1971

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Digital Object Identifier: https://doi.org/10.13023/kwrri.rr.42

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Repository Citation

Christian, Gary D.; Matkovich, Charles E.; and Schertz, W. Lynn, "Procedures for Trace Analysis of Dissolved Inorganic and Organic Constituents in Water" (1971). *KWRRI Research Reports*. 153.
https://uknowledge.uky.edu/kwrri_reports/153

PROCEDURES FOR TRACE ANALYSIS OF DISSOLVED INORGANIC AND ORGANIC CONSTITUENTS IN WATER

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Project Number A-013-KY (Completion Report)
Agreement Nos. 14-01-0001-1636
14-31-0001-3017
July 1968 - June 1971

The work upon which this report is based was supported by funds provided by the United States Department of the Interior, Office of Water Resources Research, as authorized under the Water Resources Act of 1964.

ABSTRACT

A study of different solvent systems for the atomic absorption determination of cobalt revealed that acetone results in best sensitivity. Acetone is the solvent of choice for the sensitive measurement of several metals. Hence, methods were investigated for the separation of acetone from water by salting out so that possible solvent extraction of metal chelates into this solvent could be performed. About two-thirds saturated calcium chloride proved to be the best system for salting out of the acetone. It is essentially a neutral salt and is in general a weakly complexing salt, resulting in minimum interference in solvent extractions. Solvent extraction of several elements as dithizone or APDC chelates into acetone was successful.

A new anodic stripping voltammetric method was developed for stability studies of the poorly characterized APDC chelates. The method allows the study of highly insoluble chelates.

Over sixty elements were successfully measured by flame emission spectroscopy using the nitrous oxide-acetylene flame. Optimum instrumental and flame parameters and detection limits for each element were determined.

High concentrations of neutral salts have been shown to enhance titration curve breaks of weak bases titrated in either aqueous or nonaqueous solutions. This allowed the coulometric titration of microequivalent quantities of bases with K_b values as small as 4×10^{-12}. Volumetric titration of bases with K_b values of 10^{-14} was possible in nonaqueous solvents.

KEYWORDS: atomic absorption spectroscopy, solvent extraction*, acetone*, chelate stability, flame emission spectroscopy*, nitrous oxide-acetylene flame*, concentrated salts*, acid-base titrations, nonaqueous titrations, coulometric titrations.

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CHAPTER I

INTRODUCTION

For purposes of studying pollution, it is essential to have available highly sensitive methods of analysis for the type of pollution in question. Atomic absorption spectroscopy(1) is becoming an increasingly important tool for determining trace metals. This tendency is due to the high specificity and sensitivity and ease in manipulation of atomic absorption spectroscopy. Often, little or no sample preparation is required, and this technique is relatively inexpensive and rapid compared to methods such as neutron activation analysis. However, it does not possess the sensitivity necessary for the direct analysis of several elements in natural waters. This is especially true for elements which form stable oxides in the flame (e.g., Mo, Ti, Al) and for those elements whose resonance absorption lines occur near the vacuum ultraviolet region (e.g., Se, As). One objective of this project was to investigate means of enhancing existing sensitivities for several elements.

One means of markedly increasing sensitivities when using a flame atomizer is the use of organic solvents. Cobalt is one of the more difficult to determine elements because of a non-absorbed ion line that cannot be resolved from the resonance line. Thus, several organic solvents were studied for maximum enhancement of cobalt sensitivity. In view of previous results which showed that acetone is the solvent of choice for maximum sensitivity of several elements, this solvent was included in the study.

Although acetone possesses excellent sensitivity characteristics for atomic absorption, because it is water miscible, conventional solvent extractions cannot be performed with it. Simple addition of acetone to a solution only serves to dilute it and the acetone is not in pure form. Acetone can, however, be partially separated from water by adding high concentrations of inorganic salts (e.g., saturated calcium chloride). Solvent extraction into acetone can be performed under these conditions. Therefore, methods were studied for salting out of this solvent from aqueous solutions with the idea of performing solvent extractions.

Ammonium 1-pyrrolidinecarbodithioate (APDC) is a useful chelating agent for the solvent extraction of a large number of metals from acid solution. Little is known concerning the nature of the complexes formed. Metal/ligand ratios and formation constants of several metal APDC chelates were investigated, using a new polarographic technique.

The nitrous oxide-acetylene flame has been used in recent years for the atomic absorption determination of refractory elements. This is a high temperature flame that also has a very reducing atmosphere. Flame atomic emission spectroscopy ("flame photometry") has in the past been generally limited to the alkali and alkaline earth elements because extremely high temperatures are required for the excitation of other elements. An investigation was undertaken to determine if flame emission could be obtained for a large number of elements in the nitrous oxide-acetylene flame.

Atomic absorption spectroscopy is limited in its application for the determination of nonmetals. This is because the resonance lines for these elements occur in the vacuum ultraviolet region where the flame and atmosphere absorb radiation. Hence other methods for determining traces of nonmetals in water were studied.

Constant current coulometric titrations(2) possess certain advantages over volumetric titrations for quantitative analysis. Among these are the elimination of preparation and storage of standard solutions (an important step in reducing technician error), high precision and accuracy, the ability to generate unstable titrants, direct readout, and ease of automation. They are applicable to trace analysis, and surpass nearly all other analytical methods in precision in many cases, for very small samples and for milligram samples. For example, titrations of nine nanograms of arsenic(3) or four nanograms of chromium(4) in 30 ml. have been titrated with less than 5% error. On the other hand, standard deviations of 0.003-0.005% have been attained in the titration of high purity samples of acids and bases(5), halide salts(6) and potassium dichromate(7). Because of these distinct advantages, methods of coulometric analysis of basic substances in water were investigated.

Coulometric acid-base titrations have been performed in aqueous solutions(5, 8, 9, 10) but the range of compounds which can be titrated is limited for very weak acids or bases due to a small change in pH at the endpoint. The acidity or basicity of weak acids and bases can be markedly enhanced in non-aqueous volumetric titrations. Very little work has been performed on coulometric titrations in non-aqueous solvents. Streuli and coworkers (11,12,13) and others(14,15) have titrated bases while Crisler and Conlan(16) and Streuli(17) have titrated acids in non-aqueous solvents.

Chritchfield and Johnson(18) reported that weak bases in strong aqueous solutions of neutral salts can be titrated in much the same manner as in non-aqueous solvents. While bases with ionization constants less than 10^{-9} are too weak to titrate in water, titrations in concentrated salt solutions are applicable to bases with ionization constants as low as 10^{-12}. This is apparently due to an increase in the activity of the hydrogen ion in these solutions. This is supported by further work(19) in which comparative pH and acidity function (H_o) data indicate that the decrease in pH of acids by neutral salts is accompanied by corresponding increase in acidity of the solution. Salts with the highest positive heat of solution produce the greatest change in pH. Kilpartick and coworkers have investigated the dissociation constants of benzoic acid(20), acetic acid(21), and glycolic acid(22) in salt solutions while Rosenthal and Dwyer(23) have considered the factors which affect the efficiency of the salt effect. Paul and Long(24) have reviewed H_o and related indicator acidity functions, including the effect of neutral salts on H_o.

Coulometric titrations of weak bases in neutral salt solutions have not been previously performed. Therefore, these titrations were investigated. Nonaqueous solvents are widely used to enhance the sensitivity for titrating weak bases (and acids). An investigation was undertaken to see if concentrated neutral salts might further enhance the acidity of the proton in nonaqueous solvents.

CHAPTER II

ATOMIC ABSORPTION DETERMINATION OF COBALT

A. Experimental. Solutions of cobalt in different solvents were prepared as described previously for manganese.(25)

Atomic absorption measurements were made in an Instrumentation Laboratory Atomic Absorption Spectrophotometer, Model 153. Absorption could be read on a digital counter or recorded on a mV recorder, either directly or after integrating the signal for a pre-set period of time. Westinghouse hollow cathode lamps were used as the radiation source. The 2407.2 A line was used for absorptive measurements. An air-hydrogen flame was used with a total consumption burner unless other wise specified. Some studies were made with an air-acetylene flame using a Boling premix burner.

B. Results and Discussion. The absorption characteristics of cobalt are strongly dependent on the gas pressure ratios of fuel and oxidant.(26) Effects of air and hydrogen pressures with a total consumption burner were studied for aqueous and acetone solutions of cobalt. The optimum air pressure in all cases was 20 psi. The best hydrogen pressure was 6, 8, and 8 psi, respectively, for acetone, ethanol and aqueous solutions. These are fairly oxidizing flames, as used by other workers for best sensitivity.

The burner height is also important for obtaining maximum sensitivity and minimum solvent absorbance for the different solvent systems. A study was made of the effect of burner height on absorbance by cobalt and by the solvent, using the optimum fuel and support gas pressures above. Whereas manganese absorbance increased linearly with decreasing height in the flame[25] this was not true for cobalt. A relatively low height in the flame resulted in maximum net absorption for cobalt. This occurred at 15, 12.5, and 17.5 mm. for aqueous, ethanol, and acetone solutions, respectively. The maximum net cobalt absorption for acetone solutions coincided with minimum solvent absorption. Ethanol absorption was not critically dependent on burner height except near the base of the flame, but absorption by water increased gradually with decreasing burner height. All the solvents absorbed appreciably at 10 mm. or less from the burner top. Supression of cobalt absorption by iron is less at low burner heights.[27]

It is apparent from the above studies that absorption was markedly dependent on the solvent employed. Calibration curves for cobalt in the different solvents are shown in Figure 1. As found for manganese,[25] acetone was the best solvent for enhanced sensitivity of cobalt absorption. Although cobalt cannot be dissolved easily in methylisobutyl ketone (MIBK) or ethyl acetate, absorption in these solvents should approximate that for the methanol solutions.[25]

Similar studies were done with a pre-mix burner using a Boling head. In most cases, there was not as great a dependence of the absorbance on the burner height as compared to the total consumption burner. The relative sensitivities of cobalt in the solvents were the same for the pre-mix burner as for the total consumption burner, i.e., acetone > MeOH > ETOH > H_2O. The detection limit for cobalt in acetone with the pre-mix burner was 0.002 ppm.

C. Conclusion. Excellent sensitivity can be obtained for cobalt absorbance by employing organic solvents, using either a pre-mix (Boling head) burner or a total consumption burner. Pure acetone results in maximum sensitivity with both burners. The absorbance using the total consumption burner is markedly dependent on the gas flow rates for each of the solvent systems, but not so markedly with the pre-mix burner.

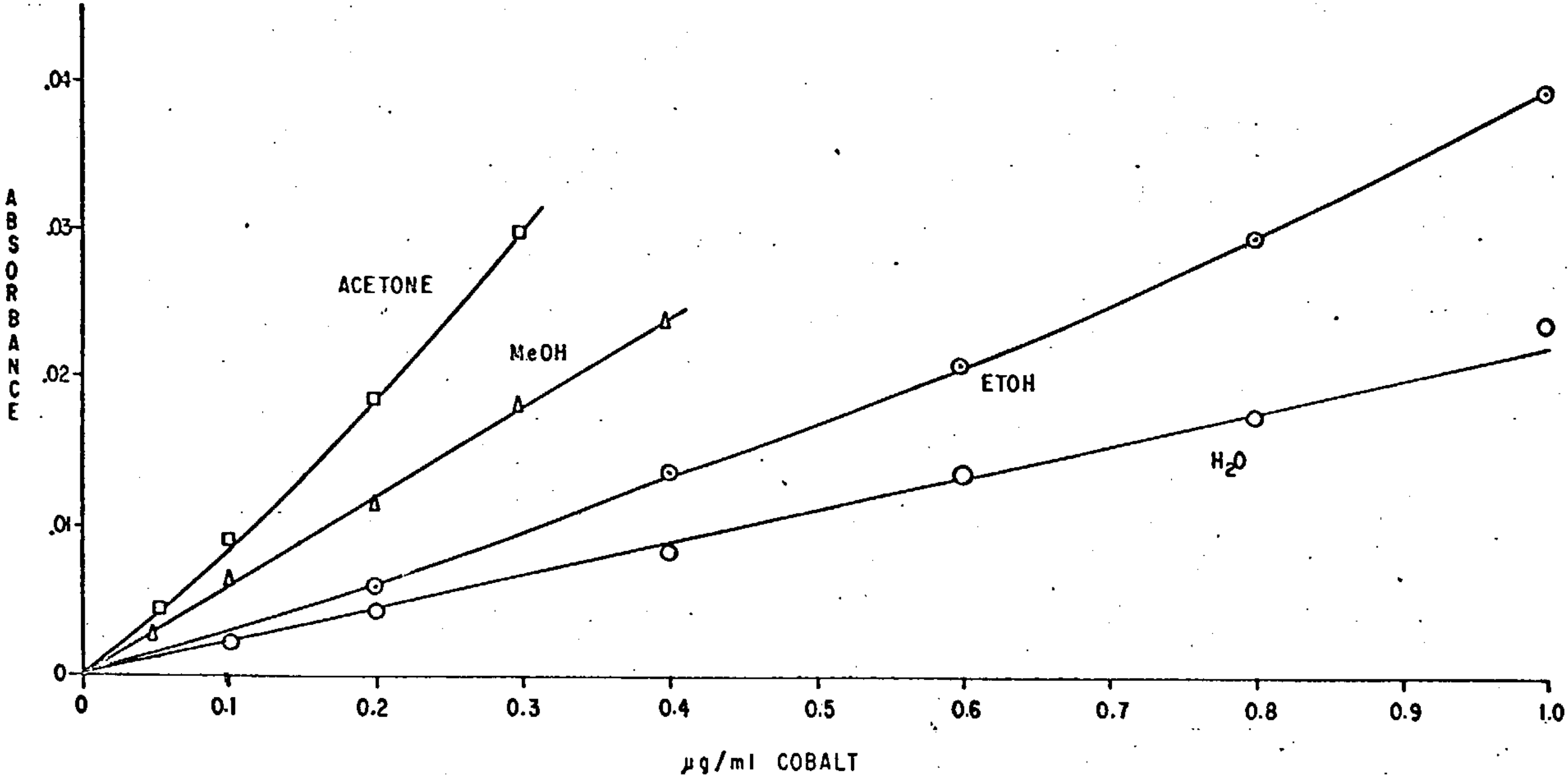

FIG. 1 CALIBRATION CURVES OF COBALT IN DIFFERENT SOLVENTS AT 2407.3 Å.

CHAPTER III

SALTING OUT OF ACETONE FROM AQUEOUS SOLUTIONS

A. Introduction. Atomic absorption analysis for trace amounts of metals in an organic solvent has been observed by Allan(28, 29) and Robinson(30) to be more sensitive than atomic absorption analysis in aqueous solution. Robinson(30) found that acetone gave the maximum sensitivity for Ni analysis. Feldman, Bosshart, and Christian(31) determined that acetone gave the best results for Mn and for Co(32). They also postulated that acetone might be "the solvent of choice" for other elements as well. Table 1 gives some of the data collected on the study of various organic solvents and their effect on the detection limits for several metals. Acetone gives the smallest detection limit in every case. Acetone usually gives a two to ten fold enhancement of detection limit over similar aqueous solutions in dilute solutions. In more concentrated solutions, 5 ppm or larger, the amount of enhancement decreases and is usually in the range of two to four fold more sensitive.

The increased sensitivity of acetone cannot be realized by solvent extraction because acetone is miscible with water. However, separation of an acetone phase is possible if a high concentration of salt is added to a mixture of acetone and water. Table 2 lists some of the results of the salting out investigation. All values listed are for room temperature.

B. Discussion. Any precipitation during the extraction procedure would probably lead to coprecipitation and therefore render the extraction process quantitatively useless. Therefore only those salts showing significant phase separation and no precipitation can be utilized in extractions into acetone by the salting out effect. Note that most of the salts showing large phase separations have a strong affinity toward water and are either deliquescent or hygroscopic.

TABLE 1

ATOMIC ABSORPTION DETECTION LIMITS IN VARIOUS SOLVENTS (ppm)

	Solvent						
Elment	Water	Acetone	MIBK	EtOH	MeOH	CCl_4	EtOAC
Ca	0.0030	0.0020	0.0020				
Cd	0.0010[A]	0.0002					
Cr	0.0020[A]	0.0008					
Co	0.020	0.0025	0.0086	0.0078	0.0180	0.2000	0.0092
Cu	0.0050[A]	0.0020					
Mn	0.0090	0.0020	0.0050	0.0050	0.011		0.0070
Mo	0.10[A]	0.010					
Ni	0.022	0.010	0.010		0.020		0.013
V	0.20[A]	0.050	0.070	0.070	0.14		0.050
Zn	0.0050[A]	0.0010					

A = Instrumentation Laboratory Inc., "Standard Conditions I. L. Model 153," Watertown, Massachusetts.

TABLE 2

RECOVERY OF 50 Ml. OF ACETONE ADDED TO 50 Ml. SATURATED SALT SOLUTIONS

Salt	% Acetone Recovered	ppt. Observed
$Al(OH)_3$	no sepn	NO
$AlCl_3$	59.6	NO
$AlBr_3$	no sepn	NO
AlI_3	no sepn	NO
$Al(OAC)_3$	no sepn	NO
$Al_2(SO_4)_3$	no sepn	NO
$Ba(OH)_2$	no sepn	NO
BaF_2	no sepn	YES
$BaCl_2$	no sepn	YES
BaI_2	no sepn	YES
$Ba(ClO_4)_2$	no sepn	NO
$Ca(OH)_2$	no sepn	NO
CaF_2	no sepn	NO
$CaCl_2$	67.6	NO
$CaBr_2$	no sepn	NO
CaI_2		
$Ca(NO_3)_2$	no sepn	NO
$CaCO_3$	no sepn	NO

TABLE 2 (Continued)

Salt	% Acetone Recovered	ppt. Observed
$CaSO_4$	no sepn	NO
$Ca(OAC)_2$	no sepn	YES
$CuSO_4$	no sepn	YES
KOH	95.6	NO
KF	99.2	NO
KCl	no sepn	YES
KBr	no sepn	YES
KI	no sepn	NO
KNO_3	no sepn	NO
K_2SO_4	no sepn	NO
KOAC	92.4	NO
K_3 citrate	105.0	NO
LiOH	no sepn	YES
LiF	no sepn	NO
LiCl	no sepn	NO
LiBr	no sepn	NO
LiI	no sepn	NO
LiOAC	88.0	
Li_2SO_4	no sepn	YES
$Mg(OH)_2$	no sepn	YES

TABLE 2 (Continued)

Salt	% Acetone Recovered	ppt. Observed
$MgCl_2$	64.0	NO
$MgBr_2$	no sepn	NO
MgI_2	no sepn	NO
$Mg(OAC)_2$	91.2	NO
$MgSO_4$	no sepn	YES
$Mg(C104)_2$	no sepn	NO
MgH citrate	no sepn	YES
$Mn (OH)_2$	no sepn	NO
$MnCl_2$	74.0	NO
$MnSO_4$	108.8	NO
NaOH	93.2	NO
NaF	no sepn	YES
NaCl	76.4	Yes
NaBr	21.6	YES
NaI	no sepn	NO
NaOAC	86.0	YES
Na_2SO_4	no sepn	YES
Na_2H citrate	118.0	NO
Na_2CO_3	131.6	YES

TABLE 2 (Continued)

Salt	% Acetone Recovered	ppt. Observed
Na_2HPO_4	no sepn	YES
NaH_2PO_4	110.4	YES
$NaNO_3$	no sepn	YES
NH_4OAC	no sepn	NO
NH_4F	99.2	NO
NH_4Cl	48.0	YES
NH_4Br	no sepn	YES
NH_4I	no sepn	NO
NH_4OAC	95.6	NO
$(NH_4)_2SO_4$	117.6	YES
NH_4NO_3	no sepn	YES
NH_4 citrate	105.2	NO
$Sr(OH)_2$	no sepn	YES
$SrCl_2$	73.3	YES
$SrBr_2$	no sepn	YES
SrF_2	no sepn	NO
$Sr(OAC)_2$	no sepn	YES
$Zn(OH)_2$	no sepn	NO
$ZnCl_2$	no sepn	NO

TABLE 2 (Continued)

Salt	% Acetone Recovered	ppt. Observed
$ZnBr_2$	no sepn	NO
ZnI_2	no sepn	NO

Those salts that showed > 100% recovery were all cloudy indicating that possibly not all of the water separated from the acetone phase during the 5-10 minutes before the readings were taken.

Three factors have to be considered when evaluating a salt and its potential salting out effect on acetone. First the solubility in acetone must be negligible. Salts such as the Li halides which might be expected to cause phase separation based on the other parameters show no separation because they are soluble in acetone. The Li halides, according to Glasstone(33), are soluble in both phases and show a negative deviation from Raoult's law, or salting in effect, and thus the two phases actually become more soluble in each other.

Secondly, the solubility of the salt in water must be large. This is probably connected with the theory that solute molecules tie up the solvent water molecules in hydration spheres thus leaving less water available to dissolve the acetone. Note that all of the salts which cause phase separation are at least 1.5 M when saturated in water.

Finally, the lyrophilic series has to be considered. It was observed several decades ago that suspended water loving substances (gels) would precipitate upon addition of electrolytes. Certain electrolytes seemed to cause more precipitation than others and thus the lyrophilic series was emperically set up. Glasstone(33) lists the series as Mg^{+2}>, $Ca^{+2} > Sr^{+2} > Ba^{+2} > Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$ for cations and $citrate^{-3} > tartrate^{-3} > SO_4^{-2} > OAC^{-} > Cl^{-} > NO_3^{-} > ClO_3^{-} > I^{-} > CNS^{-}$ for anions. A Dobry-Duclaux(34) reports a slightly different order for the cations $Mg^{+2} > Sr^{+2} > Ca^{+2} > Ba^{+2} > K^{+} > Na^{+} > NH_4^{+} > Li^{+} >$ and $SO_4^{-2} > OAC^{-} > Cl^{-} > NO_3^{-} > Br^{-} > I^{-} > CNS^{-}$ for the anions which is similar to Glasstone's order.

In conjunction with this study, it was of interest to determine how much salt was in the acetone phase after separation. If large amounts of salt are present, they can interfer with the analysis. Table 3 lists the concentration of salt found in the acetone phase for all of the salts that showed considerable phase

TABLE 3

CONCENTRATION OF DISSOLVED SALTS IN SEPARATED ACETONE LAYER

Compound	g./50 ml.	ppm
$AlCl_3$	0.0172	344
$CaCl_2$	0.0106	212
KOH	0.0036	72
$MgCl_2$	0.0146	292
NaOAC	0.0740	1480
NaOH	0.0038	76
Na_2CO_3	0.0156	312
NaCl	0.1746	392
$MnSO_4$	0.1582	3164
$SrCl_2$	0.0272	544
NaBr	0.4962	19924
NH_4OAC	0.0458	916
NaH_2PO_4	0.5160	10320

separation without precipitation and therefore might be useful in solvent extraction into acetone. The observed amount of salt is always higher than the amount predicted by the solubility of that salt in acetone. This is expected because of the water present in the acetone after extraction. A few salts such as NaBr and NaH_2PO_4 are present in considerable quantity and thus might interfere. Heiftze and Malmstadt(35) observed that the presence of 100 ppm NaCl had little effect on evaporation rate or droplet size and one could predict from that sutdy that salts present at 100 ppm or less should not interfere in atomic absorption analysis by changing the evaporation rate of the solvent.

The amount of water present in the acetone phase was determined by a modified Karl Fischer titration. The results are in Table 4. Results from the titrations of acetone samples titrated shortly after mixing and those titrated after 24 hours show large decreases in water content with time. Obviously, the water does not separate out into an equilibrium condition in a short time period of about 5 minutes. Other work with radioactive Co^{60} tracers on the extraction step support the above observation. It was found that most of the Co^{60}, greater than 90% was extracted in a time period of 15 minutes. Therefore, the time allowed for separation of the acetone phase is critical when doing an analysis. The time period can be shortened by centrifuging the water-acetone mixture.

TABLE 4

CONCENTRATION OF WATER IN SEPARATED ACETONE LAYER

Salting Out Agent	ml. of H_2O per 100 ml. of Acetone	
	After 24 hours	Right after mixing
None-Acetone Only	0.0212	0.027
$CaCl_2$	0.321	0.665
NaBr	1.580	--
NaOH	--[A]	0.052
KOH	--[A]	0.067
NH_4OAC	1.590	2.190
NaCl	1.650	--
NaOAC	1.810	--
$SrCl_2$	1.030	1.410
$AlCl_3$	0.470	0.635
Na_2CO_3	2.150	18.400
$MgCl_2$	0.304	--
$MnSO_4$	2.480	6.180
K_3 citrate	2.100	4.220
Na_2H citrate	4.209	13.5

[A] NaOH and KOH had to be tested shortly after mixing because the acetone phases underwent reactions with the production of a yellow-brown ppt, after a few hours.

CHAPTER IV

SOLVENT EXTRACTION WITH ACETONE

The nominal pH of an aqueous solution saturated with both calcium chloride and acetone was 7.67 ± 0.08. After addition of 20 ml. of water to 30 ml. of the saturated aqueous solution, the nominal pH was 8.85 ± 0.08. Small amounts of either bases or acids effectively changed the nominal pH of saturated calcium chloride solutions. However, in routine analyses, buffers would be required to maintain a reproducible pH. The solvent extraction procedure was as follows: 340 ml. of aqueous solution saturated with both calcium chloride and acetone (about 30% acetone) was added to 160 ml. of water. This represented a ratio of saturated calcium chloride solution to sample solution of 3 to 2, which was found to be near optimum condition for acetone recovery based on a phase diagram of H_2O-$CaCl_2$-acetone. The nominal pH was adjusted with hydrochloric acid before addition of the acetone. Nineteen solutions ranging in pH from about 9 to 0 at about 1/2 pH unit intervals were prepared. A third of each of the above nineteen solutions was taken for extraction studies with dithizone. The remaining two thirds of each solution were used for oxine and APDC extraction studies. The calcium chloride solutions were purified as follows: To each of the pH adjusted solutions (80 ml.) approximately 25 ml. of 50 ppm dithizone in acetone was added. The mixtures were then thoroughly shaken. After the phases completely separated, the acetone phase was discarded and a fresh portion of 50 ppm dithizone in acetone was added. The above steps were repeated five times. Dithizone extractable impurities in the calcium chloride and hydrochloric acid were thus removed. This step could also serve to saturate the aqueous phase with acetone. A similar procedure was used for studies with APDC and oxine.

Two ml. aliquots of the pH adjusted, purified, aqueous calcium chloride solution saturated with acetone were then added to either two ml. aliquots of 50 ppm dithizone in acetone to prepare blanks or to two ml. aliquots of a similar solution containing 1 - 10 ppm of the metal to be extracted. The portions were then mixed by a mechanical mixer and allowed to sit.

The concentrations of metal in the acetone phase after separation of the phases were determined for the samples and the blanks by flame spectroscopy. From the data, plots of nominal pH versus per cent metal in the acetone phase were constructed.

Scandium does not form a stable complex with dithizone. Scandium does, however, form a very strong chloride complex and has been observed to extract with 8 <u>M</u> HCl into tributylphosphate. In the present study, some distribution of scandium took place at all pH s studied with and without the presence of a chelating agent. This implies that the chloride complex of scandium was probably responsible for a large part of the observed scandium extraction into acetone.

Chromium (III) does not form a dithizonate complex and no extraction of chromium was observed in this study. Manganese (II) forms a relatively unstable complex with dithizone which extracts in basic solutions. Extractions with acetone indicated that the manganese dithizonate forms and does not extract, as one would expect to see extraction in acidic solution also for chloride complexes, and this does not occur.

Iron (II) has been observed to extract into carbon tetrachloride in the pH range 6 to 9. It has been found to extract into acetone in the present study. Iron (III) forms a very strong chloride complex and is well known to extract into various organic solvents from 6 - 7 <u>N</u> HCl. In the present study, an iron (III) dithizone complex seems to have formed. In basic medium, high concentrations of iron (III) can oxidize dithizone and can interfere in the extraction of other metals. The removal of iron (III) as the chloro complex or with other chelating agents in acidic solution prior to the extraction of other metals with dithizone is recommended.

Quantitative extraction of cobalt (II) with dithizone into carbon tetrachloride at a pH of 5.5 to 8.5 and into chloroform at a pH of 7 to 9 has been observed. In the present study cobalt extraction occurred both in very acidic solutions (possibly as a chloro complex) and in slightly acidic to slightly basic solution (probably as a dithizonate). Nickel (II) extraction at pH 8-11 was observed in acetone. Nickel, like cobalt, forms a weak chloro complex in 4.5 N HCl and 1.7 N calcium chloride and also, like cobalt, extracts at pH's lower than accountable for by dithizonate extraction.

Copper (II) quantitatively extracted into acetone and was the only one of the metals studied in the present investigation that formed stable extractable dithizonates in very acidic solution. Zinc (II) quantitatively extracted with dithizone into acetone from alkaline solution.

Irreproducible results were obtained in the extraction of titanium and vanadium with dithizone. These poor results could be due to the unstable dithizone chelates of these metals or to calcium interference in the analysis. Calcium was observed to interfere in the atomic absorption analysis of both vanadium and titanium in the nitrous oxide-acetylene flame.

In summary, the extractions of metal dithizonates into acetone with calcium chloride as a salting out agent closely resembles the extractions of these dithizonates into chloroform or carbon tetrachloride. The high per cent extractions found in acidic solution for scandium, iron, nickel and cobalt do not agree with literature data on dithizonate extractions but are probably due to extraction of ion association chloro complexes. Small shifts in pH's of maximum extraction compared to literature data are probably due to the change of solvent. Most dithizonate chelates have different optimum pH ranges for carbontetroachloride and chloroform due to differences in solubility in the two solvents and, therefore, changes in the optimum pH range for extraction into acetone as the solvent are expected.

Extractions with oxine as the chelating agent proved unsuccessful because oxine reacts with calcium and thus erratic results were obtained.

Extractions with APDC as the chelating agent were satisfactory. The procedure was similar to the procedure already described for dithizone extractions into acetone except that 0.01 ml. of freshly prepared 1% APDC solution and the correct amount of 1000 ppm stock metal solution were added to the aqueous phase rather than the acetone phase. Aqueous calcium chloride solutions were purified by extraction with APDC prior to use in the extraction studies.

The pH range for maximum metal extraction for most of the metals studied in this experiment agrees with the data presented for the same chelating agent using other organic solvents.

Titanium (IV) was observed to partially extract at all pH's studied. The nature of the extracting species is not known. Precision was not very good.

The per cent extration of chromium (III) was maximum in acidic solution and decreased to about 10% at pH 8.

Iron (III) and iron (II) were observed to partially extract in both acid and alkaline solution. Copper (II) and zinc (II) extracted efficiently with APDC at pH's 2-8 and 2-6, respectively.

Systems with large concentrations of salting out agents are much more complicated than the conventional systems with immiscible solvents. The high chloride ion concentration favors the formation of metal chloride complexes. The most general solvation form for the metal in these systems can be written as:

$$M^{n+}(H_2O)_A(\text{acetone})_B(HCl)_C(\text{chelating agent})_D$$

$$(\text{chelating agent anion})_E\ (Cl^-)_F$$

The undissociated chelating agent and hydrochloric acid probably are not important in the complex. The chloride ion concentration was primarily from the salting out agent and was, therefore, relatively independent of the pH.

As the pH changes, the exact form of the most stable solvated metal species can change from chelate to chloride complex and thus the per cent extracted can vary with the pH. In acidic solutions, the dissociation of the chelating agent is repressed whereas the chloride ion concentration remains the same. Thus, the metal has a tendency in acidic solutions to form a chloride complex rather than a chelate even though the chelate may have a stronger bond. The chloride complex may or may not be soluble in the organic phase (as an ion association complex or via salting out). The metal chelate, on the other hand, is not soluble in the aqueous phase. The formation of chloride complexes and ion pairs is believed to account for the differences between observed and literature extraction curves.

Extraction into acetone in the absence of a chelating agent such as APDC is possible. Cobalt chloride and copper chloride are soluble in acetone and would expect to find some of these metal species in the acetone phase in the absence of a chelating agent. Zinc chloride was experimentally observed to be soluble in acetone also.

CHAPTER V

STUDIES OF SLIGHTLY SOLUBLE CHELATES BY ANODIC STRIPPING VOLTAMMETRY

A. Introduction. Polarography offers a rapid and simple means for studying metal ion complexes. The change in the potential at which a metal ion is reduced at a dropping mercury electrode (DME) when it becomes complexed is related to the nature and stability of the complex. By appropriate equations(36), the metal/ligand ratio and the instability constant of the complex can be calculated. Certain difficulties limit the usefulness of conventional polarography for these determinations. First, the concentration of the metal ion must be at least 10^{-5} M and usually greater in order to obtain a well shaped polarographic wave. Since the complexing agent should be in concentrations some one hundredfold or more greater than the metal ion(36), it follows that measurements cannot be made when a small amount of complexing agent is available. Also, several metal-ion chelates, as well as the chelating agents themselves, have low solubility, and polarographic waves will not be observed. It becomes apparent that a more sensitive technique is desired.

Anodic stripping voltammetry(37, 38) is up to 1000 times more sensitive than conventional polarography for measuring metal ions in solution. Popova and Stromberg(39) have determined the composition of hydroxy-zinc complexes taking part in the electrode process at a stationary mercury-film electrode by anodic stripping voltammetry. The effects of hydroxide ion concentration on the potentials of anodic peaks of zinc were determined and results were identical with those obtained using a DME and agreed also with polarographic data of earlier investigators. Rozhdestvenskaya, et. al.(40) have determined the instability constants for thiourea and ammine complexes of copper by measuring the shift in the potential of the beginning of anodic dissolution of a copper anode in the presence of the complexing agents. They used conventional polarographic equations(36) to calculate the constants.

The present report describes an investigation of anodic stripping voltammetry at a hanging mercury drop electrode (HMDE) for the study of formation and stability of complexes, in particular, those of slight solubility. A technique is described in which polarographic waves are obtained in the presence of a ligand which forms an insoluble chelate with the metal ion.

Chelates of ammonium 1-pyrrolidinecarbodithioate (APDC) with metal ions was chosen for this study. APDC was described by Malissa and co-workers (41, 42) as a chelating agent for over thirty mietals in acid solutions. Stetter and Exler(43) at the same time described the use of sodium 1-pyrrolidinecarbodithioate for the solvent extraction of metals in soils. Because it can be employed in acid media, APDC has found wide use in atomic absorption spectroscopy for the solvent extraction of metals into methylisobutyl ketone prior to analysis(44). Despite its importance, little work has been reported on the measurement of stabilities of metal-APDC chelates. The main reason for this is because of the generally very low solubility of these chelates in aqueous solution. This is true for other dithiocarbamate chelates, and several authors have therefore established stability series based on solubility or solvent extraction(45). Jansen(46, 47, 48) has determined stabilities of copper with dialkyldithiocarbamic acids and with APDC in water and water-ethanol mixtures. The chelates were made soluble in water-ethanol mixtures of varying composition and stability constant values were extrapolated to 100 percent aqueous solution.

B. Experimental. Reagent grade chemicals were used without further purification. The purity of the APDC was determined by amperometric titration with copper(49). Mass spectral analysis indicated that the compound was of correct composition(50). There is some concern that the compound may be of a different structure(51).

Polarographic measurements were made with a Chemtrix Single Sweep Polarographic Analyzer System Model SSP-3. A Lingane H-cell(52) equipped with a saturated calomel electrode (SCE) was employed for measurements. The HMDE was prepared and used as previously described(53). Solutions were stirred by means of a magnetic stirring bar and a magnetic stirrer.

Twnety ml. of a 10^{-5} M solution of the metal ion in 0.2 M potassium nitrate were placed in the polarographic cell and were deaerated with nitrogen. The solution was preelectrolyzed for 120 sec while stirring at a constant rate. The following preelectrolysis potentials were employed (vs. S. C. E.): Zn, -1.7 V.; Cd, -1.0 V.; Pb -0.8 V. Following preelectrolysis, the stirring was stopped and an anodic stripping peak was recorded in the usual manner. This established the stripping peak potential of the unchelated metal. A fresh mercury drop was suspended from the electrode, and the preelectrolysis step was repeated. However, after preelectrolysis, the circuit was opened and an aliquot of the stock APDC solution was added to give the desired concentration (ca. 10^{-3} to 10^{-2} M). After stirring the solution briefly, the circuit was closed and the anodic stripping peak was recorded. The peak occurred at a more negative potential than that of the free metal ion. Successive peak shifts were obtained over a range of APDC concentration in increments up to 10^{-2} M by repeating the procedure starting with a fresh metal ion solution.

C. Results and Discussion. Metal/APDC ratios and instability constants were determined from the magnitude of the negative shift of the metal stripping peak in the presence of varying amounts of APDC, using conventional equations(36). A precipitate always occurred when APDC was added to the metal-ion solution, but since the APDC was in 100-to 1000-fold excess, complete solubility of the APDC was assumed. The peak potential is dependent on the peak height, and thus on the concentration of the metal ion, the stirring rate and the plating time. These variables must therefore be strictly controlled in order to maintain the activity of the metal amalgam constant for each measurement.

Reversibility criteria are of course the same here as for conventional techniques. If the metal amalgam is irreversibly stripped, the peak (if it is even recorded) will occur at a more positive potential than does the reduction peak of the free metal ion. The magnitude of the initial potential shift will depend on the stability of the chelate, the concentration of the chelating agent, and the values of n(number of electrons involved in the electrolysis) and p (the number of ligand molecules associated with each metal ion). Since here we can deal with more dilute solutions of chelating agent than in conventional methods, the magnitude of the shift may be significantly smaller. This is a limitation of the method. While quantitative data are not available, it appears that for reproducible data, a shift of 100 mV. is desirable. Based upon this assumption, limiting values of instability constants with varying values of n, p, and ligand concentration (C_x) to achieve this shift are listed in Table 5. It can be concluded from these data that the chelate must be more stable as n and p become larger and as C_x becomes smaller in order to achieve this minimal shift of the peak.

Results of this study are summarized in Table 6. The pH of the unbuffered solutions varied from 6.3 for 10^{-3} M APDC to 6.7 for 10^{-2} M APDC. The pH before adding APDC was 5.6. The results are the average of two determinations each (three for lead). Calculations were made using both the peak potential and the half-peak potential. Except for zinc, where the potential shift was smallest, results by the two methods agreed closely. Reproducibility was best using peak potentials and these are recommended for calculations.

Stability studies of these metals with other dithiocarbamates have been reported. Malatesta(54) determined some relative stabilities of diethyldithiocarbamates, based on solubility, to decrease in the order Cu (II) > Pb > Zn > Tl(I). Vedwevc and Vavsak(55) obtained the same order for Cu (II), Pb, Cd, and Zn, based on potentiometric titrations. The same order for these metals was obtained by replacement extraction procedures (56). The same order has been obtained here for lead, cadmium, and zinc with APDC. In addition, no

TABLE 5

MAXIMUM INSTABILITY CONSTANTS FOR A 100 mV INITIAL POTENTIAL SHIFT

C_x	n	p	K_i
10^{-3} M	1	1	$10^{-4.7}$
10^{-4} M	1	1	$10^{-5.7}$
10^{-3} M	1	2	$10^{-7.7}$
10^{-4} M	1	2	$10^{-9.7}$
10^{-3} M	2	1	$10^{-6.3}$
10^{-4} M	2	1	$10^{-7.3}$
10^{-3} M	2	2	$10^{-9.3}$
10^{-4} M	2	2	$10^{-11.3}$
10^{-3} M	2	3	$10^{-12.3}$
10^{-4} M	2	3	$10^{-15.3}$

TABLE 6

METAL/LIGAND RATIOS AND STABILITIES OF METAL-APDC CHELATES IN 0.2 M POTASSIUM NITRATE

Metal	(1)[a]		(2)[b]	
	p	K_i	p	K_i
Pb^{+2}	2.2	2.0×10^{-21}	2	2.0×10^{-21}
Cd^{+2}	2.3	2.6×10^{-16}	2.3	3.4×10^{-16}
Zn^{+2}	1.7	5.2×10^{-11}	2.5	4.9×10^{-10}

[a] Based on peak potential

[b] Based on half-peak potential

shift of the stripping peak for thallium (using thallium (I) solutions) was obtained, indicating that no chelate was formed with APDC. This follows the same trend above for diethyldithiocarbamate. The duplication of the order of stability is to be expected. It has been demonstrated that there is no significant differences in the chelating properties of a number of derivatives of dithiocarbamate(45). The p-values obtained here agree with these reported by Malissa and Kolbe-Rohde(57) for the APDC chelates of cadmium and zinc. It is unlikely that stepwise formation of the complexes occurs; this is negligible in most cases of formation of dithiocarbamates, due to a rather drastic shift of the equilibrium towards precipitation or extraction of the metal chelate(45).

It is difficult to determine whether a soluble metal chelate is formed at the electrode surface or whether a precipitate is formed. The numbers in Table 6 would be reasonable K_{sp} values for these chelates. Approximate calculations based upon the equations of Reinmuth (58) and Shain and Lewison(59) indicate that, for 10^{-3} <u>M</u> APDC and the conditions of electrolysis used here, the concentration of metal ion in the diffusion layer at the electrode surface would be more than sufficient to exceed a reasonable solubility product, and hence cause precipitation of the chelate in the diffusion layer. It is quite probable, then, that the numbers in the table represent K_{sp} values.

Janssen(46), by extrapolation of results obtained with nonaqueous solutions, calculated the instability constant for the copper (II)-APDC chelate in water to be 1.6×10^{-21}. The relative stability of the copper and lead chelates of diethyldithiocarbamate were shown to be close(54, 55) and the number obtained by Janssen is close to that listed for lead in Table 6. This would suggest that solubility products and instability constants for metal dithiocarbamates are not too different, and that solubility studies are a good indication of relative stabilities of slightly soluble chelates.

Other techniques of stripping analysis should be useful for studying complexes. For example, anodic stripping pulse voltammetry(60) extends the sensitivity limit ten-fold over d. c. stripping analysis. In addition, millimoler or less concentrations of supporting electrolyte can be employed so that little or negligible error results in neglecting activity coefficients in calculations, i.e., activity $\simeq$ concentration.

D. Conclusions. Anodic stripping voltammetry is employed to study chelates of ammonium l-pyrrolidinecarbodithioate with metal ions. A technique is described in which polarographic waves are obtained when the chelates are highly insoluble. The shift in the anodic stripping peaks of a metal when the chelating agent is added to the solution (after preelectrolysis) is used to calculate metal/ligand ratios and stability constants. Advantages include ability to use polarographic techniques when the chelates are insoluble (and non-reducible), increased sensitivity, and possibility of using concentrations rather than activities for calculations involving dilute solutions.

CHAPTER VI

FLAME EMISSION SPECTROSCOPY WITH THE NITROUS OXIDE-ACETYLENE FLAME

A. Introduction. Flame emission spectroscopy historically has been used for the routine determination of only a few elements, particularly since the introduction of atomic absorption spectroscopy in the late 1950's. This is primarily because of the limitations imposed on the method; the commonly used flames were insufficiently energetic to cause appreciable excitation of a large number of the elements, and so sensitiivites were poor. Also, atomic absorption appeared to offer better specificity or resolution in certain cases. It is now generally recognized that with proper instrumentation and precautions, the latter objection is not as severe as might be supposed. In 1966, Amos and Willis(61) introduced the nitrous oxide-acetylene flame for the atomization of refractory elements and their atomic absorption determination. Its advantages for atomization accrue form the highly reducing atmosphere maintained in the red feather of the flame in addition to its high temperature(62). These same factors, combined with the high excitation energy of the flame, have led to an interest in employing it for flame emission spectroscopy, and it indeed appears at present to be the flame of choice for the flame emission analyses of most elements in terms of sensitivity and convenience(63). In 1967, Amos(64) reported that the flame was superior for the emission of the rare earth elements and aluminum. In 1968, Pickett and Koirtyohann(65) described the general emission characteristics for 34 elements in aqueous solution, using this flame with a slot premix burner. In the same year Christian(66) demonstrated the emission of 52 elements in this flame; in this preliminary study, 183 emission lines and bands were investigated for possible analytical use, using both aqueous and aqueous-acetone solutions. Conditions were not optimized and relative detection limits were reported using an instrument without filtering of the photomultiplier signals. In spite of these restrictions, only selenium did not give a measurable emission in aqueous solution. Feldman(67) has compared flame emission and atomic absorption detection limits for several elements.

Pickett and Koirtyohann have more recently reported on the detailed studies for lithium and the alkaline earth metals(68) and for the elements aluminum, gallium, indium, thallium, germanium, and tin(69). Knisely, et. al. (70) recently reported detection limits for the rare earth elements using the nitrous oxide-acetylene flame.

Based on the previous preliminary investigation, (66) the present study was undertaken to determine the conditions for maximum signal/noise ratio in the flame emission spectroscopy determination of all possible elements using the nitrous oxide-acetylene flame, and a slot burner. A total of 70 elements have been investigated. Conditions reported include wavelength, slitwidth, photomultiplier voltage, flame stoichiometry, and height of measurement in the flame. Detection limits are reported for aqueous solutions of each element. Comparisons are made with atomic absorption detection limits determined using the same instrument, the same atomizer system, and the same signal/noise measurement technique (signal integration).

B. Experimental. Solutions were prepared from reagent grade or high purity salts or oxides of the elements or from high purity metals as the previously described(66). Atomic absorption and flame emission measurements were made with an Instrumentation Laboratory Model 153 Atomic Absorption/Emission Spectrophotometer. The characteristics of the monochromoter system were previously described(66). The spectral band pass for different slit settings was as follows; 40μ - 2 Å; 80μ- 4 Å; 160μ- 8 Å. A 1P28 photomultiplier was used as the detector unless otherwise specified.

The burner used for emission measurements was the Instrumentation - Laboratory 24036 nitrous oxide burner head. This has a stainless steel head with a single slot along the optic axis. The gas flow was adjusted at the inlet gauges to give the desired flame stoichiometry (ca. 10 N_2O/min. and C_2H_2 adjusted at around 8 /min). The same burner head was used for the atomic absorption measurements requiring the nitrous oxide-acetylene flame. Other atomic absorption measurements were made with an air-acetylene flame or an argon-hydrogen-entrained air flame using a triple slot Boling burner head. Solution aspiration rate was set at 4 ml/min for all measurements.

C. Results and Discussion. Optimum conditions were determined for maximum emission sensitivity. The more sensitive lines from the previous report were studied in detail(66). Table 1a summarizes the results along with the detection limits determined for aqueous solutions of the elements. Signals were integrated for 10 second periods for detection limit studies. The detection limit was defined as the concentration, in parts per million, that resulted in a signal equal to twice the standard deviation of the background fluctuations. The standard deviation of the background fluctuations was calculated from ten integrated readings. The concentration of the test element was within a factor of ten of its detection limit and the average of ten integrated readings was taken for the deflection.

A total of 68 elements are included in the table. In addition, phosphorous (5200Å) and sulfur (3837 Å) band emission were studied. The detectability of these two elements was very poor in the nitrous oxide-acetylene flame. An argon-hydrogen-entrained air flame is recommended for phosphorous and sulfur determination. A detection limit of 0.05 ppm was obtained for phosphorous and 10 ppm for sulfur.

The flame stoichiometry is important primarily for three reasons. First the intensity of background band emission from the flame changes markedly with flame stoichiometry. The flame emission spectrum of the red feather(66) is observed in the stoichiometric and the rich (luminous) flames, while the quiter background of the blue zone(66) is observed in the lean flames. The NH, CH, CN, and C_2 bands decrease as the flame is made leaner while the OH band (3064Å) increases(65). Second, ionization of the atoms is somewhat more prominent in the lean flame but this can generally be minimized by adding a high concentration of an ionization suppressant, such as potassium. Third, the formation of refractory oxides by certain elements is dependent on flame stoichiometry, and a rich reducing flame is generally preferred for these elements.

Because of the quieter flame background as well as the enhanced excitation energy, a lean or stoichiometric flame is generally preferred when possible. Thus, iridium, for example, is determined in a lean flame because a stoichiometric flame results in a very noisy signal. Lanthanum and thorium exhibit the same detectibility in a lean flame as in a rich flame or a stoichiometric respectively, but the latter two flames are preferred in order to minimize oxide formation.

Boron and uranium were determined using band emission because of the poor sensitivity of their line emission. A lean flame is used for maximum formation and excitation of their oxides coupled with minimum flame background. Determinations using band emission are, of course, less specific than by using line emission. Uranium exhibits several strong emission lines (2635.5, 2865.7, 3812.0, 4090.1 Å) but they fall on strong flame bands. Thus, a lean flame is required to eliminate background interference with these, but it results in uranium oxide formation and cannot be used.

Elements that emit at long wavelengths were determined using a red-sensitive 1P21 photomultiplier tube. These include potassium (7664.9Å), lithium (6707.8Å), and rubidium (7800.2Å). A red filter should be used with these elements to eliminate second order interference from the flame background. High concentrations of sodium exhibit an appreciable NaOH continuum in the nitrous oxide-acetylene flame and this added background emission should be corrected for(71).

Some elements exhibit maximum sensitivity using band emission, but this is limited in its selectivity. Thus, for example, marked improvement in sensitivity is found with band emission from gadolinium, iridium, lanthanum, terbium, and yttrium, in addition to boron and uranium. Berrylium also shows five-fold higher sensitivity at the BeO 4708.6Å band.

The slit width used is a compromise between resolution and response. A narrow slit is desired when possible to minimize spectral interference. But for those elements whose emission intensities are weak, a wide slit is required in order to permit the maximum amount of light to fall on the detector. Arsenic and zinc are examples. An increased photomultiplier voltage is also used to enhance the signal output, provided the electronic noise is not increased proportionately. When a 1P28 photomultiplier is used at very long or very short wavelengths (e.g., Li-6707.8Å, As-1937.0Å, Se-1960.3Å) where its sensitivity to the radiation is low, then increased slitwidth and/or photomultiplier voltage is required.

D. <u>Conclusion</u>. The optimum operating conditions were determined for maximum sensitivity using flame emission spectroscopy with the nitrous oxide-acetylene flame. A total of 70 elements were studied and the optimum wavelength, slit width, photomultiplier voltage, flame stoichiometry and red feather height, and height of observation in the flame were determined for each element. The detection limit of each element was determined under optimum conditions using signal integration.

CHAPTER VII

COULOMETRIC TITRATION OF BASES IN CONCENTRATED NEUTRAL SALT SOLUTIONS

A. Experimental. Reagent grade chemicals were used when available. Ethylenediamine was distilled prior to use. All base solutions were standardized volumetrically. Coulometric titrations were performed with a Chris-Feld Microcoulometric Quantalyzer, using a generating current of 9.65 mA. The titration cell contained 1 cm^2 platinum foil generating electrodes. The cathode was separated from the test solution via a salt bridge (3% agar-agar, 1 M potassium nitrate) which was placed in an aqueous solution of 1 M potassium nitrate. The pH indicating electrodes were a glass-SCE pair unless otherwise stated. pH measurements were made with a Corning pH meter, Model 7. Solutions were deareated with nitrogen prior to titration. The nitrogen was scrubbed by bubbling through a train consisting of 0.1 N hydrochloric acid, 0.1 N potassium hydroxide, and the solvent used for the titration. In many cases, electrode response was sluggish, and several minutes were required after each addition of titrant before stable readings were reached. Usually readings were taken 1 to 3 minutes after addition of titrant. For titrations in nonaqueous solvents, the solvent contained 1 percent water as a source of hydrogen ions; anhydrous salts were used in these solvents.

B. Results and Discussion. The use of a fiber junction SCE did not appear to introduce appreciable chloride impurities for the duration of the titrations. Concentrated solutions of lithium iodide and other halide salta have been demonstrated to provide large enhancement of acidity in volumetric titrations(72,73,74). Unfortunately, these cannot be used for coulometric titrations because the halide ions are oxidized at the anode in preference to the oxidation of water.

It has been demonstrated that the salts of sulfuric acid actually inhibit the titration break of aniline. The salts must therefore, be derived from an acid having an ionization constant greater than 10^{-2} (72). Because of the above reasons, concentrated solutions of perchlorate salts were chosen as possible electrolytes in coulometric titrations. The pH of equal concentrations of hydrochloric acid (ca. 0.01 N) in water and in the presence of the salts was measured and the results were as follows: H_2O, 2.16; 3M $LiClO_4$, 0.80; 8M $NaClO_4$, -0.5. The volumetric titration of 0.1 meq of ammonia in 6 M sodium perchlorate demonstrated an enhancement in the endpoint break of about 1.5 pH units. Volumetric titrations of 0.1 meq. aniline in 40 ml. of solution with 0.02 N hydrochloric acid showed a pH change at the endpoint of 0.5, 1.4, and 1.5 in 3 M lithium perchlorate, 8 M sodium iodide, and 8 M sodium perchlorate, respectively. Thus, sodium perchlorate compares favorably with sodium iodide for the enhancement of acidity. Readings in aqueous lithium perchlorate solutions were unstable and this salt could not be used satisfactorily for titrations in water.

Coulometric titrations of different bases are summarized in Table 7. In all coulometric titrations, the solution was pretitrated by adding the base to be titrated and then titrating to an endpoint break. The sample was then added. Aniline underwent a color change in the vicinity of the endpoint, turning from colorless to pink or violet. The color remained upon addition of more aniline to make the solution alkaline. Apparently, some of the aniline was oxidized directly at the generating anode. Results were, however, near stoichiometric, and the direct electrolysis did not detract significantly from the accuracy. This color change near the endpoint was similar to a color change observed for histidine when it was oxidized with coulometrically generated hypobromite(75). Only one endpoint break was obtained with ethylenediamine, corresponding to titration of both amine groups.

TABLE 7

COULOMETRIC TITRATIONS OF BASES IN AQUEOUS SALT SOLUTIONS

Electrolyte	Base	μeq taken	μeq found
6 M $NaClO_4$	NaOH	16.23	16.15
	NH_3	68.2	69.0
		68.2	69.2
		12.35	12.50
8 M $NaClO_4$	Aniline	62.4	61.4
	Ethylenediamine	38.2	38.4
		38.2	38.4

It was considered probable that addition of concentrated salts to nonaqueous solvents would further enhance the endpoint breaks in these solvents. An initial titration of aniline in acetonitrile containing 0.1 M lithium perchlorate was attempted, but results were very low. Lithium perchlorate was the salt chosen for nonaqueous studies because of its solubility. It has a high solubility in acetone and this neutral solvent was investigated for coulometric titrations. Volumetric titration of 0.1 meq aniline in 40 ml of acetone containing 3 M lithium perchlorate as above for aqueous solutions exhibited an apparent pH change of 2.7 at the endpoint compared to 1.4 in 8 M aqueous sodium perchlorate. Coulometric titrations of bases in this system are summarized in Table 8. Results tended to be somewhat high, particularly for m-nitroaniline. This would indicate that generating efficiency is about 99 percent, and in the case of m-nitroaniline, there may have been some direct electrolysis at the anode which was not stoichiometric with respect to consuming hydrogen ions. Aniline did not undergo the color change as found in aqueous solution. No endpoint break could be obtained for this base in acetone containing only 0.1 M lithium perchlorate. Ethylenediamine again exhibited one endpoint break, equivalent to titration of two amine groups. The ionization constant of m-nitroaniline is only 4×10^{-12}, which demonstrates the utility of the present method for titrating microequivalent quantities of weak bases. An added advantage of the combined organic solvent-concentrated salt system is that organic bases, such as aniline, have a higher solubility than in the aqueous system.

TABLE 8

COULOMETRIC TITRATIONS OF BASES IN ACETONE CONTAINING 3 *M* LITHIUM PERCHLORATE AND 1 PERCENT WATER

Base	μeq taken	μeq found
NaOH	16.23	16.50
Aniline	20.8	20.8
Ethylenediamine	38.2	38.9
m-Nitroaniline	20.1	23.5
		23.5

CHAPTER VIII

EFFECT OF NEUTRAL SALTS ON NONAQUEOUS TITRATIONS OF BASES

The coulometric titration results encouraged us to study in further detail the effects of salts on the volumetric titration of weak bases in nonaqueous solvents. The titrant was 0.1 N perchloric acid in the solvent used. In the case of acetone solvent the perchloric acid was unstable after a few hours. By dissolving it in p-dioxane, essentially the same results could be obtained, but the perchloric acid solution was stable for several weeks.

The first phase of this research involved findings salts which were sufficiently soluble in nonaqueous solvents to have an effect on the potentiometric breaks occurring during the titration of weak bases. Many salts were found to be insoluble or only very slightly soluble in acetone. Among these were potassium iodide, potassium fluoride, potassium chloride, potassium nitrate, potassium sulfate, potassium carbonate, lithium sulfate, sodium fluoride, and sodium chloride. Table 9 indicates the results of the titration of aniline in various salt solutions and the potentiometric breaks obtained. Further study was made of the more promising salts in ($Li\ Cl0_4$, LiI, $Mg(Cl0_4)_2$) in acetone and other solvents.

During the course of this study, several weak bases were employed to study the differences in the potentiometric break enhancement depending upon the strength of the weak bases being titrated. Table 10 lists the bases employed, their relative strengths in water, and the magnitudes of their potentiometric breaks in acetone. Table 11 shows the magnitude of the potentiometric breaks which were obtained for these same weak bases titrated in lithium perchlorate-acetone solutions. The concentrations of lithium perchlorate used were those

TABLE 9

EFFECT OF SALTS ON THE POTENTIOMETRIC BREAK OF ANILINE TITRATED IN ACETONE WITH ONE-TENTH MOLAR PERCHLORIC ACID

Salt	Potentiometric Break (mV)
None	245
0.07 M $LiCl$	None
Sat. $LiCl$	None
1.2 M $LiBr$	None
2.5 M $LiBr$	None
0.25 M LiI	295
0.50 M LiI	275
0.25 M $LiC10_4$	325
0.50 M $LiC10_4$	340
0.25 M $Mg(C10_4)_2$	330
0.50 M $Mg(C10_4)_2$	340
Sat. NaI	220
Sat. $NaBr$	250
Sat. $NaNO_3$	110
Sat. KBr	230
Sat. $MnCl_2$	250

TABLE 10

CORRELATION BETWEEN STRENGTHS OF WEAK BASES IN WATER AND THE MAGNITUDES OF THEIR POTENTIOMETRIC BREAKS IN ACETONE

Base	mV Break in Acetone	pK_b
Urea	None	13.80
Caffeine	None	13.39
m-Nitroaniline	70	11.40
Aniline	245	9.42
N-Dimethylaniline	185	8.79
Pyridine	250	8.81

TABLE 11

MAXIMUM POTENTIOMETRIC BREAKS OBTAINED FOR WEAK BASES TITRATED IN SOLUTIONS OF LITHIUM PERCHLORATE IN ACETONE

Base	mV Break in Acetone-$LiClO_4$	M of $LiClO_4$
Urea	20	4.0
Caffeine	315	3.0
m-Nitroaniline	250	1.0
Aniline	360	1.0
N-Dimethylaniline	365	0.5
Pyridine	340	1.5

which gave the maximum potentiometric break. A maximum potentiometric break of 365 mV. was obtained for the N-dimethylaniline and this value was approached by the strongest four bases titrated. This, in addition to the fact that N-dimethylaniline was not the strongest base titrated, seems to suggest that a break of about 365 mV. may be the absolute maximum break obtainable in the lithium perchlorate-acetone system.

The enhancements of the potentiometric break of weak bases due to the addition of lithium perchlorate are found in Table 12. Urea, the weakest base shown, has only a very small break even in strong salt solution so the enhancement is necessarily small. It appears that the lithium perchlorate-acetone system is not useful for bases weaker than caffeine, which has a pK_b of 13.39 in water. The strongest base listed, pyridine, has a rather small enhancement due to the fact that it has a good break even in acetone without salt.

Table 13 shows that the lithium perchlorate-acetone system provides a definite advantage over the usual titration of weak bases in glacial acetic acid. There appears to be no particular advantage in using the lithium perchlorate-acetone system with bases as strong as pyridine, which has a pK_b of 8.81 in water.

The effect of lithium perchlorate concentration on the potentiometric titration of aniline in acetone solvent was studied and a portion of the results are given in Figure 2. The titrant used was one-tenth molar perchloric acid in acetone. As is shown by the figure, a 0.05 M $LiClO_4$ concentration caused a considerable enhancement of the break. The potential reading tends to be decreased by the addition of salt, but the decrease is of greater magnitude before the endpoint is reached than after it is reached, causing an overall enhancement of the break. Table 14 gives the potentiometric breaks observed for aniline in the various concentrations of lithium perchlorate in acetone. These data indicate that the after a certain concentration of salt, the break is not enhanced further by using stronger concentrations of salt because the curve is shifted

TABLE 12

MAXIMUM ENHANCEMENT OF POTENTIOMETRIC BREAKS OF WEAK BASES TITRATED IN LITHIUM PERCHLORATE-ACETONE SOLUTIONS AS COMPARED TO VALUES OBTAINED IN PURE ACETONE SOLUTIONS

Base	Break Enhancement (mV.)
Urea	20
Caffeine	315
m-Nitroaniline	280
Aniline	115
N-Dimethylaniline	180
Pyridine	90

TABLE 13

COMPARISON OF MAXIMUM POTENTIOMETRIC BREAKS OF WEAK BASES OBTAINED IN LITHIUM PERCHLORATE-ACETONE SOLUTIONS WITH THOSE OBTAINED IN PURE GLACIAL ACETIC ACID SOLVENT

Base	mV. Break in Acetone $LiC10_4$	mV. Break in Acetic Acid
Caffeine	315	50
m-Nitroaniline	350	155
Aniline	360	310
Pyridine	340	370

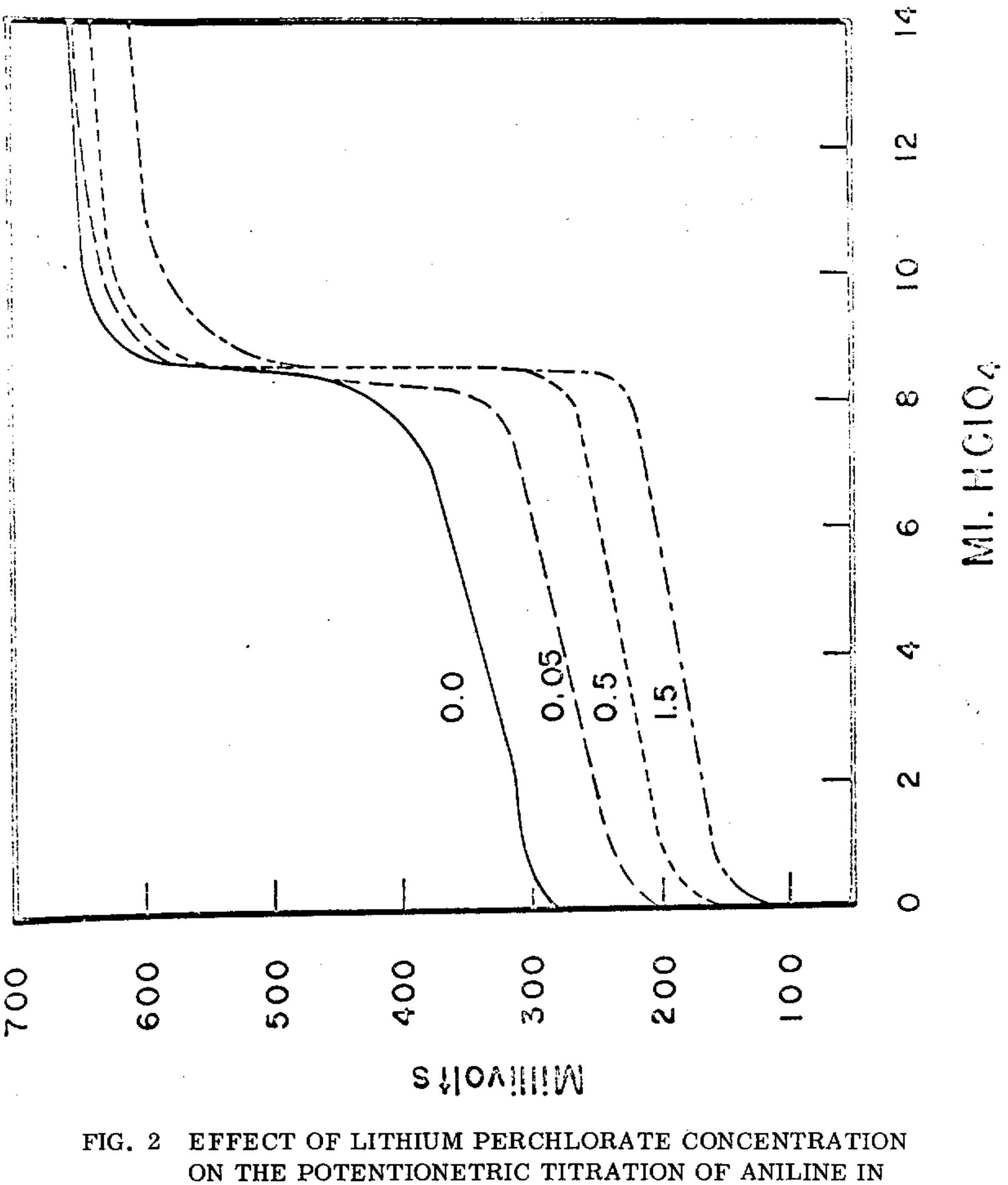

FIG. 2 EFFECT OF LITHIUM PERCHLORATE CONCENTRATION ON THE POTENTIONETRIC TITRATION OF ANILINE IN 50 Ml. ACETONE SOLVENT. NUMBERS ON THE CURVES REPRESENT MOLARITY OF SALT. THE TITRANT IS 0.1 M $HC10_4$ IN ACETONE.

TABLE 14
EFFECT OF CONCENTRATION OF LITHIUM PERCHLORATE ON THE POTENTIOMETRIC BREAK OF ANILINE IN ACETONE TITRATED WITH PERCHLORIC ACID IN ACETONE

Molar Salt Concentration	mV. Break
None	235
0.05	290
0.10	307
0.25	325
0.50	340
0.75	335
1.0	360
1.5	348
2.4	335
4.8	305

downward to a greater extent after the endpoint than it is before the endpoint. It is also evident that the endpoint comes slightly late for the higher concentrations of salt, making the higher concentrations somewhat less satisfactory than those of intermediate value, probably due to impurities in the salt.

The effect of magnesium perchlorate concentration on the potentiometric break of aniline in acetone titrated with perchloric acid in acetone is summarized in Table 15. The addition of magnesium perchlorate increased the volume of titrant required to reach the endpoint, but this disadvantage was overcome by running blank titrations and subtacting the blanks from the observed endpoints. As in the titrations with lithium perchlorate, a maximum break enhancement occurred at some intermediate concentration of salt.

It should be pointed out that small amounts of water depress the titration curves. One percent water caused nearly a 50% depression.

The effect of lithium iodide concentration on the potentiometric break of aniline in acetone titrated with perchloric acid in dioxane is given in Table 16. As with the other salts, there was an intermediate concentration of lithium iodide which gave the maximum potentiometric break. The endpoint was increased by increased concentrations of the salt and with concentrations greater than 0.5 M LiI the endpoint was so far displaced (due to impurities) that it was of no value in the determination of the amount of weak base present. The maximum break with lithium iodide was less than that which could be obtained with either lithium perchlorate or magnesium perchlorate.

Similar behavior was obtained for the titration in acetone of most of the other bases listed in Table 11, i.e., the magnitude of the break went through a maximum at a given salt concentration. In general, the weaker the base, the more salt required to reach the maximum.

The enhancement mechanism appears different from that in water, because the effect appears to be the opposite. That is, the basic end of the titration curve (at the beginning of the titration) is shifted to more basic

TABLE 15

EFFECT ON THE CONCENTRATION OF MAGNESIUM PERCHLORATE ON THE POTENTIOMETRIC BREAK OF ANILINE IN ACETONE TITRATED WITH PERCHLORIC ACID IN ACETONE

Molar Salt Concentration	mV Break
0.00	295
0.25	330
0.50	340
0.75	335
1.0	320
1.5	310

TABLE 16

EFFECT OF CONCENTRATION OF LITHIUM IODIDE ON THE POTENTIOMETRIC BREAK OF ANILINE TITRATED IN ACETONE WITH PERCHLORIC ACID IN DIOXANE AS THE TITRANT

Molar Concentration Salt	mV. Break
None	245
0.01	300
0.05	280
0.25	295
0.50	275
1.0	210

potential readings while the acid end changes to a smaller extent. Furthermore, the acid end (beyond the end point) is actually shifted slightly toward more alkaline readings rather in the other direction as in water. As the salt concentration exceeds a certain value, the alkaline shift beyond the end point becomes greater than that before the end point, causing the magnitude of the break to diminish. It is significant to note than in nearly all cases, the basic end of the titration curve was shifted to about the same potential reading, suggesting the bases were leveled to stronger bases of the same strength. This effect began to diminish with bases as weak as or weaker than caffeine, which appears to be the limit of strength of bases that can be titrated. Urea gave only a small break (20 mV) compared to no break in the absence of salt.

The same general effect was found for the titration of aniline in the solvents methylisobutyl ketone and 2-butanone containing added lithium perchlorate, although the potentiometric breaks were smaller than in acetone. The study was limited to these solvents and to the salts lithium perchlorate, lithium iodide, and magnesium perchlorate because of solubility limitations. Adding salts to glacial acetic acid solvent actually suppressed the end point breaks found when using this solvent.

The best system found was acetone solvent with added lithium perchlorate. It seems possible that the salt acts as a Lewis acid and levels the weak bases to about the strength, requiring more salt the weaker the base.

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