Solid Phase Extraction of Trace Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) Ions in Beverages on Functionalized Polymer Microspheres Prior to Flame Atomic Absorption Spectrometric Determinations

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In this study, poly(glycidyl methacrylate-methyl methacrylate-divinylbenzene) was synthesized in the form of microspheres, and then functionalized by 2-aminobenzothiazole ligand. The sorption properties of these functionalized microspheres were investigated for separation, preconcentration and determination of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) ions using flame atomic absorption spectrometry. The optimum pH values for quantitative sorption were 2–4, 5–8, 6–8, 4–6, 2–6 and 2–3 for Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II), respectively, and also the highest sorption capacity of the functionalized microspheres was found to be for Cu(II) with the value of 1.87 mmol g⁻¹. The detection limits (3σ; N = 6) obtained for the studied metals in the optimal conditions were observed in the range of 0.26–2.20 µg L⁻¹. The proposed method was successfully applied to different beverage samples for the determination of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) ions, with the relative standard deviation of <3.7%.

Keywords Trace metal sorption, solid phase extraction, functionalized polymer microspheres, flame atomic absorption spectrometry, beverages

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Introduction

In recent years, the determination, preconcentration and separation of metal ions at trace levels in food and water samples have become an important issue in the context of analytical chemistry.^{1–4} However, the direct analysis of trace metals is limited due to the presence of matrix interferences and the low metal ion concentrations, which results in low sensitivity and accuracy of analytical techniques.^{5,6} To improve the selectivity and detection limit of trace metal ions determination in complex matrices, various preconcentration and separation methods have been developed such as co-precipitation,⁷ cloud point extraction,⁸ liquid-liquid extraction (LLE),⁹ dispersive liquid-liquid micro-extraction (DLLME),¹⁰ and solid phase extraction (SPE).^{11,12} SPE offers several advantages including simplicity, rapidity, flexibility in choosing the adsorbents with different properties, high sensitivity, efficiency, preconcentration factor and safety, low cost and organic solvent consumption, short extraction time and ease of automation.^{13–17} SPE is a surface dependent method, and so the particle size and surface area of the sorbent materials directly affect the efficiency of SPE.¹⁸

Polymer materials have been of great interest as adsorbents for the solid phase extraction of metal ions from aqueous solutions, owing to their excellent mechanical, thermal and

chemical stability, and reusability.^{6,17,19–23} These polymers are functionalized by metal chelate forming agents or ligands, in which the ligand molecules are covalently bonded to the polymer active sites consisting of functional groups such as hydroxyl, carboxyl, amino, glycidyl, pyridine and chloride, in order to obtain further selectivity, affinity and capacity towards the metal ions.^{24,25} Moreover, a polymeric material designed as sorbent with a proper combination of a ligand and an insoluble polymer support can show triple functionality such as physical adsorption, chelate formation and ion exchange for target metal ions.^{24,26,27}

The functionalized polymeric materials used as solid phase sorbents for the applications of selective trace metal ion preconcentration, separation and determination can be prepared in various forms such as resin, microsphere (or bead), gel or disk. Among them, the crosslinked porous microspheres are mainly preferred due to their high surface areas, porosity, ease of preparation with desired size, durability, superior mobility and easy recovery from dispersion.^{12,24,27–33} Glycidyl methacrylate (GMA), a commercial industrial monomer possessing an epoxide ring in the side chain, is more appropriate for the preparation of functionalized porous microspheres with desired particle and pore size, and also their surfaces are easily modified *via* ring opening reaction of these glycidyl groups with various types of ligands.^{16,25,27,34} In addition, the choice of ligand chemically attached to the polymer support is of great importance in terms of achieving high metal ion selectivity and capacity. In this respect, thiazole derivatives, which are

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heterocyclic compounds containing nitrogen (N) and sulfur (S) donor atoms, have been found to be one of the efficient polydentate ligands used in the functionalization of polymeric supports.^{21,34–39} N and S donor centers in the thiazole ring exhibit excellent sorption selectivity for some metal ions including divalent transition metal ions and noble metals because of their strong affinity to form complexes with these types of metal ions, and also thiazoles show interesting physicochemical properties and remarkable biological and pharmacological activities, and have applications in different fields.^{40–45}

This study focuses on the effectiveness of 2-aminobenzothiazole (ABTAL) functionalized polymeric microspheres consisting of poly(glycidyl methacrylate-methyl methacrylate-divinylbenzene), poly(GMA-MMA-DVB) used as solid phase adsorbent for selective preconcentration/separation and sensitive determination of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) ions in different beverages by using flame atomic absorption spectrometry (FAAS). For this purpose, crosslinked porous GMA-MMA-DVB terpolymer was synthesized in the form of microsphere by suspension polymerization, and then functionalized with ABTAL via ring opening reactions of epoxide groups belonging to GMA. The determination of optimum conditions in the solid phase extraction method applied to enrich the specified metal ions on these functionalized microspheres was carried out using the column method. Lastly, the developed method was performed to determine Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) ions in various beverage samples in different types of containers.

Experimental

Chemicals

Analytical grade chemicals such as glycidyl methacrylate (GMA; 97%) (Acros Organics), methyl methacrylate (MMA; 99%) (Acros Organics), divinyl benzene (DVB; 80%) (Sigma-Aldrich), sodium sulfate (E. Merck), poly(vinyl alcohol) (PVOH; 98% hydrolyzed and $M_w \approx 100000$) (Boysan Co.), 2-aminobenzothiazole (ABTAL) (Sigma-Aldrich), toluene (E. Merck) and dimethylformamide (DMF) (Fluka) were used as received. Another chemical used was benzoyl peroxide (BPO) (E. Merck) and it was purified by crystallization in cold methanol before being used. The working solutions of aluminium; Al(III), iron; Fe(II), cobalt; Co(II), copper; Cu(II), cadmium; Cd(II) and lead; Pb(II) ions were freshly prepared by diluting their standard stock solutions appropriately (1000 mg L^{-1}) (Merck) with 0.1 M HNO_3 . All beverages consisting of cola, soda, and orange, peach, apricot and cherry juice, which are found in different containers such as plastic, can, glass and Tetra Brik, were purchased from the local markets in Istanbul, Turkey. Deionized water used for all experiments was obtained using a Milli-Q Water Purification System (Millipore, USA).

Instruments

The specific surface area of the polymer microspheres was determined according to the Brunauer-Emmett-Teller (BET) method (surface area analyzer, Quantachrome Instruments). Infrared spectra of the polymer samples were recorded in the range $4000 - 750 \text{ cm}^{-1}$ using an IR-Prestige 21, Shimadzu Fourier transform infrared (FTIR) spectrophotometer in attenuated total reflection (ATR) mode with 16 scans per sample and 4 cm^{-1} of resolution. The pH of the aqueous solutions was measured by a pH-meter having a glass-electrode (Sartorius PP-

Table 1 The operating conditions of FAAS

Parameter	Metal ion					
	Al	Fe	Co	Cu	Cd	Pb
Wavelength/nm	309.3	248.3	240.7	324.8	228.8	217.0
HCl flow rate/L min ⁻¹	6.0	4.0	6.0	4.0	4.0	5.0
N ₂ O flow rate/L min ⁻¹	4.7	—	—	—	—	—
C ₂ H ₂ flow rate/L min ⁻¹	4.2	0.8	0.8	0.6	0.6	0.6
Air flow rate/L min ⁻¹	—	6.0	6.0	6.0	4.0	4.0
Slit/nm	0.5	0.2	0.2	0.5	0.5	0.5

15). The concentrations of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) elements were determined by a flame atomic absorption spectrometer (FAAS) (Perkin-Elmer AAnalyst 700) with hollow cathode lamps. The operating conditions of FAAS instrument (previously standardized) for these trace elements are given in Table 1.

Preparation of 2-aminobenzothiazole functionalized microspheres

Crosslinked porous polymeric microspheres were obtained by suspension polymerization of GMA (8.5 mL), MMA (9.0 mL), DVB (2.5 mL) and BPO (0.3 g) mixture in 20 mL toluene using a continuous phase consisting of water (100 mL), PVOH (0.5 g) as polymeric stabilizer and sodium sulfate (1.3 g) as inorganic stabilizer according to the previous paper.⁴⁶ For the functionalization, 5 g of the obtained microspheres having $150 - 300 \mu\text{m}$ size range were placed in a glass flask containing DMF (30 mL) and left overnight to swell. After that, 12 g ABTAL was added to the flask and the reaction mixture was magnetically stirred under nitrogen atmosphere at 100°C in a thermostatic oil bath for 72 h. At the end of this period, the solid phase separated from the cooled reaction mixture at room temperature. Following washing the solid phase with DMF, water, acetone and ether, respectively, the resulting functionalized microspheres, poly(GMA-MMA-DVB)-ABTAL were kept in a vacuum oven at 40°C for 24 h in order to completely remove solvents.

Solid phase extraction procedure

A glass column, 5 mm in diameter was packed with 20 mg of ABTAL functionalized GMA-MMA-DVB terpolymer microspheres. It was treated with 3.0 mL of 3.0 M HNO_3 and washed with doubled-distilled water until the acid was completely removed from the microspheres. An appropriate aliquot of the solution having Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) in the concentration range of 0.010 to $0.10 \mu\text{g mL}^{-1}$ was passed through with an optimum flow rate after setting the appropriate pH. The stripping of the metals from the microspheres was done with appropriate eluting agents such as HCl or HNO_3 ($1.0 - 5.0 \text{ mL}$). The optimum parameters applied in this procedure are given in Table 2. The eluents were taken in a 5-mL flask and their volumes increased by double distilled water. Finally, they were aspirated into the flame for FAAS measurements.

Sampling and sample digestion

In order to remove the suspended solid before the analyses, the samples were passed through a membrane filter with $0.45 \mu\text{m}$ pore size. Special attention was given to avoid contamination at each step of the sample preparation for obtaining precise and stable analytical signals. In this study,

Table 2 Parameters optimized for sorption and desorption of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) on poly(GMA-MMA-DVB)-ABTAL microspheres

Parameter	Metal ion					
	Al	Fe	Co	Cu	Cd	Pb
pH range	2 – 4	5 – 8	6 – 8	4 – 6	2 – 6	2 – 3
Flow rate/mL min ⁻¹	2.0 – 3.0	1.5 – 2.5	2.0 – 3.0	1.5 – 2.5	2.0 – 3.0	1.5 – 2.5
Eluent concentration	4 M HCl	1 M HCl	1 M HCl	2 M HCl	2 M HNO ₃	3 M HNO ₃
Eluent volume/mL	5	4	4	5	3	2
Preconcentration factor	200	160	140	200	120	180
Average recovery, %	98	99	98	99	99	97
Relative std. deviation, %	2.8	4.2	3.7	4.6	2.3	3.5

Fig. 1 SEM images of poly(GMA-MMA-DVB) (a) and poly(GMA-MMA-DVB)-ABTAL (b) microspheres.

the digestion procedure used was based on an ultrasound-assisted method, so in summary, the samples prepared with acid solutions (as given in Table 2) were taken into glass tubes, and then they were sonicated inside the ultrasonic water bath with an ultrasonic energy of 35 kHz at 80°C for 20 min, as mentioned in the literature.⁴⁷ After that, the final solutions were collected in glass flasks for the determinations of metal ions by FAAS. Blanks were also treated in the same way. Standard reference material, NIST-SRM 1575a pine needles, was studied to confirm the accuracy and precision of the proposed method. The reference material was also prepared by applying the digestion procedure mentioned above.

Results and Discussion

Characterization of the ABTAL functionalized microspheres

Crosslinked porous GMA-MMA-DVB terpolymer microspheres were obtained by conventional suspension polymerization method, and the polymerization yield was over 90%. In order to use an appropriate particle size fraction in metal uptake experiments, the resulting microspheres were shifted using standard sieves with mesh sizes in the range from 106 to 800 µm, and among them, those sized 150 – 300 µm were chosen for use as chelating polymer sorbents. The specific surface area of the microspheres in that range was found to be 1.51 m² g⁻¹.

Figure 1a shows the SEM image of the microspheres used in the functionalization process. As can be seen, the microspheres were properly created with smooth surfaces. Then, these microspheres were treated with 2-aminobenzothiazole (ABTAL) ligand in which the primary amine groups of ABTAL are reacted

with epoxide ring groups located on the microsphere surfaces. By the ring opening reactions of epoxides, ABTAL molecules are covalently bound to the microsphere surface, and new hydroxyl and secondary amine groups occurred, as presented in Fig. 2. These reactions also changed the appearance of the microsphere surfaces; a significant roughness appeared, which proves the ligand attachment after the functionalization (Fig. 1b).

FTIR analysis is one of the simple and useful routes for determining the changes in the polymer structure. Figure 3 shows the FTIR spectra of the neat and functionalized microspheres. In Fig. 3a, the characteristic peaks indicating C-H, >C=O and -C-O- stretching and C-H bending vibrations of the GMA-MMA-DVB terpolymer structure are seen at 2935, 1722 and 1140 cm⁻¹, respectively. Also, the other peaks appearing at 904 and 837 cm⁻¹ characterize the C-O and C-O-C stretching vibrations of epoxide groups of GMA units in the polymer structure. On the other hand, the new peaks were observed in the FTIR spectrum of the functionalized polymer structure, and the existing vibration peaks were shifted and their intensities varied (Fig. 3b). The new broad peak that emerged in the range of 3600 – 3200 cm⁻¹ represents the overlapped stretching vibrations of -OH and -NH groups. These groups are formed as a result of the reactions between the epoxide groups on the polymer surfaces and ABTAL molecules. The peaks at 1537 and 1022 cm⁻¹ are also caused by N-H bending and C-N stretching vibrations of the amine groups of ABTAL, respectively.⁴⁸ In addition, the characteristic peak at 904 cm⁻¹ of the epoxide ring nearly disappeared, but there was not much change in the peak at 837 cm⁻¹ of this ring due to the overlapping of the stretching bands of the C-O-C and thiazole ring.⁴⁹ Consequently, the FTIR analysis results indicated that ABTAL

Fig. 2 Functionalization of poly(GMA-MMA-DVB) microspheres by 2-aminobenzothiazole (ABTAL) ligand.

Fig. 3 FTIR spectra of poly(GMA-MMA-DVB) (a) and poly(GMA-MMA-DVB)-ABTAL (b) microspheres.

Fig. 4 Effect of pH on the sorption of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II).

was significantly covalently bonded through the epoxide groups of the polymer microspheres.

Another effective route to analyze whether the ligand is bonded to the polymer *via* the epoxide groups is determination of the epoxide content of polymer matrix. Accordingly, the HCl-dioxane method was used to find the epoxide contents of the microspheres in this study.⁵⁰ A decrease is expected in the epoxide content of the microspheres after the functionalization process, due to the occurrence of ring opening reactions between the epoxide groups on the microsphere surfaces and the primary amine groups of ABTAL. The experimental epoxide contents of the neat poly(GMA-MMA-DVB) and poly(GMA-MMA-DVB)-ABTAL microspheres were found to be 2.73 and 0.80 mmol g⁻¹, respectively. This result indicated that 70.7% of epoxide groups of the microspheres was chemically functionalized with ABTAL. Considering the results of the FTIR analysis and the determination of the epoxide content, it can be said that a number of epoxide groups remained in the crosslinked polymer structure without being functionalized.

Effect of pH on sorption

The effect of pH on the metal sorption degree was examined using the column process. First, 30 mg of ABTAL functionalized polymer microspheres was placed in a column with 5 mm

diameter, and a proper aliquot of the solutions consisting of Al(III), Fe(II), Co(II), Cu(II), Cd(II) or Pb(II) ions was passed through this column at an appropriate flow rate and at various pH values. The metal sorption percentages were calculated by measuring the content of metals in supernatant liquid and also by stripping of metals from the microspheres with eluents composed of 4.0 M HCl for Al(II), 1.0 M HCl for Fe(II) and Co(II), 2.0 M HCl for Cu(II), 2.0 M HNO₃ for Cd(II) and 3.0 M HNO₃ for Pb, respectively. The obtained recoveries of these metal ions depending on the pH are given in Fig. 4. The maximum recovery values for each metal ion were determined at different pH ranges. For Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II), these optimum pH ranges were 2 – 4, 5 – 8, 6 – 8, 4 – 6, 2 – 6 and 2 – 3 respectively.

Effect of flow rate on sorption

The effect of the eluent flow rate on the sorption degree of metal ions onto the functionalized microspheres was investigated. The solutions were passed through the column by adjusting the flow rate between 0.5 – 5.0 mL min⁻¹. As a result, the optimum flow rate was found to be 2.0 mL min⁻¹ for all six metal ions, and above this flow rate, a decrease in percentage sorption was detected.

Adsorption capacity of the microspheres

The following procedure was applied to determine the capacity of the microspheres used for the metal ion adsorption. First, 30 mg of microspheres was stirred with 50 mL solution of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) containing 4 – 400 µg metal ions at their respective pH and at 25°C for 1 h to achieve complete equilibrium. The difference between the concentrations of metal ions before and after desorption was used to calculate the loading capacity of the polymer microspheres for each metal ion. The obtained data are given in Table 3. The values of adsorption capacity per 1 g of microspheres varied from 1.28 to 1.87 mmol depending on the type of metal ions. The microspheres showed the maximum adsorption capacity for Cu(II).

Stability test of the microspheres

The reusability of the microsphere bed in sorption-desorption processes was tested 80 times for each of the six metal ions. After the repeated use of this bed, the maximum change in its performance (sorption capacity) was found to be <3%. This indicates that it is possible to reuse these microspheres. Moreover, no change in sorption capacity of the microspheres was detected after 10 months of storage.

Effect of sample volume on the recoveries and preconcentration factor

To investigate the potential of enriching low concentrations of the analytes from the large sample volume, the metal ion sorption degree was examined by considering the effect of sample volume. Thus, 50 – 1250 mL of volumes were passed through the chelating microspheres column at a flow rate of 2.5 mL min⁻¹. The added analyte amount was constant (0.1 µg mL⁻¹). Consequently, the effect of sample volume of less than 1000 mL was insignificant on the adsorption of metal

ions using 20 mg of the microspheres. On the other hand, a decrease in the percent sorption for the analytes occurred when this volume was exceeded. Based on these results, 1000 mL of sample solution was used for the preconcentration of the working ions from the beverage samples, and the adsorbed metals could be eluted with HCl or HNO₃ (as indicated in Table 2). The highest preconcentration factor was found to be 200 for Al(III) and Cu(II) ions when the eluent volume used was 5 mL. The values found for other metals are shown in Table 2.

Effect of some cations and anions

In order to confirm the analytical application possibilities of the developed method, the effect of some cations and anions consisting of K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HPO₄²⁻, Ni²⁺, Hg²⁺, Mn²⁺ and Zn²⁺, which have the potential to interfere with the determination of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) in a real sample, were analyzed under the specified conditions. Accordingly, 1 µg mL⁻¹ solutions of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) including the interfering ions were used. The obtained recoveries data for Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) are given in Table 4. At less than 2000 µg mL⁻¹ of K⁺, Na⁺, Ca²⁺, Mg²⁺ and Cl⁻, 800 µg mL⁻¹ of SO₄²⁻ and HPO₄²⁻, and 200 µg mL⁻¹ of Ni²⁺, Hg²⁺, Mn²⁺ and Zn²⁺, there was no interfering effects of these ions on the analyte determinations. The recovery percentages for Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) were not lower than those without coexisting ions. This indicates that poly(GMA-MMA-DVB)-ABTAL microspheres have a high selectivity towards Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II), and potential for application in real sample analyses.

Analytical precision and detection limits

The standard solutions were divided into six portions (*N* = 6), and then all portions were treated and analyzed at the same time under the determined conditions. The analysis results showed that the relative standard deviations (RSD) of the method was lower than 5% [Al(III); 4.2%, Fe(II); 2.3%, Co(II); 3.8%, Cu(II); 1.7%, Cd(II); 4.6%, and Pb(II); 3.5%]. Accordingly, it is clearly seen that this method provides a good precision for the analysis of trace ions such as Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) in solution samples. In addition, it was found that the detection limits (3σ; *N* = 6) were 0.26, 0.63, 1.47, 0.85, 2.20 and 0.34 µg L⁻¹ for Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II), respectively. The linear range of the method was between 6.50 and 50.00 µg mL⁻¹ with a better correlation coefficient than 0.999.

Table 3 Adsorption capacity of poly(GMA-MMA-DVB)-ABTAL microspheres for the metal ions

Metal ion	Capacity/mmol g ⁻¹ microspheres
Al(III)	1.31
Fe(II)	1.76
Co(II)	1.81
Cu(II)	1.87
Cd(II)	1.63
Pb(II)	1.28

Table 4 Effect of coexisting ion on recovery of Al(III), Fe(II), Co(II), Cu(II), Cd(II) and Pb(II) adsorbed on poly(GMA-MMA-DVB)-ABTAL

Coexisting ion	Concentration/µg mL ⁻¹	Recovery analytes, %					
		Al(III)	Fe(II)	Co(II)	Cu(II)	Cd(II)	Pb(II)
K ⁺	2000	96.3	95.9	96.5	98.6	99.1	96.5
Na ²⁺	2000	98.5	98.2	99.8	99.2	95.3	96.8
Ca ²⁺	2000	97.4	99.8	98.5	97.7	96.2	99.5
Mg ²⁺	2000	95.8	97.5	98.9	95.3	96.5	97.4
Cl ⁻	2000	96.7	100.1	97.6	98.5	95.9	98.3
SO ₄ ²⁻	800	97.5	98.5	96.4	101.1	98.7	99.2
HPO ₄ ²⁻	800	96.8	97.9	100.4	95.9	99.3	97.7
Ni ²⁺	200	95.5	96.8	98.7	98.1	100.2	96.4
Hg ²⁺	200	96.2	99.1	96.6	97.4	96.8	100.2
Mn ²⁺	200	95.2	99.8	99.9	96.6	95.9	99.8
Zn ²⁺	200	97.5	98.6	100.1	97.2	96.7	98.2

Table 5 Results of some beverage samples from Istanbul, Turkey (V_{sample} : 1000 mL; V_{final} : 5 mL, $N = 6$)

Sample	Type of container	Metal levels in beverages/ $\mu\text{g L}^{-1}$					
		Al(III)	Fe(II)	Co(II)	Cu(II)	Cd(II)	Pb(II)
Cola	Plastic	151 $\pm$ 15	762 $\pm$ 14	14.5 $\pm$ 2.1	78 $\pm$ 17	25 $\pm$ 4.7	33 $\pm$ 5.8
	Can	417 $\pm$ 18	619 $\pm$ 20	17.8 $\pm$ 2.0	105 $\pm$ 11	31 $\pm$ 3.7	45 $\pm$ 4.9
	Glass	188 $\pm$ 12	688 $\pm$ 18	11.5 $\pm$ 2.3	150 $\pm$ 23	20 $\pm$ 2.9	27 $\pm$ 3.5
Soda	Plastic	98 $\pm$ 6	1217 $\pm$ 13	19.6 $\pm$ 3.4	218 $\pm$ 20	3.5 $\pm$ 0.2	11 $\pm$ 3.7
	Can	314 $\pm$ 13	917 $\pm$ 16	11.3 $\pm$ 3.3	220 $\pm$ 31	3.9 $\pm$ 0.6	17 $\pm$ 2.0
	Glass	115 $\pm$ 11	885 $\pm$ 12	4.7 $\pm$ 1.9	246 $\pm$ 25	4.1 $\pm$ 0.2	14 $\pm$ 2.3
Orange juice	Plastic	275 $\pm$ 17	1413 $\pm$ 18	8.5 $\pm$ 1.3	44 $\pm$ 10	0.8 $\pm$ 0.08	3.7 $\pm$ 4.8
	Can	463 $\pm$ 21	1244 $\pm$ 21	14.1 $\pm$ 1.2	17 $\pm$ 5	1.2 $\pm$ 0.3	11.3 $\pm$ 3.1
	Glass	257 $\pm$ 16	1568 $\pm$ 19	8.1 $\pm$ 1.1	38 $\pm$ 9	1.4 $\pm$ 0.4	5.5 $\pm$ 1.8
Peach and apricot juice	Tetra Brik	385 $\pm$ 18	1644 $\pm$ 22	10.5 $\pm$ 1.1	75 $\pm$ 21	2.2 $\pm$ 0.4	6.5 $\pm$ 2.2
	Can	515 $\pm$ 15	813 $\pm$ 17	8.4 $\pm$ 1.6	8 $\pm$ 2.8	13 $\pm$ 4.2	32 $\pm$ 6.7
	Glass	272 $\pm$ 22	994 $\pm$ 18	5.3 $\pm$ 1.3	19 $\pm$ 4.1	9 $\pm$ 3.2	9.9 $\pm$ 3.4
Cherry juice	Tetra Brik	319 $\pm$ 10	880 $\pm$ 24	12.6 $\pm$ 1.8	11 $\pm$ 3.8	17 $\pm$ 4.1	21 $\pm$ 4.8
	Can	419 $\pm$ 17	771 $\pm$ 13	4.8 $\pm$ 1.4	42 $\pm$ 8	1.6 $\pm$ 0.1	11 $\pm$ 1.6
	Glass	288 $\pm$ 19	916 $\pm$ 16	1.9 $\pm$ 0.6	27 $\pm$ 5.2	1.1 $\pm$ 0.1	5.4 $\pm$ 0.8
	Tetra Brik	385 $\pm$ 17	1212 $\pm$ 25	2.4 $\pm$ 0.5	14 $\pm$ 3.6	1.2 $\pm$ 0.1	8.0 $\pm$ 1.4

Table 6 Analysis of SRM 1575a (pine needles) by the presented method ($N = 6$)

Analyte	Concentration/ mg kg^{-1}	
	Certified value	Determined value
Al(III)	580 $\pm$ 30	576 $\pm$ 32
Fe(II)	46 $\pm$ 2	50 $\pm$ 4
Co(II)	0.061 $\pm$ 0.002	0.058 $\pm$ 0.001
Cu(II)	2.8 $\pm$ 0.2	2.9 $\pm$ 0.2
Cd(II)	0.233 $\pm$ 0.004	0.235 $\pm$ 0.005
Pb(II)	0.167 $\pm$ 0.015	0.169 $\pm$ 0.013

p : 0.95; $\bar{x} \pm t.s/\sqrt{N}$.

Application of the method for beverages

The feasibility of the developed method was investigated for the determination of the elements in beverage samples. The results obtained after three replicate measurements are shown in Table 5. The level of each metal ion in the beverages, which were determined by using ABTAL functionalized microspheres, showed variation depending on the type of container. Also, as expected, each metal ion level was quite different for each beverage sample in similar containers. The RSD values were in the range of 1.8 – 3.7% for the beverage samples. These results showed that the procedure was successfully applied for the selective preconcentration and determination of target elements in complex matrices. Also, the recommended method providing high accuracy and precision could be applied with high repeatability.

The validity of the presented procedure was also carried out by analyzing SRM 1576a pine needles. Table 6 includes the certified and detected values for SRM. The results were in good agreement with the SRM's certified values.

Conclusions

This study has indicated the adequacy and feasibility of the SPE method based on ABTAL functionalized GMA-MMA-DVB terpolymer microspheres prior to their FAAS determinations. This method was simple, and could be easily and rapidly applied

to different beverage samples. The separation and preconcentration procedure has a good enrichment factor, and low detection limits were achieved without using organic solvent so that environmental pollution is minimized. Consequently, this developed method can be successfully used for the preconcentration and determination of mentioned analyte ions in different real samples.

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