

Novel solid phase extraction procedure for gold(III) on Dowex M 4195 prior to its flame atomic absorption spectrometric determination

Mustafa Tuzen^{a,*}, Kadriye O. Saygi^a, Mustafa Soylak^b

^a Gaziosmanpaşa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey

^b Erciyes University, Faculty of Science and Arts, Chemistry Department, 38039 Kayseri, Turkey

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Abstract

A method for solid phase extraction (SPE) of gold(III) using Dowex M 4195 chelating resin has been developed. The optimum experimental conditions for the quantitative sorption of gold(III), pH, effect of flow rates, eluent types, sorption capacity and the effect of diverse ions on the sorption of gold(III) have been investigated. The chelating resin can be reused for more than 100 cycles of sorption–desorption without any significant change in sorption of gold(III) ions. The recovery values for gold(III) and detection limit (LOD) of gold were greater than 95% and $1.61 \mu\text{g L}^{-1}$, respectively. The preconcentration factor was 31. The relative standard deviation of the method was $<5\%$. The adsorption capacity of the resin was 8.1 mg g^{-1} . The proposed method has been applied for the determination of gold(III) in some real samples including water, soil and sediment samples.

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1. Introduction

Gold is an important element in our life due to its usage in jewelry and industry, etc. [1–3]. Trace level determination of gold by flame atomic absorption spectrometry is difficult like other metal ions due to lower levels of gold than the limit of detection of flame atomic absorption spectrometry and effects of the matrix components of the working media [4–7]. To overcome these limitations on the determination of gold by flame atomic absorption spectrometry, separation-enrichment techniques including solid phase extraction (SPE), cloud point extraction, liquid–liquid extraction, coprecipitation, etc. [8–15] have been used by the researchers around the world.

Solid phase extraction is an extraction method that uses a solid phase and a liquid phase to isolate one, or one type, of analyte from a solution [16]. SPE method had the advantages of being more sensitive, simple, environment friendly, faster and sampler saving. SPE methods employing on different solid matrices have been successfully used for the preconcentration, separa-

tion and sensitive determination of trace metal ions including gold [17–20]. Amberlite XAD resins [2,6,21], activated carbon [10], crosslinked chitosan [11], carbon nanofibers [17], YPA(4) chelating resin [19], etc. have been used as solid phase extractor for gold in real samples.

Dowex M 4195 chelating resin is based upon a special chelating amine ligand which is partially quaternized by sulfuric acid as received [22]. When in this conjugate sulfuric acid salt form, the resin is fully swollen and hydrated, and ready for scavenging metals from acidic media [22]. It was used in various studies for heavy metal separation and preconcentration from various media [23–26].

In the presented work, a SPE of gold(III) on Dowex M 4195 chelating resin has been presented. Optimal analytical conditions for the quantitative recoveries of gold(III) was investigated.

2. Experimental

2.1. Instruments

A PerkinElmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air–acetylene flame. A

* Corresponding author. Fax: +90 356 2521585.
E-mail address: mtuzen@gop.edu.tr (M. Tuzen).

10 cm long slot-burner head, a lamp and an air–acetylene flame were used. Wavelength was set at 242.8 nm and the spectral band width at 0.5 nm for gold.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.2. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore 18.2 M Ω cm⁻¹ conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1+9) and were rinsed with distilled water prior to use. One thousand and ten milligrams per liter of the stock solution of gold was purchased from Sigma. Working solutions were prepared by appropriate dilution of the stock solution with water.

Phosphate buffer solutions (H₂PO₄⁻/H₃PO₄) were prepared by mixing of appropriate volumes of 1 mol L⁻¹ sodium dihydrogen phosphate and phosphoric acid solutions for pH 2–3. Acetate buffer solutions (CH₃COO⁻/CH₃COOH) were prepared by mixing of appropriate volumes of 0.1 mol L⁻¹ acetic acid and 0.1 mol L⁻¹ sodium acetate solutions for pH 4 and 6. For pH 7, a 250 mL of borate buffer was prepared by use of 2.5 mL of 1 mol L⁻¹ HCl and 0.445 g NaBO₂. Ammonium buffer solution (NH₄⁺/NH₃) was prepared by mixing of appropriate amounts of 0.1 mol L⁻¹ ammonia and 0.1 mol L⁻¹ ammonium chloride solutions for pH 8.

Dowex M 4195 is purchased from Sigma, St. Louis, USA. It was washed successively with methanol, water, 1 mol L⁻¹ HNO₃ in acetone, water, 1 mol L⁻¹ NaOH, and water, sequentially.

Six hundred milligrams of Dowex M 4195 chelating resin was loaded after washing acetone, 1 mol L⁻¹ HNO₃ solution and water, respectively, into a 10 mm × 100 mm glass column with a glass frit resin support. The resin bed was approximately 2 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10–15 ml of the eluting solution and of water, subsequently.

2.3. Test procedure for solid phase extraction of gold(III)

Forty milliliters of solution containing 10 μ g of gold(III) ion was added to 10 mL of buffer solution (the desired pH between 2 and 8). The column was preconditioned by passing buffer solution. The solution was permitted to flow through the column under gravity at the flow rate of 5 mL min⁻¹. After passing of this solution ending, the column was rinsed twice with 2 mL of water. The adsorbed metals on the column were eluted with 8 mL portion of 2 M H₂SO₄ + 4 M NH₃. The eluent was analyzed for the determinations of gold concentrations by flame atomic absorption spectrometer.

2.4. Applications

Soil (1000 mg), sediment (1000 mg) and mine (1000 mg), were digested with 6 mL of HCl (37%) and 2 mL of HNO₃ (65%) in microwave digestion system. Digestion conditions for the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [27–29]. The residue diluted to 50.0 mL with deionized water. A blank digest was carried out in the same way. Then the pre-concentration procedure given above was applied to the final solutions. Gold was determined by flame AAS.

3. Results and discussion

3.1. pH effect on the recoveries

pH of the working media is most critical parameter on the SPE studies [30–33]. The effect of pH of the sample solution on the retention of gold(III) on Dowex M 4195 chelating resin were investigated in the pH range 2.0–8.0. The pHs of the solutions were adjusted by using buffer solutions given in Section 2.2. The results are depicted in Fig. 1. Gold was quantitatively recovered in the pH range of 3.0–6.0. All further works were carried out at pH 4.0. The mechanism of retention of gold(III) on Dowex M 4195 is chelation. The surface functional group of Dowex M 4195 is amine [22].

3.2. Eluent

Various eluent solutions were used for desorption of gold(III) from Dowex M 4195 chelating resin. The results are given in Table 1. Quantitative recoveries for gold(III) ions were obtained by using the mixture of 8 mL of 2 M H₂SO₄ + 4 M NH₃. Therefore, the volume of 8 mL of 2 M H₂SO₄ + 4 M NH₃ was used in the following experiments.

3.3. Flow rates

The effects of the sample and eluent flow rates on the retentions and recoveries of gold(III) on the resin were studied in the

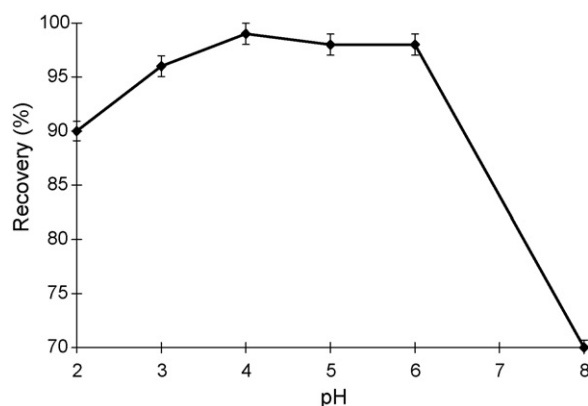


Fig. 1. Effect of pH on the recoveries of Au(III) (eluent: 2 M H₂SO₄ + 4 M NH₃, n = 4).

Table 1
Effects of eluent on the desorption of gold from Dowex M 4195 ($n=4$)

Eluent	Recovery (%)
1 M HCl	40.0 ± 2.0
2 M HCl	50.0 ± 2.0
2 M NH ₃	70.0 ± 3.0
4 M NH ₃	90.0 ± 3.0
2 M H ₂ SO ₄	67.0 ± 3.0
2 M H ₂ SO ₄ + 4 M NH ₃	99.0 ± 3.0

* Mean ± standard deviations.

Table 2
Recovery values as a function of sample volume ($n=4$)

Sample volume (mL)	Recovery (%)
25.0	97.0 ± 2.0
50.0	99.0 ± 3.0
100.0	96.0 ± 2.0
250.0	95.0 ± 3.0
500.0	70.0 ± 2.0

* Mean ± standard deviations.

flow rate range of 0.5–7.0 mL min⁻¹. Gold(III) ions were quantitatively retained and recovered in the sample and eluent flow range of 1.0–5.0 mL min⁻¹. After 5.0 mL min⁻¹, the recoveries were not quantitative due to insufficient contact between analytes and adsorbent. Five milliliters per minute was selected as sample and eluent flow rate.

3.4. Effects of amounts of Dowex M 4195 chelating resin

The effects of the amounts of Dowex M 4195 chelating resin on the adsorption of gold(III) were investigated at 5.0 mL min⁻¹ flow rates of sample and eluent solutions. The results are given in Fig. 2. The recovery values were found quantitative in the resin amounts of 500–600 mg. The recovery of gold decreased with increasing resin beyond 600 mg due to insufficient eluent volume. If the eluent volume was higher than 8.0 mL, the recoveries were quantitative. In all further studies, the short glass column was filled with 600 mg of Dowex M 4195 resin. The results are agreed with the literature values [33–36].

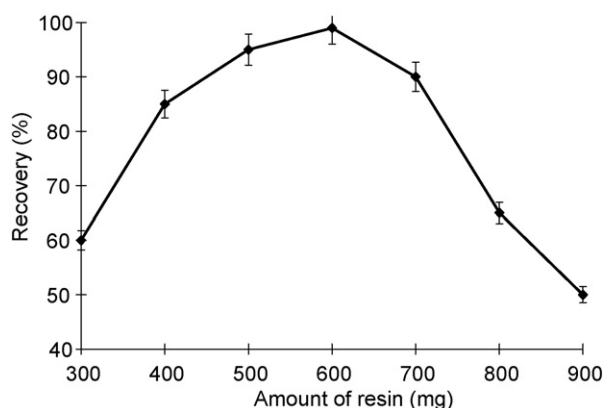


Fig. 2. Influences of amounts of resin on the recoveries of gold(III) (eluent: 2 M H₂SO₄ + 4 M NH₃, $n=4$).

Table 3
Effects of foreign ions on the recoveries of gold ($n=4$)

Ion	Added as	Concentration (mg L ⁻¹)	Recovery (%)
Na ⁺	NaCl	20,000	97.0 ± 3.0
K ⁺	KCl	3,000	95.0 ± 2.0
Ca ²⁺	CaCl ₂	5,000	96.0 ± 3.0
Mg ²⁺	MgCl ₂	5,000	95.0 ± 2.0
Cl ⁻	NaCl	25,000	95.0 ± 3.0
F ⁻	NaF	500	99.0 ± 2.0
NO ₃ ⁻	KNO ₃	2,000	95.0 ± 2.0
SO ₄ ²⁻	Na ₂ SO ₄	2,000	96.0 ± 2.0
PO ₄ ³⁻	Na ₃ PO ₄	2,500	96.0 ± 3.1
Mn ²⁺	MnSO ₄	50	97.0 ± 2.0
Fe ³⁺	FeCl ₃	50	95.1 ± 2.0
Cu ²⁺	CuSO ₄	50	95.2 ± 3.1
Pb ²⁺	Pb(NO ₃) ₂	50	96.0 ± 2.0
Zn ²⁺	ZnSO ₄	50	96.0 ± 3.0
Cd ²⁺	Cd(NO ₃) ₂	50	96.8 ± 1.0
Ag ⁺	AgNO ₃	50	98.0 ± 2.1

3.5. Effect of the sample volume

In order to obtain high preconcentration factor, the effect of sample volume on the sorption behavior of analytes on resin was investigated by passing 25–500 mL of solutions. Gold(III) ions were quantitatively recovered at the range of 25–250 mL. At the higher volumes than 250 mL, the recoveries for analytes were not quantitative. The preconcentration factor is calculated by the ratio of the highest sample volume (250 mL) and the lowest eluent volume (8 mL). The preconcentration factor was 31 Table 2.

3.6. Effect of matrix ions

In order to identify the effects of some matrix ions on the recoveries of gold(III) on Dowex M 4195 resin, model solutions containing matrix ions given in Table 3 with various concentrations were prepared then the preconcentration procedure given in Section 2 was applied. The results are given in Table 3. The efficiency of the recovery was not affected whether these ions exist or not. Hence, the presented method can be applied to real samples including sea water and samples containing transition metals at mg L⁻¹ since it was not affected by high concentrations of alkaline and earth alkaline ions.

3.7. Adsorption capacity and limit of detection

In order to study the adsorption capacity of Dowex M 4195 chelating resin, 0.1 g resin was added to 50 mL of solution containing 1.0 mg of metal ion at pH 4.0. After shaking for 30 min, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. The capacity of resin for gold(III) was 8.1 mg g⁻¹.

The detection limit (LOD) of the presented SPE study was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limits, defined as the concentration equivalent to three

Table 4

The results for tests of addition/recovery for gold determination in some real samples (sample volume: 250 mL, eluent volume: 8 mL ($n=4$))

Added (μg)	Spring water		Tap water		Sea water	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
–	BDL	–	BDL	–	BDL	–
10	9.9 ± 0.4^a	99	9.8 ± 0.5	98	9.9 ± 0.3	99
20	19.5 ± 0.6	98	19.8 ± 0.6	99	19.6 ± 0.5	98
40	39.2 ± 1.2	98	39.6 ± 0.8	99	39.1 ± 0.9	98

^a Standard deviation, BDL: Below detection limit.

Table 5

The concentration of gold in microwave digested environmental samples ($n=4$)

Added (μg)	Soil from Tokat City		Sediment from Tokat City		Mine from Tokat City	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
–	BDL	–	BDL	–	BDL	–
10	9.9 ± 0.5^a	99	9.7 ± 0.4	97	9.8 ± 0.5	98
20	19.2 ± 0.8	96	19.5 ± 0.9	98	19.9 ± 0.9	100
40	38.5 ± 1.5	96	39.1 ± 1.2	98	39.7 ± 1.4	99

^a Standard deviation, BDL: Below detection limit.

Table 6

Comparative data from some recent studies on solid phase extraction of gold

System	Eluent	PF	DL ($\mu\text{g L}^{-1}$)	R.S.D. (%)	Reference
Activated carbon/dithiophosphoric acid <i>O,O</i> -diethyl ester	$2 \text{ mol L}^{-1} \text{ NH}_3$ in acetone	20	–	10	[10]
Amberlite XAD-2000/DDTC	$1 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone	200	16.6	<6	[21]
Duolite GT-73/HCl	0.8 mol L^{-1} thiourea + 3.0 mol L^{-1} HCl	–	–	–	[37]
Amidinothioureido-silica gel chelating resin	5% thiourea	–	13	1.2	[38]
Octadecyl silica membrane disks modified with pentathia-15-crown-5	$0.5 \text{ mol L}^{-1} \text{ S}_2\text{O}_3^{2-}$	200	1	2.1	[39]
Polyoxyethylene-type nonionic surfactant-impregnated amberlite XAD-4	0.5 mol L^{-1} thiourea and 0.02 mol L^{-1} HCl	–	–	–	[40]
Dowex M-4195 chelating resin	$4 \text{ mol L}^{-1} \text{ NH}_3$ + $2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	31	1.61	5	This study

PF: preconcentration factor, DL: detection limit.

times the standard deviation ($n=13$) of the reagent blank were $1.61 \mu\text{g L}^{-1}$.

3.8. Applications of the presented procedure

Various amounts of gold(III) were spiked to water samples. Then the procedure presented was applied to the determination of gold(III) in natural water samples. The results are given in Table 4. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. Also the application of the proposed SPE procedure for the determination of gold(III) was performed to the microwave digested environmental samples. The results are given in Table 5.

4. Conclusion

The conditions for quantitative and reproducible preconcentration, elution and FAAS determinations for gold(III) on Dowex M 4195 chelating resin were studied. The method is simple, accurate and can be applied for the determination of analyte. The comparison of the results found in the presented study and

some works in literature is given in Table 6. The system showed reproducibility and reliability in analytical data, with an R.S.D. value of lower than 5% on triplicate experiment. Six hundred milligrams of Dowex M 4195 chelating resin can be used as high as greater than 100 experiments without any loss in its sorption behavior.

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References

- [1] Z.W. Li, C.L. Bao, K. Zhang, Separation and preconcentration of trace gold, platinum, palladium in geological samples with alizarin red-S chelate resin and its determination, Chem. J. Chin. Un.-Chin. 19 (1998) 1062–1064.
- [2] L. Elci, D. Sahan, A. Başaran, M. Soylak, Solid phase extraction of gold (III) on Amberlite XAD-2000 for its flame atomic absorption spectrometric determinations, Environ. Monit. Assess. 132 (2007) 331–338.

- [3] N. Pourreza, H. Parham, S. Elhami, Study of the effect of surfactants on the determination of gold by flame atomic absorption spectrometry, *Asian J. Chem.* 16 (2004) 784–790.
- [4] L. Tavakkoli, Y. Yamini, H. Ebrahimzadeh, A. Nezhadali, S. Shariati, F. Noormohamadian, Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES, *J. Hazard. Mater.*, in press.
- [5] Z.H. Sun, K. Zhu, Y. Mao, W.G. Wang, Determination of trace platinum, palladium and gold in samples by ICP-AES and fire assay preconcentration, *Spectrosc. Spectr. Anal.* 24 (2004) 233–235.
- [6] L. Elçi, M. Soylak, E.B. Büyükkşekerçi, Separation of gold, palladium and platinum from metallurgical samples using an Amberlite XAD-7 resin column prior to their atomic absorption spectrometric determinations, *Anal. Sci.* 19 (2003) 1621–1624.
- [7] B.L. Gong, X.Q. Li, F.R. Wang, X.J. Chang, Synthesis and efficiency of a spherical macroporous epoxy-dicyandiamide chelate resin for preconcentrating and separating trace Au, Hg, Pd and Ru from samples, *Chem. Res. Chin. Un.* 17 (2001) 168–174.
- [8] E.A. Moawed, N. Burham, M.F. El-Shahat, Selective separation and determination of copper and gold in gold alloy using ion exchange polyurethane foam, *J. Liquid Chrom. Related Techn.* 30 (2007) 1903–1914.
- [9] Z.J. Huang, F. Huang, X.J. Yang, Q.Y. Wei, C. Jing, Solid phase extraction and spectrophotometric determination of trace gold using 5-(4-carboxylphenylazo)-8-hydroxyquinoline, *Chemia Analytica* 52 (2007) 93–101.
- [10] M. Soylak, L. Elçi, M. Doğan, A sorbent extraction procedure for the preconcentration of gold, silver and palladium on an activated carbon column, *Anal. Lett.* 33 (2000) 513–525.
- [11] H.Y. Wang, S.H. Qian, S.B. Mo, G.Q. Huang, Application studies of crosslinked chitosan in preconcentration and separation of trace Au(III), *Chin. J. Anal. Chem.* 33 (2005) 198–200.
- [12] M.S. El-Shahawi, A.S. Bashammakh, S.O. Bahaffi, Chemical speciation and recovery of gold(I, III) from wastewater and silver by liquid–liquid extraction with the ion-pair reagent amiloride mono hydrochloride and AAS determination, *Talanta* 72 (2007) 1494–1499.
- [13] D. Rekhha, P.R. Prasad, P. Chiranjeevi, Platinum determination in environmental samples using preconcentration cloud-point extraction with flame atomic absorption spectrometry, *Environ. Monit. Assess.*, in press.
- [14] X.P. Luo, Q. Yan, H.Q. Peng, Solvent extraction of gold from polysulfide solution, *Hydrometallurgy* 82 (2006) 144–149.
- [15] F.J. Alguacil, P. Adeva, M. Alonso, Processing of residual gold (III) solutions via ion exchange, *Gold Bull.* 38 (2005) 9–13.
- [16] A. Zwir-Ferenc, M. Biziuk, Solid phase extraction technique—trends, opportunities and applications, *Polish J. Environ. Stud.* 15 (2006) 677–690.
- [17] S.H. Chen, M.F. Xiao, D.B. Lu, Z.X. Hu, X.L. Zhan, Preconcentration and separation of gold and palladium in geological samples via solid-phase extraction on carbon nanofibers prior to sample analysis by ICP-MS, *Atom. Spectr.* 28 (2007) 90–94.
- [18] Q.M. Li, X.H. Zhao, K. Jiang, G.G. Liu, Study of spectrophotometric method for determination of trace copper after the separation and enrichment with solid phase extractant-microcrystalline phenolphthalein, *Chin. Sci. Bull.* 52 (2007) 65–70.
- [19] Y.W. Wu, B. Hu, J. Chen, Z.C. Jiang, Assessment of YPA(4) chelating resin for the separation and determination of Pt, Pd, Ru, Rh, and Au in geological samples by ICP-OES, *Atom. Spectr.* 25 (2004) 257–262.
- [20] N. Rajesh, S. Manikandan, Spectrophotometric determination of lead after preconcentration of its diphenylthiocarbazono complex on an Amberlite XAD-1180 column, *Spectrochim. Acta Part A*, in press.
- [21] H.B. Senturk, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, L. Elci, M. Tufekci, Separation and enrichment of gold(III) from environmental samples prior to its flame atomic absorption spectrometric determination, *J. Hazard. Mater.* 149 (2007) 317–323.
- [22] http://www.dow.com/liquidseps/prod/dx_m4195.htm
- [23] C.V. Diniz, F.M. Doyle, V.S.T. Ciminelli, Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin Dowex M-4195, *Separation Sci. Technol.* 37 (2002) 3169–3185.
- [24] C.V. Diniza, V.S.T. Ciminelli, F.M. Doyle, The use of the chelating resin Dowex M-4195 in the adsorption selected heavy metal ions from manganese solutions, *Hydrometallurgy* 78 (2005) 147–155.
- [25] D.Y. Lee, Y.N. Shih, H.C. Zheng, C.P. Chen, K.W. Juang, J.F. Lee, L. Tsui, Using the selective ion exchange resin extraction and XANES methods to evaluate the effect of compost amendments on soil chromium(VI) phytotoxicity, *Plant Soil* 281 (2007) 87–96.
- [26] F.D. Mendes, A.H. Martins, Selective sorption of nickel and cobalt from sulphate solutions using chelating resins, *Int. J. Miner. Process.* 74 (2004) 359–371.
- [27] M. Soylak, H. Çolak, M. Tuzen, O. Türkoğlu, L. Elçi, Comparison of digestion procedures for commercial powdered soup samples for the determination of their trace metal contents by AAS, *J. Food Drug Anal.* 14 (2006) 62–67.
- [28] O.D. Uluozlu, K. Kinalioglu, M. Tuzen, M. Soylak, Trace metal levels in lichen samples from roadsides in East Black Sea region, Turkey, *Biomed. Environ. Sci.* 20 (2007) 203–207.
- [29] M. Soylak, B. Kaya, M. Tuzen, Copper (II)-8-hydroxyquinoline coprecipitation system for preconcentration and separation of cobalt(II) and manganese(II) in real samples, *J. Hazard. Mater.* 147 (2007) 832–837.
- [30] Q.X. Zhou, H.H. Bai, J.P. Xiao, Preconcentration of nickel in multi-walled carbon nanotubes pretreated with potassium permanganate for use as solid-phase extraction adsorbent and determination by flame atomic absorption spectrometry, *Atom. Spectrosc.* 28 (2007) 150–155.
- [31] D. Perez-Quintanilla, A. Sanchez, I. del Hierro, M. Fajardo, I. Sierra, Functionalized HMS mesoporous silica as solid phase extractant for Pb(II) prior to its determination by flame atomic absorption spectrometry, *J. Sep. Sci.* 30 (2007) 1556–1567.
- [32] S. Baytak, E. Kenduzler, A.R. Turker, N. Gok, Penicillium digitatum immobilized on pumice stone as a new solid phase extractor for preconcentration and/or separation of trace metals in environmental samples, *J. Hazard. Mater.*, in press.
- [33] M. Soylak, L. Elci, M. Dogan, Spectrophotometric determination of trace amounts of tungsten in geological samples after preconcentration on Amberlite XAD-1180, *Talanta* 42 (1995) 1513–1517.
- [34] M. Tuzen, K. Parlar, M. Soylak, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction, *J. Hazard. Mater.* 121 (2005) 79–87.
- [35] M. Noroozifar, M. Khorasani-Motlagh, R. Akbari, Application of pneumatic flow injection-tandem spectrometer system for chromium speciation, *J. Autom. Methods Manage. Chem.* (2007), Article ID 34373.
- [36] P. Subrahmanyam, B.K. Priya, B. Jayaraj, P. Chiranjeevi, Determination of Cd, Cr, Cu, Pb and Zn from various water samples with use of FAAS techniques after the solid phase extraction on rice bran, *Toxicol. Environ. Chem.* 90 (2007) 97–106.
- [37] M. Iglesias, E. Antico, V. Salvado, Recovery of palladium(II) and gold(III) from diluted liquors using the resin duolite GT-73, *Anal. Chim. Acta* 381 (1999) 61–67.
- [38] S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, Synthesis of amidinothioureido-silicagel and its application to flame atomic absorption spectrometric determination of silver, gold and palladium with on-line preconcentration and separation, *Anal. Chim. Acta* 452 (2002) 223–230.
- [39] M. Bagheri, M.H. Mashhadizadeh, S. Razei, Solid phase extraction of gold by sorption on octadecyl silica membrane disks modified with pentathia-15-crown-5 and determination by AAS, *Talanta* 60 (2003) 839–844.
- [40] T. Saitoh, S. Suzuki, M. Hiraide, Solid phase extraction of some precious metals from hydrochloric acid to polystyrene-divinylbenzene porous resin impregnated with polyoxyethylene-type nonionic surfactant, *J. Chromatogr. A* 1097 (2005) 179–182.