Fresenius J Anal Chem (2001) 370 : 909–912

ORIGINAL PAPER

Céline Guéguen · Janusz Dominik · Didier Perret

Use of chelating resins and inductively coupled plasma mass spectrometry for simultaneous determination of trace and major elements in small volumes of saline water samples

Received: 11 January 2001 / Revised: 27 February 2001 / Accepted: 1 March 2001

Abstract For some saline environments (e.g. deeply percolating groundwater, interstitial water in marine sediments, water sample collected after several steps of fractionation) the volume of water sample available is limited. A technique is presented which enables simultaneous determination of major and trace elements after preconcentration of only 60 mL sample on chelating resins. Chelex-100 and Chelamine were used for the preconcentration of trace elements (Cd, Cu, Pb, Zn, Sc) and rare earth elements (La, Ce, Nd, Yb) from saline water before their measurement by inductively coupled plasma mass spectrometry. Retention of the major elements (Na, Ca, Mg) by the Chelamine resin was lower than by Chelex; this enabled their direct measurement in the solution after passage through the resin column. For trace metal recoveries both resins yield the same mass balance. Only Chelex resin enabled the quantitative recovery of rare earth elements. The major elements, trace metals and rare earth elements cannot be measured after passage through one resin only. The protocol proposes the initial use of Chelamine for measurement of trace and major elements and then passage the same sample through the Chelex resin for determination of the rare earth elements. The detection limit ranged from 1 to 12 pg mL^{-1}. At concentrations of 1 ng mL^{-1} of trace metals and REE spiked in coastal water the precision for 10 replicates was in the range of 0.3–3.4% (RSD). The accuracy of the method was demonstrated by analyzing two standard reference waters, SLRS-3 and CASS-3.

Introduction

In numerous environmental applications the simultaneous determination of trace and major elements is required in saline water samples of limited volume. Slowly percolating groundwater and interstitial water of coastal marine sediments collected in some high resolution dialysis samplers are examples where only a small volume is available. Occasionally sample volume is limited by a fractionation procedure necessary to obtain information on metal speciation. For example, the filtration of turbid water of estuaries must be performed with a small volume, to avoid rapid clogging of the filter. Another example is separation of the colloidal fractions by several step-sequence separation procedures. In such applications separation of the major metals and preconcentration of trace elements using the same small volume sample is of primary importance.

In addition to the amounts of the trace metals Cd, Cu, Pb, and Zn, the concentrations of four rare earth elements (REE), La, Ce, Nd, and Yb, were investigated. Because of a coherent behavior of the group of REE, these four elements were chosen to represent light (La, Nd) and heavy (Yb) REE. In addition, Ce was investigated because of its particular redox chemistry.

Inductively coupled plasma mass spectrometry (ICP–MS) is a suitable method for multi-element analysis but it is not free from interference effects [1], specifically spectroscopic and matrix effects. The first group of effects arise as a result of isobaric overlap, polyatomic or adduct ions, refractory oxide ions, and doubly charged ions. These interferences can be corrected mainly by arithmetic algorithms. The second type of interference effect is more complex and is related to the nature of the sample matrix. These can be minimized or eliminated by careful sample preparation. They can occur for solutions containing significant amounts of dissolved solids (> 0.5 g L^{-1}) [1]. Some matrix elements, notably Na, Mg, Ca, cause enhancement of the analyte signal. A relatively high salt content can, moreover, induce instrumental problems for

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C. Guéguen (✉) · J. Dominik
Institut F.-A. Forel and Centre d'Etudes
en Sciences Naturelles de l'Environnement,
University of Geneva,
10 Route de Suisse, 1290 Versoix, Switzerland
e-mail: celine.gueguen@terre.unige.ch

D. Perret
Faculty of Chemistry, University of Geneva,
30, Ernest Ansermet, 1211 Geneva, Switzerland

ICP–MS, for example salt deposition on the torch, sampling interface, or ion lenses. In practice, these problems can be eliminated by coprecipitation [2], solvent extraction [3, 4], evaporation [5, 6] or ion-exchange [7, 8]. With the first three methods contamination is always possible because of the use of large amounts of reagent, or because of airborne particulate contamination during evaporation. Solid-phase extraction with chelating resins such as Chelex-100 and Metalfix Chelamine seems to be the best preconcentration method for determination of trace metals. The latter resin, which contains a pentamine ligand on an organic polymer, was described by Blain et al. [9]. The Chelex-100 resin is a styrene–divinylbenzene copolymer containing paired iminodiacetate ions and has been described by numerous workers (e.g. [10]).

In this work the preconcentration of trace elements and REE using the combination Chelamine/Chelex was investigated for fresh- and saline waters. The concentration of major elements after passage through the first chelating resin was determined by ICP–AES.

Experimental

The resins, 200–400 mesh Chelex-100 (Bio-Rad) and Metalfix Chelamine (Fluka), were prepared by soaking in 2.5 mol L^{-1} HNO_3 for 4 h. These slurries were poured into Teflon FEP (fluoroethylene propylene) tubing (6.4 mm i.d., 4 cm in length) closed with a polyethylene frit, left to drain, washed with HNO_3 (2.5 mol L^{-1}, 30 mL), rinsed with Milli-Q water (MQW; 30 mL), and converted to the NH_4^+ form by elution with aqueous ammonia (NH_4OH; 2 mol L^{-1}, 2 mL). Excess NH_4OH was removed by rinsing with MQW (30 mL). The column was buffered with CH_3COONH_4 (NH_4Ac; 5 mL) to pH 5.3 for Chelex and pH 8.0 for Chelamine. Additional alkaline treatment with NH_3 is needed to adjust the Chelamine buffer to pH 8.0. The resin was finally rinsed with MQW before sample preconcentration.

Sample (60 mL) was buffered with NH_4Ac (1 mol L^{-1}, 1 mL) to pH 5.3 and 8.0 for Chelex and Chelamine, respectively, before loading on to the resin column. Subsequently, to remove the salts, the Chelex column was rinsed with MQW (10 mL) and NH_4Ac (20 mL), whereas the Chelamine column was rinsed with MQW (20 mL). The columns were eluted with HNO_3 – 6 mL of 2 mol L^{-1} for Chelex and 6 mL of 0.2 mol L^{-1} for Chelamine – into preweighed 10 mL polypropylene (PP) bottles. Passage through the columns and elution were both performed at the same flow rate – 1 mL min^{-1} and 4 mL min^{-1} for Chelex and Chelamine, respectively.

Trace (Cd, Cu, Pb, Zn, Sc, La, Ce, Nd, Yb) and major (Na, Ca, Mg) elements were analyzed by ICP–MS (HP 4500 Series 100, Hewlett–Packard) and ICP–AES (Plasma 1000, Perkin–Elmer), respectively (Table 1).

Atlantic coastal water (salinity 30‰, conductivity 34 mS cm^{-1}, pH 8.2), artificially aged for several months under conditions of natural pH, natural light, and ambient temperature, was used as saline matrix for all experiments. The metal content of the artificially aged water was < 10 pg mL^{-1}. Samples of the artificially aged saline matrix were filtered through 1.2-μm filters before addition of 60 ng Ag, Cd, Cu, Pb, Zn, and 10 ng Sc, La, Ce, Nd, Yb. The final concentrations were 1 ng mL^{-1} of trace metals and 0.17 ng mL^{-1} of scandium and the rare earth elements. Organic matter was destroyed by a double UV-irradiation procedure to improve metal retention by the resins [11].

The method was validated for major and trace metal measurements with two certified waters obtained from the National Research Council of Canada (NRCC) – freshwater SLRS-3 and seawater CASS-3 (salinity 30.2‰).

All operations were performed in a class 100 laminar flow hood, in an ultra-clean room. All reagents were ultrapure quality (Merck, Germany). All tips and containers were acid-washed and stored in a double plastic bag in the clean room.

Results and discussion

All results are expressed in mass units and were obtained using the procedures described above.

Purification of buffer

During passage of the sample through the column the pH in the resin changes, which necessitates the use of a buffer. One possible source of contamination during the resin preconcentration process can be the NH_4Ac buffer [12]. Before use for column conditioning and the sample buffering, the ammonium acetate buffer was purified on Chelex-100 resin. This purification reduced the trace metal content by 41, 43, 34, and 99% for Cd, Cu, Pb, and Zn, respectively (Fig. 1). After purification the quantities of trace metals in the buffer were much lower than the metal content of the natural sample. Purification of the

Table 1 Instrument settings, limits of detection (LOD), and relative standard deviation (RSD %) for ICP–MS and ICP–AES. LOD are calculated as three times the standard deviation of the blank signal. RSD (%) is based on 10 replicate preconcentrations of 1 ng mL^{-1} trace metals and REE, and 10 replicate preconcentrations of coastal water diluted 100 times for major elements

ICP–MS Agilent HP4500			ICP–AES Perkin–Elmer Plasma 1000		
RF power (W)		1150	PMT (V)	400–850	
Plasma gas flow (L min^{-1})		14.1	Peak window (nm)	0.04	
Auxiliary gas flow (L min^{-1})		1.0	Sampling time (s)	0.1	
Nebulizer gas flow (L min^{-1})		1.14			
	LOD (pg mL^{-1})	RSD (%)		LOD (μg mL^{-1})	RSD (%)
^{111}Cd	2	0.3	Ca 393.66 nm	13	0.7
^{140}Ce	1	3.3	Na 588.99 nm	27	0.4
^{63}Cu	12	0.3	Mg 279.55 nm	3	1.2
^{139}La	8	3.4			
^{146}Nd	1	3.3			
^{206}Pb	5	0.5			
^{171}Yb	1	6.2			
^{66}Zn	12	1.0			

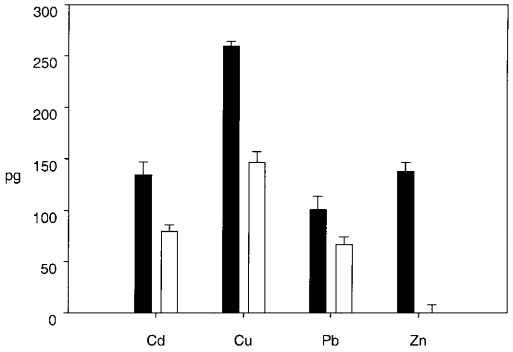

Fig. 1 Amounts (pg) of trace metals (Cd, Cu, Pb, and Zn) before (*dark bars*) and after (*white bars*) purification of Chelex resin with ammonium acetate buffer. The mass is calculated for the 5 mL buffer used during conditioning of the resin column

buffer chelated the metal ions without altering the concentrations of non-metal ions. Buffer pH was not changed by the purification process.

Blank

Procedural blanks for Chelex and Chelamine resins were determined after preconcentration of 60 mL MQW with a concentration factor of 10. Amounts of metals in the HNO_3 eluent were negligible. For both resins, the metal concentrations in the two blanks (MQW + purified buffer) for each resin were comparable and lower than in seawater (Table 2). Thus, the procedural blanks are acceptable, the major contribution being from the resin. Because in the open ocean trace metal concentrations can be lower, the total blank cannot be neglected. In such cases, the amount of resin can be optimized to reduce the resin blank. Metal recovery must also be re-checked.

Table 2 Amounts (ng) of trace metals in total blanks (n = 5) of Chelex and Chelamine resin compared with those found in seawater [13]. The errors are given at the 95% confidence level

Metal	Chelex	Chelamine	Seawater
Cu	0.75 ± 0.25	0.89 ± 0.06	52.5
Zn	4.40 ± 0.25	3.80 ± 0.12	29.7
Cd	0.13 ± 0.05	0.09 ± 0.03	2.7
Pb	0.20 ± 0.10	0.06 ± 0.02	0.96

Retention of major elements, trace metals and rare earth elements

Elimination of the saline matrix (Na, Ca, and Mg) was performed simultaneously with preconcentration of the trace elements from 60 mL coastal water spiked with metals and rare earth elements. The masses of the major elements are given for the total volumes of solutions passed through the resin (SPTR), for the different rinse solutions (MQW and NH_4Ac for Chelex, and MQW for Chelamine) and for the HNO_3 used for trace metal elution (Table 3). Chelamine resin retained less of the major elements than Chelex. Between 3% and 9% of each of the major elements was retained by Chelamine, whereas between 18% and 29% was retained by Chelex. This different affinity for the major elements is because of the chelating agent of the resin. For the Chelex resin, the chelating agent is iminodiacetic acid which has soft and hard acidic sites, whereas the Chelamine resin has a polyamine-like chelating agent which has only soft sites. MQW elution for Chelex and Chelamine was comparable: it removed 4–5% Mg, 7–9% Ca, and 3% Na for both resins. For Chelex, NH_4Ac elution enables removal of up to 19% Ca, but the resin still contained alkali and alkaline earth elements which were eluted with trace elements by HNO_3. These different solutions (MQW and NH_4Ac) are necessary to minimize interference during ICP–MS analysis, but did not remove metals. To measure major elements after preconcentration on Chelex all fractions must be measured, whereas after preconcentration on Chelamine only the SPTR was needed to obtain a result with an accuracy of approximately 10%.

For trace metals, the results were comparable for both resins (Table 4). The mass balance was between 96 and 109%. Because of the lower flow rate of loading and elution on to Chelex (1 mL min^{-1} and 4 mL min^{-1} for Chelex and Chelamine, respectively), the preconcentration process on Chelex was more time-consuming.

For these reasons, therefore, the use of the Chelamine resin for trace metal preconcentration and major element elimination is strongly recommended.

Table 3 Mass (mg) of major elements in the solutions passed through resins (SPTR) and the different rinse solutions for Chelex and Chelamine resins

	Chelex			Chelamine		
	Mg	Ca	Na	Mg	Ca	Na
SPTR	38.9 ± 0.7 (71)	10.8 ± 0.2 (74)	386.3 ± 9.0 (82)	54.6 ± 0.4 (95)	13.3 ± 0.1 (91)	456.5 ± 3.1 (97)
MQW rinse solution	2.2 ± 0.04 (4)	1.0 ± 0.1 (7)	14.1 ± 0.4 (3)	3.11 ± 0.01 (5)	1.3 ± 0.1 (9)	14.5 ± 0.03 (3)
NH_4 Ac rinse solution	8.2 ± 0.2 (15)	2.8 ± 0.1 (19)	9.4 ± 0.2 (2)	–	–	–
HNO_3 elution	5.5 ± 0.4 (10)	nd	61.3 ± 5.4 (13)	nd	nd	nd

The data in parentheses are the amounts (%) of total major elements found in the various fractions (see text for details). 100% corresponds to total major element concentrations measured before preconcentration
n.d. – not detected

Table 4 Recovery (ng) of trace elements in HNO_3 (n = 10) after preconcentration on Chelex and Chelamine

Metal	Chelex	Chelamine	Expected values
Zn	58.2 ± 0.6	57.6 ± 0.5	60
Pb	60.6 ± 0.3	62.4 ± 0.2	60
Cu	63.6 ± 0.2	60.6 ± 0.2	60
Cd	60.6 ± 0.2	58.8 ± 0.3	60

Table 5 Amounts of scandium and rare earth elements (ng) determined in HNO_3 solution after Chelex preconcentration from spiked saline water

Metal	Concentration factor			Expected mass
	2.5	3	5	
Sc	10.2	11.1	10.4	10.0
La	10.2	10.9	10.6	10.0
Ce	10.2	10.7	10.7	10.0
Nd	10.1	11.2	11.0	10.0
Yb	10.0	10.4	10.5	10.0

Table 6 Analytical results for standard certified waters (n = 5), SLRS-3 and CASS-3. Trace metal and REE concentrations are given in pg mL^{-1}, those of the major elements in μg mL^{-1}

Metal	SLRS-3		CASS-3	
	This study	Certified	This study	Certified
Cu	1436 ± 1	1350 ± 70	468 ± 5	517 ± 62
Zn	1051 ± 7	1040 ± 90	1335 ± 5	1240 ± 250
Cd	11.0 ± 0.5	13 ± 2	33.00 ± 0.02	30 ± 5
Pb	68.00 ± 0.02	68 ± 7	14.00 ± 0.02	12 ± 4
La	213 ± 10	128–814[a]	1.4 ± 0.6	1.8–5.1[b]
Ce	238 ± 13	240–308[a]	3.8 ± 1.3	2.2–3.6[b]
Nd	171 ± 10	169–224[a]	6.0 ± 0.4	
Yb	8 ± 1	8.3–13.2[a]	1.0 ± 0.4	0.61–0.94[b]
Mg	1.5 ± 0.3	1.6 ± 0.2		
Ca	5.7 ± 0.1	6.0 ± 0.4		
Na	2.3 ± 0.2	2.3 ± 0.2		

[a,b] REE concentrations were obtained from the literature [14, 15, 16]

Coastal water (60 mL) enriched in scandium and rare earth elements (La, Ce, Nd and Yb) was loaded on to Chelamine and Chelex. Chelamine resin has no affinity for these elements and they were not retained, whereas the Chelex resin has high affinity for rare earth elements. Different concentration factors (2.5, 3, and 5) were tested and had no effect on metal balance (Table 5). Chelex resin can be recommended for the determination of the concentrations of scandium and rare earth elements in saline waters.

Application to certified waters

The accuracy of results obtained after preconcentration on Chelamine was evaluated by determination of trace metals in certified freshwater (SLRS-3) and seawater (CASS-3). The concentrations of trace metals and major elements were in the certified concentration range, except for Cu (Table 6). The Cu content of SLRS-3 measured without preconcentration by ICP–MS (1.46 ± 0.03 ng mL^{-1}, n = 5) was higher than the certified value (1.35 ± 0.07 ng mL^{-1}); a similar difference has also been reported by Peart et al. [15] (1.50 ± 0.07 ng mL^{-1}; n = 5). The REE content was close to the reported data. The close agreement demonstrates the accuracy of the method for REE, trace, and major elements in the fresh and saline waters.

Conclusion

Trace metals and rare earth elements in low volumes of high-salinity samples were quantitatively determined by ICP–MS after preconcentration on chelating resins. The major elements were simultaneously separated and measured by ICP–AES. Chelamine resin was first used to separate major elements from trace metals which were retained on the resin. The effluent from Chelamine was the concentrated on Chelex to isolate the rare earth elements. Purification of the buffer solution reduced blank values, but the major contribution to the blank comes from the resin. This blank can be further reduced by optimization of resin quantity.

Acknowledgements This research was funded by the Swiss National Science Foundation (grant no 20–57189.99).

References

1. Jarvis KE, Gray AL, Houk RS (1995) Inductively Coupled Plasma Mass Spectrometry. Blackie, pp 380
2. Boniforti R, Ferraroli R, Frigieri P, Heltai D, Queirazza G (1984) Anal Chim Acta 162:33–46
3. Erel Y, Morgan JJ, Patterson CC (1991) Geochim Cosmochim Acta 55:707–719
4. Thomson M, Ramsey MH, Pahlavanpour B (1982) Analyst 107:1330–1334
5. Elbaz-Poulichet F, Holliger P, Martin JM, Petit D (1986) Sci Total Environ 54:61–70
6. Pai SC (1988) Anal Chim Acta 211:271–280
7. Groschner M, Appriou P (1994) Anal Chim Acta 297:369–376
8. Beauchemin D, McLaren JW, Mykytiuk AP, Berman SS (1987) Anal Chem 59:778–783
9. Blain S, Appriou P, Handel H (1993) Anal Chim Acta 272: 91–97
10. Pai SC, Whung PY, Lai RL (1988) Anal Chim Acta 211:257–270
11. Guéguen C, Belin C, Thomas BA, Monna F, Favarger PY, Dominik J (1999) Anal Chim Acta 386:155–159
12. Sturgeon RE, Berman SS, Desaulniers A, Russell DS (1980) Talanta 27:85–94
13. EPA (1979) Environmental Protection Agency. EPA-600/7–79–17
14. Yan XP, Kerrich R, Hendry MJ (1999) J Anal At Spectrom 14:215–221
15. Beart DB, Antweiler RC, Taylor HE, Roth DA, Brinton TI (1998) Analyst 123:455–476
16. Kühn M, Kriews M (2000) Fresenius J Anal Chem 367:440–444