

Aqueous-ethanol medium has been found to produce stable colour. Interfering ions like Fe^{3+} , Ti^{4+} , etc., are removed during carbonate fusion and subsequent aqueous extraction. The vanadium present in the solution reacts immediately with SHA under the experimental conditions and full colour is developed immediately which remains stable for more than 24 hr. This procedure is particularly suitable for the estimation of vanadium in bauxite, magnetite, ilmenite, etc. In view of purity, availability, good solvent property and better extraction efficiency, methyl isobutyl ketone (MIBK) has been preferred as the extracting solvent to alcohols or esters used by other workers. The coloured complex can be quantitatively extracted by a single extraction with MIBK at pH 3, which makes the procedure simple and rapid. The method is sensitive as well as accurate and can be applied successfully for the determination of vanadium in various types of rocks, minerals, ores, etc., where vanadium is present in the p.p.m. level.

References

1. BHADURI, A. S. & RAY, P., *Z. analyt. Chem.*, **154** (1957), 103.
2. KORISCH, J., *Modern methods for the separation of rare metal ions* (Pergamon, London) 1969, 444.
3. MAXWELL, J. A., *Rocks and minerals analysis* (Interscience, London), 1968, 273.
4. BHADURI, A. S., *Z. analyt. Chem.*, **151** (1956), 109.
5. ROUBAULT, M., ROCHE, H. L. & GOVINDARAJU, K., *Sciences Terre*, **13** (1968), 381.
6. FLANAGAN, F. J., *Geochim. cosmochim. Acta*, **33** (1969), 81.

Rapid Separation & Simultaneous Spectrophotometric Determination of U(VI) Using N-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid

SHAHID ABBAS ABBASI

Department of Chemistry, Indian Institute of Technology
Powai, Bombay 400076

Received 29 August 1975; accepted 1 November 1975

A method is presented for rapid liquid-liquid extraction and simultaneous spectrophotometric determination of U(VI) in the presence of various anions and cations which are usually associated with it using N-*m*-tolyl-*o*-methoxybenzohydroxamic acid (TMBHA) in chloroform. The effect of various parameters such as pH reagent concentration, volume of mother liquor, foreign ions, etc., on the extraction and determination of uranium is discussed. The sensitivity of colorimetric determination of U(VI) with the present method is about 8 times more than the sensitivity of the most sensitive hydroxamic acid method used hitherto.

THE first detailed examination of N-phenylbenzohydroxamic acid (PBHA) as a reagent for uranium was carried out recently¹. It was found that in the extraction of U(VI), many cations interfered and the colour of the extracted U(VI)-PBHA complex with $\lambda_{\text{max}} = 510$ nm was suitable

only for the determination of milligram quantities of uranium, the molar absorptivity at λ_{max} being as low as 230. The selectivity was also low and no attempt was made to counter the interference of various common and less-common metals which are associated with uranium in minerals and fission products. Subsequently N-phenyl-2-naphthohydroxamic acid (PNHA) was prepared and tried as a reagent for U(VI)². PNHA, though proving highly sensitive and selective for V(V)³, came off as only a marginal improvement on PBHA in case of U(VI), in both sensitivity and selectivity.

N-*m*-tolyl-*o*-methoxybenzohydroxamic acid (TMBHA) is now presented as a reagent more selective than either PBHA or PNHA and about eight times more sensitive than PNHA for the extractive colorimetric determination of U(VI).

All the chemicals used were of reagent grade unless specified. Conductivity water was used for all purpose. A stock solution of U(VI) was prepared by dissolving uranyl nitrate (0.5 g) in water (1 litre) and standardizing the solution for uranium⁴.

TMBHA was prepared by the method of Gupta and Tandon⁵, and recrystallized repeatedly, m.p. 110° (lit.⁵ m.p. 111°). The reagent is very stable if stored out of contact of light and air. A 0.1M solution of TMBHA in ethanol-free doubly distilled chloroform was used for extraction work.

pH measurements were carried out with a radio-meter pH meter type PHM-29. The absorption spectra were recorded on a Perkin-Elmer model 402 spectrophotometer and measurements at a constant wavelength were done with a SF-4 (USSR) spectrophotometer. All optical measurements were carried out using matched quartz cells with 10 mm path-length.

Extraction procedure—An aliquot solution of U(VI) containing 15 to 950 $\mu\text{g}/\text{ml}$ of uranium was adjusted at pH 4.4-5.2 with the help of dil. NaOH or HNO_3 . To it was added TMBHA solution (4 ml) in chloroform and the two phases equilibrated for about 5 min, kept aside for complete separation and the chloroform layer removed. The aqueous layer was again extracted with a fresh 4 ml portion of TMBHA for 5 min, the chloroform extract mixed with the first extract, dried (Na_2SO_4), and made up to 10 ml with TMBHA solution. The absorbance of the orange-yellow extract was measured against TMBHA solution as blank. The extracts containing 15-90 $\mu\text{g}/\text{ml}$ of uranium were measured at 360 nm and those containing 80-950 $\mu\text{g}/\text{ml}$ of uranium were measured at 520 nm. A calibration curve was set by extraction-colorimetric determination of several known amounts of uranium and plotting the optical density values against concentration of uranium. The results were found reproducible within $\pm 0.5\%$.

The absorption spectra of uranium extract of TMBHA in chloroform against reagent (TMBHA solution in chloroform) blank exhibits a sharp peak at 360 nm and a broad peak at 518-522 nm. Beer's law is obeyed in the range 15-90 $\mu\text{g}/\text{ml}$ of U(VI) at 360 nm and 80-950 $\mu\text{g}/\text{ml}$ of U(VI) at 520 nm; the molar absorptivities being 2×10^3 at 360 nm and 285 at 520 nm. Thus uranium, if present in concentrations less than 90 $\mu\text{g}/\text{ml}$ can be determined

using the 360 nm peak while milligram concentrations of uranium can be determined at 520 nm. The sensitivity of the present method, calculated according to the definition of Sandell⁶ is 0.12 $\mu\text{g/ml}$ of U(VI). This is about 8 times more than the sensitivity of PNHA method². It is to be pointed out here that for the PNHA method, the sensitivity has wrongly been reported as 0.01 $\mu\text{g/ml}$. From the optical density values the sensitivity comes out to be 1.0 $\mu\text{g/ml}$. The colour of the U(VI)-TMBHA complex, was found to be stable up to 12 days.

The extraction is quantitative in the pH range 4.4-5.1. Below and above these pH values the extraction decreases. The optimum reagent concentration is 0.1M for complete extraction. Higher reagent concentrations can be used without disadvantage.

A change in the ratio of volumes of chloroform to aqueous phases from 1 to 20 does not effect the U(VI) extraction so that the present method can be used to concentrate uranium from its dilute solutions.

The tolerance limit for 10 ml aliquot of U(VI) solution containing 760 μg of U(VI) was set at the amount required to cause $\pm 2.0\%$ error in the uranium recovery. It was observed that the presence of 30000 ppm of La(III); 20000 ppm of Mn(II), Na(I), K(I); 16000 ppm of Mg(II), bromide, iodide; 10000 ppm of Pb(II), Zn(II), Ba(II); 8000 ppm of Ca(II), Sr(II), Hg(II), Ni(II), Co(II), As(III), Ge(IV); 6000 ppm of Ga(III) and 1000 ppm of phosphate, cyanide are tolerated. The interference due to Bi(III), Th(IV) and Ce(III) can be eliminated using

EDTA and magnesium chloride as masking agents. Tungsten (VI), Zr(IV), Mo(VI), Fe(III) and V(V) should be removed prior to the extraction of U(VI).

Composition of the U(VI)-TMBHA complex — Job's method of continuous variation, as modified by Vasburgh and Cooper⁷, was employed to study the composition of the orange-yellow U(VI)-TMBHA complex. The stoichiometry was found to be 1:2 (metal-ligand).

Formation of 1:2 complex neutralizes the dipositive charges of uranyl ion and renders the complex hydrophobic and susceptible to extraction in chloroform.

In the present method, the overall extraction and determination takes less than half an hour, and it is possible to extract and determine microgram to milligram amounts of U(VI) in the presence of several ions. Thus the method is rapid, simple and selective.

The author is grateful to the CSIR, New Delhi, for a senior fellowship and to G. Kaparwan for assistance.

References

1. AGRAWAL, Y. K., *Separation Sci.*, **8** (1973), 387.
2. AGRAWAL, Y. K., *Separation Sci.*, **8** (1973), 709.
3. AGRAWAL, Y. K., *Analyt. Chem.*, **47** (1975), 940.
4. WELCHER, F. W., *The analytical use of ethylenediamine-tetracetic acid* (Van Nostrand, New York), 1958.
5. GUPTA, Y. K. & TANDON, S. G., *J. Indian chem. Soc.*, **46** (1969), 831.
6. SANDELL, E. B., *Colorimetric determination of traces of metals* (Interscience, New York), 1959.
7. VOSBURGH, W. C. & COOPER, G. R., *J. Am. chem. Soc.*, **63** (1941), 437.