Journal of Hazardous Materials 162 (2009) 333–337

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Efficient preconcentration and determination of traces of aluminum ion using silica-bonded glycerol sorbent

Afsaneh Safavi*, Safieh Momeni, Narges Saghir

Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz 71454, Iran

ARTICLE INFO

Article history:
Received 19 December 2007
Received in revised form 8 April 2008
Accepted 9 May 2008
Available online 16 May 2008

Keywords:
Silica-bonded glycerol
Solid-phase extraction
Aluminum
Hair
Tea

ABSTRACT

A solid-phase extraction system was proposed for the determination of aluminum after preconcentration with glycerol-bonded silica gel. The method is rapid and efficient for the enrichment of aluminum ions at trace levels. Optimal sorption conditions were found for sorption and desorption of aluminum ions. The effects of diverse ions on the sorption and recovery of aluminum have been studied and it was shown that the selectivity of the sorption process was very good. A very satisfactory preconcentration factor of 500 was achieved by this method. The lowest concentration of aluminum ions for quantitative recovery was 2 ng ml^{-1}. The capacity of sorbent was 400 μg per gram of sorbent. The method showed good reproducibility (R.S.D. = 2.2% for $n = 7$) and was applied to the determination of aluminum in mineral water, hair and green tea samples.

1. Introduction

Aluminum (Al) is the most important light metal and is used in a multitude of ways in industry. Aluminum alloys are especially important due to their low density and find particular use in the aerospace and automotive industries [1]. The chronical effect of Al compounds is often connected with mortality of some animals and Alzheimer's or some other human neurodegenerative diseases [2–4]. The separation of Al in soil solution is important because this factor controls the toxicity of Al to plants and living organism [5–8].

The determination of trace levels of Al has been reported by various methods, such as spectrophotometry [9–11], spectrofluorometry [12,13], graphite furnace atomic absorption spectrometry (GF-AAS) [14], absorption spectroscopy with a laser diode [15], inductively coupled plasma atomic emission spectrometry (ICP-AES) [16,17] and ICP mass spectrometry (ICP-MS). Because of possessing the advantages of high recovery, short analysis time, high enrichment factor, low consumption of organic solvent, solid-phase extraction (SPE) has been found increasing applications [18]. The solid-phase extraction of traces of metal ions from solutions by sorbent modified with analytical reagents is one of the most promising methods, especially in environmental systems [19–23]. Different solid-phase extraction methods have been recommended for the determination of aluminum [24–28]. However, many of these methods do not provide high preconcentration factors.

An easy and efficient method for the preparation of silica-based reagents has been reported previously [29–31]. The preparation of directly bonded 2-mercaptobenzothiazole–silica gel and glycerol-bonded silica gel has been reported in our previous works [32,33]. In the present work, a directly bonded glycerol–silica gel has been used as a sorbent for preconcentration of aluminum. The influence of experimental conditions was studied to establish an optimized solid-phase extraction procedure for the determination of trace levels of aluminum.

2. Experimental

2.1. Reagents

Highest grade commercially available reagents were used throughout this study without further purification. An aluminum stock solution (500 μg ml^{-1}) was prepared by dissolving 1.3894 g of $Al(NO_3)_3 \cdot 9H_2O$ (Merck, Darmstadt, Germany) in a 200 ml volumetric flask and diluting to the mark with distilled water. Standard solutions were prepared daily from the stock solution by serial dilution with water.

Ammonium acetate buffers (0.1 M) were prepared by the addition of an appropriate amount of acetic acid to ammonium acetate solution to give a solution of pH 4–6. Sodium borate (0.1 M) buffer solution was used.

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* Corresponding author. Tel.: +98 711 6137351; fax: +98 711 2286008.
E-mail address: safavi@chem.susc.ac.ir (A. Safavi).

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doi:10.1016/j.jhazmat.2008.05.044

Silica gel (60 mash size, Merck, Darmstadt, Germany), thionyl chloride (Merck, Darmstadt, Germany), KCl (Merck, Darmstadt, Germany), hydrochloric acid, glycerol and acetonitrile (Panreac Quimica SA, E.U.) were used. Triply distilled water was used throughout.

2.2. Apparatus

A Varian model SpectrAA 220 (Mulgrave, Vic., Australia) atomic absorption spectrometer equipped with an aluminum hollow cathode lamp (wavelength of 309.3 nm, nitrous oxide–acetylene flame), was used for the measurement of aluminum concentration. pH measurements were carried out by using Metrohm pH meter (model 780) with a combined pH glass electrode calibrated against standard buffer solutions at pH = 4.0 and 7.0. An Edward vacuum pump was used for filtration purposes. The column dimensions were 10 mm × 100 mm with a sintered glass plate located at the bottom of the column.

2.3. Synthesis of the sorbent

The directly glycerol-bonded silica gel, was prepared simply according to our previous report [32] and applied as a sorbent for preconcentration and determination of Al.

2.4. Recommended procedure

The glass column used had a stopcock and a porous disk. A small amount of glass wool was placed on the disc to prevent loss of the sorbent during sample loading. Then 0.1 g of the synthesized sorbent was poured into the column. Initially, for column conditioning, distilled water (5 ml) was passed through the column. Then an aliquot of aluminum(III) ion solution (between 5 and 1000 ml depending on the concentration of aluminum) was passed through the column. The solution was permitted to flow through the column at a flow rate of 0.5 ml min^{-1}. After passing the solution, the adsorbed Al on the column was eluted with 5 ml of 0.25 M hydrochloric acid at an elution rate of 1.0 ml min^{-1}. The eluent was analyzed for the determination of aluminum concentrations by a flame atomic absorption spectrometer.

2.5. Analysis of aluminum in real samples

For the human hair samples, it was immersed in acetone for 30 min, washed by water and dried. About 1.0 g of this sample was weighted accurately; 15 ml of a solution mixture of concentrated $HClO_4$ and HNO_3 (1:8, v/v) was added, and then it was digested and dried under elevated temperature. The residual was leached out with distilled water, transferred to a 500 ml measuring flask and diluted to the mark with distilled water. A proper amount of green tea solution was taken and treated as described previously [34]. Water samples were directly analyzed without any pretreatment.

3. Results and discussion

3.1. Optimization of column conditions

In order to obtain highly sensitive, accurate, and reproducible results, analytical parameters including the amount of sorbent, pH of the sample solution, type and concentration of eluent, sample and eluent flow rates, sample volume and maximum capacity of the sorbent for aluminum recovery have been studied. The optimization procedure was carried out by one-at-a-time (varying one parameter while the others were kept constant) method.

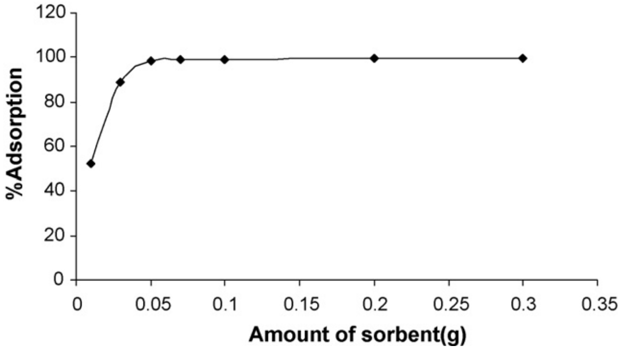

Fig. 1. Effect of the amount of sorbent on percent sorption of aluminum ion.

3.2. Effect of the amount of sorbent

The influence of various amounts of sorbent on the sorption of aluminum ions was investigated in the range of 0.01–3.0 g. For this purpose aliquots of 5 ml of 2 $\mu g\, ml^{-1}$ aluminum ion solution were separately introduced into a series of packed columns containing different amounts of sorbent. After passing solutions through the column, the percent retention of aluminum ions on the sorbent was determined by AAS. The results (Fig. 1) show that aluminum ion was completely adsorbed on the sorbent in the range of 0.05–0.3 g of the sorbent. Therefore, 0.1 g was selected as the amount of sorbent necessary for all subsequent experiments.

3.3. Effect of sample pH

The percent sorption of aluminum ion as a function of pH of sample solution was examined in the range of 4–12.

The standard solution was adjusted to the desired pH with the buffer solution. For this purpose aliquots of 5 ml of 2 $\mu g\, ml^{-1}$ aluminum ion solutions at different pH values were passed through a column containing 0.1 g sorbent. The results are depicted in Fig. 2. The recoveries of aluminum at the pH range of 6–12 were found quantitative (>98%). However, at pH values lower than 6, the retention of aluminum was not quantitative. Thus, in all further studies, the pH of the solution was kept constant at pH 8 with sodium borate buffer solution.

3.4. Effect of the sample flow rate

The degree of aluminum ion sorption of the modified silica gel packed column was studied at varying flow rates of the aluminum ion solution. The recovery was greater than 98% at flow rates between 0.1 and 3.0 ml min^{-1}. However, at a flow rate above

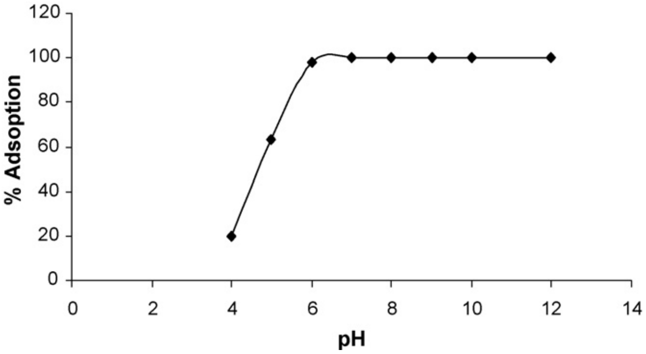

Fig. 2. Effect of pH of the sample solution on percent sorption of aluminum ion.

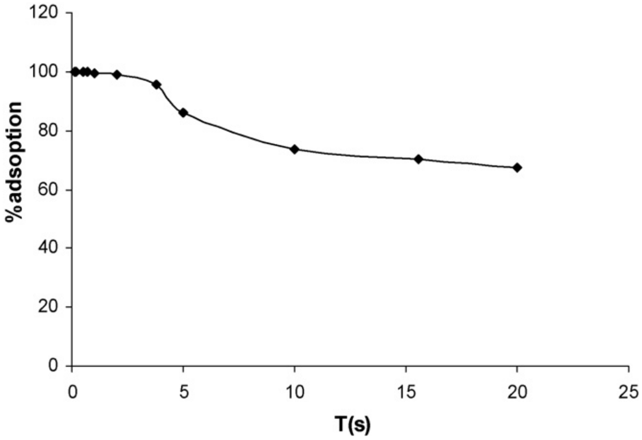

Fig. 3. Effect of the sample flow rate on percent sorption of aluminum ion.

3 ml min^{-1}, there was a decrease in the sorption percentage. A flow rate of 0.5 ml min^{-1} was selected as the optimum flow rate for further studies (Fig. 3).

3.5. Choice of eluent

The eluent type is an important factor in solid-phase extraction studies. The effect of 5 ml of various eluents on the recoveries of aluminum was studied when 5 ml of 2 μg ml^{-1} aluminum ion solution was passed through a series of columns containing 0.1 g sorbent. In order to choose the most effective eluent, a series of selected eluent solutions such as fluoride, sulfate, sodium hydroxide, nitric acid, and hydrochloric acid were used. The adsorbed aluminum ions were eluted by passing 5 ml of 0.5 M of the above selected eluents. The amount of aluminum ion back-extracted into the liquid phase by each eluent was measured using AAS. The results showed that the recovery is the best when hydrochloric acid solution was used as the eluent.

3.6. Effect of eluent concentration

The elution of 10 μg of Al(III) from a column containing 0.1 g of sorbent was studied using HCl solution at varying concentrations (0.001–0.75 M). At concentrations above 0.1 M, HCl completely (recovery of almost 100%) desorbs aluminum ion from the sorbent surface. The optimum eluent concentration selected for Al desorption was 0.25 M HCl (Fig. 4).

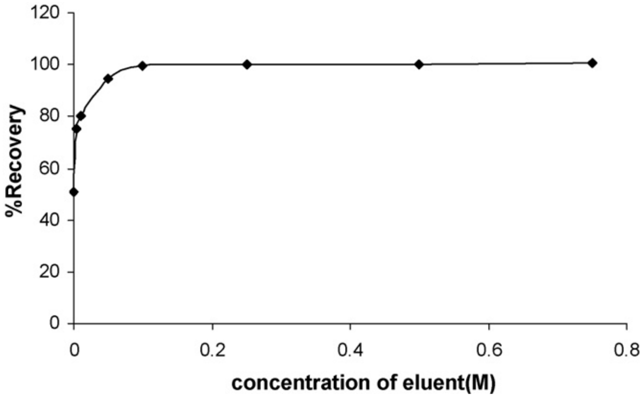

Fig. 4. Effect of eluent concentration on percent recovery of aluminum ion.

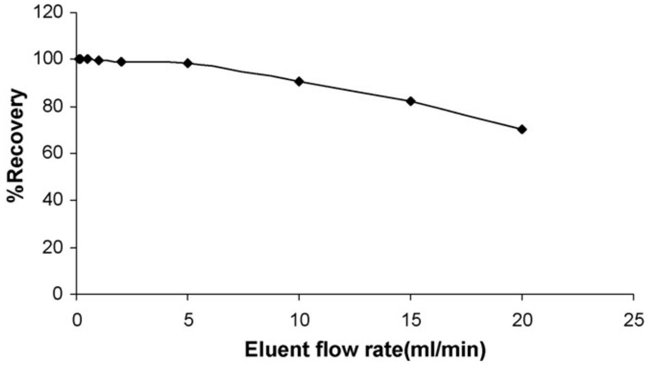

Fig. 5. Effect of eluent flow rate on percent recovery of aluminum ion.

3.7. Effect of eluent flow rate

The effect of flow rate of eluent solution on the recovery of aluminum ion from the sorbent was examined in the range of 0.1–20 ml min^{-1}. The results (Fig. 5) indicated that aluminum ion was desorbed almost completely at eluent flow rates less than 5.0 ml min^{-1}. For effective and quantitative elution, however, a flow rate of 1.0 ml min^{-1} was chosen.

3.8. Effect of adverse ions

To assess the possible application of the procedure, the effect of foreign ions which might interfere with the determination of aluminum was examined under the optimum conditions. A fixed amount of analyte was taken with different amounts of foreign ions and the recommended procedure was followed. The recoveries of analytes were higher than 95%. Tolerance limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of aluminum by combination of solid-phase extraction procedure and flame atomic absorption spectrometric determination method. The results (Table 1) show that except cobalt ion, most of the tested ions do not interfere with the determination of aluminum. The interfering effect of cobalt was eliminated by the addition of excess amounts of CN$^-$ ion (0.026 M) to the sample solution prior to its introduction into the column.

Table 1
Effects of foreign ions (in binary mixtures) on percent recovery of aluminum ion

Coexisting ion	Concentration of coexisting ions (ppm)	% Recovery of aluminum ion
K^+	100	100.1
Na^+	100	99.5
Mg^{2+}	100	101.5
Ca^{2+}	100	97.5
CH_3COO^-	100	98.0
Cu^{2+}	50	96.4
Co^{2+}	50	83.5
Co^{2+}	50	98.0[a]
Ni^{2+}	100	97.9
Cd^{2+}	50	98.8
Zn^{2+}	50	97.6
Mn^{2+}	100	99.0
Cl^-	1000	101.1

Experimental conditions:
Source: 5 ml of 2 mg l^{-1} aluminum ion solution at pH = 7.7 and flow rate 0.5 ml min^{-1}; sorbent: 0.1 g; eluent: 5 ml of 0.25M HCl and flow rate 1 ml min^{-1}.

[a] After masking Co^{2+} with CN$^-$ (0.026 M).

Table 2
Determination of aluminum(III) in real samples

Sample	Al(III) spiked (ng ml^{-1})	Al(III) detected (ng ml^{-1})[a]	% Recovery
Mineral water			
I	0.0	28.94(±0.08)	–
II	10.0	39.41(±0.21)	104.7
III	20.0	47.87(±0.18)	94.6
IV	30.0	58.14(±0.24)	97.3
Hair			
I	0.0	33.7(±0.27)	–
II	10.0	44.0(±031)	103
III	20.0	54.1(±0.11)	102
IV	30.0	62.8(±0.22)	97.0
Green tea			
I	0.0	142.5(±0.19)	–
II	50.0	195.0(±0.37)	105.0
III	100.0	248.3(±0.24)	105.8
IV	150.0	285.4(±0.25)	95.3

Experimental conditions:
Source: 200 ml mineral water, 100 ml of 0.002 g l^{-1} of hair solution, and 50 ml of 1.0 g l^{-1} green tea solution, all at pH = 7.7; flow rate: 0.5 ml min^{-1}; sorbent: 0.1 g; eluent: 5 ml of 0.25 M HCl.

[a] Mean ± standard deviation ($n = 3$).

3.9. Effect of sample volume

In order to obtain a high preconcentration factor, aluminum ions in the large sample volume has been quantitatively sorbed and desorbed by a small stripping volume. The effect of sample volume on metal sorption was studied by passing solutions containing 10 μg of aluminum in 50, 100, 200, 500 and 1000 ml water. Aluminum was quantitatively retained in all cases. At least, up to 1000 ml of aluminum ion solution and sorbed aluminum ions were eluted out by 2 ml of 0.25 M HCl. A preconcentration factor of 500 was easily achievable.

3.10. Adsorption capacity

A series of 5 ml standard solutions of 2 μg ml^{-1} Al were passed through micro-columns packed with 0.2 g glycerol-bonded silica gel, and the Al content in the eluent was estimated by flame atomic absorption spectroscopy. The maximum sorbent capacity of the method was found to be 400 μg. In this study, the sorption mechanism of aluminum ion is attributed to the complex formation of this ion with glycerol-bonded silica gel. The complexation between sorbent and aluminum is expected due to the presence of oxygen donating sites in glycerol.

3.11. Figures of merit

The limit of detection (LOD) of the present work was calculated under optimal experimental conditions. The limit of detection for Al based on three times standard deviation of the blank were 2 ng ml^{-1} .The precision of the determination of aluminum was evaluated by a solution containing 2 μg ml^{-1} of aluminum under the optimum conditions mentioned above. For this purpose, the procedure was repeated seven times. The system showed good reproducibility (R.S.D. = 2.2%).

3.12. Application to real sample analysis

The present method was applied to the preconcentration and determination of Al in mineral water, hair and green tea samples. The recoveries of the spiked aluminum ions were also determined. Table 2 indicates that the proposed method is ideal for the preconcentration of aluminum ion at ng ml^{-1} levels in real samples such as mineral water, hair and green tea.

Table 3
Comparison of preconcentration factors of the ligand-immobilized adsorbents for aluminum

Ligand	PF[a]	DL[b] (ng ml^{-1})	R.S.D. (%)	Reference
8-Hydroxyquinoline	76	0.02	<10	[22]
Tiron	20	0.3	<10	[25]
XAD-1180/pyrocatechol violet	150	0.021	<5	[14]
Cupferron	150	–	–	[23]
Glycerol	500	2.0	2.4	Present work

[a] Preconcentration factor.

[b] Detection limit.

4. Conclusion

The proposed method for solid-phase extraction is convenient, simple, and highly economic and can be applied to the determination of aluminum in real samples. The system showed good reproducibility (R.S.D. = 2.2% for $n = 7$). The advantage of this sorbent is preconcentration of analytes from large sample volumes. The preconcentration factor achieved is superior to the previously reported solid-phase extraction methods for aluminum (Table 3). The method is relatively rapid for the enrichment of aluminum ions at trace levels.

Acknowledgements

The authors wish to express their gratitude to the Third World Academy of Sciences, Iran Chapter (TWASIC) and Shiraz University Research Council for the support of this work. They are also grateful to Prof. N. Iranpoor for his valuable discussion and guidance throughout this work.

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