Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.922439

55 (2015) 1088–1095
July

Taylor & Francis
Taylor & Francis Group

A multivariate study of solid phase extraction of beryllium(II) using human hair as adsorbent prior to its spectrophotometric detection

Naeemullah Khan[a,b], Tasneem Gul Kazi[b], Mustafa Tuzen[a,*], Mustafa Soylak[c]

[a]*Faculty of Science and Arts, Chemistry Department, Gaziosmanpasa University, 60250 Tokat, Turkey, Tel. +92 022 921 4792; Fax: +92 022 9213431; email: naeemullah433@yahoo.com (N. Khan), Tel./Fax: +903562521585; email: mustafa.tuzen@gop.edu.tr (M. Tuzen)*
[b]*National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan, Tel. +92 022 92134792; Fax: +92 022 9213431; email: tgkazi@yahoo.com (T.G. Kazi)*
[c]*Fen Faculty, Department of Chemistry, Erciyes University, 38039 Kayseri, Turkey, Tel./Fax: +90 352 437 49 38; email: msoylak@gmail.com*

Received 30 September 2013; Accepted 5 May 2014

ABSTRACT

A new solid phase extraction method using hair as a adsorbent has been developed for beryllium(II) prior to its spectrophotometric determination using chrome Azurol S. The effects of various variables such as pH, sample and eluent flow rates, eluent volume and concentration, sample volume, and interfering ions on the quantitative recoveries of beryllium(II) were investigated. The multivariate strategy was applied to screen out the multifactor and estimate the optimum values of experimental factors for the recovery of beryllium(II) using solid phase extraction. Calibration graph was linear in the range of 0.046–20 $\mu g\,L^{-1}$ with correlation coefficient ($r^2 = 0.987$). The sensitivity (limit of detection (LOD)) and selectivity (preconcentration factor) of the proposed methods were 0.028 and 50, respectively. Validity and accuracy of the developed solid phase extraction method were checked by analysis of a certified reference water for Trace Elements (TM-28.3) and a real water samples by standard addition method, the relative recoveries >96% were obtained. The method was successfully applied for the determination of beryllium(II) in natural water samples.

Keywords: Beryllium; Chrome Azurol S; Solid phase extraction; Multivariate study; Spectrophotometry; Water samples

---

1. Introduction

Beryllium has wide applications in the modern world due to its unique properties [1]. It is one of the most toxic non-degradable elements to be found at trace levels in natural and waste water sample, which create a number of health problems [2,3]. Therefore, the determination of beryllium(II) ions in natural water is very important due to their wide industrial and other application [1,4]. Different national guidelines suggested that beryllium(II) concentrations should not exceed a limit of (0.1 $\mu g\,L^{-1}$) for tap water and (0.2 $\mu g\,L^{-1}$) for surface water [5]. The average concentration of beryllium(II) in natural water is in ng L^{-1} range [6]. Therefore, sensitive and accurate methods

---

*Corresponding author.

are required. Different techniques have been used for the determination of beryllium(II), which includes spectrofluorimetry [7], gas chromatography [8,9], atomic absorption spectrometry (AAS) [5,10–12], inductively coupled plasma atomic emission spectrometry [13,14], inductively coupled plasma mass spectrometry [15], and spectrophotometric method [16].

Preconcentration–separation methods are required due to trace levels of beryllium in environmental samples than the detection limits of instrument and interference of matrix components of real samples [17–21]. The SPE is an attractive and most popular method in the field of separation science. Various solid phase extractors [22–28] have been used for screening of metals from different environmental samples. Natural sorbent has become an attractive tool for SPE due to their higher retention capacity and selectivity [29–32]. It is well documented that limited work has been done on sorption of metals on hair [33]. The surface membrane of human hair is coated with a monolayer of fatty acids which mostly consists of 18-methyleicosanoic acid and it can be used as active sites for metal binding for preconcentration [34–36].

We used human hair as solid phase extractant for selective separation and preconcentration of beryllium (II) from natural water samples. A multivariate optimization strategy was employed to found the best values of experimental and theoretical values which were applied for optimum recovery of understudy analyte.

2. Experimental

2.1. Apparatus

A Hitachi 150-20 double beam spectrophotometer equipped with a pair of 1 cm pathlength quartz cuvettes was used for absorbance measurements. For pH adjustments, a pH meter, Nel pH-900 (Ankara-Turkey) model glass-electrode was used. A Perkin–Elmer Model 700 (Norwalk, CT, USA) AAS equipped with a deuterium background correction system and electrothermal atomizer (HGA-800) was used to confirm results obtained by the spectrophotometric method. Beryllium(II) was measured at 234.9 nm with a hollow cathode lamp and a slit width of 1 nm. The graphite furnace program for beryllium(II) determination was adopted from previously reported method [37].

2.2. Reagents

Chrome Azurol S dye (CAS) purchased from Sigma Co. (0.1%, w/v) stock solution was prepared by dissolving 0.1 g in ethanol in a 100 mL volumetric flask. Allow the solution to stand for several days, filter and store in dark bottle. The solution was stable and can be stored for several weeks. Standard solutions of beryllium were prepared by the dilution of certified standard solution (1,000 mg L^{-1}) from the Fluka Kamica (Bush, Switzerland). Working solutions were prepared by adequate dilution of the stock solution. All reagents and solvents used in experimental work were of analytical grade.

2.3. Adsorbent and column preparation

Human hair used as adsorbent was stirred in distilled water and the supernatant liquid was decanted to remove floating skin debris and non-hair objects. The residue was washed with synthetic liquid detergent and rinsed thoroughly with distilled water. Then hair samples were washed with 0.5 mol L^{-1} HNO_3 solutions to remove residual sorbed metals, rinsed thoroughly with distilled water and dried at 50°C. The glass column with a stopcock and porous disk, was 10 cm long and 1.0 cm in diameter. The column was filled with 1.0 g of hair. A small amount of glass wool was used to prevent the leakage of adsorbent.

2.4. General procedure

Duplicate of each aliquot (20–600 mL) of standards and samples containing beryllium(II) was taken in a beaker and diluted with deionized water to the desired volume. Subsequently, pH of the solutions were adjusted to 6.0 with 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HNO_3, then allowed to pass through the column at the rate of 3.0–7.0 mL min^{-1}. The effluent from the column was collected in a volumetric flask. The column was then washed with 5 mL of acetate buffer solution at pH 6.0. The retained metal ions were eluted from the column by 10 mL of mixture of acidic ethanol with a flow rate of 2.0–5.0 mL min^{-1}. Then effluent was treated with 1,000 μL of CAS (0.1% w/v) at pH 4.0. The solutions were kept for 6 min to allow complete color development and then absorbance was measured at 567.5 nm against a reagent blank. A blank solution was also run under the same conditions without standards and real samples. Calibration was performed using aqueous standard solutions submitted to the same SPE procedure as described above. The computer programs (Minitab 13.2 Inc., State College, PA, USA) and STATISTICA computer program 2007 (PA, USA) were used for the calculations.

2.5. Design of experiments

The designed experiments were made by statistical tools for the investigation of response of variables that influence the analytical procedure [38–40]. The designed experiments are basically consisting of four phases: planning, screening (Plackett–Burman design (PBD)), optimization (central composite design), and verification.

2.6. Plackett–Burman design

The PBD is used to screen out the multifactor and derive valid and robust statistical significant factors that influence the applied procedure. It is one of the widely applicable statistical experimental designs for data interpretation. To estimate, the optimum levels of factors, two levels PBD with only 16 experiments was developed. The low (−) and high (+) levels of all factors were specified in Table 1, while the factorial design was evaluated using the analytical signal (recovery %). The variables were screen out using a Pareto chart. The chart displays the absolute value of the effects and draws a reference line on the chart. Any effect that extends, past the reference line, is potentially important ($p = 95.0\%$) shown in Fig. 1.

Table 1
Variable and levels used in PBDs for the factorial design

Variables	Symbol	Low (−)	High (+)
pH	P	3	11
Flow rate of eluent ($mL\,min^{-1}$)	FE	2	5
Flow rate of sample ($mL\,min^{-1}$)	FS	3	9
Concentration of eluent ($mol\,L^{-1}$)	CE	1	3
Volume of eluent (mL)	VE	3	13
Sample volume (mL)	SV	20	600

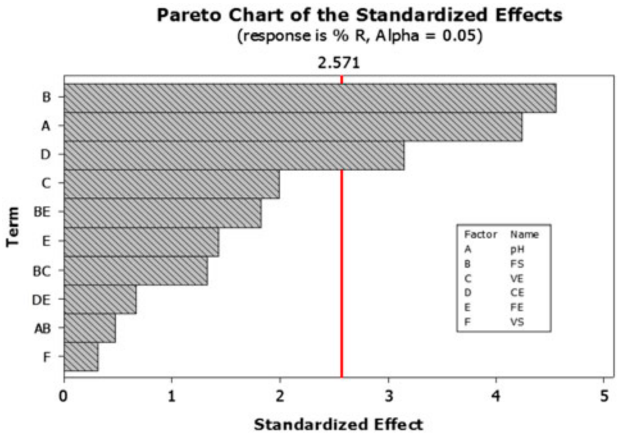

Fig. 1. Pareto chart for the significance of response of the variables: pH (P), FS, FE, VS, CE, and VE.

2.7. Central 2^{3+} star orthogonal composite design

A central 2^{3+} star orthogonal composite was used as surface response design. About 10 min for all cases. The experimental field definition for this design is given in Table 1, while Table 3 shows the central composite design together with the % response obtained for Be. After screening out the key variables with insignificant effect on the procedure were kept at optimum levels. A central 2^{3+} star, orthogonal composite design with six degree of freedom and involving 16 new experiments was performed to optimize the variables, flow rate of sample (FS), pH (P), and concentration of eluent (CE) as shown in Table 2.

3. Result and discussion

3.1. Optimization of experimental variables

Six factors, such as pH, FS and eluent, samples volume, concentration, and volume of eluent (VE) were selected to investigate the effect on the efficiency of proposed method. These variables along with their low (−) and high (+) levels are described in Table 1. The combination of all the variables from a low level to a high level was examined (Table 2) and screen out using a Pareto chart of the standardized effect (Fig. 1). From inference tests, the results produced a minimum t-value at the (95.0%) confidence interval of 2.57, and

Table 2
Central 2^{3+} star orthogonal composite design ($n = 16$) for the set of (FS), (P), and (CE)

Experiments	A (FS)	B (P)	C (CE)	% Recovery
1	$_{a}F^{o}$	$_{b}P^{o}$	$_{c}C^{o}$	99
2	+	−	−	30
3	−	+	−	32
4	+	+	−	38
5	−	−	+	31
6	+	−	+	35
7	−	+	+	37
8	+	+	+	28
9	−	−	−	16
10	$-_{a}F^{1}$	$_{b}P^{o}$	$_{c}C^{o}$	28
11	$_{a}F^{2}$	$_{b}P^{o}$	$_{c}C^{o}$	16
12	$_{a}F^{o}$	$_{b}P^{1}$	$_{c}C^{o}$	28
13	$_{a}F^{o}$	$_{b}P^{2}$	$_{c}C^{o}$	32
14	$_{a}F^{o}$	$_{b}P^{o}$	$_{c}C^{1}$	40
15	$_{a}F^{o}$	$_{b}P^{o}$	$_{c}C^{2}$	70
16	$_{a}F^{o}$	$_{b}P^{o}$	$_{c}C^{o}$	98

Notes: $_{a}F^{1} = 1.63\,mL\,min^{-1}$, $_{a}F^{2} = 8.36\,mL\,min^{-1}$, $_{a}F^{o} = 5.0\,mL\,min^{-1}$.
$_{b}P^{1} = 0.27$, $_{b}P^{2} = 12$, $_{b}P^{o} = 7$.
$_{c}C^{1} = 0.318\,mol\,L^{-1}$, $_{c}C^{2} = 3.7\,mol\,L^{-1}$, $_{c}C^{o} = 2\,mol\,L^{-1}$.

we consider that a factor is significant when the *t*-value is higher than 2.57.

We investigated the effect of six variables such as pH (P), FS, flow rate of eluent (FE), volume of sample (VS), CE, and VE on the recovery of beryllium(II) by multivariate technique. PBD was used as a screening tool to monitor the single as well as interaction of variables. The results indicated that the PS, P, and CE are statistically significant factors as shown in Fig. 1. Sampling flow rate is the most significant factor. It is directly related to the contact of solution with the solid phase, thereby providing information about the adsorption rate of beryllium(II). pH is the next important variables which have vital role on adsorption to adsorbent and subsequent extraction. CE was also statistically important variable for the optimum recovery of beryllium(II). The interaction of two variables (FS × FE) has the most significant effect as compared to other interaction (Fig. 1). Selected levels of VE, FE, and VS for the proposed procedure showed no significant effect ≤2.57. The significant effects of understudy variable on the recovery of beryllium were found in decreasing order of PS > pH > CE > VE > FE > SV as shown in Fig. 1.

3.2. Optimization by central composite design

After screening the variables, three factors (FS, P, and CE) were optimized to provide the maximum recovery of beryllium(II) and other three variable, VE, FE, and SV were kept at optimum levels. A central 2^{3+} star orthogonal composite design with six degree of freedom and involving 16 new experiments was used to optimize the effect of significant variables (Table 2). The study of estimated response surfaces data for variables, [FS]/[pH] and [FS]/[CE] on the % recovery of beryllium(II) is shown in Figs. 2(A) and 2(B).

After plotting three-dimensional (3D) surfaces response between [FS]/[P], calculation was made using quadratic equation to calculate the theoretical values of variables at which 100% recovery can be obtained. It was observed in experiments 1 and 16 that at optimum levels of all three variables ($_aP^0$, $_bE^0$, and $_cC^0$), the % recovery of beryllium(II) was 98–99%, while other variables were at optimum levels: VE (10 mL), SV (500 mL), and FE (2 mL min^{-1}).

It was observed that at low level of FS the recovery of Be was <20% (experiments 3, 5, 7, and 9 as shown in Table 2). On the other hand in experiment 10, the higher FS (8.36 mL/min) also indicate decreased recovery of beryllium(II). The pH is considered as another important factor for metal chelate formation. The results indicated that high recovery of Be was obtained at pH 7 (experiments 1 and 16), while, at (−) levels <35% recoveries was achieved at different values of other variables. Decreased beryllium(II) extraction efficiency was observed in experiment 13, where pH higher than optimized value, same trend was observed at minimum level of pH.

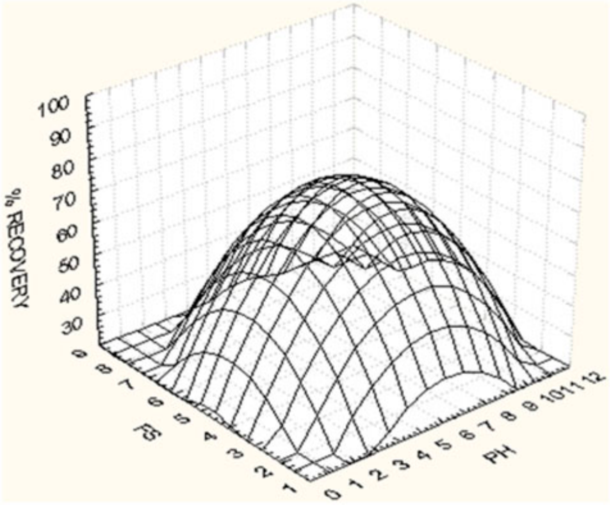

Fig. 2(A). 3D surface response for % recovery of beryllium by SPE. Interaction b/w [FS] (mL min^{-1}) and [pH].

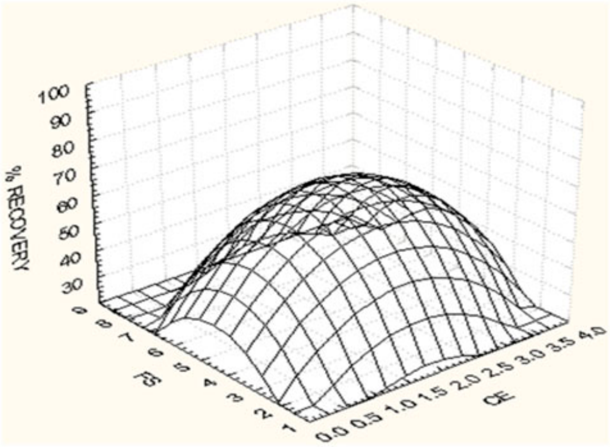

Fig. 2(B). 3D surface response for % recovery of beryllium by SPE. Interaction between [FS] (mL min^{-1}) and [CE] (mol L^{-1}).

The study of estimated 3D surfaces response for variables ([FS–pH] and [FS–CE]) was estimated by quadratic equation, indicated that the 100% recovery of Be was observed at optimum values of FS (4.62 mL min^{-1}) and CE (1.68 mol L^{-1}), and pH 6.4 was required as shown in Figs. 2(A) and 2(B).

3.3. Interferences

The influences of various cations and anions on the presented procedure were checked using model solutions contain different standards of cations. The tolerance limit of coexist ions is defined as the largest amount making variation of less than 5% in the recovery of beryllium(II). To perform this study, solution containing 5.0 μg L^{-1} of beryllium(II) at different interference to beryllium(II) ratio was subjected to the developed procedure (Table 3). Cations and anions given in Table 3, which are presented in the natural water samples, did not interfere with the subsequent extraction of beryllium(II).

Table 3
Effect of foreign ions on the preconcentration and determination of (5 μg L^{-1}) beryllium

Coexisting ions	Interference/analyte amount
Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, PO_4^{3-}, Cl^{-}, SO_4^{2-} HCO_3^{2-}	>10,000
Cr^{3+}, Fe^{3+}, Zn^{2+}	3,000
Cd^{2+}, Pb^{+2}	1,000
Al^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}	700

Table 4
Analytical characteristics of the method

Calibration equation (C in μg L^{-1})	$A = 0.062C + 0.049$
Concentration range (μg L^{-1})	0.046–20
LOD[a] (μg L^{-1})	0.028
R^2 (correlation coefficient)	0.995
Repeatability (RSD%)[b] ($n = 10$)	4.5 (5 μg L^{-1})
Preconcentration factor[c]	50.0

[a] LOD. Calculated as three times the SD (3σ) of the blank signal.

[b] Beryllium concentration was 5 μg L^{-1} for which the RSD was obtained.

[c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

3.4. Analytical figures of merit

The calibration graph was linear with a correlation coefficient (r^2) of 0.9954 at the concentration range of (0.046–20 μg L^{-1}) at optimum levels of all understudy variables. The reliability and precision of the method were checked by the relative standard deviation of 10 measurements on a solution containing 5.0 μg L^{-1} beryllium(II). LOD is defined as the concentration equivalent to three times of the standard deviation of 10 measurements of the blank and preconcentration calculated as the ratio of slope of samples to that eluent volume (Table 4).

Reliability of the method was also checked by spiking standards addition methods of beryllium(II) certified reference water for Trace Elements (TM-28.3) and at three concentration levels (0.2–1.0 μg L^{-1}) in a canal water and tap water samples as shown in Table 5. The recovery values are higher than 95% which confirmed the reliability of the methods and its independence from the matrix effects.

3.5. Application

The method was applied to spectrophotometric determination of beryllium(II) in fresh surface water samples. The fresh surface water of sea was collected

Table 5
Determination of beryllium in real water, certified reference waters for Trace Elements (TM-28.3) samples by desire method and GFAAS, $N = 4$

CRM (TM-28.3)	Certified values (μg L^{-1})	Measured values (μg L^{-1})		Recovery (%)	
		Spectrophotometry	GFAAS	Spectrophotometry	GFAAS
	3.34	3.30 ± 0.20	3.31 ± 0.30	99	99
Samples	Added (μg L^{-1})	Measured (μg L^{-1})		Recovery (%)	
Canal water	0	0.22 ± 0.04[a]	0.23 ± 0.02[a]	–	–
	0.2	0.42 ± 0.02	0.43 ± 0.04	100	100
	0.5	0.71 ± 0.05	0.70 ± 0.06	99	96
	1.0	1.20 ± 0.09	1.21 ± 0.10	98	98
Tap water	0	0.12 ± 0.01[a]	0.13 ± 0.01[a]	–	–
	0.2	0.32 ± 0.02	0.32 ± 0.03	100	97
	0.5	0.61 ± 0.03	0.62 ± 0.04	98	98
	1.0	1.09 ± 0.09	1.11 ± 0.10	97	98

[a] Mean ± SD

Table 6
Comparative data of analytical characteristics of the enrichment methods for beryllium

Preconcentration method	Techniques	Enrichment factor	LOD (μg L^{-1})	Ref.
SPE	FAAS	–	0.045	[41]
SPE	Spectrophotometry	50	0.02	[42]
SPE	FAAS	200	0.20	[4]
SPE	GFAAS	–	0.18	[43]
CPE	Spectrophotometry	20	0.51	[44]
ICM	Ion chromatography	46	3.0	[45]
CPE	Spectrophotometry	–	0.92	[46]
CPE	Spectrophotometry	–	0.9	[47]
SPE	GFAAS	–	0.0023	[21]
SPE	GFAAS	–	0.006	[48]
SPE	Spectrophotometry		0.0004	[49]
SPE	Spectrophotometry	50	0.028	Present work

in 2012 from different sampling sites of sea at Balikesir–Turkey. All water samples were filtered through a 0.45 μm pore size membrane filter, to remove suspended particulate matter. Then applied proposed method and determined spectrophotometrically. The concentrations of beryllium(II) in fresh surface water samples were found as shown in Table 5.

4. Conclusions

An effective method for enrichment and determination of beryllium(II) has been achieved by SPE using human hair as an adsorbent prior to their spectrophotometer determination. Trace- and ultratrace levels of beryllium(II) in natural water samples could be obtained with high repeatability and spiked recoveries. The recently used SPE is comparatively sensitive and superior in term of lower detection limits. The method has competitive analytical tool and an alternative of the traditional methods for the analysis of trace level of beryllium(II). The proposed extraction method has significant reproducibility and reliability by analysis GFAAS and UV–vis spectrometric methods. A high preconcentration factor and low LODs achieved in this work are comparable with literature reported works [4,21,41–49] in Table 6.

Acknowledgments

Naeemullah is grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) for awarding him “2216 Research Fellowship Programme for Foreign Citizens” and providing financial support. The authors also would like to thank the Gaziosmanpasa University and Erciyes University for excellent research laboratory facilities to carryout research work. Dr Mustafa Tuzen thanks to Turkish Academy of Sciences for financial support.

References

[1] L.S. Newman, J. Lloyd, E. Daniloff, The natural history of beryllium sensitization and chronic beryllium disease, Environ. Health Perspect. 104 (1996) 937–943.
[2] D.A. Everest, The Chemistry of Beryllium, Elsevier, New York, NY, 1964, pp. 133–140.
[3] L.R. Goldfrank, N.E. Flomenboum, N.A. Lewin, R.S. Weisman, M.A. Howland, Goldfrank’s Toxicologic Emergencies, 4th ed., Prentice-Hall, East Norwalk, CT, 1990.
[4] Y. Yamini, J. Hassan, R. Mohandesi, N. Bahramifar, 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 (2002) 375–381.
[5] J.L. Burguera, M. Burguera, C. Rondon, P. Carrero, M.R. Brunetto, Y.P. de Pena, Determination of beryllium in natural and waste waters using on-line flow-injection preconcentration by precipitation/dissolution for electrothermal atomic absorption spectrometry, Talanta 52 (2000) 27–37.
[6] P. Burba, P.G. Willmer, M. Betz, F. Fuchs, Atomic absorption determination of beryllium traces in natural waters, Int. J. Environ. Anal. Chem. 13 (1983) 177–191.
[7] U. Quandt, W. Herr, Beryllium abundance of meteorites determined by “non-destructive” photon activation, Earth Planet. Sci. Lett. 24 (1974) 53–58.
[8] C.I. Measures, J.M. Edmond, Determination of beryllium in natural waters in real time using electron capture detection gas chromatography, Anal. Chem. 58 (1986) 2065–2069.
[9] L.C. Robles, C. Garciolalla, M.T. Alemany, A.J. Aller, Flame atomic absorption spectrometric method for the determination of beryllium in natural waters after separation with N-benzoyl-N-phenylhydroxylamine, Analyst 116 (1991) 735–737.

[10] L. Haraldsen, M.A.B. Pougnet, Direct determination of beryllium in coal slurries using graphite furnace atomic absorption spectrometry with automatic injection, Analyst 114 (1989) 1331–1333.
[11] S.M. Sultan, F.E.O. Suliman, Chemometric optimization and flow injection method for the determination of norfloxacin in drug formulations, Analyst 118 (1993) 573–576.
[12] S.Q. Tao, Y. Okamoto, T. Kumamaru, Inductively coupled plasma atomic emission spectrometric determination of beryllium in aluminium-based alloys and rock samples by introducing beryllium into the plasma as ethylberyllium species, Anal. Chim. Acta 309 (1995) 379–385.
[13] L. Halicz, I.B. Brenner, O.J. Yoffe, Direct solids analysis of geological samples using slurry nebulization inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 8 (1993) 475–480.
[14] D.E. Kimbrough, I.H. Suffet, Multi-element, multimedia method for the determination of airborne elemental emissions by inductively coupled plasma atomic emission spectrometry, Analyst 121 (1996) 309–315.
[15] F. Pilon, S. Lorthioir, J.C. Birolleau, S. Lafontan, Determination of trace elements in radioactive and toxic materials by inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 11 (1996) 759–764.
[16] H.B. Singh, N.K. Agnihotri, V.K. Singh, Determination of trace amounts of beryllium using derivative spectrophotometry in non-ionic micellar medium, Talanta 47 (1998) 1287–1296.
[17] Standard Methods for Examination of Water and Waste Water, 19th ed., American Public Health Association, Washington, DC, 1995.
[18] Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Horwood, London, 1986.
[19] J.A. Adam, E. Booth, J.O.H. Strickland, The determination of microgram amounts of beryllium using acetyl acetone, Anal. Chim. Acta 6 (1952) 462–471.
[20] M. Hiraide, K. Ishikawa, Z.S. Chen, H. Kawaguchi, Coprecipitation with metal hydroxides for the determination of beryllium in seawater by graphite furnace atomic absorption spectrometry, Mikrochim. Acta 117 (1994) 7–13.
[21] H.W. Peng, M.S. Kuo, Determination of trace amounts of beryllium(II) in drinking water and of beryllium vapor in air by graphite-furnace atomic absorption spectrophotometry using acetylacetone as a chelating agent, Anal. Sci. 16 (2000) 157–161.
[22] D. Barcelo, M.C. Hennion, Determination of Pesticides and their Degradation Products in Water, Elsevier, Amsterdam, 1997, pp. 357–428.
[23] A.M. Zou, M.L. Chen, Y. Shu, M. Yang, J.H. Wang, Biological cell-sorption for separation/preconcentration of ultra-trace cadmium in a sequential injection system with detection by electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom. 22 (2007) 392–398.
[24] I. Narin, Y. Surme, E. Bercin, M. Soylak, SP70-α-benzoin oxime chelating resin for preconcentration–separation of Pb(II), Cd(II), Co(II) and Cr(III) in environmental samples, J. Hazard. Mater. 145 (2007) 113–119.
[25] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), Talanta 71 (2007) 1075–1082.
[26] R. Saxena, A.K. Singh, D.P.S. Rathore, Salicylic acid functionalized polystyrene sorbent amberlite XAD-2. Synthesis and applications as a preconcentrator in the determination of zinc(II) and lead(II) by using atomic absorption spectrometry, Analyst 120 (1995) 403–405.
[27] A.M. Naghmush, K. Pyrzyńska, M. Trojanowicz, Flame AAS determination of lead in water with flow-injection preconcentration and speciation using functionalized cellulose sorbent, Talanta 42 (1995) 851–860.
[28] M. Tuzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108, J. Hazard. Mater. 129 (2006) 266–273.
[29] H.M. Choi, R.M. Cloud, Natural sorbents in oil spill cleanup, Environ. Sci. Technol. 26 (1992) 772–776.
[30] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) 260–269.
[31] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environ. Technol. 17 (1996) 71–77.
[32] A. Nakajima, M. Yasuda, H. Yokoyama, H. Ohya-Nishiguchi, H. Kamada, Copper biosorption by chemically treated *Micrococcus luteus* cells, World J. Microbiol. Biotechnol. 17 (2001) 343–347.
[33] H.A. El-Sheikh, A.J. Sweileh, Sorption of trace metals on fish scales and application for lead and cadmium pre-concentration with flame atomic absorption determination, Jordan J. Chem. 3 (2008) 87–97.
[34] D.J. Evans, J.D. Leeder, J.A. Rippon, D.E. Rivett, Separation and analysis of the surface lipids of the wool Wbre, in: Proceedings of the 7th International Wool Textile Research Conference I, Tokyo, Japan, 1985, pp. 135–142.
[35] T. Zhao, G. Sun, Antimicrobial finishing of wool fabrics with quaternary aminopyridinium salts, J. Appl. Polym. Sci. 103 (2007) 482–486.
[36] M. Tsukada, T. Arai, G. Colonna, A. Boschi, G. Freddi, Preparation of metal-containing protein fibers and their antimicrobial properties, J. Appl. Polym. Sci. 89 (2003) 638–644.
[37] M.A. Castro, L.C. Robles, J.M. Lumbreras, B. de Celis, A.J. Aller, D. Littlejohn, Determination of beryllium by electrothermal atomic absorption spectrometry using tungsten surfaces and zirconium modifier, Anal. Chim. Acta 636 (2009) 158–162.
[38] D.C. Montgomery, Design and Analysis of Experiments, 4th ed., Wiley, New York, NY, 1997.
[39] C.K. Bayne, I.B. Rubin, Practical Experimental Designs and Optimization Methods for Chemists, VCH, Weinheim, 1986.
[40] S.N. Deming, S.L. Morgan, Experimental Design: A Chemometrics Approach, Elsevier, Amsterdam, 1987.
[41] A. Afkhami, T. Madrakian, A.A. Assl, A.A. Sehhat, Solid phase extraction flame atomic absorption spectrometric determination of ultra-trace beryllium, Anal. Chim. Acta 437 (2001) 17–22.
[42] A.S. Amin, Utilization of solid phase spectrophotometry for determination of trace amounts of beryllium in natural water, Anal. Chim. Acta 437 (2001) 265–272.

[43] P.Y. Liu, M.H. Chen, Y.Y. Tsai, M.S. Kuo, Application of acetylacetone chelation solid-phase extraction to GFAAS measurements of trace amounts of beryllium in livers and muscles of poultry and livestock, Food Chem. 126 (2011) 1460–1464.

[44] A. Afkhami, T. Madrakian, E. Bozorgzadeh, M. Bahram, Spectrophotometric determination of beryllium in water samples after micelle-mediated extraction preconcentration, Talanta 71 (2007) 1103–1109.

[45] W. Bashir, B. Paull, Sensitive and selective ion chromatographic method for the determination of trace beryllium in water samples, J. Chromatogr. A 910 (2001) 301–309.

[46] M. Bahram, T. Madrakian, E. Bozorgzadeh, A. Afkhami, Micelle-mediated extraction for simultaneous spectrophotometric determination of aluminum and beryllium using mean centering of ratio spectra, Talanta 72 (2007) 408–414.

[47] B.P. Dayananda, H.D. Revanasiddappa, T.N. Kiran Kumar, Micellanized spectrophotometric method for the determination of beryllium using haematoxylin, Spectrochim. Acta, Part A 67 (2007) 1333–1338.

[48] M.C. Valencia, S. Boudra, J.M. Bosque-Sendra, Determination of trace amounts of beryllium in water by solid-phase spectrophotometry, Analyst 118 (1993) 1333–1336.

[49] N.T. Ohba, H. Ishida, H. Satoh, K. Ohzeki, R. Ishida, Solid-phase extraction of trace amounts of beryllium (II) from natural water samples on a glass-fibre filter followed by solid-phase spectrophotometric determination using Chromazurol B, Analyst 117 (1992) 1513–1517.