Solid-phase extraction for the simultaneous preconcentration of organic (selenocystine) and inorganic [Se(IV), Se(VI)] selenium in natural waters

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Abstract

This paper describes the combined use of a new preconcentration method using the Amberlite IRA-743 resin and high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry to determine simultaneously inorganic and organic selenium species in aquatic systems. The developed enrichment procedure, whose accuracy has been checked by recovery tests, is suitable for selenium speciation at environmental levels of 10 ng (Se) l^{-1}. The method has been applied to mineral and freshwater samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Solid-phase extraction; Inorganic selenium; Organoselenium compounds; Selenium

1. Introduction

Selenium is a trace element naturally distributed in all the compartments of the environment. In waters it occurs in trace amounts as a result of natural processes such as weathering of minerals, erosion of soils and volcanic activity. Human activities (industrial and agricultural uses) also contribute to its presence. Moreover, although slightly abundant, selenium is a very important element from an ecotoxicological point of view due to the narrow concentration range between its essential and toxic effects. Its toxicity is highly dependent on its chemical form, therefore speciation becomes necessary. Assessment of selenium biogeochemical cycle also requires the precise knowledge of the different

chemical forms in which this element can exist. Selenium can be found as inorganic form showing four oxidation states: selenide [Se(-II)], elemental selenium [Se(0)], selenite [Se(IV)] and selenate [Se(VI)]. The organically bound Se(-II) forms include seleno-amino acids [selenomethionine (SeMet), selenocystine (SeCyst)...] and volatile compounds [dimethylselenide (DMSe), dimethyldiselenide (DMDSe)...] which are considered less toxic resulting from detoxification pathway.

Methods for the determination of total selenium and its speciation have been reviewed [1–4]. Some of these methods such as hydride generation atomic absorption spectrometry or differential pulse cathodic stripping voltammetry, are very sensitive but, being only Se(IV) selective, they require sample pretreatment to determine other oxidation states [5–7]. Methods that are capable of distinguishing different chemical forms without pretreatment are now preferred. The coupling of high-performance liquid

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chromatography (HPLC) separation with inductively couple plasma mass spectrometry (ICP-MS) detection is able to simultaneously determine up to seven selenium species [8].

One of the difficulties in exploring the selenium species in non polluted natural waters is their usually low concentration that prevents direct speciation. Total concentration of selenium in waters is often close to analytical detection limits. The use of solid-phase extraction (SPE) as preconcentration procedure offers the possibility of improving detectability. An overview of SPE procedures developed for selenium is given in Table 1. Most work has been done on inorganic selenium. SPE was generally used both to preconcentrate and separate inorganic selenite and selenate by fractional elution. Independent quantification of each species was achieved by analytical methods sensitive to selenite or total selenium. On the other hand, methods for preconcentration of organic compounds are scarce. Preconcentration of $TMSe^+$ and SeMet was achieved with cationic and chelating resins, respectively [10,23]. Two detailed analysis of selenium species in aquatic systems were presented by Cooke and Bruland [11] and Tanzer and Heumann [15]. In these studies, besides determination of selenite and selenate, several organic compounds were isolated by SPE. Tanzer and Heumann [15] separated basic and neutral compounds from acidic compounds by filtration on XAD-2 resin at pH 8 and 3, respectively. Cooke and Bruland [11] isolated soluble organic selenides associated with dissolved organic matter on a C_{18} column. With the help of these procedures, the authors showed that dissolved organic compounds containing selenium account for a non negligible part of the total selenium content in some aquatic samples.

Therefore it is obvious that the determination of inorganic selenium species is not always sufficient to account for complete selenium speciation in water samples. Existing methods for determination of organic and inorganic selenium species are based on successive selective filtrations, resulting in a quite long procedure that may introduce analyte losses or contamination from the reagents. Moreover, when organic compounds are isolated, their identification is not carried out. This work was focused on the simultaneous determination of inorganic and dis-

solved organic selenium species in water samples. SPE based on the use of a mixed-mode sorbent (anionic and chelating resin) was attempted for the preconcentration of selenite, selenate, selenomethionine and selenocystine. No fractional elution was needed since HPLC–ICP-MS analysis allowed the simultaneous determination of the different species.

2. Experimental

2.1. Chemicals and materials

DL-Selenocystine and DL-selenomethionine (Sigma), sodium selenite and selenate (Merck) were used without further purification. Stock standard solutions containing 1 mg (Se) l^{-1} of each compound in Milli-Q water (Millipore, 18.2 MΩ) were stored in the dark at 4 °C. Working standard solutions were prepared daily by dilution in Milli-Q water.

Citric acid (Prolabo), triammonium citrate (Aldrich) and methanol (Prolabo) were used for mobile phase preparation. The pH was adjusted by dropwise addition of 30% ammonia solution (Carlo Erba). The mobile phase was filtered (0.45 μm) and degassed before use.

The following resins were tested for selenium preconcentration: Reillex HPQ (Reilly Industries), a polyvinylpyridine cross-linked with methylchloride quaternary salt, and Amberlite IRA-743 (Rohm & Haas), a weak anion exchanger and chelating resin containing polyamine functional groups based on a macroreticular styrene–divinylbenzene matrix.

Eluents tested in the preconcentration procedure were sodium hydroxide (Merck), and sodium sulfate (Prolabo), hydrochloric, perchloric, acetic, and sulphuric acids (Merck) as eluent 1 for the Amberlite resin.

2.2. ICP-MS apparatus and HPLC conditions

The ICP-MS system consists of a Perkin-Elmer Sciex ELAN 6000 equipped with a cross-flow nebulizer mounted in a Scott-type spray chamber. The parameters settings were as follow: Ar plasma gas flow, 15 l min^{-1}; Ar auxiliary gas flow, 0.8 l min^{-1}; Ar nebulizer gas flow, 0.8–0.95 l min^{-1}; radio frequency (RF) forward power 1000 W; nickel

Table 1
Solid-phase extraction procedures for preconcentration of selenium species

Species (DL)[a]	Solid sorbent	Conditions	Elution	Detection	Ref.
Se(IV) and (VI) (20 ng)	Dionex 30589	20 to 100 ml	8 mM Na_2CO_3 (IC)	GFAAS[b]	[9]
Se(IV) and (VI) (5 ng l^{-1})	Dowex 1-X4 (OH$^-$)	1 l	35 ml 1 M HCl	GFAAS	[10]
TMSe$^+$[c] (5 ng l^{-1})	Dowex 50W-X8 (H$^+$)	2 l+15 ml 0.1 M $Na_2S_2O_3$	25 ml 4 M HCl		
DMSe$^+$	Dowex AG-50	pH 1.5 (HCl)	4 M HCl	FAAS[d]	[11]
Organic Se(-II) associated with organic matter	C_{18}		3 ml methanol		
Se(IV)	Anion exchanger	0.3–0.5 M HCl	Penicillamine or	Spectro-fluorimetry	[12]
Se(VI) (10–20 ng l^{-1})	Bismuthiol-II loaded	2M HCl+0.1 M thiourea	cysteine (0.02 M)		
Se(IV) and other species converted to Se(IV)	Amberlite IRA-400 Bismuthiol-II loaded	1 l acidified 2M HCl	20 ml 0.05 M penicillamine	HG–AAS[e]	[13]
Se(IV) (2 ng l^{-1})	D-201	pH 5 (acetate)	1 M HCl	HG–AAS	[14]
Se(IV)	Dowex AG1-X8		25 ml 1 M HCOOH	IDMS[f]	
Se(VI)	(Cl$^-$)		25 ml 3 M HCl		[15]
Other organic forms	XAD-2	pH 8: basic+neutral / pH 3: acidic	25 ml CH_3OH / 25 ml NH_3 (pH 10)		
Se(IV)	PD-102-PE	As piazselenol	1 ml toluene	GC–ECD[g]	[16]
Se(IV) and Se(VI) (6 ng l^{-1})	Alumina	25 ml in 0.01 M HNO_3	500 µl 2 M NH_3	HG–AAS	[17]
Se(IV)	Dowex 1-X8 (Cl$^-$)	100 ml, pH 9	10 ml 25 mM HCl	HG–AAS	[18]
Se(VI)			7.5 ml 5 M HCl		
Se(IV) and Se(VI) (0.08–0.42 µg l^{-1})	PRPX-100 (1.3×0.4 cm)	10 to 100 ml	Carbonate buffer (80 mM, pH 8) (HPLC)	ICP-MS	[19]
Se(IV) (2.1 µg l^{-1})	Cellex T	100 ml at pH 6	10 ml 0.01 M HNO_3	ETAAS[h]	[20]
Se(VI) (2.4 µg l^{-1})			7 ml 4 M HNO_3		
Se(IV)	Fe(III)-Chelex 100	pH 4.5 (acetate)	3 ml 1 M NaOH	DPCSV[i]	[21]
Se(VI) (49 µg l^{-1})	Alumina	100 ml (pH 4 to 7)	1 ml 0.1 M NH_3	ETAAS	[22]
Se(IV) (0.8 µg l^{-1})			6 ml 4 M NH_3		
SeMet (32 ng l^{-1})	Cu-Chelex 100	100 ml at pH 9	8 ml 1.5 M NH_3	ETAAS	[23]
Se(IV) (1.6 ng l^{-1})	SAX and C_{18},	1 l at pH 7–8	25 ml 1 M HCOOH		
Se(VI) (1.4 ng l^{-1})	connected in series		25 ml 3 M HCl	GC–MS[j]	[24]
DMSe, DMDSe, DESe, DEDSe[k] (0.6–900 ng l^{-1})			Volatile Se: 2 ml CS_2		

[a] DL=Detection limit.
[b] GFAAS=Graphite furnace atomic absorption spectrometry.
[c] TMSe=Trimethyselenonium.
[d] FAAS=Flame atomic absorption spectrometry.
[e] HG–AAS=Hydride generation–atomic absorption spectrometry.
[f] IDMS=Isotope dilution mass spectrometry.
[g] GC–ECD=Gas chromatography–electron capture detection.
[h] ETAAS=Electrothermal atomic absorption spectrometry.
[i] DPCSV=Differential pulse cathodic stripping voltammetry.
[j] GC–MS=Gas chromatography–mass spectrometry.
[k] DESe=diethylselenide; DEDSe=diethyldiselenide.

M. Bueno, M. Potin-Gautier / J. Chromatogr. A 963 (2002) 185–193

187

sampler and skimmer cones; dwell time, 200 ms; isotopes monitored: [77]Se, [78]Se, [82]Se. Since the ion intensity at m/z 82 presents a better signal-to-noise ratio than the other Se isotopes, it was used for quantification.

Chromatographic separations were carried out using a 9012 Varian HPLC pump and a Rheodyne injection valve equipped with a 100 µl polyether ether ketone (PEEK) sample loop. The analytical column was a Hamilton PRP-X-100, 10 µm particle size, 25 cm×4.1 mm I.D. The chromatographic separation of SeCyst, SeMet, Se(IV) and Se(VI) was performed by a 5 mmol l^{-1} ammonium citrate buffer as used by Ge et al. [25] and adapted to our work. Its pH was adjusted to 5.2 to obtain a better separation between Se(IV) and SeMet. The mobile phase was delivered isocratically at 1 ml min^{-1}.

The interface between the chromatograph and the ICP-MS system was simply made with a PEEK tube.

2.3. Preconcentration procedure

The selenium preconcentration was carried out in column operation. Vertical glass columns, 15×1 cm I.D., were filled with 4 or 7 g of resin. Sorbents were first washed with three resin bed volumes (BVs) of Milli-Q water (1 BV=5 ml or 9 ml for, respectively, 4 g or 7 g of resin) and conditioned, as recommended by the manufacturer, in the following sequence: 2 BVs 1 *M* NaOH solution and 2 BVs Milli-Q water for the Reillex sorbent; 1 BV 1 *M* H$_2$SO$_4$, 3 BVs Milli-Q water, 1 BV eluent 1, 3 BVs Milli-Q water, 1.5 BVs 1 *M* NaOH solution and 3 BVs Milli-Q water for the Amberlite sorbent. In this latter case different eluents 1 were tested (see below).

The solution containing the four selenium compounds was filtered through the filled column. Flow-rate during conditioning and preconcentration was in the 1–1.8 ml min^{-1} range. Filtered volumes were comprised between 1 and 2 l, the exact value being stated in the corresponding part of the study. After preconcentration, selenium was eluted at 0.4 ml min^{-1} following the entire conditioning sequence for the Reillex sorbent, and from eluent 1 step for the Amberlite sorbent. Total selenium concentrations were measured by ICP-MS in the eluates after appropriate dilution. Selenium speciation was determined by HPLC–ICP-MS only in the Milli-Q water eluates by standard addition after pH adjustment.

3. Results and discussion

3.1. Sorbent selection

A preliminary study was realised to select appropriate resin for the simultaneous pre-concentration of SeCyst, SeMet, Se(IV) and Se(VI). A solution containing 15 µg (Se) l[-1] of each compound was filtered through columns filled with 4 g of each sorbent. During the preconcentration, effluent was sampled by a fraction collector (Dynamax, FC2). After treatment of about 450 ml, selenium elution was performed. Total selenium concentrations measured in the eluates are given in Table 2.

The results of these experiments indicate that from the point of view of selenium retention, the two sorbents behave similarly and are good sorbents for selenium since its total concentration in the effluent was near the ICP-MS detection limit during the filtration. Nevertheless selenium recovery with Reillex resin is unsatisfactory. In the patent from Reilly Industries on the application of Reillex for selenium removing, it is specified that a complete regeneration is obtained with an acid–acetone (1:9, v/v) mixture [26]. We did not try this elution as the organic

Table 2
Selenium recoveries (%) obtained after elution of the two sorbents under dynamic conditions

Sorbent	Eluate				Total
	2 *M* HCl	Milli-Q	1 *M* NaOH	Milli-Q	
Amberlite	6	88	2	1	97
Reillex	–*	–*	28	6	34

* These steps are not included in the elution sequence of the Reillex sorbent.

M. Bueno, M. Potin-Gautier / J. Chromatogr. A 963 (2002) 185–193

189

mixture is not suitable for our liquid chromatography.

As shown in Table 2 the elution sequence applied to the Amberlite resin allows the complete recovery of fixed selenium. This sorbent was then selected for optimisation of the preconcentration procedure.

3.2. Optimisation of preconcentration and elution conditions with Amberlite IRA-743 resin

The preliminary experiment using Amberlite IRA-743 indicated that the greatest part of fixed selenium was eluted in the Milli-Q water eluate following acid eluate (see Table 2), this selenium enriched fraction will be called ''Milli-Q 1''. HPLC–ICP-MS analysis of Milli-Q 1 eluate showed that selenium speciation seemed to be preserved in this fraction. The chromatogram obtained showed bad resolution between SeCyst, Se(IV) and SeMet, preventing quantification of the species. Indeed the Milli-Q 1 eluate follows hydrochloric acid in the elution sequence, the acidic pore volume is then collected in Milli-Q 1 fraction. Modifications of retention times observed during chromatographic separation are explained by the important ionic strength in this sample. Different eluents 1 were then tested for elution of the four selenium species retained in the column after filtration of 2 l of Milli-Q water spiked with 0.25 µg (Se) l^{-1} of each compound. Recoveries of total selenium in Milli-Q 1 fraction are presented in Table 3. These results show that best recoveries were obtained with strong acids, i.e., when 2 M HCl or 2 M HClO$_4$ and 1 M HClO$_4$ were used as eluent 1. The other tested acids did not quantitatively elute selenium from the

column. In the case of 0.5 M Na$_2$SO$_4$ eluent, only 3% of the retained selenium was eluted in Milli-Q 1 eluate, while 93% of inorganic selenium species were present in Na$_2$SO$_4$ eluate. Injection of an acidic eluent was further needed to elute seleno-amino acids. This is indicative of the different processes involved for inorganic and organic selenium retention onto the resin which structure permits ion-exchange and sorption or affinity activities simultaneously.

1 M HClO$_4$ was selected as eluent 1 for subsequent work as a compromise between a very satisfactory selenium recovery (88% of selenium eluted in Milli-Q 1 eluate) and an acceptable molarity to not disturb HPLC separation. With these conditions, seleno-amino acids and inorganic selenium were eluted from the resin in the same fraction without speciation modification (see Fig. 1). pH is an important parameter in SPE as it controls analytes charge (cationic, anionic or zwitterionic for seleno amino acids) and therefore may affect their retention on solid sorbent. The effect of aqueous sample pH on the retention of selenium compounds was studied in the range 3.9–8.2. The results presented in Table 4 show that the pH effect was negligible in the studied range with recoveries between 80 and 100% for Se(IV), Se(VI) and SeCyst. Only SeMet seemed to be affected by this parameter, recoveries increasing from 50 to about 80% with decreasing pH from 8.2 to 4.3. For the four studied compounds, no great variation was observed between the recoveries obtained at pH 5.5, corresponding to Milli-Q water, and 6.9, which is

Table 3
Comparison of eluent 1 on selenium elution from Amberlite IRA-743

Eluent 1	Se recovery in Milli-Q 1* (%)
2 M HCl	88
2 M HClO$_4$	93
1 M HClO$_4$	88
1 M CH$_3$COOH	17
0.5 M H$_2$SO$_4$	58
0.5 M HClO$_4$	0.6
0.5 M Na$_2$SO$_4$	3

* These values are enclosed by a margin error corresponding the relative standard deviation evaluated to 8%.
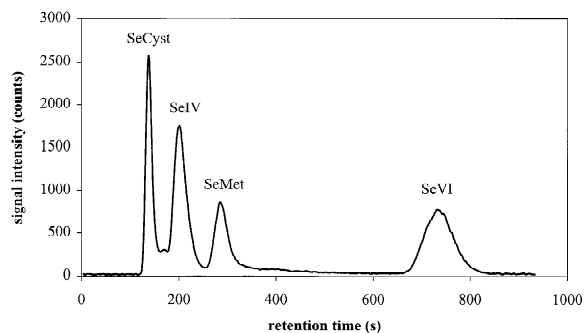

Fig. 1. HPLC–ICP-MS chromatogram of Milli-Q 1 eluate resulting from filtration of 2 l of Milli-Q water spiked with 0.25 µg (Se) l^{-1} of Se(IV), Se(VI), SeCyst and SeMet (^{82}Se isotope).

Table 4
Effect of pH on retention of selenium species on Amberlite IRA-743 resin under dynamic conditions

pH	Recovery (%)			
	SeCyst	Se(IV)	Se(VI)	SeMet
3.9	100	97	100	66
4.3	96	97	99	78
5.5	100	95	98	60
6.9	86	98	100	60
8.2	80	78	100	50

Experimental conditions: 2 l of Milli-Q water spiked with 0.25 μg (Se) l^{-1} of each compound and with pH adjusted by addition of 2 M HCl or 1 M NaOH were treated following the entire preconcentration procedure.

close to mineral waters pH, therefore no special pre-treatment of aqueous samples was performed in further experiments.

In order to examine the accuracy of the proposed method solutions containing 0.025–0.5 μg (Se) l^{-1} of each compound in Milli-Q water were treated following the entire procedure. The recovery was in the range of 92–100% for Se(IV), Se(VI) and SeCyst, whereas it decreases to 64% for SeMet. Some explanations of the weaker retention of SeMet are given in next section.

3.3. Application to mineral and freshwaters

Recovery experiments were first carried out in order to check the accuracy of the method in real water samples. The developed preconcentration procedure was applied to 2 l of commercial mineral water (Evian) spiked with 0.25 μg (Se) l^{-1} of each compound. The HPLC–ICP-MS analysis of the resulting Milli-Q 1 eluate indicated that added Se(IV) and Se(VI) were recovered with no significant losses while the greater part of seleno-amino acids was lost during the treatment (no recovery of SeMet and only 16% of SeCyst). These results suggested that seleno-amino acids suffered competitions from other ions naturally present in the mineral water matrix and that the amount of resin in the column was not sufficient for retention of selenium species.

In order to reduce competition effects the method was modified by increasing the column length (with 7 g of resin instead of 4 g). The elution sequence was also slightly modified, Milli-Q 1 eluate volume being reduced to 2 BVs in order to not dilute too much this fraction. The addition of retention sites was not sufficient since SeCyst recovery remained 21% and SeMet was not recovered. Major components of mineral water are present from 10 μM to mM. In spiking experiments, selenium compounds are in the nM range, i.e., 10^4 to 10^6 less than other components. In these conditions it is evident that competitions may occur since the resin is not supposed to be selenium selective. Nevertheless from our results it seems that the resin shows a particular affinity for selenium since it can be retained even in the presence of much higher concentrations of other anions and cations. Thus to favor selenium retention, the contact time between solid sorbent and percolating solution was increased lowering the flow-rate to 1 ml min^{-1}. On the other hand, and due to the observed competitions, the influence of filtered volume was examined. With these conditions disturbances caused by competing ions could be overcome for SeCyst if the filtered volume did not exceed 1 l of mineral water.

Accuracy of the modified method was examined after filtration of 1 l of mineral water containing 0.04–0.5 μg (Se) l^{-1} of each compound. Recoveries were in the range 92–96% for Se(IV), Se(VI) and SeCyst while SeMet remained unretained on the resin.

In order to better understand the particular behavior of SeMet, the effect from several ions present in the commercial mineral water on its preconcentration was investigated. The procedure was applied to Milli-Q water spiked with 0.25 μg (Se) l^{-1} SeMet in the presence of successively: 0.1 mM Na_2SO_4, 0.06 mM KNO_3, 0.06 mM $CaCl_2$ or 5 mM $NaHCO_3$. Concentrations of investigated ions correspond to the composition of the commercial mineral water used. HPLC–ICP-MS analysis of resulting Milli-Q 1 eluates showed SeMet recoveries close to the one obtained in Milli-Q water in the presence of Na_2SO_4, KNO_3 and $CaCl_2$ while SeMet disappeared with filtered water containing hydrogen carbonate ion which is the major ion in mineral water. Presence of dissolved carbon dioxide in Milli-Q water can also explain the weaker recovery always found for SeMet because no particular attention was taken to avoid it during filtration.

Table 5
Selenium speciation analysis in lake water samples [results in μg (Se) l^{-1}]*

Sample location	[Se(VI)]	[Se(IV)]	[SeCyst]
Gaubes lake	0.034±0.002	n.d.	n.d.
0.1 μg (Se) l^{-1} added	0.130±0.004	0.093±0.005	0.096±0.006
Estaing lake	0.073±0.003	n.d.	n.d.
Arratilles lake	0.054±0.002	n.d.	n.d.
Lourdes lake	0.0090±0.0008	n.d.	n.d.

* Se(VI) concentration quantified by HPLC–ICP-MS in Milli-Q 1 eluates resulting from preconcentration of 1 l sample.

The preconcentration procedure was applied to three groundwater samples called A, B and C for which sampling locations are not indicated for reasons of confidentiality, and to four freshwater samples collected in Pyrenean lakes. The results are given in Tables 5 and 6. Total selenium concentrations were measured by ICP-MS when possible.

Recovery of selenium species after application of the preconcentration procedure was verified in freshwater samples since this matrix was not studied up to now. Due to the limited amount of samples, a recovery test could only be performed with water collected in the Gaubes lake. The four selenium species were added to the lake water, and the sample was treated as described earlier. The results in Table 5 show that the recoveries were in the range 93–97% for SeCyst, Se(IV) and Se(VI) while SeMet was unretained on the resin like previously observed with mineral water samples. After application of the preconcentration procedure, selenate was the only selenium species detected in the four lake water samples, at very low concentrations ranging from 9 to 73 ng (Se) l^{-1}.

For mineral waters, selenium content in samples B and C was around 1 μg (Se) l^{-1} which is close to the quantification limit. No detectable selenium was
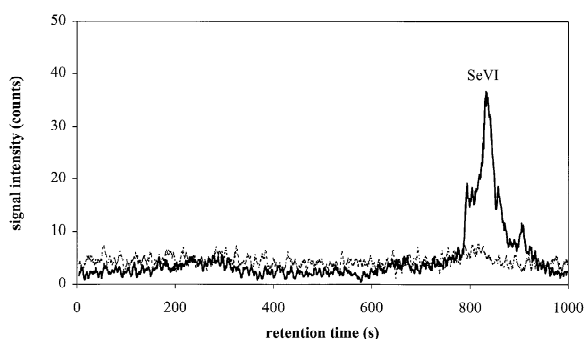

Fig. 2. Selenium speciation analysis in water A. HPLC–ICP-MS chromatograms obtained for direct injection of water A (dotted line) and for Milli-Q 1 eluate resulting from preconcentration procedure (continuous line) ([82]Se isotope).

found in water A sample. These results were confirmed by direct HPLC–ICP-MS analysis. Water A chromatogram did not show any detectable peak (see Fig. 2) while Se(VI) was detected in waters B and C at the concentration levels measured by ICP/MS as total selenium (see Figs. 3 and 4, respectively). After application of the preconcentration procedure only Se(VI) species was detected in water A sample at the low level of 76 ng (Se) l^{-1} (see Table 6 and Fig. 2). In waters B and C the presence of Se(IV) could also

Table 6
Speciation analysis of inorganic and organic selenium in groundwater samples [results in μg (Se) l^{-1}]

Water	[Se][a]$_{tot}$	[Se(VI)][b]	[Se(IV)][b]	[SeCyst][b]
A	n.d.	0.076±0.006	n.d.	n.d.
B	1.2±0.1	1.10±0.05	0.060±0.001	n.d.
C	0.9±0.1	0.92±0.01	0.0150±0.0004	0.0020±0.0001[c]

[a] Total selenium concentrations measured by ICP-MS, for waters B and C direct analysis by HPLC–ICP-MS showed that selenium was present as Se(VI).

[b] Selenium species concentrations obtained after quantification in Milli-Q 1 eluates resulting from preconcentration procedure by HPLC–ICP-MS.

[c] Indicative value since filtration of 2 l did not give quantitative recovery, SeCyst concentration in the range 0.002–0.010 μg l^{-1}.
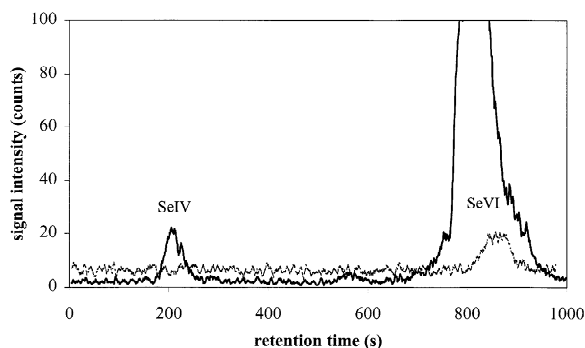
Fig. 3. Selenium speciation analysis in water B. HPLC–ICP-MS chromatograms obtained for direct injection of water B (dotted line) and for Milli-Q 1 eluate resulting from preconcentration procedure (continuous line) ([82]Se isotope).

be determined at even lower levels: 60 and 15 ng (Se) l^{-1}, respectively (see Table 6, Figs. 3 and 4). SeCyst was also detected in water C at a concentration level close to a few ng (Se) l^{-1}. To detect SeCyst 2 l of water C was filtered, in these conditions we know that recovery is not quantitative but if filtration is performed with 1 l, no SeCyst appeared in the chromatogram of the resulting Milli-Q 1 eluate. This indicated that SeCyst was present at a concentration level below 10 ng (Se) l^{-1}, which is the detectable concentration limit of SeCyst for 1 l of treated sample. This is consistent with the indicative value of 2 ng (Se) l^{-1} which was obtained without taking into account recovery correction, if we assume a recovery of 20% as obtained during experiments with spiked mineral water, SeCyst concen-
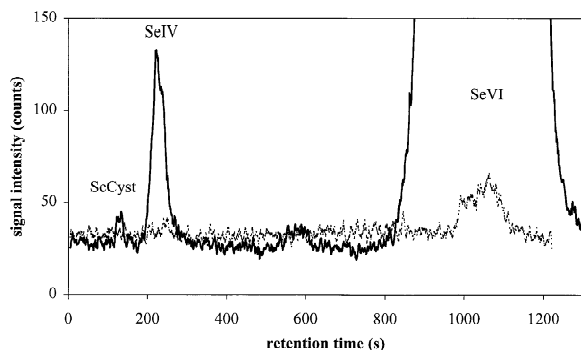
tration in water C should not exceed 10 ng (Se) l^{-1}. To our knowledge this is the first time that SeCyst was identified in a natural water sample.

4. Conclusions

The developed SPE procedure coupled to HPLC–ICP-MS described in this work appears to be a robust and sensitive method for the simultaneous preconcentration, elution and determination of organic and inorganic selenium species in natural waters. From the numerous methods developed for selenium speciation, those allowing simultaneous determination of several species are preferred because they are relatively fast and do not require sample pretreatment that may affect selenium species distribution. With this method, complex procedures like fractional elution and independent selenium species determination can be avoided.

The developed procedure is robust enough for the analysis of mineral and freshwater samples at environmental levels of 10 ng (Se) l^{-1}. The inconvenience of the method is that the sorbent used is not selenium selective and strong competitions with hydrogen carbonate prevent SeMet retention. No easy alternative was yet found to remove this interference without losses of other selenium species. Work is in progress to overcome this disturbance and will be the subject of a separate study.

SeCyst also suffers competitions that are overcome if preconcentration is made from a 1 l sample volume. For larger volumes SeCyst preconcentration is not quantitative yet but the procedure is however applicable for qualitative information.

Fig. 4. Selenium speciation analysis in water C. HPLC–ICP-MS chromatograms obtained for direct injection of water C (dotted line) and for Milli-Q 1 eluate resulting from preconcentration procedure (continuous line) ([82]Se isotope).

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M. Bueno, M. Potin-Gautier / J. Chromatogr. A 963 (2002) 185–193

193

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