



**SEPARATION OF TRACE METAL IMPURITIES FROM NUCLEAR GRADE  
URANIUM BY LONG-CHAIN AMINE EXTRACTION AND DIRECT  
DETERMINATION BY ATOMIC ABSORPTION SPECTROPHOTOMETRY**

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**PUBLICAÇÃO IEA N.º 380**  
Janeiro — 1975

**INSTITUTO DE ENERGIA ATÔMICA**  
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SAO PAULO — BRASIL

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\* Reprinted from ANALYTICAL CHEMISTRY, Vol. 46, Page 1812, October 1974.

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## ABSTRACT

The separation and determination of trace concentrations of Bi, Cd, Pb, Hg, Au and Ag in nuclear grade uranium was investigated in some detail. The elements are extracted together with tri-n-octylamine in benzene from  $UO_2Cl_2$ -HCl-KI solutions and analysed by atomic absorption spectrophotometry. Elements not extracted (Ag) or only partially extracted (Bi, Cd, Hg and Pb) by the tertiary amine from  $UO_2Cl_2$ -HCl medium had their extraction significantly improved by the addition of potassium iodide to the aqueous phase. Direct burn of the organic phase in the atomic absorption spectrophotometer using hydrogen-air flame provided enhanced absorbance for the elements. In the trace concentrations of the metals, calibrations have provided (%) in the range 2 to 12 in routine analysis of uranium.

## RÉSUMÉ

On présente une étude d'extraction de Bi, Cd, Pb, Hg, Au et Ag présents comme traces dans les matrices d'uranium avec pureté nucléaire. Ces éléments sont extraits d'une solution de  $UO_2Cl_2$ -HCl-KI par la tri-n-octylamine dissoute en benzène et ils sont déterminés par spectrométrie d'absorption atomique. L'addition de KI dans le milieu  $UO_2Cl_2$ -HCl rend meilleure l'extraction des éléments ci-dessus. La phase organique elle-même est brûlée dans le spectrophotomètre en utilisant une flamme de  $H_2$  air, ce qui rend une augmentation dans la sensibilité des lectures. La précision est comprise dans le rang de 2 à 12%.

## RESUMO

Estuda-se a separação e determinação de Bi, Cd, Pb, Hg, Au e Ag presentes como traços no urânio nuclearmente puro. Os elementos são extraídos pela tri-n-octilamina diluída em benzeno de uma solução  $UO_2Cl_2$ -HCl-KI e analisados por espectrofotometria de absorção atômica. Elementos não extraídos (Ag) ou parcialmente extraídos (Bi, Cd, Pb, e Hg) pela amina terciária do meio  $UO_2Cl_2$ -HCl têm sua extração significativamente melhorada pela adição de iodeto de potássio na fase aquosa. A queima direta da fase orgânica no espectrofotômetro de absorção atômica usando-se uma chama de hidrogênio-ar permite um aumento na sensibilidade das leituras. Os desvios padrões relativos para os elementos estão compreendidos na faixa de 2 a 12%.

## Separation of Trace Metal Impurities from Nuclear Grade Uranium by Long-Chain Amine Extraction and Direct Determination by Atomic Absorption Spectrophotometry

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The purification and conversion of uranium concentrates to nuclear grade products require the identification and determination of a series of trace metal impurities, some of which have deleteriously high thermal neutron capture cross sections. The majority of the published literature in this area has approached the problem by an initial separation of the matrix uranium using, for instance, solvent extraction, and determining the trace impurities in the raffinate. Any procedure that could primarily separate the impurities by solvent extraction, or otherwise, from the major constituent, uranium, would be advantageous and attractive. This paper deals with such an approach for the separation, concentration, and determination of microgram quantities of a series of metals present as impurities in high grade uranium.

Long-chain amines have been utilized extensively as extracting agents for various elements, including uranium.

The literature on the subject is extensive (1-9). Such procedures have also been investigated in this laboratory for isolating trace metal concentrations from hydrochloric acid media (10). Of pertinent interest is the use of tri-*n*-octyl

- (1) F. L. Moore, Rept. NAS-NS-3101 (1960)
- (2) M. Y. Mirza, M. Ejaz, A. R. Sarni, S. Ullah, M. Raschid, and G. Sandani, *Anal. Chem. Acta.* **37**, 402 (1967).
- (3) A. D. Nelson, J. L. Hasching, and R. L. MacDonald, *J. Inorg. Nucl. Chem.* **27**, 459 (1965)
- (4) W. J. Maack, G. L. Booman, M. C. Elliott, and J. E. Rein, *Anal. Chem.* **30**, 1902 (1958).
- (5) W. J. Maack, G. L. Booman, M. C. Elliott, and J. F. Ren, *Anal. Chem.* **32**, 605 (1960)
- (6) W. J. Maack, G. L. Booman, M. E. Kussy and J. E. Rein, *Anal. Chem.* **33**, 1775 (1961).
- (7) F. L. Moore, Rept. ORNL 1314 (1952)
- (8) F. L. Moore, *Anal. Chem.* **29**, 1660 (1957).
- (9) W. D. Arnold and D. J. Crouse, Rept. ORNL-3030 (1961)
- (10) A. Abrão, Ph.D. Thesis, Instituto de Química Universidade de São Paulo, Brazil, 1971.

amine (TOA), diluted with an inert solvent as extracting agent. The extractive separation of cadmium, silver, gold, mercury, lead, and bismuth from aqueous hydrochloric acid solutions of uranyl chloride by use of TOA in benzene was studied. It was demonstrated that, while Au was quantitatively extracted, Cd, Hg, Pb, and Bi were only partially extracted and Ag not at all. Addition of small quantities of potassium iodide to the aqueous acid phase overcame this difficulty and permitted high and reproducible extraction by the amine.

Atomic absorption spectrophotometry indeed appears to be the method of choice for the determination of a variety of trace elements in terms of sensitivity and convenience. In this study, the impurity elements, after extraction from uranyl chloride solutions, were determined by atomic absorption by directly burning the organic phase in the spectrophotometer.

## EXPERIMENTAL

**Apparatus.** Absorption measurements were made on a Jarell-Ash series 82-500 atomic/flame emission spectrophotometer, equipped with a 0.5-meter Ebert-type monochromator. The resolution of the instrument is 0.2 Å in the first order. The spectrophotometer has a HETCO total consumption burner and a multipass optical system to give five passes through the flame. The height of the HETCO burner was adjusted for each element to achieve optimum readings. The following spectral lines were used: (nm) Cd, 228.8; Ag, 328.1; Au, 242.8; Hg, 253.7; Pb, 283.3; and Bi, 306.8. The light source was preheated at least 15 minutes before use. Acetylene-air and hydrogen-air flames were tested. The compressed air was dried through a column of silica gel and finally filtered to remove solid particles and oil mist. Optimum fuel pressures were adjusted for maximum element sensitivities.

**Reagents.** All chemicals were reagent grade (E. Merck; B&A; Carlo Erba, São Paulo, Brazil) or of the highest purity available. Deionized water was used for the preparation of all aqueous solutions. Tri-*n*-octyl amine (Koch & Light, Eriglund) was utilized without any further treatment. It was diluted with benzene to provide a 5% (v/v) working solution. These were used immediately after preparation to avoid possible aging effects.

**Procedure.** Ammonium duramate (ADU) was dissolved in hydrochloric acid and adjusted to 0.4M in free HCl in the final dilution. Solutions that contained potassium iodide were similarly adjusted to a final 0.4M HCl-0.01M KI. Fifty ml aliquots of uranyl chloride solutions (0.300 µg/l.), to which were added microgram quantities of Cd, Ag, Au, Hg, Pb, and Bi individually or in mixtures, were extracted thrice with 3-ml portions of TOA-benzene. The organic phase was similarly washed three times with 3-ml lots of 0.4M HCl or 0.4M HCl-0.01M KI, respectively, in the two series of experiments. The final organic phase was filtered and made up to 10.0 ml with benzene.

The TOA-benzene phase was burned directly in the atomic absorption spectrophotometer to determine the concentration of extracted trace elements. Hydrogen air flame was preferentially used in view of increased sensitivity. A set of standard calibration curves were also run by the same procedure, however omitting the matrix uranium in the aqueous phase. Similarly a blank experiment was performed utilizing a previously purified uranium in which the trace metal impurities were separated by TOA-benzene extraction.

## RESULTS AND DISCUSSION

**Amine Extraction from HCl Medium.** The extraction of metals from hydrochloric acid medium with an organic phase consisting of tri-*n*-octyl amine diluted with benzene, or other diluents, depends mainly on the capacity of the metals to form anionic chloride complexes, and is considerable in the case of several metals, including Cd, Ag, Au, Hg, Pb, Bi, Pd, Cu, Zn, Sn, and U. In such systems, the influence of HCl concentration is of paramount importance on the distribution coefficients of the various metal ions. Mirza *et al.* (2), have studied the behavior of several metals toward extraction with tri-*n*-octyl amine diluted with methyl isobutyl ketone from hydrochloric acid solutions. Abrão (10) has investigated the use of tri-*n*-octyl amine for

the separation of uranium from 24 metals in HCl and  $UO_2Cl_2$ -HCl media.

An attempt was made to adapt such solvent extraction procedures for the separation, concentration, and determination of Cd, Ag, Au, Hg, Pb, and Bi from high grade uranium. Whereas the amine extraction of the pure metal ions proceeds quantitatively in HCl solutions (2, 3, 10), the presence of relatively large concentrations of uranium in the aqueous media seriously inhibited their extraction. In these experiments, the hydrochloric acid concentration was adjusted to a nominal 0.4M (free acidity) to retard appreciable coextraction of uranium. The trace metal concentrations were in the range up to: Cd, 0.67; Ag, 1.64; Au, 1.31; Hg, 191; Pb, 66; and Bi, 134 µg per gram of uranium. These experiments showed that while Au was extracted into TOA-benzene quantitatively, Cd (25%), Hg (72%), Pb (4%), and Bi (4%) were not efficiently extracted and Ag was not at all extracted from the acid-uranyl chloride solution.

**Amine Extraction from HCl-KI Medium.** The unsatisfactory extractions of the trace metals mentioned above were considerably improved by the addition of iodide ion (as KI) to the uranyl chloride-hydrochloric acid aqueous media. Although the potentiality of solvent extraction of anionic metal iodide complexes by long chain amines and quaternary ammonium salts was foreseen (11), published literature in this area is limited (12, 13). In a variation of this approach, Abrão (10) demonstrated that the extraction of pure Pb and radiotracer Pb ( $^{212}Pb$  in thorium) in TOA-benzene was improved quantitatively by the addition of small quantities of KI to the hydrochloric acid solution. Similarly, while the extraction of Ag diminishes from 97% in 0.08M HCl to 3% in 8.3M HCl, addition of KI to the acid solution brought about quantitative extractions in TOA-benzene.

Based on these observations, the solvent extraction of Cd, Ag, Au, Hg, Pb, and Bi and separation from uranium was studied. The aqueous phase containing uranium was adjusted to a final 0.4M HCl-0.01M KI. The trace element concentrations were identical to those mentioned previously. The relative extraction of the metals into TOA-benzene were: Cd, 92%; Ag, 62%; Au, 100%; Hg, 84%; Pb, 21%; and Bi, 88%. While no change in the extractability of Au was expected, considerable improvements in the extraction of Cd, Ag, Hg, and Bi into TOA-benzene were obtained.

**Atomic Absorption Determination of Trace Elements.** A significant observation in this study is the enhanced absorbance produced by burning the organic phase (TOA-benzene) directly in the atomic absorption spectrophotometer. Then, for the pure elements, the absorbance values were increased by a factor, 1.5 (Cd), 2.0 (Ag), 2.7 (Au), 1.4 (Hg), 1.6 (Pb), and 2.1 (Bi) compared to those obtainable by burning similar concentration of the aqueous acid phase. Additionally, the absorbance of the pure elements extracted into TOA-benzene from 0.4M HCl and 0.4M HCl-0.01M KI, respectively, was identical and reproducible. Calibration curves obtained (absorbance vs. concentration, µg element per ml organic phase) for Cd (0.1-1.5), Ag (0.1-1.5), Au (0.2-4.0), Hg (10-200), Pb (10-100), and Bi (10-150) were linear in the entire range. Besides enhancement of absorbance, the possibility of avoiding stripping the organic phase for the extracted elements was another convenient advantage.

(11) A. A. Prokoshov, L. K. Chuznina, B. Z. Iofa and Yu. A. Zolotov, *J. Anal. Chem. USSR, Eng. Transl.*, 27, 1230 (1972)

(12) M. I. Gao, S. C. Srivastava and F. F. Holford, Jr., *Anal. Chim. Acta*, 31, 534 (1964)

(13) D. S. Tuck and F. J. Woodhouse, *J. Chem. Soc., Suppl.* 6017 (1964)

It must be mentioned that the relative extractions of the various metals into TOA-benzene from acid solutions containing uranium, presented above, were computed on the basis of their absorbance with reference to the pure metals similarly extracted from acid media. It is believed that the matrix effect of small concentration of uranium coextracted with the trace elements into TOA-benzene is primarily the reason for an apparent lower than 100% recovery of Cd, Ag, Hg, Pb, and Bi. Repeated extraction from the aqueous raffinate did not improve the "computed" recovery values. To the extent that the calibration for the elements separated from uranium by TOA-benzene extraction and determined by atomic absorption were reproducibly linear in the entire concentration range, the analytical application of the method is evident.

### CONCLUSION

The combination of the solvent extraction and atomic absorption determination of a series of trace elements has proved to be a unique approach to the analysis of nuclear grade uranium ( $ADU$  and  $UO_2$ ). While several pure elements are well extracted by long-chain amines from hydrochloric acid solution, the presence of appreciable concentration of uranium and chloride ions constitute serious interference, lowering the activity of the metal chloro complexes. Such an interference is so marked for silver, for example, that TOA-benzene does not extract the element from  $UO_2Cl_2$ -HCl medium.

Addition of a small concentration of KI surmounted the difficulty and provided practical and reproducible extraction of the various elements in the presence of uranium.

The exact mechanism of the extraction in the presence of iodide ions is not well understood. The possibility exists for the formation of stronger iodide or even mixed iodo-chloro complexes of the metal ions. It is also pertinent to indicate that even precipitates like the chlorides and iodides of Hg, Tl, Ag, Bi, and Pb are dissolved and extracted by TOA-benzene from hydrochloric acid solution (10). Iron and cobalt were not extracted by TOA-benzene; copper was extracted, but it could be stripped quantitatively from the organic phase by washing with HCl-KI solution.

Concentrations of uranium in the aqueous phase have approached up to 300 grams per liter. However, no difficulty in phase separation with TOA-benzene was experienced. Accommodating such high concentration of the matrix uranium necessarily provides for increased analytical sensitivity for the trace elements. The enhanced absorbance obtainable in direct burning of the organic phase is an added advantage of procedure.

The technique outlined in this paper is routinely used for the analysis of Cd, Ag, Au, Hg, Pb, and Bi in uranium. Calibration curves obtained with the uranium matrix have realized relative standard deviations of approximately 2, 4, 6, 2, 12, and 3%, respectively, for these elements in the trace concentration of interest. An extension of this work is in progress for the determination of trace metals in nuclear grade thorium (14).

RECEIVED for review October 11, 1973. Accepted April 22, 1974.

(14) A. Abrão and S. de Moraes, Instituto de Energia Atômica, São Paulo, Brazil, unpublished work, 1972.