NYO-7568
CHEMISTRY — GENERAL

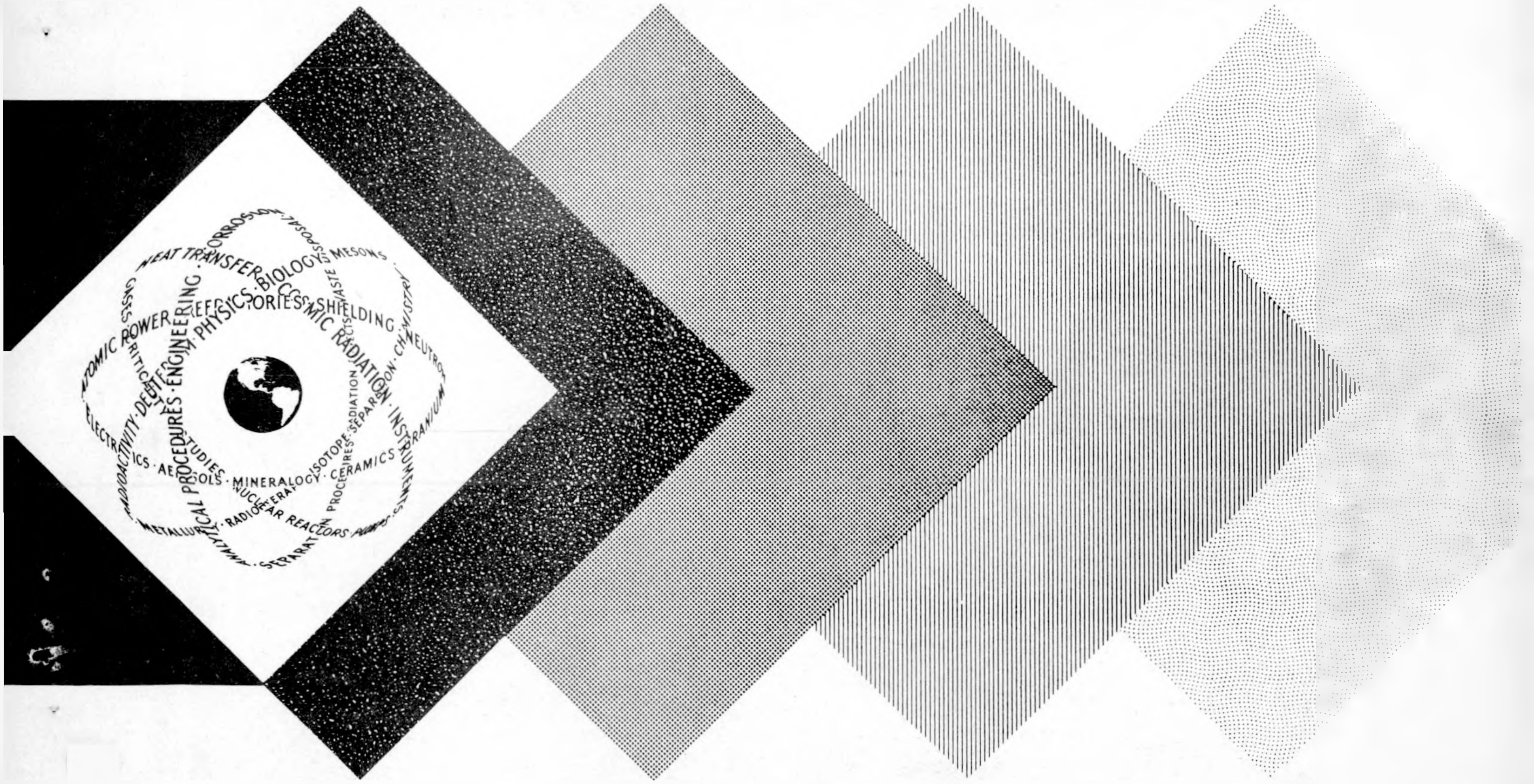
ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

Separation of Uranium from Bismuth Using Tris-(2-ethylhexyl)phosphine Oxide

By
Arno H. A. Heyn
Gurupada Banerjee

November 1, 1959

Boston University
Boston, Massachusetts



UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service

Printed in USA. Price $0.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC Technical Information Service Extension
Oak Ridge, Tennessee

NYO 7568

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

Separation of Uranium from Bismuth Using Tris-(2-ethylhexyl)phosphine Oxide

by

Arno H. A. Heyn and Gurupada Banerjee
Boston University, Boston, Massachusetts

AT(30-1)1873

November 1, 1959

Work Completed May, 1958

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

Separation of Uranium from Bismuth Using Tris-(2-ethylhexyl)phosphine Oxide

by

Arno H. A. Heyn and Gurupada Banerjee

ABSTRACT

An ultraviolet spectrophotometric method for the determination of uranium has been developed which is based on the ultraviolet absorption of the complex of uranium(VI) with tris-(2-ethylhexyl)phosphine oxide. The complex is formed by extracting uranium(VI) from an aqueous 6M sodium nitrate solution in the pH range 2.5 - 3.0 into 0.1M solution of tris-(2-ethylhexyl)phosphine oxide (TEHPO) in an inert diluent, cyclohexane. This extraction also separates the uranium from many diverse ions that otherwise interfere. The reliable range for aqueous samples is 0.0025 to 0.1 mg. of uranium per ml. The standard deviation is less than 1% for both 0.05 mg. uranium per ml. of the organic phase for 1-cm. cells and 0.005 mg. per ml. for 5-cm. cells.

Extraction of uranium from 7M nitric acid with 0.1M TEHPO, followed by stripping with sodium carbonate solution, has been successfully utilized to develop a method for the separation of uranium from 10,000-fold excess of bismuth.

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

Separation of Uranium from Bismuth Using Tris-(2-ethylhexyl)phosphine Oxide

Table of Contents

Page

Experimental

Index of Tables and Figures

Introduction

The growing interest in the liquid metal fuel reactor systems (10), using alloys of uranium in bismuth as the fuel, has made quantitative separation of uranium from bismuth and subsequent determination of the former necessary. Systematic studies on the distribution of bismuth nitrate from aqueous solutions to ethers and hexone conducted by the authors (8) have established that ethers are better extractants for uranium in presence of bismuth under comparable conditions than hexone and the separation of uranium from bismuth can be effected by using a continuous extractor. An investigation has also been made of the anion-exchange behavior of uranium and polonium-210 in sulfuric acid medium and the possibility of separation of uranium from polonium and bismuth has been discussed (1,2). A homogeneous precipitation method (17), involving thioacetamide has been applied to the separation of bismuth from uranium. Extraction with acetylacetone in the presence of ethylenediaminetetraacetate (EDTA), followed by polarographic estimation, has also been utilized to develop a method (9) for separation of uranium from bismuth.

There has appeared recently a report by Ross and White (15) in which the possibility of extraction of ions from acid solution with a new organic solvent, tris-(2-ethylhexyl)phosphine oxide (TEHPO) is indicated. These investigators have shown that uranium(VI) can be completely extracted from solutions of hydrochloric-, nitric-, sulfuric- and perchloric acids with 0.1M solution of TEHPO in a diluent of cyclohexane whereas no extraction of bismuth is possible under similar conditions. As emphasized by these workers, the results of the above-mentioned tests are qualitative in nature and do not represent absolute extraction coefficients. Blake et al (4), however, have shown that 0.1M solution of TEHPO in carbon tetrachloride gives 99.6% extraction of uranium from nitrate and sulfate solutions. The possibility of using caustic soda or sodium carbonate for stripping uranium from the organic phase has also been suggested.

With a view to utilizing the reagent, TEHPO for the separation of uranium from bismuth, an attempt has been made to study the extraction behavior of uranium and bismuth from nitric acid solutions to a 0.1M solution of TEHPO in an inert diluent, cyclohexane. Uranium cannot be completely separated from nitric acid solutions of bismuth using 0.1M TEHPO-diluent because bismuth nitrate is also extracted by the reagent to some extent. It has now been found that uranium can be completely separated from bismuth using 0.1M TEHPO in cyclohexane only if the extraction is carried out from 7M nitric acid and the organic phase is back-washed with the same acid. The uranium present in the organic phase can then be stripped with a 5% aqueous solution of sodium carbonate. The existing methods (18) for the determination of microgram quantities of uranium were not satisfactory and convenient for determining uranium in the extracts. For this reason a new method for determining uranium by ultraviolet spectrophotometry using TEHPO as the reagent was developed. This method followed the approach taken by the recent work of Paige, Elliott, Rein (13) and others (3,5,11) which has disclosed that some of the complexes of uranium absorb in the ultraviolet and can form the basis of sensitive analytical methods for the element. When it was found that the conditions which are favorable for the ultraviolet absorption of uranium(VI)-TEHPO complex are not suitable for the determination of uranium after separation from bismuth, another spectrophotometric method for the determination of uranium was developed which is based on the sensitive ultraviolet absorption of the TEHPO complex of uranium(VI).

Both uranyl nitrate and nitric acid are extracted by TEHPO and were found to absorb in the ultraviolet region. The problem of developing a sensitive and reliable spectrophotometric method for uranium was one of establishing the extraction conditions and the working wave length, so that the absorbance for the uranium(VI)-TEHPO complex was high with respect to that of nitric acid complex. 250 mμ has been chosen as the working wave length because in this region the absorption of the uranium-TEHPO complex is high as compared to that of nitric acid-TEHPO complex. The formation of the uranium complex by liquid-liquid extraction also separates uranium from many interfering diverse ions. The 7M nitric acid solution required for back-washing of the organic phase interferes with the spectrophotometric determination of uranium. For this reason, the uranium was stripped with 5% sodium carbonate solution and re-extracted into 0.1M TEHPO in cyclohexane adjusting the pH of the aqueous phase.

Our methods for uranium fall into two broad groups, in one of which the absorbance of uranium(VI)-TEHPO complex in pure uranium solution has been studied and in another the separation of uranium from bismuth has been made from 7M nitric acid using 0.1M TEHPO and the uranium content of the organic phase was stripped and then subjected to the same treatment as in the former case.

Outline of the Investigations and General Applications

The experimental studies which were made by the authors during the period March 1957 - May 1958 may be summarized as follows:

I. Investigation of the ultraviolet absorbing characteristics of the reagent TEHPO and the uranyl-TEHPO adduct in cyclohexane.

II. Study of the conditions for extraction of uranium by TEHPO.

III. Study of the conditions for minimum extraction of bismuth by TEHPO.

IV. Establishment of a method for extracting uranyl uranium in the presence of a large excess of bismuth.

V. Study of the interference of other ions with the recommended procedure.

Experimental

Apparatus: Preliminary absorption spectra were studied on a Beckman DK-1 Model spectrophotometer. All quantitative measurements were made on a Beckman Model DU spectrophotometer with ultraviolet and photomultiplier attachments. Matched 1-cm. or 5-cm. silica cells were used for absorption study. A Beckman Model G and a Beckman Zeromatic pH meters were used for all pH measurements. An International Centrifuge size 1 Model SBV of the International Equipment Company was used for separating the organic phase from the aqueous mixture, whenever needed. Pyrex separatory funnels fitted with Teflon and glass needle valves and graduated centrifuge tubes with ground glass stoppers were used for separation purposes. A Model PCC 10A Proportional Counter Converter (Nuclear Measurements Corporation) was used in conjunction with a Tracer Lab "100" scaler. Matheson Company P-10 gas (90% argon, 10% methane) was used in the gas flow system.

Preparation of Reagents

Tris-(2-ethylhexyl)phosphine Oxide: The method of Blake et al (4) was modified for the preparation of tris-(2-ethylhexyl)phosphine oxide:

A three-necked flask with ground-glass openings was mounted on a removable automatic stirrer equipped with a heating arrangement and provided with a coil type condenser and a dropping funnel with a pressure-equalizing side tube. Dry nitrogen was introduced at the top of the condenser and initially can be allowed to sweep through the apparatus and escape at the mouth of the dropping funnel. When the funnel was closed a slight positive pressure was maintained at the nitrogen tank, as indicated by the level of mecury in the escape valve.

7.3 grams of magnesium (0.3M) were placed in the flask and the apparatus was assembled and swept with nitrogen. When the air had been replaced, the flask was heated gently with a free flame under continued flow of nitrogen to insure elimination of any moisture adhering to the surface of the glass or the metal. When the flask had cooled completely, the nitrogen flow was reduced to a barely perceptible rate and 200 ml. ether and 47.6 grams of 3-(chloromethyl)-heptane (0.32M) were introduced through the funnel. The stirrer was started for the crushing of pieces of light magnesium foil in contact with the liquid. A small crystal of iodine was added to catalyze the reaction and the mixture was stirred for two hours until the liquid was clear.

The three-necked flask was cooled in ice and salt, and 15.3 grams of freshly distilled phosphorus oxychloride (0.1M) were added drop by drop.

At the end of the reaction the magnesium-halogen derivative was decomposed by adding 200 ml. 1:1 hydrochloric acid dropwise with cooling under reflux. The mixture was allowed to settle for several minutes, washed in a separatory funnel with two portions of dilute sodium carbonate solution containing small amount of sodium thiosulfate solution (to remove iodine) and then the ether layer was collected. The aqueous extract was also washed with two portions of fresh ether and the total ether extract was kept overnight over anhydrous sodium sulfate. The dried ether solution together with two portions of sodium sulfate washings with ether was distilled under reduced pressure to remove ether and the light-yellow liquid obtained was distilled at 180-200°/2 mm. on an oil-bath. The yield was 18%.

Bismuth Solution: A weighed quantity of redistilled bismuth metal prepared by W. S. Ginnell of the Nuclear Engineering Department of the Brookhaven National Laboratory was dissolved in nitric acid to give a stock solution containing 100 mg. of bismuth per ml.

Uranium Solutions: A standard 10 mg. per ml. uranium solution was prepared by dissolving a weighed quantity of uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water and diluting to volume. The uranium content was determined gravimetrically by weighing as U_3O_8. Solutions of greater dilutions were made from the stock solution as required.

4.8 mg. of radioactive uranium-233 (alpha 4.82 m.e.v., $t_{\frac{1}{2}} = 1.68 \times 10^5$ years) was obtained as a metal from Brookhaven National Laboratory. The metal was dissolved in concentrated nitric acid and the solution was evaporated nearly to dryness. The residue was treated with 1M nitric acid, 10.26 mg. natural uranium was then added as carrier and the volume was made up to 50 ml. This solution contained 96 micrograms of uranium-233 and 205 micrograms of natural uranium per ml.

One ml. of this solution was mixed with 2.052 mg. of natural uranium and the solution was diluted to 500 ml. with 0.01N nitric acid. Aliquots of the latter solution (1.92×10^{-7} grams uranium-233 per ml. plus 4.51×10^{-6} grams natural uranium per ml.) were used in the experimental work. On the basis of the activity of 0.192 micrograms of uranium-233 plus 4.51 micrograms of natural uranium as carrier, the activity per microgram of uranium-233 was determined to be 7911 ± 20 alpha counts per minute (background substracted). Measurement of alpha activity from the samples was calibrated by counting a Radium D+E standard (No. 2263, National Bureau of Standards). Correction can be made for the alpha activity of the carrier based on 0.75 disint. per minute per microgram of natural uranium (6).

TEHPO Solution: A 0.1M TEHPO solution was prepared by dissolving 9.65 grams TEHPO in Eastman Spectrograde cyclohexane (previously saturated with water) and making the total volume up to 250 ml. Eastman practical grade cyclohexane was also used after purification by passage through a column of silica gel. Unless otherwise mentioned, all other reagents were C. P. grade or met ACS reagent grade specifications.

General Procedure

Extraction of Uranium: The ability of the neutral phosphine oxide to extract uranium has been demonstrated and it has been found (4) that with the exception of dicyclohexylphosphinic acid, this is the only reagent which extracts uranium completely with an organic to uranium mole ratio as low as 10:1. It was also known from the previous experimental work that uranium(VI) at about 1 mg. per ml. is quantitatively extracted by an equal volume of 0.1M TEHPO in carbon tetrachloride from 0.008M nitrate. These experiments were designed to investigate the extraction of uranium at the micro-gram level. In each experiment, 10 ml. nitric acid solution (1M or 7M) containing 0.192 micrograms of uranium-233 and 4.51 micrograms of natural uranium, was taken in a separatory funnel and the mixture was then shaken with an equal volume of 0.1M TEHPO in cyclohexane for five minutes. The organic phase was then separated and the uranium in the aqueous phase was determined by alpha-counting. It was found that 99.4% uranium was easily extracted from the aqueous phase in a single stage extraction process and the extraction of uranium was independent of the concentration of nitric acid. Using two-stage extraction process, 99.6% uranium was extracted from the aqueous phase.

Absorption Spectra: Preliminary tests indicated that both uranyl nitrate and nitric acid are extracted by 0.1M TEHPO in cyclohexane, resulting in absorption in the ultraviolet region. For developing a sensitive and reliable spectrophotometric method for uranium, the working wave length was so chosen that the absorbance for the uranium(VI)-TEHPO complex was high with respect to that of nitric acid complex. It was also found that the extraction of nitric acid is increased as its concentration in the aqueous phase is increased.

The absorption spectra of the uranium-TEHPO and nitric acid-TEHPO complexes in 0.1M TEHPO in cyclohexane are shown in Figure 1. These complexes were formed by extraction from 6M sodium nitrate solution at pH 2.5 and were measured in 1-cm. matched silica cells. At 250 mμ, the absorbance of the uranyl complex is high, while that of the nitric acid complex is very low. The absorbance was also linear with uranium concentration. Therefore, this wave length was chosen for the recommended procedures. The molar absorptivity for the uranyl-TEHPO complex was about 2400 l mol^{-1} cm^{-1} at 250 mμ.

Effect of pH: The adjustment of pH of the aqueous phase is essential because it affects the extraction of nitric acid. A series of uranium-free 6M sodium nitrate solutions was adjusted to various pH values with dilute nitric acid and then extracted with equal volume of 0.1M TEHPO in cyclohexane. The variation of optical density against pH is shown in Table I.

TABLE I

Effect of pH on Extraction of Nitric Acid by 0.1M TEHPO

pH	Absorbance[a] at 250 m
0.5	0.151
1.0	0.147
1.5	0.089
2.0	0.052
2.5	0.050
3.0	0.050
3.5	0.051
4.0	0.054

[a] Average of duplicates

These data indicate that control of pH in the aqueous phase is necessary and the highest possible pH range should be used to minimize absorbance due to nitric acid.

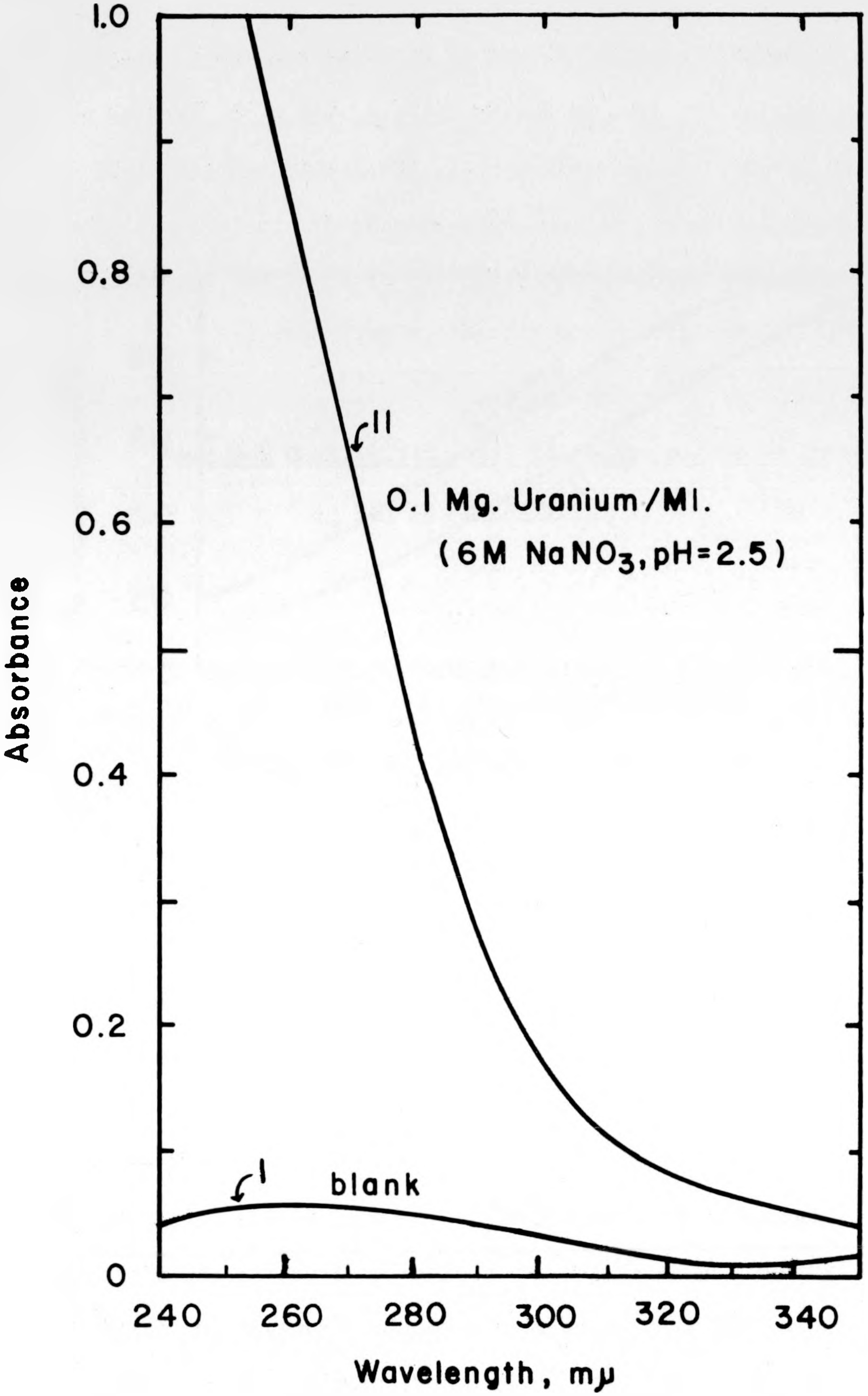


FIG. 1 ABSORPTION SPECTRA

Curve I: Nitric acid
Curve II: Uranyl nitrate } extracted with

0.1M TEHPO in cyclohexane

The variation of optical density against pH was also studied by extracting 0.05 mg. per ml. of uranium(VI) from 6M sodium nitrate into 0.1M TEHPO in cyclohexane at varying pH levels. In each experiment, the sample and its blank were adjusted to the same pH before extraction. The data given in Table II show that in the pH range 2.0-3.0, the error due to variation of pH is negligible and therefore the pH range 2.5-3.0 was chosen for extraction purposes.

TABLE II

Effect of pH on Absorbance of Uranium(VI)-TEHPO Complex

pH	Absorbance[a] at 250 mμ
1.5	0.570
2.0	0.501
2.5	0.500
3.0	0.498
3.5	0.500

[a] Average of duplicates

Recommended Procedure for Uranium

Uranium Samples, 0.01 to 0.1 Mg. per Ml.: Transfer a 10-ml. sample into a 50-ml. beaker, add 5.1 grams of solid sodium nitrate and swirl until the solution is clear. Prepare a blank containing 10 ml. of 6M sodium nitrate solution. Adjust the sample solution and the blank to a pH of 2.5-3.0 by dropwise addition of nitric acid and/or sodium hydroxide solutions, using a pH meter. The final molarity of sodium nitrate can be as low as 5M without affecting the extraction coefficient of uranium or the absorbance of the blank. Transfer the solution quantitatively to 40-ml. graduated centrifuge tubes, rinsing the electrodes and the beakers with 6M sodium nitrate solutions adjusted to pH 2.5-3.0. Pipet 10 ml. of 0.1M TEHPO in cyclohexane into the centrifuge tube. Shake the mixture vigorously for 5 minutes after closing the stopper. Allow the two phases to separate and pipet suitable aliquots of the organic phase into a 10-ml. dry volumetric flask. Transfer this organic phase carefully to a clean, dry, 1-cm. silica cell without spilling the solution on the rim or outside of the cell and then measure the absorbance at 250 m . against the blank.

Uranium Samples, Greater than 0.1 Mg. per Ml.: The procedure is the same as above except for the following changes:

A 1 to 1 aqueous to organic ratio should be used for the extraction and the sample aliquot should be chosen to give a uranium concentration in the organic phase of 0.01 to 0.1 mg. per ml. For this reason, separatory funnels should replace graduated centrifuge tubes, whenever necessary. With sample aliquots of smaller volume 6M sodium nitrate solution can be conveniently used as the salting agent.

Uranium Samples, 0.002 to 0.01 Mg. per Ml.: Either the ratio of aqueous to organic can be increased to greater than 1 to 1 or 5-cm. cells can be used. Any one of the following methods is applicable:

(a) The practical limit of the aqueous-organic ratio for quantitative extraction was found to be 4 to 1. This determines the lower limit of the procedure at 0.0025 mg. per ml. of uranium in the aqueous sample. Dissolve 10.2 grams of solid sodium nitrate in 20 ml. of sample, extract with 5 ml. of 0.1M TEHPO in cyclohexane, and measure the absorbance in 1-cm. cells.

(b) In order to have enough organic phase to fill 5-cm. cells, 20 ml. of sample solution containing solid sodium nitrate as salting agent, should be extracted with an equal volume of 0.02M TEHPO in cyclohexane. With 5-cm. cells, the concentration of TEHPO in inert diluent must be decreased to 0.02M; otherwise, the high absorbance of 0.1M TEHPO will require a large slit width and therefore decreases reliability. It has been found by using uranium-233 tracer that for low concentrations of uranium, 0.02M TEHPO gives quantitative extraction from 6M sodium nitrate. Except for these changes, the procedure is the same as (a).

Discussion of Results for Uranium

Working Curves: Calibration curves for 1-cm. and 5-cm. cells are separately prepared by processing appropriate aliquots of 0.1 mg. per ml. of uranium solutions. In each case the response is linear for the concentrations of uranium given above. The slope value for 1-cm. cells is 10 and for 5-cm. cells is 48. This value (13) is the ratio of absorbance to milligrams of uranium per milliliter in the organic phase. A Ringbom plot (14) of percent absorptance (100-% transmittance) versus log concentration is shown in Figure 2. The optimum concentration range, i.e., the range in which the present method is most precise as indicated by the approximately straight-line portion of the curve, is 10-100 mg. of uranium per liter both at 250 mμ and 270 mμ. Results obtained at 270 mμ are chosen for comparison.

Reproducibility: Some of the representative data for the recommended procedure are shown in Table III.

TABLE III

Reliability of the Recommended Procedure

Absolute Concn. of Uranium in Organic Phase	Av. Absorbance	Std. Dev. Parts per Thousand of Uranium Present
Mg./Ml.		
0.05[a]	0.50	5
0.01[a]	0.09	59
0.005[b]	0.24	6

[a] 1-cm. cells

[b] 5-cm. cells

These results are based on five replicate determinations at each of the three levels of uranium. The percentage standard deviation is less than 1 towards the midsections of the calibration curves for both 1-cm. and 5-cm. cells.

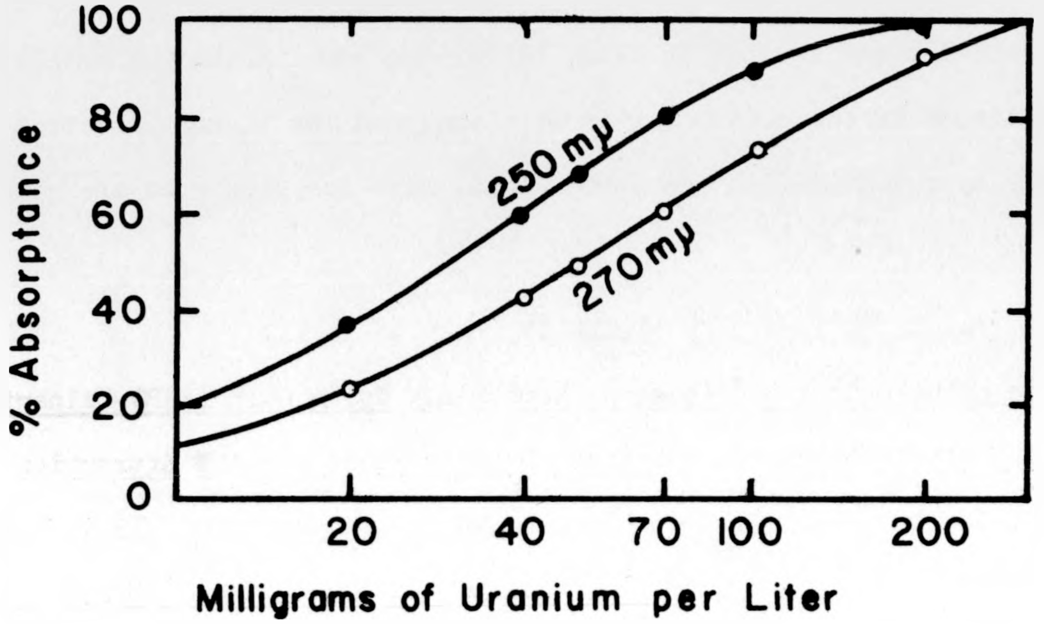


FIG.2 RINGBOM PLOT OF URANIUM(VI) SOLUTIONS

Separation of Uranium from Bismuth

With a view to finding out suitable conditions for the separation of uranium from bismuth, studies were made on the extraction of 10 mg. of bismuth in different acid media, using 0.1M TEHPO in cyclohexane under the conditions of our experimental procedure for uranium. After the equilibrium was established, appropriate aliquots of the organic layer were analyzed for bismuth spectrophotometrically by the potassium iodide method (16). Data for such runs are given in Table IV.

TABLE IV

Extraction of Bismuth from Different Acid Media Using 0.1M TEHPO-Diluent[a]

Molarity of Nitric Acid	Bismuth Organic Phase Mg.	% Extraction
1.0	1.350	13.5
3.0	0.435	4.35
5.0	0.011	0.11
7.0	0.005	0.05
10.0	0.002	0.02

[a] 10 mg. bismuth taken

When it was found that only 0.05% bismuth is extracted by 0.1M TEHPO-diluent from 7M nitric acid, experiments were made on the extraction of uranium at the microgram level from the same acid. It was found that 99.4% uranium-233 was extracted from 7M nitric acid by a single stage extraction process and a method was developed for the separation of uranium from 10,000-fold excess of bismuth. Even though less bismuth was extracted from 10M nitric acid as compared to 7M solution, the latter concentration was chosen in order to facilitate handling of the samples.

Procedure: Take suitable aliquots of uranium-bismuth solution in a graduated centrifuge tube and evaporate the solution to dryness over a Bunsen flame. Dissolve the white residue in 7M nitric acid and quantitatively transfer to a 125 ml.

pyrex separatory funnel fitted with teflon and glass needle valve, rinsing the graduated tube with 7M nitric acid and making the total volume about 10 ml. Pipet 10 ml. 0.1M TEHPO in cyclohexane into the funnel and shake the mixture vigorously for five minutes after closing the mouth of the funnel. Allow the two phases to separate and discard the aqueous phase. Backwash the separated organic phase with three (five in case of 1000 mg. bismuth present) 10-ml. portions of 7M nitric acid as in the previous manner and discard the acid. Wash the remaining organic phase with water and then strip it with a total of 50-ml. 5% sodium carbonate solution in three successive stages and collect the stripped solution in a 100-ml. beaker. Evaporate the solution to about 10 ml. and then adjust the pH of the solution to 2.5-3.0 using 7M nitric acid and caustic soda, if required. Transfer this solution quantitatively to a 40-ml. graduated centrifuge tube, rinsing the electrodes and the beaker with 6M sodium nitrate solution adjusted to pH 2.5-3.0. Adjust the aqueous to organic phase ratio according to the recommended procedure for uranium, centrifuge for 10 minutes to separate the two phases and measure the absorbance of the organic phase at 250 mμ using either a 1-cm. cell or 5-cm. cell as the case may be. There is no need for adding fresh salting agent in this case because sodium nitrate is already present in the solution. A blank run is made by extracting a sodium carbonate solution of equivalent concentration and adjusting to pH 2.5-3.0 as before. The concentration of uranium was found from suitable calibration curves. Results of such separations are shown in Table V. From these results it seems evident that the extraction with 0.1M TEHPO in cyclohexane followed by backwashing and stripping offers a clean-cut separation of uranium from 10,000 fold excess of bismuth.

TABLE V

Separation of Uranium from Bismuth

Bismuth Present Mg.	Uranium Present, Mg.	Uranium Found, Mg.	% Deviation of Average
100	0.100	0.099, 0.101, 0.100	0.0
200	0.100	0.100, 0.100, 0.101	+0.3
500	0.100	0.101, 0.099, 0.099	-0.4
500	1.000	0.996, 0.998, 0.997	-0.3
1000	0.100	0.092, 0.102, 0.103	-1.0
1000	1.000	1.030, 0.990, 1.010	+1.0

Effect of Diverse Ions

Since the extraction with TEHPO-diluent, followed by stripping can be often used for the purification of uranium in analytical procedures, an interference study at a uranium concentration level of 0.05 mg. per ml. was made to find the limitations of the recommended procedure for diverse ions commonly associated with uranium samples. Results are shown in Table VI. The diverse ions were added at levels of 0.5, 0.05 and 0.005 mg. per ml.

TABLE VI

Tolerance Level of Various Ions in Recommended Procedure

Ion	Tolerance Mg./Ml.	Ion	Tolerance Mg./Ml.
Aluminium(III)	0.500	Magnesium(II)	0.500
Barium(II)	0.500	Manganese(II)	0.050
Cadmium(II)	0.500	Nickel(II)	0.500
Cerium(III)	0.005	Potassium(I)	0.500
Chromium(III)	0.500	Silver(I)	0.500
Cobalt(II)	0.500	Sodium(I)	0.500
Copper(II)	0.050	Thorium(IV)	0.005
Iron(II)	0.500	Tin(II)	0.005
Iron(III)	0.050	Titanium(IV)	0.005
Lanthanum(III)	0.500	Zinc(II)	0.500
Lead(II)	0.050	Zirconium(IV)	0.005
Anion		**Anion**	
Acetate	0.500	Arsenate	interfere at 0.005 mg./ml.
Chloride	0.500	Bismuth	
Chromate	0.500	Oxalate	
Fluoride	0.050	Permanganate	
Perchlorate	0.500	Phosphate	
Sulfate	0.500	Tungstate	
		Vanadate	

Discussion of Results

Although 0.1M TEHPO-diluent has been successfully utilized (4) for the extraction of uranium, as yet the mechanism of the extraction has not been determined. It is most likely that TEHPO forms a strong chelate with uranium(VI) because it is also formed in very dilute nitrate solution.

No errors were encountered as a result of solvent evaporation. Hence concentration changes caused by volatilization of cyclohexane are negligible for half an hour after filling the absorption cells. If the mixture coats the outside of the cell, the absorbance reading will be affected due to the creeping effect and, therefore, the absorbance reading should be taken immediately after the cells are filled.

It was known from previous experimental work (12) that uranium cannot be stripped from the organic phase by water. Although the use of ammonium carbonate solution has been suggested (4) as a stripping agent for uranium, the quantitative recovery of the latter is only possible if sodium carbonate solution replaces ammonium carbonate.

Acknowledgment

This work was supported by the U. S. Atomic Energy Commission under the terms of Contract No. AT(30-1)1873.

The Beckman DK-1 spectrophotometer was obtained under a grant from the National Science Foundation.

The authors thank Subodh Chakravarty for his help in the preparation of TEHPO.

The authors thank Harmon L. Finston and other members of the Radiochemical Analysis Group of the Nuclear Engineering Department of the Brookhaven National Laboratory for helpful suggestions during the progress of the work.

Literature Cited

1. Banerjee, G., Heyn, A., Finston, H. L., Brookhaven National Laboratory Hot Lab Progress Report (January 1958).
2. Banerjee, G., Heyn, A., ANAL. CHEM., 30, 1795 (1958).
3. Bastian, R., Weberling, R., Palilla, F., Ibid., 25, 284 (1953).
4. Blake, C. A., Moore, J. G., Whaley, W. M., "Uranium Chemistry of Raw Materials Section Part II. Studies in Uranium Chemistry: Solvent Extraction", ORNL-1480, December 6, 1952.
5. Buck, R. P., Singhadeja, S., Rogers, L. B., ANAL. CHEM., 26, 1240 (1954).
6. Fleming, E. H., Jr., Ghioroso, A., Cunningham, P. B., Phys. Rev., 88, 642 (1952).
7. "Handbook of Chemistry and Physics", 37th Edition (1955-1956), Chemical Rubber Publishing Company.
8. Heyn, A., Banerjee, G., U. S. Atomic Energy Commission, NYO-7567 (July 1957).
9. Krishen, A., Freiser, H., ANAL. CHEM., 29, 288 (1957).
10. Liquid Metal Fuel Reactor: BNL 403 (T-88)LMFR-13, January 1957.
11. Merritt, C., Jr., Hershenson, H. M., Rogers, L. B., ANAL. CHEM., 25, 572 (1957).
12. Morrison, G. H., Freiser, H., "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, Inc., New York, p. 149 (1957).
13. Paige, B. E., Elliott, M. C., Rein, J. E., Ibid., 29, 1029 (1957).
14. Ringbom, A., Z. anal. Chem., 115, 332 (1939).
15. Ross, W. J., White, J. C., "Extraction of the Elements with Tris-2-ethylhexyl- and trihexylphosphine Oxides from Acidic Solutions", (ORNL)CF-57-1-5, January 2, 1957.
16. Sandell, E. F., "Colorimetric Determination of Traces of Metals", Second Edition, Interscience Publishers, Inc., New York, p. 213.
17. Stoner, G. A., Finston, H. L., ANAL. CHEM., 29, 570 (1957).
18. Yoe, J. H., Will, F. (III), Black, R. A., ANAL. CHEM., 25, 1200 (1953).