Determination and speciation of trace and ultratrace selenium ions by energy-dispersive X-ray fluorescence spectrometry using graphene as solid adsorbent in dispersive micro-solid phase extraction

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ABSTRACT

A dispersive micro-solid phase extraction (DMSPE) with graphene as a solid adsorbent and ammonium pyrrolidinedithiocarbamate (APDC) as a chelating agent was proposed for speciation and detemination of inorganic selenium by the energy-dispersive X-ray fluorescence spectrometry (EDXRF). In developed DMSPE, graphene particles are dispersed throughout the analyzed solution, therefore reaction between Se(IV)–APDC complexes and graphene nanoparticles occurs immediately. The concentration of Se(VI) is calculated as the difference between the concentration of selenite after and before prereduction of selenate. A central composite face-centered design with 3 center points was performed in order to optimize conditions and to study the effect of four variables (pH of the sample, concentration of APDC, concentration of Triton-X-100, and sample volume). The best results were obtained when suspension consisting of 200 μg of graphene nanosheets, 1.2 mg of APDC and 0.06 mg of Triton-X-100 was rapidly injected to the 50 mL of the analyzed solution. Under optimized conditions Se ions can be determined with a very good recovery (97.7 ± 5.0% and 99.2 ± 6.6% for Se(IV) and Se(VI), respectively) and precision (RSD=5.1–6.6%). Proposed DMSPE/EDXRF procedure allowed to obtain low detection limits (0.032 ng mL^{-1}) and high enrichment factor (1013 ± 15). The proposed methodology was successfully applied for the determination of Se in mineral, tap, lake and sea water samples as well as in biological materials (Lobster Hepatopancreas and Pig Kidney).

1. Introduction

Selenium is an essential micronutrient, necessary for the proper functioning of human and animal organisms due to its antioxidant properties and presence in selenoproteins [1]. Se captures, degrades and inhibits the formation of free radicals which protects cells from damage, metabolic disorders and premature aging [2]. Recently, large international projects are conducted in order to investigate the beneficial effect of Se on diseases such as AIDS, diabetes or cancer [3]. The daily requirement for adults ranges from 50 to 70 μg [4], however the difference between the toxic dose and the nutritious requirement is very small and exceeding the tolerable upper intake level of 400 μg per day may lead to selenosis [5]. Se can be found most frequently in natural waters as organic selenides (-II) or inorganic selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) [6]. The toxicity of inorganic Se forms is up to 40 times higher than the organic ones [7], wherein

salenates are more toxic than selenites [8]. For that matter, the development of the reliable analytical procedures enabling not only determination of total Se amount but also speciation analysis is a subject of a great importance.

The most popular analytical techniques applied for inorganic Se determination are hydride generation coupled with the atomic absorption spectrometry (AAS) [9,10], inductively coupled plasma atomic emission spectroscopy (ICP-OES) [11,12], and atomic fluorescence spectroscopy (AFS) [13,14]. Nevertheless, the direct determination of Se species in food, biological or environmental samples is usually hampered by its low concentration. Therefore, preconcentration step is usually required prior to quantitative analysis in order to improve sensitivity and precision of applied techniques. This approach is also very useful when the influence of complicated matrix should be reduced.

Different preconcentration procedures, i.e. co-precipitation with hydroxides [15], extraction [16], microextraction [17–22], anion exchange chromatography [23] and isotachophoresis [24] have been recently proposed for Se determination. Despite unquestionable advantages of the proposed methodologies, the most frequently employed procedures for Se preconcentration are based on the solid

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phase extraction (SPE). Analytical methods for the speciation and preconcentration of inorganic Se by SPE have been recently reviewed [25]. SPE is an inexpensive alternative to classical liquid-liquid extraction approach. It allows obtaining cleaner extracts, higher and more reproducible recoveries and can be also readily automated. Furthermore, SPE simplifies selective adsorption of analytes due to numerous sorbent materials and solvent mixtures that can be employed in this technique. Three different SPE strategies can be applied in order to perform speciation analysis of Se. The first one involves sorption of desired Se form while the other Se species are not retained. In the next step the captured analyte is eluted by an appropriate solvent. The second procedure bases on simultaneous sorption of selanites and selenates on the SPE adsorbent surface and subsequent elution of both species or just one Se form. In the case of simultaneous elution of both inorganic Se forms posterior speciation involving capillary electrophoresis or liquid chromatography is usually required. The last strategy involves chelates formation and subsequent sorption of complexed species. The most commonly used complexing agents are selective for only one form of Se, the most frequent Se(IV). Numerous adsorbents were successfully used in abovementioned strategies for Se determination purposes, i.e. iron(III) loaded Chelex®-100 [26], Amberlite XAD-4 grafted with DAN [27], mercapto-silica [28], activated carbon [29], Al_2O_3 [30], TiO_2 [31], Mo-form-resin [32], (CTAB)-modified alkyl silica [33], Dowex 1×2 [34]. Another types of adsorbents used for preconcentration of Se and other metal ions are nanoparticles such as nanosized-Al_2O_3 [35,36] and TiO_2 [37,38] as well as carbon-based nanomaterials such as carbon nanotubes [39,40], graphene [41,42] and graphene oxide [43,44]. Nowadays graphene is becoming more and more popular as an adsorbent due to its unique physicochemical properties [45,46]. Graphene consists of sp^2-hybridized carbon atoms organized in the honeycombed sheets providing great surface area and adsorption capacity. It is noteworthy that in contrast to carbon nanotubes both sides of planar layers are involved in adsorption process. Moreover, such a structure promotes formation of π–π stacking interaction with carbon-based ring structures.

In the present work a dispersive micro-solid phase extraction (DMSPE) with graphene as a solid adsorbent and ammonium pyrrolidinedithiocarbamate (APDC) as a chelating agent was applied for determination of trace and ultratrace Se ions by energy-dispersive X-ray fluorescence spectrometry (EDXRF). In the DMSPE a small amount of solid adsorbent is dispersed in the analyzed solution. This approach eliminates different problems that may occur in classical SPE mode such as nano-sorbent particles escaping from the cartridges or formation of high pressure inside the SPE system. Application of EDXRF spectrometry eliminates necessity of additional elution of analytes, since samples can be measured in the form of thin layers deposited onto the membrane filters.

2. Experimental

2.1. Chemicals and solutions

Stock solution (1 mg mL^{-1}) of Se(IV), nitric acid (65%, Suprapur®) and ammonium hydroxide solution (25%, Suprapur®) were purchased from Merck (Darmstadt, Germany). Hydrochloric acid (35–38%, p.a.), Triton-X-100 and reagents applied for examination of matrix elements influence, i.e. $NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$, NaCl, Na_2SO_4, $NaHCO_3$ were purchased from POCh (Gliwice, Poland). Standard solutions of 10 μg mL^{-1} of Se(IV) were prepared from the stock solution. 10 μg mL^{-1} of Se(VI) standard solution was prepared by dissolving in water proper amount of sodium selenate – Na_2SeO_4 (≥ 98%) purchased from Sigma-Aldrich (St. Louise, MO, USA).

Graphene of 8 nm thickness, ammonium pyrrolidine dithiocarbamate – APDC (> 98%) were purchased from Graphene Supermarket® (Calverton, USA) and Acros Organics (Geel, Belgium), respectively. A high purity water obtained from the Milli-Q system was used for solutions preparation.

2.2. Instrumentation

The measurements were performed using an EDXRF Epsilon 3 spectrometer (Panalytical, Almelo, The Netherlands), equipped with Rh target X-ray tube of a 50 μm Be window and a max. power of 9 W. The X-ray spectra were collected using a thermoelectrically cooled silicon drift detector (SDD) with 8 μm Be window and 135 eV resolution at 5.9 keV. The system is also equipped with 10-position removable sample changer, spinner and five primary filters that can be selected to improve measuring conditions for determined element. Evaluation of spectra was performed using non-linear least squares fitting, based on the AXIL algorithm (Epsilon 3 software).

2.3. Preconcentration procedure

The suspension of graphene/APDC/Triton-X-100 was prepared by dissolving: 10 mg of graphene, 60 mg of APDC and 3 mg of Triton-X-100 in 10 mL of high purity water. Subsequently, the mixture was sonicated for 60 min in order to obtain homogenous graphene suspension. Additionally, graphene/APDC/Triton-X-100 mixture was sonicated for 5 min before application. The rapid injection of 200 μL of graphene/APDC/Triton-X-100 suspension to 50 mL of analyzed solution was preceded by an adjustment of pH value to 1. In the next step, sample was filtered through the membrane filter with the use of filtration assembly of 5 mm in diameter. Finally, the membrane filter with graphene and Se(IV)–APDC complex adsorbed on its surface was dried under an IR heater and measured using EDXRF spectrometry.

2.4. Sample preparation

2.4.1. Water samples

All examined water samples were filtered through a Millipore cellulose acetate membrane filters (0.45 μm) and stored at 4 °C. In order to prepare an artificial sea water solution 21.03 g NaCl, 3.52 g Na_2SO_4, 0.61 g KCl, 0.088 g KBr, 0.034 g $Na_2B_4O_7 \cdot 10H_2O$, 9.50 g $MgCl_2 \cdot 6H_2O$, 1.32 g $CaCl_2 \cdot 2H_2O$, 0.02 g $SrCl_2 \cdot 6H_2O$ and 0.02 g $NaHCO_3$ was dissolved in 1 L of high purity water [47].

2.4.2. Biological samples

200 mg of Lobster Hepatopancreas Certified Material (TORT-2) and 100 mg of Pig Kidney (ERM®-BB186) were digested in 5 mL of concentrated HNO_3 using microwave-assisted digestion (closed 100 mL vassels; pressure set to 45 atm). Subsequently, digested samples were quantitatively transferred into 100 mL beakers and evaporated. Finally, 50 mL of high purity water was added to the residue and preconcentration procedure described in Section 2.3. was performed.

3. Results and discussion

3.1. Optimization of preconcentration procedure

Central composite design (CCD) was applied in order to achieve maximal information about DMSPE/EDXRF proconcentration procedure from a limited number of experiments. A face-centered central composite design (FCCCD) is one of designs commonly applied for estimating the coefficients of a model containing a

constant, the linear terms, the interactions between pairs of variables and the quadratic terms. It is obtained by combining a factorial design at two levels with a star design and n center points, and each variable is studied at three equally spaced levels, coded as -1, 0 and $+1$.

In order to optimize the conditions and to study the effect of four variables (pH of the sample, concentration of APDC, concentration of Triton-X-100, and sample volume) a FCCCD has been performed. Each of the 24 experiments of the design ($4^2 + 4 \times 2$) was run in duplicate, while the center point has been replicated 6 times. The domain of pH was set between 1 and 5 relying on experiments in which APDC was applied as a chelating agent for Se ions [48–51]. The other variables under study and their ranges (0.4, 1.2 and 2 mg of APDC; 0.02, 0.06 and 0.1 mg of Triton-X-10; and sample volume of 50, 75 and 100 mL) were determined from preliminary experiments. The variables and values used for FCCCD are listed in Table S1 in Supplementary materials. The amount of graphene (0.2 mg) was constant in all experiments. This first set of experiments (data not reported) showed very clearly the strong effect of pH, with the worst experiment at pH 1 giving a response of 96.1%, the worst experiment at pH 3 having a response of 88.3% and the best experiment at pH 5 producing a response of 18.1%. As a consequence of this, it has been decided to perform a new FCCD with three center points in which the pH was kept constant at 1 and the remaining variables had the same domain. Table S2 included in Supplementary materials shows the experimental matrix and the responses obtained (the experiments were performed in random order). By looking at the data table, it can be seen that the results are very similar for all the experiments, being in the range 97.0–103.6, with the three replicates of the center point being in the range 97.5–100.0. The standard deviation computed on the 17 experiments is 1.9, while the standard deviation of the three replicates is 1.3. The F test ($F_{exp} = 2.21$, $F_{0.95,16,2} = 19.43$) shows that the variance of the replicates is not significantly larger than the variance of the whole matrix. This means that the variability induced by modifying the experimental conditions inside the experimental domain is not larger than the pure experimental variability. Therefore, it can be said that the three variables under study have no effect. The final conditions chosen for further analysis are: pH = 1, 50 mL of sample and 200 μL of suspension of graphene/APDC/Triton-X-100 (1 mg mL^{-1} of graphene, 6 mg mL^{-1} of APDC and 0.3 mg mL^{-1} of Triton-X-100), i.e. containing 0.2 mg of graphene, 1.2 mg of APDC and 0.06 mg of Triton-X-100. It is worth noting here that the sample volume have no influence on Se recovery in the studied range. Therefore, the analysis of real samples can be performed using the sample volume from 50 to 100 mL to obtain adequate enrichment factor and in consequence detection limits fitted for the purpose.

3.2. The effect of matrix elements

The effect of different cations and anions commonly present in waters was investigated. Maximum concentrations of foreign elements and its influence on recovery of Se are listed in Table S3 in Supplementary materials. Neither the alkaline metals nor some common ions present in water samples have influence on recovery of Se, which in every case is higher than 98%. DMSPE/EDXRF procedure is characterized by an excellent resistance to presence of coexisting ions which is especially exposed for Na$^+$, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$, where matrix to analyte ratio equals or exceeds 250,000. Mg^{2+} and HCO$_3^-$ ions have the greatest impact on recovery of selenium, however obtained recoveries are still at high level ($> 98\%$) for relatively high excess of coexisting ions. This great resistance can be explained by the fact that alkali and alkaline earth elements do not react with APDC, however large amount of this ions appreciably reduce the extraction efficiency.
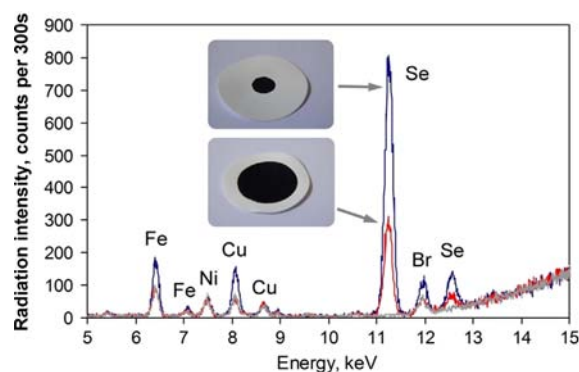

Fig. 1. Comparison between EDXRF spectra obtained for the two samples of different diameters – 5 mm (blue line) and 22 mm (red line), excited by an X-ray beam of a 5.9 mm of focal spot size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Analytical figures of merit of DMSPE procedure

The thickness and the diameter of obtained samples play very significant role for the purposes of XRF measurement. Proposed DMSPE/EDXRF procedure enables to obtain samples in form of thin layers, since small amount of adsorbent is necessary to perform the quantitative recovery of Se ions. For that matter, errors resulting from matrix effects can be neglected. The benchtop EDXRF spectrometers equipped with low-power X-ray tube usually gives X-ray beam of a relatively small spot size. Therefore, the best sensitivity can be obtained for the samples collected on the small area. In other words, if the area of the specimen is too large, only a small fraction of the preconcentrated element is excited and as a consequence a low intensity of fluorescent radiation is observed. Fig. 1 presents the EDXRF spectra of two samples of different diameters (5 and 22 mm; mass per unit area equals 1020 and 53 μg cm^{-2}, respectively) excited by an X-ray beam of 5.9 mm focal spot size calculated as full width at half maximum. It is noteworthy that 22 mm is the diameter of the sample obtained with the use of commercially available filtration assembly of 25 mm. As can be observed, when the diameter of the sample is fitted to small spot size of incident X-ray beam, a high intensity of fluorescent radiation is observed. It should be noted here that although the specimen diameter is small the specimen forms thin layer. Such thin specimen of small diameter can be obtained for only small amount of graphene (200 μg) that is sufficient for quantitative adsorption of Se ions. In consequence, the matrix effects in thin layer can be neglected and the linear relationship between radiation intensity and Se concentration is obtained. In order to obtain satisfactory detection limits and the best sensitivity, samples of 5 and 22 mm diameter were measured with the use of different measuring modes (voltage, current and beam filters). The detection limits were calculated from equation DL $= (3/k)(R_B/t)^{1/2}$, where k is the sensitivity of the method, R_B is the background count rate in counts s^{-1} and t is the counting time. The results in Table 1 show that 5 mm samples present 3.2–3.5 times better sensitivity than 22 mm samples for all examined measurement conditions. It results in very good signal to background ratio and as a consequence very low DLs values are observed for samples of smaller diameter. Generally, the lowest DLs were achieved for 5 mm samples and 100 μm Ag filter (0.032 ng mL^{-1}) and these conditions were chosen for the subsequent experiment.

Analytical figures of merit of DMSPE/EDXRF procedure for optimized preconcentration and measurement conditions are presented in Table 2. Obtained results show that the procedure is linear in the entire range of examined concentrations (up to 500 ng mL^{-1}) which reflects in a very good correlation coefficient. The recovery

Table 1
Measurement conditions, sensitivities and DLs obtained using the optimized DMSPE/EDXRF procedure.

Voltage (kV)	Current (mA)	Primary beam filter	DL (ng mL^{-1})		Sensitivity (mL ng^{-1} s^{-1})	
			5 mm	22 mm	5 mm	22 mm
30	75	None	0.15	0.40	29.6	9.31
30	300	100 μm Ag	0.032	0.088	8.07	2.33
30	300	7 μm Ti	0.11	0.21	118	33.8
30	300	200 μm Al	0.058	0.18	88	24.9
30	300	50 μm Al	0.065	0.22	109	34.3

Table 2
The parameters characterizing DMSPE/EDXRF procedure.

	Se(IV)	Se(VI)
Recovery (%) ($n=10$)	97.7 ± 5.0	99.2 ± 6.6
RSD (%)	5.1	6.6
Sensitivity, mL ng^{-1} s^{-1} (100 μm Ag)	8.07	
DL, ng mL^{-1} (100 μm Ag)	0.032	
Enrichment factor	1013 ± 15	
Maximum concentration, ng mL^{-1}	500	
Correlation coefficients	0.9995	

Table 3
Determination of Se in spiked water samples. (pH$=1$, sample volume 50 mL, 200 μL of suspension containing graphene (1 mg mL^{-1}), APDC (6 mg mL^{-1}) and Triton-X-100 (0.3 mg mL^{-1})); $n=3$; uncertainties correspond to one standard deviation.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Lake water	0	< DL	
	1	1.02 ± 0.06	102.0
	5	4.8 ± 0.27	96.0
	10	10.1 ± 0.51	101.0
	20	19.3 ± 0.44	96.5
	50	53.1 ± 1.10	106.2
Synthetic sea water	0	< DL	
	1	1.01 ± 0.06	101.0
	5	4.9 ± 0.16	98.0
	10	10.3 ± 0.21	103.0
	20	21.0 ± 0.32	105.0
	50	48.9 ± 0.84	97.8
Tap water	0	< DL	
	1	1.01 ± 0.06	101.0
	5	4.9 ± 0.16	98.0
	10	10.3 ± 0.21	103.0
	20	19.7 ± 0.52	98.5
	50	51.9 ± 1.33	103.4

Table 4
Determination of Se(IV) and Se(VI) in spiked mineral water samples.

Added (ng mL^{-1})		Found (ng mL^{-1})		Recovery (%)	
Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)
0	0	1.6 ± 0.10	< DL	–	–
10.0	0	11.4 ± 0.19	< DL	98	–
0	10.0	< DL	9.9 ± 0.65	–	99
10.0	10.0	11.0 ± 0.36	9.7 ± 0.81	94	97

values determined both for Se(IV) and Se(VI) are high and equal to 98 and 99%, respectively. Developed DMSPE/EDXRF methodology is characterized by a very good precision due to reduced number of operations and errors that may occur during the procedure performance. RSDs equal 5.1 and 6.6% for Se(IV) and Se(VI), respectively. It is worth to emphasize that according to the Polish regulations of natural mineral water, branch water and bottled water, the precision and the accuracy of the method for Se determination should not be worse than 10% [52]. It is also noteworthy here that obtained DLs are below maximum contaminant levels of drinking water established by the Polish regulations for bottled water (10 ng mL^{-1}) [52] and EPA (50 ng mL^{-1}) [53]. Such excellent DL could be obtained due to the high enrichment factor (calculated as ratio of sensitivity of DMSPE/EDXRF procedure to sensitivity of direct EDXRF analysis of liquid sample).

3.4. Analytical application

The reliability of proposed methodology was verified using spiked samples of tap, lake and sea water. The results listed in Table 3 show that the relative Se recoveries from these water samples were in the range of 96–106%. Obtained results show that no matrix effect was observed. The proposed methodology was also applied for speciation analysis of Se. Just as in the case of real water samples analysis, analyzed samples were spiked with known amount of proper Se species (10 ng mL^{-1}). Since APDC forms complexes only with Se(IV) ions, concentration of that specimen was determined with the DMSPE/EDXRF procedure. The sum of Se(IV) and Se(VI) was determined after reduction of Se(VI) to Se(IV) using reduction procedure described in Ref. 22. The concentration of Se(VI) was calculated as the difference between total amount of Se and Se(IV) concentrations. Result listed in Table 4 indicates that proposed methodology can be successfully applied for determination of Se in real water samples with good recovery and precision. The reliability of proposed methodology was also examined by an analysis of two reference materials – Lobster Hepatopancreas (TORT-2) and Pig Kidney (ERM®-BB186). Results presented in Table 5 show excellent agreement between certified and reference concentration of Se ions.

4. Conclusions

In present work graphene was applied for the first time for speciation and determination of inorganic Se in different water and biological samples. Although graphene is insoluble and hard to disperse in aqueous solutions, application of nonionic surfactant gives the possibility to use it as a solid adsorbent. Due to unique surface area and its hexagonal arrays very small amount of that nanomaterial is necessary to prepare the sample (only 200 μg per 50–100 mL of the sample). Application of DMSPE technique results in shortening of the sample preparation time, since the equilibrium state is achieved immediately and sorption time is almost time independent. In comparison to other preconcentration techniques reported in the literature for Se determination (Table 6), developed DMSPE/EDXRF procedure enables to obtain very low DLs (even better than mass spectrometry) and very good repeatability. Although, in some cases, application of ETAAS methodology allows obtaining lower detection limits, the advantage of EDXRF over ETAAS relies in the non-destructive character of the measurement. Moreover, ETAAS can be considered as an expensive and time consuming measurement technique. Enrichment factor which can be obtained after the application of the proposed procedure is very high (1013 ± 15), even if we compare it to DLLME techniques. Very good precision of DMSPE/EDXRF procedure results from the simplicity of the proposed methodology consisting only from two main steps (dispersion of the graphene suspension in analyzed solution and filtration). Another advantage which results from application of proposed methodology is the possibility of high salinity water analysis, since the combination of DMSPE/EDXRF is characterized by an excellent resistance to presence of coexisting ions.

Table 5
Analytical result of Se determination in certified reference materials with the DMSPE/EDXRF methodology; $n=3$.

Material	Coexisting elements[a] ($\mu g\,g^{-1}$)	Certified concentration of Se ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Accuracy (%)
TORT-2	As (21.6), Cd (26.7), Cu (106), Fe (105), Mn (13.6), Ni (2.5), Sr (45.2), V (1.64), Zn (180)	5.63 ± 0.67	5.8 ± 0.48	3.0
ERM[®]-BB186	Cd (1.09), Cu (36.5), Fe (256), Mn (7.26), Zn (134)	10.3 ± 0.9	10.5 ± 0.32	1.9

[a] Elements at concentration below $1\,\mu g\,g^{-1}$ are not included in the Table.

Table 6
Recent applications of different preconcentration procedures for Se determination.

Preconcentration procedure	Sample volume (mL)	DL ($ng\,mL^{-1}$)	RSD (%)	pH	EF[a]	Determine technique	Recovery (%)	Linearity ($ng\,mL^{-1}$)	Ref.
Coprecipitation with La(OH)$_3$	6.8	3	1.2	0.12% (w/v) NaOH	20	FI–GH–AAS[e]	>94	0.02–1.0	[15]
DLLME[b]	5	2.1	3	5	250	EDXRF	95	up to 400	[18]
DLLME	5	0.05	4.5	3	70	ETAAS[f]	>96	0.1–3.0	[19]
DLLME	4	0.015	5.1	0.5 mol/L HCl	20	ETAAS	>96	up to 12.5	[20]
HF-LPME[c]	10	0.005	3.1	4	480	ETAAS	>94	0.05–35	[21]
CPE[d]	10	0.5	3.5	6	50	ETV–ICP-MS[g]	>95	up to 50	[16]
DMSPE	50	0.032	5.1–6.6	1	1013	EDXRF	>98	up to 500	This work

[a] Enrichment factor.
[b] Dispersive liquid–liquid microextraction.
[c] Hollow fiber liquid-phase microextraction.
[d] Cloud point extraction.
[e] Flow injection–hydride generation–atomic absorption spectrometry.
[f] Electrothermal atomic absorption spectrometry.
[g] Electrothermal vaporization–inductively coupled plasma-mass spectrometry.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.11.036.

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