TECHNOLOGY OF THORIUM PURIFICATION ANALYTICAL CONTROL OF TRACE IMPURITIES IN NUCLEAR GRADE THORIUM BY COMBINATION OF AMINE EXTRACTION AND ATOMIC ABSORPTION TECHNIQUES

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ABSTRACT

This paper describes the results of solvent extraction of a group of elements present as trace impurities in nuclear grade thorium and their determination by atomic absorption spectrophotometry. Thorium nitrate is converted into chloride and the elements Bi, Cd, Au, Pb, Hg, Pd, Ag and Zn are extracted togheter by tri n octyl amine (TOA) from the thorium solution made 0.6 M in free HCl. The organic phase is burned directly for the determination of each element. Elements not extracted from this medium (Pb) or only partially extracted (Cd, Ag) had their extraction improved by the addition of small amount of potassium iodide to the aqueous phase.

Similarly the elements Cu, Fe, In and Sn are extracted from thorium chloride after making the solution 6 M in HCl. Cu and Sn had their extraction improved after the addition of small amount of potassium iodide.

For the calibration curves the precisions (%s) obtained are in the range 1 to 11 for routine analysis of thorium.

INTRODUCTION

The increasing importance of thorium as a nuclear fuel source has given great impulse to the development of analytical methods for determining impurities in thorium. Impurities are known to affect both the physical metallurgy and the neutron economy in the breeding reactor reaction. The selection of high quality thorium metal for reactor applications is then necessarily based on considerations of the impurity constituents which influence the physical properties as well as those which affect the usefulness of the thorium as a nuclear fuel.

The purification of thorium concentrates to nuclear grade products requires 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 have approached the problem by an initial separation of the matrix thorium 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 thorium would be advantageous and atractive. 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 thorium.

Long chain amines have been utilized extensively as extracting agents for various elements including uranium and thorium. The literature on the subject is extensive[2,4,6,7,9,12]. Such procedures have also been investigated in this laboratory for isolating trace metal concentrations from hydrochloric acid media (1). Of pertinent interest is the use of tri n octyl amine (TOA) diluted with an inert solvent

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as extracting agent The extractive separation of silver bismuth, cadmium gold, lead, mercury, palladium and zinc from aqueous hydrochloric acid solutions of thorium chloride by use of TOA in benzene was studied It was demonstrated that while Au was quantitatively extracted, Bi Cd, Hg and Ag were partially extracted and Pb not at all while Pd and Zn are well extracted Addition of small quantities of potassium iodide to the aqueous acid phase overcame this difficulty and permitted high and reproducible extraction by the amine

The separation of Cu Fe, In and Sn was previously studied[11] It was demonstrated that Cu and Sn were partially extracted while Fe and In was quantitatively extracted by tri n octyl amine from $ThCl_4$ HCl solutions Addition of small quantities of potassium iodide to the thorium chloride hydrochloric acid medium has improved the extraction for Cu and Sn

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 thorium chloride solutions were determined by atomic absorption in directly burning the organic phase in the spectrophotometer

1 – EXPERIMENTAL

Equipment

Apparatus and experimental conditions adjustment are the same as described previously[10] For Palladium and Zinc the following spectral lines (nm) were used respectively Pd 244 7 and Zn 213 8

Reagents

All chemicals were reagents 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 (Kock & Light England) 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

Thorium nitrate was converted in thorium chloride by sucessive evaporation with hydrochloric acid adjusted to be 0 5 M in free HCl in the final dilution Solutions that contained potassium iodide were similarly adjusted to a final 0 5 M HCl-0 01 M KI Fifty ml aliquots of thorium chloride solutions (300 g Th/l), to which were added microgram quantities of Bi Cd Au Pb Hg Pd, Ag and Zn individually or in mixtures were extracted thrice with 3 ml portions of TOA benzene The organic phase was similarly washed with 3 ml portions of 0 5 M HCl or 0 5 M HCl-0 01 M 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 thorium in the aqueous phase Similarly a blank experiment was performed utilizing a previously purified thorium in which the trace metal impurities were separated by TOA benzene extraction

II — RESULTS AND DISCUSSION

A — 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 metal to form anionic chloride complexes This capacity is considerable in the case of several metals including Bi Cd Cu In Pb Hg Pd Ag U and Zn In such systems the influence of HCl concentrations is of paramount importance on the distribution coefficients of the various metal ions Mirza et al [5] have studied the behavior of several metals towards extraction with tri n octyl amine diluted with methyl isobutyl ketone from hydrochloric acid solutions Abrão[1] 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 Moore[8] used the tri iso octyl amine diluted in xylene for the separation of thorium from uranium Moraes and Abrão[10] introduce iodide as complex ion in extraction of metals from matrix uranium

Attempt was made to adapt such solvent extraction procedures for the separation concentration and determination of Bi Cd Au Pb Hg Pd Ag and Zn from high grade thorium Whereas the amine extraction of the pure metals ions proceed quantitatively in HCl solutions[1 5 12], the presence of relatively large concentrations of thorium in the aqueous media however seriously inhibrted their extraction In these experiments the trace metal concentration were in the range up to Bi 120 Cd 0 5, Au 5 9 Pb 30 Hg 143 Pd 15 Ag 0 9 and Zn 3µg per gram of thorium These experiments showed that while Au was extracted into TOA benzene quantitatively Ag (18%) Bi (74%) Cd (67%) Hg (77%) were not efficiently extracted and Pb was not at all extracted from the acid thorium chloride solution Pd (95%) and Zn (86%) were better extracted in this medium

B — Amine Extraction from HCl KI Medium

The unsatisfactory extractions of any the trace metals mentioned in sec A were considerably improved by addition of iodide ion (as KI) to the thorium 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[13] published literature in this area is limited[3 14] Abrão[1] 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 08 M HCl to 3% in 8 3 M HCl addition of KI to the acid solution allowed quantitative extractions in TOA benzan Moraes and Abrão[10] demonstrated that the extraction of Bi Cd Hg Ag and Pb was improved by the addition of KI to the UO_2Cl_2 HCl media

Based on these observations the solvent extraction of Bi Cd Au Pb Hg Pd Ag and Zn and separation from thorium was studied The aqueous phase containing thorium was adjusted to a final 0 5 M HCl 0 01 M KI The trace element concentrations were identical to those mentioned previously The relative extraction of the metals into TOA benzene were Bi 86% Cd 86% Au 100% Pb 20%, Hg 84% Pd, 91% Ag 83% and Zn 84% While no change in the extractability of Au was expected considerable improvements in the extraction of Bi Cd Hg and Ag into TOA benzene were obtained Pd and Zn were not improved while partial extraction of Pb was observed

In conclusion it can be said that of all elements studied only lead has not its extraction considerably improved in the HCl KI medium its determination being not well recomended by the procedure here outlined

C — 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 2 0 (Bi) 1 6 (Cd) 1 8 (Au), 1 5 (Pb) 1 5 (Hg), 1 8 (Ag) and 1 5 (Zn) compared to those obtainable by burning similar concentration of the aqueous acid phase Calibration curves obtained (absorbance vs concentration μg element per ml organic phase) for Bi (30-120) Cd (0 1 0 5) Au (1 4 5 9) Pb (9 30) Hg (35 143) Pd (1 15) Ag (0 3 0 9) and Zn (0 5 3) 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

It must be mentioned that the relative extractions of the various metals into TOA benzene from acid solutions containing thorium, presented in sec A and B were computed on the basis of their absorbance with reference to the pure metals similarly extracted from acid media To the extent that the calibration for the elements separated from thorium 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

III — 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 thorium While several pure elements are well extracted by long chain amines from hydrochloric acid solution the presence of appreciable concentration of thorium and chloride ions contribute to lower the extractibility of some metal chloro complexes Such an interference is so marked for lead for example, that TOA benzene does not extract the element from $ThCl_4$ HCl medium

Addition of small concentration of KI surmounted the difficulty and provided practical and reproducible extraction of various elements in presence of thorium The exact mechanism of the extraction in the presence of iodine ions is not well understood The possibility exists for the formation of stronger iodide or ever mixed iodochloro complexes of the metal ions

Concentrations of thorium in the aqueous phase have approached up to 300 g per liter However, no difficult in phase separation with TOA benzene was experienced Accomodating such high concentration of the matrix thorium necessarily was required to increase the analytical sensitivity for the trace elements The enhanced absorbance obtainable in direct burning of the organic phase is an added advantage of procedure

Calibration curves for Bi, Cd Au Pb Hg Pd Ag and Zn obtained with the thorium matrix have given relative standard deviations of approximately 3 2 5 11 2 6 4 and 3% respectively for these elements in the trace concentration of interest

RESUMO

Descrevem-se os resultados dos estudos de extração de um grupo de elementos como impurezas em tório nuclearmente puro e sua determinação por espectrofotometria de absorção atomica Nitrato de tório é transformado em cloreto e os elementos Bi Cd Au Pb Hg Pd Ag e Zn são extraídos juntos por tri n-octilamina (TOA) da solução de tório acertada para ser 0 5 M em HCl livre A fase orgânica é queimada diretamente para a determinação de cada elemento Elementos não extraídos deste meio (Pb) ou apenas parcialmente extraídos (Cd Ag) tiveram sua extração melhorada pela adição de pequenas quantidades de iodeto de potássio à fase aquosa

Analogamente Cu Fe In e Sn são extraídos do cloreto de tório após acerta-lo para 5 M em HCl Cu e Sn tiveram sua extração melhorada após a adição de pequenas quantidades de iodeto de potássio

Para as curvas de calibração as precisões (%) obtidas estão no intervalo 1 11 para as análises rotineiras em tório

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