

Preconcentration of beryllium via octadecyl silica gel microparticles doped with aluminon, and its determination by flame atomic absorption spectrometry

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Abstract A simple and sensitive method is presented for solid phase extraction (SPE) and preconcentration of trace quantities of beryllium using octadecyl silica gel modified with aurin tricarboxylic acid (aluminon). Beryllium is then determined by flame atomic absorption spectroscopy. Parameters affecting SPE such as pH, sample solution and eluent flow rate, type, concentration and volume of eluent, interfering ions and breakthrough volume, were investigated. Under optimal conditions, the beryllium ions were retained on the sorbent at pH 6–6.7, while 3.0 mL of 0.05 mol L⁻¹ HNO₃ is sufficient to elute the ions. The limit of detection (LOD) based on 3σ was 0.8 μg L⁻¹ for 250 mL sample solution and 5 mL 0.05 mol L⁻¹ HNO₃ as eluent. The LOD can reach 0.1 μg L⁻¹ for 1 L sample solution and 3 mL of 0.05 mol L⁻¹ HNO₃. The accuracy and precision (RSD %) of the method is >90% and <10%, respectively. The method was applied to the determination of beryllium in aqueous samples.

Keywords Aluminon · Beryllium · SPE, AAS

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Introduction

Beryllium has been used widely in specific areas of nuclear technology because of its ability to reflect neutrons and its efficiency in the production of neutrons when exposed to alpha emitters.

Beryllium particles produced from anthropogenic processes (more than 99% of beryllium emitted into the atmosphere is the result of oil or coal combustion for electric power generation) are generally emitted as the oxide; namely, beryllium oxide (BeO). Exposure to beryllium particulate at very low levels can lead to an immune response known as beryllium sensitization, or to chronic beryllium disease (CBD) [1]. The inhalation toxicity of insoluble beryllium oxide depends to a great extent on its physical and chemical properties, which can be altered considerably depending on production conditions. Beryllium, once deposited on land as the oxide, remains bound to the soil within the environmental pH range of 4–8 and does not dissolve in water, thus preventing release to ground water. However, such particles are solubilized by a fluoride source or sources of extremely strong acids (pH<0) and strong bases (pH>14). The estimated average concentration of beryllium in any fresh surface water is 1 μg L⁻¹ (1 ppb). Be has been reported to occur in US drinking water at a concentration of 0.01–0.7 μg L⁻¹ with a mean of 0.013 μg L⁻¹ [2], therefore a sensitive and accurate method is necessary for determination of ultra-trace and trace amounts of Be⁺².

There are many techniques for preconcentration of ions such as Be⁺²: micelle-mediated extraction and

preconcentration [3, 4], SPE preconcentration [5–15] and coprecipitation [16].

Several workers have used different techniques for the determination of beryllium in waters. These include spectrophotometry [3, 10], spectrofluorometry [17, 18], ion chromatography [19, 20], flame atomic absorption spectrometry (FAAS) [4, 6, 7, 9] electrothermal atomic absorption spectrometry (ETAAS) [11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4, 5]. Today solid phase extraction is widely used because it is simple, fast, inexpensive, requires no solvents and can be automated [21–26]. Aluminon is a ligand which can form uncharged metal complexes with beryllium and some other cations [1, 27].

In this study, solid phase extraction based on modified octadecyl silica gel with aluminon acid is presented for the preconcentration of trace amounts of beryllium. Parameters affecting solid phase extraction process were investigated, and the method was applied to the determination of Be^{+2} in real samples in optimum conditions.

Experimental

Reagents

All chemicals used in this study were of analytical grade from Merck (www.merck.de) except ammonium salt of aurin tricarboxylic acid (aluminon) which was of reagent grade quality. All aqueous solutions were prepared in doubly distilled deionized water.

Working standard solutions were prepared by appropriate dilution of stock standard solution.

Apparatus

Sep-Pak C18 cartridges containing 500 mg octadecyl silica (50 mm particle size, 60Å° pore size) were obtained from

Waters Associates Co (MA-www.waters.com). The Be^{2+} determinations were carried out on a 20 plus Varian atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 234.9 nm and a slit of 1.0 nm using an N_2O -acetylene flame. The pH value was measured with a Metrohm pH meter (model 827) equipped with a combined glass-calomel electrode. An oilless vacuum pump model Rocker 600 (Today's, Taiwan) was used to pass the solution through the cartridge.

General procedure

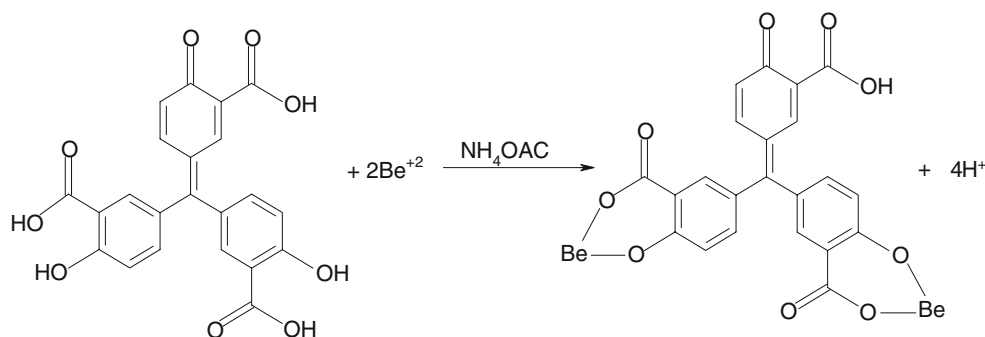
Each cartridge was washed with 5 mL methanol, 5 mL HNO_3 (0.5 mol L^{-1}), 10 mL water and then another 5 mL methanol to remove all contaminants from the manufacturing process and the environment. After drying the cartridge by passing air through it for several minutes, 2 mL of 500 ppm aluminon was introduced into the cartridge and allowed to completely penetrate into the solid phase. The solvent was evaporated at 80°C for 15 min and dried by passing air for 15 min. Extraction was carried out by passing the sample solution containing Be^{+2} ions through the cartridge. Back-extraction was performed by passing 3 mL of HNO_3 (0.1 mol L^{-1}) solution. Finally, the beryllium concentration was determined by flame atomic absorption spectrometry.

Results and discussion

Preliminary experiments

In a primary study, 50 mL of $100 \mu\text{g L}^{-1}$ ($\text{pH}=6.1$) was passed through a conditioned cartridge (without aluminon) and collected. The results showed that only 6% of Be^{+2} can be retained by the cartridge. After cartridge modification with aluminon, the tendency of the solid phase increased and approximately all of Be^{+2} was retained. This can be explained by complexation of Be^{+2} with

Fig. 1 Structure of aluminon and its complex with Be^{+2}



aluminon (Fig. 1). Recent reports have shown that Be^{+2} can form a complex with a ligand containing a CO-C-CO unit [9, 16]. To take full advantage of the procedure, the SPE conditions must be optimized. Various experimental parameters were studied in order to obtain optimized conditions. These parameters were optimized by setting all the parameters to be constant and optimizing one at a time.

Eluant selection

Due to the complex chemical structure, HCl, HNO_3 , CH_3COOH and ethanol were investigated for desorption of Be^{+2} from the cartridge. 4 ml from a separate 50 mL solution containing $50 \mu\text{g L}^{-1}$ of Be^{+2} and 0.1 mol L^{-1} ammonium acetate (pH=6.7) were passed through the cartridge and eluted with 5 mL of 1.0 mol L^{-1} of each acid solution and 5 mL of ethanol separately.

As can be seen in Fig. 2. the recovery is 100% in the case of nitric acid and hydrochloric acid, but 85% for acetic acid and 220% for ethanol. Because the atomization process increases in the organic solvent with respect to the aqueous matrix, for ethanol the recovery is above 200%. Since ethanol elutes aluminon as well as Be^{+2} from octadecyl silicagel, HNO_3 was selected as elution solvent (nitrate was a more acceptable matrix for both the flame and electrothermal atomic absorption spectrometry experiments than the other anions) [28].

Concentration and volume of eluent

For this purpose, 50 ml of six separate solutions containing $50 \mu\text{g L}^{-1}$ of Be^{+2} and 0.1 mol L^{-1} ammonium acetate (pH=6.7) each were passed through the cartridge and eluted with 5 mL of HNO_3 of varying concentration (range $0.01\text{--}2 \text{ mol L}^{-1}$). As can be seen, the recovery of

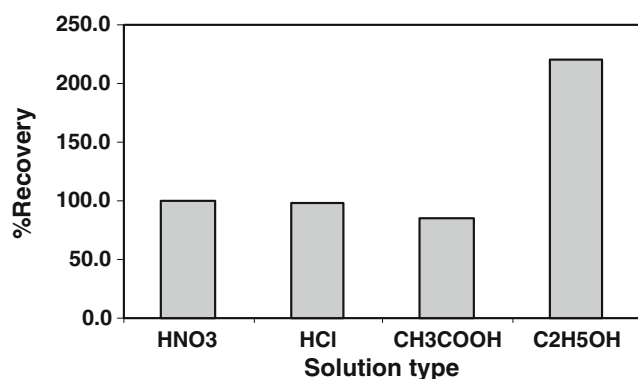


Fig. 2 Effect of eluant type on the recovery of Be^{+2} . Conditions: sample volume: 50 mL, amount of aluminon: $1.0 \mu\text{g}$, sample flow rate: 20 mL min^{-1} , eluant flow rate: 10 mL min^{-1} , concentration of eluant: 1.0 mol L^{-1} , eluant volume: 5 mL, pH of solution: 6.7

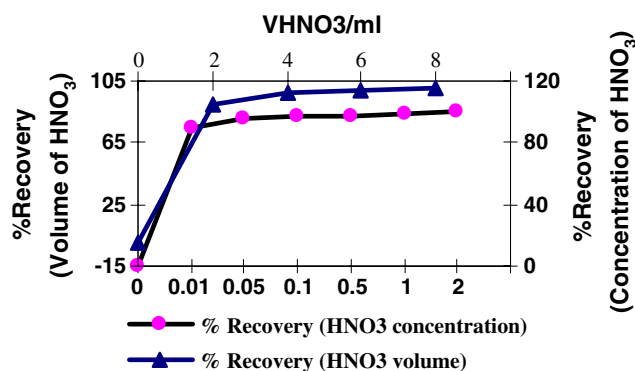


Fig. 3 Effect of concentration and amount of HNO_3 on the recovery of Be^{+2} . Conditions: sample volume: 50 mL, amount of aluminon: $1.0 \mu\text{g}$, sample flow rate: 20 mL min^{-1} , eluant flow rate: 10 mL min^{-1} , concentration of eluant: 0.1 mol L^{-1} (for volume of HNO_3), eluant volume: 5 mL (for concentration of HNO_3), pH of solution: 6.7

Be^{+2} is complete above 0.05 mol L^{-1} HNO_3 (Fig. 3). Thus, 0.1 mol L^{-1} HNO_3 was selected for subsequent experiments. The quantitative stripping of the retained Be^{+2} ions with the help of the modified cartridge was then studied by using various volumes (2–8 mL) of 0.1 mol L^{-1} HNO_3 , and the data are summarized in Fig. 3. The results show that in all cases the recovery is above 90% and above 3 mL of HNO_3 , the stripping of Be^{+2} is quantitative.

Effect of pH and ligand volume

The efficiency of aluminon to react with Be^{+2} and form uncharged metal complexes is largely dependent on pH. This is because aluminon is protonated in acid solutions and forms free acid structures and deprotonates in basic solutions. The influence of the solution pH on the

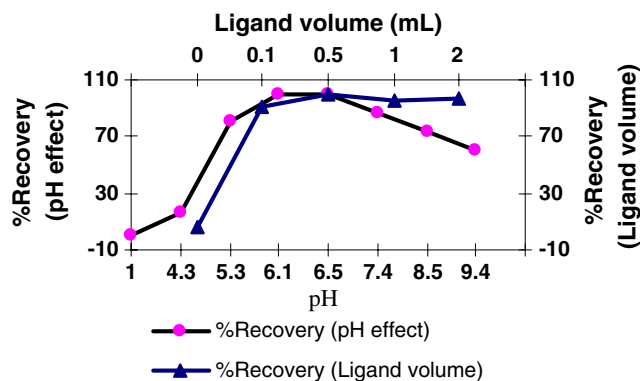


Fig. 4 Effect of pH of sample solution and amount of aluminon on the recovery of Be^{+2} . Conditions: sample volume: 50 mL, amount of aluminon: $1.0 \mu\text{g}$ (for effect of pH), sample flow rate: 20 mL min^{-1} , eluant flow rate: 10 mL min^{-1} , concentration of eluant: 0.1 mol L^{-1} (for volume of HNO_3), eluant volume: 5 mL (for concentration of HNO_3), pH of solution: 6.7 (for effect of aluminon weight)

Table 1 Effect of foreign ions on the recovery of beryllium

Foreign ion	Salt	Ratio of foreign ion to Be ⁺² ion(w/w)	Recovery%
Al ⁺³	Al(NO ₃) ₃	100	104 (±5)
Ba ⁺²	BaCl ₂ ·2H ₂ O	100	97 (±3)
Ca ⁺²	CaCl ₂	100	97 (±2)
Cd ⁺²	Cd(NO ₃) ₂	100	93 (±5)
Cl ⁻	NaCl	100	95 (±7)
Co ⁺²	Co(NO ₃) ₂	100	93 (±10)
Cr ⁺⁶	K ₂ Cr ₂ O ₇	100	100 (±2)
Cu ⁺²	Cu(NO ₃) ₂	100	93 (±4)
F ⁻	NH ₄ F	100	93 (±5)
Fe ⁺³	Fe(NO ₃) ₃	100	93 (±8)
K ⁺	KCl	100	100 (±9)
Li ⁺	LiCl	100	100 (±7)
Mg ⁺²	MgCl ₂	100	97 (±5)
Mn ⁺²	Mn(NO ₃) ₂	100	97 (±5)
Mo ⁺⁶	Na ₂ MoO ₄ ·2H ₂ O	100	93 (±3)
Na ⁺	NaCl	100	100 (±6)
Ni ⁺²	Ni(NO ₃) ₂	100	93 (±2)
Pb ⁺²	Pb(NO ₃) ₂	100	93 (±4)
SO ₄ ⁻²	Na ₂ SO ₄	100	99 (±6)
Sr ⁺²	SrCl ₂ ·6H ₂ O	100	97 (±8)
ZrO ₂ ⁺²	ZrO ₂ Cl ₂ ·8H ₂ O	20	42 (±3)
NO ₃ ⁻	KNO ₃	100	93 (±5)

retention of Be⁺² onto the column has been investigated separately. The pH of the solution was adjusted in a range of 1.0–9.4 using HCl (pH<6), NH₄OAC (6<pH<7) or NaOH (pH>7), and solutions containing Be⁺² were passed through the column. It was observed that in the pH range of 6.0–6.7 (Fig. 4) the recovery of Be⁺² is quantitative (~100%). However, at a pH value below 6.0, the extraction of metal ions is low due to the protonation of chelation sites of the ligands. In order to avoid hydrolyzing of sorbent at higher pH values, a pH of 6.7 (0.1 M ammonium acetate) was selected as optimum pH. The influence of the amount of aluminon on the recovery of Be⁺² was studied using 50 mL solutions containing 1.0 µg of beryllium ions. The recovery of Be⁺² increased

with the increase in amount of aluminon up to 0.5 mL (500 mg L⁻¹) and remained constant after that. Thus, 1.0 mL was selected to ensure a sufficient excess of the reagent throughout the experiment.

The solution and eluent flow rate

The flow rate of the solution was changed within 5–25 mL min⁻¹, and the results showed that the flow rate has no effect on the retention of Be⁺² up to 10 mL min⁻¹, and in the higher flow rates (>10 mL min⁻¹) the recovery decreased at least 30%. The eluent flow rate had no effect on the stripping of Be⁺² up to 20 mL min⁻¹, and the recovery was quantitative.

Table 2 Determination of beryllium in water samples by the proposed method

Sample i. d.	Amount of Be ⁺² (µg)			Extraction (±%RSD) ^b
	Certificated amount (%)	Amount added	Amount found (±%RSD) ^b	
^a Tap water (Tehran)	-	-	<0.2	-
Tap water (Tehran)	-	5.0	4.5 (±0.3)	90 (±6)

^a Some 250 mL of each water sample was taken

^b Mean of triplicates with percent R.S.D.

Breakthrough volume and foreign ion effect

It is important to study the dilution effect (breakthrough volume) on the process kinetics and the LOD calculation. For this purpose, 1.25 μg of Be^{+2} was added to a solution volume of 25, 50, 100, 250, 500 and 1,000 mL, respectively. These samples were passed through the cartridge according to the general procedure under the optimum conditions. The results showed that a recovery of above 90% was achieved in all cases. An enrichment factor of 300 can be obtained for a sample solution of 1,000 mL and 3 mL of eluent.

Potential interference with the present system was investigated. Interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with Be^{+2} . To evaluate the selectivity of the proposed method, the effect of typical potential interfering ions was investigated. For this purpose, 50 mL of solution containing 50 $\mu\text{g L}^{-1}$ of Be^{+2} and 0.1 mol L^{-1} ammonium acetate (pH=6.7) and foreign ions at a desired ratio (w/w) were passed through the cartridge and finally eluted with 5 mL of 0.01–2 mol L^{-1} HNO_3 separately. The results showed that the modified cartridge retained other ions without any effect on Be^{+2} recovery. Zirconium ions can interfere with the Be^{+2} recovery at a ratio above 20, and other ions have no effect on the Be^{+2} recovery (Table 1).

Figure of merit and analytical performance

The analytical figures of merit were evaluated in the optimum conditions obtained by plotting the calibration curve within eight standard solutions of beryllium and comparing to other methods (Table 3). The calibration

curve was linear in the range of 1.0–150.0 $\mu\text{g L}^{-1}$ with a coefficient correction better than 0.99. A preconcentration factor of 330 and a detection limit of 0.1 $\mu\text{g L}^{-1}$ of Be^{+2} was obtained by using 1,000 mL sample solution. The standard deviation of the method evaluated by three replicate analyses was in the range of 2.1–10.8, and the relative error was less than 10%. In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of beryllium in several water samples. The results are given in Table 2. The recoveries for the addition of different concentrations of beryllium to water samples were above 90%.

In Table 3, the figures of the merit of method are compared with other methods for preconcentration /determination of Be^{+2} ions in water samples that were reported previously. As can be seen, the present method has the highest enrichment factor with respect to other methods, and it has a limit of detection comparable to spectrofluorimetry.

Conclusion

The proposed procedure showed a selective, very sensitive and routine method for the determination of beryllium which can be applied to real samples. The conditions for preconcentration of Be^{+2} were selected using the one-at-a-time method. The accuracy and precision of the proposed SPE method was reported in terms of a recovery above 90% and an acceptable R.S.D.. The proposed method can be applied to the determination of Be^{+2} in water samples with a low detection limit, high accuracy and high precision.

Table 3 Figures of merit of comparable methods for determination of beryllium

Method	Reagent	LOD ($\mu\text{g L}^{-1}$)	Maximum enrichment factor	Determination	References
FIA	NH ₄ OH	0.025	13.8	GFAAS	16
IC	Iminodiacetate functional groups	10	-	Conductometry	19
SPE	Quinalizarine	0.2	200	FAAS	9
SPE	Anion exchange resin	0.045	125	FAAS	6
Complexation	2-hydroxy-1-naphthaldehyde-8-aminoquinoline	0.099	-	Spectrofluorimetry	18
Micelle-mediated phase	Chrome Azurol S and cetyltrimethylammonium bromide	0.51	20	Spectrophotometry	3
Polyethylene Powder	Chrome azurol S	0.8	20	GFAAS	26
SPE	Aluminon	0.1	330	FAAS	This work

FIA flow injection analysis; IC ion chromatography; GFAAS graphite furnace atomic absorption spectroscopy; SPE solid phase extraction; FAAS flame atomic absorption spectroscopy

References

- Toxicological review of beryllium and compounds, (cas no. 7440-41-7), U.S. Environmental Protection Agency Washington DC, Revised May, 2008.
- Standard Methods for Examination of Water and Waste Water, Nineteenth ed., American Public Health Association, DC, 1995.
- Afkhami A, Madrakian T, Bozorgzadeh E, Bahrami M (2007) Spectrophotometric determination of beryllium in water samples after micelle-mediated extraction preconcentration. *Talanta* 71:1103
- Beiraghi A, Saeed B (2008) Separation and preconcentration of ultra trace amounts of beryllium in water samples using mixed micelle-mediated extraction and determination by inductively coupled plasma-atomic emission spectrometry. *Anal Chim Acta* 607:183
- Maxwell SL III, Bernard MA, Nelson MR, Youmans LD (2008) New method for removal of spectral interferences for beryllium assay using inductively-coupled plasma atomic emission spectrometry. *Talanta* 76:432
- Afkhami A, Madrakian T, Afshar Assl A, Sehhat AA (2001) Solid phase extraction flame atomic absorption spectrometric determination of ultra-trace beryllium. *Anal Chim Acta* 437:17
- Guoqiang X, Yan H, Yifan L (2009) Solid phase extraction of trace cadmium and lead in food samples using modified peanut shell prior to determination by flame atomic absorption spectrometry. *Microchim Acta* 165:237
- Daorattanachai P, Unob F, Imyim A (2005) Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon. *Talanta* 67:59
- Yamini Y, Hassan J, Mohandesi R, Bahramifar N (2002) Preconcentration of trace amounts of beryllium in water samples on octadecyl silica cartridges modified by quinalizarine and its determination with atomic absorption spectrometry. *Talanta* 56:375
- Suvarthanc K, Kumarc KS, Rekha D, Jayaraj B, Naidu GK, Chiranjeevi P (2005) Extraction equilibrium of beryllium and aluminum and recovery of beryllium from Egyptian beryl solution using CYANEX 921. *Hydrometallurgy* 80:221
- Wen B, Shan XQ, Liu RX, Tang HX (1999) Preconcentration of trace elements in sea water with poly(acrylamino-phosphonic-dithiocarbamate) chelating fiber for their determination by inductively coupled plasma mass spectrometry. *Fresenius J Anal Chem* 363:251
- Tokaloğlu S, Livkebabcı A (2009) A new solid-phase extraction method for the determination of Cu(II) and Fe(III) in various samples by flame atomic absorption spectrometry using N-benzoyl-N-phenylhydroxylamine. *Microchim Acta* 164:471
- Zougagh M, Cano Pavón JM, de Torres Garcia A (2005) Chelating sorbents based on silica gel and their application in atomic spectrometry. *Anal Bioanal Chem* 381:1103
- Nascimento DB, Schwedt G (1997) Polyethylene powder as an absorbent for preconcentration of aluminium, beryllium and thallium. *Microchim Acta* 126:159
- Boussetta S, Branger C, Margailan A, Boudenne JL, Coulomb B (2006) Comparative study on metal extraction properties of empore SDB-XC and amberlite XAD-4 grafted by salicylic acid and its derivatives via different bridges. *Sep Sci Technol* 41:1619
- Burguera JL, Burguera M, Rondón CC, Carrero P, Brunetto MR, de Pena Petit Y (2000) Determination of beryllium in natural and waste waters using on-line flow-injection preconcentration by precipitation: dissolution for electrothermal atomic absorption spectrometry. *Talanta* 52:27
- Keizer TS, Sauer NN, McCleskey TM (2004) Designer ligands for beryllium. *J Am Chem Soc* 126:9484
- Jiang C, He F (2003) Spectrofluorimetric determination of trace amounts of beryllium in mineral water and human's hair. *Spectrochim Acta, Part A* 59:1321
- Voloschik IN, Litvina ML, Rudenko BA (1995) Ion chromatographic determination of beryllium in rock and waste waters with a chelating sorbent and conductimetric detection. *J Chromatogr B* 706:315
- Shaw MJ, Haddad PR (2004) The determination of trace metal pollutants in environmental matrices using ion chromatography. *Environment International* 30:403
- Yamini Y, Hassan J, Karbasi MH (2004) Solid-phase extraction of copper with cupron on octadecyl silica cartridge and its determination with atomic absorption spectrometry. *Microchimica Acta* 148:305
- Daorattanachai P, Unob F, Imyim A (2005) Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon. *Talanta* 67:59
- Xiaoguo MA, Bei H, Dee C (2007) Analysis of trace mercury in water by solid phase extraction using dithizone modified nanometer titanium dioxide and cold vapor atomic absorption spectrometry. *Rare Metals* 26(6):541
- Norisuye K, Hasegawa H, Mito S, Sohrin S, Matsui M (2000) A method for preconcentrating Zr from large volumes of seawater using MnO₂-impregnated fibers. *Talanta* 53:639
- Bagheri M, Mashhadizadeh MH, Razei S (2003) Solid phase extraction of gold by sorption on octadecyl silica membrane disks modified with pentathia-15-crown-5 and determination by AAS. *Talanta* 60:839
- Nascimento Bohrer D, Schwedt G (1997) Polyethylene powder as an absorbent for preconcentration of aluminium, beryllium and thallium. *Mikrochim Acta* 126:159
- Sharma RK, Goel A (2005) development of a Cr (III)-specific potentiometric sensor using, aurin tricarboxylic acid modified silica. *Anal Chim Acta* 534:137
- Brisson MJ et al (2006) Trace-level beryllium analysis in the laboratory and in the field: state of the art, challenges and opportunities. *J Environ Monit* 8:605