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A Novel Green Nano Determination of Aluminium in Food, Biological and Water Samples Using a Cloud Point Extraction Combined with Spectrophotometry

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Abstract

A ternary surfactant system is proposed for the first time as an extraction strategy of nano amount determination of aluminium using 6-{4-(2,4-dihydroxyphenyl)diazenyl)phenyl}-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (DDPODC), as complexing agent in presence of PONPE 5.0 as nonionic surfactant at pH 4.6 and applied for selective preconcentration of Al^{3+}. The analyte was quantified in the enriched solution by spectrophotometry. After optimization of the complexation and extraction conditions, an enrichment factor superior to 400-fold was obtained with improved sensitivity of 317 times compared to the conventional extraction system using only a nonionic surfactant. The molar absorptivity, Sandell sensitivity, calibration and Ringbom ranges, detection and quantification limits and relative standard deviation (RSD) of the complex were calculatyed. The presented procedure was successfully applied to determine aluminium content in real samples with satisfactory results.

Keyword: Cloud point extraction; Aluminium determination; Azo dyes; Spectrophotometry; Environmental analysis;

Introduction

Oxygen, silicon and aluminium being the first, second and third most abundant element in the Earth's crust. Aluminium is found in air, water, soil, plant and animal tissues in different forms. It is released to the environment due to anthropogenic activities such as mining, industrial uses and production of aluminium metal and other aluminium compounds. For several years, it was not considered as a harmful metal for humans but animal experiments in 1965 suggested a possible connection between aluminium and Alzheimer's disease [1,3]. Oral intake of foodstuffs is the most important source of aluminium. According to the data of the American scientists, daily consumption of 0.1mg of aluminium with drinking water increases the risk of dementia 2.26 times and considerably reduces intellectual abilities [2]. Oral aluminium bioavailability from the diet has been estimated to be 0.1 to 0.3%, based on daily aluminium intake and urinary elimination. Results of a few studies with a controlled diet and tea are consistent with this estimate [4]. Greater than 95% of aluminium is eliminated by the kidney. Occupational aluminium exposure increases urinary aluminium concentration above their normal levels. The aluminium body burden is distributed in decreasing order to the bone, lung, muscle, liver and brain [5-9]. The Aluminium compounds are used as antacids, antiperspirants food additives and vaccine adjuvant. Aluminium salts are also widely used in water treatment as flocculants and it is also present in treated drinking water in the form of reactive species. WHO limit for tolerable weekly intake value for aluminium is 1 mg/kg body weight/week [1]. According to the agency for toxic substances and disease registry (ATSDR) the minimal risk level (MRL) of aluminium has been established at 2.0 mg/kg/day [10]. Thus, Aluminium content control is important in the food-processing industry, agriculture and drinking water. In the studies of different foods and medicines, it is observed that aluminium is the fundamental elements in almost of all food stuffs such as cereal products, lentils, spices, tea, fruits and vegetables and medicines [4,10,11]. Medicines (antacids) contain very high amount of aluminium whereas food and food products contain aluminium in varying amounts starting from 1 mg/kg to as high as multiple of 100 mg/kg (with or without food additives) [4,10,11].

Hartwell and Pember, in 1918 studied the toxic effect of aluminium on plants due to increasing acidity in the soil substrate, and thus far several studies have been published on this topic [12,13,14]. The effect of aluminium on the human body and human health as well as aluminium intake through cosmetic preparations and pharmaceutical preparations, particularly in childhood vaccines [15,16,17,18,19], is still being discussed. Aluminium has a potential neurotoxic effect, and its intake by the human organism is connected with, for example, Alzheimer's disease, autism and breast cancer [15,20,21,23,24]. Therefore, the determination of aluminium in environmental, pharmaceutical and cosmetic preparations is very important and greatly needed [25].

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Nowadays, there are many analytical techniques for the direct detection of the Al in real samples like spectrophotometry, spectrofluorometry, flame atomic absorption spectrometry (FAAS) and the graphite furnace atomic absorption spectrometry (GFAAS) [26,30,31,32,33,34,35]. Before analytical determination of low Al concentration levels in complex samples analysis, it is necessary separation and preconcentration steps.

The most used techniques for the separation and preconcentration of this element include solid-phase extraction, conventional liquid–liquid extraction, and cloud point extraction (CPE), among others [4, 36, 37]. CPE is becoming an important and practical application of surfactants in analytical chemistry because of the versatility in recuperation of both organic and metallic analytes [31-34]. CPE has been recognized as green procedure owing to the use of inexpensive surfactant extractants, the generation of less laboratory wastes and the fact that surfactants are non-volatiles, non-toxics and non-inflammable in contrast to organic solvents [38].

To date, nonionic surfactants have been the most widely employed for CPE, although zwitter ionic surfactants and mixtures of nonionic and ionic surfactants have been also used [38, 39]. Clouding is ascribed to the efficient dehydration of hydrophilic portion of micelles at higher temperature condition. Additionally, it has been reported the ability of different substances to induce phase separation in aqueous solutions of bile salts as sodium cholate (NaC) at room temperature [40]. On the other hand, among cationic surfactants, cetyltrimethylammonium bromide (CTAB) constitutes undoubtedly an example of self-assembled ordered medium as micelles, and other structures and phases, having been widely employed in analytical chemistry with different purposes [41-47].

In the present study, 6-{4-(2,4-dihydroxy-phenyl)diazenyl) phenyl}-2-oxo-4-phenyl-1,2-dihydro- pyridine-3-carbonitrile (DDPODC), was synthesized for Al^{3+} determination using cloud point extraction and preconcentration after complexation with Al^{3+} ions. The method was based on the complexation of Al^{3+} with DMPAHPD in presence of polyethyleneglycolmono-p-nonylphenylether (PONPE 5.0) as nonionic surfactant at pH 4.6 using suitable buffer (acetate buffer). Experimental variables affecting sensitivity and precision of the proposed method were in detail investigated and optimized in order its application to determinate of nano amount of Al^{3+} in food, biological fluids and water samples.

Materials and Methods

Apparatus

A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 1.0-cm quartz cell. FAAS instrument (Perkin Elmer model Analyst 100, USA) was used. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A water bath with good temperature control and a centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

Reagents

Working standard Al^{3+} solutions were obtained by appropriate dilution of standard solution of Al(NO3)3.9 H2O (E-Merck, Darmstadt, Germany) of 1000 mg/L, using ultra pure water. A working solution containing 1.0 µg/mL of aluminium was prepared by appropriate dilution of the stock solution.

Surfactant PONPE 5.0, (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) 50% (v/v) in ethanol (Sigma Chemical Co.), was employed without further purification.

The solutions of different pH 2.75-10.63 acetate, phosphate, thiel and universal buffers were prepared as described early [48]. Acetonitrile solvent and potassium iodide salt were purchased from Merck.

6-{4-(2,4-dihydroxy-phenyl)diazenyl)phenyl}-2-oxo-4-phenyl-1,2-dihydro-pyridine-3-carbonitrile (DDPODC) used in the present investigation study was prepared according to the procedure described previously. An appropriate weight was dissolved in 100 mL of absolute ethanol (4×10^{-3} mol L^{-1}). The solution was stable for more than two weeks.

General procedure

An aliquot of cold Al^{3+} standard solution was transferred to a 100 mL polypropylene tube, 4.0 mL of the 4.0×10^{-3} M DDPODC solution and 10 mL acetate buffer solution of pH 4.6 were added. This was followed by the addition of 2.0 mL of 50% PONPE 5.0 solution and 4.0 mL of 0.5 M of KI solution. The total system was placed for 5.0 min in a thermostatic bath at 50°C. The separation of the two phases was achieved by centrifugation for 5.0 min at 4000 rpm using 25-mL calibrated centrifuge tubes. The phases were cooled in an ice bath in order to increase the viscosity of the surfactant-rich phase. The surfactant-rich phase was dissolved and diluted to 0.25 mL with acetonitrile and transferred into a 5.0-mm quartz cell. The absorbance of the solution was measured at 579 nm. The blank solution was submitted to the same procedure without Al^{3+} ions.

Samples treatment

Determination of Al^{3+} in water samples

Bottled mineral water samples were obtained from local sources. Water samples were freshly collected after allowing the water flow for 5.0 min. All samples were filtered through a 0.45 µm pore size membrane filter to remove suspended particulate matter and were stored at 4.0°C in the dark. 1.0 mL was taken of each water sample and was subjected to the above general procedure.

Determination of Al^{3+} in biological samples

Human blood (10-20 mL), urine (10-50 mL) or human gallstone (0.1-0.5 g) was added to a 100 mL micro-Kjeldahl digestion flask. A glass bead and 10 mL of conc. HNO3 were added and heated gently on the digester. When the initial brisk reaction was over, the solution was removed and cooled. Conc. H2SO3 (2.5 mL) was added carefully, followed by the addition of 70% perchloric acid (1.0 mL); heating was continued until dense white

fumes were observed, repeating HNO3 addition if necessary. Heating was continued for at least 30 min, followed by cooling. The content of the flask was neutralized (pH 4.6) with dilute NH4OH in the presence of 1.0-2.0 mL of 0.01% (w/v) tartrate and/or EDTA solution, transferred quantitatively into a 50 mL volumetric flask and made up to the mark with deionized water. An aliquot (1.0-2.0 mL) of the final solution was pipetted into a 10 mL calibrated flask and the A13+ content was determined as described above.

Determination of Al^{3+} in soil samples

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. The content of the flask was filtered through Whatman No. 40 filter paper into a 25 mL calibrated flask, neutralized (pH = 4.6) 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 and treated as in the general procedure described above.

Determination of Al^{3+} in tea sample preparation

Instant tea samples were obtained from local supermarket. Tea bag was weighed before soaking in 100 mL of boiled water (100°C) for 1.0 h and the solution was collected and adjusted to 100 mL with water. The solution was diluted 5.0 folds before applying the above general procedure. The same solution was directly aspirated into FAAS system, under the conditions as described below.

Determination of Al^{3+} food sample preparation

Various food and food products were collected from local market of Benha city, Egypt. The samples are: rice and rice products, lentils, wheat products, spices, corn, glucose and tea. Samples purchased were taken for analysis as received and thus it may contain some contaminants or additives. Wherever necessary, samples were powdered in a clean environment using a pastel and mortar. Samples (30-50 mg) were sealed in polyethylene for irradiation. Aluminium standards were prepared from high pure thin aluminium foil as well as from standard stock solution on a filter paper; air dried and sealed in polyethylene.

Determination of aluminium by FAAS

Aluminium in the above samples was determined by FAAS instrument (Perkin Elmer model Analyst 100, USA), employing the following conditions: detection wavelength 309.2 nm, air flow pressure 2.0 kg/cm^2, air flow rate 8.0 L/ min, acetylene flow pressure 0.4 kg/cm^2, acetylene flow rate 2.0 L/min, burner height, 3.25 cm. A calibration graph in the concentration range of 1–15 mg/L Al^{3+} was constructed and used for determination of aluminium content in samples.

Interferences study

Different amounts of ions, which may be present in samples, (1/1, 1/10, 1/50 and 1/100 Al^{3+}/interferent ratio) were added to the test solution containing 25 ng/mL Al^{3+} and the general procedure described above was applied. Interferences studies were realized in samples without addition of masking or anticoagulant agents.

Accuracy study

Adequate volume of each sample was spiked with increasing amounts of Al^{3+} (15 and 25 ng/mL). Analyte concentrations were determined by proposed methodology.

Results and discussion

DDPODC is often used as a chromgenic reagent for the determination of Hg^{2+} [49]. Al^{3+} forms a complex with DDPODC in the presence of PONPE 5.0 in aqueous media which has a maximum absorbance at 567 nm. By addition of iodide ion, the solution became turbid which can be extracted by CPE method. The ternary complex formed in surfactant-rich phase shows a maximum absorbance at 579 nm [Figure 1]. The absorbance was measured at 468 nm against a reagent blank as the reference, after separation of surfactant-rich phase.

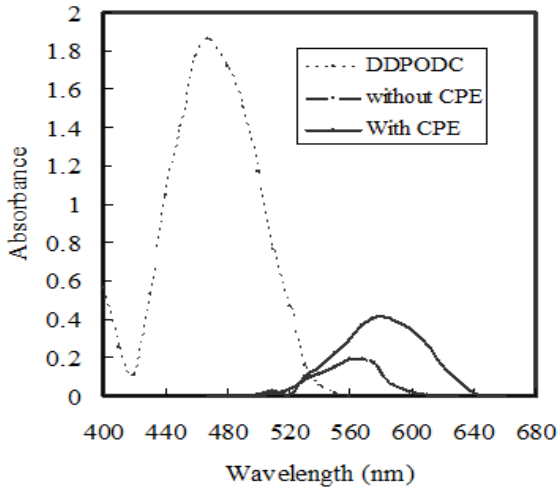

Figure 1: Absorption spectra for DDPODC and its complex with 9.0 n g/ mL Al^{3+} without CPE and 60 mg/mL Al^{3+} with CPE at the optimum conditions

Optimization of the system

To take full advantage of the procedure, reaction conditions must be optimized. Variable parameters were studied in order to achieve optimum experimental conditions. All parameters were optimized by setting these parameters to be constant and optimizing one each time.

The effect of pH on the developed colour at a constant concentration of complex in surfactant-rich phase was studied in the pH range of 2.75-10.63. The absorbance of the Al^{3+} – DDPODC–PONPE 5.0 system at 579 nm in surfactant-rich phase was investigated against the reagent blank. The absorbance was nearly constant in the range of 4.4-4.8. So, pH 4.6 was selected as the best [Figure 2]. The amount of pH 4.6 was investigated to choose the optimum volume. The highest absorbance value was achieved by addition of 8.0-12 mL of pH 4.6. For all further studies, 10 mL of pH 4.6 per 100 mL was selected.

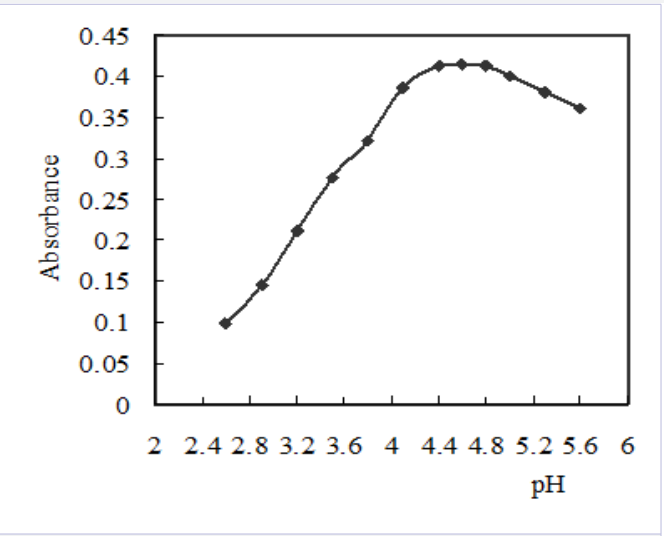

Figure 2: AEffect of pH on the CPE of 60 ng/mL Al^{3+} complexed with DDPODC at the optimum conditions

The DDPODC concentration effect on the extraction and determination of Al^{3+} was studied in the range of 0.4-4.0 × 10-4 M. The formed complex increased by increasing DDPODC concentration up to 1.6 × 10^{-4} M and decreased at higher concentrations. It was expected that increasing DDPODC causes an increase in the absorbance of complex. At concentrations ≥ 1.8 × 10^{-4}M, the concentration of uncomplexed DDPODC in surfactant-rich phase increases significantly. Therefore, much probably decrease of absorbance change at concentrations ≥ 1.8 × 10^{-4}M is due to this fact that the free DDPODC competes with the complexes in extraction to surfactant-rich phase. The optimum DDPODC concentration of 1.6 × 10^{-4} M was selected.

Effect of 50% PONPE 5 concentration on the complexation of Al^{3+} was studied in the volume range 0.5-5.0 mL. The absorbance increased by increasing PONPE 5 concentration up to 2.0 mL of 50% and decreased at higher concentrations. The absorbance of blank also increased by increasing PONPE 5 concentration. This is due to more extraction of DDPODC by increasing PONPE 5 concentration, whereas the difference between the sample and blank (ΔA) increased by increasing PONPE 5 concentration up to 2.0 mL of 50% and decreased at higher concentrations. Therefore, 2.0 mL of 50% PONPE 5 was selected.

Addition of salt can cause non-ionic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Various inorganic salts including KCl, KBr, KI, NaCl, NaF, and KNO_3, were examined and KI was found as the optimum. Therefore, iodide was added to induce micelle growth and extraction of complex. The effect of iodide concentration was investigated in the range of 0.05-0.4 M. Addition of 0.2 M iodide in the final 100 mL solution sufficed for maximum extraction of the complex and the absorbance decreased at higher concentrations. A concentration of 0.2 M iodide was selected for further studies.

Optimal equilibration temperature and incubation time were necessary to complete the reaction and to achieve as sufficient as possible for easy phase separation and preconcentration of Al^{3+}. The effect of equilibration temperature on the extraction recovery of Al^{3+} was investigated in the range of 30-60°C. It was found that the extraction recovery increased with equilibration temperature from 45-55°C and stabilized up to 60°C. Thus 50°C was ensured to get maximum absorbance. Therefore, the temperature of 50°C was employed in continuing the experiment, keeping the equilibration temperature as 50°C and the influence of the incubation time on cloud point extraction was monitored in the range of 1.0–15 min thus the obtained result showed that the 5.0 min of incubation time was sufficient for the separation process. Also a 5.0 min centrifugation at 4000 rpm was found to be enough for successful cloud point extraction (CPE).

Regarding sensitivity, different solvents were tried to select the one producing the optimal results, Because the surfactant-rich phase was precipitated. Among methanol, ethanol, acetone, acetonitrile, and DMF, acetonitrile gave the optimum results due to high sensitivity and low overlapping of spectra of components. Therefore, acetonitrile was selected in order to have appropriate amount of sample for transferring and measurement of the absorbance and also a suitable preconcentration factor. Therefore, a preconcentration factor of 250 was archived using the proposed procedure.

Stoichiometric ratio

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of DDPODC to Al^{3+}, obtained by varying the DDPODC concentration, showed inflection at molar ratio 3.0, indicating presence of three DDPODC molecules in the formed complex. Moreover, the Job method showed a ratio of DDPODC to Al^{3+} = 3.0. Consequently, the results indicated that the stoichiometric ratio was (3:1) [DDPODC: Al^{3+}]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 4.64, whereas the true constant was 4.50.

For the ternary complex with PONPE 5.0, the obtained results implied that a 1:1 complex is formed between the [(DDPODC)3Al] complex and PONPE 5.0. Consequently, the results indicated that the stoichiometric ratio was 3:1:1 [(DDPODC)3Al][PONPE 5.0], as shown in the following equations. The conditional formation constant (log K), calculated using the Harvey and Manning equation applying the data obtained from the above two methods, was found to be 5.17, whereas the true constant was 5.05.

$$3\ DDPODC + Al^{3+} \rightleftharpoons [(DDPODC)_3Al]$$

$$[(DDPODC)_3Al] + PONPE\ 5.0 \rightleftharpoons [(DDPODC)_3Al][\ PONPE\ 5.0]$$

Selectivity

The effect of various cations and anions on 60 ng/mL Al^{3+} determinations by the proposed procedure was investigated. An ion was considered to be interference when it caused difference in absorbance greater than ± 5.0%. For the determination of 60 ng/mL Al^{3+}, the foreign ions can be tolerated at the levels

Table 1: Effect of foreign ions on the determination of 60 ng aluminium (III)

Ion	Added as	Tolerance ratio	Relative error[a](%)	Ion	Added as	Tolerance ratio	Relative error[a](%)
K(I)	KCl	1750	+1.33	Pb(II)	$PbCl_2$	120	1.10
Na(I)	NaCl	1650	+1.25	W(VI)	$(NH_4)_6W_7O_{24}$	120	–2.60
Li(I)	LiCl	1600	–1.65	Mo(VI)	$(NH_4)_6Mo_7O_{24}$	120	–2.85
Ca(II)	$CaCl_2$	1000	+1.75	Cd(II)	$CdCl_2$	120	+1.80
Mg(II)	$MgCl_2$	900	+1.75	Sn(II)	$SnCl_2$	120	–1.70
B(III)	H_3BO_3	800	+2.10	Pd(II)	$PdCl_2$	120	+1.30
Si(IV)	Na_2SiO_3	750	+1.60	In(III)	$In(NO_3)_3$	100	+1.80
Ti(IV)	$Ti(SO_4)_2$	500	–1.05	Cr(VI)	$K_2Cr_2O_7$	100	+1.90
P(V)	$(NH_4)_2HPO_4$	600	+1.90	Sb(III)	$SbCl_3$	100	–2.20
Tl(I)	$TlNO_3$	450	+1.90	Cr(III)	$K_2Cr_2(SO_4)_4$	100	+2.25
Mn(II)	$MnCl_2$	400	–2.75	Pt(IV)	H_2PtCl_6	80	+1.70
Ge(IV)	K2GeO3	350	+2.40	La(III)	$La(NO_3)_3$	75	–5.0
V(V)	NH_4VO_3	300	–1.60	Y(III)	Y(NO3)3	60	+1.90
				Ga(III)	$Ga(NO_3)_3$	55	–2.70
Be(II)	$BeCl^2$	250	+2.20	Co(II)	$CoCl_2$	50	+1.75
F_2	NaF	200	+1.75	UO_2(II)	$UO_2(NO_3)_2$	50	+2.50
Ni(II)[↑]	$NiCl_2$	180	+1.90	Rh(III)	$Rh(NO_3)_3$	50	+1.50
As(III)	$NaAsO_2$	150	–2.00	Th(IV)	$ThCl_4$	40	+1.70
As(V)	Na_2HAsO_4	145	+1.25	Cu(II)	$CuSO_4$	30	+2.45
Sc(III)	$Sc(NO_3)_3$	140	–8.80	Fe(II)	$(NH_4)_2Fe(SO_4)_2$	30	–2.80

[a] Above ± 5.0% in absorbance is considered to be not tolerated.

recorded in Table 1. DDPODC forms stable complexes with different metal ions, including transition metal ions. Most of the cations and anions tested do not interfere with the extraction and determination of Al^{3+}. These results demonstrate that excess amounts of some common cations and anions do not interfere on the determinations of the analyte, putting in evidence the adequate selectivity of the developed methodology. However, Fe3+ and Cu2+ can interfere with the determination of Al^{3+} even in a ratio 5/1. The foreign ions can be removed adding masking agents as ascorbic acid and 1,10-phenanthroline, that form strong hydrophilic complexes. The masking agent form highly stable water soluble charged complexes with interfering ions and prevent them from complexing with DDPODC, thus removing their interference.

Analytical characteristics

Table 2 summarizes the analytical characteristics of the optimized method, including regression equation, linear range and limit of detection, reproducibility, and preconcentration and improvement factor. The limit of detection, defined as CL =3SB/m (where CL, SB, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.77 ng/mL [50]. Because the amount of Al^{3+} in 100 mL of sample solution is measured after preconcentration in a final volume of 0.25 mL acetonitrile, the solution is concentrated by a factor of

Table 2: Analytical features of the proposed method

Parameters	without CPE	Using CPE
Amount of acetonitrile	--	0.25
pH	4.6	4.6
Optimum [DDPODC] M	1.6×10^{-4}	1.6×10^{-4}
Reaction time (min)	20	5.0
Stirring time (min)	10	5.0
Beer's range (ng/mL)	500 - 3850	2.5–125
Ringbom range (ng/mL)	1000 - 3600	5.0 –110
Molar absorptivity (L/mol cm)	2.28×10^4	1.86×10^5
Sandell sensitivity (ng/cm^2)	45.9	0.0014
Regression equation		
Slope (µg/mL)	0.021	6.9
Intercept	- 0.012	0.04
Correlation coefficient (*r*)	0.9980	0.9990
RSD [a] (%)	3.10	1.67
Detection limits (ng/mL)	160	0.77
Quantification limits (ng/mL)	490	2.45
enhancement factor	--	400
Improvement factor	--	317

400. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the calibration graph in micellar media without preconcentration, was 317.

The relative standard deviation (RSD) and relative error for six replicate measurements of 60 ng/mL of Al^{3+} was 1.67% and 1.81% and for 100 ng/mL of platinum was 1.99% and 2.14%, respectively.

The proposed method characteristics have been compared with those of other methods. Table 2 compares analytical quality parameters of the proposed method with those reported previously for Al^{3+} determination. It was shown that the proposed method is comparable in detection limit to the previous studies for Al^{3+} determination. Therefore, CPE combined with spectrophotometric detection is a very simple and sensitive method for the preconcentration and determination of Al^{3+}.

Analytical applications

Aiming to demonstrate the usefulness of the proposed system a set of samples comprising several natural water samples was analyzed. The system was run using the optimized parameters summarized in Table 3. The results of sample are shown in Table 4. Accuracy was assessed by comparing results with these obtained using FAAS. Applying the paired t-test and F-value no significant difference at 95% confidence level was observed [51].

To test the reliability of the proposed procedure, the proposed method was employed to determine the trace amounts of Al^{3+} in different real samples containing water (i.e., tap, well, pond, river Nile, and sea water samples), and biological (i.e., blood, urine and human gallstone) samples. 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 and 5 shows the obtained results. As can be seen, recoveries between 92.7% and 101.5% were obtained, which confirm the accuracy of the proposed method.

Table 3: Comparison of the published methods employing CPE with the proposed method.

Surfactants	Detection	Comments	Ref.
Triton X-114	GFAAS	LOD = 0.09 µg/L, RSD=4.7% r^2 = 0.9981 Samples: biological and water	[34]
PONPE 7.5	ICP-OES	LOD = 0.25 µg/L r^2 = 0.9997 Samples: parenteral solutions	[27]
Triton X-114	GFAAS	LOD = 0.06 µg/L RSD = 3.6% Samples: human albumin	[35]
Tween-20	Spectrofluorimetry	LOD = 3 µg/L, RSD = 2.9% r^2 = 0.986 Samples: natural water	[32]
CTAB and Triton X-114	Spectrophotometry	LOD = 0.52 µg/L Linearity =3–100 µg/L Samples: water	[28]
Triton X-114	Spectrofluorimetry	LOD = 0.79 µg/L r^2 = 0.998 Samples: water, and food	[31]
CTAB, NaC and PONPE 5.0	Spectrofluorimetry	LOD = 0.281 µg/L LOQ = 0.853 µg L^{-1} Samples: water, serum, plasma and urine	[52]
DDPODC, KI, and PONPE 5	Spectrophotometry	LOD = 0.77 ng/L LOQ = 2.45 µg/L r^2 = 0.9992 Linearity: 2.5–125 ng/L Samples: food, biological and water samples	This work

Table 4: Determination of Al (III) in some water samples

Water sample	Added ng mL^{-1}	Al(III) "Spiked" Found[a] (ng/mL)	Al(III) "unspiked" Found[a] (ng/mL)				
		This work	FAAS	This work	FAAS	t-test[b]	F-value[b]
Tap water	70.0	79.7	79.5	9.8	9.4	1.78	3.22
	100	99.6	99.5				
Well water	50.0	75.5	76.0	25.4	26.2	1.76	3.23
	90.0	116.0	116.4				
Pond water (Helwan)	80.0	85.0	84.8	5.1	4.5	1.48	2.67
	100.0	105.5	105.2				
River Nile water							
1- Benha (upper stream)	40.0	75.5	76.0	35.5	35.9	1.66	3.13
	80.0	116.0	115.8				
2- Shoubra El-Keema (upper stream)	20.0	88.0	89.0	67.9	69.2	1.42	2.78
	40.0	107.5	108.6				
Sea water							
1- Alexandria[c] (Upper)	25.0	62.6	62.7	37.6	37.9	1.84	3.41
	50.0	86.5	87.0				
2- Safagac (Upper)	10.0	93.4	93.0	83.5	83.2	1.39	2.54
	20.0	103.2	102.9				
3- Al-Ghardaa[d] (Upper)	15.0	101.5	110.5	86.5	85.5	1.72	3.29
	30.0	115.5	116.0				

a Values given represent the average of six analysis of each sample.
b Theoretical t- and F- values for five degrees of freedom and 95% confidence level were 2.57 and 5.05, respectively.
c From Mediterranean sea.
d From Red sea.

Table 5: Concentration level (ng/mL or mg/g) of Al^{3+} in biological samples under pathological conditions.

Name of sample	Source disease	CRM	Concentration of Al^{3+} found[a]			
			FAAS	This work	t- value[b]	F- test[b]
a- Blood	Normal adult	75.0	78.7	77.9	1.45	3.23
b- Urine	Normal adult	45.0	45.5	46.0	1.51	3.48
a- Blood	Cancer (leukemia)	250	27`	270	1.40	3.16
b- Urine	Cancer (leukemia)	100	111	110	1.63	3.65
a- Blood	Cancer (lung)	300	305	295	1.73	3.72
b- Urine	Cancer (lung)	110	106.5	108	1.52	3.55
Human gallstone	Normal adult	35.0	38.9	38.5	1.60	3.74

CRM: Certified reference material.
[a] Average of six determinations.
[b] Theoretical t- and F- values for five degrees of freedom and 95% confidence level were 2.57 and 5.05, respectively.

Additionally, the accuracy of the proposed methodology was evaluated by analyzing 22 samples of food as recorded in Table 6. The concentration ranges (in mg/kg) are: 43-132 for rice and rice products; 306 for lentils; 77-418 for wheat products; 188-429 for spices and 49, 226, 306 and 725 for one each of corn powder, glucose, Lentils and tea powders, respectively. The concentration of aluminium is very high in tea sample whereas other concentrations are in the mean range of 49-418 mg/kg. The aluminium concentrations reported, in the present work, are found to be similar or slightly higher than reported elsewhere in literature, which may be due to the analysis of market samples as received [4,10,11]. Efforts are being made to collect different varieties of rice from field along with soil samples for further study. The data on Al will be of help to calculate Al intake by local people by calculating daily dietary intake (DDI) from selected food items or from total diet.

Table 6: Determined Aluminium concentrations in different food and soil samples

Food sample	Code	Name of sample	Conc. in Mg/kg
Rice and its Products	R1	Rice 1	114 ± 5.5
	R2	Rice 2	86 ± 3.5
	R3	Rice 3	82 ± 3.5
	R4	Rice 4	132 ± 3.5
	R4	White beaten rice	43 ± 2.5
Lentils	L3	Red lentil	306 ± 8.5
peas	L5	Yellow split peas	163 ± 5.5
	L6	Yellow pigeon peas	91 ± 4.2
Maize	L7	Maize 1	68 ± 2.3
	L8	Maize 2	168 ± 7.0
	L9	Maize 3	75 ± 1.6
Wheat products	WP1	Roasted vermicelli	418 ± 13
	WP2	Semolina	146 ± 6.0
	WP3	Refined wheat flour	77 ± 4.0
	WP4	Refined wheat flour	106 ± 7.0
Spices	S1	Cumin	429 ± 11
	S2	Turmeric	367 ± 19
	S3	Mustard	316 ± 15
	S4	Cinnamon	188 ± 7.0
Glucose	G1	Glucose powder	226 ± 11
Corn	C1	Corn powder	49 ± 2.0
Tea	T1	Tea powder	725 ± 21
Soil		(Benha)	92 ± 5.5
Soil		(Moshtohor)	105 ± 7.0
Soil		(Shoubra)	117 ± 9.0
Soil		(Touqh)	97 ± 5.0
Soil		(Khaha)	108 ± 6.0

The proposed method was successfully applied to the determination of Al^{3+} ion in soil samples. The average values of Al^{3+} in five different surface soil samples collected from Benha, Moshtohor, Shoubra, Touqh and Khaha was found to be 92 and 117 ng/g, respectively. The recoveries are close to 100% and indicate the proposed method was helpful for the determination of Al^{3+} in the real samples. The method is very reliable, and the concentration can be measured in a very simple and rapid way for routine analysis of Al^{3+}.

Conclusion

The proposed procedure gives a simple, very sensitive and low-cost spectrophotometric procedure for determination of Al^{3+} ion that can be applied to real samples. The surfactant has been used for preconcentration of Al^{3+} in water, and thus toxic solvent extraction, has been avoided. A comparison between the proposed methods with the previously reported methods using different instrumental techniques indicates that this method has a higher sensitivity and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of Al^{3+} to real samples.

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