

# Determination of Thorium in High Purity Aluminum by ICP-Mass Spectrometry after Matrix Removal by On-line Solid Phase Extraction

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## Abstract

A combined matrix removal by on-line solid phase extraction and ICP-MS method has been developed for the determination of thorium in high purity aluminum. The sample solution prepared as 3 M HNO<sub>3</sub> solution was loaded onto a column packed with a high-molecular quaternary ammonium loaded resin (TEVA-Spec<sup>TM</sup> resin, Eichrom Industries, Darien, IL) and thorium retained on the column was eluted by 1 M HCl solution. The effluent was directly introduced into a nebulizer of ICP-MS and thorium was measured continuously at a mass number of 232. Thorium at ppb or sub-ppb levels in high purity aluminum certified reference materials for LSI provided by Japan Society for Analytical Chemistry was determined accurately and precisely.

**Keywords** Thorium, TEVA-Spec<sup>TM</sup> resin, ICP-MS, high purity aluminum, on-line solid phase extraction.

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## 1. Introduction

Thorium in nature consists of almost 100 % of <sup>232</sup>Th, which is a radioisotope with a very long half-life ( $1.4 \times 10^{10}$  y) [1]. Therefore, even very small amounts of thorium in a large-scale integrated circuit (LSI) material induces soft errors in the CPU of a computer and the strict control of its concentration in LSI material at ppb level or less is important. For the determination of thorium at low concentration in electronics industry materials, neutron activation analysis (NAA) has been used as one of the most useful methods because of its high sensitivity [3-5]. However, NAA needs special facilities, so that it is not a universally applicable means of determining traces of elements. Recently, inductively coupled plasma-mass spectrometry (ICP-MS) is most frequently employed for trace metal

analysis. Although ICP-MS shows a high sensitivity to most of elements, it is much more subject to interferences from matrix elements [6]. Therefore, when ICP-MS is used at the final measurement step, it is absolutely necessary in advance to separate analytes from matrix components, for example, by ion-exchange chromatography [7, 8].

Flow injection (FI) techniques are carried out in closed systems. On-line separation by FI is therefore practically free from contamination from the experimental environment. Because of this advantage, on-line separation by FI has been widely used for the determination of traces of elements by coupling with various detection methods [9-11].

In this work, we have developed a precise analytical method for the determination of thorium in an electronics material using a solid phase extractant, TEVA-Spec<sup>TM</sup> resin (Eichrom, Darien, IL), for the on-line separation of thorium and ICP-MS as a detector. Thorium was adsorbed on a TEVA-Spec<sup>TM</sup> resin column

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from 3 M HNO<sub>3</sub> solution and eluted with 1 M HCl. The effluent was directly introduced into the nebulizer of ICP-MS and the signal was monitored at a mass number of 232. The peak height was used for quantification. The proposed method was successfully applied to the analysis of high purity aluminum certified reference materials.

According to our literature survey, Truscott et al. [12] have developed an on-line solid phase extraction method for the determination of thorium in certified reference biological material using ICP-MS. They employed TRU-Spec™ resin as the solid phase extractant for thorium.

## 2. Experimental

### 2.1 Reagents

A standard stock solution of thorium was prepared by dissolving thorium nitrate pentahydrate of analytical grade (E. Merck, Darmstadt) in water and standardizing by EDTA titration.

Nitric and hydrochloric acids of electronics industries grade were obtained from Kanto Chemicals (Tokyo) and used as such. Water purified with a Milli-Q SP ICP-MS system was used throughout the work.

TEVA-Spec™ resin (Eichrom Industries, Darien, IL) was used for the on-line separation of thorium.

### 2.2 Apparatus

A block diagram of the flow-injection analysis system used in this work is illustrated in Fig.1. The flow system was assembled from 1-mm bore Teflon tubing and connectors. A peristaltic pump MICROTUBE PUMP MP-3 (Tokyo Rikakikai, Tokyo) was used to propel sample solution and washing solution (3 M HNO<sub>3</sub>). A reciprocating pump of the double plunger type HITACHI L-6010 (Hitachi, Tokyo) was used to deliver eluent (1 M HCl). Six-way valves (GL Science, Tokyo) were used to switch the flow directions of the solutions in the

system. A separation column was prepared by packing 3 g of TEVA-Spec™ resin in a 4.6 × 50 mm PEEK column.

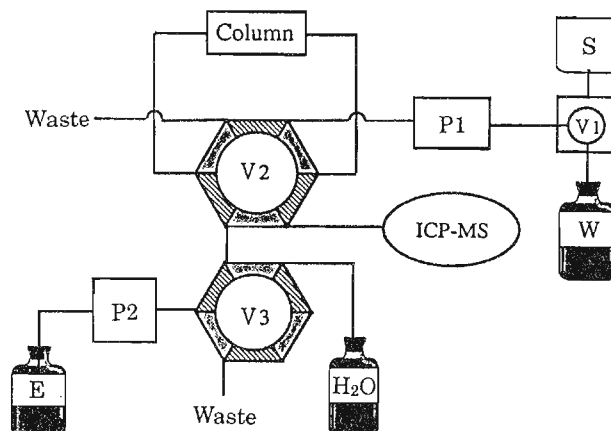


Fig. 1 Block diagram of FIA system for determination of thorium.

S: sample, P1: peristaltic pump, P2: reciprocating pump, V1, V2 and V3: six-way valve, W: washing (1 M HNO<sub>3</sub>), E: eluent (1 M HCl).

A Seiko Instruments SPQ9000 ICP-MS (Tokyo) equipped with the optional function to output a mass-number monitor file was used under the operating conditions shown in Table 1. The mass-number monitor file obtained by ICP-MS was of the "csv" form, which was converted to the elution profile by "Microsoft Excel". The peak heights were used for quantification.

Table 1 Operating conditions of ICP-MS

ICP-MS	Seiko Instruments SPQ9000
Plasma conditions	
Rf power	1.5 kw
Nebulizer gas flow	1.0 L/min
Plasma gas flow	16.0 L/min
Auxiliary gas flow	1.0 L/min
Sampling conditions	
Sampling depth	10 mm
Sampling cone	Copper, 0.80 mm orifice dia.
Skimmer cone	Copper, 0.40 mm orifice dia.
Measured isotope	<sup>232</sup> Th

## 2.2 Analytical procedures

### 2.2.1 Preparation of sample solutions

About 20-200 mg of standard high purity aluminum certified reference materials for LSI(Japan Society for Analytical Chemistry) were taken and dissolved in 3 ml each of HCl and HNO<sub>3</sub> with heating, followed by evaporation nearly to dryness. The residue was treated first with 3 ml each of HCl and HNO<sub>3</sub> and then with 3 ml of HNO<sub>3</sub>. Finally, the residue was taken up in 5 ml of 3 M HNO<sub>3</sub>.

### 2.3.2 Determination of thorium

The TEVA-Spec™ column was conditioned with 3 M HNO<sub>3</sub> for 1 min. The sample solution prepared as described above was then passed through the column to adsorb thorium on it. The column was washed with 3 M HNO<sub>3</sub> for 2 min to remove aluminum. Thorium retained on the column was eluted by passing 1 M HCl through it in the opposite direction to those for the sample and washing solutions. The effluent was directly introduced into the nebulizer of ICP-MS to detect thorium. The height of the peak at mass 232 was used for the quantification of thorium.

Prior to the succeeding run, the column was washed with 3 M HNO<sub>3</sub> for 2.5 min and 1 M HCl for 2 min to remove the residual thorium on the column. Calibration curves were constructed by varying volumes of the standard thorium solution.

## 3. Results and Discussion

### 3.1 Adsorption of thorium on TEVA-Spec™ resin

TEVA-Spec™ resin is prepared by loading high-molecular ammonium (didecyl methyl octylammonium) on Amberchrom CG-17 (Spelco) and the adsorption mechanism of thorium on it is as follows:



Di: didecyl methyl octylammonium on resin

Horwitz et al. [13] have reported the selective adsorption of plutonium(IV), neptunium(IV) and thorium(IV) on TEVA-Spec™ resin in HNO<sub>3</sub> medium. Thorium gives a capacity factor(*k'*) of about 800 on TEVA-Spec™ resin in 3 M HNO<sub>3</sub>, which is enough to retain thorium on this resin for its separation from other metals such as alkaline metals, alkaline earth metals, aluminum, transition metals, etc., which are not adsorbed on the resin in this medium. On the other hand, thorium is hardly adsorbed on TEVA-Spec™ resin in HCl medium. Based on these observations, thorium in aluminum was adsorbed on TEVA-Spec™ resin from 3 M HNO<sub>3</sub> and eluted by 1 M HCl in this work.

Passing of sample (10 ng of thorium in 10 ml) and washing (6 ml of 3 M HNO<sub>3</sub>) solutions through the TEVA-Spec™ resin column at a flow rate of 3 ml/min showed no leaks of thorium during the sample loading and following column washing steps. When 1 ng of thorium was injected into the flow system as varying volumes ( $\leq 10$  ml) of sample solution, the constant peak height was observed regardless of the sample volume. Examples of the FI signals are illustrated in Fig. 2.

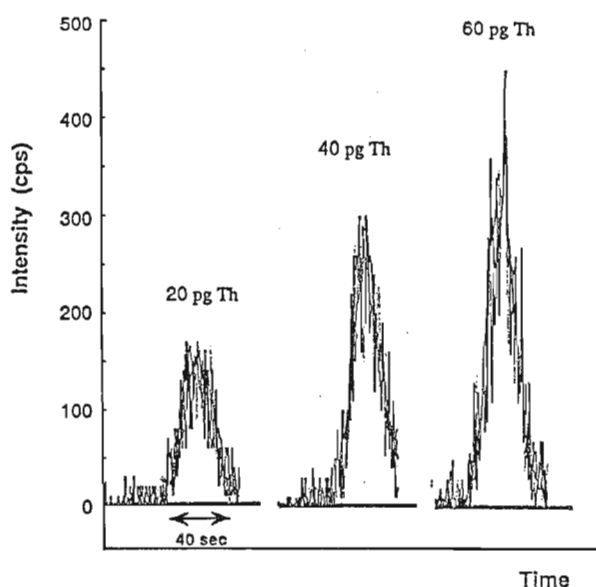


Fig. 2 FI signals for thorium.

When thorium was eluted by 1 M HCl, small amounts (< 1 %) of thorium was found to

be retained on the column and eluted at the elution step of the next run to yield an error. Therefore, the column was washed successively with 3 M HNO<sub>3</sub> and 1 M HCl after each run. The memory effect could be removed by the additional washing of the column .

### 3.2 Application to analysis of high purity aluminum

The proposed method was applied to the analysis of high purity aluminum certified reference materials for LSI (JAC-0021, JAC-0022 and JAC-0023) provided by Japan Society for Analytical Chemistry. The analytical results obtained are summarized in Table 2. Each analytical value is in good agreement with the corresponding certified value and the precision is excellent. The sample throughput is 5 h<sup>-1</sup> when the sample of 10 ml is used. The detection limit (3σ of background noise) is 8 pg.

**Table 2** Determination of thorium in high purity aluminum certified reference materials for LSI<sup>a</sup>

Sample	Taken /g	Th found /ng g <sup>-1</sup>	Certified value /ng g <sup>-1</sup>
JAC0021	0.0268	10.7	
	0.0260	11.3	
	0.0279	10.7	
	av.	10.9±0.35 <sup>b</sup>	9.8±1.7
JAC0022	0.0808	1.4	
	0.0846	1.4	
	0.0811	1.7	
	av.	1.5±0.2 <sup>b</sup>	1.7±0.4
JAC0023	0.3120	0.099	
	0.2726	0.073	
	0.2797	0.089	
	0.2608	0.084	
	0.3181	0.091	
	0.2762	0.080	
	av.	0.086±0.009 <sup>b</sup>	0.086±0.037

<sup>a</sup>Provided by Japan Society for Analytical Chemistry.

<sup>b</sup>Standard deviation.

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