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High-resolution continuum source flame atomic absorption spectrometric (HR-CS FAAS) determination of trace aluminium and lead in water and some beverage samples after separation and preconcentration procedure

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In the present study, a solid phase extraction procedure has been presented for the separation and preconcentration of aluminium (Al) and lead (Pb) in various matrixes such as water, cola and fruit juice samples. 4-[(3-amino-5-[(2-hydroxyphenyl) methylidene] amino}-1H-pyrazol-4-yl) diazenyl] benzoic acid (AHPMAPDAB) was used as a ligand. AHPMAPDAB chelates of Al and Pb ions in aqueous solutions were adsorbed on polystyrene-*graft*-ethyl methacrylate copolymer (Poly S₁₅-*g*-EMA₁₂₀). Various experimental and analytical parameters such as sample solution pH, sample volume, flow rate of sample solution and eluent, volume and concentration of eluent, amount of ligand and adsorbent, effect of common matrix ions and capacity of adsorbent were investigated. The adsorbed metal ions on resin were eluted with 6 mL of 2 mol L⁻¹ HCl solutions and their concentrations were determined by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS). Under the optimised conditions, limits of detections were 0.32 µg L⁻¹ and 0.24 µg L⁻¹ for Al and Pb, respectively. The accuracy of the procedure was confirmed by analysing certified materials (NIST SRM 1643e, Trace elements in water) and spiked real samples. The developed procedure was successfully applied to real samples.

Keywords: aluminium; beverages; continuum source atomic absorption spectrometry; graft polymer; lead; preconcentration

1. Introduction

Metal ion contaminants may present a potential hazard for human health if exposure exceeds tolerable limits. Therefore, national and international regulations, such as standards and directives on quality of drinking water, food, etc. are limiting the maximum permissible levels of toxic metals in these materials [1–4]. Al and Pb, have no known essential role in living organisms, and are toxic at even low concentrations. World Health Organization (WHO) has suggested that the maximum amount of Al and Pb in drinking water should be 0.05 mg L⁻¹ and 0.01 mg L⁻¹ respectively [5].

When human are exposed to Pb at high levels there is damage to almost all organs. Some organ systems such as the central nervous system, kidneys, and blood are affected and this can result in death at excessive levels.

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 [6]. Al plays a role in the etiology of

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several human pathologies. Some of them are dialysis dementia, amyotrophic lateral sclerosis, senile dementia of Alzheimer type and development of the brain in fetus [7–9]. It has been suggested by some previous epidemiologic studies that high aluminium levels in drinking water may be a risk factor for Alzheimer's and dementia [10,11]. Because of the toxicity of Al and Pb, the determination of them in water and food samples is important.

Line source flame atomic absorption spectrometry (LS-FAAS) has been used for the determination of trace metals in various samples. In recent years, high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) having lower limit of detection has been preferred for the determination of trace metal ions [12]. It has simultaneous background correction and can be used in multi-element analysis with continuum source [13–16].

However, direct determinations of metal ions at trace levels in environmental and food samples by many spectroscopic techniques are limited not only owing to insufficient sensitivity, but also by matrix interference. Therefore, preconcentration and/or separation methods are required for the determination of trace metals in appropriate accuracy and precision [17,18]. Separation and preconcentration procedures have a very important role for sample preparation processes in analytical methods [19].

A number of separation and preconcentration procedures for trace metals involving cloud point extraction (CPE), solid-phase extraction (SPE), co-precipitation, dispersive liquid–liquid micro-extraction have been used in literature [20–22]. Among these preconcentration techniques, SPE is an efficient, sensitive and inexpensive technique to perform removal of metal ions from environmental samples, preconcentration of metal ions for analytical purposes and speciation of the metal and metalloids [4]. SPE has some advantageous over classic extraction methods (liquid–liquid). Some of them are rapidity, simplicity, low solvent usage and lower extraction time, higher sensitivity and lower cost [23]. Many metal species can be preconcentrated and determined when SPE is used in batch or column techniques [24,25].

Numerous substances have been synthesised for solid phase extraction as an adsorbent. Recent tendency in the field of solid phase extraction is related to synthesis of the new sorbent materials having required performance. Polymeric resins have some advantages such as low cost, simple preparation, high porosity, larger surface area, stability against acidic or basic media and selectivity for some analytes [26]. In order to increase the selectivity and adsorption capacity of the sorbent, sometimes ligands or chelating agents were used to obtain metal chelates before SPE procedure [4].

In the present work, a new solid phase extraction method was developed for the preconcentration of trace Al and Pb ions in various matrixes. Some analytical parameters were investigated and optimised. 4-[(3-amino-5-[(2-hydroxyphenyl) methylidene] amino}-1H-pyrazol-4-yl) diazenyl] benzoic acid (AHPMAPDAB) as a chelating agent was used. This chelating agent has been first synthesised by our research group and it was first used for separation/preconcentration of trace metals. Polystyrene-*graft*-ethyl methacrylate copolymer (Poly S₁₅-*g*-EMA₁₂₀) was used as an adsorbent. The developed procedure was successfully applied to water samples, different brands of cola and fruit juice samples.

2. Experimental

2.1 Instrumentation

The analysis was performed by ContrAA 300 a High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (HR-CS AAS) (Analytik Jena AG, Jena, Germany) equipped with a 50 mm burner head and an injection module (SFS-6). All absorption lines of an element in the spectral range of 185–900 nm can be analytically evaluated by using a Xe short-arc lamp

Table 1. The operating conditions for HR-CS AAS.

Parameters	Al	Pb
Wavelength, nm	396.152	217.0005
Flow rate of N ₂ O-C ₂ H ₂ , L h ⁻¹	235	0
Flow rate of C ₂ H ₂ -air, L h ⁻¹	70	65
Burner height, mm	4	8
Evaluation pixels, pm	3	3
Background correction	Simultaneous	Simultaneous

as a continuum lamp source. The spectral background of the sample in the HR-CS FAAS is always corrected directly on the analysis line simultaneously and independently. All measurements were carried out under optimum conditions in three replicates using an 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. The operating conditions for Al and Pb by HR-CS FAAS are given in Table 1.

2.2 Reagents and standards

All solutions were prepared using ultra pure water (specific resistance 18 M Ω cm) from a Milli-Q purification system (Millipore Corporation, Massachusetts, USA). Standard solutions of analytes were prepared from their 1000 mg L⁻¹ stock solutions (Merck). Buffer solutions (Merck) of sodium acetate–acetic acid (for pH 3–5), sodium monohydrogen phosphate–potassium dihydrogen phosphate (for pH 6–8) and ammonium chloride–ammonia (for pH 9) were used. All glassware was cleaned using ultra-pure water, kept in nitric acid for 24 h, and washed again with ultra-pure water. As an adsorbent Poly S₁₅-g-EMA₁₂₀ was prepared with polystyrene-*co-p*-chloromethyl styrene (PS-Cl) as macro initiator in the presence of CuCl/1,2-dipiperidinoethane and ethyl methacrylate (EMA) at 130°C in *N,N*-dimethyl formamide according to literature [27]. Where, 15 and 120 are *p*-chloromethyl styrene and monomer ratios, respectively.

2.2.1 Synthesis of AHPMAPDAB

0.01 mol (2.47 g) (3,5-diamino-1H-pyrazol-4-yl) diazenyl] benzoic acid was dissolved in 15 mL dimethylformamide in a 250 mL round bottom flask. A solution of 0.01 mol (1.23 mL) 2-Hydroxybenzaldehyde in methanol was added drop-wise over a 20 min period with continuous stirring for 4 h at room temperature. Mixture was cooled and precipitated in water. The precipitate was filtered, washed with water and dried at room temperature. Data obtained from elemental analysis of AHPMAPDAB (C 58.28%, H 4.03% and N 23.99%) were comparable with the theoretically calculated values (C 58.52%, H 4.20% and N 24.48%). IR spectrum [IR(KBr) ν (cm⁻¹): 1601(Ar-CH = N), 1522 (N = N), 3270 (-NH₂); 1689 (C = O); 1561(-NH)] of AHPMAPDAB is shown in Figure 1. The AHPMAPDAB is solution of 0.01% (m/v) was prepared by dissolving 0.025 g of AHPMAPDAB in 250 mL of 0.01 mol L⁻¹ NaOH solutions.

2.3 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 on top of the column and a stopcock at the bottom of the column for separation/preconcentration of metal ions were used. Column system was prepared by placing a small portion of cleaned glass wool as a plug at one end of the column holding a certain amount

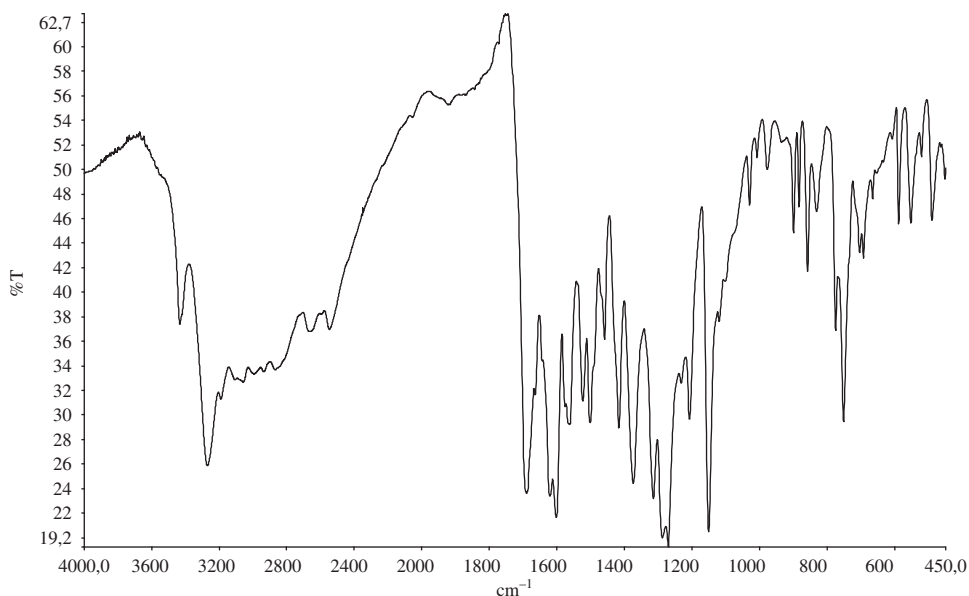


Figure 1. IR spectrum of AHPMAPDAB.

(0.3–0.6 g) of adsorbent. This system was cleaned with water, 2 mol L⁻¹ HCl and 2 mol L⁻¹ HNO₃ solutions by following a given order [28–30].

2.4 Preconcentration procedure

The proposed preconcentration procedure was tested with model solutions prior to the determination of trace Al and Pb in real samples as off-line. In order to prepare model solution 2.5 mL of 2.0 mg L⁻¹ Al³⁺ and Pb²⁺ solutions were added to 1.0 mL of 0.01%(m/v) AHPMAPDAB solution and 4 mL of buffer solutions (sodium acetate–acetic acid, sodium monohydrogen phosphate–potassium dihydrogen phosphate and ammonium chloride–ammonia) (to give the desired pH between 3 and 9) in a flask. Then, final volume was completed to 50 mL by deionised water. The column was preconditioned by passing the aqueous solutions of working pH through column and then, the model solution was passed through the column at a flow rate of 7 mL min⁻¹. Afterwards, the column was rinsed with 10 mL of water, and the metal-AHPMAPDAB chelates adsorbed on the Poly S₁₅-g-EMA₁₂₀ were eluted with 6 mL of 2 mol L⁻¹ HCl solutions. The eluent was analysed for the determination of metal concentrations by HR-CS FAAS. The recoveries of the analytes were calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically.

2.5 Analysis of samples

The tap water was collected from our research laboratory at Ahi Evran University. Most frequently consumed mineral and drinking water, cola and fruit juice samples were bought directly in local supermarkets.

2.5.1 Preparation of water samples

The water samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm . An appropriate amount of AHPMAPDAB solution, buffer solution of sodium monohydrogen phosphate – potassium dihydrogen phosphate (pH: 7.0) and known amounts of analyte ions were mixed in a volumetric flask. Then, the preconcentration procedure was applied to the obtained sample solutions.

2.5.2 Preparation of cola and fruit juice samples

50 mL each of cola and fruit juice samples were added in a beaker containing 25 mL of HNO_3 (65%(m/m)) and 5 mL of HClO_4 (60%(m/m)) solutions. Mixture was refluxed for 1 h approximately at 100°C and then the obtained solution was evaporated to approximately dryness. The residue was dissolved with water and diluted to 50 mL with water in a 50 mL volumetric flask, and the preconcentration procedure was applied to the solution.

3. Results and discussion

The effect of some experimental parameters such as the pH of sample solution, the type and concentration of eluent, volume of sample solution and the flow rate of sample and eluent solution on the recovery of Al^{3+} and Pb^{2+} were investigated. The analytical parameters such as linear dynamic range, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy were determined under optimal conditions. The effect of foreign ions has also been investigated.

3.1 Effect of pH on the recovery of Al and Pb

The dependence of the sorption conditions on pH of the solution is one of the important parameters that can have a significant influence on the overall recovery of analytes. The recovery of the analyte was determined by applying the preconcentration procedure by changing the pH of model solution in the range of 3.0–9.0. The quantitative recovery (above 95%) of analyte ions were obtained at pH 7–8.5. The recoveries of Al^{3+} and Pb^{2+} were decreased when the solutions pH is over 8.5 and less than 7.0 (Figure 2). Hence, pH 7.0 was selected as an optimum pH for solid phase extraction of the analyte ions for further experiments. At lower pH values, owing to the competition between protons and the metal ions the recoveries decrease. At higher pH values, above pH 8.5, formation of precipitates and/or anionic hydroxide complexes may occur.

3.2 Effect of eluent type and concentration on the recovery of Al and Pb

In order to choose the most effective eluent for desorbing of Al^{3+} and Pb^{2+} ions from the sorbent, different concentration and different volumes HCl and HNO_3 solutions were tested. Quantitative recovery (>95%) has been obtained by using 6 mL of 2 mol L^{-1} HCl solution (Table 2).

3.3 Effect of the sample flow rate on the recoveries of Al and Pb

The flow rate of the sample solution also effects on the recovery of Pb and Al ions. Therefore, the effect of flow rate was also investigated under the optimum conditions (pH, 7; eluent 6 mL of 2 mol L^{-1} HCl). As shown in Figure 3, the optimum value for the flow rate of the sample

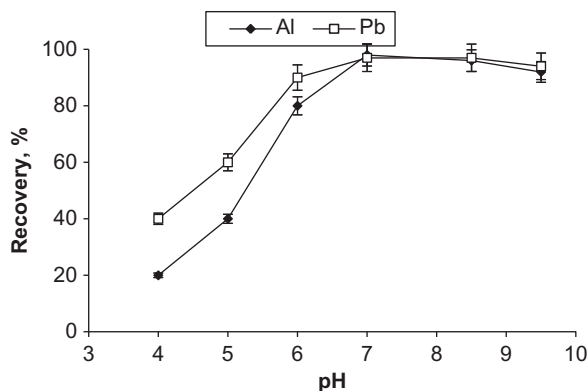


Figure 2. The effect of pH of sample solution.

solution was found as up to 7 mL min^{-1} . Above 7 mL min^{-1} , the recovery decreased gradually. Therefore, to decrease the duration time without decreasing recovery values, a rate of 7 mL/min was chosen as the optimum flow rate for subsequent experiments.

3.4 Effect of eluent flow rate on the recoveries of Al and Pb

The flow rate of eluent solution (6 mL of $2 \text{ mol L}^{-1} \text{ HCl}$) on the recovery of Al^{3+} and Pb^{2+} ions were examined in the range of $2.0\text{--}5.0 \text{ mL min}^{-1}$ at optimum conditions. The recovery of analyte ions ranged between 95% and 100% at the eluent flow rates varying up to 5.0 mL min^{-1} . To decrease the analysis time, eluent flow rate was selected as 5 mL min^{-1} .

3.5 Effect of sample volume on the recoveries of Al and Pb

For the preconcentration purposes, to achieve the higher preconcentration factor, the eluent volume should be as small as possible, and the volume of sample solution should be as high as possible [4]. In order to obtain the maximum applicable sample solution (or analyte concentration), model solutions including the same amount of analyte ions with different volumes were used. For this purpose, aqueous solutions containing $5 \mu\text{g Al}^{3+}$ and Pb^{2+} were preconcentrated

Table 2. The effect of eluent type/concentration/volume of eluent on recovery of Al and Pb.

Eluent	Recovery (%)*	
	Al	Pb
$1 \text{ mol L}^{-1} \text{ HCl}$, 5 mL	92 ± 1	88 ± 2
$1 \text{ mol L}^{-1} \text{ HCl}$, 10 mL	94 ± 2	90 ± 3
$2 \text{ mol L}^{-1} \text{ HCl}$, 5 mL	96 ± 2	95 ± 1
$2 \text{ mol L}^{-1} \text{ HCl}$, 6 mL	100 ± 1	98 ± 1
$1 \text{ mol L}^{-1} \text{ HNO}_3$, 5 mL	90 ± 2	84 ± 1
$1 \text{ mol L}^{-1} \text{ HNO}_3$, 10 mL	95 ± 2	87 ± 2
$2 \text{ mol L}^{-1} \text{ HNO}_3$, 5 mL	95 ± 2	93 ± 2
$2 \text{ mol L}^{-1} \text{ HNO}_3$, 6 mL	98 ± 2	97 ± 2

*Results are mean \pm standard deviation of three replicate analyses.

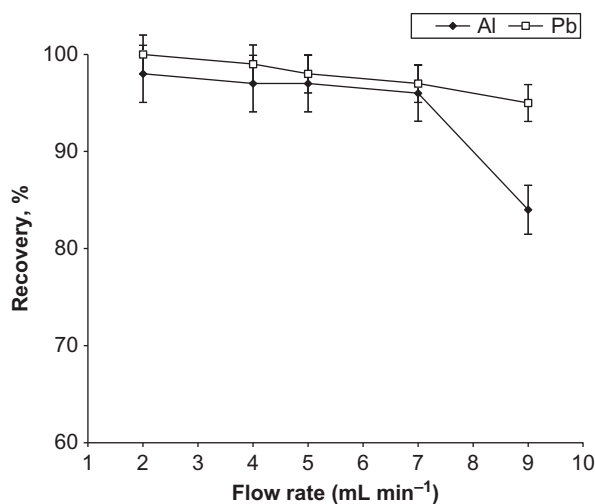


Figure 3. Effect of flow rate of sample solution.

from sample volumes of 100, 250, 500, 750 and 1000 mL corresponding to analyte concentrations of 0.100, 0.050, 0.020, 0.010, 0.006 and 0.005 $\mu\text{g mL}^{-1}$, respectively.

The recoveries of analyte were quantitative (>95%) for sample volumes up to 600 mL and 800 mL for Pb^{2+} and Al^{3+} , respectively (Figure 4). Preconcentration factors (PF) were obtained by the following equation: $\text{PF} = (V_S/V_E)$, where V_S is the volume of preconcentrated solution (600 mL for Pb^{2+} and 800 mL for Al^{3+}), and V_E is the volume of eluate (6 mL). Maximum preconcentration factors for Al^{3+} and Pb^{2+} were found to be as 100 and 133, respectively.

3.6 Effect of chelating agent amount on the recoveries of Al and Pb

In separation/preconcentration studies, various ligands which have high affinity to metal ions were used widely in adsorption process. In this study AHPMAPDAB contains imine, carbocycle, hydroxyls and amino residues as organic functional groups. These groups provide a number of different potential binding sites for the analytes. In this study, the effect of the amount of AHPMAPDAB on the recoveries of Al^{3+} and Pb^{2+} was also studied. Different

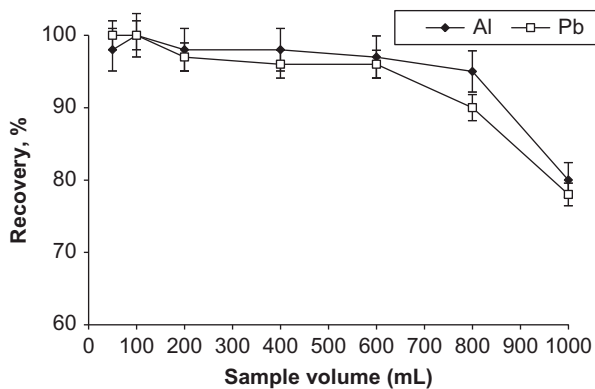


Figure 4. Effect of sample volume.

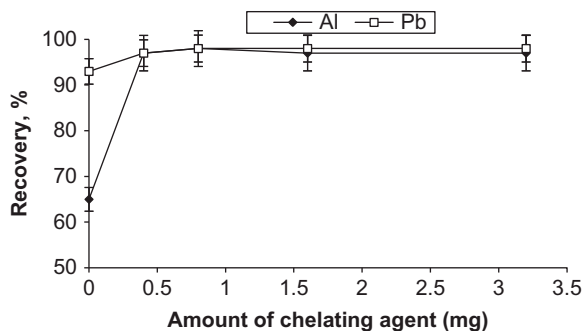


Figure 5. Effect of amount of chelating agent.

amounts of AHPMAPDAB in the range from 0 to 3.2 mg (from 0.01% (w/v) AHPMAPDAB solution with different volumes) were added to each model solutions with the same amount of analyte and preconcentration procedure was applied. The results are given in Figure 5. When AHPMAPDAB was used, the adsorption of analyte ions on Poly S₁₅-g-EMA₁₂₀ increased the performance of proposed procedure. Optimum amount of AHPMAPDAB was found as 1 mg or higher. At amount of AHPMAPDAB less than this value, the recovery was below 95%. Therefore, 1 mg of AHPMAPDAB (1.0 mL of 0.01% (m/v) AHPMAPDAB solution) was added to the solutions in subsequent studies.

3.7 Effect of sorbent amount

The effect of the amount of poly S₁₅-g-EMA₁₂₀ resin on recoveries of analytes was studied. For this purpose, different amount of sorbent (100–600 mg) was tested into the adsorption column. 50 mL of model solution including 5 µg of analytes was passed through the column at optimum experimental conditions (pH, 7; flow rate 7 mL min⁻¹; eluent, 6 mL of 2 mol L⁻¹ HCl; chelating agent, 1.0 mL of 0.01% (m/v) AHPMAPDAB). The results showed that the recovery of the analytes increase up to 300 mg of Poly S₁₅-g-EMA₁₂₀ and remain about constant above this value (Figure 6). Therefore, minimum sorbent amount (300 mg) given maximum recovery was selected for further studies.

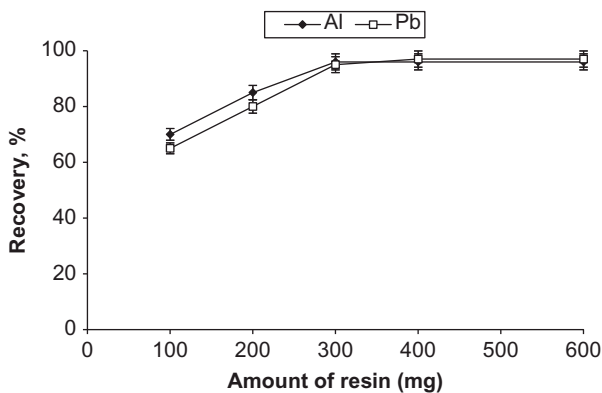


Figure 6. Effect of sorbent amount.

3.8 Matrix effect on the recoveries of Al and Pb

Matrix effects are important problem in the determination of heavy metals by atomic spectroscopic techniques in real samples. Other ions present in sample solution also affect the retention of the analytes on the sorbent and thus the recovery of them. Therefore, the effects of common coexisting ions on the determination of Al and Pb ions were investigated. For this purpose, 50 mL of test solutions containing 5 µg Pb²⁺ and Al³⁺ ions were used. The maximum concentrations of the various metal ions as their nitrate or chloride salts which are tolerable within the 5% relative error were determined by adding them to a solution containing of analyte ions and by applying the proposed procedure. The results indicated that the foreign ions tested having concentrations given in Table 3 did not interfere with recovery of Al and Pb ions.

3.9 Capacity of the resin and adsorption models

The adsorption capacity of the sorbent is an important factor in the evaluation of the property of a sorbent. Because it determines how much sorbent is required to concentrates Al³⁺ and Pb²⁺ quantitatively from a given solution [31].

Adsorption capacity of resin was obtained by batch experiments. For this purpose, 200 mg of resin was added into a 250 mL flask containing 100 mL of model solution which has various concentrations of analyte ions under the optimum experimental conditions. The prepared solutions containing different amount of analytes were shaken for 2 h at 150 rpm at room temperature. Then, 10 mL of supernatant was taken from each solution and the amount of residual Al³⁺ and Pb²⁺ in the solution was determined by using HR-CS FAAS.

There are several isotherm equations available for analysing experimental adsorption equilibrium data. In this study, the equilibrium experimental data for adsorbed Al³⁺ and Pb²⁺ ions on resin were determined using the Langmuir and Freundlich models. These isotherms are as follows:

(a) Langmuir isotherm model

The linearised equation form of the Langmuir model used to evaluate maximum metal uptake is expressed by the following equation:

$$C_e/q_e = C_e/q_{\max} + 1/K_L q_{\max} \quad (1)$$

Table 3. Effects of some foreign ions on the recovery of Al and Pb (sample solution: 50 mL, amounts of Al and Pb: 5 µg, pH: 7.0).

Foreign ions	Concentration (mg L ⁻¹)	Recovery (%)* Al	Recovery (%)* Pb
K ⁺	1000	98 ± 2	100 ± 3
Na ⁺	2000	96 ± 2	95 ± 2
Ca ²⁺	500	98 ± 1	95 ± 2
Mg ²⁺	200	100 ± 2	98 ± 3
Zn ²⁺	25	98 ± 2	96 ± 3
Cu ²⁺	25	95 ± 2	96 ± 1
Co ²⁺	25	97 ± 2	98 ± 2
Ni ²⁺	25	96 ± 2	95 ± 1
Cd ²⁺	25	97 ± 2	98 ± 2
Cr ³⁺	25	100 ± 1	96 ± 2
Fe ³⁺	50	97 ± 2	100 ± 3

*Results are mean ± standard deviation of three replicate analyses.

where C_e is the final metal concentrations in the solution at equilibrium (mg L^{-1}), q_e is the amount of sorbed metal ions per gram of sorbent at equilibriums (mg g^{-1}); K_L is a constant related to the energy of adsorption/desorption (L g^{-1}) and q_{max} is the maximum adsorption capacity of sorbent (mg/g).

(b) Freundlich isotherm model:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (2)$$

where K_F and n are Freundlich constants related to multilayer adsorption capacity and adsorption intensity, respectively [33]. A relatively $n \ll 1$ indicates that adsorption intensity is favourable over the entire range of concentrations studied, whereas $n > 1$ means that adsorption intensity is favourable at high concentrations but much less at lower concentrations [33,34].

Langmuir model had been shown to fit the experimental data well, with the correlation coefficients (R^2) in range of 0.9837–0.9906 for the analytes. The Langmuir monolayer adsorption capacities (q_{max}) were estimated as 14.6 for Al^{3+} and as 18.4 mg g^{-1} for Pb^{2+} . Constants of the energy (K_L) for Al^{3+} and Pb^{2+} were calculated as 0.10 L g^{-1} and 0.08 L g^{-1} , respectively (Figure 7). High correlations coefficients indicate that the adsorption of Pb and Al chelates on the sorbent comply with the Langmuir adsorption isotherm. This means that the solid surface presents a finite number of identical sites that are genetically uniform, and there are no interactions between adsorbed species, and a monolayer adsorption is formed when the solid surface reaches saturation [32].

As can be seen from Figure 8, adsorption of the analytes on the sorbent did not fit well to Freundlich model. The Freundlich constants (K_F) were found to be 1.27 and 1.30 for Al(III) and Pb(II), respectively. n values are calculated as 1.67 for Al(III) and 1.56 for Pb(II). The correlation coefficients (R^2) were 0.9067 for Pb(II) and 0.8991 for Al(III), respectively. These results show that the adsorption of the analytes did not comply with Langmuir isotherm well.

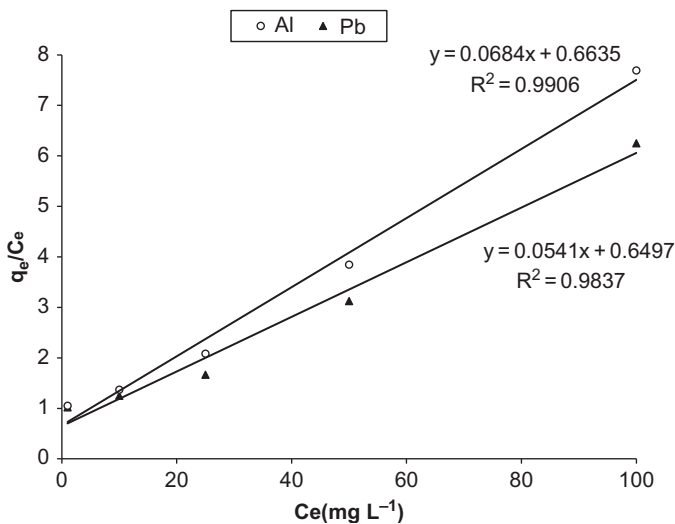


Figure 7. Linearised Langmuir adsorption isotherms of Al^{3+} and Pb^{2+} .

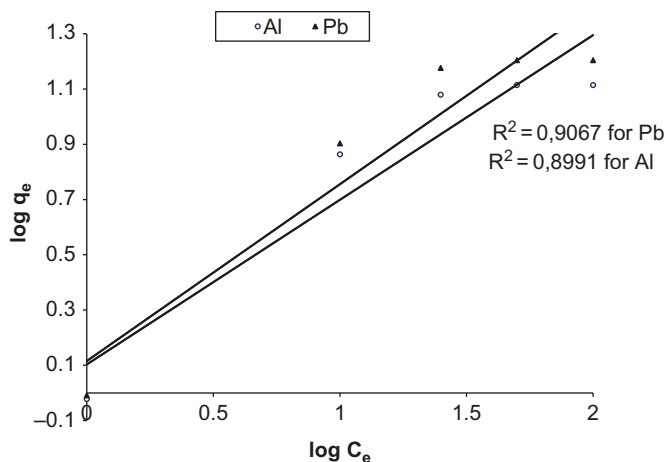


Figure 8. Freundlich adsorption isotherms of Al^{3+} and Pb^{2+} .

3.10 Analytical features

Under the optimum experimental conditions, linear dynamic range, correlation coefficient, LOD, LOQ, precision and accuracy were examined.

By using direct aspiration in FAAS without applying the preconcentration system the linear dynamic range for Pb and Al determination were $0.06\text{--}5.00\text{ mg L}^{-1}$ ($R^2 = 0.9984$) and $0.1\text{--}20.0\text{ mg L}^{-1}$ ($R^2 = 0.9992$), respectively. The dynamic ranges of the proposed method after preconcentration from 250 mL of standard solutions were $1.6\text{--}120\text{ }\mu\text{g L}^{-1}$ ($R^2 = 0.9962$) for Pb and $2.4\text{--}480.0\text{ }\mu\text{g L}^{-1}$ ($R^2 = 0.9976$) for Al.

LOD and LOQ of this procedure were determined as the concentration corresponding to three and ten times of the standard deviation (σ) of blank measurements ($N = 15$). The obtained LOD and LOQ values without applying the preconcentration procedure were divided to the preconcentration factor in order to obtain the LOD and LOQ values of the proposed method [35,36]. LOD [$3\sigma/(m \times \text{PF})$] and LOQ [$10\sigma/(m \times \text{PF})$] were found as $0.32\text{ }\mu\text{g L}^{-1}$ and $1.07\text{ }\mu\text{g L}^{-1}$ for Al and 0.24 and $0.80\text{ }\mu\text{g L}^{-1}$ for Pb, respectively. Where, m is slope of calibration curve obtained without preconcentration procedure and PF is preconcentration factor for the proposed procedure.

The precision of this procedure was examined by seven replicate measurements of 50 mL of sample solutions including $200\text{ }\mu\text{g L}^{-1}$ Al^{3+} and Pb^{2+} . The mean recoveries for Al and Pb were obtained as 97.8% and 98.4% with the relative standard deviations (RSD) of 1.8% and 1.2%, respectively.

The accuracy of the procedure was confirmed by analysing certified materials (NIST SRM 1643e, Trace elements in water). The results were in good agreement with the certified value which indicate that the accuracy of the procedure is satisfactory for trace metal analysis (Table 4). Some comparative data about Al and Pb preconcentration by other sorbents and ligands are summarised in Table 5.

Table 4. Results for certified reference material (NIST SRM 1643e, trace elements in water, 50 mL).

Element	Certified ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Relative error (%)
Al^{3+}	141.8 ± 8.6	138.2 ± 10.2	- 2.5
Pb^{2+}	19.6 ± 0.2	18.9 ± 0.8	- 3.6

^aResults are mean \pm standard deviation of three replicate analyses.

Table 5. Comparison of the proposed method for preconcentration of Al and Pb ions in aqueous solution with other methods described in the literature.

Analyte	Procedure/material	Ligand	PF	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
Al^{3+}	CPE/Triton X-114	Xylidyl Blue (XB)	50	1.43	2.7	[37]
	SPE/Glycerol-bonded silica gel	2-(2-quinolyazo)-5-diethylaminobenzoic acid	500	2	2.2	[38]
	CPE/Triton X-114	Eriochrome Cyanine R	17	60	2.8	[39]
	SPE/Activated silica gel	8-hydroxyquinoline	20	0.5	4.53	[40]
	SPE/Nano $\text{ZrO}_2/\text{B}_2\text{O}_3$	Ligandless	10	7.71	3.8	[41]
	SPE/Duolite XAD-761	4-[(dicyanomethyl)diazenyl] benzoic acid	100	0.49	2.1	[42]
	SPE/Poly $\text{S}_{15}\text{-g-EMA}_{120}$	AHPMAPDAB	133	0.32	1.8	This study
	SPE/Diaion SP-850	alpha-benzoin oxime	–	0.5	<8	[43]
	SPE/SDS	PAN	250	0.17	3.2	[44]
	FI/Triton X-114	–(2-thiazolyazo)-2-naphthol (TAN)	15.1	4.5	1.6	[45]
Membrane filtration	1-2-pyridylazo 2-naphthol (PAN)	20	3.5	–	[46]	
Membrane filtration	dicyclohexano-18-crown 6-ether (DC18C6)	76	0.003	7.0	[47]	
SPE/Poly $\text{S}_{15}\text{-g-EMA}_{120}$	AHPMAPDAB	100	0.24	1.2	This study	

Note: PF: Preconcentration factor; LOD: Limit of detection; RSD: Relative standard deviation.

3.11 Reusability of the sorbent

The stability and reusability of the sorbent were evaluated by determining the recoveries of the analytes by applying adsorption–elution cycles. One adsorption–elution cycle was considered as follow: the passage of 50 mL of the model solution, 6 mL of eluent solution and 50 mL of ultra-pure water through the column loaded with 300 mg of sorbent, respectively. The adsorbent was always stored in water when it was not in use. It was observed that the sorbent was stable up to 80 cycles without major loss in its quantities and metal recovery properties.

3.12 Analytical applications

In order to show the applicability of the method, it was applied for the determination of Al and Pb in real samples under optimal experimental conditions. The accuracy of the method was also checked by determining the percent relative error of spiked real samples. The results obtained are given in Table 6. A good agreement was obtained between added and found value of the analytes.

In tap water and drinking water samples, Al and Pb levels ranged from 2.8 to 22.6 $\mu\text{g L}^{-1}$ and 0 to 1.6 $\mu\text{g L}^{-1}$, respectively. In commercial mineral water samples, Al and Pb levels ranged

Table 6. Levels of Al^{3+} and Pb^{2+} in various samples (Volume of water and mineral water sample: 250 mL, volume of cola and juice samples: 50 mL).

Sample	Al^{3+}			Pb^{2+}		
	Added ($\mu\text{g L}^{-1}$)	Found* ($\mu\text{g L}^{-1}$)	Relative Error (%)	Added ($\mu\text{g L}^{-1}$)	Found* ($\mu\text{g L}^{-1}$)	Relative Error (%)
Drinking water A	0	2.8 ± 0.2		0	ND	
	5.0	7.6 ± 0.4	-2.6	5.0	5.1 ± 0.5	2.0
Drinking water B	0	3.5 ± 0.2		0	ND	
	5.0	8.3 ± 0.6	-2.4	5.0	5.2 ± 0.6	4.0
Tap water	0	22.6 ± 1.5		0	1.6 ± 0.2	
	20.0	43.4 ± 2.5	1.9	5.0	6.4 ± 0.5	-3.0
Mineral water A	0	6.9 ± 0.5		0	2.2 ± 0.2	
	5.0	11.4 ± 0.6	-4.2	5.0	7.4 ± 0.4	2.8
Mineral water B	0	8.7 ± 0.5		0	1.8 ± 0.4	
	5.0	14.1 ± 1.2	2.9	5.0	6.9 ± 0.6	1.5
Cola A (glass bottle)	0	258 ± 12		0	ND	
	100	346 ± 16	-3.4	10	10.5 ± 0.4	5.0
Cola A (can)	0	635 ± 24		0	12.4 ± 0.4	
	200	814 ± 25	-2.8	10	21.8 ± 1.2	-2.7
Cola B (glass bottle)	0	396 ± 18		0	ND	
	100	485 ± 26	-2.2	10	10.4 ± 0.3	4.0
Cola B (can)	0	954 ± 42		0	13.5 ± 0.5	
	300	1208 ± 64	-3.7	10	22.6 ± 1.4	-3.8
Orange juice A (paperboard)	0	320 ± 12		0	ND	
	100	432 ± 27	2.9	10	10.2 ± 0.4	2.0
Orange juice A (can)	0	875 ± 35		0	ND	
	300	1127 ± 56	-4.1	10	10.4 ± 0.5	4.0
Orange juice B (paperboard)	0	480 ± 21		0	ND	
	100	605 ± 26	4.3	10	10.2 ± 0.2	2.0
Orange juice B (can)	0	925 ± 38		0	16.1 ± 0.6	
	300	1162 ± 48	-5.1	10	25.6 ± 1.6	-1.9

Note: *Results are mean \pm standard deviation of three replicate analyses.
ND: Not detected.

from 6.9 to 8.7 $\mu\text{g L}^{-1}$ and 1.8 to 2.2 $\mu\text{g L}^{-1}$, respectively. Although the Al levels of cola samples in glass bottles were found as range of 258–396 $\mu\text{g L}^{-1}$, they were 635–954 $\mu\text{g L}^{-1}$ in can container. Whereas, although the lead levels of cola samples in glass bottles were not detected, they were found as range of 12.4–13.5 $\mu\text{g L}^{-1}$ in can container.

Although lead could not be determined in orange juice in paperboard container, aluminium was found as range of 320–480 $\mu\text{g L}^{-1}$. These values in can container were increased and were found as range of 875–925 $\mu\text{g L}^{-1}$ for Al, and 0–16.1 $\mu\text{g L}^{-1}$ for Pb. Measured Al in cola and juice is higher than the maximum aluminium level allowed in drinking water standards [1]. The maximum admitted level of Al in juice and cola has not been given in Turkish regulations and/or standards related to beverages. However, higher Al levels were also found by the other researchers. Lopez *et al.* determined that Al concentrations in fruit juices and water samples ranged from 49.3 to 1144.6 $\mu\text{g L}^{-1}$ and 4.2 to 134.1 $\mu\text{g L}^{-1}$, respectively. Aluminium levels of orange juice in glass and can containers were found as range of 220.2–470.4 $\mu\text{g L}^{-1}$ and 320.0–1053.3 $\mu\text{g L}^{-1}$, respectively. In same study, aluminium levels of cola samples in glass and can containers were found as range of 190.7–310.0 $\mu\text{g L}^{-1}$ and 279.5–985.6 $\mu\text{g L}^{-1}$, respectively [48]. Arruda *et al.* indicated that Al content in natural orange juice was found as range of 227–242 $\mu\text{g L}^{-1}$ [49].

4. Conclusion

A solid phase extraction procedure was developed for the determination of Al and Pb in water samples and some beverages on polystyrene-*graft*-ethyl methacrylate copolymer (Poly S₁₅-g-EMA₁₂₀) 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 Al and Pb. Sorbent material was stable with a period greater than 80 cycles.

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