J IRAN CHEM SOC (2013) 10:669–676
DOI 10.1007/s13738-012-0199-8

ORIGINAL PAPER

Synthesis of nano-pore size Al(III)-imprinted polymer for the extraction and preconcentration of aluminum ions

Farid Shakerian · Shayessteh Dadfarnia · Ali Mohammad Haji Shabani

Received: 18 August 2012 / Accepted: 30 November 2012 / Published online: 11 December 2012

Abstract In this study, an ion imprinted polymer (IIP) was prepared for the selective separation and preconcentration of trace levels of aluminum. Al(III) IIP was synthesized in the presence of Al(III)-8-hydroxyquinoline (oxine) complex using styrene and ethylene glycol dimethacrylate as a monomer and crosslinker, respectively. The imprinted Al(III) ions were completely removed by leaching the IIP with HCl (50 % v/v) and were characterized by FTIR and scanning electron microscopy. The maximum sorption capacity for Al(III) ions was found to be 3.1 mg g^{-1} at pH 6.0. Variables affecting the IIP solid phase extraction were optimized by the univariable method. Under the optimized conditions, a sample volume of 400 mL resulted in an enhancement factor of 194. The detection limit (defined as $3\ S_b/m$) was found to be 1.6 μg L^{-1}. The method was successfully applied to the determination of aluminum in natural water, fruit juice and cow milk samples.

Keywords Ion imprinted polymer · Aluminum · Solid phase extraction · Fruit juices · Cow milk

Introduction

During the last decades, aluminum and its distribution in the environment has been the topic of attention of many scientists. The concentrations of dissolved aluminum species in most natural waters are below the ppb level due to the relatively low solubility of aluminum minerals. However, a considerable increase in the concentration of this element has been occurred because of the increased input of acids in the environment [1, 2]. The concentrations of aluminum appear to be highest in acidified lakes, air and in the ground water of acidified soils. In acidified lakes, the number of fish and amphibians declines due to the reactions of aluminum ions with proteins in the gills of fish and the embryos of frogs. Aluminum may also accumulate in plants and cause health problems for animals that consume these plants. Aluminum has been used extensively in foodstuffs, utensils and packaging. The World Health Organization considered in 1986 that humans consumed about 30 mg of Al/day on average, through water, foods and drugs [3]. Aluminum enters the blood and accumulates in tissues such as bone, liver and the central nervous system [4]. When its concentration reaches a threshold level in the human body, it is believed to cause renal failure in patients undergoing treatment with peritoneal dialysis and hemodialysis [5]. Also, it affects the nervous system which yields to diseases such as dementia and encephalopathy [5], Alzheimer [6] and Parkinson [7]. Thus, the development of a method for the accurate determination of trace amounts of aluminum in different matrices is an important task.

Various analytical techniques such as atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry (ICP-OES) and spectrofluorimetry have been used for the determination of Al(III) in environmental samples [8–10]. Flame atomic absorption spectroscopy (FAAS) is among the most attractive techniques for the determination of metal ions due to its good selectivity, low cost, operational facilities and high speed of analyses [11]. However, FAAS lacks the sensitivity necessary for direct determination of analyte at low levels. Thus, a separation and preconcentration step is usually

---

F. Shakerian · S. Dadfarnia (✉) · A. M. H. Shabani
Department of Chemistry, Faculty of Science, Yazd University, Yazd 89195-741, Iran
e-mail: sdadfarnia@yazduni.ac.ir

required before measurement [12, 13]. The most widely used techniques for separation and preconcentration of aluminum are liquid–liquid extraction (LLE) [14], ion exchange [15], solid phase extraction (SPE) [16] and cloud point extraction (CPE) [17]. Solid phase extraction is one of the most effective preconcentration methods because of its simplicity, rapidity, ability to attain a high preconcentration factor, and its low cost from a labor and solvent consumption standpoint [18, 19]. A variety of solid materials such as titanium dioxide and L-methionine immobilized on controlled pore glass has been used for the preconcentration of aluminum in real samples [20, 21]. Currently, one of the most important focuses in relation to studies on SPE is the use of new sorbents. Among different sorbents used in SPE methods, IIPs are more convenient and effective for the selective separation and preconcentration of metal ions from real samples. In IIP, the selectivity of the sorbent is due to the three dimensional structure (3D) of the complex which is based on the coordination geometry and coordination number of the ions, and consequently is correlated to the charges and sizes of the ions. Ion imprinted polymers have found various application in the separation, preconcentration and purification of metal ions [22–27]; but, only a few studies concerning the synthesis and use of the IIP for selective extraction of aluminum have been reported in the literature [28, 29].

In this study, a selective IIP based on the Al(III)–oxine complex has been synthesized. The polymer was then used as a sorbent for the solid phase extraction of aluminum ion prior to its determination by FAAS. The factors affecting the separation and preconcentration of aluminum were optimized by the univariable method. Finally, the procedure was applied to the determination of aluminum ions in various matrices.

Experimental

Apparatus

An Analytik Jena flame atomic absorption spectrometer (model novAA®300, Jena, Germany) with deuterium lamp background correction was used for all absorption measurements. Aluminum hollow cathode lamp (Analytik Jena, Jena, Germany) and C_2H_2/N_2O flame were used for all measurements. The operating conditions were as follows: wavelength (main line) 309.3 nm, slit width 1.2 nm, and lamp current 6.0 mA. The pH measurements were carried out by a Metrohm pH meter (model 691, Herisau, Switzerland) using a combined glass calomel electrode. A Heidolph heater-stirrer (model MR 3002, Germany) was used for polymer synthesis and experiments.

Reagents

All chemicals were of the highest purity available from Merck Company (Darmstadt, Germany) and were used as received, except otherwise stated. Double distilled deionized water was used throughout the work. A stock solution of 1,000 mg L^{-1} of aluminum was prepared by dissolving appropriate amount of $AlCl_3$ in water. Working solutions were prepared daily from the stock solution by proper dilution with distilled water. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from ACROS (New Jersey, USA) and was used without further purification.

Synthesis of Al(III)-ion imprinted polymer

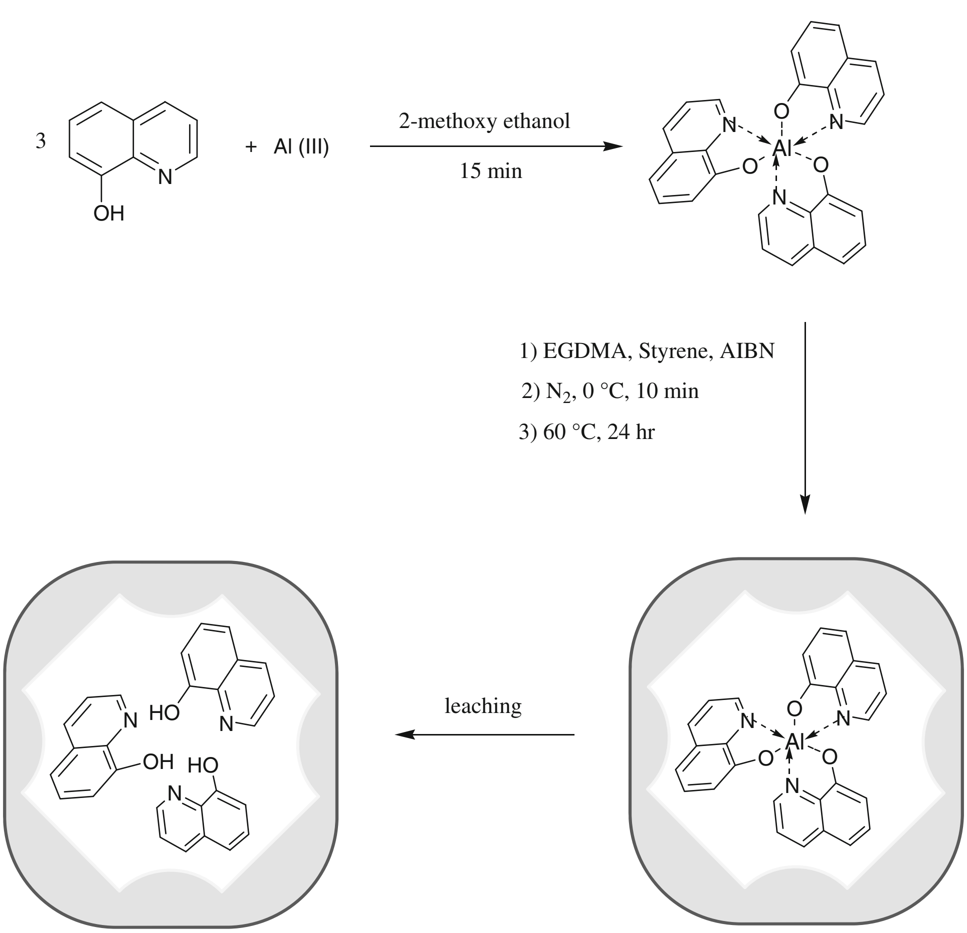
Ion imprinted polymer (Fig. 1) was prepared by thermal polymerization. The synthesis of the polymer was done in two steps, i.e. first, the stoichiometric complex between oxine and Al(III) was formed, and then monomer, cross-linker initiator was added for polymerization. The binary complex of imprinted ion Al(III) with 8-hydroxyquinoline (oxine) was prepared by stirring 3 mmol of oxine dissolved in 10 mL of 2-methoxy ethanol containing 1 mmol of aluminum for 30 min. This binary complex solution was then mixed with styrene (5 mmol) as the monomer and ethylene glycol dimethacrylate (EGDMA) as the cross-linker (20 mmol) in the presence of 50 mg of AIBN as the initiator. The solution was stirred until it was homogenized. Then, it was cooled to 0 °C, purged with N_2 for 10 min, sealed and thermally polymerized in a water bath; the temperature was slowly raised from room temperature to 60 °C and was maintained at 60 °C for 24 h. The resulting polymer material was then washed thoroughly with deionized water, dried, ground and sieved to obtain aluminum IIP particles. The synthesized IIP particles were then treated with 100 mL of HCl (50 % v/v) for 2 h and the removal of aluminum ion was followed by FAAS. This process was continued until no aluminum ion was detected. The IIP particles were then washed thoroughly with water and were dried in oven at 70 °C for further use. Control polymer (CP) particles were prepared under similar experimental conditions without the target ion.

Preparation of real samples

Water samples were filtered through 0.45 μm Millipore filter. The pH of the 400 mL of water samples were adjusted to ~6 and the analyte was determined according to the given procedure.

The processed fruit juices, which were preserved in aluminum containers, were obtained from supermarket and were digested according to the given procedure in the literature [30], i.e. 400 mL of each fruit juice was placed in a

Fig. 1 The schematic representation of synthesis of Al(III) imprinted polymer



beaker and a mixture of 20 mL of the concentrated nitric acid and 10 mL of the hydrogen peroxide (30 % w/v) was added. The mixture was heated for 30 min at 100 °C. Then, ~10 mL of the concentrated perchloric acid was added and the mixture was further heated at 150 °C with stirring, until the solution became clear. The digested sample was then diluted to 400 mL with water, the pH was adjusted to ~6 and the analyte was determined according to the given procedure. The blank sample was carried out in the same way.

The cow milk was prepared according to the previously given procedure [31] as follows: To 400 mL of homogenized cow milk, 2 mL of concentrated nitric acid was added, and the sample was centrifuged for few minutes. Then, the supernatant solution was taken, the pH was adjusted to ~6 by ammonia solution and was analyzed according to the given procedure.

An appropriate amount of the standard material EURO-Analysenkontrollprobr 678-1 (supplied by MBH Analytical Ltd) was weighed into a beaker, 7 mL concentrated nitric acid was added and the mixture was heated to near boiling point. Next, 3 mL of hydrogen peroxide was added, and the excess amount of hydrogen peroxide was removed by heating the mixture to near dryness. Then ~10 mL of double distilled water was added to the residue, and the solution was filtered; the pH was adjusted to ~6 and was diluted with water to 400 mL. The aluminum was then determined according to the given procedure.

IIP solid phase extraction

The pH of 400 mL of standard or sample solution containing not more than 0.12 mg of aluminum was adjusted to ~6 using either 1 % nitric acid or ammonia solution. 0.25 g of Al(III)-IIP was added to the solution and the mixture was stirred for 30 min. The sorbent was then separated by filtration and sorbed aluminum was eluted upon addition of 2 mL of HCl (3 mol L^{-1}) to the loaded IIP and stirring the mixture for 20 min. The IIP was then separated and the Al(III) ions in the resulting solution was measured by FAAS.

Results and discussion

Characterization studies

FT-IR spectra of oxine, unleached and leached Al(III)-IIP were recorded using KBr pellet method. Both spectra of pure oxine and Al(III)-IIP show the characteristics stretching vibration bonds of OH at 3,654.89 and 3,448.17 cm^{-1}, respectively. The shifting of OH peak toward lower wave number in case of Al(III)-IIP can be due to the formation of the complex [32]. The weakening and shift of OH-stretching in the unleached imprinted polymer in comparison with the leached polymer is due to the interaction of the deprotonated OH group of oxine with Al(III). The other characteristic peaks for the unleached and leached Al(III)-IIP are: aliphatic CH at 2,956.15 and 2,956.22 cm^{-1}; C=O at 1,732.10 and 1,731.56 cm^{-1}; C–O at 1,158.61 and 1,156.85 cm^{-1} and C=N at 1,471.51 and 1,455.95 cm^{-1}. Furthermore, the increase in the C=N bond frequency and strength in the unleached polymer in comparison with leached polymer is also an indication of complex formation between Al(III) and oxine.

The surface morphology of the resulted Al(III)-IIP and CP was characterized by scanning electron microscopy (SEM). The respective micrographs are shown in Fig. 2. The increase in roughness of the surface of imprinted polymer after removal of Al(III) ions in comparison with the surface of control polymer is an indication of the increase in the surface area. Furthermore, the pore size of the imprinted polymer is in the nano-range, corresponding to the size of the aluminum ion.

Optimization of aluminum IIP-SPE

In order to establish the best conditions for the sorption and desorption of aluminum, the procedure was optimized by the univariable method. The effect of the sample pH on the retention of aluminum was studied by varying the pH within the range of 1.5–12.5. The results of this study are shown in Fig. 3 and revealed that the recovery of aluminum is maximum in the pH range of about 4.0–9.0. The progressive decrease in aluminum absorption at lower pH is due to the incomplete complex formation and its retention to the sorbent, while the decrease in the extraction efficiency at pH $\geq$ 9 is probably due to the precipitation of aluminum as its hydroxide. An optimum pH of $\sim$6 was selected for the subsequent studies.

The desorption of aluminum from the sorbent was studied using 2.5 mL of different eluents including hydrochloric acid (1.5 mol L^{-1}), nitric acid (1.5 mol L^{-1}), sulfuric acid (1.5 mol L^{-1}) and ethanol; the recovery was found to be higher with hydrochloric acid. The concentration of hydrochloric acid was then varied between 0.5 and 5 mol L^{-1}; the recovery was found to increase with hydrochloric acid concentration up to 3 mol L^{-1} and then leveled off at higher concentration. Therefore, an optimum concentration of 3 mol L^{-1} of hydrochloric acid was employed in further experiments.

Demonstration of the preconcentration capability of the extraction system is an important aspect of the method development. A decrease in the eluent volume will increase the preconcentration factor, but it may reduce the recovery of analyte from the sorbent. The effect of different volumes (1, 2, 3 and 4 mL) of 3 mol L^{-1} hydrochloric acid as eluent on the desorption of 20 μg of aluminum from the

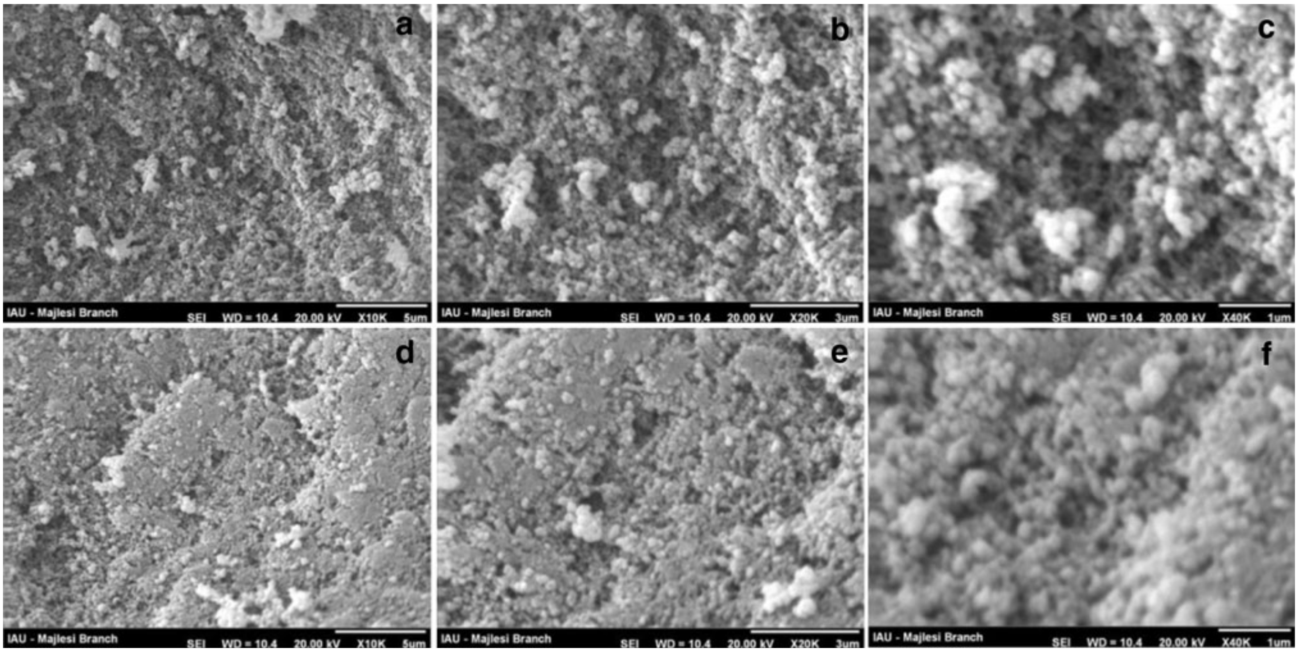


Fig. 2 Scanning electron microscopy images. **a–c** Ion imprinted polymer and **d–f** control polymer with different zoom (**a**, **d** 10 K; **b**, **e** 20 K; **c**, **f** 40 K)

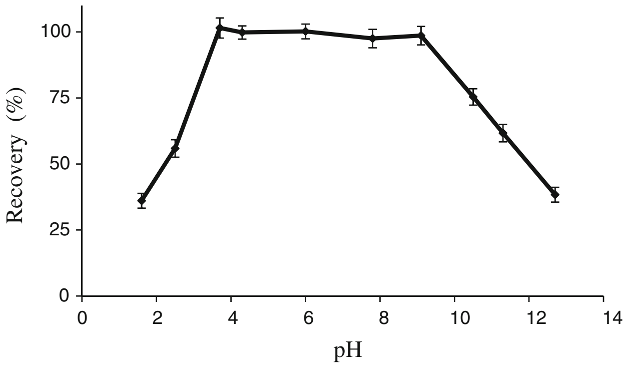


Fig. 3 Effect of the pH on the recovery of Al(III) from the sorbent. conditions: equilibrium time for sorption, 30 min; desorption time, 30 min; eluent volume, 2.5 mL; eluent hydrochloric acid, 2.5 mol L^{-1}; amount of sorbent, 0.20 g; aqueous phase volume, 200 mL; amount of aluminum, 20 μg

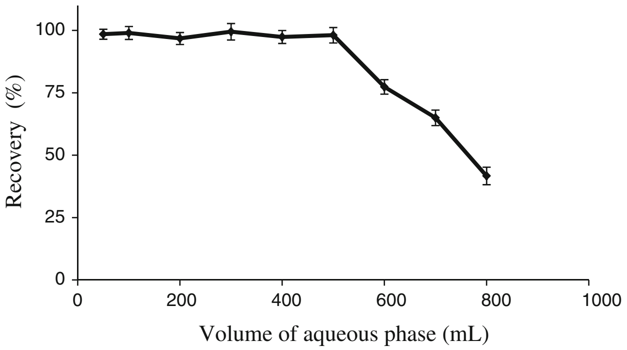


Fig. 4 Effect of the volume of aqueous phase on the recovery of Al(III) from the sorbent. Conditions: pH ~6, equilibrium time for sorption, 30 min; desorption time, 20 min; eluent volume, 2 mL; eluent concentration, 3 mol L^{-1}; amount of sorbent, 0.25 g; amount of aluminum, 20 μg

sorbent was examined and it was found that 2 mL of eluent is sufficient for the quantitative recovery of the analyte.

Another important factor influencing the extraction efficiency and speed of analysis is extraction time. In order to have a good precision, sensitivity and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between the sample and the sorbent. The effect of the extraction time on the uptake of analyte was examined by varying the extraction time from 5 to 50 min at the constant experimental conditions. The results indicated that the extraction was relatively fast and after 30 min, the uptake of aluminum was independent of the extraction time; thus, an optimum time of 30 min for the extraction was selected. Furthermore, the effect of time on desorption of analyte from the sorbent was studied by varying the elution time between 5 and 50 min. It was found that after 20 min, the absorbance signal of aluminum was maximum and independent of the elution time.

In order to explore the possibility of the enrichment of low concentration of aluminum from the large sample volume, the effect of sample volume on the extraction of 20 μg of aluminum from different aqueous volumes (50–800 mL) at optimum conditions was examined. The sorbent was then separated and the retained analyte was eluted with 2 mL of hydrochloric acid (3 mol L^{-1}) and its concentration was determined. The results (Fig. 4) showed that the recovery was quantitative ($\geq$95 %) for up to 500 mL of aqueous phase. Thus, the method has the capability of achieving high concentration factor for the separation and determination of aluminum.

Interferences study

A possible concern was that whether high enrichment factors could be realized for real samples where other cations or anions might compete with analyte and lower the extraction efficiency. For this purpose, the effect of various cations and anions on the recovery of 20 μg of aluminum from 400 mL of aqueous sample solution at an initial mole ratio of 1,000 (ion/aluminum) was studied. When interference was observed, the concentration of the interfering ion was lowered. A relative error of less than 5 % was considered to be within the range of experimental error. The results of these studies (Table 1) indicate that the presence of high concentrations of the possible interfering ions in the sample had no significant effect on the recovery of aluminum at trace levels. Thus, the method offers a high selectivity for aluminum ions.

Sorbent capacity

The capacity of the synthesized IIP for the retention of aluminum was determined by adding 1.0 g of IIP particles into 200 mL of the aluminum solution (50 mg L^{-1}) under the optimum conditions. After 30 min, the sorbent was separated and the concentration of aluminum remained in solution was determined by FAAS. The capacity of IIP for aluminum was determined from the differences in the amount of aluminum in the initial and final solutions. The capacity of IIP for aluminum was found to be 3.1 mg g^{-1} of sorbent which indicates that the sorbent has high capacity for aluminum ions.

Analytical performance

Standard solutions of aluminum (400 mL) were processed in the SPE system and the calibration graph exhibited linearity over the range of 25–300 μg L^{-1} with a determination coefficient (R^2) of 0.9995. The equation of calibration graph was $A = 9.73 \times 10^{-4}\ C + 0.01$ where A is the absorbance and C is the concentration of aluminum in μg L^{-1}. The enhancement and preconcentration factors

Table 1 Effect of diverse ions on the recovery of 20 μg aluminum from 400 mL of sample solution

Diverse ions	Mole ratio ([ion]/[Al(III)])	Recovery (%)
Ni^{2+}	1,000	95.3 ± 1.5
Co^{2+}	1,000	98.0 ± 0.9
Ag^{+}	1,000	102.5 ± 2.3
Cd^{2+}	1,000	97.9 ± 2.7
Zn^{2+}	1,000	95.8 ± 1.2
Cu^{2+}	1,000	98.4 ± 1.9
Na^{+}	1,000	95.8 ± 2.1
Mg^{2+}	1,000	99.5 ± 1.2
Pb^{2+}	1,000	103.0 ± 1.6
K^{+}	1,000	98.7 ± 2.6
Cl^{-}	1,000	99.4 ± 2.9
Br^{-}	1,000	101.2 ± 1.4
I^{-}	1,000	104.0 ± 1.5
$CO_3{}^{2-}$	1,000	96.5 ± 1.8
Ca^{2+}	750	97.5 ± 2.5
$SO_4{}^{2-}$	750	97.9 ± 1.2
Fe^{3+}	500	102.5 ± 0.8

defined as the ratio of the slope of calibration curves with and without preconcentration and the ratio of the sample volume to the eluent volume were found to be 194 and 200, respectively. Thus, the extraction is quantitative and the recovery is about 97 %. The relative standard deviation (RSD) for seven replicate measurements at 125 μg L^{-1} level was 3.2 %. The limit of detection and quantification defined as the 3 and 10 S_b/m (where S_b is the standard deviation of the blank and m is the slope of calibration curve) were 1.6 and 5.6 μg L^{-1}, respectively. The sorbent was reused in more than 20 cycles without significant change in its properties.

Application

The procedure was applied to the determination of aluminum in tap water, rain water, well water, river water [taken from (1) Zayandeh rood, Esfahan/Iran and (2) Karoon rood, Ahvaz/Iran], sea water (Persian Gulf), fruit juice (apple, cherry, peach and orange juice) and cow milk samples preserved in aluminum containers. Reliability of method was checked by the recovery experiments and by comparing the results with the data obtained by electrothermal atomic absorption spectrometry. The results of this investigation are given in Tables 2 and 3. It can be seen that the recovery of the spiked samples is good, and at 95 % confidence level, there is no significant difference between the results of this study and the data obtained by electrothermal atomic absorption spectrometry. Furthermore, the proposed procedure was applied to the determination of aluminum in a certified reference material (EURO-Analysenkontrollprobr 678-1, with the percentage composition of: Si = 1.727 ± 0.036, Ti = 0.127 ± 0.008, Al = 0.276 ± 0.026, Mn = 0.075 ± 0.005, Mg = 0.573 ± 0.025, Ca = 3.921 ± 0.092, Na = 0.107 ± 0.010, K = 0.111 ± 0.011, P = 1.608 ± 0.039, S = 0.021 ± 0.002, V = 0.115 ± 0.007, F = 0.289 ± 0.019 and Fe = 60.75 ± 0.07). The concentration of aluminum in the sample was found to be 0.271 ± 0.011 % which is in good agreement with the accepted value of 0.276 ± 0.026 %; thus, the procedure is suitable for the sample type examined.

Table 2 Determination of aluminum in water samples

Sample	Al(III) (μg L^{-1})		Recovery (%)	ETAAS (μg L^{-1})[a]
	Added	Found[a]		
Tap water	0	39.3 ± 1.2	–	38.1 ± 1.6
	20	59.0 ± 0.9	98.5	–
Rain water	0	ND	–	–
	50	49.7 ± 0.5	99.4	–
River water 1	0	78.6 ± 0.7	–	76.9 ± 2.2
	20	97.9 ± 1.5	96.5	–
River water 2	0	53.2 ± 1.3	–	53.7 ± 1.9
	20	73.5 ± 0.7	101.5	–
Spring water	0	ND	–	–
	50	48.5 ± 0.4	97.0	–
Persian Gulf water	0	85.6 ± 0.8	–	83.4 ± 2.5
	20	106.5 ± 1.5	104.5	–

[a] Mean and standard deviation of three independent analyses

Table 3 Determination of aluminum in fruit juices and cow milk samples

Samples	Al(III) (μg L^{-1})		Recovery (%)	ETAAS (μg L^{-1})[a]
	Added	Found[a]		
Cherry juice	0	42.0 ± 0.8	–	41.5 ± 1.7
	50	90.5 ± 1.2	97.0	–
Peach juice	0	35.2 ± 0.9	–	35.9 ± 1.1
	50	84.3 ± 0.7	98.2	–
Apple juice	0	40.7 ± 1.1	–	39.5 ± 1.5
	50	89.1 ± 0.9	96.8	–
Orange juice	0	31.5 ± 1.5	–	31.0 ± 0.9
	50	82.2 ± 1.2	101.4	–
Cow milk 1 (2.5 % fat)[b]	0	47.9 ± 0.6	–	47.2 ± 2.1
	50	96.6 ± 0.8	97.4	–
Cow milk 2 (2.5 % fat)[b]	0	42.5 ± 1.7	–	41.8 ± 1.5
	50	93.5 ± 1.5	102.0	–

[a] Mean and standard deviation of three independent analyses

[b] Homogenized and pasteurized cow milk from different brands

Table 4 Comparison of SPE methods used for determination of aluminum

Sample type	Sorbent	Determination technique	Sample volume (mL)	Sorbent capacity (mg g^{-1})	Enrichment factor	RSD (%)	References
Mineral water and green tea	Glycerol-bonded silica gel	FAAS	1,000	0.4	500	2.2	[33]
Water, dialysis fluids and red wine	Pyrocatechol violet (PV) immobilized on Amberlite XAD-1180	ETAAS	750	6.45	150	<10	[34]
Soil extracts and ground waters	Tiron modified resin	ECR spectrophotometry	50	5.6	20	–	[16]
Water samples	Nano-titanium dioxide	ET-AAS, ICP-OES	100	4.1	20	<5	[21]
Tea infusion	Ion-exchange resin	FAAS	25	–	–	<5	[15]
Aqueous solutions	Ion imprinted polymer	Spectrofluorometer	50	3.3	–	–	[29]
Water, wastewater, urine	Ion imprinted polymer	ICP-OES	250	–	–	6.5	[35]
Natural waters, fruit juices and milk	Ion imprinted polymer	FAAS	400	3.1	194	3.2	This work

Comparison of the proposed method with other SPE methods

The figures of merit of the proposed method were compared with some reported SPE methods for the separation and preconcentration of aluminum prior to its determination. The results are summarized in Table 4. As can be seen, the enrichment factor of the proposed method is comparable with the previously reported methods and the method is applicable for determination of aluminum in a wider range of matrices. Furthermore, the capacity of the prepared IIP is comparable to the previously synthesized IIP for Al(III) [31]. It should also be noted that although the capacity of IIP sorbents are lower than some of the other sorbents, they are more specific.

Conclusions

It has been demonstrated that the synthesized aluminum IIP adsorbed the corresponding guest Al(III) ions more effectively than did the control polymer. The cross-linked imprinted polymer has good chemical and physical stability and can be used repetitively in more than 20 cycles without significant change in properties. The Al(III)-IIP showed good selectivity for Al(III) ions even in the presence of complex matrices, such as sea water, milk and fruit juices. The procedure is simple, reproducible, and less susceptible to contamination and offers an alternative procedure to sensitive techniques such as electrothermal atomic absorption spectrometry for the determination of aluminum at trace levels.

References

1. K. Pyrazynaska, S. Gucer, E. Bulska, Water Res. **34**, 359 (2000)
2. T.N. Shilimkar, S.S. Kolekar, M.A. Anuse, Sep. Purif. Technol. **42**, 55 (2005)
3. R. Karbouj, I. Desloges, P. Nortier, Food Chem. Toxicol. **47**, 571 (2009)
4. D.G. Themelis, F.S. Kika, J. Pharm. Biomed. Anal. **41**, 1179 (2006)
5. A.C. Alfrey, Adv. Clin. Chem. **23**, 69 (1983)
6. C.N. Martyn, D.J. Barker, C. Osmond, E.C. Harris, J.A. Edwardson, R.F. Lacey, Lancet **1**, 59 (1989)
7. D. Krewski, R.A. Yokel, E. Nieboer, D. Borchelt, J. Cohen, J. Harry, S. Kacew, J. Lindsay, A.M. Mahfouz, V. Rondeau, J. Toxicol. Environ. Health B Crit. Rev. **10**, 1 (2007)
8. S. Khan, T.G. Kazi, J.A. Baig, N.F. Kolachi, H.I. Afridi, A.Q. Shah, G.A. Kandhro, S. Kumar, Talanta **80**, 158 (2009)
9. A. Sanz-Medel, A.B.S. Cabezuelo, R. Milacic, T.B. Polak, Coord. Chem. Rev. **228**, 373 (2002)
10. B. Bocca, A. Alimonti, F. Petrucci, N. Violante, G. Sancesario, G. Forte, O. Senofonte, Spectrochim. Acta Part B **59**, 559 (2004)
11. F. Shakerian, S. Dadfarnia, A.M. Haji Shabani, M. Rohani, Talanta **77**, 551 (2008)
12. G. Khayatian, S. Hassanpoor, J. Iran. Chem. Soc. (2012). doi: 10.1007/s13738-012-0131-2
13. E.K. Paleologos, C.D. Stalikas, M.I. Karayannis, Analyst **126**, 389 (2001)
14. D. Mohapatra, K. Hong-In, C.W. Nam, K.H. Park, Sep. Purif. Technol. **56**, 311 (2007)
15. S.B. Erdemoglu, K. Pyrzyniska, S. Gucer, Anal. Chim. Acta **411**, 81 (2000)
16. M. Luo, S. Bi, J. Inorg. Biochem. **97**, 173 (2003)
17. A.B. Tabrizi, Food Chem. **100**, 1698 (2007)
18. N. Pourreza, A. Mouradzadegun, S. Mohammadi, J. Iran. Chem. Soc. **8**, 951 (2011)
19. M. Jamshidi, M. Ghaedi, K. Mortazavi, M. NejatiBiareh, M. Soylak, Food Chem. Toxicol. **49**, 1229 (2011)
20. P.H. Pacheco, R.A. Gil, P. Smichowski, G. Polla, L.D. Martinez, Microchem. J. **89**, 1 (2008)

21. P. Matus, I. Hagarova, M. Bujdos, P. Divis, J. Kubova, J. Inorg. Biochem. **103**, 1473 (2009)
22. S. Dai, M.C. Burleigh, Y.H. Ju, H.J. Gao, J.S. Lin, S.J. Pennycook, C.E. Barnes, Z.L. Xue, J. Am. Chem. Soc. **122**, 992 (2000)
23. L. Ye, K. Mosbach, J. Am. Chem. Soc. **123**, 2901 (2001)
24. A. Ersoz, A. Denizli, A. Ozcan, R. Say, Biosens. Bioelectron. **20**, 2197 (2005)
25. F. Shakerian, S. Dadfarnia, A.M. Haji Shabani, Food Chem. **134**, 488 (2012)
26. M.H. Arbab-Zavar, M. Chamsaz, G. Zohuri, A. Darroudi, J. Hazard. Mater. **185**, 38 (2011)
27. M. Shamsipur, A. Besharati-Seidani, React. Funct. Polym. **71**, 131 (2011)
28. S.M. Ng, R. Narayanaswamy, Anal. Bioanal. Chem. **386**, 1235 (2006)
29. M. Andac, E. Ozyapi, S. Senel, R. Say, A. Denizli, Eng. Chem. Res. **45**, 1780 (2006)
30. M. Yaman, Mikrochim. Acta **129**, 115 (1998)
31. F. Shakerian, S. Dadfarnia, A.M. Haji Shabani, J. Iran. Chem. Soc. **6**, 594 (2009)
32. P.S. Kalsi, *Spectroscopy of Organic Compounds*, 6th edn. (New Age International (P) Ltd. Publishers, New Delhi, 2004)
33. A. Safavi, S. Momeni, N. Saghir, J. Hazard. Mater. **162**, 333 (2009)
34. I. Narin, M. Tuzen, M. Soylak, Talanta **63**, 411 (2004)
35. M. Khajeh, M. Bohlooli, H. Hashemi, J. Macromol. Sci. Part A Pure Appl. Chem. **46**, 526 (2009)