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BY ATOMIC ABSORPTION SPECTROPHOTOMETRY**

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SEPARATION OF Cu, In, Fe AND Sn FROM NUCLEAR GRADE THORIUM BY TRI-N-OCTYL AMINE-5 M HCl AND THEIR DETERMINATION BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

This work summarizes the results of solvent extraction separation of a group of metal traces in high pure thorium with the aid of tri-n-octyl amine-benzene from ThCl_4 -HCl and ThCl_4 -HCl RT solutions. Cu, In, Fe and Sn are extracted together and determined by atomic absorption spectrophotometry, burning directly the organic phase.

The behavior of Cu, In, Fe and Sn toward direct burn of the organic phase using hydrogen-air mixture was studied, an absorption enhancement being observed.

The procedure is being used routinely to perform the quality control of nuclear grade thorium and its compounds. The calibration curves have provided precisions in the range 1 to 10% in routine analysis of thorium.

INTRODUCTION

The purification and transformation of thorium concentrate into nuclear grade products requires the identification and determination of a series of elements present as trace impurities, some of which having high cross-section for thermal neutron capture, therefore interfering in the neutron economy. The separation and determination of trace impurities in nuclear grade thorium for reactor fuel is a necessity and threatened the analyst for many years. The majority of papers published had approached the problem separating first the thorium, using, for instance, the solvent extraction technique (TBP/thorium nitrate-nitric acid system) and determining the impurities in the raffinate. Definitely this is not the ideal approach for this crucial problem. Any procedure that could separate first the impurities, leaving back the major constituent, that is, the thorium matrix, should be advantageous and very attractive.

This paper deals with the extraction of a group of metal impurities from thorium chloride in hydrochloric acid medium by means of organic solutions of long-chain tertiary amine using benzene as diluent. In many laboratories long-chain amines have been tested as extracting agents for different elements, including thorium and uranium, and it is not our purpose to give here a complete literature survey of the work in this field since many other papers have done it⁽¹⁻⁷⁾. For the purpose of isolating metal traces in HCl acid solutions, long-chain amine have been successfully tested at our laboratory⁽⁸⁻¹⁰⁾ and practical application of amines as extracting agents is booming today.

The separation of copper, indium, iron and tin was studied. It was demonstrated that copper and tin were only partially extracted while indium and iron were quantitatively extracted by tri-n-octyl amine (TOA) from ThCl_4 -HCl solutions. Addition of small amounts of potassium iodide to the thorium chloride-hydrochloric acid medium has improved the extraction for copper and tin.

On the other hand atomic absorption spectrophotometry indeed appears at the moment to be the method of choice for the determination of a great number of elements in terms of sensitivity and

convenience. The use of combined solvent extraction and atomic absorption techniques continues to increase. This method has proved to be a simple and convenient way of selective extraction and concentration of the desired metal or group of metals, allowing also an enhancement of the sensitivity.

The present work summarizes the results of solvent extraction of metal traces as a group (Cu, In, Fe, Sn) from high pure thorium, with the aid of long-chain tri-n-octyl amine diluted with benzene for their separation from thorium chloride HCl and thorium chloride-HCl-KI solutions. After extraction, the four elements are determined by atomic absorption, burning directly the organic phase.

EXPERIMENTAL

Apparatus

The atomic absorption spectrophotometer (Jarrell-Ash) was described before^(9,10). The following lines (nm) were used: Cu, 324.8; In, 303.9; Fe, 248.3 and Sn, 286.3. The light source was prewarmed at least 15 minutes before use. An hydrogen-air flame was used and optimum fuel pressure for maximum sensitivity were applied. The compressed air was dried through a silica gel column and finally filtered to get rid of solid particle and oil mist.

Reagents

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

Procedure

Thorium nitrate, thorium oxalate or thorium carbonate are transformed in thorium chloride in such a way to be 5 M in free HCl at the final dilution. Aliquots of thorium chlorides containing 15 g of thorium in order to have a 50 ml final solution are introduced into a 125 ml separatory funnel.

Two extractions by manual agitation of one minute each, with 3 ml TOA-5%-benzene, are followed. With this technique it is possible to quantitatively extract In and Fe into the organic phase, while Cu and Sn are partially extracted.

Potassium iodide is added to the remaining aqueous phase ($\text{ThCl}_4\text{-HCl}$) to a final concentration of approximately 0.01 M KI. A new extraction with TOA-5%-benzene is repeated, following the same technique as indicated above and the remainder Cu and Sn are then extracted. After the disengagement, the organic phase is separated and transferred to the separatory funnel which already contained In and Fe and then the organic phases are washed with one 3 ml 5 M HCl-0.01 M KI solutions separated, filtered on filter paper and transferred into a 10 ml volumetric flask.

The organic phase containing the extracted metals is burned, using a H_2 -air flame, in an atomic absorption spectrophotometer. The elements Cu, In, Fe and Sn are determined at the wavelengths already indicated in the text. A blank for the reagents was runned similarly using a high purity thorium previously purified by the same procedure.

RESULTS AND DISCUSSION

Metals Amine Extraction from HCl Medium

The possibility of extracting metals from hydrochloric acid medium into organic phase consisting

of tri-n-octyl amine chloride diluted with benzene or other diluent depends mainly on the capacity of the metal to form anionic chloride complexes. This capacity is considerable in the case of several metals, including Cu, In, Fe and Sn. Improvement in the separation of metals by long-chain amines can be achieved by choosing the proper conditions, like free HCl concentration, salting-out agents, and the organic-to-aqueous ratio. Mainly the influence of HCl concentrations is of paramount importance.

Previous works have shown the use of long-chain amines for the purpose of isolating metals from the pure HCl solutions^(1,3) Mirza et al⁽³⁾ for instance, studied the behaviour of several metals toward extraction with tri-iso-octyl amine diluted with methyl isobutyl ketone from hydrochloric acid medium. The use of tri-n-octyl amine for the separation of uranium from 24 metals in HCl medium and UO_2Cl_2 -HCl solution have been studied⁽¹⁾. The scope of this work was to outline a technique for the separation, concentration and determination of microquantities of metals present as impurities in nuclear grade thorium.

To achieve this goal, first attempt was to apply solvent extraction using TOA-benzene as extractant for the separation and concentration of various elements, including copper, indium, iron and tin from nuclear grade thorium chloride obtained by the dissolution of thorium salts with hydrochloric acid. Our experiments showed that while indium and iron were extracted quantitatively from these solutions by TOA-benzene, copper and tin were not efficiently extracted. For these experiments the acid concentration was ascertained to 5 M HCl (free acidity), considering the advantage of thorium chloride not being extracted⁽⁴⁾ at any HCl concentration. The trace metal concentration was in the range up to: Cu, 5; In, 50; Fe, 10 and Sn, 200 μ g per gram of thorium. These experiments showed that Cu(76%), In(99%), Fe(99%) and Sn(75%) were extracted with 3 extractions into TOA-benzene from the acid-thorium chloride solution.

Metals Amins Extraction from HCl-KI Medium

The technique here outlined is based on the observation that extraction of Pb and radiolead (^{212}Pb tracer from thorium) with TOA-benzene became quantitative by the addition of small quantities of KI⁽¹⁾ to the hydrochloric acid solution. Moraes & Abrão⁽⁹⁾ demonstrated that the extraction of Bi, Cd, Pb, Hg and Ag with TOA-benzene from UO_2Cl_2 -HCl was considerably improved by the addition of KI. Keeping in mind those observed facts, in this paper the extraction of copper, indium, iron and tin was studied from $ThCl_4$ -HCl-KI system using TOA-benzene as extractant. The concentration of thorium chloride in the aqueous phase can be raised until reach 300 g Th/L with no trouble for the phases disengagement. For the routine analysis of trace metals in high pure thorium such higher concentration was used in order to get the sensitivity of the elements determined. The concentration of potassium iodide in the aqueous phase to be extracted was kept at 0.01 M level and the hydrochloric acid concentration was adjusted to a nominal 5 M (free acidity), and the trace element concentrations were identical to those mentioned in HCl medium. The extraction of the mentioned elements into TOA benzene were: Cu, 89%; In, 68%; Fe was not reproducibly extracted and Sn, 87%. Although the extractability of In was partially depressed (99% from HCl and 68% from HCl-KI) and that of Fe was almost completely depressed, considerable improvement for Cu and Sn extraction was gained.

To avoid the problem of the inhibition of the Fe extraction and the decrease of In extraction, firstly two extraction with TOA-benzene from $ThCl_4$ -HCl medium has been used. Then, KI is added to the thorium chloride solution and a third extraction with amine is done. This sequential extraction procedure allowed Cu, In, Fe and Sn be completely extracted. Cu and Sn, that were only partially extracted after the addition of KI.

Atomic Absorption Determination of Cu, In, Fe and Sn in TOA-benzene

Burning directly the organic phase an enhancement of the absorbance was obtained for copper, indium, iron and tin, when compared to those obtained by burning an aqueous acid solution having the same concentration of the studied elements. Besides that, the possibility of avoiding the stripping of organic phase for the extracted elements was another convenient advantage. All calibration curves (absorbance vs.

concentration, μg element per ml organic phase) for Cu (1.5), In (10-50), Fe (2-10) and Sn (50-200) were straight lines in the entire range and reproducible. The practical sensitivity (μg element/gram Thorium) was Cu, 0.1; In, 1; Fe, 0.3 and Sn, 16.

Application

The technique here outlined is being routinely used for the separation, concentration and determination of copper, indium, iron and tin in thorium compounds of high purity produced at the IEA, as some analysis reported in Table I.

Table I

Determination of Cu, In, Fe and Sn in nuclear grade thorium compounds. Sequential extraction from $\text{ThCl}_4\text{-HCl}$ and $\text{ThCl}_4\text{-HCl-KI}$ with tri-n-octyl amine

Sample	μg element/g Th			
	Cu	Fe	In	Sn
$\text{Th}(\text{C}_2\text{O}_4)_2$	0.41	8.1	<1*	<16*
ThCO_3	0.62	122	<1	<16
$\text{Th}(\text{NO}_3)_4$	0.66	9.5	<1	<16
$\text{Th}(\text{NO}_3)_4$	< 0.1*	4.6	<1	<16
$\text{Th}(\text{NO}_3)_4$	4.1	18	<1	<16
$\text{Th}(\text{NO}_3)_4$	5.3	40	<1	<16

* Sensitivity Limits

CONCLUSION

The sequential association of the TOA-benzene metal traces extraction from $\text{ThCl}_4\text{-HCl}$ and $\text{ThCl}_4\text{-HCl-KI}$ media with atomic absorption spectrophotometry is a valuable contribution to the analysis of metal traces present as contaminants in highly pure thorium. Burning directly the organic phase is indeed an extra advantage which has contributed to the enhancement to the absorbance for the studied elements. The technique allows the extraction and determination of a group of elements at the same time, which is undoubtedly an enormous advantage for the analyst. In this paper only Cu, In, Fe and Sn were studied.

Concentrations of thorium in the aqueous phase have approached up to 300 grams per liter. However, no difficulty in phases disengagement with TOA-benzene was experienced. Accommodating such high concentration of the matrix thorium was required to increase the analytical sensitivity for the trace elements.

The technique here outlined is routinely used for the analysis of Cu, In, Fe and Sn in thorium. Calibration curves obtained with the thorium matrix have given relative standard deviations of approximately 1%(Cu), 2%(In), 10%(Fe) and 9%(Sn). An extension of this work for determination of trace metals in nuclear grade thorium by extraction with TOA-benzene from 0.5 M hydrochloric acid medium was presented⁽⁶⁾.

RÉSUMÉ

On présente une étude d'extraction de Cu, In, Fe et Sn présents comme traces dans les matrices de thorium avec

pureté nucléaire. Ces éléments sont extraits d'une solution de $\text{ThCl}_4 \cdot \text{HCl}$ et $\text{ThCl}_4 \cdot \text{HCl} \cdot \text{KI}$ par la tri-n-octylamine dissoute en benzène et ils sont déterminés par spectrométrie d'absorption atomique. 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 a été 1% pour le Cu, 2% pour le In, 10% pour le Fe et 9% pour le Sn.

RESUMO

Apresentam-se os resultados da extração de um grupo de elementos presentes como traços em matriz de tório de elevada pureza química para uso nuclear.

Extraem-se conjuntamente os elementos Cu, In, Fe e Sn com tri-n-octilamina, diluída em benzeno, de uma matriz de tório. Os elementos Fe e In são extraídos completamente e Cu e Sn parcialmente, de uma solução de $\text{ThCl}_4 \cdot \text{HCl}$ 5 M. Após a extração de In e Fe, adiciona-se iodeto de potássio à solução de cloreto de tório a faz-se nova extração com TOA-benzeno, completando-se neste estágio a extração do Cu e do Sn.

Determinam-se os quatro elementos por absorção atômica, queimando-se diretamente a fase orgânica numa chama de hidrogênio-ar.

O procedimento é usado rotineiramente para bem controlar a qualidade dos compostos de tório produzidos na Coordenadoria de Engenharia Química. Os devidos padrões relativos encontrados foram: Cu, 1%; In, 2%; Fe, 10% e Sn, 9%.

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