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ABSTRACT

The uranium (VI) content of uranium tetrafluoride can be determined rapidly by a direct polarographic procedure. The method differs from previous methods in that total dissolution of the sample is carried out with negligible oxidation of the uranium (IV). The values obtained with the procedure agree well with calculated values.

THE POLAROGRAPHIC DETERMINATION OF URANIUM (VI) IN URANIUM TETRAFLUORIDE

M. W. Lerner and F. Jaffa

The uranium (VI) content of uranium tetrafluoride can be determined indirectly by calculation from the total uranium and the uranium (IV) values[1]. Since both the total uranium and the uranium (IV) determinations are fairly accurate, the calculated uranium (VI) values are generally regarded to be good. But, as in the case of most indirect methods, any error in the multiple determinations required results in a serious error in the uranium (VI) value.

Direct methods of determining uranium (VI) exist. Extraction of the water-soluble uranyl fluoride followed by colorimetric determination of uranium (VI) in the aqueous extract[2] generally yields values of the same magnitude as those calculated. In this procedure, contributing factors to the inaccuracy are oxidation of the uranium (IV) to uranium (VI) during the extraction period, incomplete leaching of the water-soluble uranyl fluoride and solubility of the uranium tetrafluoride. These errors are partially compensating. A method involving the extraction of the uranyl fluoride with methanol has been found to give more reliable results[3,4].

A polarographic procedure, based upon the extraction of the uranyl fluoride with dilute hydrochloric acid-sodium borate solution, has been used[5]. In our experience, this method yields erratic results, presumably because of incomplete leaching as mentioned above.

Complete dissolution of the sample with a minimum of oxidation during the dissolution step followed by the determination of the uranium (VI) polarographically practically eliminates these errors. Such a procedure has been developed.

Procedure. Add 10 ml. of concentrated hydrochloric acid to 1.5 grams of boric acid in a covered 50-ml. beaker and boil the acid gently to drive off the dissolved oxygen and nearly dissolve the boric acid. Add to this acid mixture a 0.5-gram sample of uranium tetrafluoride, previously ground in an agate mortar. Boil the mixture gently on a hot plate for 5 to 7 minutes. During the heating period, swirl the beaker occasionally. Immediately after the sample is completely dissolved, transfer the solution to a 50-ml. volumetric flask, dilute nearly to volume, add 0.5 ml. of a 0.1% solution of methyl cellulose, cool quickly to room temperature and dilute to volume.

Immediately place a 20-ml. aliquot in a polarographic cell, deaerate for 10 minutes, and record the uranium (VI) wave at about -0.20 volts vs. S.C.E. (saturated calomel electrode) at the highest sensitivity consistent with good wave form. Add 1 or 2 ml. of a standard uranium (VI) solution of 2 mg./ml. in 2 M hydrochloric acid to the polarographic cell, deaerate for 2 more minutes, and record the uranium (VI) wave again.

Calculate the uranium (VI) concentration in the solution by the following equation:

$$C = \frac{2i_1 \ v}{(i_2 - i_1)(20+v) + i_1 v}$$

where:

C = concentration of uranium (VI), mg./ml.
i_1 = wave height in first polarogram, mm.
i_2 = wave height in second polarogram, mm.
v = volume of standard solution added, ml.

Calculate the percentage of uranium (VI) as uranyl fluoride by the following equation:

$$UO_2F_2, \% = \frac{6.47 \ C}{\text{Sample Weight, grams}}$$

Oxidation of Uranium (IV). Pannell[6] has shown that the oxidation of uranium (IV) in hydrochloric acid solutions by aeration is decreased by (1) increasing the acid concentration; (2) decreasing the uranium (IV) concentration; (3) increasing the ionic strength of the hydrochloric acid solution. At the lowest pH tested, 0.9, only 4% of a 0.026 M uranium (IV) solution was oxidized to uranium (VI) by one hour of vigorous aeration at 20°C.

Although the concentration of uranium (IV) in the concentrated hydrochloric acid solution obtained in the procedure given here is greater than 0.026 M, this unfavorable factor is opposed by the favorable effect of the concentrated acid with its low pH and high ionic strength. Accordingly, it was assumed that during the 5- to 7-minute dissolution step, in which little oxygen is present, negligible oxidation occurs despite the elevated temperature. The agreement between the calculated values of uranium (VI) and those found experimentally in the samples analysed shows that this assumption is probably correct.

The importance of recording the polarogram immediately after the dilution step was shown by a brief study in which the final solution obtained after dissolution and dilution was deaerated and polarographed at various times after the dilution. The apparent uranyl fluoride percentage increased from 1.70, the value obtained with the recommended procedure, to 1.81 and 1.89 after a delay of 20 and 40 minutes, respectively. Therefore, if the polarographic deaeration is started 1 to 2 minutes after the solution is diluted to volume, the error due to oxidation is not serious.

Calibration. The standard addition method is used to calibrate the uranium (VI) wave because it has been shown by Kolthoff and Harris[7] that the wave height, in acid concentrations over 0.02 M, is dependent upon the acid concentration.

The standard addition technique, however, requires that the wave height be proportional to uranium concentration. These same authors[7] have presented data to show that this requirement is not strictly met in 2 M hydrochloric acid solutions. On the other hand, calculations with their values of i_d/C for the concentration range of uranium (VI) normally found in uranium tetrafluoride samples reveal that the error in assuming linearity between concentration and wave height generally is less than 2%.

Interferences. Commercial-grade uranium tetrafluoride generally contains less than 50 ppm each of copper, chromium, nickel and iron as the major metallic impurities. Of these elements, only copper can be expected to interfere on the basis of half-wave potentials. However, the concentration of uranium (VI) normally found is greater than 5000 ppm, or at least 100 times the copper concentration. The copper, therefore, is effectively diluted out.

The addition of 50 γ of copper to 50 ml. of hydrochloric acid-boric acid mixture, a quantity equivalent to 100 ppm of copper in the sample, gave no wave at -0.1 to -0.4 volts vs. S.C.E. with the sensitivity ordinarily used, 0.06 μa/mm. Chromium (III), chromate, molybdate, tin (II) and tin (IV), tested in the same concentration, also gave no waves. Bismuth and antimony in this concentration showed interference equivalent to slightly less than 0.05% of uranyl fluoride. These elements, however, are found in concentrations rarely exceeding 5 ppm. None of the elements tested, therefore, will ordinarily interfere.

Results. The results found on a variety of uranium tetrafluoride samples together with the calculated values are shown in Table I. In Table II are presented a series of results on a single sample to illustrate the precision of the procedure.

TABLE I

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES

	Uranyl Fluoride, %	
Sample Designation	Found[(a)]	Calculated[(b)]
C-2243	1.72	1.74
C-2377	0.98	0.97
C-2701	0.94	0.92
C-4009	4.41	4.29
C-4107	1.32	1.47
C-4401	1.75	1.73
C-4632	1.67	1.64
C-4970	1.33	1.28

(a) Average value of 2 to 4 determinations
(b) Average value calculated from the results of three different laboratories.

TABLE II

PRECISION OF SUGGESTED METHOD

	Uranyl Fluoride, %	
Sample Designation	Found	Calculated
C-7656	1.70	1.64
	1.70	
	1.66	
	1.66	
	1.66	
	1.69	
	1.79	
	1.69	
Average	1.69	
Standard deviation, absolute, %	0.04	
Standard deviation, relative, %	2.3	

Confidence limit of average (95%), % ± 0.03.

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