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ANALYTICAL METHODS MANUAL
PART I.
METHODS USED BY THE
REMOTE AND SERVICE ANALYSIS LABORATORY

R. C. Shank, Manager

J. M. Crawford, Editor

ALLIED CHEMICAL CORPORATION

IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

NATIONAL REACTOR TESTING STATION

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PART I.

METHODS USED BY THE REMOTE AND SERVICE ANALYSIS LABORATORY

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ABSTRACT

The Analytical Methods Manual Part I describes the methods used in the Remote and Service Analysis Laboratory at the Idaho Chemical Processing Plant.

CONTENTS

INTRODUCTION

The Analytical Methods Manual is a compilation of four parts derived from the organizations within the Analytical Chemistry Branch. The four parts are:

I. Methods used by the Remote and Service Analysis Laboratory.

II. Methods used by the Radio and Special Analysis Laboratory.

III. Methods used by the Mass Spectrometry Laboratory.

IV. Methods used by the Spectrochemical Laboratory.

Advantage has been taken of the opportunity to rewrite and update, as far as possible, the methods now in use within the Branch. Some of the methods now thought to be obsolete or of relatively less value have been omitted.

Over the years, contractors have changed and consequently the Technical Report Number designation also has changed. The old and new report numbers are as follows:

Old		New
IDO-14316	January 1955	Part I, ICP-1029
IDO-14315	October 1954	Part II, ICP-1030
IDO-14318	June 1955	Part III, ICP-1031
IDO-14318	June 1955	Part IV, ICP-1032

The methods manual is designed as a guide for the analytical work at the Idaho Chemical Processing Plant. The various methods described have been critically examined, and acknowledgements are made to those whose techniques have been used to make the methods in this manual applicable for the services provided by the Analytical Chemistry Branch. Each method was written for accuracy and reliability with simplicity and ease of application.

For several years, the methods that were updated during the year were published in the Annual Report. The practice of keeping our working manuals updated continuously and publishing new and revised methods annually in our annual report will be continued.

The critical examination of the methods and techniques has been maintained; and with the continual updating, the format of the manual is designed alphabetically so that the methods can be modified or new methods can be added without redoing the complete manual. For easy identification of each method, a designation of the method is printed on the top of the page, eg, U-Color-1. The U is the symbol for uranium; color designates a spectrophotometric procedure; the 1 designates that the method is the first one written to determine uranium spectrophotometrically.

DETERMINATION OF ACIDITY WITH AN n-SILICON SEMICONDUCTOR ELECTRODE

ABSTRACT

The acidity of a wide variety of ICPP process solutions is determined with an n-silicon/stainless steel cell, which is specifically sensitive to hydrofluoric acid, and associated electronics. When a sample aliquot is diluted with an ammonium fluoride solution, all strong acids present are converted to hydrofluoric acid which subsequently causes a current flow in the above cell. Over a concentration range of 0.005 to 0.03M H^+, this current flow is essentially linearly proportional to acid concentration. Matrix effects caused by some sample types are minimized by adding ferric and uranyl ions to the ammonium fluoride diluent. The response of the n-silicon/stainless steel cell is quite reproducible and acidity values accurate to within 2% are usually obtained on process samples.

APPLICABILITY

This instrumental method is applicable to any of the sample types listed below. No maximum acidity level is specified since all samples are diluted with an ammonium fluoride solution to a range of about 0.005 to 0.03M H^+. The minimum acidity determinable by the specific procedure presented herein is about 0.4M H^+.

Sample Type	Remarks
1. Strong acids (HNO_3, H_2SO_4, HCl, $HClO_4$).	
2. Weak acids (acetic, oxalic, etc.).	These are not measurable by comparison with the HNO_3 standards specified in the method. However, they are determinable by using standards of the same acid being determined.
3. Hydrofluoric acid.	This acid may be measured without the NH_4F diluent if HF standards are used for calibration. However, the diluent will provide greater sensitivity.

Sample Type	Remarks
4. Electrolytic dissolver product (4M H^+, 0.05M Fe, 0.01M Ni, 0.02M Cr, 0.4M Al, 0.09M U, 0.001M Zr, 0.006M Gd).	Samples containing ferric and uranyl ions show a positive bias when compared to HNO_3 standards diluted with NH_4F only. This error is essentially eliminated by incorporating small amounts of Fe and U in the NH_4F diluent.
5. HNO_3-$Al(NO_3)_3$	The amount of F^- present is sufficiently high that samples with Al concentrations up to 1.8M can be analyzed.
6. Zirconium dissolver product (∿3M H^+, 1M Zr, 0.4M HBF_4, ∿7M F^-, 0.004M U).	The HF only may be measured by not adding NH_4F. When the NH_4F matrix is added, a measurement of HF plus HBF_4 is obtained. Zirconium does not interfere as it is already in the form of a F^- complex.
7. Complexed dissolver product (HF, HNO_3, Al, B, Zr, F, U).	
8. Uranium nitrate product (0.4-1.6M U, ∿1M HNO_3).	Although these samples contain a large amount of U, only a small amount (0.0021M) of UO_2^{+2} is required in the standards to obtain the correct amount of cell response enhancement.

This method is simple, rapid, and accurate to 2%. The long term stability of the cell response produces reliable analyses with either frequent or occasional use. Even better accuracy may be obtained, if desired, by using two standards which closely "bracket" the sample and expanding the readout scale with the sensitivity control of the instrument.

DISCUSSION

The use of a n-silicon semiconductor crystal for monitoring acidity was first suggested by Turner[1] and further studied by McKaveney and Byrnes[2,3]. A current is generated in the presence of hydrofluoric acid at the n-silicon anode due to the formation of "excess electron holes" during the etching process. In order for the current to pass through the n-silicon/stainless steel cell, sufficient voltage must be applied between the electrodes (∿1.5 V) to cause reduction of water at the cathode (stainless steel) and to overcome the back emf generated

by iR drop in the sample solution and n-silicon crystal. The resistance of the sample is made sufficiently low when ammonium fluoride is added, that the iR drop is not a problem.

The electrode is only sensitive to unionized hydrofluoric acid. When ammonium fluoride is added as an electrolyte to an acidic solution, hydrofluoric acid is formed by replacement and a cell current flows in relation to the amount formed. Since the concentration of ammonium fluoride affects the $HF \rightleftharpoons F^- + H^+$ equilibrium, enough must be added so that after complexing all metal ions present, an excess remains. Addition of ammonium fluoride to an original 0.5M concentration is sufficient for ordinary plant samples.

Samples containing ferric and uranyl ions exhibit a positive bias when compared to nitric acid standards diluted with ammonium fluoride only. However, the bias reaches a nearly constant maximum value at a low concentration of iron or uranium and only small amounts of these two elements need be incorporated in the ammonium fluoride diluent to minimize this error. For simplicity and maximum versatility, ferric and uranyl ions are added to all standards and to all samples except when a hydrofluoric acid only measurement is desired.

The current response of the n-silicon to hydrofluoric acid is dependent on the rate of sample stirring, and a constant rate is required throughout an analysis. The current response is not completely linear over the entire range of 0 to 0.05M H^+ as shown in Figure 1, and care must be exercised to keep the acidity of the diluted samples within the concentration range of about 0.005 to 0.03M.

Changes in sample temperature also will affect the cell response. Therefore, the calibration standards, bench standard, and samples should all be allowed to come to the same room temperature before the analysis is performed.

SAFETY PRECAUTIONS

Observe all safety precautions in the handling of strong acids, especially hydrofluoric acid, which is formed in all samples. Give due regard to the poisonous and irritating ammonium fluoride diluent used in the method. Follow established procedures and guidelines in the handling of radioactive samples.

APPARATUS AND REAGENTS

A. Apparatus

1. Digital voltmeter. Three-digit readout meter capable of measuring 0.001 V.

2. Magnetic stirrer and 0.875-x 0.25-in. Kel-F-coated stir bars from Arthur H. Thomas Company.

3. n-silicon/stainless steel cell detector probe manufactured by HACH Chemical Co., Ames, Iowa.

4. Pipets, 25-ml and assorted micro sizes.

5. Readout electronics. The circuitry, shown in Figure 2, includes a 10-turn, 5000-ohm potentiometer sensitivity control.

6. Test tubes, 25- x 100-mm cylindrical plastic with snap-on lid.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water to prepare the reagents.

1. Acid bench standard, 2.000N (1.000M) H_2SO_4. Quantitatively transfer the contents of a 1-NORMAL STANDARD SULFURIC ACID CONCENTRATE to a 500-ml volumetric flask and dilute to the mark with water.

2. Acid calibration standards, 0.030, 0.025, 0.020, 0.015, 0.010 and 0.005N. Dilute the 1.000N HNO_3 stock solution (Reagent 5) with the ammonium fluoride diluent (Reagent 4) as follows:

Aliquot (ml)	Dilution (ml)	Acid Concentration (M)
3.00	100	0.030
5.00	200	0.025
2.00	100	0.020
3.00	200	0.015
1.00	100	0.010
0.50	100	0.005

Store these standards in 4-oz. polyethylene bottles containing 1 x 5/16-in. plastic-coated stir bars.

3. Acid controls. Similarly to the preparation of the acid bench standard, prepare a series of five standards with acidities in the range of 0.50 to 3.00N. Store the controls in glass bottles with polyethylene-lined screw caps.

4. Ammonium fluoride diluent, 0.5M NH_4F-0.0009M Fe(III)-0.0021M U(VI). Dissolve 18.5 g of NH_4F in water and dilute to about 900 ml in a 1-liter Nalgene volumetric flask. Add 0.355 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 1.06 g of $UO_2(NO_3)_2 \cdot 6H_2O$. Dissolve these salts and dilute to 1000 ml. Store the solution in a polyethylene bottle.

5. Standard stock solution, 1.000N. Quantitatively transfer the contents of a NORMAL STANDARD NITRIC ACID CONCENTRATE to a liter volumetric flask and dilute to the mark with water.

PROCEDURE

A. Blank

No blank is required.

B. Preparation of Calibration Curve

1. Connect the n-silicon/stainless steel detector cell to the associated electronics and with the switch S1 in the BALANCE position, check the readout. It should be zero. If not, adjust the balance resistor (screwdriver adjustment) until the readout is zero.

The balance adjustment is for "null balancing" the integrated circuit operational amplifier. Only occasional adjustment will be needed.

2. Turn switch S1 to the cell position.

3. Remove the electrode from the bottle of water in which it is stored, wipe it dry with a tissue and place it in the bottle containing the 0.030M HNO_3 calibration standard.

The electrode should be stored with the tip under water. Always wipe dry before placing it in a standard or sample solution. Examine the tip of the electrode after placing it in the bottle containing the calibration standard or sample solution to make sure there are no bubbles trapped on the surface of the n-Si electrode.

4. While using a magnetic stirrer to mix at a medium rate, adjust the sensitivity control of the electronic circuit until the readout is 0.600 V (600 millivolts). Remove the electrode and place it in an 8-oz. bottle containing distilled water.

Since the stirring rate has some effect on the readout, it should not be changed during the calibration. Allow one minute for the electrode response to stabilize before final adjustment of the sensitivity control to 600 millivolts with the 0.030M HNO_3 calibration standard. If the top of magnetic stirrer tends to heat up appreciably during operation, use a sheet of insulating material (glass, plastic, etc.) on the top of the stirrer to minimize heating of the calibration standards and samples during analysis.

5. In a similar manner, obtain readings for the 0.025, 0.020, 0.015, 0.010 and 0.005M HNO_3 calibration standards. Plot the readings vs. concentration on graph paper (10x10 to the cm).

   Because of excellent detection cell stability, it is not necessary to repeat this calibration before each acidity determination. A bi-monthly check of the curve should be sufficient. It is necessary that the sensitivity control of the instrument be adjusted each time a series of determinations are made so that the 0.03M standard reads 0.600 V. This is to compensate for temperature changes or electronic drift.

C. Analysis of Bench Standard

Analyze the acid bench standard per Procedure D with each set of samples. Use 250 µl of sample. The result must agree with the known concentration within limits set by the Quality Control Laboratory. If it does not, repeat the analysis. Seek help if trouble persists.

D. Analysis of Samples

1. Drop a magnetic stirring bar into a 25- x 100-mm cylindrical plastic test tube and add exactly 25.00 ml of the NH_4F.

2. Pipet between 100 and 250 µl of sample into the test tube.

   The recommended sample size is:
   100 µl for 3.5 to 7.5M H^+,
   200 µl for 2.5 to 3.5M H^+,
   250 µl for 0.4 to 2.5M H^+.

3. Dry the detector probe with a tissue and place it into the 0.030M HNO_3 calibration standard. While stirring, adjust the sensitivity control to give a readout of 0.600 V on the digital voltmeter. Return the probe to the bottle of clean water in which it is stored.

   The stirring rate should not be changed after this adjustment. Eliminate any bubbles which are trapped on the tip of the electrode probe and allow one minute for the electrode response to stabilize before final adjustment of the sensitivity control.

4. Dry the detector probe with a tissue and place it in the sample tube. While stirring, record the readout from the digital voltmeter. Return the probe to the bottle of rinse water.

   After placing the detector probe in the sample tube, eliminate any bubbles which are trapped by stirring on the tip of the electrode probe. Allow one minute for the electrode response to stabilize.

5. In a similar manner obtain a reading for the other samples which have been diluted for acidity measurement.

6. Graphically read the concentration of the diluted samples from the calibration curve and calculate the acidity of the original sample, $\underline{N}^a$, as shown in the example work sheet.

E. Troubleshooting

If the sensitivity control cannot be adjusted to produce a readout of 0.600 V with the 0.030$\underline{M}$ HNO_3 calibration standard or if the other calibration standards yield abnormally low readings, remove the cover from the box housing the amplifier and mercury cell. Use the digital voltmeter to check the output of the mercury cell. If this output is less than 1.30 V, replace the mercury cell with a fresh cell. The mercury cell should be long-lived (6 mo - 1 yr) under normal operating conditions.

F. Electrode Care and Cleaning

When not in use, the electrode should be stored with the tip immersed in distilled water. Although the electrode exhibits excellent stability, it may require occasional cleaning to restore its response to a useful condition. Electrode dirtiness (instability) may result in the inability to adjust the sensitivity control so that the readout is 0.600 V with the 0.030$\underline{M}$ HNO_3 calibration standard. Cleaning of the electrode can be accomplished by immersing its tip in a solution of equal parts of nitric acid, glacial acetic acid, and 48% hydrofluoric acid for 5 seconds. This acid mixture must be prepared just prior to use and discarded afterwards. Use extreme caution in cleaning the electrode. This acid mixture is very corrosive and rapidly etches the n-Si electrode surface. Following the acid cleaning, the electrode should be rinsed thoroughly and stored with the tip immersed in distilled water. The calibration curve should be checked after cleaning the electrode because its response will likely be changed during this acid etching process.

REFERENCES

1. D. R. Turner, "A Simple and Rapid Method for Fluoride Ion Determination", Anal. Chem., 33 (June 1961) pp 959-960.

2. J. P. McKaveney, C. J. Byrnes, "Apparatus Using Semiconductor Electrodes for the Measurement of Acid Concentration", Anal. Chem., 42 (August 1970) pp 1023-1028.

3. J. P. McKaveney, C. J. Byrnes, "Analytical Monitors Using Electrodes of Semiconductors", Anal. Chem., 44 (February 1972) pp 290-295.

S. D. Reeder
D. R. Kendall
December 1972

Acidity-Amp-1

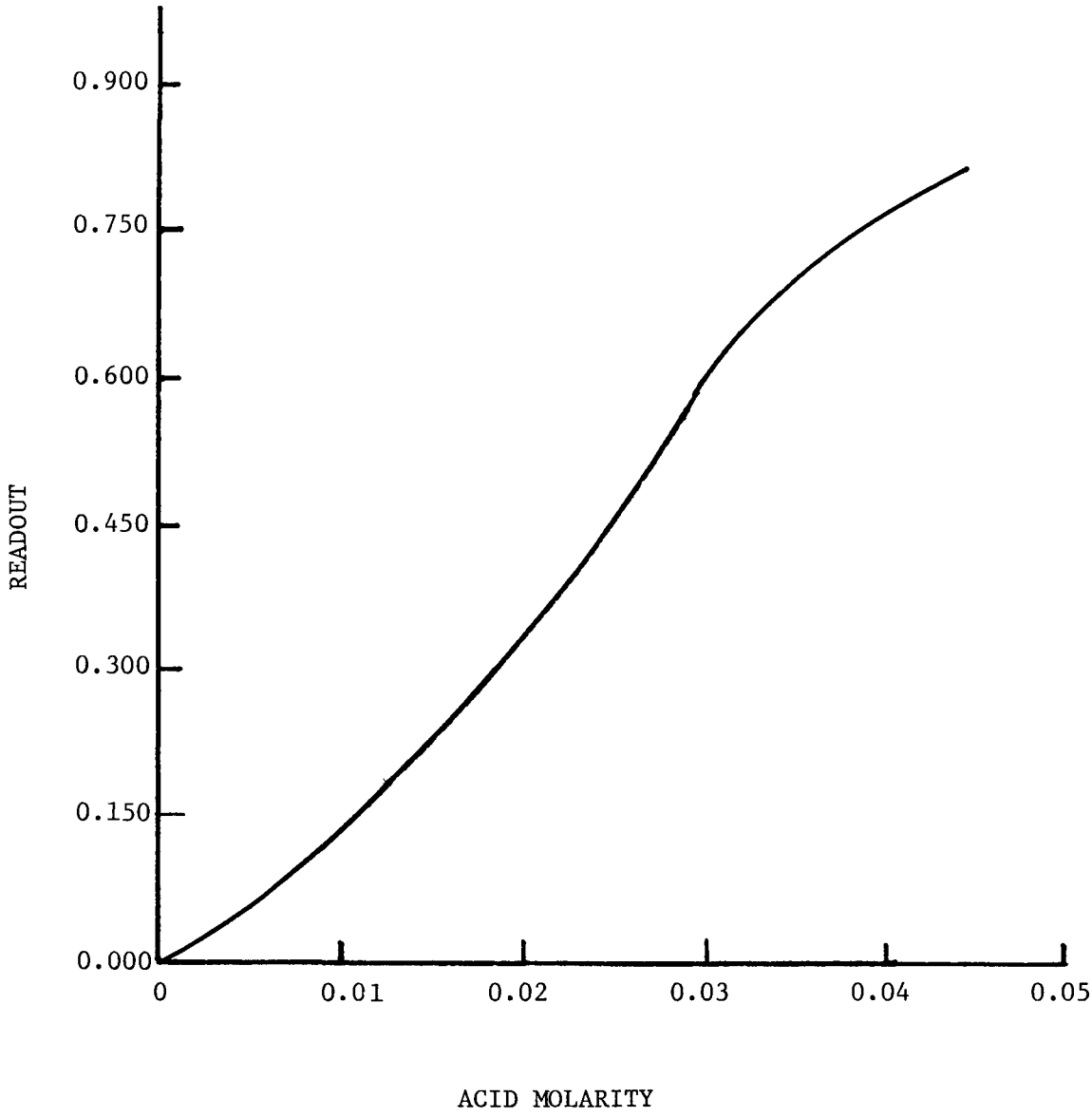

Fig. 1 Response of n-silicon/stainless steel cell to acid concentration.

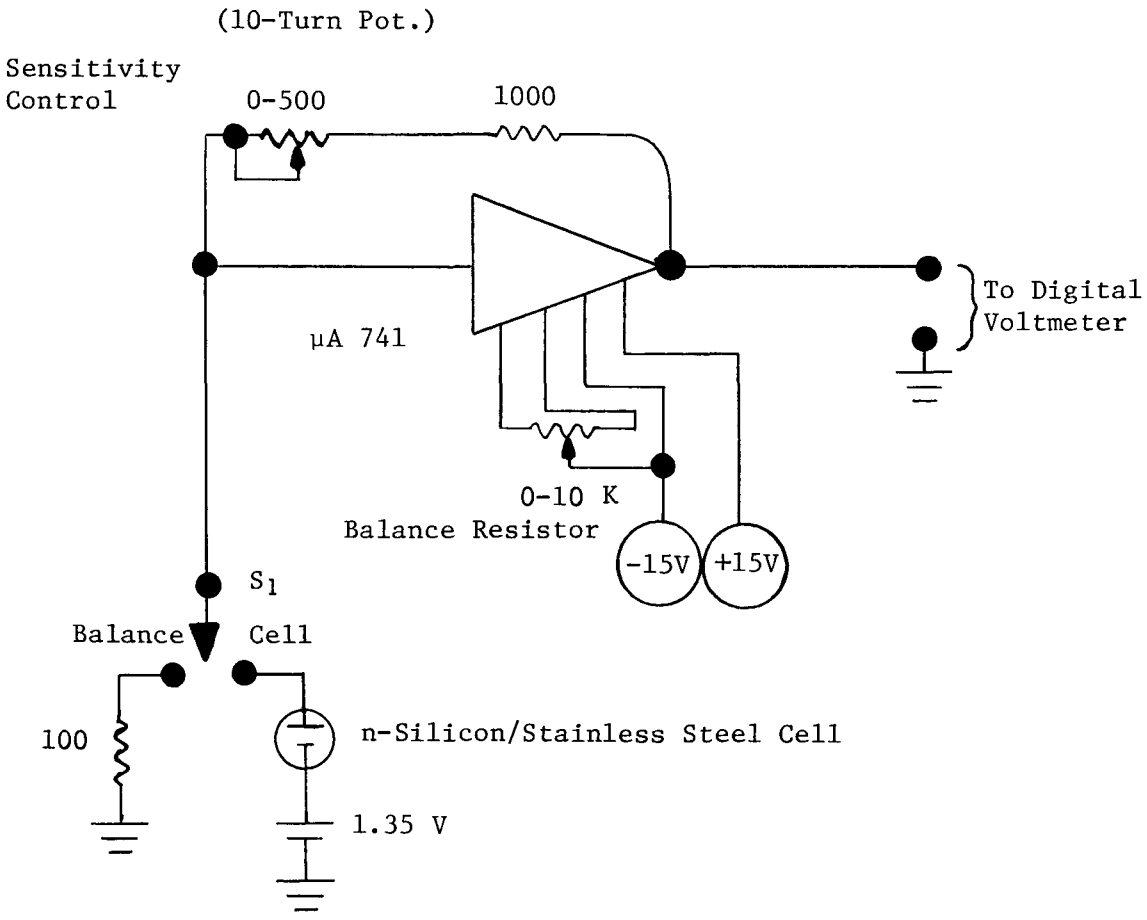

Fig. 2 Readout electronics.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Acidity

CHARGE NUMBER _____ PROCEDURE Acidity-Amp-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Readout	Value from curve, M						RESULT
Bench Std	250 µl/25 25ml	280	0 0195						1 97 $\underline{N}^a$
342	250 µl/25 25ml	178	0 0137						1 38 $\underline{N}^a$

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\underline{N}^a = \frac{(\text{Value from curve})(\text{Volume of Sample} + 25)(10^3)}{\text{ml of Sample}}$$

$$\text{Bench Std} = \frac{(0\,0195)(25\,25)(10^3)}{250} = 1\,97\ \underline{N}^a$$

$$342 = \frac{(0\,0137)(2525)(10^3)}{250} = 1.38\ \underline{N}^a$$

APPROVED BY _____

TITRIMETRIC DETERMINATION OF THE ACIDITY OF AQUEOUS SOLUTIONS CONTAINING HYDROLYZABLE METAL IONS

ABSTRACT

Hydrolyzable metal ions are complexed with oxalate, and acidity is determined by titration with standard sodium hydroxide to pH 5.55 (Al-Zr-U matrix samples) or pH 5.80 (Fe-Cr-Ni matrix samples). Acid-deficient or feebly acidic samples that contain metal hydroxide complexes or stable hydrolysis polymers are reacted initially with excess acid, then back titrated with sodium hydroxide to the reference pH.

APPLICABILITY

The various types of samples analyzable by the method[1], the recommended procedure, and pertinent remarks relative to the determination are summarized in Table I.

The titration range varies with each procedure. It is 0.12- to 1.2-meq acid for Procedure B, 0.12- to 1.2-meq acid for Procedure D, and 0 to 1.2-meq acid for Procedure F. The usual sample aliquot for these three procedures is 200 µl; hence, the lowest determinable acidity concentrations are 0.85N, 0.6N, and 0N, respectively. Procedures C and E involve the addition of an acid spike and back titration with sodium hydroxide so their titration ranges are difficult to define. The approximate determinable concentration range for these two procedures is 2.5N acid-deficient or basic to 0.75N acid.

TABLE I

TYPES OF SAMPLES ANALYZABLE

Principal Sample Components	Procedure and End Point pH	Remarks
1. Al(III), U(VI), Zr(IV), (HF must accompany Zr.)	B, 5.55	Any of the four ions can be together in mixtures. The polymerization of Zr is usually negligible in solutions containing HF. Mercury at concentrations less than 0.01M does not interfere. For Hg concentrations greater than 0.01M, use 20 ml of the 0.45M potassium oxalate (K_2Ox) reagent saturated with KCl.

TABLE I (Cont'd)

Principal Sample Components	Procedure and End Point pH	Remarks
		Samples of this type often contain Cr. The Cr can be neglected if its concentrations is less than 5% of the major metal constituent(s).
2. $M(OH^{+x})$ such as $Al(OH)_y^{+(3-y)}$	C, 5.55	The addition of an acid-deficient Al sample to the K_2Ox reagent usually results in the precipitation of $Al(OH)_3$. Acid-deficient samples should be treated initially with a measured excess of acid.
3. Fe(III), Cr(III) Ni(II)	D, 5.80	Applicable only to acidic samples in which polymerization is negligible. Procedure C should be used to analyze acid-deficient samples. Stainless steel constituents, especially Cr, are complexed very slowly by oxalate. For this reason, wait at least 2 hr after the addition of the sample to the K_2Ox before titrating.
4. Zr(IV) without HF present	E, 5.55	In the absence of complexing anions such as F^-, Zr forms stable hydrolysis polymers. Breaking them requires a preliminary digestion with H_2SO_4 in a sealed container.
5. Metal ions, such as Al(III), U(VI), and Zr(IV), with both B and F^- present	F, 5.55	The acidity of these samples is dependent on the relative concentrations of the metal ions, B (H_3BO_3), and F^- (See the DISCUSSION section). This procedure provides the answer to the question, "What would be the acidity of the sample if there were no reaction between the H_3BO_3 and F^-?" Actually, there is some reaction between F^- and H_3BO_3 and the question, "What is the free acidity of the sample?" might be raised. Procedure B provides the answer to this second question.

DISCUSSION

Free acid, $\underline{N}^a$ is defined as that amount of acid which would remain if the hydrolyzable metal ions were removed from the solution as neutral salts. Analogously, acid-deficiency, $\underline{N}^b$, or "free-base" is defined as that amount of base which would remain if the hydrolyzable metal ions were removed from the solution as neutral salts.

In this method, hydrolyzable metal ions are removed effectively by complexation with potassium oxalate (K_2Ox). This is illustrated by Reaction 1 which describes the reaction of K_2Ox with an acidic solution of aluminum nitrate. In practice, the direction reaction of K_2Ox with

$$HNO_3 + Al(NO_3)_3 + 3K_2Ox \rightleftarrows K_3Al(Ox)_3 + 3KNO_3 + HNO_3 \quad (1)$$

$$Al(OH)_2NO_3 + 3K_2Ox \rightleftarrows K_3Al(Ox)_3 + KNO_3 + 2KOH \quad (2)$$

dibasic aluminum nitrate (Diban), Reaction 2, usually is not practical, and the hydroxy complex must first be converted with excess standard acid to the neutral salt which then reacts with K_2Ox according to Reaction 1.

Actually, the determination of acidity using oxalate complexation is quite complicated and requires a careful consideration of several equilibria. Oxalic acid is a dibasic acid which ionizes to give the

$$H_2Ox \rightleftarrows HOx^- + H^+ \quad (3)$$

$$HOx^- \rightleftarrows Ox^- + H^+ \quad (4)$$

$$M^+ + Ox^= \rightleftarrows MOx^- \quad (5)$$

$$M^+ + HOx^- \rightleftarrows MHOx \quad (6)$$

$$MOx^- + H^+ \rightleftarrows MHOx \quad (7)$$

$$M^+ + H_2O \rightleftarrows MOH + H^+ \quad (8)$$

monovalent binoxalate and bivalent oxalate anions according to the reversible Reactions 3 and 4, respectively. Reaction 5, similar to Reaction 1, is the desired, predominant reaction, but is is accompanied by Reactions 6, 7, and 8. Reaction 6 together with the reverse of Reaction 4 and Reaction 7 shows the consumption of hydrogen ions accompanying the formation of the metal binoxalate complex. These reactions, causing a negative bias, are observed especially at moderate acidities where monovalent binoxalate ions are stable and predominant. Reaction 8, particularly troublesome at high pH, shows the hydrolysis of the metal ion and the release of acid.

In the recommended procedures, the pH of the oxalate complexing solution is controlled at a value where the release of acid via Reaction 8 is offset by the consumption of acid via Reactions 6 and 7. The optimum pH values are pH 5.80 for stainless steel samples and pH 5.55 for Al, U, and Zr samples. The pH of the stock complexing solutions are preadjusted to these values; however, the pH should be checked for each sample and readjusted where necessary.

Besides pH, the sample to oxalate ratio must be controlled to guarantee reliable results. Significant differences have been noted with changes in the sample to oxalate ratio. In Procedure B, sample aliquots up to 10 ml can be taken if the total hydrolyzable metal ion content in the aliquot does not exceed 1.5 meq. Large dilution of the oxalate reagent with water also affects the results.

Mercury undergoes considerable hydrolysis even in the presence of oxalate. A special oxalate reagent saturated with potassium chloride is used to prevent this.

The determination of the acidity of zirconium-uranium fuel solutions that contain both boric acid and fluoride (Sample 5, Table I) is a unique problem because the acidity is dependent on the relative concentrations of the fluoride, the boric acid, and the metal ions. The following equilibria illustrate this.

$$H_3BO_3 + nF^- \rightleftarrows BF_n(OH)_{3-n} + nOH^- \qquad (9)$$

$$M^{+x} \downarrow$$

$$MF_n^{+(x-n)} \qquad (10)$$

The reversible reaction of boric acid with fluoride ions (Reaction 9) to form a fluoborate complex and hydroxyl ions is especially significant. High fluoride concentration favors formation of the fluoborate complex with the accompanying release of hydroxyl ions. Low fluoride concentration and high hydroxyl ion concentration favor the reverse reaction. Fluoride-complexing metal ions also favor the reverse reaction by effectively reducing the fluoride concentration (Reaction 10).

The routine acid Procedure B for zirconium samples containing hydrofluoric acid provides acidity values which are probably close to, but slightly higher than, the free acidities of these solutions. However, these acidity values do not provide an acid material balance because of the usual variations in the compositions of the process solutions and the dependence of the acidity on the relative concentrations of fluoride, boric acid, and metal ions as noted above.

The fact that fluoride complexing metal ions eliminate the complicating effect of boric acid by the reversal of Reaction 9 led to the development of a modified Procedure, F, which provides an acid material balance. The principal modifications are the addition of 1 mM of aluminum nitrate and the use of 1M K_2Ox solution in place of the 0.45M solution prescribed for Procedure B. Essentially Procedure F determines the sum of nitric acid and hydrofluoric acid in the sample with no reaction between boric acid and fluoride.

SAFETY PRECAUTIONS

Wear rubber gloves to avoid acid burns from concentrated sulfuric acid in Procedure E. When heating the sealed tubes containing sulfuric acid, Procedure E, use a safety glass shield. Glass, screw-cap test tubes can break when strong pressure is applied. Wrap the test tubes in a cloth to avoid cuts (and sulfuric acid burns).

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, assorted sizes.

2. Buret, micro, 10-ml, graduated in 0.02-ml increments.

3. Ice bath.

4. pH meter, Corning Model 12 or other expanded scale meter with attached recorder and glass-calomel electrode system. An Arthur H. Thomas Company combination electrode, 4858-L60, and the combination of standard glass (Beckman 4970 or L&N Std 1199-30) and calomel (Beckman 4990 or L&N Std 1199-31) electrodes are satisfactory. If the highest precision is not required, pH meters without expanded scales, such as the Beckman Model H-2 or the L&N Model 7664, may be used.

5. Parafilm. This paraffin-coated film (Marathon Division, American Can Company) is a stock item.

6. Pipets, macro and micro, assorted sizes with syringe and rubber suction bulb.

7. Stirring bars, magnetic, plastic-coated.

8. Syringe Microburet, Model No. SB2, with assorted syringes (Micrometric Instrument Co., Cleveland, Ohio).

9. Test tubes, 15- to 25-ml, glass, with polyethylene-lined screw caps.

10. Thermometer, 0 to 110°C.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Aluminum nitrate solution, 1M aqueous solution. Dissolve 375 ± 1 g of $Al(NO_3)_2 \cdot 9H_2O$ in water, filter the solution through a 0.45-μ membrane filter, and dilute to 1 liter with water.

2. Buffer solution, pH 7.00.

3. Hydrochloric acid solution, standard, 0.200N±0.001N.

4. Nitric acid, 1M.

5. Potassium oxalate reagent I, 0.45M, unadjusted. Dissolve 82.9 g of potassium oxalate monohydrate ($K_2Ox \cdot H_2O$) in water and dilute to 1 liter with water. Adjust portions of this solution as needed to pH 5.55 or 5.80 with 1M HNO_3. If subsequent readjustment to a higher pH is necessary, use 1M NaOH.

6. Potassium oxalate reagent II, 0.45M, unadjusted, saturated with KCl. Prepare the solution as directed above except dilute nearly to volume, saturate the oxalate solution with KCl then dilute to volume. Crystals of KCl should be visible at the bottom of the container. Adjust portions of this solution as needed to pH 5.55 or 5.80 with 1M HNO_3.

7. Potassium oxalate reagent III, 1.00M, unadjusted. Prepare the 1.00M solution using 184.2 g of $K_2Ox \cdot H_2O$ in water and dilute to 1 liter. Adjust portions of this solution as needed to pH 5.55 or 5.80 with 1M HNO_3.

8. Sodium hydroxide solutions, standards, 0.200±0.001N and 1.000± 0.001N.

9. Sulfuric acid solution, standard, 1.000±0.001N.

10. Sulfuric acid, 26N (13M). Add cautiously, with cooling, 360 ml of conc H_2SO_4 to 140 ml of water. Cool, dilute to 500 ml with water, and mix well. Transfer the H_2SO_4 solution to 20-ml ampoules and flame seal the ampoules.

PROCEDURES

A. Bench Standard

Select a bench standard with a matrix similar to that of the sample and process a single determination. Allowable limits will be specified by the Quality Control Laboratory.

B. Analysis of Samples Containing Major Amounts of Aluminum, Uranium, and Zirconium, and Small Amounts of Mercury.

NOTE: This procedure is applicable to zirconium samples only if the samples contain hydrofluoric acid which prevents the polymerization of zirconium through complexation. In the absence of fluoride, Procedure E must be used.

1. Wash the pH meter electrodes with distilled water and dry them with absorbent tissue paper.	For highest precision, use an expanded scale pH meter, preferably one with a recorder. Standardize the expanded scale pH meter at the pH 6 to pH 7 range with pH 7 buffer, then switch the instrument to the pH 5 to pH 6 range for titrations.
2. Standardize the pH meter against a pH 7.00 buffer solution, then wash the electrodes with water and wipe with tissue paper.	
3. Pipet 20 ml of the 0.45M K_2Ox Reagent I, preadjusted to pH 5.55, into a 50-ml beaker containing a stirring bar. If the Hg concentration of the sample is greater than 0.01M, use instead 20 ml of the 0.45M K_2Ox Reagent II.	Adjust a suitable portion of the 0.45M K_2Ox Reagent I or II to pH 5.55±0.05 with 1M HNO_3 or 1M NaOH before analyzing the bench standard or samples.
4. Lower the pH electrodes into the solution and stir the solution for about 3 min.	
5. Measure the pH of the solution and record the pH.	The pH must be in the range of 5.50 to 5.60; if not, adjust per Step 3.
6. Pipet 200 µl of sample into the oxalate solution, stir, then observe the pH.	If the pH is below 5.20, continue with Step 7. If the pH is above 5.2, discard the solution and analyze the sample according to Procedure C for

samples containing hydroxy-metal complexes. Sample aliquots up to 10 ml may be taken with no adverse effect if the aliquot does not contain more than 1.5 meq of hydrolyzable metal ion.

7. Titrate with 0.200N NaOH to the exact pH recorded in Step 5.

8. Record the data and calculate the results as shown on the example work sheet. Report results to the second decimal place.

C. Analysis of Low Acid or Acid-Deficient Samples such as Diban.

1. Standardize the pH meter against pH 7.00 buffer solution, then adjust the 0.45M K_2Ox to pH 5.55± 0.5 or to pH 5.80±0.05. Record the pH of the oxalate reagent.

For highest precision, use an expanded scale pH meter, preferably one with a recorder. Standardize the expanded scale pH meter at pH 6 to pH 7 range with pH 7 buffer, then switch the instrument to the pH 5 to pH 6 range for the titrations. Adjust to 5.55 for Al samples and to 5.80 for Fe-Cr-Ni stainless steel samples. Use 0.45M K_2Ox reagent I for samples containing less than 0.01M Hg and reagent II for samples with Hg concentrations above this. Use the same reagent for the acid spike standardization, Step 2, and sample analysis, Step 3.

2. Standardize the 1.00N H_2SO_4 spike as follows:

   a. Pipet 1.00 ml of the 1.000±0.001N H_2SO_4 into a 50-ml beaker containing a stirring bar.

   b. Pipet 20 ml of the 0.45M K_2Ox reagent I or II into the beaker.

c. Titrate with 0.200N NaOH to the exact pH recorded in Step 1.

d. Record the volume of 0.200N NaOH used and proceed with Step 3.

3. Analyze the samples as follows:

a. Pipet 1.00 ml of the 1.000N H_2SO_4 into a 50-ml beaker.

b. Pipet 200 µl of the sample into the beaker. Cover the beaker with a watch glass and swirl the beaker intermittently for 2 to 3 min.

c. Pipet 20 ml of the 0.45M K_2Ox reagent I or II into the beaker.

If the sample is of the stainless steel type that contains large amounts of Cr, cover the beaker with a 3- x 3-in. sheet of Parafilm, swirl to mix, then let stand for 2 hr.

d. Immerse the pH electrode into the solution and stir for 3 min.

e. Titrate with 0.200N NaOH to the exact pH recorded in Step 1.

f. Record the data and calculate the results as shown on the example work sheet. Report results to the second decimal place.

D. Analysis of Samples Such as Stainless Steel that Contain the Major Constituents Iron, Chromium, and Nickel.

1. Standardize the pH meter against a pH 7.00 buffer solution, then adjust the 0.45M K_2Ox reagent I to pH 5.80±0.05 with 1M HNO_3 or 1M NaOH. Record the exact pH.

For highest precision, use an expanded scale pH meter, preferably one with a recorder. Standardize the expanded scale pH meter at the pH 6 to pH 7 range with pH 7 buffer, then switch the instrument to the pH 5 to pH 6 range for the titrations.

2. Analyze the sample as follows:

   a. Pipet 20 ml of the pH adjusted 0.45M K_2Ox reagent into a 50-ml beaker.

   b. Pipet 200 µl of the sample into the beaker, then mix well by swirling or with magnetic stirring. Cover the beaker tightly with a 3- x 3-in. sheet of Parafilm and allow to stand for 2 hr.

   The 2-hr waiting period is necessary for the oxalate to complex Cr.

   c. Remove the Parafilm covering, insert the pH electrode, and observe the pH.

   If the pH is below 5.4, continue with Step d. If it is above 5.4, discard the solution and analyze the sample according to Procedure C.

   d. Titrate with 0.200N NaOH to the exact pH recorded in Step 1.

   e. Record the data and calculate the results as shown on the example work sheet. Report results to the second decimal place.

E. Analysis of Samples Containing Polymeric Species Such as Polymers of Zirconium.

NOTE: In this procedure, results are obtained from the difference of two large titration volumes; therefore, standardize the sulfuric acid spike and analyze the sample in duplicate. Allowable limits for the difference between duplicates is 0.1N. If these limits are adhered to, results will be reliable to ±0.1N standard deviation.

Strong sulfuric acid absorbs atmospheric moisture and loses strength. The 26N H_2SO_4 will be supplied in small, sealed ampoules. Transfer the acid to a small, screw-cap bottle and keep the bottle tightly capped when the acid is not being used. Request a new ampoule of 26N H_2SO_4 after 2 weeks.

1. Standardize the pH meter against pH 7.00 buffer solution, then adjust the 0.45M K_2Ox reagent I to pH 5.55± 0.05 with 1M HNO_3 or 1M NaOH. Record the exact pH.

   For highest precision, use an expanded scale pH meter, preferably one with a recorder. Standardize the expanded scale pH meter at the pH 6 to pH 7 range with pH 7 buffer, then switch the instrument to the pH 5 to pH 6 range for the titrations.

2. Standardize the 26N H_2SO_4 spike as follows:

   a. Standardize the pH meter against pH 7.00 buffer solution, then rinse the electrodes with water and dry them with tissue paper.

   b. Pipet 20 ml of the 0.45M K_2Ox reagent from Step 1 into a 50-ml beaker.

   c. With the Syringe Microburet, pipet 200 µl of the 26N H_2SO_4 solution into the beaker.

      Do not use the common hand micro-pipet. The H_2SO_4 does not drain completely and the use of water rinses is not allowed because complete depolymerization is obtained only with strong H_2SO_4.

   d. Immerse the pH electrodes into the solution and titrate with 1.000N NaOH to the exact pH recorded in Step 1.

   e. Record the data on the work sheet and continue with the analysis of the sample, Step 3.

3. Analyze the sample as follows:

a. With the Syringe Microburet, pipet 200 µl of the 26N H_2SO_4 solution into a glass screw-cap test tube.	Use a small screw-cap polyethylene bottle for samples containing HF.
b. Pipet 200 µl of the sample, cap tightly, then swirl the test tube to mix the acid and the sample.	
c. Heat the test tube in boiling water for 1 to 2 hr.	Do not heat over 2 hr because insoluble sulfate salts may form and volatile acids may be lost.
d. Remove the test tube from the boiling water bath and quickly immerse it into an ice bath. Chill to room temperature.	
e. Open the test tube and quantitatively rinse the sample into a 50-ml beaker with 20 ml of the K_2Ox reagent from Step 1.	
f. Immerse the pH electrode into the solution and titrate with 1.000N NaOH to the exact pH recorded in Step 1.	Because pH drifts near the end point, approach the end point slowly to avoid over titration. If the sample is over titrated, back titrate with 0.200N HCl allowing ample time for equilibration.
g. Record the data and calculate the results as shown on the example work sheet. Report results to the second decimal place.	

F. Analysis of Metal Ion Solutions That Contain Both Fluoride and Boron

1. Standardize the pH meter against the pH 7.00 buffer solution, then adjust the 1.0M K_2Ox reagent III to pH 5.55±0.05. Record the exact pH.	For highest precision, use an expanded scale pH meter, preferably one with a recorder. Standardize the expanded scale pH meter at the pH 6 to pH 7

range with pH 7 buffer, then switch the instrument to the pH 5 to pH 6 range for the titrations.

2. Analyze the sample as follows:

   a. Pipet 1.00 ml of the 1M $Al(NO_3)_3$ solution into a 50-ml beaker.

   b. Pipet 200 µl of the sample into the beaker.

   c. Cover the beaker with a 3- x 3-in. sheet of Parafilm, swirl the beaker to mix the sample thoroughly with the 1M $Al(NO_3)_3$, and let stand for 3 min.

   d. Remove the Parafilm and pipet 20 ml of the K_2Ox reagent from Step 1 into the beaker.

   e. Immerse the pH electrodes into the solution, stir the solution about 2 min, then titrate with 0.200N NaOH to the exact pH recorded in Step 1.

3. Determine the acid blank of the 1M $Al(NO_3)_3$ spike solution according to Steps 2a, 2d, and 2e.

4. Record the data from Steps 1, 2e, and 3 and calculate the results as shown on the example work sheet. Report results to the second decimal place.

REFERENCES

1. G. L. Booman, M. C. Elliot, R. B. Kimball, F. O. Cartan, J. E. Rein, "Determination of Free Acid in the Presence of Hydrolyzable Ions", Anal. Chem., 30 No. 2 (February 1958) pp 284-287.

November 1968
S. S. Yamamura
R. Fullerton

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION N^a or N^b

CHARGE NUMBER _____ PROCEDURE Acidity-Vol-1

SPECIAL INSTRUCTIONS:

For Analysis via Procedure C

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	0.2N NaOH Spike ml	0.2N NaOH Sample ml	H^+ meq	meq H^+ corrected				RESULT
II	0.200 ml	4.95	5.95	0.20	0.02±0.01				1.00±0.05 N^a
	0.200 ml	4.95	3.95	-0.20	-0.20±0.01				1.00±0.05 N^b

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = 0.200(B-A) = 0.200(5.95-4.95) = 0.20$$

$$\text{Result} = \frac{D}{\text{Sample Vol.}} = \frac{0.20 \pm 0.01}{0.200} = 1.00 \pm 0.05$$

$$C' = 0.200(B-A) = 0.200(3.95-4.95) = -0.20$$

$$\text{Result} = \frac{D}{\text{Sample Vol.}} = \frac{-0.20 \pm 0.01}{0.200} = -1.00 \pm 0.05$$

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION N^a

CHARGE NUMBER _____ PROCEDURE Acidity-Vol-1

SPECIAL INSTRUCTIONS:

For Analysis via Procedures B and D

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	0.2N NaOH ml	0.2N HCl ml	H^+ meq	meq H^+ corrected				RESULT N^a
I	0.200 ml	3.00	0	0.60	0.61 ± 0.01				3.05 ± 0.05

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = 0.200\,(A-B) = 0.60$$

$$\text{Result} = \frac{E}{\text{Sample Vol.}} = \frac{0.61 \pm 0.01}{0.2} = 3.05 \pm 0.05\ N^a$$

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION N^a or N^b

CHARGE NUMBER _____ PROCEDURE Acidity - Vol - I

SPECIAL INSTRUCTIONS:

For Analysis via Procedure E

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	1.0 N NaOH Spike ml	1.0 N NaOH Sample ml	0.2 N HCl ml	H^+ meq	meq H^+ corrected			RESULT N^a
III	0.200 ml	5.20	5.35	0.20	0.11	0.11 ± 0.05			0.55 ± 0.05

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = (1.0B - 1.0A) - 0.2D$$

$$= (1.0)(5.35) - (1.0)(5.20) - (0.2)(0.2) = 0.11$$

$$\text{Result} = \frac{E}{\text{Sample Vol}} = \frac{0.11 \pm 0.01}{0.200} = 0.55 \pm 0.05$$

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION N^a

CHARGE NUMBER _____ PROCEDURE Acidity-Vol-1

SPECIAL INSTRUCTIONS:

For Analysis via Procedure F

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	0.2 N NaOH Al Blank ml	0.2 N NaOH Sample ml	0.2 N HCl ml	H^+ meq	meq H^+ corrected			RESULT N^a
IV	0.200 ml	0.20	3.00	0.15	0.53	0.54±0.01			2.70±0.05

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = 0.200\,(B-A) - (0.200)(C)$$

$$= 0.200\,(3.00 - 0.20) - (0.200)(0.15) = 0.53$$

$$\text{Result} = \frac{E}{\text{Sample vol.}} = \frac{0.54 \pm 0.01}{0.200} = 2.70 \pm 0.05\ N^a$$

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TITRIMETRIC DETERMINATION OF ACID

ABSTRACT

Total acidity is determined by titration with standard sodium hydroxide to a phenolphthalein end point.

APPLICABILITY

This method is intended primarily for the determination of the total acidity of mineral acids, such as hydrochloric, hydrofluoric, nitric, perchloric, and sulfuric acids, in aqueous solutions devoid of hydrolyzable ions. The color change of the phenolphthalein indicator occurs at a pH of about 9; hence, all other acids with pK_a values less than 11[1] (ionization constants greater than 10^{-11}) are titrated totally or in part. The titration is quantitative for acids with pK_a values less than about 6; hence, these are determinable by the method. The titration is partial for acids with pK_a values above 7. The latter also interfere by diminishing the sharpness of the end point.

The range of the method is 0.5 to 4.5 meq of acid. The practical maximum sample aliquot is 50 ml; hence, the lower concentration limit is 0.01N.

As stated above, this method is intended primarily for aqueous samples devoid of hydrolyzable metal ions. For samples that do contain hydrolyzable metal ions, method Acidity-Vol-1 of this manual is applicable. Method Acidity-Vol-3 is applicable to organic samples.

DISCUSSION

This method is one of the simplest performed in analytical chemistry. For this very reason, it is taken for granted and carelessness, which leads to decreased reliability, is the result. Factors that control the reliability are the use of dirty burets that do not drain cleanly and the use of glassware that has not been washed and rinsed free of interfering ions and soaps or detergents. The latter buffers in the basic region to cause low results.

A source of imprecision is the difference between individuals in judging the phenolphthalein end point. An attempt has been made to prepare a stable comparison standard that has the hue of a properly titrated sample; however, this, to date, has not been successful. A titrated sample itself cannot be used because the color fades due to the absorption of CO_2 from the air. Until such a comparison standard can be made, the stated conditions for the end point, titration to the faint pink color that persists for 30 sec, should be followed closely.

SAFETY PRECAUTIONS

Wear rubber gloves when handling strong acid samples. If the sample is strong sulfuric acid, pipet the aliquot into the water rather than adding water to the acid as the heat of reaction can cause the acid to splatter. Wash any areas of the skin or the eyes contacted by acids or bases with copious amounts of water.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 50-ml, graduated in 0.1-ml increments.

2. Flask, Erlenmeyer, 125-ml.

3. Magnetic stirrer with plastic-coated stirring bars.

4. Pipets, macro and micro, assorted sizes, with syringe and suction bulb.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Phenolphthalein indicator solution, 1%. Dissolve 1 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml with water.

2. Sodium hydroxide, standard, 0.1N.

PROCEDURE

A. Blank

A blank is not required in this procedure.

B. Bench Standard

Process a 25-ml aliquot of 0.1000N H_2SO_4 according to Procedure C. Limits will be specified by the Quality Control Laboratory.

C. Analysis of Samples

1. Pipet an aliquot of sample that contains 0.5 to 4.5 meq of acid into a 125-ml Erlenmeyer flask.

If the sample is strong H_2SO_4 or HF acid, pipet it into a flask containing 40 ml of water.

2. Add distilled water to a total volume of 50 ml.

3. Add 2 drops of phenolphthalein indicator solution.

4. Using magnetic stirring, titrate with 0.1N NaOH solution to the appearance of a faint pink color which persists for 30 sec.

5. Record the data and calculate the results as shown on the example work sheet. Report all results to three significant figures.

REFERENCES

1. N. A. Lange, Handbook of Chemistry, 8th Ed., Sandusky, Ohio: Handbook Publishers Inc., 1952.

March 1968

S. S. Yamamura
J. E. Rein

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Acidity

CHARGE NUMBER _____ PROCEDURE Acidity - Vol - 2

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Normality of NaOH	ml NaOH used	Acid in Samp Aliquot, Meq	Acid Corr'd for Bias				RESULT Normality
I	25.00 ml	0.1012	24.85	2.51	2.51 ± 0.02				0.100 ± 0.001

ANALYZED BY _____ DATE _____

CALCULATIONS:

$C = AB = (0.1012)(24.85) = 2.51$ meq

$\text{Result} = \frac{D}{\text{Samp Vol}} = \frac{2.51 \pm 0.02}{25.00} = 0.100 \pm 0.001$ N

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VOLUMETRIC DETERMINATION OF ALKALINITY BY ACID TITRATION

ABSTRACT

This method describes three procedures for the determination of total alkalinity of aqueous solutions of ammonium hydroxide, sodium carbonate, and sodium hydroxide by hydrochloric acid titration. Ammonium hydroxide is titrated in boric acid medium to a bromocresol green - methyl red mixed indicator end point. Carbonate and hydroxide are titrated in plain aqueous medium to methyl orange and phenolphthalein end points, respectively.

APPLICABILITY

The three procedures in this method are intended primarily for verifying the concentrations of ammonium hydroxide, sodium carbonate, and sodium hydroxide solutions used in the plant uranium recovery processes. None of the methods are specific. All three procedures are applicable to other bases of comparable strength[1]; most basic substances will contribute to the measured alkalinity and "interfere".

The contribution of other basic substances is quantitative or partial depending on their basicity and the pH range where the indicator undergoes observable color change. Table I lists the indicators used in this method and discusses the behavior of bases of varying strength in each of the three procedures.

Aside from bases, metal hydroxides and metallates (oxygenated metal anions) that consume acid constitute the major interference. Soluble metallates cannot be removed but insoluble metal hydroxides can be removed by centrifugation or filtration.

The range of all three procedures is 0.5 to 4.5 meq of base. Assuming a maximum sample limit of 50 ml, the lowest concentration determinable is 0.01 meq/ml.

DISCUSSION

The determination of alkalinity by acid titration is simple and usually very reliable. It is, however, subject to errors. Possible sources of error that should be considered include: absorption of carbon dioxide by strong bases, faulty equipment, partial neutralization of samples by acids from the pipet wash train, and improper sampling (particularly with volatile ammonium hydroxide samples).

TABLE I

EFFECT OF OTHER BASES IN PROCEDURES C, D, AND E

Procedure & Indicator	Color Transition and pH Range for Transition	Observed Color Change and Approximate pH at End Point	Effect of Other Bases [a]
C; bromocresol green plus methyl red	Blue to yellow; pH 5.4 to 3.8 and yellow to red; pH 6.0 to 4.8	Green to gray to gray-pink; pH 4.5±0.1	All bases with pK_b below 6.5 are expected to be titrated quantitatively. Weaker bases with pK_b above 6.5 will be titrated partially.
D; Special Methyl Orange	Blue to pink; pH 4.5 to 3.0, estimated	Blue to pink; pH 4.0±0.1	All bases with pK_b below 7 are expected to interfere quantitatively. Weaker bases with pK_b above 7 will be titrated partially.
E; phenolphthalein	Pink to colorless; pH 10.0 to 8.3	Pink to colorless; pH ~9.0 to 8.5	All bases with pK_b below about 3 are expected to be titrated quantitatively. Weaker bases with pK_b above 3 will be titrated partially.

[a] A quantitative titration is assumed to be one where the ratio of titrated base to untitrated base is 1000:1 or greater. The contribution of so-called weaker bases varies from 99.9% to 1% depending on their basicity.

SPECIAL SAFETY PRECAUTIONS

Handle strong solutions of bases with caution. Ammonium hydroxide samples may be pressurized. Chill all such samples before opening the containers.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 50-ml.
2. Dropping bottles.
3. Erlenmeyer flasks, 125- and 250-ml.
4. Magnetic stirrer with plastic-coated stirring bars.
5. Pipets, macro and micro, assorted sizes with syringe and suction bulb.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Boric acid solution, 4%(w/v). Dissolve 40 g of H_3BO_3 in water and dilute to 1 liter.
2. Bromocresol green - methyl red mixed indicator. Dissolve 0.50 g of bromocresol green and 0.25 g of methyl red in 250 ml of ethanol.
3. Hydrochloric acid, 0.1N standard solution. A standardized solution will be provided by the Quality Control Laboratory.
4. Phenolphthalein indicator solution, 1%. Dissolve 1.0 g of the solid reagent in 100 ml of ethanol.
5. Sodium carbonate, anhydrous, granular.
6. Special Methyl Orange Indicator Solution No. 260 (Flox Company, Inc., Minneapolis, Minnesota).
7. Trishydroxy methyl aminomethane (THAM).

PROCEDURE

A. Blank

A blank need not be determined for any of the procedures in this method.

B. Bench Standard

Process an appropriate bench standard before analyzing samples. The recommended standards are accurately weighed 0.3- to 0.4-g samples of THAM for Procedure C, accurately weighed 0.13- to 0.15-g samples of Na_2CO_3 for Procedure D, and 25.00 ml of standard 0.1N NaOH for Procedure E. Report the results for THAM and Na_2CO_3 as milliequivalents per gram as described in the example work sheet. For NaOH, report total milliequivalents. Acceptable limits for the analyses results will be specified by the Quality Control Laboratory.

C. Titration of Ammonium Hydroxide

1.	Chill the entire sample in an ice bath for 10 min or until the temperature drops to 10°C or less.	Samples must be chilled to reduce the volatility of NH_3. The volume change due to chilling is to be ignored.
2.	Meanwhile, with a graduated cylinder, deliver 50 ml of the H_3BO_3 solution to a 250-ml Erlenmeyer flask.	
3.	Pipet a sample aliquot containing 0.5 to 4.5 meq of NH_3 to the H_3BO_3 solution.	To avoid loss of NH_3, deliver the sample directly into the H_3BO_3 solution while mixing it continuously with a magnetic stirrer. For best reliability, select a sample with more than 1.5 meq of base.
4.	Add 5 drops of the bromocresol green - methyl red mixed indicator solution.	
5.	Titrate with standard 0.1N HCl to a gray-pink color.	The color transition is green to gray-pink to pink.
6.	Record the data and calculate the results as described on the example work sheet. Report all results to three significant figures.	

D. Titration of Sodium Carbonate

1. Pipet a sample aliquot containing 0.5 to 4.5 meq of Na_2CO_3 into a 125-ml Erlenmeyer flask. For best results, select a sample with more than 1.5 meq of CO_3.
2. Dilute to 50 ml with water.
3. Add 2 drops of Special Methyl Orange Indicator.
4. Using magnetic stirring, titrate with standard 0.1N HCl to a pink color. The color transition is blue to pink.
5. Record the data and calculate the results as described on the example work sheet. Report all results to three significant figures.

E. Titration of Sodium Hydroxide

1. Pipet a sample aliquot containing 0.5 to 4.5 meq of hydroxide into a 125-ml Erlenmeyer flask. For best results, select a sample with more than 1.5 meq of hydroxide.
2. Dilute to 50 ml with water.
3. Add 2 drops of phenolphthalein indicator.
4. Using magnetic stirring, titrate with standard 0.1N HCl to the disappearance of the pink color.
5. Record the data and calculate the results as described on the example work sheet. Report all results to three significant figures.

REFERENCES

1. N. A. Lange, Handbook of Chemistry, 8th ed., Sandusky, Ohio: Handbook Publishers, Inc., 1952, pp 1233-1235.

March 1968

S. S. Yamamura

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(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Total Alkalinity

CHARGE NUMBER _____ PROCEDURE Alkalinity - Vol - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Tare wt, g	Tare Plus THAM, g	Net Wt of THAM, g	Normality of HCl Titrant	Volume of HCl Used, ml	Meq Base in Sample	Meq Base Corr'd for Bias	RESULT
THAM Bench Standard	—	0 5250	0 8583	0 3333	0 1000	27 51	2751	2 75 ± 0.02	825 ± 006 meq/gram
NH_4OH-1	5 00 ml (Entire Sample Used)	—	—	—	0 1000	27 50	2 750	2 75 ± 0.02	0.550 ± 0 004 meq/ml

ANALYZED BY _____ DATE _____

CALCULATIONS:

Bench Standard

$F = DE = 0\,1000(2751)$

$= 2751$ meq

$\text{Result} = \frac{G}{\text{wt of standard}} = \frac{2\,75 \pm 002}{0\,3333}$

$= 8\,25 \pm 006$ meq/gram

Sample NH_4OH-1

$F = DE = 0\,1000(27\,50)$

$= 2\,750$

$\text{Result} = \frac{G}{\text{Samp Vol}} = \frac{2\,75 \pm 0.02}{5\,00}$

$= 0\,550 \pm 0\,004$ meq/ml

APPROVED BY _____

DETERMINATION OF ALUMINUM IN CERTAIN PLANT SAMPLES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

ABSTRACT

Aluminum in certain plant samples is determined by comparing the atomic absorption of a sample to the atomic absorption of a known set of standards. Samples and standards are aspirated as a 0.05M NH_4F-0.006M KCl-0.1M HBF_4 solution into a nitrous oxide-acetylene flame system.

APPLICABILITY

This method is applicable to the determination of any plant samples described in the following table:

TABLE I

PLANT SAMPLES ANALYZABLE BY THIS METHOD

Type of sample	Approximate Composition
Al-IFU, Al dissolver product	1.5M Al; 1.5M H^+; 6M NO_3^-; 0.007M Hg; ∿ 4 mg U/ml.
Al-IFD, Al dissolver product heel	Similar to Al-IFU above.
PM-175, Al nitrate complexer	1.4-2.0M Al; ∿ 1.4M H^+; 5.5-7.5M NO_3^-; ∿ 2.5 mg Cr(VI)/ml.
IFU, complexing solution	Similar to PM-175 above.
Al-Zr IFU, complexed dissolver product	0.5M Zr; 3.4M F^-; 0.7M Al; 2M H^+; 2.7M NO_3^-; ∿ 0.2M B; ∿ 2.5 mg U/ml.
WC-101, waste calciner raw feed, Zr type	Similar to Al-Zr IFU above plus calcium at about 0.6M.

All samples should be diluted with an accurately measured volume of NH_4F-KCl-HBF_4 solution to an aluminum concentration of 50 to 350 µg/ml. Optimum results are obtained in the 100 to 250 µg/ml range.

Although this dilution matrix was developed for the atomic absorption determination of zirconium where the absorbance is considerably enhanced by the presence of ammonium fluoride, it is also suitable for the determination of aluminum. Possible interferences are reduced to a level which eliminates the need for special standards compounded to match the composition of the sample. When the samples are diluted at least 1 to 100, there is no adverse effect when the concentration of the elements Zr, F, B, Cr, Ca, Hg, Sn, and U are varied individually or as a mixture by a factor of two or more from the expected concentrations.

Sulfate is a strong suppressant and should not be present in the sample if the analysis is to be accomplished with the set of standards provided with this method. If pyrosulfate or sulfate fusion is involved in the sample preparation, or if the original sample contains sulfate, appropriate sulfate-containing standards must be used or a prior separation of aluminum must be performed.

DISCUSSION

In establishing the optimum conditions for aluminum absorption, burner height was found to be the most critical parameter. In Figure 1, the flame profile shows that aluminum absorbance increases almost sevenfold as the burner height vernier setting is increased from 5 to 9. While there is a slight gain in absorbance for vernier settings above 9, this gain is offset by the increase in flame noise for all higher vernier settings.

Carbon deposits may build up on the perimeter of the burner slot. These deposits change both the shape and the path length of the flame and should be removed often. The absorption is sufficiently linear over the working range of 50 to 350 µg Al/ml to allow the analyst to use a bracketing or calibration procedure.

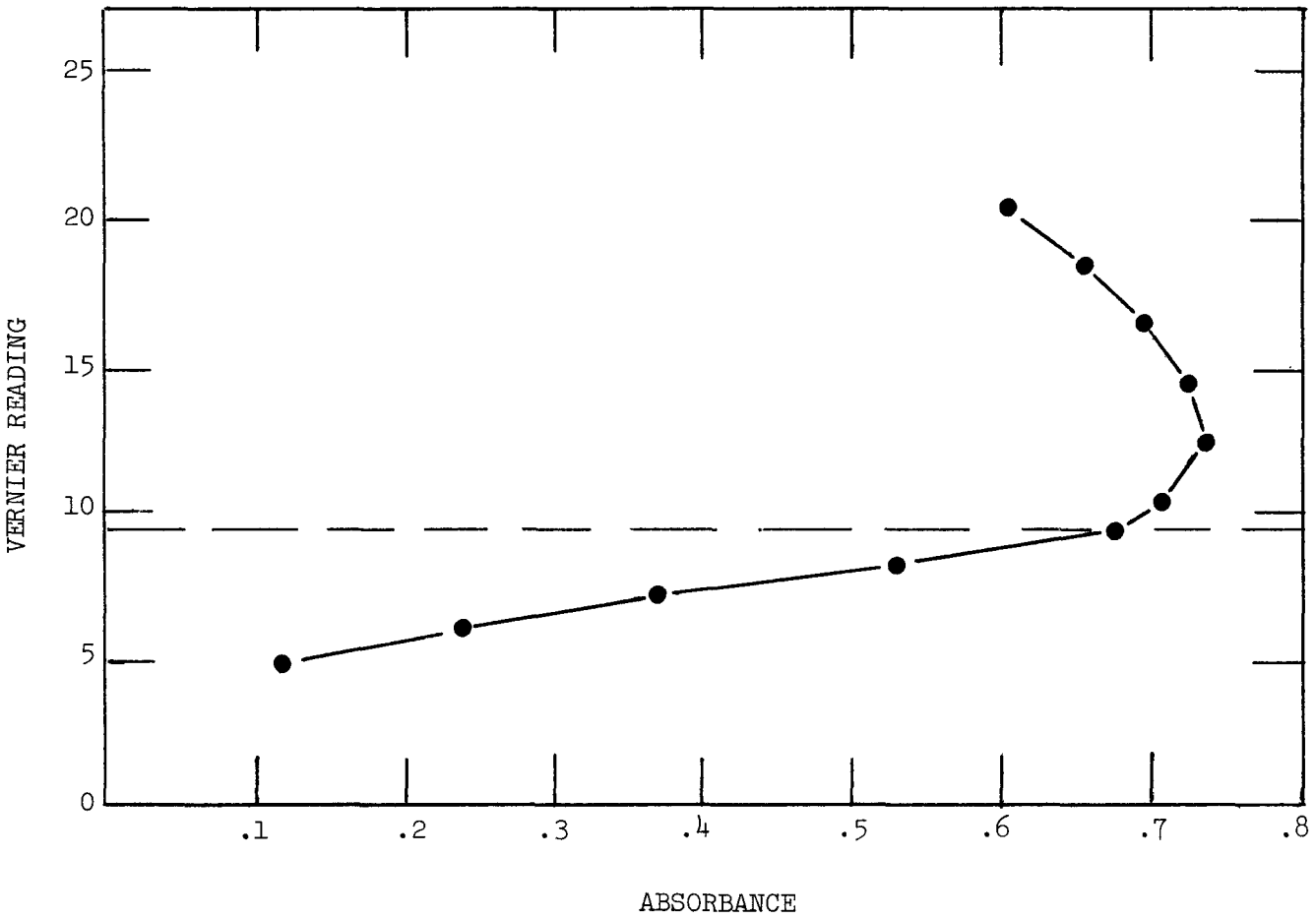

Fig. 1 Flame profile of aluminum absorbance.

SPECIAL SAFETY PRECAUTIONS

Explosions of nitrous oxide-acetylene mixtures are common; therefore, follow carefully all instructions for lighting and extinguishing the flame. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of the drain tube must extend below the surface of the liquid in the waste receptacle. Spills can be prevented by only partially filling the sample cups.

APPARATUS AND REAGENTS

A. Apparatus

1. Bottles, plastic, 2-oz.

2. Burner, nitrous oxide-acetylene, 6-cm slot.

3. Cups, plastic, caplugs No. 12X.

4. Spectrophotometer, atomic absorption, Techtron AA-5 or equivalent instrument with attachments.

5. Pipets, 100-µl and 20-ml, with control syringe and rubber suction bulb.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagent and matrix solutions.

1. Aluminum standard stock solution, 10.00 mg/ml. Dissolve 10.0000 g of high purity aluminum wire with hydrochloric acid and dilute to 1 liter. Use sufficient hydrochloric acid to give a final concentration ∿ 1M.

2. Sample diluent, 0.05M NH_4F-0.006M KCl-0.1M HBF_4. This matrix is used for the dilution of all samples and the preparation of aluminum standards and controls. To a 1-liter Nalgene volumetric flask, add 7.4 g of NH_4F and 1.79 g of KCl. Dissolve these salts in about 500 ml of water and add 71.7 g of 48% HBF_4. Dilute to volume with water and mix. Pour the contents into a 4-liter polyethylene bottle and, using the same 1-liter flask, add three more liters of water and mix.

3. Aluminum calibration standards. Dilute 5.00-, 10.00-, 15.00-, 20.00-, 25.00-, 30.00-, and 35.00-ml portions of the 10.00 mg/ml aluminum stock solution to 1 liter with the sample diluent. These seven standard solutions, which should be stored in polyethylene bottles, cover the concentration range 50 to 350 µg Al/ml in 50-µg increments.

4. Aluminum controls and bench standards. Following the directions given above for preparing calibration standards, prepare a series of 6 controls with aluminum concentrations in the range of 50 to 350 µg/ml. Designate two of the six, one around 75 µg/ml and another around 200 µg/ml, as bench standards for use in trouble-shooting or method checkout.

PROCEDURE

A. Sample Preparation

1. Plant Samples

Pipet 100 µl of sample to 200 ml of the sample diluent in to a 2-oz polyethylene bottle and mix well. Highly radioactive samples must be diluted remotely.

2. Bench-Controls Standards

No dilution is required on the controls. Process the controls as supplied.

B. Calibration

The analyst has an option of two methods of calibration. One method is to process the calibration standards for construction of a calibration curve. This is the preferred approach when there are many samples. The other approach is to process two standards that bracket the concentration of the sample. In either case, the standards are processed per Procedure D in the same manner as any sample.

C. Analysis of Controls

Analyze one control per Procedure D each time an analysis is performed. The result for the control must fall within specified limits. If it does not, process another control. Seek help if troubles continue.

D. Analysis of Samples

The analysis should be carried out in accordance with normal instrument operating procedures. Verify that the correct shut-down procedure was followed. If any control or condition is not as it should be, correct it.

	Operation	Specific Instructions
1.	Turn on power.	Three switches, one each on monochromator, readout unit and hollow cathode supply.
2.	Rotate hollow cathode into position.	Al hollow cathode.
3.	Set hollow cathode current.	Set at 10 ma and allow warmup of at least 10 min.
4.	Adjust hollow cathode position.	Circle of light should center on monochromator slit.
5.	Mount proper burner head.	Nitrous oxide-acetylene, 6-cm slot.
6.	Align burner with respect to light beam.	Adjust burner horizontal movement and rotation.
7.	Set burner height.	Set vernier at 9. Bottom of focused beam should be 0.078-in. above burner top.
8.	Set the wavelength dial.	Set at 3092.7 Å.
9.	a. Set the backing control.	Zero.
	b. Set the damping switch.	D
	c. Set the select switch.	Normal
	d. Set the mode switch.	% T
	e. Set the scale expand.	X 1
	f. Set the monochromator slit.	25 μ
	g. Set the coarse gain.	To give meter reading of about 50.

10.	Adjust wavelength to give maximum meter deflection.	Change gain as required to keep meter on scale.
11.	Verify that drain tube extends below surface of liquid in waste receptacle.	
12.	Set exhaust control at open.	
13.	Turn on supply valves.	Air, acetylene (C_2H_2), and N_2O are needed.
14.	Adjust regulator settings.	Air - 15 gauge C_2H_2 - 13 gauge N_2O - 24 gauge
15.	a. Turn support valve to air.	Adjust support pressure to 15 psi.
	b. Turn support valve to N_2O.	Support pressure should read 15 psi.
	c. Turn support valve off.	
	d. Turn fuel valve to C_2H_2.	Adjust flowmeter setting to 3.
	e. Turn support valve to air.	
	f. Light the burner.	Allow air to flow for at least 5 sec before lighting the burner.
	g. Raise fuel flowmeter setting to 9.	
	h. Rapidly switch support valve to N_2O.	
	i. Adjust flowmeter settings. (1) N_2O - 5.5 (flow) (2) C_2H_2 - $\sim$ 7.5 (flow)	Flow should be adjusted to obtain a pink inner cone about 0.625-in. high. Check by aspirating a standard.

16.	Adjust the exhaust control.	Close exhaust as necessary to stabilize flame, but never close exhaust completely.
17.	Block the light beam and set the readout zero.	Adjust with the backing control if necessary.
18.	With light beam unobstructed, adjust the gain controls.	Set for readout of 100.
19.	Turn mode switch to ABS.	Set for readout of zero with fine gain controls.
20.	Set select switch to auto 100 and the auto/read switch to auto. Aspirate blank solution.	Reset the readout to zero with the set 100 control.
21.	Set the scale expand control while aspirating standard solution with auto/read switch on read.	Set readout to 0.5 absorbance for 300 µg Al/ml standard.
22.	Aspirate blank solution with auto/read switch on auto.	
23.	Switch auto/read switch to read.	
24.	Move atomizer capillary to sample solution.	Wait for readout to reach a stable value.
25.	Record readout value on worksheet.	
26.	Transfer capillary to blank solution.	
27.	Switch auto/read switch to auto.	Repeat Steps 22-27 for all standard and sample solutions.

See instructions in the operating manual for calibration and use of curve corrector and direct readout attachment.

CALCULATIONS

The concentration of aluminum in the diluted sample can be obtained by either of two methods. A calibration curve relating absorbance to concentration can be plotted from the calibration standards data. The concentration of aluminum in µg/ml corresponding to the sample absorbance can be read from the calibration curve. The two standard, bracket method may also be used. The aluminum concentration of the diluted sample is then calculated from the following equation:

$$C = x_1 - \frac{[y_1 - y_s]}{[y_1 - y_2]} [x_1 - x_2] \qquad (1)$$

where

C = aluminum concentration of sample in µg/ml

Y_s = sample absorbance

x_1 = concentration of high standard

x_2 = concentration of low standard

y_1 = absorbance of high standard

y_2 = absorbance of low standard.

The result to be reported is calculated by substituting the concentration in µg/ml in the formula below and solving the equation.

$$\underline{M} = \frac{[(C + \text{bias}) \pm \text{sd})](201)}{1000(26.98)} \qquad (2)$$

where

$\underline{M}$ = molarity of aluminum in the sample

C = aluminum concentration in µg/ml

bias = µg of aluminum added or subtracted as shown by control data

sd = standard deviation of the control data

201 = dilution factor

26.98 = atomic weight of aluminum.

December 1970
T. R. Lyon
S. D. Reeder

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Aluminum

CHARGE NUMBER _____ PROCEDURE Al-AA-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Conc μg	Absorbance	μg in Sample	correction	Standard Deviation			RESULT M
Sample	01/201		0 357	1304	0 0	3 3			0 97±0 02
Std 1		100	0 275						
Std 2		150	0 410						

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\mu g\ Al\ in\ Sample = 150 - \left(\frac{0.410 - 0.357}{0.410 - 0.275}\right)(150 - 100) = 130.4$$

$$Result = \frac{(130.4 \pm 3.3)(201)}{(1000)(26.98)} = 0.97 \pm 0.02\ M$$

APPROVED BY _____

GRAVIMETRIC DETERMINATION OF ALUMINUM BY DIRECT IGNITION TO THE OXIDE

ABSTRACT

Aluminum in various aluminum salts and solutions is determined gravimetrically as the oxide following ignition at 1000°C. When maximum accuracy is needed, impurity elements are determined spectrographically and an appropriate correction is applied.

APPLICABILITY

This method, based on an ORNL method[1], is applicable to relatively pure aluminum salts or solutions, such as dibasic aluminum nitrate and aluminum nitrate used in the plant process, containing only small amounts of extraneous metals. In addition to nitrate, the aluminum can be accompanied by or be in the form of the Br^-, $CO_3^=$, Cl^-, F^-, OH^-, IO_3^-, I^-, NO_2^-, $S^=$, $SO_4^=$, $S_2O_3^=$, and organic complexes or precipitates such as cupferrate, ethylenediaminetetraacetic acid (EDTA) oxalate, and oxinate. Phosphate must not be present for aluminum phosphate is not converted to the oxide[2]. Low concentrations of spectrographically determinable elements do not interfere because corrections can be applied for their presence. Mercury, even in moderate amounts volatilizes completely and is not an interference. Uranium, if present in appreciable amounts, is removed initially by extraction with tributyl phosphate (TBP). The sample aliquot taken for analysis should contain between 75 to 150 mg of aluminum. This provides 140 to 280 mg of aluminum oxide accurately weighable on a balance sensitive to 0.1 mg.

Occasionally it may be desirable or necessary to determine the aluminum concentration more rapidly than is possible by this gravimetric procedure. Method Al-Vol-1 and Th-Vol-1 (Procedure D) in this manual may be suitable for these rapid determinations.

DISCUSSION

This method, though very simple and usually very reliable, will give faulty results if appropriate precautions are not exercised. Special attention should be directed to the evaporation of aqueous samples and to the initial ignition of the solid salt. These manipulations should be done slowly with moderate heat to minimize spatter losses. Aluminum oxide is hygroscopic and should be protected from atmospheric moisture after ignition.

SAFETY PRECAUTIONS

Use asbestos gloves and long platinum-tipped tongs when inserting crucibles into the furnace or removing them from the furnace.

APPARATUS AND REAGENTS

A. Apparatus

1. Balance, analytical with at least 100-g capacity and sensitivity to 0.1 mg.

2. Crucibles, platinum or porcelain with covers.

3. Culture tubes, 25- to 50-ml capacity with polyethylene-lined screw caps.

4. Desiccator.

5. Furnace, muffle, capable of providing 1100°C temperatures.

6. Heat lamp.

7. Meker burner.

8. Pipets, macro and micro, assorted sizes, with syringe and suction bulb.

9. Test tubes, borosilicate glass, 15- x 125-mm with fitting polyethylene stoppers.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagents.

1. Aluminum bench standard I, 25.00 mg Al/ml. Dissolve 12.500±0.005 g of pure aluminum metal in 200 ml of 8M HCl under reflux. Chill the solution to room temperature, then dilute to 500 ml with water.

2. Aluminum bench standard II, 25.00 mg Al/ml, with uranium. Prepare as above except add 10.6 g of $UO_2(NO_3)_2 \cdot 6H_2O$ dissolved in 100 ml of water to the aluminum solution before dilution to volume.

3. n-Hexane.

4. Nitric acid, conc.

5. Tributylphosphate(TBP)-n-hexane solution, 25% by volume TBP equilibrated with 6M HNO_3. Mix 100 ml of TBP with 300 ml of n-hexane. Contact the mixture for 3 min in a 1-liter separatory funnel with 100 ml of 6M HNO_3. Drain the nitric acid, then transfer the TBP-hexane solution to a stoppered bottle.

PROCEDURE

A. Bench Standard

Process a 5.00-ml aliquot of the appropriate bench standard per Procedure C (bench standard without uranium) or Procedures B and C (bench standard with uranium). Acceptable limits will be specified by the Quality Control Laboratory.

B. Removal of Uranium by Extraction

1. Pipet a sample aliquot containing 75 to 150 mg of Al into a test tube or culture tube.

2. Add sufficient conc HNO_3 to adjust the HNO_3 concentration to 6±1M.

The HNO_3 concentration must be 6±1M to obtain adequate extraction of uranium. If the sample volume is large, evaporate it to a small volume, then add the HNO_3.

3. Add an equal volume of TBP-hexane solution, stopper, and extract vigorously for 3 min.

4. Let the two phases separate, then remove the majority of the top organic phase without removing any of the aqueous phase.

Use a fine-tipped pipet or medicine dropper on a vacuum train to remove the TBP-hexane extractant. Complete removal of the organic phase is not essential.

5. Repeat Steps 3 and 4.

6. Repeat Steps 3 and 4 using pure n-hexane in place of the TBP-hexane solution.

If the sample contains enriched U, consult the laboratory supervisor.

7. Proceed to Procedure C. Tare a crucible per C-1, transfer the extracted sample to the crucible with small water rinses, then continue beginning at Step C-3.

C. Gravimetric Determination of Aluminum

1.	Ignite the crucibles and covers at 1000°C to constant weight (within ±0.3 mg) and record the exact tare weight to the nearest 0.1 mg.	Platinum crucibles are recommended except for samples which yield Cl that attacks Pt.
2.	Pipet a sample aliquot containing 75 to 150 mg of Al to the tared crucible.	
3.	Carefully evaporate to dryness under an infrared lamp.	A hot plate at low heat may be used to hasten the evaporation; however, precautions should be taken to prevent spatter losses.
4.	Ignite the dry residue slowly and cautiously over a small flame of a Meker burner.	
5.	Ignite the crucible without its cover for 30 min in a muffle furnace at 1000°C.	
6.	Remove the crucible from the furnace, replace the lid on the crucible, and let the crucible cool to room temperature in a desiccator.	
7.	Weigh to the nearest 0.1 mg.	
8.	Repeat Steps 5, 6, and 7 until the weight is constant to within ±0.3 mg.	
9.	Record the data and calculate the results as described under CALCULATIONS.	
10.	If the result is to be corrected for impurities, submit the ignited oxide to the Spectroscopy Laboratory.	

CALCULATIONS

Record the data and calculate the results as described on the example work sheet. Report four significant figures for all results.

If the gravimetric results are to be corrected for impurities, the ignited oxide is submitted for spectrographic analysis. The spectrographic results normally are reported as parts per million (µg/g) of the impurity element in the aluminum oxide and must be converted to equivalent µg/g element oxide. Listed below in Table I are the conversion factors for those elements most likely to be encountered. These conversion factors are obtained by dividing the formula weight of the oxide by the atomic weight of the element taken as many times as it appears in the formula of the oxide.

TABLE I

FACTORS FOR CONVERSION OF µg/g ELEMENT TO µg/g ELEMENT OXIDE

Element and Assumed Oxidation State	Conversion Factor	Element and Assumed Oxidation State	Conversion Factor
Ba, +2	1.12	Mo, +6	1.50
Bi, +3	1.11	Na, +1	1.35
Ca, +2	1.40	Ni, +2	1.27
Cd, +2	1.14	Pb, +2	1.08
Ce, +4	1.23	Si, +4	1.57
Co, +3	1.41	Sn, +4	1.27
Cr, +3	1.46	Sr, +2	1.18
Cu, +2	1.25	Ti, +4	1.67
Fe, +3	1.43	U, +5.3	1.18
K, +1	1.20	W, +6	1.26
Mg, +2	1.66	Zn, +2	1.24
Mn, +4	1.58	Zr, +4	1.35

To calculate the appropriate impurities correction:

(1) Convert µg/g element values to µg/g element oxides by applying the appropriate conversion factor.

(2) Add the individual µg/g element oxide values to obtain total µg/g element oxides.

(3) Multiply the result obtained in (2) by 10^{-6} to convert the element oxides concentration from µg/g to g/g. The number obtained here will generally be a decimal fraction such as 0.0021 g/g.

(4) Multiply the value obtained in (3) by the weight of the ignited aluminum oxide to obtain the appropriate impurity correction.

The gravimetric conversion factor for converting aluminum oxide to aluminum is $2Al/Al_2O_3 = 0.5292$.

REFERENCES

1. J. G. Surak, P. F. Thomason, ORNL-1931 (1955).

2. G. Duval, Inorganic Thermogravimetric Analysis, New York: Elsevier Publishing Company, 1953, p 226ff.

March 1968

S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Al

CHARGE NUMBER _____ PROCEDURE Al-Grav-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Wt of Crucible, Grams	Wt of Crucible plus Oxide	Wt of Oxide, Grams	Impunty Correction, Grams	Net Wt of Oxide	Mg Al in Aliq Analyzed	Mg Al Corr'd for Bias	RESULT mg Al/ml
Diban - 1	2 00 ml	534777	536685	01908	None	0.1908g	101 0	101.0± 05	5050±025

ANALYZED BY _____ DATE _____

CALCULATIONS:

$F = (\text{wt of oxide})(1000)(0.5292) = 5292(E)$

$= 1010$ mg Al

$\text{Result} = \frac{G}{\text{Samp Vol}} = \frac{1010 \pm 05}{200} = 5050 \pm 025$ mg Al/ml

APPROVED BY _____

VOLUMETRIC DETERMINATION OF ALUMINUM

ABSTRACT

Aluminum is determined indirectly by titrating the hydroxyl ions released when aluminum, in the basic aluminate form, is complexed with an excess of fluoride. The end point of the titration is determined potentiometrically. Various interferences are eliminated by an initial perchloric acid fuming and by oxalate complexing.

APPLICABILITY

This adaptation of Hay's method [1] is fairly selective and applicable to a variety of samples. These samples include solutions from the processing of both aluminum-clad and zirconium-clad uranium fuels and could contain some or all of the ions: BO_2^-, Ca(II), Cr(III), F^-, NO_3^-, Sn(IV), U(VI) and Zr(IV).

Potential interferences are: (a) anions such as citrate, EDTA, fluoride, phosphate, and tartrate that complex aluminum; (b) large concentrations of common anions such as chloride and nitrate that adversely affect reliability; and (c) metal ions that form insoluble hydroxides, especially those metal ions that also are complexed by fluoride.

The interference of anions except phosphate is avoided by fuming the sample with perchloric acid. The fuming also effectively breaks up hydroxy complexes of aluminum and eliminates Cr(III) interference by oxidizing it to noninterfering Cr(VI) [2].

Phosphate buffers the titration medium and decreases both the precision and accuracy of the determination [3]. At a phosphate to aluminum molar ratio less than 5:1, the phosphate effect can be minimized by standardizing the titrant against aluminum standards containing phosphate in amounts similar to that of the sample. At higher ratios, aluminum must be determined by other techniques such as spectrophotometry or emission spectrography.

Most metal ions are potential interferences. They may, like aluminum, convert to a hydroxide or an oxy anion, then react with fluoride to release hydroxide. Others may precipitate under the analysis conditions and coprecipitate aluminum. Therefore, metal ions must be removed by actual physical separation or rendered inactive by in-situ masking. This method employs oxalate for masking which effectively prevents the interference of Ca(II) at a 4:1 molar ratio, Hg(II) at 15:1, Pb(II) at 3:1, and the metal ions: Bi(III), Ce(III, IV), Cu(II), La(III), Mo(VI), U(VI), V(V), and Zr(IV) at 1:1 (Table I).

Oxalate masking is inadequate for 1:1 ratios of Fe(III) and Ni(II) which precipitate as the hydroxide and carry down aluminum even in the presence of oxalate. Oxalate masking also is inadequate for Cr(III);

however, as discussed previously, the initial perchloric acid fuming oxidizes Cr(III) to noninterfering Cr(VI). One gram of iron, for example, carries 30 mg of aluminum. Table I lists the known tolerance levels for these ions. Cadmium(II), Co(II), and Zn(II) also interfere at the 1:1 metal to aluminum molar ratio. Tolerance ratios for these ions have not been established. Thorium(IV) which behaves like aluminum interferes at 1:1, but its interference can be avoided by filtering off thorium oxalate at pH 2. In the filtration, the pH must be held at about 2. At higher pH, aluminum partially hydrolyzes to filterable aluminum hydroxide and results will be low.

TABLE I

TOLERANCE RATIOS OF DIVERSE METAL IONS

Ion	Permissible Metal to Aluminum Molar Ratio
Bi(III), Ce(III, IV), Cu(II), La(III), Mo(VI), U(VI), V(V), Zr(IV)	At least 1 for each ion individually.
BO_2^-	0.2[a]
Ca(II)	4
Cr(III)[b]	0.5
Cr(VI)	10[a]
Fe(III)	0.3
Hg(II)	15
Ni(II)	0.05
Pb(II)	3[a]
Sn(IV)	0.02[a]

[a] Highest ratio studied. Aluminum level was held at 8 mg (0.3 mM) in the study of diverse ion effects.

[b] This is the interference level without the initial perchloric acid fuming. See text.

Ions, such as acetate, ammonium, carbonate, and dichromate, that buffer at a low pH will have little effect at the high pH (10.5) used in this procedure.

Occasionally, stainless steel and other very complex samples with high diverse ion concentrations may be involved. Mercury cathode

electrolysis is recommended for the removal of metal ions from these samples. This technique efficiently removes Ag, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, Ir, Mo, Ni, Pd, Po, Pt, Re, Rh, Sn, Tl, and Zn. It also converts As, Os, Pb, Se, and Te into forms removable by filtration.

The range of the titration procedure is 1.5 to 25 mg of aluminum. From a practical standpoint, the largest sample aliquot is 50 ml. This permits the analysis of solutions as low as 0.03 mg/ml in aluminum. When the diverse metal ion content is low, the aluminum present in large sample volumes may be concentrated by evaporation. The upper range of the method is fixed by the 0.4M strength of the titrant and the 10-ml capacity of the buret. However, by refilling the buret during a titration, up to at least 40 mg of aluminum can be determined in the absence of metal ions.

DISCUSSION

Aluminum ions are converted to aluminate at a high pH(>12.5), then reacted with potassium fluoride to release hydroxyl ions by the reaction:

$$NaAlO_2 + 6KF + 2H_2O \longrightarrow \underline{K_2NaAlF_6} + 4KOH \qquad (1)$$

Titration of the hydroxyl ions with a standard acid provides a measure of the aluminum present. Theoretically 4 moles of hydroxyl ions are released per mole of aluminum. In practice, however, the reaction is not stoichiometric and only about 3.9 moles of hydroxide are released per mole of aluminum. To correct for this nonstoichiometry, an aluminum standard is titrated with the acid titrant and an aluminum titer or conversion factor is assigned to the titrant. The factor with the units, mg Al/ml, must be determined for each new batch of titrant.

The principal steps of this procedure are:

(1) Evaporation of the sample with perchloric acid

(2) Addition of oxalate

(3) Conversion of Al(III) to aluminate at pH 12.75 ± 0.25

(4) Readjustment of the pH to 10.55 ± 0.05

(5) Addition of potassium fluoride

(6) Titration of the hydroxyl ions released with standard hydrochloric acid to the preadjusted pH of 10.55 ± 0.05.

Each step is critical and should be carried out as prescribed.

As noted under APPLICABILITY, the perchloric acid fuming removes anionic interferences, breaks up hydroxy complexes of aluminum,

and oxidizes Cr(III) to Cr(VI). This is a critical step because results will be low if the aluminum is converted to insoluble species by excessive heating. Of course, if the sample contains organic matter, there must be nitric acid present at the start of the digestion to prevent an explosion.

Oxalate in acid medium reduces noninterfering Cr(VI) to Cr(III) which cannot be tolerated except in small amounts (Table I). It is important, therefore, to adjust the pH to 12.75±0.25 immediately after the addition of oxalate. In basic medium, Cr(VI) is not reduced by oxalate.

Aluminum is converted to aluminate when the pH is raised to 12.75±0.25. If the pH goes above 13, the results tend to be low and the sensitivity decreases. As noted under APPLICABILITY, high concentrations of common anions decrease precision and accuracy; hence, a large excess of base should be avoided. In some samples such as those containing high amounts of uranium the pH may not rise above 12.5. If the pH does not rise after the addition of 2 to 3 drops of 50% (w/w) NaOH, discontinue the addition and continue with the procedure.

The readjustment of the pH to 10.55±.05 must be done slowly as the pH approaches 12. If the pH is lowered too rapidly, the tendency is to drop below 10.5 where some aluminate reverts to aluminum hydroxide. This aluminum hydroxide does not always convert to the aluminate form on reajustment to pH 10.55±0.05 and the results may be low.

The volume of potassium fluoride reagent added must be closely controlled especially if there is an appreciable titration blank. Though prepared identically, different potassium fluoride solutions yield blanks ranging from 0.03 ml to 0.25 ml. A fresh solution must be prepared and a blank determination must be performed each shift.

The final titration must be performed at room temperature with efficient stirring. High temperatures cause high results while inadequate stirring leads to low results, especially when copious amounts of precipitate are present.

SAFETY PRECAUTIONS

Extreme care should be taken in the fuming of samples with perchloric acid to make sure there are no organics present. Fuming should be done in a special perchloric acid hood. Dilute all acid solutions carefully, especially after fuming. Concentrated sodium hydroxide and conc $HClO_4$ can cause serious burns. Wash contacted areas with copious amounts of water.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, low-form, 50-ml with 10-ml graduations.

2. Buret, 10-ml, graduated in 0.02-ml increments.

3. Electrode, combination calomel-glass, high pH range (to pH 13). The Thomas electrode has proved satisfactory.

4. Hot plate.

5. Magnetic stirrer with plastic-coated magnetic stirring bars.

6. pH meter.

7. Pipet, volumetric, macro and micro; assorted sizes with control syringe and suction bulb.

8. Ring stand with buret clamp.

9. Watch glass, 3-in., Speedyvap.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water throughout.

1. Aluminum calibration standard, 13.00 mg Al/ml. Dissolve 13.00 g of pure aluminum metal in HNO_3 and dilute to 1 liter. Catalyze the dissolution with $Hg(NO_3)_2$. About 3 drops of a 1M solution is usually sufficient.

2. Aluminum bench and control standards. Prepare standards by dissolving aluminum metal in nitric acid as described for reagent 1.

3. Buffer solution, pH 10.

4. Hydrochloric acid, 6M.

5. Hydrochloric acid titrant, 0.4M.

6. Diverse ion matrix, 0.4M Zr, 0.008M Cr, 2.4M HF and 1.3M Ca. Place 19 g of Zircaloy II and 25 ml of water in a 500-ml Teflon beaker. Add slowly 42 ml of conc HF. After the Zircaloy has dissolved, add 72.1 g of $CaCl_2$ and 1.24 g of $Cr(NO_3)_3 \cdot 9H_2O$. Dilute to 500 ml with water. Filter the solution and store the filtrate in a polyethylene bottle.

7. Perchloric acid, conc.

8. Potassium fluoride solution. Using a Teflon beaker, dissolve 30 g of $KF \cdot 2H_2O$ in 20 ml of water. Bring the solution to room

temperature and adjust the pH to 11.25±0.15 with silica-free 1M KOH. Prepare a fresh solution each shift and store it in a screw-cap polyethylene bottle.

9. Potassium hydroxide, 1M, silica-free.

10. Potassium oxalate solution, 2M. Dissolve 368.5 g potassium oxalate, monohydrate, in 500 ml of water and dilute to 1 liter in a volumetric flask.

11. Sodium hydroxide solution 50% (w/w).

PROCEDURE

A. Blank

A blank determination is required each time a fresh solution of potassium fluoride is made. Process the blank per Procedure D beginning at Step 2. If the pH drops when the potassium fluoride is added, record the blank as zero. Add 0.5 ml of matrix to the blank if it is also added to the bench and control standard.

B. Standardization of 0.4M HCl Titrant

Each new batch of 0.4M HCl must be standardized against the 13.00 mg/ml aluminum standard. To standardize a new titrant, each crew is to analyze two 1.00-ml aliquots of the 13.00 mg/ml aluminum standard per Procedure D. Report the data to the Quality Control Laboratory for calculation of the conversion factor.

C. Analysis of Bench and Control Standard

Process a bench standard according to Procedure D with each series of samples. If the samples contain metal ions, add 0.50 ml of the diverse ion matrix to the bench standard. The result for the bench standard must fall within limits specified by the Quality Control Laboratory. If not, process another bench standard. Contact your supervisor if troubles persist.

D. Analysis of Samples

1. Pipet a sample aliquot containing 1.5 to 25 mg of Al into a 50-ml beaker graduated in 10-ml increments.	Steps 2 through 6 may be omitted if the sample is known to be free of F^-, Cr(III), high concentrations of acids, and hydroxy aluminum species.
2. Add 1 ml of conc $HClO_4$.	
3. Cover with a Speedyvap watch glass and evaporate to near dryness on a hot plate set at low heat. Do not bake the sample.	The ideal time for terminating the fuming is when liquid $HClO_4$ is not visible but the residue is still moist and perchloric fumes are still being evolved.

4.	Remove the beaker from the hot plate and allow it to cool.	
5.	Add 5 drops of conc $HClO_4$ and about 1 ml of water.	
6.	Dissolve the residue by warming the solution on a hot plate set at low heat. Swirl the contents occasionally and heat until water vapor just starts to evolve.	If the residue does not dissolve, add 1 or 2 drops of conc HCl.
7.	Cool the sample and dilute to 15 ml with water. Let the diluted sample cool to room temperature.	Best results are obtained if the final volume at the end of the titration is less than 40 ml; therefore, the volume at this stage must not exceed 15 ml. The sample must be cooled to room temperature or the results will be high.
8.	Standardize the pH meter with pH 10 buffer.	
9.	Add a plastic-coated magnetic stirring bar to the beaker, place the beaker on the stirrer, and adjust the stirrer speed to give satisfactory mixing.	Thorough stirring is necessary to obtain good results.
10.	Insert the tip of the electrode into the solution.	
11.	Add 5 ml of the 2M potassium oxalate solution and immediately adjust the pH to 12.75 ± 0.25 with 50% (w/w) NaOH.	In acidic medium, oxalate reduces Cr(VI) to Cr(III) so the NaOH must be added without delay. Do not exceed pH 13 because high salt concentrations cause low erratic results. If the pH rises above 13, discard the sample and process a new one.

12.	Immerse the buret tip into the solution. To adjust the pH to 10.55±0.05, add 6M HCl dropwise until the pH approaches 12, then add the 0.4M HCl titrant from the buret until the pH is within the range 10.55±0.05. Record the exact pH to the nearest 0.01 pH unit.	The pH should not drop below 10.5. If it does, results will likely be low so discard the sample and process a new one.
13.	Pipet 2.0 ml of the KF solution into the sample.	
14.	Fill the buret with the 0.4M HCl titrant and titrate the solution to the exact pH recorded in Step 12.	Some titrations are characterized by drifting pH near the end point. Wait 30 sec between increments of titrant and continue the titration until the drifting stops.
15.	Record the data and calculate the results as shown on the example work sheet. Report all results to 3 significant figures.	

REFERENCES

1. S. A. Hays, "The Acidimetric Determination of Aluminum with Fluoride at pH 10-11", HW-18178, Richland, Washington (1950).

2. D. R. Trammell, Personal Communication.

3. M. A. Wade, Personal Communication.

January 1969

J. A. Rindfleisch
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Aluminum

CHARGE NUMBER _____ PROCEDURE Al-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Volume 0.4M HCl used, ml	Blank, ml	Acid Factor mg Al/ml	mg Al	mg Al corrected for Bias	mg Al/ml		RESULT M
#1	0.500 ml	3.41	0.03	2.64	8.92	8.80±0.15	17.6±0.3		0.65±0.01

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = (A-B)(C) = (3.41 - 0.03)(2.64) = 8.92 \text{ mg Al}$$

$$F = \frac{E}{0.500} = \frac{8.80 \pm 0.15}{0.500} = 17.6 \pm 0.3 \text{ mg Al/ml}$$

$$\text{Result} = \frac{F}{26.98} = \frac{17.6 \pm 0.3}{26.98} = 0.65 \pm 0.01 \text{ M}$$

APPROVED BY _____

COLORIMETRIC DETERMINATION OF BARIUM WITH METALPHTHALEIN

ABSTRACT

Barium(II) reacts with metalphthalein (o-cresolphthalein complexone) in an ammoniacal medium at pH 11.3 to form a violet complex. The absorbance of the complex is measured spectrophotometrically at 575 mμ.

APPLICABILITY

This method based on published reports[1, 2] has been adapted to water samples of high purity such as reactor coolant water with little or no interferences. Interferences are of three main types: those that complex or precipitate barium(II), those that react with metalphthalein, and those that alter the pH of the color development medium. Examples of the first type are carbonate, oxalate, phosphate, and sulfate. These produce low results. Metalphthalein is a very unselective reagent hence most metal ions with the exception of the alkali metals represent the second type of interference. The effect of metal ions varies depending on the absorbance characteristics of the diverse ion-metalphthalein complex relative to that for the barium(II)-metalphthalein complex and/or the free indicator. If the diverse ion-metalphthalein complex absorbs more strongly than the barium(II)-metalphthalein complex or metalphthalein at the working wavelength for barium, the interference will be positive. If the reverse is true, results will be biased low. The intensity of the barium(II)-metalphthalein complex is very sensitive to pH. Acidic or basic samples, therefore, must be neutralized prior to analysis.

The range of this method is 20 to 100 μg of barium. The maximum sample size is 50 ml; hence, the concentration sensitivity limit is 0.4 ppm barium in the original sample.

DISCUSSION

At pH 11.3, the absorbance spectrum of free metalphthalein is similar to that for the barium(II) complex and absorbs strongly at 575 mμ[2]. The addition of metalphthalein, therefore, should be made accurately and all samples must be measured against the reagent blank.

Metalphthalein and its barium complex are unstable. A fresh solution of chromogen must be used for each run. Also, samples should be read within 20 min after color development.

The harmful effect of carbonate has been noted in the preceding section. During the sampling process, care must be taken to prevent absorption of carbon dioxide. The absorption of carbon dioxide is particularly serious under basic conditions. Color development, therefore, should be carried out as rapidly as possible after the addition of ammonium hydroxide and in the final mixing, vigorous agitation should be avoided[2].

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, Pyrex, 5-cm.
2. Bottle, sampling, polyethylene.
3. Erlenmeyer flasks, 125-ml.
4. Flasks, volumetric, 100-ml.
5. Graduated cylinders, assorted sizes.
6. Medicine droppers.
7. pH meter with glass-calomel electrode system.
8. Pipets, micro, assorted sizes, with control syringe.
9. Pipets, volumetric, assorted sizes, with suction bulb.
10. Spectrophotometer, Beckman Models B, DU, or DK, or Cary Model 14.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium hydroxide, 0.75M.
2. Barium stock solution, 10.00 mg Ba/ml. Dissolve 19.05±0.01 g of barium nitrate in 500 ml of distilled water. Dilute to 1 liter with distilled water.
3. Barium calibration standard I, 50 µg Ba/ml. Pipet 5.00 ml of the barium stock solution into a 1-liter volumetric flask and dilute to volume with distilled water.

4. Barium calibration standard II, 75 µg Ba/ml. Pipet 7.50 ml of the standard stock solution into a 1-liter volumetric flask and dilute to volume with distilled water.

5. Metalphthalein indicator solution, 0.1% (w/v). Dissolve 0.050 g metalphthalein in 14 ml of 0.75M NH_4OH. Dilute to 50 ml with water and mix. Prepare a fresh solution for each series of samples.

6. Nitric acid, 8M.

7. Sodium hydroxide, 8M.

PROCEDURE

A. Reagent Blank

Process a reagent blank per Procedure D beginning at Step 4.

B. Calibration

1. A separate calibration is required for each series of samples. Process 1 ml of two of the bench standards according to Procedure D.

2. Divide the micrograms of Ba in each aliquot by its respective absorbance.

This establishes the conversion factor to calculate the concentration of Ba in the sample.

3. The difference between the conversion factors and their average should agree within limits set by the Quality Control Laboratory.

If the difference or the average does not agree, process another pair. If these disagree, contact your supervisor.

C. Sampling

1. Let the sample flow at a moderate rate from the sample line for 1 min.

A health physicist and a reactor engineer must be present when sampling. The health physicist measures the activity level of the sampling area and the reactor engineer establishes the rate of flow through the sampling station

2.	Rinse the inside of the sample bottle with the sample.	Prevent splashing to avoid possible contamination of the area.
3.	Fill the sample bottle with the sample and tightly cap it.	Prevent unnecessary absorption of CO_2 by keeping the sampling tubing beneath the surface of the sample.
4.	Rinse the outside of the sample bottle with demineralized water.	
5.	Place the sample bottle in the standard radiation measurement holder.	Request the health physicist to measure the radiation level.
6.	Transport the sample to the laboratory in a rubber safety bucket lined with a plastic bag.	If the sample reads greater than 1 R/hr, transport it in a shielded container.

D. Analysis of Samples

1.	Measure the pH of the sample. If within the range 5 to 12, proceed to Step 3. If outside the range, proceed to Step 2.	
2.	Transfer 100 ml of sample to a 125-ml Erlenmeyer flask. Adjust the pH to 10.0±0.5 with 8M NaOH or 8M HNO_3.	The dilution will be neglected in the calculation. If more than 1 ml of 8M NaOH and 8M HNO_3 is used, contact your supervisor.
3.	Pipet an aliquot of the sample containing from 20 to 100 µg of Ba into a 100-ml volumetric flask.	The maximum volume is 50 ml. Highest reliability is obtained at a level of 60 µg. Select the aliquot volume accordingly. Simultaneously process the reagent blank, the 2 calibration standards, and the samples from Steps 4 through 9. The color of the Ba-metalphthalein complex in unstable and must be read within 20 min after color develop-

		ment. Limit the number of samples to remain within this time period.
4.	Dilute to 50 ml with water.	
5.	Pipet 25 ml of 0.75M NH_4OH.	
6.	Add 3 ml of the metalphthalein indicator solution.	The metalphthalein reagent is unstable. Prepare a fresh reagent just prior to use per the directions given under APPARATUS AND REAGENTS.
7.	Dilute to volume with distilled water and stopper the flask.	
8.	Mix by gently inverting the flask at least 7 times.	Do not shake vigorously. Absorbance decreases with strong mixing [2].
9.	Measure the absorbance against the reagent blank within 20 min after the addition of the metalphthalein indicator solution (Step 6) at 575 mμ in 5-cm cells.	Set the absorbance at 0.000 with the reagent blank.
10.	Record the data and calculate the results as shown on the example worksheet. Report results to 2 significant figures.	

REFERENCES

1. Greenaway, W. R., Letter WAPD-C1(cc)-112, attachment A, "Procedure for Determining Barium in High Purity Water", February 8, 1966.

2. Pollard, F. H., and Martin, J. V., "The Spectrophotometric Determination of the Alkaline-earth Metals with Murexide, Eriochrome Black T, and with o-Cresolphthalein Complexone", Analyst 81,(1956) p 348.

H. A. Shogren
S. S. Yamamura

August 1967

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Barium

CHARGE NUMBER _____ PROCEDURE Ba-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance VS Reagent Blank	Conversion Factor, µg/A	µg Ba in Aliquot Analyzed	µg Ba corrected For Bias				RESULT µg Ba/ml
Std, 50 µg		0.482	103.7						
Std, 75 µg		0.726	103.3						
		$\bar{X}$	103.5						
Sample X	50 ml	0.573		59.3	56.8±2.6				1.1 ± 0.05
Sample Y	5ml/25ml/5ml	0.623		64.5	62.0±2.6				62 ± 2.6

ANALYZED BY _____ DATE _____

CALCULATIONS:

B = Conversion Factor = $\frac{\mu g\ Ba}{A}$

$B' = \frac{50}{0.482} = 103.7$, $B'' = \frac{75}{0.726} = 103.3$

$\bar{X} = 0.5(B' + B'') = 0.5(103.7 + 103.3) = 103.5\ \mu g\ Ba/absorb.\ unit.$

For Sample X: µg Ba Analyzed = $AB = 0.573(103.5) = 59.3$

Result = $\frac{56.8 \pm 2.6}{50} = 1.1 \pm 0.05\ \mu g\ Ba/ml$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH CURCUMIN

ABSTRACT

Boron is reacted with curcumin in a 2:1 acetic acid-sulfuric acid medium to form the red boron-curcumin complex. The red complex is precipitated with aqueous 3M HCl, separated on a membrane filter, redissolved in ethanol, and measured spectrophotometrically at 555 mμ. The method is applicable to aqueous chloride and sulfate solutions that do not contain oxidants such as nitrate and perchlorate. With proper precautions to minimize contamination, the method can be used to determine 0.125-ppm concentrations of boron in aqueous solutions.

APPLICABILITY

This method, adapted from a published report[1], is applicable for the determination of microgram and submicrogram levels of boron in aqueous solutions. The range of the method varies between 0.025 to 5 μg of boron depending on the dilution and the length of the optical cell (Figure 1). The 0.025-μg value is the practical lower limit with a 25-ml dilution and absorbance measurements in 5-cm cells.

Fluoride which complexes boron and oxidants such as nitrate and perchlorate that destroy the curcumin reagent interfere seriously even at very low concentrations. Zirconium and stainless steel in amounts less than 20 mg do not interfere. Aluminum in the range 2 to 15 mg appears to suppress the color development by a slight constant amount. Therefore, when analyzing aluminum samples, aluminum matrix controls must be processed simultaneously to establish the necessary bias correction.

DISCUSSION

The principal steps of this procedure are: (a) development of the boron-curcumin complex in a 2:1 acetic acid-sulfuric acid medium, (b) removal of excess curcumin, and (c) measurement of the red boron-curcumin complex at 555 mμ. In each step there are a number of variables that must be understood and controlled.

The two important variables of the complex formation, step (a), are water concentration and reaction time. Water, one of the products of the boron-curcumin reaction, affects the color development. Up to 0.25 ml of water has no effect, 0.25 to 0.45 ml has a slight suppressing effect, and greater than 0.45 ml of water decreases the color development markedly. For maximum sensitivity and high versatility, a procedure based on the control of water at 0.4 ml has been adopted in this method. With the water level at 0.4 ml and a 6-ml 2:1

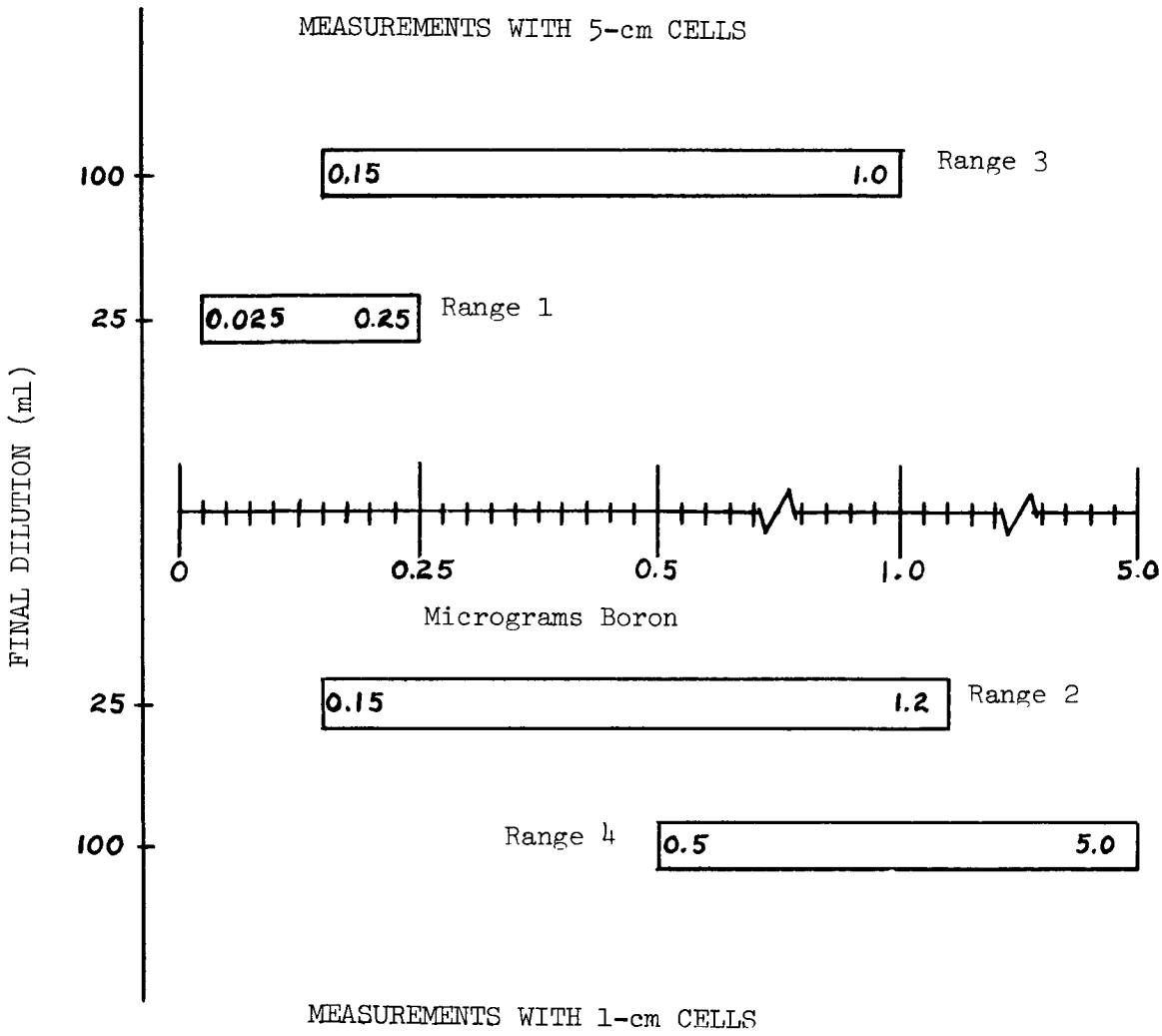

Fig. 1 Ranges of the method.

acetic acid-sulfuric acid reaction medium, the boron-circumin reaction is complete in 15 min. Once formed the complex is stable for an additional 45 min in the acetic acid-sulfuric acid medium. The satisfactory color development period is, therefore, 15 to 60 min.

In strongly acidic medium, curcumin is a dark red protonated species which absorbs at the 555-mμ peak of the boron-curcumin complex. Two techniques can be used to "remove" the curcumin: the boron-curcumin complex can be precipitated with water and isolated by filtration or the red protonated curcumin can be reverted to the yellow unprotonated curcumin (which does not absorb significantly at 555 mμ) by extensive dilution with ethyl alcohol. The filtration procedure which is the better of the two for micro determinations is used in this method. The addition of water (actually, 3M HCl is used in this method to prevent the interference of tin which also reacts with the reagent) quantitatively precipitates the boron-curcumin complex in 2 min. The addition of water also promotes the decomposition of the boron-curcumin complex. The precipitate, therefore, must be filtered within the interval of 2 to 4 min after the addition of the 3M HCl and the 3M HCl addition must be staggered for a series of samples to meet this requirement. Some curcumin also is precipitated by the 3M HCl. This residual curcumin is removed with an ether wash. The isolated boron-curcumin complex is redissolved in ethyl alcohol for measurement. Because water decomposes the boron-curcumin complex, absolute alcohol is best, but if absorbance measurements are made within 4 hr, 95% ethyl alcohol is satisfactory.

Boron contamination will be the primary source of problem in this method especially when determining submicrogram amounts of boron. Control the addition of reagents and whenever possible, use fused quartz glassware and plasticware for the preparation and storage of reagents and for all analytical manipulations up to the addition of the 3M HCl. The boron-curcumin reaction proceeds only under dehydrating conditions; thus, after the addition of 3M HCl, boron contamination is no longer a problem.

Fume quartz glassware with hydrochloric and sulfuric acids and rinse with quartz-distilled water immediately before use. Plastic ware is best cleaned with warm 3M HCl followed by water rinses. Borosilicate glassware use should be kept to a minimum, and when used, the manipulation should be done rapidly to minimize the introduction of boron. Boron in the form of boric acid will volatilize at elevated temperatures under moist, acidic conditions. Boiling steps, therefore, should be kept to a minimum. If prolonged boiling or high temperature heating is necessary, the operation should be performed under reflux in quartzware. Boron is not volatilized from basic media even at high temperatures, but mechanical losses still can occur, especially in carbonate fusions. Incline the fusion crucible at a 45° angle and use a lid to prevent spatter losses.

SAFETY PRECAUTIONS

Glacial acetic acid, sulfuric acid, and the acetic acid-sulfuric acid mixture will cause skin burns. Ether is toxic and highly flammable.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, plastic (polyethylene or polypropylene), assorted sizes.

2. Burner, Meker, or muffle furnace.

3. Crucible, zirconium, 60-ml, with lid.

4. Filtration apparatus, Millipore, 47-mm and 1-in. diam with 47-mm and 1-in. diam 0.45-μ Gelman Alpha-6 membrane filters. Attach 5 in. of 7-mm borosilicate glass tubing to the base of the 47-mm diam filter holder and 5 in. of 6-mm borosilicate glass tubing to the base of the 1-in. diam holder. For high efficiency, four units of each size should be available.

5. Fisher filtrator. A 1-liter suction flask with the bottom removed is a satisfactory substitute.

6. Fused quartz glassware such as round bottom flasks and condensers. These are necessary for the dissolution of solid samples.

7. Graduated cylinder, 10-ml.

8. Hot plate.

9. Pipets, micro, assorted sizes with control syringe.

10. Pipets, plastic (polyethylene or polypropylene) or fused quartz, assorted sizes.

11. Platinum ware, miscellaneous crucibles and dishes with lids.

12. Spectrophotometer, Beckman DU or DK, or Cary Model 14.

13. Volumetric flasks, borosilicate glass, assorted sizes.

14. Volumetric flasks, fused quartz, assorted sizes.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and fused quarts or plastic ware for the preparation and storage of all reagents. Clean the ware immediately before use as discussed previously under DISCUSSION.

1. Acetic acid, glacial.

2. Acetic acid-sulfuric acid, 1:1 mixture. Mix, with appropriate ice-bath chilling and swirling, equal volumes of glacial acetic acid and conc H_2SO_4. Add the sulfuric acid to the acetic acid slowly. Store the acid mixture in a well-stoppered fused-quartz flask.

3. Alcohol, ethyl, absolute or 95%. Add 1 ml of glacial acetic acid per liter of alcohol. Storage in a glass container is satisfactory.

4. Aluminum matrix solution, 1M. Dissolve 27 g of pure aluminum metal with a minimum of hydrochloric acid in a quartz flask. Dilute with quartz-distilled water to 1 liter. This solution is used to prepare the bias controls for aluminum samples.

5. Boron stock solution, 1.000 mg B/ml. Dissolve 2.859 ±0.001 g of 99.9% boric acid in water and dilute to 500 ml. Store in a polyethylene bottle.

6. Boron calibration standard I, 1 µg B/ml. Dilute 0.500 ml of the stock solution to 500 ml with quartz-distilled water. The shelf life of this solution has not been established. Prepare a fresh solution monthly and store in a screw-cap polyethylene bottle.

7. Boron calibration standard II, 10 µg B/ml. Dilute 5.00 ml of the stock solution to 500 ml with quartz-distilled water. The shelf life of this solution has not been established. Prepare a fresh solution every month and store in a screw-cap polyethylene bottle.

8. Dimethylformamide.

9. Ether.

10. Hydrochloric acid, conc and 3M.

11. Potassium pyrosulfate.

12. Sodium carbonate, anhydrous.

13. Water, quartz-distilled. Distill water into a polyethylene bottle with an all-fused-quartz still. Add about 0.5 g of calcium oxide to the water in the still pot to retain boron.

PROCEDURE

A. Reagent Blank

Pipet 0.40 ml of quartz-distilled water into a plastic beaker and process it per Procedure D beginning at Step 2.

B. Calibration and Bench Standard.

It is usally very difficult to select a sample aliquot with the desired amount of boron; therefore, five levels of calibration standards are recommended for this method. These five standards cover the four working ranges (Figure 1) and promote efficiency by minimizing repeat analyses. Of course, if only samples with similar concentrations are being run, two or three appropriate standards will suffice.

Process a separate calibration with each series of samples. The recommended standards are 0.10-, 0.20-, and 0.40-ml portions of the 1 µg/ml standard I and 0.10- and 0.40-ml portions of the 10 µg/ml standard II. Dilute each to 0.40 ml with quartz-distilled water and process each per Procedure D, beginning at Step 2. Divide the micrograms in each standard by its respective absorbance to obtain the conversion factor. For each range, the difference between the two conversion factors should not exceed limits set by the Quality Control Laboratory and the average of the two factors should agree with the established factor for the range within specified limits. If either or both of the specifications are not met, reprocess the calibration standards. Contact your supervisor if further difficulties are encountered.

C. Dissolution of Solid Samples.

Metal alloys such as 1100-S aluminum, stainless steel, and Zircaloy, refractory oxides such as calcined alumina and plastics such as polyethylene tape are the types of solids that heretofore have been encountered. These materials must be dissolved without introducing interferences such as fluoride, nitrate, or perchlorate, without introducing boron contamination, and without loss of boron through volatiliza-

tion (Refer to the APPLICABILITY and DISCUSSION Sections).

Aluminum alloys should be dissolved with hydrochloric acid under reflux in a fused quartz apparatus. If a residue persists, it should be isolated on a 0.45-μ membrane filter (acid-resistant Gelman VM-6 membrane filter is best), decomposed by fusion with sodium carbonate in a platinum dish, then combined with the original filtrate after dissolution in hydrochloric acid.

Stainless steel samples should be dissolved with sulfuric acid under reflux in a fused quartz apparatus. If a residue persists, filter it on a membrane filter, dissolve it with a sodium carbonate fusion -hydrochloric acid treatment, and combine the residue fraction with the original filtrate.

Zircaloy is best dissolved with a sulfuric acid-ammonium sulfate mixture under reflux in a fused-quartz apparatus. A mixture of 15 ml of conc H_2SO_4 and 5 g of ammonium sulfate will dissolve 1 g of Zircaloy. If high sensitivity is desirable in the analysis, dilute the dissolved sample with conc H_2SO_4 rather than water. This will permit the use of an aliquot larger than 0.4 ml for the determination.

Refractory oxides of amphoteric metals such as aluminum are best dissolved with a sodium carbonate fusion -hydrochloric acid dissolution process. Zirconia, on the other hand, requires a pyrosulfate fusion-hydrochloric acid treatment. Fused pyrosulfate is acidic so the fusion should be carried out under reflux in a fused quartz apparatus.

Plastics such as polyethylene tape should be charred slowly in a tared platinum dish. The residue is then fused with 30 to 50 times its weight of sodium carbonate and dissolved with dilute H_2SO_4.

D. Analysis of Samples.

Note: Contamination of samples with boron from apparatus and reagents is a major problem until the 3M HCl is added in Step 5 (see the discussion on contamination). Use plastic or fused-quartz apparatus whenever possible. If borosilicate glass apparatus must be used, perform the operation as rapidly as possible. All equipment used prior to Step 5 should be cleaned, preferably just before use. This is particularly important in the determination of submicrogram amounts of boron.

1. Pipet an aliquot (0.4 ml or less) with 0.025 to 5 µg of B into a 30- or 50- ml plastic beaker. Dilute, where necessary, to 0.4 ml with water.	The range of the method varies widely depending on the selection of the volumetric flask in Step 10 and the choice of optical cell in Step 15. The number of samples that can be processed simultaneously is governed by the availability of filtration setups. Two samples can be processed per setup. Four setups is about the maximum that can be handled satisfactorily.
2. Add 2 ml of 0.125(w/v) % curcumin solution.	
3. Add 4 ml of 1:1 acetic acid-H_2SO_4, mix well by swirling, then let stand for 15 min.	The color development is complete in 15 min. The complex is stable for another 45 min in the acetic acid-H_2SO_4 medium.
4. Set up the filtration apparatus.	Use a Gelman Alpha-6 type membrane filter. The choice of filter size depends on the level of boron. Amounts of B less than 1 µg give best results filtered on the 1-in. filter.
5. Add 10 ml of 3M HCl to precipitate the boron-curcumin complex. Mix well by swirling and let stand for 2 min.	Time is critical because the complex hydrolyzes gradually. Stagger the addition of 3M HCl to permit filtrations soon after the 2-min period. Hereafter, B contamination is no longer a problem and borosilicate glassware can be used.
6. Pass the sample through the filtration assembly with suction. Collect the waste filtrate in a suitable container.	

7. Rinse the beaker with 3M HCl and pass the rinses through the filter.	Some red complex will cling to the beaker. This will be recovered in Step 11.
8. Rinse the beaker with ethyl ether and pass the rinses through the filter.	Occassionally it will take several minutes for the ether to penetrate the wet filter. If the ether refuses to pass through add 1 or 2 drops of glacial acetic acid.
9. Rinse the filter assembly reservoir with ether.	
10. Replace the waste container with a dry 25- or 100-ml volumetric flask.	Select the flask on the basis of the intensity of the red boron-curcumin complex on the filter. The ability to make correct appraisals must be gained through experience.
11. Rinse the beaker with the 95% ethanol-0.1% acetic acid solution and pass the rinses through the filter. Wash the reservoir and filter with the ethanol-acetic acid.	Keep the vacuum off, then turn it on gradually after the addition of each portion of alcohol. The alcohol can be dispensed from a polyethylene squirt bottle.
12. With the vacuum off, add 1 to 2 ml of dimethylformamide to dissolve the residual boron-curcumin complex.	
13. Draw the dimethylformamide through the filter, then rinse well with the ethanol-acetic acid solution.	Disregard the small amount of red complex which remains on the filter.
14. Dilute to volume with the ethanol-acetic acid solution and mix well.	

15. Measure the absorbance within 4 hr against the ethanol-acetic acid solution. Use either 1- or 5-cm cells depending on the level of B in the sample (see Figure 1).

16. Record the data and calculate the results as shown in the example work sheet. Report results to 3 significant figures or to the nearest third decimal.

Keep in mind that samples and calibration standards must be processed identically.

REFERENCE

1. M. R. Hayes and J. Metcalf, "The Boron-Curcumin Complex in The Determination of Trace Amounts of Boron", Analyst, 87 (1962) p 956.

August 1967

S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Boron

CHARGE NUMBER _____ PROCEDURE B-Color 2

SPECIAL INSTRUCTIONS:

Dilute to 25 ml and use 1-cm cells.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	wt of Sample (no Tare)	Absorbance vs Solvent	Net Absorbance	Conversion Factor µg B/ Abs Unit	µg B in Sample Aliquot			RESULT
Reagent Blank			0.010						
std, 0.4 µg			0.270	0.260	1.538				
std, 1.0 µg			0.655	0.645	1.550				
				$\bar{x}$	1.544				
A1-001	0.500g/50ml/0.30ml	0.500g	0.425	0.415		0.641			2.14 µg B/g

ANALYZED BY _____ DATE _____

CALCULATIONS:

$D = \text{Conversion Factor} = \frac{\mu g\ B\ in\ Std}{Net\ Absorbance} = \frac{0.4}{0.260} = 1.538,\ D' = \frac{1.0}{0.645} = 1.550$

$\text{Ave Conversion Factor} = 0.5(D + D') = 0.5(1.538 + 1.550) = 1.544$

$E = \mu g\ B\ in\ Sample\ Aliquot = (Net\ Absorbance)(Ave\ Conv\ Factor)$

$= (0.415)(1.544) = 0.641$

$\text{Result} = \frac{(\mu g\ B\ in\ Sample\ Aliquot)(d_1)}{(a_0)(a_1)}$

$= \frac{(0.641)(50)}{(0.500)(0.30)} = 2.14\ \mu g\ B/g$

APPROVED BY _____

DETERMINATION OF BORON IN ATR FUEL PLATE PUNCHINGS

ABSTRACT

The fuel plate punching is decomposed with concentrated hydrochloric acid under reflux in a fused quartz apparatus. The residue is filtered, dissolved by a sodium carbonate fusion-hydrochloric acid dissolution process, then recombined with the original filtrate. Boron is determined by a simplified curcumin procedure based on a method developed by Hayes and Metcalf[1,2]. A 300-µl aliquot of the prepared sample is reacted with curcumin in an acetic acid-sulfuric medium and the absorbance of the red boron-curcumin complex is measured in an ethanol-acetic acid-sulfuric acid medium at 555 mµ.

APPLICABILITY

This procedure is designed specifically for the determination of low concentrations of boron in ATR fuel plate punchings; however, it also is applicable to uranium-stainless steel and uranium-zircaloy samples[2]. Aluminum at 4 mg or less, Cr, Fe, Ni, U, and Zr and trace levels of metallic constituents normally present in aluminum, stainless steel, and zirconium alloys do not interfere. Principal interferences are fluoride which complexes boron and oxidants such as nitrate and perchlorate that react with the curcumin reagent. These should not be present even in small amounts. Oxidizing metal ions like cerium(IV), chromium(VI), and manganese (VII) cannot be tolerated and must be reduced prior to color development.

The range of the colorimetric procedure is 0.25 to 3.5 µg of boron. The maximum aliquot is 300 µl so the lowest determinable boron concentration is about 0.8 µg/ml in the prepared solution. In terms of the solid plate punching, the lowest determinable boron concentration is 80 µg/g. This assumes a dilution of 1 g to 100 ml. If greater sensitivity is desirable, refer to Method B-Color-2[2].

DISCUSSION

The critical facets of this method are: the dissolution of the plate punchings, the introduction of boron contamination through reagents and apparatus, and the variables (water level, reaction time, and reagents) affecting formation and measurement of the boron-curcumin complex. The 0.5-in. diam punchings contain less than 1 mg of boron as boron carbide so extreme care should be exercised to recover all the boron carbide from the dissolution flask and to dissolve it

completely without boron losses. The curcumin and acetic acid-sulfuric acid reagents should be prepared and stored in fused quartz flasks previously cleansed with boiling hydrochloric acid and water rinses. Though low in boron, fused quartz ware still introduces boron into the reagents so weekly preparations are recommended. Under the prescribed conditions, quantitative color development will be obtained in the interval 15 to 60 min after the addition of the acetic acid-sulfuric acid reagent. After dilution with 95% ethanol, the boron-curcumin complex is stable for 4 hr.

SAFETY PRECAUTIONS

Use caution in the handling of the acetic acid-sulfuric acid reagent.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 100-ml, fused quartz or Teflon.

2. Bottles, polyethylene, 2-oz capacity, with screw-caps. Before use, clean thoroughly by rinsing successively with 2 to 4M HCl and water. Those bottles that are used to dilute the dissolved sample should be calibrated.

3. Condenser, fused quartz, straight water-jacketed type approximately 15-in in length with ₹ joint to fit the 100-ml flasks.

4. Cover glasses, plastic.

5. Cuvettes (optical cells), 1-cm

6. Filter paper, Whatman 42, 11-cm diam.

7. Flasks, round bottom, fused quartz, 100-ml, with female ₹ joint.

8. Flasks, round bottom or Erlenmeyer, 500-ml.

9. Flasks, volumetric, fused quartz, 250- or 500-ml.

10. Funnels, plastic.

11. Funnel rack.

12. Hot Plate

13. Medicine droppers, polyethylene.

14. Meker burner.

15. Muffle furnace.

16. Pipets, micro, assorted sizes, with syringe.

17. Pipets, volumetric or Mohr type of fused quartz or plastic, suitable for delivery of constant 3-ml aliquots of reagents.

18. Platinum crucible, 15-ml.

19. Ringstand.

20. Spectrophotometer, Beckman Models DU or DK or Cary Model 14.

21. Tongs, platinum-tipped.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for all reagents.

1. ATR fuel matrix solution. Dissolve 1.5 g of NBS U_3O_8 in a quartz beaker or flask with 5 ml of conc HCl plus 10 drops of conc HNO_3. Heat gently to hasten dissolution. If complete dissolution of the U_3O_8 is not obtained, add another 5 ml of conc HCl and 5 drops of conc HNO_3 and continue heating. When dissolution is complete, evaporate to dryness. Add 5 ml of conc HCl and evaporate to dryness, repeat the evaporation to dryness with 3 ml of conc HCl, and dissolve the residue in 500 ml of water. Meanwhile, using a 1-liter polyethylene bottle, dissolve 16.7 $\pm$ 0.5 g Na_2CO_3 in about 500 ml of water and cautiously with intermittent mixing, add 110 ml of conc HCl. Dissolve 62.7 $\pm$ 1 g $AlCl_3 \cdot 6H_2O$ in this solution, add the uranium solution, and dilute the mixture to 1 liter with water.

2. Boron stock standard, 1.000 mg B/ml. Prepare an aqueous solution 1.000 mg/ml in boron and store the solution in a screw-cap polyethylene bottle. For 100% assay boric acid, use 2.8589 $\pm$ 0.0005 g per 500 ml of solution.

3. Boron calibration standard I, 4.00 µg B/ml. Dilute 400 µl of the 1.000 mg B/ml stock standard to 100 ml with the ATR fuel matrix solution. Transfer to a 4-oz polyethylene screw-cap bottle.

4. Boron calibration standard II, 8.00 µg B/ml. Dilute 800 µl of the 1.000 mg B/ml stock standard to 100 ml with the ATR fuel matrix solution. Transfer to a 4-oz polyethylene bottle.

5. Curcumin reagent, 0.125 (W/v)%. Dissolve 0.3125 ± 0.0010 g of curcumin in 250 ml of glacial acetic acid. Prepare and store the reagent in a fused quartz flask.

6. Ethyl alcohol, 95% or absolute.

7. Hydrochloric acid, conc.

8. Sodium carbonate, anhydrous powder.

9. Sulfuric acid-acetic acid solution, 1:1 mixture. Mix, with appropriate ice-bath chilling and swirling, equal volumes of glacial acetic acid and conc H_2SO_4. Prepare and store the acid mixture in a fused quartz flask.

PROCEDURE

A. Blank

Process a 300-µl aliquot of the ATR fuel matrix solution per Procedure D beginning at Step 2 with each series of standards and samples.

B. Calibrations and Bench Standards

Process two calibration standards with each series of samples. Use 300 µl of calibration standards I and II and follow Procedure D beginning at Step 2. Divide the micrograms of boron in the standard by its respective absorbance to obtain the conversion factor. The difference between the two should be within limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the theoretical factor within established limits. For the boron-curcumin complex, the molar absorptivity is about 170,000; hence, the calibration factor should be 4.01 µg B per unit absorbance for this method. If both or either specification is not met, discard the samples and reprocess another pair of standards. Notify your supervisor if difficulties continue.

C. Dissolution of Plate Punchings

1. Weigh the sample to ± 0.1 mg.

2. Transfer the sample to a 100-ml quartz round bottom flask, connect the water-cooled condenser, and add 7.5 ml of conc HCl through the top of the condenser.

3. When decomposition of the sample is complete, rinse the condenser with 5 ml of water, and disconnect it.

4. Swirl the flask to mix its contents and filter the sample through a Whatman-42 filter paper supported in a plastic funnel. Transfer the undissolved residue quantitatively to the filter, then wash the filter with small water rinses. Collect the filtrate in a 100-ml fused quartz or Teflon beaker.

   The total volume of filtrate plus washings should not exceed 40 ml.

5. Fold the filter paper and place it in a 15-ml platinum crucible. Place the crucible in an oven or on a hot plate to dry the filter

6. Ash the filter and residue as follows: With the crucible inclined at 45°, char the filter paper over a low blue flame of a Meker burner until flames no longer are observed. Carefully, continue the ashing at the mouth of a 950°C muffle furnace. Complete the ashing by placing the crucible in

   Steps 6 and 7 are extremely critical for the ashing and fusion must be done without any loss of the minute 0.3-mg B_4C residue. In the ashing process, Step 6, avoid drafts that tend to carry particles of residue from the crucible. In the fusion, Step 7, place a lid over the crucible to prevent spatter losses. The Na_2CO_3 melt does not dissolve

	the furnace for 30 min.	
7.	Let the crucible cool and add 1 g of anhydrous Na_2CO_3. With a small platinum wire, intimately mix the Na_2CO_3 with the ashed residue. Place a lid on the crucible and fuse the sample in a 950°C muffle furnace for 20 min. Let the melt cool and examine the fused sample. It should be free of black matter. If not, continue the heating until the black coloration disappears.	the residue completely. The fusion shuld be continued until all lumps break down and black particles disappear.
8.	Let the crucible cool to room temperature, then lay it in the 100-ml beaker containing the original filtrate. Add 3-ml of conc HCl.	
9.	When the Na_2CO_3 cake disintegrates completely, heat the beaker on a hot plate without boiling the solution until the solution clears, then chill the sample to room temperature.	
10.	Transfer the dissolved sample with water rinses to a precalibrated 2-oz polyethylene screw-cap bottle. Dilute to volume with water and mix well.	Use the bottom of the first ring as the reference point. The capacity of the 2-oz polyethylene bottles is sufficiently uniform ($\bar{X}_6$ = 61.73 ml; s.d. = 0.84 ml) so calibration is not necessary when a relative precision of 4 to 10% is satisfactory.
11.	Record the sampling data on the work sheet and continue with the determination per Procedure D.	

D. Determination of Boron in the Dissolved Sample

1. Pipet 300 µl of the dissolved sample to a precalibrated, clean, dry 2-oz polyethylene screw-cap bottle.

   A borosilicate pipet is satisfactory for delivering the sample.

   When a precision of 4 to 10% is satisfactory, precalibration of the polyethylene bottles is unnecessary.

2. Pipet 3.00 ml of the 0.125 (w/v)% curcumin reagent.

3. Pipet 3.00 ml of the 1:1 sulfuric acid-acetic acid mixture.

   Use plastic or quartz pipets to dispense the curcumin and sulfuric acid-acetic acid reagents.

4. Mix additives 1, 2, and 3 thoroughly by swirling the bottle.

5. Let stand for 25 min.

6. Dilute to volume with 95% ethanol and mix thoroughly.

   Use any reference point, such as the bottom of the first ring, but dilute all standards and samples identically.

7. Measure the absorbance of the sample in a 1-cm cell at 555 mµ against 95% ethanol within 4 hr.

8. Record the data and calculate the results as shown on the attached work sheet. Report all results to 3 significant figures.

REFERENCES

1. M. R. Hayes and J. Metcalf, "The Boron-Curcumin Complex in the Determination of Trace amounts of Boron", Analyst, 87 (1960) p. 956.

2. S. S. Yamamura, Method B-Color-2 of this manual.

S. S. Yamamura
August 1968

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Boron

CHARGE NUMBER _____ PROCEDURE B-Color-3

SPECIAL INSTRUCTIONS: The requestor may ask for results in terms of total micrograms boron per plate punching. If so, disregard the sample weight in the calculation of the final result.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Sample weight, g	Absorbance Vs ETOH	Net Absorbance	Conv Factor µg B/abs	µg B in Sample Aliquot	µg B Corrected for Bias		RESULT µg B/g
Blank			0.065						
Std I, 1.2 µg B			0 368	0.303	3 960				
Std II, 2.4 µg B			0 658	0.593	4.047				
				$\bar{X}$ =	4.004				
Punching B-1	0 5050g/61 7ml/300µl	0.5050	0 385	0 320	4 004	1 28	1 28 ± 004		522 ± 17

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Conv Factor} = \frac{12}{0\,303} = 3\,960$$

$$= \frac{24}{0\,593} = 4\,047$$

$$\bar{X} = 0.5(3960 + 4.047) = 4\,004 \text{ µg B/abs unit}$$

Sample

µg B in Sample Aliquot = CD = 0 320 (4.004) = 1 28 µg B

$$\text{Result} = \frac{F\,(\text{Dilution volume})}{(\text{wt of punching})(\text{Size of Aliquot})} = \frac{(1\,28 \pm 004)(61.7)}{(0\,5050)(0\,30)} = 522 \pm 17 \text{ µg B/g}$$

APPROVED BY _____

DETERMINATION OF BORON IN PLANT CHARGE WATER, SUPPLEMENTAL CHARGE WATER, AND DISSOLVENT MAKEUP SOLUTIONS BY FLAME EMISSION SPECTROPHOTOMETRY

ABSTRACT

Boron in plant solutions is determined by comparing the emission from band systems in the green portion of the spectrum for a solution of boron in dilute hydrofluoric acid with the band emission from a known set of standards of similar composition. Samples and standards are aspirated into a nitrous oxide-acetylene flame system, and the resultant emission is measured at 5480 Å.

APPLICABILITY

This method is applicable to the determination of boron in supplemental charge water makeup [9 g/l B added as H_3BO_3], charge water (E-101, ∿ 5 g/l B), dissolvent makeup (PM-180, 4.1M B and 6.8M HF), or other samples characterized by high boron content and few, if any, additional metals or anions. Interference may be encountered from band emission (in the case of Ca, K, and probably Ba) and from radiation background emission (principally from the sodium continuum). Direct spectral line interference can occur in the presence of Cr, Co, Cu, Eu, Fe, Lu, Ni, Sr, Th, U, and Zr when either the element is present at relatively high concentrations or the spectral bandwidth is too great. Because the maximum buildup of dissolver product in the charge water is expected to be about 5%, only zirconium is likely to contribute significantly to boron emission. Uranium, tin and other metals are below 1 µg/ml.

DISCUSSION

Emission by boron at the wavelength of 5480 Å is probably attributable to emission by the species, BO_2[1]. This is one of a series of narrow bands called boric acid fluctuation bands. While there are slight differences in the reported maxima, the band heads appear at about 4520, 4710, 4920, 5180, 5470, and 5800 Å. Because these band systems overlap, difficulty arises in applying background corrections, and many elements present at relatively high concentration may exhibit general background radiation. The sodium continuum completely overlies the spectral region used.

Although fluoride has been reported not to affect boron emission in other flame systems[2], the effect of fluoride ion on boron emission in a nitrous oxide-acetylene system needed investigation. Possible interference from the presence of zirconium also needed study. Four solutions, each containing 40 µg B/ml, were made up in the following: (a) distilled water, (b) 0.068M HF, (c) charge water containing fluoride and zirconium at maximum expected levels, and (d) charge water containing fluoride and zirconium at twice the expected levels. Boron emission from the three samples containing fluoride was significantly greater than that from the simple aqueous solution. No significant difference in the emission from these three samples was noted when flame conditions were optimized. For these reasons, hydrofluoric acid should be added to any sample which does not already contain fluoride ion.

The working range of the method is from 10 to 100 µg B/ml and the calibration curve should be linear over this range.

SPECIAL SAFETY PRECAUTIONS

Explosions of nitrous oxide-acetylene mixtures are common; therefore, follow carefully all instructions for lighting and extinguishing the flame. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of the drain tube must extend below the surface of the liquid in the waste receptacle. Spills can be prevented by only partially filling the sample cups.

APPARATUS AND REAGENTS

A. Apparatus

1. Bottles, plastic, 2-oz.

2. Burner, nitrous oxide-acetylene, 6-cm slot.

3. Cups, plastic, 5-ml, caplugs No. 12X.

4. Spectrophotometer, atomic absorption, Techtron AA-5 with chopper mechanism for flame emission or equivalent instrument with attachments.

5. Pipets, 100-µl, 10-ml, and 20-ml with control syringe and rubber suction bulbs.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagent and matrix solutions.

1. Boron stock solution, 1.000 mg/ml. Dissolve 5.7178 g of 99.9% H_3BO_3 in distilled water and dilute to 1 liter.

2. Boron calibration standards. To each of five calibrated 1-liter polyethylene bottles, add 25 ml of water and 2.3 ml of conc HF. Dilute the first with water to 1 liter and mix. This solution is the blank. Add 20.00 ml, 40.00 ml, 60.00 ml, and 80.00 ml, respectively of the 1.000 mg/ml boron stock solution to the remaining four bottles and dilute each solution to 1 liter with water. The boron concentrations of these four solutions are 20, 40, 60, and 80 µg/ml.

3. Boron controls. Following the directions given for the preparation of the calibration standards, prepare a series of four or five unknowns to cover the concentration range 10 to 70 µg B/ml.

PROCEDURE

A. Conversion of Instrument for Flame Emission

Mount the chopper on the optical bench as near to the monochromator slit as possible. Connect the two cables from the chopper to the plugs on the monochromator base and the back of the digital readout unit. Set the hollow cathode mount so that no light reaches the slit from any hollow cathode lamp.

B. Sample Preparation

1. Supplemental charge water. Add 100 µl of sample to 20.00 ml of 0.068M HF in a 2-oz polyethylene bottle and mix well.

2. E-101 charge water. Add 100 ml of sample to 10.00 ml of 0.068M HF in a 2-oz polyethylene bottle and mix well.

3. PM-180 dissolvent makeup. Add 100 µl of sample to 10 ml of distilled water in a 2-oz polyethylene bottle and mix well.

4. Controls. No dilution is required on the controls. Process the controls as supplied.

C. Calibration

The analyst has an option of two different methods of calibration. One method is to process the blank and all four calibration standards for construction of a calibration curve. The other approach is to process two standards that bracket the concentration of the sample. In either case, the standards are processed per Procedure E in the same manner as any sample.

D. Analysis of Bench-Control Standards

Analyze one control per Procedure E each time an analysis is performed. The result for the control must fall within the specified limits. If it does not, process another control. Seek help if troubles continue.

E. Analysis of Samples

	Operation	Detailed Instructions
1.	Turn on power.	Two switches - one each on read-out and monochromator units.
2.	Mount proper burner head.	Nitrous oxide-acetylene, 6-cm slot.
3.	Adjust burner height.	Set vernier at 15.
4.	Set the wavelength dial.	Set at 5480 Å. Do not peak in.
5.	Check that drain tube extends below surface of liquid in waste receptacle.	
6.	a. Set backing control.	Zero
	b. Set damping control.	D
	c. Set select switch.	High gain position
	d. Set mode switch.	% T
	e. Set scale expand control.	X 1
	f. Set monochromator slit.	50 μ
7.	Open exhaust control.	
8.	Open supply valves.	Turn on air, C_2H_2 and N_2O.
9.	Set gas regulators.	Air - 15 gauge C_2H_2 - 13 gauge N_2O - 24 gauge
10.	a. Turn support valve to air.	Adjust support pressure to 15 psi.
	b. Turn support valve to N_2O.	Support pressure should read 15 psi.

	c. Turn support valve off.	
	d. Turn fuel valve to C_2H_2.	Adjust to 3 on flowmeter.
	e. Turn support valve to air.	
	f. Light burner.	Allow air to flow for 5 sec before ignition.
	g. Increase C_2H_2 flow.	Raise to 9 on flowmeter.
	h. Rapidly rotate support valve to N_2O.	
	i. Adjust flow rate settings.	N_2O - 5.5 (flow) C_2H_2 - 4.5 (flow) Auxiliary Support - 6.0 (flow)
11.	Adjust exhaust control.	Set at 2/3 closed. Never close exhaust completely.
12.	Cover slit and adjust readout zero.	Adjust zero with backing control.
13.	Aspirate high standard.	Set gain controls to give half scale meter deflection.
14.	Adjust burner horizontal movement and rotation.	Image of flame should be centered on the slit.
15.	Adjust wavelength setting to maximize meter deflection.	Change gain as necessary to keep meter on scale.
16.	Depress "Trans" switch on readout unit.	
17.	Set "Concn" control.	Turn fully counter-clockwise.
18.	Set "Zero" control.	"Zero Set" light should flash intermittently.
19.	Set 100% T on meter with gain control.	Flame should be burning with no sample solution.
20.	Set "Concn" control to 100.0 on readout unit.	
21.	Turn "Avg" control until "Zero Set" light flashes each 5 sec.	

22. Atomize high standard and set ∿ 80% T with gain controls.

Run samples and standards. Atomize either the blank or water between each pair. Record the readout value obtained for each sample or standard on worksheet.

CALCULATIONS

The concentration of boron in the diluted sample can be obtained by either of two methods. A calibration curve relating % T to concentration can be plotted from the calibration standard data. This calibration curve will show the concentration of boron in µg/ml which corresponds to the sample % T readout value. The two standard, bracket method may also be used. The boron concentration of the diluted sample is then calculated from the following equation:

$$C = \frac{Y_s - \left[\frac{y_1(x_1-x_2) - x_1(y_1-y_2)}{x_1 - x_2}\right]}{\frac{y_1 - y_2}{x_1 - x_2}} \qquad (1)$$

where:

C = boron concentration of sample in µg/ml

Y_s = % T of sample

x_1 = concentration of high standard

x_2 = concentration of low standard

y_1 = % T of high standard

y_2 = % T of low standard.

The result to be reported is calculated by substituting the concentration in µg/ml in the appropriate formula below and solving the equation.

Dissolvent makeup (PM-180): $\underline{M} = \frac{[(C + \text{bias}) \pm sd](101)}{1000(10.81)}$ (2)

where:

$\underline{M}$ = molarity of boron of PM-180 sample

C = boron concentration of sample in µg/ml

bias = µg of boron added or subtracted as shown by control data

sd = standard deviation of control data

101 = dilution factor

10.81 = atomic weight of boron.

$$\text{Charge water (E-101): } g/l = \frac{[(C + \text{bias}) \pm sd](101)}{1000} \quad (3)$$

where:

g/l = grams of boron per liter of charge water

C = boron concentration of sample in µg/ml

bias = µg of boron added or subtracted as shown by control data

sd = standard deviation of control data

101 = dilution factor.

$$\text{Supplemental charge water: } g/l = \frac{[(C + \text{bias}) \pm sd](201)}{1000} \quad (4)$$

where:

g/l = grams of boron per liter of supplemental charge water

C = boron concentration of sample in µg/ml

bias = µg of boron added or subtracted as shown by control data

sd = standard deviation of control data

201 = dilution factor.

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2. J. A. Dean, Flame Photometry, New York: McGraw-Hill Book Co., Inc., 1960, p 229.

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T. R. Lyon
W. A. Ryder

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(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Boron

CHARGE NUMBER _____ PROCEDURE B-Flame Emission-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	conc µg	Asorb	µg in Sample	correction	Std deviation			RESULT g/l
Sample	0.1/10.1		0.575	50	0.0	±1.5			5.05 ±0.15
Std 1		40	0.450						
Std 2		60	0.700						

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\mu g \text{ in Sample} = \frac{0.575 - \left[\frac{0.700(60-40) - 60(0.700-0.450)}{60-40}\right]}{\frac{0.700-0.450}{60-40}} = 50$$

$$\text{Result} = \frac{(50 \pm 1.5)(101)}{1000} = 5.05 \pm 0.15 \text{ g/l}$$

APPROVED BY _____

DETERMINATION OF BORON BY FLAME EMISSION SPECTROPHOTOMETRIC MEASUREMENT AFTER EXTRACTION FROM AQUEOUS SOLUTIONS INTO METHYL ISOBUTYL KETONE

ABSTRACT

Submilligram quantities of boron are extracted from aqueous solutions into methyl isobutyl ketone (MIBK) as the tetrabutylammonium boron tetrafluoride ion association complex. Boron is determined in the organic phase by comparing the emission from band systems in the green portion of the spectrum for a sample with the band emission of a set of known standards similarly extracted. Samples and standards are aspirated into a nitrous oxide-acetylene flame system, and the resultant emission is measured at 5480 Å.

APPLICABILITY

A great many direct spectral interferences and interelemental effects are encountered in direct flame emission analysis of aqueous solutions. Method B-Flame Emission-1 is only applicable to aqueous solutions of boron characterized by few, if any, additional elements which must be present only at low concentrations. Reliable results for boron in aqueous solutions containing other elements depends upon a good separation between the boron and the other elements in the sample. This extraction procedure is very selective for boron[1], so this method is applicable to a wide variety of solutions. A study of the effects of diverse ions[2] shows that only five of 30 cations studied and two common anions cannot be tolerated. The five interfering cations are Mo, Nb, Pt, V and W; the two interfering anions are $PO_4^{=}$ and ClO_4^{-}. Possible interferences from Fe(III) and Cr(VI) are prevented by reduction with hydroxylamine hydrochloride. Sample aliquots which contain more than 10 mmole of nitrate require a sulfuric acid fuming pretreatment. No interference is reported for 5 mmole of Be, Cd, Cr, Cu, Fe, K, Mg, Na, Zn or Zr per sample aliquot. The tolerance level for Al and Ca is 2.5 mmole, and that for La is 2 mmole. One mmole of Th or U, 0.8 mmole of Si, 0.4 mmole of Ni or Pd, and 0.2 mmole of Bi or Sn are tolerated by the procedure. Mercury, Pb, and Ru do not interfere at a 1:1 mole ratio to boron. Above these tolerance levels, enhancement effects are noted from all metals except Hg, La, Ni, Pb, and Th. Nitrate suppresses emission, while perchlorate prevents complete extraction of the boron. Phosphate enhances the emission signal by increasing the background.

The working range of the procedure is from 100 to 1000 µg of boron. The lower concentration limit for an unknown sample is 21 µg/ml without prior evaporation. Prior evaporation is performed as described in Procedure D.

The prevalence of boron in laboratory glassware necessitates the use of inert plasticware for the measurement and delivery of reagents reactive to glass.

DISCUSSION

Increasing the concentration of either hydrogen ion or fluoride ion increases the extraction of the tetrabutylammonium borontetrafluoride complex. Sulfuric acid is used to increase the hydrogen ion concentration because it forms few extractable metal complexes[2], and the specificity of the extraction is increased. Perchlorate forms a stable salt with the tetrabutylammonium ion and interferes with the complete extraction of boron by consuming the reagent. This perchlorate salt also extracts and consititutes a potential explosion hazard. The volume of the organic phase increases in the extraction from 10 ml to about 11.5 ml because of the distribution of tetrabutylammonium salts and acid into the organic phase. This volume change is constant, however, and has no adverse effect on the results.

Boron emission at the 5480 Å wavelength is probably attributable to emission by the species, BO_2[3]. This system is overlapped by other boric acid fluctuation bands, which complicates the problem of background correction, but the organic solvent provides a reproducible matrix with a reproducible flame background. Reliable analytical results are, therefore, attainable by measuring only the peak intensity of the flame emission. The selectivity of the extraction procedure also frees the emission signal from most spectral line interference and most band emission interference. Solutions exposed to air for more than 5 min give high readings due to evaporation of MIBK.

SPECIAL SAFETY PRECAUTIONS

Extractable perchlorate complexes constitute a potential explosion hazard; therefore, this method should not be used for samples that contain perchloric acid. Explosions of nitrous oxide-acetylene mixtures are common; therefore, carefully follow all instructions for lighting and extinguishing the flame. Reduce the acetylene flow to the prescribed rate before aspirating any sample solution. Additional fuel is provided by the organic solvent in the sample. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of the drain tube must extend below the surface of the liquid in the organic waste receptacle. Use rubber gloves for the extraction work.

APPARATUS AND REAGENTS

A. Apparatus

1. Burner, nitrous oxide-acetylene, 6-cm slot.

2. Centrifuge.

3. Centrifuge tubes, polypropylene, 50-ml.

4. Extraction wheel, 33-rpm.

5. Pipets, glass, 250-µl, 1-ml and 10-ml with control syringes and rubber suction bulb.

6. Pipet, Mohr, 5-ml.

7. Pipets, plastic, 1-ml and 5-ml.

8. Spectrophotometer, atomic absorption, Techtron AA-5 with chopper mechanism for flame emission or equivalent instrument with attachments.

9. Stoppers, polyethylene, No. 5.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Boron bench standard. Follow the directions given below for preparing the calibration standards.

2. Boron calibration standards. Weigh into 500-ml volumetric flasks, 0.2860 g, 0.8580 g, 1.4300 g, 2.1450 g and 2.8600 g, respectively of H_3BO_3, dissolve and dilute to the mark with distilled water. This provides standards of 100, 300, 500, 750, and 1000 µg B/ml, respectively. The specified weights are for 100.0% H_3BO_3. Adjust accordingly for H_3BO_3 purity less than 100%.

3. Boron controls. Follow the directions given above for preparing the calibration standards, but add other elements to simulate an unknown sample. Prepare a series of four controls with boron in the range of 100 to 1000 µg/ml. Use 1 ml for each determination.

4. Hydrofluoric acid, conc.

5. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution, 1M. Dissolve 6.95 g of $NH_2OH \cdot HCl$ in water and dilute to 100 ml. Store in polyethylene bottle.

6. Methyl isobutyl ketone.

7. Sulfuric acid, 15M.

8. Tetrabutylammonium hydroxide, 1M, titration grade (Southwest Analytical Chemicals, Austin, Texas, or Eastman Organic Chemicals, Rochester, New York).

PROCEDURE

Note: The extracted samples must be flame-analyzed within 30 min of the extraction separation, so the spectrophotometer should be in operating condition before the separation is made.

A. Reagent Blank

Process a 4.75-ml portion of distilled water in the same manner as the calibration standards and the samples.

B. Calibration Standards

For each set of samples, process one complete set of five calibration standards in the same manner as any sample.

C. Bench Standard

For each set of samples, process one bench standard in the same manner as any sample. If the result falls outside the specified limits, discard all results and repeat the entire series of blank, standards, bench standard, and samples. Seek help if trouble persists.

D. Extraction-Separation of Boron

1. Pipet a sample containing 100 to 1000 µg of boron into a 50-ml polypropylene centrifuge tube.

Plastic pipets should be used for samples containing HF, for the delivery of HF in Step 6 and of tetrabutylammonium hydroxide in Step 7. Glass pipets are satisfactory otherwise. If the sample aliquot is 4.75 ml or less, omit Step 2. If the nitrate level exceeds 10 mmole, use Procedure E.

2.	Evaporate the sample under a heat lamp and with the aid of a stream of filtered air to a volume of 2±0.5 ml.	
3.	Dilute to 4.75 ml with water.	
4.	Add 250 µl of 1M $NH_2OH \cdot HCl$ to reduce possible interferences from Fe(III) and Cr(VI).	
5.	Add 1 ml of 15M H_2SO_4.	If Procedure E has been used to remove NO_3^-, add 1 ml of water.
6.	With a plastic pipet, add 1 ml of conc HF and mix.	
7.	Add 3 ml of 1M tetrabutylammonium hydroxide and mix.	To prevent crystallization of the reagent in the pipet, warm the reagent to about 40°C in a water bath.
8.	Pipet exactly 10 ml of methyl isobutyl ketone, cap tightly with a polyethylene stopper and extract for 3 min using the extraction wheel or 2 min manually.	To minimize errors due to loss of the methyl isobutyl ketone through evaporation or leakage, tightly stopper the tube immediately after the delivery of the solvent. Loosen the stopper just before the flame analysis is to be performed.
9.	Centrifuge for 3 min.	
10.	Flame-analyze the extracted samples and calculate the results per Procedures F and G.	The flame analysis should be concluded within 30 min after the extraction.

E. Evaporation of Samples Containing Nitrate

Note: This procedure should only be used when the minimum sample aliquot to contain 100 µg of boron exceeds a nitrate level of 10 mmole.

B-Flame Emission-2

1.	Pipet a sample aliquot containing 100 to 1000 μg of B into a 50-ml glass centrifuge tube.	This procedure is not applicable to samples containing HF.
2.	Pipet an equal sample aliquot into a second 50-ml test tube.	
3.	Add 1 ml of 15M H_2SO_4 to both test tubes.	
4.	Evaporate the solution in both test tubes to fumes at 140° or less in a glycerol bath.	Cease fuming when the volume in the second tube is reduced to 0.5 ml or less.
5.	Quantitatively transfer the sample in the first test tube with 4.25 ml of distilled water into a 50-ml polypropylene centrifuge tube.	The sample is now ready for the extraction of B, Procedure D. See note on Step 5.

F. Adjustment of Flame Spectrophotometer and Analysis of Extracted Samples and Standards.

All five standards and a reagent blank must be processed and verified by construction of a working curve. Because samples must be analyzed within 30 min after extraction, no time is available to extract additional standards as they are needed, and processing all standards and the blank ensures that the samples concentration will fall within the range of the standards used. The analysis should be carried out in accordance with normal instrument operating procedures. Verify that the correct shutdown procedure was followed. If any control or condition is not as it should be, correct it.

	Operation	Specific Instructions
1.	Turn on power.	Two switches - one each on readout and monochromator.
2.	Mount proper burner head.	Nitrous oxide-acetylene, 6-cm slot.
3.	Adjust burner height.	Set vernier at 15.

	Operation	Specific Instructions
4.	Set the wavelength dial.	Set at 5480 A. Do not peak in.
5.	Transfer drain tube to organic waste receptacle.	Check that drain tube extends below surface of liquid.
6.	a. Set backing control.	Zero.
	b. Set damping control.	D.
	c. Set select switch.	High gain position.
	d. Set mode switch.	% T.
	e. Set scale expand control.	X 1.
	f. Set monochromator slit.	50 μ.
	g. Turn on chopper.	
7.	Open exhaust control.	
8.	Open supply valves.	Turn on air, C_2H_2 and N_2O.
9.	Set gas regulators.	Air - 15 gauge C_2H_2 - 13 gauge N_2O - 24 gauge
10.	a. Turn support valve to air.	Adjust support pressure to 15 psi.
	b. Turn support valve to N_2O.	Support pressure should read 15 psi.
	c. Turn support valve off.	
	d. Turn fuel valve to C_2H_2.	Adjust to 3 on flowmeter.
	e. Turn support valve to air.	
	f. Light burner.	Allow air to flow for 5 sec before ignition.
	g. Increase C_2H_2 flow.	Raise to 9 on flowmeter.
	h. Rapidly rotate support valve to N_2O.	

	Operation	Specific Instructions
	i. Adjust flow rate settings.	N_2O - 6.0 (flow) C_2H_2 - 2.5 (flow) Auxiliary Support - off.
11.	Adjust exhaust control.	Set at 2/3 closed. Never close exhaust completely.
12.	Cover slit and adjust read-out zero.	Adjust zero with backing control.
13.	Aspirate high standard.	Set gain controls to give half scale meter deflection.
14.	Adjust burner horizontal movement and rotation.	Image of flame should be centered on the slit.
15.	Adjust wavelength setting to maximize meter deflection.	Change gain as necessary to keep meter on scale. Note settings.
16.	Remove high standard and replace stopper.	Evaporation of MIBK gives erroneous results.
17.	Depress "Trans" switch on readout unit.	
18.	Set "Concn" control.	Turn fully counter-clockwise.
19.	Set "Zero" control.	"Zero Set" light should flash intermittently.
20.	Set 100% T on meter with gain control.	Flame should be burning with no sample solution.
21.	Set "Concn" control to 100.0 on readout unit.	
22.	Turn "Avg" control until "Zero Set" light flashes each 5 sec.	
23.	Reset the gain controls.	Return gain controls to settings for Step 15.
24.	Reset the gain controls.	Turn backing on about 50%.

Operation	Specific Instructions
25. Using high standard and reagent blank alternately, calibrate readout meter at about 100% T and 0.0% T.	Turn backing on about 50%. Set high standard at 100% T by adjusting gain control, then set reagent blank at 0% by adjusting backing. Continue to alternate standards until no significant change is noted.
26. Record value for last high standard reading.	

Loosen stoppers on remaining standards and samples. Aspirate each solution into the flame directly from the centrifuge tube, being careful that the aspirator tube does not extend into the aqueous phase. Record the readout value obtained for each sample or standard on a work sheet.

G. CALCULATIONS

A calibration curve relating % transmittance to concentration can be plotted from the calibration standards data. The concentration of boron in µg in the sample aliquot corresponding to the % transmittance value for the sample can be read from the calibration curve and the calculations completed as on the sample chemical analysis work sheet.

REFERENCES

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3. R. W. B. Pearse and A. G. Gaydon, The Identification of Molecular Spectra, New York: John Wiley and Son, Inc., 1963, p 75.

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January 1972

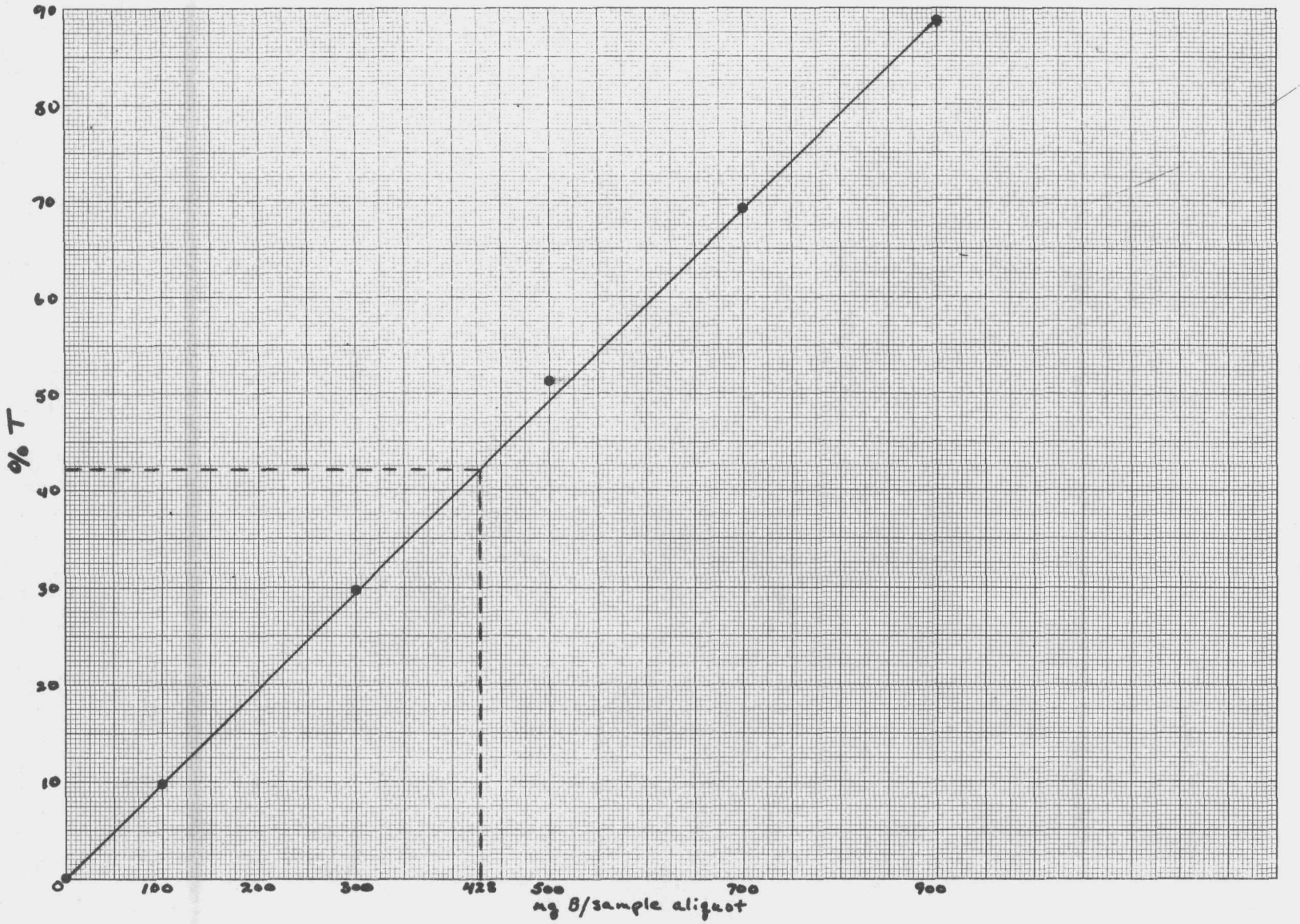

Fig. 1 Calibration curve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Boron

CHARGE NUMBER _____ PROCEDURE B-Flame Emission-2

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	%T		µg B in Test Aliquot	µg B/ml				RESULT mg B/ml
Reagent Blk		0.0							
Std, 100µg B		9.6							
Std, 300µg B		29.8							
Std, 500µg B		51.2							
Std, 700µg B		69.0							
Std, 900µg B		88.7							
Sample	0.25 ml	42.3		428	1712				1.7

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Result} = \frac{C4}{1000} = \frac{(428)(4)}{1000} = 1.712$$

APPROVED BY _____

SEPARATION OF BORON FOR THE DETERMINATION OF ISOTOPIC DISTRIBUTION BY MASS SPECTROMETRY

ABSTRACT

The mass spectrometric determination of the isotopic distribution of boron requires a clean boron sample. The boron is distilled as methyl borate from a sulfuric acid medium into water and the solution is evaporated to dryness.

APPLICABILITY

This method is applicable to acidic or basic aqueous solutions and solid samples that can be dissolved to yield solutions compatible with the distillation-separation procedure. Potential interferences are volatile anions which may codistill. Anion carryover, however, can be avoided or kept to a tolerable level by careful temperature control. At the recommended bath temperature of 75 ± 5°C, sulfate codistillation is nil as is the carryover of chloride and nitrate when these are present alone. When both chloride and nitrate are present, some chloride and nitrate codistill because of the interaction of chloride and nitrate and the resultant formation of volatile chlorine and nitrogen dioxide. Fortunately, chloride and nitrate can be driven off during the ensuing evaporation with only slight boron losses. Fluoride, which complexes boron, is a serious interference. Preliminary precipitation of fluoride as cerous fluoride per method F-Vol-1 enables separation of boron from solutions containing fluoride.

DISCUSSION

The overall methanol distillation-evaporation procedure must provide a boron sample free of interfering levels of sulfate and free of boron contamination from reagents and apparatus. It also must provide adequate recovery of boron to enable the analysis of samples with microgram concentrations of boron.

From the standpoint of cleanliness of the methyl borate distillate, the critical variable is the distillation pot temperature which must be maintained at 75 ± 5°C. At these temperatures, the flow rate of the air purge is not critical and an easy to obtain rate of 2 ± 1 bubble per second has been arbitrarily adopted. Sulfate carryover increases as the distillation pot temperature rises above 80°C. It is nil at 70-80°C as noted above.

The amount of water introduced through the sample, the sulfuric acid concentration, and the volume of methanol affect the distillation of boron. If the aqueous sample volume is 1 ml or less and acidic (it

matters not what mineral acid), no sulfuric acid need be added provided a minimum of 35 ml of methanol is added and half of the methanol is distilled. For aqueous samples above 1 ml, the volume ratio of sulfuric acid to sample and methanol to sample must be at least 1.5 and 6, respectively; however, a minimum of 35 ml of methanol must be used. In this method, the methanol addition is fixed at 60 ml to accommodate all samples up to 10 ml. When a number of samples less than 5 ml are to be processed, some time could be saved by reducing the methanol addition to 35 ml and collecting 20 ml of distillate.

Contamination of samples with boron from the reagents and the apparatus can be a serious problem, especially when microgram amounts of boron are being distilled. Quartz-distilled water should be used. Commercial methanol and sulfuric acid generally are satisfactory. If the methanol or sulfuric acid is found to contain significant amounts of boron (per Apparatus and Reagent Checkout Procedure B) it is best (a) to find new uncontaminated methanol and sulfuric acid or (b) to run a reagent blank because complete removal of boron from sulfuric acid and methanol is difficult. Distillation of methanol through a quartz still from a basic medium should reduce the boron level considerably. The distillation and subsequent evaporation of samples should be carried out with quartz apparatus.

SAFETY PRECAUTIONS

Methanol is flammable and poisonous. Poisoning may occur from ingestion, inhalation, or absorption through the skin. Concentrated sulfuric acid causes serious burns. Exercise caution when using both methanol and sulfuric acid. Particular caution is directed to Procedure C, Steps 2 and 4.

APPARATUS AND REAGENTS

A. Apparatus

1. Bath, constant temperature. For few infrequent samples, use a magnetic stirrer-hot plate and an 800-ml beaker of water.

2. Bath, ice.

3. Bottles, polyethylene, 2-oz with caps.

4. Distillation apparatus, quartz, see Figure B-2.

5. Graduated cylinders, assorted sizes (either glass or plastic is satisfactory).

6. Pipets, macro and micro, assorted sizes with control syringe and suction bulb.

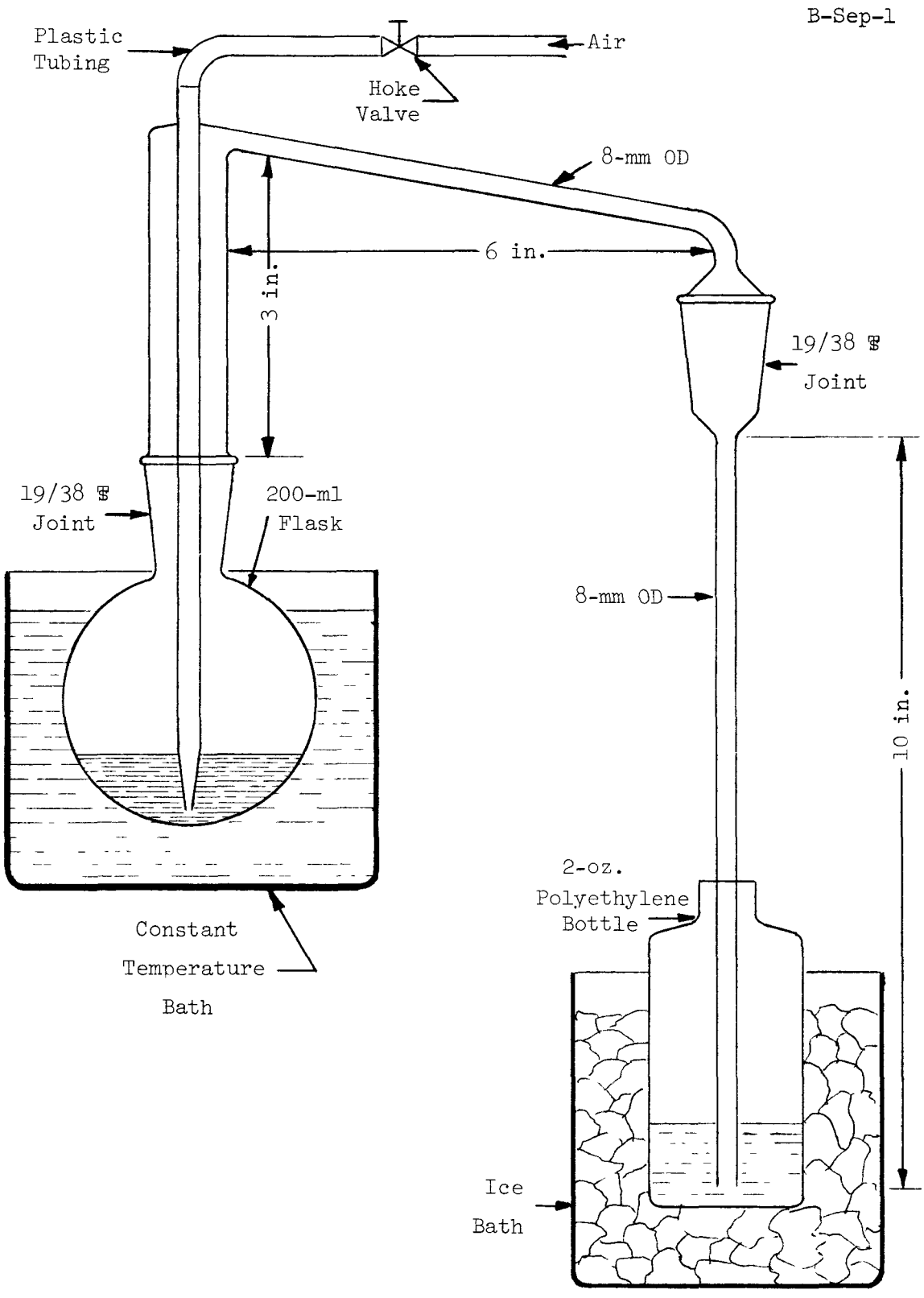

Fig. 1 Quartz distillation apparatus.

7. Tubing, polyethylene, equipped with Hoke valve for close control of the air flow.

B. Reagents

1. Boron, ^{10}B enriched. The mass laboratory usually has a supply of ^{10}B enriched boron.

2. Methyl alcohol (methanol), absolute.

3. Sulfuric acid, conc.

PROCEDURE

NOTE: Use quartz distillation apparatus and quartz distilled water.

A. Procedure for Cleaning the Distillation Apparatus

Add 50 ml methanol to the 200-ml distillation flask. Attach the condensor and the delivery tube and distill about 25 ml of methanol through the apparatus into a polyethylene bottle immersed in an ice bath. Discard the residual methanol in the flask and distillate and rinse the flask thoroughly with water.

B. Checkout of Apparatus and Reagents for Boron Contamination

When highest reliability is desired and when small amounts of boron are to be separated, initial checkout of the apparatus and reagents for boron contamination is recommended. Obtain a sample of ^{10}B enriched boron from the mass laboratory, separate the boron per Procedures A and C, and submit the distillate to the mass laboratory for analysis. Any deviation of the observed isotopic composition from the original composition is indicative of boron contamination.

C. Distillation of Methyl Borate

1. Into a clean 200-ml distilling flask immersed in an ice bath, pipet a sample aliquot of 10 ml or less containing at least 100 µg of boron. Add 60 ml of absolute methanol and mix.	If a number of samples less than 5 ml are to be processed, some time can be saved by using 35 ml of methanol and collecting 20 ml of distillate in Step 5.
2. Carefully add 1.5 ml of conc H_2SO_4 for each ml of sample. Keep the flask inclined at a 45° angle and let the acid run beneath the methanol.	Add 1 ml of H_2SO_4 for samples less than 1 ml.

3. While the acid chills, add 10 ml of water to a clean 2-oz polyethylene bottle and place the bottle in an ice bath. Also, assemble the distillation apparatus and adjust the air flow to 1 bubble per sec.

4. While maintaining the flask at a 45° angle, slowly rotate the flask to mix the H_2SO_4 and methanol.

   Methyl borate boils around 50°C. Keep the solution cold to minimize B loss.

5. Attach the flask to the distillation apparatus and lower it into the constant temperature bath. Distill 30 ml of methanol into the 2-oz polyethylene bottle.

   Adjust the height of the collecting bottle so that the tip of the delivery tube is immersed in the water. The bath temperature should be 75±5°C.

6. Remove the distillate from the ice bath, place a cap on the bottle. Identify this bottle by log number and sample identification. Transfer the distillate and work sheet to the mass laboratory.

June 1970

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TITRIMETRIC DETERMINATION OF BORON

ABSTRACT

Methods are described for the determination of milligram amounts of boron in reactor materials such as aluminum, stainless steel, and Zircaloy. With aluminum and stainless steel samples, hydrolyzable cations are removed by ion exchange. With Zircaloy-type samples, the boron is separated initially by distillation from sulfuric acid medium as methyl borate. In either case, the treated sample solution then is adjusted to pH 7.00, mannitol is added to complex the boric acid, and the acidic boric acid-mannitol complex is titrated with standard sodium hydroxide.

APPLICABILITY

In this method, designed primarily for aluminum, stainless steel, and zirconium alloys and solutions, boric acid is reacted with mannitol to form an acidic complex which is measured by titration with base [1]. As such, the method is subject to various interferences. These include: (a) metal ions that react with mannitol to release titratable acids, (b) metal ions that react with base to form hydroxy complexes, (c) buffering anions such as carbonate that consume acid, and (d) substances, such as fluoride, that complex boric acid and prevent its reaction with mannitol.

Cation exchange and distillation are used to remove interfering metal ions. The cation exchange procedure is applicable to solutions of aluminum and stainless steel provided the solutions do not contain complexing anions that convert the metal ions to uncharged or negatively charged complexes not retained by the resin. The complexing tendency of common anions increases in the order ClO_4^-, NO_3^-, Cl^-, $SO_4^{=}$, and $PO_4^{\equiv}$. Also, the stability of complexes increases with increasing anion concentrations. Thus, in sample preparation, least complexing acids should be used at lowest permissible concentrations. Organic complexers such as citrate and tartrate likewise interfere. If it is necessary to analyze samples containing these substances, the ligands first must be destroyed by a nitric acid-perchloric acid digestion with a digestion apparatus, such as that described in Method Hg-Color-1 of this Manual, which enables acid digestion under total reflux conditions.

The distillation technique, more specifically methanolic distillation of methyl borate from sulfuric acid medium, is applicable to zirconium-base samples that require high concentrations of complexing acids for dissolution. Methanol does not affect the alkalimetric titration so the isolated boric acid can be titrated directly without evaporation of the methanol.

Carbonate (for carbonic acid, $pK_{a_1} = 6.37$) interferes even at a 0.05-mmole level. Its interference is eliminated by expelling the carbonate as carbon dioxide at pH 4.0. Carbon dioxide is slowly absorbed by water so that in precise analyses, an inert nitrogen blanket should be maintained during the titration.

Fluoride complexes boric acid and interferes seriously. Samples containing fluoride, therefore, must be analyzed by the extraction-flame photometric method [2].

The range of this method is 0.1 to 4.25 mg of boron. The sensitivity varies with the nature of the sample. It is estimated to be 0.013 wt% for aluminum alloys, 0.033 wt% for stainless steel alloys, and 0.01 wt% for zirconium-based alloys. Samples with lower concentrations of boron should be analyzed by Methods B-Color-1 and B-Color-2 of this Manual.

DISCUSSION

Boric acid, $pK_a = 9.24$, is too weak to be titrated directly with sodium hydroxide. In the titration, therefore, mannitol is added to complex the boric acid releasing one hydrogen ion per mole of boric acid. The release of the hydrogen ion is complete and reproducible at a mannitol concentration of 0.6M. This is equivalent to 1.2 g of mannitol per 10 ml of the sample solution after removal of cations and carbon dioxide.

Although the boric acid is too weak to be determined directly with sodium hydroxide, it is titrated partially when the sample is adjusted to pH 7.00 with base. For this reason, the sodium hydroxide solution must be standardized against a standard boric acid solution using the same procedure that is used for samples. A difference of about 3% is observed when the normality obtained by standardization against potassium acid phthalate is compared with the normality obtained against standard boric acid.

The principal sources of error are: (a) loss of boron during sample preparation, (b) introduction of boron during sample preparation via reagents and apparatus, (c) incomplete removal of hydrolyzable cations, (d) incomplete removal of carbonate, and (e) insufficient addition of mannitol.

Boron, as boric acid, is volatilized under acidic conditions. This is especially severe at high temperatures such as that encountered with boiling sulfuric acid or fusions. Whenever possible, basic fusions should be used and if acid fusions are necessary, the fusion should be performed in fused quartz ware under total reflux. With reference to boiling acidic solutions, the volatilization of boron is slow enough that any losses from brief boiling usually can be neglected. One noteworthy exception to this is the boiling of nearly dry solutions where significant serious losses will occur.

Borosilicate glassware, used routinely for milligram-level boron determinations, is the principal source of boron contamination. Generally, the amount of boric acid leached by acidic solutions is of no consequence. On the other hand, basic solutions will leach significant quantities of boron from borosilicate glassware. The highly basic sodium hydroxide titrant should be stored in a plastic container and used soon after it is delivered to a buret of borosilicate glass. Sodium hydroxide left in contact with borosilicate glass for some time should not be used.

SPECIAL SAFETY PRECAUTIONS

The analysis of boron samples frequently involves high temperature fusions and dissolutions with various concentrated acids. Use appropriate protective equipment and follow routine safe practices.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Berzelius, 600-ml. Mark the beaker at 200 and 250 ml. These marks will facilitate sample dilution.

2. Beakers, Griffin, assorted sizes.

3. Buret, 10-ml, calibrated in 0.02-ml divisions.

4. Crucibles, zirconium, 60-ml with lids; platinum, 15-ml with lids.

5. Dissolution and distillation apparatus (for analysis of Zircaloy-type samples). The description of a suitable apparatus is given in Figure 1.

6. Filter paper, Whatman 41.

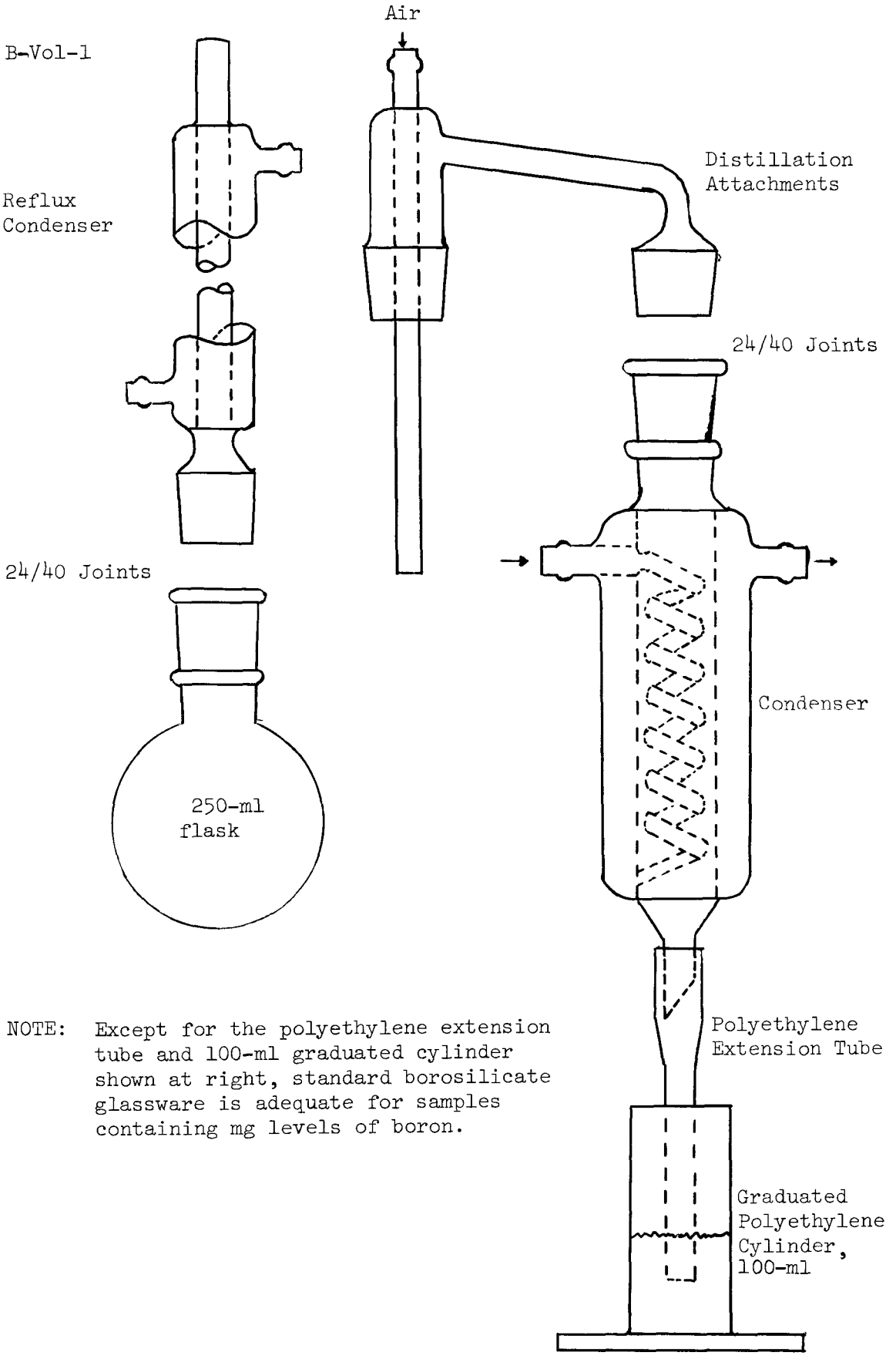
7. Flask, round or flat bottom, 100- and 250-ml.

8. Flasks, volumetric, assorted sizes.

9. Funnels, polyethylene or polypropylene, with ringstand and funnel rack.

10. Heating mantles, assorted sizes, with a Variac or Powerstat.

11. Hot plate, such as a Thermo-Stir hot plate, equipped with a magnetic stirrer.



NOTE: Except for the polyethylene extension tube and 100-ml graduated cylinder shown at right, standard borosilicate glassware is adequate for samples containing mg levels of boron.

Fig. 1 Dissolution and distillation apparatus for zircaloy-type samples.

12. Ion exchange column, 20-mm OD x 17-in. with a 35-mm OD x 4-in. reservoir, a 1- to 2-mm stopcock with a 2-in. stem, and a glass wool plug to retain the resin.

13. Magnetic stirrer and Teflon-coated stir bars.

14. Medicine droppers, polyethylene or polypropylene.

15. Membrane filter holder, 25.4-mm and 47-mm diam (Millipore Filter Corporation, Bedford, Mass.) with 0.45-μ pore size membrane filters from either Millipore or Gelman (Gelman Instrument Co., Ann Arbor, Mich.). To facilitate direct filtrations into a volumetric flask, attach 4 to 5 in. of 6- or 7-mm borosilicate glass tubing to the Millipore filter holder base. The glass tubing should be long enough to extend just below the shoulder of the flask.

16. pH meter with glass-calomel electrode system.

17. Pipets, macro and micro, assorted sizes, with rubber suction bulb and syringe.

18. Quartz dissolution apparatus. The description of a suitable apparatus is given in Figure 2.

19. Suction filtration flask, 2-liter. Remove the bottom of the flask by cutting horizontally around its circumference, 1 in. from the bottom. Grind the edge with carborundum on a piece of plate glass. This apparatus will enable filtrations directly into 100- or 200-ml volumetric flasks.

20. Wash bottles, polyethylene.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water. Except for strong acids, store all reagents in polyethylene bottles.

1. Aluminum matrix solution. Dissolve 50 g of 1100-S aluminum in 500 ml of conc HCl and dilute to 2 liters with water. One ml of this solution contains approximately 25 mg of aluminum.

2. Ammonium sulfate.

3. Ammonium sulfate (0.25 g/ml) - sulfuric acid (12M) matrix solution. Dissolve 125 g of $(NH_4)_2SO_4$ in 12M H_2SO_4 and dilute to 500 ml with 12M H_2SO_4.

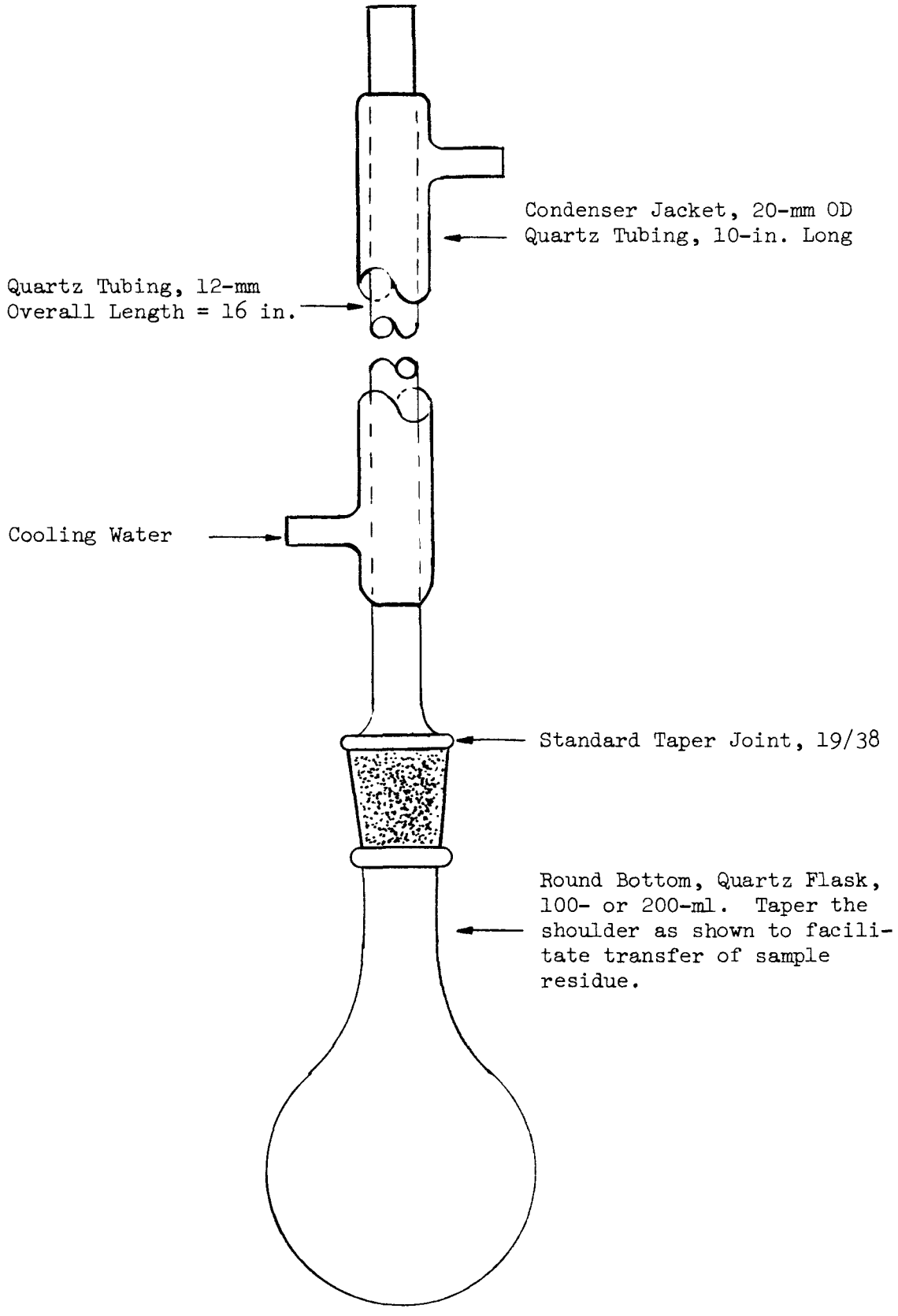


Fig. 2 Quartz dissolution apparatus.

4. Boron standard solution, 1.500 mg B/ml. Dissolve 8.588±0.001 g of 99.9% H_3BO_3 in water and dilute to 1 liter.

5. Hydrochloric acid, conc and 1M.

6. Ion exchange resin, Dowex 50W-X8, 50-100 mesh, hydrogen form.

7. Iron, pure, granulated (G. Frederick Smith Chemical Co., Columbus, Ohio).

8. Mannitol.

9. Nitric acid, conc.

10. Sodium carbonate, anhydrous.

11. Sodium hydroxide, 0.02N. Dilute 8 ml of 10N carbonate-free NaOH (obtainable from Fisher Scientific Company) to 4 liters with preboiled water. Standardize against the 1.5 mg/ml standard boron solution according to Procedure B.

12. Sodium hydroxide, 19M and 1M. Prepare as needed using commercial sodium hydroxide and distilled water. (DO NOT USE BOROSILICATE GLASSWARE)

13. Sodium peroxide, Na_2O_2.

14. Stainless steel matrix solution. Dissolve 75 g of Na_2CO_3 in about 500 ml of water. Add cautiously, 130 ml of conc HNO_3. Stir to expel CO_2. Add 164.6 g of $FeCl_3 \cdot 6H_2O$, 69.2 g of $Cr(NO_3)_3 \cdot 9H_2O$, and 34.6 g of $Ni(NO_3)_2 \cdot 6H_2O$. Stir to dissolve. Filter through a 0.45-μ Millipore filter and dilute to 2 liters with water. One ml of this solution contains 25 mg of stainless steel constituents.

15. Sulfuric acid, conc and 12M.

PROCEDURE

NOTE: Use distilled water throughout the procedure.

A. Blanks

1. Standardization of 0.02N NaOH.

   No blank is required. The usual titration blank for 250 ml of preboiled water is 0.01 ml.

2. Analysis of bench standards and samples per Procedures F and H.

Process an appropriate blank with each bench standard and with each series of samples per Procedures F and H. Use 20 ml of the aluminum matrix solution or 10 ml of the stainless steel matrix solution for the bench standards and 20 ml of water for samples.

3. Analysis of bench standard and samples per Procedures G and H.

To prepare a blank for the bench standard, process 10 ml of the $(NH_4)_2SO_4$-H_2SO_4 matrix solution per Procedures G and H beginning with Step G-4.

To prepare a blank for samples, deliver 5 ml of water, 25 g of $(NH_4)_2SO_4$, and 15 ml of conc H_2SO_4 to the 250-ml flask of the distillation apparatus and process the mixture per Procedures G and H beginning at Step G-4.

B. Standardization of 0.02N NaOH

Initially, standardize the 0.02N NaOH solution by titrating 1.00-ml portions of the 1.5 mg/ml boron standard in quadruplicate. Thereafter, run duplicate standardizations each time a sample is analyzed. The average of the duplicates should agree with the previous standardization value within 0.5%. If it does not, process another pair, then average the four results.

Pipet 1.00 ml of the 1.500 mg/ml standard boron solution into 250 ml of preboiled water contained in a 600-ml Berzelius beaker and continue according to H. Calculate the normality of the sodium hydroxide solution using the equation

$$\underline{N} = \frac{1.50}{10.82(\text{ml NaOH})} \qquad (1)$$

C. Bench Standard

NOTE: Analyze a bench standard with each series of samples. Limits will be specified by the Quality Control Laboratory. The bench standard must be analyzed as directed below by the same procedure as that used for the analysis of samples.

1. Bench standard for analysis of samples according to Procedures F & H.

Pipet 1.00 ml of the 1.500 mg/ml standard boron solution into a clean 100-ml beaker. Add 20 ml of the aluminum matrix solution or 10 ml of the stainless steel matrix solution (see the note above) and dilute to approximately 40 ml with water. Continue beginning at Procedure F-1.

2. Bench standard for analysis of samples according to Procedures G & H.

Pipet 1.00 ml of the 1.500 mg/ml standard boron solution into the round bottom distillation flask (Figure 1) and add 10 ml of the

$(NH_4)_2SO_4$-H_2SO_4 matrix solution. Continue beginning at Procedure G-4, then complete the determination according to Procedure H.

D. Resin Purification and Column Preparation

"Baker Analyzed" Reagent Dowex resin, although purified, often contains residual dyes and small amounts of metal ions such as iron(III). Before using, wash the resin thoroughly in a large column with 6M HCl and copious volumes of water.

The ion exchange column has a resin capacity of approximately 110 ml. Fill the column to within 2 to 3 in. of the reservoir with clean resin.

E. Sample Dissolution

1. Aluminum Alloy Samples

a. Weigh a sample of 3 g or less containing greater than 0.4 mg of B.	
b. Transfer the sample to a clean 100- or 200-ml quartz flask and dissolve it under reflux using 10 ml of conc HCl per gram of sample.	If the sample yields a residue, continue with Step c. If not, omit Steps c through g and continue with Step h.
c. Filter the residue on a 0.45-μ membrane filter or a Whatman 41 filter paper. Use water to transfer and wash the residue. Collect the filtrate and washes in a 200-ml volumetric flask.	
d. Ignite the filter and residue in a platinum crucible to destroy the filter.	If a Millipore filter apparatus and membrane filter is used to filter the residue, recover all residue adhering to the inside walls of the reservoir with pieces of moist Whatman 41 filter paper.
e. Add 1 g of anhydrous Na_2CO_3, cover the crucible with a platinum lid, and fuse the sample over an air-fed Meker	

burner or in a muffle furnace at 900°C.

f. Deliver 2 ml of conc HCl and 25 ml of water to a 150-ml beaker. Lay the COOL platinum crucible in the acid solution and dissolve the melt.

Use a cover glass over the beaker to prevent loss of boron through spattering.

g. Transfer the solution to the 200-ml volumetric flask containing the original filtrate (Step c).

h. Dilute to 200 ml with water and mix well.

i. Continue per Procedure F.

2. Stainless Steel Alloy Samples

a. Weigh a sample of 1.2 g or less containing more than 0.4 g of boron.

b. Transfer the sample to a clean 100- or 200-ml quartz flask and dissolve it under reflux using 3 ml of conc HCl, 2 ml of conc HNO_3, and 5 ml of water per gram of sample.

If the sample yields a residue, continue with Step c. If not, omit Steps c through l and continue with Step m.

c. Filter the residue on a 0.45-μ membrane filter or a Whatman 41 filter paper. Use water to transfer and wash the residue and collect the filtrate in a 200-ml volumetric flask.

d. Ignite the filter and residue in a zirconium crucible.

If membrane filtration is employed, recover the residue adhering to the walls of the filtration apparatus with pieces of moist Whatman 41 filter paper.

e.	Cover the residue with 1 g of Na_2O_2, then cover the Na_2O_2 with 0.5 g of Na_2CO_3.	
f.	Fuse the contents of the crucible slowly over a Meker burner until all lumps disintegrate.	To minimize spatter losses, incline the crucible at a 45° angle and swirl the melt continuously. The use of a zirconium lid is suggested; however, this hampers visual inspection.
g.	Cool the crucible. Add 15 ml of water to the crucible, then heat gently on a hot plate to dissolve the melt.	
h.	Filter the sample through a Whatman 41 filter paper supported on a plastic funnel. Collect the filtrate in a 4-oz polyethylene bottle.	
i.	Thoroughly wash the residue on the filter with water.	Use the yellow color of the chromate ion as a guide to the completeness of the washing.
j.	Neutralize the filtrate with 3 ml of conc HNO_3 and stir the solution (magnetic stirring) for 3 to 5 min to expel gases.	
k.	Add 4 to 5 g of pure granulated iron metal and stir until all the Cr(VI) is reduced to Cr(III).	Complete reduction is indicated by a color change from orange to blue or olive.
l.	Filter the solution through a 0.45-μ membrane filter or Whatman 41 filter paper and combine the filtrate and water washings with the original filtrate from Step c.	

m. Dilute to 200 ml with water and mix well.

Solutions treated per Step n must be analyzed right away. If it is necessary to hold the solution, defer Step n until the solution can be analyzed.

n. Contact the diluted solution with 4 to 5 g of iron granules and proceed immediately per Procedure F.

3. Zirconium Alloy Samples

The dissolution of zirconium-type samples is described under Procedure G.

F. Removal of Diverse Ions via Ion Exchange and Removal of Carbonate

1. Transfer an aliquot (50 ml or less) of the sample solution containing between 0.1 and 4.25 mg of B into the reservoir of the ion exchange column prepared per Procedure D.

The sample aliquot can have up to 750 mg of Al or 300 mg of stainless steel.

For best results, select a sample with more than 1 mg of B.

2. Pass the sample through the column at a rate of 2 to 3 drops/sec and collect the effluent in a 600-ml Berzelius beaker. Wash the sample through with water until a total of 200 ml of effluent is collected.

For convenience, the beaker should be marked at 200-ml and at 250-ml.

3. Using magnetic stirring and a pH meter, adjust the pH to 3.9±0.1 with saturated 1M NaOH. If the pH rises above 4.0, acidify with 1M HCl to the proper pH.

Samples should be titrated as soon as possible after decarbonation per Steps 3 to 5. If the sample cannot be titrated right away, defer Steps 3 to 5.

4. Place a 250-ml round- or flat-bottomed flask filled with ice on the beaker, and using continuous magnetic stirring to prevent bumping, heat to boiling and boil for 5 min.

5. Cool the beaker in a cold water bath then rinse the "condenser" flask with water.

   Avoid excessive use of wash water. The volume of this point should be well below 250 ml.

6. Continue with the titration per Procedure H without prolonged delay.

G. Distillation-Separation of Boron for Zirconium Alloy Samples

NOTE: This method is not applicable to samples that contain boron in the form of boron carbide, B_4C.

1. Weigh a sample, 1 g or less, containing 0.1 to 4.25 mg of boron.

   For best results, select a sample with more than 1 mg of B.

   Aqueous Zr samples void of F^- also can be analyzed. Pipet an aliquot of 5 ml or less containing 0.1 to 4.25 mg of B into the distillation flask, carefully add 10 ml of conc H_2SO_4 and 65 ml of methanol, and continue beginning at Step 7.

2. Transfer the sample to the flask of the distillation apparatus (Figure 1).

3. Add 2.5 g of $(NH_4)_2SO_4$ and 15 ml of conc H_2SO_4 for each 0.5 g of sample or fraction thereof.

4. Add 3 ml of conc HNO_3 and heat (using a heating mantle) under reflux until complete dissolution occurs.

   Set the Variac at about 80.

5. Remove the heating mantle, cool the flask in air, then chill it to room temperature in an ice bath.

6. Slowly add 65 ml of methanol to the flask through the condenser.

7.	Set up the apparatus for distillation (Figure 1). Deliver 5 ml of 1M NaOH and 25 ml of water to a 100-ml polyethylene graduated cylinder and immerse the condenser tip in the basic solution.	
8.	Adjust the air flow to about 5 bubbles/sec and distill 50 ml of methanol. Use a heating mantle for the distillation.	If the sample contains high concentration of volatile anions such as Cl^-, add 2 drops of 0.2% phenolphthalein indicator to the basic absorber solution and add saturated NaOH as required to maintain a basic solution.
9.	Rinse the condenser with water and collect the water rinses in a 600-ml Berzelius beaker. Transfer the distillate from the graduated cylinder to the beaker with water rinses.	Proceed without delay to Steps 10 and 11.
10.	Dilute to 200 ml with water.	
11.	Adjust the pH to 3.9±0.1 with 1M HCl. If the pH drops below 3.8, add 1M NaOH to return the pH to the desired range.	
12.	Place a 250-ml round-bottom flask filled with crushed ice on the beaker, and using continuous magnetic stirring to prevent bumping, heat to boiling and boil for 5 min.	
13.	Cool in a cold water bath, then rinse the outside of the flask with a few ml of water collecting the rinsings in the beaker.	The volume at this point should be well below 250 ml.
14.	Titrate the sample without delay per Procedure H.	

H. Titration of Samples

1. Rinse down the walls of the beaker with water and adjust the pH to 7.00 with the 0.02N NaOH titrant. If necessary, dilute HCl also may be used to obtain the desired pH.

   The sample volume at this point should be 250 ml or less.

   For precise work, use a nitrogen purge during the titration to minimize absorption of CO_2.

2. Add 30 g of mannitol.

   The mannitol concentration must be at least 0.6M. This is equivalent to 1.2 g of mannitol for each 10 ml of solution. If the volume of the treated sample solution exceeds 250 ml, increase the addition of mannitol appropriately.

   With a 10-ml buret, it will be necessary to refill the buret for samples containing more than 2.15 mg of B. If the sample contains more than 4.3 mg of B (requires more than 20 ml of 0.02N NaOH), discard the sample and process a smaller aliquot. If additional sample is not available, report to your supervisor.

3. Fill the buret with fresh 0.02N NaOH and titrate immediately to exactly pH 7.00.

4. Record the data and calculate the results as described under CALCULATIONS.

CALCULATIONS

Record the data and calculate the results as shown on the example work sheet. Report all results to three significant figures.

The answer is calculated in terms of milligrams of boron per unit volume or unit weight of sample using the atomic weight, 10.82, for natural boron. If the boron is not natural, the isotopic composition of the boron must be determined by mass spectrometry and appropriate corrections should be applied.

REFERENCES

1. J. R. Martin and J. R. Hayes, "Application of Ion Exchange to Determination of Boron", Anal. Chem., 24 (1952) p 182.

2. W. J. Maeck, M. E. Kussy, B. E. Ginther, G. V. Wheeler, J. E. Rein, "Extraction-Flame Photometric Determination of Boron", Anal. Chem., 35 (1963) pp 62-65.

October 1967

S. S. Yamamura
M. A. Wade

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Boron

CHARGE NUMBER _____ PROCEDURE B- Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Sample wt, g	NaOH N	NaOH ml	B in Aliquot mg	B in Aliquot Corrected mg			RESULT mg B/g
11- A1-1	3.5000g/200ml/20ml	3.5000	0.01995	4.50	0.971	0.950 ± 0.030			2.71 ± 0.086

ANALYZED BY _____ DATE _____

CALCULATIONS:

$D = 10.82\,BC = 10.82\,(0.01995)\,(4.50) = 0.971$ mg B

$$\text{Result} = \frac{E(200\text{ml})}{(3.5000\text{g})(20\text{ml})} = \frac{(0.950 \pm 0.030)(200)}{(3.5000)(20)} = 2.71 \pm 0.086 \text{ mg B/g}$$

APPROVED BY _____

DETERMINATION OF CALCIUM IN WCF SOLUTIONS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

ABSTRACT

Calcium in WCF solutions is determined by comparing the atomic absorption of a sample to the atomic absorption of a known set of standards. Samples and standards are aspirated into a nitrous oxide-acetylene flame system after the addition of potassium as potassium chloride to a concentration of 2 mg/ml.

APPLICABILITY

This method is used for the determination of calcium in Waste Calcination Facility (WCF) or pilot plant solutions. Samples should be diluted to contain between 5 and 10 µg Ca/ml, and the final dilution should contain 2 mg/ml of potassium added as the chloride to prevent ionization of the calcium neutral atomic species.

In addition to providing increased sensitivity by preventing ionization of neutral calcium atoms, this addition of potassium helps to overcome some residual interelemental effects and to extend the applicability of the method. In the absence of potassium, aluminum at 100 µg/ml and zirconium at 200 µg/ml cause significant suppression of the calcium response. Free fluoride ion also results in a slight suppression of calcium absorbance. In combination, some suppression occurs even at much lower concentrations of these elements. Boron enhances calcium absorbance. The presence of potassium at a level of 1 mg/ml is adequate to remove the effect of Zr, Fe, B, Sn, NO_3^-, and F^- at concentrations twenty times higher than those expected in WCF samples diluted to bring calcium concentration within the required range; however, an additional 1 mg/ml potassium is necessary to prevent enhancement by aluminum or by a combination of elements.

Figure 1 shows the effect of added potassium on the absorbance by calcium in the nitrous oxide-acetylene flame in the presence of aluminum, zirconium, and the combination of ions expected in WCF solutions. The concentrations indicated represent a level sixteen times greater than that expected in samples diluted to the proper concentration for the calcium determination. Base absorbance, represented by a dashed line, is for 5 µg Ca/ml in the presence of 1 mg/ml added potassium. Each solution contained an equal amount of calcium. While 1 mg/ml of added potassium restores the absorbance

to the base level for a combination of other ions, an equal addition of potassium did not fully compensate for 100 µg/ml of aluminum. Even though the observed suppression by aluminum is not statistically significant, the recovery of the calcium absorbance in the combined matrix could be partially attributed to the enhancement effect of the boron in that combined matrix. A 2 mg/ml potassium concentration, therefore, has been selected to prevent aluminum suppression in the absence of boron.

DISCUSSION

Calcium determinations by atomic absorption methods are reported in the literature to be flame sensitive, especially when an air-acetylene flame system is used. In order to optimize calcium absorbance, even with a nitrous oxide-acetylene flame, care should be taken to adjust the flow of fuel and oxidant. This adjustment should be made at the beginning of each analysis run. The normal nitrous oxide-acetylene flame (pink cone about five-eighths inches high) is best for calcium absorbance. Richer or leaner flames result in lower sensitivities or higher noise levels. Burner height adjustments are also critical if the light passes through the flame close to the burner head. Figure 2 shows flame profiles for aqueous solutions of calcium in both air-acetylene and nitrous oxide acetylene as well as aqueous solutions of calcium in the nitrous oxide-acetylene flame with and without added potassium. In all cases, optimum absorbance is obtained relatively high in the flame, and in the cases for the nitrous oxide-acetylene flame, these maxima tend to stabilize when the bottom of the focused beam is more than 11 mm above the top of the burner head. This stability helps to reduce variations in absorbance arising from changes in flame conditions which may occur during a sample analysis run.

Any carbon desposits which may build up on the perimeter of the burner slot should be removed immediately to prevent alteration of the path length and the shape of the flame. Calibration curves over the working range of 0 to 12.0 µg Ca/ml show only slight curvature as is shown in Figure B-4.

SPECIAL SAFETY PRECAUTIONS

Explosions of nitrous oxide-acetylene mixtures are common; therefore, follow carefully all instructions for lighting and extinguishing the flame. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of the drain tube must extend below the surface of the liquid in the waste receptacle. Spills can be prevented by only partially filling the sample cups.

APPARATUS AND REAGENTS

A. Apparatus

1. Burner, nitrous oxide-acetylene, 6-cm slot.

2. Cups, plastic, 5-ml, caplugs No. 12X.

3. Flask, volumetric, 10-ml.

4. Pipets, 250-µl, with control syringe.

5. Spectrophotometer, atomic absorption, Techtron AA-5 or equivalent instrument with attachments.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagent and matrix solutions.

1. Calcium standard stock solution, 1.00 mg/ml. Dissolve a slurry of 2.497 g $CaCO_3$ in 300 ml of water by careful addition of nitric acid. Boil to expel CO_2, cool and dilute to 1 liter.

2. Potassium diluent solution. Dissolve 3.911 g KCl with water and dilute to 1 liter.

3. Calcium calibration standards. Dissolve 3.815 g KCl in each of seven 1-liter volumetric flasks. Dilute the first flask to 1 liter with water and mix well. This is the blank solution. To the remaining six flasks add 2.00 ml, 4.00 ml, 6.00 ml, 8.00 ml, 10.00 ml, and 12.00 ml, respectively of the 1 mg/ml calcium standard stock solution and dilute each to volume with water. These standards cover the concentration range 0 to 12 µg Ca/ml in 2-µg increments.

4. Calcium bench standard. Prepare a 250 µg/ml bench standard following the directions given above for preparing the calibration standards.

5. Calcium controls. Following the directions given above for preparing the calibration standards, prepare a series of four controls with calcium concentrations in the range 80 to 400 µg/ml. No blank is required.

PROCEDURE

A. Sample Preparation

1. Plant Samples

Pipet a 250-µl aliquot of the sample dilution available for radiochemical analysis (0.1/10.1 ml in 1M HNO_3) into a 10-ml volumetric flask and dilute to the mark with the potassium diluent solution.

2. Bench Standards and Controls

Pipet a 250-µl aliquot of the bench standard or control solution into a 10-ml volumetric flask and dilute to the mark with the potassium diluent solution.

B. Calibration

The analyst has an option of two methods of calibration. One method is to process the blank and six calibration standards for construction of a calibration curve. The other approach is to process two standards that bracket the concentration of the sample. In either case, the standards are processed per Procedure D in the same manner as any sample.

C. Analysis of Bench Standards and Controls

Analyze the bench standard per Procedure D each time an analysis is performed. If the bench standard result does not fall within specified limits, make another analysis run. Seek help if this second result is still outside the limits.

D. Analysis of Samples

Perform analysis in accordance with normal instrument operating procedures. Verify that the correct shutdown procedure was followed. If any control or condition is not as it should be, correct it.

Operation	Specific Instruction
1. Turn on power.	Three switches, one each on monochromator, readout unit, and hollow cathode supply.
2. Rotate hollow cathode into position.	Ca hollow cathode.

3.	Set hollow cathode current.	Set at 6 ma and allow warmup of at least 10 min.
4.	Adjust hollow cathode position.	Circle of light should center on monochromator slit.
5.	Mount proper burner head.	Nitrous oxide-acetylene, 6-cm slot.
6.	Align burner with respect to light beam.	Adjust burner horizontal movement and rotation.
7.	Set burner height.	Set vernier at 22. Bottom of focused beam should be 13.5 mm above burner top.
8.	Set the wavelength dial.	Set at 4226.7Å.
9a.	Set the backing control.	Zero
b.	Set the damping switch.	D
c.	Set the select switch.	Normal
d.	Set the mode switch.	%T
e.	Set the scale expand.	X1
f.	Set the monochromator slit.	25 μ
g.	Set the coarse gain.	To give meter reading of about 50.
10.	Adjust wavelength to give maximum meter deflection.	Change gain as required to keep meter on scale.
11.	Verify that drain tube extends below surface of liquid in waste receptacle.	
12.	Set exhaust control.	Open
13.	Turn on supply valves.	Air, acetylene (C_2H_2), and N_2O are needed.
14.	Adjust regulator settings.	Air - 15 gauge C_2H_2 - 13 gauge N_2O - 24 gauge

15a.	Turn support valve to air.	Adjust support pressure to 15 psi.
b.	Turn support valve to N_2O	Support pressure should read 15 psi.
c.	Turn support valve off.	
d.	Turn valve to C_2H_2.	Adjust flowmeter setting to 3.
e.	Turn support valve to air.	
f.	Light the burner.	Allow air to flow for at least 5 sec before lighting the burner.
g.	Raise fuel flowmeter setting to 9.	
h.	Rapidly switch support valve to N_2O.	
i.	Adjust flowmeter settings. (1) N_2O - ∿5.5 (flow) (2) C_2H_2 - ∿7.5 (flow)	Flow should be adjusted to obtain a pink inner cone about 0.625-in. high. Check by aspirating a standard.
16.	Adjust the exhaust control.	Close exhaust as necessary to stabilize flame, but never close exhaust completely.
17.	Block the light beam and set the readout zero.	Adjust with backing control if necessary.
18.	With light beam unobstructed, adjust the gain controls.	Set for readout of 100.
19.	Turn mode switch to ABS.	Set for readout of zero with fine gain control.
20.	Set select switch to auto 100 and the auto/read switch to auto. Aspirate blank solution.	Reset the readout to zero with the set 100 control.
21.	With auto/read switch on auto, aspirate 12 µg/ml standard. Adjust flame or scale expand to obtain readout of 1.000.	If readout exceeds 1.0, rotate burner slightly. If readout is less than 1.0, adjust with scale expand.
22.	Aspirate blank solution with auto/read switch on auto.	

23. Switch auto/read switch to read.

24. Move atomizer capillary to sample solution. Wait for readout to reach a stable value.

25. Record readout value on work sheet.

26. Transfer capillary to blank solution.

27. Switch auto/read switch to auto. Repeat Steps 22-27 for all standard and sample solutions.

See instructions in the operating manual for calibration and use of curve corrector and direct readout attachment.

CALCULATIONS

The concentration of calcium in the diluted sample can be obtained by either of two methods. A calibration curve relating absorbance to concentration can be plotted from the calibration standards data. The concentration of calcium in µg/ml corresponding to the sample absorbance can be read from the calibration curve. The two-standard bracket method may also be used. The calcium concentration of the diluted sample is then calculated from the following equation:

$$C = \frac{Y_s - \frac{y_1(x_1-x_2) - x_1(y_1-y_2)}{x_1-x_2}}{\frac{y_1-y_2}{x_1-x_2}} \qquad (1)$$

where

C = calcium concentration of sample in µg/ml

Y_s = sample absorbance

x_1 = concentration of high standard

x_2 = concentration of low standard

y_1 = absorbance of high standard

y_2 = absorbance of low standard.

The result to be reported is calculated by substituting the concentration in µg/ml in the formula below and solving the equation.

$$\underline{M} = \frac{[(C+bias)\pm sd](4040)}{1000(40.08)} \qquad (2)$$

where

$\underline{M}$ = molarity of calcium in the sample

C = calcium concentration in µg/ml

bias = µg of calcium added or subtracted as shown by control data

sd = standard deviation of the control data

4040 = dilution factor

40.08 = atomic weight of calcium.

May 1972
T. R. Lyon

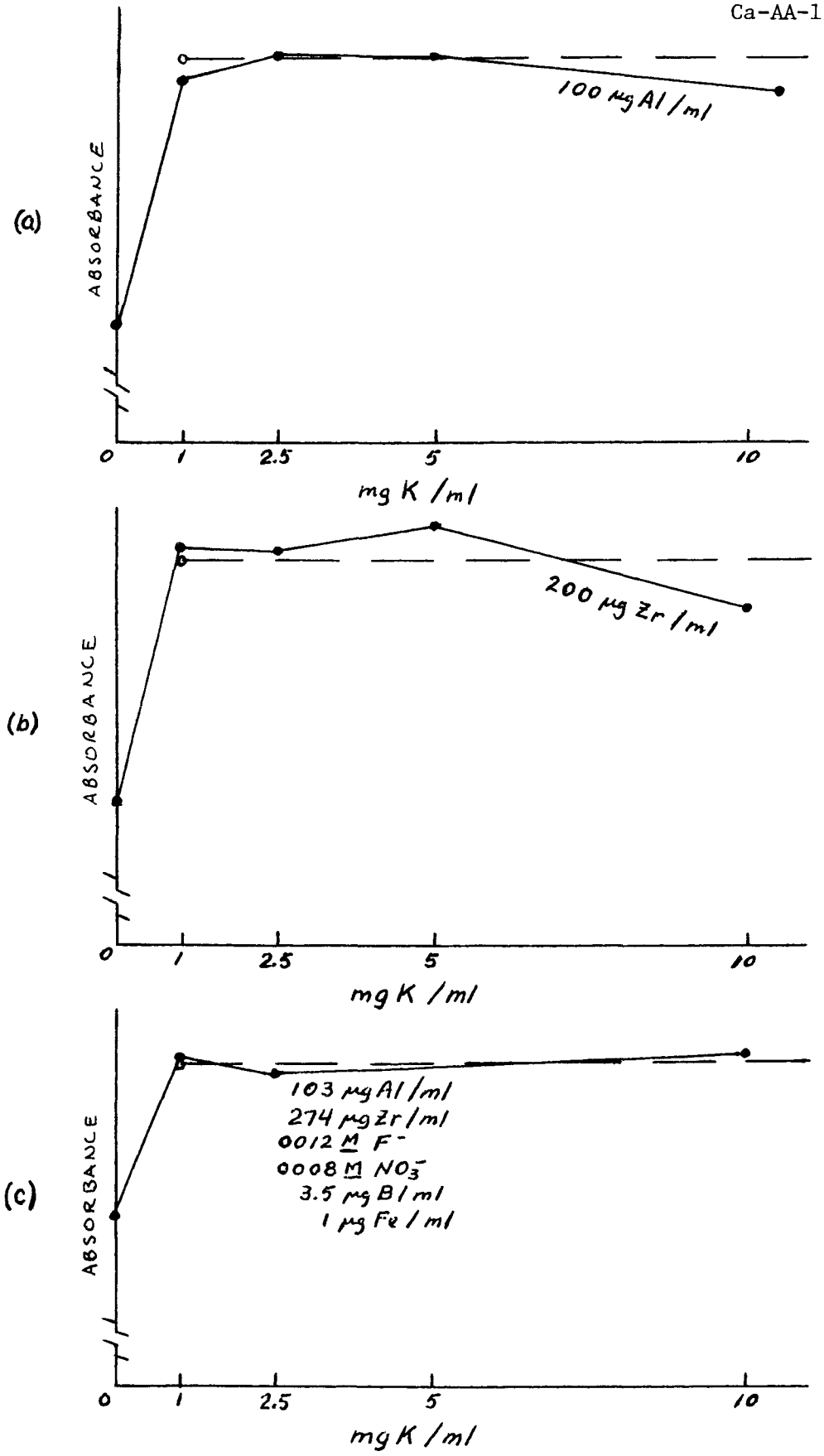


Fig. 1 Effect of added K on absorbance of Ca in N_2O-C_2H_2 flame in the presence of other ions.

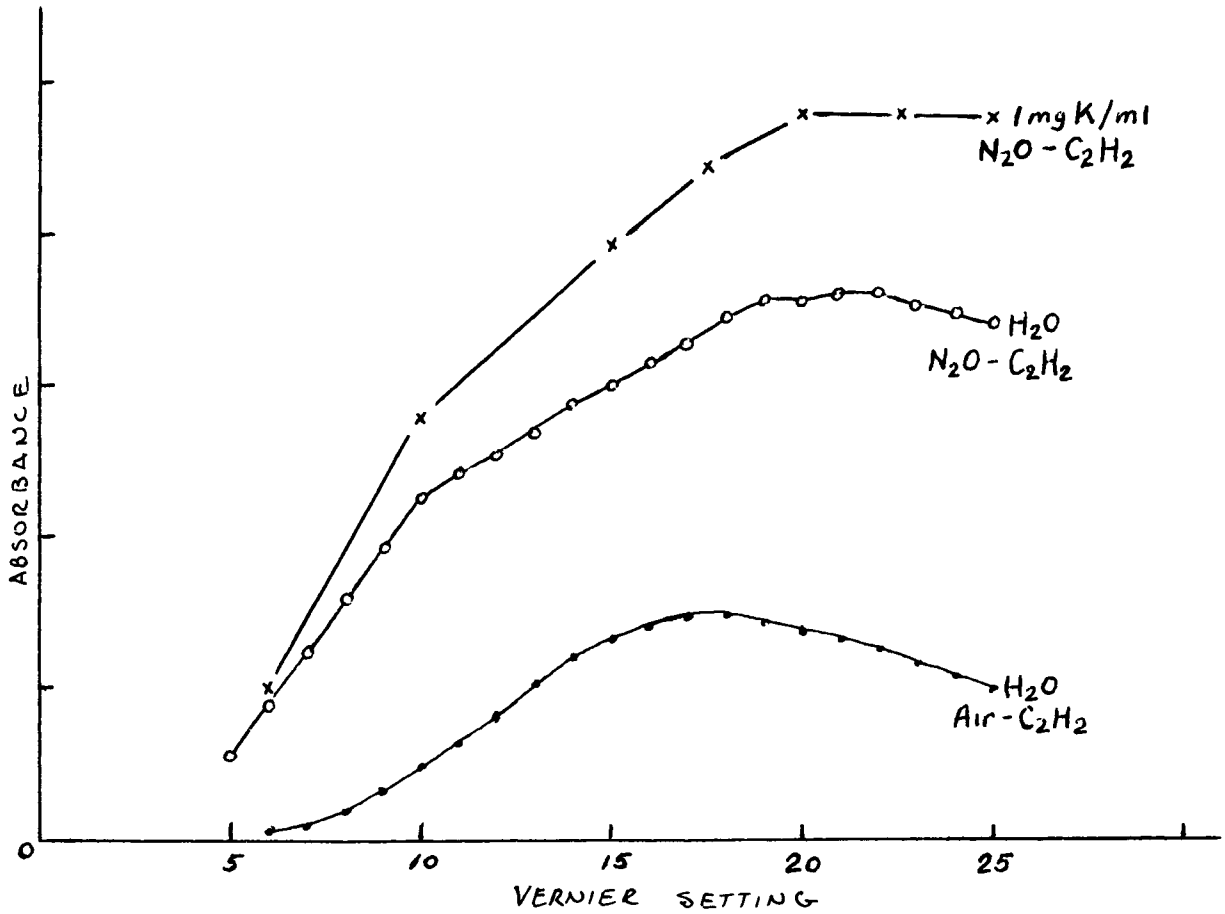


Fig. 2 Flame profiles for Ca absorbance under varying conditions.

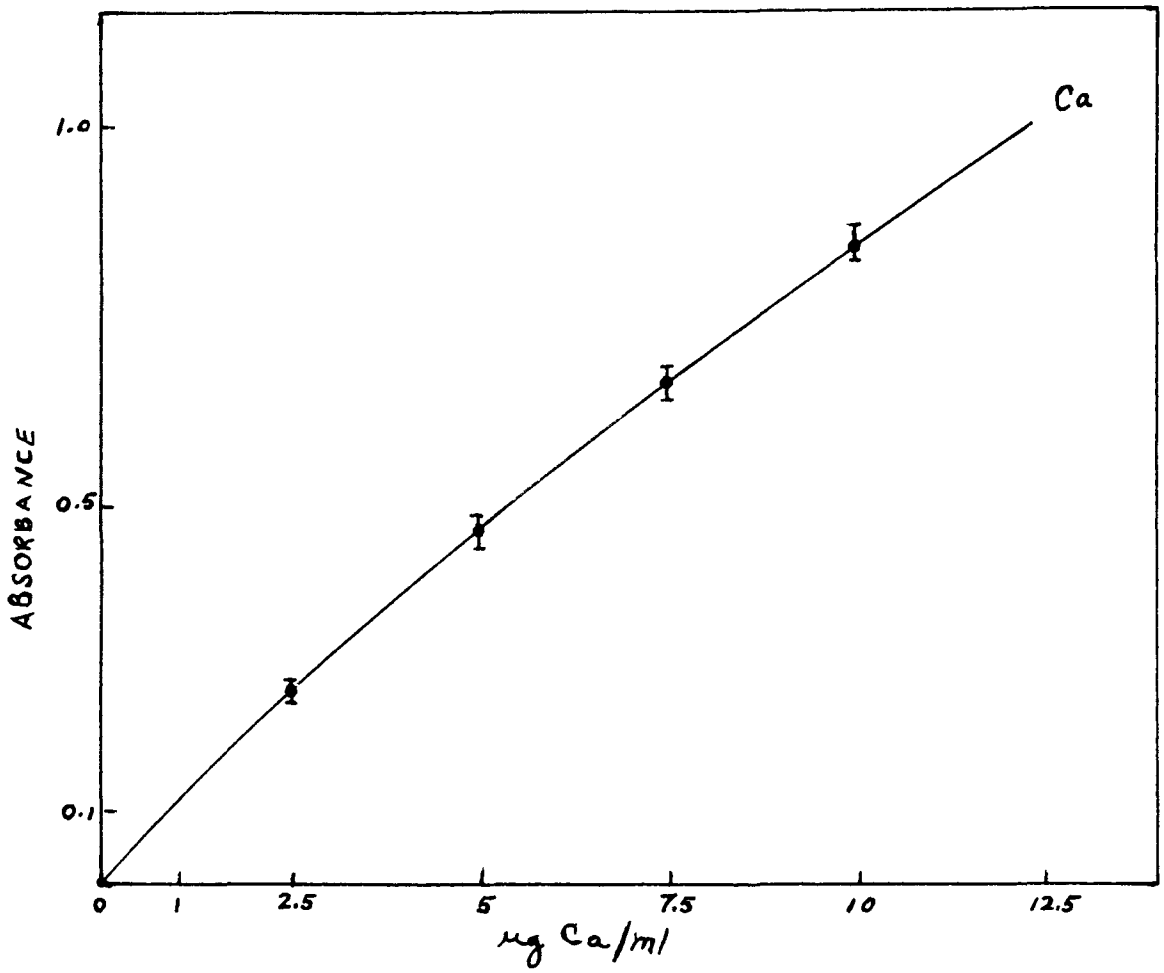


Fig. 3 Typical Ca Calibration curve for N_2O-C_2H_2 flame.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Calcium

CHARGE NUMBER _____ PROCEDURE Ca-AA-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Ca, mg/ml	Bias correction	dilution factor	std. dev.			RESULT M
WC-101	a1/10.1/0.25/10	0.539	5.95	-0.05	4040	0.31			0.59±0.03
7.5 mg Ca/dl		0.660							
5.0 mg Ca/dl		0.465							

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$B = \frac{0.539 - \left[\frac{0.660(7.5-5.0) - 7.5\,(0.660-0.465)}{(7.5-5.0)}\right]}{\frac{(0.660-0.465)}{7.5-5.0}} = 5.95$$

Bias = +0.05 std. dev. = 0.31

$$\text{Result} = \frac{[(5.95-0.05)\pm 0.31]\,4040}{1000\,(40.08)} = 0.59 \pm 0.03\ M$$

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APPROVED BY _____

VOLUMETRIC DETERMINATION OF CALCIUM WITH EDTA

ABSTRACT

A titrimetric method is described for the determination of calcium in the milligram range. Calcium is titrated with standard EDTA (ethylenediamine tetraacetic acid) in 20- to 40-volume percent ethanol at pH 10 to 10.5 to a metalphthalein end point.

APPLICABILITY

This method is applicable to the determination of calcium in relatively pure solutions that contain only minor amounts of diverse metal ions. Most polyvalent metal ions react with EDTA and interfere. Also, complexing anions such as carbonate, citrate, and tartrate interefere.

DISCUSSION

Calcium reacts with EDTA in a 1:1 ratio at pH 10 to 10.5. The end point is indicated by the decomposition of the purple calcium-metalphthalein complex. In aqueous medium, the end point color transition is purple to light pink. The addition of alcohol diminishes the pink color of the uncomplexed indicator so that in 20- to 40-volume percent ethanol the end point is essentially purple to colorless, and the titration is not affected adversely by marked increase in the addition of indicator.

After the pH is raised to 10.5, the titration must be done as rapidly as possible to minimize absorption of carbon dioxide. Calcium is complexed by carbonate and high carbonate levels cause precipitation of calcium with subsequent low results.

SAFETY PRECAUTIONS

Use normal safety precautions when handling conc HCl and conc NH_4OH. When dissolving the calcium carbonate, do not add the acid too rapidly.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150-ml. For convenience, use beakers with etched graduations.

2. Buret, 25-ml, calibrated in 0.1-ml divisions.

3. Dropping bottle.

4. Magnetic stirrer and stir bars.

5. pH meter with high pH range, glass-calomel electrode system.

6. Pipets, macro and micro, assorted sizes, with suction bulbs and syringes.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents and throughout the method.

1. Ammonium hydroxide, conc, in a dropping-bottle.

2. Buffer, standard, pH 10.

3. Calcium bench standard, 1.00M. Dry reagent grade $CaCO_3$ at 105°C for overnight or longer. Weigh 50.005±0.001 g into a 500-ml Erlenmeyer flask. Add 100 ml of water. Place a funnel in the neck of the flask and add 100 ml of conc HCl a little at a time to dissolve the $CaCO_3$. Boil for 10 min to expel CO_2, cool the solution; then, dilute, to volume in a 500-ml volumetric flask.

4. EDTA solution, 0.05M. Prepare a large batch of 0.05M EDTA using 18.65 g of $Na_2EDTA \cdot 2H_2O$ per liter of solution. Dissolve the salt in a minimum volume of water, filter through a 0.45-μ membrane filter; then dilute the filtrate to the appropriate volume with water. Standardize the solution against a standard zinc solution per Method EDTA-1 of this Manual.

5. Ethanol, 95%.

6. Hydrochloric acid, conc.

7. Metalphthalein indicator, 0.1%. Add 0.1 g of metalphthalein to 95 ml of water; then add 3 ml of conc NH_4OH to dissolve the indicator. This reagent is stable for about 1 week. Alternatively, grind 0.5 g of metalphthalein with 100 g of NaCl. This salt mixture is stable indefinitely.

PROCEDURE

A. Blank

A blank is not required for this procedure.

B. Bench Standard

Process a 1.00-ml aliquot of the calcium bench standard per Procedure C.

C. Analysis of Samples

1.	Pipet a sample aliquot containing 8 to 40 mg of Ca (0.2 to 1 mM) into a graduated 150-ml beaker.	For maximum accuracy, select the aliquot to contain at least 20 mg, if possible.
2.	Add 0.5 ml of conc HCl and dilute to 60 ml with water.	If CO_3 is suspected, boil gently for 4 min before diluting to 60 ml.
3.	Add 40 ml of 95% ethanol.	
4.	Standardize the pH meter with the pH 10 buffer.	
5.	Adjust the sample to pH 10.5 with conc NH_4OH.	After adjusting the pH to 10.5, titrate as rapidly as possible to minimize absorption of CO_2 from the atmosphere.
6.	Add sufficient metalphthalein indicator solution (or metalphthalein-NaCl solid mixture) to give a purple color. Usually 7 to 10 drops of the solution is sufficient.	
7.	Titrate with standard 0.05M EDTA solution to a change from purple to colorless.	As the sample is titrated, the pH drops. Add conc NH_4OH dropwise to maintain the pH within the range 10 to 10.5

8. Record the data and calculate the results as shown on the example work sheet. Report three significant figures.

REFERENCES

1. J. R. McCallum, "Analysis for Small Amounts of Calcium, Magnesium, Barium, and Sulfate Using Phthalein Purple", Can. J. of Chem., 34 (1956) pp 921-925.

October 1967
D. R. Trammell

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Calcium

CHARGE NUMBER _____ PROCEDURE Ca-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	EDTA, M	EDTA, ml	Ca in Aliquot Analyzed, mg					RESULT mg Ca/ml
ST-1	0.3 ml	0.05033	23.53	1.184					157.9
	(NO Dilution)								or
									3.95 M

ANALYZED BY _____ DATE _____

CALCULATIONS:

$C = A\,B\ (23.53)(0.05033) = 1.184$

$\text{Result} = \frac{40\,C}{\text{Sample Vol}} = \frac{(40)(1.184)}{0.3} = 157.9$ mg Ca/ml

or, $= \frac{C}{\text{Sample Vol}} = \frac{1.184}{0.3} = 3.95$ M

APPROVED BY _____

GASOMETRIC DETERMINATION OF CARBON

ABSTRACT

In this gasometric method for the determination of carbon in materials of relatively low level carbon content, the sample is ignited in a LECO induction furnace under an oxygen atmosphere. The carbon dioxide and excess oxygen are collected in a measuring buret, then exposed to a potassium hydroxide absorber for removal of the carbon dioxide. The final gas volume is measured and the decrease in volume calculated as percent carbon.

APPLICABILITY

This method uses an induction furnace to melt the samples and to oxidize the carbon to carbon dioxide. It is, therefore, designed primarily for the analysis of conducting metals such as steel. Nonconducting samples such as metal oxides and miscellaneous deposits are analyzable by adding a conducting accelerator.

The range of the method is 0.3 to 15 mg of carbon. Best results are obtained in the 2- to 15-mg range. The maximum sample size is 1 g giving a lower limit of 0.03% carbon. The upper limit of 15 mg is set by the volume (28 ml) of the measuring buret.

DISCUSSION

The LECO gasometric carbon analyzer [1] is schematically illustrated in Figure 1. Its individual components are shown in detail in Figures 2 through 5. Oxygen is purified by passing it through the purification train which contains (a) conc H_2SO_4 to remove moisture, (b) Ascarite to remove acid gases, and (c) anhydrous magnesium perchlorate (Anhydrone) to protect the Ascarite from moisture when the apparatus is idle. The oxygen then flows through the rotameter at a controlled rate of 2 cu ft/hr over the heated sample in the induction furnace where combustion takes place. The gaseous combustion products, carbon monoxide, carbon dioxide, sulfur dioxide, and water are carried by the oxygen stream over the manganese dioxide in the sulfur dioxide absorber, and then to the catalytic furnace where carbon monoxide is oxidized to carbon dioxide. The gas enters the carbon analyzer (Figure 5 through the buret valve shown in detail in Figure 6. The gas is collected and its volume is measured in the buret bulb at atmospheric pressure and room temperature. The gas then is transferred via the buret valve to the caustic absorption vessel where the carbon dioxide is removed as potassium carbonate. The gas is returned to the buret bulb and the volume is measured. The decrease in volume is corrected to standard temperature and pressure and converted to percent carbon.

Leaks in the train constitute a very serious source of error. A leak test should be made prior to each series of analyses.

SAFETY PRECAUTIONS

Handle the ignited crucibles with tongs and always set hot crucibles in the crucible holder. Do not touch the crucibles after ignition.

APPARATUS AND REAGENTS

A. Apparatus

1. Barometer.

2. Carbon Analyzer Apparatus, LECO (Figure 1), including crucible holder, induction furnace, catalytic furnace, and oxygen purification train.

3. Crucibles, as obtained from LECO, Cat. No. 528-25.

4. Forceps, 12-in., steel.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ascarite.

2. Caustic solution. Dissolve 900 g of KOH in 1800 ml of water with appropriate chilling.

3. Iron accelerator, as obtained from LECO, Cat. No. 160.

4. Leveling solution. Add 40 ml of conc H_2SO_4, 10 drops of methyl orange indicator, and 2 ml of LECONAL wetting agent to 500 ml of water, and mix.

5. Magnesium perchlorate, anhydrous, such as Anhydrone.

6. Manganese dioxide, specially prepared for SO_2 absorption, as obtained from Fisher Scientific Company, Cat. No. M-103.

7. Sulfuric acid, conc.

8. Tin accelerator, as obtained from LECO, Cat. No. 155.

9. Wetting agent, LECONAL, as obtained from LECO, Cat. No. 501-79.

PROCEDURE

A. Test for Leaks

1. Turn on the oxygen.	Avoid excess oxygen pressure from the line by opening the rubber diaphragm valve (Figure 5) one full turn and adjusting the oxygen flow to 2 cu ft/hr as indicated by the rotameter.
2. Turn the buret valve to the furnace position and the pressure valve to the empty position.	See Figure 6 for the valve operating positions.
3. Close the raising mechanism of the furnace and open the rubber diaphragm valve to allow oxygen into the system.	See Figure 3 for the raising mechanism. See Figure 5 for the location of the rubber diaphragm valve.
4. Close the rubber diaphragm valve when the top of the leveling solution is in the calibrated stem of the buret. If the solution level remains steady indicating the system is leak-free, continue with Procedure B. If the solution level continues to fall, continue with Step 5.	See Figure 5 for the location of the buret.
5. Progressively pinch off sections of the line from the carbon analyzer to the oxygen supply to locate the leak.	When the level of the solution remains steady, the leak is in the last section pinched off.

6.	Repair the leak and again test the apparatus for leaks.	A leak between the buret and the absorption vessel (Figure 5) will be detected in Procedure B and repaired at that point.

B. Zero the Apparatus

This procedure (a) removes any residual CO_2 from the system, (b) insures the cleanliness of the measuring buret, and (c) tests the buret and absorption vessel portion of the apparatus for leaks. This operation must be done before beginning an analysis. Proceed according to Procedure E, Steps 3 through 13. Repeat these steps a minimum of three times or until a zero reading is obtained on the calibrated buret stem (Figure 5). If a zero reading is not obtained after three attempts, test the tubing connectors between the buret and the absorption vessel and replace the tubing, if necessary. Also test the buret valve and apply a high vacuum stopcock grease, if necessary. Repeat the procedure to obtain a zero reading on the buret. If further trouble is encountered, contact your supervisor.

C. Blank

1.	Process a blank prior to each series of samples. Use the same amount and type of accelerator that is used for the sample and proceed with Steps 3 through 13 of Procedure E.	See note Procedure E, Step 1.
2.	Record the buret reading as the blank.	

D. Bench Standards

Process an NBS bench standard according to Procedure E. Choose a bench standard that has approximately the same carbon content as the sample.

E. Analysis of Samples

1.	Weigh a sample to ± 1 mg into a tared (to ± 1 mg) crucible, add accelerator, and place the crucible on the raising mechanism of the furnace. The sample should contain 0.3 to 15 mg of C.	If less than 0.75 g of sample is used, add 1 scoop each of the Fe and Sn accelerators. If greater than 0.75 g of sample is used, add only the Sn accelerator. If the sample is a nonconductor, both Fe and Sn accelerators are required, regardless of the sample weight.
2.	Turn on the filament switch and then the high voltage switch.	
3.	Turn the buret valve to the exhaust position and the pressure valve to the empty position and allow the leveling solution to drain to zero.	Note the level of the leveling solution. If it is not at zero on the calibrated stem, add leveling solution to the reservoir.
4.	Turn the pressure valve to the fill position and allow the leveling liquid to fill the buret.	When the buret is full, the float valve will seat. This valve must be observed to insure that H_2SO_4 solution does not flow into the KOH solution. If the H_2SO_4 does flow into the absorption vessel, the absorption vessel must be emptied, washed thoroughly with water, and a new KOH solution prepared and added. If this occurs, begin again with Procedure B.
5.	Turn the pressure valve to the lock position and turn the buret valve clockwise to the furnace position.	
6.	Open the rubber diaphragm valve until the rotameter reads 2 cu ft/hr. Then simultaneously close the raising mechanism of the furnace and turn the pressure valve to the empty position.	Gas will displace the leveling solution in the buret.

7.	When the leveling solution is 2/3 of the way down the calibrated stem of the buret, immediately close the rubber diaphragm valve and open the raising mechanism.	
8.	Turn the buret valve counter-clockwise to the exhaust position and let the leveling solution settle to the zero point on the buret.	The buret should drain for 20 sec. This drain time must be consistent to obtain reproducible results.
9.	Note the level of the caustic around the float valve in the absorption vessel.	The caustic level must be closely observed so that the same level may be reached in Step 11.
10.	Turn the buret valve to the caustic position and the pressure valve to the fill position. Allow the leveling solution to force the trapped gas into the absorption vessel until the float valve in the buret seats.	
11.	Turn the pressure valve to the empty position and the gas will return to the buret until the float valve seats.	The level of the caustic around the float valve must be the same as that noted in Step 9.
12.	Turn the buret valve to the lock position and let the leveling solution drain for 20 sec. Adjust the level in both columns of the buret to the same level by turning the pressure valve to either empty or fill position, whichever is necessary.	The pressure valve is turned to the fill position if the right column is the higher and to the empty position if the left column is the higher. Turn the valve cautiously and approach the level position slowly.
13.	Read the percent carbon directly from the left hand side of the buret.	This reading must be made 20 sec after the buret valve was turned to the lock position in Step 12.

CALCULATIONS

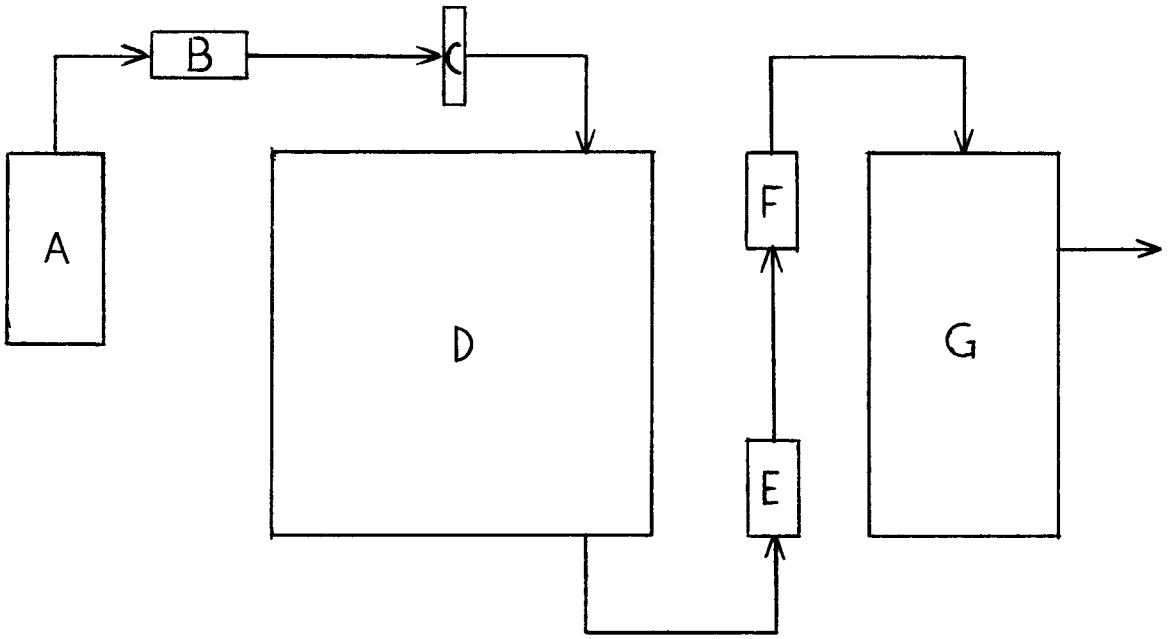
The buret is graduated in percent carbon based on a 1-g sample. The buret reading must be divided by the sample weight when other than 1-g samples are analyzed. A gas volume is being measured in the buret; therefore, the results must be converted to standard temperature and pressure.

The value 0.359 shown in the calculations on the example worksheet is the ratio 273/760 that corrects the gas volume to standard conditions.

REFERENCES

1. Instruction Manual for Operation of LECO Carbon Determinators, Laboratory Equipment Corporation, St. Joseph, Michigan, November 1953.

March 1969
D. E. Savage



A. oxygen supply
B. purification train
C. rotameter
D. induction furnace
E. sulfur dioxide absorber
F. catalytic furnace
G. carbon analyzer

Fig. 1 Schematic of LECO carbon analysis.

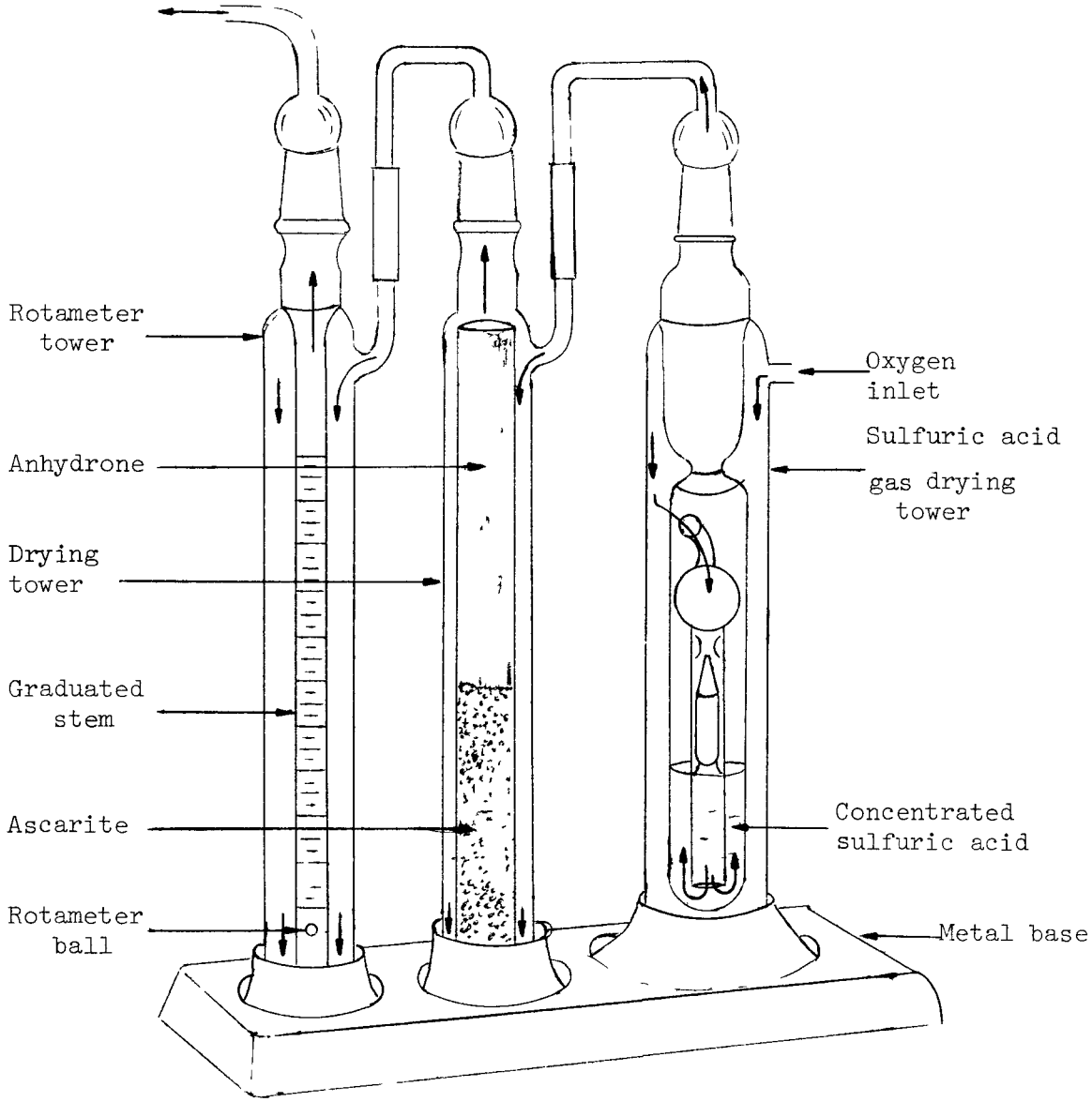


Fig. 2 LECO oxygen purification train.

* Combustion Gas Outlet for Analyzing Carbon and the Oxygen Inlet when Analyzing Sulfur

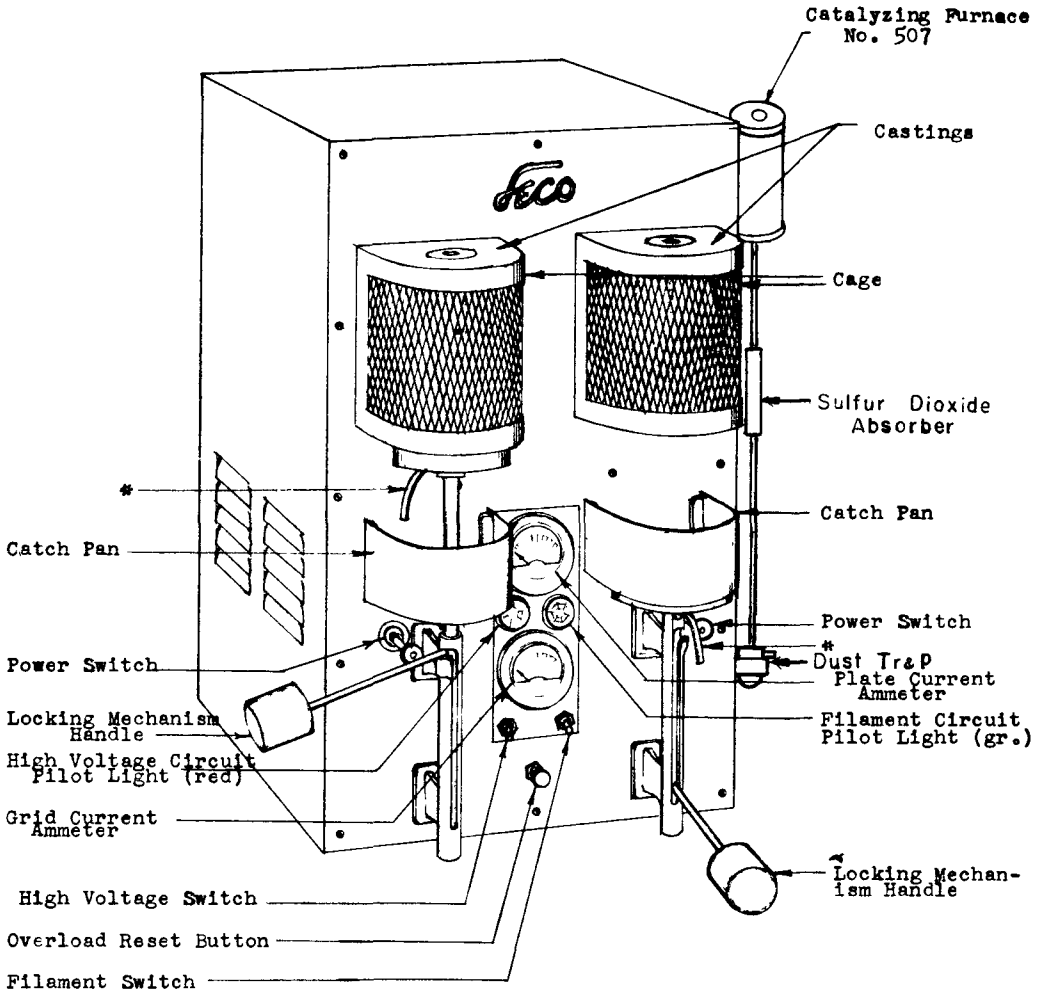


Fig. 3 LECO induction furnace.

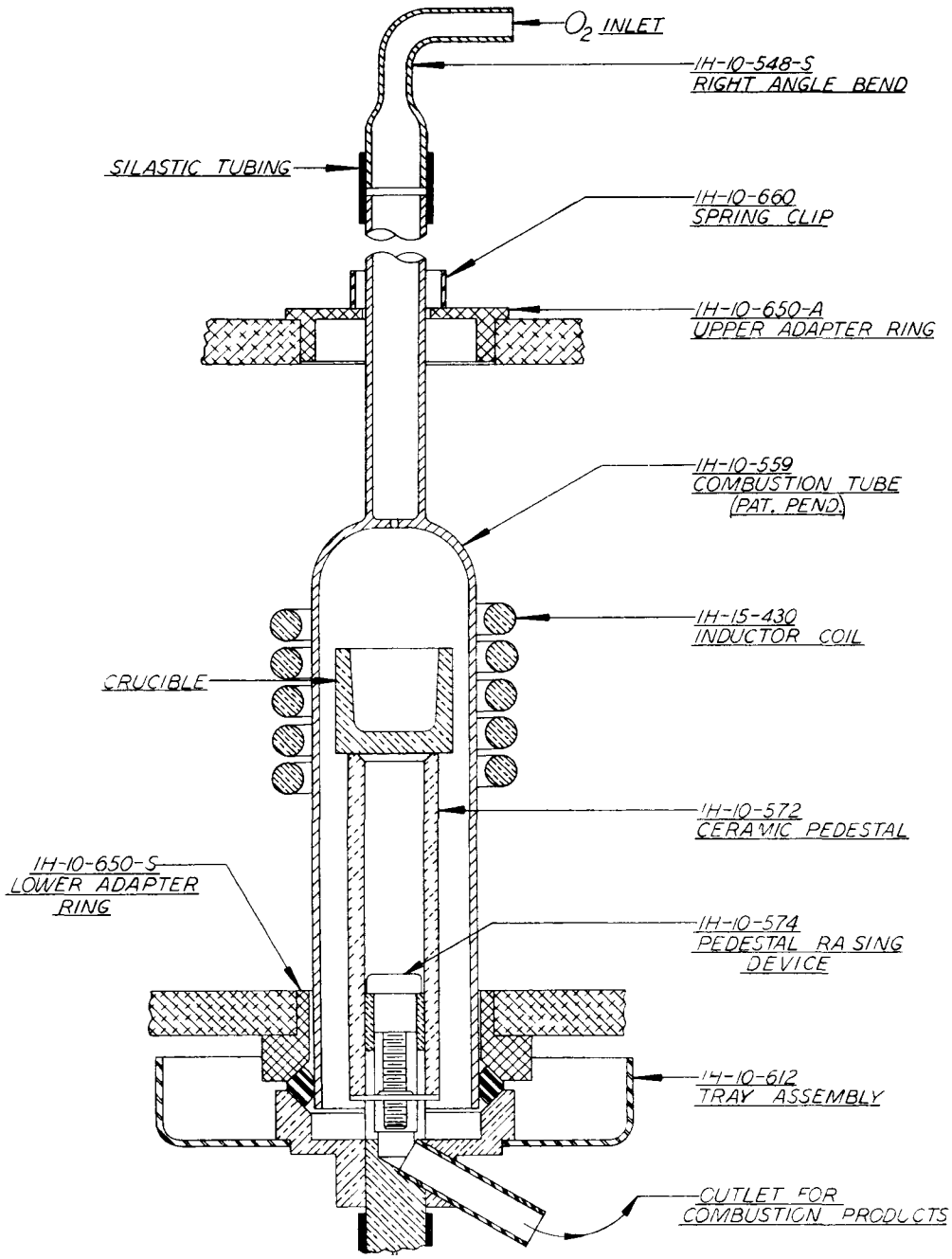


Fig. 4 Combustion tube.

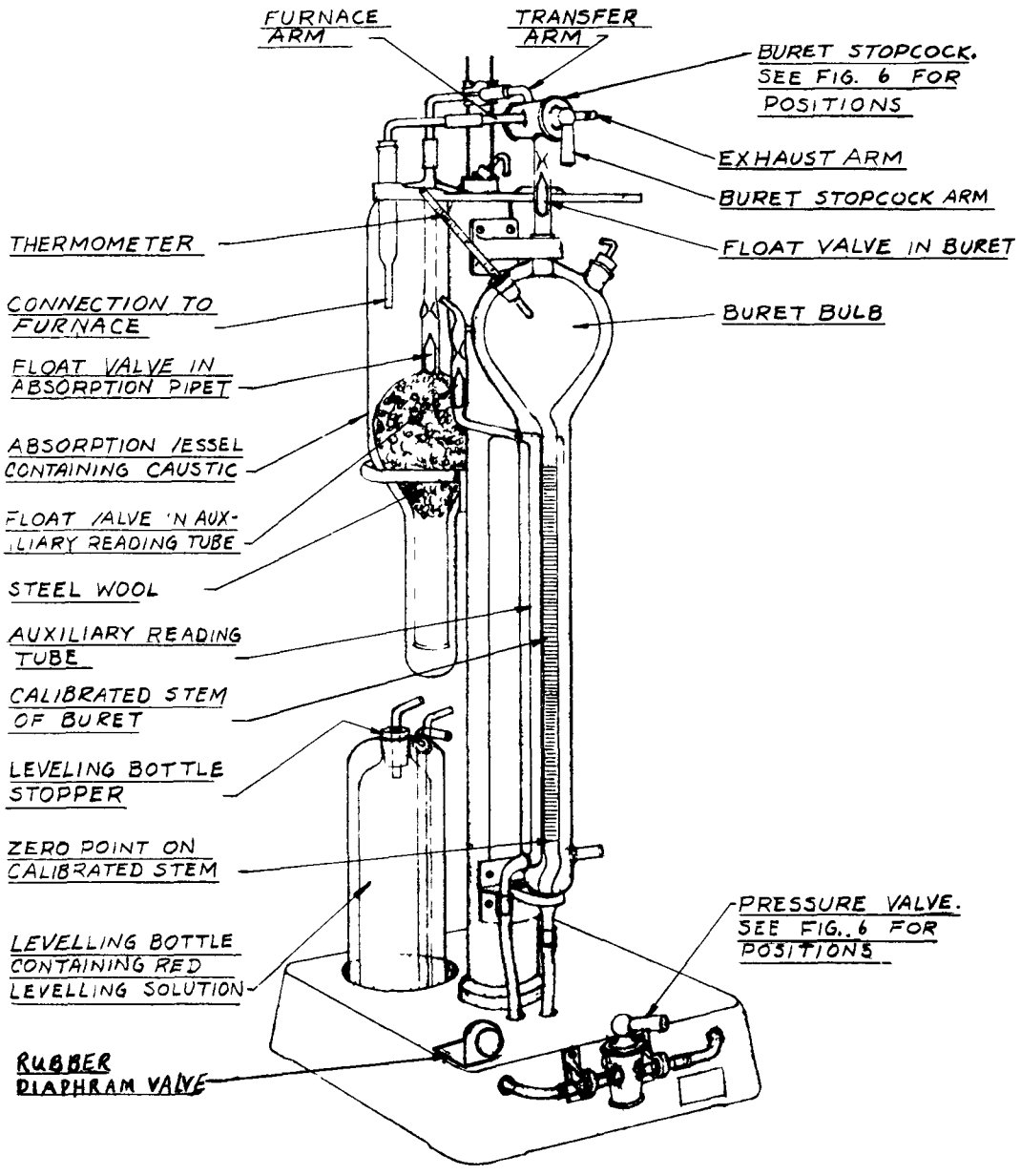


Fig. 5 LECO carbon analyzer.

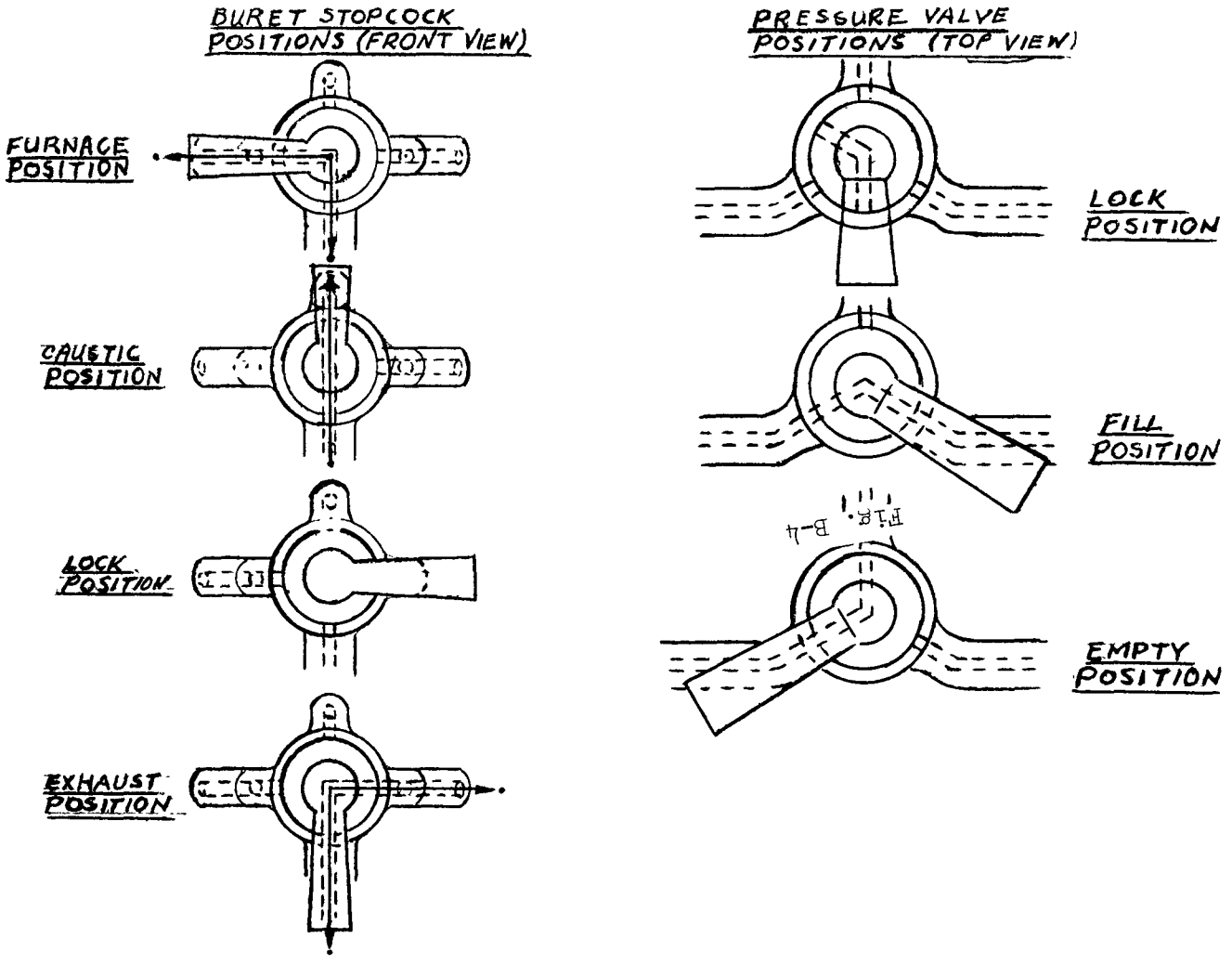


Fig. 6 Buret valve and pressure valve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Carbon

CHARGE NUMBER _____ PROCEDURE C-Gas-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$ Sample wt	Buret Reading	Blank	Net Buret Reading	Pressure in mm of Hg	T, °K	STP Factor		RESULT wt% C
#1	0.997	0.090	0.015	0.075	645	297	0.781		0.059
	1.014	0.095		0.080					0.062
#2	1.035	0.180		0.165					0.129
	1.006	0.170		0.155					0.120

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{STP Factor} = (0.359)\left(\frac{D}{E}\right) = (0.359)\left(\frac{645}{297}\right) = 0.781$$

#1) $$\text{Result} = \frac{(A-B)F}{\text{Sample wt}} = \frac{(0.090-0.015)\,0.781}{0.997} = 0.059 \text{ wt\%}$$

APPROVED BY _____

COLORIMETRIC DETERMINATION OF TOTAL CHROMIUM AND CHROMIUM(VI)

ABSTRACT

Chromium(VI) reacts with diphenylcarbazide in an acid medium to form a red-violet chromium(III)-diphenylcarbazone complex with an absorbance maximum at 540 mμ. This is the basis of two sensitive, selective, spectrophotometric procedures for (a) the determination of total chromium, and (b) the specific determination of chromium(VI) in aqueous solutions that contain both chromium(III) and chromium(VI). To determine total chromium, the chromium is oxidized to the (VI) oxidation state with excess cerium(IV), the excess cerium(IV) is destroyed with sodium azide, and the chromium(VI) is reacted with diphenylcarbazide. To determine chromium(VI) selectively, the sample is reacted directly with diphenylcarbazide without prior oxidation.

APPLICABILITY

Diphenylcarbazide is reported to be highly selective for hexavalent chromium[1,2] This has been confirmed in comprehensive studies of the effects of foreign ions which show that numerous ions do not interfere at diverse ion to chromium molar ratios 250 to 1 or greater (Table I). There are, however, a number of common ions that interfere at low concentrations. These include Cu(I, II), Hg(I, II), Fe(II, III), Mn(II), Mo(VI), and V(IV, V). Copper suppresses the color development seriously at levels exceeding 0.01 mmole. Mercury(II), Fe(III), Mo(VI), and V(V) react with the reagent to produce blue, yellowish-brown, violet, and red complexes, respectively, that absorb at 540 mμ and produce high results. Their tolerance limits are listed in Table I. The red vanadium complex fades rapidly so its interference can be avoided by allowing sufficient time, about 15 min, for the complex to decompose. Manganese at levels above 0.1 mg causes results to be low. It is oxidized by cerium(IV) to manganese dioxide and permanganate. These interfere in two different ways: the manganese dioxide occludes chromium(III) and prevents quantitative oxidation to chromium(VI); the permanganate destroys the diphenylcarbazide chromogen.

Other potential interferences are colored ions that absorb at the working wavelength of 540 mμ and ions that precipitate in the color development. An example of the former is cobalt(II) which in amounts exceeding 0.1 mmole must be compensated by a sample blank. Examples of ions that precipitate are Ba(II), Pb(II), and Sr(II) which form insoluble sulfates and Bi(III), Sn(II, IV), and Nb(V) which form hydrous oxides.

TABLE I

TOLERANCE OF METHOD FOR DIVERSE IONS[a]

Diverse Ion Studied	Known Tolerance Level	Remarks
Al(III), Cd(II), Co(II), Mg(II), Ni(II), Zn(II)	At least 0.4 mM for each ion individually.	Co(II) absorbs at 540 mμ. If the Co(II) level exceeds 0.1 mM, process a sample blank.
		On the basis of their chemical properties, similar tolerance is expected for BO_2^-, Ga(III), and In(III).
Ho(III), La(III), Sr(II)[b], Th(IV)	Max. 0.2 mM	On the basis of their chemical properties, similar tolerance is expected for Ca(II), other lanthanides, Sc(III), and Y(III).
Pb(II)[b], U(VI), Zr(IV)	Max. 0.1 mM	On the basis of their chemical properties, similar tolerance is expected for Hf(IV), Np(IV,VI), and Pu(IV, VI).
Ba(II)[b], Bi(III)[b]	Max. 0.05 mM	On the basis of their chemical properties, similar tolerance is expected for Ge(IV), Sb(III, V), and Ti(IV).
Cu(II), Mo(VI)	Max. 0.01 mM	
Hg(I, II), Sn(II, IV)[b]	Max. 0.025 mM	
K(I)	At least 1 mM	Similar tolerance is expected for Li(I), Na(I) and NH_4(I). Because of the limited solubility of $CsClO_4$ and $RbClO_4$, the practical tolerance level for Cs(I) and Rb(I) is expected to be about 0.5 mM.

TABLE I (continued)

Diverse Ion Studied	Known Tolerance Level	Remarks
Fe(II, III), Nb(V)	Max. 0.5 mg	Similar tolerance is expected for Ta(V) and W(VI).
Mn(II)	Max. 0.1 mg	
V(V)	Max. 0.05 mg	Before measuring, wait 15 min after color development to allow the V complex to decay.
Cl^-	At least 6 mM	This tolerance level applies to Procedure C wherein Cl^- is expelled in the initial evaporation step. It's effect on Procedure D has not been studied.
PO_4^-	At least 0.02 mM	Similar tolerance is expected for $AsO_4^{\equiv}$.

[a] Based on an interference study at a chromium level of 4×10^{-4} mM (20 µg).

[b] Under the conditions of the determination, these ions precipitate as the sulfate or hydrous oxide. The precipitate is settled by centrifugation before measurement.

Within the limitations described in the preceding two paragraphs, this method is applicable to a wide variety of inorganic aqueous samples. For either procedure, the range is 0.5 to 50 µg of chromium and the maximum practical sample aliquot is about 20 ml. The lowest determinable concentration is, therefore, about 0.05 µg Cr/ml. Samples with chromium concentrations above 1 mg/ml are best analyzed by Method Cr-Vol-1 of this manual. Where greater tolerance for diverse ions is desirable, the extraction-spectrophotometric procedure of Method ECF-1 of this manual may be useful.

DISCUSSION

In the presence of chloride, chromium in the (VI) oxidation state volatilizes as chromyl chloride. Hydrogen peroxide, therefore, must be present during evaporations to maintain the chromium in its nonvolatile (III) oxidation state. Also, if the sample must be dissolved under oxidizing conditions, a reflux condenser should be used.

The red-violet chromium(III)-diphenylcarbazone complex is reported to form instantly and remain stable for several hours.[2] Independent studies show that the color forms immediately, then fades slowly. For best results, therefore, samples should be measured within 1 hr after color development.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1- and 5-cm, Pyrex.
2. Burner, Meker.
3. Dropping bottles.
4. Hot plate.
5. pH meter with glass-calomel electrode system.
6. Pipets, macro and micro, assorted sizes with control syringe and suction bulb.
7. Redy-Dispenser or Canti-Pet, 10-ml, with 500-ml Florence flask.
8. Spectrophotometer, Beckman Model DU or DK, or Cary Model 14.
9. Tongs and test tube holder.
10. Transite board.
11. Volumetric flasks, 50-ml.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium hexanitratocerate, $(NH_4)_2Ce(NO_3)_6$, 0.10M. Dissolve 11.0 g of the solid reagent (G. Frederick Smith Chemical Company, Columbus, Ohio) in 100 ml of 0.5M H_2SO_4 and dilute to 200 ml with water.

2. Chromium standard stock solution, 0.5000 mg Cr/ml. Dissolve 1.4144±0.0005 g of $K_2Cr_2O_7$ in water and dilute to 1 liter with water.

3. Chromium calibration standards. Prepare aqueous dilutions as follows:

   a. Standard I, 4 µg Cr/ml. Dilute 4.00 ml of the stock solution to 500 ml.

   b. Standard II, 8 µg Cr/ml. Dilute 4.00 ml of the stock solution to 250 ml.

   c. Standard III, 15 µg Cr/ml. Dilute 15.00 ml of the stock solution to 500 ml.

   d. Standard IV, 30 µg Cr/ml. Dilute 15.00 ml of the stock solution to 250 ml.

4. Diphenylcarbazide solution, 0.25%(w/v). Dissolve 0.5±0.01 g of diphenylcarbazide in 200 ml of 95% ethyl alcohol. Add 2 drops of conc HCl and mix well. This solution is usually stable for 1 week. If significant coloration appears, prepare a fresh solution at more frequent intervals.

5. Hydrogen peroxide, H_2O_2, 30% (w/v).

6. Nitric acid, conc.

7. Perchloric acid, conc.

8. Phenol, 0.1M.

9. Potassium bromide, 0.1M.

10. Sodium azide (NaN_3) solution, 0.10M. Dissolve 1.30±0.01 g of NaN_3 in water. Filter, if necessary, then dilute to 200 ml with water.

11. Sodium hydroxide, 3M.

PROCEDURE

A. Blanks

The absorbance of the diphenylcarbazide reagent is negligible at 540 mμ; however, blanks are necessary to correct for (a) the introduction of chromium via the reagents, and (b) the absorbance of colored ions such as cobalt(II) at 540 mμ. The former is corrected with a reagent blank, the latter with a sample blank.

Prepare the reagent blank per Procedure C or D beginning at Step 2. Prepare the sample blank per Procedure C or D omitting the addition of diphenylcarbazide (Step 15 of Procedure C or Step 4 of Procedure D).

B. Calibration

Samples usually vary widely in their chromium content. To minimize repeat analyses, the use of four calibration standards (standards I and II for 5-cm cell measurements and standards III and IV for 1-cm cell measurements) is recommended. If only samples with similar concentrations are being processed, two appropriate standards are sufficient.

Process a new calibration with each series of samples as follows:

(1) Procedure C. Process 1.00-ml portions of the standards beginning at Step 2.

(2) Procedure D. Obtain freshly prepared calibration standards. Process 1.00-ml portions of the standards beginning at Step 2.

In either case, divide the micrograms of chromium in each standard by its corresponding absorbance to obtain the conversion factor. The difference between the two factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average factor for each pair of standards should agree with the established conversion factor for each group within specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties are encountered again.

C. Determination of Total Chromium

NOTE: Use distilled water throughout the procedure.

1. Pipet a sample aliquot containing 0.5 to 50 μg of Cr into a 50-ml volumetric flask. If the

For best results, select a sample with 15 to 50 μg of Cr and measure the absorbance in a 1-cm cell.

	sample is highly colored, pipet an equal aliquot into a second 50-ml flask for the sample blank.	
2.	Add 0.5 ml of conc HNO_3.	The HNO_3 helps to remove Cl^-.
3.	Add 0.75 ml of conc $HClO_4$.	
4.	Add 0.5 ml 30% H_2O_2.	
5.	Evaporate the sample on a Chromalox hot plate (set on MEDIUM with a sheet of asbestos on it) to the appearance of $HClO_4$ fumes within the flask.	Do not continue the heating to the expulsion of $HClO_4$ fumes from the flask.
6.	Cool the sample, then carefully add 10 ml of water.	
7.	Heat the sample until the ring of condensation reaches the mouth of the flask.	The purpose of this boiling step is to expel oxides of nitrogen that reduce the Ce(IV) oxidant.
8.	Add cautiously 2 drops of conc H_2SO_4 and 5 drops of 0.10M $(NH_4)_2Ce(NO_2)_6$ and mix by swirling.	If the yellow Ce(IV) color bleaches in Steps 8 or 9, add another 5 drops. If the color again fades, there is too much residual H_2O_2 and/or nitrogen oxides. Discard the sample and start over with a new one.
9.	Heat the sample on a Chromalox hot plate (set on MEDIUM with a 0.25-in. thick Transite board on it) for 20 min.	
10.	Cool the sample, then examine it visually for Mn. If Mn is present, continue with Step 11. If Mn is absent, omit Step 11 and continue with Step 12.	The presence of Mn is indicated by the presence of dark MnO_2 and/or purple coloration of the permanganate ion.

11.	Add, with swirling, 0.1M KBr dropwise until the sample clears, then add 2 drops more.	
12.	Chill the sample to room temperature, then dilute it to about 45 ml with water.	
13.	Add 5 drops of 0.1M NaN_3 and swirl to mix.	The sample must be diluted with water per step 12 before the addition of NaN_3; otherwise, Cr(VI) will reduce.
14.	If KBr was added per Step 11, add 5 drops of 0.1M phenol solution; otherwise, omit the phenol and continue with Step 15.	
15.	Add 1 ml of 0.25% diphenylcarbazide reagent, then dilute to volume with water and mix. Do not add diphenylcarbazide to the sample blank.	
16.	Read the absorbance within 1 hr at 540 mμ against water.	Use a 1-cm cell for samples with greater than 10 μg of Cr and a 5-cm cell for samples with less than 5 μg. In between 5 μg and 10 μg, either cell may be used.
17.	Record the data on the worksheet and calculate the results as shown on the example worksheet. Report three significant figures.	Compare samples read in 5-cm cells against standards I and II also read in 5-cm cells. Compare samples read in 1-cm cells against standards III and IV.

D. Selective Determination of Chromium(VI)

1.	Pipet a sample aliquot containing 0.5 to 50 μg of Cr(VI) into a 50-ml beaker. If the sample is highly	For highest precision, use an aliquot with greater than 15 μg of Cr(VI) and measure the absorbance with a 1-cm cell.

colored, pipet an equal aliquot into a second 50-ml beaker for the sample blank.

2. Dilute to about 40 ml with water and adjust the pH to 1.5±0.2 with conc $HClO_4$ or 3M NaOH.

   For convenience, use magnetic stirring in Steps 2 through 4.

3. Add 5 drops of 0.1M NaN_3 and mix.

4. Add 1 ml of 0.25% diphenylcarbazide reagent and mix. Do not add diphenylcarbazide to the sample blank.

5. Transfer the sample with water rinses to a 50-ml volumetric flask, dilute to volume with water, and mix well. If solution is cloudy, filter through a 0.45-μ membrane filter.

6. Measure the absorbance within 1 hr against water at 540 mμ.

   Use a 5-cm cell for samples with less than 5 μg of Cr(VI) and a 1-cm cell for samples with greater than 10 μg of Cr. In between 5 and 10 μg, either cell may be used.

7. Record the data and calculate the results as shown on the example worksheet. Report three significant figures.

REFERENCES

1. E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd Ed., Interscience, New York, 1959, pp 392-397.

2. F. D. Snell, C. T. Snell, Colorimetric Methods of Analysis, 3rd Ed., Van Nostrand, New York, 1949, pp 274-277.

June, 1967

S. S. Yamamura
E. M. Fortsch

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Chromium

CHARGE NUMBER _____ PROCEDURE Cr-Color-1

SPECIAL INSTRUCTIONS:

Sample 002 contains cobalt and requires a sample blank.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance VS H_2O	Net Absorbance	Conv. Factor	mg Cr in Aliquot Analyzed	mg Cr corrected for Bias			RESULT mg Cr/ml
Rgt Blank		0.003							
Std 15 mg		0.247	0.244	61.48					
Std 30 mg		0.503	0.500	60.00					
			$\bar{x}$	60.74					
001	3 ml	0.370	0.367		22.3	22.3 ± 1.1			7.43 ± 0.37
002, BLK	5 ml	0.022							
002	5 ml	0.275	0.250		15.2	15.2 ± 0.9			3.04 ± 0.18

ANALYZED BY _____ DATE _____

CALCULATIONS:

C = Conv. Factor = $\frac{\text{mg Cr in Std}}{\text{Net Absorbance}}$

$C' = \frac{15}{B} = \frac{15}{0.244} = 61.48$ $\quad C'' = \frac{30}{B} = \frac{30}{0.500} = 60.00$

$\bar{x} = 0.5(C' + C'') = 0.5(61.48 + 60.00) = 60.74$ mg Cr/abs unit

Sample 002

Net abs = 0.275 − 0.022 − 0.003 = 0.250

mg Cr = 0.250 (60.74) = 15.2 mg

Result = $\frac{E}{\text{Sample Vol}} = \frac{15.2 \pm 0.9}{5} = 3.04 \pm 0.18$ mg Cr/ml

APPROVED BY _____

4

VOLUMETRIC DETERMINATION OF TOTAL CHROMIUM, CHROMIUM(VI), AND CHROMIUM(III)

ABSTRACT

A volumetric method is described for the determination of milligram levels of total chromium, chromium(VI), and chromium(III) in aqueous solutions. Total chromium is determined by an iron(II) titration after a silver-catalyzed persulfate oxidation of the chromium to the (VI) oxidation state. Chromium(VI) is determined by direct titration without prior removal of chromium(III). Chromium(III) then is obtained by subtracting the chromium(VI) result from the total chromium result.

APPLICABILITY

This method is applicable for the determination of total chromium, chromium(VI), and chromium(III) in aqueous samples. It consists of two procedures, one for the determination of total chromium and another for the selective determination of chromium(VI). Chromium(III) is obtained by difference. For total chromium, the sample is evaporated to sulfuric acid fumes, and the chromium is oxidized to the (VI) oxidation state with silver-catalyzed ammonium persulfate. The chromium(VI) is titrated with iron(II) to a ferroin, iron(II)-1,10-phenanthroline, end point. For chromium(VI), the sample is titrated directly with iron(II) to a ferroin end point.

Principal interferences are high concentrations of colored metal ions which may obscure the end point and metals such as Ce, Mn, and V which oxidize with persulfate and subsequently titrate. Of the latter, manganese is the most serious because it is present in concentrations up to about 2% in many chromium steels. Its interference is avoided by selectively reducing the permanganate that forms in the persulfate oxidation step to nonreactive manganese dioxide with hydrochloric acid prior to the titration. Up to 17 mg of manganese dioxide (equivalent to 11 mg of manganese) does not interfere in the titration and need not be removed. Above this, the end point is obscured and the manganese dioxide must be removed by filtration. At least 55 mg of manganese can be tolerated when the reduction and filtration treatments are used. The addition of the hydrochloric acid also precipitates the silver catalyst as silver chloride. This does not obscure the end point.

The range of the method is 1.6 to 16 mg of chromium for either total chromium or chromium(VI). The practical limit of sample volume for both procedures is 100 ml. Thus, the lowest determinable concentration is about 0.016 mg/ml of either total chromium or of chromium(VI). The lowest determinable concentration for chromium(III) is very dependent on the precisions of the procedures for total chromium and for chromium(VI). It is estimated to be about 0.02 mg/ml. The recommended method for lower levels of chromium is Method Cr-Color-1 of this manual.

DISCUSSION

The initial treatment in the determination of total chromium is to evaporate the sample to sulfuric acid fumes. Hydrogen peroxide and nitric acid are added prior to the evaporation. The hydrogen peroxide maintains chromium in the nonvolatile (III) oxidation state and nitric acid helps to remove chloride. The removal of chloride is necessary to prevent loss of chromium as chromyl chloride.

Hydrochloric acid is used to reduce permanganate. The acidity of the sample must be reduced to 1N or less prior to the addition of the hydrochloric acid to prevent partial reduction of chromium(VI).

In the titration of chromium(VI) in the presence of chromium(III), the color transitions throughout the titration vary widely with changes in the Cr(VI):Cr(III) ratio. Nevertheless, a color change at the equivalence point can be seen satisfactorily in the presence of 100 mg of initial chromium(III). Other colored ions such as Fe(III), Ni(II), and Co(II) have no adverse effect on the titration at the levels normally encountered with metal alloys such as stainless steel.

Useful references for this method are Kolthoff and Elving[1] and Smith and Richter[2].

SAFETY PRECAUTIONS

Exercise caution when handling strong, concentrated acids. Dilute acid solutions carefully to avoid spattering, especially after fuming steps.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, low-form, 250-ml.
2. Buret, 10-ml graduated in 0.05-ml increments.
3. Cover glasses, Speedyvap.
4. Filtering apparatus: Fisher Filtrator with 47-mm diam filter holders (Millipore Filter Corporation, Bedford, Massachusetts) and 47-mm diam membrane filters (type VM-6, 0.45-μ, Gelman Instrument Company, Chelsea, Michigan).
5. Graduated cylinder, pharmaceutical, 25-ml.
6. Ice bath.
7. Magnetic stirring apparatus.
8. Pipets, volumetric, assorted sizes.
9. Stirring bars, Teflon-coated.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent grade chemicals and distilled water.

1. Ammonium persulfate, $(NH_4)_2S_2O_8$, solid reagent.
2. Bench standard I, 1.73 mg Cr/ml with manganese. Dissolve the following in 500 ml of distilled water.
   a. 5 ml of conc H_2SO_4.
   b. 4.9035 g of dried (for at least 1 hr at 110°C) NBS $K_2Cr_2O_7$.
   c. 0.46 g of $MnSO_4.H_2O$.
   d. 48.3 g of $Fe(NO_3)_3 \cdot 9H_2O$.
   e. 5.41 g of $Ni(NO_3)_2 \cdot 6H_2O$.
   Dilute the solution to 1 liter with water.
3. Bench standard II, 8.67 mg Cr/ml, without manganese. Prepare the same as Bench Standard I, except omit the $MnSO_4 \cdot H_2O$.
4. Ferroin indicator, 0.025M. (Reagent number 165, G. F. Smith Chemical Company, Columbus, Ohio).
5. Ferrous ammonium sulfate, 0.1N (0.1M). Dissolve 39.2 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 500 ml of cold 0.5M H_2SO_4 and dilute to 1 liter with 0.5M H_2SO_4.
6. Hydrochloric acid, 3M.
7. Hydrogen peroxide, H_2O_2, 30%.
8. Nitric acid, conc.
9. Phosphoric acid, 7.3M.
10. Potassium dichromate, 0.1N (0.0167M). Dissolve 4.9035 g of dried (for at least 1 hr at 110°C) NBS $K_2Cr_2O_7$ in distilled water and dilute to 1 liter with water.
11. Silver nitrate, 0.06M. Dissolve 10.2 g of $AgNO_3$ in water and dilute to 1 liter with water. Store in a dark-colored bottle.
12. Sulfuric acid, 9M.

PROCEDURE

A. Blank

No blank determination is required for this method because significant levels of oxidizing contaminants usually are not present in the reagents. To detect possible reagent contamination, mix 100 ml of water, 20 ml of 9M H_2SO_4, 10 ml of 7.3M H_3PO_4, and 1 drop of the ferroin indicator solution in a 250-ml beaker. The color should be orange. If it is not, the glassware, reagents, or both are contaminated. Do no further work until the source of contamination is found and eliminated.

B. Standardization of Ferrous Ammonium Sulfate Solution For Procedures D and E

Do in duplicate each shift. Limits will be specified by the Quality Control Laboratory. This standardization serves as the Bench Standards for Procedure E.

1. Pipet 5.00 ml of the 0.1N $K_2Cr_2O_7$ solution into a 250-ml beaker that contains a stirring bar.

2. Add 50 ml of water.

3. Add 20 ml of 9M H_2SO_4.

4. Add 10 ml of 7.3M H_3PO_4.

5. Add 1 drop of the ferroin indicator solution.

6. While stirring, titrate with the 0.1N $Fe(NH_4)_2(SO_4)_2$ solution to an orange-colored end point that is stable for 1 min.

7. Record the volume of titrant on the worksheet and calculate the normality of the Fe(II) titrant as described under CALCULATIONS and as shown in the example worksheet.

C. Bench Standards (for Procedure D only).

Analyze a 5.00-ml aliquot of one of the two bench standards according to Procedure D. Limits will be specified by the Quality Control Laboratory.

Two bench standards are provided for this method. Bench standard I contains Mn; bench standard II does not. If the sample contains Mn, process bench standard I; otherwise, process bench standard II.

D. Analysis of Samples for Total Chromium Content

1. Pipet a sample that contains 1.6 to 16 mg of Cr into a 250-ml beaker.

The precision improves with increasing amounts of Cr. If possible, use an aliquot that contains at least 5 mg of Cr.

2. Add 10 ml of 9M H_2SO_4.

3. Add 4 ml of 30% H_2O_2.

4. Add 2 ml of conc HNO_3.

5.	Heat on a hot plate just until copious fumes of SO_3 are evolved.	Use a Speedyvap cover glass in Steps 5 through 12.
6.	Cool slightly, then chill in an ice bath to room temperature.	
7.	Add 50 ml of water. To avoid spattering and excessive heat evolution, add the water carefully, running it down the sides of the beaker while swirling.	
8.	Add 3 g of $(NH_4)_2S_2O_8$ and 5 ml of 0.06M $AgNO_3$ and swirl until the persulfate dissolves.	
9.	Heat on a hot plate to oxidize chromium to the (VI) oxidation state and to destroy the excess persulfate. Boil the solution until the small bubbles cease, then continue boiling for 10 min.	The extra 10-min boiling guarantees complete destruction of the persulfate. Up to 20 min of boiling is permissible.
10.	Cool and dilute to 100 ml with water.	If the absence of Mn has not been established, continue with Step 11. If Mn is known to be absent, omit Step 11 and continue with Step 12.
11.	Add 5 ml of 3M HCl, heat solution for 5 min.	As noted under APPLICABILITY, no filtration is necessary when the Mn level is less than 11 mg. If the Mn level exceeds this, filter the sample through a 0.45-μ VM-6 filter.
12.	Add a Teflon-coated stirring bar.	
13.	Add, with continuous stirring, 10 ml of 9M H_2SO_4 and 10 ml of 7.3M H_3PO_4.	Stirring prevents local high concentrations of acidity which causes reduction of Cr(VI) by Cl^- and low results.
14.	Add 1 drop of ferroin indicator solution and titrate with the 0.1N $Fe(NH_4)_2(SO_4)_2$ solution to an orange-colored end point that is stable for 1 min.	

15. Record the data on the worksheet and calculate the result as described under CALCULATIONS and as shown in the example worksheet.

E. Determination of Chromium(VI)

1. Pipet a sample that contains 1.6 to 16 mg of Cr(VI) into a 250-ml beaker.

2. Add a Teflon-coated stirring bar.

3. Dilute to about 100 ml.

4. Add, with continuous stirring, 20 ml of 9M H_2SO_4 and 10 ml of 7.3M H_3PO_4.

5. Add 1 drop of ferroin indicator solution and titrate with the 0.1N $Fe(NH_4)_2(SO_4)_2$ solution to an orange-colored end point that is stable for 1 min.

The end point color is altered by the presence of high concentrations of colored metal ions. For example, 100 mg of Cr(III) plus 500 mg of Fe(III) produce a reddish-brown end point.

6. Record the data and calculate the results as described under CALCULATIONS and as shown in the sample worksheet.

F. Determination of Chromium(III)

1. Determine total Cr by Procedure D.

2. Determine Cr(VI) by Procedure E.

3. Determine Cr(III) by difference.

CALCULATIONS

Record the data and calculate the results as shown on the example worksheet. Report three significant figures.

The factor 17.34 appears in the equation for the calculation of results. This is the factor to convert millequivalents chromium to milligrams chromium.

REFERENCES

1. W. H. Hartford, Treatise on Analytical Chemistry, I. M. Kolthoff and P. J. Elving, Eds., New York: Interscience Publishers, Part II, Vol 8, 1963, p 327.

2. G. F. Smith and F. P. Richter, Phenanthroline and Substituted Phenanthroline Indicators, The G. Frederick Smith Chemical Company, Columbus, Ohio (1944).

May 1967
R. Fullerton

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Total Cr

CHARGE NUMBER _____ PROCEDURE Cr-Vol-1, D

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Gross wt., g	Tare wt., g	Net wt., g	Fe(II) ml	Fe(II) N	Cr in Aliquot, mg	Cr in Aliquot corrected, mg	RESULT Cr mg/g
Cr(VI) - 0.1000 N	5.00 ml				5.09				
	5.00 ml				5.11				
					$\bar{x}$ = 5.10	0.09804			
SS1	1.5000g/100/3.0	5.8260	4.3260	1.5000	4.75		8.07	8.05±0.14	179±3 mg/g
AQS	4.0 ml				4.50		7.70	7.68±0.12	1.92±0.03 mg/g

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$E = \frac{[\text{Vol Cr(VI)}]\,[\text{N Cr(VI)}]}{D} = \frac{(5.00)(0.1000)}{5.10} = 0.09804\ N$$

SS1 $F = 17.34\,DE = (17.34)(4.75)(0.09804) = 8.07$

$$\text{Result} = \frac{G d_1}{a_1 a_2} = \frac{(805 \pm 0.14)(100)}{(1.5000)(3.0)} = 179 \pm 3\ \text{mg Cr/g}$$

AQS $F = (17.34)(4.50)(0.09804) = 7.70$

$$\text{Result} = \frac{7.68 \pm 0.12}{4.0} = 1.92 \pm 0.03\ \text{mg/g}$$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH NEOCUPROINE

ABSTRACT

Copper is extracted into chloroform as a copper(I)-neocuproine complex and measured spectrophotometrically at 457 mμ.

APPLICABILITY

When the copper(I)-neocuproine (2,9-dimethyl-1,10-phenanthroline) complex is initially extracted into chloroform from citrate medium at pH 5.0 as in this method, neocuproine is extremely specific for copper and the determination is unaffected by many metals and high concentrations of most common anions[1,2,3,4]. For example, Luke and Campbell[4] found that 50-μg amounts of 56 metals have no harmful effect, and Gahler[3] observed that satisfactory results are obtainable even in the presence of 120 mM of perchloric acid, 70 mM of phosphoric acid, 36 mM of sodium fluoride, 160 mM of ammonium chloride, and significant amounts of niobate, molybdate, tantalate, tungstate, and vanadate. Frank et al[2] found that 15-mg amounts of Al(III), Fe(III), Mn(II), Mo(VI), and V(IV) do not interfere. The only serious interferences are cyanide in amounts exceeding 1 mg and sulfide in all amounts. Cyanide and sulfide, however, can be removed easily by evaporating the sample initially with perchloric acid. Frank et al[2] also note that chromium(III) in amounts exceeding 2 mg interfere; however, independent studies show that up to 15 mg of chromium(III) do not interfere.

With reference to the preceding paragraph, this method is applicable to nearly all types of samples including aluminum alloys, iron, various steels, various solders, various uranium compounds, and tungsten.

The range of the method is 1 to 70 μg of copper. Five-cm cells are used for the range of 1 to 14 μg of copper, 1-cm cells for the range of 5 to 70 μg of copper. The maximum permissible sample aliquot is about 50 ml; hence, the lowest concentration determinable is about 0.02 μg Cu/ml.

DISCUSSION

The critical variables of this method are the amount of ethyl alcohol present in the aqueous phase and the organic-to-aqueous volume ratio. A minimum of 2 ml of ethyl alcohol must be present for maximum reproducible color development. With the ethyl alcohol addition maintained at 3 ml and the volume of chloroform extractant at 10 ml, the absorbance increases significantly as the volume of the aqueous phase is increased from 20 ml to 80 ml. Dilution to 80±10 ml, therefore, is recommended in all cases. This provides satisfactory precision and maximum

versatility. The pH during color development is not critical. Gahler[3] and Frank et al[2] report a suitable pH range of about 2 to 9. Studies in this laboratory indicate a satisfactory pH range of 4 to 8.

The absorbance of the copper(I)-neocuproine complex increases linearly with increasing copper concentrations up to 8 µg/ml. Once extracted, the complex is stable for at least 4 days.

SAFETY PRECAUTIONS

Chloroform is toxic. Work in a well-ventilated room or in a hood.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, assorted sizes.
2. Cells for absorbance measurements, borosilicate glass or silica, 1- and 5-cm.
3. Graduated cylinder, 10-ml.
4. Flasks, volumetric, assorted sizes.
5. pH meter with glass-calomel electrode system.
6. Pipets, macro and micro, assorted sizes with rubber suction bulb and syringe.
7. Pipet, Mohr, 10-ml.
8. Separatory funnels, pear-shaped type, with Teflon-plugged stopcocks and polyethylene stoppers, 125-ml.
9. Spectrophotometer, Beckman Models DU or DK or Cary Model 14.
10. Test tubes, 13- x 100-mm, with polyethylene stoppers, or culture tubes, 25-ml, with polyethylene-lined screw caps.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water to prepare all reagents.

1. Ammonium hydroxide, conc and 3M.

2. Chloroform.

3. Copper stock solution, 1.000 mg Cu/ml. Dissolve 1.0000±0.0005 g of copper in a mixture of 10 ml of conc HNO_3 and 10 ml of water then dilute to 1 liter with water.

4. Copper calibration standard I, 30 µg Cu/ml. Dilute 15.00 ml of the 1 mg/ml stock solution to 500 ml with water.

5. Copper calibration standard II, 50 µg Cu/ml. Dilute 25.00 ml of the 1 mg/ml stock solution to 500 ml with water.

6. Hydroxylamine hydrochloride solution, 10% (w/v). Dissolve 50 g of $NH_2OH \cdot HCl$ in water and dilute to 500 ml.

7. Neocuproine solution, 0.1% (w/v). Dissolve 0.50 g of neocuproine in 500 ml of 95% ethanol.

8. Perchloric acid, 3M.

9. Sodium citrate solution, 30% (w/v). Dissolve 300 g of sodium citrate dihydrate in water and dilute to 1 liter. Transfer the solution to a 2-liter separatory funnel, add 5 ml of 10% (w/v) $NH_2OH \cdot HCl$ and 5 ml of 0.1% neocuproine solution, and extract with 75-ml portions of chloroform until the chloroform extract is colorless.

PROCEDURE

A. Blank

Process a reagent blank with each series of calibration standards and samples. Substitute 10 ml of water for the sample aliquot and follow Procedure C.

B. Calibration and Bench Standard

Measurements with either 1- or 5-cm cells are recommended in this method. For measurements with 1-cm cells, use 1.00-ml portions of copper calibration standards I and II. For 5-cm cell measurements, use 200-µl portions of these same standards. If only samples of uniform copper concentrations are being analyzed, one appropriate pair of standards is sufficient. However, if samples of varying or unknown copper concentrations are being analyzed, process both pairs of standards to minimize repeat determinations and to save time.

Process the standards per Procedure C beginning at tep 2. Divide the micrograms of copper by the corresponding absorbance to obtain the conversion factor. Within each group, the difference between the two factors should not exceed specified limits, and the average of the two factors should agree with the established factor within specified limits. If either or both of these specifications are not met, reprocess the pair or pairs of standards. Contact your supervisor if difficulties persist.

C. Analysis of Samples

1. Pipet a sample aliquot of 50 ml or less containing 1 to 70 µg of Cu into a beaker of suitable size.

2. Add 10 ml of 30% (w/v) sodium citrate solution.

3. Add 5 ml of 10% (w/v) $NH_2OH \cdot HCl$ to reduce copper to the cuprous state.

   If the volume of sample is small, add 10 to 15 ml of water to facilitate pH adjustment in the next step.

4. Using a pH meter, adjust the pH to 5.0±1.0 with conc NH_4OH, 3M NH_4OH, or 3M $HClO_4$ as required.

   The pH is not critical. The pH range of 5.0±1.0 is a convenient, suitable range for citric acid - citrate buffer.

5. Transfer the solution to a 125-ml separatory funnel with several rinses.

6. Pipet 3 ml of 0.1% neocuproine.

7. Dilute to 80±10 ml with water.

8. Pipet exactly 10.00 ml of chloroform and extract vigorously for 1 min.

9. Let the layers separate, then jiggle the funnels to settle the chloroform.

10. Drain the lower chloroform phase into a test tube or screw-cap culture tube.

    The glass test tube or culture tube effectively adsorbs accompanying water droplets.

11. Measure the absorbance of the chloroform solution against pure chloroform at 457 mμ.

    Use 5-cm cells for samples with less than 5 μg of Cu and 1-cm cells for samples with more than 14 μg of Cu. Between 5 μg and 14 μg, either cell may be used. In doubtful cases, use the 5-cm cell first for this enables subsequent 1-cm cell measurement.

12. Record the data and calculate the results as shown on the example work sheet. Report all results to three significant figures.

REFERENCES

1. H. Diehl and G. F. Smith, The Copper Reagents: Cuproine, Neocuproine, Bathocuproine, Columbus, Ohio: The G. Frederick Smith Chemical Company (1958) pp 23-32.

2. A. J. Frank, A. B. Goulston, A. A. Deacutis, "Spectrophotometric Determination of Copper in Titanium", Anal. Chem., 29 (1957) p 751.

3. A. R. Gahler, "Colorimetric Determination of Copper with Neo-cuproine", Anal. Chem., 26 (1954) p 577.

4. C. L. Luke and M. E. Campbell, "Determination of Impurities in Germanium and Silicon", Anal. Chem., 25 (1953) p 1588.

S. S. Yamamura
April 1968

Cu-Color-1

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Cu

CHARGE NUMBER _____ PROCEDURE Cu-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance vs Chloroform	Net Absorbance	Conv Factor µg Cu/abs Unit	µg Cu in Samp Aliquot	µg Cu Corr'd for Bias			RESULT µg Cu/ml
Std, 30µg		0 425	0 414	7246					
Std, 50µg		0 688	0 677	7386					
Blank		0 011							
			$\bar{X}$ =	7316					
Dissolved Coolant	15 00 ml	0 375	0 364	7316	26 63	26 9 ± 0 6			1 79 ± 0 04

ANALYZED BY _____ DATE _____

CALCULATIONS:

$C = \text{Conv Factor} = \frac{\mu g\ Cu}{\text{Net Abs}}$

$C_1 = \frac{30}{0\ 414} = 72\ 46$; $C_2 = \frac{50}{0\ 677} = 73\ 86$

$\bar{X} = 0\ 5(72\ 46 + 73\ 86) = 73\ 16$

$D = BC = 0\ 364(73\ 16) = 26\ 63\ \mu g\ Cu$

$\text{Result} = \frac{E}{\text{samp vol}} = \frac{26\ 9 \pm 0\ 6}{15.00} = 1\ 79 \pm 0\ 04\ \mu g\ Cu/ml$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF DIBUTYLPHOSPHATE FOLLOWING ALUMINA COLUMN SEPARATION

ABSTRACT

Dibutylphosphate (DBP) is oxidized to orthophosphate with fuming perchloric acid and the orthophosphate is determined spectrophotometrically as the molybdenum blue complex. The DBP is separated initially from tributylphosphate (TBP) and orthophosphate with an alumina column. Monobutylphosphate (MBP) is only partially removed by the alumina column separation but is not a serious problem because its concentration is normally considerably lower than that of DBP.

APPLICABILITY

This method is designed primarily for the determination of DBP in streams associated with the TBP extraction process for uranium. It is applicable to organic (TBP-kerosene) and aqueous samples.

Organic TBP-Kerosene Samples. Tributylphosphate, when present in the usual 5 (v/v) % concentration, occasionally holds up on the alumina column, even after thorough washing, to cause erratic high results. This problem is avoided by extracting the DBP into dilute sodium hydroxide prior to the alumina column separation. Inorganic ions are present in TBP-kerosene samples usually in low concentrations only so the recommended method (Procedures E plus G) adequately circumvents interference from these substances. Monobutylphosphate partially accompanies DBP and represents a potential interference.

Aqueous Samples. Two analysis schemes are employed for aqueous samples. These schemes are represented by Procedure G and by the combination of Procedures F and G. Procedure G includes the alumina column separation of DBP and the spectrophotometric measurement of DBP as orthophosphate. Procedure F describes the extraction of DBP into hexone from 3M HCl-0.12M HF medium and the subsequent sodium hydroxide strip. When Procedure G alone is used, uranyl nitrate alone at 600:1 U:DBP molar ratio, aluminum nitrate alone at 200:1 or zirconyl nitrate at 200:1 does not interfere. Higher ratios of these ions cause low results. Zirconium at 200:1 interferes seriously when accompanied by aluminum and/or uranium. The effect of other metal ions has not been studied; however, metals that form strong complexes with phosphate should be considered as potential

interferences. In addition to DBP, the alumina column has a strong affinity for the anions $Cr_2O_7^{=}$, F^-, $C_2O_4^{=}$, $PO_4^{\equiv}$, $SO_4^{=}$, and $SO_3^{=}$ when present in amounts approaching or exceeding the break-through capacity of the column, causes incomplete retention of DBP and low results. The breakthrough capacity of the alumina column in this method is something less than the estimated column capacity of 8 meq. The interference of the aforementioned cations and anions is avoided by initially extracting the DBP into hexone from 3M HCl-0.12M HF medium per Procedure F. Again, comprehensive studies have not been made to determine the tolerance levels of many diverse ions. The method gives satisfactory results on a synthetic mixture containing Al, U, and Zr.

As in the case of the organic samples, MBP partially accompanies DBP and will interfere if present in appreciable amounts (see Discussion Section).

The range of the molybdenum blue spectrophotometric measurement procedure in this method is 10 to 100 µg of phosphate (approximately 20 to 200 µg DBP).

DISCUSSION

Dibutylphosphate is formed along with MBP and phosphate in the degradation of TBP per the sequence:

$$\text{TBP} \xrightarrow{k_1} \text{DBP} \xrightarrow{k_2} \text{MBP} \xrightarrow{k_3} PO_4^{\equiv} \qquad (1)$$

where

$$k_1 = 7.5 \times 10^{-3}/\text{hr}$$
$$k_2 = 3.4 \times 10^{-3}/\text{hr}$$
$$k_3 = 1.6 \times 10^{-3}/\text{hr}.$$

The alumina column separation procedure removes TBP completely and MBP partially. The incomplete removal of the latter is not a serious problem; however, because the DBP concentration is usually much greater than the MBP concentration as the hydrolysis rate constants, k_1 and k_2, in 0.05M HNO_3 - 0.25M $UO_2(NO_3)_2$ medium at 76°C indicates. Singly and doubly charged DBP and MBP are retained by the alumina quantitatively; whereas, neutral TBP is not retained and readily eluted from the alumina column with acetone (Figure 1). Dibutylphosphate is eluted quantitatively in a sharp band with five column volumes of 1M NH_4OH. Monobutylphosphate is eluted partially (approximately 50%) during the DBP elution (Figure 1). Fortunately, as noted above, the level of MBP is much less than the level of DBP and the interference of MBP is not serious. The presence or absence of MBP can be confirmed by analyzing the next 10- to 15-ml portion of ammoniacal column effluent for phosphate. Phosphate, the ultimate

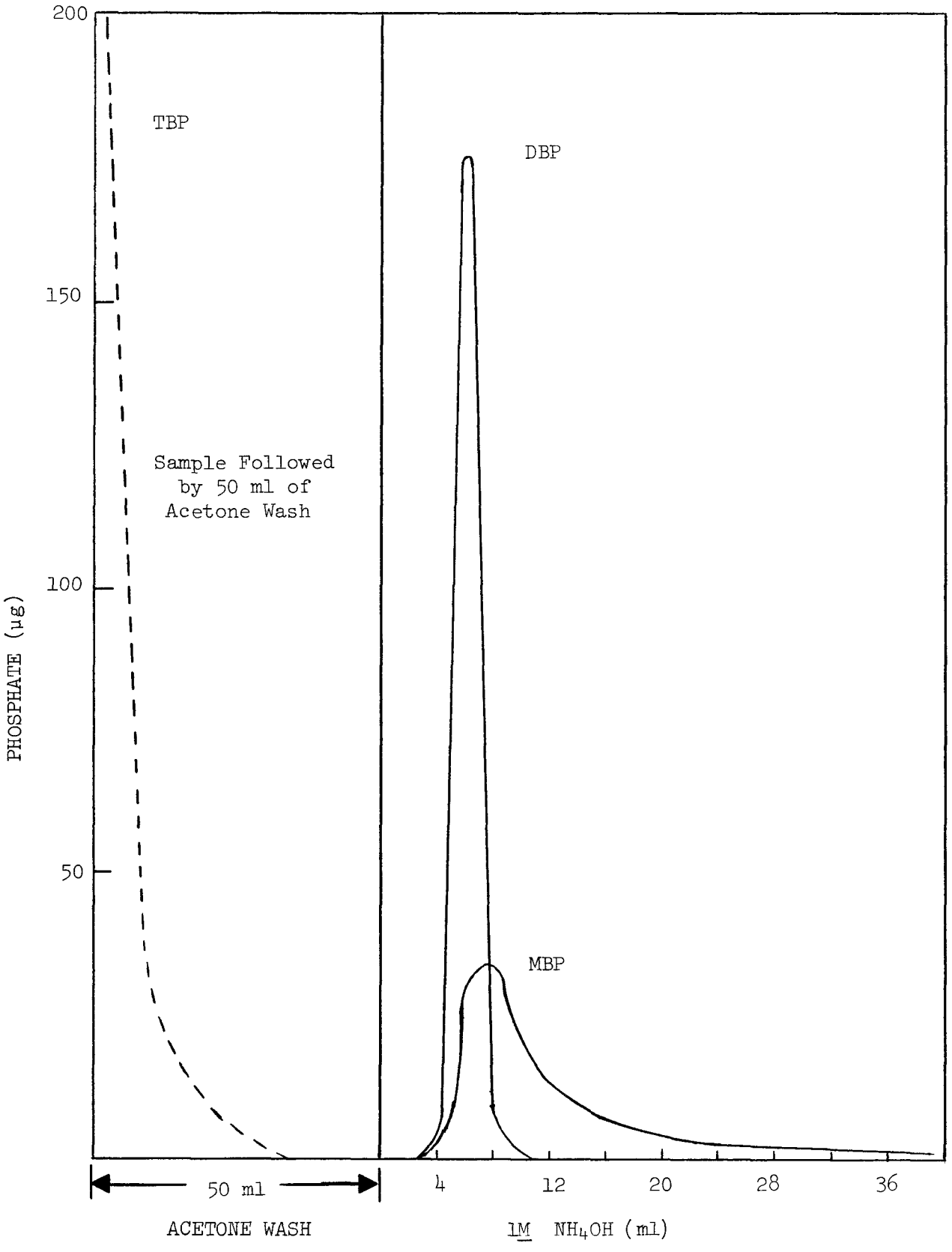


Fig. 1 Elution curves for DBP, MBP, and TBP.

degradation product of MBP, also is retained by the alumina column but does not interfere because it is not eluted with 1M NH_4OH[1].

When interfering amounts of metal ions are present, the DBP is separated initially from the metal ions by extraction into hexone from a 3M HCl-0.12M HF medium. Both fluoride and hydrochloric acid help to break up metal-DBP complexes while hydrochloric acid produces the strongly acidic medium required for the extraction of DBP as the nonionized acid.

The measurement of DBP as orthophosphate by the molybdenum blue spectrophotometric procedure presents several potential trouble areas. These areas, covered in detail in Method P-Color-1 of this manual, are:

(1) Phosphate contamination. Phosphate contamination through apparatus and reagents (perchloric acid, especially) is a frequent problem. Glassware can be cleaned effectively with a 7M NH_4OH soak and water rinse.

(2) Color development and measurement. The reduction of the yellow phosphomolybdate complex to molybdenum blue and the intensity of the blue color are affected by molybdate reagent level, acidity, and the presence of anions other than that of the reduction medium (HCl). At room temperature, the reduction is complete in 15 min, and thereafter, the blue color is stable for several hours. Once prepared, the hexone solution of the blue complex should not be diluted because the color intensity is sensitive to change in acidity and salt concentration.

SAFETY PRECAUTIONS

Perchloric acid is used in this method to oxidize DBP to orthophosphate. The digestion of milligram amounts of organic matter with perchloric acid is generally a smooth, safe operation; however, caution should still be exercised. Perform all perchloric acid digestions behind a safety shield in the perchloric acid hood. Use rubber gloves when handling acids and other injurious chemicals.

APPARATUS AND REAGENTS

A. Apparatus

Note: All apparatus that contacts the sample between the DBP elution and the stannous chloride reduction must be cleaned thoroughly before use. Soak the items in 7±1M NH_4OH, then rinse well with distilled water.

1. Absorbance cells, borosilicate glass or silica, 1-cm.

2. Alumina Column. Prepare the alumina column by attaching 3.5 in. of 39-mm glass tubing and a 1-mm Teflon-plugged stopcock to 4 in. of 11-mm glass tubing. Transfer a sufficient amount of the alumina slurry to the column to make a bed 3-in. high. Use a glass-wool plug to retain the alumina.

3. Beakers, assorted sizes.

4. Centrifuge tubes, 50-ml.

5. Cylinders, graduated, assorted sizes.

6. Glass beads.

7. Hot plate.

8. Pipets, macro and micro, assorted sizes, with suction bulb and syringe controls.

9. Pipet, mohr, 5- and 10-ml.

10. Separatory funnels, 125-ml, with Teflon stopcocks.

11. Spectrophotometer, Beckman DU, Cary Model 14, or equivalent.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium hydroxide, 1M.

2. Aluminum nitrate-uranyl nitrate matrix solution. Dissolve 125 g of $UO_2(NO_3)_2 \cdot 6H_2O$, 94 g of $Al(NO_3) \cdot 9H_2O$, and 6.7 g of $ZrO(NO_3)_2 \cdot 2H_2O$ in 0.5M HNO_3 and dilute to 250 ml with 0.5M HNO_3.

3. Ammonium hydroxide, 1M.

4. Chlorostannous acid solution. Dissolve 1.2 g of $SnCl_2 \cdot 2H_2O$ in 85 ml of conc HCl and dilute to 500 ml with water. Add several pellets of metallic tin and store in a polyethylene bottle. This reagent is good for about 2 weeks. Prepare only half when a few samples are to be analyzed.

5. Dibutylphosphate bench-control standards. Prepare dilutions of DBP with kerosene (organic samples) or with 0.001M NaOH (aqueous samples) to cover the concentration range 20 to 200 µg DBP/ml. Store both types of solutions in glass screw-cap bottles.

6. Hexone (4-methyl-2-pentanone).

7. Hydrochloric acid, conc and 1M.

8. Hydrofluoric acid, 3M (Use rubber gloves when preparing this reagent.)

9. Kerosene.

10. Molybdate solution. Dissolve 73±0.5 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in water. Filter if turbid, dilute to 1 liter with water, and store in a polyethylene bottle.

11. Nitric acid, conc.

12. Perchloric acid, conc and 1M, phosphate-free. Vacuum distill reagent grade perchloric acid, if necessary.

13. Phenolphthalein.

14. Phosphate standard stock solution, 1.000 mg $PO_4^{\equiv}$/ml. Dissolve 0.7165±0.0005 g of KH_2PO_4 in water and dilute to 500 ml with water.

15. Phosphate calibration standards I and II, 50.0 and 75.0 µg $PO_4^{\equiv}$/ml, respectively. Dilute 10.00 ml and 15.00 ml of the stock standard to 200 ml with water.

16. Sodium hydroxide, 0.02M, 0.05M, and 1M.

PROCEDURE

A. Blank

A blank solution must be prepared with all samples. Process 10 ml of water according to Procedure G beginning at Step 6.

B. Calibration

Process 1.00-ml aliquots of the two phosphate calibration standards according to Procedure G beginning at Step 6. Record the absorbances of the two standards and the blank on the worksheet. Divide the micrograms of phosphate in each standard by the respective net absorbance to obtain the conversion factor. The difference between the two conversion factors should not exceed limits shown on the control chart. Also, the average of the two factors must agree with the established conversion factor within specified limits. If either or both specifications are not met, reprocess the calibration standards. Seek help if difficulties continue.

C. Analysis of Bench-Control Standards

Because DBP is determined only at infrequent intervals, this method is not included in the continuous surveillance. Consult your supervisor to determine the type and number of standards that should be processed prior to and during the analysis of samples.

D. Preparation of Alumina Column

1. Swirl about 50 ml of anionotropic alumina with about 75 ml of water, wait 2 to 3 min for the large particles to settle, then decant the fines. Repeat the washing until most of the undesirable slow-to-settle fines are removed.

2. Transfer an amount of the washed alumina slurry to the column to make a bed 3-in. high.

   If the column is not equipped with a sintered glass support, use a glass-wool plug to retain the alumina.

3. Pass 20 ml of 1M NaOH through the column.

4. Pass 10 ml of water through the column.

5. Convert the column to the perchlorate form by passing 10 ml of 1M $HClO_4$ through it.

6. Pass 10 ml of water through the column.

E. Pre-extraction of DBP from Organic Samples

1. Pipet a sample aliquot containing 20 to 200 µg of DBP into a 125-ml separatory funnel.

2. Dilute to about 25 ml with kerosene.

3. Add 15 ml of 0.02M NaOH and extract for 1 min.

   Extract gently to minimize emulsion formation.

4. Swirl the funnel to get the kerosene away from the stopcock and drain the aqueous lower layer into a beaker.	Try not to get any more organic in the beaker than necessary; however, some will be there.
5. Repeat Steps 3 and 4 two more times and combine the aqueous extracts.	
6. Add 1 drop of phenolphthalein to the combined aqueous extract, neutralize with 1M $HClO_4$, and continue with Procedure G.	

F. Pre-extraction of DBP from Aqueous Samples Containing Interfering Ions.

1. Pipet a sample containing 20 to 200 g of DBP into a 125-ml separatory funnel.	
2. Dilute to 19±1 ml with water.	For convenience, mark the funnel at the 19-ml level.
3. Add 6 ml of conc HCl and 1 ml of 3M HF.	The HF is added to complex the Zr and break any Zr-DBP complex.
4. Add 25 ml of hexone, extract for 3 min, then drain and discard the aqueous bottom layer.	Shake gently to avoid emulsion formation. Do not drain any hexone out of the funnel. DBP will be lost.
5. Gently scrub the residual hexone solution for 30 sec with 25 ml of 1M HCl. Discard the bottom phase.	
6. Add 20 ml of 0.05M NaOH and 1 drop phenolphthalein. If the solution is not basic add more 0.05M NaOH dropwise until basic. Shake gently for 1 min, drain the bottom aqueous layer into a 100-ml beaker.	
7. Complete the DBP strip with 15 ml of 0.02M NaOH and then with 10 ml of water. Combine the strip solutions.	Use a gentle 30-sec contact.

8. Neutralize the combined aqueous strip with 1M $HClO_4$ and continue with Procedure G.

G. Separation and Determination of DBP

1. Pass the combined strips from Step E-6, F-8, or an aliquot of an aqueous sample containing 20 to 200 µg of DBP through the prepared alumina column at a rate up to 5 ml/min.

2. Wash the column with five 10-ml portions of acetone to remove all traces of TBP.

For most effective washing, let the acetone level drop to about 0.5 in. above the alumina before adding the next portion.

3. Pass 15 ml of water through the column.

4. Elute the DBP into a clean 150-ml beaker with four 3-ml portions of 1M NH_4OH followed by 10 ml of water.

5. Add 1 drop of phenolphthalein and evaporate the solution on a hot plate until it turns colorless.

6. Add 1 ml conc HNO_3 and 6 ml of conc $HClO_4$.

7. Add 2 to 3 glass beads to prevent bumping, place a cover glass on the beaker, evaporate to fumes of $HClO_4$, and fume for 5 min.

Phosphate losses may occur if the fuming is prolonged much over 5 min. Perform the fuming behind a safety shield and in the perchloric acid hood.

8. Cool, transfer quantitatively with water washing to a 125-ml separatory funnel, and dilute to 35 ml with water.

9. Add 5 ml of the ammonium molybdate reagent, mix by swirling, then let stand for 5 min.

10. Pipet exactly 25 ml of hexone and extract vigorously for 1 min.

11. Let the two phases separate, then drain and discard the lower aqueous layer.

Hereafter, the hexone is not diluted to a given volume so small losses of hexone are permissible in ensuing steps.

12. Add 15 ml of water, contact gently for 30 sec, then drain and discard the lower phase.

13. Repeat Step 12.

In the absence of acids or salts, hexone-water mixtures form a difficult-to-separate emulsion when shaken vigorously. Use a gentle rocking motion to mix the two phases.

14. Swirl the hexone solution to settle water droplets clinging to the walls of the funnel. Drain the water completely.

15. Add 15 ml of the chlorostannous acid reagent, extract vigorously for 15 sec, and drain and discard the lower aqueous layer.

16. Wait 15 min for color development.

17. Measure the absorbance against hexone at 625 mμ.

If the solution is cloudy, transfer to a 50-ml tube and centrifuge.

18. Record the data and calculate the results as shown on the example worksheet.

Use 1-cm cells for all samples.

REFERENCES

[1] M. A. Wade, S. S. Yamamura, "Determination of Dibutylphosphate in Tributylphosphate-Kerosene Solutions - An Alumina Column Separation Procedure", Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, October 1962.

May, 1970
J. A. Rindfleisch
M. A. Wade

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION DBP

CHARGE NUMBER _____ PROCEDURE DBP-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Net Absorbance	Factor	mg PO4 in Aliquot	mg PO4 Corrected	DBP conversion Factor		RESULT mg DBP/ml
Blank		0.022							
Std, 50		0.474	0.452	110.62					
Std, 7.5		0.710	0.688	109.01					
			$\bar{X}$	109.82					
Sample	5.0ml	0.372	0.350		36.44	36.54±1.3	2.213		16.17 ± 0.58

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = \frac{\text{mg PO}_4}{B} = \frac{50}{0.452} = 110.62 \qquad C' = \frac{75}{0.688} = 109.01$$

$$\bar{X} = \frac{C + C'}{2} = \frac{110.62 + 109.01}{2} = 109.82$$

$$D = C_{\bar{x}} B = (109.82)(0.352) = 36.44$$

$$\text{Results} = \frac{EF}{a_0} = \frac{(36.54 \pm 1.3)(2.213)}{5.0}$$

$$= 16.17 \pm 0.58$$

APPROVED BY _____

PREPARATION OF EDTA STANDARD SOLUTION

ABSTRACT

An aqueous solution of ethylenediamine tetraacetic acid (EDTA) is prepared from the disodium salt and standardized via titration of standard solutions of zinc(II) and/or mercury(II).

APPLICABILITY

This method deals specifically with the preparation of a standard EDTA solution; however, the directions given also are applicable with minor changes to the preparation of standard solutions of diethylenetriamine pentaacetic acid (DTPA), cyclohexanediamine tetraacetic acid (CDTA or DCTA), N-hydroxyethylethylenediamine triacetic acid (most often referred to as Versenol), and triethylenetetramine hexaacetic acid (TTHA).

The directions given in this method deal specifically with the preparation of a 0.05M solution; however, these directions with minor changes are applicable to the preparation of a 0.10M solution.

DISCUSSION

Nitrilotriacetic acid (NTA), EDTA, Versenol, CDTA, DTPA, and TTHA (Table I) are the most important members of a series of related aminopolycarboxylic acid "complexones" popularized by Schwarzenbach and others[1,2]. Of these, EDTA (alias enta, Calsol, Chelaton, Complexone(III), Idranal(III) Iminol D, Nervanaid, Nullapon, Sequestrene, Titraver, Trilon B, and Versene) is the compound most often and most widely used in analysis. EDTA (as the doubly-ionized anion, $H_2Y^{=}$) reacts with most cations to form 1:1 complexes of high stability (Equation 1).

$$M^{+x} + H_2Y^{=} \leftrightarrow MY^{-(4-x)} + 2H^{+} \qquad (1)$$

This is the basis of numerous "complexometric" methods for the determination of metallic elements[1,2]. Many techniques can be used to signal that point in the titration where just the right amount of EDTA standard has been introduced[2]. The one employed in this method uses a metal-complexing chromogen which bears a different color when complexed by a metal and when not complexed. Complexometric titration procedures based on EDTA and related "chelons" also are referred to as "chelometric" procedures. This arises from the fact that the EDTA molecule, through multiple coordination, binds a metal ion in a special kind of complex wherein the metal is clutched in a ring structure called a chelate.

TABLE I

EDTA AND SOME RELATED AMINOPOLYCARBOXYLIC ACIDS

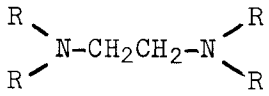
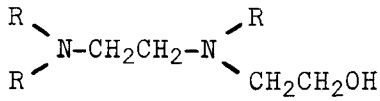
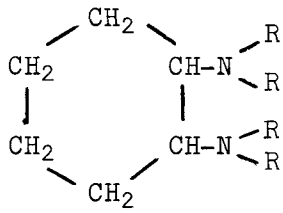
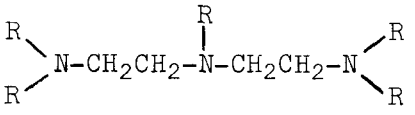
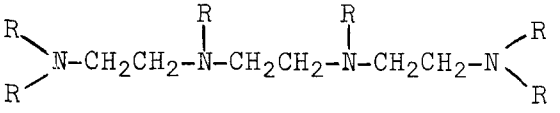
Compound	Structural Formula[a]	Remarks
NTA (Nitrilotriacetic Acid)		
EDTA		EDTA, a tetrabasic acid, often is represented by the formula H_4Y. The negative logarithms, pK's, of the successive dissociation constants are: 2.0, 2.67, 6.16, and 10.26.
N-Hydroxyethyl-ethylenediamine Triacetic Acid (Versenol)		The presence of the ethanolic group makes Versenol more soluble than EDTA, especially in acidic media. Its metal complexes are slightly less stable than the corresponding EDTA complexes.
CDTA		

TABLE I (Cont'd)

Compounds	Structural Formula[a]	Remarks
DTPA		The metal complexes of DTPA are generally 100- to 1000-fold more stable than the corresponding EDTA complexes.
TTHA		

[a] R = $-CH_2COOH$

EDTA is available commercially in an Analytical Reagent Grade as the tetraacid and as $Na_2EDTA \cdot 2H_2O$. These Reagent Grade chemicals are sufficiently pure that standard solutions with nearly the correct (within 1%) concentration can be prepared from weighed portions of the acid or salt. For precise work, however, it is best to prepare an aqueous solution of the disodium salt, then standardize the solution against high purity metal standards. Reliable reference materials include metallic Bi, Cu, Hg, In, and Zn, $CaCO_3$, and ZnO[2]. Standardization of a given solution of EDTA against a series of supposedly pure metal standards may give a range of concentration values for the EDTA. In such a case, the most correct values are those at the lower end of the range. The reason for this is that as the actual purity of the reference material increases, the volume of EDTA required to titrate a given weight of the material increases and the calculated EDTA molarity decreases. This can be seen readily from the relationship:

$$\text{EDTA Molarity} = \frac{(\text{Wt of Reference Material})(N)}{(\text{Formula Wt of Ref Material})(\text{Vol EDTA})} \qquad (2)$$

where

N = the number of metal atoms in the formula of the reference material.

Chelometric titrations are simple and reliable; however, there are a number of causes for titration failure. The most important are: (a) deterioration of indicator; (b) indicator blocking attributable to the presence of traces of metal ions that react irreversibly with the indicator; (c) improper pH; (d) metal ion hydrolysis; and (e) introduction of contaminants through apparatus and reagents. All of these affect the clarity of the end point and the reliability of the titration. EDTA solutions leach significant amounts of metal ions from all glass including borosilicate glass and are best stored in thick-walled polyethylene containers. Because of their inherent ability to attract magnetic materials, bar magnets for magnetic stirrers constitute a frequent source of metallic contamination. All stir-magnets should be examined routinely for adhering particles and cleaned periodically with warm 6M HCl.

SAFETY PRECAUTIONS

There are no particularly hazardous chemicals or operations. Pyridine is somewhat toxic. Work in a hood or well-ventilated room.

APPARATUS AND REAGENTS

A. Apparatus

1. Ampoules, glass, 20-ml capacity.
2. Beakers, assorted sizes.
3. Buret, 10-ml, with 0.05-ml graduations.
4. Dropping bottles.
5. Flasks, Erlenmeyer or round-bottom, with 24/40 ℧ joint.
6. Flasks, volumetric.
7. Hot plate.
8. Membrane filters, 0.45-μ pore size, 47-mm diam.
9. Millipore filter holder, 47-mm diam.
10. Muffle furnace.
11. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.
12. Platinum crucible or dish.
13. Reflux head.
14. Suction flasks, 1-, 2-, or 4-liter capacity.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Disodium ethylenediaminetetraacetic acid dihydrate, $Na_2EDTA \cdot 2H_2O$.

2. Hydrochloric acid, 6M.

3. Mercury metal, freshly distilled.

4. Nitric acid, conc, 8M, and 0.1M.

5. Pyridine.

6. Sodium-cerium-EDTA octahydrate, $NaCeEDTA \cdot 8H_2O$. Prepare as described in Method Fe-Vol-1 of this Manual.

7. Xylenol orange, 0.2% (w/v). Dissolve 0.20 g of the reagent in 100 ml of water.

8. Zinc oxide, ZnO, high purity (Johnson, Matthey, and Company).

PROCEDURE

NOTE: Use distilled water for all procedures.

A. Titration Blank

No titration blank is necessary.

B. Preparation of 0.07500M Zinc Reference Standard

1. Place approximately 3.5 g of ZnO in a platinum dish or crucible.

2. Ignite the oxide for 1 hr at 1000°C.

Caution: The furnace should be in a well-ventilated hood.

3. Transfer the platinum dish to a desiccator and cool to room temperature.

4. Weigh 3.0518±0.0005 g of the ignited oxide into a 125-ml Erlenmeyer flask.

5. Place a reflux head on the flask and dissolve the oxide with 25 ml of 6M HCl with gentle heating.

6. Chill the solution to room temperature, then transfer it quantitatively to a 500-ml volumetric flask with water rinses. Dilute exactly to volume with water and mix thoroughly.

7. Transfer the solution to clean, dry 20-ml glass ampoules in units of about 18 ml, draw seal the ampoules, and label properly.

This sealed standard is known to be stable for at least 2 yr.

C. Preparation of 0.07500M Mercury Reference Standard

1. Weigh 7.5229±0.0005 g of freshly distilled Hg metal into a 250-ml flask with a 24/40 ℧ joint.

2. Fit a water-cooled condenser onto the flask and admit 100 ml of 8M HNO_3 through the top of the condenser.

The condenser prevents loss of Hg by volatilization.

3. Heat gently until the Hg dissolves completely, then boil the solution for 5 min.

4. Chill the Hg solution to room temperature, then rinse the condenser with 0.1M HNO_3 and remove the solution and flask.

5. Transfer the solution with 0.1M HNO_3 rinses to a 500-ml volumetric flask. Dilute exactly to volume with 0.1M HNO_3 and mix until homogeneous.

6. Transfer the Hg solution to clean 20-ml glass ampoules in units of about 18 ml, draw seal the ampoules, and label properly.

The stability of this standard has not been established. It is believed to be stable for at least 2 yr.

D. Preparation of 0.05M EDTA

NOTE: The directions below are for the preparation of 1 liter of 0.05M solution. For larger volumes and higher concentrations of EDTA, scale up accordingly.

1. Weigh 18.75±0.05 g of $Na_2EDTA \cdot 8H_2O$ into a 400-ml beaker.

The solution is intentionally made to be slightly above 0.05M.

2. Add 200 ml of water and stir until the salt dissolves completely.

3. Filter the solution through a 0.45-μ membrane filter, then wash the filter with water.

Analytical Reagent Grade $Na_2EDTA \cdot 2H_2O$ contains significant amounts of insoluble residue which are best removed by filtration.

4. Transfer the filtrate with water rinses to a 1-liter polyethylene bottle, dilute to 1 liter with water, and mix until homogeneous.

5. Standardize the solution via Procedure E and/or F.

E. Standardization of EDTA by the Zinc Reference Standard

1. Pipet 5.00 ml of the 0.07500M Zn reference standard into a 150-ml beaker.

Use 10 ml of the reference standard to standardize a 0.10M EDTA solution.

2. Add 5 drops of conc HCl and dilute to 125 ml with water.

3. Add 5 drops of 0.2% (w/v) xylenol orange indicator solution.

4. Noting the number of drops, add pyridine dropwise to the appearance of a violet or red coloration, then add two times as much additional pyridine. If the red or violet coloration does not appear after the addition of 1 ml of pyridine, add conc NH_4OH dropwise until it appears, then add 2 ml of additional pyridine.

   The pH should be 5.60±0.25.

5. Titrate the zinc with the 0.05M EDTA solution prepared per Procedure D to a color change from violet to yellow.

   The end point color transition is violet to red to yellow. Titrate to the complete disappearance of the red coloration.

   Burets with grease-free Teflon-plugged stopcocks are used frequently in the laboratory. To avoid errors caused by leakage, remove the Teflon plug and clean the plug and the barrel of the stopcock before using the buret.

6. Calculate the molarity to four significant figures as described in the example work sheet.

F. Standardization of EDTA by the Mercury Reference Standard

1. Pipet 5.00 ml of the 0.07500M Hg reference standard into a 150-ml beaker.

   Use 10 ml of the reference standard to standardize 0.10M EDTA solution.

2. Add 5 drops of conc HNO_3 and dilute to 125 ml with water.

3. Add 0.5 g of $NaCeEDTA \cdot 8H_2O$ and stir for 1 to 2 min.

   Mercury(II) quantitatively releases an equivalent amount of Ce(III).

4. Add 5 drops of 0.2% (w/v) xylenol orange indicator solution.

5. Noting the number of drops, add pyridine dropwise to the appearance of a violet or red coloration, then add two times as much additional pyridine. If the red or violet coloration does not appear after the addition of 1 ml of pyridine, add conc NH_4OH dropwise until it appears, then add 2 ml of additional pyridine.	The pH should be 5.60±0.25
6. Titrate the solution with the 0.05M EDTA solution prepared per Procedure D to a color change from violet to yellow.	The end point transition is violet to red to yellow. Titrate to the complete disappearance of the red coloration.
7. Calculate the molarity to four significant figures as described in the example work sheet.	

REFERENCES

1. F. J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, Princeton, New Jersey: D. Van Nostrand Company, Inc., 1958.

2. L. Meites (ed) Handbook of Analytical Chemistry, New York: McGraw-Hill Book Company, Inc., 1963, pp 3-76 to 3-99.

January 1968
S. S. Yamamura

EDTA-Prep-1

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Standardization of EDTA

CHARGE NUMBER _____ PROCEDURE EDTA - Prep - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Molarity of Reference Standard	ml of Ref. Std. Used	ml of EDTA Used					RESULT EDTA Molarity
		0.07500	5.00	7.43					0.05047

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{EDTA Molarity} = \frac{(\text{Molarity of Ref. Std.})(\text{ml of Ref. Std})}{\text{ml of EDTA}} = \frac{AB}{C}$$

$$= \frac{(0.07500)(5.00)}{7.43}$$

$$= 0.05047\ \underline{M}$$

APPROVED BY _____

POTENTIOMETRIC DETERMINATION OF FLUORIDE USING A SPECIFIC FLUORIDE ELECTRODE

ABSTRACT

The concentration of free fluoride ions is determined by measuring the potential produced by a specific fluoride ion electrode with reference to a standard calomel electrode. This potential is proportional to the fluoride concentration. Interfering metal ions are removed by diluting the sample in a pH 7 buffer-complexer solution containing sodium citrate and triethanolamine. For samples containing boron, a special pretreatment with aluminum is necessary to break the strong boron fluoride (BF_4^-) complex.

APPLICABILITY

This method is applicable to the determination of fluoride in most samples resulting from the operation of the Idaho Chemical Processing Plant (ICPP) and the Waste Calcination Facility (WCF). The source of fluoride is the hydrofluoric acid used to dissolve Zircaloy clad fuel. Aluminum is added to the dissolved fuel to complex excess fluoride. The resulting solution (complexed dissolver product) has the approximate composition 0.5M Zr, 0.7M Al, 0.008M U, 0.2M B, 2.4M NO_3, and 3.4M F, and can be analyzed for fluoride by this method. After the uranium is extracted, the waste is calcined in the WCF. Calcium is added to the feed to complex excess fluoride before calcination; the added calcium does not interfere in this method. Other samples that can be analyzed include niobium-uranium and niobium-zirconium-uranium fuels that are dissolved in hydrofluoric acid. The following ions at a F^-/ion mole ratio of 13 do not interfere: Cr(III), Cd(II), Co(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Zn(II), $MoO_4^=$, and VO_3^-. This method is not applicable to solid samples; they must be analyzed by the pyrohydrolysis procedure of Method F-Vol-1.

The range of the method (Table I) is 0.001M to 10M F^-. The lower limit assumes the presence of boron which requires the addition of Al(III) to break the BF_4 complex. If boron is not present and complexing metal ions are low, samples of a lower concentration (about 2×10^{-6}M F^-) can be analyzed. At this level, a 1:1 dilution with the buffer-complex solution will give a solution 10^{-6}M F^- which is the lower limit of the electrode.

Except for the effect of ionic strength on the activity coefficients of fluoride ion, the anions such as Cl^-, NO_3^-, HCO_3^-, Br^-, $PO_4^{\equiv}$, and $SO_4^=$ do not interfere. Hydrogen and hydroxyl ions will interfere if they exceed the buffering capacity of the buffer-complexer solution.

TABLE I

SUGGESTED DILUTIONS FOR SAMPLES OF VARIOUS CONCENTRATIONS OF FLUORIDE

F^-		First Dilution			Second Dilution			
M	mg/ml	Aliquot	Vol Al^{+++}	Volume Complexer	Aliquot	Volume Complexer	Dilution	Dilution Factor
10	190	.200	1.0	50	.100	25	.2/51.2/.1/25.1	64256
6	114	.200	1.0	50	.200	25	.2/51.2/.2/25.2	32256
5	95	.200	1.0	50	.200	25	.2/51.2/.2/25.2	32256
4	76	.200	1.0	50	.250	25	.2/51.2/.25/25.25	25856
3	57	.200	1.0	50	.300	25	.2/51.2/.3/25.3	21589
2	38	.200	1.0	50	.500	25	.2/51.2/.5/25.5	13056
1	19	.200	1.0	50	1.000	25	.2/51.2/1.0/26	6656
.5	9.5	.200	1.0	25	1.000	25	.2/26.2/1.0/26	3406
.1	1.9	.200	0.4	25	1.000	25	.2/25.6/1.0/26	3328
.05	.95	.500	0.2	25	1.000	25	.5/25.7/1.0/26	1336
.01	.19	.300	0.2	50			.3/50.5	168
.005	.095	.500	0.2	50			.5/50.7	101.4
.001	.019	1.000	0.2	50			1.0/51.2	51.2

DISCUSSION

The fluoride sensitive electrode consists of a single crystal of lanthanum fluoride (solid membrane) doped with europium and cast into an epoxy body. The internal solution is a mixture of about 10^{-3}M F^- and 0.1M NaCl. The internal electrode is a silver-silver chloride electrode, and its potential is fixed by the chloride ion activity. The fluoride ion activity controls the potential of the inner surface of the lanthanum fluoride membrane. When the electrode is in a fluoride solution, a potential difference occurs across the membrane, and its magnitude depends on the ratio of fluoride ion activities in the inner and outer solutions.

Two procedures are described for the analysis of fluoride. Procedure C is for direct measurement, and Procedure D uses a standard addition technique. In the simpler Procedure C, the sample is diluted with the buffer-complexer solution to about 10^{-4}M. The potential of the solution is measured and compared to standards prepared in the same matrix. Figure 1 is a typical standard curve. The linear portion of the curve extends down to about 2×10^{-5}M F^-; the linear part is defined by Equation 1.

$$\log \text{conc} = (-0.016799)(MV) - 2.8917 \qquad (1)$$

This equation is fairly constant and can be used to calculate the concentration of samples. However, to guard against possible change of electrode response, calibration standards are processed with each set of samples. The 10^{-4}M F^- standard is measured first followed by the sample. The second standard is chosen to bracket the sample, and the concentration is calculated from Equation 2.

$$\log \text{conc} = A + \left[\frac{(A-B)(C-D)}{(D-E)}\right] \qquad (2)$$

where

A = log of the concentration of standard 1

B = log of the concentration of standard 2

C = sample reading, MV

D = standard 1 reading, MV

E = standard 2 reading, MV.

The sample aliquot selected for analysis should be such that the final dilution contains 10^{-4} to 2×10^{-4}M F^-. This range gives the largest change in potential for a given change in fluoride concentration. Table I gives sample dilutions for various concentrations of fluoride to achieve the desired range.

The standard addition procedure (Procedure D) may be used for more accurate analysis of samples that differ from the standards. This technique may be necessary if the complexer is not of sufficient strength to free the fluoride or the ionic strength is not the same as the standards. This should occur only at the low fluoride levels which prevent adequate dilution. In Procedure D a known volume of a standard fluoride solution is added to the sample after it has been diluted with the buffer-complexer solution. The volume of standard added should not exceed 1% of the diluted sample volume; this permits neglecting of volume corrections for the added standard. The concentration of the sample is calculated from Equation 3.

$$C = \frac{\Delta C}{(\text{antilog } \frac{\Delta MV}{S} - 1)} \qquad (3)$$

where

C = concentration of diluted sample (This concentration must be corrected for dilution factors to obtain the concentration of the sample.)

ΔC = change in concentration due to addition of NaF

ΔMV = change in potential of solution caused by addition of NaF

S = slope of electrode response curve. Theoretically, it is 59.12 but should be determined experimentally.

For this technique to work, the potentials must fall on the linear portion of the electrode response curve (Figure 1), and the slope of the curve for the sample solution must be the same as that determined experimentally for the electrode.

Another standard addition technique that may be used requires the addition of two increments of the fluoride standard with each addition giving the same potential change. This allows the use of the following simplified equation that does not contain the slope of the electrode response curve or the logarithmic function:

$$C = \frac{(\Delta C)^2}{(\Delta C' - \Delta C)} \qquad (4)$$

where

C = concentration of diluted sample (This concentration must be corrected for dilution factor to obtain the concentration of the sample.)

ΔC = change in concentration due to first addition of NaF

ΔC' = change in concentration due to second addition of NaF.

This method may be used in the nonlinear portion of the curve if the changes in concentrations are kept small so that the changes in potential approximate a straight line.

The standard deviation of the double addition method, obtained while doing the experimental work, was almost 3 times that of the results obtained by the single addition method. This difference is probably attributable to the two additions and the two readings which double the chances for error. Therefore, it is normal to see small differences between the values obtained by different procedures on a given sample.

SAFETY PRECAUTIONS

Hydrofluoric acid is very corrosive to body tissue and can cause deep subcutaneous burns if the acid or its vapors come in contact with the skin. Take all precautions necessary to avoid contact with this acid. If contact does occur, wash thoroughly with water and immediately notify the dispensary.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, plastic, 50-ml.
2. Bottles, plastic, 2- and 4-oz.
3. Electrode, calomel, Leeds and Northrup Model 117208. This electrode must make good contact with the sample. Force air through the liquid junction with a rubber bulb; if the junction is plugged, obtain a new electrode.
4. Electrode, fluoride. Orion Model 94-09A or equivalent. Wipe the crystal and lower part of the electrode once each shift with a tissue covered with special silicon oil. The oil is supplied with the electrode.
5. Lab jack (need 2).
6. Micro buret, Gilmont, and syringe calibrated to deliver 0.2 µl/div.
7. Magnetic stirrer with stirring bars.
8. pH meter, expanded scale. Corning Model 12, or equivalent.
9. Pipets, glass, 50- and 25-ml, and assorted micro pipets with suction bulb and syringe.
10. Pipets, plastic, 0.100, 0.200, 0.500, and 1.00-ml.

11. Recorder, 10-MV range.

12. Ringstand.

B. Reagents

Note: Use reagent grade chemicals and distilled water.

1. Aluminum nitrate, 1M. Dissolve 37.514 g of $Al(NO_3)_3 \cdot 9H_2O$ in water and dilute to 100 ml.

2. Buffer complexer solution I. 1M sodium citrate, 2M NaCl, 0.1M thiethanolamine (TEA). To prepare 4 liters, weigh 1176.4 g of sodium citrate dihydrate and 467.6 g NaCl, place into a 4-liter beaker and add water to the 3.5-liter mark. Stir until nearly dissolved and add 59.6 g of triethanolamine. Adjust the pH to 7.0 ± 0.1 with 6M HCl. If the pH drops below 7, use 6M NaOH. DO NOT USE AMMONIUM HYDROXIDE. Dilute to 4 liters and transfer to a 4-liter polyethylene bottle.

   Each time a new buffer-complexer solution is prepared, a blank must be processed. Add 25.0 ml of the buffer-complexer solution to 25.0 ml of water and measure the potential of the solution as described in Procedure C. If this potential is more negative than 150 MV (See Figure 1), a new set of calibration standards must be prepared.

3. Buffer-complexer solution II. Dilute 500 ml of reagent 2 to 1 liter with water.

4. Sodium fluoride. Purify NaF as follows: Prepare 100 ml of a saturated solution of NaF and filter off the excess NaF crystals. To the filtrate, add an equal volume of ethanol. Filter through a 0.45-μ filter and wash with alcohol. Dry at 150°C and store in a plastic bottle.

5. Standard fluoride solution, 0.5000M. Dissolve 20.995 g of the purified NaF (Reagent 4) in water and dilute to 1 liter. Store in a polyethylene bottle.

6. Standard fluoride solutions, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}M. Prepare 250 ml of each. Dilute 50 ml of reagent 5 to 250 ml with water to prepare the 10^{-1}M standard. Dilute the 10^{-1}M standard 1/10 to prepare the 10^{-2}M standard; dilute the 10^{-2} standard 1/10 to prepare the 10^{-3}M standard, etc.

7. Standards, calibration, 10^{-3}, 10^{-4}, 4×10^{-5}, and 10^{-5}M F^-. Prepare by adding standard fluoride solutions to 250 ml of the buffer-complexer solution I and diluting to 500 ml with water. Use the following table to prepare these standards.

TABLE II

PREPARATION OF CALIBRATION STANDARDS

Concentration of F^- Standard (M)	Volume of F^- Standard (ml)	Concentration of Calibration Standard (M)
10^{-3}	5	10^{-5}
10^{-2}	2	4×10^{-5}
10^{-2}	5	10^{-4}
10^{-1}	5	10^{-3}

8. Bench Standard

   (a) Dilute 28M HF 1:1 with water and standardize with sodium hydroxide. Prepare 1 liter of solution.

   (b) Transfer 100 ml (measured in a polyethylene volumetric flask) of the standardized HF to a 250-ml polyethylene volumetric flask and add 6 g of boric acid. Dilute to volume with water. Rinse the 100-ml volumetric flask into the 250 ml volumetric flask to achieve a quantitative transfer of the HF. To assure formation of HBF_4, do not dilute the HF standard before the boric acid is added. This will be used as a stock solution.

   (c) Dilute the stock solution to give a working bench standard with a concentration of about 2.3M F.

   Note: The stock solution can be used to prepare controls in the range of 0.25M to 5M F.

PROCEDURE

A. Standard Curve

Prepare a standard curve for each fluoride electrode before using the electrode and intermittently during the life of the electrode to determine whether the electrode is responding satisfactorily. The standard curve can be used to estimate fluoride concentrations and guide further dilutions.

1. Pipet aliquots of the fluoride standards (Reagents 5 and 6), as shown in Table III, into 100-ml polyethylene volumetric flasks.

TABLE III

PREPARATION OF STANDARD CURVE

Concentration of F^- Standard (M)	Volume of F^- Standard (ml)	Concentration of Calibration Standard (M)
5×10^{-1}	20	10^{-1}
10^{-1}	10	10^{-2}
10^{-2}	10	10^{-3}
10^{-3}	10	10^{-4}
10^{-4}	10	10^{-5}
10^{-5}	10	10^{-6}

2. Add 50.0 ml of buffer-complexer solution I and dilute to volume with water. Mix thoroughly and store in 4-oz. polyethylene bottles.

3. Measure the potential of each solution, starting with the 10^{-6}M standard, as described in Procedure C, Step 7. At the low concentrations, 10^{-4}M and below, it will require up to 20 min for the electrode to reach equilibrium. Measure each solution and plot the data on 5 cycle semi-log graph paper. A straight line should be obtained from 10^{-1} to 10^{-4}M F^-. A non-linear or a nonreproducible curve generally indicates a bad electrode.

B. Bench Standard

The bench standard is processed with a dilution of 0.2/51.2/.3/25.3. Process 0.200 ml of the bench standard as described in Procedure C beginning at Step 2. If the value obtained does not fall within the limits specified by the Quality Control Laboratory, repeat the analysis. If trouble still exists, contact your supervisor.

C. Analysis of Samples, Direct Procedure

1. From the expected F^- concentration of the sample and the data in Table I determine the sample aliquot, the sample dilutions, and the volume of $Al(NO_3)_3$ required.

   Record the sample size and dilution data on the sample work sheet.

2. Using a plastic pipet, transfer the sample aliquot to a 60-ml polyethylene bottle, if two dilutions are required or to a 50-ml polyethylene beaker if only one dilution is to be made.

3. Add the amount of 1M $Al(NO_3)_3$ determined in Step 1, cover, mix thoroughly by swirling the contents, and let stand for 5 min to insure complete reaction.	The Al(III) reacts with F^- and breaks the BF_4^- complex. A precipitate of AlF_3 may form at this point. It will dissolve in Step 4.
4. Pipet the amount of buffer-complexer solution II determined in Step 1 into the sample and mix on a magnetic stirrer. If two dilutions are required, continue with Step 5. If only one dilution is to be made, continue with Step 7.	If two dilutions are required, the sample will be in a bottle. In this case, mix by shaking.
5. Prepare for the second dilution by pipeting the required amount (as determined in Step 1) of buffer-complexer solution II into a 50-ml polyethlene beaker.	
6. Make the second dilution by pipeting the required amount (as determined in Step 1) of the diluted sample of solution from Step 4 into the beaker prepared in Step 5. Mix thoroughly on a magnetic stirrer.	A glass pipet may be used for this aliquot.
7. Measure the potentials of the 10^{-4}M calibration standard, the sample, and another calibration standard chosen so that the sample is bracketed with the two standards.	Between each measurement, rinse the electrodes thoroughly with distilled water and wipe dry with a soft tissue.
Set the pH meter to the +MV mode and expanded scale to make the measurement. Allow the potential to come to equilibrium; take the reading after the potential remains steady for at least one min.	Once each shift, wipe the crystal and lower body of the fluoride electrode with a tissue coated with silicon oil.

8. Wash the electrode and leave it immersed in the 10^{-5}M standard solution.

   If the potential of the 10^{-5}M standard falls below 115 MV, replace it with fresh solution.

9. Calculate the concentration of the sample as shown on the sample work sheet.

D. Analysis of Samples, Standard Addition Procedure

1. Dilute the sample to about 10^{-4}M F^- with buffer-complexer solution II. If a 1:1 dilution is made, use buffer-complexer solution I.

   Do not dilute below 2×10^{-5}M F^-.

2. Measure the potential of the solution as described in Procedure C, Step 7.

3. Add an amount of 0.25M F^- that will cause a potential change of about 20 MV. Use a 0.2 µl/div Gilmont microburet for the addition. Calculate the concentration as shown in the sample work sheet.

   If a double addition is to be used, continue with Step 4.

   The slope of the equation must be known to calculate concentrations from a single addition. Dilute reagent 5 (0.5M) 1:1 to obtain the 0.25M F^- solution.

4. If two additions are to be made, repeat Step 3. Continue the second addition so the potential change is exactly the same as for the first addition.

   Calculate the concentration as shown in the sample work sheet.

D. R. Trammell
May 1971

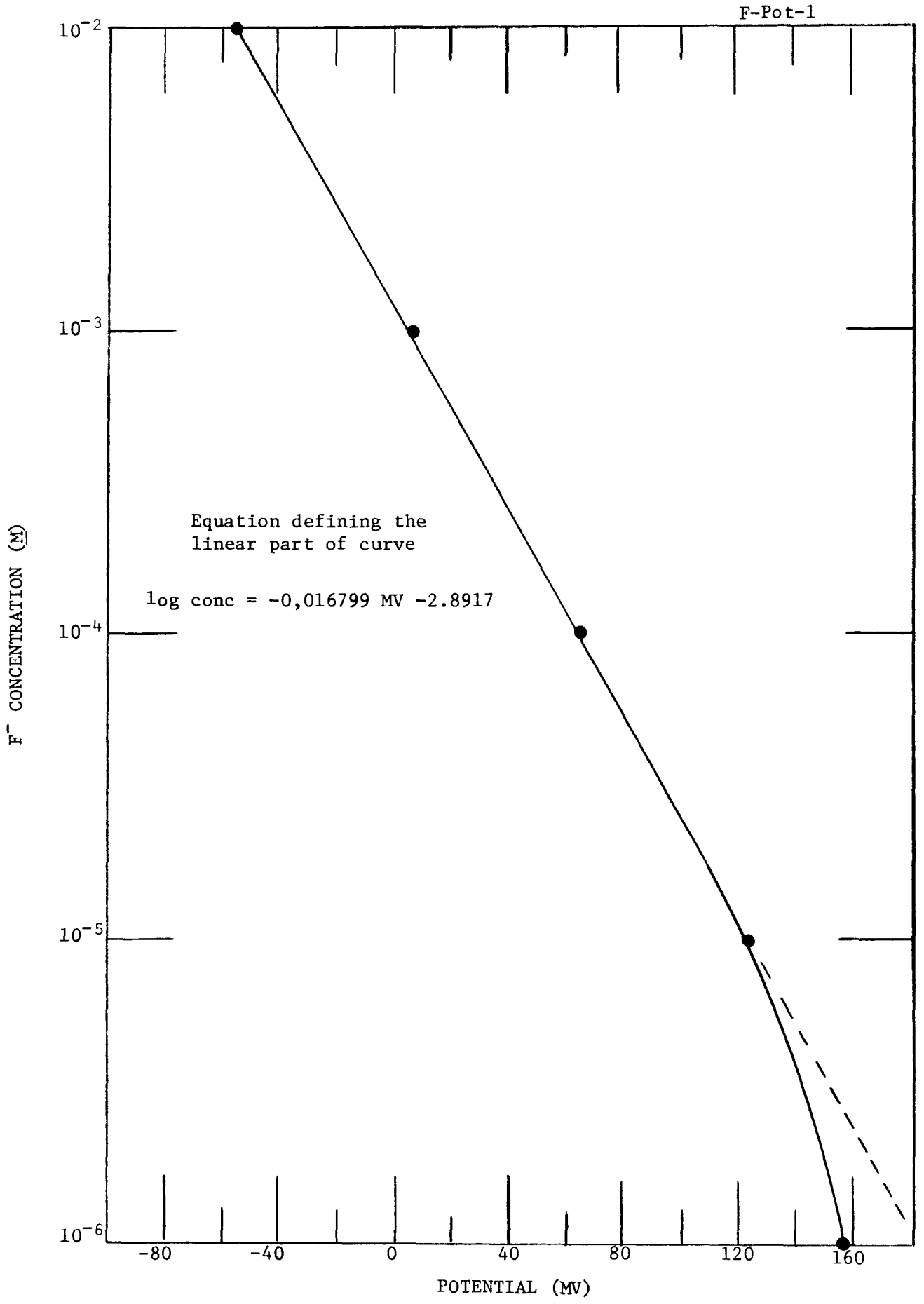


Fig. 1 Standard curve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Fluoride

CHARGE NUMBER _____ PROCEDURE E-Pot-1, Procedure C

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	MV	log Conc	Conc of Dilution	Dilution Factor from Table				RESULT MF^-
I-A	0.2/51.2/0.2/25.2	53	-3.788	1.63×10^{-4}	32256				5.26
Std 1	10^{-4} M	65.6	-4.00						
Std 2	10^{-3} M	6.3	-3.00						

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\log \text{Conc Sample} = \log \text{Conc Std 1} + \left[\frac{(\log \text{Conc Std 1} - \log \text{Conc Std 2})(MV_2 - MV_1)}{MV_1 - MV_2}\right]$$

$$\log \text{Conc Sample} = -4.00 + \left[\frac{(-4.00) - (-3.00)\ (53 - 65.6)}{65.6 - 6.3}\right]$$

$$= -4.00 + \left[\frac{-1.00\ (12.6)}{59.3}\right] = -3.788$$

$$\text{Conc Sample} = (10^{-4})(\text{antilog } 0.212)$$

$$= 1.63 \times 10^{-4}$$

$$\text{Result} = DE = (1.63 \times 10^{-4})(32256) = 5.26\ ppm$$

APPROVED BY _____

FORM 1NC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Fluoride

CHARGE NUMBER _____ PROCEDURE F-Pot-1, Procedure D

SPECIAL INSTRUCTIONS:

(1) Dilution Factor = $\left(\frac{25.3}{0.3}\right)\left(\frac{26.25}{0.25}\right) = 8855$

(2) Sample Conc = $DFC_o = 8855\,C_o$.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Potential of Dilution, MV	Potential After First Addition MV_1	Potential After Second Addition MV_2	Volume 0.25 M NaF, V_1	ΔC	Volume 0.25 M NaF V_2	$\Delta C'$	RESULT M F^-
	0.25/26.25/0.3/25.3	27.0	20	-13.0	0.048	4.74×10^{-4}	0.103	10.18×10^{-4}	
Standard	Addition								3.59
Double	Standard	Addition							3.65

ANALYZED BY _____ DATE _____

CALCULATIONS:

Standard Addition

C_o = Conc of Dilution

$$= \frac{\Delta C}{\left(\log^{-1}\frac{\Delta MV - 1}{59.44}\right)}$$

$$= \frac{4.74\times10^{-4}}{\left(\text{Antilog}\frac{20}{59.44} - 1\right)}$$

$$= 4.05\times10^{-4}$$

Sample Conc = $(4.05\times10^{-4})(8855)$

= 3.59

Double Standard Addition

$$C_o = \frac{(\Delta C)^2}{\Delta C' - \Delta C}$$

$$= \frac{(4.74\times10^{-4})^2}{(10.18 - 4.74)(10^{-4})}$$

$$= 4.13\times10^{-4}$$

Sample Conc = $(4.13\times10^{-4})(8855)$

= 3.65

APPROVED BY _____

PYROLYSIS SEPARATION-INDIRECT COMPLEXOMETRIC DETERMINATION OF FLUORIDE

ABSTRACT

Milligram amounts of fluoride are separated by pyrolysis and quantitatively precipitated as cerium trifluoride with an excess of standard cerium(III). The excess cerium is titrated with ethylenediaminetetraacetic acid (EDTA) to a xylenol orange end point in a pyridine-buffered medium.

APPLICABILITY

This method is based on work at this laboratory [1] and is designed for the analysis of milligram amounts of fluoride in liquids and solids containing such fluoride-complexing ions as Al, B, Ca, and Zr.

Most metal ions, with the exception of the alkali metals, interfere in the titration procedure by reacting with either fluoride or EDTA. When such ions are present, the samples must be pyrolyzed. CPP process streams containing Al, B, Ca, Hg, and Zr are analyzed with the complete method. Mercury and boron codistill with the fluoride during pyrolysis but do not interfere in the titration. The mercury precipitates in the caustic solution used to collect the pyrolysate and is filtered off. The boron-fluoride complex is dissociated during the digestion with cerium(III).

Anions are not separated from fluoride during the pyrolysis. The titration procedure, however, has a high tolerance for most common anions. The tolerances expressed as mole ratio to fluoride are: acetate, 4; chloride, 19; perchlorate, 16; silicate, 0.5; and tetraborate, 0.25. Anions that complex cerium(III) interfere. Two such common ones are sulfate and phosphate. Method F-Color-1 of this manual tolerates them.

The range of the titrimetric procedure is 3 to 40 mg of fluoride. The maximum aliquot volume is about 20 ml; thus, the lowest determinable fluoride concentration is about 0.15 mg/ml. When the pyrolysis separation is used, the maximum aliquot volume is 3 ml for aqueous samples and about 3 g for most solid samples. The lower limit is, therefore, 1 mg/ml or 1 mg/g. For solid samples such as ZrO_2, ZrF_4, ZrO_2F_2, NbF_5, and UO_2, that do not require the addition of an accelerator (see DISCUSSION), 15- to 20-g portions can be analyzed.

DISCUSSION

In the pyrolysis separation,[2] moist air is passed over a mixture of the sample and the accelerator in a quartz tube furnace at 950°C. The accelerator, tungstic oxide, is added to catalyze the hydrolysis of fluoride salts to volatile hydrofluoric acid. The effluent stream is passed through a caustic absorber where the hydrofluoric acid is trapped. The pyrolysis separation is dependent on such variables as (a) pyrolysis temperature, (b) air flow rate, (c) moisture content of the air, (d) dimensions of the pyrolysis tube and its location in the furnace, (e) location of the sample boat in the pyrolysis tube, (g) sample preparation, and (h) pyrolysis time. These variables must be closely controlled.

The caustic absorber solution is acidified with nitric acid to pH 3.5 before the addition of standard cerium(III). This is necessary to prevent the hydrolysis of the cerium. Monochloroacetic acid is added to catalyze the cerous fluoride precipitation, and gelatin is added to hasten the agglutination of the precipitate. The pH is adjusted to 1.85 ± 0.10 to obtain complete and stoichiometric precipitation. The solution containing the precipitate is placed in a boiling water bath and digested until cloudiness disappears. When boron is present, the precipitation is slow and a digestion period of 20 min is required.

SAFETY PRECAUTIONS

Use care when working around the hot tube furnace to avoid burns. Wear rubber gloves when handling the caustic and strong acid reagents.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150-ml.
2. Buret, 15-ml with 0.05-ml divisions.
3. Centrifuge tube, 50-ml, round bottom.
4. Combustion boats, nickel, chamber size 0.6-in. wide x 0.4-in. deep x 3.6-in. long.
5. Fisher Filtrator assembly or equivalent.

6. Flowmeter, Tru-Taper, size 6-15-2.

7. Tube furnace capable of continuous operation at 1000°C, chamber size 1.25-in. diam x 12-in. long.

8. pH Meter with a Thomas combination electrode or equivalent.

9. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.

10. Stirrer, magnetic, with plastic-coated stirring bars.

11. Tamping tool. Weld a 1-in. O.D. x 4-in. aluminum rod to a 0.5-in. x 0.75-in. x 3.5-in. stainless steel bar. Round the edges of the steel bar to fit the combustion boat. See Figure 1.

12. Teflon splatter plate and Teflon cover. See Figure 1. splatter plate sets about 1 in. from the top of the pyrolysis collection tube to break up bubbles. The cover sets on top of the collection tube.

13. Tube, pyrolysis, quartz. See Figure 1.

B. Reagents

NOTE: Prepare all reagents from Analytical Reagent Grade chemicals. Use distilled water for the preparation of all reagents and throughout the analysis.

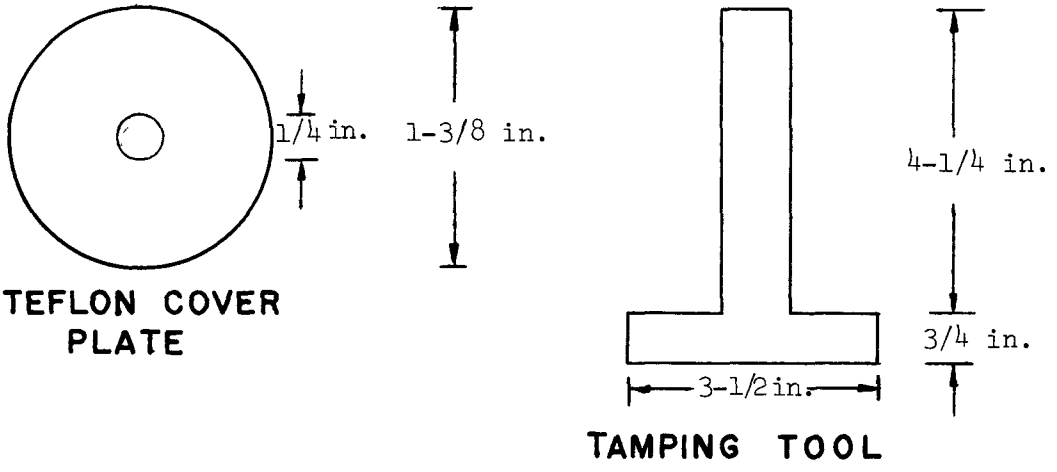
1. Aluminum nitrate, saturated solution, approximately 2M. Prepare in 0.1M HNO_3 using 75 g of $Al(NO_3)_3 \cdot 9H_2O$ per 100 ml of solution.

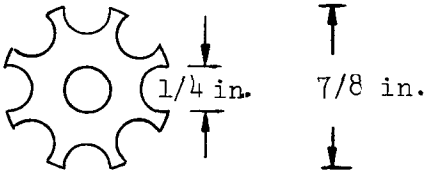
2. Ammonium hydroxide, conc and 2M.

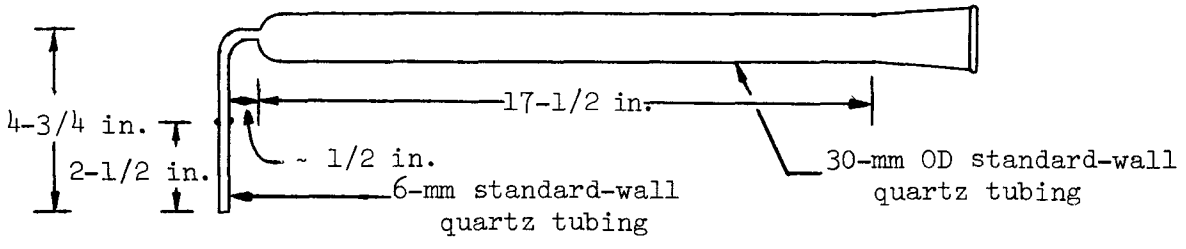
3. Cerium standard solution, 0.075M. Dissolve 65.14 g of $Ce(NO_3)_3 \cdot 6H_2O$ in 1.5 liters of 0.01M HNO_3. Filter through a 0.45-μ membrane filter and dilute to 2 liters with 0.01M HNO_3. Standardize the solution against EDTA per Method Metals-Vol-1 of this Manual.

4. Chloroacetic acid, 1M. Dissolve 47.13 g of chloroacetic acid in water and dilute to 500 ml.

5. EDTA standard solution, 0.05M. Prepare a standard 0.05M solution of the disodium salt per Method EDTA Standard Prep-1 of this Manual.







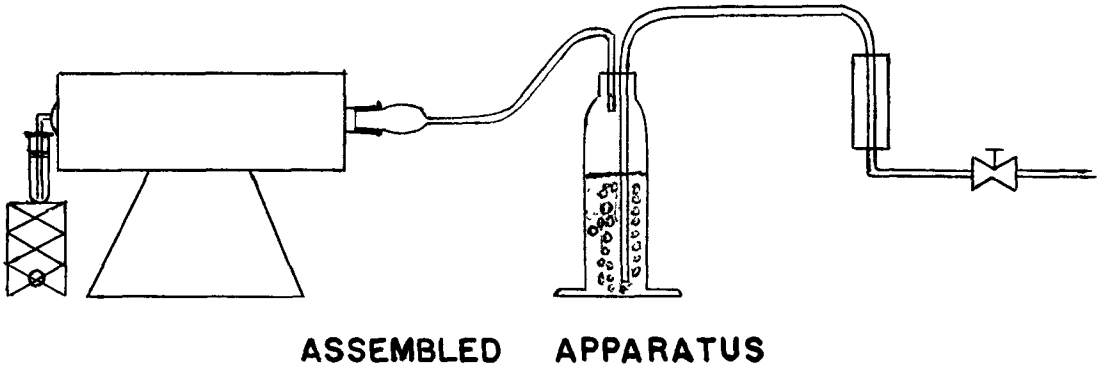


Fig. 1 Special apparatus for fluoride analysis.

6. Fluoride bench and control standards. A series of standards covering the range of the method will be prepared by the Quality Control Laboratory.

7. Gelatin solution, 1%. Dissolve 1 g of gelatin in 100 ml of water. Prepare a fresh solution each week.

8. Nitric acid, conc and 2M.

9. Phenolphthalein indicator solution, 0.5%. Dissolve 0.500 g of the solid reagent in 100 ml of 90% ethanol.

10. Pyridine.

11. Sodium hydroxide, 3.6M and 2M. Prepare by diluting the commercially obtained 50% (w/w) NaOH.

12. Tungstic anhydride.

13. Xylenol orange indicator, 0.2% in water. Dissolve 0.200 g of solid reagent in 100 ml water.

PROCEDURE

A. Determination of Titration Blank

A blank determination is not necessary.

B. Analysis of Bench and Control Standard

Analyze one of the bench standards by the procedure used for the sample analysis. If the result is out of limits, repeat the analysis. If trouble persists, contact your supervisor.

C. Analysis of Aqueous Samples

1. Weigh 15 g of WO_3 into a 50-ml beaker. Transfer about 10 g to a nickel boat and pack down firmly with the tamping tool.

2. Make a small furrow down the middle of the packed WO_3 bed. The sample will be added to this furrow.

3. Pipet 3 ml or less of sample, containing 3 to 40 mg of F^-, evenly along the length of the furrow.

4.	Add 1 ml of the saturated $Al(NO_3)_3$ solution evenly along the entire length of the boat.	The Al aids the conversion of F^- to HF.
5.	Cover the sample with the remaining 5 g of WO_3.	
6.	Pack the WO_3 firmly with the tamping tool.	
7.	Add 1 ml of water evenly over the surface of the WO_3 and continue with Procedure E.	The water helps to prevent WO_3 from blowing out of the boat.

D. Analysis of Solid Samples

1.	Weigh 15 g of WO_3 into a 50-ml beaker and transfer about 3 g to a mortar.	A small ball mill can be substituted for the mortar.
2.	Transfer 3 g or less of sample, containing 3 to 40 mg of F^-, to the mortar and grind intimately with the WO_3.	Grind the sample until it is as finely divided as the WO_3.
3.	Transfer the sample-WO_3 mixture to a nickel boat containing about 2 g of WO_3 spread evenly along the bottom. Use about 5 g of the WO_3 to quantitatively transfer the sample into the boat.	Use several small portions of the WO_3 to transfer the sample.
4.	Add 1 ml of saturated $Al(NO_3)_3$ evenly along the entire length of the boat.	Aluminum aids the conversion of F^- to HF.
5.	Cover the sample with the remaining 5 g of WO_3 and pack firmly with the tamping tool.	

6. Add 1 ml of water evenly along the surface of the WO_3 and continue with Procedure E.	The water helps to prevent WO_3 from blowing out of the boat.

E. Separation of Fluoride by Pyrolysis

NOTE: Assemble the pyrolysis apparatus as shown in Figure 1.

1. Position the pyrolysis tube in the furnace so that the exit tube is 0.5 in. from the end of the furnace.	If the exit tube is further than 0.5 in. from the furnace, recovery of F^- may be incomplete.
2. Add 10 ml of 3.6M NaOH to a 50-ml centrifuge tube and immerse the exit tube in the solution.	The exit tube must extend well below the surface of the NaOH, and the Teflon splatter plate should be about 1 in. from the top of the tube.
3. Adjust the rate of air flow to 2.5 liters/min.	With a Tru-Taper size 6-15-2 flow meter, a float setting of 2 cm corresponds to a flow rate of 2.5 liters/min.
4. Place the nickel boat, containing the prepared sample, in the center of the pyrolysis tube.	The temperature of the furnace must be less than 200°C.
5. Attach the pyrolysis tube to the air supply.	
6. Turn on the furnace and heat rapidly to 950°C. Maintain this temperature for 10 min.	The total heating time will be about 35 to 45 min.
7. Turn off the furnace and, with the air flow still on, lower the centrifuge tube.	
8. Wash the inside of the exit tube with a fine stream of water from a wash bottle equipped with a long hypodermic needle. Finally, rinse down the outside of the exit tube and the Teflon splatter plate.	Some F^- adsorbs on the inside walls of the exit tube and must be removed by washing with a minimum amount of water. The final volume should not exceed 35 ml after Step 9. If there is no precipitate, continue with Step 11. A precipitate in the pyrolysate indicates that the sample contains Hg.

9.	Filter the pyrolysate through a 0.45-μ membrane filter using the Fisher Filtrator assembly. Collect the filtrate in a 50-ml centrifuge tube. Wash the residue with a minimum amount of water and collect the washings in the centrifuge tube.	Omit this step and proceed to Step 10 if a precipitate does not form.
10.	Remove the pyrolysis tube and while still hot, rinse with water to clean it.	Use an asbestos glove to hold the pyrolysis tube. Pour water slowly down the sides of the tube.
11.	Analyze the pyrolysate per Procedure F.	

F. Titration of Fluoride

NOTE: This procedure is applicable to aqueous samples that do not require pyrolysis. For such samples, pipet 20 ml or less of sample containing 3 to 40 mg of fluoride into a 50-ml centrifuge tube and begin with Step 1.

1.	Place the centrifuge tube containing the pyrolysate from Procedure E in an ice bath on a magnetic stirrer, and with the aid of a pH meter, adjust the pH to 3.0 ± 0.5 with conc HNO_3.	
2.	Add 2 drops of 1M monochloroacetic acid.	The monochloroacetic acid catalyzes the precipitation of CeF_3.
3.	Add exactly 10.00 ml of the 0.075M $Ce(NO_3)_3$ solution.	
4.	Add 1 ml of 1% gelatin solution.	Gelatin hastens the precipitation of CeF_3.
5.	Adjust the pH to 1.85 ± 0.10 with 2M HNO_3 or 2M NaOH and stir for 1 min.	CeF_3 precipitation is complete and stoichiometric at pH 1.85.
6.	Remove the electrodes and stirring bar from the sample and rinse with water. Collect the rinsings in the centrifuge tube with the sample.	

7.	Digest the sample in a boiling water bath until the CeF_3 precipitate settles.	Normally, a 5-min digestion is sufficient. If B is present, digest for 20 min.
8.	Centrifuge the sample at medium speed for 5 min.	The CeF_3 precipitate will pack at the bottom of the centrifuge tube.
9.	Carefully decant the supernatant solution into a 150-ml beaker.	
10.	Rinse the walls of the centrifuge tube with water and decant the washings into the 150-ml beaker containing the sample.	Use a squeeze bottle and direct the stream of water at the walls of the tube. Do not break up the precipitate in the bottom of the tube. If the precipitate does break up, centrifuge the sample again. Do not transfer any solid material to the 150-ml beaker.
11.	Repeat Step 10 three times.	
12.	Place the beaker on a magnetic stirrer and add 5 drops of xylenol orange indicator.	Place a plastic-coated stirring bar in the beaker.
13.	Add 2 drops of conc HNO_3.	
14.	Add pyridine dropwise to the appearance of a violet color. Count the drops.	
15.	Add two times the pyridine added in Step 14 to bring the pH in the range 5.60 ± 0.25.	
16.	Titrate with EDTA to a yellow end point.	The color change is violet to red to yellow.
17.	Record the data and calculate the results as shown on the sample work sheet. Report all results to three significant figures.	

REFERENCES

1. Stanley S. Yamamura, Maxine Elliott Kussy, and James E. Rein, "Complexometric Determination of Fluoride with Cerium(III), Anal. Chem., 33 (November 1961) p 1655.

2. R. H. Powell and Oscar Menis, "Separation of Fluoride from Inorganic Compounds by Pyrolysis," Anal. Chem., 30 (September 1958), p 1546.

E. M. Fortsch
S. S. Yamamura
May 1969

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Fluoride

CHARGE NUMBER _____ PROCEDURE F-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	EDTA, ml	Molarity of EDTA	mM Ce 10(M of Ce)	mg F⁻ in Aliquot Analyzed	mg F⁻ corrected For Bias			RESULT mg/ml
#1	3.0 ml	5.0	0.0500	0.7500	28.5	29.8±2.0			9.93± 0.67

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = 57^{*}(c - AB) = 57[0.750 - (5)(0.0500)] = 28.50$$

$$\text{Result} = \frac{E}{\text{vol sample}} = \frac{29.8 \pm 2.0}{3.0} = 9.93 \pm 0.67 \text{ mg F}^{-}/\text{ml}$$

* The factor 57 converts mM cerium to milligrams Fluoride.

APPROVED BY _____

Gd-Color-1; April 1973

COLORIMETRIC DETERMINATION OF GADOLINIUM IN ELECTROLYTIC DISSOLVER SOLUTION

ABSTRACT

Arsenazo-III [2,2'-(1,8-dihydroxy-3,6-disulpho-2,7-naphthylenebis(azo)) dibenzene-arsonic acid] is a very sensitive colorimetric reagent for gadolinium. The red-violet complex is developed in a chloroacetate medium at pH 2.3 and measured spectrophotometrically at 654 nm. Unfortunately, Arsenazo-III is not specific for gadolinium. Iron and uranium, the major interferences expected in electrolytic dissolver solutions, are removed by extraction into tri-iso-octylamine and xylene. Aluminum and chromium interfere less seriously. These are removed as soluble aluminate and chromate ions in a sodium hydroxide-hydrogen peroxide media prior to the solvent extraction of iron and uranium.

APPLICABILITY

Gadolinium is added as a neutron absorber to maintain "critically safe" conditions in the dissolution of nuclear fuel by the electrolytic dissolver process. This method is designed specifically for the determination of gadolinium in electrolytic dissolver solution of the following approximate composition:

	g/l			g/l
Al	16.0	Fissium Elements		4.0
Cr	10.0	Mo	2.0	
Fe	35.0	Pd	0.4	
Gd	2.6	Rh	0.24	
Ni	5.0	Ru	1.2	
U	75.0	Zr	0.16	

The method also is applicable to uranium product solutions containing about 250 g/l of uranium and 1 g/l of gadolinium.

All lanthanides behave like gadolinium; consequently, other lanthanides must be absent or be present in amounts less than 1 or 2% of the gadolinium.

The sample aliquot taken for analysis should contain between 10 to 45 µg of gadolinium. An aliquot containing 20 to 40 µg of gadolinium provides the best precision. The electrolytic dissolver solution is expected to be about 2.6 mg/ml in gadolinium. Assuming an initial dilution of 100 µl of the "hot" solution with 10.0 ml of water, a 1-ml aliquot of the dilution will contain about 26 µg of gadolinium.

The method effectively removes Al, Cr, Fe, and U which are the predominant interfering ions. Arsenazo-III is a sensitive reagent for zirconium, but very little interference is expected with its low abundance among the fissium elements. Analysis of a synthetic dissolver solution, identical to the dissolver solution described at the outset of this section except for the absence of rhodium and palladium, has given results generally within ± 2% of the known value.

DISCUSSION

The basic operations in this method are (a) treatment of the sample aliquot with sodium hydroxide containing hydrogen peroxide to remove aluminum and chromium; (b) dissolution of the precipitate containing the gadolinium in hydrochloric acid and extraction of uranium and iron into tri-iso-octylamine-xylene; (c) evaporation of the extracted aqueous sample to dryness; and (d) development and measurement of the gadolinium-arsenazo-III colored complex. Sufficient sodium hydroxide should be used in (a) to assure the conversion of aluminum to aluminate. Chromium(III) is oxidized to soluble chromate. The hydroxide precipitate contains Fe, Ni, and U besides gadolinium. When these elements are not present in sufficient amount to quantitatively carry the gadolinium, about 1 mg of iron should be added.

Better than 99% of the iron and uranium are removed in a single extraction. Centrifuging gives good separation of the phases. A xylene wash is used to extract most of the dissolved residual tri-iso-octylamine from the aqueous phase. This reagent must be completely removed because it causes the gadolinium-arsenazo-III color complex to fade rapidly. The aqueous phase is evaporated with perchloric acid to remove any remaining traces of tri-iso-octylamine.

The gadolinium-arsenazo-III-complex is developed in a medium of perchloric acid and ammonium monochloroacetate at a pH of 2.3. The perchloric acid portion of this buffer also is used to dissolve the residue resulting from the evaporation of the extracted aqueous phase.

A calibration curve is provided with this method. The analyst should verify that the reagents are good and that the spectrophotometer is working properly by running a reagent blank and a single standard with each set of samples.

SAFETY PRECAUTIONS

With radioactive samples, apply the usual precautions necessary to avoid spread of contamination and unnecessary exposure to radiation. Exercise care in the use of hydrogen peroxide and perchloric acid which can cause severe skin irritations.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, 30- and 250-ml.
2. Centrifuge, with holders for 15x125-mm tubes.
3. Hot plate, adjustable temperature.
4. Mixer, vortex or equivalent.
5. Pipets, volumetric, assorted sizes.
6. Pipets, transfer.
7. Spectrophotometer, Cary Model 14, with 1-cm optically matched cells.
8. Test tubes, borosilicate glass, 15x125-mm, with Teflon-lined screw caps.
9. Vacuum assembly, with liquid trap.
10. Volumetric flasks, 25-ml.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium monochloroacetate, 1.3M. Dissolve 61.4 g of monochloroacetic acid in 400 ml of water using magnetic stirring. Add slowly, 43 ml of conc NH_4OH. Allow the solution to cool and adjust the pH to 7.0±0.3 by dropwise addition of conc NH_4OH. Dilute to 500 ml with water.
2. Ammonium hydroxide, conc.
3. Arsenazo-III, 0.1% (w/v). Dissolve 0.10 g of arsenazo-III in 50 ml of water using magnetic stirring. Filter through a 0.45-μ membrane filter and dilute to 100 ml with water.
4. Electrolytic dissolver matrix. Weigh 94 g of $Al(NO_3)_3 \cdot 9H_2O$, 79 g of $UO_2(NO_3)_2 \cdot 6H_2O$, 127 g of $Fe(NO_3)_3 \cdot 9H_2O$, 12.4 g of $Ni(NO_3)_2 \cdot 6H_2O$, 38.5 g of $Cr(NO_3)_3 \cdot 9H_2O$, 0.2 g of $ZrO(NO_3)_2 \cdot nH_2O$, 1.8 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and 1.2 g of $RuCl_3$ into a 1-liter Erlenmeyer flask. Add 400 ml of water and 125 ml of conc HNO_3, stopper the flask, and shake until the salts are completely dissolved. Heat gently if necessary. Filter the solution through 0.45-μ membrane filters with water rinses. Dilute to

1 liter with water and mix. This solution represents a "composite" electrolytic dissolver product solution diluted 1 to 2 with water.

5. Gadolinium calibration standard, ∿125 µg Gd/ml. Prepare a gadolinium stock solution by dissolving "spec-pure" Gd_2O_3 in 4M HNO_3. Standardize the stock solution by titration with EDTA per Method Metals-Vol-1, then dilute the stock solution to the desired 125 µg/ml concentration.

6. Gadolinium bench standard, ∿1.3 mg Gd/ml. Deliver a sufficient quantity of the gadolinium stock solution to a volumetric flask and dilute to volume with the electrolytic dissolver matrix solution. Specify a dilution of 0.2 to 10.2 for analysis.

7. Gadolinium controls. As per Reagent 6, prepare controls containing gadolinium in the concentration range 0.5 to 2.0 mg/ml. Specify an initial dilution of 0.2 to 10.2 for analysis.

8. Hydrochloric acid, conc and 6N.

9. Hydrogen peroxide, 15%. Dilute 10 ml of 30% H_2O_2 with 10 ml of water.

10. Nitric acid, 8N.

11. Perchloric acid, conc and 0.5M.

12. Sodium hydroxide, 2M.

13. TiOA-Xylene, 5% v/v. Add 5.0 ml of tri-iso-octylamine to 95 ml of xylene and mix.

14. Xylene.

PROCEDURE

A. Blank.

A reagent blank is processed only to check the suitability of the reagents. It is not used in any of the calculations since a predetermined calibration curve or factor is used. To prepare the blank, add 4.0 ml of 0.5M $HClO_4$ and about 10 ml of water to a 25-ml volumetric flask and continue beginning with Step 16 of Procedure D. An absorbance outside the range 0.033-0.040 is an indication of trouble and your supervisor should be consulted.

B. Calibration

A careful determination of gadolinium concentration vs absorbance and a corresponding calibration factor have already been prepared for the analyst. However, with each set of samples, the analyst will verify that the reagents and instrument will duplicate this calibration by running a single calibration standard.

Pipet exactly 0.2 ml of the ∿125 µg Gd/ml standard into a 25-ml volumetric flask and add 4.0 ml of 0.5M $HClO_4$. Dilute to about 15 ml with water and proceed with Step 16 of Procedure D. Using Equation 1

$$\mu g\ Gd = (\text{sample absorbance} - 0.022)(89.9) \qquad (1)$$

calculate a value for the standard. This value should not exceed limits specified by the Quality Control Laboratory. If necessary, repeat the calibration check and if difficulties are still experienced, consult your supervisor who should request a fresh standard and fresh reagents from the Quality Control Laboratory. The precalibration is made as follows. Pipet aliquots of a gadolinium standard: 10, 20, 30, 40 µg of Gd into 25-ml volumetric flasks. Add 4.0 ml of 0.5M $HClO_4$. Dilute to 15 ml with water and proceed with Step 16, Procedure D. Repeat this calibration at least four times to obtain a good statistical average for each concentration. Plot the absorbance vs concentration. The data should give a straight line with the relationship mentioned above. Departure from this calibration is indicative of instrument or reagent changes which will be evaluated by the Analytical Research Section.

C. Bench Standard

Pipet exactly 200 µl of the Gd bench standard stock solution into a bottle containing 10.00 ml of water. Analyze a 1-ml aliquot of this solution per Procedure D. The results should agree within limits set by the Quality Control Laboratory.

D. Determination of Gadolinium

1. Dilute the electrolytic dissolver solution with water to contain 20 to 40 µg/ml of Gd.

2. Pipet an aliquot of the diluted sample into a 12x125-mm screw cap culture tube and dilute to about 3 ml with water.

3. Add 2 drops of 15% H_2O_2 and 2 ml of 2N NaOH and mix. Digest for 5 min in a boiling water bath.	If the sample is a U product solution, add 0.5 mg of Fe(III) carrier then the peroxide and hydroxide. Mix well. Do Not Digest. Chromium(III) is oxidized to Cr(VI). Uranium forms a soluble peroxide complex which is destroyed by digestion with heat.
4. Centrifuge and draw off the supernate using a transfer pipet connected to a vacuum assembly.	Care must be taken to prevent loss of the precipitate which contains $Gd(OH)_3$.
5. Dissolve the precipitate with 1 drop of conc HCl and wash the walls of the tube down with about 4 ml of water.	
6. Add 0.5 ml conc NH_4OH and mix by swirling.	Excess Na ion is removed by the reprecipitation.
7. Centrifuge and draw off the supernate.	
8. Dissolve the precipitate with 3 drops conc HCl, then add 5 ml of 6N HCl, and mix.	
9. Add 5 ml of TiOA-Xylene solution and extract for 1 min using a vortex mixer. Centrifuge and draw off the organic (top) phase.	
10. Add 5 ml of xylene and extract for 30 sec. Centrifuge and carefully draw off the organic phase.	It is better to leave a little organic than take the chance of drawing off some of the aqueous phase. TiOA causes fading of the gadolinium-arsenazo-III complex.
11. Transfer the aqueous phase to a clear 30-ml beaker. Rinse the centrifuge tube with two 2-ml portions of water and add the rinses to the beaker.	

12. Add 1 drop conc $HClO_4$ and evaporate the sample to dryness on a hot plate.	Keep the heat low enough to prevent splatter and excessive baking.
13. Rinse down the beaker walls with 8N HNO_3, add 1 drop conc $HClO_4$, and evaporate to dryness to destroy residual organic matter.	Adjust temperature of hot plate to medium to remove all moisture and $HClO_4$.
14. Allow the beaker to cool then add 4.0 ml 0.5M $HClO_4$. Heat slightly to dissolve all salts.	
15. Transfer the sample to a 25-ml volumetric flask with water rinses.	
16. Pipet 2.0 ml of 1.3M ammonium chloroacetate into the flask and mix.	
17. Pipet 2.0 ml of the Arsenazo-III indicator into the flask, dilute to volume, and mix.	
18. Read the absorbance within 30 min at 652.5 nm (Shift Lab Cary Model 14). 654 nm (Room 211 Cary Model 14). Use a 1-cm cell and read against water.	
19. Record the absorbance on a work sheet and determine the results as shown on the example work sheet.	

REFERENCES

1. H. Onishi and C. V. Banks, "Separation and Spectrophotometric Determination of Rare Earths", Talanta, 10(1963) pp 399-406.

2. H. Onishi and K. Sekine, "Spectrophotometric Determination of Zirconium, Uranium, Thorium, and Rare Earths with Arsenazo-III After Extractions with Thenoylthifluoroacetone and Tri-n-Octylamine", Talanta, 19(1972) pp 473-478.

S. D. Reeder
D. Schneidmiller
April 1973

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Gadolinium

CHARGE NUMBER _____ PROCEDURE Gd - Color - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: a_0/d_1 a_1 d_2/a_2	Absorbance vs H_2O							RESULT
Blank		0 037							OK
Standard	2/10 X 1256 mg	0 300							24.99 mg
	(25 12 mg Gd)								
EDP-105	01/101/1	0 313							2.64 g/l

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CALCULATIONS:

FACTOR (F) = 899 , INTERCEPT (I) = 0 022

mg Gd = (Absorbance - I) F

Std = (0.300 - 0 022) 899 = 2499 -0.56%

EDP-105 = (0 313 - 0 022) 89.9 $\left[\frac{10\ 1}{(0.1)(1)}\right]$ = 2642 mg/ml

or 264 g/l

APPROVED BY _____

5

DETERMINATION OF GADOLINIUM BY FLAME EMISSION SPECTROMETRY

ABSTRACT

Gadolinium in dilute nitric acid solutions is determined by comparing the flame-induced emission (the emission of the sample produced by flame excitation) with the emission of standards of similar composition. The solutions are aspirated into a lean nitrous oxide-acetylene flame, and the resultant emission is measured at both 461.7 and 580.7 nm. The two wavelengths are used to verify that the emission is from gadolinium.

APPLICABILITY

This method is designed for the determination of gadolinium added as a neutron poison in the processing of nuclear fuels. It is limited to dilute nitric acid solutions of gadolinium that do not contain other metal ions. For best results, the nitric acid concentration should be kept below 2M. The concentration of the solution aspirated into the flame should be between 0 to 60 µg Gd/ml.

DISCUSSION

Gadolinium is used as a primary safeguard and is added to the nitric acid used to dissolve nuclear fuel; the gadolinium serves as a neutron poison to prevent criticality in the dissolver. Thus, it is mandatory that the analysis procedure be specific for gadolinium. This specificity is achieved by determining the concentration at two wavelengths. Those elements that will interfere at one wavelength either will not interfere at the other wavelength or will interfere to a different degree. The results of the analysis at the two wavelengths must agree within analytical error. (If they do not agree, the sample is either not gadolinium or there is interference from sample constituents). In either case, the cause of the discrepancy must be identified and corrected.

Samples and standards should be prevented from coming in contact with black "Bakelite" caps commonly used on plastic bottles. The solution rapidly leaches calcium from the cap and calcium will interfere at 580.7 nm.

SPECIAL SAFETY PRECAUTIONS

Explosions of nitrous oxide-acetylene mixtures are common; therefore, follow carefully all instructions for lighting and extinguishing the flame. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of

the drain tube must extend below the surface of the liquid in the waste receptacle. Partial filling of the sample cups will help prevent spills.

APPARATUS AND REAGENTS

A. Apparatus

1. Burner, nitrous oxide-acetylene, 6-cm slot.

2. Cups, plastic, 5-ml, Caplugs No. 12X.

3. Spectrophotometer, atomic absorption, Techtron AA-5 with chopper mechanism for flame emission or equivalent instrument with attachments.

4. Pipets, assorted sizes, with control syringe and rubber suction bulbs.

5. Volumetric flasks, assorted sizes.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagent and matrix solutions. Use only Gd_2O_3 which has been shown by DC arc emission spectrography and chemical assay to be at least 99.9 wt% Gd_2O_3. For best results, ignite the oxide at 950°C for 30 min initially.

1. Gadolinium stock solution, 1.000 mg/ml. Dissolve 1.153 g of $\geq$99.9 wt% Gd_2O_3 in 50 ml of 0.1M HNO_3 and dilute with distilled water to 1 liter.

2. Gadolinium calibration standards. To each of four 1-liter volumetric flasks, add 0, 20.0, 40.0, and 60.0 ml, respectively, of the 1 mg Gd/ml stock solution. Add to each 7 ml of conc HNO_3. Dilute to volume with distilled water. The gadolinium concentrations of these solutions are 0, 20, 40, and 60 µg/ml. Store the solution in 1-liter polyethylene bottles. DO NOT USE BAKELITE CAPS.

3. Gadolinium controls. To a 1-liter volumetric flask add a volume of 1.000 mg/ml gadolinium stock to give a concentration of 10 to 55 µg/ml. Add 7 ml of conc HNO_3 and dilute to volume with distilled water.

PROCEDURE

A. Instrument Operating Conditions for Techtron AA-5

1. Chopper on
2. Burner vernier height: 20
3. Wavelength: 461.7 and 580.7
4. Slit width: 100 μ
5. Support gas: N_2O_2 at 14 lb
6. Fuel gas: Acetylene. Minimize background while aspirating water. Pink cone in flame should be about 0.375-in. high.
7. Gain: about 11
8. Damping Switch: D
9. Select Switch: High gain
10. Mode Switch: %T
11. Digital Indicator settings:
    a. Transmission: ON
    b. Average: ON
    c. Average control knob set so light blinks every 3 to 4 seconds.

B. Analysis of Bench Standard

Process a bench standard with each series of samples as described in Procedure C. If the results do not fall within the limits specified by the Quality Control Laboratory, repeat the analysis. Seek help if trouble persists.

C. Analysis of Samples

1. Dilute the sample, if necessary, with water to obtain a concentration of 10 to 60 μg/ml. For best results dilute to 40 μg/ml.

2. Allow the instrument to "warm up" with the flame ignited for about 15 min to minimize drifting.

3. Check the waste bottle to see that it contains at least 1 in. of liquid and that it is not more than one-half full.

4. Measure the emission of the calibration standards and sample twice at each wavelength. Duplicate readings at the same wavelength should not disagree by more than 2.0 %T units.

5. Record the data and calculate the results as shown on the sample work sheet. Plot the curve at each wavelength and obtain the concentration from the graph. If the two results obtained from the two wavelengths do not agree within limits specified by the Quality Control Laboratory, contact your supervisor.

REFERENCES

1. J. Ramirez-Munoz, Atomic Absorption Spectroscopy, Elsevier, New York, 1968, pp 244, 246, 402.

April 1973
L. E. Trejo
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J. M. Baldwin
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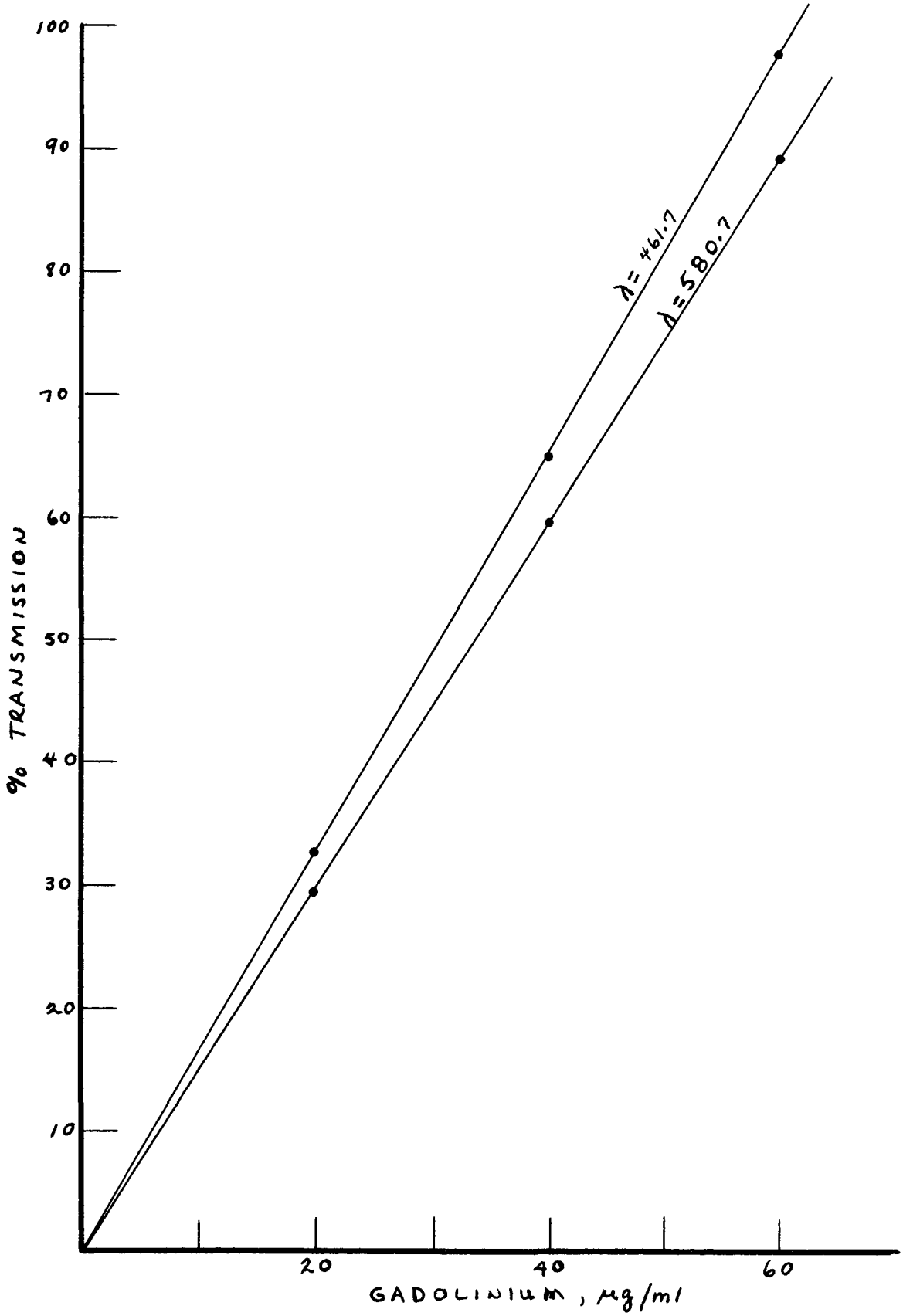

Fig. 1 Calibration curve for gadolinium.

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CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Gadolinium

CHARGE NUMBER _____ PROCEDURE Gd-Flame-1

SPECIAL INSTRUCTIONS

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA a_0 $d_1/a_1/d_2/a_2$	% T λ = 4617	Ave % T	% T λ = 5807	Ave % T	μg/ml λ = 4617	μg/ml λ = 5807	$\bar{X}$ μg/ml	RESULT
0 μg/ml		0 0	0	0 0	0				
20		32 5 32 6	32 6	29 3 29 3	29 3				
40		64 8 65 2	65 0	58 0 59 6	58 8				
60		97 2 97 4	97 3	88 0 88 8	88 4				
NO 1	1/100	48 8 49 0	48 9	44 8 45 2	45 0	30 1	30 5	30 3	3 03 g/l
NO 2		81 8 81 5	81 6	73 4 74 0	73 7	50 3	50 1	50 2	50 2 μg/ml

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CALCULATIONS

Sample No 1

$$\text{Result} = \frac{(G)(d_1)}{a_0} = \frac{(30\ 3)(100)}{1} = 3030 \text{ μg/ml}$$

Sample No 2

$$\text{Result} = (G) = 50.2 \text{ μg/ml}$$

NOTE: The data in column E and F are taken from a graph of the plot of the data in Column B and D

APPROVED BY _____

DETERMINATION OF HYDROXYLAMINE IN THIRD CYCLE A COLUMN (IIIAS) SCRUB SOLUTIONS

ABSTRACT

Hydroxylamine is indirectly determined by reaction with ferric ion, followed by titration of the resulting ferrous ion with cerium(IV) to a visual ferroin indicator end point. Sulfamic acid and an inert gas purge are used to minimize interference from nitrite and oxygen, respectively.

APPLICABILITY

The method is specifically designed for the determination of hydroxylamine in third cycle A column scrub solutions of the composition: 2.0M Al(III), 6M NO_3^-, 0.1M sulfamic acid, 0.05M hydroxylamine sulfate, and 0.32 N^b with ammonium hydroxide. Reductants like sulfite and iron(II), and oxidants like chromium(VI) must not be present. The useful range of the method is 0.05 to 0.25 mM; however, as little as 0.02 mM is determinable.

DISCUSSION

The chemical reactions involved are: oxidation of the hydroxylamine

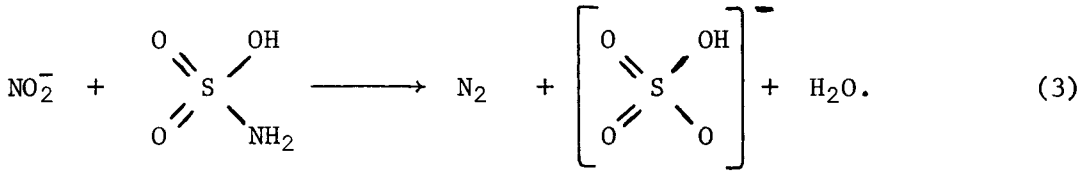
$$2\ NH_2OH + 4\ Fe^{+3} \longrightarrow N_2O + 4\ Fe^{+2} + 4H^+ + H_2O \qquad (1)$$

and titration of the resulting ferrous iron with cerium(IV)

$$Fe^{+2} + Ce^{+4} \longrightarrow Ce^{+3} + Fe^{+3} \qquad (2)$$

The reducing normality of hydroxylamine is twice its molarity. In this determination, each mole of hydroxylamine, therefore, is equivalent to two moles (equivalents) of cerium(IV). If the sample matrix contains reductants, ferrous ions may be produced over and above that formed from Reaction (1). Additionally, if the sample contains oxidants, such as dissolved oxygen or nitrite, ferrous ions would be oxidized in competition with Reaction (2). In III AS scrub solutions containing the reductant hydroxylamine and sulfamic acid, most strong oxidants are absent, and the potential interferences are oxygen and nitrite which is produced by the decomposition of nitrate. Oxygen interference is eliminated with an inert gas purge. Nitrite interference is minimized by the addition of sulfamic acid to the sample.

The sulfamic acid reacts with and destroys the nitrite ion per the equation



(3)

The high nitrate concentration (6M) and the heating of the sample to effect the hydroxylamine oxidation make the nitrite interference problem particularly severe for the III AS solution. The effect of various amounts of sulfamic acid upon the hydroxylamine results obtained in a nitrate-ammonia matrix are shown in Table I

TABLE I

EFFECT OF SULFAMIC ACID ON THE DETERMINATION OF HYDROXYLAMINE

Molar Ratio of Sulfamic Acid to Nitrate	% Error in Hydroxylamine Determination
0	-100
0.017	-7.8
0.17	-3.8
0.43	-1.7
0.83	-1.1

It is doubtful that the interference of nitrite ion can be completely eliminated for high nitrate samples. However, the small error that does remain can be automatically corrected for by standardizing the cerium titrant with hydroxylamine standards containing a matrix comparable to that of the samples.

SAFETY PRECAUTIONS

Sulfuric acid can cause severe eye and skin damage, and if the acid is contacted, the affected area should be washed immediately with copious quantities of water. Safety glasses should be worn during the preparation of the standard cerium solution. Tongs or asbestos gloves should be used to handle the hot Erlenmeyer flask.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 5-ml, graduated in 0.01-ml divisions.
2. Deaerator tube, 4-mm ID by 15-cm long.
3. Flask, Erlenmeyer, 250-ml.
4. Hot plate.
5. Magnetic stirrer and plastic-coated stir bars.
6. Nitrogen regulator.
7. Pipets, Mohr, 10-ml.
8. Pipets, macro and micro, assorted sizes with control syringe and suction bulb.
9. Rubber stopper, size 6.5.
10. Titration ring stand with attached buret clamp and extension clamp.

B. Reagents

1. Cerium sulfate solution. Weigh out 54.811 g of primary standard grade $(NH_4)_2Ce(NO_3)_6$, which has been dried for 2 hr at 100°C. Place in a 1-liter beaker. Slowly and carefully add 56 ml of conc H_2SO_4 and stir for 2 min. Very slowly, while mixing the contents with a magnetic stirrer, add 100 ml of distilled water in small increments. CAUTION. Do this by pouring a small stream of water down the side of the beaker. After a mixing period of 5 min, add more water until dissolution is complete. Finally, cool the solution and dilute to exactly 1 liter. Standardize against 4-ml aliquots of 0.1000N NH_2OH bench standard to which 4 ml of III AS sample matrix has been added. Store the standard solution in a bottle with a polyethylene-lined screw cap.
2. Ferric ammonium sulfate, saturated aqueous solution.
3. Ferroin indicator, 0.025M as obtained commercially.
4. Hydroxylamine bench standard. Dissolve 4.1035 g of hydroxylamine sulfate, $(NH_2OH)_2 \cdot H_2SO_4$, in water and dilute to 1 liter. This standard is 0.0500M in hydroxylamine and 0.1000N in reducing power.

5. Hydroxylamine controls. Prepare four standards as in Reagent 4 to cover the concentration range of 0.02M to 0.06M.

6. Inert gas. Nitrogen, carbon dioxide, or argon.

7. Synthetic III AS sample matrix for bench standards and controls. Transfer 750 g of aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, and 9.705 g of sulfamic acid, HSO_3NH_2, to a 2-liter beaker. Add 50 ml of water and 21.6 ml of conc NH_4OH, stir and dilute to 1 liter with water. This solution is 2.0M in $Al(NO_3)_3$, 0.32N[b] (with NH_4OH), and 0.1M in sulfamic acid.

PROCEDURE

A. Determination of Titration Blank

Process 4.00 ml of the III AS matrix solution per Procedure C.

B. Analysis of Bench Standard

Analyze 4.00 ml of the hydroxylamine bench standard plus 4 ml of the III AS matrix solution per Procedure C. The result must fall within limits specified by the Quality Control Laboratory. If it does not, repeat the analysis. Seek help if trouble persists.

C. Analysis of Samples

1. Pipet 4.00 ml of the III AS sample into a 250-ml Erlenmeyer flask.	The aliquot should contain between 0.05 and 0.25 mM of NH_2OH and about 25 mM of NO_3^-. Aliquots other than 4 ml may be used if the sample is less than 6M in NO_3^-; however, because the amount of NO_3^- in the sample aliquots affects the NO_2^--caused bias, the NO_3^- level should be kept constant at about 25 mM. If necessary, additional NO_3^- can be added by adding the III AS sample matrix.
2. Add 10 ml of 1M HSO_3NH_2 and mix flask contents by gentle swirling.	This high concentration of HSO_3NH_2 is required to minimize interference from NO_2^- ion.

3.	Add 1 ml of 6M H_2SO_4 and mix flask contents by gentle swirling.	If the sample contains more than about 0.5M of base, add sufficient H_2SO_4 to bring the base concentration below 0.5M.
4.	Place the flask on a hot plate, insert the deaerator tube clamped to the titration ringstand into the flask, and adjust its height so that the end of the tube rests 2-3 cm above the sample surface. Turn on the inert gas and set the flow rate so that the surface of the sample is slightly indented.	The heat furnished by the hot plate should be sufficient to bring the sample to a quiet boil only. Oxygen must be excluded from the sample flask to prevent oxidation of Fe^{++} ion. Care must be taken not to have so great an inert gas flow rate that sample is splattered onto the deaerator tubing.
5.	Heat the sample to nearly boiling, then add 10 ml of saturated $FeNH_4(SO_4)_2$ solution.	
6.	Heat to gentle boiling and boil the sample for 5-7 min.	
7.	Remove the flask from the hot plate, loosely stopper, and quickly cool by holding the flask under a cold water tap.	
8.	Remove the stopper, again insert the deaerator tube, and add 1 drop of ferroin indicator. Place the flask on the magnetic stirrer. Rinse down the side of the titration flask until the sample volume is 30 to 50 ml.	It is essential that only 1 drop of indicator be used as additional amounts increase the titration blank.
9.	Titrate with the Ce(IV) solution to a green end point.	
10.	Record the data and calculate the results as shown on the example work sheet.	

REFERENCES

1. D. A. Skoog, D. M. West, Fundamentals of Analytical Chemistry, New York: Holt, Rinehart and Winston, 1966.

D. R. Kendall
October 1972

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Hydroxylamine

CHARGE NUMBER _____ PROCEDURE NH_2OH-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Normality of Ce(IV) Titrant	Titrant for Blank, ml	Titrant for Sample, ml					RESULT N^r
Blank		0.1017	0.013						
III AS	400 ml	0.1017		4.673					0.118

ANALYZED BY _____ DATE _____

CALCULATIONS:

Reducing Normality

$$N^r = \frac{A\,(C-B)}{\text{Sample Aliquot}} = \frac{0.1017\,(4.673 - 0.013)}{4.00} = 0.118$$

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COLORIMETRIC DETERMINATION OF IRON WITH 1,10-PHENANTHROLINE

ABSTRACT

Two procedures are described for the determination of iron with 1,10-phenanthroline. In one, the direct procedure, the color is developed directly in an aqueous EDTA-citrate medium using hydroxylamine hydrochloride for the reduction of Fe(III) to Fe(II). In the second, a column extraction-colorimetric measurement procedure, the iron is separated initially by selective extraction from 7M HCl into 2-octanone sorbed on a column of Fluoropak. The Fe(III)-2-octanone solution is stripped from the column with 2-propanol, and the iron is determined in situ in the effluent with 1,10-phenanthroline using hydroquinone for the reduction of Fe(III) to Fe(II). In both procedures, the absorbance of the red Fe(II)-1,10-phenanthroline complex is measured spectrophotometrically at 507 mμ.

In general, both procedures are highly selective. The column extraction procedure tolerates higher ratios of diverse ions. Each method tolerates a few ions that interfere in the other one.

APPLICABILITY

Each of the two procedures for the colorimetric determination of iron is highly selective and applicable to a wide variety of samples. The effects of diverse ions on each of the two procedures and the iron concentration limits for the two procedures are described below.

A. Direct Procedure (A) Using EDTA-Citrate Masking[1]

This procedure is recommended for all samples except those containing Co(II) and Ru(III,IV) and those containing diverse ions at ion to iron molar ratios exceeding the tolerance ratio.

Figure 1 gives the tolerance ratios of 54 elements. These ratios were established by analyzing synthetic samples containing 54.6 μg of iron and varying concentrations of the diverse ions. A "t" test at the 95% confidence level was used to establish interference. For a single determination at the 54.6-μg iron level, the allowable limits were ±0.60 μg of iron.

Figure 1 shows that most cations and anions do not interfere at diverse ion to iron molar ratios greater than 100:1. In most cases, the tolerance ratio given is the highest ratio that was studied and does not represent the maximum tolerance ratio. Maximum tolerance ratios are given for the metal ions Ag(I), Co(II), Cr(III,VI), and Ni(II). The effects of these ions at higher ratios are shown in Table I. The ions As(III), Ga(III), Ge(IV), Ir(IV), Sb(III,V),

Fe-Color-1

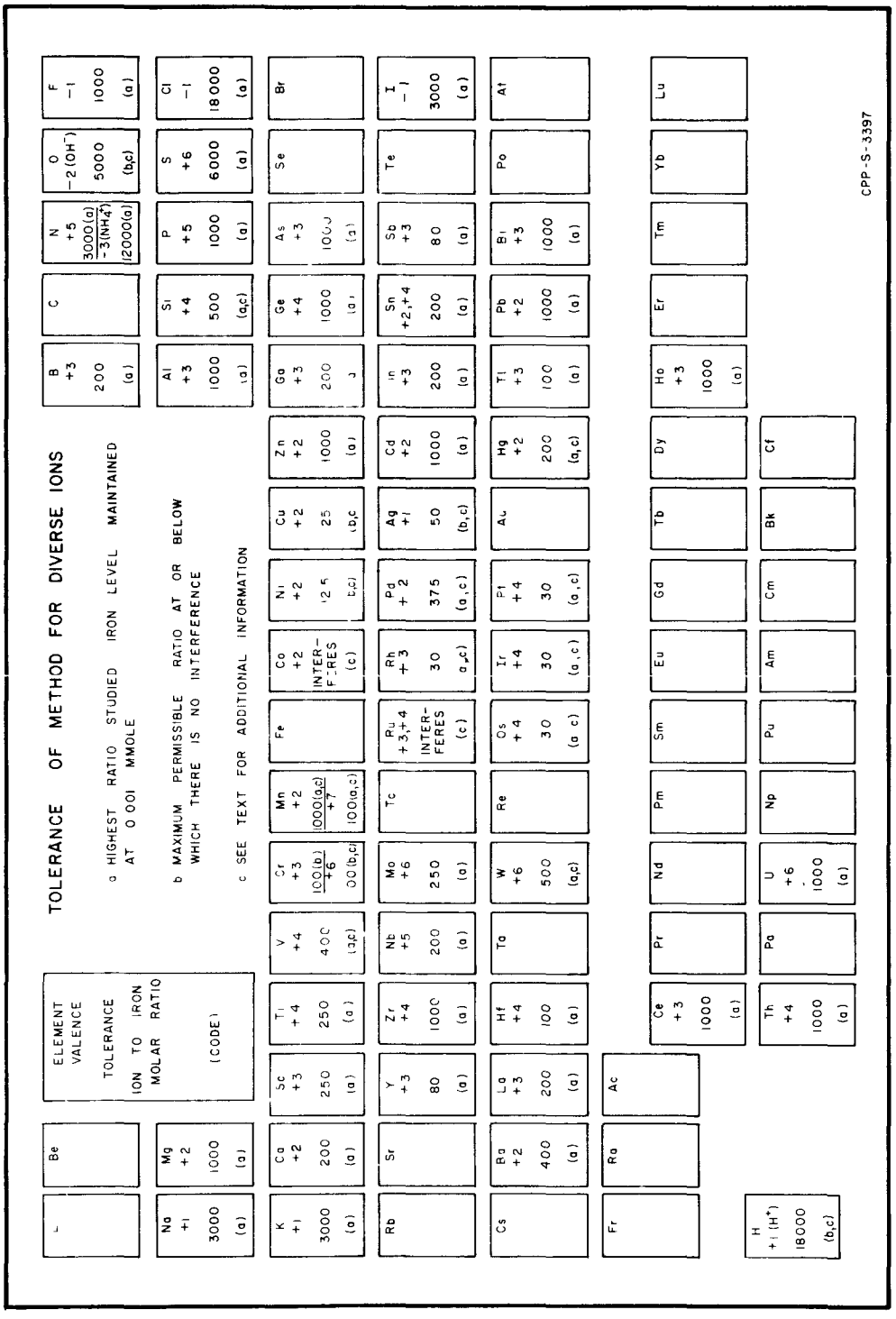

Fig. 1 Tolerance of the Direct Procedure for Diverse Ions

Sn(II,IV), and Tl(III), which are potential interferences in the column extraction-colorimetric measurement procedure, do not interfere.

The effects of the noble metals, Ir, Os, Rh, Ru, Pd, and Pt were studied at approximately 30:1 molar ratios. Ruthenium interfered at this ratio. However, at tracer levels, ruthenium is not expected to interfere.

TABLE I

EFFECT OF DIVERSE METAL IONS AT ION TO IRON MOLAR RATIOS ABOVE THE MAXIMUM TOLERANCE RATIO

Diverse Ion	Diverse Ion to Iron Molar Ratio[a]	Interference (%)
Ag(I)	200.0	- 5.2
Co(II)	12.5	- 1.6
	25.0	- 1.8
	50.0	- 4.1
	100.0	- 6.1
Cr(III,VI)	200.0	+ 2.7
Ni(II)	25.0	- 2.0
	50.0	- 12.5

[a] These data were obtained using 54.6 µg (~0.001 mM) of iron.

In the procedure, 1.25 mM of EDTA and 2.50 mM of citrate are used for masking. As much as 2.50 mM of citrate or EDTA or 1.0 mM of oxalate or tartrate can be present in addition without any adverse effect.

A precipitate is formed under the recommended analysis conditions in the presence of the ions Ag(I), Hg(II), and silicate. The precipitate must be removed by centrifugation or filtration prior to measurement of the absorbance of the iron complex.

Tungsten(VI) precipitates as tungstic acid in acid medium and coprecipitates iron. The precipitation is avoided by adding the EDTA-citrate reagent to the sample first, then adding the pyridine before the addition of the hydrochloric acid.

Many metal ions are colored or form colored complexes with EDTA under the analysis conditions. These include Co(II), Cr(III), Cu(II), Dy(III), Ho(III), Ir(IV), Mn(II), Mo(V,VI), Nd(III), Ni(II), Os(IV), Pd(II), Pt(II,IV), Rh(III), Ru(III,IV), Ti(IV), U(IV,VI), and V(IV,V). The preparation of a sample blank is included in the recommended procedure to correct for the absorbance of these ions

at the 507-mμ wavelength. The sample blank is similar to the sample and contains all the reagents except the 1,10-phenanthroline chromogen. The net absorbance of the sample is then the gross absorbance of the sample versus water less the total absorbance of the reagent blank plus the sample blank, each measured versus water.

Cobalt(II) and Ru(III,IV) are the only known interferences. The interference of cobalt is somewhat unusual. The pink Co(II)-EDTA complex absorbs at the 507-mμ wavelength. The yellowish-orange Co(II)-1,10-phenanthroline complex, apparently more stable than the Co(II)-EDTA complex, also absorbs at 507 mμ but not as much as the Co(II)-EDTA complex. The net effect is that the subtraction of the sample blank results in an overcorrection, hence, a negative bias. Samples that contain cobalt should be analyzed according to the column extraction-spectrophotometric measurement Procedure B. As an alternative, simulated standards containing cobalt can be processed to obtain correction factors for cobalt.

The absorbance of the red Fe(II)-1,10-phenanthroline complex is linear with iron concentrations up to at least 200 μg/25 ml of final solution (8 ppm); however, the range specified for this procedure is 2 to 100 μg of iron. Without prior evaporation by concentration, 10 ml is the largest sample that can be analyzed. Therefore, as specified, the lowest concentration determinable is 0.1 μg Fe/ml. For sample aliquots that contain a total of less than 10 μg of iron, 5.00-cm cells are recommended.

Column Extraction-Colorimetric Measurement Procedure (B)

This procedure, somewhat longer than the direct procedure, is recommended for samples containing diverse ions at ion to iron molar ratios exceeding the tolerance ratios given in Figure 1 for the direct procedure. It is also recommended for samples containing Co(II) and Ru(III,IV) which interfere in the direct procedure even at low concentrations.

As in the macro procedure for iron, Method Fe-Vol-1, selectivity is obtained through a preliminary extraction of the iron into 2-octanone[2,3]. The sample is adjusted to 7±1M in hydrochloric acid and passed through a column of Fluoropak saturated with 2-octanone. Iron(III) is extracted quantitatively and diverse cations and anions are washed from the column with additional 7M HCl.

A study of the effects of diverse ions has shown that the metal ions Bi(III), Cd(II), Ce(III), Cr(III), Cu(II), Co(II), Hg(II), Ni(II), Th(IV), U(VI), and Zn(II) at a 5000:1 diverse ion to iron molar ratio, V(IV) at a 2500:1 ratio and Mo(VI), Ti(IV), and Zr(IV) at a 1000:1 ratio do not interfere. Molybdenum(VI), which partially coextracts with iron is complexed with hydrogen peroxide, and vanadium(IV), which partially coextracts even in the presence of

hydrogen peroxide, must be eluted during the 7M HCl wash with additional hydrogen peroxide.

The complexing anions citrate, oxalate, and tartrate at 2500:1 anion to iron molar ratio and phosphate at a 5000:1 ratio do not interfere. Fluoride at a 5000:1 ratio gives high erratic results because iron is introduced from the Pyrex column through etching. No fluoride interference is expected if columns of polyethylene or Teflon are used.

Potentially interfering elements are Ga, Au, and Tl which coextract quantitatively and Sb, As, Ge, Ir, and Te which partially coextract. A special study was made of the effects of Ga, Au, Te, and Tl on the determination of iron with 1,10-phenanthroline. This study showed that gallium did not interfere at a 100:1 molar ratio, but did interfere at 200:1. Gold at 50:1 does not interfere; however, because gold solutions absorb at the working wavelength of 507 mμ, a comparison against a sample blank without chromogen is necessary. Tellurium interferes even at a 10:1 ratio. With chloride masking, thallium at 500:1 does not interfere.

The range of this procedure is 5 to 100 μg of iron. The lowest concentration determinable depends on the volume of sample used. Assuming a practical sample limit of 50 ml, it is 0.1 μg Fe/ml. For sample aliquots that contain a total of less than 10 μg of iron, 5.00-cm cells are recommended.

DISCUSSION

A. Direct Procedure

The development of the Fe(II)-1,10-phenanthroline complex is dependent on the concentrations of the 1,10-phenanthroline chromogen, the hydroxylamine reductant, and the EDTA and citrate masking agents. Because changes in pH alter the "effective" concentrations of these reagents, the color development also is dependent on pH.

In the procedure, the pH is controlled at 5.0 to 6.5 by a mixture of pyridine and conc HCl. The capacity of this buffer is large enough to maintain the pH at 5.0 to 6.5 even upon the addition of samples with up to 18 meq of acid or 5 meq of base.

The hydroxylamine and 1,10-phenanthroline levels are maintained at 2 mM and 0.10 mM, respectively, and the EDTA and citrate levels are maintained at 1.25 mM and 2.50 mM, respectively. Under these conditions, complete color development is obtained in 25 min at room temperature. At much higher EDTA-citrate levels, complete color development is obtained only with heating. Heating at 60°C for 15 min, cooling, then allowing to stand for 25 min has been found to

be satisfactory. The 25-min standing period is necessary because the Fe(II)-1,10-phenanthroline complex dissociates at elevated temperatures. Once formed, the Fe(II)-1,10-phenanthroline complex is stable for at least 24 hr.

B. Column Extraction-Colorimetric Measurement Procedure

In the column separation procedure, the iron is extracted from a 7M HCl medium into 2-octanone sorbed on Fluoropak. The extracted iron and the 2-octanone solvent are then eluted with 2-propanol and the iron is determined colorimetrically with 1,10-phenanthroline in the 2-propanol-2-octanone medium.

For quantitative extraction, the iron must be in the (III), ferric, oxidation state. Proper preparation of the column also is essential. The column packing should not contain excessive amounts of free 2-octanone, and in packing the column, excessive pressure which tends to "squeeze out" sorbed 2-octanone should be avoided.

Hydroquinone rather than hydroxylamine hydrochloride is used for the reduction of Fe(III) to Fe(II) because the latter reacts with 2-octanone to form the oxime. This side reaction results in insufficient reductant and incomplete color development.

The rate of color development of the iron complex is fairly slow so that a 15-min waiting period is used. Once formed, the color is stable for at least 24 hr.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1.00-cm and 5.00-cm.

2. Beakers, glass, assorted sizes.

3. Beakers, polyethylene, 50-ml.

4. Extraction columns, 7.2-mm ID x 15-cm with a 25-ml reservoir, a Teflon-plugged stopcock, and a glass wool plug to support the column packing.

5. Flasks, volumetric, 25-ml, and other sizes.

6. Glass stirring rods, 6-mm x 10-in.

7. Pipets, macro and micro, assorted sizes, with suction bulb and syringe.

8. Pipets, Mohr, 5- and 10-ml.

9. Polyethylene wash bottles.

10. Spectrophotometer, Beckman B, DU, or DK, or Cary Model 14 recording spectrophotometer.

11. Thermometer, Centigrade.

12. Water bath, at 60°C.

B. Reagents

Note: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Reagents for both procedures.

a. Hydrochloric acid, conc.

b. Iron standard stock solution, 1.000 mg Fe/ml. Dissolve 7.025 ±0.001 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 100 ml of 0.05M HCl and dilute to 1 liter with water.

c. Iron calibration standard I, 40.0 µg Fe/ml. Dilute 10.00 ml of the iron stock standard stock solution to 250 ml with 0.005M HCl.

d. Iron calibration standard II, 60.0 µg Fe/ml. Dilute 15.00 ml of iron standard stock solution to 250 ml with 0.005M HCl.

e. Iron calibration standard III, 6.00 µg Fe/ml. Dilute 3.00 ml of the iron standard stock solution to 500 ml with 0.005M HCl.

f. Iron calibration standard IV, 12.0 µg Fe/ml. Dilute 3.00 ml of the iron standard stock solution to 250 ml with 0.005M HCl.

g. 1, 10-Phenanthroline reagent, 0.05M. Dissolve 4.96 g of 1,10-phenanthroline monohydrate in 500 ml of 2-propanol or 95% ethanol.

h. Pyridine.

2. Reagents used in direct procedure only.

a. EDTA-Citrate reagent. Dissolve 93 g of $Na_2H_2EDTA \cdot 2H_2O$ and 113 g of diammonium citrate in water and dilute to 1 liter.

b. Hydroxylamine hydrochloride solution, 2M. Dissolve 70 g of $NH_2OH \cdot HCl$ in 500 ml of water.

3. Reagents used in the column extraction-colorimetric measurement procedure only.

a. Fluoropak, 20-to 70-mesh, coated with 2-octanone. Half fill a 600-ml beaker with new 20- to 70-mesh Fluoropak (Wilkens Instrument and Research, Inc., Box 313, Walnut Creek, California) and drench the Fluoropak with 2-octanone. Filter the 2-octanone-coated Fluoropak on a large Buchner funnel and suck air through it for 10 to 15 min. Store in a screw-cap wide mouth jar.

b. Iron bench standard, 50.0 µg Fe/ml. Prepare a matrix solution containing 0.10 mole of each of the metals: Cd, Cr, Cu, Hg, Ni, U, and Zn. Introduce all the metals except uranium as nitric acid solutions of the spectrographic grade metals. Admit the uranium as the nitrate salt. Pipet 50.00 ml of the 1.00-mg Fe/ml standard stock solution to the matrix solution and dilute to 1 liter with water. Store in a borosilicate glass bottle.

c. Hydrochloric acid, 7M.

d. Hydrogen peroxide, 30%.

e. Hydroquinone, 0.1M aqueous solution. Prepare a new solution when significant discoloration occurs.

f. 2-Propanol.

g. 2-Octanone.

PROCEDURE

A. Direct Procedure

1. Blank

Process a reagent blank with each series of standards and samples. In addition, process a sample blank if the sample contains colored ions other than iron. The reagent blank contains all the reagents used in the procedure except the sample aliquot. The sample blank contains the sample aliquot and all the reagents except the 1,10-phenanthroline chromogen.

Most reagent grade acids and salts contain traces of iron. Therefore, when large amounts of reagents are used to dissolve or prepare the sample, prepare a solution of the reagents, and process an aliquot of the solution as a sample to enable appropriate correction.

2. Calibration and bench standard

The use of four calibration standards is intended to promote efficiency by eliminating many repeat analyses. If only samples with similar concentrations are being run, the use of two appropriate standards will suffice.

Process a set of calibration standards with each series of samples. Use 1.00-ml portions of each of the four calibration standards and process these according to Procedure A-3, Step f. Use 1.00-cm cells for standards I and II (40 and 60 µg Fe/ml, respectively). Divide the micrograms of iron by the absorbance to obtain the conversion factors. The difference between the two conversion factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties still are experienced.

3. Analysis of samples

a. Pipet a sample aliquot of 10 ml or less containing 2 to 100 µg of Fe into a 25-ml volumetric flask. If the sample contains colored ions, pipet an identical aliquot into another 25-ml flask for the sample blank.

If the sample is a solid, dissolve a weighed portion of the solid with a minimum of reagents (fusion fluxes, acids, etc.) and dilute with water to a convenient volume. If large amounts of reagents are used to dissolve the sample, it will be necessary to determine the iron introduced through them (See Procedure A-1).

b. Pipet 0.5 ml of conc HCl.

If a cloudy precipitate forms, the sample could contain W. Discard the sample, pipet a new one, continue with Steps c through f, then add the acid after Step f. This modification is only for samples suspected to contain W. The procedure as written should be used in all other cases because the addition of acid at the beginning

		breaks up metal-hydroxy complexes if any are present.
c.	Pipet 5 ml of the EDTA-citrate reagent and mix by swirling the flask.	
d.	Pipet 1 ml of 2M $NH_2OH \cdot HCl$.	
e.	Pipet 2 ml of the 0.05M 1,10-phenanthroline reagent.	
f.	Pipet 3 ml of pyridine and mix by swirling the flask.	If the HCl was omitted at Step b, add it at this point.
g.	Cool the sample to room temperature, dilute to volume with water, and mix well. If the sample contains large amounts of organic complexing agents such as citrate, EDTA, and tartrate, proceed to Step h; otherwise, proceed to Step i.	
h.	Heat the sample for 15 min at 60°C (water bath), then chill the sample to room temperature.	
i.	Let stand for 25 min for color development.	
j.	Measure the absorbance of the sample against water at 507 mμ in 1- or 5-cm cells.	Use 1-cm cells for samples that contain more than 10 μg of Fe and 5-cm cells for samples that contain less than 10 μg of Fe In doubtful cases, measure the absorbance in 5-cm cells first. This will permit subsequent 1-cm cell measurements when necessary. The Fe(II)-1,10-phenanthroline color is stable for at least 24 hr.

k. Record the data and calculate the results as described on the example work sheet. Report all results to three significant figures.

In the calculation, it is essential that samples be compared against standards that were measured under identical conditions.

B. Column Extraction Procedure

1. Blank

Process a blank with each series of samples substituting 2 ml of distilled water for the sample aliquot.

2. Bench standard

Process a single determination on 1.00 ml of the bench standard per Procedure B-4 and 5. Limits will be specified by the Quality Control Laboratory. This standard is to be processed in addition to the calibration standards to ensure that the column separation of iron is proceeding correctly.

3. Calibration

The use of four calibration standards is intended to promote efficiency by eliminating many repeat analyses. If only samples with similar concentrations are being processed, the use of two appropriate standards will suffice.

A separate calibration is required for each series of samples. Use 1.00-ml portions of each of the four calibration standards and process these according to Procedure B-4 and 5. Use 1.00-cm cells for standards I and II (40 and 60 µg Fe/ml, respectively) and 5.00-cm cells for standards III and IV (6 and 12 µg Fe/ml, respectively). Divide the micrograms of iron by the absorbance to obtain the conversion factors. The difference between the two conversion factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties still are experienced.

4. Preparation of extraction column

a. Deliver about 15 ml of 7M HCl to the empty extraction column.

b. With a plastic scoop, transfer the treated Fluoropak to the column reservoir. Slurry the Fluoropak with the 7M HCl using a 6-mm glass stirring rod.

c. Open the column stopcock, and as the Fluoropak settles, tamp it down gently with the glass rod. Prepare a bed 5-in. high.

Do not allow the column to run dry. Add additional 7M HCl if necessary.

d. Drain the 7M HCl until its surface is within about 1 in. of the top of the Fluoropak bed.

5. Samples

a. Prepare the column as described in Procedure B-4.

b. Pipet a sample aliquot containing 5 to 100 µg of iron into a 50-ml polyethylene beaker.

Conc HCl normally contains trace levels of Fe so this procedure is limited to sample aliquots up to about 10 ml. When aliquots greater than 10 ml must be taken, pipet the aliquot into a glass beaker, evaporate the aliquot to about 3 ml, cool it, then proceed with Step c.

c. Add a volume of conc HCl equal to the aliquot volume plus 1 ml, then add 3 drops of 30% H_2O_2. Swirl to mix.

d. Quantitatively transfer the solution with 7M HCl rinses to the column reservoir.

e. Pass the solution through the column at a rate of 3 to 5 ml/min.

Collect the waste column effluent in any suitable glass container such as a 250-ml Erlenmeyer flask.

f.	Wash the column well with 7M HCl to remove foreign ions. Use 25 ml of 7M HCl in 5-ml increments.	Be sure to rinse the entire reservoir. Also, for most efficient washing, let the wash solution recede to the top of the bed before admitting the next wash.
g.	Pipet 0.5 ml of 0.1M hydroquinone into a 25-ml volumetric flask.	
h.	Elute the Fe and 2-octanone into the 25-ml flask with 15 to 18 ml of 2-propanol added in small increments.	Save the used Fluoropak in a wide-mouth screw-cap jar for subsequent reuse in Method Fe-Vol-1.
i.	Pipet 2 ml of the 0.05M 1,10-phenanthroline reagent. Mix.	
j.	Add 3 ml of pyridine. Mix.	
k.	Cool to room temperature and dilute to volume with 2-propanol. Mix well.	
l.	Let stand 15 min for color development.	
m.	Measure the absorbance of the sample against water at 507 mμ using 1- or 5-cm cells.	For best results, use 5-cm cells for samples that contain less than 10 μg of Fe. The Fe(II)-1,10-phenanthroline is stable for at least 24 hr.
n.	Record the data and calculate the result as shown on the example worksheet. Report all results to three significant figures.	

REFERENCES

1. S. S. Yamamura and J. H. Sikes, "Use of Citrate-EDTA Masking for Selective Determination of Iron with 1,10-Phenanthroline", Anal. Chem., 38 (1966), p 793.

2. J. S. Fritz and C. E. Hedrick, "Separation of Iron by Reversed-Phase Chromatography", Anal. Chem., 34 (1962), p 1411.

3. M. A. Wade and S. S. Yamamura, "Column Extraction Spectrophotometric Determination of Iron", Anal. Chem., 36 (1964), pp 1861-1862.

S. S. Yamamura
M. A. Wade
October 1967

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Iron

CHARGE NUMBER _____ PROCEDURE Fe-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance VS water	Net Absorbance	Conversion Factor μg/Abs	μg Fe in Aliquot	μg Fe corrected for Bias			RESULT μg Fe/ml
Blank		0.015							
Std, 40 μg Fe		0.333	0.318	125.8					
Std, 60 μg Fe		0.505	0.490	122.4					
			$\bar{X}$	124.1					
Bench Std	10 ml	0.420	0.405		50.3	50.2±1.7			5.02 ± 0.17

ANALYZED BY _____ DATE _____

CALCULATIONS:

Conversion Factor = $\frac{\mu g\ Fe}{net\ Abs} = \frac{40}{0.318} = 125.8$, $C' = \frac{60}{0.490} = 122.4$

Ave Factor = $\frac{125.8 + 122.4}{2} = 124.1$

μg Fe = BC = 0.405 (124.1) = 50.3

Result = $\frac{50.2 \pm 1.7}{Sample\ Vol} = \frac{50.2 \pm 1.7}{1.00} = 50.2 \pm 1.7\ \mu g\ Fe/ml$

APPROVED BY _____

COLUMN-EXTRACTION COMPLEXOMETRIC DETERMINATION OF IRON

ABSTRACT

Iron at milligram levels is separated from diverse cations and anions by extraction from 6 to 8M HCl medium into 2-octanone solvent supported on an inert column of fluorocarbon polymer particles. The iron subsequently is eluted from the column and determined by direct EDTA replacement titrimetry wherein equimolar cerium(III)-EDTA is added in excess and the liberated cerium(III) is titrated with EDTA to a visual xylenol orange end point. The method is highly selective and is applicable without special adaptation to a wide variety of complex inorganic samples.

APPLICABILITY

This method, based on published reports[1,2], is applicable to the determination of macro levels of iron in many types of complex inorganic samples such as stainless steels and iron ores. The wide applicability is due primarily to the high selectivity of the preliminary extraction-separation process. Comprehensive studies of the effects of diverse ions[2] show that Al, Bi, Cd, Ce, Co, Cr [as Cr(III)], Cu, Hg, Ni, U, and Zn at a 35:1 diverse metal to iron molar ratio do not interfere. Also, Mo (as molybdate) at 2:1, Pb at 8.5:1, V at 5:1, and Th, Ti, and Zr at 20:1 are without adverse effect. Partial extraction of Mo(VI) and V(V) is noted, but in the presence of hydrogen peroxide, no coextraction of these elements occurs. Metal ions which coextract are As(III), Au(III), Ga(III), Ge(IV), Ir(IV), Sb(III,V), Sn(II,IV), Te(IV), and Tl(III). Of these, As, Ge, Sb, and Sn can be removed initially by volatilization with a mixture of hydrochloric and hydrobromic acids from sulfuric acid medium. Interference is limited, therefore, to a few elements only infrequently encountered. Sulfuric acid at a 120:1 mole ratio to iron, phosphoric acid at a 100:1 ratio, and the complexing anions citrate, fluoride, oxalate, and tartrate at 17:1 ratios do not interfere.

The range of the method is 2.5 to 25 mg (0.045 to 0.45 mM) of iron. With a preliminary evaporation step, samples up to about 50 ml may be analyzed; hence, the lowest determinable concentration is about 0.05 mg Fe/ml. In actual practice, samples with iron concentrations less than 0.5 mg/ml are best analyzed by Method Fe-Color-1 which is equally reliable at low levels of iron and requires no preconcentration of samples by evaporation.

DISCUSSION

The overall method involves an initial column-extraction separation of the iron and subsequent titration of the separated iron with EDTA (ethylenediamine tetraacetic acid). In the extraction process, the sample is adjusted to about 7M in hydrochloric acid and passed through a column of fluorocarbon polymer particles coated with 2-octanone. Diverse cations and anions are washed through with additional 7M HCl; then, the extracted iron plus the 2-octanone solvent are eluted with acetone. The determination is concluded by diluting the column eluate with water, adding an unmeasured excess of equimolar cerium(III)-EDTA salt, and titrating the cerium(III) displaced by the iron with EDTA.

Attention is called to the following potential trouble spots of the method:

(1) Proper column preparation is essential. The column packing should not contain excessive amounts of free unsorbed 2-octanone. Also, excessive tamping should be avoided in packing the column. In both cases 2-octanone may bleed through the column carrying varying amounts of iron with it.

(2) For quantitative extraction, the iron must be in the (III), ferric, oxidation state. Hydrogen peroxide is used in the recommended procedure to assure this.

(3) Incomplete removal of diverse cations will give high results. Incomplete removal of strong complexing anions will give low results. The use of many small rinses is recommended over the use of a few large rinses. Channeling and thus incomplete washing will result when the column is allowed to drain dry.

(4) In the titration, excess cerium(III)-EDTA is added to the eluted sample and the cerium released is titrated with EDTA. After the addition of the cerium(III)-EDTA reagent, the sample must be titrated within a period of about an hour. After much longer standing, the end point color change is indistinct and high results are obtained. If the analysis is to be completed at a later time, do not add the cerium(III)-EDTA reagent, for in its absence the eluted sample can be held for at least 24 hr without harmful effect. Aqueous solutions of $NaCeEDTA \cdot 8H_2O$ decompose upon standing for reasons yet undetermined. The reagent, therefore, should be stored and used as the solid salt.

SAFETY PRECAUTIONS

Hydrogen peroxide, 7M HCl, and conc HCl are used in this method. Also, other strong acids may be used in sample dissolution. All of these can cause severe skin burns.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, assorted sizes.

2. Beakers, polyethylene or polypropylene, 50-ml.

3. Buret, 10-ml with 0.05-ml graduations.

4. Glass stirring rods, 7-mm diam by 10-in.

5. Graduated cylinders, assorted sizes.

6. Ion exchange column. Fabricate the column by attaching a 1-mm Teflon-plugged stopcock (with a 1-in. stem) and 3 in. of 38-mm glass tubing (the reservoir) to the ends of a 6-in. piece of 12-mm OD glass tubing (the column). Insert a glass-wool plug to retain the column packing.

7. Magnetic stirrer and Teflon-coated stirring bars.

8. Pipets, volumetric, macro and micro, assorted sizes, with suction bulb and syringe.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Acetone.

2. EDTA solution, 0.05M standard solution. Prepare a standard 0.05M solution per Method EDTA Prep-1 of this manual.

3. Hydrochloric acid (HCl) conc and 7M.

4. Hydrogen peroxide (H_2O_2) 30%.

5. Iron bench standard, 15.00 mg Fe/ml. Prepare a matrix solution by dissolving 15 g of $Cr(NO_3)_3 \cdot 9H_2O$, 20 g of $Ni(NO_3)_3 \cdot 6H_2O$, 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ and 20 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 20 ml of conc H_2SO_4 and 500 ml of water. Filter through a 0.45-μ membrane filter, to remove any insoluble residue. Weigh exactly 105.34±0.01 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a 400-ml beaker. Add approximately 200 ml of the matrix solution and 15 ml of conc HNO_3. Stir to dissolve, then boil gently for 5 to 10 min to oxidize the Fe(II) to Fe(III). Transfer quantitatively to a 1-liter volumetric flask using the remainder of the matrix solution for the rinses. Finally wash the balance of the matrix solution into the flask with water and dilute to volume with water. Store in a borosilicate glass bottle.

6. 2-Octanone-coated Fluoropak. Half fill a 600-ml beaker with 20- to 70-mesh Fluoropak (Wilkens Instrument & Research, Inc., Box 313, Walnut Creek, Calif.) and drench the Fluoropak with 2-octanone. Filter the 2-octanone-saturated Fluoropak on a large Buchner funnel and suck air through it for 10 min. Store the treated Fluoropak in a wide-mouth screw-cap jar.

7. Pyridine.

8. Sodium cerium(III)-EDTA reagent, solid. Dissolve 74.5 g of $Na_2H_2EDTA \cdot 2H_2O$ in about 1600 ml of water contained in a 2-liter graduated cylinder. Dissolve 87 g of $Ce(NO_3)_3 \cdot 6H_2O$ in 150 ml of water. If the cerium solution is not clear, filter it through a 0.45-μ membrane filter, then add it gradually to the clear EDTA solution in the 2-liter graduated cylinder. Add 10M NaOH intermittently throughout the cerium addition to maintain the pH at 5 to 7. Use vigorous stirring during this step to prevent the hydrolysis of cerium. Generally, 0.4 eq (40 ml of 10M NaOH) will be required.

   Pipet a 5-ml aliquot of the solution into a 150-ml beaker. Add 5 drops of conc HNO_3, 15 drops of pyridine, and 5 drops of 0.2% xylenol orange. If the solution is yellow, the EDTA is in excess. Titrate (a Mohr pipet is adequate) with 0.05M $Ce(NO_3)_3$ to a change from yellow to reddish-purple. If the original indicator color is purple, the cerium is in excess. Titrate then with 0.05M EDTA to a change from reddish-purple to yellow. In either case, note the volume of the reagent in the graduated cylinder and add the calculated volume of 0.05M cerium(III) or 0.05M EDTA to the graduated cylinder. Stir well, then repeat the titration process until a 10-ml aliquot of the solution requires no more than 0.01 ml of 0.05M cerium(III) or 0.05M EDTA to change the indicator from yellow to reddish-purple or vice versa.

Adjust the pH to 7 with 10M NaOH, then precipitate the equimolar NaCe(III)-EDTA salt by diluting with two volumes of acetone. Filter the salt on a Buchner funnel, air dry, and store in a screw-cap, wide-mouth jar. Based on cerium(III) and EDTA determinations, the formula for the salt is $NaCeEDTA \cdot 8H_2O$ with a molecular weight of 595.5

9. Xylenol orange, 0.2% (w/v). Dissolve 0.20 g of the solid reagent in 100 ml of water.

10. Other reagents which are not specified but which are useful in sample preparation are:

    a. Hydrobromic acid

    b. Hydrofluoric acid

    c. Nitric acid

    d. Potassium pyrosulfate

    e. Sodium carbonate

    f. Sulfuric acid.

PROCEDURE

A. Titration Blank

The Fluoropak column support is salvaged and reused. The 2-octanone-saturated Fluoropak, therefore, can contain small but significant levels of iron. Pipet 3 ml of distilled water to a 30-ml beaker and process it per Procedure E omitting Step 2.

B. Bench Standard

Process a 1-ml aliquot of the bench standard per Procedure E omitting Step 2. Acceptable limits will be specified by the Quality Control Laboratory.

C. Column Preparation

1.	Deliver about 15 ml of 7M HCl to the empty column.	
2.	Transfer the 2-octanone-coated Fluoropak to the column with a plastic (polyethylene is ideal) scoop and with the aid of a glass stirring rod, slurry the treated Fluoropak with the 7M HCl.	
3.	Open the stopcock, and as the Fluoropak settles, tamp it down gently with the glass rod.	Avoid excessive packing.
4.	Repeat Steps 2 and 3 to form a bed 5-in. high.	
5.	Drain the 7M HCl to within 1 in. of the top of the column packing.	Do not allow the column to run dry.

D. Dissolution of Stainless Steel Samples

Note: Because stainless steel type samples are most frequently encountered, a brief discussion of stainless steel dissolution is presented. For different types of alloys and solid samples, consult other appropriate sources.

Dissolve stainless steel samples with mixtures of sulfuric acid and nitric acid or of hydrochloric acid and nitric acid. When employing the latter, add the hydrochloric acid to the sample then admit the nitric acid in small portions until dissolution is complete. Boil to expel oxides of nitrogen. Filter any residue remaining on a Whatman 41 filter paper. Char, ignite, then fuse the ignited residue with sodium carbonate. Dissolve the carbonate melt with hydrochloric acid. If necessary, heat to dissolve the metal oxides. When samples contain silica, add conc HF dropwise to solubilize the silica. Combine the solutions and dilute to volume. Mix well and continue according to Procedure E.

E. Analysis of Samples

1.	Prepare the extraction column per Procedure C.	
2.	Pipet a sample aliquot containing 2.5 to 25 mg (0.045-0.45 mM) of Fe into a 50-ml polyethylene beaker.	Samples up to 10 ml can be analyzed conveniently. Those above 10-ml should be concentrated by evaporation before analysis or analyzed by Method Fe-Color-1. For best reliability, select a sample with greater than 10 mg of Fe.
3.	Add 3 drops of 30% H_2O_2, then add a volume of conc HCl equal to the sample volume plus 1 ml.	
4.	Quantitatively transfer the sample to the column reservoir with 7M HCl rinses.	
5.	Pass the sample through the column at a rate of 3 to 5 ml/min.	Use a 250-ml beaker or Erlenmeyer flask to collect the waste column effluent.
6.	Wash the column well with 7M HCl to remove diverse ions. Use four 5-ml rinses initially then complete the washing with four 10-ml rinses.	For most effective washing, allow the liquid level to drop to just above the column packing before admitting the next wash. Do not let the column run dry.
7.	Elute the Fe with acetone. Use three 5-ml portions of acetone followed by two 10-ml rinses. Collect the column eluate in a 150-ml beaker.	High salt concentrations tend to lessen the clarity of the end point transition. To minimize the level of HCl in the effluent, watch the descent of the yellow Fe band and start the collection when the band descends to within 1 in. of the glass wool plug.

8.	Dilute the sample to about 100 ml with water.	This is a convenient stopping place. After the addition of NaCeEDTA in step 9, the sample should be titrated within 1 hr, preferably right away.
9.	Add 0.5 g of solid $NaCeEDTA \cdot 8H_2O$ and stir for 1 to 2 min.	The weight of $NaCeEDTA \cdot 8H_2O$ is not critical. A scoop may be improvised to deliver 0.50±0.05 g of the reagent. For convenience, use continuous magnetic stirring from Step 9 through Step 12.
10.	Add 3 drops of 0.2% xylenol orange solution.	
11.	Add 1 ml of pyridine, then add conc NH_4OH dropwise to the appearance of a reddish-purple color, then add 2 ml of pyridine.	The 1 ml of pyridine must be added before any NH_4OH is introduced.
12.	Titrate with standard 0.05M EDTA to a change from red to yellow.	In the vicinity of the end point, wait 5 to 10 sec after each increment of titrant. Titrate to the complete disappearance of the red color.
13.	Record the data on the worksheet and calculate the results as described under CALCULATIONS.	
14.	Transfer the used Fluoropak with acetone rinses from the column to a wide-mouth screw-cap bottle for subsequent rinse.	Surplus 2-octanone-coated Fluoropak often is admitted along with 7M HCl to the collection jar. In acid medium, the 2-octanone undergoes condensation to form a dark compound which is not easily removed. Periodically, wash the salvaged Fluoropak with acetone and decant the acetone wash.

CALCULATIONS

Record the data and calculate the results as shown on the example work sheet. Report all results to four significant figures.

The factor 55.85 appearing in the calculation is the atomic weight of iron and converts the results from mmole to mg.

REFERENCES

1. J. S. Fritz and C. E. Hedrick, "Separation of Iron by Reversed-Phase Chromatography", Anal. Chem., 34 (1962) p 1411.

2. S. S. Yamamura, "Determination of Iron(III) by (Ethylenedinitrilo) Tetraacetic Acid Replacement Titrimetry Following Selective Separation by Column Extraction", Anal. Chem., 36 (1964) p 1858.

September 1967

S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Iron

CHARGE NUMBER _____ PROCEDURE Fe- Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	EDTA, M	EDTA used, ml	EDTA Net, ml	Fe in Sample Aliquot, mg	Fe corrected For Blas mg			RESULT mg Fe/ml
Blank		0.05025	0.01						
SS-1	3.00 ml	0.05025	5.33	5.32	14.93	15.10±0.25			5.033±0.083

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = 55.85\,AC = 55.85\,(0.05025)(5.32) = 14.93 \text{ mg Fe}$$

$$\text{Result} = \frac{E}{\text{Sample Vol}} = \frac{15.10 \pm 0.25}{3.00} = 5.033 \pm 0.083$$

APPROVED BY _____

RADIOMETRIC DETERMINATION OF KRYPTON-85

ABSTRACT

Krypton-85 gas samples from the Idaho Chemical Processing Plant (ICPP) Rare Gas Recovery Plant is determined by counting on a Beta proportional counter[1]. The samples, submitted in stainless steel bombs, are aliquotted, diluted with ethylene to atmospheric pressure, and counted in a special gas beta counting cell.

APPLICABILITY

This method is designed specifically for the determination of ^{85}Kr in gas samples received from the ICPP Rare Gas Recovery Plant. Gaseous beta emitters other than ^{85}Kr, if present, will interfere.

DISCUSSION

The samples, varying in pressure from a few centimeters of mercury to greater than one atmosphere, are received in stainless steel gas bombs. An aliquot (20 to 40 cm of mercury pressure) of the sample is transferred to an evacuated glass sample bomb; its approximate pressure is measured with a manometer (Figure 1). An aliquot of the reduced pressure subsample is then transferred to the gas dilution apparatus (Figure 2), and the pressure is accurately measured with the McLeod gauge (Figure 3). Ethylene is added to bring the sample to atmospheric pressure. The sample and the ethylene are mixed by alternately solidifying and vaporizing the gases, using liquid nitrogen coolant. It is necessary to bring the sample to atmospheric pressure to prevent implosion of the sample cell window (Figure 4) when the cell is removed from the gas dilution apparatus. The sample cells are fabricated to contain 3.21 ml; by measuring the pressure of the gas, the amount of gas in the cell at standard temperature and pressure (STP) can be calculated.

SAFETY PRECAUTIONS

Use extreme care when handling the evacuated glass collecting tubes and when using the gas dilution apparatus. This apparatus is under vacuum when in use and operating the stopcocks incorrectly can cause the sample to be lost or mercury to be sprayed through the apparatus. If the apparatus is stressed beyond its limit, an implosion will result, causing severe damage to the apparatus and possible injury to the operator. Clean and relubricate sticky stopcocks. Exercise care when handling liquid nitrogen. It is extremely cold and injury to the skin will result if contacted with the liquid nitrogen. Do not wear gloves while handling liquid nitrogen; if an accidental spill occurs

and the liquid nitrogen gets inside the glove, very serious skin injury will result.

APPARATUS AND REAGENTS

A. Apparatus

1. Beta proportional counter.

2. "Crescent" wrench for attaching the adaptor to the steel sample bombs.

3. Dewar flasks, pint and quart.

4. Gas collecting bomb, 250-ml with stopcocks on both ends.

5. Gas counting cell (Figure 4).

   The windows on the cells are repaired by scraping off the old window and dissolving the old cement with acetone. A new cellophane window is then cemented on using a thin coat of cement. The cement is allowed to dry, then the excess cellophane is trimmed off.

6. Gas dilution apparatus (Figure 2).

   Two units are required. When the apparatus is being stored for an extended time, it is recommended that grease be removed from all stopcocks and a piece of paper be placed between the outer and inner parts of the stopcock. These precautions are necessary to prevent the stopcocks from "freezing".

7. Gas sampling apparatus (Figure 1).

8. Regulator for ethylene tank.

9. Slotted aluminum card (2.50 x 3.25-in.).

   Cut a slot in the aluminum card so the gas counting cell will slip into the middle of the card.

10. Steel gas bomb adaptor (Figure 5).

11. Storage rack for steel gas bombs.

12. Vacuum pumps. Three pumps are required....one for each gas dilution apparatus and an auxiliary pump for the McLeod gauges and the gas sampling apparatus.

B. Reagents

1. Cellophane for windows of gas counting cells.

2. Cellulose nitrate base cement for gluing the windows on the cells.

3. Ethylene, CP reagent grade in 2.5-pound cylinders.

4. Liquid nitrogen.

5. Vacuum grease (Apiezon-N).

PROCEDURE

A. Set up and Check of Gas Dilution Apparatus

Place the two gas analysis apparatus in the hood and connect a vacuum pump to each unit. Keep the tubing as short as possible from the pump to the connector at stopcock 1 (Figure 2); the longer the tubing, the longer the time required for evacuation of the system. Use hose clamps to ensure good joints. The pump should be checked and oil replaced if it is dirty. If possible, a test should be made to determine how low the pump will evacuate. If the pump will not pump below 0.001-mm Hg pressure, it should be replaced or repaired. The pump used as the auxiliary does not have to be this good. The Mass Spectrometry Section has a portable gauge for checking pumps. Check all tubing on the apparatus to make sure it is in good condition and forming good connections. Remove, clean, and grease all stopcocks with Apiezon-N vacuum stopcock grease. Use a minimum amount of grease to lubricate the stopcocks. Check the system for leaks; a sample cell is not required in the cell filler for this check. Open stopcocks 2 and 8 (Figure 2) and 5 (Figure 3). Close stopcocks 1 and 4 (Figure 2), and stopcock 7 (Figure 3). Turn stopcock 6 (Figure 3) to the left position (◣) and stopcock 3 (Figure 2) to the right position (▶); connect a sample gas bomb to stopcock 3 with a section of vacuum tubing. The vacuum pump is turned on and stopcock 1 is slowly opened so that the level of mercury in the manometer slowly changes. After the system has been evacuated for 10 min, stopcock 1 is closed, and the level of mercury in the manometer is observed; if it doesn't change, there are no large leaks in the system. The pressure is then measured using the McLeod gauge according to Procedure B. If the pressure is below 0.01-mm Hg, everything is okay. However, if it is not below this pressure, remove the mercury from the gauge, open stopcock 1, and evacuate for an additional 5 min. Check the pressure and if it is not below 0.01-mm Hg pressure, the system has leaks or the vacuum pump is not pumping down to a low enough pressure. If the pump wasn't checked in the setup, do so now. The system is then checked for leaks by evacuating again with stopcock 5 closed and measuring the pressure,

if the pressure is now low enough, the leak is below stopcock 5. Pull the mercury out of the gauge, close stopcock 7, and open stopcock 5. Let air into the system and remove and clean stopcocks 5, 6, and 7 (Figure 3). Evacuate the system and check the pressure again. If the system still has a leak with stopcock 5 closed, check for a leak in the sampling system by evacuating the system with stopcock 2 closed; check the pressure. If the leak is isolated here, let air in then clean and regrease stopcocks 2 and 3. Remove the mercury from the sample chamber and clean and regrease the stopcock on the sample chamber. Check the tubing connections to ensure a tight fit. If this does not cure the leak, remove and grease stopcocks 1, 4, and 8 and also the stopcock on the cell filler. Check the cell filler cover and the ball joint connection to determine if they have good seals. Check the pressure and if it is still not low enough, the glass should be checked for pin hole leaks with a Tesla coil; this is done while the system is evacuated. If a hole is found, have it repaired by a glass blower.

B. Operation of McLeod Gauge

Figure 3 is a drawing of a McLeod gauge. The gauge has three calibrated columns for measuring pressure. The right column is for measuring pressures from 0 to 25 mm, the middle column is for measuring pressures from 0 to 5 mm, and the left column is for measuring pressures from 0 to 0.5 mm. The right and middle columns are open at the top while the left one is sealed at the top.

To operate the gauge, close stopcock 5, open stopcock 7 to the auxiliary vacuum pump, and slowly turn stopcock 6 to allow air to enter the top of the mercury reservoir. Because the vacuum in the gas dilution system is applied to the gauge through stopcock 8, the atmospheric pressure forces the mercury down in the reservoir and up into the tube. The mercury rises in the gauge. The rate of rise is controlled by touching a finger to the capillary at the right of stopcock 6. At point A the rising mercury traps a calibrated volume of air at the pressure being measured and starts compressing it into the left hand side of the gauge. If the pressure is greater than 5 mm, the mercury in the left column is stopped at point B (the zero point for the right or high pressure scale) by finger pressure on the capillary and/or closing stopcock 6. The level of the mercury in the extreme right hand scale is read to obtain the pressure. If the pressure is less than 5 mm, stopcock 6 is again opened to the atmosphere and the mercury is allowed to rise to point C on the left hand column. This is the zero point for the middle column. The level of the mercury in the middle column is read for the pressure in millimeters of mercury. If the pressure is below 0.5 mm, the mercury is allowed to rise in the gauge until it reaches the zero at the top of the middle column, point D. The pressure is then found by reading the level of mercury in the left column.

The mercury is removed from the column by slowly rotating stopcock 6 to vacuum; the pressure on the reservoir is reduced and the mercury is drawn into the reservoir.

One of the problems associated with the operation of this gauge is that mercury tends to hang up in the capillary of the low pressure scale. This will occur if the mercury is allowed to drop out of the capillary too quickly. Also, if atmospheric pressure is allowed to displace all of the mercury in the reservoir, the air will then bubble through the mercury in the tube and splatter it into the capillary. Regardless of how the mercury gets there, it is difficult to remove. A fairly effective method to remove entrapped mercury is to evacuate the system, then allow air to enter through stopcock 6 and force the mercury up into the capillary. Rapidly turn stopcock 6 to the vacuum; as the mercury is pulled out of the gauge, place a Vibra-tool against the capillary and follow the mercury down. This will usually cause the mercury to fall out of the capillary. If this doesn't work, the next alternative is to evacuate the system completely and then slowly raise the mercury from the reservoir into the small bulb below the capillary. Do this without causing the trapped mercury drop to go up into the capillary. Get the mercury level as close to the drop as possible. Then apply the Vibra-tool to the glass bulb.

C. Check of Instrument Performance

Place the gross beta calibration standard on the fifth shelf of the counting chamber and activate the counter. Allow the counter to accumulate 10,000 counts. Enter the time on the work sheet as shown in the sample work sheet. Calculate the performance factor by dividing the known counting time by the determined value.

D. Determination of Cell Background

1. Place an empty sample cell on the special slotted aluminum card.	Visually inspect the cell window to be sure it is intact. Two types of samples are normally analyzed....a "hot" feed sample and a "cold" exit-gas sample. Use separate cells for "hot" samples and "cold" samples and do not interchange them.
2. Place the card and cell in the counter on the fourth shelf and count for 1000 sec. Record the background on the work sheet as counts/1000 sec.	If the cell is contaminated, it must be purged before use. The "cold" cell should be <400 c/1000 sec and the "hot" cell should be <600 c/1000 sec.

3. The exit gas sample cells are usually counted in "Homer" and the feed gas sample cells are counted in "Jethro".

4. After obtaining the background on a pair of cells, start counting the background on another pair of cells.

E. Sampling of the Steel Gas Bomb

Note: While the background is being determined on the cells, take a sample from the steel gas bomb as described below. Two glass bombs are used to take these samples. One is used only for the "hot" feed samples and the other is used only for the "colder" exit-gas samples. Before taking a sample, be sure that the glass sampling bomb does not contain sample from the previous analysis. Clean these bombs by opening both stopcocks and applying vacuum for a few minutes. Always sample the cooler exit gas first to minimize contamination of the cold exit-gas by the hot feed gas.

1. Attach the special adaptor (Figure 5) to the steel gas bomb and then attach the glass sampling bomb to the adaptor. The other end of the glass bomb is connected to the manometer. Open the valves on the glass bomb and the valve on the adaptor.

2. Turn the stopcock on the manometer to the down position (⊤) and start the auxiliary vacuum pump. Pump until the column of mercury stops rising.

   Before disconnecting the line of the auxiliary pump to the vacuum apparatus, make sure stopcock 7 is closed on both systems.

3. Turn the stopcock to the left position (⊣) and observe the mercury column. If it does not drop, slowly open the valve on the bomb and allow gas to enter until the mercury drops about 40 cm.

   If the feed gas is running about 10^7 d/m/ml, take only 20 cm of gas pressure.

4. Close all valves except the one on the adaptor, remove the sample bomb, and clean the sample out of the sampler by applying house vacuum with the manometer stopcock in the down position (⊤).

F. Analysis of Samples

1. Attach the glass bomb to the tubing on stopcock 3 of the gas dilution apparatus (Figure 2). Attach the auxiliary vacuum pump to stopcock 7 (Figure 3).

2. Put the counting cell, with its stopcock open, into the cell filler. Put the cover on and turn the stopcock on the cell filler to the right position (⊢).

Start counting the background on another cell.

3. Adjust the following stopcocks to the positions indicated:

Stopcocks 1 and 4 (Figure 3) are closed, stopcocks 2 (Figure 2) and 5 and 8 (Figure 3) are open, stopcock 3 (Figure 2) is to the right position (⊢) and stopcock 6 (Figure 3) is to the left position (>).

4. Turn the vacuum pumps on and slowly open stopcock 1 (Figure 2) so that the mercury level slowly changes in the manometer.

If the valve is opened too fast the sudden drop in pressure may cause the cell window to rupture or stretch.

5. Pump the system down for 5 to 10 min.

6. Close stopcock 5 and open stopcock 7.

7. Measure the pressure using the McLeod gauge. Slowly turn stopcock 6 to the down position (^) until mercury starts rising in the gauge. Control the rate of rise by placing a finger over the capillary on stopcock 6.

8. Let the mercury rise until the level in the center column reaches zero, point D in Figure 3.

9. If the pressure is not below 0.01 mm, turn stopcock 6 slowly to the left position (>). If the pressure is below 0.01 mm go to Step 12.

   This allows the auxiliary vacuum pump to draw the mercury out of the gauge. Do not allow mercury to drop too fast.

10. Evacuate the system for another 5 min.

11. Repeat Steps 7-9 and measure the pressure in the vacuum system.

    If the pressure is not below 0.01 mm, check system for leaks as described in Procedure A.

12. If the pressure is below .01 mm, close stopcock 1 and lower the mercury in the gauge by turning stopcock 6 to the left position (>).

13. Transfer a sample from the glass bomb using the following procedure.

    The level of the mercury in the bulb below stopcock 3 determines the amount of sample taken. This volume is small for the feed and large for the exit gas.

    a. Turn stopcock 3 to the down position (T).

    b. Momentarily open the stopcock on the sample bomb.

    c. Turn stopcock 3 to the left position (-|).

    d. After a second, close stopcock 2.

14.	Measure the pressure in the system as described in Steps 7 and 8. Record this pressure on the work sheet as sample pressure.	For feed samples, the pressure should be below 1.0 mm. If it is too high, reduce it by momentarily opening stopcock 1. Then remeasure the pressure. For exit samples the pressure should be at least 10 mm. If it is not high enough, take additional sample starting at Step 13. The desired pressures, of course, depend on the sample activity.
15.	After the pressure is measured, lower the mercury again by turning stopcock 6 to the left position (>).	
16.	Let the system pump until all the mercury has been drawn out of the gauge.	
17.	Close stopcock 8.	
18.	Admit ethylene to the system by opening stopcock 4. Use the needle valve on the regulator to control the rate of addition.	Before opening stopcock 4, open the valve on the tank and the regulator. Admit some ethylene to the line by momentarily opening the needle valve.
19.	Add ethylene until the pressure in the vacuum system reaches atmospheric pressure.	Both columns on the mercury manometer will be at the same level. Do not let the pressure exceed one atmosphere.
20.	Close stopcock 4.	
21.	Condense as much gas as possible by immersing the cold finger in liquid nitrogen.	
22.	After the manometer shows no further change, revolatilize the gas by warming the cold finger with water.	
23.	Repeat Steps 21 and 22 three more times.	

24.	Remove the cover from the cell filler.	
25.	Remove the counting cell and immediately close the cell's stopcock.	
26.	Open stopcock 1 and evacuate a few seconds.	Clean the vacuum system by replacing the cell filler cover and evacuating. Let air in and evacuate again. Repeat twice.
27.	Open stopcock 8, and 5 and close stopcock 7. Open stopcock 2 and turn stopcock 3 to the right position (⊢).	The sample bomb is still attached and is not removed until it has been determined that a good sample has been taken, Step 29.
28.	Place the cell on the special slotted aluminum plate and place the plate in the counter on the fourth shelf.	This requires the use of third shelf geometry in the calculation.
29.	Observe the counting rate. If it changes significantly, the cell leaks. Repair the cell as discussed under apparatus and process another sample. The repaired cell should not be used until the glue is dry.	If the sample counts in less than 15 sec, take a new sample at a lower pressure. Begin with Step 2, Procedure F.
30.	Record the counts and counting time on the work sheet. Calculate the activity as d/m/ml as shown on the sample work sheet.	
31.	After counting a sample, place the cell in the gas apparatus and purge by alternately applying vacuum and admitting air to the system.	Check the background to determine if the cell is clean.
32.	Clean the glass sampling tubes by drawing air through with the vacuum.	

G. Calculations

Report result as disintegrations per min per ml of gas at standard condition.

The brass cells are 1 in. dia x 1/4 in. deep, having a capacity of 3.21 ml. The volume of sample taken may be computed at standard conditions from the general gas law:

$$\frac{P_o V_o}{T_o} = \frac{P_1 V_1}{T_1} \qquad (1)$$

Where: V_o = volume of the sample taken at standard conditions, ml.

P_o = 760 mm.

T_o = 273° K.

P_1 = pressure observed on McLeod gauge, in mm.

V_1 = 3.21 ml.

T_1 = room temp. 298° K may be used in all calculations.

Thus: $$V_o = P_1 \left[\frac{(3.21)\ (273)}{(760)\ (298)} \right] \qquad (2)$$

$$V_o = 0.00387\ P_1$$

Then, $$\text{C/min/ml} = \left(\frac{\text{observed counts}}{\text{observed time sec}} - \text{BKGD} \right) \left(\text{Vol factor} \right) \qquad (3)$$

$$\text{d/min/ml} = (\text{C/min/ml})\ \ (\text{PF})\ \ (\text{Geometry factor}) \qquad (4)$$

REFERENCES

1. B. R. Hunter and G. A. Huff (ed.), Remote and Service Analysis Group Operating Manual, PTR-729, pp 74-77.

D. R. Trammell
April 1972

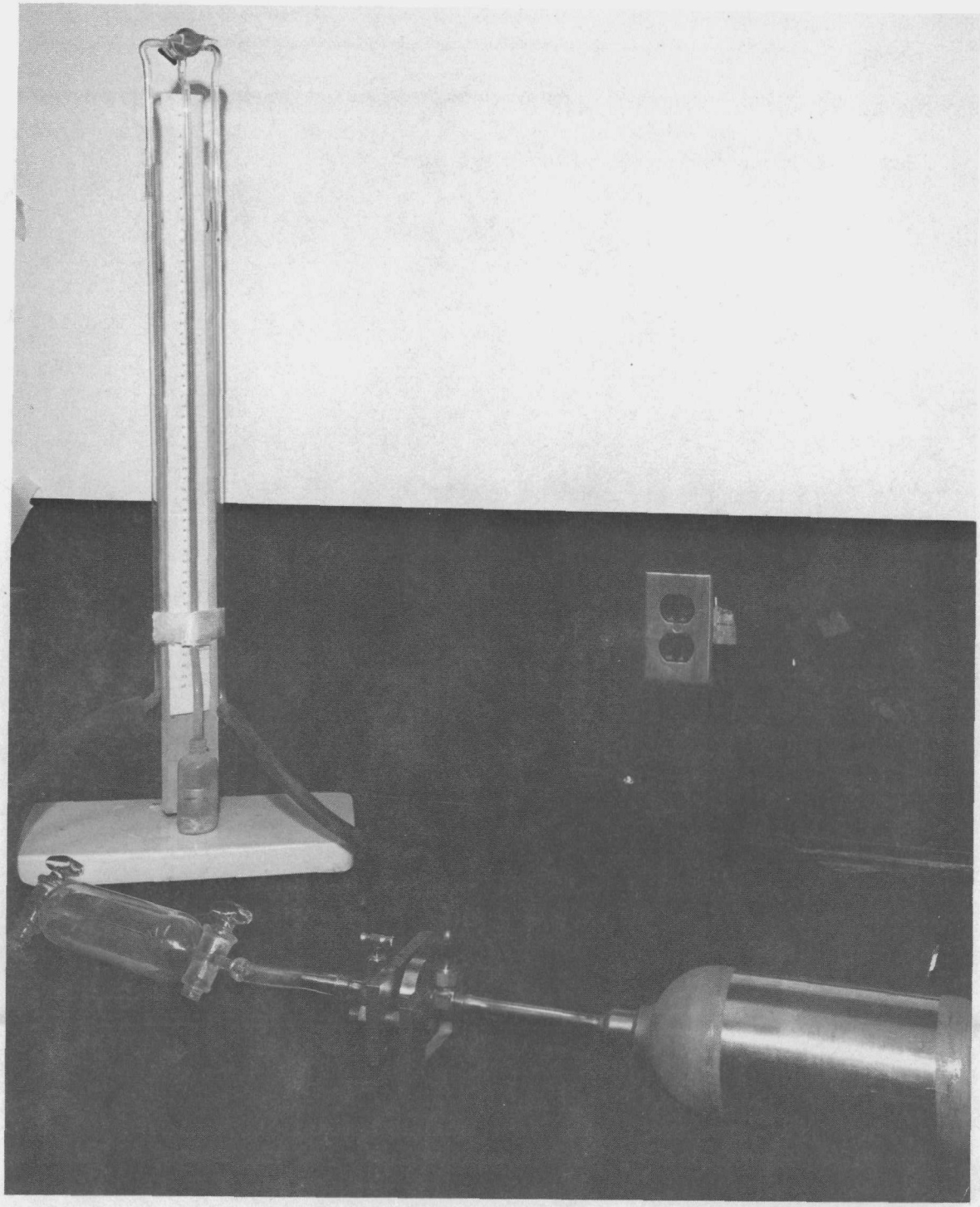

Fig. 1 Apparatus to take sample from steel gas bomb.

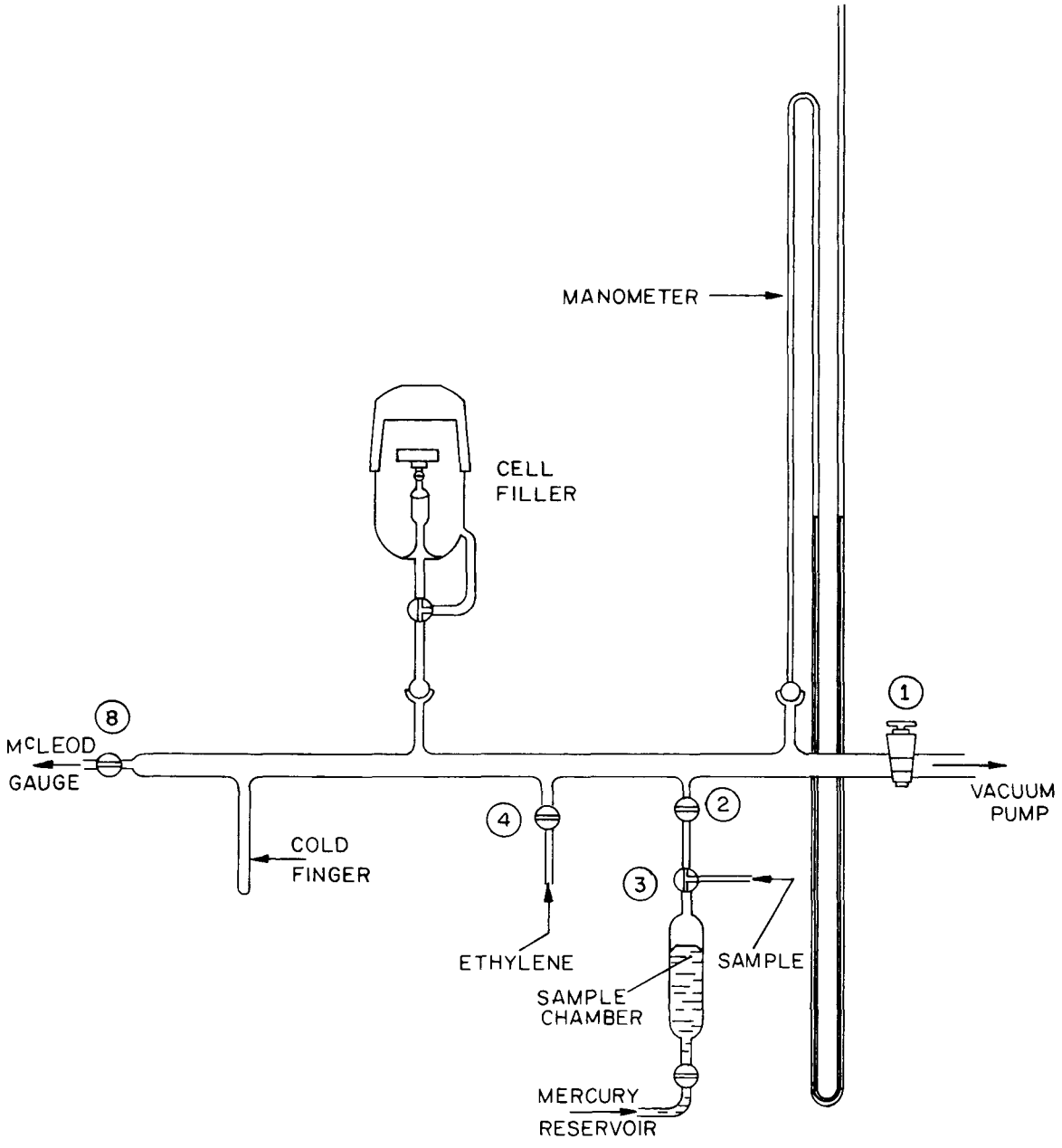

Fig. 2 Gas dilution apparatus.

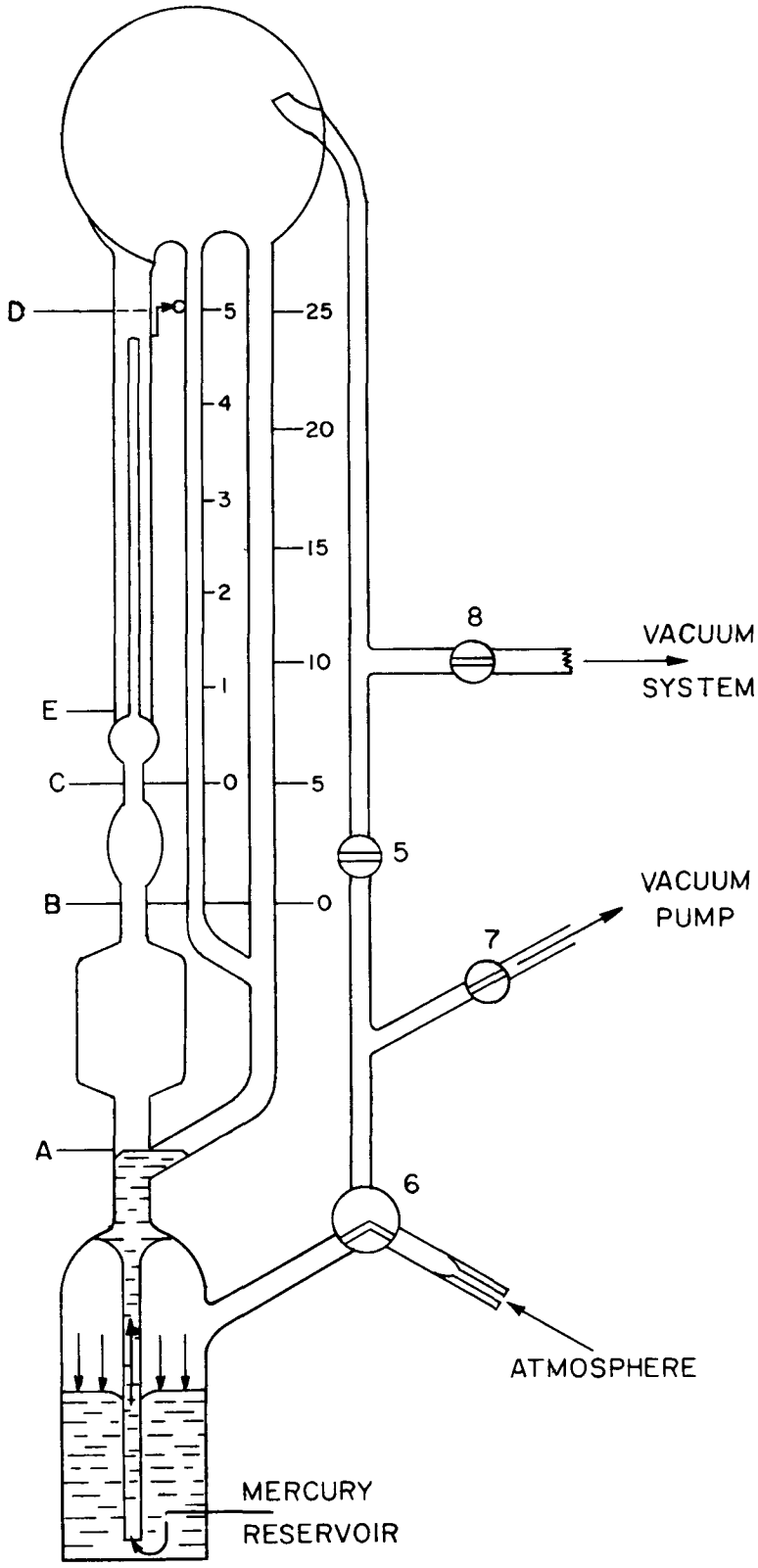

Fig. 3 McLeod gauge.

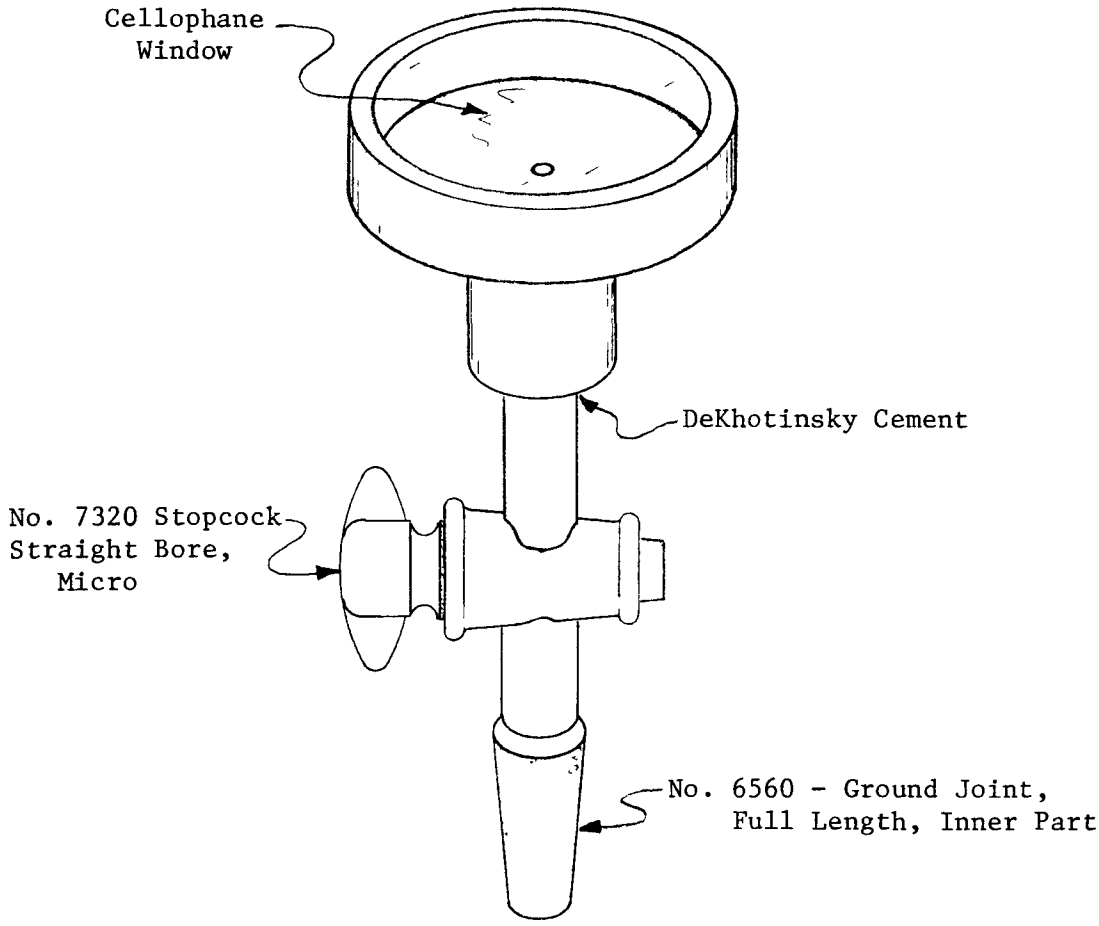

Fig. 4 Gas counting cell.

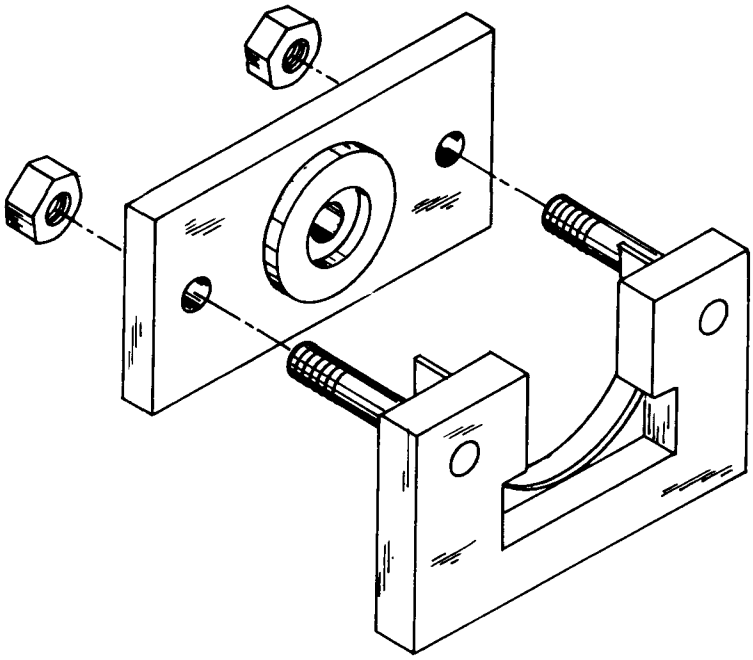

Fig. 5 Steel gas bomb adaptor.

ACC-A-0221

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION ^{85}Kr

CHARGE NUMBER _____ PROCEDURE ^{85}Kr-Beta Counting-1

SPECIAL INSTRUCTIONS:

Counter - Homer

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Standard Counting Time, 10,000	Performance Factor	Background c/s	Sample counts	Sample Counting Time, sec	Pressure of Sample, mm	Vol Factor $1/V_0$	RESULT d/m/ml
Cell NO.									
Exit NO. 1		59.96	1.11	0.400	9797	1000	17.8	14.52	4.4×10^4

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Performance Factor (PF)} = \frac{\frac{184.9}{10000}}{59.96} = 1.11$$

$$V_0 = 0.00387\, P_1 = (0.00387)(17.8) = 0.0689$$

$$\text{Vol Factor} = 1/V_0 = 1/0.0689 = 14.52$$

$$\text{c/m/ml} = \left(\frac{\text{observed counts}}{\text{seconds}} - \text{Background c/s}\right)\left(1/V_0\right)(60\ \text{sec/min})$$

$$= \left(\frac{9797}{1000} - 0.400\right)(14.52)(60) = 8187$$

$$\text{d/m/ml} = \frac{(\text{c/m/ml})(\text{PF})}{\text{Geometry}} = \frac{(8187)(1.11)}{0.208} = 4.4 \times 10^4$$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEEL

ABSTRACT

Manganese in dissolved steel is oxidized to permanganate ion by potassium periodate in a perchloric-nitric-phosphoric acid medium. The oxidized sample is measured spectrophotometrically at 545 nm and then remeasured at the same wavelength after reduction of the permanganate to nonabsorbing manganese(II) with nitrite. The difference in absorbances is proportional to the manganese in the sample. The steel samples are dissolved initially in a mixture of nitric and hydrochloric acid.

APPLICABILITY

This method adapted from published procedures [1,2,3] is applicable to carbon and stainless steels and to other samples which do not contain nitrite-reducible ions which absorb significantly at 545 nm. Chromium at a 40 to 1 chromium-to-manganese molar ratio, copper and cobalt at 200 to 1, and nickel at 100 to 1 are without effect.

The working range of the spectrophotometric procedure is from 75 to 1000 µg of manganese. The lowest determinable concentration is 3 µg/ml using a maximum sample aliquot of 25 ml. Lower limits can be obtained by prior evaporation of the sample aliquot.

DISCUSSION

Immediately before the perchloric acid fuming, nitric acid is added to eliminate the danger of a perchloric acid explosion with any organic material that might be present in the sample. This precaution is incorporated into this method because it may be used for samples other than steel. It is necessary to heat the sample until dense perchloric acid fumes appear to completely expel nitric acid, which if present in large quantities, will retard color development.

The method of obtaining a sample blank by reducing the sample with nitrite is not applicable to samples containing tungsten. Then a desirable reference solution consists of a sample aliquot plus the appropriate mineral acids omitting the potassium periodate.

Permanganate has several absorption peaks. Here, 545 nm is preferred over higher absorbing 526 nm because chromate ion absorbancy is minimized.

SAFETY PRECAUTIONS

This procedure employs potentially explosive perchloric acid. Form 2063 (Safe Handling of Perchloric Acid) is required. All heating steps are performed in a perchloric acid hood with a water scrubber. Gloves should be worn for the handling of all acid solutions.

APPARATUS AND REAGENTS

A. Apparatus

1. Flasks, Erlenmeyer, 125-ml with reflux head.
2. Flasks, volumetric, 50-ml.
3. Hot plate.
4. Petri dish, large, for use as a boiling water bath container.
5. Pipets, macro and micro, assorted sizes with syringe control and suction bulb.
6. Pipets, Mohr, 5- and 10-ml.
7. Spectrophotometer, Cary Model 14 or Beckman DU or equivalent with 1-cm cuvettes.

B. Reagents

1. Hydrochloric acid, conc.
2. Manganese standard stock solution, 5.000 mg Mn/ml. Dissolve 2.500 g of manganese metal in 100 ml of 2M HNO_3 and dilute to 500 ml with water. Confirm the concentration by EDTA titrimetry.
3. Manganese calibration standard I, 500 µg Mn/ml. Dilute 10.00 ml of manganese standard stock solution with water to 100.0 ml.
4. Manganese calibration standard II, 750 µg Mn/ml. Dilute 15.00 ml of the manganese standard stock solution with water to 100.0 ml.
5. Manganese bench standard, 500 µg Mn/ml. Dilute 10.00 ml of manganese standard stock solution to 100.0 ml with a solution prepared by the Quality Control Laboratory to provide a typical steel matrix.

6. Controls. Prepare controls containing from 75 to 1000 µg Mn/ml in a typical steel matrix.

7. Nitric acid, conc.

8. Perchloric acid, conc.

9. Potassium periodate solution. Dissolve 7.5 g of KIO_4 in 200 ml of hot 1:1 HNO_3. Add 400 ml of conc H_3PO_4, cool, and dilute to 1 liter. This reagent is usually stable for months.

10. Sodium nitrite. Dissolve ∿0.5 g of $NaNO_2$ in 10 to 15 ml of distilled water. Prepare this reagent fresh daily.

PROCEDURE

A. Preparation of a Reagent Blank

Process a 1-ml portion of water by the same procedure used to process the calibration standards and the sample(s).

B. Preparation of calibration standards.

Process a set of calibration standards with each series of samples. Use 1.00-ml portions of each calibration standard (500 and 750 µg Mn/ml). Divide the micrograms of manganese by the absorbance to obtain the conversion factors. The difference between the two conversion factors should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor within the specified limits. If either or both specifications are not met, reprocess the pair of calibration standards. Contact your supervisor if difficulties are still experienced. The molar absorptivity of the permanganate ion is about 2,700. The expected conversion factor is, therefore, about 1010 as the procedure is written.

C. Analysis of Bench Standard

Process a 1.00-ml portion of the bench standard per Procedure E beginning with Step 1. If desired, a known NBS steel standard may be processed per Procedure D, beginning with Step 1.

D. Dissolution of Steel Samples

1. Weigh ∿1.0 g of sample into a 125-ml Erlenmeyer flask.

2. Place a reflux head on the flask and add 10 ml of conc HCl in small increments. After the initial reaction subsides, heat on a hot plate until the reaction ceases.

3. Add 10 ml of conc HNO_3 and continue heating until digestion is complete.

If the sample does not dissolve completely after digestion with HCl and HNO_3, consult your supervisor for further dissolution steps.

4. Cool, transfer to an appropriate volumetric flask, dilute to volume, and mix.

5. Proceed to Step 1 of Procedure E.

E. Analysis of Samples

1. Pipet a sample aliquot of 25 ml or less containing 75 to 1000 µg of Mn into a 50-ml volumetric flask.

2. Add 2 ml of conc HNO_3 and 4 ml of conc $HClO_4$ using a Mohr pipet.

In the case of steel or any other sample known to contain no organic material, the HNO_3 may be omitted.

3. Heat on a hot plate in a perchloric acid hood until heavy white $HClO_4$ fumes appear.

4. Cool and dilute to about 25 ml with distilled water.

5. Add 10 ml of KIO_4 solution.

6. Heat in a boiling water bath for 20 to 30 min.

7. Cool, dilute to volume with water and mix thoroughly.

8.	Measure the absorbance within 2 hr in 1-cm cells against water at 545 nm.	Continue to Step 9 with all samples other than the blank and calibration standards.
9.	Add one drop of $NaNO_2$ solution to the residual solution in each flask, swirl to mix, then measure the absorbance of the bleached solution as per Step 8.	One drop of $NaNO_2$ solution should cause the purple to fade completely after 10 sec of swirling. If there is any doubt, add another drop.
10.	Record the data and calculate the results as shown on the example work sheet.	

REFERENCES

1. ASTM, "Manganese by the Periodate (Photometric) Method", ASTM Methods for Chemical Analysis of Metals, Philadelphia: American Society for Testing Materials, 1960, pp 168-170.

2. E. B. Sandell, Colorimetric Metal Analysis, New York: Interscience Publishers, Inc., 1959, pp 606-620.

3. F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, Princeton: D. Van Nostrand Co., Inc., 1959, p 308.

P. A. Anderson
April 1972

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Manganese

CHARGE NUMBER _____ PROCEDURE Mn-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance VS H_2O	Sample Blank Absorbance VS H_2O	Net Absorbance	Conversion Factor	µg Mn in Aliquot Analyzed			RESULT wt% Mn
Reagent BK		0.000							
Std, 500µg		0.493		0.395	1014.20				
Std, 750µg		0.741		0.741	1012.15				
				$\bar{X}$ =	1013.18				
Sample	1.0201g/500/15.00	0.621	0.029	0.592		599.8			1.96

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = \frac{\mu g\ Mn\ in\ Std}{Net\ Abs.} \qquad D' = \frac{500}{0.493} = 1014.20$$

$$D'' = \frac{750}{0.741} = 1012.15$$

$$\bar{X} = 0.5(D' + D'') = 0.5(1014.20 + 1012.15) = 1013.18\ \mu g\ Mn/abs.\ unit$$

Sample

Net Abs. = 0.621 − 0.029 = 0.592

µg Mn = 0.592 (1013.18) = 599.80 µg in sple Aliquot.

$$wt\% = \frac{(\mu g\ Mn\ in\ Aliquot)(ml\ in\ Sample\ Dilution)(100)}{(wt\ sample)(10^6\ \mu g/g)(ml\ in\ Sample\ Aliquot)}$$

$$= \frac{(599.80)(500)(100)}{(1.0201)(10^6)(15)} = 1.9599\ wt\%\ Mn$$

APPROVED BY _____

DETERMINATION OF MERCURY IN STACK GAS CAUSTIC SCRUB SOLUTIONS BY FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRY

ABSTRACT

Mercury in stack gas caustic scrub solution is determined by a modification of the method of Hatch and Ott[1]. The Hg^{2+} and Hg_2^{2+} are reduced to Hg^o by either hydrazine hydrate or Sn^{2+}. Elemental mercury is purged from the solution by an air stream. Mercury is determined by passing the air through a 10-cm quartz-window cell and measuring the absorbance at 253.7 nm.

APPLICABILITY

The method is applicable to the determination of mercury in stack gas caustic scrub solutions (~500 ng/ml of Hg in 7N NaOH). It is also useful, with proper sample preparation, for analysis of a wide variety of samples containing from 10 to 500 ng of mercury. The requirements for a suitable sample are that it contains from 10 to 500 ng of mercury in a maximum volume of about 50 ml and that the sample is acidified to contain about 10% HCl by volume. Possible interferences should be anticipated if the sample contains more than 1% of other easily reducible ions. The technique may not be usable if the mercury is strongly complexed in solution. It is relatively free from interference by other metal ions present at 100 ppm, but a serious depression by iodide has been reported[2]. It is important that the mercury be in a form reducible to elemental mercury by Sn^{2+} or hydrazine hydrate.

Any volatile substances in the sample may absorb at 253.7 nm and interfere with the determination (eg, benzene, other aromatic hydrocarbons, sulfur dioxide). Samples free from organic matter are acidified to contain 10% HCl. Samples in which the organic content is less than 0.05% can be analyzed directly if the acidification is performed at least 16 hr prior to the analysis. Samples with higher organic content must undergo a digestion per Method Hg-Color-1 prior to analysis.

DISCUSSION

Directions for connecting the air supply should be followed explicitly. The nebulizing air supply on most atomic absorption instruments and specifically on the Techtron AA-5 is poorly suited to provide a controlled flow into a low impedance, so special arrangements must be made. On the AA-5, it is possible to obtain adequate flow control

by using the auxiliary support gas valve as the controlling element.

It is essential that a blank determination be made on the scrub reagent. Reagent grade sodium hydroxide contains enough mercury to give a blank of about 100 ng/ml on 7N NaOH.

The useful range of the method for caustic scrub solutions is limited by this blank, and extends upward to about 500 ng in the sample taken for analysis. The inherent detection limit of the method is about 5 ng. Accuracy and precision of about 1% are attainable at the 250-ng level but are critically dependent on syringe injection technique.

APPARATUS AND REAGENTS

A. Apparatus

1. Chart recorder, 10-mv full scale, 1-sec or faster full scale pen movement.
2. Cups, plastic, 5-ml, caplugs No. 12X.
3. Glass wool.
4. Hypodermic needles, 24-ga, 2- or 2.5-in., Huber point preferred.
5. Mercury analysis kit, Techtron part No. FJ-Hg-1, or equivalent (Figure 1).
6. Mercury hollow cathode lamp.
7. Pipets, volumetric, assorted sizes with suction bulb.
8. Spectrophotometer, atomic absorption, Techtron AA-5, or equivalent.
9. Volumetric flasks, 10-ml and 1-liter.

B. Reagents

1. Desiccant, anhydrous magnesium perchlorate or barium perchlorate.
2. Hydrochloric acid, conc.
3. Mercury stock solution, 1.000 mg/ml. Dissolve 1.354 g of reagent grade $HgCl_2$ in distilled water and dilute to one liter with 10% (v/v) HCl. Standardize by EDTA titrimetry per Method Metals-Vol-1.

4. Mercury calibration standard, 0.500 µg/ml. Immediately before performing the determination, dilute 0.500 ml of the mercury stock solution to one liter with 10% (v/v) HCl. Dilute solutions of mercury are not stable[3] and should not be stored. Discard unused solutions and prepare fresh dilutions daily or more frequently.

5. Reducing reagent, 4% (w/v) $NaHCO_3$ and 40% (v/v) hydrazine hydrate in distilled water [or 10% (w/v) $SnCl_2$ in 20% (v/v) HCl].

PROCEDURE

A. Conversion of the Instrument for Mercury Analysis

1. Insert and align the mercury hollow cathode lamp. Adjust the current to 4 ma. Allow 30 min for warmup.

2. Fill the drying tube on the mercury analyzer with anhydrous magnesium perchlorate or barium perchlorate. Place a small plug of glass wool in each end cap.

3. Remove the burner head from the burner body and insert the cell holder and 10-cm quartz cell. Align the cell so it is centered in the optical path.

4. If the gas lines are equipped with quick-disconnect fittings with check valves, disconnect the nebulizing gas line. Otherwise, clamp off the nebulizing gas line with a screw-type pinch clamp. Disconnect the auxiliary support gas line from the burner and attach it to the inlet of the mercury analyzer.

5. Connect the outlet of the mercury analyzer to the quartz cell.

6. Check the condition of the rubber septum and replace it, if necessary.

B. Sodium Hydroxide Scrubber Blank

Pipet 5 ml of the 7N NaOH provided by the requester into each of two 10-ml volumetric flasks. Add 4 ml of conc HCl, dilute to volume with water, and mix well. Process each per Procedure E.

C. Sample Preparation

Pipet 5 ml of the sample into each of two 10-ml volumetric flasks. Add 4 ml of conc HCl, dilute to volume with distilled water, and mix. Process each per Procedure E.

D. Calibration

Use the working curve method of calibration. Process 50, 100, 250, and 500 ng of Hg (ie, 0.1, 0.2, 0.5, and 1.0 ml of the calibration standard) in duplicate per Procedure E.

E. Analysis of Samples

	Operation	Detailed Instruction
1.	Peak in wavelength.	Nominal 253.7 nm; adjust for maximum meter reading in %T mode.
2.	Set backing control.	Full counter clockwise.
3.	Set damping control.	A
4.	Set select switch.	Normal
5.	Set mode switch.	%T
6.	Set slit width.	150 μ
7.	Fill flask with reducing reagent.	100 ml
8.	Turn on and adjust air flow.	15 psig; 3 lpm.
9.	Adjust coarse and fine sensitivity.	Meter deflection 100.
10.	Set mode switch.	ABS
11.	Set scale expansion.	X10
12.	Set zero.	Fine gain control.
13.	Inject sample.	0.5 ml for sample or blank; specified volumes (Procedure D) for standards.
14.	Observe signal on recorder. Wait until signal returns to baseline (about 3 min) before injecting next sample.	If baseline drift is severe, correct with fine sensitivity control between samples.

CALCULATIONS

Draw the baseline for each peak by interpolating with a straight edge. Instrument response is read as peak absorbance minus baseline. Construct a working curve of absorbance vs. concentration and read sample concentrations from the working curve. Average the result from the two or more determinations per sample and report the average corrected for the scrub solution blank. Original sample concentrations are twice the value read from the working curve.

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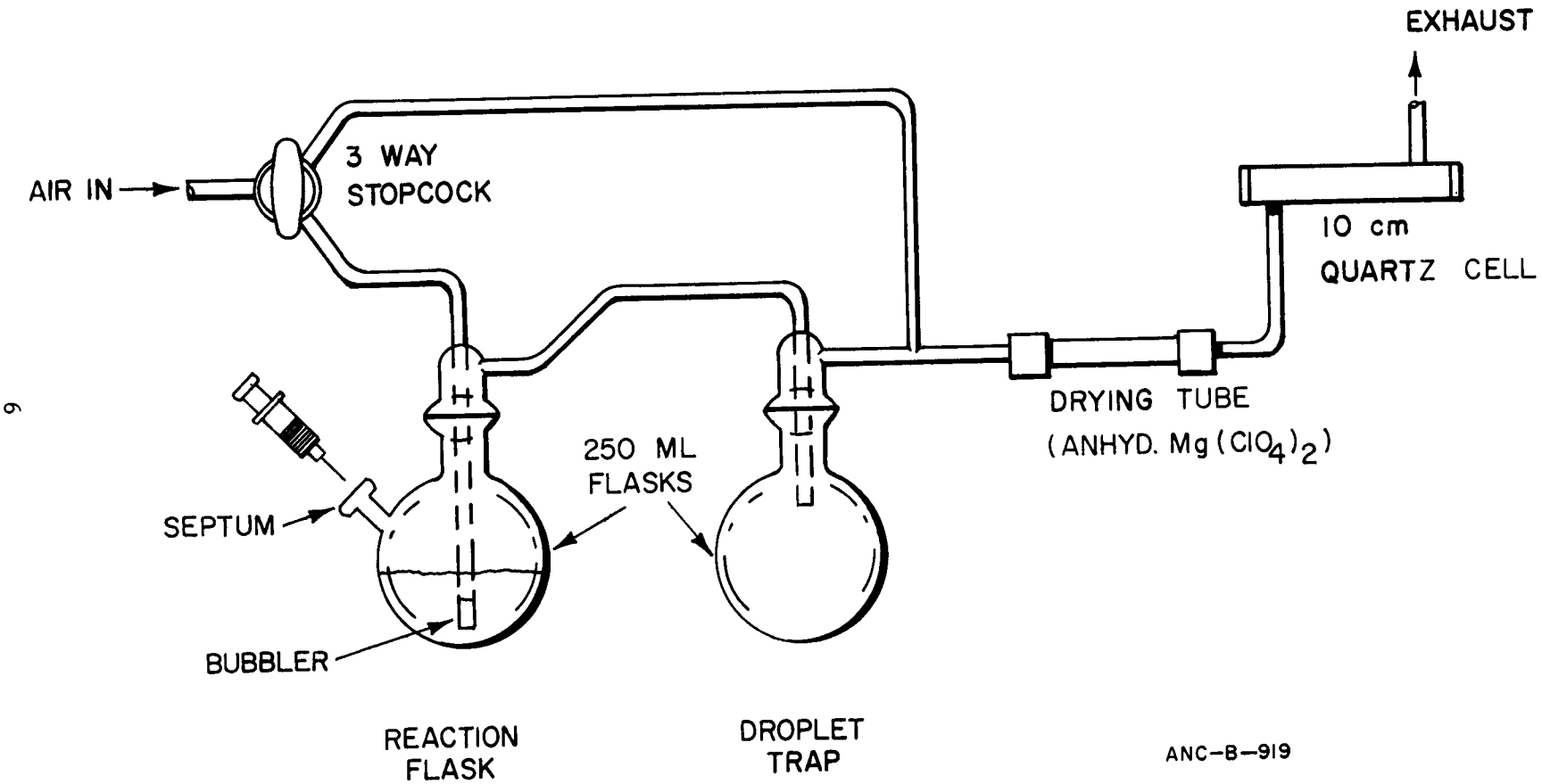

Fig. 1 Mercury analysis kit.

COLORIMETRIC DETERMINATION OF MERCURY WITH DITHIZONE

ABSTRACT

A sensitive, versatile, colorimetric method based on a dithizone extraction is described for the determination of mercury in inorganic and organic samples. Five procedures are included: two for organic solutions, two for inorganic solids, and one for organic materials and aqueous solutions containing dissolved organic matter. The effects of diverse ions on the method are discussed.

APPLICABILITY

This method is applicable to a wide variety of samples including fuel dissolver product, calciner feeds, and calciner off-gas scrub solutions. Also, with appropriate pretreatment, the method is applicable to such samples as calciner feeds containing sucrose, alumina-zirconia calciner solids, and organic materials such as vegetation, cardboard, polyethylene, inks, and paints.

Five procedures, C, D, E, F, and G are recommended for the analysis of the many different types of samples mentioned in the preceding paragraph. Procedures C, D, E and F, patterned after a method recently reported[1], are identical except for differences in the initial steps (Figure 1). Procedure C, the principal procedure, is intended for aqueous samples, especially those with unknown compositions where maximum selectivity is desirable. Procedures D and E are designed for solid inorganic samples (especially waste calciner solids) and Procedure F for organic samples and inorganic samples containing organic matter. In all four procedures, C, D, E, and F, the mercury is initially extracted into dithizone-chloroform, stripped out of the chloroform with sodium nitrite, then reextracted into dithizone-chloroform after destruction of the excess nitrite with hydroxylamine and aniline. Procedure G is simpler and faster than Procedure C and differs from the latter in that only a single extraction is made using twice as much complexer-buffer solution. It is specifically designed for aqueous inorganic samples of known composition, such as the aluminum nitrate calciner feed samples from the Chemical Engineering Section that are free of interferences, or that contain only noninterfering concentrations of potential interferences such as copper. Procedure G should not be used for uncharacterized samples.

The effect of diverse ions for Procedure G are summarized in Table I which lists the known tolerance levels of numerous ions present individually and in groups that simulate the composition of samples actually encountered. Silver(I) at greater than 0.1:1 silver-to-mercury molar ratios and copper(II) at greater than 150:1 ratios are the only known cationic interferences. Iodide and thiosulfate above 50:1 interfere.

Solid Inorganic Samples (Procedure D for High Hg)

Fuse with $K_2S_2O_7$.

↓

Reflux with HNO_3.

↓

Dilute to appropriate volume with water.

↓

Pipet aliquot containing 1 to 35 µg Hg.

↓

Continue per Procedure C, starting at *.

Aqueous Inorganic Samples (Procedure C)

Pipet aliquot containing 1 to 35 µg Hg.

↓

Heat with HNO_3 to oxidize all Hg to Hg(II).

↓

*Extract Hg(II)-dithizonate into $CHCl_3$ from EDTA-citrate medium at pH 2.85±0.35.

↓

**Strip Hg(II) from $CHCl_3$ with $NaNO_2$.

↓

Destroy excess $NaNO_2$ with $NH_2OH \cdot HCl$ and aniline·HCl.

↓

Extract Hg(II)-dithizonate into $CHCl_3$ from EDTA-citrate-monochloroacetate medium at pH 2.85±0.35.

↓

Measure absorbance at 495 mµ.

Organic Samples and Inorganic Samples Containing Organics (Procedure F)

Digest sample with HNO_3 - H_2SO_4.

↓

Dilute with H_2O until $N^a \leq 0.75$.

↓

Destroy N-oxides with $NH_2OH \cdot HCl$ and aniline·HCl.

↓

Extract Hg(II)-dithizonate into $CHCl_3$.

↓

Continue per Procedure C, starting at **.

Solid Inorganic Samples (Procedure E for Low Hg)

Fuse sample with $K_2S_2O_7$ and reflux with HNO_3.

↓

Dilute with water until $N^a \leq 0.75$.

↓

Add $NH_2OH \cdot HCl$ and aniline·HCl and extract Hg(II)-dithizonate into $CHCl_3$.

↓

Continue per Procedure C, starting at **.

Aqueous Inorganic Samples (Procedure G)

Pipet aliquot containing 1 to 35 µg Hg.

↓

Digest with HNO_3 to oxidize all Hg to Hg(II).

↓

Extract Hg(II)-dithizonate into $CHCl_3$ from EDTA-citrate medium at pH 2.85±0.35.

↓

Measure absorbance at 495 mµ.

Fig. 1 Outline of Procedures C, D, E, F, and G.

TABLE I

EFFECT OF INDIVIDUAL IONS AND ION COMBINATIONS
ON PROCEDURE G (AND C)

Ion or Mixture Investigated	Tolerance Level, Ion to Hg Molar Ratio[a,b]
Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cr(III), Cs(I), Fe(III), Ge(IV), Ho(III), In(III), La(III), Mg(II), Mn(II), Mo(VI), Ni(II), Pb(II), Sn(II,IV), Sr(II), Th(IV), Ti(IV), U(VI), V(V), Y(III), Zn(II), Zr(IV).	Each ion individually at 1000
Ag(I)	0.1[c]
Au(III), Pd(II), Pt(IV)	Each ion individually at 50
Cu(II)	150[c], 750[d]
BO_2^-	2000
Br^-	1000
Cl^-	7.5×10^5
I^- , $S_2O_3^=$	50[c]
$PO_4^{\equiv}$	3.0×10^4
$SO_4^=$	1.3×10^5
Synthetic Aluminum - Zirconium Matrix	
Al(III), Zr(IV)	Each at 2000
Cr(VI), U(VI)	Each at 50
Cl^- plus NO_3^-	1×10^4

TABLE I (Continued)

Simulated aluminum fuel dissolver product	
Al(III)	4×10^{4}
Cu(II)	150[c]
Cr(III), U(VI)	Each at 50
Fe(III)	200
Mn(II), Ni(II)	Each at 100
NO_3^-	12×10^{4}
Simulated calciner product fused with $K_2S_2O_7$.	
Al(III), Zr(IV)	Each at 2000
Cr(VI)	50
K(I)	2.4×10^{5}
$SO_4^=$	1.3×10^{5}

[a] Mercury level maintained at 20 μg (1×10^{-4} mM).

[b] Except where noted otherwise, the tolerance level listed is the highest level studied and does not represent the maximum permissible level.

[c] Maximum tolerance level.

[d] Maximum tolerance level, Procedure C.

Procedure C is similar to Procedure G except for the use of two dithizone-chloroform extractions in C. The tolerance levels of diverse ions for Procedure C are therefore expected to be higher than those for Procedure G. For example, the tolerance level of copper(II) is 150:1 for Procedure G and 750:1 for Procedure C.

In all five procedures, strong oxidants that oxidize dithizone interfere when present in sufficiently high concentrations. Oxides of nitrogen formed during the digestion of samples and the oxidation of mercury are the most common interferences. These are removed effectively by hydroxylamine hydrochloride and aniline hydrochloride. After the digestion or oxidation step, brown nitrogen oxide fumes are often observed above the solution. These should be removed by gentle suction prior to the addition of the hydroxylamine and aniline.

With the use of both 1- and 5-cm absorbance cells, the range of the method is 1 to 35 µg of mercury. The maximum sample size for aqueous solutions is 5 ml; for inorganic solids, 0.1 g; and for organic samples, 2 g. Accordingly, the lower limit of determinability is about 0.2 ppm, 10 ppm, and 0.5 ppm, respectively.

DISCUSSION

Potential sources of error include: (a) use of mercury-contaminated glassware, (b) loss of mercury by volatilization during sample preparation and analysis, (c) use of too large a sample aliquot, and (d) incomplete destruction of nitrite prior to the final extraction.

Use of mercury-contaminated glassware is a frequent and serious source of error. All glassware, including new glassware, should be boiled in 4M HNO_3 and rinsed thoroughly with distilled water before use. Do not rely upon the purity of demineralized water. Always use distilled water for all reagents and throughout the method.

Mercury and mercury compounds are quite volatile and can be lost under many conditions. They are volatilized slowly but in significant amounts from boiling acid solutions. They are volatilized quantitatively or nearly so in acidic and basic fusions. Use a reflux condenser for all fusions and lengthy boiling steps.

In this method, the chloroform extract contains blue-green unreacted dithizone and yellow-orange mercury dithizonate, so the observed color varies from blue-green at low levels of mercury to yellow-green when 25 to 35 µg of mercury are present. If the final extract lacks the greenish cast, the capacity of the dithizone could have been exceeded and another, smaller sample should be processed.

Nitrite and nitrogen oxides (NO_2 and NO) that yield nitrite in the presence of water and air oxidize dithizone rapidly and cause erratic, low results. The presence of nitrite is indicated by a gradual "bleaching" of the blue-green dithizone to a golden-yellow oxidation product. The function of the hydroxylamine and aniline during the initial and final extractions is to destroy the nitrite.

Digest organic samples in a hood behind a safety shield to guard against possible explosion and to confine the nitrogen oxide fumes evolved during the digestion. Wear safety glasses.

After each extraction, remove the separatory funnel stoppers carefully to avoid spattering of chloroform or the acidic aqueous solution. This precaution applies to the extractions carried out with the large separatory funnels in Procedures D, E, and F.

Wear latex gloves when handling concentrated acids.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, Pyrex, matched pairs, 1-cm and 5-cm, with covers.
2. Beakers, assorted sizes.
3. Centrifuge tubes, 50-ml.
4. Culture tube, with Teflon-lined screw cap.
5. Digestion apparatus for organic samples (Figure 2).
6. Filter paper, Whatman 41.
7. Fisher Filtrator.
8. Funnels, assorted sizes.
9. Graduated cylinders, 10-ml.
10. Hot plate.
11. Magnetic stirrer, with Teflon-coated stirring bars.
12. Meker burner.
13. Membrane filter, 0.45-μ pore size, with Millipore filtering apparatus.
14. Micro burner.
15. pH Meter, Leeds and Northrup or Beckman, with capillary glass-calomel electrodes or a single-probe glass-calomel electrode.
16. Pipets, macro, volumetric, assorted sizes, with suction bulb.

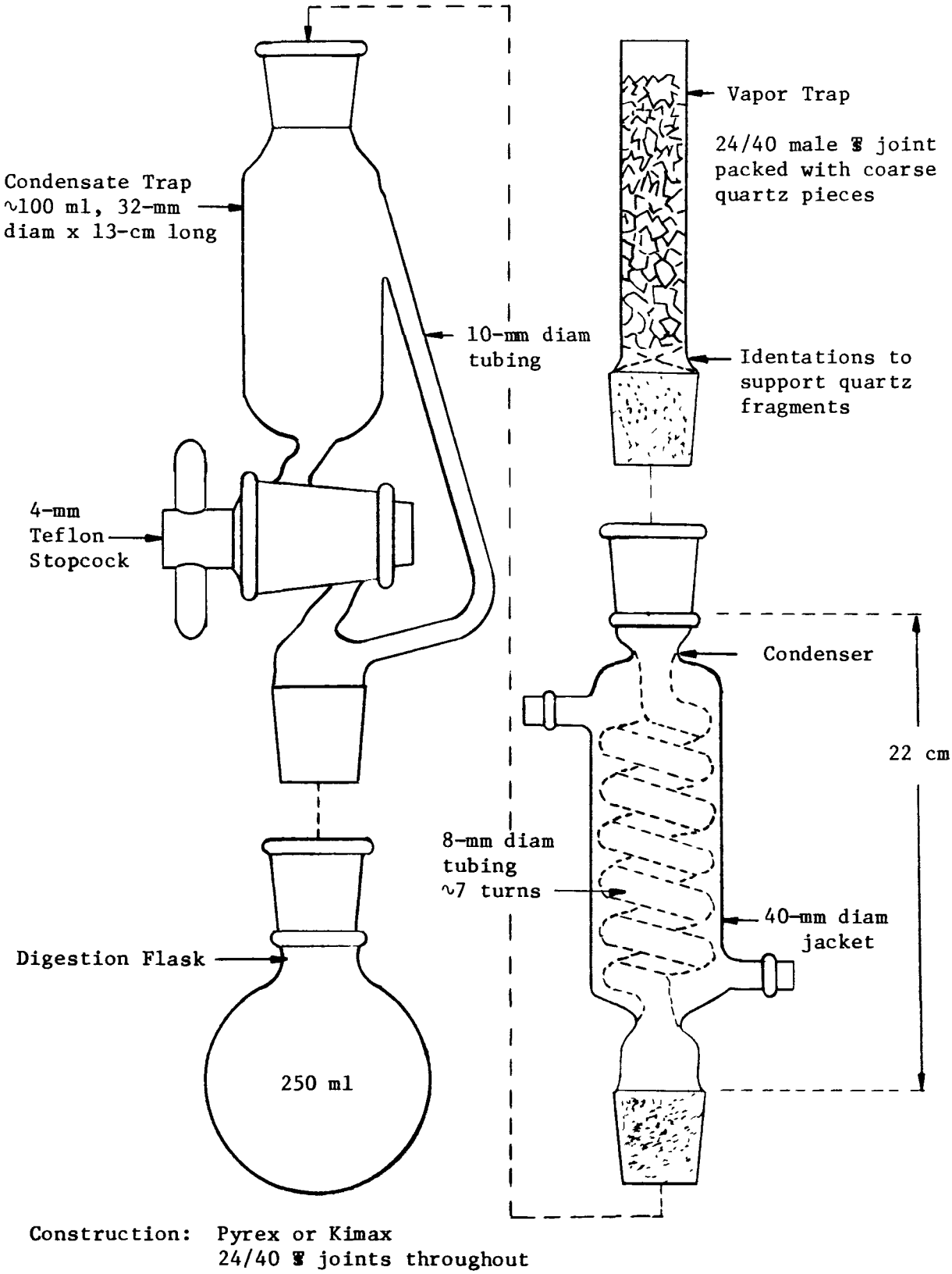

Fig. 2 Digestion apparatus for organic samples.

17. Pipets, micro, assorted sizes, with control syringe.

18. Pipets, Mohr, 5- and 10-ml.

19. Quartz fusion apparatus for inorganic solids. Use a 100-ml round bottom quartz flask or a 35-mm diam x 6-in. quartz test tube with a 24/40 outer joint in conjunction with the condenser illustrated in Fig. 2.

20. Separatory funnels, 60-ml, with Teflon stopcocks.

21. Separatory funnels, 500-ml, with ground glass stoppers and Teflon stopcocks.

22. Spectrophotometer, Beckman Model DU, DK, or B, or Cary Model 14.

23. Variac.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents and throughout the procedure.

1. Ammonium hydroxide, conc.

2. Aniline hydrochloride solution, 0.5M. Add 45 ml of conc HCl to 500 ml of water. Add 46 ml of freshly distilled aniline SLOWLY with efficient stirring. Transfer to a 1-liter volumetric flask and dilute to volume with water. The final solution should be colorless or have only a faint pink or yellow tinge. Store in the dark and prepare a fresh solution every month.

NOTE: The aniline must be added slowly to dilute HCl solution to avoid excessive coloration of the solution.

3. Buffer-complexer reagent. Dissolve 37.22 g of $Na_2EDTA \cdot 2H_2O$, 94.50 g of monochloroacetic acid, and 90.48 g of ammonium citrate in a 2-liter beaker with 1500 ml of distilled water. Use sufficient conc NH_4OH to insure complete dissolution (pH ≈3.5). Dilute to 2 liters with water.

4. Chloroform.

5. Dithizone stock solution, 0.0105 (w/v)% (4×10^{-5} M). Dissolve 0.0525 g of dithizone in chloroform and dilute to 500 ml with chloroform. Store in a refrigerator when not in use.

6. Dithizone solution, 0.00105 (w/v)% (4×10^{-6} M). Pipet 50.00 ml of the 0.0105% stock solution into a 500-ml volumetric flask and dilute to 500 ml with chloroform. Store in a refrigerator when not in use.

7. Hydrochloric acid, 1.0M.

8. Hydroxylamine hydrochloride, 2.5M. Dissolve 174 g of $NH_2OH \cdot HCl$ in 800 ml of distilled water. Filter the solution through a 0.45-μ membrane filter and dilute to 1 liter with water.

9. Mercuric nitrate stock solution, 500 μg/ml. Dissolve 0.5000 g of redistilled mercury metal in 20 ml of 7.5M HNO_3 with heating. Boil gently for 10 min, cool, then dilute to 1 liter with water. Store as 40-ml units in sealed glass ampoules.

10. Mercury calibration standard solutions.

    a. Standard I, 30.00 μg Hg/ml. Dilute 15.00 ml of the mercury stock solution to 250 ml with 0.25M HNO_3.

    b. Standard II, 20.00 μg Hg/ml. Dilute 10.00 ml of the mercury stock solution to 250 ml with 0.25M HNO_3.

    c. Standard III, 8.00 μg Hg/ml. Dilute 4.00 ml of the mercury stock solution to 250 ml with 0.25M HNO_3.

    d. Standard IV, 6.00 μg Hg/ml. Dilute 3.00 ml of the mercury stock solution to 250 ml with 0.25M HNO_3.

11. Nitric acid, conc and 1M.

12. Nitric acid-sulfuric acid digestion mixture. Mix, as needed, conc H_2SO_4 and conc HNO_3 in the ratio of 1:5.

13. Potassium pyrosulfate, $K_2S_2O_7$.

14. Sodium hydroxide, 0.80M. Dissolve 32.0 g of NaOH in water and dilute to 1 liter with water.

15. Sodium nitrite solution, 0.75M. Dissolve 51.76 g of $NaNO_2$ in 500 ml of water and dilute to 1 liter with water. Prepare a fresh solution every month. Store in the dark.

PROCEDURE

NOTE: Use distilled water throughout the procedure.

Mercury(II) reduces to mercury(I) or (0) by reaction with hydroxylamine, especially in weakly acidic or basic solution. Also, it may precipitate as the hydroxide from weakly acidic or neutral solutions. For these reasons, the procedure, once begun, may be interrupted only at those points where the acidity is high and hydroxylamine is absent. These points are at the end of each pretreatment procedure before any dilution or pH adjustment (Steps C-2, D-9, E-2, F-9, and G-2) and at the end of the stripping Step (C-12) when the hydrochloric acid concentration is about 0.9M.

Failure to observe these precautions will lead to low and erratic results.

A. Blank

Process a reagent blank with each set of samples per the procedure selected for the analysis of samples. For aqueous samples, use 3 ml of distilled water in place of the sample. With inorganic solids and organic samples, omit the addition of a sample substitute, but introduce all reagents used for the samples in amounts equal to those used for the samples.

B. Calibration and Bench Standard

Four standards are recommended for this method - two for the high range (to be measured in 1-cm cells) and two for the low range (to be measured in 5-cm cells). If only one type of sample is to be analyzed, two appropriate standards will suffice. However, if the mercury concentrations of the samples vary over a wide range, the use of all four calibration standards will minimize repeat analyses.

Process calibration standards with each run by the same procedure as that used to analyze the samples. Use 1.00-ml aliquots of the appropriate standards. Divide the micrograms of mercury in the standard by the absorbance to obtain the conversion factor. For each of the two groups of standards, the difference between the two factors should not exceed established limits and the average of the two factors should agree with the established conversion factor within specified

limits. If either of these requirements is not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties are still experienced.

C. Analysis of Aqueous Inorganic Samples of Unknown Composition

NOTE: If the levels of diverse ions are known not to exceed the tolerance limits (see APPLICABILITY section), the shorter single extraction procedure (Procedure G) may be used.

1. Pipet an aliquot, 5 ml or less, containing 1 to 35 µg of Hg into a 50-ml centrifuge tube.	The use of a wide-mouth test tube such as a 50-ml centrifuge tube facilitates pH adjustment in Step 6. Refer to the APPLICABILITY section for information on tolerance levels for diverse ions.
2. Add 1 ml of conc HNO_3 and immerse the centrifuge tube in a boiling water bath for 5 min.	Nitric acid oxidizes Hg(0,I), to Hg(II). Prolonged digestion will lead to loss of Hg by volatilization. If brown NO_2 fumes are observed, aspirate the fumes with mild suction before adding the $NH_2OH \cdot HCl$.
3. Cool, dilute to about 15 ml with water, add a small stirring bar and 2 ml of 2.5M $NH_2OH \cdot HCl$, then let stand for 5 min with intermittent stirring.	If the analysis must be interrupted, defer Step 3.
4. Add 1 ml of 0.5M aniline hydrochloride.	

5.	Add 5 ml of the buffer-complexer solution.	
6.	With the aid of a pH meter, adjust the pH to 2.85±0.35 with conc NH_4OH.	The pH is critical. Above 3.5, results are low; below 2.5, EDTA precipitates.
7.	Transfer the sample quantitatively to a 60-ml separatory funnel with water rinses.	
8.	Add approximately 15 ml of 0.00105% dithizone-chloroform solution and shake vigorously for 30 sec. Let the two layers separate, then swirl the separatory funnel to settle the floating droplets of chloroform.	Use polyethylene stoppers.
9.	Drain the lower chloroform layer into a clean 60-ml separatory funnel.	Do not transfer any of the aqueous phase. A small amount of the chloroform layer left in the separatory funnel will be recovered in Step 10. Observe the color of the chloroform solution. If it is golden-yellow or nearly so with very little blue-green color of free dithizone, extract the residual aqueous phase in the original separatory funnel with 10 ml of the 0.00105% chloroform-dithizone solution and drain the chloroform extract into the clean separatory funnel. If the second extract still lacks the blue-green color of free dithizone, discard the sample and process a new, smaller aliquot.
10.	Extract the residual aqueous phase in the original separatory funnel for 15 sec with 5 ml of chloroform and drain the chloroform into the clean separatory funnel.	Do not transfer any of the aqueous phase. Discard the aqueous phase. The two organic phases (Steps 9 and 10) are combined.
11.	To the dithizone-chloroform extract, pipet 10 ml of 1.0M HCl with a volumetric pipet and 1 ml of 0.75M	The NO_2^- destroys the dithizone and returns the mercury to the aqueous phase.

	$NaNO_2$ solution. Stopper and shake for 30 sec.	
12.	Let the two phases separate, then drain and discard the lower chloroform layer.	Take care that none of the aqueous layer is lost in the separation.
13.	To the residual aqueous phase, add 2 ml of 2.5M $NH_2OH \cdot HCl$. React for 5 min with intermittent swirling.	If the analysis must be interrupted, defer Step 13.
14.	Rinse the separatory funnel with a little water, then add 1 ml of 0.5M aniline hydrochloride solution. Swirl to mix.	Rinse the stopper and the neck of the flask carefully to remove any traces of $NaNO_2$ present.
15.	Add 5 ml of the buffer-complexer solution, swirl to mix, then pipet 10 ml of 0.80M NaOH with a volumetric pipet to adjust the pH to the range 2.85±0.35.	The pH at this step is critical. Measure the pH of the blank with a pH meter to see if it is within the required range. If it is not, measure the pH of all samples. Adjust the pH, as necessary, to 2.85±0.35 with 1M HCl or 0.80M NaOH.
16.	Pipet precisely 15.00 ml of 0.00105% dithizone-chloroform solution, stopper, and extract for 15 sec.	The extraction time must be kept short to minimize the extraction of Cu.
17.	Let the phases separate, then drain the lower chloroform phase into a 25-ml screw-cap culture tube. Measure the absorbance of the chloroform phase at 495 mμ against the reagent blank in 1-cm (5 to 35 μg of Hg) or 5-cm (1 to 10 μg of Hg) cells.	When in doubt, measure the absorbance with 5-cm cells first. This will permit subsequent measurements with 1-cm cells. The color of the chloroform-dithizone extract should show the presence of excess unreacted dithizone, i.e., a bluish-green cast. If not, discard the sample and process a new smaller aliquot. The walls of the tube adsorb water droplets which otherwise interfere. If necessary, centrifuge the tube.

Under proper conditions, the color of the chloroform extract is stable for at least 2 hr. If slow but noticeable "bleaching" is observed, the NO_2^- probably was not destroyed adequately in Steps 13 and 14. Discard the sample and process a new one.

18. Record the data on the work sheet and calculate the results as shown on the example work sheet. Report three significant figures.

D. Analysis of Inorganic Solids With Greater Than 100 ppm Levels of Mercury

1. Transfer a 0.1-g sample containing greater than 10 µg of Hg to the quartz fusion apparatus.

This procedure is intended primarily for inorganic solids such as alumina and alumina-zirconia calcined materials that are difficult to dissolve. Dissolve metals and alloys under reflux in appropriate mineral acids and analyze per Procedure C.

2. Add 3.0 g of $K_2S_2O_7$.

3. Assemble the fusion apparatus. Turn on the cooling water and tilt the apparatus to about a 45° angle.

4. With a Meker burner, fuse the sample repeatedly until the melt clears.

5. Turn off the cooling water and return the apparatus to the upright position.

6. Add 6 ml of conc HNO_3 through the condenser and heat the mixture with a micro burner until the point of condensation just reaches the top of the condenser or until the start of bumping.

During fusion, Hg is volatilized into the condenser possibly as metallic Hg. The purpose of the HNO_3 reflux is to recover the volatilized Hg.

7. Cool slightly, turn on the cooling water, and rinse the condenser with 20 to 25 ml of 1M HNO_3.

8. Remove the fusion flask or tube and place it in a boiling water bath until the liquid clears and most of the solids dissolve.

   It is not necessary to dissolve the solids completely.

9. Cool the solution and filter it through a 0.45-μ membrane filter directly into a 250-ml volumetric flask. Use at least three 10-ml portions of 1M HNO_3 for the transfer and washing and a Fisher Filtrator-Millipore setup for the filtration.

10. Dilute to volume with water and mix well.

11. Pipet an aliquot, 25 ml or less, containing 1 to 35 μg of mercury into a 50-ml beaker.

12. Continue per Procedure C beginning at Step 3.

    If the observed net absorbance of the sample corresponds to less than 1 μg of Hg, select a larger aliquot (if this is permissible) in Step 11. With a 25-ml aliquot of the diluted sample, the lower limit of determinability is 100 ppm of Hg in the original solid sample. If greater sensitivity is required, reanalyze the original solid sample per Procedure E.

E. Analysis of Inorganic Solids With Less Than 100 ppm Levels of Mercury

1. Dissolve a 0.1-g sample per Steps 1 through 8 of Procedure D.

2. Cool the solution, then filter the solution through a Whatman 41 filter paper into a 500-ml separatory funnel. Use three 10-ml portions of 1M HNO_3 to rinse the fusion flask and the filter paper.	If the analysis must be interrupted, this is a permissible stopping place.
3. Dilute to 250 ml with distilled water.	The acidity must be reduced to 0.75N or less.
4. Add 5 ml of 2.5M $NH_2OH \cdot HCl$ and let stand for 5 min with intermittent swirling.	
5. Rinse the separatory funnel with water, then add 2 ml of 0.5M aniline hydrochloride solution.	
6. Extract for 30 sec with 10 ml of 0.00105% dithizone-chloroform solution. Drain the lower chloroform phase into a 60-ml separatory funnel.	Considerable pressure is often built up within the separatory funnel. Cover the stopper with a tissue paper and remove the stopper carefully.
7. Repeat Step 6.	
8. Repeat Step 6 using 10 ml of chloroform in place of the dithizone-chloroform solution. Discard the aqueous phase.	
9. Continue per Procedure C beginning at Step 11.	

F. Analysis of Organic Samples and Inorganic Samples Containing Organic Matter

1. Weigh or pipet a sample containing 1 to 35 µg of Hg into the flask of the digestion apparatus (Figure 2).	This procedure has been found to be satisfactory for 2-g samples of organic matter such as vegetation. If larger samples must be processed to reach the desired sensitivity, process separate 2-g samples per Steps F-1 through F-15, combine the dithizone-chloroform and chloroform

		extracts of Steps F-13 through F-15, then complete the determination per Step 16.
2.	Add 15 ml of freshly prepared HNO_3-H_2SO_4 digestion mixture.	
3.	Assemble the digestion apparatus per Fig. 2, turn on the cooling water, and heat the sample with a heating mantle controlled by a Variac. Boil vigorously and collect the distillate in the condensate trap. Continue the digestion until only 2 to 3 ml of acid remains and H_2SO_4 fumes and charring observed.	A Variac setting of 105 to 110 is recommended.
4.	CAUTIOUSLY return the condensate to the digestion flask through the stopcock. If necessary, swirl the flask to loosen solids adhering to the walls of the flask.	
5.	Continue the digestion to the reappearance of H_2SO_4 fumes and charring.	
6.	Repeat Steps 4 and 5 until charring is no longer observed.	The entire digestion normally requires about 1.5 hr.
7.	Return the condensate to the digestion flask, cool slightly, then admit about 50 ml of water through the top of the digestion apparatus.	Admit the water slowly.
8.	Reflux for 5 min, or longer if necessary, to dissolve precipitated sulfate salts.	

9.	Disassemble the digestion apparatus. Rinse each component with water and collect the rinses in the flask.	Rinse the side arm of the condensate trap also. If the analysis must be interrupted, this is a permissible stopping place.
10.	Transfer the contents of the flask quantitatively to a 500-ml separatory funnel with water rinses and dilute to about 400 ml with water.	For quantitative extraction of the Hg, the acidity must be 0.75N or less.
11.	Add 10 ml of 2.5M $NH_2OH \cdot HCl$, mix well, then let stand for 5 min. Swirl intermittently during the 5-min period.	
12.	Add 2 ml of 0.5M aniline hydrochloride solution and mix well.	
13.	Extract the mercury with a 10-ml portion of 0.00105% dithizone-chloroform solution for 30 sec. Drain the lower chloroform layer into a 60-ml separatory funnel.	Considerable pressure is often built up during the extraction. Cover the stopper with a tissue paper and remove the stopper carefully.
14.	Repeat Step 13.	Combine the organic phases.
15.	Repeat Step 13 using 10 ml of chloroform in place of the dithizone-chloroform solution. Discard the aqueous phase.	Combine this organic phase with the two previous organic phases in the 60-ml separatory funnel.
16.	Continue per Procedure C beginning at Step 11.	

G. Analysis of Aqueous Inorganic Samples of Known Composition (Single Extraction Procedure)

NOTE: If the composition of the sample is unknown or is known to contain diverse ions at concentrations that exceed the tolerance limits (see APPLICABILITY section), Procedure C must be used.

1.	Pipet an aliquot, 5 ml or less, that contains 1 to 35 µg of Hg into a 50-ml	The sample must not contain more than 4 mM of Al nor more than 0.03 mM of Cu(II). See

centrifuge tube.	Table I for the tolerance levels of other ions.
2. Add 1 ml of conc HNO_3 and immerse the centrifuge tube in a boiling water bath for 5 min.	Nitric acid oxidizes Hg(0,I) to Hg(II). Prolonged digestion will lead to loss of Hg by volatilization.
3. Cool, dilute to about 25 ml with water, add 2 ml of 2.5M $NH_2OH \cdot HCl$, then let stand 5 min with intermittent swirling.	If much brown NO_2 fumes are observed, aspirate the fumes with mild suction before adding the $NH_2OH \cdot HCl$.
4. Add 1 ml of 0.5M aniline hydrochloride.	
5. Add 10 ml of the complexer-buffer solution and adjust the pH to 2.85±0.35 with conc NH_4OH.	The pH is critical. Above 3.50 results are low; below 2.50 EDTA precipitates.
6. Transfer the sample quantitatively to a 60-ml separatory funnel with water rinses.	
7. Add exactly 15.0 ml of 0.00105% dithizone-chloroform solution and extract for exactly 15 sec.	The extraction time must be kept short to minimize the extraction of Cu.
8. Drain the lower chloroform layer into a 50-ml culture tube.	The walls of the culture tube adsorb water droplets which otherwise interfere. If necessary, centrifuge the tube.
9. Measure the absorbance of the chloroform extract against the reagent blank at 495 mμ in 1-cm (5 to 35 μg of Hg) or 5-cm (1 to 10 μg of Hg) cells.	When in doubt, measure the absorbance with 5-cm cells first. This will permit subsequent measurements with 1-cm cells. The color of the chloroform-dithizone extract should show the presence of excess unreacted dithizone, i.e., a bluish-green cast. If not, discard the sample and process a new smaller aliquot.

Under proper conditions, the color of the chloroform extract is stable for at least 2 hr. If slow but noticeable "bleaching" is observed, the nitrite probably was not destroyed adequately in Steps 3 and 4.

10. Record the data and calculate the results as shown on the example work sheet. Report three significant figures.

REFERENCES

1. Analytical Methods Committee, "The Determination of Small Amounts of Mercury in Organic Matter", Analyst, 90 (1965) p 515.

October 1967

R. Fullerton
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Mercury

CHARGE NUMBER _____ PROCEDURE Hg - Color-I

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance vs water	Net Absorbance	Conversion Factor µg/Abs	Hg in Aliquot Analyzed µg	Hg Corrected for Bias µg			RESULT µg Hg/ml
Reagent Blank		0.281							
Std, 30 µg		0.809	0.528	56.82					
Std, 20 µg		0.631	0.350	57.14					
			$\bar{X}$	56.98					
1051	2ml	0.689	0.408	56.98	23.2	24.5 ± 1.3			12.2 ± 0.65
	(No Dilution)								

ANALYZED BY _____ DATE _____

CALCULATIONS:

C = Conversion Factor = $\frac{\text{µg Hg in Std}}{\text{Net Absorbance}}$

$C' = \frac{20}{0.350} = 57.14$; $C'' = \frac{30}{0.528} = 56.82$

$\bar{X} = 0.5(C' + C'') = 0.5(57.14 + 56.82) = 56.98$ µg Hg/Abs Unit

Sample 1051

Net Absorbance = 0.689 − 0.281 = 0.408

µg Hg = 0.408 (56.98) = 23.2 µg

$\text{Result} = \frac{E}{\text{Sample Vol}} = \frac{24.5 \pm 1.3}{2} = 12.2 \pm 0.65$ µg Hg/ml

APPROVED BY _____

TITRIMETRIC DETERMINATION OF METALS BY NaCeEDTA "REPLACEMENT" EDTA TITRIMETRY

ABSTRACT

A versatile, reliable EDTA titration procedure is described for the determination of 37 metallic elements. In this method, an unmeasured excess of a stoichiometric sodium-cerium-EDTA octahydrate ($NaCeEDTA \cdot 8H_2O$) salt is added to an acidic solution of the metal to be determined, the solution is adjusted to pH 5.6 with pyridine, and titrated with standard EDTA to a xylenol orange or arsenazo end point. With but few exceptions, the method is not selective, hence is suitable only for relatively pure metal ion samples.

APPLICABILITY

This versatile procedure, based on a recent investigation[1], is applicable to the determination of 37 metallic elements (Table I). Except for the alkali and alkaline earth metals which do not form stable EDTA complexes at pH 5.6, the method is not selective and is intended primarily for the analysis of individual pure metals, metal salts, and metal salt solutions. It is, however, extremely reliable, hence suitable for the standardization of solutions of titratable metals.

In this method, the metal being determined reacts with NaCeEDTA to release cerium(III). The effects of diverse anions on the titration depend on the complexing ability of the anion and the chemical properties of cerium(III) and the metal ion. The complexing tendency of common inorganic anions increases in the order $ClO_4^- < NO_3^- < Cl^- < SO_4^= < F^- \approx H_xPO_4^{-(3-x)}$. Sulfate in large amounts, fluoride, and phosphate should not be present. Also, citrate, oxalate, tartrate and other organic complexing agents that form stable complexes will interfere and should be absent. Noncomplexing anions at very high concentrations adversely affect the titration; hence, samples with high levels of acid should be evaporated initially. Prior digestion with nitric and perchloric acids adequately destroys organic complexers.

Table I lists, for each of the 37 determinable metals, the required oxidation state and pertinent remarks concerning the determination. Samples of various pure metals, oxides, and salts frequently are received for purity verification. To facilitate such analyses and the preparation of standard metal solutions, suggested dissolution procedures for the most frequently encountered sample types are included in Table I.

As described in this method, the sample aliquot taken for titration should contain 0.05 to 0.45 mM of metal. Assuming a practical sample volume limit of 50 ml, the lowest concentration determinable is 0.001M. The precision of the determination increases with increasing amounts of metal.

TABLE I

METALS DETERMINABLE AND PERTINENT REMARKS

Metal	Required Oxidation State	Remarks
Am, Bk, Cm, Cf	+ 3	Serious alpha hazards; work in glove box.
Bi	+ 3	Chloride interferes.
		Bismuth metal dissolves readily in hot conc HNO_3. Salts such as $Bi(NO_3)_3 \cdot 5H_2O$ should be dissolved in ~0.5M HNO_3 to prevent hydrolysis.
Cd	+ 2	The metal and oxide dissolve readily in warm 8M HNO_3.
Co	+ 2	At high Co(II) levels, the pink Co(II)-EDTA complex imparts a reddish tinge to the yellow xylenol orange.
		The metal is soluble in warm 8M HNO_3.
Cu	+ 2	Use arsenazo indicator. Copper(II) reacts "irreversibly" with xylenol orange at the end point.
		Dissolve Cu metal with hot 8 to 12M HNO_3.
Fe	+ 3	For selectivity (see Method Fe-Vol-1 of this Manual), Fe(III) can be preseparated by extraction into 2-octanone from 7M HCl[2].
		Dissolve Fe metal with hot 8M HNO_3 or aqua regia; Fe_2O_3 with hot conc HCl.
Ga	+ 3	

TABLE I (Cont'd)

Metal	Required Oxidation State	Remarks
Hf	+ 4	This method is not suitable for the determination of Hf metal which requires complexing acids for dissolution. Nitrate and chloride solutions of Hf should be adjusted to 3M in HNO_3 and boiled for 10 min to break up polymers[3].
Hg	+ 2	See Method EDTA Std Prep-1 of this Manual. Dissolve Hg metal with hot 8M HNO_3 under reflux.
In	+ 3	Dissolve In metal with hot 8 to 12M HNO_3, the oxide with warm 6M HCl or conc $HClO_4$.
Lanthanides (La - Lu)	+ 3	The lanthanides are determinable by direct EDTA titration to a xylenol orange end point; hence, NaCeEDTA·$8H_2O$ may be omitted. Lanthanide oxides are soluble in warm 6M HCl. Reduce Ce(IV) to Ce(III) with NH_2OH·HCl.
Mn	+ 2	Manganese(II) is determinable by this method; however, it is best determined by direct EDTA titration to an Eriochrome Black T end point in ammoniacal tartrate-hydroxylamine medium[4].
Ni	+ 2	For selectivity, Ni(II) can be preseparated by precipitation with dimethylglyoxime from tartrate medium (See Method Ni-Vol-1 of this Manual). Dissolve Ni metal with hot 8 to 12M HNO_3.

TABLE I (Cont'd)

Metals	Required Oxidation State	Remarks
Pb	+ 2	Dissolve the metal with hot 8M HNO_3, PbO with warm 3M HNO_3 or 6M $HClO_4$. PbO_2 is dissolved best by a conc HCl-conc $HClO_4$ sequential treatment.
Sc	+ 3	See Lanthanides.
Tl	+ 3	For selectivity, preseparate thallium from EDTA medium as TlI. Hot fuming HNO_3 expels I^- and converts Tl(I) to Tl(III)[5].
V	+ 4	Reduce V(V) to V(IV) in warm acid medium with $NH_2OH \cdot HCl$.
Y	+ 3	Like the lanthanides and Zn, Y(III) is determinable by direct EDTA titration to a xylenol orange end point and does not require the addition of NaCeEDTA. Dissolve the oxide with hot 6M HCl.
Zn	+ 2	See Method EDTA Std Prep-1 of this Manual. Like the lanthanides and Y, Zn(II) is determinable by direct EDTA titration to a xylenol orange end point and does not require the addition of NaCeEDTA. Titrate slowly near the end point to avoid overshooting it.
Zr	+ 4	This method is not applicable to Zr metal which must be dissolved in complexing acids. To depolymerize nitrate and chloride solutions of zirconium, adjust the sample to 3M in HNO_3 and boil for 10 min[3].

DISCUSSION

Except in the case of copper where arsenazo must be used, xylenol orange, 3',3"-Bis{[bis(carboxymethyl)amino]methyl}-5,5"-dimethylphenolsulfonephthalein, or arsenazo, o-(1-dihydroxy-3,6-disulfo-2-naphthylazo) benzenearsonic acid, may be used interchangeably. The preferred indicator is xylenol orange which gives a violet to red to yellow end point transition with better color contrast than the violet to red to reddish-orange transition of arsenazo.

The most serious potential source of error is diverse metal contamination through water and reagents and through apparatus, especially magnetic stirring bars that attract magnetic materials. If burets with Teflon-plugged stopcocks are used, the stopcock should be disassembled and cleaned before use.

In aqueous medium buffered at pH 5.60±0.25 with pyridine, cerium(III) can be titrated with EDTA to a sharp, easily discernible xylenol orange (violet to yellow) or arsenazo (violet to reddish-orange) end point. This is the basis of this method for the determination of metallic elements by EDTA titrimetry. The titration is basically a replacement titration procedure. A stoichiometric 1:1 cerium(III)-EDTA salt is added to an acidic solution of a metal to be determined. The metal preferentially reacts with the EDTA and liberates cerium(III) which subsequently is titrated with EDTA. The release of cerium(III) is dependent on the relative stabilities of the cerium(III)-EDTA complex ($K_f = 10^{16}$) and the EDTA complex of the metal being determined. If the test metal has an EDTA complex with more than 10^3 higher stability than cerium(III)-EDTA, cerium(III) is released in an amount equal to the test metal and its measure is a measure of the metal being determined. If the test metal forms an EDTA complex weaker than cerium(III)-EDTA or equal in stability or only slightly stronger, the release of cerium(III) is not quantitative. However, sufficient cerium(III) is released, even by metals with EDTA complex stabilities as low as 10^{14}, to react with the indicator and provide a distinct end point.

SAFETY PRECAUTIONS

There are no particularly hazardous operations. Use caution in the handling of strong acids. Avoid excessive inhalation of pyridine vapors.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150-ml.

2. Buret, 10-ml with 0.05-ml graduations.

3. Hot plate.

4. Magnetic stirrer and Teflon-coated stir bars.

5. Medicine dropper bottles.

6. pH Meter, with glass-calomel electrode system.

7. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents. Reagents for the dissolution of solid samples are not included.

1. Ammonium hydroxide, conc.

2. Arsenazo indicator, 1% (w/w) mixture with NH_4NO_3. Intimately grind 0.5 g of arsenazo with 50 g of NH_4NO_3. Supply the indicator mixture in a small screw-cap jar with a small glass or plastic spatula.

3. EDTA, standard 0.05M solution. Prepare as directed in Method EDTA Std Prep-1 of this Manual.

4. Perchloric acid, conc.

5. Pyridine.

6. Sodium cerium EDTA salt. Prepare $NaCeEDTA \cdot 8H_2O$ per the directions given in Method Fe-Vol-1 of this Manual. Supply the salt in a wide-mouth screw-cap jar with a small plastic or glass scoop designed to deliver 0.5±0.05 g of the reagent.

7. Xylenol orange, 0.2% (w/v). Dissolve 0.2 g of xylenol orange in 100 ml of water.

PROCEDURE

A. Blank

No blank determination is necessary for this method. If properly prepared $NaCeEDTA \cdot 8H_2O$ is used, the indicator blank is generally 0.01 ml or less.

B. Titration of Metals

1. Pipet a sample aliquot containing 0.05 to 0.45 mM of metal into a 150-ml beaker.	For best precision, select an aliquot with more than 0.2 mM of metal.
2. Consider the acidity of the sample. If the sample aliquot contains more than 15 meq of acid or if the sample acidity is unknown, continue with Step 3, then proceed to Step 5. If it contains less than about 3 mM of acid, continue with Step 4. If it contains 4 to 15 mM of acid, continue with Step 5.	
3. Add 0.5 ml (10 drops) of conc $HClO_4$ and evaporate the solution with moderate heat to the appearance of $HClO_4$ fumes.	Because Hg(II) is partially volatilized from boiling acid solutions, mercury samples should not be evaporated.
4. Add 0.5 ml (10 drops) of conc $HClO_4$.	If the $HClO_4$ was added in Step 3, omit it here.
5. Dilute to 125 ml with water.	
6. Add 0.5 g of NaCeEDTA·$8H_2O$ and stir for 2 min.	The NaCeEDTA·$8H_2O$ may be omitted in the determination of lanthanides, yttrium, and zinc. For convenience, use continuous magnetic stirring from this step on.
7. Add 5 drops of 0.2% xylenol orange. If Cu(II) is being determined, substitute arsenazo for xylenol orange. Add sufficient arsenazo - NH_4NO_3 mixture to give a reddish-orange color.	
8. Noting the number of drops, add pyridine dropwise to the appearance of a red or violet coloration, then add two times as much additional pyridine. If the red or violet coloration	This procedure adjusts the pH to the desired value of 5.60±0.25. Periodically, check the pH of the solution to ascertain that the pH is within the range 5.35 to 5.85.

	does not appear after the addition of 1 ml of pyridine, add conc NH_4OH dropwise until it appears, then add 2 ml of additional pyridine.	
9.	Titrate with 0.05M EDTA to a change from violet to yellow (xylenol orange) or violet to reddish-orange (arsenazo).	The end point color transition is altered by the presence of colored metal-EDTA complexes. See Table I. The titration must be carried to that point where no color change occurs after the addition of another increment of titrant, i.e., to the complete dissociation of the violet cerium-xylenol orange or cerium-arsenazo complexes.
10.	Record the data and calculate the results as described on the example work sheet. Report all results to four significant figures.	The results are calculated in terms of molarity. To convert molarity to mg/ml, multiply the molarity by the atomic weight of the metal.

REFERENCES

1. S. S. Yamamura, "Use of Sodium Cerium EDTA for the Titrimetric Determination of Metallic Elements with EDTA", Anal. Chem., 40 (October 1968) pp 1898-1901.

2. S. S. Yamamura, "Determination of Iron(III) by (Ethylenedinitrilo)-tetraacetic Acid Replacement Titrimetry Following Selective Separation by Column Extraction", Anal. Chem., 36 (1964), p 1858.

3. B. C. Sinha and S. DasGupta, "Direct Complexometric Determination of Zirconium(IV) in Relation to Polymerization", Analyst, 92 (1967), p 558.

4. F. J. Welcher, The Analytical Uses of EDTA, New York: Van Nostrand, 1958, pp 217-220.

5. See Reference 4, pp 182-183.

S. S. Yamamura
January 1968

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION "Metal X"

CHARGE NUMBER _____ PROCEDURE Metals - Vol - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA. $a_0/d_1/a_1/d_2/a_2$	Molarity of EDTA	Volume of EDTA Used, ml	mMole "Metal X" in Samp Aliquot	mMole "Metal X" Corr'd for Bias				RESULT Molarity
"Metal X"	5.00 ml (All used)	0.05025	7.00	0.3518	0.3520 ±0.0009				0.07040 ± 0.00018M

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = AB = 0.05025(7.00) = 0.3518 \text{ mmole}$$

$$\text{Result} = \frac{D}{\text{Samp Vol}} = \frac{0.3520 \pm 0.00092}{5.00}$$

$$= 0.07040 \pm 0.00018 \text{ M}$$

APPROVED BY _____

Ni-Color-1; June 1972

COLORIMETRIC DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME

ABSTRACT

Nickel is complexed with dimethylglyoxime in an alkaline carbonate-tartrate medium containing potassium persulfate oxidant. The absorbance is measured at 465 nm.

APPLICABILITY

Dimethylglyoxime is highly selective for nickel(III) in the presence of other cations. This procedure is applicable to steel solutions, aluminum and magnesium alloys, uranyl salts, and other electrolytes which are soluble in a tartrate-carbonate solution at a high pH.

Highly colored solutions can be analyzed without interference by processing a sample blank without chromogen in addition to the usual blank. The color from the nickel itself in the sample blank is negligible at the concentrations involved in this procedure.

Chromium(III) has no effect up to at least a 1:1 chromium-to-nickel mole ratio. Cobalt and manganese are without effect up to a 1:2 ratio. Up to 6 mg of uranium can be tolerated. The maximum tolerance limits of these ions have not been established.

Known interferences are silver and copper, but both of these can effectively be removed by electrolysis.

The working range is 2 to 150 µg of nickel using 1-cm cells for the 20- to 150-µg range and 5-cm cells for the 2- to 25-µg range. With a maximum sample volume of 20 ml, the lowest determinable concentration is 0.10 µg Ni/ml.

DISCUSSION

The nickel(III)-dimethylglyoxime is formed in a tartrate-carbonate medium containing persulfate. For full color development, the pH must be controlled at 12.0±0.5. Below 11.5 pH, other complexes with varying optical properties may form. A high concentration of carbonate is necessary to complex diverse cations which would otherwise precipitate at high pH. Tartaric acid is used specifically to complex iron; hence, it could be omitted if iron is absent. This method specifies the use of tartaric acid in all cases because tartrate has no detrimental effect. At least 20 min must be allowed for complete color development. The fully developed color is stable for at least 24 hr.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 50-ml.

2. Flasks, volumetric, 50-ml.

3. pH meter, Fisher Accumet or equivalent.

4. Pipets, macro and micro, assorted sizes with control syringe and suction bulb.

5. Spectrophotometer, Beckman DU, Cary Model 14, or equivalent with 1-cm and 5-cm cells.

B. Reagents

Note: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium carbonate solution, 20%. Dissolve 200 g of $(NH_4)_2CO_3$ in water and dilute to 1000 ml. Filter to remove undissolved particles.

2. Dimethylglyoxime solution, 1%. Dissolve 5 g of dimethylglyoxime $(CH_3CNOH)_2$ in 500 ml of 95% ethanol.

3. Nickel standard stock solution. Dissolve 1.0000±0.0005 g of nickel metal in 50 ml of 1:1 HNO_3 and dilute to 1000 ml. Confirm the concentration by EDTA titrimetry per Method Metals-Vol-1. Use the EDTA-determined value if the difference exceeds 0.1%.

4. Nickel calibration standards.

   a. Calibration standard I, 50 µg Ni/ml. Dilute 5.00 ml of the stock solution to 100.0 ml.

   b. Calibration standard II, 100 µg Ni/ml. Dilute 10.00 ml of the stock solution to 100.0 ml.

5. Nickel bench standard, 60 µg Ni/ml. Dissolve 0.63291 g of NBS SRM number 101E (use a Teflon beaker with cover) in 20 ml of 7M HCl with heat. Add 10 ml of 8M HNO_3 and heat gently for 20 min. Add 4 drops conc HF and heat gently for 10 min then cool and dilute to 1 liter with water.

6. Nickel controls. Prepare controls to cover the method range using the same procedure given in Step 5 for the Bench standard.

7. Sodium hydroxide solution, 5N. Dissolve 100 g of NaOH in 100 ml of water, cool, and dilute to 500 ml. Filter and store in a polyethylene bottle.

8. Potassium persulfate solution, 5%. Dissolve 50 g of $K_2S_2O_8$ in water and dilute to 1000 ml.

9. Tartaric acid solution, 25% (w/v). Dissolve 250 g of tartaric acid in water and dilute to 1000 ml.

PROCEDURE

A. Blanks

Blanks are necessary to correct for (a) the introduction of nickel via the reagents and (b) the absorbance of colored ions at 465 nm. The former is corrected with a reagent blank, the latter with a sample blank.

Prepare the reagent blank using a 2-ml portion of water, per Procedure D beginning with Step 2. Prepare the sample blank, using an aliquot identical to that used for the sample itself, per Procedure D omitting Step 7.

B. Calibration Standards

Process a set of calibration standards with each series of samples per Procedure D beginning with Step 1. Use a 1-ml portion of each for samples to be measured in 1-cm cells (20- to 150-µg range) and a 200-µl portion of each for samples to be measured in 5-cm cells (2- to 25-µg range). Divide the micrograms of nickel by the net absorbance to obtain the conversion factors. The difference between the two conversion factors should not exceed the limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor within the specified limits. The conversion factor is about 210 µg Ni/Abs unit when absorbance measurements are made in 1-cm cells with a Cary Model 14 or Beckman DU spectrophotometer. If either or both specifications are not met, reprocess the calibration standards. Contact your supervisor if difficulties persist.

C. Bench Standards

Process a bench standard (1-ml aliquot of nickel plus an aliquot of an appropriate diverse ion matrix as provided by the Quality Control Laboratory) each time the calibration standards are processed. If the result of the bench standard does not fall within specified limits, reprocess the bench standard and samples. Contact your supervisor if difficulties persist.

D. Sample Analysis

1. Pipet an aliquot of 20 ml or less containing 2 to 150 µg of Ni into a 50-ml beaker.

   For best results, select a sample with 20 to 150 µg of Ni and measure the absorbance in a 1-cm cell.

   If the sample is colored, pipet an identical aliquot into another 50-ml beaker and process it as a sample blank.

2. Add 1 ml of tartaric acid and mix.

3. Add 10 ml of $(NH_4)_2CO_3$ reagent. Mix by swirling.

4. Add 10 ml of $K_2S_2O_7$ reagent. Mix by swirling.

5. Using magnetic stirring, adjust the pH of the solution to 12.0±0.5 by the addition of 5N NaOH.

   For maximum reliability, maintain the pH within the range 11.8 to 12.3.

6. Transfer the solution to a 50-ml volumetric flask with distilled water rinses.

7. Add 1 ml of dimethylglyoxime reagent to all samples except those intended to be sample blanks.

8. Dilute to volume with distilled water and mix well.

9. Allow at least 20 min for color development and measure the absorbance at 465 nm in the appropriately sized cells after setting the absorbance of the reagent blank at 0.000.

   The developed color remains stable for at least 24 hr.

10. Record the data and calculate the results as shown on the example worksheet. Report 3 significant figures.

P. A. Anderson
June 1972

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Nickel

CHARGE NUMBER _____ PROCEDURE Ni Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Net Absorbance	Conversion Factor	mg Ni in Aliquot Analyzed	mg Ni corrected for Bias			RESULT mg Ni/ml
Rgt Blank		0.000							
50 µg std		0.234		213.68					
100 µg std		0.446		214.59					
			$\bar{X}$ =	214.14					
Sample	2.00 ml	0.502	0.424		90.80	89.23 ± 3.61			44.6 ± 1.8
Sample Blank		0.078							

ANALYZED BY _____ DATE _____

CALCULATIONS:

C = conversion factor = $\frac{\text{mg Ni in std}}{\text{Net Absorbance}}$

$C' = \frac{50}{0.234} = 213.68$ $\quad C'' = \frac{100}{0.466} = 214.59$

$\bar{X} = 0.5(C' + C'') = 0.5(213.68 + 214.59) = 214.14$ mg Ni/Abs.unit

Sample

Net Absorbance = 0.502 - 0.078 = 0.424

mg Ni = 0.424 (214.14) = 90.80 mg

Result = $\frac{E}{\text{Sample Volume}} = \frac{89.23 \pm 3.61}{2.00} = 44.62 \pm 1.80$ mg Ni/ml

APPROVED BY _____

COMPLEXOMETRIC DETERMINATION OF NICKEL FOLLOWING SEPARATION WITH DIMETHYLGLYOXIME

ABSTRACT

Nickel at milligram levels is separated selectively as the dimethylglyoxime complex from ammoniacal tartrate medium, then determined by EDTA (ethylenediamine tetraacetic acid) replacement titrimetry using sodium cerium EDTA.

APPLICABILITY

In ammoniacal solutions containing tartrate, dimethylglyoxime is a highly selective, quantitative precipitant for nickel[1]. Most metals including most members of the acid sulfide group at moderate (few milligrams) levels, are not precipitated by dimethylglyoxime. Some, such as Co, Cu, and Zn consume reagent by the formation of soluble complexes and necessitate the addition of extra reagent for quantitative precipitation of the nickel[2]. The most serious interferences are Co(II) at high levels, Au, Fe(II), and Pd. Gold and palladium are encountered only infrequently and iron normally exists in the noninterfering (III) oxidation state or is oxidizable to it. The method is, therefore, essentially specific for nickel and is applicable to a wide variety of complex samples. It is particularly well suited for the determination of nickel in aqua regia or nitric acid-sulfuric acid solutions of Fe-Cr-Ni steels. This has been confirmed by interference studies, at a constant 0.25-mmole nickel level, which show that iron(III) at a 10:1 iron-to-nickel molar ratio and chromium at a 5:1 ratio do not interfere. In the presence of both iron and chromium at these same ratios, cobalt at a 1:2 ratio give results about 4% high. The covalent nickel(II)-dimethylglyoxime complex is soluble in ethanol. To avoid losses through solubility, the ethanol concentration must be kept below 50%.

The range prescribed for this method is 2 to 28 mg ($\sim$0.03 to 0.45 mM) of nickel. Assuming a practical sample limit of 50 ml, the lowest determinable concentration is 0.04 mg Ni/ml. Samples with nickel concentrations less than this are to be analyzed by Method Ni-Color-1. In fact, for best results, all samples with nickel concentrations less than 0.1 mg/ml should be analyzed by the spectrophotometric method.

DISCUSSION

The final titrimetric measurement of the nickel involves the addition of excess sodium cerium EDTA salt ($NaCeEDTA \cdot 8H_2O$) and titration of

the liberated cerium with EDTA to a xylenol orange (XO) end point. The reactions involved are:

$$Ni^{+} + NaCeEDTA \xrightarrow{H^{+}} NiEDTA^{=} + Ce^{+} + Na^{+} \quad (1)$$

$$Ce^{+++} + H_2EDTA^{=} \xrightarrow{pH5.6\pm0.25} CeEDTA^{-} + 2H^{+} \quad (2)$$

$$\underset{\text{(violet)}}{Ce(III)\text{-}XO} + H_2EDTA^{=} \xrightarrow{pH5.6\pm0.25} CeEDTA^{-} + \underset{\text{(yellow)}}{XO} \quad (3)$$

Nickel(II) stoichiometrically reacts with NaCeEDTA per Equation 1 to release an equivalent quantity of cerium(III) which is titrated with EDTA per Equation 2 . The end point is indicated by the release of yellow uncomplexed XO from the violet cerium(III)-XO complex as shown in Equation 3 . Reaction 1 is slow and incomplete in neutral solution. Increasing the acidity favors the decomposition of the less stable cerium(III)-EDTA complex and the quantitative complexation of the nickel. The end point color transition is violet to red to orange to amber in the presence of nickel. The titration must be carried to the amber color which corresponds to the complete dissociation of the cerium(III)-XO complex.

In aqueous solution, sodium cerium EDTA slowly decomposes, presumably through air oxidation of cerium(III)-EDTA to cerium(IV)-EDTA and subsequent degradation of EDTA by cerium(IV). The reagent, therefore, should be stored and used as the solid.

SAFETY PRECAUTIONS

Strong nitric acid is used to dissolve the nickel-dimethylglyoxime precipitate. Use of rubber gloves is recommended.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150- and 250-ml.
2. Buret, 10-ml, calibrated in 0.05-ml divisions.
3. Dropping bottles.
4. Filter paper, 11-cm diam, Whatman 41 or equivalent.
5. Funnels.
6. Hot plate, Chromalox or equivalent. If available, a combination stirrer-hot plate is ideal.

7. Stirring rods, glass, 6-in.

8. Magnetic stirrer and stirring bars.

9. pH meter with glass-calomel electrode system.

10. Pipets, macro and micro, assorted sizes, with suction bulb and syringe.

11. Speedyvap watch glasses, 3-in.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium hydroxide, conc (in a dropping bottle).

2. Ammonium tartrate, 2M. Dissolve 368 g of diammonium tartrate in water and dilute to 1 liter with water.

3. Dimethylglyoxime reagent, 0.15M. Dissolve 17.4 g of dimethylglyoxime in 95% ethanol and dilute to 1 liter with 95% ethanol. Store in a dark bottle.

4. EDTA solution, 0.05M. This reagent, prepared and standardized per Method EDTA-Prep-1 of this manual, is continuously stocked by the Quality Control Laboratory.

5. Hydrochloric acid, conc.

6. Nickel bench standard, 3.00 mg/ml (0.05112M). Dissolve 3.0000 ±0.0005 g of pure nickel in 25 ml of conc HCl and 5 ml of conc HNO_3. Transfer the solution quantitatively to a 1-liter volumetric flask with water rinses. Add 44.4 g of $Cr(NO_3)_3 \cdot 9H_2O$, 165.8 g of $Fe(NO_3)_3 \cdot 9H_2O$, and 11.0 g of $UO_2(NO_3)_2 \cdot 6H_2O$. Dissolve and dilute to volume with water. This solution is 0.11M in Cr(III), 0.41M in Fe(III), and 0.022M in U(VI).

7. Nickel controls. Prepare per the directions for the bench standard except vary the nickel concentrations to cover the range 0.5 to 5.5 mg Ni/ml. Provide 4 controls.

8. Nitric acid, conc (in a dropping bottle).

9. Pyridine.

10. Sodium cerium EDTA salt. A stoichiometric sodium cerium EDTA salt ($NaCeEDTA \cdot 8H_2O$) prepared according to the directions given in Method Fe-Vol-1 will be supplied by the Quality Control Laboratory.

11. Xylenol orange indicator solution, 0.2%($^{W}/_{V}$). Dissolve 0.10 g of the solid reagent in 50 ml of water.

PROCEDURE

A. Blank.

A blank need not be processed for this method.

B. Bench Standard.

Process a 5-ml aliquot of the nickel bench standard per Procedure C beginning at Step 2. Acceptable limits will be specified by the Quality Control Laboratory.

C. Analysis of Samples.

1. Pipet a sample aliquot containing 2 to 28 mg (∿0.03 to 0.45 mM) of Ni into a 150-ml beaker.

   The reliability of the results increases with increasing amounts of Ni. For best results, select a sample aliquot with greater than 10 mg of Ni.

   This sample should not contain more than 15 meq of acid. This is equivalent to 1 ml of conc HNO_3.

2. Add 5 ml of 2M ammonium tartrate, dilute with water to about 100 ml.

3. Heat the sample on a hot plate just to boiling.

4. Remove the sample from the hot plate and using magnetic stirring, add 3 ml of conc NH_4OH. The sample should be ammoniacal at this point. Test for the presence of ammonia vapor above the solution with moist red litmus paper. If NH_3 vapors are detected, proceed to Step 5. If NH_3 vapors are not observed, add conc NH_4OH in 0.5-ml increments until basic.

   Before testing for NH_3 siphon or blow off the vapors above the solutions.

5. Pipet 10 ml of 0.15M dimethylglyoxime reagent and stir.

6. Rinse down the walls of the beaker with water, then let the sample stand, without stirring, for a minimum of 30 min.

Protect the samples from rust and dust particles with any appropriate cover.

7. Filter the nickel-dimethylglyoxime precipitate on a Whatman 41 filter supported on a funnel. Use water rinses to transfer the precipitate. Collect the waste filtrate in a 250-ml beaker.

Quantitative transfer of the precipitate is not necessary; however, by the end of Step 9, extraneous metal ions must be removed completely. Do not remove the magnetic stirring bar.

8. Rinse the beaker thoroughly with water and pass the rinses through the filter.

The flocculent nickel-dimethylglyoxime precipitate tends to creep and run down the sides of the beaker. To prevent this, use a glass stirring rod to transfer the sample to the filter funnel.

9. Wash the filter and precipitate thoroughly with water to remove diverse metal ions.

10. Transfer the filter plus precipitate to the original 150-ml beaker, then using the medicine dropper, soak the filter evenly with 20 to 25 drops (1 ml) of conc HNO_3. Do not add too much HNO_3 because it will cause a poor end point.

11. Add about 60 ml of water, and using a combination stirrer-hot plate, heat the solution to boiling while stirring it continuously. Stir until the filter disintegrates.

If a stirrer-hot plate is not available, heat the solution to boiling on a conventional hot plate, then stir the solution on a magnetic stirrer until the filter breaks up. Use a cover glass and avoid loss of sample through excessive boiling.

12.	Chill to ambient temperature and dilute to about 120 ml with water.	
13.	Add 0.5 g of NaCeEDTA salt and stir for 2 min.	
14.	Add 10 drops xylenol orange indicator and 10 drops of conc NH_4OH.	To prevent localized hydrolysis of Ce(III), the solution should be stirred continuously when the NH_3 is being added.
15.	Counting the drops, add pyridine until the olive solution just turns color (bluish-purple), then add twice as much additional pyridine.	This method of pH adjustment gives a 2:1 pyridine to pyridinium ratio and a pH of about 5.6.
16.	Titrate with standard 0.05M EDTA to a change from violet to olive. Toward the end of the titration, take a buret reading, then add another small increment of titrant. The end point is that point where the next increment does not produce a noticeable change in color.	The color transition is violet to red to orange to olive. The final orange to olive transition requires about 0.02 ml of titrant.
17.	Record the data and calculate the results as shown in the example worksheet. Report all results to three significant figures.	

REFERENCES

1. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Applied Inorganic Analysis, New York: Wiley, 1953, pp 404-412.

2. G. E. F. Lundell and J. I. Hoffman, Outlines of Methods of Chemical Analysis, New York: Wiley, 1938, pp 111-112.

November 1971
J. A. Rindfleisch
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Nickel

CHARGE NUMBER _____ PROCEDURE Ni-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	wt of Tare, g	wt of Tare + Sample, g	wt of Sample, g	EDTA, M	EDTA, ml	Ni in sample Aliquot, mg	Ni Corrected for Bias, mg	RESULT
SS-1	0.5550g/50ml/ml	0.5000	1.0550	0.5550	0.05033	5.31	15.7	15.4±0.6	139±5mgNi/g
SS-2	5.00 ml (Entire Aliquot Used)				0.05033	5.52	16.3	16.0±0.6	3.2±0.1 mgNi/ml

ANALYZED BY _____ DATE _____

CALCULATIONS:

SS-1 $F = 58.69^{*} DE$

$= 58.69(0.05033)(5.31) = 15.7$ mg Ni

$$\text{Result} = \frac{Gd_1}{0.5550\,a_1} = \frac{(15.4 \pm 0.6)(50)}{(0.5550)(10)} = 139 \pm \text{mg Ni/g}$$

* 58.69 = atomic weight of nickel.

APPROVED BY _____

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM

ABSTRACT

Niobium is extracted as a yellow benzoylphenylhydroxylamine (BPHA)[a] complex into toluene from a 1OM HCl medium containing fluoride and thiourea. The yellow Nb-BPHA complex is measured directly at 375 mμ or converted to a more intensely yellow Nb-BPHA-thiocyanate complex and measured at 365 mμ.

APPLICABILITY

This method, based on an Argonne National Laboratory method [1] for the determination of niobium in fissium alloys, is highly selective, hence is applicable to a wide variety of samples including solutions of uranium and solutions of uranium-aluminum, uranium-stainless steel, and uranium-zirconium fuels.

As noted in the abstract, two procedures are described, Procedure D based on measurement of the Nb-BPHA complex and Procedure E based on measurement of the Nb-BPHA-SCN complex. Extensive studies of the effects of diverse ions have been conducted for both procedures. Table I lists the tolerance levels of diverse ions for each procedure and Table II defines the effects of ions that do or could interfere. For both procedures, the most serious interferences are ions of Ta, Ti, V, and W which cannot be tolerated except in microgram amounts. The observed effects are strong negative interference for high levels of tungsten and all levels of vanadium and strong positive interference for low levels of tungsten and all levels of tantalum and titanium. Nitrate, because of its common occurrence, is a serious potential interference. When its level exceeds 2 mM, the nitrate must be expelled by evaporating the sample to sulfuric acid fumes per Procedure F.

The working range is 5 to 160 μg of niobium in Procedure D and 1 to 35 μg of niobium in Procedure E. If no preliminary evaporation is made, the maximum sample volume is 4 ml for Procedure D and 5 ml for Procedure E. With these volumes, the lowest determinable concentrations are 1.25 μg Nb/ml and 0.2 μg Nb/ml by Procedures D and E, respectively. With prior evaporation, which is permissible, concentrations down to about 0.02 μg Nb/ml are determinable.

[a] Benzoylphenylhydroxylamine also is identified as N-phenylbenzohydroxamic acid.

TABLE I

KNOWN DIVERSE ION TOLERANCE LEVELS FOR PROCEDURES D AND E [a]

Ion[b]	Tolerance Level (mM) Procedure D	Procedure E	Ion[b]	Tolerance Level (mM) Procedure D	Procedure E
Al(III)	1.0	0.75	Ni(II)	1.0	0.3
Actinides[c]	0.5[c]	0.5[c]	Platinum Metals	0.05	0.05
Alkalies(I)	2.0	1.0	Re(VII)	not studied	0.025
Alkaline Earths(II)	1.0	0.5	Si(IV)	not studied	0.04
Bi(III)	0.25	0.05	Sn(II,IV)	3.5	3.5
Cd(II)	1.0	0.2	Ta(V)	interferes; tolerance level not established	
Ce(IV)	0.25	0.1	Th(IV)	0.5	0.25
Co(II)	1.0	0.2	Ti(IV)	not established	0.0002[d]
Cr(III)	1.0	0.6	U(VI)	1.0	1.0
Cr(VI)	0.25	0.1	V(IV,V)	0.005[d]	0.005[d]
Cu(II)	0.5	0.5	W(VI)	0.005[d]	0.0025[d]
Fe(III)	0.5[d]	2.0[d]	Y(III)	0.5	0.1
H(I)	30	30	Zr(IV)	1.0	1.0
Hg(II)	0.25	0.2	Borate	1.0	1.0
In(III)	0.25	0.1	Citrate	5.0	5.0
Lanth-anides(III)	0.5[d]	0.5[d]	Fluoborate	8	8
Mg(II)	2.0	0.4	Fluoride	10[d]	10[d]
Mn(II)	1.0	0.2	Nitrate	2[d]	2[d]
Mo(VI)	0.5	0.1	Oxalate	2.5	5.0
Perchlorate	12	12			
Phosphate	7.5[d]	5[d]			
Sulfate	18	18			

[a] Based on data of R. Villarreal and S. A. Barker of Argonne National Laboratory and also from independent studies by the authors. Except where noted, the tolerance values listed are the highest levels studied and do not represent the maximum tolerance level. In the studies of the effects of diverse ions, the niobium level was maintained at 100 µg for Procedure D and 10 µg for Procedure E.

[b] Metal ions were studied as chloride, sulfate, or alkali metal salts; anions as the acid.

[c] Thorium and uranium were the only actinides studied; neptunium, plutonium, and the transplutonics are not expected to interfere at levels up to about 0.5 mM.

[d] Maximum tolerance above which interference is observed.

TABLE II

EFFECTS OF IONS THAT INTERFERE

	Procedure D[a]		Procedure E[b]	
Ion	Level of Ion	Effect	Level of Ion	Effect
Fe(III)	1.0 mM	+3.5%		
NO_3^-	>2 mM	erratic high results	>2 mM	erratic high results
Ta(V)	1.0 mg	+20%	0.005 mg	+11%
Ti(IV)	0.05 mg	+8%	0.020 mg	+7%
	0.5 mg	+75%		
	10 mg	+125%		
V(IV, V)	0.5 mg	-5.6%	1.0 mg	-20%
	12.5 mg	no extraction of Nb		
W(VI)	5 mg	+12%		
	10 mg	-20%		
	100 mg	no extraction of Nb		

[a] Based on studies at a niobium level of 100 µg.

[b] Based on studies at a niobium level of 10 µg.

DISCUSSION

Procedure D, based on measurement of the Nb-BPHA complex, involves an extraction of the Nb-BPHA complex into toluene from a 10M HCl medium containing fluoride and thiourea, a scrub of the toluene extract with 10M HCl, and a spectrophotometric measurement of the Nb-BPHA complex in the toluene. Procedure E is similar to Procedure D except that after the scrub step, the Nb-BPHA-toluene solution is contacted with thiocyanate (SCN^-) in an approximately 3M HCl medium to form the Nb-BPHA-SCN complex. For both procedures, the reactivity of the niobium is very important. The hydrochloric acid concentration must be greater than 9M during the extraction and scrub steps. The 10M HCl scrub is a necessary step in Procedure D.

Although the niobium extracts quantitatively, the Nb-BPHA color is not developed fully during extractions from fluoride media. The full color develops when the Nb-BPHA-toluene solution is scrubbed with 10M HCl devoid of fluoride.

Unless complexed by strong complexers such as oxalate, niobium readily hydrolyzes in dilute acid media including those containing fluoride. Standards and, when possible, solid samples, therefore, should be prepared with an oxalic acid medium. When hydrolysis or polymerization is suspected, an initial fuming with sulfuric acid must be performed.

Other potential sources of difficulty are the introduction of color-producing contaminants and the occasional appearance of cloudiness during the absorbance measurements. Glass should not be used in the sample preparation or in the final determination under conditions where the glass is attacked. The occasional cloudiness of the toluene solution, attributed to water-toluene-emulsions, can be minimized by close adherence to the recommended procedures.

SPECIAL SAFETY PRECAUTIONS

Use protective equipment while handling the acids and during the extraction. Toluene is quite volatile and may generate pressure during the extraction. Uncap the extraction bottle cautiously.

APPARATUS AND REAGENTS

A. Apparatus

1. Constant, rapid delivery dispensing equipment, 4-, 10-, and 15-ml, such as Cantipets.

2. Graduated cylinders, 10- and 25-ml.

3. Pipets, macro and micro, assorted sizes with syringe control and rubber suction bulb.

4. Pipets, Mohr, 5- and 10-ml.

5. Pipets, Mohr, 5-ml, plastic.

6. Platinum crucible or dish.

7. Polyethylene bottles, screw-cap, 2- and 4-oz.

8. Spectrophotometer, Beckman Models DU or DK or Cary Model 14 with 1-cm cuvettes made of borosilicate glass or silica (quartz).

9. Vacuum wash train equipped with a 1-liter suction flask and a 2-ft length of plastic tubing terminating with a drawn-out, fine-tipped polyethylene tube.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium thiocyanate (NH_4SCN) solution, 25% (w/v). Dissolve 250 g of NH_4SCN in water and dilute to 1 liter. Transfer the solution to a 2-liter separatory funnel and extract with 100 ml of hexone (methylisobutyl ketone) for 2 to 3 min. Separate and discard the hexone and extract the NH_4SCN solution with 100 ml of chloroform to remove residual hexone. Drain and discard the chloroform, then transfer the solution through a fluted filter paper into a 1-liter reagent bottle.

2. Benzoylphenylhydroxylamine (BPHA) solution, 1% (w/v) in acetone. Dissolve 2.00 ± 0.05 g of BPHA in acetone and dilute to 200 ml with acetone.

3. Diverse ion matrix solution. Prepare 1M solutions of $AlCl_3$, $CrCl_3$, $FeCl_3$, $NiSO_4$, $UO_2(NO_3)_2$, and $ZrOCl_2$, each in 1M HCl. Mix these solutions in the ratio: 15 Zr, 10 Al, 10 Fe, 5 Cr, 5 Ni, and 5 U. This mixture is 0.3M in Zr, 0.2M in Al and Fe, and 0.1M in Cr, Ni, and U.

4. Fluoride complexer solution, 14M in HF and 2M in HBF_4. Dilute 125 ml of 48% HF plus 88 g of 49% HBF_4 to 250 ml with water. Store this solution in an 8-oz polyethylene bottle.

5. Hydrochloric acid, conc (12M), 10M, and 4M.

6. Niobium stock standard, 1.000 mg Nb/ml. Dissolve 0.2500±0.0005 g of pure niobium metal in a 2-oz polyethylene bottle with a minimum of a 4 to 1 mixture of conc HF and conc HNO_3. Using 10 ml of 9M H_2SO_4 for rinsing, quantitatively transfer the niobium solution to a platinum crucible or dish. Evaporate to fumes of sulfuric acid, then let the sample fume for 10 min without spattering. Cool slightly, add 5 ml of conc H_2SO_4 and continue the evaporation until a clear solution is obtained. Cool the sulfuric acid solution, then transfer it to a 250-ml volumetric flask with 0.3M oxalic acid rinses. Dilute to volume with 0.3M oxalic acid and mix thoroughly.

7. Niobium calibration standards I and II, 100 and 125 µg Nb/ml, respectively, for Procedure D. Dilute 20.00 ml and 25.00 ml of the 1 mg/ml stock standard to 200 ml with 0.3M oxalic acid solution.

8. Niobium calibration standards III and IV, 20.0 and 25.0 µg Nb/ml, respectively, for Procedure E. Dilute 4.00 ml and 5.00 ml of the 1 mg/ml stock standard to 200 ml with 0.3M oxalic acid solution.

9. Niobium bench and control standards. Per the calibration standards, prepare dilutions from the 1.000 mg/ml niobium stock standard to cover the concentration range 0.0005 to 0.16 mg Nb/ml.

10. Oxalic acid solution, 1M. Dissolve 22.5 g of oxalic acid in water and dilute to 250 ml with water.

11. Stannous chloride solution, 40% (w/v). Dissolve 40 g of $SnCl_2 \cdot 2H_2O$ in 75 ml of conc HCl, then dilute to 100 ml with conc HCl. If necessary, heat gently to obtain a clear solution. Prepare a fresh solution after 2 weeks.

12. Sulfuric acid, conc.

13. Thiourea, saturated aqueous solution. Add 12 g of thiourea to 100 ml of water and mix until no more dissolves.

14. Toluene.

PROCEDURES

A. Preparation of Reagent Blank

Process a 2-ml portion of water by the same procedure used to process the calibration standards and to analyze the sample(s).

B. Preparation of Calibration Standards

Two pairs of calibration standards are provided: Standard I and II (100 and 125 µg Nb/ml, respectively) for analyses by Procedure D and standards III and IV (20.0 and 25.0 µg Nb/ml, respectively) for analyses by Procedure E. Process an appropriate pair of standards with each series of samples.

Divide the weight of niobium in each standard by its net absorbance to obtain the calibration factor. The difference between the factors for the two standards should not exceed established limits. Also, the average of the two factors should agree with the established calibration factor within specified limits. If either or both of these specifications are not met, reprocess another pair of standards. Consult your supervisor if difficulties persist.

The molar absorptivities of the Nb-BPHA and Nb-BPhA-SCN complexes are 10,900 and 33,875, respectively; hence, the theoretical calibration factors are 171 for Procedure D and 41.0 for Procedure E.

C. Analysis of Bench and Control Standard

Process a bench standard (1 ml of the niobium bench standard plus 1 ml of the diverse ion mixture) each time calibration standards are processed. Separate bench standards are provided for each procedure. If the result for the bench standard does not fall within specified limits, reprocess the bench standard and samples. Notify your supervisor if difficulties persist.

D. Analysis of samples (Nb-BPHA Procedure)

Note: The range of this procedure is 5 to 160 µg of niobium.

1.	With a graduated cylinder or constant-volume dispenser, deliver 15 ml of conc HCl to a 2-oz polyethylene bottle.	If the analysis must be interrupted, stop after Step 5. Use Procedure F for samples high in NO_3^- and for samples that are suspected to contain hydrolyzed species of Nb.
2.	Add 2 ml of the 40% $SnCl_2$ reagent and mix.	
3.	Pipet a sample aliquot of up to 4 ml containing between 5 and 160 µg of Nb.	
4.	Add 4.75 ml of conc HCl for every 1 ml of sample above 2 ml to adjust the HCl concentration to 10M, then mix.	The HCl concentration must be above 9M for quantitative extraction of the Nb. If the sample volume is 2 ml or less, proceed to Step 5.
5.	Add 0.5 ml of the 14M HF-2M HBF_4 solution and mix.	Mohr pipets are adequate for Steps 5, 6, and 7. Use a plastic pipet for the HF-HBF_4 solution.
6.	Add 0.5 ml of the saturated thiourea solution and mix.	
7.	Add 2 ml of the 1% (w/v) BPHA solution, mix well, and let stand for a minimum of 2 min.	The BPHA must be reacted with the Nb for a minimum of 2 min before extraction. After the 2 min period, the extraction should be carried out without delay.
8.	Pipet exactly 20.00 ml of toluene into each bottle.	Proceed to Step 8 while waiting.
9.	Cover the bottle securely with a screw-cap and extract vigorously for 2 min.	
10.	Let the phases separate, then remove the lower aqeous layer with a fine-tipped plastic medicine dropper attached to a vacuum train.	Here as well as in Step 14, it is permissible to remove a small portion of the upper toluene phase.

11. With a graduated cylinder or constant-volume dispenser, deliver 15 ml of 10M HCl.

12. Extract vigorously for 30 sec.

13. Centrifuge the bottle for several minutes.

14. Remove and discard the lower layer.

15. Transfer the clear toluene solution to a dry 1-cm cell (with a micro transfer pipet or by pouring) and measure the absorbance against toluene at 375 mμ.

    The Nb-BPHA-toluene solution in the extraction bottle is stable for at least 1 hr. Once transferred to a cell and placed in the spectrophotometer, the color gradually fades; hence, the measurement should be made right away.

    Transfer the solution to the cell without agitating the solution in the bottle. For best results, flow the solution onto the nonoptical sides of the cell.

16. Record the data and calculate the results as described on the example worksheet. Report all results to three significant figures.

E. Analysis of Samples (Nb-BPHA-SCN Procedure)

Note: The range of this procedure is 1 to 35 μg of niobium.

1. To a 2-oz polyethylene bottle, deliver 15 ml of conc HCl with a graduated cylinder or constant-volume dispenser.

   If the analysis must be interrupted, stop after Step 5. Use Procedure E for samples high in NO_3^- and for samples suspected to contain hydrolyzed species of Nb.

2. Add 1 ml of 40% $SnCl_2$ solution.

3. Pipet a sample aliquot up to 5 ml containing 1 to 35 μg of Nb.

4.	Add 4.75 ml of conc HCl for every 1 ml of sample above 2 ml and mix.	This adjusts the HCl concentration to the necessary 10M level. If the sample volume is 2 ml or less, proceed to Step 5.
5.	Add 0.5 ml of the 14M HF-2M HBF_4 solution and mix.	A Mohr pipet is adequate for Steps 5, 6, and 7. Use a plastic pipet for Step 5.
6.	Add 0.5 ml of the saturated thiourea solution and mix.	
7.	Add 1 ml of the 1% BPHA solution, mix well, and let stand for a minimum of 2 min.	After the 2-min reaction, the extraction should be carried out as soon as possible. Perform Step 8 while waiting for the BPHA to react.
8.	Pipet exactly 15.00 ml of toluene into the bottle.	
9.	Cover the bottle securely with a screw-cap and extract vigorously for 2 min.	
10.	Let the phases separate, then with a fine-tipped plastic medium dropper attached to a vacuum train, remove and discard the lower layer.	Here and in Steps 12 and 16, it is permissible to remove a small amount of the upper toluene phase.
11.	Let the phases separate and remove and discard the lower phase.	
13.	With a graduated cylinder or dispenser, deliver 15 ml of 4M HCl to the bottle.	
14.	Deliver 4 ml of the 25% thiocyanate solution to the bottle.	
15.	Extract vigorously for 1 min to develop the Nb-BPHA-SCN complex.	
16.	Centrifuge for several minutes and remove the lower aqueous phase.	

17.	Transfer the clear toluene solution (with a micro transfer pipet or by pouring) into a 1-cm cell and measure the absorbance against toluene at 365 mμ.	Transfer the solution to the cell without agitating the solution in the bottle. For best results, flow the solution onto the non-optical sides of the cell. The color is stable for at least 1 hr.
18.	Record the data on the worksheet and calculate the results as described on the example worksheet. Report all results to three significant figures.	

F. Analysis of Samples That Require Prior Sulfuric Acid Fuming

1.	Pipet a suitable aliquot (i.e., suitable for either Procedure D or E) into a platinum dish or crucible.	This procedure is designed to expel nitrate and to dissociate hydrolyzed Nb species. A platinum vessel is recommended because most Nb samples will contain F^-. The use of platinum limits this procedure to solutions other than aqua regia. In the absence of F^-, aqua regia solutions can be processed with glass apparatus.
2.	Add 1 ml of conc H_2SO_4, evaporate the sample to the appearance of SO_3 fumes without spattering, then fume for 5 min.	
3.	Chill the crucible, then cautiously add 2 ml of water and 5 ml of conc HCl.	
4.	Heat the crucible GENTLY and swirl the contents of the crucible to dissolve the salts.	Strong heating causes undesirable excessive volatilization of HCl.
5.	Quantitatively transfer the clear solution to a 2-oz polyethylene bottle using 10 ml of conc HCl for the rinses.	
6.	Add 2 ml of 40% $SnCl_2$ (Procedure D) or 1 ml of 40% $SnCl_2$ (Procedure E) and continue per Procedure D or E beginning at Step 5.	

REFERENCES

1. Robert Villarreal, Spencer A. Barker, "A Rapid and Selective Method for the Spectrophotometric Determination of Niobium", Anal. Chem., 41 (April 1969) pp 611-613.

S. S. Yamamura
M. E. Kussy
January 1969

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Niobium

CHARGE NUMBER _____ PROCEDURE Nb-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance vs Toluene	Net Abs.	Calib Factor	µg Nb in Test Aliquot	µg Nb Corr'd for Bias			RESULT mg Nb/ml
Rgt Blank		0.012							
Std, 100 µg Nb		0.611	0.599	166.9					
Std, 125 µg Nb		0.757	0.745	167.8					
				$\bar{X}_2$ = 167.35 µg Nb/abs unit					
Sample X	0.50ml /100ml /4.00ml	0.392	0.380		63.6	64.0 ± 0.6			

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Calib Factor} = C = \frac{\mu g\ Nb}{\text{Net abs}} = \frac{100}{0.599} = 166.9 \quad ; \quad C' = \frac{125}{0.745} = 167.8$$

$$\bar{X}_2 = \frac{166.9 + 167.8}{2} = 167.35\ \mu g\ Nb/\text{abs unit}$$

$$D = BC = (0.380)(167.35) = 63.6\ \mu g\ Nb$$

$$\text{Result} = \frac{E\ (100)}{0.50\ (4)} = \frac{64.0 \pm 0.6\ (100)}{0.50\ (4)} = 3200 \pm 30\ \mu g\ Nb/ml$$

$$= 3.20 \pm 0.03\ mg\ Nb/ml$$

APPROVED BY _____

DETERMINATION OF INORGANIC NITRATE AND AMMONIA

ABSTRACT

Inorganic nitrate is reduced to ammonia with Devarda's alloy in a sodium hydroxide medium, the ammonia is distilled, collected in boric acid, and titrated with standard acid. Ammonia is determined separately by omitting the Devarda's alloy.

APPLICABILITY

This method is applicable to aqueous solutions and to solids that either are soluble in sodium hydroxide or from which nitrate and ammonia are leachable by sodium hydroxide. Nitrite also reduces to ammonia and therefore is an interference. However, the procedure is used for many samples which contain both nitrate and nitrite with the results reported as total nitrate equivalent. Ammonia and compounds which release alkaline vapor during the distillation also are interferences when nitrate is determined.

By omitting the Devarda's alloy, ammonia can be determined in the presence of nitrate.

Nitrate and ammonia can be determined separately. The result with Devarda's alloy present is the sum of the two. The result for ammonia, with Devarda's alloy omitted, is subtracted to give nitrate.

The range of the method is 0.25 to 4.5 mM of distillable ammonia. The maximum, practical sample aliquot volume is about 450 ml. Thus, the lower concentration limit is 5×10^{-4} M.

DISCUSSION

In sodium hydroxide media, inorganic nitrate and nitrite are reduced to ammonia by Devarda's alloy, an alloy of aluminum, copper, and zinc. The ammonia is distilled and absorbed in a boric acid solution. This solution then is titrated with standard acid to a bromcresol green - methyl red mixed indicator end point. Boric acid is not ionized significantly at the pH value of the titration end point to affect the titration. The end point transition of the bromcresol green - methyl red mixed indicator is green to gray to gray-pink to pink. Best results are obtained by controlling the addition of indicator and titrating to the first noticeable appearance of pink [4].

Major causes of low recovery are poor connections in the distillation apparatus, failure to seal the system immediately after adding the sodium hydroxide and the Devarda's alloy, and incomplete absorption of ammonia by the boric acid absorbing solution[4]. Ammonia losses from incomplete absorption are minimized by using a delivery tube with small orifices and increasing the depth of the boric acid absorber solution by dilution with water. Occasionally, ammonia losses through faulty connections are apt to occur. These losses can be kept to a minimum by processing the samples without delay as directed in Procedure C. Causes of high results are a carry over of sodium hydroxide due to too vigorous distillation and absorption of ammonia fumes from the laboratory atmosphere caused mainly by having bottles of ammonium hydroxide near the apparatus.

SAFETY PRECAUTIONS

Concentrated sodium hydroxide damages eyes and skin severely. Wear rubber gloves when handling the reagent and when washing the Kjeldahl flasks from completed analyses. If the reagent contacts the skin or eyes, wash immediately with copious quantities of water followed by boric acid rinsings. In case of eye incidents, contact the nurse or Health Physics personnel.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 50-ml, graduated in 0.1-ml increments.

2. Distillation apparatus, Kjeldahl, consisting of electric heaters, condenser section, and connections. Commercial units are available from most laboratory supply companies.

3. Flasks, Erlenmeyer, 500-ml.

4. Flasks, Kjeldahl, 800-ml.

5. Graduated cylinders, assorted sizes.

6. Pipets, macro and micro, assorted sizes, with suction bulbs and control syringes.

7. Traps, Kjeldahl.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Bench standard. Dilute 128 ml of conc HNO_3 to 1 liter. Standardize against Tris(hydroxymethyl)aminomethane using methyl red indicator.

2. Boric acid solution. Dissolve 40 g of H_3BO_3 per liter of water.

3. Bromcresol green-methyl red mixed indicator. Dissolve 2 g of bromcresol green and 1 g of methyl red per liter of ethanol.

4. Devarda's alloy.

5. Sodium hydroxide, 15M.

6. Sulfuric acid, standard, 0.1000N.

PROCEDURE

A. Blank

Process a blank per Procedure C omitting Step 5.

B. Bench Standard

Analyze a 1.00-ml aliquot of the bench standard per Procedure C. Acceptable limits will be specified by the Quality Control Laboratory.

C. Samples

NOTE: To determine alkaline volatile matter such as ammonia, omit the Devarda's alloy, Step 8.

1. Add 50 ml of the boric acid solution plus 50 ml of water to a 500-ml Erlenmeyer flask.	
2. Add exactly 5 drops of the indicator solution to the Erlenmeyer flask.	Add exactly 5 drops to obtain reproducible end points.
3. Immerse the exit tube of the distillation apparatus into the bottom of the Erlenmeyer flask.	If not immersed deeply, NH_3 will be lost.

4.	Start the flow of cooling water through the condenser.	
5.	Pipet a sample aliquot or weigh a solid sample that contains 0.25 to 4.5 mM of distillable NH_3 into an 800-ml Kjeldahl flask.	The usual maximum sample aliquot is about 450 ml; however, see Step 7. Highest reliability is obtained toward the upper level of this range.
6.	Dilute to a total volume of 450 ml with distilled water.	
7.	Add 50 ml of 15M NaOH. If the sum of NO_3 and NH_3 is being determined, proceed immediately to Step 8. If only NH_3 is being determined, immediately attach the flask to the distillation apparatus and proceed to Step 9.	The total volume of solution in the flask is limited to 50 ml. The sample aliquot volume in Step 5 must be selected accordingly. Ammonia rapidly volatilizes at room temperature from NaOH solutions.
8.	Add 5 g of Devarda's alloy and immediately attach the flask to the distillation apparatus.	Nitrate is reduced rapidly to volatile NH_3. Secure the Kjeldahl flask tightly to the distillation apparatus.
9.	Heat rapidly on high heat to boiling, then turn off the power briefly (1 to 2 min) to let the reaction subside.	In Steps 9 and 10, droplets of solution or particles of Devarda's alloy occasionally carry over from the flask into the Kjeldahl trap and the condenser. If this occurs, discard the sample and process a new one. To clean the apparatus after an NaOH carryover, distill 250 ml of water. If Devarda's alloy carries over, disassemble and clean the apparatus, then distill 250 ml of water.
10.	Using high heat, distill 300 ml.	
11.	Lower the Erlenmeyer flask containing the H_3BO_3 solution until the exit tube is exposed.	The flask is lowered before the heat is turned off (next step) to avoid back suction.
12.	Stop the heat, and let the distillate drip into the H_3BO_3 solution as the system cools.	

13. Disconnect the Kjeldahl flask and rinse the exit tube with distilled water.

14. Titrate with the standard 0.1000N H_2SO_4 to the first appearance of pink. The color transition is green to gray to gray-pink to pink. Titrate to the gray-pink color.

15. Rinse the strong NaOH solution from the distillation flask carefully, and dissolve the Devarda's alloy with HNO_3 in a hood.

16. Record the data and calculate the results as shown in the example work sheet. Report results to three significant figures.

REFERENCES

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3. H. A. Lyper, Methods of Analysis, Association of Official Agricultural Chemists, 7th Ed, Washington, D. C., 1950, p 14.

4. F. D. Snell and F. M. Biffen, Commercial Methods of Analysis, New York: McGraw-Hill, 1944, p 150.

December 1967

H. A. Shogren
S. S. Yamamura
J. E. Rein

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Nitrate + Ammonia

CHARGE NUMBER _____ PROCEDURE $NO_3 - NH_3 - 1$

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	H_2SO_4 N	H_2SO_4 ml	H_2SO_4 corrected for Blank, ml	mM NO_3 or NH_3 in Aliquot Analyzed	mM NO_3 or NH_3 corrected for Bias			RESULT M
Blank		0.1000	0.15						
XYZ ($NO_3 + NH_3$)	5 ml (No Dilution)	0.1000	17.55	17.40	1.74	1.80 ± 0.05			0.360 ± 0.010
XYZ (NH_3 Only)	100 ml (No Dilution)	0.1000	36.72	36.57	3.66	3.83 ± 0.09			0.0383 ± 0.0009
XYZ (NO_3 Only)									0.322 ± 0.010

ANALYZED BY _____ DATE _____

CALCULATIONS:

M $NO_3 + NH_3 = D = AC = (0.1000)(17.40) = 1.74$

$$\text{Result} = \frac{E}{\text{Sample Vol.}} = \frac{1.80 \pm 0.05}{5} = 0.360 \pm 0.010$$

M NH_3 Only $= D = AC = (0.1000)(36.57) = 3.66$

$$\text{Result} = \frac{E}{\text{Sample Vol.}} = \frac{3.83 \pm 0.09}{100} = 0.0383 \pm 0.0009$$

M NO_3 Only $= \underline{M}\ NO_3 + NH_3 - \underline{M}\ NH_3$

$= (0.360 \pm 0.010) - (0.0383 \pm 0.0009)$

$= 0.3217 \pm 0.010$

APPROVED BY _____

COLORIMETRIC DETERMINATION OF NITRATE

ABSTRACT

Nitrate is reacted with phenoldisulfonic acid in a strong sulfuric acid medium to form a nitrophenol which turns intensely yellow in alkaline medium. The yellow nitrophenolate species is measured spectrophotometrically at 403 mμ[1,2]. Two procedures are described. One is a general method for the determination of nitrate in samples that do not contain high levels of interfering ions. The other, applicable to samples that contain large amounts of interfering ions such as zirconium and fluoride, employs direct color development on aqueous samples and a standard addition calibration technique to compensate for the suppressive effect of these ions and water on the color development.

APPLICABILITY

In the general Procedure A, the sample first is made basic and evaporated to dryness. It then is reacted with phenoldisulfonic acid in conc H_2SO_4 medium to form the nitrophenol which subsequently is measured in an ammoniacal medium at 403 mμ. Interferences are metals that precipitate and occlude nitrate during color development, reducing agents such as chloride, colored metal ions such as uranium(VI) and other colored substances that absorb at 403 mμ, and nitrite which partially oxidizes to nitrate in the evaporation and nitration steps. The effect of diverse metal ions at high ratios has not been studied; however, moderate to high levels of most metal ions are expected to introduce some harmful effect for the reasons indicated above. Chloride even in very small amounts causes results to be low. For example, at a nitrate level of 60 μg, 60 μg of chloride cause results to be low by 5%. The tolerance limit for chloride is about 15 μg. Nitrite at nitrite to nitrate molar ratios below 1:1 does not interfere; however, at ratios above 2:1, it interferes seriously, especially at low nitrate levels.

The standard addition method, Procedure B, is especially designed for aqueous samples that contain appreciable amounts of substances such as zirconium(IV) and fluoride that interfere in the general procedure. As in Procedure A, chloride, nitrite, and colored metal ions that absorb at the working wavelength interfere and must be absent.

The range of the method is 6 to 80 μg ($1x10^{-4}$ to $1.3x10^{-3}$ mM) of nitrate for both procedures. In Procedure A, where samples up to 50 ml may be analyzed, the lowest determinable nitrate concentration is about 0.1 μg/ml ($1.6x10^{-6}$ M). For Procedure B, the maximum sample volume is 0.4 ml and the lowest determinable concentration is 15 μg/ml ($2.4x10^{-4}$ M). Five-centimeter cells are used for all measurements.

NO_3-Color-1

This method, designed for high sensitivity, is intended primarily for samples with nitrate concentrations below 150 µg/ml (2.5×10^{-3} M) and for samples with higher nitrate concentrations that, because of sample limitations, require a sensitive method. Two other useful methods are available for the analysis of samples with nitrate concentations above 150 µg/ml. One is the distillation-titration method, Method NO_3^--NH_3-Vol-1 described in this Manual. The other is a direct spectrophotometric measurement of nitrate at its absorbance peak of 300 to 310 mµ[1].

DISCUSSION

The general Procedure A, consists of four broad operations: (a) the sample is made alkaline and evaporated to dryness; (b) the dry sample residue is reacted with phenoldisulfonic acid to form the corresponding nitrophenol; (c) the acidic sample is made alkaline to convert the nitrophenol to the intensely yellow nitrophenolate form; and (d) the absorbance of the nitrophenolate is measured at 403 mµ. In the evaporation step, (a), the evaporation should be performed slowly over a steam bath and protected from nitric acid vapors in the laboratory. In Step b, the critical factors are the purity of the phenoldisulfonic acid reagent, the manner of addition of the reagent, and the reaction conditions. The reagent should be free of the monosubstituted sulfonic acids and should be added rapidly to the bulk of the evaporated sample residue, then brought in contact with the entire inner surface of the reaction vessel. Nitration is complete in 5 min over a steam bath or in 10 min at room temperature. In Step c, ammonium hydroxide is recommended over potassium hydroxide. Ammonium sulfate is considerably more soluble than potassium sulfate and ammonium hydroxide seems to improve the sensitivity. The addition of ammonium tartrate before the addition of ammonium hydroxide prevents precipitation of metal hydroxides. The nitrophenolate, Step d, is stable indefinitely.

In Procedure B, the nitration reaction is carried out in the presence of water with a special phenoldisulfonic acid reagent containing excess fuming sulfuric acid to counteract the suppressive effect of water. Water, a by-product of the nitrate-phenoldisulfonic acid reaction, affects the nitration in spite of the excess fuming sulfuric acid, so its level must be controlled at 0.5 ml at which level the color development is nearly complete and sufficiently reproducible after 30 min at room temperature.

SAFETY PRECAUTIONS

Fuming sulfuric acid and the sulfuric acid solution of the phenoldisulfonic acid attack the skin and react with water or base to release tremendous amounts of heat. Wear protective rubber gloves and perform all dilutions or neutralizations with caution.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, borosilicate glass, 5-cm.
2. Casseroles (porcelain) or evaporating dishes of borosilicate glass, 30- and 60-ml sizes.
3. Centrifuge.
4. Centrifuge tubes, 50-ml.
5. Flasks, volumetric, 50-ml.
6. Pipets, macro and micro, assorted sizes with suction bulb and syringe.
7. Pipet, Mohr, 10-ml.
8. Spectrophotometer, Beckman Models B, DU or DK, or Cary Model 14.
9. Steam bath.
10. Stirring rods, glass, 4-mm x 4-in.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium tartrate, 10% (w/v). Dissolve 100 g of ammonium tartrate in water and dilute to 1 liter with water.
2. Nitrate calibration standard I, 30 µg NO_3^-/ml. Dissolve 0.0489 g of KNO_3 in water and dilute to 1 liter.
3. Nitrate calibration standard II, 60 µg NO_3^-/ml. Dissolve 0.0978 g of KNO_3 in water and dilute to 1 liter.
4. Nitrate calibration standard III, 300 µg NO_3^-/ml. Dissolve 0.1223 g of KNO_3 in water and dilute to 250 ml.
5. Phenoldisulfonic acid reagent. Dissolve 50 g of pure white phenol in 370 ml of conc H_2SO_4. Add 110 ml of fuming sulfuric acid (20 to 23% sulfur trioxide), mix thoroughly, and heat for 2 hr over a steam bath. Test the reagent by processing 1 ml of nitrate calibration standard II. Follow Procedure A-3 except at Step 3-d, heat the standard for 5 min over a steam bath. The

appearance of a green coloration, indicative of the presence of monosubstituted sulfonic acids, indicates the need for further heating. If the green coloration persists after lengthy heating, the fuming sulfuric acid may be faulty.

6. Special phenoldisulfonic acid reagent, SO_3-rich. Mix 75 ml of the phenoldisulfonic acid reagent with 25 ml of 20 to 23% fuming sulfuric acid.

7. Sodium hydroxide, 0.1M. The chloride content of this reagent should not exceed 0.001% of the sodium hydroxide.

PROCEDURE

NOTE: Because nitric acid and nitrate salts are used routinely in the laboratories, exercise care to prevent sample contamination. Rinse all glassware thoroughly with distilled water before use.

A. General Procedure

1. Blank

Process a reagent blank with each set of samples and standards. Substitute 3 ml of water for the sample aliquot.

2. Calibration and bench standard

Process a pair of standards with each set of samples. Use 1.00-ml aliquots of nitrate calibration standards I and II and follow Procedure A-3 beginning at Step h. Divide the micrograms of nitrate in each standard by the respective net absorbance to calculate the calibration factor. The two factors must agree within limits specified by Quality Control and the average factor must agree with the established conversion factor within specified limits. If either of these specifications are not met, process another pair. Consult your supervisor if difficulties persist.

3. Analysis of samples

a. Pipet a sample aliquot containing 6 to 80 µg ($1x10^{-4}$ to $1.3x10^{-3}$ mM) of NO_3^- into a 30- or 100-ml casserole.

For small-volume samples, the 30-ml casserole is recommended.

7

b.	Add 0.1M NaOH dropwise until the sample is basic.	Use a pH meter with miniature electrodes or litmus paper to ensure the addition of sufficient base. Avoid adding excess base. If a pH meter is used, rinse the electrodes with water just before use and carry out the neutralization rapidly to minimize the introduction of Cl^- from the calomel reference electrode.
c.	Evaporate the sample to dryness on a steam bath.	
d.	Cool the casserole, add 2 ml of the phenoldisulfonic acid reagent, mix thoroughly, and let stand for 10 min at room temperature.	Add the reagent rapidly by using a 2-ml pipet which has had the tip removed. For maximum color development, try to add the reagent so that it contacts as much of the sample as possible, then rotate the casserole to wet its entire inner surface with the reagent.
e.	Transfer the sample to a 50-ml volumetric flask with water rinses. Do not exceed 35 ml.	If the analysis must be interrupted, this is a permissible stopping place. After dilution, the introduction of NO_3^- has no harmful effect.
f.	Add 5 ml of 10% ammonium tartrate and mix.	
g.	With a Mohr pipet, add 7 ml of conc NH_4OH slowly while continuously swirling the sample.	
h.	Chill to room temperature, then dilute to volume with water, and mix.	
i.	Transfer the sample solution to a 5-cm cell and measure the absorbance against water at 403 mμ.	If solids are present, settle the solids by centrifugation and decant the clear supernatant solution.

j. Record the data and calculate the results as described in the example work sheet. Report all results to three significant figures.

B. Modified Procedure

1. Blank

Process 0.5 ml of water per Procedure B-2 beginning at Step e.

2. Calibration and analysis of samples

a. Label four, dry, 50-ml volumetric flasks as CS-1, CS-2, S-1, and S-2 (calibration standards 1 and 2 and samples 1 and 2, respectively).

Once the analysis is begun, complete the determination without interruption.

b. To flasks CS-1 and CS-2, pipet 0.10 ml of the 300 µg/ml NO_3^- standard III.

c. To each of the four flasks, pipet identical aliquots of the sample up to 0.4 ml and containing 6 to 50 µg ($1x10^{-4}$ to $8x10^{-4}$ mM) of NO_3^-.

d. Dilute the contents of each flask to 0.5 ml with water.

The volume of water is critical. Use a micro pipet or a small Mohr pipet to measure the water.

e. Pipet 3 ml of the special phenoldisulfonic acid reagent to each of the flasks.

f. Stopper, mix thoroughly, and let stand for 30 min at room temperature.

g.	Dilute the sample with about 10 ml of water, then add 5 ml of 10% ammonium tartrate.	
h.	While swirling the sample continuously, add conc NH_4OH 1 ml at a time until the solution is definitely alkaline.	The nitrophenol turns yellow when the solution is basic.
i.	Chill to room temperature, dilute to volume with water, and mix thoroughly.	
j.	Transfer the solution to a 5-cm cell and measure the absorbance against the blank at 403 mμ.	
k.	Record the data and calculate the results as described in the example work sheet. Report three significant figures for all results.	

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January 1968

F. A. Duce
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FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION NO_3

CHARGE NUMBER _____ PROCEDURE A, Method NO_3-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA, $a_0/d_1/a_1/d_2/a_2$	Absorbance vs H_2O	Net Absorbance	Calib. Factor	$\mu g\ NO_3$ in Samp Aliq	$\mu g\ NO_3$ Corrected for Bias			RESULT $\mu g\ NO_3$ /ml
Blank		0015	–						
Std, 30 µg		0 361	0 346	8671					
Std, 60 "		0 708	0 693	8658					
			$\bar{x}$ =	8665	µg NO_3/abs unit				
Sample	0 300 ml	0 430	0 415		360	368 ± 12			123 ± 4

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = \frac{\mu g\ NO_3}{abs} = \frac{30}{0346} = 8671 \quad , \quad C' = \frac{60}{0693} = 86.58$$

$$\text{Average} = 0.5(C + C') = 0.5(8671 + 8658)$$

$$= 8665\ \mu g\ NO_3/\text{abs unit}$$

$$D = CB = (8665)(0415) = 360\ \mu g\ NO_3$$

$$\text{Result} = \frac{368 \pm 12}{\text{samp aliquot}} = \frac{368 \pm 12}{0.30} = 123 \pm 4\ \mu g\ NO_3/ml$$

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FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION NO_3

CHARGE NUMBER _____ PROCEDURE B, Method NO_3-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance vs Blank	Average Absorbance	Net Absorbance of 30 μg NO_3	Calib Factor	μg NO_3^- in samp. Aliquot	μg NO_3 Corrected for Bias		RESULT μg NO_3 /ml
Sample plus 30 μg NO_3 spike		0.530	0.538	0.333	90.09				
		0.545							
Sample	0.40 ml.	0.215	0.205			18.5	192 ± 22		480 ± 55
	"	0.195							

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Calib Factor} = D = \frac{30}{(\text{Ave. Abs of Spiked Samp.}) - (\text{Ave. Abs. of Samp})}$$

$$= \frac{30}{0.538 - 0.205} = \frac{30}{0.333} = 90.09 \ \mu g\ NO_3/\text{abs unit}$$

$$\mu g\ NO_3 \text{ in Samp Aliq} = E = BD = 0.205(90.09) = 18.5$$

$$\text{Result} = \frac{19.2 \pm 2.2}{\text{Samp Vol.}} = \frac{19.2 \pm 2.2}{0.4} = 480 \pm 55\ \mu g\ NO_3/ml$$

APPROVED BY _____

REMOTE DETERMINATION OF MMPD AND BULK DENSITY OF CALCINER PRODUCT

ABSTRACT

The volume of a monolayer of particles on a given surface area is linearly proportional to the size of the particles. This is the basis of a rapid method for the determination of mass mean particle diameter (MMPD) of radioactive calciner product from the Waste Calcining Facility[1]. A weighed sample is transferred to a 60° funnel equipped with a calibrated stem, and its as-poured and tap-packed volumes are measured. Then the sample is contacted with a circle of adhesive attached to the face of the funnel and the tap-packed volume of the nonadhering particles is again measured. The volume of the adhering particles, determined by difference, is converted to MMPD by reference to a calibration curve constructed with sieve-analyzed standards. Bulk density is calculated from the weight of the sample and its as-poured volume.

APPLICABILITY

This method is designed specifically for waste calciner product particles with an MMPD in the range 0.2 to 0.7. It can be applied to other particulate matter; however, because particle shape is one of the important variables affecting the analysis, the apparatus should be calibrated against sieved samples of the same or similar material.

DISCUSSION

The volume of a monolayer of particles within a defined area is linearly proportional to the mean particle diameter (MPD) and the mass mean particle diameter (MMPD). Particle shape and particle size distribution are the two most serious factors that cause deviations from this proportionality. The waste calciner product is sufficiently uniform in shape and size distribution to enable reliable use of this simple, rapid technique. Indeed, comparison of the results by this method with the results by sieve analysis indicate good agreement. Fine powder, which is known to stick to the adhesive preferentially and cause low results, is not present in the calciner material in adverse amounts. The effect of particle shape, particle size distribution, and other factors are minimized by processing the calibration standards and the samples in the same way.

Particle Size-1

APPARATUS

1. Adhesive paper, clean-stick. Adhesive paper similar to that used for bumper stickers in political campaigns is available from Eastern Idaho Farmer Printing in Idaho Falls. To accommodate remote use, cut 4- to 5-in. diam skillet-shaped pieces and prepare them as illustrated in Figure 1.

2. Balance, top loading, with 1-mg sensitivity.

3. Funnel, modified. Attach a 10-ml Mohr pipet to the funnel portion of a 3-in. diam 60° funnel as shown in Figure 2. Seal the pipet exactly at the 10-ml mark and seal the pipet section to the funnel at the zero end.

4. Sample transfer jig. Fabricate the jig with stainless steel as shown in Figure 3.

5. Settling ring and ringstand. Connect 10 in. of 0.25-in. ID galvanized or stainless steel pipe to a 1- x 1- x 1/4-in. pipe tee and mount this on a ringstand with the 1-in. hole aligned vertically.

PROCEDURE

A. Calibration

The calibration curve and equation have been established by the analysis of many cold run samples also analyzed with standard sieves. During any cold startup preceding a hot campaign, it is recommended that samples be analyzed with sieves also to confirm the suitability of the existing curve or equation. If the new data is similar to previous data, the new and old data are combined to derive the calibration equation or curve for the succeeding hot run. If the new data is significantly different, the new data alone are used to derive the calibration equation and curve.

B. Analysis of Bench Standard

Analyze the bench standard per Procedure C before analyzing the samples. The result should fall within the specified limits and if it does not, repeat the analysis. Consult your supervisor if trouble persists.

C. Analysis of Samples

1. Insert the funnel into the pipe tee funnel support.

2.	Insert the sample transfer jig into the sample bottle through the slit in the neoprene cap liner and weigh the sample bottle plus jig to the nearest milligram and record the weight.	
3.	Pour about 8 ml of the sample into the funnel apparatus.	Position the funnel upright. Sample size may vary between 7 and 10 ml.
4.	Weigh the sample bottle plus jig to the nearest milligram and record the weight.	
5.	Record the level of the sample.	This reading is used to calculate bulk density. Do not settle the particles before making the reading.
6.	Settle the particles in the funnel to a constant level by raising and dropping the funnel 10 times. Raise the funnel 2 to 3 in. each time.	It is best to raise the funnel by pushing up on the funnel stem from below.
7.	Record the level of the sample.	
8.	Obtain a piece of the adhesive paper, remove the protective cover, and center the paper on the funnel with the sticky side down. Apply firm pressure around the entire rim of the funnel to secure the paper to the funnel. A large rubber stopper fitted with a handle is provided for this.	Store the prepared supply of adhesive paper on a hook placed in a convenient, accessible location.
9.	Invert the funnel quickly and with a circular motion.	The idea is to expose the sample to the adhesive without preferential exposure of either large or fine particles.

10. Return the funnel to the funnel support and settle the nonadhering particles as in Step 6.

11. Record the level.

12. Remove the used adhesive paper and place it in the waste can provided.

13. Calculate the results as shown on the example work sheet.

REFERENCES

1. F. O. Cartan, G. J. Curtis, "New Rapid Method for Average Particle Size Measurements", Anal. Chem., 41, (October 1969), p 1719.

F. O. Cartan
G. J. Curtis
E. M. Fortsch
November 1971

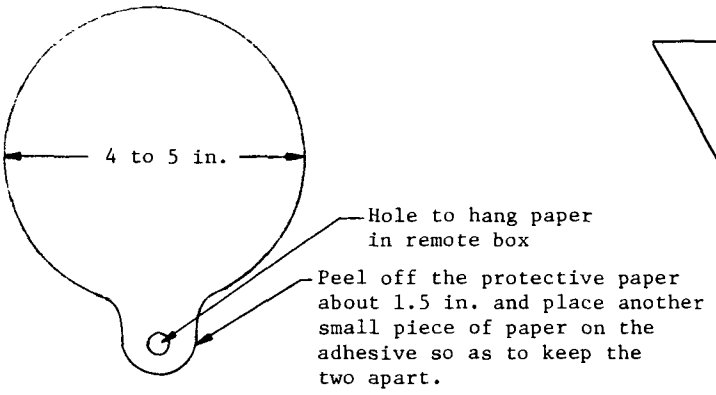

Fig. 1 Precut adhesive paper.

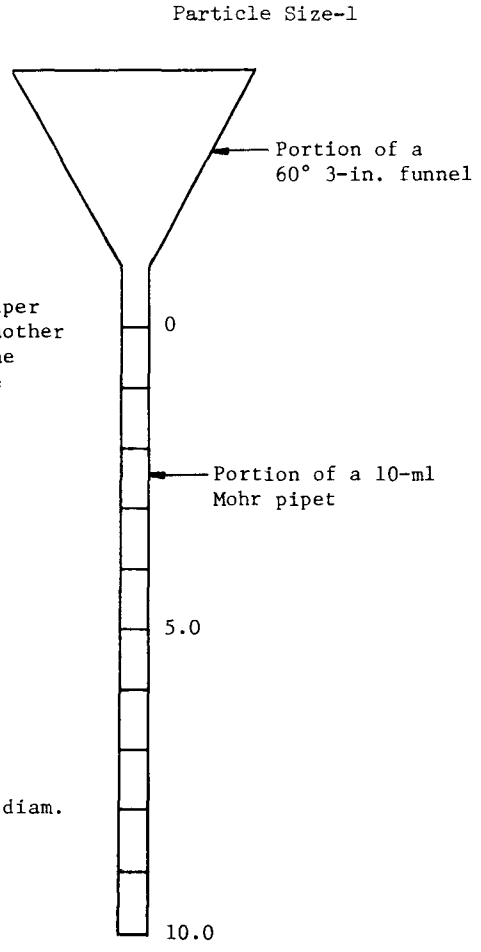

Fig. 2 Funnel apparatus.

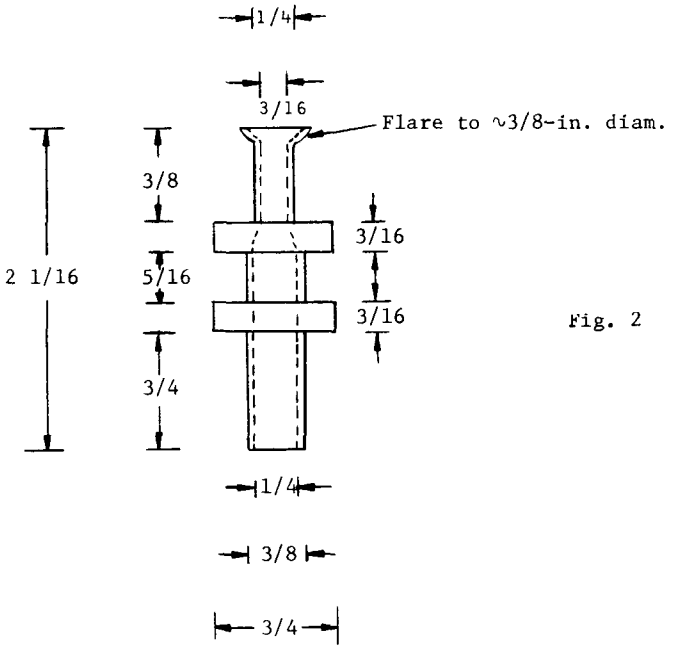

Fig. 3 Stainless steel sample transfer jig.

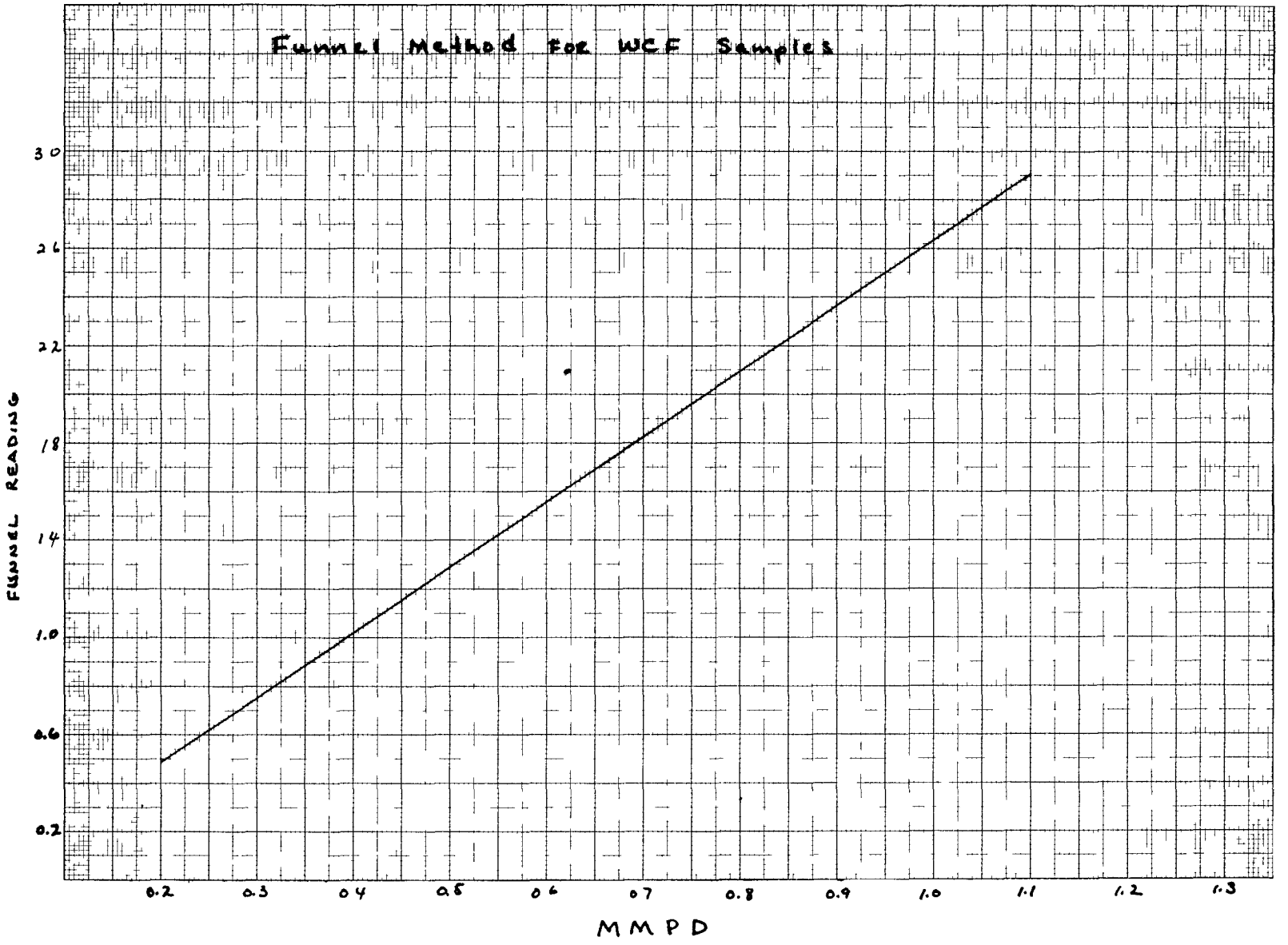

Fig. 4 Calibration curve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION MMPD; BD

CHARGE NUMBER _____ PROCEDURE Particle Size - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Initial wt, g	Final wt, g	Initial unpacked Funnel Reading	Initial Packed Funnel Reading	Final Packed Funnel Reading	Net Vol on Adhesive		RESULT MMPD from chart or Equation
WCF		77.731	64.216	1.95	2.28	3.30	1.02		.398
									Bulk Den.
									1.68 g/ml

ANALYZED BY _____ DATE _____

CALCULATIONS:

MMPD

F = E - D = 3.30 - 2.28 = 1.02 ml

Convert F to MMPD by reference to the calibration curve or by calculation using the calibration equation.

Bulk Density

$$\text{Bulk Density} = \frac{A-B}{10.00-C} = \frac{77.731-64.216}{8.05} = 1.68 \text{ g/ml}$$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS

ABSTRACT

In this versatile method for the determination of microgram amounts of phosphorus, orthosphosphate phosphorus is extracted selectively as the yellow phosphomolybdic acid complex into methyl isobutyl ketone (hexone) from a 2M $HClO_4$ medium. The yellow complex is then reduced to the more sensitive molybdenum blue complex and measured at 625 mμ. A perchloric acid digestion converts organophosphorus compounds and inert phosphates to determinable orthophosphate. Prior extraction with cupferron eliminates such interferences as vanadium(V) and zirconium(IV).

APPLICABILITY

In this method, the widely-used molybdenum blue spectrophotometric method [1] for phosphate is used alone and in combination with a perchloric acid pretreatment and a cupferron extraction pretreatment (Figure 1) to determine orthophosphate phosphorus and total phosphorus in a wide variety of inorganic and organic samples. The various combinations of the spectrophotometric measurement procedure and the two pretreatment procedures give rise to four different analysis schemes or methods (Figure 1 and Table I). The applicability of each analysis scheme is different (Table I) because the perchloric acid pretreatment, Procedure E, and the cupferron extraction, Procedure F, produce chemical changes and eliminate certain interferences. Analysis Schemes 2 and 3 include the perchloric acid treatment while analysis Schemes 1 and 4 do not. Analysis Schemes 3 and 4 include a cupferron extractable whereas Schemes 1 and 2 do not.

With reference to Table I, the effect of niobium and tungsten in analysis Schemes 3 and 4 and the effect of chromium(III) require further clarification. Niobium and tungsten at a level of 25 μg interfere seriously despite the application of the cupferron extraction. The difficulty with niobium is attributed to the coprecipitation of phosphate by the niobium precipitate that forms in acidic medium devoid of suitable complexing anions. The difficulty with tungsten is that it is not extracted quantitatively by cupferron from a 2M $HClO_4$ medium. Extraction from 0.3M $HClO_4$ medium yields satisfactory results with 25 μg of tungsten; however, this condition is not satisfactory for zirconium and is not used in this method.

The tolerance of the method for chromium(III) depends on whether the perchloric acid fuming is performed and whether iron(III) is present. In the absence of iron(III), chromium(III) does not interfere at a 550 to 1 chromium(III) to phosphate molar ratio if the sample is not fumed. If it is fumed, the chromium(III) tolerance is only about 25 to 1 or about 0.01 mmole per sample aliquot. In the presence of phosphate, chromium(III) apparently is not oxidized quantitatively to chromium(VI) by fuming perchloric acid. Heating promotes the formation of stable chromic phosphate which does not react with molybdate to form the extractable phosphomolybdic acid complex. When sufficient iron(III) is present, the initial perchloric acid fuming has no effect on the behavior of chromium(III). The explanation is that iron(III) reacts preferentially with phosphate and prevents the formation of nonreactive chromic phosphate.

As stated in Table I, a minor modification in the method, centrifugation of the hexone phase before reading the absorbance, is necessary when mercury is present in the sample. Mercury extracts into the hexone phase, then is reduced to mercury(I) when the hexone phase is contacted with the chlorostannous reagent. This produces a suspension of insoluble mercurous chloride in the hexone phase which, if not centrifuged out, would cause high absorbance readings.

The range of this method is 5 to 100 µg of phosphate (1.6 to 33 µg of phosphorus); however, with extreme care, the range can be extended to 1 µg of phosphate. Both 1- and 5-cm cells are used to cover this range. The maximum sample size is 0.5 ml or 0.5 g for organic samples and about 25 ml for aqueous solutions. Therefore, the minimum determinable phosphate concentrations are 2 ppm with organic samples and 0.04 ppm with aqueous samples.

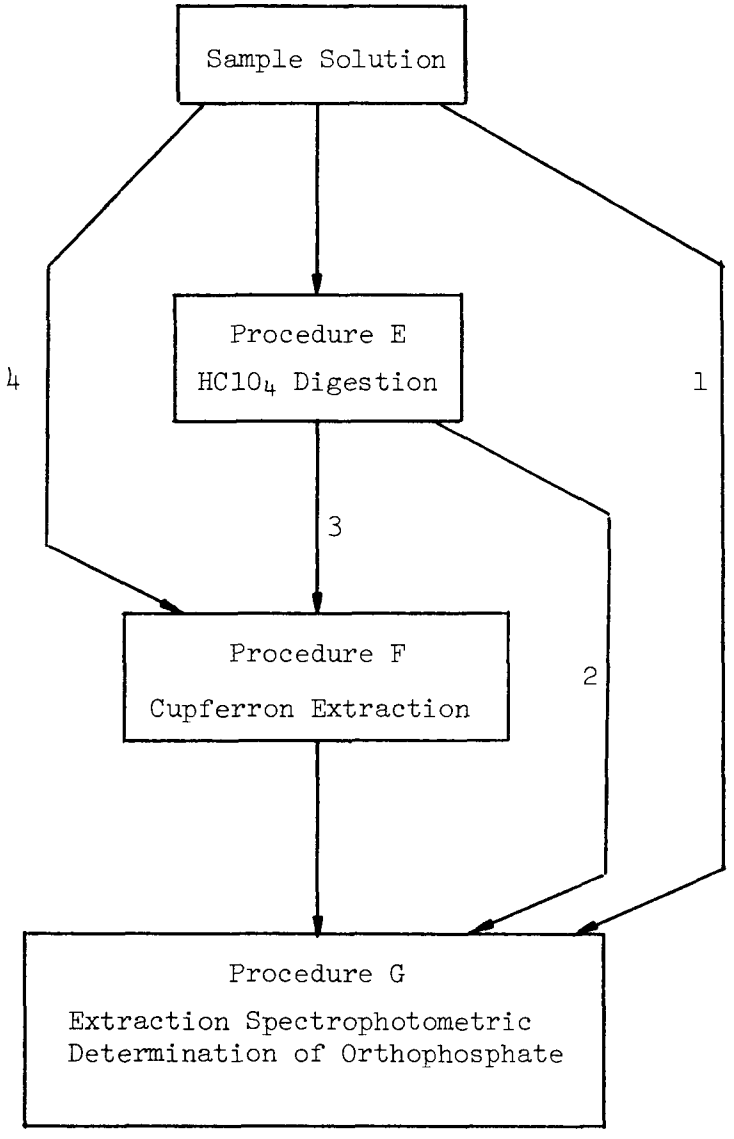

Fig. 1 Diagram of analysis schemes.

TABLE I

APPLICABILITY OF THE VARIOUS ANALYSIS SCHEMES

Analysis Scheme	Applicability	Summary of Diverse Ion Effects[a]
1. Procedure G	Selective determination of orthophosphate in aqueous solutions which do not contain metallic interferences and which may or may not contain organophosphorus compounds such as TBP.	The tolerance expressed as mole ratio of impurity to phosphate is 50,000 for U(VI); 3,500 for Al; at least 1,400 for Na and Mg; at least 550 for Ba, Bi(III), Co, Cr(III), VI), Cs, Cu, Fe, Hg(II), K, Lanthanides(III), Mn(II), Ni, Pb, Th, and Zn; and at least 175 for Si. This tolerance for Hg(II) is based on centrifuging the hexone phase before absorbance measurement as explained in the APPLICABILITY section. As for common anions, the tolerances in terms of mM per sample aliquot are 8mM for Cl^-, NO_3^-, and $SO_4^=$ and 4 mM for F^-. The metals Hf, Nb, Ti, V, W, and Zr interfere seriously even at a 1:1 metal to phosphate weight ratio.
2. Procedures E + G	Determination of total phosphorus in organic and inorganic samples that do not contain interfering metal ions.	Same as analysis Scheme 1 with the following exceptions: a. Cr(III) tolerance is only 0.01 mM (see text). b. Perchloric acid fuming expels volatile anions such as Br^-, Cl^-, F^-, and NO_3^-. c. High levels of silicate may interfere in analysis Scheme 1. Perchloric acid fuming converts silicate to noninterfering silica.

TABLE I (Cont'd)

Analysis Scheme	Applicability	Summary of Diverse Ion Effects[a]
3. Procedures E + F + G	Determination of total phosphorus in all types of organic and inorganic samples.	Same as analysis Scheme 1 except a. Hf, V, and Zr do not interfere at a 550 to 1 metal to phosphate molar ratio. b. The comments for analysis Scheme 2 apply. Niobium, Ti, and W interfere despite the cupferron extraction (See Text).
4. Procedures F + G	Selective determination of orthophosphate in aqueous solutions which contain interfering metal ions and which may contain organophosphorus compounds such as TBP.	Same as analysis cheme 1 except that Hf, V, and Zr do not interfere at a 550 to 1 metal to phosphate molar ratio. Niobium, Ti, and W still interfere (See Text).

[a] In the study of the effects of diverse ions, the phosphate level was maintained at 34 µg (4×10^{-4} mM). The diverse metal ions were added as chloride or nitrate salts or, in the case of Nb, V, and W, as alkali metal salts of the oxyanions. The anions were introduced as the acid.

DISCUSSION

The principal operations involved in this method are:

(1) digestion of samples with perchloric acid

(2) removal of certain metal ions by cupferron extraction

(3) formation of the phosphomolybdic acid complex

(4) extraction of the phosphomolybdic acid complex into hexone

(5) reduction of the yellow complex to molybdenum blue with a hydrochloric acid solution of stannous chloride

(6) measurement of the intensity of the blue complex at 625 mµ.

The perchloric acid digestion converts silicate to silica; converts organophosphorus compounds, metaphosphate, pyrophosphate, and other phosphorus species to determinable orthophosphate; depolymerizes

hydrous metal polymers to cupferron-reactive monomers; expels volatile acids; destroys organic complexing agents; and oxidizes certain elements to higher oxidation states. The cupferron extraction removes metal ions, e.g. V(V) and Zr(IV), that interfere by tying up phosphate.

The formation and extraction of the phosphomolybdic acid complex is carried out in a 1.8M $HClO_4$ medium. Warm dilute perchloric acid oxidizes cupferron to a yellow-green substance which also extracts into the hexone to give high and erratic results. Chilling the solution minimizes this undesirable side reaction. The formation of the phosphomolybdic acid complex is complete in less than 5 min in 1.8M $HClO_4$ medium. Only a slight excess of molybdate is necessary. The reduction of the yellow complex to molybdenum blue and the intensity of the blue color are affected by excess molybdate reagent, acidity, and the presence of anions other than that of the acid medium (HCl) used in the reduction. At room temperature, the color development is complete in 15 min and thereafter, the blue color is stable for several hours. Once prepared, the hexone solution of the molybdenum blue complex must not be diluted because the color intensity is sensitive to change in acidity and salt concentration.

In the analysis of zirconium-containing samples that require a perchloric acid digestion, it has been found necessary to deliver the cupferron reagent to the digestion vessel. The cupferron apparently "dissolves" zirconium phosphate adhering to the vessel walls enabling quantitative transfer of the phosphate to the separatory funnel.

Phosphate contamination through glassware is a constant problem. Many detergents contain phosphate or phosphate-bearing chemicals. All glassware should be soaked initially in 7±1M NH_4OH, then thoroughly rinsed with distilled water.

When determining phosphorus in metallic samples, carry out the dissolution under oxidizing conditions to prevent loss of phosphorus as phosphine.

SAFETY PRECAUTIONS

Perchloric acid is a very useful reagent in analytical chemistry. It is a safe chemical when used properly but because of the large amount of chemical energy in perchloric acid, it can react violently and explosively and represents a serious potential danger[2]. Perchloric acid, a weak, docile oxidant when cold and dilute, becomes a gradually stronger oxidant as it is heated and concentrated. It is an extremely powerful oxidant in the boiling 72.5% ($HClO_4 \cdot 2.4H_2O$) azeotrope form which is stable and safe but which can react explosively when there is a substance (e.g. organic material and certain inorganic material) that can trigger a sudden release of the chemical energy.

The trigger is generally an easily oxidizable substance, so nitric acid which is a good oxidant and sulfuric acid which chars organic material to not-so-readily oxidizable carbon are added with or before the perchloric acid to prevent explosion. The use of nitric acid does not guarantee that explosions cannot occur because nitric acid volatilizes before perchloric acid. A perchloric acid explosion is often preceded by a gradual darkening of the solution from yellow to brown. When in doubt, the reaction can be quenched with a little water, then continued after the addition of more nitric acid. PERFORM ALL DIGESTIONS IN THE PERCHLORIC ACID HOOD BEHIND PROTECTIVE GLASS. DO NOT ATTEMPT A PERCHLORIC ACID DIGESTION WITHOUT PRIOR SUPERVISED TRAINING.

APPARATUS AND REAGENTS

A. Apparatus

NOTE: All apparatus that contacts the sample prior to the stannous chloride reduction must be cleaned thoroughly before use. Soak the items in $7 \pm 1 M$ NH_4OH, then rinse well with distilled water.

1. Absorbance cells, borosilicate glass or silica, 1- and 5-cm.
2. Beakers, assorted sizes.
3. Centrifuge tubes, 50-ml.
4. Cylinders, graduated, assorted sizes.
5. Glass beads.
6. Hot plate.
7. Pipets, macro and micro, assorted sizes, with suction bulb and syringe controls.
8. Pipets, Mohr, 5- and 10-ml.
9. Separatory funnels, 125-ml, with Teflon stopcocks.
10. Spectrophotometer, Beckman DU, Cary Model 14, or equivalent.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Chloroform.

2. Chlorostannous acid solution. Dissolve 2.38 g of $SnCl_2 \cdot 2H_2O$ in 170 ml of conc HCl and dilute to 1 liter with water. Add several pellets of metallic tin and store in a polyethylene bottle. Prepare a new solution every 2 weeks. Because of instability, it might be advisable to cut the recipe by at least 2.

3. Cupferron solution, 0.25M. Dissolve 3.88±0.05 g of ammonium cupferrate in 100 ml of water. Store in a refrigerator in a dark bottle. Prepare a fresh solution after 2 weeks.

4. Diverse ion matrix for phosphate bench standards analyzed by Schemes 3 and 4 (Table I). Dissolve 5.0±0.1 g of $ZrOCl_2 \cdot 8H_2O$ and 1.0±0.1 g of NH_4VO_3 in 75 ml of 2M HCl and dilute to 100 ml with water.

5. Hexone (4-methyl-2-pentanone).

6. Molybdate solution. Dissolve 73±0.5 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water. Filter if turbid, dilute to 1 liter with water, and store in a polyethylene bottle.

7. Nitric acid, conc.

8. Perchloric acid, conc, phosphate-free. Vacuum distill reagent grade perchloric acid.

9. Phosphate standard stock solution, 1.000 mg $PO_4^{\equiv}$/ml. Dissolve 0.7165±0.0005 g of KH_2PO_4 in water and dilute to 500 ml with water.

10. Phosphate calibration standards I and II, 50.0 and 75.0 µg $PO_4^{\equiv}$/ml, respectively. Dilute 10.00 ml and 15.00 ml of the stock standard to 200 ml with water.

11. Phosphate ($PO_4^{\equiv}$) bench and control standards. Dilute the 1.000 mg $PO_4^{\equiv}$/ml standard with water to the desired concentrations.

PROCEDURE

A. Blank

Process a 5-ml aliquot of water by the same analysis scheme as that used to analyze the samples. The usual blank absorbance is about 0.020 compared against water. If the blank absorbance greatly exceeds this, check first the perchloric acid, then the glass apparatus.

B. Calibration

The use of four calibration standards will promote efficiency by reducing repeat analyses. If only samples with similar concentrations are being analyzed, the use of two appropriate standards will suffice.

Process at least one pair of calibration standards with each series of samples. Use 1.00-ml portions of the 50 and 75 µg/ml phosphate standards for measurements in 1-cm cells and 200-µl portions of the same standards for measurements in 5-cm cells. Record the absorbance for each standard and the blank. Divide the micrograms of phosphate by the net absorbance to obtain the conversion factor. The difference between the two conversion factors for each pair of standards should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both specifications are not met, reprocess the pair or pairs of calibration standards. Report problems to your supervisor if difficulties continue.

C. Analysis of Bench-Control Standards

Analyze a bench standard each time samples are analyzed. Process the bench standard by the same analysis scheme used to analyze the samples. If the analysis scheme involves a cupferron extraction, add 1 ml of the diverse ion matrix to the bench standard. The result obtained must fall within specified limits. If it does not, process another bench standard. If trouble continues, report to your supervisor.

D. Determination of Presence of Organic Matter

The method requires that all samples be fumed with perchloric acid to hydrolyze silicon which would otherwise give high results. The potential danger of heating an organic sample with perchloric acid makes it necessary to determine if organic material is present. If the sample is POSITIVELY known to be free of organic material, proceed with Procedure E, Step 1. If in doubt, determine the presence or absence of organic material by one or all of the following techniques.

1. Smell Test. Some organics such as alcohol, acetone and hexone can be detected by smelling. The lack of an odor does not confirm the absence of an organic.

2. Miscibility Test. Some organics such as Amsco, hexone, and chloroform will not mix with water. Add a drop or two of the sample to a test tube containing about 1 ml of water. If the sample does not mix with the water, it should be considered organic. A negative test does not confirm the absence of organic material.

3. Flame Test. All organics will either burn or char in a flame. Place a drop of the sample on the tip of a micro spatula and heat in an open flame. Volatile organics such as alcohol and acetone will burst into flame. Non-volatiles such as EDTA will char.

4. Acid Test. If the above tests do not confirm the presence or absence of organic material, add ONE drop of the sample to a 100 ml beaker containing 0.5 ml of perchloric acid. Heat the sample on a hot plate behind glass shielding. If organic material is present, the sample will either turn brown then black or produce a small explosion when the perchloric acid begins fuming. The lack of any reaction confirms the absence of any reactive organic material. DO NOT USE THIS TEST UNLESS THE OTHER THREE LEAVE YOU IN DOUBT. THE LABORATORY SUPERVISOR MUST BE PRESENT DURING THIS TEST.

E. Digestion of Samples with Perchloric Acid

1. Pipet a sample aliquot containing 5 to 100 µg of total $PO_4^{\equiv}$ (1.6 to 33 µg P) into a 150-ml beaker.

   Organic samples should be 0.5 ml (0.5 g) or less. Aqueous samples can be as much as 25 ml.

2. Using a Mohr pipet, add 6 ml of conc HNO_3.

3. Using a Mohr pipet, add 6 ml of conc $HClO_4$.

   For safety, add the HNO_3 before the $HClO_4$. When the sample is predominantly organic, digest the sample with conc HNO_3 for awhile, then admit the conc $HClO_4$. Perform the digestion in a perchloric acid hood equipped with safety glass.

4. Place a cover glass on the beaker, evaporate to fumes of $HClO_4$ and fume for 5 min.

5. Cool the sample to room temperature. If the sample contains Hf, V, or Zr, proceed to Step 6. If these metals are not present, quantitatively transfer the digested sample to a 125-ml separatory funnel with 25 ml of water, then continue with the analysis per Procedure G beginning at Step 3.

6. Rinse the cover glass and the beaker walls with 15 ml of water, mix by swirling, then chill the solution in an ice bath for 2 to 3 min.

   The solution must be chilled to minimize $HClO_4$ oxidation of cupferron to yellow-green products that coextract and interfere.

7. Add 5 ml of 0.25M cupferron solution, swirl the beaker to mix the solution and to wet the beaker walls with the reagent, then let stand for 3 min to permit the cupferron to break up insoluble metal phosphates.

8. Transfer the solution quantitatively with 10 ml of water to a 125-ml separatory funnel.

9. Continue per Procedure F beginning at Step 5.

F. Removal of Interfering Metals by Cupferron Extraction

1. To a 125-ml separatory funnel, add 6 ml of conc $HClO_4$ and 15 ml of water.

2. Pipet a sample aliquot (10 ml or less) containing 5 to 100 µg of orthophosphate.

3. Dilute to 30 ml with water, mix by swirling the solution, then immerse the funnel in an ice bath for 3 min.

   The solution must be chilled to minimize $HClO_4$ oxidation of cupferron to yellow-green products that coextract and interfere.

4. Add 5 ml of 0.25M cupferron mix, and let stand for 3 min.

5. Add 30 ml of chloroform, extract vigorously for 1 min, and discard the lower chloroform phase.

6. Repeat Step 5.

7. Rinse the walls of the funnel with about 5 ml of chloroform, swirl the funnel to settle the chloroform, then drain the chloroform completely without removing any of the aqueous phase.

8. Continue the analysis per Procedure G beginning with Step 3.

G. Extraction-Spectrophotometric Determination of Orthophosphate

1. Pipet a sample aliquot of 25 ml or less containing 5 to 100 µg of orthophosphate into a 125-ml separatory funnel.

2. Add 6 ml of conc $HClO_4$ and dilute to 35 ml with water.

   Measurements at Steps 2, 3, 6, 7, and 9 are not critical. Either Mohr pipets or appropriate graduated cylinders are adequate.

3. Add 5 ml of the ammonium molybdate reagent, mix by swirling, then let stand for 5 min.

4. Pipet exactly 25.00 ml of hexone and extract vigorously for 1 min.

5. Let the two phases separate, then drain and discard the lower aqueous layer.

6. Add 15 ml of water, contact gently for 30 sec, then drain the lower phase.

   In the absence of acids or salts, hexone–water mixtures form a difficult-to-separate emulsion when shaken vigorously. Use a gentle rocking motion to mix the two phases.

7. Repeat Step 6

8. Swirl the hexone solution to settle water droplets clinging to the walls of the funnel. Drain the water completely.

9. Add 15 ml of the chlorostannous acid reagent, extract vigorously for 15 sec, and drain and discard the lower aqueous layer.

10. Wait 15 min for color development.

11. Measure the absorbance against hexone at 625 mμ.

    If the solution is cloudy, centrifuge it in a 50-ml centrifuge tube.

    Use 5-cm cells for samples in the 1- to 15-μg $PO_4^{\equiv}$ range and 1-cm cells for samples in the 20- to 100-μg range. In between 15 and 20 μg, either cell may be used.

12. Record the data and calculate the results as shown on the example worksheet.

REFERENCES

1. D. F. Boltz, Colorimetric Determination of Nonmetals, New York: Interscience, 1951, pp 32-36.

2. G. F. Smith, "The Wet Ashing of Organic Matter Employing Hot Concentrated Perchloric Acid", G. Frederick Smith Chemical Company, Columbus, Ohio, 1954.

February 1970

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F. A. Duce
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FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Phosphate

CHARGE NUMBER _____ PROCEDURE P-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance Vs Hexone	Net Absorbance	Conversion Factor mg/abs.unit	mg PO_4 in Aliquot	mg PO_4 corrected for Bias			RESULT mg PO_4/ml
Blank		0.022							
Std, 50 mg PO_4		0.474	0.452	110.62					
Std, 75 mg PO_4		0.710	0.688	109.01					
			$\bar{X}$	109.82					
Bench Std.	1.00 ml	0.644	0.622		68.31	69.1 ± 2.4			69.1 ± 2.4

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\text{mg } PO_4}{\text{Net Abs.}} = \frac{50}{0.452} = 110.62$$

$$C'' = \frac{75}{0.688} = 109.01$$

$$\bar{X} = \frac{110.62 + 109.01}{2} = 109.82$$

$$D = BC = (0.622)(109.82) = 68.31 \text{ mg } PO_4$$

$$\text{Result} = \frac{E}{\text{Sample Vol.}} = \frac{69.1 \pm 2.4}{1.00} = 69.1 \pm 2.4 \text{ mg } PO_4/\text{ml}$$

APPROVED BY _____

PLUTONIUM SEPARATION FOR THE ISOTOPE DILUTION MASS SPECTROMETRIC ANALYSIS OF IRRADIATED FUELS

ABSTRACT

This method is designed to separate plutonium from irradiated fuel dissolver samples in a form suitable for analysis in surface ionization mass spectrometers. The sample aliquot and ^{242}Pu spike added for the isotope dilution concentration analysis is made 10M in hydrochloric acid; the plutonium is stabilized at the (IV) valence state by sequential treatments with iodide and bromate, and is adsorbed on an anion exchange resin column as the negatively charged chloride [$PuCl_6^{=}$] complex. The column is washed sequentially with 8M HCl, 8M HNO_3, and 2M HNO_3 to remove diverse ions including fission products, neptunium, and transplutonics[1,2]. The plutonium then is eluted with 0.2M HNO_3, evaporated to dryness, and dissolved in 3M HNO_3 for transfer to the filament of the mass spectrometer.

APPLICABILITY

This method is applicable to existing nuclear fuels including UO_2 pellets, uranium metal alloys, various uranium cermets, and u[illegible] plutonium mixed fuels. The known tolerance for uranium is 100[illegible] the plutonium. Dissolution schemes are not included; however [illegible] inorganic acids and fusion melts are acceptable. The procedure designed for high decontamination of fission products rather [illegible] for the quantitative recovery of plutonium. Before separation isotope spike which normally is ^{242}Pu is added, and treatment included to guarantee isotopic identity. The procedure is de[illegible] to separate about 0.5 to 5 µg of total plutonium which is the used for triple filament mass spectrometer sources. Smaller can be separated with no changes; larger amounts require sc reagents.

The procedure may be used to separate plutonium solely f distribution analysis merely by omitting the spike isot ^{242}Pu is formed by consecutive neutron captures on ^{2} irradiated fuels require an unspiked analysis to corr spike addition for the ^{242}Pu in the sample.

DISCUSSION

Based on quality control samples and on the results of duplicate sample analysis, the main source of error is the remote pipetting apparatus used to deliver the sample. The relative standard deviation at the 1-µg/ml Pu level with a fully automatic remote pipetter[3] delivering 500 µl is 0.8%, and for hand-operated, 500-µl micropipets (Ultrapette-type) is 0.37%. Bias for both the remote pipetter and micropipets is insignificant.

A shielded alpha-tight facility is required to protect personnel against beta-gamma penetrating radiation and alpha contamination when the fuel dissolver sample is handled. This facility need not be elaborate because the only special equipment required is the remotely operated pipetter for the delivery of the initial sample aliquot. Other operations can be performed with simple tong-type manipulators. After the ion exchange column separation of the plutonium from the fission products, an unshielded glove box can be used.

A successful isotope dilution analysis requires chemical identity of the determined component in the sample and added spike before the separation is initiated. In this method, the mixture of sample and spike in a 10M HCl medium is treated sequentially with iodide and bromate. Iodide reduces the plutonium(V) and-(VI) oxidation states to the (IV) state and bromate oxidizes the (III) state to the (IV) state. The (IV) state is stabilized as the hexachloro plutonium(IV), $PuCl_6^{=}$, complex in this medium.

SAFETY PRECAUTIONS

The samples will contain plutonium and higher transuranics. Take every precaution possible to prevent absorption through the skin or ingestion of these materials (See DISCUSSION).

APPARATUS AND REAGENTS

A. Apparatus

1. Heat Lamp.

2. Ion Exchange Column. A polyethylene column, about 5-mm diam, 25-mm long with a 2.5-ml reservoir at the top, is recommended. A convenient source is the Nalgene Unitary Dropper, manufactured by the Nalge Company, which has a molded bulb. The bulb is easily snipped with a scissors to provide the 2.5-ml

reservoir. Place a small wad of glass wool at the delivery end and add the resin slurry to occupy 1 ml. Wash the resin with 4 ml of 10M HCl.

3. Medicine droppers.

4. Pipets, micro, assorted sizes with control syringe.

5. Pipets, transfer (throwaway type).

6. Stoppers, polyethylene or rubber, size 0.

7. Test tube, centrifuge, 5-ml.

B. Reagents

Note: Prepare all reagents with Analytical Reagents Grade chemicals and distilled water.

1. Anion exchange resin. Use a distilled water slurry of Bio-Rad AG-1 X8, 100 to 200 mesh, chloride-form resin, or equivalent.

2. Hydriodic acid. Dilute 25 ml of 57% HI to 100 ml with water. Keep well stoppered. Discard when the brown color of elemental iodine, caused by air oxidation, is visible.

3. Hydrochloric acid, conc, 10M, and 8M.

4. Nitric acid, 8M, 3M, 2M, and 0.2M.

5. Plutonium-242 spike solution. Plutonium-242 is obtained through the Division of Research, AEC. The material usually is in the form of a low-fired oxide. Dissolve a quantity of the material in a minimum amount of hot, concentrated perchloric acid and dilute with 6M HCl to a final plutonium concentration of 1 µg/ml. Mix until homogeneous. Distribute the solution to 5-ml glass ampoules and flame seal. This provides long-term storage stability. When aliquots are desired, break open an ampoule and deliver the entire contents, as 500-µl aliquots, into 5-ml test tubes. Evaporation of the solvent hereafter causes no error; however, polyethylene stoppers should be placed in the test tubes to minimize the contamination hazards.

6. Potassium bromate solution. Prepare a saturated solution in water.

7. Standard plutonium solution. Transfer about 500 mg (one issue unit) of highly pure plutonium metal (NBS sample 949) to a 500-ml volumetric flask. The weight of each issue unit is provided with the sample. Dissolve the plutonium in 6M HCl using slight heat after the violent reaction subsides. Dilute to volume with 6M HCl and mix until homogeneous. Transfer a 1000-µl aliquot to a 1000-ml volumetric flask, dilute to volume with 6M HCl, and mix until homogeneous. Distribute this solution to 5-ml glass ampoules and flame seal for storage stability.

   Calculate the exact concentration of the standard plutonium solution by:

$$C = \frac{WP}{500} \qquad (1)$$

   where

   C = µg/ml of plutonium

   W = weight in mg of the plutonium metal

   P = fractional purity of the plutonium metal.

PROCEDURE

A. Calibration of ^{242}Pu Spike Solution

Pipet 500 µl each of the ^{242}Pu spike solution and the standard plutonium solution into a clean 5-ml centrifuge tube. The same dry-filmed pipet is recommended for both solutions to obtain maximum accuracy. Rinse the inside walls of the tube with 6M HCl to ensure that no droplets of the solutions remain unmixed. Evaporate slowly, without spattering, nearly to dryness and transfer the tube to the mass spectrometry laboratory. A minimum of six mixtures is recommended for this calibration.

B. Separation of Plutonium

Note: Steps 2 through 11 require a shielded, alpha-tight facility designed to handle irradiated fuel dissolver solutions. See DISCUSSION.

1. Pipet 500 µl of the ^{242}Pu spike solution into a 5-ml test tube.

   Omit this step if only the isotopic distribution of the Pu is to be determined.

2. Add 1.5 ml of conc HCl.

3. Transfer the tube to the shielded facility. Pipet a sample aliquot containing from 0.5 to 5 µg of Pu into the tube.

   The volume of the aliquot should be 200 to 1000 µl.

   If the concentration of Pu in the original sample exceeds 25 µg/ml, first prepare accurate dilutions using 10M HCl as the diluent.

4. Add 3 drops of the HI solution, then swirl the tube to mix the contents until homogeneous.

   Iodide reduces the (V) and (VI) oxidation states of Pu to the (IV) state in 10M HCl.

5. Heat the solution to about 80°C for 10 min under an infrared lamp.

6. Let the solution cool for about 10 min; and while slightly above ambient temperature, add 5 drops of saturated $KBrO_3$ solution, swirling the solution between each drop.

   Plutonium(III) is oxidized to Pu(IV) giving chemical identity of the Pu in the sample and the ^{242}Pu spike. The $KBrO_3$ causes gas formation. Swirling between added drops relieves the gas pressure

7. Transfer the solution to the ion exchange column collecting the effluent in any convenient container for disposal.

8. Pass three 1-ml portions of 8M HCl through the column and discard the effluent.

   Most extraneous ions, fission products and fuel components, elute from the column.

9. Pass ten 1-ml portions of 8M HNO_3 through the column and discard the effluent.

   Uranium elutes from the column in this step and Step 10.

10. Pass three 500-µl portions of 2M HNO_3 through the column and discard the effluent.

11. Place a 5-ml centrifuge tube under the column and elute the Pu with four 500-µl portions of 0.2M HNO_3.

12. Slowly evaporate to dryness under an infrared lamp.

13. Dissolve the residue in 1 drop of 3M HNO_3, stopper with a polyethylene stopper, and transfer the tube to the mass spectrometry laboratory.

REFERENCES

1. I. K. Kressin and G. R. Waterbury, "The Quantitative Separation of Plutonium from Various Ions by Anion Exchange," Anal. Chem., 34 (1962) pp 1598-1601.

2. J. P. Faris and R. F. Buchanan, "Anion Exchange Characteristics of Elements in Nitric Acid Medium," Anal. Chem., 36 (1964) pp 1157-1158.

3. F. W. Dykes, J. P. Morgan, W. G. Rieder, The Remote Analytical Facility Model "B" Pipetter, USAEC Report IDO-14456, Atomic Energy Division, Phillips Petroleum Company, (October 1958).

W. A. Emel
J. E. Rein
April 1969

TITRIMETRIC DETERMINATION OF REDUCING NORMALITY OF FERROUS SULFAMATE SOLUTIONS

ABSTRACT

In this method, iron(II) is titrated with standard potassium dichromate solution with diphenylaminesulfonate as the indicator.

APPLICABILITY

The method, designed for aqueous inorganic solutions of ferrous sulfamate, is applicable to other ferrous solutions. Interferences include oxidizable substances which react with the titrant, cations which form precipitates with phosphoric acid, and colored materials which obscure the end point color transition.

The range of the method is 0.09 to 0.9 meq of iron(II). Best precision is obtained toward the upper limit of this range. The maximum practical sample aliquot is 25 ml; therefore, the lowest determinable concentration is 0.0036N.

DISCUSSION

Sulfamate even at a 4:1 sulfamate to iron(II) molar ratio does not react with dichromate at temperatures up to 60°C.

Useful references for this method are Kolthoff and Belcher[1] and Furman[2].

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 10-ml, graduated in 0.05-ml increments.
2. Erlenmeyer flasks, 125-ml.
3. Graduated cylinder, 10-ml.
4. Magnetic stirring apparatus with Teflon-coated stirring bars.
5. Pipets, macro and micro, assorted sizes, with control syringe and suction bulb.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Phosphoric acid, 7.4M.

2. Potassium dichromate, 0.1000N standard solution. Dissolve 4.9035±0.0005 g of $K_2Cr_2O_7$ (dried for 1 hr at 110°C) in water and dilute to 1 liter with water.

3. Diphenylaminesulfonate indicator solution, 0.005M. Dissolve 0.26 g of sodium diphenylaminesulfonate in 100 ml of water. If only the barium salt is available, suspend 0.32 g of barium diphenylaminesulfonate in 100 ml of water, add 0.5 g of $Na_2SO_4 \cdot 10H_2O$, mix, allow the barium sulfate precipitate to settle, then decant off the clear solution.

PROCEDURE

A. Blank

No blank determination is required because significant levels of reducing contaminants usually are not present in the reagents and the indicator blank is negligible.

B. Analysis of Samples

1. Pipet a sample aliquot containing 0.09 to 0.9 meq of Fe(II) into a 125-ml Erlenmeyer flask which contains a stirring bar.	The largest practical aliquot size is 25 ml. Best precision is attained with samples containing 0.9 meq of Fe(II).
2. Dilute to approximately 25 ml with water and start stirring.	
3. Add 10 ml of 7.4M H_3PO_4.	
4. Add 2 drops of diphenylaminesulfonate indicator solution.	
5. Titrate with standard 0.1000N $K_2Cr_2O_7$ to the appearance of a purple color which persists for 15 sec.	The color transition is green to greenish-gray to gray to purple.

6. Record the data and calculate the results as shown on the example work sheet. Report results to three significant figures.

REFERENCES

1. I. M. Kolthoff and R. Belcher, Volumetric Analysis, New York: Interscience Publishers, Vol 3, 1957, p 170.

2. N. H. Furman, Scott's Standard Methods of Analysis, 6th ed., New York: Van Nostrand, Vol 1, 1962, p 542.

R. Fullerton
December 1967

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Reducing Normality

CHARGE NUMBER _____ PROCEDURE Red. Norm - Vol. - I

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	$K_2Cr_2O_7$, $\sim N$	$K_2Cr_2O_7$, ml	Fe(II), meq	Fe(II) meq corrected for Bias				RESULT $\sim N$
2A5-654	2.00 ml	0.1000	7.65	0.765	0.766 ±	0.10			0.383 ± 0.005

ANALYZED BY _____ DATE _____

CALCULATIONS:

$C = AB = (0.1000)(7.65) = 0.765$

$$\text{Result} = \frac{D}{2.00\ ml} = \frac{0.766 \pm 0.010}{2.00} = 0.383 \pm 0.005\ \sim N$$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH THIOUREA FOLLOWING SEPARATION BY DISTILLATION

ABSTRACT

Ruthenium at microgram levels is distilled as ruthenium tetroxide from a sulfuric acid - sodium bismuthate medium into an ethanol-hydrochloric acid medium. It is determined by spectrophotometric measurement of the blue ruthenium(III)-thiourea complex at 620 mμ.

APPLICABILITY

This method, based on a thiourea spectrophotometric procedure [1] for the determination of microgram amounts of ruthenium preceded by a distillation-separation of ruthenium tetroxide [2], is applicable to a wide variety of samples. The only major metal interference is osmium which also distills as the tetroxide and reacts with thiourea. Very high levels of extraneous metals interfere as explained in the DISCUSSION section.

Chloride and nitrate interfere with the development of the ruthenium(III)-thiourea complex. The pretreatment procedure is designed to adequately remove both these ions.

The range of the method is 10 to 500 μg of ruthenium. Two optical cell path lengths are used to cover this range: 5-cm cells for samples containing 10 to 120 μg of ruthenium and 1-cm cells for samples containing 50 to 500 μg of ruthenium. The volume of sample that may be taken for analysis depends on the nitrate and diverse metals content of the sample. If both diverse metal ions and nitrate are low, sample volumes up to about 50 ml are permissible and for such samples, the lowest concentration determinable is 0.2 μg Ru/ml.

DISCUSSION

The method consists of three basic steps: (a) preliminary evaporation of samples to sulfuric acid fumes to expel nitrate, (b) distillation of ruthenium as the tetroxide from dilute sulfuric acid medium containing sodium bismuthate and absorption of the ruthenium tetroxide in ethanol-hydrochloric acid medium, and (c) development and spectrophotometric measurement of the blue ruthenium(III)-thiourea complex. At each of these steps, there are critical variables and potential trouble spots.

In the preliminary evaporation step, the sample is evaporated to sulfuric acid fumes to expel nitrate. Hydrochloric acid is present during the evaporation to help expel nitrate by reducing it to volatile nitrogen oxides and to prevent volatilization of ruthenium by keeping the ruthenium in a reduced state. Ruthenium partially volatilizes from

nitrate-rich aqua regia so sufficient hydrochloric acid must be added to maintain a high chloride to nitrate ratio. A two-step, hydrochloric acid followed by hydrochloric acid-sulfuric acid, evaporation procedure is necessary to completely expel nitrate from samples containing large amounts of metals. When sulfuric acid is admitted at the beginning of the evaporation, extraneous metal sulfates precipitate and occlude nitrate. Large amounts of extraneous metals interfere. The ruthenium tetroxide is distilled from 2.5M H_2SO_4 containing sodium bismuthate into an ethanol-hydrochloric acid medium. A slow flow of air is used to carry the ruthenium tetroxide. The critical variables are the concentration of sulfuric acid, the volume of distillate, and the flow rate of the air sweep. The maximum sulfuric acid concentration is 3M. Above this, bismuthate is reduced by water. The ruthenium is oxidized rapidly so the delivery tube of the still must be immersed in the ethanol-HCl collection medium before the addition of bismuthate. It is distilled quantitatively in the first 4 ml of distillate. The effect of sweep-gas flow rate on ruthenium recovery has not been studied extensively for the ethanol-hydrochloric absorbing solution; however, quantitative recovery is known to be obtained at a flow rate of 1 to 2 bubbles/sec. A 1:1 (v/v) mixture of 95% ethanol and conc HCl absorbs ruthenium tetroxide satisfactorily without chilling; however, the volume of distillate collected is important so an ice bath is specified in the method to reduce evaporation.

The blue ruthenium(III)-thiourea complex is developed in the ethanol-hydrochloric acid absorbing medium at 85°C and its absorbance is measured at 620 mμ. The critical variables are the relative concentrations of hydrochloric acid, ethanol, and water, temperature, time, and the age of the thiourea solution. Color development is complete in 10 min at 85°C at a hydrochloric acid concentration of about 4.25M and an ethanol concentration of about 33%. In the recommended procedure, which differs slightly from that of Ayres and Young[1], 15 ml of a 1:1 conc HCl-95% ethanol mixture is used to collect the ruthenium distillate and 1.25 ml of 10% (w/v) thiourea solution is added for color development. These conditions, which give complete color development in the presence of 5 ml of water, enable direct color development on the distillate without an evaporation. Water effects the color development so the total volume of distillate plus rinse should be controlled at 5±1 ml. Aqueous thiourea solutions are not stable and old solutions produce a cloudiness during color development. Until its shelf life is established, prepare a fresh solution each week.

SAFETY PRECAUTIONS

In the evaporation-distillation phase of this method, water must be added to conc H_2SO_4. Chill the conc H_2SO_4 to minimize spatter. Use caution when handling all acidic reagents.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1- and 5-cm.
2. Beakers, Berzelius, 600-ml.
3. Distillation apparatus and associated equipment (Figure 1).
4. Erlenmeyer flasks, 125-ml.
5. Funnel, small.
6. Graduated cylinders, 10-ml.
7. Graduated cylinders, 25-ml, with glass stoppers.
8. Hot plate.
9. Meker burner.
10. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.
11. Pipets, Mohr, 5-ml.
12. Reflux splash heads for 125-ml Erlenmeyer flasks.
13. Spectrophotometer, Beckman Models DU or DK or Cary Model 14.
14. Tongs.
15. Water bath, 85°C. (A 2- or 4-liter beaker of water and a hot plate equipped with a magnetic stirrer can be used to set up a satisfactory bath.)

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ethanol-conc HCl mixture. Mix 250 ml of 95% ethanol with 250 ml of conc HCl.
2. Ethanol-6M HCl mixture. Mix 500 ml of 95% ethanol with 500 ml of 6M HCl.
3. Hydrochloric acid, conc.

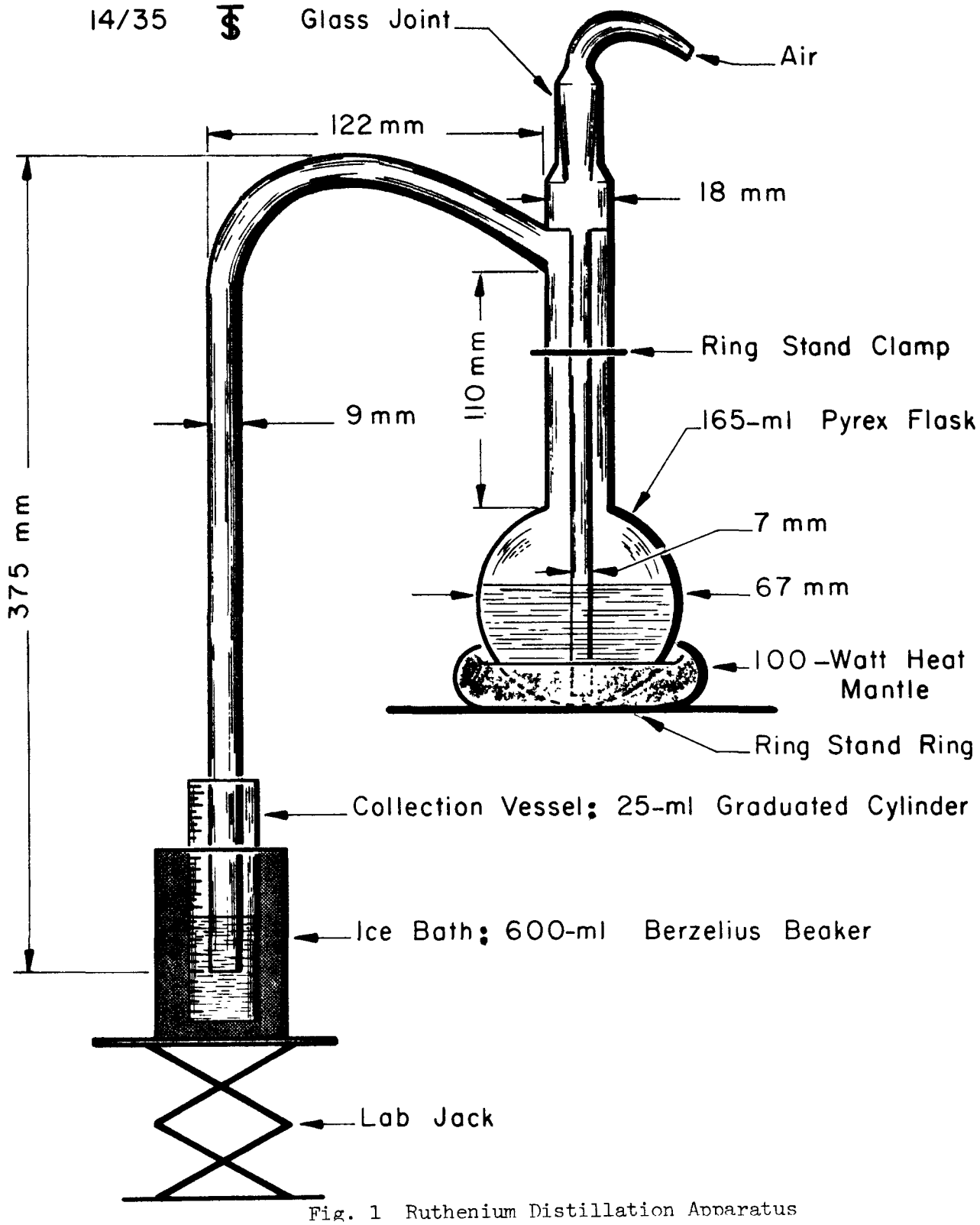

Fig. 1 Ruthenium Distillation Apparatus

4. Ruthenium stock solution, 10 mg/ml. Prepare an approximately 10 mg/ml solution with $RuCl_3$ and 1M HCl. Standardize the solution gravimetrically by evaporating weighed aliquots to dryness in a quartz boat and reducing the ruthenium to the metal in a hydrogen atmosphere [3].

5. Ruthenium calibration standard I, 200 µg Ru/ml. Dilute an appropriate (weighed) aliquot of the 10 mg/ml stock solution with 0.1M HCl.

6. Ruthenium calibration standard II, 400 µg Ru/ml. Dilute an appropriate (weighed) aliquot of the 10 mg/ml stock solution with 0.1M HCl.

7. Sodium bismuthate, $NaBiO_3$.

8. Sulfuric acid, 12M.

9. Thiourea solution, 10% (w/v). Dissolve 10 g of thiourea in 85 ml of cold water. Filter through a 0.45-µ membrane filter and dilute to 100 ml with water. Prepare a fresh solution weekly.

PROCEDURE

A. Blank

Process a blank with each series of standards and samples per Procedure C using 1 ml of water in place of the sample aliquot.

B. Calibration and Bench Standards

Two calibration standards are provided to cover the range 10 to 500 µg Ru. Use 0.20-ml portions of calibration standards I and II for measurements in 5-cm cells and 1.00-ml portions of standards I and II for measurements in 1-cm cells.

Depending on the concentration range of the samples, process two appropriate calibration standards or all four calibration standards per Procedure C. Divide the micrograms of ruthenium in each standard by its respective absorbance to obtain the calibration factor. With each pair of standards, the difference between the two factors should not exceed specified limits and the average of the two factors should agree with the established factor within specified limits. If either or both of these specifications are not met, reprocess the standards. If difficulties still persist, contact your supervisor.

C. Analysis of Samples

1.	Pipet a sample aliquot containing 10 to 500 µg of Ru into a 125-ml Erlenmeyer flask. Place a reflux head on the flask.	
2.	Add 10 ml of conc HCl and evaporate to about 2 ml over a Meker burner.	Use a small flame and swirl constantly to avoid baking the sample.
3.	Let cool, add 5 ml of conc HCl and 10 ml of 12M H_2SO_4, then evaporate to the appearance of SO_3 fumes. Continue heating the sample until the H_2SO_4 is condensing at the neck of the Erlenmeyer flask.	
4.	Let cool, then chill the sample in an ice bath.	If the analysis must be interrupted, this is a permissible stopping place.
5.	Pour the H_2SO_4 solution of the sample into the distillation flask, then quantitatively rinse the sample into the distillation flask with 30 ml of water.	The H_2SO_4 concentration is a critical factor in the distillation. At this step and Step 8, use a graduated cylinder to measure the water.
6.	Pour 15 ml of 1:1 ethanol-conc HCl into a 25-ml graduated cylinder and immerse the delivery tube of the distillation flask into the solution.	Adjust the immersion of the tube so that with the sweep air coming through the tube, the surface of the ethanol-HCl solution is at 19 ml.
7.	Adjust the flow rate of the air sweep to 1 to 2 bubbles/sec at the orifice of the delivery tube.	
8.	Weigh 0.5 g of $NaBiO_3$ into the original 125-ml Erlenmeyer flask. Add 15 ml of water and swirl the flask until a uniform slurry is obtained.	

9.	Pour the $NaBiO_3$ slurry into the distillation flask and quickly replace the air inlet plug.	
10.	Heat the mixture and distill over 4 ml.	With a setup as illustrated in Figure 1, 4 ml of distillate has been collected when the level of the ethanol-HCl solution rises from the 19-ml position, tep C-6, to the 25-ml position of the graduated cylinder.
11.	Turn off the power. Immediately lower the graduated cylinder and rinse the delivery tube with 1 ml (1 medicine dropper full) of water.	Rinse the distillation flask thoroughly with demineralized water. If solids remain, fill the distillation flask with water and immerse it in an ultrasonic bath. If the analysis must be interrupted, this is a permissible stopping place.
12.	Add 1.25 ml of 10% (w/v) thiourea solution.	It is not necessary to intimately mix the thiourea reagent and the sample solution.
13.	Place the graduated cylinder in an 85°C water bath for 10 min.	
14.	Chill the graduated cylinder and contents to room temperature with cold water.	
15.	Dilute to 25 ml with 1:1 ethanol-6M HCl, stopper, and mix until homogeneous.	
16.	Measure the absorbance in a 1- or 5-cm cell against water at 620 mμ.	Use 5-cm cells for samples that contain less than 50 μg of Ru, 1-cm cells for samples that contain more than 120 μg of Ru. In between, either cell may be used. The blue Ru(III)-thiourea complex is stable for at least 4 hr.

17. Record the data and calculate the results as described on the example work sheet. Report results to 3 significant figures.

REFERENCES

1. G. H. Ayres and F. Young, "Spectrophotometric Study of the Ruthenium-Thiourea Complex", Anal. Chem., 22 (1950), p 1277.

2. R. E. Foster, M. E. Kussy, R. E. McAtee, G. D. Workman, "Procedure for the Separation and Mass Spectrometric Analysis of Fission Product Ruthenium", Burnup Determination of Nuclear Fuels - Project Report for the Quarter October 1 - December 31, 1965, Edited by W. J. Maeck, R. M. Abernathey, and J. E. Rein, IDO-14676 (May 1966), pp 19-24.

3. C. V. Banks and J. W. O'Laughlin, "Spectrophotometric Determination of Ruthenium with 1,10-Phenanthroline", Anal. Chem., 29 (1957), p 1412.

S. S. Yamamura
December 1967

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Ruthenium

CHARGE NUMBER _____ PROCEDURE Ru - Color - 1

SPECIAL INSTRUCTIONS:

Samples are about 10 µg/ml in ruthenium
Use 5-ml samples and 5 cm cells

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA. $a_0/d_1/a_1\ d_2\ a_2$	Absorbance vs H_2O	Net Absorbance	Conversion Factor µg Ru/Abs	µg Ru in Aliquot Analyzed	µg Ru corrected for Bias			RESULT µg Ru/ml
Blank		0.014							
Std I, 40 µg		0.294	0.280	142.9					
Std II, 80 µg		0.564	0.550	145.5					
			$\bar{X}$	144.2					
Ru-1	5.00 ml	0.334	0.320	144.2	46.1	47.0 ± 2.4			9.40 ± 0.48

ANALYZED BY _____ DATE _____

CALCULATIONS:

C = Conversion Factor = $\frac{\text{µg Ru in Std}}{\text{Net Absorbance}}$

$C' = \frac{40}{B} = \frac{40}{0.280} = 142.9$ $\quad C'' = \frac{80}{B} = \frac{80}{0.550} = 145.5$

$\bar{X}\ \ 0.5(C' + C'') = 0.5(142.9 + 145.5) = 144.2$ µg Ru/Abs unit

Sample Ru-1

Net Absorbance = 0.334 − 0.014 = 0.320

D = µg Ru = BC $(0.320)(144.2) = 46.1$ µg

Result = $\frac{E}{\text{Sample vol}} = \frac{47.0 \pm 2.4}{5.00} = 9.40 \pm 0.48$ µg Ru/ml

APPROVED BY _____

PREPARATION OF DESCALING SOLUTIONS FOR CHEMICAL ANALYSIS

ABSTRACT

Procedures are described for the preparation of two types of descaling solutions, alkaline permanganate (AP) solutions and aqueous solutions of organic complexing agents, for chemical analysis. The solutions are filtered and the residues are dissolved and recombined with the filtrate for organic samples or maintained in a separate solution for AP samples.

APPLICABILITY

This method is designed specifically for AP solutions and aqueous solutions of organic complexing agents. It is applicable but not limited to the following organic solutions: monoammonium citrate-Versenol (MAC/HEDTA), hydrazine-Versene (HV), diammonium citrate (AC), and thioglycolic acid-Versenol (THIO/HEDTA). The procedure for organic samples also is applicable to 2:1 mixtures of AP and MAC/HEDTA solutions.

The descaling solutions generally contain varying amounts of radioactivity. Samples with an activity >5 R/hr are processed in a shielded cave equipped with masterslave manipulators while samples with an activity of <5 R/hr are processed behind lead bricks in a hood.

DISCUSSION

The organic solutions are filtered through membrane filters and the filter and solids are ignited in a Vitreosil beaker. The residue is then fused with sodium bisulfate ($NaHSO_4$) and the melt is dissolved in the filtrate. Preparation of the AP solution differs from the preparation of the organic solutions in the handling of the separated solids; the solids are composed primarily of metal oxides and silica and cannot be recombined with the alkaline filtrate because metal hydroxides will precipitate. These solids are dissolved and analyzed separately from the filtrate. They are ignited, transferred to a Teflon beaker, and treated with hydrofluoric acid and sulfuric acid to volatilize the silicon. The solution is heated to fumes of sulfur trioxide, cooled, transferred back to the Vitreosil beaker, and heated to dryness to remove the excess sulfuric acid. The remaining solids then are dissolved with hydrochloric acid and hydrogen peroxide. Iron and cobalt are usually determined only in the residue, while nickel and chromium are determined in both residue and filtrate.

Two procedures are used for filtering the descaling solutions. The first method[1], adaptable for remote operation, uses the three-vessel filtration apparatus shown in Figure B-15 and requires a minimum amount of manipulation in separating the solids and in rinsing. The second method involves the use of a special vacuum flask as shown in Figure 2. It is simpler to use than the three-vessel system but should not be used for samples having an activity >1 R/hr due to more frequent contact during the filtration.

SAFETY PRECAUTIONS

Protective clothing, gloves, and safety glasses should be worn while handling radioactive materials and strong acids. Safe Work Permits shall be obtained from the job supervisor when handling samples with an activity >1 R/hr. All work should be conducted behind adequate shielding. Sample containers should be washed to minimize external contamination.

APPARATUS AND REAGENTS

A. Apparatus

1. Balance, platform or equivalent.
2. Beakers, Griffin, 250-ml.
3. Beakers, Teflon, 100-ml.
4. Beakers, Vitreosil, 100-ml.
5. Burner, Meker.
6. Filters, Millipore membrane, 47-mm diam, 0.45-μ pore size.
7. Filters, Whatman, ashless, 7-cm.
8. Filtration equipment (see Figures 1 and 2).
9. Flasks, volumetric, 50-ml and 100-ml.
10. Furnace, muffle or equivalent.
11. Graduated cylinders, 500-ml and 100-ml.
12. Hot plates, Chromalox.
13. Lab jack containing a rubber mat on the top surface area (See Figure 2).
14. Medicine dropper.
15. Polyethylene bottles, 2-, 4-, 16-, and 32-oz.
16. Ring stands with clamps and braces and ring clamp.
17. Rubber policeman.
18. Speedyvap cover glass, 3.5- and 4.5-in.
19. Tongs, large and medium.

20. Transite boards.
21. Triangles, glass.
22. Tweezers.
23. Wash bottles, 8- and 16-oz.
24. Watch glass, Pyrex, 2.5-in.
25. Weighing dishes, aluminum.

B Reagents

NOTE: Use reagent grade chemicals throughout this method.

1. Acetone.
2. Hydrochloric acid, 12M, 7M.
3. Hydrofluoric acid, 48%.
4. Hydrogen peroxide, 30%.
5. Sodium bisulfate.
6. Sodium hydroxide.
7. Sulfuric acid, 18M.

PROCEDURE

A. Blanks

Reagent blanks are not routinely processed with this method. If a reagent blank is requested, process a Millipore filter in the same manner as the samples and dissolve the treated filter in a matrix solution prepared by the Quality Control Laboratory.

B. Preparation of Organic Samples.

1. Remove the samples from their shipping containers and wash to remove external contamination.

Store the samples behind a lead brick barricade if the samples are reading >20 mR/hr.

2.	Measure the sample volume with a graduated cylinder and record it on the sample work sheet.	
3.	Filter the sample by either Procedure D or Procedure E and then continue with Step 4.	
4.	To the ignited solids from Procedure D or E, add $NaHSO_4$ at the rate of 3 g/l of original sample volume.	Weigh the $NaHSO_4$ into a 50-ml plastic or glass beaker. Use a single pan balance.
5.	Cover the beaker with a 2.5-in. "Pyrex" watch glass.	
6.	Heat the beaker in a moderate flame using a Meker burner. Swirl the melt to contact all of the residue.	The flame should have a blue cone about 1.5 in. high to melt the flux and fuse the residue without driving off the SO_3 before the fusion is complete.
7.	Heat until all of the solids are dissolved. The watch glass should provide adequate reflux; if the sample bakes dry the addition of a few drops of conc H_2SO_4, after the beaker is cooled, may aid in completing the fusion.	If the fusion requires the use of additional $NaHSO_4$, make a note of this on the sample prep work sheet.
8.	Cool the beaker and add ∿70 ml of the filtrate to dissolve the melt.	The addition of a few pellets of NaOH may be required when processing HV samples; the Versenol precipitates if the solution becomes too acidic.
9.	Digest this mixture on a hot plate set on low until the melt is dissolved.	

10. Remove the beaker from the hot plate and transfer the solution to the filtrate bottle. Rinse the beaker with sample solution, pouring it back and forth to obtain a homogeneous mixture.

    If the beaker contains undissolved melt, repeat Steps 8 and 9. Do not add any water to this solution because it would dilute the sample.

11. Mix the solution thoroughly and decant two 50-ml aliquots of the solution into two properly labeled 2-oz. polyethylene bottles. Transfer one of the bottles to the Spectrochem Lab for Cr and Ni analyses, and transfer the other to the Radiochem Lab for radiochemical analyses.

12. Store the samples in a shielded area to minimize exposure to laboratory personnel.

C. Preparation of Alkaline Permanganate (AP) Samples

1. Wash the sample bottles to remove external contamination and store behind a lead barricade if >20 mR/hr.

2. Measure the sample volume in a graduated cylinder and record this volume on the work sheet.

    Frequently the requester will ask for two or more of these samples to be composited in equal volumes. If one of the solutions has a smaller volume, use it first to obtain equal volumes.

3. Filter the sample as described in either Procedure D or Procedure E and then continue with Step 4.

    If one of the samples has precipitated MnO_2, process the samples separately, allowing the compositing to take place in the filtrate receiving vessel. Mixing the samples before will cause more MnO_2 to precipitate and will make filtering difficult.

4.	Transfer the ignited residue from either Procedure D or E to a Teflon beaker. Use water rinses to make the transfer. Retain the Vitreosil beaker for later use.	If the samples were not received in glassware, silica should not be present and Steps 4 through 9 can be omitted.
5.	Moisten the residue with 1 ml of distilled water and add 1 ml of 18M H_2SO_4.	Do not use platinum ware for the HF treatment because Pt interferes with the Co analysis.
6.	Add 5 ml of 48% HF and heat to fumes of SO_3.	
7.	Repeat Step 6.	
8.	Cool and transfer with distilled water back to the Vitreosil beaker.	
9.	Heat the beaker until all of the H_2SO_4 is fumed off and a dry residue remains.	
10.	Moisten the residue with 1 ml of distilled water and add 10 ml of 7M HCl.	
11.	Cover with a watch glass and gently heat the beaker to dissolve the residue.	
12.	If the residue does not dissolve after 15 min of digesting add 2 ml of 30% H_2O_2 dropwise with a dropper and continue digesting.	Too much H_2O_2 will react violently and may foam out of the beaker. USE CAUTION.
13.	After the dissolution appears complete, digest an additional 15 min to dispel H_2O_2.	
14.	Cool the solution and transfer it to a 50-ml volumetric flask.	
15.	Dilute to volume with water and mix well.	

16. Transfer the solution to a 2-oz. polyethylene bottle and store the filtrate and residue in a shielded area.

Allow 30 ml for Fe and Co analyses, 15 ml for radiochemical analyses and 5 ml for Ni and Cr analyses. Do not exceed these volumes unless all other work is completed.

D. Three-Vessel Filtration System

1. Assemble the equipment (Figure 1) behind a lead barricade in a hood.

2. Place a 47-mm diam membrane filter on the filter holder and clamp the chimney in place.

3. Turn on both vacuum lines.

4. Close valves B, C, and D and open valve A.

This will send the filtrate to the filtrate vessel.

5. Agitate the sample to loosen insoluble material.

If an AP sample has precipitated, decant most of the sample into the receiver vessel before shaking.

6. Pour the sample into the receiving vessel.

If large quantities of solids are evident, pour small increments of the solution into the vessel. If the filter clogs, change the filter as described in Steps 10, 11, and 2 and continue the filtration.

7. When the entire sample has been filtered, close valve A and open valve B.

8. Rinse the sample bottle and/or graduate with distilled water and pour the rinse onto the filter.

9. Rinse down the walls of the receiving vessel with distilled water to wash the insoluble material onto the filter.

10. Remove the clamp from the filter holder and lift the receiver vessel up to facilitate washing the solids onto the filter from the junction edges.

    This step does not require any special care to wash down all of the solids. A damp piece of Whatman ashless filter paper can be used to wipe the vessel clean.

11. Close valve B and remove the filter with a pair of tweezers and transfer it to a damp piece of Whatman filter paper.

    Remote - Close valve B. Remove filter holder at the quick disconnect and invert holder over a Vitreosil beaker, then attach an air line to the quick disconnect to force the filter into the beaker.

    The membrane filter is wrapped in a Whatman filter paper to prevent a rapid combustion of the membrane and possible sample loss during the subsequent ignition step.

12. Fold up the filter paper and place it into a Vitreosil beaker for ashing.

13. Place a polyethylene bottle under valve C and open valves A and C. Turn off the vacuum to drain the filtrate. Cap and save the filtrate for later use.

14. Remove the stopper from the filtrate vessel and rinse the walls down with distilled water followed by an acetone rinse. Discard these rinses.

    Remote - Replace the filter holder on the vacuum line and place Millipore filter on the holder, connect holder to receiver vessel, fill receiver vessel half full of water. Turn vacuum on. Turn valve A on. After all of the water has been down into the filtrate vessel, place polyethylene bottle under valve C.

Turn valve A off and open valve C; action of air entering through valve C will cause water to splash inside and rinse out filtrate vessel. Turn off vacuum and let water out.

15. Replace the stopper, close valves A and C. Turn on the vacuum to dry the system before filtering another sample.

16. Ignite the beaker containing the filtered residue in a Meker burner or muffle furnace to completely destroy the filter paper.

17. Continue with Procedure B-4 for organic samples or Procedure C-4 for AP samples.

E. Single Filtration Vessel

1. Assemble the apparatus as shown in Figure 2.

2. Place a 47-mm diam membrane filter on the holder and clamp on the chimney.

3. Place a polyethylene bottle for collecting washes on the rubber covered lab jack and lower the vacuum flask over it. For AP samples omit Steps 4 and 5.

Organic sample bottles will require rinsing and filtration of the rinses to ensure complete recovery of solids. AP samples will be transferred directly from the graduated cylinder to the filter.

4. Turn on the vacuum and wash the residue from the sample bottle onto the filter. Discard the washings.

At this point the sample is in a graduated cylinder. (See Procedure B, Step 2.)

5. Turn off the vacuum and replace the polyethylene bottle with the original sample bottle.

6. Turn on the vacuum and pour the solution from the graduated cylinder into the chimney.

7. Continue filtering until the solution is filtered or the filter clogs.

   If the filter clogs, replace the filter as described in Steps 10, 11, and 2 without rinsing any water into the filtrate.

8. Turn off the vacuum and remove the filtrate bottle and replace it with a bottle for collecting washes.

9. Rinse down the graduated cylinder and the walls of the chimney.

10. Remove the clamp, lift up the chimney and rinse the junction edges with distilled water.

11. Transfer the filter with a pair of tweezers to a damp piece of Whatman filter paper. Fold the paper over and use it to wipe out any particles adhering to the chimney or filter holder.

    The membrane filter will burst into flames when heated. To prevent this and a subsequent sample loss, a slow burning ashless paper like Whatman is used to wrap the membrane filter.

12. Transfer the residue to a Vitreosil beaker and ignite over a Meker burner or in a muffle furnace.

    If a batch of samples is being ashed, start them in a cold muffle furnace and heat them to 600°C for $\sim$ 1 hr.

13. Continue with Procedure B-4 for organic samples or Procedure C-4 for AP samples.

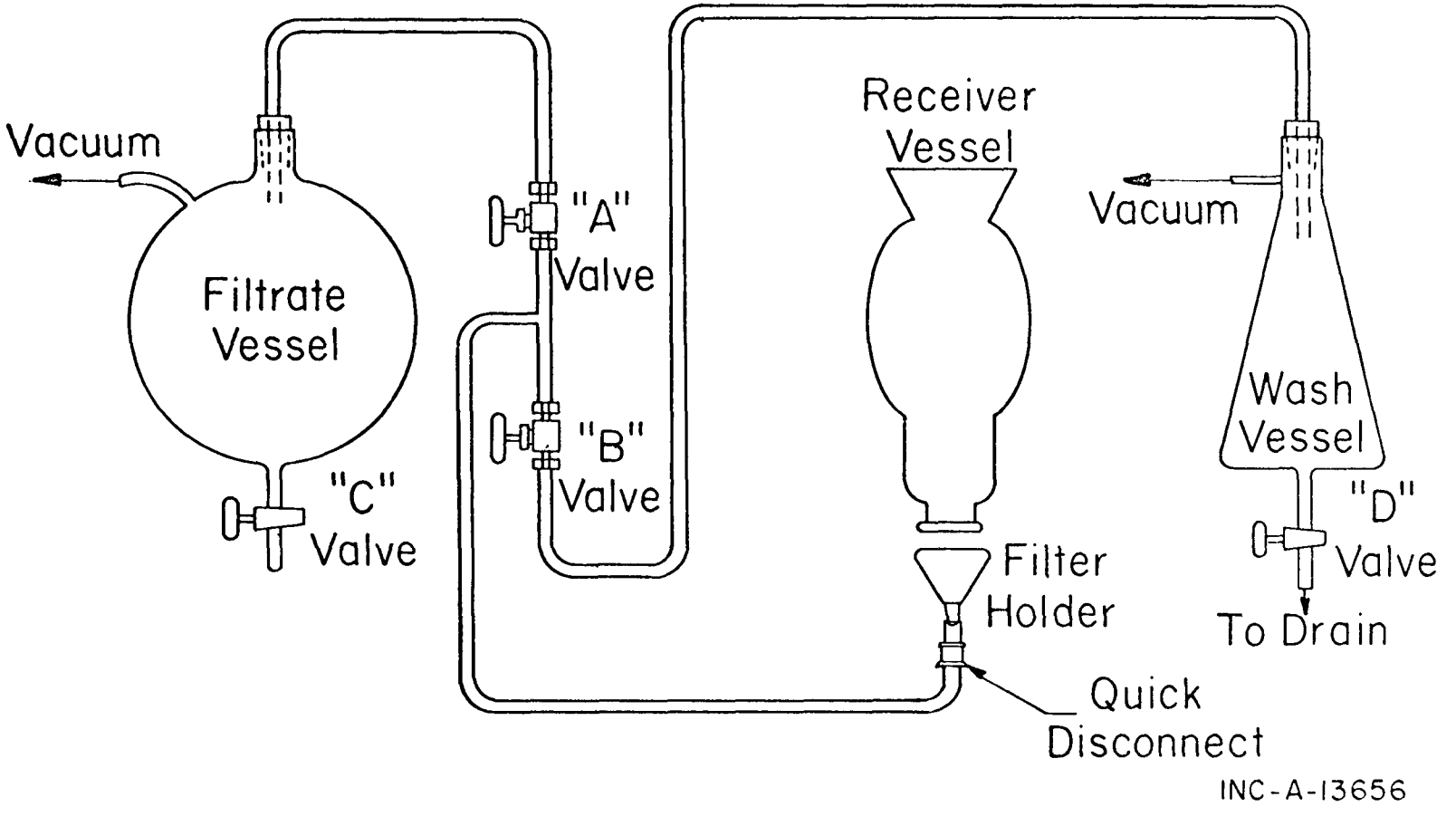

Fig. 1 Three-vessel filtration apparatus.

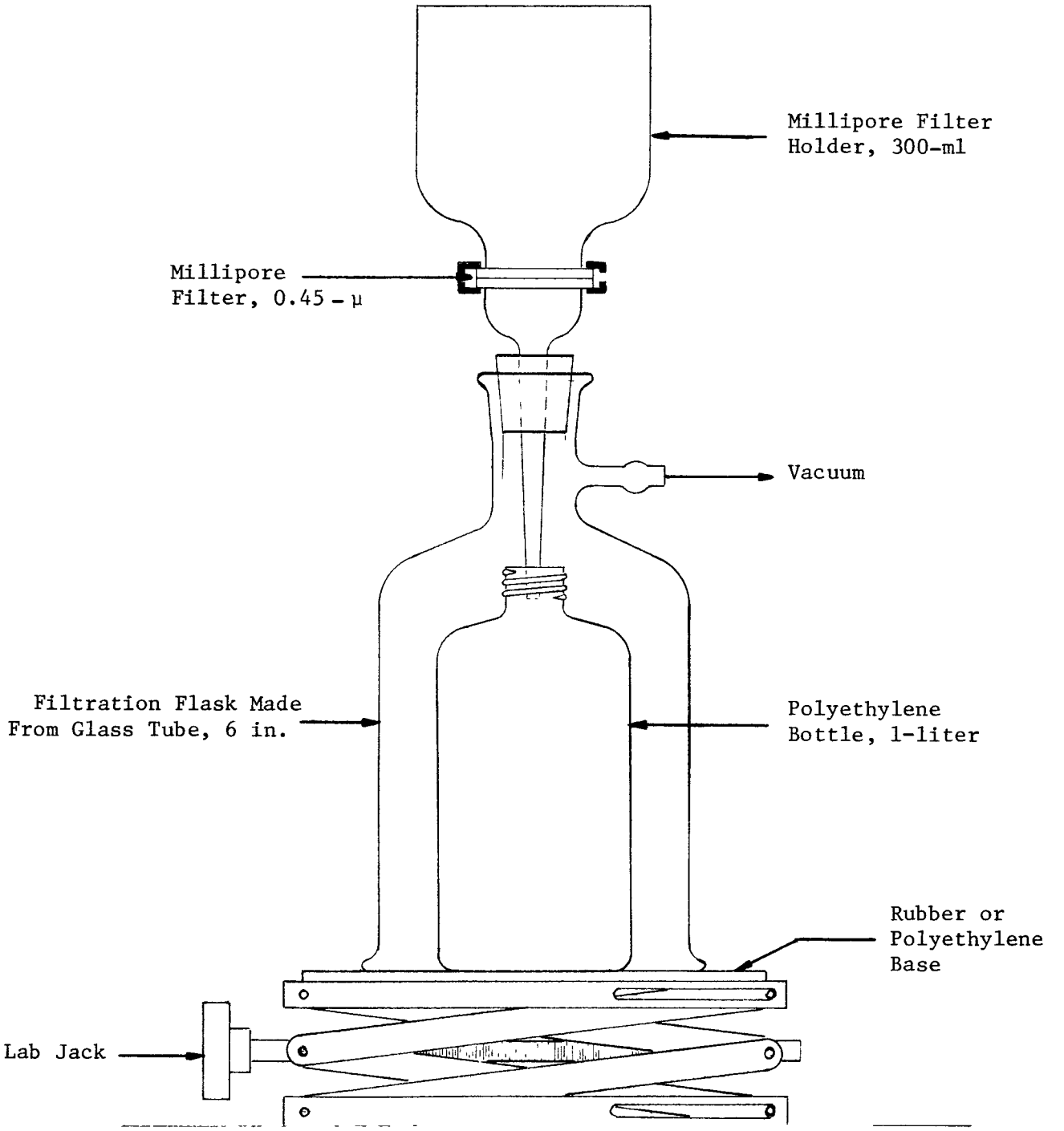

Fig. 2 Single-vessel filtration apparatus.

REFERENCE

1. R. C. Shank et al, Analytical Chemistry Branch Annual Report for Fiscal Year 1969, IN-1316 (September 1969), pp 57-59.

J. P. Clark
D. R. Trammell
June 1972

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Sample Prep

CHARGE NUMBER _____ PROCEDURE Sample Prep - 1

SPECIAL INSTRUCTIONS:

* Combine in Equal proportions

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Total Sample Volume, ml	$NaHSO_4$ to use, g	Dissolved Sol'd volume, ml	Radio Chem	Spec Lab	complete	Date	RESULT Prepared By
HV-923		750	225		✓	✓	✓	7-3	DRT
AP-225 *	500 ml								
AP-227 *	500 ml	1000*		50	✓	✓	✓	7-8	DRT

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$B = \frac{(A)(30\text{ g } NaHSO_4)}{1000} = \frac{(750)(3)}{1000} = 225\text{ g}$$

APPROVED BY _____

SPECTROPHOTOMETRIC DETERMINATION OF SILICON

ABSTRACT

Silicon, as monosilicic acid and disilicic acid, is reacted with molybdate in an acid medium to form silicomolybdate. The yellow silicomolybdate is reduced to molybdenum blue and measured at 810 mμ. This basic procedure is used alone or in various combinations with three pretreatments to accommodate different sample types. Selective determinations of reactive (monosilicic and disilicic acids) silicon, total soluble silicon (reactive silicon species plus polysilicic acids), and total silicon (reactive silicon plus polysilicic acids plus particulate silicon) are possible.

APPLICABILITY

This method, designed for maximum versatility, is applicable to natural and plant water and to samples of aluminum, stainless steel, and zirconium with or without uranium or solutions of these alloys. Silicon exists as monosilicic acid, disilicic acid, a variety of higher polysilicic acids, and colloidal silica in aqueous medium. This method, with a few exceptions, can be used to determine total silicon and to selectively determine the sum of the reactive monosilicic acid and disilicic acid.

The great versatility of this method stems from the use of a cation resin treatment (Procedure F), a sodium hydroxide treatment (Procedure G), and a boric acid-cation resin treatment (Procedure H) in conjunction with the familiar molybdenum blue colorimetric measurement of silicon (Procedure I). The molybdenum blue procedure is used alone and in various combinations with Procedures E, F, G, and H to provide five analysis schemes (Figure 1 and Table I). Table I defines the applicability of each analysis scheme and summarizes the effects of diverse ions on each. Careful study of Table I shows that analysis Scheme IV (Procedures F plus G plus I) is limited to the determination of total soluble silicon, rather than total silicon and that Scheme V (Procedures H plus I) is limited to the determination of total silicon only. The limitation on analysis Scheme IV is imposed by the resin treatment which employs a filtration that removes particulate silica. In fluoride solutions, silicon exists predominantly as a fluosilicate which yields the reactive monomer upon the addition of boric acid.

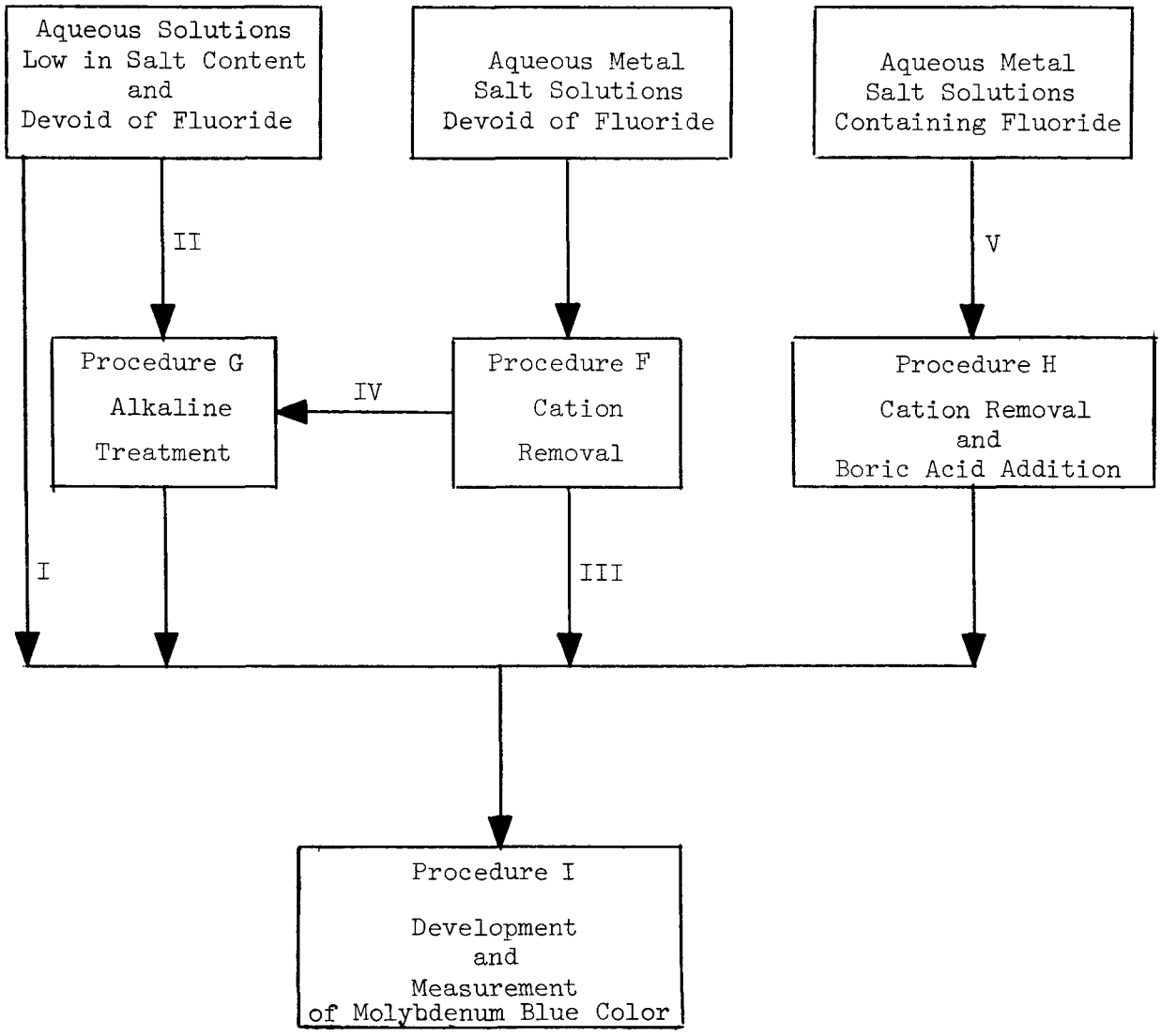

Fig. 1 Diagram of analysis schemes.

TABLE I

APPLICABILITY OF THE VARIOUS ANALYSIS SCHEMES

Analysis Scheme and Application	Diverse Ion Effects[a]
I. Procedure I; Determination of the sum of the reactive monosilicic and disilicic acids in aqueous solutions of low salt content and devoid of F^-. Samples containing interfering amounts of Cu(II) must be analyzed by analysis Scheme III. Samples containing Fe are most conveniently analyzed by analysis Scheme III.	The tolerance limits expressed as the diverse ion to Si molar ratio are at least 950 to 1 for Al; at least 185 to 1 for Co, Cr(III, VI), Fe[b], lanthanides[c], Mn, Ni, and Zn, and at least 25 to 1 for As(V), Hg, Sn(IV), U(VI), and V(V). Copper absorbs at 810 mμ; hence, its tolerance ratio is only 20 to 1. Tin(II) immediately reduces the molybdate and must be absent. Up to 10 mM of Cl^-, ClO_4^-, NO_3^-, and $SO_4^=$ and 0.005 mM of $PO_4^{\equiv}$ per sample aliquot do not interfere. Citrate, fluoride, oxalate, and tartrate must be absent.
II. Procedures G plus I; Determination of total Si in aqueous solutions of low salt content and devoid of F^-. Samples containing interfering amounts of Cu(II) must be analyzed by analysis Scheme IV.	Anion tolerance same as analysis Scheme I. Cations which form insoluble hydroxides must be absent. Use analysis Scheme IV for samples containing cations that form insoluble hydroxides.
III. Procedures F plus I; Determination of the sum of reactive monosilicic and disilicic acids in aqueous mineral salt solutions devoid of F^-.	Anion tolerance same as analysis Scheme I. Metals, except those in the form of anionic complexes, are removed by the cation resin. For example, 2 mM of Al, 1.5 mM of an equimolar Fe, Cr, Ni mixture, 0.8 mM U, and 0.5 mM Bi are removed sufficiently to enable application of the alkaline treatment. The tolerance for metals that form anionic complexes is the same as analysis Scheme I.

TABLE I (Cont'd)

	Analysis Scheme and Application	Diverse Ion Effects[a]
IV.	Procedures F plus G plus I; Determination of total soluble Si in aqueous metal salt solutions devoid of F^-.	As analysis Scheme III.
V.	Procedures H plus I; Determination of total Si in metal salt solutions containing F^-.	Except for those that exist as stable anionic complexes, cations are removed by the resin. This analysis scheme has been applied successfully to fluoride solutions of Zircaloy, to synthetic "Coprocess" Zr-Al fuel solutions, and to various metal solutions obtained per Procedure E. Niobium at 10 to 1 and Sn(IV) and Ti at 25 to 1 molar ratio do not interfere. At least 5 mM of F^- can be present in the sample aliquot without adverse effect.

[a] Based on diverse ion studies at a Si level of 30 µg (0.001 mM).

[b] Because the Mo blue color is slow to form, the minimum color development time is 1.5 hr.

[c] Lanthanide oxalates are insoluble, so the sample must be centrifuged or filtered.

The practical range of the method is 5 to 100 µg of silicon; however, the lower limit may be dropped to 1 µg of silicon with extreme care against contamination. The volume of samples analyzed by analysis Scheme I is up to 75 ml; hence, the practical lowest determinable silicon concentration is 0.07 µg/ml (2.5×10^{-6} M). The maximum sample volume for Schemes II, III, and IV is 25 ml and the lowest practical determinable silicon concentration is 0.2 µg/ml. The maximum sample volume for Scheme V is 5 ml and the lowest practical determinable silicon concentration is 1 µg/ml.

A method for the determination of macro concentrations of silicon is Method Si-1, "Gravimetric Determination of Silicon", in this Manual.

DISCUSSION

The principal pretreatments in the method are (a) the dissolution of metal samples, (b) the removal of cations with a cation exchange resin in the acid form, (c) the alkaline conversion of all silicon species to the reactive monomer, and (d) the decomposition of silicon fluoride complexes with boric acid in the presence of cation exchange resin. In the color development phase of the method, silicic acid is reacted with molybdate at pH 1.3 to form the yellow silicomolybdate; an oxalic acid-tartaric acid complexing reagent is added; and the yellow silicomolybdate is reduced to molybdenum blue which is measured at 810 mμ. The alkaline pretreatment, Step c, is omitted if a selective determination of the sum of monosilicic and disilicic acid is to be performed. Boric acid is added, treatment d, to samples containing fluoride to convert nondeterminable fluosilicates to monosilicic acid.

Cations affect the determination in several ways. They may hydrolyze at pH 1.3, form insoluble molybdates, form insoluble hydroxides that prevent complete conversion of soluble silicon to monosilicic acid, form insoluble oxalates or tartrates, or absorb at 810 mμ. Cation exchange removal is used to circumvent these difficulties. To minimize the introduction of common anions, the cation exchange resin is also used to neutralize the base from the alkaline conversion treatment.

The common anions chloride, nitrate, perchlorate, and sulfate do not interfere at levels up to 10 mM per sample aliquot. Above this level, they prevent quantitative formation of silicomolybdate and cause low results. Only the monosilicic acid and disilicic acid react with molybdate; hence, the higher polysilicic acids must be converted to monosilicic acid if total silicon is to be determined. This conversion can be accomplished by reaction with hydrofluoric acid, by a basic fusion, or by reaction with a hot sodium hydroxide solution. The decomposition in a hot alkaline solution at pH 12 to 13 was found to be best.

Silicic acid and molybdate react in a dilute acid solution. The optimum pH for this reaction is 1.3 ± 0.1. Because the addition of molybdate to alkaline samples gives low results, the pH of the sample must be adjusted to between pH 1.0 and 1.3 before the molybdate reagent is added. The reaction of molybdate with monosilicic acid and disilicic acid is reported to be complete in 75 sec and 10 min, respectively[1]. These differing reaction rates can be used to establish the presence and approximate level of the monomer and/or the dimer.

In fluoride solutions, silicon exists as a fluosilicate which does not react with the molybdate reagent. The silicon-fluoride complex is decomposed by a saturated solution of boric acid. When boric acid is added to a Zr-Al-F solution such as that from the "Coprocess", a precipitate forms upon the addition of the molybdate reagent. The precipitate formation and low recovery of silicon is avoided by reacting the sample with the boric acid in the presence of cation exchange resin.

The oxalic acid-tartaric acid complexing reagent is added to the sample to complex the excess molybdate reagent and to selectively break up reducible molybdate complexes such as phosphomolybdate. The complexing reagent also slowly breaks up the silicomolybdate complex; therefore, the time interval between the addition of the complexing reagent and the reducing reagent must be controlled between 30 sec and 1 min. If both the complexing and reducing reagents are added together, the phosphomolybdate complex is not completely destroyed.

A tricomponent reducing mixture of bisulfite, sulfite, and 1-amino-2-naphthol-4-sulfonic acid is recommended[2] for this method. It was confirmed to be the most reliable of the many reducing reagents suggested in the literature. Maximum color intensity (complete reduction of the silicomolybdate complex to molybdenum blue) is obtained in 20 min and the color is stable for at least 16 hr.

Variations in temperatures over the range 24°±12°C[3] do not affect the color development.

Silica (glass) is very soluble in alkaline medium and sparingly soluble in water. Basic solutions should be diluted by weight in plastic ware and stored in plastic ware. All reagents must be stored in polyethylene bottles. The cation exchange resin must be freshly charged with 6M HCl, washed with water until the effluent is neutral, then stored in a plastic container.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1- and 5-cm, of borosilicate glass or silica.

2. Beakers, polyethylene, 50- and 100-ml, Teflon, 50-ml.

3. Bottles, polyethylene, assorted sizes.

4. Cover glass, polyethylene.

5. Filtrator, Fisher, low form.

6. Flasks, volumetric, 100-ml and 50-ml polypropylene.

7. Graduated cylinder, pharmaceutical, 10-ml.

8. Hot plate, Chromalox.

9. Magnetic stirrer and plastic-coated magnetic stirring bars.

10. Medicine droppers, polyethylene.

11. Millipore filtering apparatus, 25-mm with 25-mm, 0.45-μ Millipore filters. The stem of the filter holder base is extended with 6- or 7-mm tubing to a total length of 7 in. to facilitate filtrations into beakers or bottles.

12. pH meter with a glass-calomel electrode system.

13. Pipets, macro and micro, assorted sizes, with control syringe and rubber suction bulb.

14. Pipets, polypropylene, assorted sizes.

15. Spectrophotometer, Beckman DU or DK, or Cary Model 14.

B. Reagents

Note: Prepare all reagents with Reagent Grade chemicals and distilled water. Store all reagents in polyethylene bottles.

1. Ammonium hydroxide, silicon-free, 6±1M. Deliver 500 ml of conc NH_4OH to a large crystallizing dish and 250 ml of water to a 1-liter plastic beaker. Place the beaker in the center of the crystallizing dish and add a magnetic stirring bar to the beaker. Place the crystallizing dish plus beaker, enclosed in a sealed polyethylene bag, on a magnetic stirrer and let stand overnight with continuous stirring. Transfer the ammonium hydroxide solution from the beaker to an 8-oz screw-cap, polyethylene bottle.

2. Ammonium molybdate, 10% (w/v) solution. Dissolve 50 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 500 ml of water and filter through a 0.45-μ membrane filter.

3. Boric acid, saturated solution. Add 50 g of H_3BO_3 to 950 ml of water in a 32-oz polyethylene bottle, place the bottle in a hot water bath, stir until dissolution is complete, then cool to room temperature.

4. Buffer, standard, pH 2.00.

5. Complexing reagent, 0.75M oxalic acid-0.75M tartaric acid. Dissolve 49 g of oxalic acid and 56 g of tartaric acid in water and dilute to 500 ml with water.

6. Diverse ion matrix for silicon bench-control standards. Appropriate matrices will be furnished by the Quality Control Laboratory as samples are received for analysis.

7. Hydrochloric acid, 8M.

8. Hydrofluoric acid, conc, and ∿ 8M.

9. Nitric acid, 12M and 6M.

10. Phenolphthalein indicator solution, 1%. Dissolve 1.0 g of the solid reagent in 100 ml of ethanol.

11. Reducing reagent. Dissolve 27 g of $NaHSO_3$ and 2 g of NaOH in 225 ml of water, add 0.5 g of 1-amino-2-naphthol-4-sulfonic acid, stir until dissolved, dilute to 250 ml, and filter through a 0.45-μ membrane filter.

12. Resin, cation, acid-form. Purify Dowex 50W-X8 (or equivalent), 50- to 100-mesh resin as described in Procedure D.

13. Silicon standard stock solution, 1.000 mg Si/ml. Fuse 0.5350 g of SiO_2 with 2 g of anhydrous Na_2CO_3 in a platinum crucible. Dissolve the melt in water with mild heating. Meanwhile, dissolve 1 g of NaOH in 50 ml of water in a 100-ml polyethylene beaker. Quantitatively transfer the silicon solution to a 250-ml volumetric flask with water rinses. Dilute the solution to about 200 ml with water, add the sodium hydroxide solution, dilute to volume with water, mix well, then immediately transfer the solution to an 8-oz polyethylene bottle.

14. Silicon calibration standard solution I, 75 μg Si/ml. Pipet 15 ml of the silicon stock solution into a 200-ml volumetric flask. Add about 100 ml of water and 1 g of NaOH dissolved in 50 ml of water, dilute to volume with water, mix well, then immediately transfer the solution to an 8-oz polyethylene bottle.

15. Silicon calibration standard solution II, 50 μg Si/ml. Prepare as above except use 10.00 ml of the silicon stock solution.

16. Silicon bench-control standards. Prepare dilutions of the silicon stock solution in the same manner as for the calibration standards, 14 and 15, to cover the concentration range 5 to 100 µg Si/ml. For the analysis of solid samples carried through Procedure E, use available NBS standards.

17. Sodium hydroxide, 50% (w/w), silicon-free. Fisher's 50% (w/w) NaOH has been found to be satisfactory.

PROCEDURE

Note: Use distilled water throughout the procedure and use plasticware wherever possible.

A. Preparation of Reagent Blank

This method requires two types of reagent blanks. The first type, which must be prepared at all times, is for the calibration standards and for samples submitted as solutions. The second type of blank is for solid samples dissolved per Procedure E and accounts for any silicon that may be introduced by the reagents used in the dissolution. Only one appropriate blank is to be subtracted for any given sample to obtain the net absorbance.

1. Blank for calibration standards and solution samples.

   Process 5 ml of water through the same analysis scheme as that used to analyze the sample. When several analysis schemes are used simultaneously in any given run, process the blank per analysis Scheme III. Generally, there is very little difference among blanks prepared by the various analysis schemes. The usual blank absorbance is about 0.015.

2. Blank for solid samples dissolved per Procedure E.

   When solid samples are dissolved per Procedure E, the reagents introduced are compounded for preparation of an appropriate blank. Process an aliquot of this solution, equal in size to the sample aliquot, through the same procedure as the sample.

B. Calibration

Process a pair of standards with each series of samples. Use 1.00-ml aliquots of standards I and II with sample aliquots containing more than 10 µg of silicon and 200-µl aliquots of the same standards for sample aliquots containing less than 20 µg of silicon. Either set of standards is applicable in the range 10 to 20 µg of silicon. Divide the micrograms of silicon in each standard by its respective net absorbance to obtain the calibration factor. The two factors must agree within specified limits and the average of the two factors must agree with the established conversion factor within the specified limits. If both or either of these specifications are not met, process another pair of standards. Report to your supervisor if difficulties persist.

The method may be used only infrequently so sufficient current calibration data may not be on hand to specify realistic requirements for the calibration. During the development of this method, a precision of 1.25% relative standard deviation was observed by one chemist on measurements of 30- to 40-µg amounts of silicon with a Cary Model 14 recording spectrophotometer. On the basis of this observation, the difference between the two calibration factors should not exceed about 4 relative percent. The observed factor is 113.8 ± 1.4 µg Si/abs unit for 1-cm cell measurements on the Cary Model 14 spectrophotometer. It will be slightly higher if a less sensitive instrument is used.

C. Analysis of Bench-Control Standards

Process the bench standards, spiked with diverse ion matrix when necessary, using the same analysis scheme as that used to analyze the samples. Report the results to the Quality Control Laboratory for calculation of bias and precision.

D. Resin Purification

Fill a large column capable of holding 200 ml of resin to within 3 in. of the top with the resin slurry. Pass 1 liter of 6M HCl slowly through the column, then 1 liter of distilled water. Store the resin in a plastic container.

E. Dissolution of Steel Samples

1. Weigh 0.100 to 0.250 g of the steel sample into a 50-ml Teflon beaker.

2. Add 8 ml of the 8M HCl and heat on a hot plate. Set at low heat until the reaction ceases.

A Teflon beaker containing the same amounts of acids should be carried through the dissolution procedure. This solution is used to prepare the blank (A-2) for solid samples.

3. Add 8 ml of the 12M HNO_3 and continue heating until the dissolution is complete.

4. Cool for 5 min then add 5 drops of conc HF. Mix thoroughly and let stand for 15 min to insure dissolution and depolymerization of Si.

Some batches of HF contain large amounts of Si. If the blank absorbance is high, the reliability of the analysis result is lowered, and it may be necessary to repeat the analysis with a new batch of HF containing less Si.

5. Transfer the solution to a 50-ml polypropylene volumetric flask and dilute to volume with distilled water.

6. Transfer the solution to a 2-oz polyethylene bottle.

7. Proceed to Step 1 of Procedure H.

F. Cation Removal for Analysis Schemes III and IV

1. Add 10 ml of cation resin to a 50-ml polyethylene beaker.

The wet resin is easily dispensed with a small plastic scoop.

2. Pipet a sample aliquot, 25-ml or less, containing 5 to 100 µg of Si, onto the resin and mix by magnetic stirring for 1 min.

3. Using a Fisher filtrator and a Millipore filtering apparatus, filter the sample through a 0.45-μ membrane filter. Collect the filtrate in a 100-ml polyethylene beaker for analysis Scheme III or in a 2-oz polyethylene bottle for analysis Scheme IV.

4. For analysis Scheme IV, proceed to Step 2 of Procedure G. For analysis Scheme III, proceed to Step 2 of Procedure I.

G. Alkaline Treatment for Analysis Schemes II and IV

1. Pipet a sample aliquot, 25-ml or less, containing 5 to 100 μg of Si, into a 2-oz. polyethylene bottle. A glass pipet can be used.

2. Add 2 drops phenolphthalein indicator, then add 19M NaOH with a polyethylene medicine dropper until the sample turns pink. Add 5 drops more.

3. Heat the sample in a boiling water bath for 20 min.

4. Cool the sample to room temperature, add Dowex 50W-X8 resin until the pink color disappears, then add an additional 5 ml. The wet resin is easily dispensed with a tiny plastic scoop.

5. Filter the sample through a 0.45-μ membrane filter into a 100-ml polyethylene beaker. Use a Fisher filtrator and a Millipore filtering apparatus. The sample is acid at this point so glass filtering apparatus may be used. The volume of the filtered sample should not exceed 70 ml.

6. Proceed to Step 2 of Procedure I.

H. Cation Removal and Boric Acid Addition for Analysis Scheme V

1.	Add 10 ml of cation resin to a 50-ml polyethylene beaker.	The wet resin is easily dispensed with a small plastic scoop.
2.	With a polyethylene pipet, add a sample aliquot, 5-ml or less, containing 5 to 100 µg of Si, to the beaker and mix.	
3.	Add 40 ml of the H_3BO_3 reagent, mix by magnetic stirring, let stand for 30 min, then mix again.	The H_3BO_3 will decompose the $Si-F^-$ complex in about 30 min.
4.	Filter the sample through a 0.45-µ membrane filter into a 100-ml polyethylene beaker. Use a Fisher filtrator and a Millipore filtering apparatus.	Boric acid has complexed the F^-; so a glass filtering apparatus may be used. The volume of the filtered sample should not exceed 70 ml.
5.	Proceed to Step 2 of Procedure I.	

I. Development and Measurement of the Molybdenum Blue Color

1.	Pipet a sample aliquot, 75-ml or less, containing 5 to 100 µg of Si, into a 100-ml polyethylene beaker.	A glass pipet can be used. Steps 1 through 6 must be completed without interruption.
2.	Adjust the pH to 1.1±0.1 with 6M HNO_3.	
3.	Add 10 ml of the molybdate reagent with a pharmaceutical graduated cylinder.	If a precipitate forms, the sample must be analyzed by analysis Scheme IV.
4.	Adjust the pH to 1.3±0.1 with either 6M HNO_3 or 6M NH_4OH. Use a polyethylene medicine dropper.	
5.	Wait 10 min for the yellow silicomolybdate to form.	The silicomolybdate is stable for about 30 min, so proceed to Step 6 immediately after the 10-min wait.

6.	With a graduated cylinder, add 10 ml of the complexing reagent. Wait 30 sec and\ add 2 ml of the reducing reagent. Stir the solution continuously during this step.	The time between the addition of the complexing reagent and the addition of the reducing agent is critical and must be controlled. Low results will be obtained if the interval is much over 1 min.
7.	Wait 20 min for color development.	If the sample contains Fe and the Fe has not been removed, wait 1.5 hr for color development.
8.	Transfer the sample to a 100-ml volumetric flask and dilute to volume with water.	
9.	Measure the absorbance against water at 810 mμ (infrared source and detector) or at 790 mμ (visible source and detector).	Best results are obtained with an IR source and detector. Use 1-cm cells for samples containing more than 20 μg of Si and 5-cm cells for samples with less than 10 μg of Si. In between, either cell may be used; however, standards and samples must be read alike. The color is stable for at least 16 hr.
10.	Record the data and calculate the results as described in the example work sheet. Report 3 significant figures but not more than 2 decimal places.	

REFERENCES

1. Ralph K. Iler, The Colloidal Chemistry of Silicon and Silicates, Ithaca, New York: Cornell University Press, 1955.

2. Anton B. Carlson, Charles V. Banks, "Spectrophotometric Determination of Silicon in The Presence of Zirconium, Beryllium, Aluminum, and Calcium", Anal. Chem., 24 (March 1952), pp 472-477.

3. D. F. Boltz, Colorimetric Determination of Nonmetals, New York: Interscience Publishers, Inc., 1958.

October 1970
F. A. Duce
S. S. Yamamura
D. M. Lund

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Silicon

CHARGE NUMBER _____ PROCEDURE Si-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Conversion Factor	µg Si in Aliquot Analyzed	µg Si Corrected For Bias				RESULT µg Si/ml
Si Std, 75µg		0.663	113.12						
Si Std, 50µg		0.447	111.86						
			$\bar{X}$ = 112.49						
Dissolver Feed	100µl	0.372		38.47	385 ± 20				385 ± 20

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\mu g\ Si\ in\ Std}{Absorbance}$$

$$B = \frac{75}{0.663} = 113.12$$

$$B' = \frac{50}{0.447} = 111.86$$

$$\bar{X} = 0.5(B + B') = 0.5(113.12 + 111.86) = 112.49$$

Dissolver Feed:

$$C = AB = 0.372\ (112.49) = 38.47\ \mu g\ Si$$

$$\text{Result} = \frac{D}{\text{Sample Vol}} = \frac{385 \pm 20}{0.100} = \frac{385 \pm 2.0}{0.100}$$

$$= 385 \pm 20\ \mu g\ Si/ml$$

APPROVED BY _____

DETERMINATION OF SPECIFIC GRAVITY WITH THE WESTPHAL BALANCE

ABSTRACT

Specific gravity of liquids is measured with the Westphal balance.

APPLICABILITY

The Westphal balance can be used to measure the specific gravity of aqueous and organic liquids with specific gravity values in the range 0 to 2[1]. Exceptions are liquids that attack the glass plummet or the suspension wire. Hydrofluoric acid is particularly bad on the plummet and strong acids could attack the suspension wire which usually is nichrome or platinum. Radioactive samples that result in excessive radiation exposure to personnel and samples lacking sufficient volume also are exceptions. The minimum permissible volume is 10 ml. Samples less than 10 ml or excessively radioactive should be analyzed by Method Sp Gr-2 of this manual or the alternate methods mentioned below.

In routine use, the precision of this method is 0.003 specific gravity unit. Though more time consuming, better precision is attainable with pycnometer measurements. Weighing a measured aliquot of solution is also a rapid, convenient method for determining specific gravity. The precision of this technique depends mainly on the precision of the volume measurement.

DISCUSSION

The operation of the Westphal balance is based on the principle that an object immersed in a liquid is buoyed up by a force equal to the weight of liquid displaced by the object. In the Westphal balance, a movable rider sits on the balance beam. A hollow glass plummet suspended by a wire hangs on one end of the balance beam and a variable chain-vernier weight system attaches to the other end. The specific gravity measurement involves initial adjustment of the balance to show zero deflection with the rider-chain-vernier setting at 0.0000, then the plummet is immersed in the sample and the balance is again restored to zero deflection by moving the rider and chain. The balance reading is the specific gravity of the sample. The reference is water at 20°C and the adjusted sample temperature is normally 25°C; therefore, the specific gravity value obtained is designated 25/20.

The terms absolute density, relative density, and specific gravity are often used incorrectly. Absolute density is the weight in grams of one cubic centimeter (cc) of something at a given temperature. The absolute density of water is 0.999973 at 4°C. Relative density (or simply density) is the ratio of the mass of 1 ml of something at a certain temperature to the mass of 1 ml of water at 4°C. At 4°C 1 ml of water weighs 1.00000 g and at 20°C 1 ml of 8.15N HNO_3 weighs 1.2527 g; hence, the relative density of 8.15N HNO_3 at 20°C is 1.2527. Specific gravity is the ratio of the mass of a certain volume of something at a specified temperature to the mass of an equal volume of water at a specified temperature. At 20°C, the density of water is 0.99823 g/ml and the density of 8.15N HNO_3 is, therefore, 1.2549 relative to water at 20°C and 1.2527 relative to water at 4°C. Specific gravity and relative density (density) are numerically equal (interchangeable) only when the comparison is against water at 4°C. For most chemical applications, 1 ml of water equals 1 cc; hence, absolute density equals relative density. The following is a useful relationship:

$$\text{Absolute density}^{T} \simeq \text{density}^{T} = (\text{Sp Gr } 25/20) \cdot (D_{H_2O} \text{ @20°C}) \quad (1)$$

where

T is any given temperature.

Major sources of error are (a) failure to adjust the balance prior to use, (b) dirty plummet (touching the plummet or suspension wire with bare hands leaves a film), (c) presence of bubbles on the plummet, (d) failure to immerse the plummet to the same depth during the water adjustment and sample measurement, and (e) letting the plummet touch the walls of the sample container.

SAFETY PRECAUTIONS

Normal hazards associated with the chemical and toxic properties of the samples being analyzed.

APPARATUS AND REAGENTS

A. Apparatus

1. Centrifuge tubes, equipped with specially-fabricated holder to stand them upright.

2. Test tubes, 15- x 125-mm, equipped with holder.

3. Tissue, absorbent paper.

4. Westphal Balance, Model SG-1, Christian Becker or equivalent. The plummet support wire should have a reference mark (loop, node, etc.) 0.5 in. above the plummet.

B. Reagents

1. Acetone

2. Nitric acid, 1M

3. Water, distilled.

PROCEDURE

Note: Lock the balance beam after each reading to protect the knife edge of the balance.

A. Procedure for Cleansing the Plummet and Wire

The plummet and supporting wire must be clean to obtain accurate results. Clean the plummet by consecutive immersion in 1M HNO_3, distilled water, and acetone, then dry carefully and thoroughly with absorbent tissue. Do not use fingers to touch the plummet or wire at any time. Change the 1M HNO_3, water, and acetone at least every shift.

B. Balance Checkout

Note: Calibrate and check the balance at least once per shift when in use.

1. Set the rider at 0.0 and the chain at 0.0000.	The plummet and wire must be clean (See Procedure A).
2. Release the beam, adjust the chain position so the pointer rests at the center of the scale (zero deflection), then set the vernier to show a chain reading of 0.0000. Lock the beam.	
3. Transfer 10 ml of distilled water at room temperature to a 15- x 125-mm test tube and repeatedly immerse and raise the plummet to remove all air bubbles that may be adhering to the plummet.	When the samples are large enough, 50-ml centrifuge tubes can be used in place of the 10-ml tubes to minimize the probability of the plummet touching the container wall. The centrifuge tube requires 40 ml of sample. Use absorbent tissue or ivory-tipped forceps to handle the wire.

5. Using aluminum counting plates as shims, adjust the height of the tube so the water level is at the referance mark on the suspension wire (0.5 in. above the plummet).

   The plummet should be centered in the tube so that it does not contact the tube wall.

6. Set the rider at 0.9 and the chain setting at 0.99.

7. Unlock the beam and adjust the chain to obtain zero deflection. Lock the beam.

8. Rotate the tube 180° and repeat Step 7.

   The allowable difference between the two readings is 0.0003. If the difference exceeds this, repeat Step 8 until two successive readings agree to within 0.0003.

9. Note the temperature shown by the thermometer on the plummet and compare the specific gravity of water at that temperature with the result obtained in Step 8.

   The specific gravities of water at various temperatures relative to water at 20°C are tabulated on the rear wall of the balance case. The tabulated value and the observed value should agree within 0.0003. If not, clean the plummet per Procedure A and repeat B. If disagreement persists, use freshly-boiled distilled water. Should this second remedy fail, consult your supervisor.

10. Clean and dry the plummet per Procedure A.

C. Analysis of Sample

1. Transfer the sample to a 15- x 125-mm test tube or a 50-ml centrifuge tube.

   A 10-ml portion is adequate for the test tube. The centrifuge tube requires 40 ml.

2. Using absorbent tissue or a pair of forceps to handle the plummet wire, immerse the plummet until there are no bubbles adhering to the plummet or wire.

3. Note the temperature and adjust to 25.0±0.2°C. Warm the sample by grasping the tube with bare hands. Chill it by immersion in acetone.	Room temperature is usually less than 25°C so it is advisable to attain a temperature on the high side of 25°C.
4. Keeping the plummet immersed in the sample, replace the plummet on the beam. Adjust the height of the tube so the surface of the sample is at the reference mark on the support wire.	The plummet should not touch the tube wall.
5. Move the rider to the estimated specific gravity of the sample. Set the chain at 0.0000.	
6. Unlock the beam slightly, note the direction that the pointer swings, then relock the beam.	
7. Reset the rider and repeat Step 6. Do this until the rider is at a position corresponding to a specific gravity just less than that of the sample.	
8. Note the temperature. If it is in the range 25.0±0.2°C, unlock the beam and adjust the chain to give zero deflection.	
9. Lock the beam, rotate the tube 180°, and repeat the measurement. Relock the beam.	The two results should agree to within 0.0003. If they don't, repeat Step 9 until two successive readings agree. If the temperature strays outside the range 25.0±0.2°C, appropriate corrective actions must be taken.

10. Record the specific gravity to four decimal places as shown on the worksheet.

11. Clean the plummet per Procedure A.

REFERENCES

1. A. Weissberger, Editor, Physical Methods of Organic Chemistry, Vol I, Part I, Chapter VI, "Determination of Density" by N. Bauer, New York: Interscience, 1949.

J. M. Dietz
S. S. Yamamura
June 1970

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Specific Gravity

CHARGE NUMBER _____ PROCEDURE Sp Gr - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Sp Gr	Correction						RESULT
I		1.1412	+0.0002						1.1414

ANALYZED BY _____ DATE _____

CALCULATIONS:

APPROVED BY _____

INDIRECT DETERMINATION OF SULFATE BY FLAME EMISSION OF BARIUM

ABSTRACT

Small amounts of sulfate are determined by precipitation with barium and subsequent determination of the barium by flame emission[1].

APPLICABILITY

This procedure is applicable to many types of samples. Samples that have been analyzed by this method are CPP samples containing Al, Zr, F^-, NO_3^-, and B. It is also applicable to stainless steel and water samples. Almost all metals interfere in the emission step of the procedure; however, most of them are removed by the precipitation separation. Uranium above 100 mg/ml interferes by preventing precipitation of the barium sulfate; these samples can be analyzed by Method SO_4-Vol-1. Phosphate will not interfere up to 100 mg; this was the highest level studied. Some phosphate will precipitate as barium phosphate, but the barium phosphate is redissolved in the water washes. Chloride, F^-, NO_3^-, ClO_4^- do not interfere. The aliquot to be analyzed should contain between 250 and 1000 μg of sulfate and should be less than 3.5 ml.

DISCUSSION

Small amounts of sulfate are determined by precipitation of the sulfate from 5 ml of a 0.6±0.2M acid solution with 1M $BaCl_2$. This acidity is controlled by initial neutralization, measured addition of acid, and dilution to a constant volume. After the formation of the barium sulfate, the solution is centrifuged, and the supernate is decanted. The barium sulfate is washed and centrifuged twice with water, and once with acetone. The acetone wash makes the decantation more complete, avoiding carry-over of diverse ions. The barium sulfate is dissolved in a warm EDTA solution of pH 10.5. The solution is transferred to a 10-ml volumetric flask, diluted to volume, and compared against standard barium solutions by flame emission. The procedure requires approximately 2 hr for 12 samples. The accuracy and precision is within 2%.

APPARATUS AND REAGENTS

A. Apparatus

NOTE: Detergents may contain sulfate. Clean all glassware by fuming with perchloric acid and rinsing with distilled water.

1. Atomic absorption unit, Techtron AA-5 or equivalent.
2. Centrifuge.
3. Centrifuge tubes, 15-ml, graduated.
4. Glass stirring rod, tapered end.
5. pH meter.
6. Pipets, assorted sizes.
7. Wash bottle, fine-tipped.

B. Reagents

NOTE: Prepare all reagents with C.P. or Analytical Reagent Grade stock and distilled water.

1. Acetone.
2. Ammonium hydroxide, conc.
3. Barium chloride, 1M. Dissolve 122 g of $BaCl_2 \cdot 2H_2O$ in distilled water and dilute to 500 ml.
4. Barium standards 30, 50, 60, 75, 90, 120, 130, and 140 µg Ba/ml. Prepare from a stock solution containing 1000 µg Ba/ml. The sulfate equivalents are 20.97, 34.94, 41.93, 52.42, 62.90, 73.38, 83.87, 90.86, and 97.85 µg SO_4/ml, respectively.
5. EDTA, 0.05M. Use the material prepared in Method EDTA-Prep-1 of this manual.
6. Nitric acid, 5M. Dilute 156 ml of conc HNO_3 to 500 ml with distilled water.
7. Sulfate bench standard, 0.01M (960 µg SO_4/ml). Dilute about 6 ml of conc H_2SO_4 to 1 liter with distilled water and standardize against THAM tris(hydroxymethyl)aminomethane. This solution should be about 0.1M sulfate. Dilute 1:10 with distilled water to obtain bench standard.
8. Controls. Prepare controls as described in No. 7 to cover the range of the method.

PROCEDURE

A. Blank

No blank is required for this method.

B. Bench Standard

Process 0.5 ml of the bench standard as described in Procedure C.

C. Separation Procedure

1. To a graduated 15-ml centrifuge tube, add a sample aliquot containing 250 to 1000 µg of SO_4.	The volume of the sample should not exceed 3.5 ml.
2. Add 1 drop of phenolphthalein indicator, then add 5M HNO_3 or conc NH_4OH to adjust to the neutral point and then add 0.6 ml of 5M HNO_3. Dilute to 4 ml with water and mix.	
3. Add 1 ml of 1M $BaCl_2$ with a Mohr pipet and mix.	
4. Let the solution stand for 5 min, then centrifuge for 1 min at 2500 rpm.	Higher rpm may break the centrifuge tube.
5. Carefully decant the supernate.	
6. Wash the precipitate with a fine spray of water from a wash bottle and centrifuge.	The precipitate must be broken up for a good wash. The sonic bath may be used.
7. Carefully decant the supernate and repeat Step 6 once more with water and then once with acetone.	The acetone wash makes the decantation more complete, avoiding carryover of diverse ions.
8. Decant the acetone and break up the precipitate with a fine stream of water.	

9. Add 1 drop of conc NH_4OH and 0.5 ml of 0.05M EDTA solution to the tube and place the tube in a hot water bath until the precipitate dissolves.

10. Transfer the solution to a 10-ml volumetric flask with small water rinses and dilute to volume.

11. Compare the solution against the Ba standards by flame emission with the Techtron AA-5.

The Ba standards are reported as equivalent weights of sulfate.

D. Flame Emission Procedure

The analysis should be carried out in accordance with normal operating procedures. Verify that the correct shutdown procedure was followed.

1. Turn on the power to the monochromator, chopper, and the readout units.

2. Set the burner height vernier at 10.

3. Set the wavelength dial at 5535.5 A°.

4. Set the damping switch at D.

5. Set the select switch at high gain.

6. Set the mode switch at % T.

7. Set the monochromator slit at 50 μ.

8. Set the course gain at 7.

9. Verify that the drain tube extends below the surface of the liquid in the waste receptable.

10. Set the exhaust control at 1/3 open.

11. Turn the support valve to air and adjust to 5.5 on flowmeter.

12. Turn the fuel valve to acetylene and light the burner. Adjust the fuel to 2 on the flowmeter.

13. Block the monochromator slit and adjust the readout meter and display unit to zero.

14. With the slit unobstructed, adjust the gain controls for a readout of 100. Adjust the display unit if necessary.

15. Aspirate blank solution and adjust to zero with the backing control.

16. Read a standard before and after each sample. One standard should be higher and one lower than the sample.

CALCULATIONS

The concentration of sulfate in the sample can be obtained by either of two methods. A calibration curve relating % emission to concentrations can be plotted from the calibration data and the concentration of sulfate in µg/ml corresponding to the sample absorbance can be read from the calibration curve. The two standard bracket method may also be used. The sulfate concentration of the sample is then calculated from the following equation:

$$c = \left[x_1 - \left(\frac{y_1 - y_3}{y_1 - y_2} \right) \left(x_1 - x_2 \right) \right] \frac{10d}{a} \qquad (1)$$

where

a = aliquot of sample

c = sulfate concentration in µg/ml

d = dilution of sample

x_1 = concentration of high standard

x_2 = concentration of low standard

y_1 = % emission of high standard

y_2 = % emission of low standard

y_3 = % emission of sample.

REFERENCE

1. D. C. Cullum, D. B. Thomas, "The Flame-Photometric Determination of Barium and Sulfate: An Improved Technique", Analyst 85, (March 1960) pp 688-689.

D. E. Savage
January 1973

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION SO4

CHARGE NUMBER _____ PROCEDURE SO4 - Flame - 1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: a_0/d_1 $a_1/d_2/a_2$	concentration µg	% T	µg in Aliquot	Correction	Std Deviation			RESULT mg/ml
Sple 1	0.5/10		56 4	47.7	0	2.0			0.954±004
Std 1		41 93	52 1						
Std 2		52 42	59 9						

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\mu g\ SO_4 \text{ in Aliquot} = 52\,42 - \frac{[59.9 - 56\,4]}{[59.9 - 52.1]}\,[52\,42 - 41\,93] = 47\,7$$

$$\text{Result: } mg\ SO_4/ml = \frac{[47.7 \pm 2\,0]\,[10]}{[1000]\,[0.5]} = 0.954 \pm 0\,04$$

APPROVED BY _____

TITRIMETRIC DETERMINATION OF SULFATE

ABSTRACT

Small amounts of sulfate are determined by titration with barium perchlorate to a photometric thorin end point. The titration is carried out in an 80% ethanol solution buffered with pyridine. The sulfate is separated from interfering ions by both anion and cation exchange procedures.

APPLICABILITY

The range of the titration procedure is 0.2 to 2 mg of sulfate. With a maximum sample size of 20 ml, samples as low as 10 µg/ml can be analyzed. More dilute solutions can be analyzed by concentrating the sulfate on an alumina column. Sulfate at levels above 2 mg/aliquot produce a visible precipitate which interferes in the photometric measurement.

Interfering ions are removed by a combination of anion and cation exchange. An alumina (anion) column in the perchlorate form is used to separate sulfate from most interfering ions [1]. This separation is followed by a Dowex-50 cation exchange separation to remove aluminum and ammonium hydroxide introduced in the alumina column separation.

The adsorption affinity of anions on activated alumina is as follows: $OH^- > PO_4^{\equiv} > C_2O_4^{=} > F^- > SO_3^{=} = Fe(CN)_6^{\equiv} = CrO_4^{=} > S_2O_3^{=} > SO_4^{=} > Fe(CN)_6^{\equiv} = Cr_2O_7^{=} > NO_2^- = CNS^- > I^- > Br^- > Cl^- > NO_3^- > MnO_4^- ClO_4^- > CH_3COO^- > S^{=}$ [2]. Of the ions commonly associated with sulfate, the greatest error in the titration is due to phosphate with fluoride nearly as serious[3]. As can be seen from the relative adsorption affinities of the various anions, activated alumina has greater affinity for phosphate, fluoride, and sulfite than for sulfate and a somewhat low affinity for chloride and nitrate. Separation is effected by washing the chloride and nitrate through the column while the sulfate, sulfite, fluoride, and phosphate are retained. The sulfate, sulfite and fluoride are eluted with ammonium hydroxide. Ammonium hydroxide is not a strong enough base to elute the phosphate[4]. If fluoride is present, its interference can be suppressed by adding boric acid to the sample aliquot before separation. Sulfite is a serious interference, but its interference can be corrected by inhibiting its oxidation to sulfate with a glycerol solution. Sulfite can be determined by oxidizing it to sulfate with sodium peroxyborate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$).

Most metal ions interfere and must be removed. The interference is due primarily to coprecipitation during titration with barium perchlorate and to the formation of colored complexes with thorin. Nearly all cations are successfully removed by the alumina column during the sulfate separation. When the alumina column has been used, a Dowex 50W-X8 cation column (Figure 2) in the hydrogen form must be employed to remove aluminum and ammonium hydroxide introduced in the alumina column. Samples such as ground water that contain only interfering cations can be passed directly through the Dowex column omitting the alumina column.

Chromium, zirconium and thorium form strong complexes with sulfate and are not separated by ion exchange. These ions can be removed by complexing them with Versenol (N-hydroxyethylethylenediamine triacetic acid) before separation[5].

Sulfur in organic materials can be released by oxidation in a Parr bomb, and the sulfate is determined by this procedure.

DISCUSSION

Small amounts of sulfate are determined by titration with barium perchlorate to a photometric thorin end point. The barium reacts with the sulfate to form insoluble barium sulfate. At the end point[6], excess barium reacts with thorin to form a colored complex which is detected by a spectrophotometer. The titration is carried out in an 80% ethanol medium to decrease the solubility of barium sulfate. The nonaqueous medium also reduces the reaction time.

The pH drops during the titration as moderately acidic bisulfate ($pK_a \simeq 2$) is replaced by strongly acidic perchloric acid ($pK_a < 0$), and the absorbance decreases to give a negative slope to the pre-end point portion of the titration curve. The negative slope is avoided by buffering the solution to pH 6.0±0.5 with pyridine and perchloric acid before the addition of alcohol. At this range, small pH changes have little effect on the absorbance.

APPARATUS AND REAGENTS

A. Apparatus

NOTE: Detergents may contain phosphate and/or sulfate. Clean all glassware by fuming with perchloric acid and rinsing with distilled water.

1. Alumina column (Figure 1).

2. Beakers, assorted sizes.

3. Buret, 10 ml.

4. Dowex 50W-X8 column (Figure 2).

5. Flasks, 25-ml volumetric.

6. Parr peroxide or oxygen bomb.

7. pH meter.

8. Pipets, volumetric, assorted sizes.

9. Spectrophotometer, Spectronic 20 and special cell (Figure 2).

10. Wash bottle.

B. Reagents

NOTE: All reagents are made from C. P. or Analytical Reagent Grade stock and distilled water.

1. Alumina, WOELM; anionotropic, 80- to 200-mesh. Remove the very fine particles by repeatedly washing the reagent with water and decanting the fines.

2. Alcohol, ethanol, 95%.

3. Ammonium hydroxide, 1M and 0.1M.

4. Barium perchlorate, 0.01M. Dissolve 3.9 g of $Ba(ClO_4)_2 \cdot 3H_2O$ in 200 ml of water and dilute to 1 liter with ethanol.

5. Barium perchlorate, 0.001M. Dilute 10 ml of the 0.01M reagent to 100 ml with ethanol. Standardize by titrating 0.5 ml of the sulfate calibration standard beginning with Step 9 of Procedure D.

6. Dowex 50W-X8, 50- to 100-mesh.

7. Perchloric acid, conc, 1M and 0.1M.

8. Pyridine.

9. Sulfate bench and bias control standards. Dilute conc H_2SO_4 with water and standardize against THAM (tris-hydroxymethyl-aminomethane).

10. Thorin, 0.5%. Dissolve 0.5±0.01 g of thorin [0-(2-hydroxy-3, 6-disulfo-1-naphthylazo)benzenearsonic acid] in 100 ml of water.

11. Versenol, 0.5M. Dissolve 69.5 g of Versenol (N-hydroxyethyl-ethylene diamine triacetic acid) in water using sodium hydroxide pellets to aid dissolution. Adjust the pH to 5.5±0.5 with 2M NH_4OH or 2M $HClO_4$ and dilute to 1 liter with water.

PROCEDURE

A. Preparation of the Alumina Column

Fill the column with water, and using gentle suction, adjust the stopcock to give a flow rate of 2 drops/sec. Admit sufficient washed alumina as a slurry to make a bed about 6 cm high. Convert the column to the perchlorate form by washing it with three successive 5-ml portions of 1M NH_4OH and then 10 ml of 2M $HClO_4$. It is not necessary to repack the column after it has been allowed to go dry.

B. Preparation of Cation Exchange Column

Place approximately 12 cm of acid-form Dowex 50W-X8, 50- to 100-mesh resin into the column and rinse thoroughly with water. Convert spent columns to the hydrogen form by passing 50 ml of 3M HCl through the column. Wash with water until traces of chloride are gone. Check for chloride by adding silver nitrate to the column effluent.

C. Analysis of Bench Standard

Process 250 µl of the known bench standard according to the procedure used for the sample. If the limits specified by the Quality Control Laboratory are exceeded, process another standard.

D. General Procedure for Sulfate Employing Ion Exchange Separation.

This procedure is designed for samples of metal salts, metal salt solutions or water samples of very low sulfate content.
Note: Use distilled water throughout the procedure.

1. Pipet a sample aliquot containing 0.005 to 0.10 mM of $SO_4^=$ and less than 10 mM of diverse cations into a 250-ml beaker.

If complexing cations such as Cr, Zr or Th are known to be absent, proceed to Step 4.

For samples such as ground water that contain no interfering anions, proceed to Step 9; if these samples are too low in $SO_4^=$, concentrate on the alumina column beginning at Step 4.

2. Pipet 25 ml of 0.5M Versenol into the sample and adjust the pH to 5.5± 0.5 with dilute NH_4OH.

3. Boil the solution for 10 min. Cool.

4. Adjust pH to 0.5 to 1.0 by diluting with water or by adding $HClO_4$ or NH_4OH.

5. Pass the sample through the alumina column at the rate of 2 drop/sec. Discard the effluent.

6. Wash with 10 ml of 0.1M $HClO_4$ and three 8-ml portions of water. Discard the washings.

7. Place a clean 25-ml vol flask under the column and elute the SO_4 by adding successively 3 ml of 1M NH_4OH, three 3-ml portions of 0.1M NH_4OH, and 10 ml of water.

8. Add 2 ml of conc $HClO_4$ to the flask and dilute to volume with water. Mix well.

9. Pipet an aliquot of up to 15 ml containing 0.0002 to 0.01 mM of SO_4 from the vol flask into the prepared cation column.

10. Place the special titration cell under the column and collect the effluent. Wash the column with small portions of water until a total volume of 20 ml is reached.

The column will handle many samples before needing to be recharged. See Step 13 for indication of spent column.

11.	Add 2 ml of pyridine and adjust the pH to 6.0±0.5 with conc $HClO_4$.	Use a pH meter equipped with a combination electrode.
12.	Add 80 ml of ethanol, 10 drops of 0.5% thorin indicator, mix well by shaking, and after the air bubbles rise out of the optical path, zero the spectronic 20 at 520 nm.	Zero by adjusting the dark current to 0%T with the cell chamber empty. Place the cell containing sample solution into the chamber and adjust to 100% T with the slit control. If the solution turns red upon addition of thorin, the cation column is spent. Start over at Step 9.
13.	Add 0.2 ml of the standardized 0.001M $Ba(ClO_4)_2$ and determine the absorbance.	Mix well after each addition of $Ba(ClO_4)_2$. If the absorbance value is increasing, calculate a less than value or take a larger sample aliquot.
14.	Add 0.3 ml of the titrant and determine the absorbance. The end point is reached when the absorbance values begin to increase.	
15.	Add 0.5 ml of titrant and determine the absorbance. If no end point is reached continue adding titrant at the rate of 1 ml per increment until it is reached. When the end point is reached, titrate in 0.5 ml increments for 1.5 ml past the end point.	
16.	Plot the absorbance values vs volume of titrant on 10x10 chart paper. The end point is found by intersecting the two straight portions of the curve.	

17. Enter the data on the work sheet and calculate as shown on the sample work sheet. Report results to three significant figures.

E. Procedure for Samples Containing no Interfering Ions.

1. Pipet an aliquot of the sample containing 0.002 to 0.01 mM of SO_4 directly into the titration cell. Mix with water and dilute to the 20-ml mark.

2. Proceed with Step 11 of Procedure D.

REFERENCES

1. F. Nydahl, "Determination of Sulfur in Iron and Steel by Barium Chloride Method After Chromatographic Separation of Sulfuric Acid", Anal. Chem., 26 (March 1954) pp 580-584.

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3. J. S. Fritz and S. S. Yamamura, "Rapid Microtitration of Sulfate", Anal. Chem. 27, (September 1955) pp 1461-1464.

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6. D. C. M. Squirrell, Automatic Method in Volumetric Analysis, New Jersey: D. Nostrand Co. Inc., 1964.

7. A. F. Colson, "The Removal of Phosphate in Barium Perchlorate Titration of Sulphate", Analyst 88, (January 1963) pp 26-29.

D. E. Savage
S. S. Yamamura
January 1972

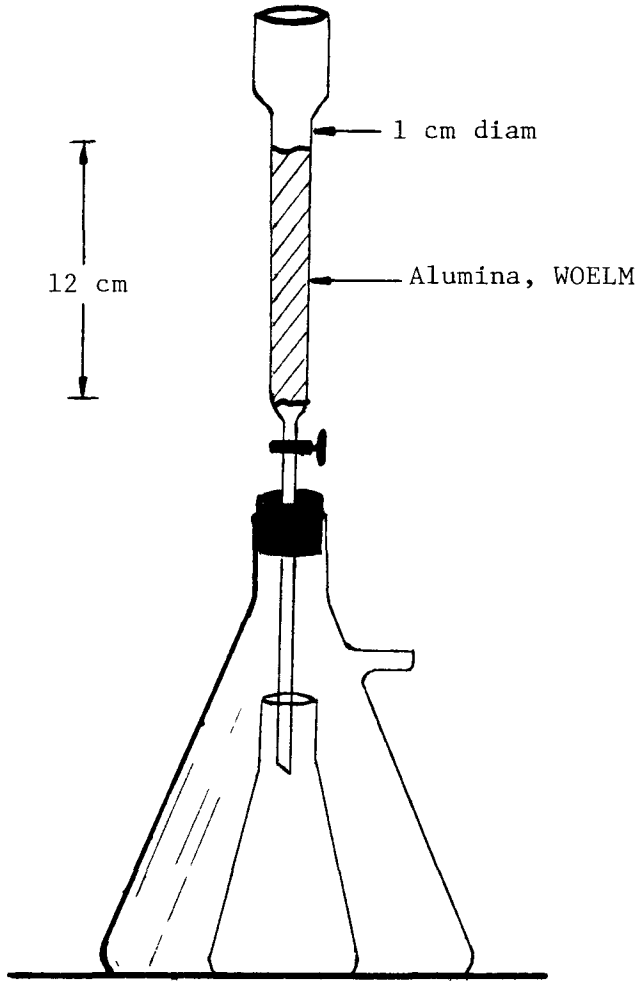


Fig. 1 Alumina column.

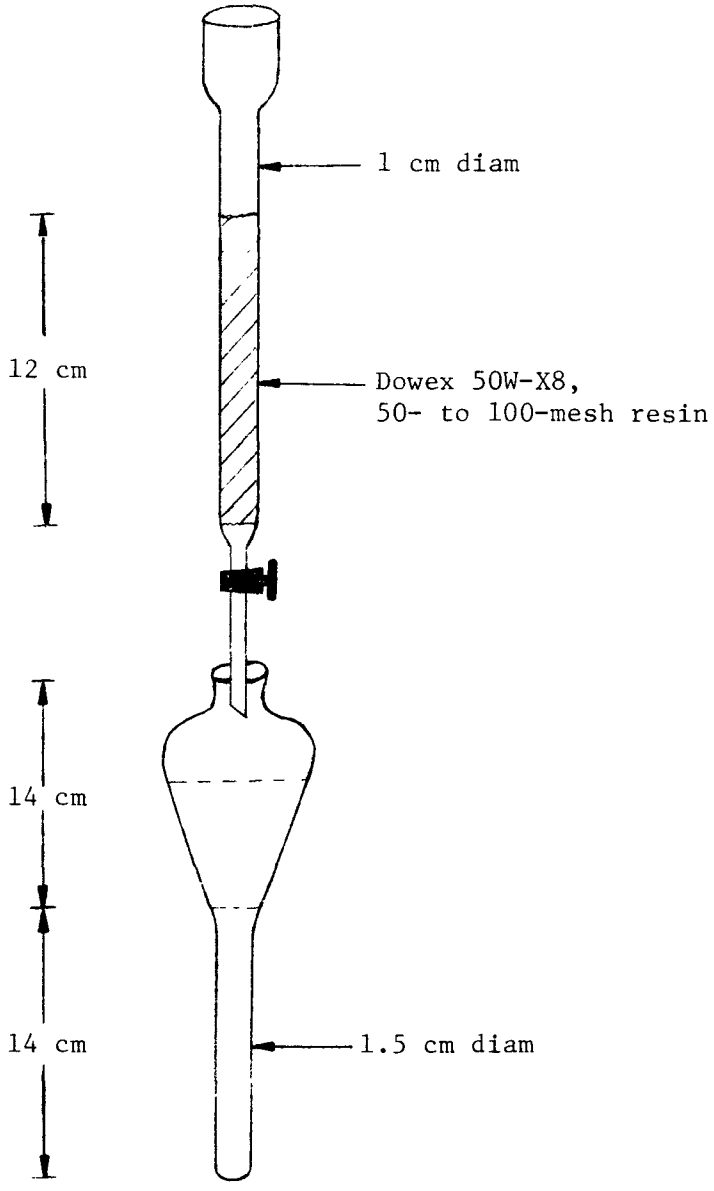


Fig. 2 Cation column and special titration cell.

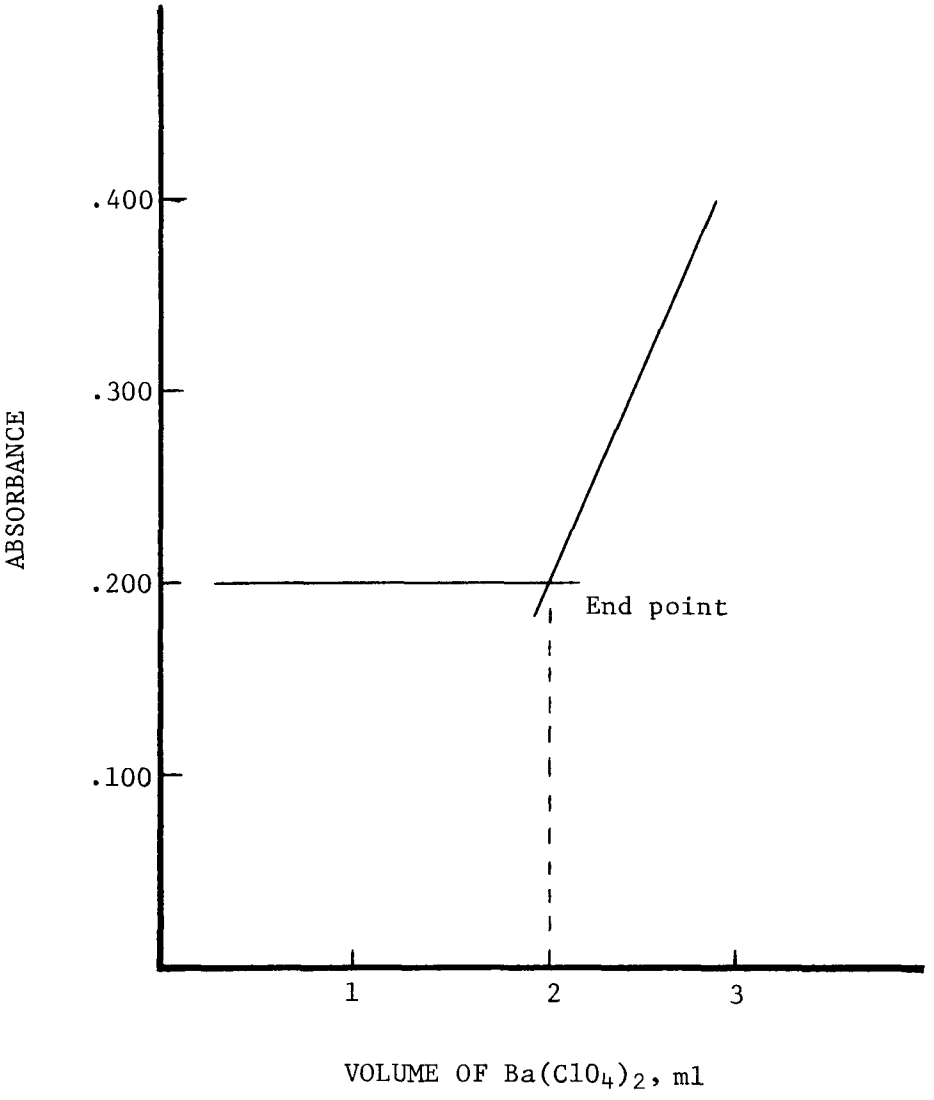


Fig. 3 Titration curve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Sulfate

CHARGE NUMBER _____ PROCEDURE SO_4-V01-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2$ a_2	Standardization Vol Ba^{++}, ml	Vol $SO_4^{=}$, ml	Ba^{++} M	Sample Vol Ba^{++}, ml	$SO_4^{=}$ in Aliquot, mg			RESULT
	1/25/10	2.50	0.250	0.001	2.0	0.1922			0.005 M SO_4
									0.480 mg/ml SO_4

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Molarity} = \frac{DC}{1/25/10} = \frac{(2.0)(0.001)}{0.4} = 0.005\ M\ SO_4$$

$$\text{Concentration} = \frac{DC\ 96}{1/25/10} = \frac{(2.0)(0.001)(96)}{0.4} = 0.480\ mg/ml\ SO_4$$

APPROVED BY _____

TITRIMETRIC DETERMINATION OF TRIBUTYLPHOSPHATE IN KEROSENE BY AN ACID SATURATION METHOD

ABSTRACT

When contacted with 8M HNO_3, a tributylphosphate (TBP)-kerosene solution extracts nitric acid in amounts directly proportional to the TBP concentration. Titrimetric measurement of the extracted acid with standard base gives a measure of the TBP concentration. The proportionality is constant for TBP concentrations in the range 3 to 12 volume percent. Above this range, a correction is required. TBP-kerosene solutions containing interfering levels of extractable metal ions are scrubbed with a 0.1M ammonium citrate solution before analysis.

APPLICABILITY

This method based on the procedures of Allen and DeSesa[1] and Brown[2] is designed specifically for the determination of tributylphosphate (TBP) in kerosene medium. Tributylphosphate concentrations between 3 and 50 (v/v)% are determinable. Most metal ions are not extracted into TBP-kerosene solutions at high enough concentrations to cause interference. Exceptions are Np(IV, VI), Pa(V), Pu(IV,VI), Th(IV), and U(IV, VI). Uranium, for example, interferes at concentrations exceeding 0.5 g/liter and must be scrubbed out initially with a 0.1M citrate solution.

DISCUSSION

A TBP-kerosene solution extracts nitric acid in amounts proportional to the TBP concentration. This relationship holds for TBP concentrations up to about 12% when the TBP-kerosene solution is contacted three times with 8±0.5M HNO_3. At TBP concentrations above 10%, results tend to be slightly low and corrections based on quality control data are applied. This is caused by a significant increase in the volume of the TBP-kerosene phase due to the extraction of nitric acid; hence, less than a proportionate amount of acid is present in a unit volume of the acid-contacted TBP-kerosene solution that is titrated with the standard sodium hydroxide.

Two potential sources of error are incomplete separation of the TBP-kerosene and 8M HNO_3 phases and too rapid titration near the bromthymol blue end point. As the end point is approached, the blue color appears, then fades slowly. The titration must be taken to a blue color that remains for 2 min.

SPECIAL SAFETY PRECAUTIONS

The extraction of the TBP-kerosene sample with 8M HNO_3 is potentially hazardous. Wear rubber gloves and tightly secure the stopper of the separatory funnel. Release the pressure in the separatory funnel periodically to eliminate excessive pressure build up.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, low form, 250-ml.
2. Buret, 10-ml, graduated in 0.05-ml increments.
3. Buret, 25-ml, graduated in 0.10-ml increments.
4. Funnels, separatory, 125-ml, with Teflon-plugged stopcocks.
5. Magnetic stirrer and plastic-coated stirring bars.
6. Pipets, volumetric, 5- and 25-ml.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium citrate solution, 0.1M. Dissolve 5.65 g of di-ammonium hydrogen citrate in water and dilute to 250 ml.
2. Bromthymol blue indicator, 0.05 (w/v)%. Triturate 0.1 g of the dry indicator with 7.5 ml of 0.02M NaOH and dilute to 200 ml with water.
3. Nitric acid, 8.0$\pm$0.5M.
4. Sodium hydroxide, standard, 0.200N.
5. Tributylphosphate standard 5.0 (v/v)%. Measure 50 ml of reagent grade TBP in a 50-ml volumetric flask. Transfer the TBP to a 1-liter volumetric flask with kerosene rinses and dilute to volume with kerosene.
6. Tributylphosphate bench standards. Prepare four bench standards with TBP concentrations in the range of 2 to 15 (v/v)%. Measure the appropriate volume of TBP for each standard and dilute to 1 liter with kerosene.

PROCEDURE

A. Determination of Titration Blank

A blank determination is not required for this method.

B. Determination of TBP Conversion Factor

The TBP conversion factor must be determined in duplicate by each shift for every new batch of 8M HNO_3. Use 25-ml aliquots of the 5.0 (v/v)% TBP standard and follow Procedure D. Report the results to the Quality Control Laboratory which will assign a TBP conversion factor to the 8M HNO_3.

$$\text{TBP Conversion Factor} = \frac{(\text{TBP conc of std, in \%})}{(\text{ml } 0.2\underline{N}\ \text{NaOH})(\text{Normality of NaOH})} = \frac{\text{\% TBP}}{\text{meq NaOH}} \quad (1)$$

C. Analysis of Bench Standard Control

Analyze one of the bench standards with each series of samples. The result obtained must fall within the specified limits. If the result is outside the limits, reprocess the bench standard. Contact your supervisor if difficulties persist.

D. Analysis of Samples

1. Pipet a 25-ml aliquot of the sample into a 125-ml separatory funnel. Proceed to Step 2 if the sample contains interfering levels of metal ions. If not, proceed to Step 3.

2. Add 10 ml of 0.1M diammonium hydrogen citrate solution, extract vigorously for 2 min, let stand for 5 min, then drain and discard the lower aqueous phase.

   If the sample contains enriched U, follow the established salvage procedures.

3. Contact the sample with three 25-ml portions of 8M HNO_3; each time, extract vigorously for 2 min, let the phases separate, then drain the lower phase.

4.	Wait 15 min to obtain complete phase separation.	
5.	Pipet 5.00 ml of the TBP-kerosene solution into a 250-ml beaker containing a plastic-coated stirring bar.	Do not transfer any of the aqueous phase. Let the pipet drain for 30 sec.
6.	Add 100 ml of distilled water and 10 drops of the bromthymol blue indicator solution.	
7.	Place the beaker on a magnetic stirrer and adjust the stirring to give good mixing of the two phases without loss of solution.	
8.	Immerse the tip of the buret into the sample and titrate with the 0.2N NaOH to the permanent blue color of the yellow to blue bromthymol blue end point that remains for 2 min.	Use the 10-ml buret for samples containing 10% TBP or less. Use the 25-ml buret for samples containing greater than 10% TBP. Titrate slowly in the vicinity of the end point to avoid undertitration. The blue color appears, then slowly fades.
9.	Record the data and calculate the results as described on the example worksheet. Report 3 significant figures.	

REFERENCES

1. Robert J. Allen and Michael A. DeSesa "Determination of Tributyl Phosphate", U. S. Atomic Energy Commission, WIN-52 (1956).

2. E. A. Brown, "The Determination of Tributyl Phosphate By An Acid Saturation Method", U. S. Atomic Energy Commission, FMPC-66 (1952).

3. R. A. Schneider and K. M. Harmon, "Analytical Solvent Extraction", Chemical Processing Department Analytical Technical Manual, U. S. Atomic Energy Commission, HW-53368 (1957).

January 1969

D. M. Lund

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION % TBP

CHARGE NUMBER _____ PROCEDURE TBP-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Volume of NaOH required ml	Normality of NaOH	TBP Conversion Factor %/meq	% TBP	% TBP Corrected for Bias			RESULT % TBP
IAS		8.24	0.201	5.43	8.99	8.99±0.10			8.99±0.10
IBS		14.15	0.201	5.43	15.4	15.6±0.1			15.6±0.1

ANALYZED BY _____ DATE _____

CALCULATIONS:

Sample IAS.

D = ABC

D = 8.24 x 0.201 x 5.43 = 8.99

E = 8.99 ± 0.10

Sample IBS:

D = ABC

D = 14.15 x 0.201 x 5.43 = 15.4

E = 15.6 ± 0.1

APPROVED BY _____

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF MILLIGRAM AMOUNTS OF URANIUM

ABSTRACT

A rapid, highly selective method is described for the determination of milligram amounts of uranium in a wide variety of inorganic and organic samples. For aqueous samples, the uranium is extracted directly into hexone as the neutral tetrapropylammonium trinitratouranate ion pair from an acid-deficient aluminum nitrate salting medium, then measured at 452 mμ on a recording spectrophotometer. For organic solvent samples, the uranium first is stripped with an ammonium citrate solution, then extracted as aqueous samples. For both cases, standards are processed simultaneously and the uranium concentration of the samples is determined by comparison.

APPLICABILITY

This versatile method is applicable to a wide variety of inorganic samples including those of the aluminum, stainless steel, and Zircaloy types. It is also applicable to liquid organic samples such as hexone and tributylphosphate (TBP)-kerosene. Two basic analysis procedures, D and E (see comparison of the two in Table I), are used. Procedure D which uses smaller volumes of samples and reagents is simpler, more adaptable to remote use, and more economical. Its sensitivity limit is 1 mg U/ml. Procedure E is especially suitable for samples either with complex unknown compositions or with low levels of uranium. Its sensitivity is 0.1 mg/ml. A special Procedure F is provided for the analysis of water-immiscible organic solvent samples[1]. This procedure, based on a citrate strip of the uranium, is coupled with Procedure E.

The range is 1 to 40 mg of uranium for Procedures D and E. As written, the maximum sample aliquot for aqueous samples is 1 ml for Procedure D and 10 ml for Procedure E; hence, the lowest concentration determinable is 1 mg U/ml by Procedure D and 0.1 mg U/ml by Procedure E. When highest precision is desirable, Procedure E should be used for samples with uranium concentrations less than 5 mg/ml. For organic solvent samples, a limit of 25 ml is specified and the lowest concentration that can be determined is 0.04 mg U/ml.

The effects of diverse ions have been studied extensively under the conditions of Procedure D[2,3] and Procedure E; and on the basis of these studies, the tolerance levels of 43 metal ions and 18 anions have been established (Table II). Careful examination of Table II will show that most ions do not interfere even at high levels. Some identified in Table II by the letter "b" may interfere under given

TABLE I

COMPARISON OF PROCEDURES D AND E

Item Compared	Procedure D	Procedure E
Volume of salting solution	6 ml	40 ml
Maximum sample volume	1 ml [a]	10 ml
Maximum volume of water permissible during extraction	1.75 ml	12 ml
Range of procedure	1 to 40 mg U for "cold" samples 5 to 40 mg U for samples that require remote handling.	1 to 40 mg U
Lowest concentration determinable	1 mg U/ml ("cold" samples) 5 mg U/ml (samples that require remote handling)	0.1 mg U/ml
Diverse ion tolerance	Excellent, but generally less than Procedure E; greater than moderate amounts of Cl^- interfere.	Excellent, including high levels of Cl^-.

[a] The sample volume can exceed 1 ml if the sample is evaporated prior to extraction.

TABLE II
EFFECTS OF DIVERSE IONS[a]

Ion	Tolerance Level, mM Procedure D	Procedure E	Ion	Tolerance Level, mM Procedure D	Procedure E
Metal Ions					
Al(III)	2.0[c]	15.0	Mg(II)	0.75	5.0
Ag(I)	1.2	2.0[c]	Mn(II)	0.50	5.0
Au(III)	Expected to Interfere		Mn(VII)	1.0[d]	1.0[d]
Ba(II)	0.025	1.0[c]	Mo(VI)	0.10[b]	0.35[b]
Be(II)	1.0	2.0[c]	Na(I)	1.2	5.0[c]
Bi(III)	0.025	0.05[b]	Nb(V)	0.1[b]	0.1[b]
Ca(II)	0.75	5.0[c]	Nd(III)	0.10	0.55
Cd(II)	0.50	5.0	NH_4(I)	0.5[c]	3.0
Ce(III)	0.50	5.0	Ni(II)	1.0	5.0
Ce(IV)	0.008[b]	0.025[b,d]	Np(VI)	Expected to Interfere	
Co(II)	1.2	5.0	Pb(II)	0.25	5.0
Cr(III)	1.5	5.0	Pt(IV)	0.0003[c]	0.024
Cr(VI)	0.1[b,d]	0.5[b,d]	Pu(IV,VI)	Expected to Interfere[f]	
Cu(II)	1.0	5.0	Ru(III,IV)	0.01[c]	0.13
Dy(III)	0.10[c]	0.55	Sm(III)	0.10	0.52
Er(III)	0.10[c]	0.52	Sn(II,IV)	0.02[c]	0.05[b]
Fe(III)	0.50	5.0	Sr(II)	0.50	5.0
H(I) as HNO_3	10[b]	50[b]	Th(IV)	0.008[b]	0.025[b]
			V(V)	0.012[b]	0.025[b]
Hg(I,II)	0.50	2.5	W(VI)	0.01[c]	0.06[b]
Ho(III)	0.015[c]	0.025[b]	Y(III)	0.02[c]	0.10
K(I)	0.50	8.0	Zn(II)	1.0	2.5
La(III)	0.50	5.0[c]	Zr(IV)	0.25	2.5

TABLE II (Cont'd)

Ion	Tolerance Level, mM Procedure D	Procedure E	Ion	Tolerance Level, mM Procedure D	Procedure E
Anions					
Acetate	1.2	8.7[b]	I^-	0.05[c,e]	0.10[b,e]
$BO_3^{\equiv}$	0.025	3.0	NO_3^- (as acid)	10	50
BrO_3^-	0.50	1.0[c]	Oxalate	0.050	4.0
Br^-	0.2[c]	1.0	ClO_4^-	0.10[b]	0.50[b]
Cl^- (low Fe samples)	0.25	24.2[b]	Peroxide (H_2O_2)	0.10[b]	0.50[b]
Cl^- (high Fe samples)	Expected to Interfere	6.0[b]	$S_2O_8^=$	0.25	---
Citrate	0.25	2.5[b]	$PO_4^{\equiv}$	0.25[b]	1.0[b]
CN^-	0.25	0.25[c]	$SO_4^=$	0.25[b]	12[b]
F^-	5.0	20	Tartrate	0.05[c]	2.5
Formate	1.2	5.0[c]			

[a] Unless noted otherwise, the tolerance level listed is the highest level studied and does not represent the maximum tolerance level.

[b] Maximum tolerance level below which the error is 1% or less.

[c] Conservative estimate based on the chemical properties of the elements and the observed effect of the ion in the other procedure.

[d] Tolerance level with no hydroxylamine reduction. With reduction, tolerance is about same as lower valence ion listed.

[e] After the extraction, wait 30 min before color measurement to allow the iodine to bleach out.

[f] The interference of plutonium possibly could be eliminated or reduced by scrubbing the hexone phase with a salting solution containing organic complexing reagents[4].

conditions and maximum tolerance levels are listed for these. The maximum tolerance level is defined as that level where the observed effect becomes 1%. The effects of a number of the interfering ions at levels above the maximum tolerance level also have been studied for Procedure E. The data are summarized in Table III. Noteworthy is the fact that sulfate does not interfere seriously even at the 24 mM (1.25 ml of the concentrated acid) level.

The diverse ions that do interfere affect the determination in different ways. Bismuth, perchlorate, tungstate, and vanadate precipitate under the conditions of the analysis and carry uranium. Cerium(IV), chloroaurate ($AuCl_4^-$), perchlorate, vanadate, and Th(IV) form stable complexes with the tetrapropylammonium ion and prevent the complete extraction of uranium. Others such as Ho(III), Np(VI), and Pu (all valences) coextract with the uranium and absorb at 452 mμ, the working wavelength. Complexing anions such as citrate, phosphate, and sulfate above certain levels complex uranium to prevent quantitative extraction. Chloride alone does not interfere except at very high levels; however, when major amounts of iron(III) also are present, the chloride level must be less than 6 mM for Procedure E and less than 1 mmole for Procedure D. Above these limits, the iron(III)-chloride complex coextracts and interferes by altering the spectrum of the uranium complex. The extraction of iron is strongly dependent on the chloride concentration as well as the total chloride level. In Procedure E, the addition of water effectively reduces the chloride concentration and the coextraction of iron.

The harmful effect of some of the interferences can be minimized or eliminated with simple manipulations. In the recommended procedures, a sequential potassium permanganate-hydroxylamine sulfate treatment is used routinely to guarantee that the uranium is in the extractable (VI) valence state. This treatment automatically reduces Ce(IV), Cr(VI), Mn(VII), and peroxide to eliminate their interferences. Volatile interferences such as perchloric acid can be removed by repeated evaporation of the sample with sulfuric acid. Sulfate, however, tends to suppress the absorbance so that the final fuming should be to a small volume and standards should be processed with the samples through the same treatment. The tolerance for thorium can be increased by the use of a modified salting solution with a higher tetrapropylammonium nitrate (TPAN) concentration.

TABLE III

EFFECT OF DIVERSE IONS AT LEVELS ABOVE THE MAXIMUM TOLERANCE LEVEL, PROCEDURE E[a]

Metal Ion	mM Present	Effect, %	Anion	mM Present	Effect, %
Au(III)	0.04	- 9.0	Acetate	17.4	- 1.7
Bi(III)	0.50	- 2.6	Cl^- (low Fe)	36.3	- 1.1
H(I) as HNO_3	63 78	- 1.1 - 4.3	Citrate	5.0	- 2.0
Ho(III)	0.10	+ 2.3	I^-	0.5	Iodine Coextracts and Interferes
Mo(VI)	0.70	- 2.0	ClO_4	2.0	- 2.7
Sn(II,IV)	0.25	- 2.3	Peroxide (H_2O_2)	1.0	- 3.5
Th(IV)	0.05	- 1.5	$PO_4^{\equiv}$	7.3	- 1.5
V(V)	0.05	- 1.5	$SO_4^=$	18	- 1.5
	0.10	- 4.4		24	- 2.1
W(VI)	0.10	- 4.4			

[a] The uranium level was maintained at 0.1 mM (25 mg). Similar effects can be expected for Procedure D at diverse ion levels approximately 20% of the levels listed above.

DISCUSSION

The uranium must be in the (VI) oxidation state to quantitatively extract. A permanganate oxidation step is specified in both Procedures D and E to accomplish this. If the uranium is definitely known to be in the (VI) state only, the addition of potassium permanganate is not necessary. The uranium can be assumed to be totally in the (VI) state when the sample contains strong oxidants such as chromium(VI) and when the prior history of the sample precludes the existence of uranium in oxidation states other than (VI).

The extraction of uranium(VI) and the absorbance of the extracted uranium complex are dependent on temperature, the TPAN concentration, the age and concentration of the salting solution, and the volume of hexone. Thus, standards must be processed each time a sample is processed. Recent studies have shown that the calibration factors for D and E are slightly, but significantly, different so standards must be processed by the same procedure as that used for the analysis of the samples. The reasons for the observed difference between the factors for D and E are thought to be differences in the level and concentration of TPAN in the two extraction systems and differences in the distribution of hexone into the aqueous phase. The latter is particularly important in the analysis of hexone samples wherein uranium is stripped from the hexone sample with 9 ml of 0.1M diammonium hydrogen citrate, reextracted into 6 ml of hexone per Procedure E, then compared against standards also processed via Procedure E. To minimize errors associated with increases or decreases in the volume of the final hexone extract, the calibration standard must be diluted with 9 ml of 0.1M diammonium hydrogen citrate preequilibrated with hexone. This practice is not necessary in the analysis of samples of TBP-kerosene with only limited solubility in water.

Two potentially serious sources of error are the improper measurement of the hexone and the loss of hexone in the extraction process before equilibration is attained. It should be kept in mind that a difference of one drop (~0.05 ml) of hexone will cause an error of nearly 1%. Freshly prepared salting solution contains a significant amount of suspended hexone which seriously effects the results. For this reason, requests for salting solution should be made well in advance so that properly aged salting solutions can be provided.

In Procedure E, up to 75 mg of uranium is extracted quantitatively, so that in emergencies (for example, when resamples are not available), the hexone extract can be diluted with 1 or 2 parts of hexone to enable measurement. This approach will give results within about 3% of the true value....about 1.5% low when diluted twofold and about 2 to 3% low when diluted threefold.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, Aminco, 5-cm, 13-mm OD, 4.9-ml capacity. These cells should be fitted with Teflon sleeves with a diameter similar to that of standard 22-mm OD 5-cm cells.

2. Absorbance cells, Corex, 1-cm. Teflon spacers should be placed in the bottom of the cell if scaled-down volumes are used in the method.

3. Beakers, assorted sizes.

4. Cary Model 14 Recording Spectrophotometer, Beckman DK Recording Spectrophotometer, or equivalent.

5. Centrifuge, International Clinical, Model C1, or equivalent.

6. Culture tubes, 25-ml, with polyethylene-lined screw caps.

7. Dropping bottles.

8. Extraction apparatus for test tubes; pin wheel type[2] is recommended.

9. Graduated cylinder, 50-ml.

10. Hot plate.

11. Pipets, micro, assorted sizes, with control syringe.

12. Pipets, Mohr, 5- and 10-ml, with suction bulb.

13. Pipets, transfer.

14. Pipets, volumetric, assorted sizes, including 6-ml, with suction bulb.

15. Polyethylene stoppers for test tubes and separatory funnels.

16. Separatory funnels, 125- and 60-ml, with Teflon stopcocks.

17. Test tubes, glass, 16-x 150-mm, or slightly larger.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade Chemicals and distilled water. Use distilled or treated water throughout the method.

1. Acid-deficient aluminum nitrate salting solution, 2.8M, 0.8% (0.04M) in TPAN. Dissolve 1050 g of $Al(NO_3)_3 \cdot 9H_2O$ in 75 ml of water and 135 ml of conc NH_4OH with the aid of heating and stirring. Cool to room temperature, dilute to 900 ml with water, add 20 ml of 10% tetrapropylammonium hydroxide (Eastman Organic), and mix well. Extract the solution with 100 ml of hexone for 3 min. Let stand for about 1 hr to allow the phases to separate, then drain off the lower phase into a 1-liter bottle. Finally, add 80 ml of 10% tetrapropylammonium hydroxide and mix well. THE SOLUTION IS SUITABLE FOR USE AFTER 3 DAYS (see the DISCUSSION section). The preparation of a 4-liter batch is recommended. To prepare a 4-liter batch, multiply all additions by four and extract the solution one half at a time with 200-ml portions of hexone.

2. Acid-deficient aluminum nitrate salting solution, 2.8M, 5.0% in TPAN. Neutralize 100 ml of 10% tetrapropylammonium hydroxide solution to pH 7 with 5M HNO_3. Transfer to a large evaporating dish and allow the TPAN solution to stand until a thick slurry of crystals forms. This may take as long as 4 days. Transfer the crystals to a 400-ml beaker with 20 ml of water. Add 210 g of $Al(NO_3)_3 \cdot 9H_2O$. Stir and add water until a volume of approximately 165 ml is reached. Add 27 ml of conc NH_4OH and stir without heating until solution is complete. Filter and dilute to 200 ml with water.

3. Ammonium citrate solution, 0.1M. Dissolve 22.62 g of diammonium hydrogen citrate in water and dilute to 1 liter.

4. Hexone (methyl isobutyl ketone, 4-methyl-2-pentanone).

5. Hydroxylamine sulfate, 1M. Dissolve 32.8 g of $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 200 ml.

6. Nitric acid, conc.

7. Potassium permanganate solution, 0.2M. Dissolve 3.16 g of $KMnO_4$ in 100 ml of water. Store in a dark bottle.

8. Uranium stock solution, 250 mg U/ml. Ignite approximately 300 g of NBS U_3O_8 at 900°C for 1 hr. Let cool, then weigh to the nearest 0.001 g, 295±1 g of the oxide into a 500-ml Erlenmeyer flask. Cover the flask with a reflux head and dissolve the U_3O_8 in nitric acid with the aid of heat. Lengthy digestion

may be necessary to completely dissolve the oxide. When the dissolution is complete, evaporate the solution to the appearance of uranyl nitrate crystals. Cool slightly, then quantitatively transfer the contents of the Erlenmeyer flask with water rinses to a tared (to ±0.001 g) 1-liter volumetric flask. Cool the flask and contents to room temperature, dilute to volume with water, mix thoroughly, and weigh. Store the solution in sealed ampoules in 50-ml units. From the weight of the U_3O_8, its purity, and the weight of the solution, calculate the uranium concentration in mg/g. Label the ampoules accordingly.

9. Uranium calibration standards I and II, ~25 and ~20 mg U/ml, respectively. Dilute 25 ml and 20 ml (weighed to ±0.001 g) of the stock solution to 250.0 ml with 0.1M HNO_3. Calculate the concentration of uranium of the two solutions from the weight of the aliquot and the concentration of the stock solution.

10. Uranium bench-control standards. Prepare a series of dilutions of the stock solution, per item 9 above, to cover the concentration range 1 to 40 mg U/ml.

A. Blank

A blank is not necessary in this method. All absorbances are measured against air.

B. Calibration

To cover the range of 1 to 40 mg U, both 1- and 5-cm cells are used... 5-cm cells for the range 1 to 9 mg U and 1-cm cells for the range 5 to 40 mg U. If samples of widely varying uranium concentrations are being analyzed, the preparation of four calibration standards, 200 µl and 1.00 ml of standard I and 200 µl and 1.00 ml of standard II, will assure the presence of one suitable pair of comparison standards and minimize repeat analyses. If only samples with similar concentrations are being analyzed, two appropriate standards will suffice.

Calibration standards should be processed with each series of samples by the same procedure as that used to analyze the samples. Process the appropriate standards as follows:

1. Aqueous samples that do not require fuming. Use Procedure D or E with reference to samples.

2. Aqueous samples that require sulfuric acid fuming. Because high levels of sulfate exert a slight lowering effect, standards must be carried through the same treatment to compensate for the effect. Process the standards per Procedure G.

3. TBP-kerosene samples. Pipet the calibration standard into a 125-ml separatory funnel, add 5 drops of conc HNO_3 and 9 ml of 0.1M ammonium citrate, and process the mixture per Procedure E beginning at Step 4.

4. Hexone samples. Contact 50 ml of 0.1M ammonium citrate with 10 ml of hexone in a 125-ml separatory funnel for 3 min. Let the two phases separate then drain the hexone-equilibrated 0.1M ammonium citrate into a 100-ml beaker. Pipet the calibration standard into a 125-ml separatory funnel, add 5 drops of conc HNO_3 and 9 ml of hexone-equilibrated 0.1M ammonium citrate and then process the mixture per Procedure E beginning at Step 4.

Divide the milligrams of uranium in each standard by its respective absorbance to obtain the conversion factor. For each of the two groups of standards, the difference between the two factors should not exceed limits set by the Quality Control Laboratory and the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards immediately. Contact your supervisor if difficulties still are experienced.

C. Analysis of Bench-Control Standards

Each time samples are analyzed by Procedures D, E, or G, process one of the bench-control standards by the same procedure used to analyze the samples. The result obtained must fall within specified limits. If it does not, process another standard. Report to your supervisor if further difficulties are encountered.

The analysis of organic solvent samples is expected only at infrequent intervals. When such samples are received, request special bias controls from the Quality Control Laboratory.

D. Analysis of Aqueous Samples (Procedure D)

NOTE: Procedure D is recommended for radioactive samples that require remote handling and for all other samples except those with complex unknown compositions or those with appreciable amounts of chloride. For samples requiring analysis, the uranium concentration must be at least 1 mg/ml. For samples requiring remote analysis, only 1-cm cells can be used for the absorbance measurement. Thus the uranium concentration must be greater than 5 mg/ml. If greater sensitivity is needed, concentrate the sample initially by evaporation or use Procedure E. The tolerance of

Procedure D for diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1.	Pipet a sample, 1 ml or less, containing 1 to 40 mg of U and less than 10 meq of acid, into a 16- x150-mm test tube or a 25-ml screw-cap culture tube.	If the extraction of U is done remotely, the sample aliquot must contain at least 5 mg of U. If the evaporation step is used in Step 5, the sample can be slightly larger than 1 ml. For best precision, select a sample aliquot with at least 10 mg of U.
2.	Add 1 drop of conc HNO_3.	If it is known definitely that the U is in the (VI) valence state only, omit Step 3 and continue with Step 4.
3.	While swirling the tube continuously, add 0.2M $KMnO_4$ one drop at a time until the pink color persists for 30 sec.	
4.	Add 0.2 ml of 1M $(NH_2OH)_2 \cdot H_2SO_4$ and mix.	The purpose of the $(NH_2OH)_2 \cdot H_2SO_4$ is to reduce oxidants such as $KMnO_4$, Cr(VI), and Ce(IV).
5.	Using the approximation that one drop ≈0.05 ml to determine the volume of reagents added in Steps 2 to 4, estimate the total volume of the treated sample. If the volume exceeds 1.5 ml, evaporate the sample to less than 1.5 ml, then cool it to room temperature.	
6.	Add 6 ml of the 0.8% TPAN, aluminum nitrate salting solution with a Mohr pipet.	If the sample contains interfering levels of thorium, use the 5.0% TPAN salting solution.
7.	Pipet exactly 6.00 ml of hexone, stopper, and extract for 3 min with the extraction wheel or manually.	Erratic results will be obtained when there is inadequate mixing. Preferably, extract vigorously by hand for 2 min.

8. Centrifuge for 1 min to separate the two phases.

9. With a transfer pipet, transfer the hexone phase to a 5-cm (1 to 9 mg of U) or a 1-cm (5 to 40 mg of U) optical cell.

   Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, select the 5-cm cell for this will enable subsequent measurement in a 1-cm cell. For best results, the observed net absorbance should be 0.1 or higher.

10. Place the cell in the recording spectrophotometer and adjust the instrument so that the absorbance versus air is 0.0 to 0.5 at 480 mμ.

    One cell is recommended for a series of measurements of standards and samples. Clean the cell between measurements by rinsing it three times with water and three times with acetone, then dry the cell with clean air.

    After the final measurement, rinse the cell thoroughly with water, then acetone, and then air dry.

11. Scan the sample versus air from 480 mμ to 440 mμ at a scan speed of 0.5 mμ (5Å) per sec.

12. Determine the U concentration of the sample by comparison to the standards as described under CALCULATIONS.

E. Analysis of Aqueous Samples (Procedure E)

NOTE: This procedure is intended primarily for samples that contain between 0.1 and 2 mg of uranium per ml; however, it also is applicable to samples with higher uranium concentrations. Procedure E is recommended for samples with unknown compositions and samples that contain large amounts of chloride. The effects of diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1. Pipet a sample aliquot containing 1 to 40 mg of U and less than 50 meq of acid into a 60-ml separatory funnel.

   For best precision, select an aliquot with more than 10 mg of U.

2. Add 5 drops of conc HNO_3.

3. If the aliquot volume is less than 5 ml, dilute to 5 ml with water. Otherwise, proceed to Step 4 or 5 (see note).

   If it is known definitely that U is in the (VI) valence state only, omit Step 4 and continue with Step 5.

4. While swirling the funnel continuously, add 0.2M $KMnO_4$ one drop at a time until the MnO_4 color persists for 30 sec.

5. Add 0.5 ml of 1M $(NH_2OH)_2 \cdot H_2SO_4$ to reduce excess MnO_4 and other oxidants such as Cr(VI) and Ce(IV). Mix by swirling.

   If the sample contains high concentrations of Cr(VI) or Ce(IV), warm the funnel in a hot water bath to hasten reduction, then chill to room temperature.

   The total volume of sample plus added reagents must be less than 12 ml at this point. If the volume exceeds 12 ml, start again with a smaller aliquot. If a resample is not available, evaporate the sample to less than 12 ml under a heat lamp, chill to room temperature, then proceed with Step 6.

6. With a graduated cylinder, add 40 ml of the 0.8% TPAN aluminum nitrate salting solution.

7. Pipet exactly 6.00 ml of hexone, stopper, and extract fairly vigorously for 1 min.

   Low results will be obtained if the extraction is performed too gently.

8. Let the two phases separate, then drain off the lower aqueous phase.

9. Pour (or transfer with a transfer pipet) the hexone phase to a 5-cm (1 to 9 mg U) or a 1-cm (5 to 40 mg U) optical cell. If a precipitate or emulsion persists, drain the organic phase

   Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, select the 5-cm cell first for this will enable subsequent measurements in 1-cm cells. For best results, the

into a clean 16- x 150-mm test tube and centrifuge for 1 min.	observed net absorbance should be 0.1 or higher.
10. Place the sample in the recording spectrophotometer and adjust the instrument so that the absorbance versus air is 0.0 to 0.5 at 480 mμ.	One cell is recommended for a series of measurements of standards and samples. Clean the cell between measurements by rinsing it three times with water and three times with acetone, then dry the cell with clean air. After the final measurement, rinse the cell thoroughly with water, then acetone, and then air dry.
11. Scan the sample versus air from 480 mμ to 440 mμ at a scan speed of 0.5 mμ (5Å) per sec.	
12. Determine the U concentration of the sample by comparison to the standards as described under CALCULATIONS.	

Analysis of Organic Samples

NOTE: This procedure is designed specifically for the analysis of hexone and TBP-kerosene samples.

1. Pipet a sample aliquot (25 ml or less) containing 1 to 40 mg of U into a dry 60-ml separatory funnel.	For best results, select a sample with greater than 10 mg of U.
2. If the aliquot volume is less than 5 ml, dilute to 5 ml with the solvent.	Use hexone for hexone samples and kerosene for TBP-kerosene samples.
3. Pipet 5 ml of the 0.1M ammonium citrate solution, stopper, and extract for 2 min.	

4.	Let the two phases separate, then drain the lower aqueous phase into a clean, dry 60-ml separatory funnel.	The phase separation must be complete. Carryover of the organic solvent to the aqueous phase causes low results.
5.	Repeat steps 3 and 4, except use 2 ml of the 0.1M ammonium citrate solution. Combine the aqueous strip with the first 5-ml strip.	
6.	Repeat Step 5.	The total volume of the aqueous strip must not exceed 12 ml after Step 7. Do not use more than 2 ml of water to rinse the tip of the separatory funnel.
7.	Add 5 drops of conc HNO_3 to the combined aqueous citrate strip and mix.	
8.	Complete the determination per Procedure E beginning at Step 5.	

G. Analysis of Aqueous Samples Requiring Sulfuric Acid Fuming

NOTE: This treatment is designed to remove volatile interferences such as chloride, perchlorate, and peroxide. Occasionally for reasons not known, the uranium spectra climbs sharply away from the base line as the wavelength decreases. Sulfuric acid fuming has been found to correct this.

1. Pipet a sample aliquot containing 1 to 40 mg of U into a small beaker.

2. Add 0.5 ml of conc HNO_3 and 1 ml of conc H_2SO_4, evaporate the sample to H_2SO_4 fumes, and fume for 5 min.

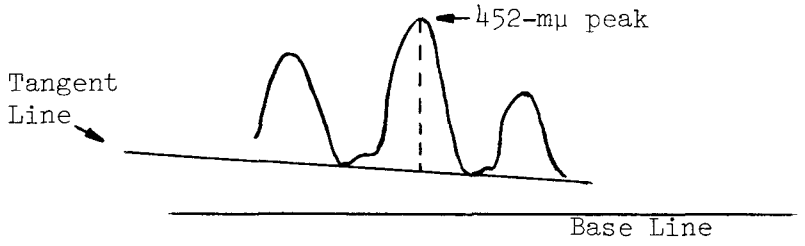
3. Cool the sample, add 5 ml of water, and heat gently until the salts dissolve completely. Additional water may be added to effect dissolution and to replenish that lost through evaporation.

4. Evaporate the solution slowly to a volume of 3 ml or less, then transfer the sample quantitatively to a 125-ml separatory funnel with small water rinses. The volume of the solution should not exceed 12 ml after the transfer.

5. Continue with the determination per Procedure E beginning at Step 6.

CALCULATIONS

A. Determine the absorbance of the calibration standards and the samples by drawing a line tangent to and connecting the absorbance minimums on each side of the 452-mμ peak as shown below.



The absorbance is the height of the peak in absorbance units and is equal to the difference between the absorbance reading at the 452-mμ peak and the absorbance reading on the tangent line at 452 mμ.

B. Record the sampling and absorbance data and calculate the results as shown on the example work sheet. Report all results to three significant figures.

The calibration standards are prepared with natural uranium so a correction must be applied for enriched uranium samples. The factor for this correction is the ratio of the average atomic weight of the uranium in the sample to the average atomic weight of the natural uranium (238.04). Table IV lists corrections factors for different enrichment levels. The effects of varying ^{236}U and ^{234}U are considered negligible.

TABLE IV

CORRECTION FACTORS FOR DIFFERENT ^{235}U LEVELS

^{235}U Isotope Abundance, %	Correction Factor	^{235}U Isotope Abundance, %	Correction Factor
		50	0.9937
100	0.9875	40	0.9950
90	0.9887	30	0.9962
80	0.9900	20	0.9975
70	0.9912	10	0.9987
60	0.9925	0	1.0000

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April, 1969
S. S. Yamamura

FORM INC-121
(REC 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Uranium

CHARGE NUMBER _____ PROCEDURE U-Color-1, Procedure E

SPECIAL INSTRUCTIONS:

The sample is a dilute solution of product uranyl nitrate with 84.5% ^{235}U enrichment.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA $a_0/d_1/a_1/d_2/a_2$	Absorbance	Conversion Factor	mg U in Aliquot Analyzed	Enrichment Factor	mg U Corrected for Enrichment	mg U Corrected for Bias		RESULT mg U/ml
U std, 20 mg		0.384	52.08						
U std, 25 mg		0.478	52.30						
			$\bar{X}$ = 52.19						
Prod-UN-1	3.00 ml								
	(Entire Sample used)	0.598	52.19	31.21	0.9894	30.88	31.23±0.65		10.41±0.22

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\text{mg U in Std}}{\text{Absorbance}} = B = \frac{20}{0.384} = 52.08$$

$$B' = \frac{25}{0.478} = 52.30$$

$$\bar{X} = 0.5(B + B') = 0.5(52.08 + 52.30) = 52.19 \text{ mg U/abs unit}$$

Prod-UN-1

$$C = AB = 0.598\,(52.19) = 31.21 \text{ mg U}$$

$$E = CD = 31.21\,(0.9894) = 30.88 \text{ mg U}$$

$$\text{Result} = \frac{F}{\text{Sample Vol}} = \frac{31.23 \pm 0.65}{3.00} = 10.41 \pm 0.22 \text{ mg U/ml}$$

APPROVED BY _____

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM

ABSTRACT

Uranium, as the tetrapropylammonium uranyl trinitrate complex, is extracted into methyl isobutyl ketone from an acid-deficient aluminum nitrate salting solution. The organic phase is scrubbed with an aluminum nitrate solution which contains tartaric acid, oxalic acid, ethylenediamine tetraacetic acid, and ferrous sulfamate. The chromogen, dibenzoylmethane, in an ethanol-pyridine medium, is added to an aliquot of the separated organic phase and the absorbance is measured at 415 mμ. The only significant cation interferences are thorium(IV) and cerium(IV), and a special procedure is described for samples containing them.

APPLICABILITY

The effects of diverse cations and anions have been established as summarized in Table I[1]. The only serious metal ion interferences are thorium(IV) and cerium(IV). A special procedure is included which tolerates large levels of these two ions. No common anion interferes seriously. Total uranium, including all oxidation states, is determined.

With the described procedure, the maximum aliquot volume is 1 ml and the maximum amount of acid in the aliquot is 16 meq. Larger volumes can be analyzed by evaporating a known volume to a known smaller volume and then selecting the aliquot. This same technique can be used to reduce the total amount of acid. Sulfate, in high concentrations, causes the precipitation of aluminum sulfate when the salting solution is added to the sample. The recovery of uranium, in such a case, tends to be low because the gel-like precipitate adsorbs uranium. Again, evaporation of a sample aliquot is the means of reducing the interference. The evaporation should be to near dryness and the residue is taken up in hot, 8M HNO_3.

The range of the method is 0.005 to 0.075 mg of uranium. With a maximum aliquot volume of 1 ml, the lower concentration limit is 0.005 mg/ml. The pellet fluorophotometric method (Method U-Fluor-1) is 100 times more sensitive.

TABLE I

TOLERANCES OF DIVERSE IONS

Metal Ion	Known Tolerance Level[a] (mM)	Anion	Known Tolerance Level[a] (mM)
Ag(I)	1.2	Acetate	1.2
B(III)	See Anion	$BO_3^{\equiv}$	0.025
Ba(II)	0.025	$BrO_3^{\equiv}$	0.5
Be(II)	1.0	Cl^-	0.25
Bi(III)	0.5	Citrate	0.25
Ca(II)	0.75	CN^-	0.25
Cd(II)	0.5	$CrO_4^=$	0.012
Ce(III)	0.5	Formate	1.2
Ce(IV)	0.25[b]	F^-	0.25
Co(II)	1.2	$Fe(CN)_6^{\equiv}$	0.25
Cr(III)	1.5	$Fe(CN)_6^{\equiv}$	0.00025
Cr(VI)	See Anion	$MoO_4^=$	0.025
Cu(II)	1.0	Oxalate	0.05
Fe(III)	0.5	ClO_4^-	0.25
Hg(I or II)	0.5	$S_2O_8^=$	0.25
K(I)	0.5	$PO_4^{\equiv}$	0.25
Lanthanides(III)	0.5	$SO_4^=$	0.25
Mg(II)	0.75	SCN^-	0.025
Mn(II)	0.5	$WO_4^{\equiv}$	0.0012
Mo(VI)	See Anion	VO_3^-	0.012
Na(I)	1.2		
Ni(II)	1.0		
Pb(II)	0.25		
Pu(III,IV, or VI)	0.1		
Sr(II)	0.5		
Th(IV)	0.25[b]		
V(V)	See Anion		
W(VI)	See Anion		
Zn(II)	1.0		
Zr(IV)	0.25		

[a] Level of U for all tests was 1.05×10^{-3} mM (0.025 mg). The tolerance level given for each diverse ion is the highest value studied. The actual tolerance level may be higher.

[b] This tolerance level is for the special procedure designed to minimize the interference of Th(IV) and Ce(IV).

DISCUSSION

The high selectivity of this method is attributable to the combination of an extraction procedure selective for uranium and a chromogen relatively selective for uranium. The extractant, hexone, has high distribution coefficients for oxygenated cations and for the higher valence simple cations. By using an acid-deficient aluminum nitrate salting solution, the higher valence cations form hydrolyzed species with lower distribution coefficients. The extraction, thus, becomes selective for such oxygenated cations as UO_2^{+2} and PuO_2^{+2}. The limitation of 16 meq of acid in the sample simply is that above this level the acid-deficiency of the salting solution is exceeded and the hydrolysis ability is lost.

To increase the distribution of uranium(VI) into hexone, tetrapropylammonium nitrate is included in the salting solution. The ion-association complex tetrapropylammonium uranyl trinitrate $[(C_4H_9)_4N]^+[UO_2(NO_3)_3]^-$, forms which is soluble in organic solvents. A single batch contact under the prescribed procedure conditions gives >99.8% extraction of uranium(VI).

To remove coextracted plutonium and traces of diverse ions, the hexone phase is scrubbed with an aluminum nitrate solution containing tartaric acid, oxalic acid, EDTA, and ferrous sulfamate. This last reagent reduces plutonium to the (III) valence state which has a low distribution coefficient. The ferrous sulfamate cannot be incorporated into the aluminum nitrate scrub solution because it is unstable to nitrate for other than short periods.

After the scrub, an aliquot of the hexone phase is mixed with the chromogen, dibenzoylmethane (DBM) in pyridine solution to produce the uranium(VI)-DBM complex which has a molar absorptivity of $\sim$ 23,000 at the wavelength of 415 mμ. Pyridine is miscible with hexone to permit this "in situ" color development. Full color develops in 10 min and is stable for at least 24 hr. To obtain maximum sensitivity, the mixture of the hexone aliquot and the DBM-pyridine reagent are not diluted to a volume. Pyridine also serves as a buffer to neutralize coextracted acid which otherwise would decrease the intensity of the uranium(VI)-DBM color.

The oxidant used to ensure that uranium is in the (VI) valence state is potassium permanganate. Large excesses must be avoided as permanganate reacts with hexone to form manganese dioxide as a reduction product. Manganese dioxide collects at the interface between the salting solution and the hexone to hinder the phase separation. It also adsorbs uranium. Many analytical methods rely on nitric acid oxidation to produce uranium (VI). But certain complexes of lower valence uranium, particularly fluoride complexes of uranium(IV) in the presence of oxalate, are sufficiently stable to resist boiling nitric acid.

Thorium and cerium(IV) interfere by forming stable tetrapropylammonium nitrate complexes, thus competing for the reagent with uranium(VI). In the special procedure for samples that contain these two diverse ions, the tetrapropylammonium nitrate is omitted from the salting solution. The lowered extraction of uranium is accounted for in the procedure by processing the calibration standards the same as samples. However, even with the tetrapropylammonium nitrate omitted, sufficient thorium and cerium(IV) extract to interfere in the color development. The hexone phase, therefore, is scrubbed with a diethyldithiocarbamate (DDC)-ammonium acetate mixture. Thorium and cerium transfer to the scrub solution and uranium, as the DDC complex, remains in the hexone. DDC then in stripped from the hexone with an aqueous solution of mercury(II). The mercury(II) displaces uranium(VI) from the uranium(VI)-DDC complex to form a stable mercury(II)-DDC complex that distributes in favor of the aqueous phase. The uranium remains in the hexone phase. An aliquot of the hexone then is mixed with the DBM-pyridine reagent to form the uranium(VI)-DBM colored complex.

Many volumetric measurements are involved in this method. Those that affect the reliability of the analyses, and therefore must be exact, are (a) the sample aliquot, (b) the hexone for the extraction, (c) the aliquot of hexone removed for color development, and (d) the DBM-pyridine reagent.

Others, such as the measurement of the salting and scrub solutions, may be done with automatic dispensing devices or graduated cylinders.

SAFETY PRECAUTIONS

Hexone is flammable. Keep it away from open flames. Pyridine is mildly toxic. Avoid excessive inhalation of pyridine fumes.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, borosilicate glass, 5-cm, calibrated to ±0.002 absorbance units at 415 mμ with a processed standard.
2. Bottles, glass, ∿ 20-ml, S stopper.
3. Centrifuge for 15-x 125-mm test tubes.
4. Extraction apparatus. Pin wheel type[1] is recommended.
5. Graduated cylinders, 5- and 10-ml.
6. Medicine droppers.

7. Pipets, micro, assorted sizes, with control syringe.

8. Pipets, macro, 2-, 4-, 5-, and 15-ml.

9. Spectrophotometer, Beckman DU, Beckman DK, Cary Model 14, or equivalent.

10. Stoppers, polyethylene, 11- x 17-mm.

11. Test tubes, glass, 15- x 125-mm.

B. Reagents

Note: Use Analytical Reagent Grade Chemicals, high purity organic chemicals, and distilled water for all reagents. Use distilled water throughout the procedure.

1. Aluminum nitrate salting solution. Slurry 1050 g of $Al(NO_3)_3 \cdot 9H_2O$ with a small amount of water. Add 135 ml of conc NH_4OH, 10 ml of 10% tetrapropylammonium hydroxide and dilute with water to about 950 ml. Stir until dissolved (disregard any fine colloidal suspension), then extract with 250 ml of hexone in a separatory funnel. Filter the aqueous phase through a large, fine-porosity, sintered-glass Buchner funnel, add 10 ml of 10% tetrapropylammonium hydroxide, and dilute to 1 liter with water.

2. Dibenzoylmethane-pyridine reagent. Dissolve 0.114 g of dibenzoylmethane in 400 ml of pyridine. Add 25 ml of ethanol and dilute to 500 ml with pyridine.

3. Ferrous sulfamate solution. Add $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ to a saturated solution of sulfamic acid until no more dissolves. Prepare fresh once a week.

4. Hexone.

5. Nitric acid, conc and 1M.

6. Potassium permanganate solution, 0.002M. Dissolve 0.063 g of $KMnO_4$ in 200 ml of water.

7. Scrub solution. Add 940 g of $Al(NO_3)_3 \cdot 9H_2O$, 33 g of tartaric acid, 31 g of oxalic acid, and 64 g of EDTA (tetraacidic form) to 800 ml of water and 150 ml of conc NH_2OH. Heat mildly and stir until dissolved, then cool. Extract with 250 ml of hexone in a separatory funnel. Filter the aqueous phase through a large, fine-porosity, sintered-glass Buchner funnel, and dilute to 1 liter with water.

8. Special reagents for Procedure D.

   a. Aluminum nitrate salting solution. Prepare as described for Reagent 1 except omit the tetrapropylammonium hydroxide.

   b. Mercuric nitrate solution. Dissolve and dilute 0.063 g of $Hg(NO_3)_2$ in 100 ml of 1M HNO_3.

   c. Scrub solution. Dissolve 154 g of ammonium acetate and 20 g of the sodium salt of diethyldithiocarbamate in 900 ml of water. Adjust the pH to 7 with acetic acid, filter, and dilute to 1 liter with water.

9. Uranium standard stock solution, 25.00 mg U/ml. Dissolve 12.491 ± 0.001 g of standard NBS natural U_3O_8 (preignited for 1 hr at 900°C, then cooled) in 20 ml of 8M HNO_3 with the aid of heat, then dilute the clear solution to exactly 500 ml with water. Store the stock solution in sealed glass ampoules in units of 10 to 15 ml.

10. Uranium calibration standard I, 0.050 mg U/ml. Dilute 2.00 ml of the 25.00 mg U/ml stock solution to 1 liter with water.

11. Uranium calibration standard II, 0.125 mg U/ml. Dilute 5.00 ml of the 25.00 mg U/ml stock solution to 1 liter with water.

PROCEDURE

A. Blank

Process a reagent blank with each series of standards and samples. Use 0.5 ml of 1M HNO_3 as the blank sample aliquot.

B. Calibration and Bench Standard

Process the two uranium calibration standards with each series of samples. Use 500-µl aliquots of each calibration standard, 0.050 mg U/ml and 0.125 mg U/ml. Divide the milligrams of uranium in the aliquots by the respective absorbance to obtain the conversion factors. The difference between the two factors must agree within limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the established factor within specified limits. If either or both limitations are not met, process another pair of standards before reporting any sample results. If this second pair also is unsatisfactory, contact your supervisor.

C. Analysis of Samples Void of Thorium and Cerium(IV)

1.	Pipet 1.00 or less of the sample, containing 0.005 to 0.075 mg of U and less than 16 meq of acid, into a test tube.	Samples may be evaporated to increase the concentration of U or to reduce the acidity level. If the U is in the (VI) oxidation state, proceed to Step 4.
2.	Add 1 drop of conc HNO_3, then dropwise add 0.002M $KMnO_4$ with continuous swirling until the purple $KMnO_4$ color remains for 5 sec.	In this step, U oxidizes to the (VI) oxidation state which is the only oxidation state that extracts completely.
3.	If more than 9 drops of 0.002M $KMnO_4$ were added evaporate without spattering to a volume of less than 1 ml, then let cool to room temperature.	The extraction of U is not complete if the volume is greater than 1.5 ml at this point because the salting concentration is too low.
4.	Add 8 ml of the salting solution (Reagent 1).	A graduated cylinder provides adequate accuracy.
5.	Pipet 2.00 ml of hexone, stopper with a polyethylene stopper, and mix for 3 min on the pin wheel apparatus.	Rubber stoppers introduce colored contaminants that extract and cause high results.
6.	Centrifuge for 1 min, then transfer nearly all of the hexone phase to another test tube which contains 5 ml of the scrub solution (Reagent 7).	This transfer does not have to be quantitative because 1.00 ml is eventually used (see Step 8). The scrub solution can be added from a graduated cylinder.
7.	Add 5 drops of the saturated porous sulfamate solution to the test tube containing the transferred hexone phase, stopper with a polyethylene stopper, and mix for 3 min on the pin wheel apparatus.	Diverse metals such as Pu are scrubbed from the hexone phase.

8.	Centrifuge for 1 min, then transfer with a micropipet 1.00 ml of the hexone phase to a glass-stoppered glass bottle of at least 20-ml capacity.	A 25-ml volumetric flask is a handy bottle for this step.
9.	Pipet 15.00 ml of the dibenzoylmethane-pyridine reagent, stopper the bottle, mix until the solution is homogeneous, then let stand for at least 15 min.	Color development is relatively slow and requires this waiting period. Once developed, the color is known to be stable for at least 24 hr.
10.	Transfer the solution into a dry 5-cm absorbance cell and measure the absorbance at 415 mμ against water set at an absorbance of 0.000.	
11.	Record the data on the work sheet and calculate the results as described under CALCULATIONS.	

D. Analysis of Samples that Contain Thorium or Cerium(IV)

1.	Pipet 1.00 ml or less of the sample, containing 0.005 to 0.075 mg of U and less than 16 meq of acid, into a test tube.	Samples may be evaporated to increase the concentrations of U or to reduce the acidity level.
		If the uranium is in the (VI) oxidation state, proceed to Step 4.
2.	Add 1 drop of conc HNO_3, then dropwise add 0.002M $KMnO_4$ with continuous swirling until the purple $KMnO_4$ color remains for 5 sec.	In this step, U oxidizes to the (VI) oxidation which is the only oxidation state that extracts completely.
3.	If more than 9 drops of 0.002M $KMnO_4$ were added, evaporate without spattering to a volume of less than 1 ml, then let cool to room temperature.	The extraction of U is not complete if the volume is greater than 1.5 ml at this point because the salting concentration is too low.

4.	Add 8 ml of the salting solution without tetrapropylammonium nitrate (Reagent 8-a).	A graduated cylinder provides adequate accuracy.
5.	Pipet 4.00 ml of hexone, stopper with a polyethylene stopper, and mix for 3 min on the pin wheel apparatus.	Rubber stoppers introduce colored contaminants that extract and cause high results.
6.	Centrifuge for 1 min, transfer nearly all of the hexone phase to another test tube which contains 5 ml of the scrub solution (Reagent 8-c), stopper with a polyethylene stopper, and mix for 20 min on the pin wheel apparatus.	This transfer does not have to be quantitative because 2.00 ml is eventually used (see Step 8). The scrub solution can be added from a graduated cylinder.
7.	Centrifuge for 1 min, transfer nearly all of the hexone phase to another test tube which contains 5 ml of the salting solution without tetrapropylammonium nitrate (Reagent 8-a), add 0.5 ml of the mercuric nitrate solution (Reagent 8-b), stopper with a polyethylene stopper, and mix for 10 min on the pin wheel apparatus.	The transfer does not have to be quantitative as explained in the previous step. The salting solution and mercuric nitrate solution can be added from graduated cylinders.
8.	Centrifuge for 1 min, then transfer, with a microPipet, 2.00 ml of the hexone to a glass-stoppered glass bottle of at least 20-ml capacity.	A 25-ml volumetric flask is a handy bottle for this step.
9.	Pipet 15.00 ml of the dibenzoylmethane reagent, stopper the bottle, mix until the solution is homogeneous, then let stand for at least 15 min.	Color development is relatively slow and requires this waiting period. Once developed, the color is known to be stable for at least 24 hr.
10.	Transfer the solution into a dry 5-cm absorbance cell and measure the absorbance at 415 mμ against water set at an absorbance of 0.000.	

11. Record the data on the work sheet and calculate the results as described under CALCULATIONS.

CALCULATIONS

Record the data and calculate the results as shown on the example work sheet. Report three significant figures.

The calibration standards are prepared from normal uranium so a correction must be applied for enriched uranium. The following table lists correction factors as a function of ^{235}U enrichment to be used for samples other than natural uranium.

TABLE II

CORRECTION FACTORS FOR VARIOUS ^{235}U ENRICHMENT LEVELS

Enrichment (%)	Factor	Enrichment (%)	Factor
0.7 (normal)	1.0000	88.1 - 90.0	0.9889
80.0 - 82.0	0.9899	90.1 - 92.0	0.9887
82.1 - 84.0	0.9897	92.1 - 94.0	0.9884
84.1 - 86.0	0.9894	94.1 - 96.0	0.9882
86.1 - 88.0	0.9892	98.1 - 98.0	0.9879
		98.1 -100.0	0.9877

$$\text{Correction Factor} = \frac{\text{Average Atomic Weight of U in Sample}}{238.03}$$

REFERENCES

1. W. J. Maeck, G. L. Booman, M. C. Elliott, J. E. Rein, "Spectrophotometric Extraction Methods Specific for Uranium", Anal. Chem., 31 (July 1959), pp 1130-1134.

2. S. S. Yamamura, M. A. Wade, Personal Communication, December 1964.

October 1967
J. E. Rein
S. S. Yamamura

U-Color-2

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Uranium

CHARGE NUMBER _____ PROCEDURE U-Color-2

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance VS H_2O	Net Absorbance	Conversion Factor	Mg U in Aliquot Analyzed	Mg U Corrected For Bias			RESULT mg U/ml
Blank		0.015							
Std, 0.025 mg		0.289	0.274	0.0901					
Std, 0.0625mg		0.695	0.680	0.0902					
			$\bar{X}$	0.0902					
001	0.500ml	0.400	0.385		0.0347	0.0347 ± 0.0020			0.0694 ± 0.0040

ANALYZED BY _____ DATE _____

CALCULATIONS:

Conversion Factor = $\frac{\text{mg U in Std}}{\text{Absorbance}}$ = C = $\frac{0.025}{0.274}$ = 0.0901

C' = $\frac{0.0625}{0.680}$ = 0.0902

$\bar{X}$ = 0.5 (C + C') = 0.5 (0.0901 + 0.0902) = 0.0902 mg U/abs unit

001

D = BC = (0.385)(0.0902) = 0.0347

Result = $\frac{E}{0.500ml}$ = $\frac{0.0347 \pm 0.0020}{0.500}$ = 0.0694 ± 0.0040 mg U/ml

APPROVED BY _____

EXTRACTION-FLUOROPHOTOMETRIC DETERMINATION OF URANIUM

ABSTRACT

This method for uranium, highly selective and sensitive to nanogram levels, is applicable to a wide variety of aqueous and organic samples including plant processing streams that contain high levels of fission products. Its only undesirable feature is limited precision.

Uranium in aqueous samples is separated by extraction as the tetrapropylammonium uranyl trinitrate salt into methyl isobutyl ketone from an acid-deficient aluminum nitrate salting solution[1,2]. Solid samples are fused with potassium pyrosulfate, dissolved in dilute nitric acid and then extracted. Organic samples are analyzed directly. The organic phase is evaporated on a sodium fluoride-lithium fluoride pellet which then is fused over a burner[3]. The pellet, after cooling, is irradiated with ultraviolet light at 365 nm from a mercury lamp and the resulting fluorescence, which is proportional to the amount of uranium, is measured at 555 nm.

APPLICABILITY

The method covers the concentration ranges of 5×10^{-5} to 0.1 mg/ml for aqueous samples and 2.5×10^{-5} to 5.0×10^{-2} for organic samples. Aqueous samples containing more uranium than 0.1 mg/ml may be diluted with dilute nitric acid. Organic samples may be diluted with a pure solvent identical to samples.

Serious interference is caused by components that decrease the fluorescence of uranium. This effect is termed quenching. Metals that seriously quench include Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Pu, Si, Th, W, V, and Zn. The preliminary extraction used in this method is highly selective for uranium to separate it from these and other cations. Anions can interfere by inhibiting the extraction of uranium. The only significant common anion interference is sulfate in that large amounts precipitate aluminum as aluminum sulfate in the salted aqueous phase and the precipitate carries uranium to cause low recovery. The tolerance for sulfate is 2.5 mM in the sample aliquot. Large levels of fluoride, chloride, and nitrate, the anions usually present in nuclear fuel processing solution, do not interfere. The tolerance for acid is 8 meq in the sample aliquot. Above this, the acid deficiency of the aluminum nitrate salting solution is exceeded and the decontamination factors for some fission products are decreased. With a 0.5-ml aqueous sample aliquot, as specified in the procedure, the tolerances

are 5M for sulfate and 16N for acid. If either the level of sulfate or the level of acid exceeds these limits, the sample aliquot should be evaporated to near-dryness, then redissolved in 6M HNO_3 before extraction. Water solutions and acid-deficient solutions should be acidified with concentrated nitric acid before proceeding with the analysis.

Total uranium in samples containing solids (e.g., PEW samples from the CPP) is determined by evaporating the sample to dryness, fusing with potassium pyrosulfate and dissolving the melt with dilute nitric acid. The solution is then processed as an aqueous sample.

DISCUSSION

The conditions of the extraction were designed for the quantitative recovery of uranium, with high separation factors from other components including fission products. The only fission product that measurably extracts is ruthenium. Upon fusion, the ruthenium alloys with the platinum dish resulting in a buildup of beta activity, mainly from 1-yr ^{106}Ru. For this reason, a separate set of dishes should be used for the analysis of highly radioactive samples. These dishes should be checked periodically for radiation buildup and set aside if radiation levels become excessive.

The platinum dishes must be handled with care because scratches adversely affect the fluorescence response. Variations in the amount of light reflected by different dishes cause significant variations in the amount of uranium fluorescence measured. This problem of variable dish reflectivity may be resolved by tapping the fused melt out of the fusion dish and transferring it to one unscratched dish that is used for all pellets including the calibration. This practice improves the precision of the method by a factor of about 2. The disadvantage is that pellets tend to fracture, requiring repeat analyses. Because most of the samples analyzed by this method do not require this improved precision, this practice is not incorporated in the method.

Variations in flux weight and pellet thickness cause minor variations in uranium fluorescence. It is important, therefore, to make fusion pellets of uniform size and weight. Fusion conditions and cooling time are important factors that must be controlled[4]. The flux should remain molten sufficiently long for the uranium to uniformly distribute in the melt. However, the melt corrodes the platinum dish so there is a compromise time. Quenching by dissolved platinum is a major source of error. Fusions, therefore, should be made at temperatures only slightly higher (by about 50°C) than the melting point of the flux and the time of fusion should not exceed 3 min. Also, a minimum cooling period is necessary to obtain reproducible fluorescence readings. The sodium fluoride-lithium fluoride flux used in the procedure may be cooled rapidly without danger of fractured crystals. By removing the platinum fusion dishes, containing the fused melt, from the burner and placing them on a cool Transite board a minimum cooling period of 1 min is satisfactory. Shorter cooling time will cause erratic results.

APPARATUS AND REAGENTS

A. Apparatus

1. Fluorophotometer.
2. Forceps, large 8-in. and small 4 1/2-in.
3. Infrared heat lamps, 250-W.
4. Pelletizer, syringe-type, to deliver ∿216 mg of the sodium fluoride-lithium fluoride flux.
5. Pipets, micro, 100-, 200-, and 500-µl.
6. Pipets, volumetric, 2- and 4-ml.
7. Platinum fusion dishes. (See Procedure A for cleaning technique.)
8. Ribbon burner with nichrome-wire fusion rack. A stainless steel wire bow is welded to each end of the ribbon burner to support the nichrome wire mesh fusion rack ∿3/8 in. above the top surface of the burner.
9. Rotating wheel stirrer.
10. Spatula, glass, fabricated to hold 220±20 mg of $K_2S_2O_7$. The accelerator scoop used with the LECO carbon analyzer is suitable.
11. Stoppers for 13-x100-mm test tubes, rubber or plastic.
12. Transite boards for carrying platinum dishes.
13. Test tubes, 13-x100-mm.

B. Reagents

1. Acetone.
2. Calibration standards; 0.05, 10, and 100 µg U/ml.
3. Fusion flux. Homogeneously mix by weight 98% of NaF and 2% of LiF.
4. Hydroxylamine hydrochloride, 2M. Dissolve 13.9 g of $NH_2OH \cdot HCl$ in distilled water and dilute to 100 ml.
5. Methyl isobutyl ketone (4-methyl-2-pentanone) (Hexone).
6. Nitric acid, conc and 6M.
7. Potassium permanganate, 0.2M. Dissolve 7.9 g of $KMnO_4$ in distilled water and dilute to 250 ml.
8. Potassium pyrosulfate ($K_2S_2O_7$).

9. Salting solution. 2.8M Al, 2N[b], plus 0.1% tetrapropylammonium nitrate. Prepare by dissolving 1050 g of $Al(NO_3)_3 \cdot 9H_2O$, in 135 ml of conc NH_4OH (heat to dissolve). Cool to room temperature and add 10 ml of a 10% solution of tetrapropylammonium hydroxide and dilute to about 950 ml with water. Stir until dissolved, then extract with 250 ml of methyl isobutyl ketone in a separatory funnel. Allow the two phases to separate and discard the organic. Add 10 ml of the 10% tetrapropylammonium hydroxide, and dilute to 1 liter with water.

PROCEDURE

A. Cleaning and Checking Platinum Dishes

Clean and check all platinum dishes before use as follows:

1. Remove the residual solids by gently tapping the platinum dish on a Transite board.	If the solids cannot be removed by gentle tapping, place the dish in a beaker of warm water until the solids are dissolved.
2. Boil the platinum dishes in 6M HNO_3 for 20 min.	
3. Rinse the dishes thoroughly with distilled water and dry them under the infrared lamp.	
4. Add a pellet of fusion flux to each dish and fuse according to Procedure F, Steps 6 and 9 - 11.	
5. Measure the fluorescence of each dish according to Procedure H.	Any dishes having a fluorescence reading of greater than 1 µa should be recleaned.

B. Blank

There is no blank for this procedure; the 0.05 µg/ml calibration standard is used as a blank control. The reading for the 0.05 standard should not exceed 0.20 µA. High readings are the result of uranium. If contamination is present, clean the pipets and then clean the platinum dishes according to Procedure A and repeat the analysis.

C. Calibration

The fluorophotometers are calibrated each day by the person doing the analysis. If the sample concentration is between 0.05 and 15 µg/ml, the 0.05-and 10-µg/ml calibration standards are used. If the sample concentration is higher, the 10-and 100-µg/ml calibration standards are used. The calibration is to be performed once each shift according to Procedure F. Leave the pellets from the calibration standards in the fluorophotometer until the end of the shift.

D. Bench Standards

Process a known bench standard once each shift. If the bench standard is out of limits, repeat the analysis. If trouble still persists, contact your supervisor for help.

E. Analysis of Aqueous Samples Containing Solids for Total Uranium

Note: Process a bench standard through this procedure.

1. Shake the sample and pipet 500 µl into a 13-x100-mm test tube.	Thorough mixing is essential to obtain a representative sample.
2. Place the test tube under an infrared lamp and evaporate to dryness.	
3. Cool and add 1 level spatula of $K_2S_2O_7$.	A special scoop, made to deliver 220±20 mg of $K_2S_2O_7$, is provided.
4. Tilt and heat the test tube gently over a mild flame until the $K_2S_2O_7$ melts. Continue heating gently until the residue dissolves and the melt is clear.	Do not heat too fast or the reaction may cause the sample to bump out of the tube. Swirl the tube as it cools so the $K_2S_2O_7$ will solidify on the walls.
5. Cool and add 1 drop conc HNO_3 and 500 µl of distilled water.	
6. Place the test tube in a boiling water bath and heat until the melt dissolves.	It may be necessary to swirl the tube periodically to keep the residue moist and to hasten the dissolution.

7. Cool and continue the analysis with Procedure F, Step 2.

F. Analysis of Aqueous Samples

1. Pipet 500 µl of the sample into a 13x100-mM test tube. For neutral or acid-deficient samples, add 100 µl of conc HNO_3.	As pointed out in the APPLICABILITY section, the tolerance limits for SO_4 and acid are 2.5 mM and 8 meq, respectively. If either of these limits is exceeded, evaporate the sample to near-dryness without baking. Redissolve the residue in 0.5 ml of 6M HNO_3 (with heating, if necessary), cool the test tube and contents to room temperature, then continue with Step 2.
2. While swirling, add 0.2M $KMnO_4$ 1 drop at a time until the pink color just persists.	The addition of the 0.2M $KMnO_4$ and the 2M $NH_2OH \cdot HCl$ (Step 3) may be omitted when analyzing plant raffinate solutions I, II, and III ARm samples, because the U is in the VI oxidation state.
3. While swirling, add 1 drop of 2M $NH_2OH \cdot HCl$. If the pink color persists, add a second drop.	If more than 2 drops of the 2M $NH_2OH \cdot HCl$ is required to discharge the pink color, too much 0.2M $KMnO_4$ was used in Step 2. Start again with a fresh sample aliquot.
4. Add 4 ml of the salting solution.	The volume of salting solution is not critical and, therefore, may be added with a dispensing device.
5. Pipet 2.00 ml of methyl isobutyl ketone into the test tube, stopper, and mix on the rotating wheel for 3 min, then let stand until the phases separate.	If complete separation does not occur, centrifuge for 2 min.

6.	Place a pellet of the fusion flux into each of two platinum dishes with the pelletizer.	To insure maximum and uniform size pellets, turn the plunger handle counter-clockwise as far as possible. Insert the pelletizer into the flux material three times (pressing down firmly each time), then scrape the excess flux from the bottom of the pelletizer on the lip of the beaker containing the flux, before dropping the pellet into the platinum dish.
7.	Pipet 200 µl of the organic phase onto each of the two pellets. Each time rinse the pipet with acetone and add the rinsings to the pellet.	If the pipet is Dri-filmed and drains thoroughly, the acetone rinse may be omitted. Methyl isobutyl ketone slowly dissolves Dri-film so that frequent treatment of pipets is necessary.
8.	Place the dishes containing the pellets on a Transite board under an infrared lamp and evaporate to dryness.	The lamp should be set on low heat for 2 min, then on high heat for 2 min. This prevents spattering and gives complete dryness.
9.	Light the ribbon burner and adjust it so that the tip of the blue flame is approximately 0.25 in. below the nichrome wire mesh fusion rack.	
10.	Fuse the pellets for 3 min.	Do not let the dishes touch each other because they will fuse together.
11.	Remove the dishes from the burner and place them on a Transite board to cool.	Let cool for at least 1 min.
12.	Measure the fluorescence according to Procedure H.	The allowable limit for the difference between duplicates is 12%. If this is exceeded, reject the data and start again at Step 7.

G. Analysis of Organic Samples

1.	Place a pellet of the fusion flux into each of the two platinum dishes with the pelletizer.	See remark in Procedure F, Step 6.
2.	Pipet 100 µl of the sample onto each of the two pellets. Each time rinse the pipet with acetone and add the rinsings to the pellet.	See remark in Procedure F, Step 7.
3.	Place the dishes containing the pellets on a Transite board under an infrared heat lamp and slowly evaporate to dryness.	The lamp should be set on low heat for 3 min, then on high heat for 3 min. This gives complete dryness without spattering.
4.	Light the ribbon burner and adjust it so that the tip of the blue flame is approximately 0.25 in. below the nichrome-wire fusion rack.	
5.	Fuse the pellets for 3 min.	Do not let the dishes touch each other because they will fuse together.
6.	Remove the dishes from the burner and place them on a Transite board to cool.	Let cool for at least 1 min.
7.	Measure the fluorescence according to Procedure H.	The allowable limit for the difference between duplicates is 12%. If this is exceeded, reject the data and start again at Step 2.

H. Operation of the Model 11 Laboratory Photometer

1.	The fluorophotometer should be left on at all times.	
2.	Check the Number 1 pellet slot to make sure it is empty and clean. The Number 2 pellet slot should contain the permanent fluorescence standard.	

3. Turn the sensitivity knob to the extreme right and lock into position. Once it is locked, it does not need to be adjusted for future analyses.

4. Turn the HV switch to 500. Do not exceed this setting.

5. Place the meter display switch to the INPUT position and turn the input current knob to the 0.1 position.

6. Rotate the sample wheel to the Number 1 position and zero the meter on the 0-100 scale with the cancellation current knob.

7. Rotate the sample wheel to the Number 2 position which contains the standard and adjust the meter to read 25 using the high voltage knob.

8. Repeat Steps 6 and 7 until the instrument is accurately set at each position.

9. Rotate the sample wheel to position the sample and adjust the input current knob to bring the meter on scale.

10. Multiply the meter reading by the scale factor from the input current knob to obtain the sample reading.

11. Record this value on the work sheet.

CALCULATIONS

Record the data and calculate the results as shown on the following example work sheet.

Report the results to two significant figures, as 2.1×10^{-3} mg/ml.

For organic samples, divide the calculated results by 2.

Note that the column "Sampling and Dilution Data" is used only for dilutions prior to the pipetting of the 500-µl aliquots of aqueous samples for extraction and of 100-µl aliquots of organic samples directly on pellets. These volumes are used for all samples including the aqueous calibration standards. The calibration standards are prepared by the same procedure as that used for aqueous samples, therefore, dilution factors in the procedure are not necessary for calculations.

The calculations are made from the bracketing equation

$$X_s = \frac{Y_s - \left[\frac{Y_1(X_1-X_2) - X_1(Y_1-Y_2)}{X_1-X_2}\right]}{\frac{Y_1-Y_2}{X_1-X_2}} \qquad (1)$$

where

X_s = conc of sample

Y_s = % T of sample

X_1 = conc of standard 1

X_2 = conc of standard 2

Y_1 = % T of standard 1

Y_2 = % T of standard 2.

REFERENCES

1. R. J. Jones, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle. TID-7029, USAEC, Division of Technical Information, Method 1.402, pp 147-155, (1963).

2. ORNL Master Analytical Manual, Method Nos. 1 003080, 9 003080, 1960.

3. F. A. Centanni, A. M. Rose, M. A. DeSesa, Anal. Chem. 28, 1651 (1956).

4. B. R. Hunter, Private Communication, February 1960.

D. M. Lund
J. A. Rindfleisch
January 1972

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Uranium

CHARGE NUMBER _____ PROCEDURE U-Fluor-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Standard Reading	Scale	Net Reading					RESULT µg/ml
NO 1	0.05 = X_1	7	0.1	0.7 = Y_1					1.0132
		7							
		A'		C'					
	10 = X_2	54	1	57 = Y_2					
		60							
		A''		C''					
	Sample = X_s	19	0.3	6.15 = Y_s					
		22							

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$X_s = \frac{C'' - \left[\frac{C(.005-10) - .005(C-C')}{.005-10}\right]}{\frac{C-C'}{.005-10}}$$

$$= \frac{6.15 - \left[\frac{0.7(0.05-10) - 0.05(0.7-57)}{0.05-10}\right]}{\frac{0.7-57}{0.05-10}}$$

$$= \frac{6.15 - 0.4171}{56582} = 1.0132 \text{ µg U/ml}$$

APPROVED BY _____

U-Grav-1; August 1972

GRAVIMETRIC DETERMINATION OF URANIUM IN RELATIVELY PURE URANIUM SALT SOLUTIONS

ABSTRACT

Uranium in relatively pure uranium salt solutions is determined gravimetrically as U_3O_8. The sample solution is evaporated to dryness in the presence of hydrofluoric acid, then ignited at 900°C in a muffle furnace to obtain stoichiometric U_3O_8. Residual impurities are determined spectrographically, and an impurity correction is applied.

APPLICABILITY

This method is applicable to uranium solutions that do not contain significant amounts of phosphate which yields uranyl pyrophosphate rather than U_3O_8 on ignition. The common anions Cl^-, F^-, NO_3^-, and $SO_4^=$ do not interfere. Because metallic impurities must be determined spectrographically and a correction applied for them, the concentration of the metallic impurities must be low, especially if highly precise uranium measurements are required. The permissible metal content has not been defined. Impurity concentrations up to about 0.2 wt% are believed tolerable. The correction is generally 0.1 wt% or less.

Assuming a permissible uncertainty of ±0.3 mg on the weighings, at least 0.85 g of uranium (1 g U_3O_8) should be taken for analysis. Larger amounts, which are permissible and in fact desirable, will provide improved precision.

DISCUSSION

The gravimetric determination of uranium as U_3O_8 is a simple, straightforward procedure; however, the high precision and accuracy usually demanded of this method necessitate careful attention to several facets of the analysis. Of paramount importance is the use of proper ignition conditions to yield stoichiometric U_3O_8. The major factors that affect stoichiometry are the nature of the sample, the nature of the U_3O_8 produced (i.e., particle size and the surface area-to-volume ratio of the particles), the ignition temperature, the duration of the ignition, and the ignition atmosphere[1]. According to Duval[2], the general pyrolysis curve for uranium(VI) compounds containing nitrate shows the following transitions upon heating: loss of water, loss of oxides of nitrogen, gradual formation of UO_3, formation of U_3O_8, a level corresponding to stable U_3O_8, and finally dissociation to UO_2.

Duval reports this dissociation of U_3O_8 to UO_2 starts at 946°C and cautions analysts not to exceed this temperature even in the presence of air or oxygen. Also, below the range of 750 to 800°C, the rate of conversion to U_3O_8 is relatively slow, so the optimum temperature appears to be about 900°C. Other thermogravimetric and muffle furnace ignition studies have verified the above. The addition of hydrofluoric acid before ignition of uranyl nitrate is claimed[3] to aid the stoichiometric conversion to U_3O_8, and it serves to remove silica. Recent studies by S. Kallman at Ledoux and Company has shown that the formation of stoichiometric U_3O_8 is also facilitated and assured by taking the uranium through an intermediate UO_2 state[4]. This conversion, accomplished with hydrogen in a porcelain Rose crucible, yields upon final ignition a fluffy powder with large surface area.

Another potential problem area is loss of sample through spatter during the evaporation of the sample to dryness. Sample preparations, sample aliquotting and all weighings require special care. As the level of impurities increase, there should be sufficient replication in the spectrographic impurity measurement to provide the required accuracy.

SAFETY PRECAUTIONS

Handle solutions and precipitates of uranium with care to avoid contamination of equipment and personnel. Wear rubber or plastic gloves when handling hydrofluoric acid which causes serious skin burns. Use asbestos gloves while removing samples from hot plates or muffle furnaces.

APPARATUS AND REAGENTS

A. Apparatus

1. Analytical balance, with at least 0.1-mg sensitivity.

2. Burets, weighing, 10-ml, stopcock at each end, and one end with extended tip of 4 cm.

3. Crucibles, platinum, 15-ml.

4. Desiccator, with Anhydrone (magnesium perchlorate) desiccant.

5. Filtration accelerators, Fisher Scientific Company.

6. Furnace, muffle.

7. Heat lamp, infrared, with support plate for crucibles. A Fisher Infra-Rediator or equivalent is ideal.

8. Tongs, platinum-tipped.

B. Reagents

1. Hydrofluoric acid, 48% Analytical Reagent Grade.

2. Nitric acid, 8M.

PROCEDURE

A. Blank

A blank is not required for this method.

B. Bench Standard

A bench standard is not required because this method requires no standard reagents that may change with time. However, control samples should be analyzed concurrently with samples per the frequency designated in the Analytical Branch Quality Control Standard Operating Procedure.

C. Analysis of Samples

1. Tare the 15-ml crucibles(s). Ignite the crucible(s) at 900°C for 10 min, cool in a desiccator for 20 min, then weigh to the nearest 0.1 mg. Repeat this until a weight constant to ±0.3 mg is obtained.

2. Add two circles of filtrator accelerator, each broken in half, to each crucible.

3. Accurately weigh or pipet into the crucible, a sample aliquot containing between 0.85 and 3 g of U.

Aliquotting by weight with a weight buret is preferred. A volumetric pipet dry-filmed and calibrated and used on a "to contain" basis will give satisfactory precision on volumes exceeding 3 ml

4. Add approximately 1 ml of conc HF to the crucible.

5.	Evaporate the sample to dryness under a heat lamp.	Evaporate carefully at a rate where spatter losses are nil. Samples must be completely dry. This can be assured by applying heat from above and below toward the end.
6.	Char the filtrator accelerator, then ignite the crucible in a 900°C muffle furnace for at least 1 hr but no longer than 3 hr.	Slow charring without flashing of the filtrator accelerator is essential to prevent loss of U.
7.	Remove the crucible from the furnace, hold it in the air for 30 sec, then let it stand in a desiccator for 20 min.	
8.	Weigh the crucible plus contents to the nearest 0.1 mg.	
9.	Repeat Steps 6, 7, and 8 until successive weighings agree to within ±0.3 mg.	
10.	Send the original sample solution or a portion to the Spectroscopy Laboratory for the impurities measurement. Also, send a portion of the sample to the Mass Laboratory for an isotopic distribution measurement.	The former is required for the impurities correction....the latter for determining the atomic weight.
11.	Dissolve the U_3O_8 in the crucible with 8M HNO_3.	Enriched U should be placed in the salvage container. Normal or depleted U should be disposed of in accordance with established procedures.
12.	Record the data and calculate the results as described under CALCULATIONS and as shown on the example work sheet.	

CALCULATIONS

A. Calculation of the Average Atomic Weight and the Gravimetric Factor for the Uranium Being Determined.

1. Obtain the isotopic distribution results from the Mass Laboratory. Either atom % or weight % is sufficient.

2. Multiply the percent of each isotope by its respective isotopic weight. Use the recognized atomic weights (^{234}U = 234.0409, ^{235}U = 235.0439, ^{236}U = 236.0456, and ^{238}U = 238.0508) rather than 235, 236, etc.

3. Sum the four products obtained in A-2.

4. Divide the sum by 100. This is the atomic weight.

5. Calculate the gravimetric factor for converting U_3O_8 to U.

$$\text{Fraction U} = \frac{3U}{3U+80} \qquad (1)$$

where

U = calculated atomic weight of uranium

O = atomic weight of oxygen (15.9994).

B. Correction of the Observed U_3O_8 Weight for Metallic Impurities and Calculation of the Result.

The metallic impurities determined by emission spectroscopy are normally reported as microgram of element per gram U_3O_8 (ppm element in U_3O_8). The gravimetric factors for converting ppm element to ppm element oxide are:

Element	Oxide	Gravimetric Factor
Al	Al_2O_3	1.89
Cr	Cr_2O_3	1.46
Cu	CuO	1.25
Fe	Fe_2O_3	1.43
Mn	MnO_2	1.58
Na	Na_2O	1.35
Ni	NiO	1.27
Zr	ZrO_2	1.35

Correct the observed U_3O_8 weight for impurities and calculate the result as follows:

1. Multiply the ppm element concentration value for each element by its respective gravimetric factor to obtain the metal oxide impurity concentration.

2. Sum the products obtained in B-1.

3. Multiply the sum by 10^{-6}, i.e., move the decimal 6 places left.

4. Calculate the decimal fraction 1.0000 minus the product of B-3. (Example: 1.0000 - 0.0053 = 0.9947.)

5. Calculate the result per the relationship:

$$\text{mg U/Sample Unit} = 1000 \frac{(\text{decimal fraction from B-4})(\text{Wt } U_3O_8)(\text{Grav Factor})}{\text{Wt or Vol of Sample}} \quad (2)$$

$$\text{Ex: mg U/g} = 1000 \frac{(0.9947)(2.5000\text{ g})(0.8480\text{ g U/g } U_3O_8)}{2.6000\text{ g}} \quad (3)$$

$$= 811.1$$

REFERENCES

1. G. L. Booman and J. E. Rein, Chapter "Uranium", Treatise on Analytical Chemistry, I. M. Kolthoff and P. J. Elving, Eds., New York: Interscience Publishers, Inc., Part II, Vol 9, 1963, pp 74-76.

2. C. Duval, Inorganic Thermogravimetric Analysis, New York: Elsevier Publishing Co., 1963, pp 661-662.

3. F. S. Voss and R. E. Greene, "Determination of Uranium", AECD-4030 (August 1953), Declassified with deletions November 3, (1955).

4. S. Kallman, Ledoux and Company, private communication (August 1972).

August 1972
S. S. Yamamura
D. M. Lund

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Uranium

CHARGE NUMBER _____ PROCEDURE U Graw-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: a_0 d_1 a_1/d_2 a_2	Original weight of Buret + Solution, g	Final weight of Buret + Solution, g	Crucible Tare weight, g	weight of Crucible + U_3O_8, g	weight of U_3O_8, g	Graw Factor	Impurity Correction Factor	RESULT mgU/g
UNO_3-1	2.6000 g	46.3600	43.7600	11.8834	14.3834	2.5000	0.84652	0.9947	809.6

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{Result} = \frac{1000\,E\,F\,G}{\text{Sample weight}}$$

$$= \frac{(1000)(2.5000)(0.84652)(0.9947)}{2.6000}$$

$$= 809.6$$

APPROVED BY _____

GRAVIMETRIC DETERMINATION OF URANIUM IN UO_3 DENITRATOR PRODUCT

ABSTRACT

Uranium in relatively pure UO_3 is determined gravimetrically as stoichiometric U_3O_8 after direct ignition at 900°C for 2 hr. The U_3O_8 is analyzed for metallic impurities by emission spectroscopy and a correction is applied.

APPLICABILITY

This method is designed specifically for the analysis of Chemical Process Plant UO_3 denitrator product. Sample sizes can vary between 1 and 20 g; however, a 10-g sample is recommended for best results.

DISCUSSION

This method is similar to Method U-Grav-1 for the gravimetric determination of uranium in uranyl nitrate solutions. Method U-Grav-1 should be referred to for further discussions on the conditions for obtaining stoichiometric U_3O_8.

The UO_3 is converted to U_3O_8 with loss of oxygen, as illustrated by the equation:

$$6\ UO_3 \xrightarrow{900°C} 2\ U_3O_8 + O_2 \qquad (1)$$

The UO_3 in a platinum crucible is ignited at 900°C for 2 hr in a muffle furnace; longer heating will not affect the results. The conversion is accompanied by a "popcorn popping" action so the crucible must be covered with a platinum lid to prevent loss of sample. The crucible must be weighed with the lid on because some of the sample adheres to the lid after the ignition.

Some of the UO_3 may be in the form of a fine powder that could become airborne during sample transfer. This presents two problems. One is that of alpha contamination. The other problem is the resettling of powder on the outside wall of the crucible. The powder will drop off or be rubbed off in subsequent handling of the crucible causing erroneous results. These problems have been minimized by using an appropriate sample transfer jig (see item 13 under Apparatus).

For the subsequent spectroscopic determination of impurities and determination of uranium isotopic distribution, the ignited U_3O_8 is dissolved in 5M HNO_3. Residual solids are filtered, ignited, and weighed, then the solids and filtrate are analyzed for impurities. The mass analysis is performed directly on the filtrate. Care must be exercised when dissolving the U_3O_8 because when the samples are large (>10 g) there is a tendency for the samples to foam. Samples over 10 g should be watched closely and removed from the hot plate if foaming starts.

The UO_3 is hygroscopic; so care must be taken to avoid moisture uptake. Sample bottles with screw caps containing conical polyethylene liners are best from the standpoint of moisture leakage; however, there is still some moisture absorption even with these caps. The sample bottle should be placed in a secondary "Titeseal" vial during storage. This secondary containment also helps prevent the spread of alpha contamination.

SAFETY PRECAUTIONS

The denitrator samples are approximately 83% uranium and 75% ^{235}U which make alpha contamination and criticality two important potential safety hazards. No more than 400 g of ^{235}U is allowed in one room. All work on the UO_3 powders should be performed in a glove box.

APPARATUS AND REAGENTS

A. Apparatus

1. Balance, accurate to 0.1 mg.
2. Crucibles with platinum lids, 35-ml.
3. Desiccator.
4. Filtering apparatus (Millipore Corporation), 47-mm diam. Cut the filter funnel to a height of 1 in. and attach 6 in. of 5-mm glass tubing to the filter base.
5. Filter paper, Millipore HAWP 47-mm, HA 0.45-μ, or equivalent.
6. Flask, Erlenmeyer, 50-ml.
7. Flask, volumetric, 50-ml.
8. Funnel, 2-in.
9. Furnace, muffle with capability of continuous operation at 900°C.
10. Glove box.

11. Hot plate with variable heat control.
12. Polyethylene bottles, 2-oz.
13. Sample transfer jig (Figure 1). The sample transfer device is a thin-walled metal tubing of about 8 mm O D equipped with two stoppers. Select the size of the stoppers and the distance a to suit the sample bottle and the platinum crucible. The stem of a No. 4 cork borer is satisfactory.

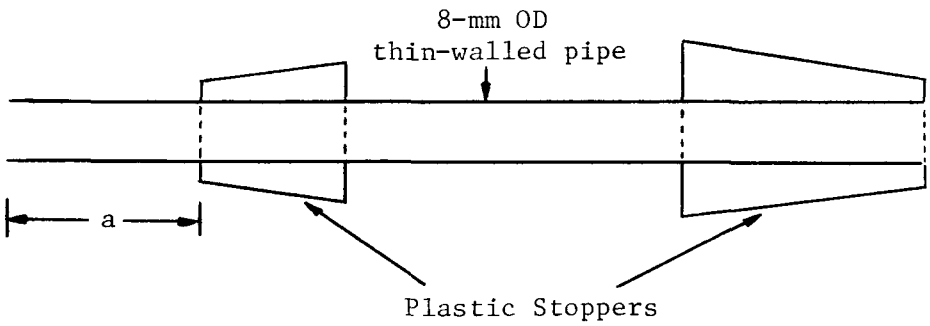

Fig. 1 Sample transfer jig.

14. Vial, Titeseal, 12-dram.
15. Wash bottle, polyethylene, 250-ml.

B. Reagents

1. HNO_3, 5N.

PROCEDURE

A. Blank

A blank is not required for this method.

B. Analysis of Sample

1. Tare an ignited 35-ml platinum crucible and lid.

2. Using the recommended sample transfer jig, transfer 5 to 15 g of UO_3 to the crucible, then replace the lid.	If the samples are enriched, a glove box should be used for the transfer.
3. Obtain a gross weight on the crucible plus sample	
4. Place the crucible in a muffle furnace at 900°C for 2 hr.	The samples must be in the furnace at least 2 hr. Heating for a longer period will not affect the results.
5. Remove the crucible from the furnace and place it in a desiccator for 30 min.	
6. Weigh the crucible and transfer the U_3O_8 to a 50-ml Erlenmeyer flask with 5N HNO_3 washes.	
7. Dilute to approximately 30 ml with 5N HNO_3 and place the flask on a hot plate set on low heat.	Care should be taken to prevent loss of sample by foaming. All samples greater than 10 g should be watched during the initial dissolution period to make sure they do not foam over.
8. Heat the flask until the uranium oxide is dissolved. This usually requires about 30 min. If impurities need not be determined, omit Steps 9 through 11.	A white residue may remain which will give the solution a cloudy appearance. If duplicate samples are analyzed, it is usually necessary to determine impurities on only one sample.
9. Cool slightly and filter the solution through a 0.45-μ membrane filter using 5N HNO_3 for washing. Use a 2-liter vacuum flask with the bottom removed for the filtration and collect the filtrate in a 50-ml volumetric flask.	Moisten the entire filter with 5N HNO_3 before filtering the sample. This must be done before the filter chimney is assembled.
10. Submit the filter plus residue to the Spectroscopy Laboratory for a spectrochemical analysis.	

11. Dilute the filtrate to volume with 5N HNO_3.

12. Transfer the solution to a 2-oz polyethylene bottle and submit the solution for spectrochemical and isotopic analyses.

    A volume measurement is not required on any sample that is not filtered.

13. Calculate the results as shown on the sample work sheet.

J. A. Rindfleisch
M. A. Wade
July 1971

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME Denitrator Product

LOG NUMBER _____

ACTIVITY (mR/hr) _____

DETERMINATION Uranium

CHARGE NUMBER _____

PROCEDURE U.-Grav-2

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$ crucible Lid	Crucible Gross wt. before heat	Crucible tare	Crucible Gross wt. after heat	Sample wt.	U_3O_8 wt.	Grav. factor		RESULT mg U/g spl
478	119 121	39.6841	30.1484	39.3445	9.5357	9.1961	.84656		815.46
480	130 117	40.0708	30.2240	39.7210	9.8468	9.4970	.84656		815.53
		A'	B'	C'	D'	E'	F'	G'	
	Impurities	Element	Filtrate PPM	grav. factor	PPM Oxide	Residue wt.	PPM residue	Total impurities	
		Al	115	1.89	217	5.3mg	576	1171	
		Na	141	1.35	190				
		Fe	4	1.43	6				
		Si	85	2.14	182				

ANALYZED BY _____ DATE _____

CALCULATIONS:

$C - B = E$

$39.3445 - 30.1484 = 9.1961$

$A - B = D$

$39.6841 - 30.1484 = 9.6357$

$(B')(C') = D'$

$(115)(1.89) = 217$

$\frac{1000E'}{E} = F'$

$\frac{(5.3)(1000)}{9.1961} = 576$

$F' + (\Sigma D') = G'$

217
190
6
182
576
1171

$$\frac{\left\{E - \left[\frac{(E)(G')}{(1000)^2}\right]\right\} 1000F}{D} = \text{Result}$$

$$\frac{\left\{9.1961 - \left[\frac{(9.1961)(1171)}{(1000)^2}\right]\right\}(1000)(.84656)}{9.5357} = 815.46$$

APPROVED BY _____

SEPARATION OF URANIUM FOR MASS SPECTROMETRIC ANALYSIS

ABSTRACT

Uranium, with added spike isotope when concentration is to be determined by the isotope dilution technique, is extracted from an acid-deficient aluminum nitrate salting solution into methyl isobutyl ketone (hexone). The organic phase is scrubbed with a special complexing solution to remove coextracted plutonium when it is present in significant quantities in the sample. The organic phase then is contacted with hydrogen peroxide to precipitate milligram levels of uranium as uranium peroxide or evaporated to dryness for microgram levels of uranium. The uranium peroxide or evaporated residue is solubilized with nitric acid for the mass spectrometric analysis.

APPLICABILITY

This method, designed for samples that contain high levels of fission products, is applicable to existing nuclear fuels including the alloying and cladding constituents present in aluminum, various stainless steels, zirconium, and most cermets. The manipulations are simple, hence, suitable for shielded facilities with Castle-type manipulators. The extraction conditions give about 10^5 decontamination of aged fission products so the separated organic phase containing the extracted uranium can be moved to a nonshielded hood for the remainder of the procedure. The degree of extraction of uranium is about 90%. As discussed further in the next section, the degree of extraction of such fission products as zirconium and cerium will increase for highly (more than 10 meq per sample aliquot) acid samples. This effect can be overcome by adding ammonium hydroxide to the extraction mixture. However, because uranium extraction decreases with increasing aqueous volume, the acidity tolerance level is about 12N acid. The acidity of fuel dissolver samples rarely exceeds this.

The usual isotopic compositions of uranium in fuel samples at the time of writing this procedure (1971) are normal and enriched. The added isotope (hereafter called spike) for the isotope dilution determination of uranium concentration as described in this method, therefore, is ^{233}U. Another isotope is required for samples such as irradiated thorium that contain ^{233}U. The spike for these samples usually is ^{238}U. Because of natural uranium contamination, especially in thorium, samples without spike also should be analyzed to provide the means to

correct for this contamination. If this natural contamination is high, ^{235}U may be superior as the spike.

Two uranium concentration ranges are covered: Procedure B is for the uranium concentration range of 0.001 to 0.1 mg/ml and Procedure C is for the range 0.1 to 10 mg/ml. There are two additional Procedures D and E. These are for remote processing of highly radioactive samples on volume (Procedure D) and weight (Procedure E) bases.

Without prior treatment such as evaporation, the maximum sample aliquot is 1 ml. Above 1 ml, the salting strength is lowered and the uranium recovery decreases from ∿ 90% at the 1-ml level to ∿ 35% at the 3-ml level. Samples requiring more than a 1-ml aliquot can be analyzed by either of two ways. They can be concentrated by evaporation in the extraction tube or prior to sampling, or solid aluminum nitrate can be added at the rate of 1.5 g for each milliliter of sample above 0.5 ml. For practical reasons, evaporation in the test tube is limited to aliquots up to about 5 ml and the aluminum nitrate addition technique is limited to aliquots up to approximately 3 ml. If a residue appears in the test tube evaporation, 6M HNO_3 is the recommended dissolvent, of course, its addition should be confined to 1 ml or less.

In the procedures as described, the amount of ^{233}U added is 0.005 mg for sample aliquots with 0.001 to 0.1 mg of uranium and 0.5 mg for samples with 0.1 to 10 mg of uranium. Highest reliability is obtained at a sample (major isotope) to spike ratio of 1. The reliability decreases significantly when this ratio falls outside the range of 0.2 to 5.

Of the analytical methods used for uranium, this method is the most widely applicable one with high reliability. It does, however, require a minimum of 2 man hours. If less reliable results are acceptable, the more rapid spectrophotometric methods (U-Color-1 and U-Color-2, this Manual) should be used.

DISCUSSION

The basis of the extraction procedure is the preferential extraction of the ion association complex $[H]^+[UO_2(NO_3)_3]^-$ into hexone from a highly salted medium. The extraction serves to isolate the uranium from various interfering substances, particularly the highly radioactive fission products that are present in irradiated fuel samples. Actually, the extraction procedure is designed for such samples, i.e., to give adequate extraction of uranium, yet good separation from long-lived fission products surviving > 3 mo cooling. The prescribed salting solution, 3.0M monohydroxy aluminum nitrate with an acid deficiency of 3 meq/ml, provides > 90% uranium extraction and a 10^5 decrease in sample activity. The acid-deficiency of the salting solution promotes decontamination by decreasing the coextraction of

hydrolyzable fission products such as Ce(IV), Nb(V), and Zr(IV). When the recommended 4 ml of salting solution is used, the total acid-deficiency is 12 meq and up to about 8 meq of acid can be added through the sample without seriously diminishing the decontamination. If desired, conc NH_4OH can be added to the sample-spike mixture; however, additions of conc NH_4OH must be limited to keep the uranium recovery at a satisfactory level.

The oxidation state of the uranium in the extracted ion association complex is +6. The ^{233}U spike is usually in this oxidation state. Because the isotope dilution technique depends on chemical identity of the sample isotope species and added spike species, an oxidation with Cr(VI) (potassium dichromate) is included in the procedures to assure a uniform +6 oxidation state that promotes thorough mixing of spike and sample uranium. The oxidation may be omitted only when the uranium in the sample is known to be in the +6 oxidation state. Normally, nitric acid is a sufficiently strong oxidant to provide this oxidation state. However, nitric acid samples of uranium have been encountered which contain +4 uranium stabilized by such complexing agents as fluoride and oxalate. Although previous methods call for the addition of dichromate oxidant to the sample-spike mixture prior to the addition of the salting solution, quantitative results have been obtained even when the sample of +4 uranium is added after the addition of dichromate and salting solution to the spike. This demonstrates that the order of reagent addition has little effect on the method and simplifies the remote processing of samples.

For easier remote operation, the organic reagent aluminon (aurin tricarboxylic acid) is added to the extraction mixture. It forms a deep red complex with the aluminum ion of the salting solution, and hence, provides an easily seen demarcation of the aqueous and organic phases through the thick, shielded, viewing windows. This aids the analyst to separate more of the organic phase after the completion of the extraction. Also, the use of a 15-ml spike tube allows the use of 4 ml of hexone for remote extraction.

The extraction, though highly selective for uranium, will coextract such transuranics as neptunium and plutonium. These elements do not directly interfere in the subsequent mass spectrometric analysis, but do constitute a health hazard in the mass spectrometry laboratory, so there is a provision for scrubbing the separated organic phase with a mixture of hydrazine, oxalic acid, and EDTA in an aluminum nitrate matrix. This mixture reduces neptunium and plutonium to the low extractable +3 oxidation states and complexes them as aqueous-soluble complexes. The scrub step is not necessary for fuels processed at the CPP in which the initial ^{235}U abundance is above about 20%. Scrubbing is necessary, especially when low-enrichment fuels are taken to high burnup.

Organic matter in the uranium fraction sent to the Mass Laboratory causes erratic behavior in the mass spectrometer and even loss of material from the filament. Sources of organic matter are: (a) rubber stoppers used in the extraction, (b) lint or other packing material in the test and centrifuge tubes, and (c) extractant. Hexone leaches organic matter from rubber stoppers. This organic matter is removed by an acetone wash, but acetone too, is a good solvent, so it is important not to let the acetone wash come in contact with the rubber stopper. All tubes should be rinsed with water (and dried) to remove lint. The final uranium fraction from Procedure B should be digested with nitric acid until no visible residue remains.

Some samples taken through the extraction do not yield a precipitate when treated with hydrogen peroxide. The failure to obtain a precipitate is associated with the use of certain combinations of acids and/or a sulfate fusion in sample preparation. When the normal procedure fails, ammonium hydroxide precipitation of the uranium from the original sample-spike mixture followed by a 6M HNO_3 dissolution of the separated precipitate yields a solution that can be processed by the normal separation procedure.

SAFETY PRECAUTIONS

Samples processed by this procedure usually will contain ^{223}U, plutonium, and higher transuranics. Observe the necessary handling procedures to prevent either absorption through the skin or ingestion of these materials.

Hydrogen peroxide severely burns the skin. Wear rubber gloves when handling this reagent and wash any contacted skin areas immediately with copious quantities of cold water.

APPARATUS AND REAGENTS

A. Apparatus

1. Analytical balance.

2. Centrifuge, International Clinical Model CL, with 15-ml head and 5-ml adapter, or equivalent.

3. Centrifuge tubes, glass, 5-ml.

4. Dispensing heads, 4-ml and 2-ml, for adding the salting solution, scrub solution, and hexone.

5. Heat lamp.

6. Meker burner.

7. Phase mixing apparatus, 10-in. disc with clamps to hold four 10-ml tubes mounted on a stand and rotated at 60 rpm by an electric motor.

8. Pipets, micro, calibrated, assorted sizes. Constricted-stem pipets as Ultrapette. Use only pipets calibrated by the Quality Control Laboratory.

9. Pipets, transfer, 1-ml glass, uncalibrated.

10. Pipets, volumetric, assorted sizes, with control syringes and suction bulbs.

11. Stoppers, rubber or polyethylene, size 00.

12. Test tubes, glass, 10-ml, 13- x 100-mm and 15-ml, 15- x 100 mm.

Reagents

Note: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Acetone.

2. Aluminum nitrate salting reagent, 3.0M in aluminum nitrate and 3N acid-deficient. Slurry 1125 g of $Al(NO_3)_3 \cdot 9H_2O$ with 100 ml of water, add 203 ml of conc NH_4OH, and stir vigorously until dissolution is complete. Dilute to 1 liter with water. Contact this solution with 100 ml of hexone in a large separatory funnel (with a Teflon-greaseless-stopcock) to remove traces of natural uranium impurity. Discard the organic phase.

3. Aluminon reagent, 0.2% (w/v). Dissolve 0.2 g of the ammonium salt of aurin tricarboxylic acid (MW 473.43) in 100 ml of water.

4. Ammonium hydroxide, conc.

5. Hexone (methyl isobutyl ketone, 4-methyl-2-pentanone).

6. Hydrogen peroxide, 30%. Keep in refrigerator when not in use.

7. Nitric acid, conc and 6M.

8. Plutonium scrub solution 2.0M in aluminum nitrate, 2N acid-deficient, 0.25M each in oxalic acid, EDTA, and hydrazine. Slurry 750 g $Al(NO_3)_3 \cdot 9H_2O$ with 100 ml of water, add 134 ml of conc NH_4OH, and stir vigorously until dissolution is "complete". Add 31 g of oxalic acid dihydrate, 64 g of EDTA (tetraacid form) and 15 ml of 85% hydrazine hydrate. Dilute

to 1 liter with water, mix, and contact this solution with 100 ml of hexone in a large separatory funnel (with a Teflon-greaseless-stopcock) to remove traces of natural uranium. Discard the organic phase.

9. Potassium dichromate solution, 0.1M. Dissolve 29.4 g of $K_2Cr_2O_7$ in water and dilute to 1 liter with water.

10. Uranium-233 spike solution I, 1 mg/ml, in 3M HNO_3. Standardize the spike against NBS U_3O_8, high purity natural uranium metal, and high purity fully-enriched ^{235}U metal. Store the spike as 15- and 40-ml portions in flame-sealed glass ampoules. When spikes are needed, break open an ampoule and with a 500λ calibrated constricted stem-type pipet, deliver the entire contents without interruption and very reproducibly into pre-cleaned 10- or 15-ml test tubes. Take four of the test tubes at random, deliver a weighed aliquot of uranium standard into each and carry out the spike verification test. The spike verification test is as follows:

    Thoroughly mix two of the four, evaporate the solution to dryness. Thoroughly mix the other pair and carry them through Procedure B. Submit the four samples to the Mass Spectrometry Lab for analysis. The Mass Lab is to analyze one evaporated and one separated sample initially.

NOTE ON REAGENTS 10 AND 11: Store the test tubes containing these reagents in a hood or glove box. Discard any tube that tips over because solution will creep around and adhere to the stopper and will not be available for mixing with the sample. If used, the results will be biased high.

11. Uranium-233 spike solution II, 0.01 mg/ml in 3M HNO_3. Prepare an exact 100-fold dilution of Reagent 10 using NBS-calibrated volumetric ware. Store the solution and dispense the spikes as described for Reagent 10.

12. Uranium Controls and Bench Standards. On a weight basis, prepare a suitable stock solution of natural uranium (use either NBS U_3O_8 or high purity natural uranium metal) and fully-enriched uranium (use the pure metal). Dilute the stock solutions on weight/weight and weight/volume bases to obtain solutions about 2 mg/ml. Identify one each of the natural and fully enriched uranium standards as bench standards or "knowns". Keep the acidity of the stock solution and 2 mg/ml solutions at about 3 M HNO_3. Store all of the standards in sealed glass ampoules.

PROCEDURES

A. Known and unknown controls will be processed on a schedule established by the quality control program for the procedure being used.

B. Low-Level Uranium Separation

NOTE: See Procedures D and E for remote operations.

1. Deliver by weight or volume a sample aliquot containing 0.0005 to 0.05 mg of U into a test tube that contains 500 µl of ^{233}U spike solution II.

   Select the sample aliquot to give a sample to spike ratio close to 1. The amount of ^{233}U in the tube is 0.005 mg. Deliver the sample aliquot deep into the tube but do not let the pipet tip touch the spike solution. Refer to the APPLICABILITY section for information on sample aliquot limits.

2. Mix the contents of the tube by swirling, add 2 drops of 0.1M $K_2Cr_2O_7$ to oxidize the uranium in the sample to the +6 oxidation state, and again swirl the contents.

   The $K_2Cr_2O_7$ addition may be omitted only when the oxidation state of the U in the sample is known to be +6.

3. If the sample aliquot was larger than 1 ml, do either of the following:

   a) Add solid $Al(NO_3)_3$ at the rate of 1.5 g for each milliliter of sample above 0.5 ml and mix until the salt dissolves.

   b) Evaporate the sample to a few drops, then dissolve any residue formed with a minimum of 6M HNO_3. Use heat lamp and a tiny stream of air.

4. Add 4 ml of the salting (Reagent 2) solution, 2 drops of the aluminon reagent, and 2 ml of hexone, insert a stopper, and mix the contents for 1 min on the phase mixing apparatus.

Steps 5, 6, and 7 are provided to scrub out transuranics and to scrub out interfering Cr(VI) which extracts when it is used in Step 2 and the sample contains Cl^-. If neither of these exist, proceed directly to Step 8.

5. Transfer as much as possible of the organic phase (with none of the aqueous phase) with a new transfer pipet to a 10-ml test tube. Discard the aqueous phase to the hot waste drain.

6. Add 2 ml of the Pu scrub (Reagent 7) solution, insert a stopper, and mix the contents for 3 min on the phase mixing apparatus.

7. Centrifuge for 1 min at 2/3 speed.

8. Transfer as much as possible of the organic phase (with none of the aqueous phase) with a new transfer pipet to a new, cleaned 5-ml conical centrifuge tube. Discard the aqueous phase to the hot waste drain.

9. Slowly, without spattering, evaporate the hexone in a glove box or hood to dryness under a heat lamp with the aid of a gentle stream of air directed into the tube.

10. Heat the tube with a Meker burner until the tip of the tube just glows red to decompose all the organic matter.

11.	After the tube cools, add 2 drops of conc HNO_3 and evaporate to dryness as described in Step 9.	
12.	Repeat Step 11.	
13.	Insert a clean stopper and measure the gross beta-gamma activity with a portable meter in contact with the tube.	If the reading is less than 30 mR/hr, continue with Step 16. If more than 30 mR/hr, continue with Step 14.
14.	Add 0.5 ml of 6M HNO_3 to the tube, swirl it for 1 min, and transfer the solution with the aid of another 0.5 ml of 6M HNO_3 wash to a clean 10-ml test tube.	Use a new transfer pipet for this transfer. Make sure that a new unused 10-ml test tube is used.
15.	Repeat Steps 4 through 13.	
16.	Write the log number and sample code on the tube and prepare for the mass spectrometry laboratory a work sheet which includes all data necessary to calculate the final results.	

C. High-Level Uranium Separation

NOTE: See Procedure D for remote techniques.

1.	Deliver a sample aliquot containing 0.05 to 5 mg of U into a test tube that contains 500 µl of ^{233}U spike solution I.	Select the sample aliquot to give a sample to spike ratio close to 1. The amount of ^{233}U in the tube is 0.5 mg. Deliver the sample aliquot deep into the tube but do not let the pipet tip touch the ^{233}U solution. Refer to the APPLICABILITY section for information on sample aliquot limits.

2. Mix the contents of the tube by swirling, add 2 drops of 0.1M $K_2Cr_2O_7$ to oxidize the U in the sample to the +6 oxidation state, and again swirl the contents.

   The $K_2Cr_2O_7$ addition may be omitted only when the oxidation state of the U in the sample is known to be +6.

3. If the sample aliquot was larger than 1 ml, do either of the following:

   a. Add solid $Al(NO_3)_3$ at the rate of 1.5 g for each milliliter of sample above 0.5 ml and mix until the salt dissolves.

   b. Evaporate the sample to a few drops, then dissolve any residue formed with a minimum of 6M HNO_3. Use heat lamp and a tiny stream of air.

4. Add 4 ml of the salting (Reagent 2) solution, 2 drops of aluminon reagent, and 2 ml of hexone, insert a stopper, and mix the contents for 1 min on the phase mixing apparatus.

   Steps 5, 6, and 7 are provided to scrub out transuranics and to scrub out interfering Cr(VI) which extracts when it is used in Step 2 and the sample contains Cl^-. If neither of these reasons exist, proceed directly to Step 8.

5. Transfer as much as possible of the organic phase (with none of the aqueous phase) with a new transfer pipet to a 10-ml test tube. Discard the aqueous phase to the hot waste drain.

6. Add 2 ml of the Pu scrub (Reagent 7) solution, insert a stopper, and mix the contents for 3 min on the phase mixing apparatus.

7. Centrifuge for 1 min at 2/3 speed.

8. Transfer as much as possible of the organic phase (with none of the aqueous phase) with a new transfer pipet to a new, cleaned 5-ml centrifuge tube. Discard the aqueous phase to the hot waste drain.

9.	Add 1 ml of 30% H_2O_2, insert a clean stopper, and mix the contents for 1 min or until the precipitation of uranium peroxide appears complete.	If no precipitate forms, add 1 drop of conc NH_4OH and again mix the contents. This may be repeated, 1 drop at a time up to about 5 drops. If this does not work, obtain a new sample-spike mixture, and precipitate the U with NH_4OH. Centrifuge and discard the supernatant solution, dissolve the residue with 6M HNO_3, then carry this solution through the extraction beginning at Step 4.
10.	Centrifuge at 2/3 speed for 5 min.	
11.	With a clean transfer pipet connected to a vacuum wash train, remove the supernatant solution without disturbing the precipitate.	
12.	Add 2 drops of acetone and vigorously agitate the tube until the precipitate is dispersed.	In Steps 12 and 13, do not let acetone contact the rubber stopper.
13.	Wash down the tube with 3 ml of acetone.	
14.	Centrifuge at 2/3 speed for 5 min.	
15.	With the transfer pipet used in Step 11, remove the acetone without disturbing the precipitate.	If the acetone is highly colored, organic matter is present. Repeat Steps 13, 14, and 15.
16.	Insert a clean stopper and measure the gross beta-gamma activity with a portable meter in contact with the tube.	If the reading is less than 30 mR/hr, continue with Step 19. If more than 30 mR/hr, continue with Step 17.
17.	Add 0.5 ml of 6M HNO_3 to the tube, swirl it for 1 min, and transfer the solution with the aid of	Use a new transfer pipet for this transfer. Make sure that a new unused 10-ml test tube is used.

another 0.5 ml of 6M HNO_3 wash to a clean 10-ml test tube.

18. Repeat Steps 4 through 16.

19. Write the log number and sample code on the tube and prepare for the Spectrometry Laboratory a work sheet which includes all data necessary to calculate the final results.

D. Remote Operation: Separation-Analysis on a Volume Basis

1. Add 2 drops of 0.1M $K_2Cr_2O_7$ to a 15-ml test tube that already contains 500 µl of either ^{233}U spike solution I or ^{233}U spike solution II.

   Select the spike solution depending on the U content of the sample. See Step 1 in both Procedures B and C.

2. Add 4 ml of the salting (Reagent 2) solution, and 2 drops of the aluminon reagent, and 4 ml of hexone to a clean 10-ml test tube.

3. Transfer the 2 tubes prepared in Steps 1, 2, and 3 to the Remote Analytical Facility.

4. Deliver the sample aliquot into the 15-ml tube containing the spike. The aliquot should contain between 0.0005 and 0.05 mg of U (low-level separation) or between 0.05 and 5 mg of U (high-level separation).

   Adjust the pipetter tip to a height of 1 in. above the liquid in the tube before delivering the sample. Also, adjust the tube position so the pipetter tip is not touching the tube. The recommended delivery volume for dissolved fuel samples from the plant process is 500 µl. Use the calibrated 200 to 700 position of the pipetter to deliver 500 µl.

5. Wash the pipet tip with 5 to 10 drops of water.	The salting strength will be decreased too much if more than 10 drops is used. This will result in unsatisfactory low extraction of U.
6. Remove the tube from the pipetter and mix the contents by swirling the tube.	Take care no solution is lost from the tube in this operation.
7. Add the premeasured salting solution-hexone-aluminon reagent mixture from Step 2. Set the empty tube aside for later use in Step 9.	
8. Insert the stopper and mix the contents for <u>at least 1 min</u> by repeatedly inverting the tube.	Use the tong that has a special bracket to hold the stopper in place.
9. Decant as much as possible of the organic phase (with none of the aqueous phase) to the empty tube that had contained the salting solution, hexone, and aluminon reagent.	
10. Insert a clean stopper and transfer the tube to the Warm Laboratory.	
11. Continue either with Procedure B, Step 8, or with Procedure C, Step 8.	If a scrub is necessary to remove transuranics or Cr(VI), begin at Step 6.

E. Remote Operation: Separation-Analysis on a Weight Basis

1. Add 2 drops of 0.1M $K_2Cr_2O_7$ to a 15-ml test tube that already contains 500 µl of either ^{233}U spike solution I or ^{233}U spike solution II.	Select the spike solution depending on the U content of the sample. See Steps 1 in both Procedures B and C.
2. Add 4 ml of the salting (Reagent 2) solution, 4 ml of hexone, and 2 drops of the aluminon reagent to a clean 10-ml test tube.	

3.	Transfer the 2 tubes prepared in Steps 1 and 2 to the Remote Analytical Facility.	
4.	Weigh the spike tube on the remote balance and record the weight on the mass analysis work sheet.	See the Remote and Service Analysis Group Operating Manual (PTR-729, p 184-1) for operating instructions. Zero the balance immediately before weighing the tube.
5.	Invert a No. 3 polyethylene stopper over the tube and transfer it to the pipet box.	The polyethylene stopper will help prevent contamination that might change its weight.
6.	Remove the polyethylene cover and then remove the rubber stopper and place it in the special stopper holder.	The rubber stopper holder is designed to prevent contamination of the stopper.
7.	Deliver the sample aliquot into the 15-ml tube containing the spike. The aliquot should contain between 0.0005 and 0.05 mg of U (low-level separation), or between 0.05 and 5 mg of U (high-level separation).	Adjust the pipetter tip to a height of 1 in. above the liquid in the tube before delivering the sample. Also, adjust the tube position so the pipetter tip is not touching the tube. The recommended delivery volume for dissolved fuel samples from the plant process is 500 µl. Use the calibrated 200 to 700 position of the pipetter to deliver 500 µl.
8.	Touch the tip of the pipet to the walls of the tube and then remove the tube from the pipetter.	Wash and dry the pipet thoroughly before pipetting another sample.
9.	Mix the contents by gently swirling the tube.	Take care no solution is lost from the tube in this operation.
10.	Return the tube to the tube carrier.	Do not allow the tubes to drop into the carrier. This may cause solution to spatter out of the tube.

11.	Replace the rubber stopper and the polyethylene cover and transfer the tube to the remote balance box.	
12.	Remove the polyethylene cover and weigh the tube. Record the weight on the mass analysis work sheet.	Zero the balance before weighing the tube.
13.	Add the prepared salting solution-hexone-aluminon reagent mixture from Step 2. Set the empty tube aside for later use in Step 15.	
14.	Insert the stopper and mix the contents for <u>at least 1 min</u> by repeatedly inverting the tube.	Use the tong that has a special bracket to hold the stopper in place.
15.	Decant as much as possible of the organic phase (with none of the aqueous phase) to the empty tube from Step 13.	
16.	Insert a clean stopper and transfer the tube to the Warm Laboratory	
17.	Continue either with Procedure B, Step 8, or with Procedure C, Step 8.	If a scrub is necessary to remove transuranics or Cr(VI), begin at Step 6.

<u>REFERENCES</u>

1. W. J. Maeck, G. L. Booman, M. C. Elliott, J. E. Rein, "Separation of Uranium From Diverse Ions: Methyl Isobutyl Ketone Liquid-Liquid Extraction System", <u>Anal. Chem.</u>, <u>30</u> (December 1958) pp 1902-1907.

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DETERMINATION OF URANIUM BY REDOX TITRIMETRY

ABSTRACT

A precise, selective titrimetric method is described for the determination of uranium. The uranium is reduced to the (IV) state with excess Fe(II) in a strong phosphoric acid medium containing sulfamic acid; the excess Fe(II) is oxidized by nitrate with Mo(VI) catalysis; and the U(IV) is titrated with potassium dichromate to a potentiometric end point.

APPLICABILITY

This method, based on studies at Dounreay[1] and the New Brunswick Laboratory[2,3], is particularly useful for the determination of uranium in uranyl nitrate solutions such as plant final product and evaporator concentrate samples from the J, H, and E cells. The method is quite selective (see Table I), so it is applicable to other types of samples such as aluminum-, stainless steel-, and Zircaloy-clad uranium fuels[2,3] and solutions of Rover fuel containing niobium, hydrofluoric acid, and nitric acid.

Davies and Gray[1] and New Brunswick Laboratory personnel made fairly comprehensive studies of the effects of diverse substances. Their data, confirmed and broadened through independent studies at this laboratory, are presented in Table I. Principal interferences are Cl^-, Br^-, I^-, Ag(I), and Sn(II). Nitrate, even at very high levels, and molybdenum are without effect when present alone; however, both interfere significantly in the presence of significant amounts of the other. For example, 48 mM of nitrate as nitric acid does not interfere at a molybdenum level of 1 mg or less but causes about a 12% negative bias at a molybdenum level of 10 mg; 100 mg of molybdenum has no effect in the presence of 2.5 mM of nitrate, but introduces negative errors of approximately 2% and 25% in the presence of 8 and 48 mM of nitrate, respectively. In this method, approximately 23 mg of molybdenum is used in the determination to catalyze the nitrate oxidation of Fe(II) to Fe(III). This molybdenum has no bearing on the effect of nitrate in the initial reduction step. With reference to the foregoing remarks, samples should be evaporated to sulfuric acid fumes routinely if the absence of interferences has not been established. It has been found that fuming effectively eliminates the interference of volatile anions like Cl^-, Br^-, I^-, and NO_3^-.

TABLE I

EFFECTS OF DIVERSE SUBSTANCES[a]

Substance and Level Studied	Remarks
Br^- (0.2 g)	Interferes. Avoid interference by fuming sample with H_2SO_4.
Cl^- (1 g)	No adverse effect; Larger interfering amounts can be fumed off.
F^- (1 g)	No adverse effect.
NO_3^- (many levels)	The effect of NO_3^- depends on its level and the concentration of Mo. See text under APPLICABILITY.
H_2O_2(0.02 g), ClO_4^- (1 g), $SO_4^=$ (5 g), TBP(5 ml of a 35% (v/v) TBP-kerosene solution)	No adverse effect.
H_2O	Up to 15 ml of water has no adverse effect. Results are low by about 3% at 20 ml.
Al^{+3}(0.2 g), Fe^{+3}(0.2 g), Pu^{+4}(0.11 g), Ti^{+4}(0.1 g), W^{+6}(0.2 g)	No adverse effect.
Cr^{+3}(0.05 g), Cu^{+2}(0.2 g), Ni^{+2} (0.2 g)	No adverse effect.
Pb^{+2}(0.2 g), Hg^{+2}(0.2 g)	A precipitate forms during the determination, but there is no adverse effect.
Mn, V	Davies and Gray[1] report that V interferes seriously at the 40-mg level. Studies at New Brunswick Laboratory[2] show that the tolerance limit for V and Mn are 5 mg and 10 mg, respectively. Above these levels, V interferes positively and Mn interferes negatively.
Mo^{+6}(0.1 g)	The effect of Mo depends on its level and the level of NO_3^-. See text under APPLICABILITY.
Ag^{+1}(0.2 g), Sn^{+2}(0.1 g)	Serious positive interference.

TABLE I (Cont'd)

Substance and Level Studied	Remarks
Nb (1 mM) + HF (28 mM) + HNO_3 (50 mM)	No adverse effect.
Solution of 1100-S Al	No adverse effect at 90-mg alloy level.

[a] Based on the analysis of binary mixtures containing the diverse substance and 100 to 300 mg of uranium. These data have been confirmed in diverse ions studies at this laboratory.

A range of 25 to 300 mg of uranium has been selected for this titrimetric method. With an initial evaporation step, there is no specific limit to the maximum sample aliquot. Assuming a practical limit of 100 ml, the lower limit of determinability is 0.25 mg of uranium per ml (1×10^{-3} M).

DISCUSSION

The principal steps and reactions involved in this method are:

(1) Sampling

(2) Evaporation of samples with sulfuric acid (optional)

(3) Reduction of U(VI) to U(IV) with Fe(II) in H_3PO_4-sulfamic acid medium

$$U(VI) + Fe(II) \text{ in excess } \xrightarrow[H_2NSO_3H]{H_3PO_4} U(IV) + Fe(III) + \text{excess } Fe(II) \quad (1)$$

(4) Destruction of excess Fe(II) by molybdate-catalyzed nitrate oxidation

$$Fe(II) + HNO_3 \text{ in excess } \xrightarrow[H_2NSO_3H]{Mo(VI)\ \text{catalyst}} Fe(III) + \text{N-oxides} + \text{excess } HNO_3 \quad (2)$$

(5) Dilution of sample with 1M H_2SO_4 and titration of U(IV) to U(VI) with Cr(VI), in the presence of vanadium catalyst, to a potentiometric (Pt-calomel) equivalence point.

$$U(IV) + Cr(VI) \xrightarrow{V\ \text{catalyst}} U(VI) + Cr(III). \quad (3)$$

Close adherence to prescribed directions and conditions at each step is necessary to obtain the highly reliable (±0.05%) results that this method is capable of delivering.

In the sampling Step (1), 15 ml is the maximum permissible volume of aqueous sample if no evaporation is performed. Above this, results are low, presumably because of the lowering of the phosphate concentration which leads to incomplete reduction of U(VI) to U(IV) by Fe(II) in Step (3). Results are about 3% low at the 20-ml level.

A preliminary evaporation with sulfuric acid is used to expel volatile interferences and to lower the water content of the sample to below 15 ml. Temperature is a critical factor in the Fe(II) destruction and Cr(VI) titration steps that follow. The evaporated sample should be rinsed down with water, then cooled to 20-25°C before the analysis is continued. The heat of dilution alone is sufficient to cause partial reoxidation of U(IV) to U(VI) and low results.

The reduction of U(VI) to U(IV) with Fe(II) per Step (3) is complete in 1 min at room temperature. Adequate but not overly energetic stirring should be provided and the Fe(II) reagent should be added to the solution, not to the container wall. These precautions assure complete destruction of excess Fe(II) in the succeeding step.

The molybdenum-catalyzed nitrate oxidation of excess Fe(II) reductant, Step (4), and the titration of uranium with dichromate, Step (5), are the two most critical steps in the determination. The temperature of the reaction medium must be about 35°C to obtain complete destruction of excess Fe(II) without simultaneous reoxidation of U(IV) to U(VI). Using a 5-ml standard made up in a dilute nitric acid medium, the temperature remains constant at about 35°C from the time the phosphoric acid is admitted to the time 1M H_2SO_4 diluent is added. The reaction time for the nitrate oxidation of Fe(II) must be controlled closely at 3 min and the titration must be started immediately after dilution and concluded within at least 5 min. With a total titration plus delay time of 10 min, results are low by almost 1.5%. Chilling the 1M H_2SO_4 diluent or rapid addition of the bulk of the dichromate reagent (either as the solid or from a squeeze bottle by weight) may minimize the criticalness of time, but as yet, these changes have not been evaluated. The oxidation of U(IV) to U(VI) by Cr(VI) is not rapid enough near the equivalence point for rapid equilibrium and rapid, sensitive indication of potential. Vanadium catalyst provides a rapid, readily-distinguishable potential break. Because V(IV) in solution is reported to air oxidize to V(V) which is capable of oxidizing U(IV) to U(VI), the vanadium is best added as the $VOSO_4$ salt. Between 150±15 mg is satisfactory. The platinum electrode seems to "poison" readily and give erroneous responses. It should be rinsed with nitric acid and flamed before use.

Sulfamic acid plays a vital role in the method. It prevents undesirable oxidation of Fe(II) by nitrate and subsequently the oxidation of U(IV) to U(VI) by the same oxidant.

APPARATUS AND REAGENTS

A. Apparatus

1. Analytical balance.

2. Beakers, assorted sizes.

3. Buret, specially made, 20-ml. Attach a 9-ml capacity oblong bulb to a 10-ml microburet about 0.5 in. above the zero calibration line, then attach 3 in. of 9-mm OD tubing to the top end of the bulb. Etch a new zero calibration line on the 9-mm OD tubing so that the capacity of the reservoir between the two lines is between 9.5 and 10.0 ml. Accurately calibrate the volume of the reservoir (to the nearest 0.001 ml) with water or mercury.

4. Buret, 50-ml, with ringstand and buret holder.

5. Hot plate, Chromalox.

6. Magnetic stirrer and stirring bars.

7. pH Meter, with fiber tip calomel-platinum wire electrode pair.

8. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.

9. Thermometer (to measure room temperature in the range 15 to 30°C).

10. Watch glasses, Speedy-Vap, for 400-ml beakers.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ferrous sulfate solution, 1.0M. CAREFULLY, with stirring, add 100 ml of conc H_2SO_4 to 750 ml of water. Add 280 g of $FeSO_4 \cdot 7H_2O$ to the hot acid solution, stir until the salt dissolves, cool, then dilute to 1 liter with water. Mix well, then add about 20 g of cadmium metal chips to maintain the iron in the (II) oxidation state.

2. Nitric acid-sulfamic acid-ammonium molybdate reagent. Dilute 500 ml of conc HNO_3 to 800 ml with water. Add 100 ml of the 1.5M sulfamic acid (HSO_3NH_2) solution and mix well. Dissolve 4 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 100 ml of water (heat to dissolve); add this to the solution and dilute to 1 liter. This solution, 8M in nitric acid, 0.15M in sulfamic acid, and 0.4% in ammonium molybdate, is stable for at least 2 mo.

3. Phosphoric acid, conc.

4. Potassium dichromate solution, 0.05000N(0.008333M). Dissolve 2.45144±0.00005 g of NBS 136b $K_2Cr_2O_7$ in water, dilute to 1 liter with water at 22.5°C, and mix thoroughly. The specified weight, adjusted for air buoyancy and reagent purity, is for exactly 1 liter. Use a calibrated flask and assign the exact normality or alter the weight of dichromate.

5. Sulfamic acid, 1.5M. Dissolve 150 g of sulfamic acid in water and dilute to 1 liter.

6. Sulfuric acid, conc, 9M, 1M.

7. Uranium bench and bias control standards. Prepare a series of standards from NBS Standard 950a U_3O_8 on both weight and volume basis to cover the range 50 to 300 mg of uranium. Dissolve the oxide with 8M HNO_3, then dilute to volume with 2M HNO_3.

8. Vanadyl sulfate salt ($VOSO_4\cdot 2H_2O$). For convenience, provide a tiny glass scoop that delivers 150±50 mg of the salt.

PROCEDURE

A. Treatment of Platinum Electrode and Checkout of pH Meter-Electrodes Assembly.

Prior to the analysis of samples, flame the platinum wire electrode over a full blue flame of a Meker burner. Flaming cleans the electrode and makes it sensitive to potential changes. If desired, the electrodes-pH meter assembly can be checked for response by immersing the calomel-platinum electrode pair into a solution prepared by mixing 5 ml of 9M H_2SO_4, 40 ml conc H_3PO_4, 10 ml of the nitric acid-sulfamic acid-molybdate reagent, 5 ml of 0.1M $VOSO_4$, and 100 ml of 1M H_2SO_4, then adding in order one drop of 1M $FeSO_4$ and 0.05N $K_2Cr_2O_7$ dropwise. At the equivalence point, there should be a 300 to 400 MV change for 1 drop (0.05 ml) of the dichromate solution.

B. Titration Blank

No blank determination is necessary. Under proper conditions, the blank is 0.01 ml or less.

C. Dichromate Titrant Volume Corrections at Different Temperatures.

The titrant is diluted to volume at 22.5°C and the buret is normally calibrated at 20°C so a volume correction must be applied to the dichromate titrant for titrations at temperatures other than 22.5°C. Correction values for the temperature range 19 to 30°C are given in Table II. These values were calculated on the assumption that the expansion or contraction of the buret is negligible in the range 19 to 30°C.

TABLE II

DICHROMATE TITRANT VOLUME CORRECTIONS AT DIFFERENT TEMPERATURES

Room Temperature (°C)	Correction to Apply at Different Titrant Volumes (ml)				
	10	20	30	40	50
19	+0.01	+0.02	+0.02	+0.03	+0.04
20	+0.01	+0.01	+0.02	+0.02	0.03
21	0.00	+0.01	+0.01	+0.01	+0.02
22.5	0.00	0.00	0.00	0.00	0.00
24	0.00	-0.01	-0.01	-0.01	-0.02
25	-0.01	-0.01	-0.02	-0.02	-0.03
26	-0.01	-0.02	-0.03	-0.03	-0.04
27	-0.01	-0.02	-0.03	-0.05	-0.06
28	-0.01	-0.03	-0.04	-0.06	-0.07
29	-0.02	-0.03	-0.05	-0.07	-0.09
30	-0.020	-0.040	-0.06	-0.08	-0.10

D. Analysis of Bench Standard

Process a bench standard with each series of samples. The result should be within the specified range. If not, process another standard. If problems persist, contact your supervisor.

E. Analysis of Samples

1. Transfer an aliquot containing 25 to 300 mg (0.1 to 1.3 mM) of U to a 400-ml beaker.	See Table I for limitations on other substances. For maximum precision, select a sample aliquot containing between 80 and 100 mg of U when working with the modified micro buret, and between 225 and 275 mg of U when working with the 50-ml buret.
2. Add 5 ml of 9M H_2SO_4, place a Speedy-Vap cover glass on the beaker, and evaporate to the appearance of strong SO_3 fumes. Continue fuming for 3 to 5 min.	If the sample aliquot is less than 15 ml and does not contain interfering levels of Br^-, Cl^-, I^-, NO_3^-, or $MoO_4^=$, add 1 ml of 9M H_2SO_4 and proceed directly to Step 5. Samples of uncertain compositions should always be fumed.
3. Remove the sample(s) from the hot plate and let them cool.	
4. Rinse the cover glass and beaker walls with a measured 5 ml of water.	After rinsing the beaker and swirling the solution to obtain mixing, cool the solution to 20-25°C before continuing.
5. Add 5 ml of 1.5M sulfamic acid.	Process the samples, ONE AT A TIME, from Step 5 through Step 11 using continuous magnetic stirring.
6. With a graduated cylinder, add 40 ml of conc H_3PO_4. Use the H_3PO_4 to wash down the beaker wall.	
7. Add the 1M $FeSO_4$ solution and wait 1 min. Add 5 ml for samples with more than 110 mg of U and 2 ml for samples with less than 110 mg of U.	Use a pipet and deliver the $FeSO_4$ into the sample solution.

8.	Add 10 ml of the 8M HNO_3-0.15M sulfamic acid-0.4% ammonium molybdate reagent.	Use the reagent to wash down the wall of the beaker. It is imperative that all of the Fe(II) reductant is brought in contact with the HNO_3 oxidant. A brown coloration appears when this reagent is introduced. Time is critical in this and subsequent steps (See DISCUSSION).
9.	Continue the stirring for 3 min after the brown coloration disappears.	
10.	Add 100 ml of 1M H_2SO_4 and 150±15 mg of $VOSO_4 \cdot 2H_2O$.	
11.	Without delay, titrate the sample with 0.05N $K_2Cr_2O_7$ titrant to a potentiometric end point. Titrate rapidly from the starting potential of about 400 MV to a potential of about 475 MV, then add successively smaller increments until a potential of 590 MV is reached or surpassed. Near the end of the titration, add 0.01-ml increments and wait 15 sec between increments.	Conclude the titration within 5 min after dilution with the 1M H_2SO_4. Use the modified microburet for samples containing less than 110 mg of U and the 50-ml buret for samples containing more than 110 mg of U. If the sample contains less than 0.25 mM of U, fill the microburet only to the 10-ml mark. The break begins at about 500 MV. Only about 0.10 ml of titrant is required to go from 500 MV to 590 MV.
12.	Record the data and the ambient temperature and calculate the results as shown in the example work sheet. Report all results to 4 significant figures.	

REFERENCES

1. W. Davies and W. Gray, UKAEA Report TRG-716 (D), 1964; Talanta 11, 1203 (1964).

2. C. F. Hedrick, United States Atomic Energy Commission, New Brunswick Laboratory, New Brunswick, New Jersey, private communication (June 1969).

3. C. J. Rodden, "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle", revised edition, (revision in process, September 1971).

D. M. Lund
S. S. Yamamura
October 1971

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Uranium

CHARGE NUMBER _____ PROCEDURE U-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Room Temp, °C	Volume 0.0500 N $K_2Cr_2O_7$ used, ml	Temp Volume Correction, ml	Net $K_2Cr_2O_7$ Volume, ml	mM U in Aliquot	mM corrected for Bias		RESULT mM U/g
Product UO_3	0.2560 g	25	33.63	-0.04	33.59	0.8398	0.8398 ± 0.0017		3.280 ± 0.007

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$D = \text{Net } K_2Cr_2O_7 \text{ Volume} = B + C$$
$$= 33.63 + (-0.04)$$
$$= 33.59 \text{ ml}$$

$$E = \frac{0.05000^*}{2} D = 0.2500(33.59) = 0.8398 \text{ mM}$$

$$\text{Result} = \frac{F}{\text{sample wt}} = \frac{0.8398 \pm 0.0017}{0.2560 \text{ g}} = 3.280 \pm 0.007 \text{ mM U/g}$$

* 0.0500 is the normality of the $K_2Cr_2O_7$ titrant and 2 is the number of equivalents of U/mole of U.

APPROVED BY _____

DETERMINATION OF ZIRCONIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

ABSTRACT

Zirconium is determined by comparing the atomic absorption of a sample to the atomic absorption of a known set of standards. Samples and standards are aspirated as a 0.05M NH_4F-0.006M KCl-0.1M HBF_4 solution into a nitrous oxide-acetylene flame system.

APPLICABILITY

The method is applicable to the determination of zirconium in the following sample types:

Sample	Approximate Composition
Al-Zr IFU, complexed dissolver product	0.5M Zr; 3.4M F^-; 0.7M Al; 2M H^+; 2.7M NO_3^-; ∿ 0.2M B; ∿ 2.5 mg U/ml.
WC-101, waste calciner feed, Zr type	Similar to above plus Ca at about 0.6M.
HF solutions of PWR type fuel	Samples contain Zr, Nb, U, and HF at various concentrations.

For maximum precision, all samples should be diluted with an accurately measured amount of 0.05M NH_4F-0.006M KCl-0.1M HBF_4 solution to a zirconium concentration of 50 to 400 µg/ml. Best results are obtained at about 200 µg/ml.

The recommended 0.05M NH_4F-0.006M KCl-0.1M HBF_4 sample diluent greatly reduces sample matrix effects by enhancing zirconium sensitivity[1,2]. For example, it has been found that where samples are diluted 1 to 100 with the diluent, several-fold variations in the concentrations of Al, B, Ca, Cr, F, Hg, and U, individually or as a mixture, have no adverse effect on the zirconium results.

DISCUSSION

Flame composition is a critical parameter in obtaining maximum sensitivity for the determination of zirconium. A fuel rich flame is essential. This flame is characterized by a pink inner cone about 0.75-in. high. Any increase in acetylene flow should cause luminescent streaks to appear in the flame. Increases in the acetylene flow rate may be necessary during the life of an acetylene tank in order to obtain the proper fuel-oxidant ratio. This can be tested by making flame adjustments while aspirating a standard solution.

With the fuel rich flame used for the zirconium determination, carbon deposits must be removed frequently to prevent changes in the shape and length of the flame. Calibration curves constructed for the range 50 to 400 µg Zr/ml should show good linearity if the instrument is operating properly.

SPECIAL SAFETY PRECAUTIONS

Explosions of nitrous oxide-acetylene mixtures are common; therefore, follow carefully all instructions for lighting and extinguishing the flame. Test the waste elimination system to ensure that it is functioning properly before converting from air to nitrous oxide. The tip of the drain tube must extend below the surface of the liquid in the waste receptacle. Spills can be prevented by only partially filling the sample cups.

APPARATUS AND REAGENTS

A. Apparatus

1. Bottles, plastic, 2-oz.

2. Burner, nitrous oxide-acetylene, 6-cm slot.

3. Cups, plastic, 5-ml, caplugs No. 12X.

4. Spectrophotometer, atomic absorption, Techtron AA-5 or equivalent instrument with attachments.

5. Pipets, 100-µl and 20-ml, with control syringe and rubber suction bulb.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for preparation of all reagent and matrix solutions.

1. Zirconium stock solution, 10.00 mg/ml. Dissolve 10.0000 g of high purity zirconium metal in a 500-ml Teflon beaker with 40 ml of conc HF (use rubber gloves and add the HF slowly in small portions) and dilute to 1-liter with water in a calibrated Nalgene volumetric flask.

2. Sample diluent, 0.05M NH_4F-0.006M KCl-0.10M HBF_4. This matrix is used for the dilution of all sample types and the preparation of zirconium standards and controls. To a 1-liter Nalgene volumetric flask, add 7.4 g of NH_4F and 1.79 g of KCl. Dissolve these salts in about 500 ml of water and add 71.7 g of 48% HBF_4. Dilute to volume with water and mix. Transfer the contents to a 4-liter polyethylene bottle and with the 1-liter flask, add 3 liters of water and mix.

3. Zirconium calibration standards. Dilute 5-, 10-, 15-, 20-, 25-, 30-, 35-, and 40-ml portions of the 10.0000 mg/ml zirconium stock solution and dilute to 1 liter with the sample diluent. These eight standards, which should be stored in polyethylene bottles, cover the concentration range 50 to 400 µg Zr/ml in 50-µg increments.

4. Zirconium controls and bench standards. Following the procedure given above for the zirconium calibration standards, prepare a series of 6 controls with zirconium concentrations in the range 50 to 350 µg/ml. Designate two, one at about 100 µg/ml and another at 250 µg/ml as bench standards for use in methods trouble shooting or checkout.

PROCEDURE

A. Sample Preparation

1. Plant Samples

Dilute the sample with the sample diluent to give a zirconium concentration of about 200 to 300 µg/ml. The usual dilution procedure for plant samples is to pipet 100 µl of the sample into 20 ml of the sample diluent. Of course, highly radioactive samples must be diluted remotely.

2. Bench-Control Standards

No dilution is required on the controls. Process the controls as supplied.

B. Calibration

The analyst has an option of two different methods of calibration. One method is to process the necessary zirconium calibration standards for the construction of a calibration curve. This is the preferred approach when there are many samples. The other approach is to process two standards that bracket the concentration of the sample. In either case, the standards are processed per Procedure D in the same manner as any sample.

C. Analysis of Controls

Analyze one control per Procedure D each time an analysis is performed. The result for the control must fall within the specified limits. If it does not, process another control. Seek help if troubles continue.

D. Analysis of Samples

The analysis should be carried out in accordance with the normal instrument operating procedures. Verify that the correct shutdown procedure was followed. If any control or condition is not as it should be, correct it.

Operation	Detailed Instructions
1. Turn on power.	Three switches, one each on monochromator, readout unit and hollow cathode supply.
2. Rotate hollow cathode into position.	Zr hollow cathode.
3. Set hollow cathode current.	Set at 20 ma and allow warmup of at least 10 min.
4. Adjust hollow cathode position.	Circle of light should center on monochromator slit.
5. Mount proper burner head.	Nitrous oxide-acetylene, 6-cm slot.

6.	Align burner with respect to light beam.	Adjust burner horizontal movement and rotation.
7.	Set burner height.	Set vernier at 11. Bottom of focused beam should be 0.25 in. above burner top.
8.	Set the wavelength dial.	Set at 3601A.
9.	a. Set the backing control.	Zero
	b. Set the damping switch.	D
	c. Set the select switch.	Normal
	d. Set the mode switch.	% T
	e. Set the scale expand.	X 1
	f. Set the monchromator slit.	25 μ
	g. Set the coarse gain.	To give meter reading of about 50.
10.	Adjust wavelength to give maximum meter deflection.	Change gain as required to keep meter on scale.
11.	Verify that drain tube extends below surface of liquid in waste receptacle.	
12.	Set exhaust control at open.	
13.	Turn on supply valves.	Air, C_2H_2 and N_2O are needed.
14.	Adjust regulator settings.	Air - 15 gauge C_2H_2 - 13 gauge N_2O - 24 gauge
15.	a. Turn support valve to air.	Adjust support pressure to 15 psi.
	b. Turn support valve to N_2O.	Support pressure should read 15 psi.
	c. Turn support valve off.	
	d. Turn fuel valve to C_2H_2.	Adjust flowmeter setting to 3.
	e. Turn support valve to air.	

	f. Light the burner.	Allow air to flow for at least 5 sec before lighting the burner.
	g. Raise fuel flowmeter setting to 9.	
	h. Rapidly switch support valves to N_2O.	
	i. Adjust flowmeter settings. (1) N_2O - 5.5 (flow) (2) C_2H_2 - ∿ 7.5 (flow)	Flow should be adjusted to obtain a pink inner cone about 0.75 in. high. Check by aspirating a standard. Carbon buildup is normal for this flame.
16.	Adjust the exhaust control.	Close exhaust as necessary to stabilize flame, but never close exhaust completely.
17.	Block the light beam and set the readout zero.	Adjust with the backing control if necessary.
18.	With light beam unobstructed, adjust gain controls.	Set for readout of 100.
19.	Turn mode switch to ABS.	Set for readout of zero with fine gain control.
20.	Set select switch to auto 100 and the auto/read switch to auto. Aspirate blank solution.	Reset the readout to zero with the set 100 control.
21.	Set the scale expand control while aspirating standard solution with auto/read switch on read.	Set readout to 0.5 absorbance for 300 µg Zr/ml standard.
22.	Aspirate blank solution with auto/read switch on auto.	
23.	Switch auto/read switch to read.	
24.	Move atomizer capillary to sample solution.	Wait for readout to reach a stable value.

25. Record readout value on worksheet.

26. Transfer capillary to blank solution.

27. Switch auto/read switch to auto.

Repeat Steps 22-27 for all standard and sample solutions.

See instructions in the operating manual for calibration and use of curve corrector and direct readout attachments.

CALCULATIONS

The concentration of zirconium in the diluted sample can be obtained by either of two methods. A calibration curve relating absorbance to concentration can be plotted from the calibration standard data and the zirconium in µg/ml corresponding to the sample absorbance can be read from this curve. The two standard, bracket method may also be used. The zirconium concentration of the diluted sample is then calculated from the following equation:

$$C = x_1 - \frac{[y_1 - y_s]}{[y_1 - y_2]} [x_1 - x_2] \qquad (1)$$

where

C = zirconium concentration of sample in µg/ml

y_s = sample absorbance

x_1 = concentration of high standard

x_2 = concentration of low standard

y_1 = absorbance of high standard

y_2 = absorbance of low standard.

The result to be reported is calculated by substituting the concentration in µg/ml in the formula below and solving the equation.

$$\underline{M} = \frac{[(C + \text{bias}) \pm \text{sd}](201)}{1000(91.22)} \qquad (2)$$

where

M	=	molarity of zirconium in the sample
C	=	zirconium concentration in µg/ml
bias	=	µg of zirconium added or subtracted as shown by control data
sd	=	standard deviation of control data
201	=	dilution factor
91.22	=	atomic weight of zirconium.

REFERENCE

1. W. Slavin, A. Venghiattis, D. C. Manning, "Some Recent Experience with the Nitrous Oxide-Acetylene Flame", Atomic Absorption Newsletter, 5, No. 4, July-August 1966, p 87. (Perkin-Elmer Corporation, Norwalk, Connecticut).

2. A. M. Bond, "Use of Ammonium Fluoride in Determination of Zirconium and Other Elements by Atomic Absorption Spectrometry in the Nitrous Oxide-Acetylene Flame", Analytical Chemistry, Vol. 42, No. 8 (July 1970) p 932.

December 1970
T. R. Lyon
S. D. Reeder

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Zirconium

CHARGE NUMBER _____ PROCEDURE Zr-AA-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: a_0 d_1 $a_1/d_2/a_2$	conc, µg	Absorbance	µg in Sample	Correction	Standard Deviation			RESULT M
Zr-1	01 / 201		0470	311	-04	131			068 ± 0.03
Std 1		300	0455						
Std 2		350	0525						

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$\text{µg Zr in Sample} = 350 - \left(\frac{0525 - 0470}{0525 - 0455}\right)(350 - 300) = 311$$

$$\text{Result} = \frac{[(311 - 0.4) \pm 131](201)}{(1000)(9122)} = 068 \pm 003\ M$$

APPROVED BY _____

TITRIMETRIC DETERMINATION OF ZIRCONIUM WITH CUPFERRON

ABSTRACT

Zirconium is titrated with cupferron in a 3.6M $(NH_4)_2SO_4$-2M H_2SO_4 medium to an amperometric end point[1].

APPLICABILITY

Though quite selective, cupferron (ammonium salt of nitrosophenylhydroxylamine) reacts[1,2] with a number of common metal ions in 2M H_2SO_4 medium (Table I). This method, therefore, is limited to samples that contain only negligible amounts of metallic interferences. Examples of samples that can be analyzed are solutions of zirconium salts, solutions of Zircaloy and Zircaloy-clad fuels, and solutions such as those encountered in fuel processing and waste calcination that contain zirconium and aluminum or aluminum plus calcium.

Other potential interferences are strong oxidants that destroy the cupferron and complexing anions that keep the zirconium from reacting quantitatively and rapidly with cupferron. Examples of oxidants are nitrate above 10 mM per sample aliquot, cerium(IV), chromium(VI), and large amounts of perchlorate. Cupferron forms an extremely stable complex with zirconium so most anions including chloride, citrate, fluoride, nitrate, oxalate, sulfate, and tartrate can be tolerated at mmole levels[1]. Fluoride which often is present in zirconium-containing solutions, is tolerated up to a molar ratio of 30 to 1. Phosphate at 1 to 1 seriously retards the formation of zirconium cupferrate but can be tolerated if sufficient time is allowed for equilibrium to be established[1].

The harmful effects of oxidants and large amounts of fluoride can be reduced or eliminated by evaporating the sample to sulfuric acid fumes initially, then reducing residual oxidants with hydroxylamine. The addition of aluminum also removes fluoride interference[1].

The overall range of this method is 0.01 to 0.10 mM of zirconium Best precision is obtained above 0.025 mM.

TABLE I

PRECIPITATION OF METAL IONS BY CUPFERRON
IN 2M H_2SO_4 MEDIUM

Metal Ions	Extent of Precipitation and Effect of Ion on the Method
Bi(III), Fe(III), Ga(III), Hf(IV), Mo(V,VI), Nb(V), Sb(III), Sn(IV), Ta(V), Ti(IV), U(IV), V(IV,V), W(V,VI).	Complete or nearly complete precipitation; Serious positive interference.
Cu(II), lanthanides(III), Th(IV), Tl(III).	Partial precipitation; Positive interference increases as level of ion increases.
Alkali metals(I), alkaline earths (II), Al(III), Ag(I), As(III), Be(II), Ca(II), Cd(II), Co(II), Cr(III), Fe(II), Hg(II), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Ru(III,IV), Sc(III), Tl(I), U(VI), Y(III).	No precipitation; No interference expected even at high levels except that some ions may precipitate as the sulfate and carry down Zr. Examples of these are the alkaline earths and Pb(II).

DISCUSSION

Cupferron reacts with zirconium at a stoichiometric 4 to 1 ratio when the zirconium is in the form of the reactive monomer. Fuming the sample with sulfuric acid assures this. The end point of the titration is determined by monitoring the concentration of uncomplexed cupferron amperometrically at a potential of -0.75 V versus the standard calomel electrode. When all available zirconium is complexed and free cupferron appears, the cupferron is reduced at the surface of a dropping mercury electrode resulting in a current that rises linearly with increasing free cupferron concentration. The end point is the intersection of this straight line and the straight line constructed through the current versus volume of titrant points before the appearance of free cupferron. The titration conditions originally recommended by Olson and Elving[1], i.e., titration in 1.8M H_2SO_4 medium at -0.84 V, gave a titration curve characterized by a pre-end point hump that introduced much uncertainty in the location of the end point. This difficulty has been corrected by lowering the potential to -0.75 V[3] and by loading the titration medium with ammonium sulfate[4]. The solidification of the 1% gelatin solution also has been a problem. Solid gelatin, a highly satisfactory substitute[5], therefore is used.

SAFETY PRECAUTIONS

The initial steps of the analysis involve the addition of 9M H_2SO_4 and the evaporation of the sample to sulfuric acid fumes. Wear rubber gloves when handling the sulfuric acid and perform the fuming in a fume hood behind a safety shield. Cool the fumed sample before adding the 4M $(NH_4)_2SO_4$ solution; however, do not immerse the fuming beaker directly into cold water. The beaker is likely to shatter resulting in dangerous spattering.

APPARATUS AND REAGENTS

A. Apparatus

1. Ampot, Sargent, modified with compensator or Model III Sargent Polarograph, or equivalent.

2. Beakers, Berzelius tall-form, 200-ml.

3. Buret, 10-ml, graduated in 0.05-ml increments.

4. Electrode assembly, standard calomel and dropping mercury electrodes (with attached mercury reservoir) mounted through a Teflon plug which fits the 200-ml tall-form beaker. This assembly also contains two polyethylene tubing inlets for the nitrogen purge and sweep gas.

5. Graduated cylinders, assorted sizes.

6. Hot plate.

7. Magnetic stirrer, with plastic-coated magnetic stirring bars.

8. Pipets, macro and micro, assorted sizes with rubber suction bulb and control syringe.

9. Valve, 2-way valve for directing the nitrogen gas to either purge or sweep as desired. Valve is mounted on the Ampot.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium sulfate solution, 4M. Dissolve 1060 g of $(NH_4)_2SO_4$ in 1800 ml of water and dilute to 2 liters with water.

2. Cupferron solution, 0.0500M. Dissolve 7.7580 g of cupferron in water and dilute to 1 liter. Store the solution in the refrigerator when not in use. Prepare a new solution after 5 days. Cupferron stored over ammonium carbonate as obtained from J. T. Baker is satisfactory. If purification is necessary, purify the reagent as follows:

   Dissolve 25 g of the reagent in 250 ml of water in a 1-liter separatory funnel. Add 15 ml of conc HCl and shake. Add 75 ml of diethyl ether and mix thoroughly

by shaking. Reject the aqueous phase. Add ammonium hydroxide until basic to litmus and sufficient water until the precipitate solubilizes. Transfer small portions of the ammonium hydroxide phase to large beakers and precipitate the purified ammonia salt with acetone. Collect the product on a Buchner funnel, rinse several times with acetone, and air dry.

3. Gelatin, solid powder.

4. Hydroxylamine sulfate, 2M. Dissolve 32.8 g of $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 200 ml.

5. Nitrogen, water-pumped, in large cylinders.

6. Sulfuric acid, 9M.

7. Zirconium Bench and Control Standards. Prepare these standards from pure crystal bar zirconium to cover the range 0.01 to 0.1 mM of zirconium. Dissolve the zirconium metal in a minimum of hydrofluoric acid in a plastic container and dilute to volume with water. The standards are best stored in screw-cap polyethylene bottles.

PROCEDURES

A. Preliminary Operations

1. Connect the black-tipped wire of the Sargent Ampot to the dropping mercury electrode and the red-tipped wire to the Calomel electrode.

2. Start the dropping mercury electrode, making sure that no air bubbles exist in the mercury lines.

3. Open the nitrogen valve and adjust the flow to a rate of about 2 bubbles per sec.

4. Keep the "Rev. Cell" switch on the position (- +).

5. Set the "Current Mult" on "X_1".

6. Leave the "Current" switch on normal.

7. Leave the helipot labeled "App. E.M.F." at "750".

8. Turn "Battery" to "On" and set the "Range E.M.F." to 1.00 V.

9. Leave the "Circuit" "Open" until ready to take readings and then throw the switch to "Damped".

B. Blank

Recent experience indicates that no blank determination is necessary for this method.

C. Analysis of Bench-Control Standard

Process a bench standard with each series of samples per Procedure D. The result obtained must fall within the limits specified. If not, reprocess the standard. Consult your supervisor if difficulties persist.

D. Analysis of Samples

NOTE: The cupferron titrant is stored in a refrigerator. Take it out of the refrigerator enough in advance to allow the solution to warm to room temperature.

1. Pipet a sample aliquot containing 0.01 to 0.10 mM of Zr into a 200-ml beaker.

   For best precision, work at the high end of the range 0.025 to 0.10 mM.

2. Add 20 ml of 9M H_2SO_4, evaporate to the appearance of H_2SO_4 fumes, and fume for 5 min.

   Most Zr samples contain F^- so do not use a cover glass. Evaporate carefully without spattering the sample.

3. Let the beaker and contents cool to room temperature, add 80 ml of 4M $(NH_4)_2SO_4$, and 1 ml of 2M $(NH_2OH)_2 \cdot H_2SO_4$, and mix by magnetic stirring.

4. Chill the solution to 25°C or less in a cold water bath.

   Above 25°C, cupferron decomposes readily. Measure the temperature with a thermometer.

5. Add about 1/2 micro spatula full of solid gelatin powder.

6. Rinse the electrode assembly with water and fit it onto the beaker.

7. Bubble nitrogen through the solution for at least 5 min with the stirrer on.	The purpose of this step is to remove oxygen.
8. Change the nitrogen to sweep over the solution and with the stirrer off, measure the mercury drop time. It should be between 2 and 5 sec per drop. If necessary, adjust the height of the mercury reservoir to obtain the required drop time.	If readjustment of the mercury reservoir height fails to give the desired drop time, the length of the capillary electrode must be altered.
9. Fill the buret with fresh 0.0500M cupferron solution and titrate the sample "amperometrically" with the "Circuit" switch in the "Damped" position. 10. Record the data and calculate the results as described under CALCULATIONS.	"Amperometric" titration involves (a) the addition of a constant increment of titrant with the nitrogen bubbling through the solution and the stirrer on, (b) the passage of nitrogen through the solution for another 30 sec with the stirrer on, (c) waiting 60 sec with the stirrer off and the nitrogen sweeping over the solution, and (d) recording the galvanometer (current) reading and the corresponding volume of titrant. This four-step process is repeated until 5 points are obtained beyond the break or end point. The recommended titrant increments are 0.10 ml, 0.25 ml, and 0.50 ml for the zirconium levels 0.01 to 0.025, 0.025 to 0.050, and 0.050 to 0.100 mM, respectively.

CALCULATIONS

Record the titration (titrant volumes and galvanometer readings) data on a columnar sheet of paper, then determine the end point by plotting galvanometer readings on the vertical axis against titrant volume on the horizontal axis (Figure 1). The end point is the intersection of the two lines defined by the points before and after the break.

Record the titrant volume and the sampling data on the work sheet and calculate the results as described on the work sheet. Report all results to 3 significant figures.

The factor 0.25 appears in the equation for the calculation of the mmole of zirconium in the sample aliquot. This factor converts mmole cupferron to mmole zirconium, for as noted in the discussion, cupferron reacts with zirconium in the ratio 4 to 1.

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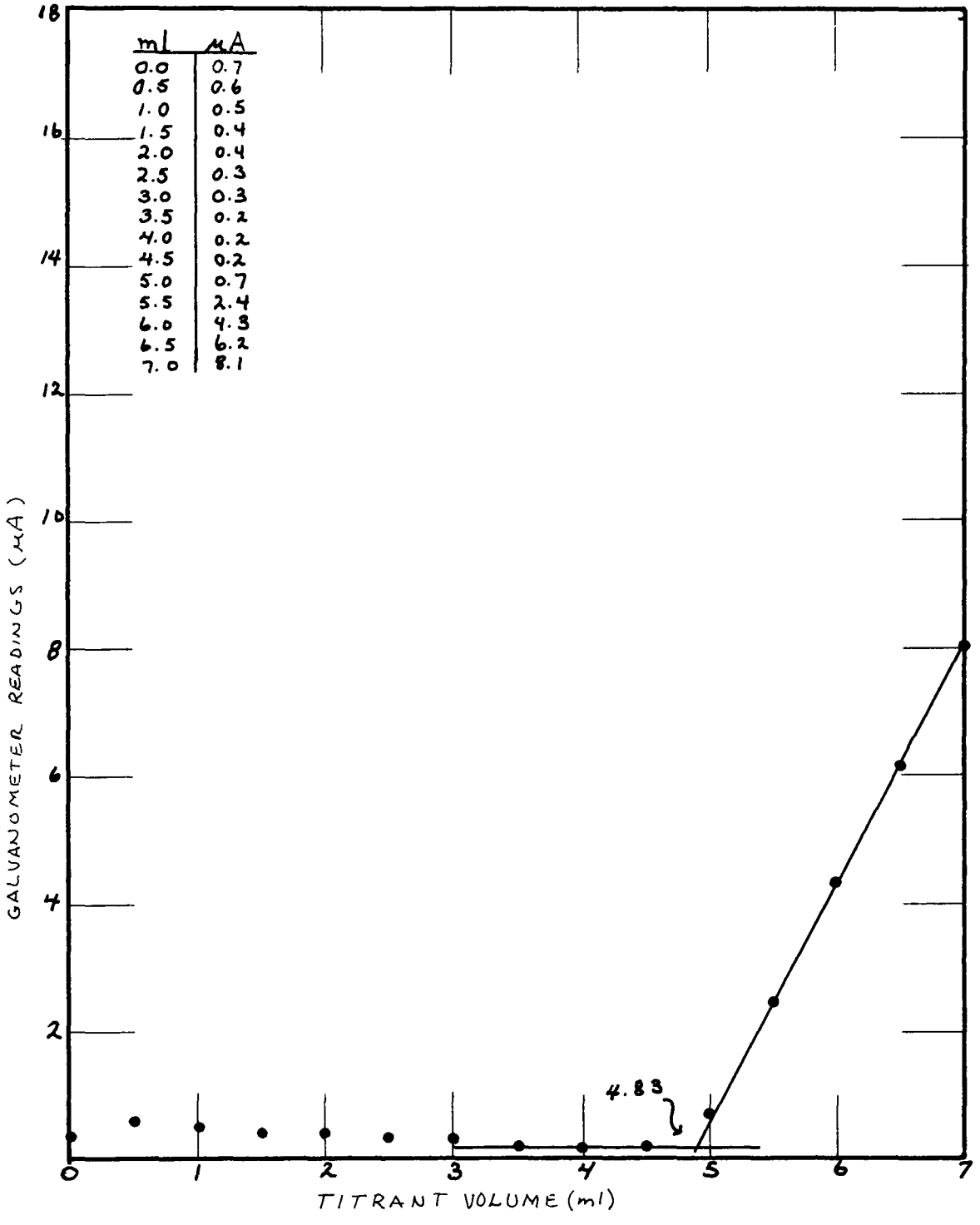

Fig. 1 Titration data.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

ACTIVITY (mR/hr) _____ DETERMINATION Zirconium

CHARGE NUMBER _____ PROCEDURE Zr-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Cupferron M	End Point From Graph ml	mM Zr in Aliquot Analyzed	mM Zr Corrected For Bias				RESULT M
No. 101	0.100 ml	0.0500	4.83	0.060	0.059 ± 0.002				0.59 ± 0.02

ANALYZED BY _____ DATE _____

CALCULATIONS:

$$C = AB(0.25) = (0.0500)(4.83)(0.25) = 0.0604 \text{ mM Zr}$$

$$\text{Result} = \frac{D}{\text{Vol. Sample}} = \frac{0.059 \pm 0.002}{0.100} = 0.59 \pm 0.02 \text{ M}$$

APPROVED BY _____