CLOUD POINT EXTRACTION COUPLED WITH ICP-MS FOR TRACE-ELEMENT AND ISOTOPIC ANALYSIS

Oleksandra Horban

Taras Shevchenko National University of Kyiv, 01033 Kyiv, Volodymyrska St, 64;
e-mail: gorban.sh.sasha@gmail.com

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is considered one of the most suitable techniques for trace metal analysis. However, the direct determination of elements and their isotopic composition can be complicated by spectral interferences arising from isotopes of other elements [1-3].
Cloud point extraction (CPE) has gained widespread application in the separation and preconcentration of organic and inorganic compounds over recent decades, owing to its numerous advantages [1-4].
The combination of CPE with ICP-MS represents a promising approach that integrates efficient analyte separation and preconcentration with high analytical sensitivity and the capability for isotopic analysis. This combination can improve the reliability of analytical results obtained for complex matrices [1-4].

STABLE ANALYTICAL PERFORMANCE

The proposed CPE–ICP-MS approach offers excellent instrumental compatibility, high plasma tolerance, and an environmentally friendly, cost-effective alternative to conventional liquid–liquid extraction, without carbon deposition during prolonged operation. [4].

ADVANTAGES OF CPE COUPLED WITH ICP-MS

The high enrichment factors achieved by CPE, combined with the sensitivity of ICP-MS, enable the attainment of satisfactory detection limits for the analysis of natural water and soil samples [1-4].
Meanwhile, the good reproducibility of measurement results and the performance characteristics of calibration curves demonstrate the analytical suitability of the proposed methods [1–4].

Table 1. Comparison of Nd, Sm, and Eu extraction efficiencies from the NIST-2709a reference material using CPE and solid-phase extraction (SPE) (n = 4) [2].

Element	CPE, %	SPE, %
Nd	101 ± 10	45 ± 10
Sm	99 ± 5	51 ± 10
Eu	99 ± 5	68 ± 10

Table 2. Analytical figures of merit for the of the method for the determination of rare earth elements [3].

Sample type	Instrumentation	LOD, ng/L	Preconcentration factor	Extraction efficiency, %
Soils	ICP-MS	0,2 - 30	>140	>97

Table 3. Results of the determination of rare earth element concentrations in an environmental sample and a reference material (mg/kg) [3].

Element	NIST-2709a: Measured (n = 4)	NIST-2709a: Expected (n = 4)	Bauxite residue (n = 4)	IAEA-384 (n = 4)
Sc	11,8 ± 0,6	11,1 ± 0,1	50 ± 1	10 ± 5
Y	12,1 ± 0,2	H.з.	71 ± 1	2,0 ± 0,8
La	20 ± 4	21,7 ± 0,4	50 ± 1	19 ± 2
Ce	43 ± 4	42 ± 1	93 ± 1	0,22 ± 0,05
Pr	5,4 ± 0,4	N.A.	8,8 ± 0,4	0,052 ± 0,009
Nd	22 ± 2	17	28,2 ± 0,9	0,04 ± 0,009
Sm	4,3 ± 0,2	4	5,9 ± 0,4	0,017 ± 0,004
Eu	0,9 ± 0,1	0,83 ± 0,02	1,3 ± 0,4	0,014 ± 0,001
Gd	4,3 ± 0,2	3,0 ± 0,1	8,0 ± 0,3	0,032 ± 0,005
Tb	0,50 ± 0,02	0,5	1,3 ± 0,4	0,030 ± 0,003
Dy	3,2 ± 0,4	3	11,2 ± 0,3	0,020 ± 0,003
Ho	0,60 ± 0,06	N.A.	2,3 ± 0,2	0,029 ± 0,003
Er	2 ± 0,4	N.A.	8,5 ± 0,3	0,018 ± 0,002
Tm	—	N.A.	1,3 ± 0,2	0,017 ± 0,002
Yb	2,0 ± 0,2	2	10,3 ± 0,3	0,012 ± 0,004
Lu	0,5 ± 0,09	0,3	1,2 ± 0,2	0,016 ± 0,005

ADVANTAGES OF CPE COUPLED WITH ICP-MS.
Reduction of spectral interferences in ICP-MS analysis

The use of appropriate chelating agents in CPE offers the important advantage of effectively separating lanthanides from coexisting barium, which can cause spectral interferences during ICP-MS analysis, while also reducing other polyatomic interferences [1].

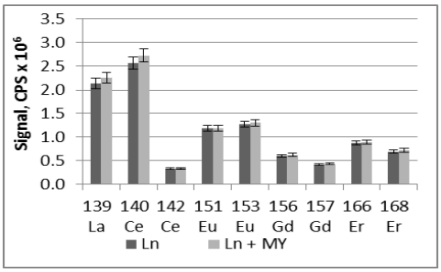


Fig.1. Analytical responses of lanthanides after CPE in the presence (Ln + MY) and absence (Ln) of concomitant elements; ligand used: En [1].

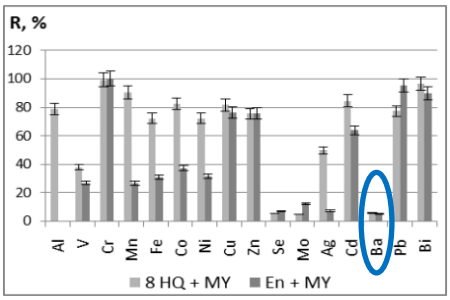


Fig. 2. Extraction efficiencies of concomitant elements (C = 10 µg/L) after CPE using 8HQ and En ligands [1].

ISOTOPIC ANALYSIS

Table 4. Lanthanide isotope ratios in environmental samples and standard reference materials (n = 4) [2].

Sample CRM- code	Sample origin	Sample type	$^{143/145}$Nd		$^{147/149}$Sm		$^{151/153}$Eu	
			R (±1σ)	δ, ‰ (±1σ)	R (±1σ)	δ, ‰ (±1σ)	R (±1σ)	δ, ‰ (±1σ)
NIST-2709a	San Joaquin, California, USA	Agricultural soil	1,468 ± 0,002	-1 ± 1	1,084 ± 0,001	-0,4 ± 0,7	0,915 ± 0,001	-1 ± 1
IAEA-384	Fangataufa Lagoon, French Polynesia	Sediments	1,490 ± 0,002	14 ± 2	1,099 ± 0,004	13 ± 4	0,903 ±0,008	-14 ± 9
CRL-082005	Chalk River, Ontario, Canada	Sediments	1,435 ± 0,002	-23 ± 2	1,076 ± 0,003	-8 ± 3	0,915 ± 0,001	-1 ± 2
IAEA-360	Chernobyl, Ukraine	Soil	1,440 ± 0,002	-20 ± 4	1,074 ± 0,002	-10 ± 2	0,913 ± 0,001	-4 ± 1

CONCLUSION

Combining cloud point extraction with inductively coupled plasma mass spectrometry is a promising approach for metal analysis, enabling efficient extraction and preconcentration alongside highly sensitive determination. Further optimization of CPE conditions, expansion of the range of analytes that can be extracted using this technique, and refinement of ICP-MS parameters will help improve the effectiveness of this approach for analysing complex environmental matrices and monitoring environmental quality.

REFERENCES

1. Varbanova E. K., Angelov P. A., Simitchiev K. K., Kaynarova L. I., Stefanova V. M. Cloud point extraction of lanthanides with 3-ethylamino-but-2-enoic acid phenylamide from water samples prior to ICP-MS determination. Bulgarian Chemical Communications. 2017. Vol. 49, Special Issue G. P. 49–54.
2. Labrecque C., Lebed P. J., Larivière D. Isotopic signature of selected lanthanides for nuclear activities profiling using cloud point extraction and ICP-MS/MS. Journal of Environmental Radioactivity. 2016. Vol. 155–156. P. 15–22. 10.1016/j.jenvrad.2016.02.002
3. Labrecque C., Larivière D. Quantification of rare earth elements using cloud point extraction with diglycolamide and ICP-MS for environmental analysis. Analytical Methods. 2014. Vol. 6, No. 23. P. 9291–9298. 10.1039/C4AY01911C.
4. Simitchiev K., Stefanova V., Kmetov V., Andreev G., Kovachev N., Canals A. Microwave-assisted cloud point extraction of Rh, Pd and Pt with 2-mercaptobenzothiazole as preconcentration procedure prior to ICP-MS analysis of pharmaceutical products. Journal of Analytical Atomic Spectrometry. 2008. Vol. 23, No. 5. P. 717–726. 10.1039/B715133K