

Solid-phase extraction and separation procedure for trace aluminum in water samples and its determination by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS)

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Abstract In the present study, a separation/preconcentration procedure for determination of aluminum in water samples has been developed by using a new atomic absorption spectrometer concept with a high-intensity xenon short-arc lamp as continuum radiation source, a high-resolution double-echelle monochromator, and a charge-coupled device array detector. Sample solution pH, sample volume, flow rate of sample solution, volume, and concentration of eluent for solid-phase extraction of Al chelates with 4-[(dicyanomethyl)diazanyl] benzoic acid on polymeric resin (Duolite XAD-761) have been investigated. The adsorbed aluminum on resin was eluted with 5 mL of 2 mol L⁻¹ HNO₃ and its concentration was determined by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS). Under the optimal conditions, limit of detection obtained with HR-CS FAAS and Line Source FAAS (LS-FAAS) were 0.49 μg L⁻¹ and 3.91 μg L⁻¹, respectively. The accuracy of the procedure was confirmed by analyzing certified materials (NIST SRM 1643e, Trace elements in water)

and spiked real samples. The developed procedure was successfully applied to water samples.

Keywords Preconcentration · Trace metal · Aluminum · Separation

Introduction

Aluminum is one of the most abundant elements in the earth. It enters into the body from the environment, diet, drinking waters, sprays, and medication (Yokel 2000; Liu et al. 2005). Al is a highly neurotoxic element and has been suggested to play a role in degeneration of nerve cells in the brain of human and experimental animals (Yumoto et al. 2001). It was also reported that Al was involved in the etiology of several human pathologies like dialysis dementia, amyotrophic lateral sclerosis (Linton et al. 1987), senile dementia of Alzheimer type, and development of the brain in fetus and suckling (Paternain et al. 1988; Muller et al. 1992).

Despite the several Al exposure reports, foods and water are the most important sources. 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 (WHO 1997). EPA has recommended a secondary maximum contaminant level of 0.05–0.2 mg L⁻¹ for aluminum in drinking water (EPA 2000). Some previous epidemiologic studies have

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suggested an association between aluminum from drinking water and dementia (Flaten 1990; McLachlan et al. 1996). Rondeau et al. (2000) have found that when concentration of aluminum in drinking water is higher than 0.1 mg L^{-1} it may be a risk factor for Alzheimer's disease.

Direct analyses of these concentrations without using a separation/preconcentration technique are impossible due to high limits of detection (LOD) of flame atomic absorption spectrometry (FAAS) and matrix effects. Therefore, sample preparations are required for separation and preconcentration determination of metal ions (Narin et al. 2004).

A number of separation and preconcentration procedures for trace metals involving cloud point extraction, solid-phase extraction (SPE), coprecipitation, dispersive liquid–liquid micro-extraction have been used in literature (Baytak and Türker 2009; Baysal et al. 2009; Ciftci 2010a; Rezaee et al. 2010). Among the preconcentration techniques, SPE has been widely used for the separation and sensitive determination of metal ions, mainly in water samples. SPE has some advantages such as rapid, simple, low solvent usage and lower extraction time and being sensitive and economic (Ulusoy et al. 2011; Pacheco et al. 2008).

Some analytical techniques as neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GF-AAS), and FAAS have been used for the determination of trace elements in different matrixes (Narin et al. 2004; Yenisoys-Karakaş and Tuncel 2008; Xia et al. 2005; Frankowski et al. 2011; Bianchi et al. 2007; Bulut et al. 2010). ICP-AES has a low detection limit for metals. However, the technique does suffer from the problem of spectral overlap from various elements present in the sample. For example, cadmium, boron, and tungsten have interfering effects on the determination aluminum (Tria et al. 2007). GF-AAS has successfully been applied to determine trace aluminum levels in various samples. Detection limits for this technique for trace elements are very low (in micrograms per liter). There are some disadvantages such as serious matrix interferences and formation of refractory carbides in GF-AAS analyses (Magalhaes et al. 2002). NAA and ICP-MS have good sensitivity, but uses of these methods are limited because of expensive instrumentation and high cost for routine analysis.

LS-FAAS and HR-CS AAS have been popularly used for this purpose. The detection limits of analytical methods for determination of trace element have been improved in recent years. For this reason, HR-CS AAS was developed as a new atomic absorption spectrometer concept. HR-CS AAS is a promising option for element analysis because of its relatively low cost and it allows obtaining detection limits five times better than those obtained by LS-FAAS (Welz 2005). This is due to the combined use of the high radiation intensity xenon short-arc lamp, a high-resolution Echelle double monochromator and a charge-coupled device (CCD) array as detector. The entire spectral environment of the analytical line is available, giving more information and possibilities of background correction and elimination of interferences than conventional LS-FAAS. Moreover, the most obvious advantage is the need for only one single lamp for all elements and wavelengths, compared with one lamp for each element, as it is necessary in LS-FAAS (Welz et al. 2003; Becker-Ross et al. 2006; Welz et al. 2007; Villanueva-Alonso et al. 2009).

In this work, a new SPE procedure for the determination of aluminum by using HR-CS AAS was developed. In previous studies, different chelating agents such as quercetin, morin, pyrocatechol violet, eriochrome cyanine, lumogallion, 8-hydroxyquinoline, and salicylaldehyde picolinoylhydrazone have been used for separation and determination of trace aluminum (Tria et al. 2007). As different from these chelating agents we have firstly used 4-[(dicyanomethyl) diazenyl] benzoic acid (DSMDABA) as chelating agents for separation/preconcentration of aluminum ions. Al-DSMDABA chelates can be adsorbed on Duolite XAD-761 polymeric resin in column and needed analytical parameters for recovery of aluminum were optimized. Detection and quantification limits of proposed procedure were calculated by using HR-CS AAS and LS-FAAS.

Experimental work

Sampling, analysis, and quality control

An Analytik Jena Model ContrAA 300 High-Resolution Continuum Source Flame Atomic Absorption Spectrometer (GLE, Berlin, Germany) equipped with a xenon short-arc lamp XBO 301 with a nominal

power of 300 W operating in a hot-spot mode as a continuum radiation source was used for the analysis. A N₂O-acetylene flame was used for atomization of Al. All measurements were carried out under optimum conditions in three replicates using an injection module (SFS 6) enabling the computer controlled aspiration of blanks, analytical solutions and samples. All pH measurements were made with an Orion Star (Thermo Fisher, USA) model pH meter. A Varian (Palo Alto, CA, USA) AA240 FS model flame atomic absorption spectrometer equipped with a deuterium-lamp background corrector, aluminum hollow cathode lamp (Varian) was used as line source for FAAS. The operating conditions for HR-CS FAAS and LS-FAAS are given in (Tables 1 and 2), respectively.

Reagents

All solutions were prepared using ultra pure water (specific resistance 18 MΩ cm) from a Milli-Q purification system (Millipore Corporation, MA, USA). Duolite XAD-761 which is an ester acrylic polymer (Sigma-Aldrich) was used as a polymer resin. The resin particles were between 20–60 mesh. The DSMDABA monosodium salt hydrate was used as a ligand and it was obtained from Firat University (Turkey), Inorganic Chemistry Division. Molecule formula of DSMDABA is given (Fig. 1). DSMDABA solution of 0.1 % (w/v) was prepared by dissolving 0.1 g of DSMDABA monosodium salt in 100 mL water.

Standard solutions of used metals were prepared from the correspondent 1,000 mg L⁻¹ stock solutions (Merck). All glasswares were cleaned using ultra-pure water, kept in nitric acid for 24 h, and washed again with ultra-pure water.

Table 1 The operating conditions for HR-CS AAS

Parameters	
Wavelength (nm)	396.152
Flow rate of N ₂ O–C ₂ H ₂ (L/h)	225
Flow rate of C ₂ H ₂ –air (L/h)	70
Flow rate of oxidant (L/h)	400
Burner height (mm)	4
Evaluation pixels (pm)	3
Background correction	Ne lamb, simultaneous

Table 2 The operating conditions for LS-FAAS

Parameters	
Wavelength (nm)	309.3
Slid width (nm)	0.5
Lamp current (mA)	10
Acetylene flow rate (L/min)	6.95
N ₂ O flow rate (L/min)	10.24
Background correction	On (deuterium lamb)

Preparation of separation column

A glass column which was 10.0 cm in length and 0.8 cm in internal diameter and had a 250-mL tank for separation/preconcentration of metal ions were used. The resin was treated with nitric acid (2 mol L⁻¹) and water. Then, it was washed with deionized water until pH of the supernatant was neutral. Afterwards it was dried in an oven at 80 °C. A small amount of glass wool was placed at the bottom of the column in order to hold resin; 0.5 g dried resin was placed and another small glass wool plug was inserted on the top of the resin. After each use, the resin for the removal of impurities was rinsed with 10 mL of 2 mol L⁻¹ HCl, 10 mL of 2 mol L⁻¹ HNO₃, and 50 mL water, respectively (Baytak et al. 2011; Ciftci et al. 2011; Ciftci 2010b; Kalfa et al. 2009).

Preconcentration procedure

Model solutions were used for preconcentration of Al³⁺. The model solutions were prepared as follows: Firstly, 2.5 mL of 2.0 mg L⁻¹ Al³⁺ solution was put into the volumetric flask then 1.0 mL of DSMDABA solution and 2 mL of acetic acid/sodium acetate buffer solutions (pH 5.5) were added. Afterwards, final volume was diluted to 50 mL by deionized water. The column was preconditioned by passing the aqueous solutions of pH 5.5 through column and then, the model solution was passed through the column at a flow rate of

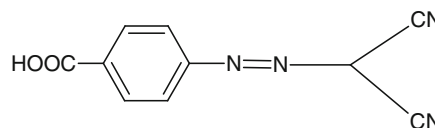


Fig. 1 Molecule formula of DSMDABA

10 mL min⁻¹. The adsorbed metal ions on the column were eluted with 5 mL of 2 mol L⁻¹ HNO₃ solutions at a flow rate of 10 mL min⁻¹ and, were determined by HR-CS AAS.

Analysis of water samples

The tap water was collected from our research laboratory at Ahi Evran University. Commercial drinking water and mineral water were collected from the local market in Turkey. For analysis, a 500-mL sample was placed in a beaker and filtered through 0.45 μm cellulose nitrate membrane filters to remove suspended organic and other particles. Afterwards, 20 mL buffer solutions (pH 5.5), 1.0 mL of DSMDABA solution, and known amounts of Al³⁺ were spiked into this sample. Finally, the preconcentration procedure was applied and the concentration of the Al³⁺ was determined by HR-CS AAS.

Results and discussion

For the maximum recovery of Al³⁺, the pH of sample solution, the type and concentration of eluent, volume of sample solution, and the flow rate of sample and eluent solution and interfering ions have been investigated and optimized. The analytical parameters such as LOD, limit of quantification (LOQ), precision, accuracy, and dynamic range have been determined under optimal conditions.

Effect of test solution pH on recovery of Al ions

The pH of the medium is of prime importance for efficient retention and recovery of the metal ions on the resin. Its influence strongly depends on the nature of the adsorbent used. The recovery of the analyte was determined by applying the preconcentration procedure by changing the pH of model solution in the range of 4.0–8.5. The pH of each model solutions was adjusted with different buffer solutions, such as sodium acetate-acetic acid, sodium mono hydrogen phosphate-potassium dihydrogen phosphate and ammonium chloride-ammonia. The quantitative recovery (above 95 %) of Al³⁺ was obtained at pH 5.0–7.5. The recoveries of Al³⁺ were decreased when the solutions pH is over 7.5 and less than 5.0 (Fig. 2). Hence, pH 5.5 was selected

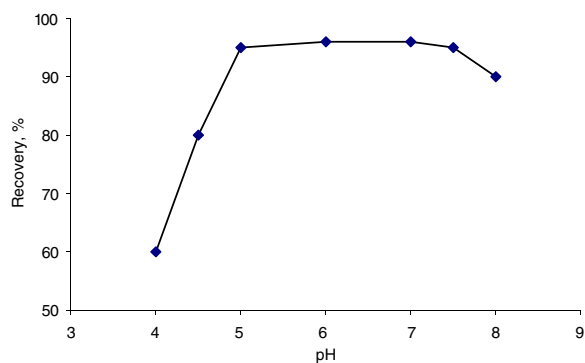


Fig. 2 The effect of pH of sample solution on the recovery of Al

as an optimum pH for SPE of the analyte ions for further experiments.

Effect of eluent type and concentration

In order to choose the most effective eluent for desorbing, different concentration and different volume of eluent agents, such as, HCl, HNO₃ and mixture of Ethanol-HNO₃ have been studied. Quantitative recovery (>95 %) has been obtained by using 5 mL of 2 mol L⁻¹ of HNO₃ solutions (Table 3).

Effect of the sample flow rate

The sample flow rate should be optimized to ensure quantitative recovery along with decreased sample processing time. The effect of the flow rate of sample solutions on the recovery of analyte was examined in the range of 1–12 mL min⁻¹. Under optimum conditions, the aluminum ions were quantitatively recovered up to

Table 3 The effect of eluent type/concentration/volume of eluent on recovery of aluminum

Eluent	Recovery (%) ^a
1 mol L ⁻¹ HCl (5 mL)	92±2
1 mol L ⁻¹ HCl (10 mL)	94±3
2 mol L ⁻¹ HCl (5 mL)	90±1
1 mol L ⁻¹ HNO ₃ (5 mL)	94±1
1 mol L ⁻¹ HNO ₃ (10 mL)	96±2
2 mol L ⁻¹ HNO ₃ (5 mL)	99±2
2 mol L ⁻¹ HNO ₃ (in ethanol; 5 mL)	97±2

^a Results are mean±standard deviation of three replicate analyses

10 mL min⁻¹ of the flow rates (Fig. 3). Above this value, the recovery decreased gradually. Accordingly, the optimum flow rate was recommended as 10 mL min⁻¹ to decrease time of preconcentration time.

Effect of eluent flow rate

The flow rate of eluent solution (5 mL of 2 mol L⁻¹ HNO₃) on the retention of Al³⁺ was examined in the range of 2.0–10.0 mL min⁻¹ at optimum conditions. The recovery of Al³⁺ ranged between 95 and 100 % at the eluent flow rates varying from 2.0 to 10.0 mL min⁻¹. To decrease the analysis time, eluent flow rate was selected as 10 mL min⁻¹.

Effect of sample volume

In order to obtain the maximum applicable sample solution (or analyte concentration), model solutions including the same amount of aluminum ions with different volumes were used. For this purpose, Al³⁺ solutions containing 5 µg Al³⁺ were preconcentrated from sample volumes of 50, 100, 250, 500, and 750 mL according to preconcentration procedure (corresponding to analyte concentrations of 0.1, 0.05, 0.02, 0.01, and 0.0066 µg mL⁻¹, respectively).

The recovery of Al³⁺ was quantitative (>95 %) for sample volumes up to 500 mL (Fig. 4). After the preconcentration of 500 mL sample solution, if 5 mL of eluent solution was used for the analysis, the preconcentration factor was found to be 100 for Al³⁺.

Effect of foreign ions

The effects of common coexisting ions on the adsorption of aluminum ions were investigated. Various

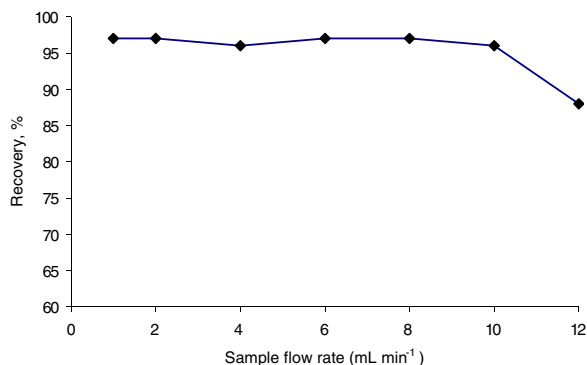


Fig. 3 Effect of the sample flow rate on the recovery of Al

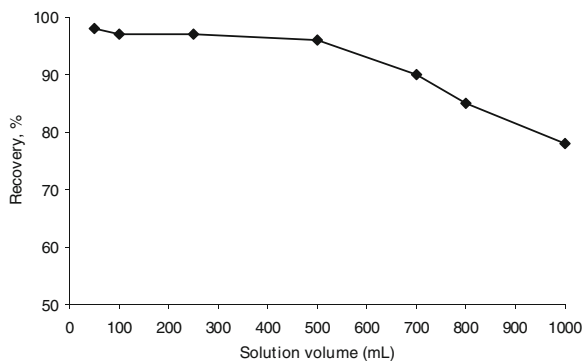


Fig. 4 The effect of sample volume on the recovery of Al

amounts of foreign ions (their nitrate or chloride salts) were added into 50 mL of model solutions containing 5 µg of Al³⁺ and the procedure described in the experimental section was applied. The results indicated that concentrations of all the ions tested did not interfere on recovery of aluminum ions (Table 4).

Effect of ligand amount

In separation/preconcentration studies, various ligands which have high affinity to metal ions were used widely in adsorption process. In this study, DSMDABA that contains imine and cyano residues as an organic functional group which provides various numbers of different potential binding sites for metal ions

Table 4 Effects of the some foreign ions on the recovery of Al

Interfering ions	Concentration (mg L ⁻¹)	Recovery ^a (%)
K ⁺	1,000	96±2
Na ⁺	1,000	102±2
Ca ²⁺	500	98±1
Mg ²⁺	200	96±2
Zn ²⁺	5	100±2
Cu ²⁺	5	102±2
Co ²⁺	5	97±2
Ni ²⁺	5	99±2
Pb ²⁺	5	95±2
Cr ³⁺	5	102±1
Fe ³⁺	5	98±2
NO ₃ ⁻	1,000	96±2
Cl ⁻	1,000	102±2

^a Results are mean±standard deviation of three replicate analyses

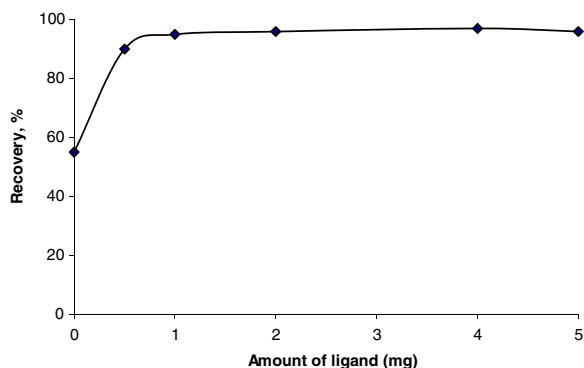


Fig. 5 Effect of ligand amount on the recovery of Al

under investigation was used as a ligand. Effect of the amount of DSMDABA on the recovery of Al^{3+} was studied. Different amounts of DSMDABA in the range from 0.5 to 5.0 mg (from 0.1 % (w/v) DSMDABA solution with different volumes) were added to different model solutions with the same amount of analyte and preconcentration procedure was applied. The results are given in (Fig. 5). When DSMDABA was used the adsorption of aluminum ions on Duolite XAD-761 resin was stimulated and this effect increased the performance of proposed procedure. Quantitative recoveries were obtained for aluminum ions when the amount of DSMDABA was 1.0 mg or higher. At an amount of DSMDABA of less than 1.0 mg, the recovery was below 95 %. As a result, 1.0 mg of DSMDABA (1.0 mL of 0.1 % (w/v) DSMDABA solution) was added to the solutions in further works.

Effect of resin amount

The influence of XAD-761 resin amount on recoveries of aluminum ions was studied. For this aim, different amounts of adsorbent were added in the

range of 300 and 600 mg into the adsorption column. The test solution of 50 mL sample including 5 μg of aluminum was passed through the column at optimum conditions. The results showed that the amount of optimum sorbent was in the range of 500–600 mg of XAD-761 for maximum recovery of Al^{3+} , was selected 500 mg.

Capacity of the resin

The capacity of the resin is an important factor that determines which amount of adsorption material is required to quantitatively accumulate a specific amount of analyte from the samples solution (Ciftci 2010c; Roldan et al. 2004). For investigation of adsorption capacity, 250 mL aluminum–DSMDABA chelates/complexes solution including 50 mg L^{-1} of Al^{3+} was passed from column including 0.50 g of Duolite-XAD-761 resin at optimized conditions. The adsorbed metal ions on the column were eluted with 5 mL of 2 mol L^{-1} HNO_3 solutions and were determined by HR-CS AAS. The results showed that the capacity of resin was 9.6 mg g^{-1} . The capacity of the adsorbent was checked again after using approximately a hundred times. It was found that sorbent capacity did not significantly change.

Analytical features

Under the optimum experimental conditions, analytical parameters of the proposed procedure, such as linear range, calibration curve, equation of calibration curve, correlation coefficient, LOD, LOQ, and precision were examined.

The linear range of calibration graph was found to be 0.2 to 20 mg L^{-1} with a correlation coefficient of

Table 5 Comparison of some analytical performance parameters that obtained by using HR-CS AAS and LS-FAAS

Parameters	HR-CS AAS	LS-FAAS
Calibration equation (mg L^{-1})	$A=0.0043480 \times C+0.0001131$	$A=0.00417 \times C+0.00050$
Correlation coefficient (R^2)	0.9992	0.9993
Dynamic range (mg L^{-1})	0.2 to 20	1.0 to 20
Standard deviation of absorbance of blank solutions ($N=15$)	0.00011	0.00071
Detection limit ($\mu\text{g L}^{-1}$)	0.49	3.91
Quantification limit ($\mu\text{g L}^{-1}$)	1.63	12.90

Table 6 Results for certified reference material (NIST SRM 1643e, trace elements in water, 50 mL)

Element	Found ^a ($\mu\text{g L}^{-1}$)	Certified ($\mu\text{g L}^{-1}$)	Recovery (%)
Al	139.6±9.2	141.8±8.6	98.4

^aMean and standard deviation from three determinations

0.9992 for standard aluminum solutions. LOD and LOQ of this procedure were defined as the concentration corresponding to three times and ten times of the standard deviation (σ) measurements of blank solution ($N=15$) using the preconcentration procedure. LOD ($3\sigma/(mPF)$) and LOQ ($10\sigma/(mPF)$) for aluminum ions were found to be 0.49 and $1.63 \mu\text{g L}^{-1}$, respectively. Where, m is slope of calibration curve and PF is preconcentration factor for proposed procedure. Similar calculations of LOD and LOQ were reported by other researchers (Kartal et al. 2007; Yalçinkaya et al. 2011). These solutions were also analyzed by LS-FAAS. Analysis of results obtained by HR-CS AAS and LSAAS are given in (Table 5). When HR-CS AAS was used in analyses it was obtained that LOD and LOQ were decreased approximately eight times and sensitive was increased according to results of LS-FAAS. HR-CS AAS has high signal-to-noise ratio because of the high intensity of the radiation source and linear CCD array detector with 512 pixels. Hence, HR-CS AAS will be advantaged latest preconcentration studies.

The precision of this procedure was examined by seven replicate measurements of 50 mL sample solutions including $100 \mu\text{g L}^{-1}$ of Al^{3+} . The mean

Table 8 Concentration and recovery of Al^{3+} in water samples

Sample	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
Drinking water A	0	2.4±0.2	98.6
	5.0	7.3±0.6	
Drinking water B	0	4.2±0.4	101.1
	5.0	9.3±0.7	
Tap water	0	74.6±5.8	102.9
	50.0	128.3±9.5	
Mineral water A	0	5.2±0.5	101.9
	5.0	10.4±0.8	
Mineral water B	0	2.8±0.4	96.1
	5.0	7.5±0.5	

^aMean±ts/ \sqrt{N} with 95 % confidence level

recovery and the relative standard deviation (RSD) of recovery values were found to be 98.2 and 2.1 %, respectively.

The accuracy of the procedure was confirmed by analyzing certified materials (NIST SRM 1643e, trace elements in water). The results were in good agreement with the certified value (Table 6).

Comparison to other procedure

A comparison of the proposed procedure with other reported preconcentration procedures is given in (Table 7). Analytical characteristics obtained for our study are comparable to many procedures in the table. The LOD and RSD of proposed procedure are lower than that of the most procedures in the literature. The enrichment factor was 100 and is higher than those published in the literature (Ulusoy et

Table 7 Comparison of enrichment factors, LOD and RSD of purposed procedure and with other studies in literature for aluminum

Procedure/material	Ligand	Enrichment factor	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	References
CPE/Triton X-114	XB	50	1.43	2.7	Ulusoy et al. (2011)
SPE/glycerol-bonded silica gel	2-(2-quinolylozo)-5-diethylaminobenzoic acid	500	2	2.2	Safavi et al. (2009)
CPE/Triton X-114	Eriochrome Cyanine R	17	60	2.8	Satiroglu and Tokgoz (2010)
SPE/activated silica gel	8-hydroxyquinoline	20	0.5	4.53	Khan et al. (2009)
SPE/nano-ZrO ₂ /B ₂ O ₃	Ligadless	10	7.71	3.8	Yalçinkaya et al. (2012)
SPE/duolite XAD-761	4-[(dicyanomethyl)diazenyl] benzoic acid	100	0.49	2.1	Present paper

LOD limits of detection, CPE cloud point extraction, SPE solid-phase extraction, XB Xylidyl blue

al. 2011; Satiroglu and Tokgoz 2010; Khan et al. 2009; Yalçinkaya et al. 2012).

Analytical applications

The suitability of the proposed procedure for the analysis of water samples was checked by spiking samples of water samples with different concentrations of aluminum ions. The results are given in (Table 8). A good agreement was obtained between added and found value of the analyte.

Conclusions

A SPE procedure was developed for the determination of aluminum in water samples on Duolite XAD-761 resin using DSMDABA by high-resolution continuum source atomic absorption spectrometry. The developed method provides a simple, accurate, economical, rapid, and precise procedure for preconcentration and determination of aluminum. The time required for the preconcentration procedure was approximately 11 min (for 100 mL of sample solution in 10 min, at a flow rate of 10 mL min⁻¹; elution in 1 min, at a flow rate 10 mL min⁻¹). Sorbent material was stable with a period greater than 100 cycles, without major loss in its quantities and aluminum recovery property. In additionally, precision and detection limits was improved for determination of aluminum in various water samples by using a new atomic absorption spectrometer concept with a high-intensity xenon short-arc lamp as continuum radiation source, a high-resolution double-echelle monochromator and a CCD array detector.

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