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SUBJECT: Direct Spectrophotometric Determination of Uranium in Cyclohexane Solutions of Tri-n-Octylphosphine Oxide

TO: See Distribution

FROM: J. C. White

WJR-150

ABSTRACT

A method for the direct determination of uranium in a cyclohexane solution of tri-n-octylphosphine oxide (TOPO) is presented. The adduct, $UO_2Cl_2 \cdot 2TOPO$, that is formed when uranium(VI) is extracted from hydrochloric acid solutions by tri-n-octylphosphine oxide absorbs light in the ultraviolet region. This absorbance is measured at 230 mμ versus a TOPO-cyclohexane solution that has been contacted with hydrochloric acid of the same concentration as that in the test aliquot. The molar absorbance index is 5500. The method is not selective; of the elements that are extracted by TOPO from hydrochloric acid, iron(III), zirconium, molybdenum, tin and thorium, only thorium can be tolerated.

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DIRECT SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN CYCLOHEXANE SOLUTIONS OF TRI-n-OCTYLPHOSPHINE OXIDE

W. J. Ross

The adducts of tri-n-octylphosphine oxide (TOPO) and $H_2Cr_2O_7$,(1) $FeCl_3$,(2) $ZrCl_4$,(3) and $SnCl_4$(4) have been observed to absorb energy in the ultraviolet region. Such absorption indicates a possible means for the direct determination of chromium(VI), iron(III), zirconium, and tin(IV) by spectrophotometric measurement of the organic phase. A cursory study of the visible and near-ultraviolet spectral characteristics of the $UO_2Cl_2 \cdot 2TOPO$ species has also been made previously.(5) The intense absorption band that was initially observed at 320 mμ could not be reproduced in subsequent spectral studies and is now recognized as being caused, at least partially, by the presence of microgram amounts of iron in the UO_2Cl_2 solution that was used in these earlier tests. The $UO_2Cl_2 \cdot 2TOPO$ adduct absorbs at wavelengths greater than 300 mμ; however, no absorption maximum is present in the near-ultraviolet region.

Banerjee and Heyn(6) observed that the complex that was formed when uranium was extracted from nitrate solutions by tris(2-ethylhexyl) phosphine oxide (T2EHPO) absorbed ultraviolet light. They made this absorbance the basis of a spectrophotometric method for the determination of 0.0025 to 0.1 mg of uranium.

Horton and White(7) have determined uranium in TOPO extracts colorimetrically with dibenzoylmethane. The range of uranium in this method is 0.015 to 2.5 mg.

A fluorometric procedure for the determination of uranium in TOPO extracts has also been published.(8)

This report is a summary of the investigations on the spectra of $UO_2Cl_2 \cdot 2TOPO$ that were performed with a Cary, Model 14-M, recording spectrophotometer. This species of uranium is extracted into the organic phase when hydrochloric acid solutions of uranium are equilibrated with the extractant.(9) A similar adduct, $UO_2(NO_3)_2 \cdot 2TOPO$ is extracted from HNO_3 systems. Previous studies(5) have revealed that nitrate, in the TOPO-cyclohexane phase, absorbs ultraviolet light strongly below 300 mμ whereas chloride exhibits very little absorbance at wavelengths higher than 230 mμ; consequently, hydrochloric acid was selected for these spectral studies.

EXPERIMENTAL

Reagents

Uranyl Sulfate Stock Solution, 1.8 mg of uranium per ml. This solution was a dilution of a more concentrated uranyl sulfate solution, 19 mg of uranium per ml, that was originally prepared by dissolving 2.6 g of U_3O_8 in HNO_3, removing the HNO_3 by fuming with H_2SO_4, and diluting the residual H_2SO_4 solution to 100 ml with H_2O. The diluted stock solution was standardized colorimetrically.

Thorium Chloride Stock Solutions, 10.8 and 1.13 mg of thorium per ml. These solutions were prepared by diluting a more concentrated solution of $ThCl_4$ with 1 M HCl and standardizing the solutions by the Thoron colorimetric method. The original stock solution had been prepared by repeatedly evaporating 100 ml of 0.5 M $Th(NO_3)_4$ solution to dryness in the presence of 12 M HCl until all nitrate had been expelled.

Hydrochloric Acid, ~12 M. Reagent-grade acid was equilibrated with TOPO-cyclohexane in order to remove iron(III) from the acid prior to its use.

Tri-n-Octylphosphine Oxide, 0.1 M solution in cyclohexane. Commerical grade, Eastman No. 7440, TOPO was purified further to remove traces of phosphinous and phosphinic acids and other impurities that absorb light at wavelengths greater than 200 mμ. The diluent was Eastman "Spectra Grade" cyclohexane (No. S702). A petroleum ether solution of TOPO is washed with 1 N $KMnO_4$ to oxidize phosphinous acid to phosphinic acid; the excess $KMnO_4$ is destroyed by oxalic acid, then the phosphinic acid is removed either by an extraction into NaOH solution or by contact with Al_2O_3. The purified TOPO is recrystallized from the ether.

Ultraviolet Spectrum of $UO_2Cl_2 \cdot 2TOPO$

A cyclohexane solution of this adduct that contained 36 μg of uranium per ml was prepared as follows. Five ml of a 3 M HCl solution that contained 1.8 mg of uranium was extracted with 5 ml of 0.1 M TOPO for 10 minutes. The aqueous phase was analyzed fluorometrically and found to contain 6 μg of uranium. A 1-ml aliquot of the organic phase was transferred to a 10-ml volumetric flask and diluted to volume with cyclohexane.

The amount of hydrochloric acid that is extracted by 0.1 M TOPO is a function of the initial concentration of acid present. This acid adduct has been observed to absorb energy in the ultraviolet region.(10) A reference solution was prepared, accordingly, that contained the same concentration of the acid adduct as was present in the uranium solution; i.e. 5 ml of 3 M HCl was extracted with 5 ml of 0.1 M TOPO, following which a one-ml aliquot of the organic phase was diluted to 10 ml with cyclohexane.

The spectrum of the uranium adduct was measured versus the reference solution (~0.01 M $HCl \cdot TOPO$) between 350 and 210 mμ. The major portion of this spectrum is presented in Figure 1; the remainder of the ultraviolet spectrum (310 to 350 mμ) consists merely of a continuation of the decreasing absorbance as the wavelength is increased.

The spectrum of $UO_2Cl_2 \cdot 2TOPO$ exhibits only one absorbance maximum in the ultraviolet region, 230 mμ, at which the molar absorbance index is 5500.

Calibration Curve for the Direct Determination of Uranium as $UO_2Cl_2 \cdot 2TOPO$

The precision with which the absorbance of $UO_2Cl_2 \cdot 2TOPO$ follows Beer's law was determined with aliquots of a stock solution that contained 43 μg of uranium per ml and was 0.001 M with respect to HCl·TOPO. This stock solution was prepared by repeating the extraction described above and then diluting a 3-ml aliquot of the organic phase to 25 ml with cyclohexane. One to 7-ml aliquots of this stock solution were diluted to 10 ml with cyclohexane, following which the absorbance of each solution was measured at 230 mμ versus a reference solution of 0.001 M HCl·TOPO (Figure 2, Curve A).

The absorbance values shown in Curve A were obtained with a single reference solution, i.e. 0.001 M HCl·TOPO, although the concentration of the acid adduct in the $UO_2Cl_2 \cdot 2TOPO$ solutions varied from 0.001 M to 0.007 M. As mentioned above, the absorbance of HCl·TOPO in the ultraviolet region increases with the concentration of this acid adduct. The contribution to the absorbance of the $UO_2Cl_2 \cdot 2TOPO$ adduct produced by the acid adduct was determined as follows. The absorbance of 0.010 M HCl·TOPO was found to be 0.040. The absorbance of 0.002 M, 0.003 M, 0.004 M, 0.005 M, and 0.007 M HCl·TOPO versus 0.001 M HCl·TOPO was calculated by interpolation. These prorated errors were then subtracted from the absorbances presented in Curve A. The corrected curve, Curve B, has a reciprocal slope, $\frac{\mu g/ml}{absorbance}$, of 42.5 as compared to 40.8 for Curve A.

These tests reveal that significant errors are incurred in the measurement of the absorbance of $UO_2Cl_2 \cdot 2TOPO$ when the sample and reference solution contain different amounts of HCl·TOPO. These errors have been minimized (Curve C) by duplicating exactly the dilutions and size of aliquots of both sample and reference solutions. When the acid adduct concentrations in the sample and reference solutions are identical, the calibration curve intersects the origin with a reciprocal slope of 45.5 and varies from linearity by 3 per cent over the uranium concentration range of 0 to 30 μg per ml.

Interferences from Extraneous Elements

In general, any element that is extracted from HCl solutions by TOPO and which absorbs light in the ultraviolet region will interfere with this direct method for the determination of uranium. Previous studies have shown that chromium(VI), iron(III), zirconium, molybdenum(VI), tin(IV), and thorium, can be extracted from HCl by 0.1 M TOPO. All these elements, except molybdenum and thorium, have been investigated previously and observed to absorb atat wavelengths in the ultraviolet region.

A series of extractions was performed to determine the extent to which the absorbance of the TOPO adducts of $FeCl_3$, $ZrCl_4$, $SnCl_4$, and $H_2Cr_2O_7$ would interfere with the measurement of $UO_2Cl_2 \cdot 2TOPO$ at 230 mμ. Five-ml solutions of 3 M HCl that contained one mg of each of these elements were extracted with 5 ml of 0.1 M TOPO. The organic phases were then diluted with cyclohexane until the concentration of iron, zirconium, tin, and chromium was 10 µg per ml and the concentration of HCl·TOPO was 0.005 M. The absorbance of each of these dilute solutions was measured at 230 mµ versus a reference solution of 0.005 M HCl·TOPO. Each of these adducts absorbed energy at 230 mµ as shown in Table I.

Table I

Absorption of Energy by the TOPO Adducts of $FeCl_3$, $ZrCl_4$, $SnCl_4$, and $H_2Cr_2O_7$ at 230 mµ

Concentration of metal - 10 µg/ml
Reference - 0.005 M HCl·TOPO
Wavelength - 230 mµ
Cell length - 1 cm
Cary, Model 14-M, Recording Spectrophotometer

Element	Absorbance	Uranium Equivalence, µg/ml
Fe(III)	1.40	63
Zr	0.280	13
Sn(IV)	.380	17
Cr(VI)	.088	4

These results reveal that tin(IV), chromium(VI), zirconium and especially iron(III) cause serious interference with the measurement of the absorbance of $UO_2Cl_2 \cdot 2TOPO$. The TOPO adducts of $ZrCl_4$ exhibit absorbance maxima at 220 mµ, the adduct of $FeCl_3$ has an absorbance maximum at 245 mµ, while the $H_2Cr_2O_7$ complex exhibits a broad absorbance band between 220 mµ and 300 mµ.

Interference of Thorium

The interference of thorium with the determination of uranium was investigated with two types of solutions. In the first test, 5 ml of 3 M HCl that contained 1.13 mg of thorium was extracted for 10 minutes with 5 ml of 0.1 M TOPO. Three ml of the organic phase was diluted to 25 ml with cyclohexane and then a 4-ml aliquot of the dilute solution was diluted further to 10 ml to yield a solution that contained 10.8 µg of thorium per ml. The absorbance of this solution was measured at 230 mµ versus 0.004 M HCl·TOPO and observed to be less than 0.005.

In a similar test wherein 10.8 mg of thorium was extracted into 5 ml of 0.1 M TOPO, the organic phase (~2.2 mg of Th per ml) did not absorb at wavelengths between 350 and 220 mµ.

A third test consisted of extracting 5 ml of 3 M HCl that contained 1.8 mg of uranium and 1.13 mg of thorium with 5 ml of 0.1 M TOPO. The organic phase was diluted with cyclohexane to yield a solution that contained 17.2 μg of uranium and 10.8 μg of thorium per ml. The absorbance of this solution was measured versus 0.004 M HCl·TOPO and observed to be 0.380. This absorbance was corrected to be 0.388 versus 0.001 M HCl·TOPO and, therefore, deviated from the calibration curve by less than two per cent.

These tests prove that thorium is not an interference in this direct method for the determination of uranium.

Interference of Molybdenum(VI)

The ultraviolet spectral characteristics of the molybdenum-TOPO adduct, which has the approximate formula $MoOCl_3 \cdot 2TOPO$, were investigated briefly. Five ml of a 3 M HCl solution that contained 10 mg of molybdenum, as $(NH_4)_2MoO_4$, were extracted for 10 minutes with 5 ml of 0.1 M TOPO. The absorbance of the organic phase, 2 mg of Mo per ml, was greater than 2.0 when measured versus 0.1 M HCl·TOPO between 320 mμ and 220 mμ. These solutions were subsequently diluted with cyclohexane until the concentration of molybdenum was ~20 μg per ml in 0.001 M HCl·TOPO. The spectrum of this solution exhibited an absorbance maximum (1.520) at 226 mμ and another maximum (0.855) at 255 mμ.

The absorbance of the molybdenum-TOPO adduct in the ultraviolet region is, therefore, sufficiently high to cause serious interference with the determination of uranium in TOPO extracts.

Summary

An ultraviolet spectrophotometric method for the determination of uranium has been developed that is based on the absorbance of the $UOCl_2 \cdot 2TOPO$ adduct. The relationship between absorbance and concentration of uranium follows Beer's law in the concentration range below 30 μg per ml with a coefficient of variation of three per cent when the reference and sample solution consist of identical dilutions of the organic phase. All elements [Fe(III), Cr(VI), Zr, Mo(VI), and Sn(IV)], except thorium, that are readily extracted by 0.1 M TOPO from 3 M HCl also absorb in the ultraviolet region, and, thus interfere with this method. The extraction and interference of the $FeCl_3$ and $ZrCl_4$ adducts can be reduced considerably by extracting uranium from 1 M HCl, although the extraction coefficient of uranium is also decreased from ~1000 to ~100.(11)

This method appears to be a rapid means of determining uranium in the presence of thorium or other non-interfering elements and can be used effectively, in conjunction with the fluorometric method, for the determination of uranium in milligram or sub-milligram amounts. The presence of sulfate, perchlorate, or phosphate in the original aqueous phase causes no interference except through inhibition of the uranium extraction.

Acknowledgement

The purified tri-n-octylphosphine oxide, used in this work, was secured from Messrs. J. M. Schmitt and C. A. Blake.

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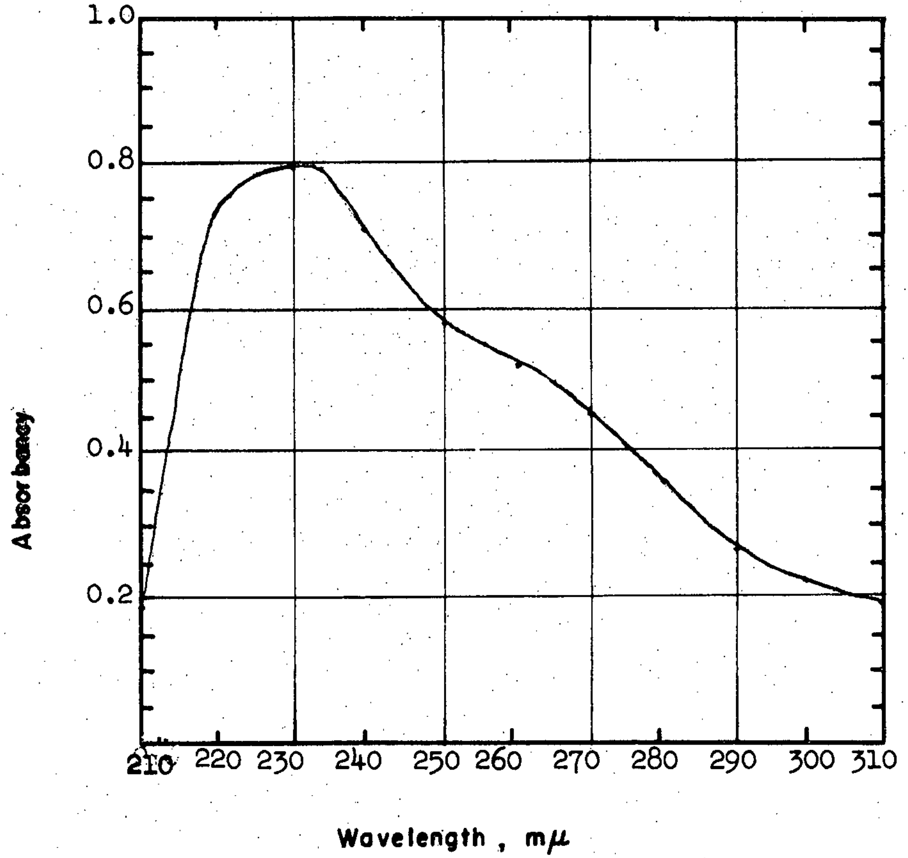
FIGURE 1

TITLE: Absorption Spectra of $UO_2Cl_2 \cdot 2(TOPO)$ in Cyclohexane

Molar Absorbancy Index 5500 at 230 mμ



TEST CONDITIONS

Concentration 36 μg of U per ml
Medium 0.01 M TOPO in cyclohexane
Chromophore
pH
Temperature, °C, 20
Reference
Instrument Cary, Model 14-M
Slit Width, mm. 0.08 mm at 230 mμ
Cell Thickness, Cm 1
Blank 0.01 M HCl·TOPO in cyclohexane
Remarks Slit sensitivity - 3 Slit width of 0.7 mm at 230 mμ when sensitivity is 1.

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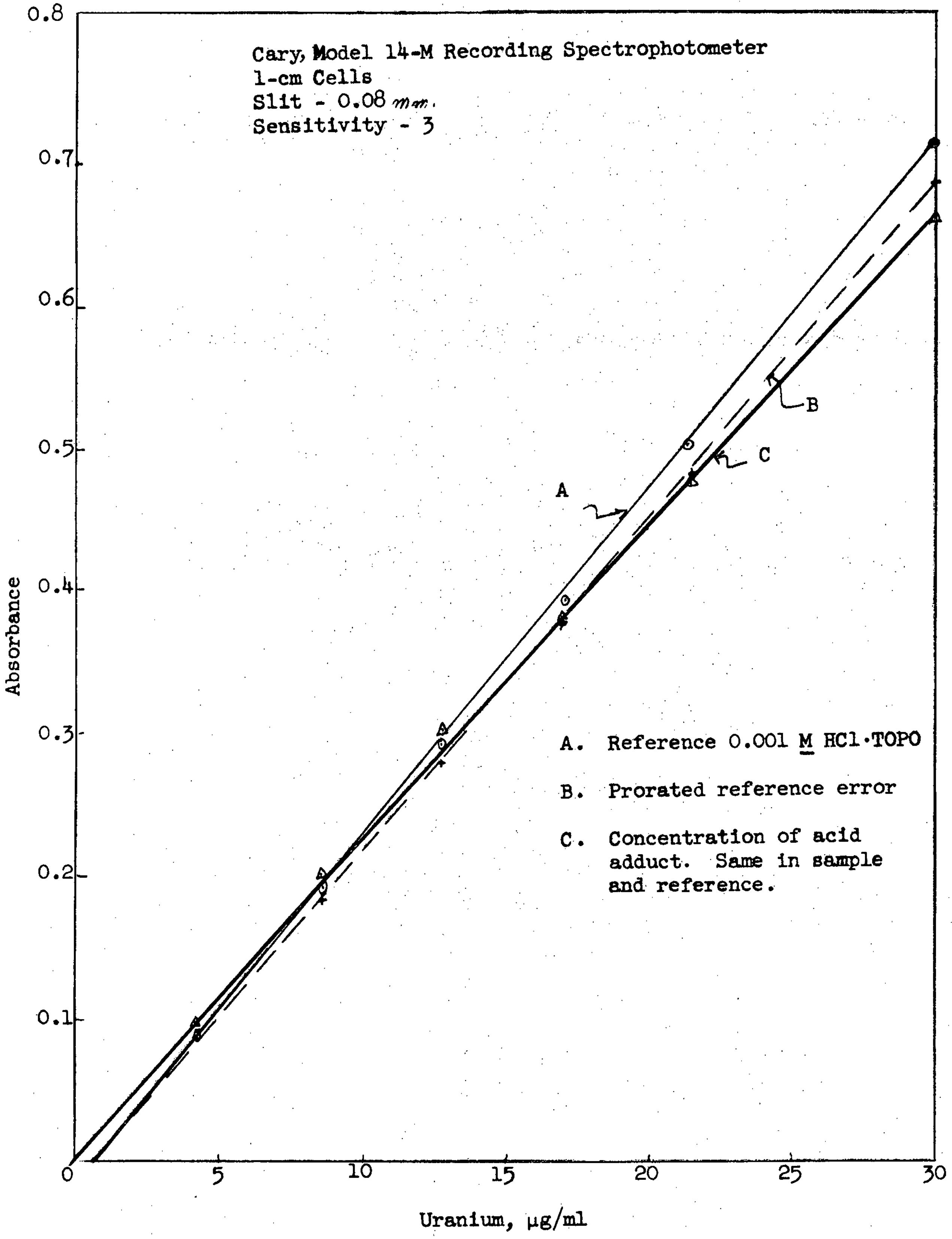
Figure 2

Calibration Curve for $UO_2Cl_2 \cdot TOPO$ in Cyclohexane



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