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Publication date:
2009

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Citation (APA):

Qiao, J., Hou, X., Roos, P., & Miro, M. (2009). *Simultaneous Determination of Plutonium and Neptunium by on-line Extraction Chromatography and Sequential Injection*. Poster session presented at NKS-R and NKS-B Joint Summary Seminar, Stockholm, Sweden.

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Simultaneous Determination of Plutonium and Neptunium by on-line Extraction Chromatography and Sequential Injection



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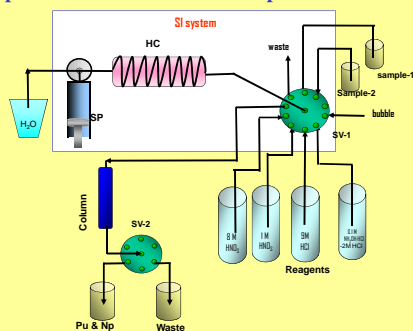
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Abstract

Pu and Np were released into the environment by the nuclear activities of human beings, especially the nuclear weapon testing in the years of 1950-1980, and would exist in the environment for a very long period due to their extremely long half-lives. Consequently, they are regarded as highly radiological and biological toxic pollutants in the environment. Therefore, to be able to quantitatively determine the content of Pu and Np in various environmental samples is necessary for the environmental risk assessment and monitoring, especially the area around the nuclear facility sites, and for the radiological emergency preparedness as well as the nuclear waste treatment.

The simultaneous determination of Pu and Np in one analytical procedure is based on the similar chemical separation behaviour of the Np(IV) and Pu(IV) in the nitric and hydrochloric acid media. It offers the advantages including reducing the consumption of samples and chemical reagents, and remarkably saving the analytical time. Moreover, using ²⁴²Pu (sometimes ²³⁶Pu or ²⁴⁴Pu) as a tracer to calculate the chemical yield of Np can avoid the difficulties of obtaining Np tracer (such as ²³⁶Np or ²³⁹Np). However, to our best knowledge, due to the bottle-neck of valence adjustment and maintenance for Pu(IV) and Np(IV) during the whole separation procedure, only few works have been reported for the simultaneous analysis of Pu and Np in the environmental samples.

Separation scheme for Pu and Np determination



Instrumentation



FIAlab system 3500



Thermo X-series ICP-MS

Typical operation conditions for ICP-MS

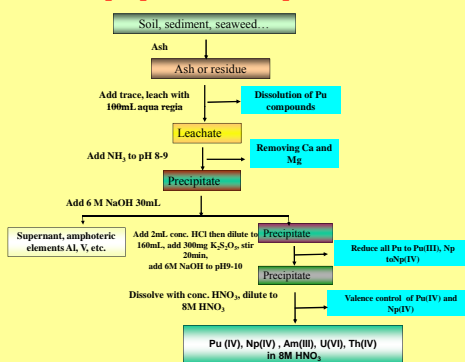
Forward power (W)	1400
Ion masses (m/z)	¹¹³ In, ¹⁸⁹ Hg, ²⁰⁹ Pb, ²⁰⁴ Pb, ²⁰⁹ Pb, ²³⁷ Np, ²³⁸ U, ²³⁹ Pu, ²⁴⁰ Pu, ²⁴² Pu, ²⁴³ Am
Gas flow (L/min)	
Coolant	13.8
Auxiliary	0.80
Nebuliser	1.03
Operation pressures (mbar)	
Expansion	1.0 × 10 ⁵
Analysis	8.3 × 10 ⁻⁸
Time resolved data acquisition	
Sweeps	800
Dwell time (ms)	10000
Channels Per Mass	1
Acquisition Duration (ms)	161041

Sample analyzed throughout the work

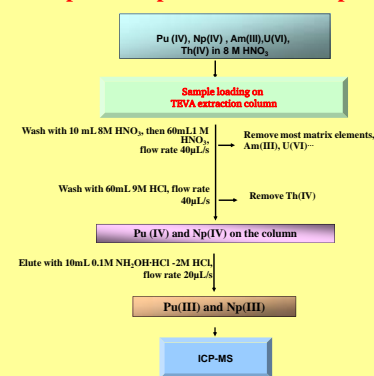
Sample name	Sample amount	Description	Area, location	Rec. or info. of ²³⁷ Np activity, Bq/kg	Rec. or info. of ²³⁹⁺²⁴⁰ Pu activity, Bq/kg
Danish soil	10g	Low-level sample (<1 mBq/g of ²³⁹ Pu)	The top 10cm of 2mm sieved soil from 12 different Danish locations collected during 2003	(5.08 ± 0.158) × 10 ⁻⁴	0.238 ± 0.0135
IAEA-135 certified reference material	0.5g	Soil	Soil sample	0.846 ± 0.045	205-226
Irish Sea Sediment	1g	High level Sediment	Surface sediment from Irish Sea	0.987 ± 0.048	419 ± 10.6
Thule soil	1g	Contaminated soil	Surface soil from, Thule, Greenland	-	1.87 ± 0.17*
NIST Seaweed	20g	A blend of <i>Fucus vesiculosus</i> , <i>Laminaria saccharia</i> and <i>Ascophyllum nodosum</i>	Collected from the western coast of Ireland and from the White Sea	0.152-0.198	0.1296 ± 0.0075
Seaweed	20g	<i>Fucus vesiculosus</i>	Collected from the Klint, Danish coast in the Kattegat	-	-

* Given by α-spectrometry measurement

Sample pre-treatment procedure



Chemical separation/pre-concentration procedure



Comparison of various methods for valence adjustment of Pu(IV) and Np(IV)

Redox reagent	Addition of ²³⁷ Np, mBq	Recovery of Pu, %	Recovery of Np, %	²³⁹⁺²⁴⁰ Pu measured, Bq/kg	²³⁷ Np measured, Bq/kg	Rec. or info. of ²³⁷ Np activity, Bq/kg	Decontamination factor		
							²³⁸ U	²³² Th	Pb
K ₂ S ₂ O ₅ -4M HNO ₃	1.14 ± 0.01	3.6 ± 2.8	54.1 ± 13.9	0.35 ± 0.31	1.78 ± 0.64	0.117 ± 0.001	4.9E+04	1.5E+04	2.1E+04
K ₂ S ₂ O ₅ -conc. HNO ₃ dilute to 1M HNO ₃	1.17 ± 0.01	5.6 ± 3.8	74.1 ± 19.9	0.45 ± 0.31	1.53 ± 1.64	0.117 ± 0.001	4.9E+04	1.5E+04	2.1E+04
K ₂ S ₂ O ₅ -conc. HNO ₃ dilute to 4M HNO ₃	1.15 ± 0.06	76.7 ± 13.2	73.2 ± 11.7	0.25 ± 0.01	0.12 ± 0.01	0.116 ± 0.006	4.1E+04	5.4E+03	1.5E+04
K ₂ S ₂ O ₅ -conc. HNO ₃ dilute to 8M HNO ₃	1.20 ± 0.02	98.1 ± 3.4	95.7 ± 3.9	0.23 ± 0.01	0.11 ± 0.01	0.120 ± 0.002	1.0E+04	7.0E+03	1.0E+04
K ₂ S ₂ O ₅ -conc. HNO ₃ dilute to 1M HNO ₃ -300mg ascorbic acid	1.22 ± 0.07	0.2 ± 0.1	43.7 ± 41.2	5.54 ± 7.37	11.63 ± 19.80	0.123 ± 0.007	1.6E+04	9.1E+03	1.4E+04
K ₂ S ₂ O ₅ -conc. HNO ₃ dilute to 4M HNO ₃ -300mg ascorbic acid	1.26 ± 0.22	53.2 ± 7.5	58.5 ± 9.7	0.27 ± 0.04	0.14 ± 0.02	0.127 ± 0.022	1.5E+04	1.1E+04	1.7E+04
4M HNO ₃ -300mg ascorbic acid (stay for 1h)	1.31 ± 0.10	2.3 ± 2.8	53.8 ± 14.7	0.78 ± 0.63	8.03 ± 6.94	0.132 ± 0.010	8.0E+03	2.4E+04	2.6E+04
4M HNO ₃ -300mg ascorbic acid (stir for 1h)	1.22 ± 0.09	84.5 ± 27.7	48.7 ± 8.9	0.25 ± 0.01	0.09 ± 0.02	0.122 ± 0.009	7.1E+04	1.7E+04	1.0E+05

* Each sample used in the investigation was 10g Danish Soil.

**All the values are the average of three replicate (± standard deviation)

Analytical results of reference materials and real samples for Pu and Np

Sample name	Addition of ²³⁹ Pu, mBq	Addition of ²³⁷ Np, mBq	Recovery, %	²³⁹⁺²⁴⁰ Pu measured Bq/kg	Rec. or info. of ²³⁹⁺²⁴⁰ Pu activity, Bq/kg	²³⁷ Np measured Bq/kg	Rec. or info. of ²³⁷ Np activity, Bq/kg	Decontamination factor		
								²³⁸ U	²³² Th	Pb
IAEA-135 soil	0	0	79.7 ± 7.6	220.0 ± 7.9	205-226	0.78 ± 0.045	0.846 ± 0.045	4.8 × 10 ³	1.1 × 10 ³	1.3 × 10 ³
Irish Sea Sediment	0	0	75.7 ± 15.9	427.2 ± 56.6	419 ± 10.6	1.02 ± 0.037	0.987 ± 0.048	5.4 × 10 ³	2.3 × 10 ³	1.2 × 10 ⁴
NIST Seaweed	0	0	72.8 ± 4.0	0.131 ± 0.005	0.1296 ± 0.0075	1.34 ± 0.09	0.152-0.198	2.8 × 10 ⁴	1.5 × 10 ³	2.2 × 10 ³
Thule soil	0	1.02 ± 0.12	70.0 ± 10.5	1.95 ± 0.29	1.87 ± 0.17	1.14 ± 0.16	1.02 ± 0.14	2.4 × 10 ⁴	3.6 × 10 ³	1.5 × 10 ⁴
Seaweed	8.13 ± 0.10	1.67 ± 0.03	87.9 ± 16.7	0.62 ± 0.03	0.61 ± 0.01	0.06 ± 0.01	0.08 ± 0.01	1.8 × 10 ⁴	1.3 × 10 ³	1.9 × 10 ³
Notes: All values are the average of three replicates (± standard deviation)								4.0 × 10 ⁴	7.5 × 10 ³	1.1 × 10 ³

Summary

An automated analytical method for the simultaneous determination of Pu and Np in the environmental samples was developed. Extraction chromatographic column packed with TEVA resin was used as a separation column, which was incorporated in a sequential injection system to actualize the automated separation of Pu and Np from the matrix elements and interfering radionuclides.

The comparison of various valence adjustment methods showed that using K₂S₂O₅-conc. HNO₃ (dilute to 8M HNO₃) as redox reagents was the most effective one for the valence adjustment and maintenance of Pu(IV) and Np(IV).

The analytical results for both Pu and Np in three reference materials showed good agreement with the reference or informative values.

The total time of separation for a single sample was < 1.5 hours, which extremely improve the analysis efficiency and reduces the labor intensity, as well as enables a rapid determination of Pu and Np especially in emergency situations.