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N. H. Furman and G. P. Haight, Jr.

Experimental Work Done By: G. P. Haight, Jr.

Contribution of the
Princeton University Analytical Group
Frick Chemical Laboratory
Princeton, N. J.

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Introduction.

Uranium tetrafluoride, prepared from pure materials, almost invariably contains both uranium dioxide and uranyl fluoride together with other uranium oxides or fluorides, depending on the conditions of preparation. For certain types of preparations it has been shown that the simple test of the solubility of the material in hot 2.5 per cent ammonium oxalate solution gives an approximate indication of the content of uranium dioxide in the substance.(1) The present study was made to find alternative methods for the characterization of the uranium tetrafluoride.

In preliminary experiments, attempts were made to dissolve the tetrafluoride rapidly by using a mixture of ammonium oxalate and boric acid or oxalic acid. Although uranium dioxide is not soluble in a warm mixture of 0.4 per cent oxalic acid and 2 1/2 per cent oxalic acid, it was found that the use of such a material gave low results for "oxide_ in a previously analyzed tetrafluoride. It was found that pure uranium dioxide was appreciably soluble in a mixture of sodium fluoride, sulfuric acid and boric acid:, it seems likely that the presence of oxalate, fluoride and hydrogen ion accounted for the increased solubility of the oxide in the tetrafluoride preparation over that observed when ammonium oxalate solution was used.

The use of mixtures of boric acid and either hydrochloric or sulfuric acid was tested as a possible method for dissolving the tetrafluoride without appreciably attacking any dioxide that might be present. Boric acid has long been used to bind fluoride ion in the form of a stable complex.(2) Mixtures of fluoboric and other acids attack Pyrex glass rather slightly,(3) and use of this fact has been made in other modifications of methods of analysis of tetrafluoride preparations.(4) If the use of boric acid is objectionable, an aluminum salt may be used to complex the fluoride.(5)

It was found that mixtures containing 2 per cent of boric acid and concentrations of sulfuric acid up as high as 4 N dissolved the tetrafluoride more or less rapidly and left a brownish-black residue, presumably the dioxide. When hydrochloric acid was used instead of sulfuric acid, it was found that the oxide dissolved readily at concentrations as high as 4 N and fairly readily at about 1 N. The residual "oxide" in good tetrafluoride preparations is more resistant to the solvent action of acids in the presence of fluoride ion than is the brown dioxide prepared by the reduction of the trioxide. Mellor(6) states that the dioxide varies markedly in its reactivity depending upon its history and gives many conflicting reports regarding the solubility of the dioxide in various acid solutions. In the preparations of the tetrafluoride when the oxide content is less than 1.5 per cent, it apparently has been converted to a more resistant form.

It was thought that the procedure of Dobratz(7) for determining the total quadrivalent metal in the sample by digesting the sample with an excess of ceric sulfate in 10 per cent sulfuric acid solution might be combined with a direct solution and titration of the tetrafluoride. The latter estimation was first attempted by dissolving the tetrafluoride in a solution 1 N in sulfuric acid and containing 2 grams per 100 ml. of boric acid. The mixture was heated and later cooled in a carbon dioxide atmosphere, filtered to remove the dioxide and the filtrate and washings were made 4 N in sulfuric acid. It was shown by experiment that sulfuric acid might be substituted for hydrochloric acid in the titration of uranium (IV) solution (Table I). Titration with standard ceric sulfate after addition of 3 ml. of 85 per cent phosphoric acid and 2 drops of ortho-phenanthroline ferrous sulfate indicator (0.025 M) might be expected to give a direct estimation of the tetrafluoride and an estimation of the dioxide either by subtraction of the latter titration from the titration of the total quadrivalent metal on a sample of the same weight, or by ignition and weighing of insoluble matter. It was found that in the filtration, a small and variable part of the quadrivalent material is oxidized by the air. This rather simple procedure tends to give, therefore, results that are variable and somewhat low for the tetrafluoride and high for the dioxide.

It was found that portions of a standard solution of uranium sulfate, ($U(SO_4)_2$), to which were added the sulfuric, hydrofluoric and boric acids to duplicate the conditions of the determination, could be heated and cooled under purified carbon dioxide and then made 4 N in sulfuric acid and titrated with ceric sulfate after adding phosphoric acid and indicator (Table II).

TABLE I.

Substitution of 4N H_2SO_4 for 4N HCl in the Titration of Uranium (IV) Solution

Normality of Solution from H_2SO_4 Titration		Normality of Solution from HCl Titration		
0.09747	0.09743	0.09747	0.09743	0.09751

TABLE II.

Results on a Standard Solution Run Through the Conditions of the Determination

Method	Uranium (IV) added. Grams	Uranium (IV) recovered. Grams
UF_4 - Haight	0.5799	0.5798
	0.2900	0.2900
Total U^4 - Dobratz	0.2900	0.2903
	0.2900	0.2917
	0.2900	0.2906
	0.2900	0.2898

The foregoing studies finally led to the simple method here proposed, namely, to heat the sample with a solution 1 N in sulfuric acid and containing 2 grams of boric acid per 100 ml. in a carbon dioxide atmosphere until the tetrafluoride is dissolved. Usually from 15 to 30 minutes are needed for 0.3 to 0.5 gram sample. After cooling in the carbon dioxide atmosphere the solution is adjusted to proper acidity and titrated with ceric sulfate. After the end point is reached and recorded a measured extra volume of ceric sulfate is added and the dioxide is dissolved by boiling the solution for as short a period as is necessary to complete this process. The solution is then cooled and the excess of ceric sulfate is titrated with freshly standardized ferrous sulfate. The per cent of the tetrafluoride is calculated from the data of the first titration and that of the dioxide from the amount of ceric sulfate that is reduced in the process of dissolving the dioxide. The details of the method follow:

Apparatus and Materials. Source of carbon dioxide or nitrogen freed from air.

Purification Train. Two gas washing bottles of Friedrichs type (or equivalent) charged with chromous chloride or sulfate prepared in the bottles by adding zinc amalgam as used in Jones reductors to chromic chloride or sulfate acidified with hydrochloric or sulfuric acid. The wash bottles are followed by one or more wash bottles filled with distilled water.

Erlenmeyer Flasks. Several 250 ml. flasks fitted with stoppers and inlet and exit tubes for carbon dioxide. Thus far three samples have been analyzed here simultaneously with the flasks in series.

Ceric Sulfate. 0.1 M in $Ce(SO_4)_2$ and 1 molar in sulfuric acid, standardized against arsenious oxide.(e) Sulfato-ceric acid from the G. F. Smith Chemical Co. and arsenious oxide from the National Bureau of Standards were used.

The process of dissolving the samples was carried out in a well ventilated hood because of the presence of fluorides and boric acid.

Conditions Under Which the Procedure Gives Favorable Results as Compared to the Ammonium Oxalate Insoluble Method for UO_2. When samples contain more than 1.5 per cent of UO_2, the method here proposed had been found to give lower results in the determination of UO_2 than the ammonium oxalate insoluble method, and it is suggested that when a sample is found to contain a large amount of oxide that the ammonium oxalate insoluble method be applied. This evidence, coupled with the evidence that uranium dioxide, UO_2 dissolves under the experimental conditions of the new method, leads to speculation as to the exact nature of the residue found in each method. Apparently the residues are either not pure UO_2 or are entirely different from each other. The new method gives results very comparable to those obtained by combining the results of the ammonium oxalate insoluble method for UO_2, and the procedure of Dobratz for obtaining total quadrivalent uranium, in the case of samples containing less than 1.5 per cent UO_2. In the case of results obtained on samples 1, 2, 3, 4, 5 (Table III), results by the new method for UF_4 and UO_2 were in very excellent agreement with those obtained independently by the procedures previously used for this determination.

Procedure: Place in each Erlenmeyer flask 100 ml. of a solution containing 2 ml. of concentrated sulfuric acid and 2 - 3 grams of boric acid per 100 ml. Weigh accurately into each flask from 0.3 to 0.5 grams of the tetrafluoride previously ground in an agate mortar. Immediately start bubbling the purified carbon dioxide through the solutions and continue for 20 - 30 minutes at a rate adequate to sweep out the air. Then heat each solution, while continuing the passage of carbon dioxide, until the tetrafluoride has dissolved and only a small residue of brown-black "oxide" remains. Cool each solution, with the carbon dioxide passing, by surrounding the flask with the cold water or an ice bath. Remove the flasks, rinsing each inlet tube into the proper solution; add enough sulfuric acid to make the solution approximately 4 N in this acid; add 1.5 ml. of 85 per cent phosphoric acid and 2 drops of 0.025 M o-phenanthroline ferrous sulfate indicator and titrate with the standard ceric sulfate, using a calibrated buret.(8) We have found by tests of $U(SO_4)_2$ solution prepared by passage through a Jones reductor and freed of trivalent ions by aeration that 4N sulfuric may be substituted for 4N hydrochloric acid in this titration.

Record the end-point and then add about 10 ml. of ceric sulfate in excess and note the volume added. Boil the solution until the oxide dissolves. There is a tendency for the solution to begin to bump at about the time the solution is complete. Cool, add 2 drops of the indicator and titrate back with freshly standardized ferrous sulfate solution.

$$\text{Per cent } UF_4 = \frac{\text{ml. } Ce(SO_4)_2 \text{ X N of } Ce(SO_4)_2 \text{ x } 157}{\text{Wt. of sample in g. x } 10}$$

$$\text{Per cent } UO_2 = \frac{[(\text{ml. excess } Ce(SO_4)_2 \text{ X N } Ce(SO_4)_2 - (\text{ml. } FeSO_4 \text{ X N of } FeSO_4)] \text{ X } 135}{\text{Wt. of sample X } 10}$$

Because of the ease of solution of the oxide in a solution 4 N in hydrochloric acid containing 2 per cent by weight of boric acid, it was decided that the total uranium content could be easily measure by simply dissolving the whole sample, passing the solution through a silver reductor and titrating according to the method of Birnbaum and Edmonds.(9) In this way UO_2F_2 as well as UF_4 and UO_2 could be estimated. This is similar to a method compiled by C. D. Wilder(10) But involves fewer steps and materials.

Apparatus and Materials. Silver reductor prepared according to Walden, Hammett and Edmonds.(11)

Stock solution of 4 N hydrochloric acid.

Standard $Ce(SO_4)_2$ solution about 0.1 N.

Calibrated 50 ml. buret.

Procedure. Weigh accurately into a 250 ml. beaker a 0.4 - 0.6 gram sample of the tetrafluoride. Add 2 grams of boric acid and 50 ml. of 4 N HCl solution. Heat in a well ventilated hood until sample is dissolved (10 - 15 minutes usually required). Pass the solution through the silver reductor into a 500 ml. Erlenmeyer flask following through with 150 ml. of hot 4 N HCl solution. Cool and titrate with standard $Ce(SO_4)_2$ solution using 3 ml. of 85 per cent phosphoric acid catalyst and 2 drops of o-phenanthroline ferrous indicator. The level of the liquid in the reductor should always be above the top of the silver if good results are to be obtained. A blank determination is required. A blank of 0.05 - 0.10 ml. of 0.1 N ceric sulfate was found present in the work here cited.

Typical Results are shown in Table III.

TABLE III.

Results Obtained by the Proposed Procedures

Sample	Quadrivalent Fluoride Per Cent	Dioxide Per Cent	Uranyl Fluoride Per Cent	Total (Average)	Ammonium Oxalate Insoluble Per Cent
1.	97.25				
	97.34	0.54	1.94	99.94	0.49
	97.45	0.68	2.04		0.55
2.	97.33	0.63	1.65		
	97.25	0.60	1.81	99.74	0.48
	97.58				0.49
3.	96.87	0.82	2.23		
	97.00	0.41	2.03	99.60	0.63*
	96.71	0.59			
4.	97.51	0.67	1.33		
	97.74	0.49	1.33	99.49	0.58*
		0.43	~~See low~~		
5.	97.59	0.74	1.88		
	97.31	0.49	1.83	99.90	0.65*
	97.45	0.56			
6.	94.91	0.67	4.16		
	95.05	0.56	4.20	99.95	0.56*
	95.24	0.88			
7.	97.63	1.34	1.3		
	97.02	1.46	1.3	100.01	1.61*
8.	97.14	0.60	1.73		
	97.27	0.64	1.78	99.59	0.50*
9.	97.01	0.47	2.31		
	97.14	0.49	2.43	99.94	0.56*
10.	96.74	0.42	2.58		
	97.17	0.60	2.52	100.01	0.47*
11.	93.57	1.98	1.99		
	93.41	2.08	2.07	99.76	2.93**

* Average of duplicate determinations by C. K. Wolfe, Jr.
** Sample too large in oxide content for new method.

The present method compares favorably with the ammonium oxalate test in cases where the amount of material that is insoluble in ammonium oxalate is of the order of 1 per cent or less.

In a cooperative test of two samples of uranium tetrafluoride the average obtained for UO_2 by all methods was 1.55 per cent and the value obtained by the present method was 1.15 per cent, on one sample whereas on a second sample the result here was 0.21 as compared with an average result of 0.17.

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Summary.

It has been shown that uranium tetrafluoride may be dissolved in a mixture of boric acid and sulfuric acid without attacking the residue that is ordinarily reported as oxalate-insoluble material in nearly pure preparations of uranium tetrafluoride. The soluble U(IV) may be titrated with ceric sulfate after which an excess of that reagent is added and after warming to dissolve the dioxide, etc. the excess of ceric sulfate is determined. The data are then used to calculate the percentages of uranium tetrafluoride, "dioxide", and uranyl fluoride (by difference). The results compare favorably with other procedures for evaluating nearly pure preparations of uranium tetrafluoride.

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