

# **Applications of ICP-MS to the Determination of Trace Np and Pu in Environmental Samples with Extraction Chromatography**

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## **ABSTRACT**

An unique extraction chromatographic column (TOA: Tri-n-octylamine on Teflon powder) with a two-stage sample loading was prepared to separate Np and Pu from the environmental matrix. Np and Pu were efficiently retained in 4 M HNO<sub>3</sub> medium on the column and easily eluted with 0.02 M oxalic acid in 0.16 M HNO<sub>3</sub> at 95°C. The separated solutions were free from most of the matrix elements and were aspirated into the ICP-MS directly. The decontamination factor for <sup>238</sup>U is more than 104. The instrumental detection limit for <sup>237</sup>Np was 0.46 pg mL<sup>-1</sup> ( 1.2 × 10<sup>-5</sup> Bq mL<sup>-1</sup>), and for <sup>239</sup>Pu was 0.48 pg mL<sup>-1</sup> ( 1.1 × 10<sup>-3</sup> Bq mL<sup>-1</sup>). The feasibility for the determination of both elements was proved by analysing IAEA-135 reference samples, the measured values agreed with the recommended reference value.

## **INTRODUCTION**

Small amounts of radioactive materials are lost inevitably to the environment during any processing of nuclear material. With the development of nuclear power industry the corresponding waste has been grown. In order to evaluate the radioactive waste, which could

affect the environment, and to devise projects for the nuclear waste disposal, the behaviour of long-lived artificial radionuclides in the environment are subject to detailed studies and are of increasing concern to environmental researchers. However, the concentration of neptunium and plutonium is extremely low in environmental samples, and such samples have a complex matrix composition, which is to be taken into account for a proper analysis. Conventional radiochemical methods such as alpha spectrometry, neutron activation analysis, liquid scintillation system, fission track and gamma spectrometry for the quantitative determination of neptunium and plutonium often require complicated and time-consuming sample preparation and separation procedures. Due to the large amount of the complex and often unknown matrix, the analysis may also be covered by naturally occurring radionuclides.

With the development of new analysis techniques, non-radioactive methods are increasingly used for the determination of trace or ultra-trace radionuclides in environmental samples. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most suitable analysis techniques for the measurement of the long-lived radionuclides with its high sensitivity, low detection limits, short analysis time, less chemical interferences and multi-elemental capability. The main objective of the present study was to set up of a simple, fast separation procedure to measure Np and Pu in the environmental samples by ICP-MS. Based on our research results[1, 2], an unique TOA extraction chromatographic column was prepared to separate Np and Pu in the environmental samples. Preliminary studies were performed to determine both Np and Pu by ICP-MS simultaneously. The method is considered suitable for environmental monitoring of ultra trace Np and Pu.

## EXPERIMENTAL

### Instrumentation

VG Elemental PlasmaQuad PQ2+ was used for this work with a conventional pneumatic nebulization system for the sample uptake. The sample is delivered using a peristaltic pump (Minipuls3, Gilson, France). The instrumental operating conditions that were chosen are listed in Table 1.

**Table 1 Instrumental operating conditions for VG PQ2+ ICP-MS**

RF Forward power	1350 W
Reflected power	<5 W
Nebuliser	Pneumatic
Chamber	Scott double-pass spray type
Torch	Fassel type
Nebuliser argon gas flow	0.795 L/min
Coolant gas flow	13 L/min
Auxiliary gas flow	0.6 L/min
Sample uptake rate	0.85 mL/min
Mass range (scan)	208.6 ~ 240.4 amu
Channels per m/z =1	24
Dwell time	160 $\mu$ s
Sampling distance coil sample cone	10 mm
Time, acquisition	60 s; 30 s

### Standard solutions and reagents

The stock solution of  $^{237}\text{Np}$  (121.5 ng mL<sup>-1</sup>, CIAE, China) and  $^{239}\text{Pu}$  (34.999 Bq mL<sup>-1</sup>, CIAE, China) were prepared and stored in Teflon bottles. All calibration standards were freshly prepared by successive dilution of the stock solution with 5% nitric acid. Spike  $^{242}\text{Pu}$  (IRMM-044) was used for isotope dilution method calculated plutonium. A blank solution,

which contains only 5% HNO<sub>3</sub> was also prepared. 209Bi (GBW080135, China) as an internal standard was added to all the solutions prior to the measurement giving a concentration of 2 ng mL<sup>-1</sup>.

#### **Preparation of the extraction chromatographic column (TOA)**

150 mL 15% Tri-n-octylamine (TOA) in xylene (v/v) was mixed with 100 g Teflon powder and stirred for 1h with a magnetic bar. After stirring the liquid was removed and the remaining xylene was volatilized. The extraction chromatographic powder was stored for later use. The bottom of the glass columns (i.d., 3.5 mm, 50 mm high) were packed with a small Teflon wool plug treated with 1% HNO<sub>3</sub>. After thorough draining and rinsing with doubly deionized distilled water, 0.5 g of the prepared chromatographic powder suspended in water, was slurry-packed slowly and another small Teflon wool plug was inserted on the top of the solid phase bed. The column was rinsed with 50 mL of distilled water for later use.

#### **Sample preparation**

The initial sample dried at 110°C for 12 h, ashed at 450°C for 6 h, 242Pu was added to the samples as a yield tracer and for calculation of total plutonium by isotope dilution. Samples Digested with 8M HNO<sub>3</sub> three times, centrifugation of the leaching solutions, then combined and evaporated to near dryness, finally dissolved in 4 M HNO<sub>3</sub>. Chemical separation suggested overall analysis scheme is presented in Figure 1.

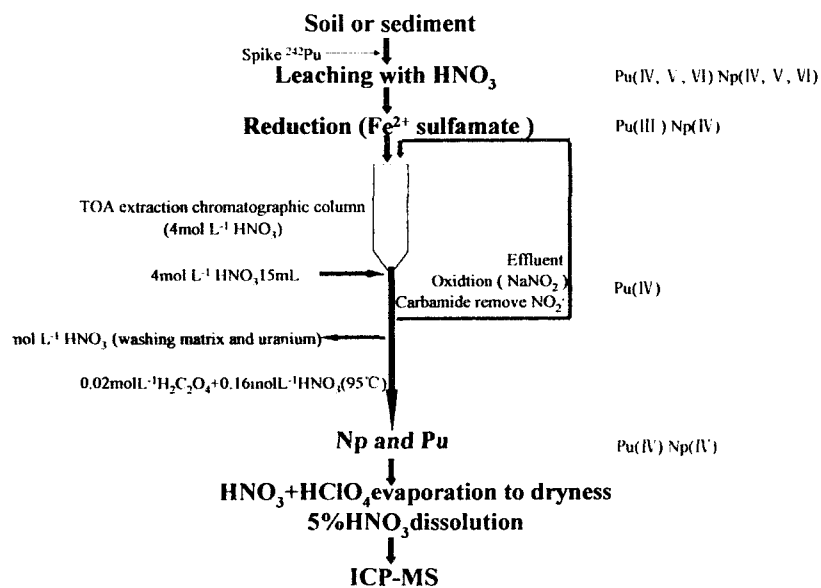
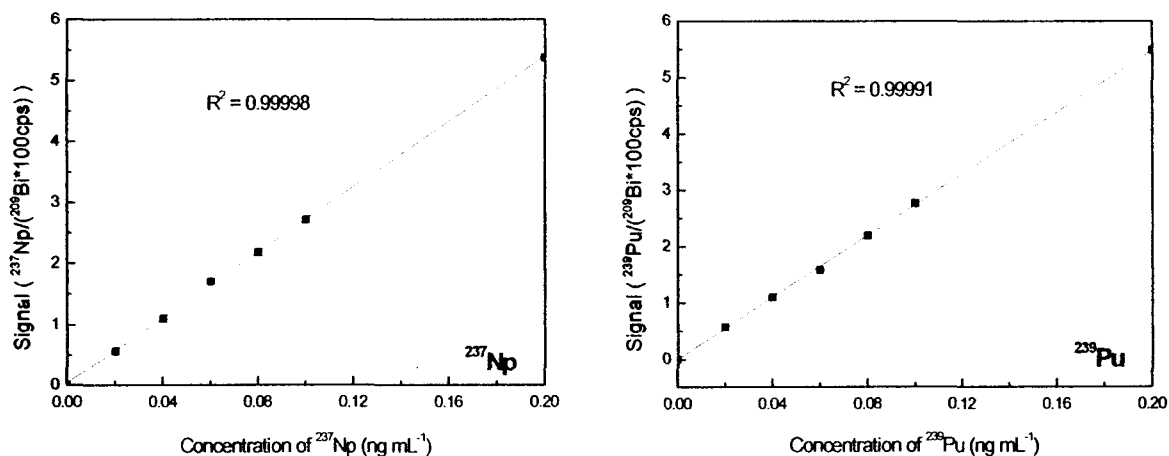


Figure 1. Flow chart showing separation procedure for the determination of Np and Pu by ICP-MS

## RESULTS AND DISCUSSION

### Determination of detection limit (DL)

Figure 2 shows the calibration curve for  $^{237}\text{Np}$  and  $^{239}\text{Pu}$  by ICP-MS. A good linearity was observed in the range of  $10 \text{ pg mL}^{-1}$  to  $1 \text{ ng mL}^{-1}$ . The detection limit, defined as three times the standard deviation of the blank solution, was about  $0.46 \text{ pg mL}^{-1}$  ( $1.2 \times 10^{-5} \text{ Bq g}^{-1}$ ) for  $^{237}\text{Np}$  and  $0.48 \text{ pg mL}^{-1}$  ( $1.1 \times 10^{-3} \text{ Bq g}^{-1}$ ) for  $^{239}\text{Pu}$ . The relative standard deviation (RSD) for three analyses of the same sample solution was usually less than 5% for a concentration greater than  $10 \text{ pg mL}^{-1}$ . These data indicated that the precision of the ICP-MS measurements was reasonable for the determination of Np and Pu in environmental samples.



**Figure 2** Calibration curve for  $^{237}\text{Np}$  and  $^{239}\text{Pu}$ ;  $^{209}\text{Bi}$  (2ng mL $^{-1}$ ) was added to each sample

### **Decontamination factors using TOA extraction chromatography**

Total cation concentrations in the final solution for ICP-MS should be less than 1000  $\mu\text{g/mL}$  to avoid any matrix suppression and sample cone interface clogging [3]. Therefore, it is necessary to reduce the concentrations of matrix element in the sample solution without losing any of the Np and Pu trace contents. In addition to the separation of Np and Pu from major matrix elements,  $^{238}\text{U}$  should also be removed to avoid any peak tail overlapping of the  $^{238}\text{U}$  peak on  $^{237}\text{Np}$  or  $\text{UH}^+$  interference to  $^{239}\text{Pu}$  (see Figure 3). Selected matrix elements in soil (U, Na, Mg, Al and the rare earth elements Nd, Eu, Er) were measured after a sample was processed through the extraction chromatographic column (TOA). The observed mass range was  $m/z = 22.6$  to  $27.4$ ;  $m/z = 113.6$  to  $116.4$ ;  $m/z = 142.6$  to  $167.4$  under normal operating conditions using  $^{115}\text{In}$  as an internal standard. The decontamination factors measured for these elements listed in Table 2.

**Table 2 The decontamination factors for TOA extraction chromatography**

Matrix element	Added as	Concentration of matrix in the sample	Concentration of matrix in eluent (ng mL <sup>-1</sup> )	Decontamination factor
U	UO <sub>2</sub> <sup>2+</sup> (GBW080173, China)	20 µg/mL	0.2	3.3×10 <sup>4</sup>
Na	NaCl	50 mg/mL	1100	1.5×10 <sup>4</sup>
Mg	Mg powder + HNO <sub>3</sub>	5 mg/mL	320	5.2×10 <sup>3</sup>
Al	Al(NO <sub>3</sub> ) <sub>3</sub>	5 mg/mL	31	5.4×10 <sup>4</sup>
Nd	Nd <sup>3+</sup> (GSBG62050, China)	100 ng/mL	0.16	2.1×10 <sup>2</sup>
Eu	Eu <sup>3+</sup> (GSBG62052, China)	100 ng/mL	0.098	3.4×10 <sup>2</sup>
Er	Er <sup>3+</sup> (BW3139, China)	100 ng/mL	0.097	3.4×10 <sup>2</sup>

**Recovery of separation procedure**

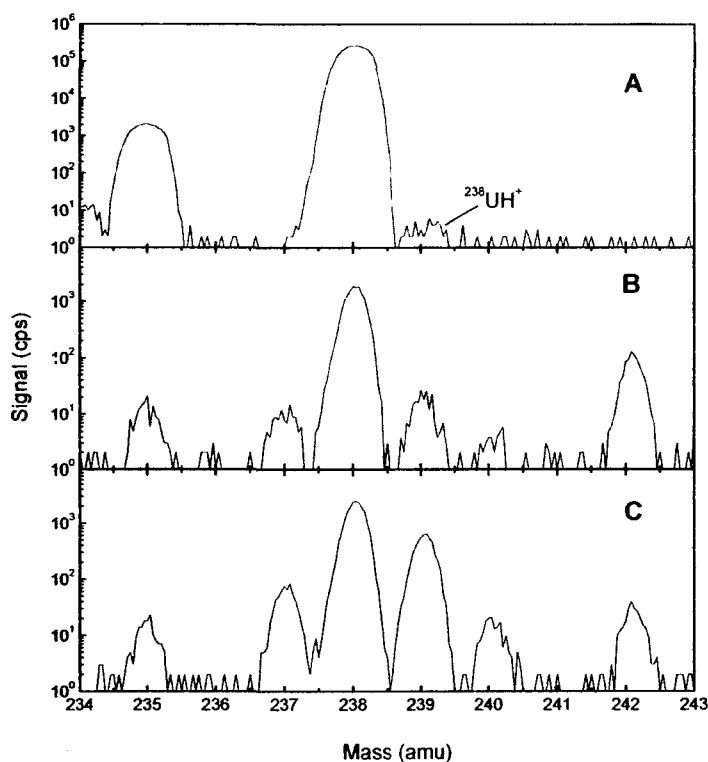
In order to validate the analytical method and to obtain data on the concentration of Np and Pu, blanks were analysed by ICP-MS following the separation procedure. Table 3 shows the recovery of Np and Pu for TOA extraction chromatography is more than 90 percent.

**Table 3 Recovery of Neptunium and Plutonium for TOA extraction chromatography**

Sample	<sup>239</sup> Pu			<sup>237</sup> Np		
	Measured (ng mL <sup>-1</sup> )	Added (ng)	Recovery (%)	Measured (ng mL <sup>-1</sup> )	Added (ng)	Recovery (%)
blank	0.00102	-	-	0.00059	-	-
1#	0.22149	1.217	91	0.23668	1.215	97.4
2#	0.23426	1.217	95.6	0.22791	1.215	93.8
3#	0.211	1.217	90.8	0.24104	1.215	99.2
Mean recovery:				<sup>239</sup> Pu (%)	=	92.7±3.1 ;
<sup>237</sup> Np (%)	= 96.8±2.7					

**Certified reference material and soil sample**

The method was applied to the determination of Np and Pu in soil sample. Table 4 shows the results obtained for IAEA-135 (Irish Sea sediment). The sum of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations ( $^{239}+^{240}\text{Pu}$ ) was calculated for comparison with the value recommended by the IAEA. Our analytical results for  $^{239}+^{240}\text{Pu}$  agreed well with the recommended value given by the IAEA (no Np standard value available) [4]. The result of soil sample from safeguards environment was identified in table 4. Figure 3 shows the ICP-MS scanning spectrum.



**Figure 3** Mass spectrum of 500 ng mL<sup>-1</sup> uranium in 5% HNO<sub>3</sub> (A),  
 **$^{237}\text{Np}$  and Pu in IAEA-135 (B),  $^{237}\text{Np}$  and Pu in soil-3# sample (C)**



**Table 4 Analytical results for  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in environmental samples**

Samples	$^{239}\text{Pu}$ ( $\text{Bq g}^{-1}$ )	$^{240}\text{Pu}$ ( $\text{Bq g}^{-1}$ )	$^{239+240}\text{Pu}$ ( $\text{Bq g}^{-1}$ )	$^{237}\text{Np}$ 含量( $\text{ng g}^{-1}$ )
Soil-3#	157.3	17.7	175	1.2915
IAEA-135	$0.116\pm 0.005$	$0.091\pm 0.006$	$0.203\pm 0.010$	$0.0144\pm 0.0005$

IAEA recommended (IAEA-135):  $^{239+240}\text{Pu}=0.213 \text{ Bq g}^{-1}$

## CONCLUSIONS

This paper suggests that the separation procedure outlined is appropriate and applicable to the determination of environmental levels of Np and Pu. The decontamination factor for the interfering  $^{238}\text{U}$  is more than 104. The instrumental detection limit was  $0.46 \text{ pg mL}^{-1}$  ( $1.2 \times 10^{-5} \text{ Bq mL}^{-1}$ ) for  $^{237}\text{Np}$ , and  $0.48 \text{ pg mL}^{-1}$  ( $1.1 \times 10^{-3} \text{ Bq mL}^{-1}$ ) for  $^{239}\text{Pu}$ . A considerable advantage is the significantly shorter measurement time in comparison to the traditional radiometric detection techniques. The method presented is considered to be highly suitable for the environmental monitoring of Np and Pu.

## REFERENCES

- 1) Ji, Y. Q., Li, J. Y., Luo, S. G. et al, "Determination of Traces of  $^{237}\text{Np}$  in Environmental Samples by ICP-MS after Separation Using TOA Extraction Chromatography". *Fresenius' J. Anal. Chem.*, 371: 49~53 (2001).
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