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# Determination of trace elements in sea water by ion chromatography–inductively coupled plasma mass spectrometry<sup>☆</sup>

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## Abstract

The determination of trace elements in sea water was carried out by means of ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS). The elimination of the matrix by the chromatographic technique allowed the determination of about twenty elements (rare earths, Co, Cu, Mn, Ni, Zn Pb and U) at ultra-trace levels. The calibration of the ICP-MS system was carried out using multi-elemental standard aqueous solutions. The use of a multi-elemental technique such as ICP-MS permitted the throughput of samples to be increased because the separation of the different analytes was not required. The detection limits obtained for most of the elements were in the range 1–50 ng/l and the recovery for all the elements under analysis was quantitative.

## 1. Introduction

The determination of trace elements, particularly heavy metals, in samples from uncontaminated areas requires powerful techniques to detect extremely low concentrations of analytes. Inductively coupled plasma mass spectrometry (ICP-MS) is applicable to trace multi-elemental and isotopic analysis of a wide range of matrices [1–4], although highly saline samples can cause both spectral interferences and matrix effects [5,6]. Typically, the elements of interest (transition metals and metalloids) are present at trace levels, and the high concentrations of alkaline

earth and alkali metals can cause significant interferences in trace element determinations. In this situation, separation of the matrix components and preconcentration of analytes are frequently necessary. In the preconcentration step, metals are generally complexed by chelating agents. The chelating agent could be used in an immobilized form in a resin and packed into a chromatographic column. Metals can be released either by digesting the resin with acid [7] or by changing the ionic form of the resin. One of the most useful and frequently used methods employs an iminodiacetate chelating resin [8,9]. Recently, great importance was assumed by the development of a highly cross-linked macroporous poly(styrene–divinylbenzene) (PS–DVB) resin containing iminodiacetate functional groups with a high degree of physical integrity and

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therefore with the possibility of operating at high pressures without physical degradation or alteration of the chemical properties of the resin. In this paper, the use of an automatic chelation system is described for matrix elimination and on-line preconcentration of rare earth elements (REE) and first-row transition metals in sea water prior to determination by ICP-MS.

## 2. Experimental

### 2.1. Instrumentation

A metal-free high-pressure chelation system (Chelation System 2; Dionex, Sunnyvale, CA, USA) including a gradient pump (GPM-2, Dionex) and a sample concentration module (SCM-1, Dionex) and equipped with a MetPac CC-1 column was used. The operation of all the components in the system is controlled by the operating program in the chromatography automation system (Autoion-400, Dionex), running on a microcomputer (IBM PS/50) interfaced through a computer interface module (CIM). The gradient pump was employed for delivering reagents during the matrix elimination, metal elution and chelating column reconditioning steps. A single reciprocating piston pump (DPO, Dionex) was used for sample preconcentration on to the MetPac CC-1 column. The IC system was connected directly to the cross-flow nebulizer of the ICP-MS system with PTFE tubing.

Preconcentration and matrix elimination were carried out on a MetPac CC-1 (Dionex) column (50 mm × 4 mm I.D.) packed with a styrene-based macroporous 12% cross-linked imino-diacetate-functionalized chelating resin. The particle size was about 20 μm and the capacity of the resin was about 0.9 mequiv. Cu(II)/g.

All the elemental measurements were made on a Perkin-Elmer Elan 5000 ICP-mass spectrometer (Perkin-Elmer Sciex, Norwalk, CT, USA), equipped with two mass-flow controllers, a personal computer (IBM PS/2 70/386) and a printer (Epson EPL 7100). The element elution peaks were recorded in real time and stored on a

hard disk with Elan V2.2 transient signal analysis software.

### 2.2. Reagents

Nitric acid (65%, w/v) and ammonia solution (25%, w/v), Suprapur, were obtained from Merck (Darmstadt, Germany) and 2.0 M ammonium acetate buffer (pH 5.5), Ultrapure, from Dionex. Deionized water (18 MΩ) was prepared with a Millipore water-purification system.

Synthetic sea water was prepared according to the ASTM D 1141 procedure [10] and subsequently purified by treatment at pH 5.5 with Chelex-100 resin (NH<sub>4</sub><sup>+</sup> form) [11].

Multi-elemental standard solutions were prepared from a 10 mg/l multi-elemental atomic absorption standard, ICP-MS Calibration Standard No. 1–2–3–4 (Perkin-Elmer), by dilution with demineralized water or synthetic sea water.

In the literature there are many examples of contamination derived from the pH probe, glass bottles and the reagents [12]. For this reason, all the sample and reagent preparations and handlings were conducted under a laminar-flow cleanhood (class 100) in order to reduce blank contaminations.

### 2.3. Procedure

A volume of 90 ml of the sample was buffered to 5.5 pH by adding 10 ml of 2.0 M ammonium acetate buffer solution (pH 5.5). An aliquot of 10 ml of this solution was loaded on to the Dionex MetPac-CC1 chelation column at 3 ml/min. The alkali and alkaline earth metals were eliminated by elution for 3 min at 3.0 ml/min with the ammonium acetate solution, and finally the elements under investigation were eluted with 2 M HNO<sub>3</sub> for 2 min at 3.0 ml/min. The operating programme and a scheme of the apparatus are reported in Table 1 and Fig. 1, respectively. The use of a multi-elemental technique such as ICP-MS allowed us to elute all the analytes in a single step with 2 M HNO<sub>3</sub> without considering the chromatographic separation,

Table 1  
Ion chromatographic preconcentration programme

Step No.	Time (min)	Flow-rate (ml/min)	Eluent composition (%)			Valve position		Comments
			H <sub>2</sub> O	CH <sub>3</sub> COONH <sub>4</sub>	HNO <sub>3</sub>	V <sub>1</sub>	V <sub>6</sub>	
1	0.0	1.0	100	–	–	0	0	Start
2	0.1	3.0	–	100	–	1	1	Alkali metal elution
2f	2.9	3.0	–	100	–	1	1	
3	3.0	3.0	–	–	100	0	1	ICP-MS start reading
3f	5.5	3.0	–	–	100	0	1	ICP-MS end reading
4	5.6	3.0	–	–	100	1	1	Column washing
4f	7.5	3.0	–	–	100	1	1	
5	7.6	3.0	–	100	–	1	1	Column reconditioning
5f	11.0	3.0	–	100	–	1	1	
6	11.1	3.0	100	–	–	1	1	
7	14.0	3.0	100	–	–	0	0	Stand-by

therefore reducing the analysis time (see Table 2).

### 3. Results and discussion

In order to check the retention efficiency of the column with highly saline matrices, a series

of preliminary off-line tests were performed. In these experiments we used the IC preconcentration unit separately from the ICP-mass spectrometer, and therefore the analysis consisted of two different steps: (1) loading of the sample and elution of the analytes from the column; and (2) the instrumental determination.

A multi-elemental standard solution (1 µg/l) was prepared in synthetic sea water by diluting the 10 mg/l multi-elemental atomic absorption standards (Perkin-Elmer). Different volumes (10, 100 and 500 ml) of the 1 µg/l multi-elemental synthetic sea water standard solution were loaded on the column, the alkali and alkaline earth metals were washed out according to the procedure described above and the elements under investigation were eluted with 10 ml of 2 M HNO<sub>3</sub>. In this way, concentration factors of 1, 10 and 50 were obtained. The quantitative recoveries, calculated on the basis of three replicates and reported in Table 3, confirm that under the conditions tested the column permits the treatment of large volumes of highly saline samples.

In a second phase, in order to lower the volume of acid used for the elution of the metals, the handling of the samples and the consequent contamination of the system, we directly connected the IC and ICP-MS systems by means of PTFE tubing about 500 mm long. The IC concentration system is shown in Fig. 1. An increase

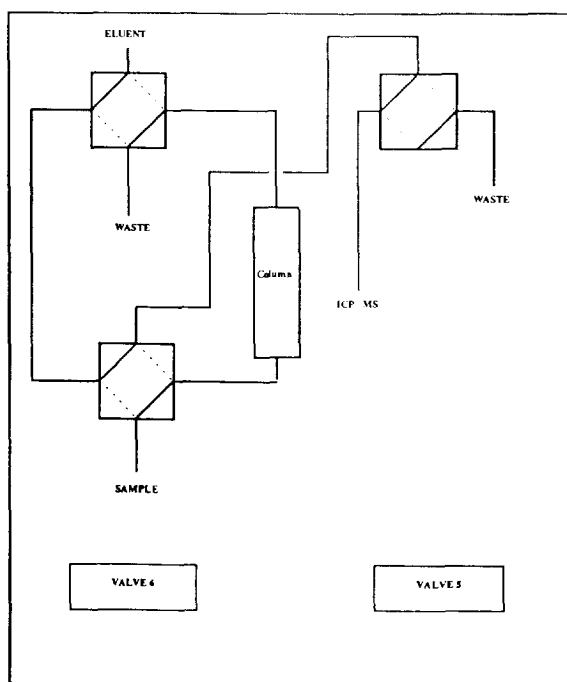


Fig. 1. Schematic diagram of the IC concentration system

Table 2  
Instrumental conditions for ICP-MS

Argon plasma flow (l/min)	14.5
Argon auxiliary flow (l/min)	0.95
Argon nebulizer flow (l/min)	1.00
Power (W)	1050
Sample uptake (ml/min)	1.0
Resolution (u)	0.8
Sweeps/readings	1
Readings/replicates	150
Point across peak	1
Dwell time (ms)	20
Scanning mode	Peak hop transient
Signal profile processing	Area integration

Element	Mass	Elemental equations
Mn	55	
Co	59	
Ni	60	
Cu	63	
Zn	66	
Y	89	
Cd	114	$Cd^{114} = Cd^{114} - 0.02747 \cdot Sn^{118}$
La	139	
Ce	140	
Pr	141	
Nd	144	$Nd^{144} = Nd^{144} - 0.2064 \cdot Sm^{147}$
Sm	152	$Sm^{152} = Sm^{152} - 0.01276 \cdot Gd^{157}$
Eu	153	
Gd	158	$Gd^{158} = Gd^{158} - 0.003604 \cdot Dy^{163}$
Tb	159	
Dy	164	$Dy^{164} = Dy^{164} - 0.04669 \cdot Er^{166}$
Ho	165	
Er	166	
Tm	169	
Yb	174	$Yb^{174} = Yb^{174} - 0.006632 \cdot Hf^{178}$
Pb	208	$Pb^{208} = Pb^{208} + Pb^{207} + Pb^{206}$
U	238	

Table 3  
Recoveries (%) for pre-concentration off-line tests on the MetPac-CCl column

Element	Sample loaded (ml) <sup>a</sup>		
	10 ( <i>f</i> = 1) <sup>b</sup>	100 ( <i>f</i> = 10)	500 ( <i>f</i> = 50)
Mn	105	102	102
Co	105	101	99
Ni	103	98	98
Cu	112	103	101
Zn	132	93	91
Y	106	111	100
Cd	85	95	96
La	101	102	100
Ce	104	104	99
Pr	103	99	99
Nd	106	99	98
Sm	102	96	96
Eu	99	96	96
Gd	102	100	99
Tb	97	96	96
Dy	88	96	97
Ho	87	95	95
Er	88	97	95
Tm	81	95	94
Yb	83	92	93
Pb	106	101	93
U	100	85	82

<sup>a</sup> Concentration of the multi-elemental solution = 1 µg/l (buffered at pH 5.5).

<sup>b</sup> *f* = Concentration factor: ml of solution loaded/ml of HNO<sub>3</sub> eluted.

in the sensitivity of detection and lower blank values were observed with this instrumental configuration.

A series of preliminary tests was carried out by loading various sample volumes in the range 5–200 ml. A sample volume of 10 ml was chosen as a compromise between the necessity for having detection limits adequate for the analytical needs and not too long analysis times. As an example, calibration with a blank and three standard solutions needs about 3.5 h: 3.3 min for

the loading and 14 min for the analysis of each replicate, with three replicates for four solutions.

With very low concentrations of the analytes, as good retention on the column was observed, it will be possible to increase the enrichment factor by loading larger volumes of the samples.

Calibration of the ICP-MS system was performed by loading three times 10 ml of blank solution and three different multi-elemental standard solutions (1, 5, and 10 µg/l) in synthetic sea water. The linearity of the system was checked by calculating, on different days, the correlation coefficients of the curves; for all the elements these were better than 0.990.

The decrease in matrix interferences was con-

firmed by loading on the column 10-ml volumes of 1  $\mu\text{g/l}$  multi-elemental standard solutions prepared in demineralized water and in synthetic sea water and comparing the respective intensities. The ratios of the instrumental signals (count/s), reported in Table 4, are close to 1 for all the elements.

These results confirm the possibility of using the Chelex 100 resin to eliminate the saline matrix of samples and to determine the analytes by ICP-MS after elution of trace metals with 2 *M*  $\text{HNO}_3$ .

In order to check the contamination that occurs in the system, we compared the contents of each analyte in the blank solutions: 10 ml of ammonium acetate buffer and 90 ml of demineralized water or synthetic sea water. As can be seen in Table 5, whereas for the REE there is no significant difference between the two matrices, the concentrations of the most common transition metals vary dramatically, confirming the presence of these elements in the salts used for the preparation of the synthetic sea water. This fact negatively influences the detection limits.

The detection limits for all the elements, calculated as three times the standard deviation of three replicates of the blank solution, are

Table 4  
Signal ratio between 1  $\mu\text{g/l}$  multi-elemental standard in demineralized water and sea water solution

Element	Ratio: sea water/ demineralized water	Element	Ratio: sea water/ demineralized water
Mn	1.05	Sm	0.93
Co	0.91	Eu	0.94
Ni	0.88	Gd	0.93
Cu	0.85	Tb	0.92
Zn	0.85	Dy	0.91
Y	0.89	Ho	0.92
Cd	0.90	Er	0.89
La	0.98	Tm	0.90
Ce	0.99	Yb	0.92
Pr	0.90	Pb	0.86
Nd	0.92	U	0.85

Table 5  
Typical values for a blank solution

Element	Concentration (ng/l)	
	Demineralized water	Sea water
Mn	80	141
Co	80	154
Ni	70	250
Cu	90	250
Zn	90	250
Y	3	7
Cd	20	186
La	4	14
Ce	20	82
Pr	1	4
Nd	3	8
Sm	10	19
Eu	4	13
Gd	10	10
Tb	1	5
Dy	10	7
Ho	1	3
Er	4	7
Tm	2	5
Yb	5	6
Pb	20	85
U	3	8

Sample volume loaded: 10 ml.

reported in Table 6, where the results obtained by loading a sample volume of 10 ml (demineralized and sea water solutions) and 100 ml of sea water solution are compared. The values obtained for the REE in demineralized and sea water are similar to those determined using the continuous pneumatic aspiration system. This means that the matrix elimination achieved by the IC system permits the determination of REE in sea water with the same detection limits as in demineralized water. An increase in the sample volume loaded resulted in a sensitive improvement of the performance.

The same behaviour was not observed for the transition and heavy metals, for which we noted higher contamination problems when using synthetic sea water. In this case only the values obtained in the demineralized water are similar to those determined by continuous aspiration; a

Table 6  
Detection limits (ng/l) for on-line concentration method

Element	Continuous aspiration: demineralized water	On-line concentration		
		Demineralized water, 10 ml	Sea water	
			10 ml	100 ml
Mn	7	9	56	189
Co	19	8	14	25
Ni	36	49	102	104
Cu	11	50	63	37
Zn	44	100	123	102
Y	5	3	8	3
Cd	15	9	40	58
La	2	7	7	38
Ce	5	10	13	17
Pr	3	5	1	1
Nd	6	8	2	2
Sm	2	2	1	1
Eu	2	3	5	1
Gd	6	4	3	1
Tb	3	3	4	1
Dy	5	1	6	1
Ho	1	4	8	1
Er	4	3	9	1
Tm	2	4	3	1
Yb	3	1	5	18
Pb	5	16	50	145
U	2	15	12	21

worsening of the results was observed on increasing the sample volume from 10 to 100 ml.

We determined the precision of the determination by analysing three replicates of a 1  $\mu\text{g/l}$  multi-elemental standard solution and calculating the relative standard deviation (R.S.D.). The precision was about 1% for Y, La, Ce, Pr, Nd, Sm and Eu, 2% for Gd, Tb, Tm and U, 3% for Dy, Ho, Er and Yb, 5% for Co, Cd, Mn and Pb and 10% for Ni, Cu and Zn.

Further purification of synthetic sea water and the insertion of a Chelex column in the buffer solution line significantly reduced the amount of metal ions introduced with the buffer or avoided large blank values for certain metals owing to accidental contamination of the buffer. This is particularly true for Zn, which usually gives high blank levels and is often subject to contamination from the laboratory environment.

#### 4. Conclusions

Ion chromatography can be successfully used with ICP-MS for the simultaneous determination of transition metals and REE in sea water. The system makes it possible to remove the saline matrix and concentrate the analytes of interest. The instrumental conditions adopted allow 22 elements to be detected with detection limits, for 10 ml of sample, in the range 1–50 ng/l.

The precision of the results found for 1  $\mu\text{g/l}$  of different analytes in sea water varied between 0.5 and 3% for REE and between 5 and 10% for transition elements. The use of a multi-elemental technique such as ICP-MS, moreover, permitted the throughput of the samples to be increased, as no separation of the different analytes was required.

This work confirmed that on-line preconcent-

tration is one of the best methods of sample pretreatment in ICP-MS. The procedure requires very few sample manipulations and reagent additions and for this reason very low blank levels are obtained.

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