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Preconcentration of Aluminum on Nano ZrO_2/B_2O_3 and Its Determination by Flame Atomic Absorption Spectrometry

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ABSTRACT This study presents a chelating agent free solid phase extraction method for preconcentration of Al(III) using hybrid nano zirconium dioxide–boron oxide (ZrO_2/B_2O_3) sorbent. This method is based on the sorption of Al(III) ions directly onto nano sorbent, followed by the elution with 10 mL of 4 mol L^{-1} HNO_3 and determination by flame atomic absorption spectrometry (FAAS). Preconcentration parameters, including pH of the sample solution, volume and concentration of the eluent, sample volume, and flow rate of the sample solution, that affect the recovery of the Al(III) ions have been optimized. Under the optimized experimental conditions, analytical parameters such as limit of detection, limit of quantification, linear working range, precision, and accuracy were determined. The analytical limit of detection for Al(III) was found as 7.71 μg L^{-1}. The reusability and adsorption capacity of the new hybrid sorbent for Al(III) ions were also investigated. Interfering effects of matrix constituent on the recovery of the Al(III) ions were studied. The accuracy of the method was checked by determining Al(III) ions in a certified reference water sample (SPS-WW1 Waste Water). The proposed procedure was applied for the determination of Al(III) ions in dam waters.

KEYWORDS aluminum, flame atomic absorption spectrometry, nano sorbent, preconcentration, solid phase extraction

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INTRODUCTION

Aluminum is the richest element in the earth's crust (8.1% by weight) and is a redundant element to which humans are frequently exposed.[1] Aluminum is most commonly used in the food industry as packing materials[2] and in other industry arms such as aerospace and the automotive and metal industries due to its special properties, especially its corrosion resistance and easy processing properties.[3] Accumulation of Al in tissue may increase the risk of neurological and bone diseases, such as Alzheimer disease, Parkinson disease, encephalopathy/dialysis dementia, and osteomalacia.[4] Determination of trace levels of aluminum in water and food samples is very important in environmental chemistry because of aluminum's negative effect on human health.[5,6]

The levels of aluminum in natural waters can vary significantly depending on various physicochemical and mineralogical processes. Aluminum levels in waters with near-neutral pH values usually range from 0.001 to 0.05 mg L^{-1}.[7] Direct determination of these concentrations by flame atomic absorption spectrometry (FAAS) without using a separation/preconcentration technique is impossible due to the low detection limits of FAAS.[8]

Various methods are used for the determination of trace levels of aluminum in food and environmental samples. These methods can be classified as electrochemical methods, chromatographic methods, and spectrometric methods. Especially, spectrometric methods such as FAAS,[9,10] electrothermal atomic absorption spectrometry (ETAAS),[11,12] inductively coupled plasma optical emission spectrometry (ICP-OES),[13] and ultraviolet-visible spectrophotometry (UV-VIS)[14] were commonly used for aluminium determination. The direct determination of trace aluminum by these techniques is generally difficult because of the low concentration of aluminum and possible matrix interference problems. These problems can be overcome by using a preconcentration and/or separation procedure before the detection procedure. A number of separation and preconcentration procedures for preconcentration and/or separation of trace metals involving cloud point extraction,[15] solid phase extraction,[16,17] coprecipitation,[14] and dispersive liquid–liquid microextraction[18] have been proposed to overcome this problem. Among the preconcentration techniques, solid phase extraction (SPE) has become the preferred method for concentrating the analyte prior to its analysis by FAAS and other techniques. Its advantages over classical liquid–liquid extraction methods are simple procedure, high enrichment factor, reduced solvent usage, permitting to combine with different detection techniques, reduced disposal costs, shorter extraction times for sample preparation,[8,19–21] and the availability of a wide variety of sorbent materials that mainly affect the extraction efficiency.

In this work, nano ZrO_2/B_2O_3 hybrid material was used as a nano sorbent for preconcentration of aluminum. This hybrid sorbent was first used for the preconcentration of aluminum in the literature. Experimental parameters including pH of the sample, flow rate of the sample, sample volume, eluent type, volume, and concentration were optimized. Analytical parameters such as accuracy, precision, limit of detection (LOD), limit of quantification (LOQ), and linear dynamic range were also studied. The proposed procedure was applied for the determination of trace aluminum in dam waters.

MATERIALS AND METHODS

Apparatus

A Varian (Palo Alto, CA, USA) AA240FS model flame atomic absorption spectrometer equipped with a deuterium-lamp background corrector, aluminum hallow cathode lamp (Varian), and N_2O-C_2H_2 flame were used for the determination of Al under the conditions suggested by the manufacturer. The wavelength, lamp current, slit width, acetylene flow rate, and nitrous oxide flow rate were 309.3 nm, 10 mA, 0.5 nm, 6.95 L min^{-1}, and 10.24 L min^{-1} for Al, respectively. All pH measurements were made with a WTW 720 model pH meter (Weilheim, Germany). A thermostat shaker (Nüve ST-402), ultrasonic bath (Sonicator) (Bandelin electronic RK100H), and peristaltic pump (Watson Marlow 323) were used for preconcentration experiments.

Reagents and Solutions

All reagents were of analytical grade unless otherwise stated. All solutions were prepared in ultrapure water (18.3 μΩ cm). Various concentrations of aluminum standard and model solutions were prepared by dilution of single-element stock solutions (1000 mg/L, Merck) of Al(III). Nitric acid (65%), hydrochloric acid (37%), and ammonia solutions (25%) were also purchased from Merck. The laboratory glassware was washed with 5% nitric acid solution before every use. Afterward, it was rinsed thoroughly with water and dried. Nano ZrO_2/B_2O_3 was synthesized and characterized by the methods given in our previous paper.[22]

Column Preparation

A glass column (150 mm length and 8 mm i.d.) having a stopcock at the bottom and a tank of 250 mL on top of the column was used. A small amount of glass wool was placed over its stopcock in order to hold the sorbent. Two hundred

milligrams of dry hybrid nano material (ZrO_2/B_2O_3) was made into a slurry with water and then placed into the column. Then, another small glass wool plug was inserted onto the top of the sorbent to avoid disturbance during sample passage. The column was preconditioned by passing blank solution having the same pH with the sample solution prior to use. After each use, the nano material in the column was washed with dilute HCl ($0.5\,mol\,L^{-1}$), HNO_3 ($4\,mol\,L^{-1}$), and water, respectively, and stored in water until the next experiment.

General Procedure for the Preconcentration of Al(III) on Nano ZrO_2/B_2O_3

Preconcentration performance for Al was investigated with model solutions before analyzing the real samples and certified reference materials (CRMs). Twenty-five milliliters of model solutions containing of 25 μg Al(III) was taken and pH was buffered to working value (pH 5.0, with acetic acid/acetate buffer). The resulting solution was drawn through the column by using a peristaltic pump adjusted to the desired flow rate ($4\,mL\,min^{-1}$). After passing model solution through the column, it was washed at the aqueous solutions of the working pH. Finally, Al(III) ions were eluted from solid phase with 10 mL of $4\,mol\,L^{-1}$ HNO_3. Aluminum was determined by FAAS by applying a direct calibration method. Using the procedure described above, percent recovery was calculated from the following equation:

$$R(\%) = \frac{C_E x V_E}{C_S x V_S}$$

where C_E is the concentration of analyte in eluent in $mg\,L^{-1}$, V_E is the volume of eluent in L, C_S is the concentration of analyte in sample solution in $mg\,L^{-1}$, and V_S is the volume of sample solution in L.

RESULTS AND DISCUSSION

Under optimized experimental conditions, analytical parameters including limit of detection, limit of quantification, linear dynamic range, precision, and accuracy were determined. Interfering effects of matrix constituent on the recovery of the aluminum were studied. The reusability and adsorption capacity of the hybrid sorbent were also investigated.

Effect of pH of Sample Solutions

The pH value is the most important experimental parameter for metal ion adsorption on solid phase. It strongly influences the sorption availability of the metal ions. Therefore, pH was the first optimized parameter. The effects of the pH on the recoveries of aluminum ions were investigated in the pH range of 2.0–8.0 due to the occurrence of $Al(OH)_3$ precipitate at high pH values. For this purpose, 25 mL of model solutions containing 25 μg Al(III) were taken and pHs of the solutions were adjusted to 2 with $0.01\,mol\,L^{-1}$ HCl; to 4, 5, and 6 with acetic acid/acetate buffer; and to 8 with phosphate buffer. The effect of the pH value on the recovery of Al(III) ion is shown in Figure 1. The results show that high recovery values were obtained for Al(III) in the pH range of 5.0–8.0. Therefore, pH 5 was chosen for further experiment. To study in acidic media minimizes possible precipitation of metal hydroxides, and this is one of the advantages of the method.

Effect of Eluent Type and Concentration

The kind and concentration of eluent are the other important parameters for such studies. To determine the optimum value of these parameters, 25 mL of model solutions containing 25 μg Al(III) ions were used. pH of the model solution was adjusted to 5.0 with acetic acid/acetate buffer and the general preconcentration procedure was applied. For the elution process, first HCl and HNO_3 solutions having various concentrations and various volumes were

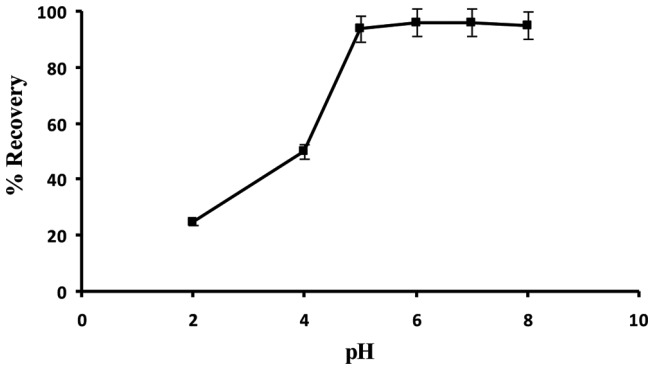

FIGURE 1 The effects of pH value on the recovery of Al(III).

TABLE 1 Effect of Eluent Type and Concentration

Eluent concentration and volume	Recovery %[a]
3 mol/L 10 mL HNO_3	79 ± 2
4 mol/L 10 mL HNO_3	96 ± 3
4 mol/L 5 mL HNO_3	83 ± 5
4 mol/L 10 mL HCl	65 ± 3

[a]The average ± standard deviation of three measurements.

tested. Ten milliliters of 4 mol L^{-1} HNO_3 solution that gives maximum recovery was found as the optimal eluent solution to desorption of Al(III) from the hybrid nano ZrO_2/B_2O_3 material (Table 1). For subsequent experiments, 10 mL of 4 mol L^{-1} HNO_3 was used for elution of Al(III).

Effect of the Sample Flow Rate

The effect of flow rates of sample solution on the recovery of aluminum was investigated by controlling the flow rate of sample solution with a peristaltic pump. Flow rate not only affects the retention of the analytes but also determines the duration of analysis. Because a large volume of sample solution is needed for obtaining a high preconcentration factor, it is always expected that sample solution can be passed through the column at higher flow rates without reducing the recovery. Therefore, the effect of flow rate of sample solutions on the recovery of aluminum was examined in the range of 1–7 mL min^{-1}. Under optimum conditions (pH: 5, eluent: 10 mL of 4 mol L^{-1} HNO_3), Al(III) was quantitatively recovered up to 4 mL min^{-1} of the flow rates (Fig. 2). Above 4 mL min^{-1} the recoveries were decreased gradually.

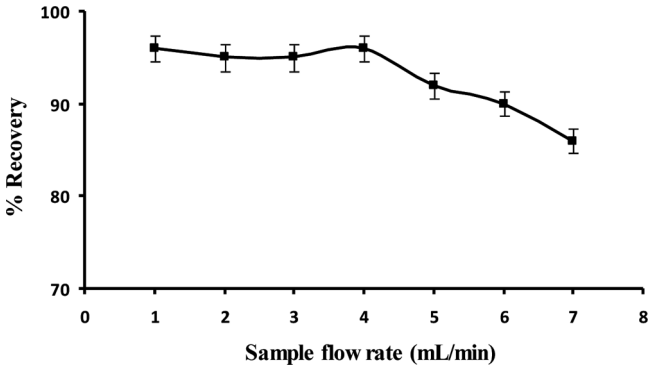

FIGURE 2 The effects of sample flow rate on the recovery of Al(III).

Effect of Volume of Sample Solution

The influence of the sample volume on recovery of the aluminum was also examined in order to determine the maximum applicable sample volume or minimum analyte concentration. For this purpose, Al(III) ions were preconcentrated from volumes of 25, 50, 100, and 250 mL of sample solution containing 25 μg Al(III) ions, which corresponds to an aluminum concentration of 1.00, 0.50, 0.25, and 0.10 μg mL^{-1}, respectively. These solutions were passed through the column at optimum experimental conditions by applying the general procedure mentioned above. Results show that aluminum could be recovered quantitatively up to 100 mL of sample solution (0.25 μg mL^{-1} Al(III)). At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Since the original sample volume and final volume of solution (after preconcentration) are 100 mL and 10 mL, respectively, an enrichment factor of 10 can be achieved for Al(III).

Analytical Figures of Merits

By using direct aspiration in FAAS without the preconcentration system, the linear range for aluminum determination was between 1 and 20 μg mL^{-1}. The calibration equation was $A = 0.0015 + 0.042C$, where C is the aluminum concentration in μg mL^{-1} and A is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

As analytical figures of merit, LOD, LOQ, precision, and accuracy for the proposed method have been determined. In order to determine the instrumental detection limit for aluminum, 50 mL of blank solution was passed through the column under the optimum experimental conditions (pH: 5, eluent: 4.0 mol L^{-1} HNO_3, flow rate: 4 mL min^{-1}). Blank solutions were prepared by adding a minimum amount of the analyte to the water in order to obtain readable analyte signals. The sorbed analyte was eluted by 50 mL of 4.0 mol L^{-1} HNO_3 solution (there is no preconcentration) and the signal of this blank solution was measured about 20 times. The instrumental detection limit based on three times the standard deviation of the blank ($LOD_i = 3\sigma/m$, where m is the slope of the calibration curve) was found to be 77.1 μg L^{-1} for aluminum (n = 20). The analytical

limit of detection (LOD_a) has been calculated by dividing the instrumental detection limit by the enrichment factor (10 in the present work).[23–25] The LOD_a for aluminum was 7.71 $\mu g\,L^{-1}$. The analytical LOQ based on $10\,\sigma/m$ was 25.7 $\mu g\,L^{-1}$. As it is well known, this Al(III) concentration cannot be determined directly by FAAS with sufficient accuracy and precision.

Influence of Foreign Ions

The preconcentration of Al(III) on solid phase may be affected by the other ions in samples. For this reason, the reliability of the proposed method should be examined in the presence of possible interfering ions of the samples. To investigate the effect of other constituents on the recovery of Al(III), the possible interfering elements (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, and Co^{2+}) were added to 25 mL of model solutions containing 25 μg of Al(III). Interfering ion concentrations causing ±5% deviation in recovery of the Al(III) is considered as the tolerance limit. Influence of foreign ions on the recovery of Al(III) ions was shown in Table 2. These results show that the proposed hybrid nano ZrO_2/B_2O_3 as solid phase extractor could be applied for preconcentration of Al(III) from the various samples that contain other metal ions at mg L^{-1} levels.

TABLE 2 The Effect of Foreign Ions

Ions	Tolerance limit mg/L	Recovery, %[a]
Na^+	1000	95 ± 3
K^+	500	98 ± 4
Ca^{2+}	500	96 ± 2
Mg^{2+}	50	93 ± 3
Ni^{2+}	25	93 ± 2
Cu^{2+}	25	94 ± 3
Fe^{3+}	25	94 ± 2
Mn^{2+}	25	96 ± 3
Co^{2+}	25	94 ± 3

[a]The average ± standard deviation of three measurements.

Application of Proposed Method

The proposed preconcentration method was applied for the determination of Al(III) in water samples, under optimal experimental conditions. The accuracy of the method was also checked by measuring the recovery of Al(III) in spiked real samples and analyzing certified reference material (SPS WW1, Waste Water). A good agreement was obtained between the certified (or added value for real samples) value and the found value of the analyte. The results obtained are given in Table 3. Relative errors below 5% demonstrate the applicability of the method and indecency from matrix constituents of the samples.

Reusability of the Sorbent

The proposed nano sorbent can be used alone many times due to its strong structure. The stability and potential reusability of nano ZrO_2/B_2O_3 were investigated by monitoring the change in the recoveries of the Al(III) ion through several adsorption–elution cycles. The passage of model solutions (25 mL containing 25 μg Al(III)), buffer solution, elution solution (10 mL of 4 mol L^{-1} HNO_3), and water through the column packed with 200 mg of hybrid sorbent was defined as one adsorption–desorption cycle. The adsorbent was always stored in water when it was not in use. It was observed that the column could be reused up to about 100 times without a decrease in the recovery of Al(III) ions. This is another advantage of the proposed method. Classic sorbents usually loaded with chelating agent cannot

TABLE 3 Determination of Aluminum in CRM and Water Samples

Sample	Certified or added value mg L^{-1}	Found value[a] mg L^{-1}	Relative error, %
(SPS-WW1) Waste Water	2.00 ± 0.1	2.04 ± 0.06	+2
Dam Water[b]	—	0.31 ± 0.06	—
	1	1.28 ± 0.04	−3
Dam Water[c]	—	0.46 ± 0.05	—
	1	1.39 ± 0.04	+5

[a]Mean of five determinations at 95% confidence level.
[b]Kurt Boğazı.
[c]Çubuk.

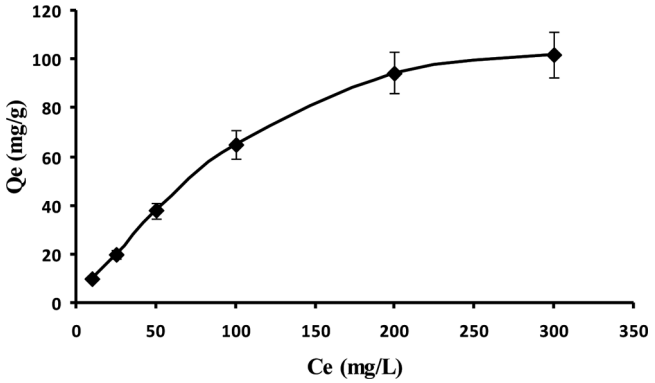

FIGURE 3 Adsorption isotherm of Al(III) on hybrid nano ZrO_2/B_2O_3.

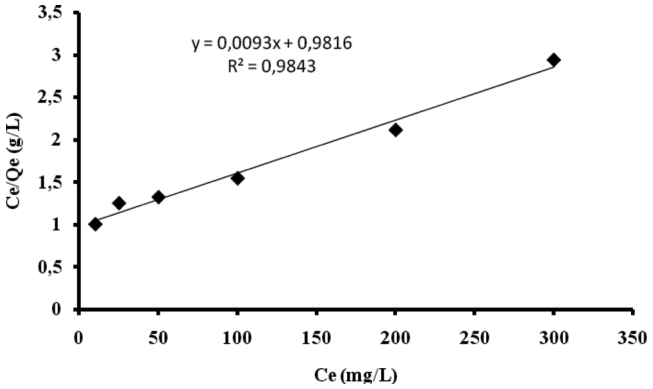

FIGURE 4 Linearized Langmuir adsorption isotherm of Al(III) on hybrid nano ZrO_2/B_2O_3.

be used repeatedly due to the probable loss of chelating agent with every adsorption–desorption cycle.

Adsorption Isotherm and Adsorption Capacity

The adsorption capacity of hybrid nano ZrO_2/B_2O_3 was determined by the batch technique.[26] The adsorption behavior of hybrid nano ZrO_2/B_2O_3 was determined by studying the amount of adsorbed aluminum as a function of equilibrium aluminum concentration. For this purpose, 50 mL of sample solutions having the aluminum the concentrations in the range of 10 to 300 mg L^{-1} at pH 5 were shaken for 50 min with a constant weight (100 mg) of nano sorbent. The profile of the adsorption isotherm of the nano sorbent for aluminum is shown in Figure 3, representing the amounts of adsorbed aluminum versus the aluminum concentration of the supernatant under equilibrium conditions. The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. When the adsorption profile reaches a plateau, a monolayer adsorption is supposed to be established. The data of the isotherm reveal that the adsorption process conforms to the Langmuir model. In Figure 4, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. A modified Langmuir equation conformed to this kind of adsorption isotherm is represented below:

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0\, b}$$

where C_E is the concentration of Al(III) in the solution at equilibrium (mg L^{-1}), Q_E is the amount of sorbed aluminum per gram of nano sorbent at equilibrium (mg g^{-1}), b is the "affinity" parameter or Langmuir constant (L mg^{-1}), and Q_0 is the "capacity" parameter (mg g^{-1}). Based on the linear form of the adsorption isotherm derived from plots of C_E/Q_E versus C_E, the constant Q_0 values were calculated from the slope of the graph. The value of Q_0 (adsorption capacity) and b were found to be 107.7 mg g^{-1} and 0.0094 L mg^{-1}, respectively.

Comparison of the Method with Others

The analytical performance of the sorbent is comparable with the other sorbents. Some comparative

TABLE 4 Comparative Data for Various SPE Preconcentration Methods

Preconcentration system	LOD (μg L^{-1})	Adsorption capacity (mg g^{-1})	PF	Determination technique	Ref.
Amberlite XAD-1180/pyrocathecol	0.02	6.45	150	ETAAS	[8]
Silica-glycerol sorbent	2	0.4	500	FAAS	[10]
Pseudomonas aeruginosa- Cromosorb 106	0.03	10.5	50	ETAAS	[11]
Nanometer-sized TiO_2	40	4.1	20	ETAAS	[27]
Nano ZrO_2/B_2O_3	7.71	107.7	10	FAAS	This work

PF, preconcentration factor; ETAAS, electrothermal atomic absorption spectrometry; FAAS, flame atomic absorption spectrometry.

data about sorption is summarized in Table 4. The present work has relatively high adsorption capacity when compared to other methods. The limit of detection and preconcentration factor are relatively lower than those of the other methods. However, the stability of the proposed sorbent is higher than the others.

CONCLUSION

Nano ZrO_2/B_2O_3 composite material as a new solid phase extractor provides a simple, selective, accurate, economical, rapid, and precise method for the preconcentration and determination of Al(III). This nano material was first used as adsorbent for enrichment of the Al(III) ion. The proposed solid phase extraction method has sufficiently good recoveries, a high tolerance limit of interfering ions, and a low detection limit for determination of Al(III) ions in various water samples. The other advantage of the proposed preconcentration procedure is the applicability of it in acidic media, which minimizes possible precipitation of metal hydroxides. There is no need for loading any chelating and/or complexing agent before the preconcentration procedure to obtain quantitative recovery of Al(III). The adsorbent was stable up to 100 cycles, without a major loss in its quantities or metal recovery properties.

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REFERENCES

1. Merian, E.; Anke, M.; Ihnad, M.; Stoeppler, M. *Bowie, Elements and their Compound in the Environment*; Wiley-Vch Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004; p. 641.
2. de Amorim, F. R.; Bof, C.; Franco, M. B.; da Silva, J. B. B.; Nascentes, C. C. Comparative study of conventional and multivariate methods for aluminum determination in soft drinks by graphite furnace atomic absorption spectrometry. *Microchem. J.* **2006**, *82*, 168–173.
3. Welz, B. *Atomic Absorption Spectrometry*; 3rd Ed.; VCH: Weinheim, 1999.
4. Buratti, M.; Valla, C.; Pellegrino, O.; Rubino, F. M.; Colombi, A. Aluminum determination in biological fluids and dialysis concentrates via chelation with 8-hydroxyquinoline and solvent extraction/fluorometry. *Anal. Biochem.* **2006**, *353*, 63–68.
5. Mehra, A.; Baker, C. L. Leaching and bioavailability of aluminum, copper and manganese from tea (Camellia sinensis). *Food Chem.* **2007**, *100*, 1456–1463.
6. Carpani, I.; Scavetta, E.; Tonelli, D. Spectrophotometric determination of aluminum and nickel. *Ann. Chim.* **2004**, *94*, 365–372.
7. WHO. *Aluminum.* World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 194): Geneva, 1997.
8. Narin, I.; Tüzen, M.; Soylak, M. Aluminum determination in environmental samples by graphite furnace atomic absorption spectrometry after solid phase extraction on Amberlite XAD-1180/pyrocatechol violet chelating resin. *Talanta* **2004**, *63*, 411–418.
9. Shokrollahi, A.; Ghaedi, M.; Niband, M. S.; Rajabi, H. R. Selective and sensitive spectrophotometric method for determination of submicro-molaramounts of aluminum ion. *J. Hazard. Mater.* **2008**, *151*, 642–648.
10. Safavi, A.; Momeni, S.; Saghir, N. Efficient preconcentration and determination of traces of aluminum ion using silica-bonded glycerol sorbent. *J. Hazard. Mater.* **2009**, *162*, 333–337.
11. Tuzen, M.; Soylak, M. Biosorption of aluminum on *Pseudomonas aeruginosa* loaded on Chromosorb 106 prior to its graphite furnace atomic absorption spectrometric determination. *J. Hazard. Mater.* **2008**, *154*, 519–525.
12. Knezevia, S.; Milaeie, R.; Veber, M. ETAAS determination of aluminum and copper in dialysis concentrates after microcolumn chelating ion-exchange preconcentration. *Fresenius J. Anal. Chem.* **1998**, *362*, 162–166.
13. Bianchi, F.; Maffini, M.; Mangia, A.; Marengo, E.; Mucchino, C. Experimental design optimization for the ICP-AES determination of Li, Na, K, Al, Fe, Mn and Zn in human serum. *J. Pharma. Biomed. Anal.* **2007**, *43*, 659–665.
14. Bulut, V. N.; Arslan, D.; Ozdes, D.; Soylak, M.; Tufekci, M. Preconcentration, separation and spectrophotometric determination of aluminum(III) in water samples and dialysis concentrates at trace levels with 8-hydroxyquinoline–cobalt(II) coprecipitation system. *J. Hazard. Mater.* **2010**, *182*, 331–336.
15. Kazi, T. G.; Khan, S.; Baig, J. A.; Kolachi, N. F.; Afridi, H. I.; Kandhro, G. A.; Kumar, S.; Shah, A. Q. Separation and preconcentration of aluminum in parenteral solutions and bottled mineral water using different analytical techniques. *J. Hazard. Mater.* **2009**, *172*, 780–785.
16. Ciftci, H.; Tunc, T.; Tasdemir, I. H.; Ciftci, E. The development of new enrichment method for simultaneous determination of copper and zinc in water samples. *Environ. Toxicol. Chem.* **2011**, *30*, 616–621.
17. Ciftci, H. Separation and preconcentration of cobalt using a new Schiff base derivative on XAD-7. *Clean-Soil, Air, Water* **2010**, *38*, 657–662.
18. Rezaee, M.; Yamini, Y.; Khanchi, A.; Faraji, M.; Saleh, A. A simple and rapid new dispersive liquid–liquid microextraction based on solidification of floating organic drop combined with inductively coupled plasma-optical emission spectrometry for preconcentration and determination of aluminum in water samples. *J. Hazard. Mater.* **2010**, *178*, 766–777.
19. Ulusoy, H. İ.; Gürkan, R.; Aksoy, Ü.; Akçay, M. Development of a cloud point extraction and preconcentration method for determination of trace aluminum in mineral waters by FAAS. *Microchem. J.* **2011**, *99*, 76–81.
20. Türker, A. R. New sorbents for solid-phase extraction for metal enrichment. *Clean-Soil, Air, Water* **2007**, *35*, 548–557.
21. Pacheco, P. H.; Gil, R. A.; Smichowski, P.; Polla, G.; Martinez, L. D. Trace aluminum determination in biological samples after microwave digestion followed by solid phase extraction with L-methionine on controlled pore glass. *Microchem. J.* **2008**, *89*, 1–6.
22. Yalcinkaya, Ö.; Kalfa, O. M.; Türker, A. R. Chelating agent free-solid phase extraction (CAF-SPE) of Co(II), Cu(II) and Cd(II) by new nano hybrid material (ZrO_2/B_2O_3). *J. Hazard. Mater.* **2011**, *195*, 332–339.
23. Akl, M. A. A.; Kenawy, I. M. M.; Lasheen, R. R. Organically modified silica gel and flame atomic absorption spectrometry: employment for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems. *Microchem. J.* **2004**, *78*(2), 143–156.

24. Dubiella-Jackowska, A.; Polkowska, Ż.; Lech, D.; Pasławski, P.; Staszek, W.; Namieśnika, J. Estimation of platinum in environmental water samples with solid phase extraction technique using inductively coupled plasma mass spectrometry. *Cent. Eur. J. Chem.* **2009**, *7*(1), 35–41.
25. Yalçınkaya, Ö.; Kalfa, O. M.; Türker, A. R. Chelating agent free solid phase extraction (CAF-SPE) method for separation and/or preconcentration of iron(III) ions. *Turk. J. Chem.* **2010**, *34*(2), 988–992.
26. Eren, E.; Cubuk, O.; Ciftci, H.; Eren, B.; Caglar, B. Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study. *Desalination*, **2010**, *252*(1–3), 88–96.
27. Matus, P.; Hagarova, I.; Bujdos, M.; Divis, P.; Kubava, J. Determination of trace amounts of total dissolved cationic aluminium species in environmental samples by solid phase extraction using nanometer-sized titanium dioxide and atomic spectrometry techniques. *J. Inorg. Biochem.* **2009**, *103*(11), 1473–1479.