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AN INDIRECT COLORIMETRIC METHOD FOR THE DETERMINATION OF URANIUM

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Index No. ORNL-1476
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AN INDIRECT COLORIMETRIC METHOD FOR THE DETERMINATION OF URANIUM

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January 13, 1953

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ABSTRACT

An indirect colorimetric method has been developed for the determination of uranium in the range 50 to 400 γ in a volume of 50 ml. The method is based on the oxidation of uranium(IV) to uranium(VI) with iron(III) and determination of the iron(II) thus formed by application of the o-phenanthroline method. A concentration of 1 γ U/ml will produce an absorbancy of 0.08 in 1-cm cells. The standard deviation is 11 per cent. Application has been made to carnotite ores, phosphate rocks, Bartow clay and organic and aqueous extracts.

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AN INDIRECT COLORIMETRIC METHOD FOR THE DETERMINATION OF URANIUM

INTRODUCTION

Methods for the determination of uranium in the colorimetric range are extremely limited in general application. Rodden[3] gave a thorough discussion of the reagents that have been used for this determination. The major criticism of all of these reagents is their marked insensitivity. Recently Crouthamel and Johnson[1] reported an improved procedure based on the thiocyanate[4] method. The authors state that about 10 γ U/ml will develop an absorbance of about 0.20 in 1-cm cells. Although this method is a distinct improvement with respect to sensitivity, a need exists for still more sensitive colorimetric methods.

The quantitative oxidation of uranium(IV) with iron(III) has led to the investigation of a possible indirect colorimetric method based on the following reactions:

(1) $U^{+4} + Fe^{+3} \longrightarrow U^{+6} + Fe^{+2}$

(2) Fe^{+2} + o-Phenanthroline $\longrightarrow$ (Fe-o-Phenanthroline Complex)$^{+2}$

By means of a spectrophotometric measurement of the ferrous-o-phenanthroline complex, uranium may be determined indirectly. The sensitivity of the proposed method is theoretically the sensitivity of the o-phenanthroline method for iron, approximately 0.2 γ/ml[6], which is greater than that of existing colorimetric methods for uranium. Such a high sensitivity would permit the determination of uranium in concentrations where presently only the fluorescence technique is applicable.

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EXPERIMENTAL

The major problem which was encountered in the successful development of the indirect ferrous-o-phenanthroline method for the determination of uranium was to separate uranium from traces of iron. If iron is present in the solution during the reduction of uranium(VI) to uranium(IV), it will also be reduced, thereby producing iron(II) ions other than those formed when iron(III) is reduced by uranium(IV). The concentration of phosphate should also be reduced to a minimum since uranium(IV) and phosphate form a slightly soluble compound.

These two major interfering ions, iron and phosphate, are found in significant concentration in numerous uranium-bearing ores. The investigation of efficient, practical methods of separating these and other possible interferences was undertaken initially. Experiments included separation by precipitation with cupferron, separation by anion-exchange resins, and separation by extraction with tributylphosphate.

Separation of Uranium from Iron and Phosphate by Precipitation with Cupferron. A preliminary separation with cupferron removes iron, copper, and vanadium by precipitation. Uranium(VI) is not precipitated and remains in the filtrate. A procedure was devised in which the filtrate, containing uranium free from iron, was treated with nitric and perchloric acids in order to destroy unreacted cupferron, and finally with sulfuric acid. Following evaporation of the solution to fumes of sulfur trioxide, uranium(VI) was reduced in the diluted sulfate solution.

Attempts to apply this procedure to solutions containing iron and aluminum phosphate to which traces of uranium had been added were not successful. A dense precipitate (mostly $AlPO_4$), which caused severe bumping

and spattering, formed upon evaporation and hindered the complete decomposition of excess organic reagent with nitric and perchloric acids. Attempts to remove the bulk of the aluminum by a carbonate precipitation resulted in the precipitation of NH_4ClO_4 upon further evaporation.

Other workers[5] investigating the separation of iron from uranium with cupferron have stated that the method is not to be recommended for the removal of large amounts of iron prior to determining traces of uranium.

Separation by Anion Exchange. Separation of uranium from interfering ions based on the retention of uranium(VI) in the form of a complex uranium(VI) sulfate on a strong base anion exchange resin was attempted. Preliminary results indicated that this approach was unsuccessful since the uranium was not quantitatively retained on the resin.

Separation by Extraction with Tributylphosphate. The separation of uranium from iron and phosphate by extraction with tributylphosphate[2] was also attempted. By using certain specific conditions, this method proved the most feasible of those tested. Uranium(VI) was extracted from a 10 per cent solution of nitric acid in the presence of aluminum nitrate. In order to insure complete removal of uranium, a double extraction was required. The organic phase was washed with ammonium carbonate solution, which stripped the uranium as the soluble uranyl tricarbonate anion. The stripping solution also served as an hydrolytic agent for traces of iron and aluminum that had been extracted by TBP.

Reduction of Uranium(VI) to Uranium(IV). Another factor of utmost importance to the success of the proposed method was the quantitative reduction of uranium(VI) to uranium(IV). In order for the iron(II) ions formed to

be equivalent to uranium(IV) present, it is imperative that uranium exist in the quadrivalent state only after reduction. The more common methods of reduction include the zinc reductor, cadmium reductor and electrolysis with the mercury cathode. A small amount of uranium(III) is formed in each of these methods. Uranium(III) is oxidized to uranium(IV) by aeration; however, excessive aeration must be avoided because oxidation of microgram quantities of uranium(IV) to uranium(VI) often occurs.

Tests employing zinc and cadmium micro-reductors (0.5 by 8 to 12 cm) as a means of reducing standard uranium solutions (50 to 400 γ of uranium) demonstrated that either could be used satisfactorily. Suction is recommended to assure an even flow rate of solution through the reductor. Further tests using these reductors on solutions of aluminum and iron phosphates containing known amounts of uranium, which were extracted twice with TBP, gave erratic results. A cause of this behavior may be due in part to the presence of a small trace of iron in the final solution which was not separated. This supposition was verified by applying the TBP extraction procedure to synthetic solutions of aluminum and iron phosphates containing no uranium. In each case an appreciable amount of iron was found in the final solution.

In an effort to avoid contamination by iron, the mercury cathode was used to affect the reduction of uranium(VI) to uranium(IV). Traces of iron that were not previously removed should deposit in the mercury during the electrolysis period. Although preliminary tests yielded erratic results, reproducible results were obtained using an increased volume of solution for electrolysis and immersing only a minimum portion of the platinum gauze anode in the solution. The purpose of partial immersion of the anode was to minimize anodic oxidation. A study of the separation

of iron by the mercury cathode showed that 0.2 mg of iron in a solution containing uranium was deposited quantitatively in one hour when the solution was electrolyzed at two amperes and six volts.

RESULTS

Standard solutions of uranyl sulfate were reduced with the mercury cathode using small, water-cooled, electrolytic cells of the type described by Rodden[7]. A 25-ml solution was made 1 N in H_2SO_4 and electrolyzed for 1 hour at 6 to 8 volts and 2.0 to 2.5 amperes using a mercury pool with a surface area of 12.6 sq. cm. as the cathode. A Fisher electroanalyzer was used to provide the d.c. power. The reduced solutions were transferred to 50-ml volumetric flasks then aerated for 1-1/2 minutes by swirling to oxidize any uranium(III) that had been formed to uranium(IV). An excess of iron(III) was added followed by the addition of the o-phenanthroline reagent. The pH was adjusted to 4 ± 0.5 with ammonium hydroxide. The optical density was measured in 1-cm cells at 515 mμ after 20 minutes with a Beckman Model DU spectrophotometer. The results are given in Table 1.

Table 1

Determination of Uranium in Standard Solutions of Uranyl Sulfate by the Indirect Ferrous-o-Phenanthroline Method

Final Volume of Solution - 50 ml

Uranium γ/ml	Optical Density	Factor γ/ml/Optical Density
1	0.079	12.7
	0.078	12.8
	0.077	13.0
	0.088	11.4
2	0.154	13.0
	0.125	16.0
4	0.314	12.7
	0.304	13.2
	0.332	12.0
6	0.501	12.0
	0.418	14.4
	0.370	16.2
8	0.589	13.6
	0.545	14.7
	0.522	15.3
	0.609	13.1
	0.641	12.5
Average		13.5
Standard Deviation		1.5
Coefficient of Variation, per cent		11.0

A second series of standard uranyl sulfate solutions was tested which contained a matrix solution of aluminum and iron phosphates approximating 0.5 gram of phosphate ore. These standards were extracted twice with TBP, the uranium was stripped with ammonium carbonate and the acidified extracts evaporated to dryness with sulfuric acid. The remainder of the procedure was followed as described previously. The results are given in Table 2.

Table 2

Determination of Uranium in Solutions of Aluminum Phosphate by the Indirect Ferrous-o-Phenanthroline Method Following Extraction with TBP

Final Volume of Solution - 50 ml

Uranium γ/ml	Optical Density	Factor γ/ml/Optical Density
1	0.092	10.9
2	0.168	11.9
	0.211	9.5
4	0.315	12.7
	0.284	14.1
	0.286	14.0
	0.277	14.4
	0.270	14.8
	0.283	14.1
6	0.393	15.3
	0.430	14.0
8	0.620	12.9
	0.540	14.8
	0.513	15.6
Average		13.5
Standard Deviation		1.5
Coefficient of Variation, per cent		11.0

DISCUSSION

The results indicate that 50 to 400 micrograms of uranium in the presence of high concentrations of aluminum phosphate in volumes of 50 ml is quantitatively extracted by TBP. The same factor was obtained on these solutions as was obtained on standard solutions of uranyl sulfate. The standard deviation of the factor was also equivalent for both solutions. The standard deviation encountered here is higher by a factor of approximately two than that usually found for the determination of iron(II) with o-phenanthroline. This relatively high deviation is probably due in part to the experimental error of the reduction step with the mercury cathode in which some uranium(III) is formed in addition to uranium(IV). The customary procedure for oxidizing uranium(III) back to uranium(IV) is to aerate the solution. Aeration is known, however, to cause oxidation of microgram quantities of uranium(IV) to uranium(VI). Since these oxidations occur simultaneously, rigid control of the aeration time was practiced in an effort to standardize conditions. There is no assurance however, that the extent of reduction to the trivalent state is duplicable.

The method is of significant value for the determination of uranium in the concentration range interval in which the available colorimetric procedures are not sufficiently sensitive and the fluorometric technique is not sufficiently precise. The precision of this method compares favorably with the best precision which can be obtained with existing methods.

Application of this method was made to the determination of uranium in standard samples of carnotite ores, and phosphate rocks. The results are shown in Table 3.

Table 3

Determination of Uranium in Standard Samples of Carnotite Ore and Phosphate Rock by Indirect Ferrous o-Phenanthroline Method

	U_3O_8, Per Cent		
	A Present	B Found	A-B Difference
Carnotite Ore No. 4	0.170	0.206	
		0.192	
		0.165	
		0.173	
		0.173	
		0.166	
	Average	0.178	-0.008
Phosphate Rock No. 1	0.030	0.027	
		0.025	
	Average	0.026	0.004

Further application was made to the determination of uranium in organophosphorus-kerosene extracts of uranium and sodium carbonate strippings of these extracts. In the case of the organic extracts, the organic compounds were first charred and then oxidized with nitric and perchloric acids and the uranium determined in the usual manner. A comparison of the results by this method and by the ascorbic acid[8] method is shown in Table 4.

Table 4

Comparison of Uranium Content in Organic and Sodium Carbonate Extracts by Indirect Ferrous o-Phenanthroline Method with Ascorbic Acid Method

Organic Extracts, mg/ml

		1	2	3	4	5	6
A. Indirect Ferrous		0.20	0.23	0.32	0.33	1.94	2.16
		0.18	0.23	0.31	0.33	1.91	1.96
		0.21				1.88	
		0.20				1.60	
						1.74	
	$\bar{x}$	0.20	0.23	0.32	0.33	1.81	2.06
B. Ascorbic	$\bar{x}$	0.20	0.21	0.32	0.34	1.74	2.10
A-B. Difference		0.00	0.02	0.00	-0.01	0.07	-0.04

Sodium Carbonate Extracts, mg/ml

A. Indirect Ferrous		3.3	3.5	3.4	3.5
		3.9	3.6	3.4	3.6
		3.3	3.4	3.8	4.0
		3.4	3.5	3.3	3.8
	$\bar{x}$	3.2	3.5	3.6	3.7
B. Ascorbic	$\bar{x}$	3.4	3.5	3.8	3.9
A-B. Difference		-0.2	0.0	-0.2	-0.2

In general the agreement between methods is good. The results which were obtained by the indirect method show a tendency to be slightly lower at increasing concentrations than those by the ascorbic acid method, but not by any significant factor.

SUMMARY

An indirect colorimetric method has been developed for the determination of uranium in the range 50 to 400 γ in a volume of 50 ml. The method is based on the oxidation of uranium(IV) to uranium(VI) with iron(III) and determination of the iron(II) thus formed by application of the o-phenanthroline method. A concentration of 1 γ U/ml will produce an absorbancy of 0.08 in 1-cm cells. The standard deviation is 11 per cent.

Uranium is separated from iron and phosphate, the major interfering ions, by extraction with tributylphosphate. The last traces of iron are deposited by electrolysis in a mercury cathode which also accomplishes the reduction of uranium(VI) to uranium(IV). Application has been made to carnotite ores, phosphate rocks, Bartow clay and organic and aqueous extracts.

ACKNOWLEDGEMENT

The authors acknowledge the assistance of W. K. Miller in contributing to the technical phases of the problem, and the assistance of Miss Shirley Weindl in the performance of the experimental work.

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APPENDIX

PROCEDURE FOR THE DETERMINATION OF URANIUM BY THE INDIRECT FERROUS-O-PHENANTHROLINE COLORIMETRIC METHOD

Reagents

Hydrofluoric acid - HF, 48 per cent.
Nitric acid - HNO_3, concentrated and 5 N solutions.
Perchloric acid - $HClO_4$, concentrated, 72 (W/V) per cent.
Ammonium hydroxide - NH_4OH, concentrated solution (W/V).
Ammonium nitrate - $(NH_4)NO_3$, 2 (W/V) per cent.
Aluminum nitrate - $Al(NO_3)_3$, saturated solution.
Ammonium carbonate - $(NH_4)_2CO_3$, 1 M.
Tributylphosphate reagent, 30/70 (V/V) tributylphosphate and isopropyl ether.
Ammonium hydroxide, concentrated.
Sulfuric acid, 1 N.
o-Phenanthroline, 0.2 per cent - Dissolve 0.2 grams o-phenanthroline monohydrate in 100 ml of water.
Iron(III) solution - Dissolve 0.5 g. iron wire in 10 per cent H_2SO_4 solution and dilute to 1 liter. Each ml contains 500 micrograms of iron.
Alkacid test paper.
Triple-distilled mercury.

Apparatus

D. C. power supply.
Water-jacketed electrolytic cells.
Platinum gauze anodes, circular (approx. 3-1/2 cm diameter and 3 cm in length).

Procedure

A. Dissolution of Sample

Steps	Comments
1. Weigh approximately 0.5 g sample to the nearest 0.1 mg and transfer to a platinum dish.	
2. Add 5 ml conc. HNO_3, 5 ml conc. $HClO_4$, 3 ml conc. H_2SO_4 and 10 ml HF.	
3. Heat the sample to fumes of SO_3 and evaporate nearly to dryness.	

4. Dissolve the residue in 20 to 25 ml of 5 N HNO_3 and dilute to about 80 ml with distilled water.

5. Heat the solution nearly to boiling and add conc. NH_4OH slowly until the solution is basic and digest for 1 minute on a hot plate.

6. Filter through Whatman No. 40 paper and wash the precipitate with 15 to 25 ml of 2 per cent NH_4NO_3.

6. The filtrate and washings are discarded.

7. Dissolve the precipitate in 10 to 15 ml of 10 per cent nitric acid solution and dilute to 30 ml with distilled water.

7. This step is best accomplished by using hot nitric acid solution which dissolves the precipitate off the filter paper.

B. Extraction of Uranium

8. Add 6 ml of saturated $Al(NO_3)_3$ reagent.

8. The purpose of this reagent prior to TBP extraction is to "salt out" and complex phosphate.

9. Add 30 ml of TBP reagent, extract for 5 minutes. Separate the phases; add 20 ml TBP reagent to the aqueous phase and extract for 3 minutes.

9. A double extraction is necessary if appreciable phosphate is present.

10. Combine the TBP extracts and discard the aqueous phases.

11. Strip the organic phase by shaking with 50 ml of 1 M $(NH_4)_2CO_3$ for 5 minutes.

11. Ammonium carbonate strips uranium from the TBP phase by the formation of the uranyl tricarbonate ion. Any iron(III) and aluminum(III) "carry through" will hydrolyze at this point.

12. Separate the phases, add 20 ml of 1 M $(NH_4)_2CO_3$ to the organic phase and shake for 3 minutes.

13. Combine the aqueous phases and discard the organic phase.

14. Evaporate to about 50 ml and filter again if any precipitate is evident.

15. Wash the precipitate with 15 to 20 ml of 1 M $(NH_4)_2CO_3$.

16. Continue evaporating to a volume of approximately 5 ml, then add 2 to 3 ml of conc. H_2SO_4 and take to dryness.

17. Dissolve the residue in 25 ml of 1 N H_2SO_4.

17. The solution is now ready for the electrolysis step.

C. Reduction with the Mercury Cathode

18. Transfer the mercury to the electrolytic cell and connect the anode and cathode leads.

18. About 20 ml of mercury is sufficient.

19. Transfer the solution to be electrolyzed into the cell.

20. Start the stirrer and stir the mercury just enough to agitate the surface.

21. Adjust the anode until the bottom rim is below the surface of the solution.

21. Further immersion is to be avoided due to anodic oxidation during electrolysis.

22. Turn on the current and adjust to two amp.

23. Electrolyze for 30 minutes to 1 hour.

23. If the sample is known to contain no iron(III), an electrolysis period of 30 minutes will be sufficient. If, however, a trace of iron is suspected, an electrolysis period of 1 hour is necessary.

24. At the end of the electrolysis period adjust the current to one-half amp., and with the current on, quickly drain the mercury from the electrolytic cell. Turn off current.

24. The purpose of leaving the current on is to prevent any leaching of iron with acid or other impurities, back into solution during the time the mercury is being drained off.

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25. Transfer the solution to a 50-ml volumetric flask and aerate for 1-1/2 to 2 minutes by swirling the flask.

25. During the electrolysis step uranium(VI) is reduced to a mixture of uranium(IV) and uranium(III). The aeration step is necessary to oxidize the uranium(III) to uranium(IV).

D. Formation of the Ferrous-o-Phenanthroline Complex

26. After the aeration step, add 1 ml of iron(III) solution.

26. The amount need not be accurate as long as a slight excess of iron(III) is added.

27. Add 1 ml of o-phenanthroline reagent.

28. Add NH_4OH drop by drop with shaking until the solution is just basic to alkacid paper.

29. Add 1 N H_2SO_4 until the solution is at a pH of about 4 as noted by the alkacid paper. Dilute to the mark.

30. Let stand 20 minutes.

31. Measure the optical density of the solution against a reference solution on a spectrophotometer at 515 mμ.

31. The reference solution contains the same amount of iron(III) and o-phenanthroline as the sample and is adjusted to the same acidity.

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PROCEDURE FOR CLEANING THE MERCURY
FROM THE ELECTROLYTIC CELLS

Reagents

Nitric acid, 10 (W/V) per cent
Sulfuric acid, 5 (W/V) per cent

Procedure

Steps	Comments
1. Add 200 ml of 10 per cent HNO_3 to the used mercury.	1. If the samples to be electrolyzed contain traces of iron, the mercury cathode should be renewed after every fourth or fifth electrolysis. The mercury need not be changed as often when essentially pure solutions are electrolyzed.
2. Pass air through the mercury for 3 hours.	
3. Decant the HNO_3 and add 200 ml of 5 per cent H_2SO_4.	
4. Continue passing air through the mercury for 2 hours.	
5. Decant the H_2SO_4 and wash the mercury thoroughly with distilled water.	

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