Simultaneous determination of inorganic arsenic, antimony, selenium and tellurium by ICP-MS in environmental waters using SPE preconcentration on modified silica

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This paper deals with a simplified multi-element profiling of inorganic arsenic, antimony, selenium and tellurium in the form of ^{75}As, ^{82}Se, ^{121}Sb and ^{125}Te by ICP-MS for amounts less than $10\,\mu g\,L^{-1}$. Internal standards such as ^{72}Ge and ^{209}Bi were successfully used for the suppression of both influence of macro elements Na^+, K^+, Ca^{2+}, Mg^{2+} or Al^{3+}, and interference of limited concentrations of heavy metal ions. Modified silica sorbents Separon^{TM} SGX C18, C8, CN, NH$_2$, RPS and Phenyl were tested for the preconcentration of As, Sb, Se and Te ($0.25-5\,\mu g\,L^{-1}$) in the form of ion associates with cationic surfactants from 50–250 mL sample volume. 1-etoxycarbonyl-pentadecyltrimethylammonium bromide (Septonex®, $0.005\,mol\,L^{-1}$) was suitable for this purpose in the presence of 4-(2-pyridylazo) resorcinol, 2-pyrrolidinecarbodithioate and 8-hydroxyquinoline-5-sulphonic acid. The quantitative retention occurred at pH 7 ± 0.2 and the mixture of acetone with ethanol in ratio 1:1 in the presence of $0.1\,mol\,L^{-1}$ HCl was used for the quantitative elution. Organic solvents and the excess of acid were removed by evaporation prior to the determination by ICP-MS. The determination of the above trace metalloids in various kinds of water with enrichment factor till 50 times on silica Separon^{TM} SGX C18 and the above reagents were compared with the standard addition method.

Keywords: arsenic; antimony; selenium; tellurium; solid-phase extraction (SPE); ICP-MS, waters

1. Introduction

The inorganic species of As, Sb, and Se, Te are often characterised by two valences which are M (III) and M (V) for As and Sb and M (IV) and M (VI) for Se and Te. There are no considerable differences in toxicity between compounds of the above elements with particular valences. A complicated affection of the human organism is described for arsenic; skin cancer can be caused by its large concentrations in water [1,2]. Tellurium is more toxic than selenium but is rarely found in toxic amounts in food or in samples of biologic importance [3]. For a long time, selenium has been known for its ambivalence and particular essentiality for human and animal organisms [4,5].

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The determination of more than 60 trace elements in various environmental samples including waters by using inductively coupled plasma mass spectrometry [6–10] was described but limited attention was paid to various inorganic species of Sb and Te. On the other hand, the determination of arsenic by ICP-MS was mentioned in some of the literature [11] and negative influence of high amounts of chloride and sodium was indicated by Colon *et al.* [12]. Optimisation of ICP-MS collision/reaction cell conditions for the simultaneous removal of argon based interferences of arsenic and selenium in different kinds of matrix was described [13,14]. Mononuclear and oligonuclear hydroxycomplexes soluble in aqueous medium at various pH show little influence on the determination of metalloid traces of As, Sb, Se, and Te by ICP-MS [15].

The previous separation of Se (IV) and Se (VI) from water samples on active carbon [16], polyurethane foam and silica C18 [17] as well as some preconcentration of inorganic species of As, Se and Sb in the form of complexes with 2-pyrrolidinecarbodithioate [18,19] or 8-hydroxyquinoline [20] has been described prior to ICP-MS analysis; As (III), As (V) and Sb (III) and Sb (V) could also be preconcentrated on mesoporous TiO_2 in the presence of organic reagent from sea water [21].

The modified silica is a very useful sorbent whose capacity may increase in the presence of aliphatic and aromatic organic reagents. Modified silica has proved higher efficiency, especially for the preconcentration of transient element ions than organic based polymer sorbents. A suitable summarisation of used reagents has been recently published by Chinese authors [22], but the description of detailed behaviour of As (III, V), Sb (III, V), Te (II, IV) and Se (II, IV) with modified silica is still missing.

The organic reagent can involve covalent bonds inside the synthesised silica species with organic reagents but a sufficient sorption capacity is also observed during surface interaction of reagent with the sorbent.

This paper focuses on the separation and preconcentration of inorganic forms of As, Sb, Se and Te. For the preconcentration, various kinds of derived hydrophobised silica in the presence of cationic surfactants and selected organic reagents were tested. The retention of ion associates of anionic As(V), Sb(III), Se(IV) and Te(IV) with cationic surfactants in the presence of 4-(2-pyridylazo)resorcinol (PAR), 2-pyrrolidinecarbodithio-ate (APDC) and 8-hydroxyquinoline-5-sulphonic acid (8-HQS) was nearly quantitative and the determination by ICP-MS was proved after elution with acetone-ethanol mixture (1 : 1) in the presence of $0.1\,mol\,L^{-1}$ HCl and subsequent evaporation. The optimisation procedure on Separon^{TM} SGX C18 was used for the determination of arsenic, antimony, selenium and tellurium in drinking, surface, mineral and sea waters.

2. Experimental

2.1 *Reagents and solutions*

Standard solutions of Se, Te, As and Sb $(100\,\mu g\,L^{-1})$ were prepared by dilution from purchased standard solutions with $1.000 \pm 0.002\,g$ of the respective metalloid per litre and the multi-component standard containing Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Ti and Zn with $1.000 \pm 0.002\,g$ of each above metal per litre were purchased from Analytica, Prague, Czech Republic. The suprapure acids were delivered by Merck, Darmstadt, Germany and the tuning solutions for ICP-MS $(1\,\mu g\,L^{-1}$ of Ce^{3+}, Li^+, Y^+ and Tl^+ in 2% $HNO_3)$ by Agilent (HPST s.r.o.), Prague, Czech Republic. Solutions of Ge and Bi internal standards (Analytica s.r.o., Prague, Czech Republic) were prepared by dilution

from Ge and Bi standard solutions with $1.000 \pm 0.002\,g\,L^{-1}$. The cationic surfactant 1-ethoxy-carbonyl-pentadecyl-trimethylammonium bromide (Septonex®) was from Tamda, Olomouc, Czech Republic, benzyl-dimethyl-tetradecylammonium chloride (Zephyramin), anionic surfactant sodium dodecylsulphate and non-ionic surfactant Brij 35 were from Merck, Darmstadt, Germany. (4-(2-Pyridylazo)-resorcinol (PAR) and 2-pyrrolidincarbodithioate (APDC) were from Lachema, Brno, Czech Republic, and 8-hydroxyquinoline-5-sulphonic acid (8-HQS) was from Aldrich, Steinheim, Germany. Modified sorbents Separon™ SGX C18, C8, SGX NH$_2$, SGX CN, SGX RPS and SGX Phenyl with particle size $60\,\mu m$, were used as the original columns (Tessek™, Prague, Czech Republic).

The synthetic drinking, mineral, surface and sea water samples used in this study were prepared by correct weighing of particular pure chemicals and dilution with ultrapure water of selected volume [23–25]. These standards contained defined spikes of studied trace elements. Surface water from the Morava River, sea water from the Mediterranean, Vincentka mineral water from Luhačovice, Czech Republic and potable water from the Brno water supply served as real samples. These water samples were taken away in dark bottles and acidified with ultrapure HNO$_3$ to 0.5% content. The samples were filtered through a membrane filter with $0.40\,\mu m$ pores and saved in a dark and cold place. A quantity of $0.01\,mol\,L^{-1}$ EDTA was added to sea water only. The amounts of matrix elements (Na, K, Ca, Mg, Al, Fe) were additionally proved by ICP-AES.

2.2 *Instruments*

An ICP-MS spectrometer Agilent 7500ce, Tokyo, Japan with a plasma generator of 27.12 MHz and the power output of 1500 W was used. A three-channel peristaltic pump produced $0.4\,mL\,min^{-1}$ of the sample for the nebuliser. A concentric silica nebuliser MicroMist™ with a cooled Scott chamber was used and the nebulised sample entered the plasma through an injector of 2.5 mm diameter. The flow of the argon carrier trough the nebuliser was $1\,L\,min^{-1}$; the sample flow rate was $0.33\,L\,min^{-1}$. Constant temperature of $2°C$ was maintained in the nebulising chamber. Various mass ranges were characterised by Li$^+$ for low masses, by Y$^+$ for medium masses and by Tl$^+$ for large masses. The supposed signal values were higher than 3000/8000/4000 impulses per s and the RSD% was lower than 5%. The ICP-MS spectrometer contains an octapole collision-reaction cell, the quadrupole analyser and the electron multiplier detector working in a pulse-analogous mode. The tuning solutions were adjusted for high signal response across the mass range for the normal mode, signal stability, low background and a low signal of metal oxide and doubly charged ions. The extraction ion lenses of the spectrometer were optimised prior to each measurement. For authentic samples, the octapole collision cell in the helium mode was used both to reduce polyatomic interference from the matrix and to secure the minimum decrease of analyte signals. The Co containing solution was used for tuning this cell. The signal ratio ClO/Co was followed during nebulisation. The He flow was set at $4\,mL\,min^{-1}$ during tuning octobias; the entrance into the cell, QP focus and QP bias lens were maintained at the minimum value of the mass ratio 51/59 which was less than 2%; the aim was to keep the intensity of the mass signal ^{59}Co for at least 10,000 impulses s^{-1}.

The vacuum manifold system Dorcus™ (Tessek, Prague, Czech Republic) was used for the sorption and preconcentration. The PCD 81/82.4 K peristaltic pump (Kouřil™,

Kyjov, Czech Republic) was attached with 3 mm wide silicon tubing to the cartridges containing the sorbent.

2.3 *Sorption process*

The sorption on columns with various derivatives of silica has been usually tested at different flow rates between 1.0–3.0 mL min^{-1} at various pH for 50 mL solution containing 1 µg of metalloid or less in the presence and absence of cationic surfactant and organic reagents were employed. Prior to the sorption the columns of sorbent were successively conditioned with 10 mL of ultrapure water and 10 mL of surfactant Septonex® in concentration 5×10^{-4}–1×10^{-2} mol L^{-1}. The column was rinsed with 10 mL of ultrapure water prior to the elution with 10 mL or less of elution mixture of acetone and ethanol (1 : 1) in the presence of 0.1 mol L^{-1} hydrochloric acid.

2.4 *Limit of detection*

Two ways of calculation were used for the evaluation of detection limit (a) from the ten times measured blank signal according to IUPAC [26] and (b) values of X_D^{α} and X_D^{β} according to Graham calculated from confidence intervals of the calibration plots [27]. Instrumental and practical detection limits are given in Table 1.

3. Results and discussion

Eight-points calibration plots for the following selected isotopes [75]As, [82]Se, [121]Sb and [125]Te were strictly linear for concentrations less than 100 µg L^{-1} in aqueous solutions containing 0.5% HNO$_3$ when no previous sorption was used. Each concentration value was always prepared in triplicate and evaluated according to Dean-Dixon statistics [28]. No interfering polyatomic clusters such as Ar-Ar^{2+}, ArH^{+}, ArO^{+} and ArN were observed.

Table 1. Instrumental and practical detection limits [µg L^{-1}] calculated from the calibration plot.

	[75]As	[121]Sb	[82]Se	[125]Te
Isotope concentration [%]	100	57.3	9.70	7.14
Instrumental detection limit				
$X_D^{\alpha 1}$	0.032	0.025	0.027	0.030
$X_D^{\beta 1}$	0.096	0.080	0.080	0.091
$X_{3\sigma}^{2}$	0.061	0.017	0.081	0.058
Practical detection limits				
Drinking water[1]	0.033	0.018	0.063	0.020
Surface water[1]	0.042	0.012	0.052	0.021
Mineral water[1]	0.069	0.022	0.040	0.027
Sea water[1]	0.102	0.052	0.053	0.042

Notes: [1]According to Graham [25].
[2]According to IUPAC [26].

3.1 *Effect of acids, surfactants and organic reagents on the intensity of ICP-MS signal*

The signal intensity considerably decreases with the increasing concentration of acids. With 5% HCl, the decrease was 5–11% for all monitored elements. With 5% HNO_3, the decrease was 30% for ^{82}Se and ^{125}Te but 15% for ^{75}As and 5% for ^{121}Sb. Cationic surfactants Septonex®, Zephyramin and organic reagents used for complexation and following sorption show influence on some processes in the cloud chamber. 5×10^{-4}–$1 \times 10^{-2}\,mol\,L^{-1}$ of Septonex® increases the intensity of signal up to 120%. Anionic surfactant sodium dodecylsulphate and non-ionic Brij 35 gave lower effect. This was observed because more sample solutions were brought into plasma discharge per unit of time due to lower surface tension of solution with surfactant in the cloud chamber. The signal also increased up to 110% in the presence of 1.75×10^{-4}–$1.75 \times 10^{-3}\,mol\,L^{-1}$ of PAR and 2.77×10^{-4}–$2.77 \times 10^{-3}\,mol\,L^{-1}$ of 8-HQS. For the concentration range 2.43×10^{-4}–$2.43 \times 10^{-3}\,mol\,L^{-1}$ of APDC, the intensity of signal only decreased to 90% for all trace elements. The concentration of organic reagents corresponded with 5–50 mass excess against $10\,\mu g\,L^{-1}$ of ^{75}As, ^{82}Se, ^{121}Sb, and ^{125}Te. Higher amounts of reagents decreased the signals.

3.2 *Effect of interferents*

The effect of Na, K, Ca, Mg, Al, Fe(III) (1–$250\,mg\,L^{-1}$), on the signal intensity was evaluated for trace elements ($100\,\mu g\,L^{-1}$) in 0.5% HNO_3. The relative signal for the element isotope was calculated according to Equation (1):

$$Ir = \frac{I_{A+M} - I_M}{I_A - I_{Bl}} \cdot 100. \tag{1}$$

I_{A+M} is the total intensity of the solution signal, I_M is the intensity of the matrix signal, I_A, I_B is the intensity of analyte and blank solution signals.

For 1–$10\,mg\,L^{-1}$ of the matrix element the error for the trace element signal did not exceed 5%. For $50\,mg\,L^{-1}$ of the matrix element the error for the trace elements increased by 15–20% in the presence of Ca, Mg, Al and Fe(III). On the other hand, $250\,mg\,L^{-1}$ of Na and K caused less than 10% error when no internal standard was used. In the presence of multi-component solution containing 10–$100\,\mu g\,L^{-1}$ of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Ti, Zn with $100\,\mu g\,L^{-1}$ of ^{75}As, ^{82}Se, ^{121}Sb and ^{125}Te a considerable interference was observed, resulting in a 70% signal decrease for ^{75}As, ^{121}Sb and 65% decrease for ^{82}Se, ^{125}Te. The decrease of signal was successfully suppressed by using internal standard ^{72}Ge for ^{75}As in the He collision mode and ^{82}Se in the normal mode. ^{209}Bi was suitable for the remaining trace elements in the normal mode. These internal standards were always used in the measurements.

3.3 *Optimisation of the sorption process of trace elements with surfactants on different sorbents*

The anionic species of metalloids are assumed in solution for the preconcentration on Sepharon™ SGX C18, SGX C8, SGX CN, SGX NH$_2$, SGX Phenyl or SGX RPS from 50–$250\,mL$ with $5 \times 10^{-3}\,mol\,L^{-1}$ cationic surfactant Septonex® and organic reagents PAR, 8-HQS, APDC were retained. The optimal retention of $1\,\mu g\,L^{-1}$ or less amount of a metalloid was found at pH 7.0 ± 0.2 in flow rate 1–$3\,mL\,min^{-1}$.

The elution with acetone-ethanol $(1:1)$ mixture in the presence of $0.1\,mol\,L^{-1}$ HCl showed the highest elution efficiency. When the sorbent Separon^{TM} SGX C18 was used, the elution was quantitative with 4–5 mL of eluent; for Separon SGX C8 3 mL of eluent was already sufficient. The organic eluent was always removed by evaporation to 1 mL of solution under an infra-red lamp in a suitable Teflon^{TM} dish. 500 µL of concentrated (67%) HNO$_3$ were added to each solution for stabilising the solution during evaporation. The residual solution was diluted to 10 mL with ultrapure water and analysed by ICP-MS with respect to the corresponding calibration plot.

The recovery for Sb(III), Se(IV) and Te(IV) was nearly 90% on Separon^{TM} SGX C18. For As(III), the efficiency of retention was 60% only. When As(III) was previously oxidised with 500 µL of 30% H$_2$O$_2$ to As(V). Thus, the recovery of the As has been improved to 100.2 ± 2.4, 93.3 ± 1.3 or 96.5 ± 3.2 in the presence of PAR, 8-HQS, APDC for the most suitable Separon SGX C18. About 20% retention for As(III) and 50% for As(V) and Te(IV) was observed on the Separon^{TM} SGX NH$_2$, but for Sb(III) it increased up to 70–80%. The recoveries on SGX NH$_2$, RPS and Phenyl for Se(IV) were about 90%. The recovery efficiency on Separon^{TM} SGX CN for As(III, V), Se(IV) and Te(IV) was nearly 20% and about 50% for Sb(III) only. More than 15% of As(III), 40% of As(V) and Te(IV) were retained on the SGX RPS sorbent, in the case of Se(IV) and Sb(III) the recovery reached nearly 70%.

3.4 *The effect of organic reagents on the sorption process*

The retention of monitored elements on sorbents was also tested in the presence of various organic reagents after conditioning the column with 10 mL of ultrapure water and 10 mL of $5 \times 10^{-3}\,mol\,L^{-1}$ Septonex$^®$.

A quantity of 50–250 mL of solution containing 0.25–5.0 µg L^{-1} of each trace element with PAR, 8-HQS or APDC at pH 7 ± 0.2 was pumped through the column with the $1\,mL\,min^{-1}$ flow rate. 10 mL of the mixture of acetone with ethanol (in ratio $1:1$) in the presence of $0.1\,mol\,L^{-1}$ HCl was suitable for the elution. The eluate was partly evaporated and diluted with demineralised water prior to ICP-MS analysis.

The complexes of metalloids with 0.85×10^{-4}–$3.38 \times 10^{-3}\,mol\,L^{-1}$ of PAR (2.5–10 mass excess of reagent for each microelement) showed about 100% retention on Separon^{TM} SGX C18, SGX CN and SGX RPS for all trace elements. The efficiency of sorption by PAR on Separon^{TM} SGX NH$_2$ was up to 95% for As(V), Sb(III) and Te(IV) whereas only 82% for Se(IV). The recoveries on Separon^{TM} SGX Phenyl were 82–90% for antimony, selenium and tellurium. In the case of As(V) it reached less than 65%.

The concentration range of 8-HQS 2.77×10^{-4}–$8.31 \times 10^{-3}\,mol\,L^{-1}$ (5–15 mass excess of reagent) was sufficient for 100% retention of all elements on Separon^{TM} SGX RPS. The efficiency of retention for these complexes on Separon^{TM} SGX C18 and SGX NH$_2$ was about 95% for As(V), Sb(III) and Te(IV). Almost 100% of Se(IV) was retained. The recoveries on Separon^{TM} SGX CN were under 85% for selenium and As(V) but for antimony and tellurium the efficiency was more than 90%. Separon^{TM} SGX Phenyl was not effective for each sorption.

The concentration between 2.43×10^{-4}–$7.29 \times 10^{-3}\,mol\,L^{-1}$ was suitable for APDC. For antimony and tellurium, the recoveries on all Separon^{TM} sorbents except Separon^{TM} SGX Phenyl were 100%. On Separon^{TM} SGX C18 and SGX RPS, the recovery for As(V) and selenium was 100%. For Separon^{TM} SGX NH$_2$ and Separon^{TM} SGX CN, the

efficiency was less than 95% and 85% only. The retention values of microelements As, Sb, Se and Te ($1\mu g\,L^{-1}$) from $50\,mL$ of sample solution in the presence of some organic reagents are compared in Figure 1. Prior to the measurement, the samples were conditioned with Septonex® ($5\times10^{-3}\,mol\,L^{-1}$), sorbed at pH 7 and eluted with acetone-ethanol mixture ($10\,mL$) in the presence of $0.1mol\,L^{-1}$ HCl. The recoveries were summarised in Table 2.

At least 900-fold of Na^+ and K^+, 800-fold of Mg^{2+} and Ca^{2+}, 150-fold of Al^{3+}, 100-fold of Fe^{3+} and 100-fold mass excess of Cl^-, Br^-, F^-, NO_3^-, SO_4^{3-}, PO_4^{3-} does not interfere with the sorption of $1\,\mu g\,L^{-1}$ of each trace element, when the most suitable Separon SGX C18 has been used from $50\,mL$ solution at pH 7 in the presence of $1.7\times10^{-4}\,mol\,L^{-1}$of PAR and $0.01\,mol\,L^{-1}$ EDTA.

3.5 *Analyses of synthetic waters*

Calibration plots of synthetic water samples containing 1, 2 and $5\,\mu g\,L^{-1}$ of trace element spikes were evaluated. The intensity of signal was measured by ICP-MS in the presence or absence of internal standard. The slopes of the regression lines were compared with those of ultra pure water to evaluate the influence of the matrix. The slopes decreased by 2–4% for drinking and surface water, by 7% for mineral water and by up to 10% for sea water models. However, if internal ^{72}Ge standards for ^{75}As in the He collision mode, for ^{82}Se in the normal mode and ^{209}Bi for the remaining elements were used, this error and depression
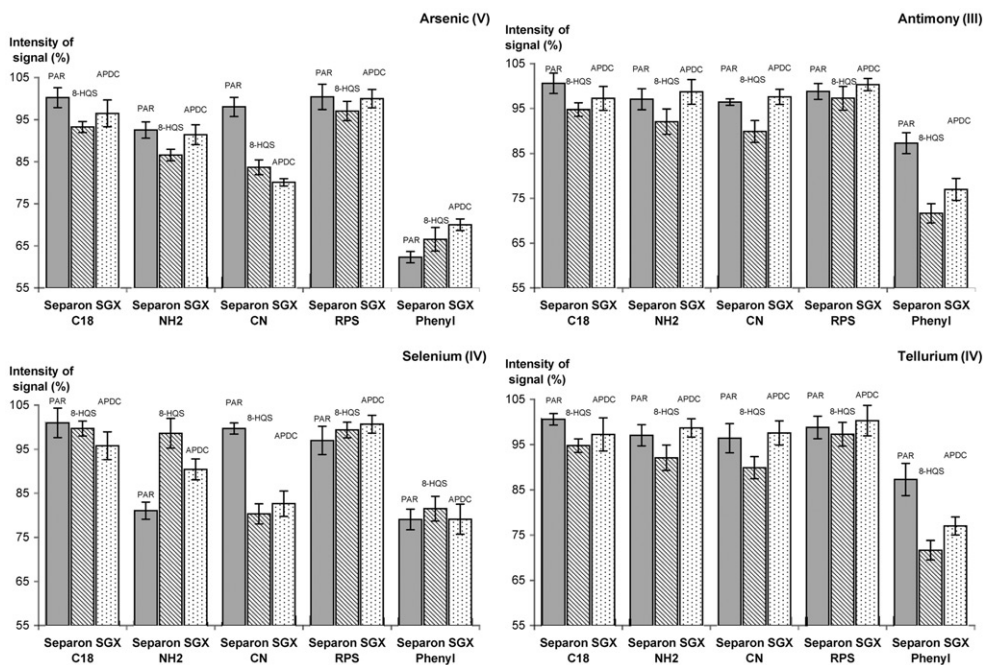

Figure 1. Retention (%) of $1\,\mu g\,L^{-1}$ of trace elements in the presence of some organic reagents. ($50\,mL$ of sample solution after previous conditioning with $5\times10^{-3}\,mol\,L^{-1}$ Septonex at pH 7, after elution with $10\,mL$ of acetone with ethanol (1 : 1) in the presence $0.1\,mol\,L^{-1}$ HCl).

Table 2. Recoverability (%) for each element on modified silica.

	As(III)		Sb(III)		Se(IV)		Te(IV)	
	$1\,\mu g\,L^{-1}$	$10\,\mu g\,L^{-1}$	$1\,\mu g\,L^{-1}$	$10\,\mu g\,L^{-1}$	$1\,\mu g\,L^{-1}$	$10\,\mu g\,L^{-1}$	$1\,\mu g\,L^{-1}$	$10\,\mu g\,L^{-1}$
SGX C 18	68.5±2.7	65.2±2.5	102.1±2.7	99.1±1.8	99.0±3.1	97.7±2.6	96.0±3.5	97.9±3.1
SGX C 8	59.9±2.0	53.6±3.4	97.2±2.1	100.3±2.7	99.7±3.2	99.5±3.2	96.5±14.8	95.0±2.7
SGX CN	64.5±3.0	64.0±2.7	100.6±3.0	98.9±2.9	94.0±2.9	98.4±2.7	95.6±3.1	97.4±3.1
SGX HN₂	44.1±2.7	49.5±2.6	102.0±3.0	99.2±2.3	76.8±2.6	79.1±3.0	100.0±3.2	99.3±3.3
SGX RPS	42.1±2.1	40.0±3.1	98.8±3.2	101.4±3.0	99.0±2.1	100.8±2.8	97.6±1.8	100.0±3.1
SGX Phe	4.2±3.4	5.1±3.1	81.1±2.9	85.2±3.0	102.1±3.3	99.8±2.6	42.1±2.9	49.1±2.2

Note: 1 and $10\,\mu g\,L^{-1}$ of trace elements in the presence of $1.70 \times 10^{-3}\,mol\,L^{-1}$ PAR from 50 mL of sample solution under previous conditioning with $5 \times 10^{-3}\,mol\,L^{-1}$ Septonex at pH 7, after elution with 10 mL of acetone with ethanol in the presence of $0.1\,mol\,L^{-1}$ HCl were used for the sorption.

of signal diminished to 1.5% only, especially for sea and mineral water models. Macroelements Ca^{2+}, Mg^{2+}, Fe^{3+} were sufficiently screened with $0.01 \, mol \, L^{-1}$ EDTA.

The Separon[TM] SGX C18 give quantitative sorption of As(V), Sb(III), Se(IV) and Te(IV) from synthetic waters. Prior to analyses, 250 mL of the samples were conditioned with $5 \times 10^{-3} \, mol \, L^{-1}$ Septonex®, 0.5, 1 and $5 \, \mu g \, L^{-1}$ of trace element spikes and $1.70 \times 10^{-3} \, mol \, L^{-1}$ of PAR were added. The flow rate was $1 \, mL \, min^{-1}$ and pH 7 ± 0.2 in all solutions.

3.6 *Analyses of real water samples*

The concentrations of trace elements in real water samples were evaluated directly by standard addition method using 1, 2 and $5 \, \mu g \, L^{-1}$ standard additions; each of them was carried out in triplicate and evaluated with Dean-Dixon statistics in addition, the amounts of matrix elements had been always previously proved by ICP-AES. The preconcentration on modified silica Separon[TM] SGX C18 from 250 mL solutions without standard additions was also used. No influence of potentially present Cl^-, CO_3^{2-} and SO_4^{2-} in various kinds of water was observed. The sorbent was firstly activated by both 10 mL of ultrapure water and $5 \times 10^{-3} \, mol \, L^{-1}$ Septonex®. Quantities of $1.70 \times 10^{-3} \, mol \, L^{-1}$ of PAR and $0.01 \, mol \, L^{-1}$ EDTA were added into solution and samples were equilibrated at laboratory temperature for 1 hour. Then, the solutions were pumped through the sorbent at the flow rate of $1 \, mL \, min^{-1}$ at pH 7 ± 0.2. After the analyte retention on the sorbent, the sorbent was rinsed with 10 mL of distilled water to wash off undesirable sample components. This step also ensured that the entire sample came in contact with the sorbent. A quantity of 5–10 mL of acetone with ethanol (in the ratio 1 : 1) in the presence of $0.1 \, mol \, L^{-1}$ HCl was used for quantitative elution. The organic solvents were removed by evaporation on the infrared lamp in the presence of $500 \, \mu l \, HNO_3$ and the solution filled up to 10 mL prior to evaluation by ICP-MS. The results were recalculated to 1 L volume and compared with the results from the standard addition method (see Table 3).

Table 3. The comparison of concentrations of trace elements ($\mu g \, L^{-1}$) in real water samples after preconcentration on the Separon[TM] SGX C18 sorbent and standard addition method.

Kind of water	As(V)[a]	Sb(III)	Se(IV)	Te(IV)
Standard addition method with $1.7 \times 10^{-4} \, mol \, L^{-1} \, PAR$				
Drinking water	0.26 ± 0.06	0.34 ± 0.12	1.22 ± 0.21	0.27 ± 0.05
River water	0.42 ± 0.09	0.72 ± 0.06	0.71 ± 0.08	0.14 ± 0.02
Mineral water	0.32 ± 0.02	0.81 ± 0.06	1.46 ± 0.46	0.11 ± 0.03
Sea water	0.61 ± 0.05	0.51 ± 0.09	2.18 ± 0.31	0.84 ± 0.06
Preconcentration on Separon[TM] SGX C18 with $1.7 \times 10^{-4} \, mol \, L^{-1} \, PAR$				
Drinking water	0.25 ± 0.09	0.36 ± 0.14	1.26 ± 0.20	0.30 ± 0.12
River water	0.40 ± 0.10	0.67 ± 0.10	0.77 ± 0.13	0.18 ± 0.07
Mineral water	0.37 ± 0.15	0.87 ± 0.11	1.40 ± 0.15	0.14 ± 0.05
Sea water	0.64 ± 0.10	0.55 ± 0.14	2.21 ± 0.21	0.91 ± 0.16

Note: [a]As(III) was oxidised to As(V) with H_2O_2.

4. Conclusion

The multi-elemental profiling of arsenic, antimony, selenium and tellurium was provided in detail by ICP-MS using ^{75}As, ^{82}Se, ^{121}Sb and ^{125}Te isotopes. The determination of the trace element in 0.25–5.0 μg L^{-1} concentration range was carried out in aqueous solutions containing 0.5% HNO$_3$ in the absence and presence of internal standard. The above trace elements (100 μg L^{-1}) can be determined in the presence of Ca, Mg, Al and Fe(III) (50 mg L^{-1}) with 15–20% error or in the presence of Na and K (200 mg L^{-1}) with 10% error only. Fifteen macro elements (250 mg L^{-1}) in multi-componental mixture caused a considerable depression of signals for 100 μg L^{-1} micro elements diminished in the presence of internal standards (all in 100 μg L^{-1}) such as ^{72}Ge for ^{75}As in the helium collision mode, ^{82}Se in normal mode and ^{209}Bi for the remaining elements in normal mode. The instrumental and practical detection limits were evaluated by using various kinds of synthetic waters.

Trace elements As(V), Sb(III), Se(IV) and Te(IV) (0.25–5.0 μg L^{-1}) were successfully retained and preconcentrated from 50–250 mL of aqueous solutions on modified silica sorbents Separon^{TM} SGX after conditioning the column with cationic surfactant Septonex$^{®}$ and in the presence of 4-(2-pyridylazo)resorcinol, 2-pyrrollidincarbodithioate and 8-hydroxyquinoline-5-sulphonic acid at pH 7. Separon^{TM} SGX C18 or Separon^{TM} SGX RPS showed the best retention characteristics. The formation of ion associate between the reagent chelate and the cationic surfactant is assumed during the sorbent interaction while the surfactant is later displaced from the sorbent surface. The elution from the columns with a mixture of acetone and ethanol in ratio 1 : 1 in the presence of HCl (0.1 mol L^{-1}) was found optimal. The determination of the micro elements by ICP-MS followed after the evaporation of the excess of solvents nearly to the residue and final dilution to 10 mL.

The contents of As(V), Sb(III), Se(IV) and Te(IV) in various synthetic and real waters were evaluated in the form of selected isotopes from the recoveries of spikes in triplicate and from the method of standard addition, whose results were compared with those after previous retention on the modified silica Separon^{TM} SGX C18. Tests of six kinds of modified silica preceded the preconcentration. Separon^{TM} SGX C18 and SGX RPS in the presence of PAR and APDC demonstrated the best retention characteristics but As(III) had to be previously oxidised to As(V) by 30% H$_2$O$_2$ (500 μL). The SPE with the 1:25–1:50 enhancement factor was not interfered by the matrix elements in the water samples in the presence of EDTA (0.01 mol L^{-1}).

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