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## PRECONCENTRATION AND DETERMINATION OF HEAVY METALS BY ICP-MS

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### ABSTRACT :

Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most sensitive analytical techniques for fast multi-element determination of heavy metals in trace and ultra-trace concentration different sample matrices. This technique is widely used for the accurate and precise determination of trace elements in environmental materials due to its low detection limits, analytical speed and multi-elemental capability. However, one of the main limitations of this technique is the need for sample preparation prior to analysis, as high levels of matrix components, such as Na, K, Ca, Mg, can give serious damage to mass spectrometer and the disposition of matrix constituents on the sampler and skimmer cones of the Spectrometer, which can seriously affect the accuracy analytical results. Therefore, the matrices must be removed from the sample solutions before measurement by ICP-MS. In addition the preconcentration procedure is necessary when heavy metals exist at extremely low level to achieve more accurate measurement.



**Keywords** – Preconcentration, Determination, Heavy Metals, ICP-MS .....etc.

### INTRODUCTION -

**Preconcentration of Uranium, Thorium and Lanthanum and Determination By ICP - MS -** Determination of the uranium (U), thorium (Th) and lanthanum (La) in environmental samples has great importance in order to assess the human exposure to these elements. These elements present in soil, rocks, plants and water in considerable quantities and can be incorporated into human food chains through various pathways. While ingestion is the main pathway for uptake in non-exposed subjects, incorporation due to occupational exposure occurs most probably by inhalation. Nephrological damage had been reported mainly after uranium and thorium intoxication. Exposure to thorium and uranium can also occur in the mining and milling of elemental ore materials and at various other stages of metal refining. In addition, nuclear tests and multiple military conflicts during the last few years have led to a real need to conduct studies of military and civilian contamination by uranium and thorium as part of risk assessment of the biosphere. There are several studies on the determination of uranium, thorium and lanthanum in environmental and biological samples by ICP-MS.

### Content -

All these studies revealed the importance of separation and preconcentration of methods for the determination of uranium, thorium and lanthanum in environmental and biological matrices by ICP-MS. In preconcentration methods, solid-phase extraction technique in which polymeric matrix Amberlite

XAD series modified suitable complexing agent are more convenient and efficient determination of metals by ICP-MS.

Here attempts are made to develop two solid-phase extraction methods for the determination of U, Th and La environmental samples. The methods are based on the application of hydroxyacetophenone-3-thiosemicarbazone (HAPTSC) on solid support XAD-3 for determination of U, Th and [1-(2-hydroxyphenyl)ethyl]camino]acetate (PHPEAA) on solid support XAD-16 for preconcentration of metals U, Th and La and determination by ICP-MS.

### **Application of Amberlite XAD-2-HAPTSC For Preconcentration of U, Th in Environmental Samples And Determination By ICP-MS**

Hydroxyacetophenone-3-thiosemicarbazone (HAPTSC)

Preparation and characterization of hydroxyacetophenone-3-thiosemicarbazone (HAPTSC) and functionalization of Amberlite XAD-2.

### **Procedure for pre-concentration of metal ions by column solid-phase extraction and determination by ICP-MS**

A glass column (15 cm long and 0.90 cm in diameter) with a stopcock was filled with 500 mg of Amberlite XAD-2-HAPTSC resin. A small amount of glass wool was placed on the disk to prevent loss of resin beads during sample loading. Then the resin was treated with 4.0 M HCl and washed with doubly distilled water until free from HCl. 100 ml of water sample containing 2.0-200  $\mu\text{g l}^{-1}$  of metal ions U(VI) and Th(IV) was passed through the column at a flow rate of 1.5 ml min<sup>-1</sup> controlled by peristaltic pump after adjusting the pH 5.0 by adding borate buffer. The column was washed with doubly distilled water to remove free ions. The bound metal ions were stripped from the column with 10 ml of 2.0 M HNO<sub>3</sub>. The concentration of metal ions in elutes were determined by ICP-MS after suitable dilution if required. The operating parameters of ICP-MS are given in Table 2.2.

## **Results and Discussion**

### **Effects of pH-**

The effect of pH on the retention of metal ions on the HAPTSC functionalized Amberlite XAD-2 resin column was carried out over a wide range of pH (1.0-8.0) by applying the proposed solid-phase extraction procedure and analysis ICP-MS. The variation in sorption of metal ions on the sorbent with pH is shown in fig. 4.1. 1 and the optimum pH range for two metal ions is given in Table 4.1.1. The results demonstrate that the sorption is maximum and quantitative (98 %) in pH range 4.0-5.0 for U(VI) and 4.0-7.0 for Th (IV) respectively. Hence pH 5.0 was chosen as the optimum pH for solid-phase extraction of both metal ions.

### **Effect of dose of resin on pre-concentration of metals**

The effect of amount of Amberlite XAD-2-HAPTSC resin loaded in column on recovery of analytes U(VI) and Th (IV) was evaluated by filling varying amounts of resin (0.2-0.8 g) in the column. It was found that maximum recoveries for two analytes were obtained with 0.5 g of resin. Therefore 0.5 g of Amberlite XAD-2-HAPTSC resin was used for solid-phase extraction of two metal ions and subsequent determination.

### **Effect of flow rate and element**

The retention of the metal ions U (VI) and Th (IV) on Amberlite XAD-2-HAPTSC resin also depends on the flow rate of the sample solution. The dependence of metal ion sorption at various flow rates was studied at optimum pH. The studies show that these ions can be sorbed quantitatively by the resin at a flow rate of 1.5 ml min<sup>-1</sup>, an increase in flow rate causes a gradual decrease in sorption. Metal elution from the column was studied by using different concentrations (0.5-3.0 M) of HNO<sub>3</sub> and the results are presented in Table 4.1.2 and graphically presented in Fig. 4.1.2. The results indicate that the

optimum concentration for the maximum recovery of metals was 2.0 M. Hence 2.0 M HNO<sub>3</sub> was selected as the eluent the analysis metals.

**Sorption Capacity**

The sorption capacity of Amberlite XAD-2-HAP'TSC resin was determined by batch method. The resin (1.0 g) was saturated with U(VI) and Th (IV) solution (concentration 50 ug ml<sup>-1</sup>) by equilibrating on a mechanical shaker under optimum conditions. The solid matrix was filtered and washed with distilled water. The remaining metals in supernatant liquid were determined by ICP-MS, after appropriate dilution. The amounts of metals sorbed onto Amberlite XAD-2- HAP'TSC resin were obtained by mass balance. The sorption capacities in mmolg<sup>-1</sup> are 0.91 for U(VI) and 0.86 for Th(IV) respectively

**Kinetics of sorption**

The rate of loading of metal ions U(VI) and Th(IV) on the Amberlite XAD- 2-HAP'TSC resin was carried out by batch experiments. 0.5 g of Amberlite XAD-2- HAP'TSC resin was added to the 50 ug/ml of individual metal ion solution and **Table 1** Effect of pH on the complication of metals from Amberlite XAD-2- HAP'TSC

**Table-1**  
**Effect of HNO<sub>3</sub> concentration on the elution of metals from Amberlite XAD-2-HAP'TSC**

pH	% recovery	
	U	Th
1.0	68.20	61.70
2.0	80.20	71.20
3.0	88.70	79.20
4.0	99.50	99.80
5.0	99.90	99.86
6.0	95.90	99.56
7.0	90.17	99.53
8.0	81.45	80.25

**Table 2**  
**Effect of HNO<sub>3</sub> concentration on the elution of metals from Amberlite XAD-2-HAP'TSC**

HNO <sub>3</sub>	% recovery	
	U	Th
0.5	58.72	53.10
1.0	69.30	65.20
1.5	83.40	80.50
2.0	99.95	99.90
2.5	99.92	99.87
3.0	99.85	99.82

stirred for 2, 5, 10, 20, 30, 40, 50, 60 and 90 min at room temperature. The concentration of metal ions in the supernatant solution was determined by ICP-MS after appropriate dilution and the amount of metal ions sorbed onto the resin phase was determined by mass balance. The loading half-time  $t_{1/2}$  defined as the time needed to reach 50 % of the resin total loading capacity was estimated from the curves (Fig. 4.1.3 and it is found to be less than 5 min for two metal ions 3.14 min for U(VI) and 3.40 min for Th(IV)]. The kinetics of the resin-metal interaction is sufficiently rapid for two metal ions at optimum

pH. The faster uptake of these metal ions on Amberlite **XAD-2-HAPTSC** resin reflects good accessibility of the chelating sites of the resin to metal ions.

### Pre-concentration Factor

Pre-concentration factor was determined by increasing the volume of the sample solution and keeping the metal ion concentration fixed at 20/ug and eluent volume constant to 10 ml. The recovery of U(VI) and Th (IV) with 500 mg of functionalized resin was not affected by sample volume below 1500 ml. Above 1500 ml the percent recovery was decreased considerably. Hence a pre-concentration factor of 150 is achieved for both metal ions.

### Resin Stability And Reusability.

The stability of resin loaded with Amberlite **XAD-2-HAPTSC** was studied in acid (1.0-4.0 M HNO<sub>3</sub>). It was shaken with acid solutions of varying concentrations for 4 h and filtered. The solid was washed with distilled water until free from acid, air-dried and its sorption capacity was determined using batch method. The sorption capacity of the acid treated resin was found to be similar (variation 3 %) to that of the untreated one. This shows that the present resin can resist to acid concentration up to 4.0 M HNO<sub>3</sub>. The reusability of the resin was tested by sorption of metal ions U(VI) and Th (IV) onto a column loaded with Amberlite **XAD-2-HAPTSC** from a solution having a concentration 25 ug/l at a flow rate of 1-2 ml/min and eluting with 2.0 M HNO<sub>3</sub> and determined by the recommended procedure. It was found that the sorption capacity after 20 cycles of sorption and desorption did not vary more than 2% for any metal ion. Therefore the resin showed good reusability and stability for the determination of metal ions. The sorption capacity of the resin stored for more than three months under ambient conditions has been found to be practically unchanged.

### Effect of matrix ions

The effect of the matrix ions, electrolytes and cations on the sorption of the metal ions U(VI) and Th(IV) was studied. The limits of tolerance defined as the amount of electrolyte/foreign ions causing an error of 1% in the recovery of metal ions. Metal ions are presented in Table 4.1.3. The results indicate that various electrolytes and cations present in water samples do not interfere in the analysis of metals under the reported conditions.

### Accuracy of the Method -

The accuracy of the proposed solid-phase extraction method was ascertained by determining uranium in standard reference materials **NASS-4** (Open Ocean Sea Water) and **SLRS-3** (River Water) and determining U(VI) and Th(IV) in synthetic water samples. The synthetic mixtures were prepared by taking large number of metal ions based on their possible interference effects. The synthetic samples containing U(VI) and Th(IV) and other metal ions were prepared in 50 ml of HNO<sub>3</sub>. The results are presented in Table. The recovery of uranium from reference materials by proposed method is in good agreement with certified values of the standard reference materials. The results of spiked water samples show the quantitative recoveries of 99% for two metal ions with a RSD of below 5%.

### (A) Applications Determination of Uranium and thorium in water samples

The applicability of the proposed method for the determination of U(VI) and Th(IV) in real samples was checked. Different amounts of U(VI) and Th(IV) ions were spiked in tap water and determined by the proposed method. The results are given in Table 4.1.6. Good agreement was found between the added and found concentrations of two metal ions. The recoveries are in the range of 99.4-99.8% for U and 98.9-99.7% for Th with the standard deviation in the range of 3.48-4.36 for U and 3.28-4.12 for Th. These values suggest that the proposed solid-phase extraction method is suitable for the analysis of uranium and thorium in real water samples.

**Table 3**  
**Tolerance limits of matrix ions**

Matrix ions	Tolerance limits (mol l <sup>-1</sup> )	
	U(VI)	Th(IV)
NaSO <sub>4</sub>	0.60	0.62
Na <sub>3</sub> PO <sub>4</sub>	0.29	0.31
NaF	0.08	0.11
CH <sub>3</sub> COONa	0.09	0.05
Ca <sup>2+</sup>	0.52	0.54
Mg <sup>2+</sup>	0.49	0.50
Co <sup>2+</sup>	4.8	5.1
Cd <sup>2+</sup>	4.2	4.6
Zn <sup>2+</sup>	3.2	3.4
Pb <sup>2+</sup>	31	3.3
Mo <sup>6+</sup>	5.6	5.2
Zr <sup>4+</sup>	6.3	5.4

**Table No. 4.**

**Results fox the determination of uranium in certified reference materials NASS-4, SLRS-3 by ICP-MS**

Certified reference material	Certified value/ng ml <sup>-1</sup>	Analysed by ICP-MS
NASS-4 Open ocean sea water	2.68 ± 0.12	2.67±0.07
SLRS-3River Water	0.045*	0.044 ±0.09

Certified reference material Certified value/ng m l ' Analysed by ICP-MS

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\* uncertified indicative value the values reported are the means of three readings

**Table 5**  
**Determination U(V1) and Th(1V) in synthetic samples**

Composition of synthetic sample (ug/50 ml, 0.5 g resin)	Cone of U(V1) and Th(IV) (ug1.50 ml)	Added		Found"	
		U(VI)	Th(IV)		
		U(VI)	Th(IV)	U(VI)	Th(IV)
Co(20),Ni(20),Zn(25)	1	1		0.97 ±0.02	0.92± 0.06
Fe(10), Pb(12), Cu(25)	1	10		0.90 ±0.10	9.84± 0.14
Cd(2),Ni(15),Co(8),Mn(15)	10	1		9.94 ±0.15	0.97 ±1.02
Fe(10), Pb(5), Zn(15), Cu(10)	25	25		24.50± 0.30	23.96± 1.02

"Average and standard deviation fix triplicate mn

**(B) Extraction of thorium from monazite sand (Travancore, India)**

The resin's applicability in extracting Th(1V) from monazite sand was studied. 0.1 g of monazite sand sample was digested with conc. **H2S04** at 250 °C for 4 h. Further, it was digested using 5 ml of HF followed by conc. HNO<sub>3</sub> to remove excess HF. Subsequently, the digested solution was evaporated to dryness and the residue was re-dissolved in minimal volumes of diluted HCl and passed through the resin column. The amount of **Th(IV)** extracted was found to be 80.7 **mg g<sup>-1</sup>** which was comparable with the certified value of 81 mg g<sup>-1</sup>. The data was further confirmed by the standard addition method, and the values were within 3.4 % **RSD** for triplicate measurements.

**Table- 6**  
**Recovery of U(VI) and Th(IV) from spiked tap water samples after**  
**Pre-concentration on Amberlite XAD-2-HAPTSC resin Analyte Added ( $\mu\text{g l}^{-1}$ ) Found ( $\mu\text{g l}^{-1}$ )**  
**Recovery (%)' RSD (%)" ND: Not detected.**  
**"Percent recovery and percent R.S.D fir four determinations**

Analyte	Added ( $\mu\text{g l}^{-1}$ )	Found ( $\mu\text{g l}^{-1}$ )	Recovery (%)	RSD (%)"
U(VI)	0.0	ND		
	10.0	9.98	99.8	3.48
	25.0	24.85	99.4	3.98
	50.0	49.85	99.7	4.36
Th(IV)	0.0	ND		
	10.0	9.97	99.7	4.12
	25.0	24.73	98.9	3.64
	50.0	49.55	99.1	3.28

**ND:Not detected**

Percent recovery and percent R.S.D for four determinations

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