New SPE Sorbent for the Rapid and Sensitive Quantification of Aluminium in Food, Soil Extracts and Water Samples

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ABSTRACT

An on-line solid-phase extraction (SPE) technique, linked to spectrophotometry, has been developed to overcome the problem of high matrix concentration, which is thought to interfere with the determination of low levels of aluminum in environmental samples. Aurintricarboxylic acid (ATCA) modified resin was prepared and used as a SPE absorbent, which can quantitatively adsorb Al(III) at pH 4.5–6.5 with an adsorption capacity of 10.8 mg g^{-1} resin. The main advantages of this novel method are: (1) a much higher sensitivity has been obtained by SPE technology; and (2) a large amount of Na, K, Ag, Hg, Ca, and Mg, can be removed and the interference of Fe(III) and F^{-} can be efficiently eliminated by eluting with 0.30 mol L^{-1} NaOH. It is a highly selective and sensitive method for simple and quick determination of Al in food samples (rice, tea and potato), soil, waste water, river waters, spring water and ground water samples.

Keywords: Aluminum determination; solid-phase extraction; spectrophotometry; soil extracts; food and water analysis; Quinoxaline azo dyes;

1. INTRODUCTION

The development of the new determination methods is among the subject of the analytical chemists. For this reason extensive research has been focused on the developing sensitivity, relative simplicity, accurate, speed and costly effective methods for determination

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of metals which have industrial importance and affect human health. Although, none of the group 13 elements qualifies as essential to life, aluminium is of large biological interest. Aluminium is of great concern due to its large natural abundance and its possible toxic effects (Yokel, 2000; Exley et al., 1996; Flaten et al., 1996; Yokel, 1994; Corani et al., 1990; Wisniewski and Wen, 1992; Fleming and Joshi, 1987). Aluminium is the third most abundant element at the Earth's crust. It is commonly found in living organism consumed as food by human beings. The naturally occurring forms are usually stable and do not interfere with biological processes. Although, excessive use of aluminium preparations influences negatively the human organism causing disturbances in calcium and phosphate metabolism and resulting in damage to the bone system. In addition, accumulation of considerable aluminium amounts in the brain is observed in Alzeheimer disease, as well senescence symptoms and amnesia of young people (Zareba and Melke, 2000). Therefore, the determination of trace aluminium is very important and during the last 20 years, there are many investigations in this area (Tria et al., 2007; Zheng et al., 2007; Safavi et al., 2007; Alieva et al., 2006; Zaijun et al., 2007; Themelis and Kika, 2006; Rodrigues et al., 2005; Madrakian et al., 2005).

Several techniques such as atomic absorption, atomic fluorescence, X-ray fluorescence, voltammetric, electrothermal atomic absorption or inductively coupled plasma mass spectrometry, gas chromatography have been used for the determination of aluminium in different samples (Gündüz et al., 2005; Pierson and Evonson, 1986; Hirata et al., 1986; Korenaga et al., 1980; Di et al., 2004; Albendin et al., 2003). Spectrophotometric methods are widely used due to their simplicity, rapidity, low costs and wide applications (Fakhari et al., 2005; Filik et al., 1998; Reddy et al., 2008). UV spectrophotometry amongst the optical methods seems to be most appropriate analytical approach for the determination of toxic metals, as it provides sensitive, precise and accurate measurement of suitable analytes. Besides, visible spectrophotometric detection is much more viable as useful technique to develop a portable, on-line or at-line system (Suresha et al., 2002).

Many spectrophotometric methods have been proposed using various azo dyes and other chromogenic reagents such as aluminon, xylenol orange, stilbazo, chlorophosphonazo I, methylthymol blue, erichrome cyanine R, chrom azurol KS, pyrocatechol violet, 8-hydroxyquinoline and alizarine (Ying-Quan et al., 1983; Marczenko, 1976; Tagashira, 1984; Martire and Hainberger, 1985; Wyganowski et al., 1983, Shao-pu, 1982; Chamsaz et al., 2000; Samaritan et al., 1993; Shokrollahi et al., 2008) for the determination of aluminium. However, most of these methods lack sensitivity or selectivity, the procedures are sometimes rather complicated because of the need for extraction to separate interfering ions or expensive surfactants. Similarly, bromooxine, pyridylazoresorcinol (PAR), 1-(2-pyridylazo)-2-naphtol (PAN) have been used for spectrophotometric determination of indium. But, these reagents are less sensitive (ε = 8.8×10^3, 4.3×10^4, 1.9×10^4 L mol^{-1} cm^{-1}, respectively) (Marczenko, 1976).

Monoazo systems were successfully used for the determination of some metals (Marczenko, 1976; Al-Kindy et al., 2007; Güray et al., 2005; Huseyinli and Atilir, 2001; Huseyinli et al., 2001). These reagents enhance the stability of the formed band with the metals, because of high electron density between the –OH groups ortho to azo group and nitrogen atom of the azo group. For this purpose, the new method has been developed for the determination of aluminium with 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo) quinoxaline (DCHNAQ) which have synthesized by us (Azhari and Amin, 2007) and the method has been applied to the determination of aluminium in certified steel, alloys, waste water, river waters, spring water and ground water samples.

Recently, the solid phase extraction (SPE) technique has become increasingly popular. It has advantages over traditional liquid–liquid extraction such as a higher preconcentration factor, better efficiency and greater reproducibility (Mondal et al., 2001; Scindia et al., 2002; Garg et al., 1999; Pozzebon et al., 2003; Sarzanini et al., 1987). The aim of this paper was to develop a simple and fast SPE spectrophotometry, which is free from the interference of Fe(III) and F$^-$ for the determination of Al(III) in food samples (rice, tea and potato), soil, waste water, river waters, spring water and ground water samples.

2. EXPERIMENTAL DETAILS

2.1 Apparatus and Chemicals

The absorption spectra of the solutions were recorded on a Perkin-Elmer lambda 3B spectrophotometer (Nor walk, CT, USA) in the range 350 – 750 nm using 10 mm matched stopper quartz cells. Values of pH were measured with an Orion research model 601 A/digital ionalyzer. The pH meter was calibrated regularly before use with standard buffer solutions. A homemade micro-column (70 mm 32.5 mm i.d.) was made from polypropylene. A peristaltic pump (HL-1, Shanghai Huxi Instrumentation Factory, Shanghai, China) was used to control the flow rate. An ICP-atomic emission spectrometer (Atomscan16, TJA, USA) was used for the determination of metal elements.

An Al stock solution (500 µg mL^{-1}) was prepared by dissolving 0.1250 g high purity Al foil in 10 mL of concentrated HCl and heated until the Al was completely dissolved. Then the solution was cooled and transferred to a 250-mL flask, and diluted to the mark with deionized- distilled water. A 5.0 µg mL^{-1} Al working standard solution was prepared by diluting 10 mL stock solution to 1000 mL with deionized-distilled water. A 0.0826 g DCHNAQ was dissolved in 100 mL of absolute ethanol (2 x 10^{-3} M). A series of buffer solutions were prepared by dissolving 150 g hexamethylenetetramine to 500 mL of doubly distilled water, and the solution was adjusted to the desired pH (from 4.5 to 6.5) with 6.0 M HCl and 6.0 M NH$_3$.H$_2$O, checked by glass electrode; 201 X 8 strong base anion-exchange resin (100–120 mesh, styrene–di-vinylbenzene copolymers containing quaternary ammonium) was purchased from Shanghai Yaolong Chemical Factory (Shanghai, China). All reagents used were of analytical-reagent grade, and the solutions were prepared with deionized-distilled water.

2.2 Modified Resins and Micro-Column Preparation

2.2.1 Modified resins preparation

The appropriate amount of 201 X 8 strong base anionic exchange resin was immersed in 0.1 M NaOH for 10 h and then in 1.0 M HCl for another 10 h. The treated resin was washed to be neutral with water and dried at 60 ^{o}C, then stored in a desiccators. Three grams of the treated 201 X 8 resin was weighed into the solution containing 100 mL of 1.0 % ATCA (Fluka), and settled for 12 h. Then the mixture was filtered and washed with 3.0 M HCl and 1.0 M NaOH, respectively, then conditioned to neutrality with deionized-distilled water, and finally dried at 60 ^{o}C. Then it was stored in a desiccator before use.

2.2.2 Resin regeneration

The micro-column can be reused by regeneration with 3.0 mL of 3.0 M of HCl, 0.5 mL of 0.5 M of HCl, and 5.0 mL distilled water. The desired pH value was adjusted with the buffer solution at the same pH as that of the samples.

2.2.3 Resin stability

According to the procedure, the capacity of the resin was found to be constant before its repeated use at least 40 times for ATCA modified resin. While here the resin will usually be adopted for 30 times before it is renewed.

2.2.4 Micro-column preparation

Packed 0.20 g ATCA modified resins into a homemade micro-column 6–7 cm high using the slurry technique.

2.3 Solid-Phase Extraction

The resin modified by ATCA was filled into a micro-column, which was connected to a peristaltic pump. The resin column was equilibrated with the buffer solution at pH 5.5 before analysis. If the pH of the sample solution is in the pH range 4.5–6.5, it can be directly pumped through the micro-column, otherwise it should be adjusted to pH 5.5 with 10% (v/v) HCl and then passed through the micro-column packed with modified resin at 1.0 mL min^{-1}, and rinsed with 3.0 mL of water, and then desorbed with 2.0 ml 0.30 M of NaOH. The Al in the eluent was estimated by DCHNAQ spectrophotometry.

2.4 DCHNAQ Spectrophotometry

A simplified DCHNAQ procedure was used. An appropriate volume of sample solution containing Al(III) was pipetted into a 10-mL calibrated flask, A 1.0 mL of 2 x 10^{-3} M DCHNAQ, 1.0 mL of NaClO$_4$, and 2.0 mL of zephiramine solutions were then added successively. The whole was mixed well by swirling and then allowed to stand for about 10 min. The Al(III)–DCHNAQ–zeph complex together with the zephiramine–perchlorate was collected on a membrane filter of 0.2 mm pore size (for economy, a membrane filter of 47 mm was divided into two halves and each half was used) by filtration under suction. Hence, the ternary complex was concentrated on the membrane filter as a circular thin layer 17 mm in diameter. The membrane filter was stored wet for about 10 min on a filter paper impregnated with water. A blank thin layer was prepared using the same procedure except that no Al(III) was added. The wet membrane filter holding the Al(III)–DCHNAQ–zeph complex was placed on a glass attached to the sample channel, and the wet membrane filter holding the blank thin layer was placed on a glass plate attached to the reference channel of the spectrophotometer. The absorbance was measured at 655 nm.

2.5 Sample Preparation

2.5.1 Waste, river, spring and ground water samples

Four water samples were collected from Shobra El-Keema and Benha cites in the delta Nile of Egypt. They were stored in closed poly-ethylene bottles and analyzed within 10 h of sampling. Before analysis samples were filtered through a 0.45-mm membrane filter.

2.5.2 Soil extracts

A 10–20 g amount of air-dried soil sample was weighed accurately and placed in as 100 mL micro-Kjeldahl flask. The sample was digested according to the method recommended by Jackson (Jackson, 1965). The content of the flask was filtered through Whatman No. 40

filter paper into a 25 mL calibrated flask, neutralized (pH = 5.5) with 10 M NaOH and diluted to the volume with H_2O suitable aliquots (1.0–2.0 mL) were then, diluted to 20 mL.

2.6 Determination of Aluminum in Rice

Twenty gram of rice or flour sample was accurately weighed and placed into quartz crucible. Ten milliliter of concentrated sulfuric acid was added to it and evaporated to near dryness; then 10 mL of nitric acid (1 + 1, volume ratio) was added and evaporated to dryness. Under the heating conditions, concentrated hydrogen peroxide was added by drop till the solution clearness and evaporated. Water was added and continued to heat to remove the hydrogen peroxide. The residue cooled and was transferred into a 50-mL calibrated flask and diluted to the mark with water. Volumes of 2.00 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions.

2.7 Determination of Aluminum in Tea

Tea sample (3.9883 g) was accurately weighed and placed into ceramic crucible. Six milliliter of concentrated nitric acid and 2.0 mL of concentrated hydrochloric acid were added. After 20 min, the sample was gently heated to digest till near dryness. It is transferred into muffle furnace for ashing at 600 for 1.0 h. The sample was taken out to cool and 5.0 mL of nitric acid (1 + 1, volume ratio) was added and evaporated to near dryness by gently fire heating. Two gram of ammonium peroxydisulfate was added to cover the residue. The sample was transferred to muffle furnace at 800 ^{o}C for ashing for 1.0 h. It cooled and was taken out. Ten milliliter of nitric acid (1 + 99, volume ratio) was used to dissolve the residue and transferred to a 100-mL calibrated flask and diluted to the mark with water. Volumes of 2.00 mL of each of the aliquots were taken for the determination of aluminum.

2.8 Determination of Aluminum in Potato

The potato samples were washed and cut into bar. Then the samples were dried at 110 ^{o}C for 4.0 h. Ten grams of the dried samples were accurately weighed and placed into ceramic crucible. The samples were put into muffle furnace for ashing at 650 ^{o}C for 8 h. After the ashing was completed, the furnace was opened and the samples cooled and were taken out. After the samples cooled to a room temperature, a few drops of water were added and 4.0–5.0 mL of hydrochloride acid (1 + 1, volume ratio) was added to dissolve the residues. The above substances were transferred to a 50-mL calibrated flask and diluted to the mark with water. Volumes of 2.0 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions.

2.9 Preparation of Fruit Juice Samples

Packed fruit juice samples including orange, sour cherry and grape juices were purchased from the local market. For determination of aluminum in each sample, a 1.0 mL sample portion, 3.0 mL of HNO_3 (65%) and 5.0 mL of H_2O_2 (30%) was heated on a hot plate at a fairly low temperature in the glass beaker to dryness. After that, the sample was cooled, and 3.0 mL of H_2O_2 was added and the heating was repeated to obtain about 0.5 mL sample solution. After cooling down the resulting solution to room temperature and dilution with deionized water, pH was adjusted to pH 5.5 by adding diluted NaOH solution (Wyganowski

et al., 1983). Then, the solution was transferred into a 25 mL volumetric flask and diluted to the mark with deionized water.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on Sorption

The influence of pH on the metal recovery was determined. The standard solution was adjusted to the desired pH with the buffer solution. These solutions were then passed through the micro-column at 1.0 mL min^{-1} according to the fore-mentioned procedure. It was found that maximum retention of Al was achieved at pH 4.5–6.5. As is shown in Fig. 1, the recovery of Al (defined as Al in eluent/total Al) begins to decrease when the solution is over pH 6.5. Therefore, the buffer solution at pH 5.5 must be pumped simultaneously through the micro-column with the sample solution.
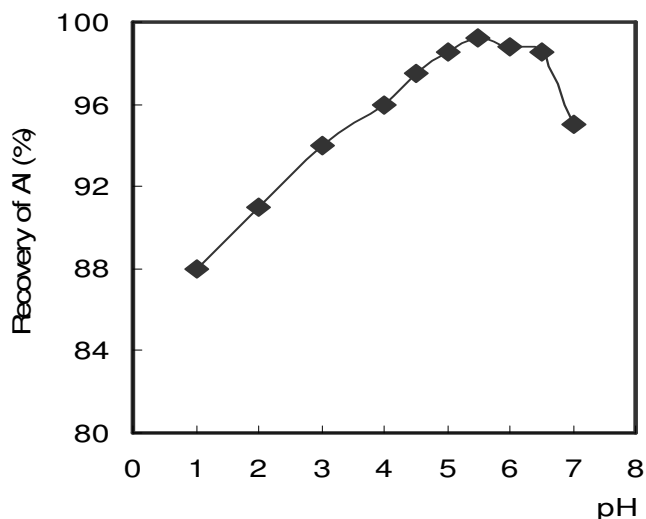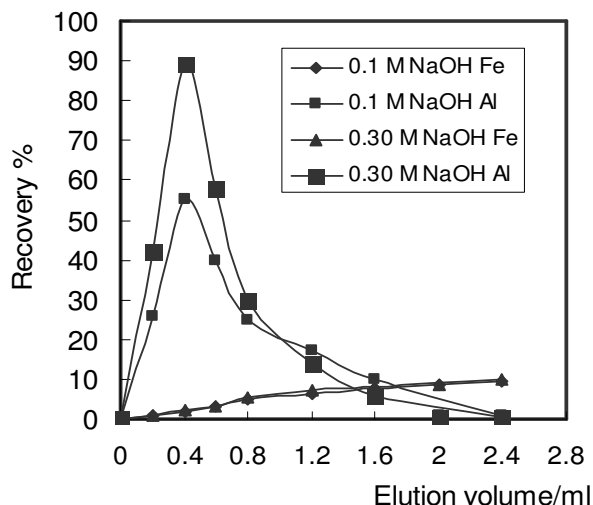

Fig. 1. Effect of pH on the sorption of Al concentration of Al 6.0 µgml^{-1}, resin 0.2 g, flow rate 1.0 ml min^{-1}

3.2 Influence of Elution Agent Concentration and the Separation of Ag(I), Hg(II), Fe(III), Mn(II) and Al(III)

The elution of Al(III) from the column was studied by using NaOH solution at varying concentrations (0.1–0.30 M) as a stripping agent. The optimum eluant concentration found for Al(III) was 0.30 M NaOH. The concentration of Al(III) in the eluent was determined by DHCNAQ spectrophotometry, and Ag(I), Hg(II), Fe(III) and Mn(II) can be eluted by using 3.0 mL of 1.0 M of HCl. The principal interferent for analysis in environmental samples is Fe(III). ATCA can form stable complexes with Al(III) and Fe(III). Fig. 2, shows that 50 µg of Fe(III) retained on the resin was not eluted with 2.0 mL of 0.30 M NaOH and thus did not interfere in down-line Al chemistry, but Al(III) was removed from the resin. This result was consistent with the much lower stability of the ferrate complex [Fe(OH)$_4^-$] compared with aluminate [Al(OH)$_4^-$] (Simpson et al., 1997). An experimental retention of Ag(I), Hg(II), Fe(III) and Mn(II) by the column was confirmed. The 50 µg Ag(I), Hg(II), Fe(III) and 10 µg Mn(II)

adsorbed on resin were eluted completely with 3.0 M HCl and detected by ICP-AES in eluent. Results were in good agreement with those obtained by ICP-AES.

Fig. 2. Eluting curves for Al and Fe. Concentration of Al is 6.0 µgml⁻¹; concentration of Fe is 50 µgml⁻¹; resin 0.2 g; flow rate 1.0 ml min⁻¹

3.3 Effect of Flow Rate on Sorption

The retention of Al(III) on the ATCA modified resin was studied at different flow rates. The recovery was greater than 98.8 % at a flow rate between 0.5 and 5.0 mL min^{-1}. However, at a flow rate above 5.0 mL min^{-1}, there was a decrease in the sorption percentage. Some Al(III) cannot be adsorbed on the ATCA modified resin if the flow rate is too high. The experimental results showed that the recovery would decrease if the flow rate was over 5.0 mL min^{-1}. In this work, a 1.0 mL min^{-1} flow rate was selected as optimum flow rate for the further study.

3.4 Breakthrough Studies

The breakthrough volume and the sorption capacity by column method were investigated. A series of 20-mL standard solutions of 10 µg mL^{-1} Al were passed through the micro-column packed with 0.20 g of modified resin, and the Al in the effluent was estimated by DCHNAQ spectrophotometry. The breakthrough curve was obtained and is shown in Fig. 3. The maximum sorption capacity (C/C$_o$ = 0.5) by the column method was found to be 10.8 mg Al g^{-1} resin.
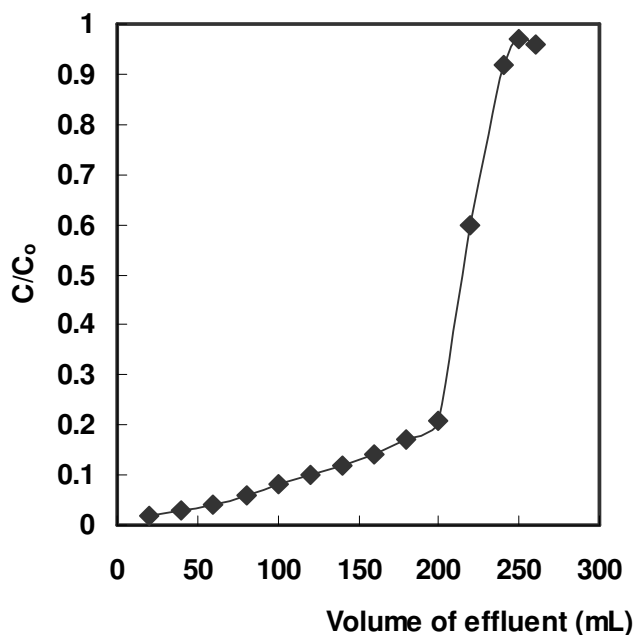
Fig. 3. Breakthrough curve for Al. C_0, concentration of Al is 10 µgml^{-1}; C, concentration of Al in effluent; resin 0.2 g; flow rate 1.0 ml min^{-1}

3.5 Tolerance of Foreign Ions

Five micrograms of Al and a certain amount of concomitant metal were added to 50 mL of the chromomeric system and determined by DHCNAQ spectrophotometry. The tolerance levels of the main concomitant ions with and without the separation of SPE are given in Table 1, when the recovery of Al was defined as over 97.5%. As recorded in Table 1, the tolerance levels of Ag(I), Hg(II), Fe(III), Mn(II), F^- had increased 100, 25, 100, 40, and 150 times, respectively. The reason is that ATCA can form stable complexes with Ag(I), Hg(II), Fe(III) and Al(III) and F^-. This made it possible to eliminate the main interfering ions such as F^-, alkali metal and alkali earth metal ions after passing through the SPE. Although Fe(III) is still adsorbed, it can be separated if 0.5 M of NaOH is selected as the eluant, which results in the first elution of Al(III) and the detention of the majority of Fe(III) on the micro-column. Therefore, the tolerance levels of Fe(III) were increased 100 times.

3.6 Preconcentration Limit, Preconcentration Factor, Detection Limit and Precision

The limits of preconcentration and preconcentration factors were investigated by using the column procedure. For this purpose, a series of 100, 250, 500 and 1000 mL of standard solutions containing 2.0 µg of Al, were passed through a micro-column by using a continuous column procedure. The concentration range of Al was between 2.0 and 20 µgL^{-1}. The results showed that the limit of preconcentration was 4.0 µgL^{-1} when the quantitative recovery was considered up to 97.5%. Recoveries from more dilute solutions were not quantitative.

Table 1. Effect of foreign ions on the determination of Aluminium(III).

Ion	Added as	The tolerance levels without the SPE/mg		The tolerance levels with the SPE/mg	
		Tolerance ratio	Relative error[*] %	Tolerance ratio	Relative error[*] %
K(I)	KCl	100	+ 1.25	250	+ 2.85
Li(I)	LiCl	100	+ 2.20	250	+ 2.60
Na(I)	NaCl	150	+ 1.10	400	- 2.00
Ag(I)	$AgNO_3$	50	- 2.50	500	+ 1.50
Mg(II)	$MgCl_2$	1000	+ 0.75	2000	+ 0.90
Ca(II)	$CaCl_2$	200	+ 1.30	500	- 1.25
Pd(II)	$PdCl_2$	30	+ 2.50	100	- 1.70
Fe(III)	$(NH_4)_2Fe(SO_4)_3$	1.0	+ 1.80	100	- 2.20
Co(II)	$CoCl_2$	30	+ 2.90	500	+ 2.90
Ni(II)	$NiCl_2$	30	- 2.65	500	+ 1.70
Cu(II)	$CuSO_4$	30	- 1.60	500	+ 1.90
Zn(II)	$ZnCl_2$	20	+ 1.30	1000	+ 25.5
Mn(II)	$MnCl_2$	25	+ 1.10	1000	+ 3.50
Cd(II)	$CdCl_2$	25	+ 0.80	100	+ 1.60
Hg(II)	$HgCl_2$	15	- 1.75	375	- 2.25
F$^-$	NaF	1.0	+ 2.20	80	+ 3.90

Above ± 4.0 % in absorbance is considered to be not tolerated.

The preconcentration factor was up to 250 times because 2.0 µg of Al from a 500-mL standard solution on the micro-column could be eluted with 2.0 mL 0.30 M of NaOH. However, in practice, 10–25-mL samples were studied in the analysis and procedure and the preconcentration factor was found to be 30 times.

According to the definition of the IUPAC, the detection limit (3s) is determined by performing 10 repeated measurements of the blank value. The detectable minimum Al concentration was found to be 16 µg L^{-1} by DHCNAQ spectrophotometry (Azhari and Amin, 2007). In the present paper, it was found to be 0.53 µg L^{-1} Al if the preconcentration factor of 30 times was adopted. The precision of the determination was measured by five successive retention and elution cycles for 2.0 µg of Al in 10 mL of solution. It was found that the recovery was 99.7 ± 1.1% at the 95% confidence level.

3.7 Practical Applications to Determine Dissolved Al Concentration in Waters and Soil Extracts

In order to establish the validity of the method, natural waters were selected for analysis of Al(III). The proposed method and ICP-AES (Tagashira, 1984) method have been applied to the analysis of Al(III) in synthetic and natural waters, respectively. The results are shown in Table 2.Both methods obtained consistent results indicating the proposed SPE approach is accurate and reliable.

Table 2. Determination of Al(III) in some water samples

Water sample	Added ng ml^{-1}	Al(III) "Spiked" Found [a] ng ml^{-1}		Al(III) "unspiked" Found [a] ng ml^{-1}	
		This work	**ICP-AES**	**This work**	**ICP-AES**
Tap water	30.0	39.7	39.6	9.7	9.6
	50.0	59.5	59.5	9.6	9.6
Well water	20.0	45.5	46.0	25.5	26.0
	40.0	66.0	65.7	25.9	25.8
Pond water (Helwan)	80.0	85.0	85.5	5.0	4.5
	120.0	125.2	124.7	5.2	4.8
River Nile water					
1- Benha	40.0	75.5	76.0	35.5	35.9
(upper stream)	100.0	136.0	135.8	36.0	35.8
2- Shobra El-Keema	50.0	118.0	119.0	67.9	69.0
(upper stream)	90.0	157.5	158.6	67.5	68.7
Sea water					
1- Alexandria [b]	35.0	71.6	72.0	36.6	37.0
(Upper)	85.0	121.5	122.0	36.5	37.0
2- Safaga [c]	30.0	113.4	113.0	83.4	83.0
(Upper)	30.0	113.2	112.9	83.3	83.0
3- Jedda [c]	25.0	111.5	110.5	86.5	85.5
(Upper)	45.0	130.8	131.0	85.7	86.0

[a]: Values given represent the average of six analysis of each sample
[b]: From Mediterranean sea
[c]: From Red sea

Six soil extracts were analyzed in the recovery study (Table 3). The experimental results indicated that the interferences of Ag(I), Hg(II), Fe(III) and Mn(II) were removed and the selectivity as well as sensitivity were improved with this method.

Table 3. Determination of Al in some surface soil samples[a,b]

Serial no.	Al (ng g^{-1}) [a]	Sample source
S$_1$ [c]	112.7 ± 1.2 [b]	Traffic soil (Makkah bus terminal, Makkah)
S$_2$	73.5 ± 1.5	Agricultural soil (Benha University campus)
S$_3$	104.0 ± 1.8	Paint soil (Shoubra Paint, Qhalubia)
S$_4$	76.5 ± 2.0	Industrial soil (Catron Company, Benha)
S$_5$	105.3 ± 1.5	Roadside soil (Makkah–Jedda highway)
S$_6$	84.5 ± 1.6	Marine soil (Bay of Makkah)

[a] Average of five analyses of each sample.
[b] The measure of precision is the standard deviation.
[c] Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu, Fe, Pb, NO$_3$, NO$_2$, Zn, SO$_4$, Mn, Mo, Co, etc.

The proposed method were found to be in excellent agreement with those obtained by and ICP-AES (Tagashira, 1984) method and are recorded in Table 3. The average values of Al(III) in different surface soil samples of Benha and Makkah El-Mokarama was found to be 84.5 and 112.6 ng g^{-1}, respectively. The method is very reliable, and the concentration can be measured in a very simple and rapid way for routine analysis of Al(III).

To test the reliability of the proposed procedure, the proposed method was employed to determine the trace amounts of Al^{3+} in different fruit juice samples (i.e., orange, sour cherry and grape juices), and food samples (rice, tea and potato). In order to verify the accuracy of the established procedure, recovery experiments were also carried out by spiking the samples with different amounts of aluminum before any pretreatment. Table 4 shows the obtained results It can be concluded that the proposed method is accurate and free from systematic errors. Statistical analysis of these results using Student's t-test showed that there was no significant difference between actual and found concentrations at 95% confidence level (Miller and Miller, 2005).

The performance of the proposed method was assessed by calculation of the t- value for accuracy and the F- test for the assessment of precision compared with those obtained from AAS method on the same sample for five degrees of freedom and a 95% confidence level (Miller and Miller, 2005). The calculated values of t-and F- obtained did not exceed the corresponding theoretical values (Table 4) indicating no significant differences between the method compared.

4. CONCLUSION

From the above experiments, we can make the following conclusions:

(i)   DHCNAQ is a very sensitive chromogenic reagent for Al. However, the concentration of sodium in leaching solution often exceeds 10 mg mL^{-1}. Furthermore, the concentrations of Fe(III) and F$^-$ are sometimes also much higher. This seriously interferes with the determination of Al(III) by the above method. Therefore, it is necessary to find a suitable new way to solve these problems. DHCNAQ spectrometry coupled with SPE is one such promising method.

(ii)   The tolerance levels of Fe(III) and F$^-$, by using SPE technology–ATCA modified resin, can be increased 80, 10 and 100 times, respectively. This resolves the long-term critical problem of the interferences of Fe(III) and F$^-$ for determining Al(III) by spectrophotometry.

(iii)   A large concentration factor (20 times for a 50-mL sample volume) can be reached using SPE technology and a much higher sensitivity (20 times) has been obtained by DHCNAQ spectrophotometry coupled to SPE technology. This enables DHCNAQ spectrophotometry to reach the sensitivity requirement for determining dissolved Al in soil extracts and ground waters.

Table 4. Determination of aluminum in different real samples

Name of sample	Added Al ($\mu g \ l^{-1}$)	Found Al [a] ($\mu g \ l^{-1}$)			
		ICP-AESAAS	This work	t- value [b]	F- test [b]
Orange juice	--	276.50 ± 2.43	275.7 ± 1.67	1.19	2.83
	100	369.20 ± 2.40	370.0 ± 1.77	1.36	3.14
	200	373.60 ± 1.95	376.80 ± 1.56	0.96	2.11
Sour cherry juice	--	160.50 ± 2.44	160.29 ± 1.43	1.05	2.42
	100	258.50 ± 2.10	260.8 ± 1.85	1.36	3.18
	200	257.80 ± 2.25	258.70 ± 1.55	1.23	2.68
Grape juice	--	347.50 ± 2.86	346.90 ± 1.95	1.58	3.41
	100	443.80 ± 2.34	445.80 ± 1.51	1.40	3.31
	200	542.60 ± 2.05	447.10 ± 1.77	0.89	1.98
Rice	--	90.25 ± 2.56	89.90 ± 1.43	1.11	2.58
	100	190.50 ± 2.17	190.20 ± 1.65	1.45	3.52
	200	291.20 ± 2.34	290.80 ± 1.81	1.20	2.88
Tea	--	168.80 ± 1.95	170.00 ± 1.54	1.07	2.66
	100	269.5 ± 2.25	169.70 ± 1.27	1.33	3.24
	200	368.0 ± 2.62	268.90 ± 1.47	1.06	2.57
Potato	--	125.5 ± 2.22	125.1 ± 1.33	1.41	3.39
	100	224.7 ±1.88	224.8 ± 1.18	1.23	3.01
	200	324.4 ± 2.04	325.9 ± 1.46	1.17	2.76

[a]: Mean of sex results.
[c]: Theoretical t- and F- values for five degrees of freedom and 95 % confidence level were 2.57 and 5.05, respectively.

In summary, the proposed method possesses distinct advantages such as the simplicity in handling and transferring, the rapidness, and the economic advantages. Its sensitivity and selectivity are satisfactory for the determination of total reactive Al in soil extracts and other complex environmental samples.

REFERENCES

Albendin, G., Manuel-Vez, M.P., Moreno, C., Garcia-Varas, M. (2003). Reverse flow injection manifold for spectrofluorimetric determination of aluminum in drinking water. Talanta, 60, 425–431.

Alieva, R.A., Alieva,S.F., Chyragov, F.M. (2006). Bis-(2,3,4-trihydroxy phenylazo)-benzidine as a reagent for the photometric determination of aluminum. J. Anal. Chem., 61, 630–633.

Al-Kindy, S.M.Z., Al-Ghamari, S.S., Suliman, F.E.O. (2007). A sequential injection method for the fluorimetric determination of aluminum in drinking water using 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid. Spectrochim. Acta (A), 68, 1174–1179.

Azhari, S.J., Amin, A.S. (2007). High sensitive and selective spectrophotometric determination of aluminium after collection on a membrane filter using 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline and zephir-amine. Anal. Lett., 40, 2959–2973.

Chamsaz, M., Zavar, A.M.H., Hosseini, M.S. (2000). Flotation spectrophotometric determination of aluminum with alizarin. Anal. Lett., 33, 1625–1633.

Corani, B., Bombi, G.G., Tapparo, A., Nicolini, M., Zatta, P., Perazzolo, M., Favarato, M. (1990). Alzheimers-disease and aluminum toxicology, Envir. Health Per., 89, 233–235.

Di, J., Bi, S., Yang, T., Zhang, M. (2004). Voltammetric determination of aluminum(III) using a reagentless sensor fabricated by sol–gel process. Sensors. Actuators B: Chem., 99, 468–473.

Exley, C., Burgess, E., Day, J.P., Jeffrey, E.H., Melethil, S., Yokel, R.A. (1996). Aluminum toxicokinetics, J. Toxicolog. Envir. Health, 48, 569–584.

Fakhari, A.R., Khorrami, A.R., Naeimi, H. (2005). Synthesis and analytical application of a novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples. Talanta, 66, 813–817.

Filik, H., Tütem, E., Apak, R., Ercag, E. (1998). Spectrophotometric determination of gallium(III) with carminic acid and hexadecylpyridinium chloride. Mikrochim. Acta., 129, 57–63.

Flaten, T.P., Alfrey, A.C., Birchall, J.D., Savory, J.R., Yokel, A. (1996). Status and future concerns of clinical and environmental aluminum toxicology. J. Toxicolog. Environ. Health., 48, 527–541.

Fleming, J., Joshi, J.G. (1987). Ferritin-isolation of aluminum ferritin complex frombrain. Proc. Natl. Acad. Sci. U.S.A., 84, 7870–8766.

Garg, B.S., Sharma, R.K., Bhojak, N., Mittal, S. (1999). Chelating resins and their applications in the analysis of trace metal ions. Microchem. J., 61, 94–99.

Gündüz, S.B., Kücükkolbas, S., Atakol, O., Kilic, E. (2005). Spectrofluorimetric determination of trace aluminum in diluted hemodialysis solutions. Spectrochim. Acta (A)., 61, 913–921.

Güray, T., Uysal, U.D., Huseyinli, A.A., Gedikbey, T. (2005). 2,2,3,4-tetra- hydroxy-3-sulpho-5-nitroazobenzene for spectrophotometric determination of aluminium in pharmaceutical suspensions and granite. Anal. Chim. Acta, 545, 107–112.

Hirata, S., Umezaki, Y., Ikeda, M. (1986). Determination of chromium(III), titanium, vanadium, iron(III), and aluminum by inductively coupled plasma atomic emission-spectrometry with an online preconcentrating ion-exchange column. Anal. Chem., 58, 2602–2606.

Huseyinli, A.A., Atilir, A. (2001). Determination of toxic elements in some natural samples. Toxicology., 164, 229–233.

Huseyinli, A.A., Koseoglu, F., Uysal, U.D. (2001). Rapid spectrophotometric determination of zirconium(IV) with 2,2,3,4-tetrahydroxy-3-sulpho-5-chloroazobenzene in alloys. Anal. Sci., 17, 793–796.

Jackson, M.L. (1965). Soil Chemical Analysis; Prentice-Hall: New Jersey, p. 297.

Korenaga, T., Motomizu, S., Toei, K. (1980). Modified extraction procedure for the spectrophotometric determination of trace amounts of aluminum in sea-water with pyrocatechol violet and removal of excess of reagent. Analyst., 105, 328–332.

Madrakian, T., Afkhami, A., Borazjani, M., Bahram, M. (2005). Partial least-squares regression for the simultaneous determination of aluminum and beryllium in geochemical samples using xylenol orange. Spectrochim. Acta (A)., 61, 2988–2994.

Marczenko, Z. (1976). Spectrophotometric Determination of Elements, Wiley, New York.

Martire, C., Hainberger, L. (1985). Sensitive and selective spectrophotometric determination of aluminum with chrome fast pure blue-b and cetyltrimethyl-ammoniumbromide. Mikrochim. Acta, 11, 223–229.

Mendham, J., Denney, R.C., Barnes, J.D., Thomas, M. (2000). Vogel's Textbook of Quantitative Chemical Analysis, 6th ed., Prentice-Hall, London/ New York/ Toronto., p. 473.

Miller, J.N., Miller, J.C. (2005). "Statistics and Chemometrics for Analytical Chemistry" 5th ed., Prentice Hall, England.

Mondal, B.C., Das, D., Das, A.K. (2001). Application of a new resin functionalised with 6-mercaptopurine for mercury and silver determination in environmental samples by atomic absorption spectrometry. Anal. Chim. Acta, 450, 223–230.

Pierson, K.B., Evonson, M.A. (1986). Measurement of aluminum in neuronal tissues using electrothermal atomization atomic-absorption spectrophoto-metry. Anal. Chem., 58, 1744–1748.

Pozzebon, J.M., Queiroz, S.C.N., Melo, L.F.C., Kapor, M.A., Jardim, I.C.S.F. (2003). Application of new high-performance liquid chromatography and solid-phase extraction materials to the analysis of pesticides in human urine. J. Chromatog. (A), 987, 381–385.

Reddy, S.A., Reddy, K.J., Lakshminaraya, S., Priya, D.L., Rao, Y.S., Reddy, A.V. (2008). Extractive spectrophotometric determination of trace amounts of cadmium(II) in medicinal leaves and environmental samples using benzildithiosemicarbazone (BDTSC). J. Hazard. Mater., 152, 903–909.

Rodrigues, J.L., Magalhaes, C.S., Luccas, P.O. (2005). Flow injection spectrophotometric determination of Al in hemodialysis solutions. J. Pharm. Biomed. Anal., 36, 1119–1123.

Safavi, A., Abdollahi, H., Mirzajani, R. (2007). Simultaneous spectrophotometric determination of Fe(III), Al(III) and Cu(II) by partial least-squares calibrationmethod. Spectrochim. Acta (A), 63, 196–199.

Samaritan, J.M., Wehr, J.D., Buccafuri, M.A., Sahn, M. (1993). Automated measurement of aqueous aluminum by the pyrocatechol violet method. Inter. J. Environ. Anal. Chem., 50, 173–182.

Sarzanini, C., Mentasti, E., Porta, V., Gennaro, M.C. (1987). Comparison of anion-exchange methods for preconcentration of trace aluminum. Anal. Chem., 59, 484–486.

Scindia, Y.M., Pandey, A.K., Manohar, A.V.R. (2002). Selective preconcentration and determination of chromium(VI) using a flat sheet polymer inclusion sorbent: potential application for Cr(VI) determination in real samples. Anal. Chem., 74, 4204–4212.

Shao-pu, L. (1982). Highly sensitive spectrophotometric determination of trace amounts of aluminium with chromazol KS and cetylpyridinium bromide. Analyst., 107, 428–432.

Shokrollahi, A., Ghaedi, M., Niband, M.S., Rajabi, H.R. (2008). Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium ion. J. Hazard. Mater., 151, 642–648.

Simpson, S.L., Powell, K.J., Nilsson, N.H.S. (1997). Flow injection determination of Al^{3+} and Al$_{13}$O$_4$(OH)$_{24}$(H2O)$_{12}$$^{7+}$ species using a 1.3-s reaction with 8-quinolinol-derivatised Fractogel. Anal. Chim. Acta, 343, 19–32.

Suresha, S., Silwadi, M.F., Syed, A.A. (2002). Sensitive and selective spectrophotometric determination of Hg(II), Ni(II), Cu(II) and Co(II) using iminodibenzyl and 3-chloroiminodibenzyl as new reagents and their applications to industrial effluents and soil samples. Inter. J. Envir. Anal. Chem., 82, 275–289.

Tagashira, S. (1984). Distribution equilibria of aluminum pyrocatechol violet quaternary onium salt ion-pairs in micellar systems—spectrophotometric determination of aluminum. Anal. Chim. Acta, 157, 343–348.

Themelis, D.G., Kika, F.S. (2006). Flow and sequential injection methods for the spectrofluorimetric determination of aluminium in pharmaceutical products using chromotropic acid as chromogenic reagent. J. Pharm. & Biomed. Anal., 4, 1179–1185.

Tria, J., Butler, E.C.V., Haddad, P.R., Bowie, A.R. (2007). Determination of aluminium in natural water samples. Anal. Chim. Acta, 588, 153–165.

Wisniewski, H.M., Wen, G.Y. (1992). Aluminum in Biology and Medicine, Wiley, New York.

Wyganowski, C., Motomizu, S., Toei, K. (1983). Spectrophotometric determination of aluminum with bromopyrogallol red and a quaternary ammonium salt—determination of aluminum in river water. Mikrochim. Acta, 1, 55–64.

Ying-Quan, Z., Lin, Z., Jun-Yi, L. (1983). Spectrophotometric determination of aluminium with chlorophosphonazo I. Talanta, 30, 291–293.

Yokel, R.A. (1994). Aluminum chelation-chemistry, clinical and experimental studies and the search for alternatives to desferrioxamine. J. Toxicolog. Envir. Health., 41, 131–174.

Yokel, R.A. (2000). The toxicology of aluminum in the brain: a review, Neurotoxicology, 21, 813–828.

Zaijun, L., Naping, L., Xia, Z., Qijun, S. (2007). Extraction spectrophotometric determination of aluminum in dialysis concentrates with 3,5-ditertbutylsalicylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate. J. Pharm. & Biomed. Anal., 43, 1609–1613.

Zareba, S., Melke, J. (2000). Spectrophotometric determination of aluminium in pharmaceutical preparations by azo dyes of 1,2,4-triazole series. Pharm. Acta Helv., 74, 361–364.

Zheng, H.L., Xiong, W.Q., Gong, Y.K., Peng, D.J., Li, L.C. (2007). Catalytic spectrophotometric determination of trace aluminium with indigo carmine. Spectrochim. Acta (A), 66, 1243–1247.

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