



Utilization of Ionic Liquid Cold-Induced Aggregation Micro Extraction Technique for Preconcentration and Determination of Aluminum in Food, Water, and Biological Sample

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Abstract

Cold induced aggregation micro extraction technique combination with spectrophotometry was used to preconcentrate and detect aluminum in biological and environmental samples. The procedure is depending on Al (III) complexation with 2-amino-4-(m-tolyazo) pyridine-3-ol (ATAP), and entrapped in non-ionic surfactant octylphenoxy polyethoxy ethanol (Triton X-114). In the present method, sodium hexafluorophosphate (NaPF₆) was brought to the sample solution having smallest levels of 1-hexyl-3-methylimidazolium hexafluoro-phosphate [Hmim] [PF₆] as extraction solvent. The preconcentration and extraction efficiency were influenced and optimized by factors as pH, amount of ionic liquid, ionic strength, and temperature. Under the optimum experimental conditions, the calibration graph was linear in the range 3.0–230 ng mL⁻¹ with correlation coefficient (r²) of 0.9992. The molar absorptivity and Sandell sensitivity are evaluated to be 1.15x10⁵ L mol⁻¹ cm⁻¹ and 0.024 ng cm⁻², respectively. For 150 ng mL⁻¹ (n= 10) aluminum, the relative standard deviation (RSD) was 1.79%. The enhancement factor of 500 was achieved, whereas, the detection and quantification limits were reported to be 0.87 and 2.98 ng mL⁻¹, respectively. The applicability was evaluated to determine ultra-trace amount of Al (III) in various types of biological, environmental water, soil, and food samples.

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Introduction

Throughout the environment, aluminum is a nontoxic element and essential metal, which is widespread throughout the environment. Some studies suggest that aluminum accumulated in the brain through various routes (drinking waters, food, and medicines) and tolerated with the normal activities of nervous system. For human health, aluminum causes problems due to it was considered as a possible cause of renal osteodystrophy, Parkinson and Alzheimer's diseases [1]. Therefore de-

tection of ultra-trace amounts of Al³⁺ in food, biological and environmental samples is essentially importance.

Different instrumentation have been reported to determine aluminum at trace amounts. These include Flame Atomic Absorption Spectrometry (FAAS) [2], Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [3], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [4,5], Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [6] and

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spectrophotometry [7-10]. ICP-MS and ICP-AES are expensive instruments with high costs of operation [11].

Spectrophotometric procedures are facile, rapid and low cost that have been widely used to determine metal ions which could form a color complex with chromogenic reagents [12-26]. However, the sensitivity is very small to detect low amounts of aluminum and a preconcentration step is needed. Various procedures to separate and preconcentrate of aluminum with extraction methods is recommended, e.g., liquid-liquid extraction [27], cloud point extraction [28] liquid-liquid microextraction [29] and solid phase extraction [30,31]. Over other preconcentration procedure, solid phase extraction has several advantages including simplicity, rapidity, low cost of reagents, and high preconcentration factor [32]. Various solid phase extractants as naphthalene [33], titanium dioxide nanomaterial [34] and modified Tiron resin [30], have been applied to preconcentrate and determine ultra- trace levels of aluminum.

A good negligible vapor pressure and selective solubility with Room Temperature Ionic Liquids (RTILs) have become important for their promising role as alternative solvents in synthesis, separation and electrochemistry [32-34]. They are used to be green solvents because their very wide liquid phase range, good dissolving and extracting abilities thermal stability, and negligible vapor pressure [35-37]. They have been used with success instead of solvents to separate organic and biologically important compounds [38,39] and metal ions [40,41]. Many efforts was used via extraction with an ionic liquid, as ionic liquid-based headspace liquid phase microextraction [42], ionic liquid-based single-drop microextraction [43,44], and temperature-controlled ionic liquid dispersive liquid phase microextraction [36,45]. These methods have advantages of high enrichment factors in addition to little consumption of volatile organic solvents and. Another useful procedure which is termed cold-induced aggregation microextraction (CIAME) and is depended on applying of ILs for homogeneous liquid-liquid micro-extraction (HLLME), was performed [37] and modified further [46-48]. The mechanism of the procedure is likely to DLLME, whereas, the dispersal is accomplished by temperature-dependent dissolution instead of injection. Optimum temperature is applied to fully dissolve the RTIL in the sample solution without applying disperser solvent [49].

In comparison using CIAME, IL-based DLLME is more efficient and suitable for dispersing the RTILs throughout the sample, thus significantly reducing the extraction time and increasing the recovery. To the best of our knowledge, there is no previous literature survey on the Cold-Induced CIAME applied to preconcentrate Al (III) ions in real samples. In this article, the CIAME technique coupled with spectrophotometry was used for reasonably selective and sensitive Al (III) determination in biological, and environmental samples. The effects of different experimental conditions on the extraction and preconcentration were also illustrated.

Experimental

Apparatus

A water bath with a centrifuge with 10-mL calibrated centrifuge tubes and good temperature control (Superior, Germany) was supplied to increase the process of the phase separation. Tabletop Low Speed Large Capacity Centrifuge model L-550 was applied. An Orion research model 601 A/digital ionalyzer pH meter was used for examining the pH of the media. All ICP-AES

measurements was reported by a Perkin Elmer model 5300 DV; ICP-AES (Waltham, MA, USA). Absorbance spectra was recommended applying a Perkin-Elmer Lambda 12 UV/Vis spectrometer with 1.0-mm quartz cell.

Reagents and solutions

Deionized water was introduced for preparation of the sample solutions, whereas, all reagents and chemical were of analytical-reagent grade. A 1000 $\mu\text{g mL}^{-1}$ stock solution of Al (III) was prepared by dissolving 1.38 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) in 5.0 mL of 5.0 M HNO_3 and diluted to 100 mL in a measuring flask, and then standardized with EDTA titration. By appropriate dilution of stock solution, working solutions were prepared daily.

Triton X-114 (octylphenoxy polyethoxyethanol) and sodium hexafluoro-phosphate (NaPF_6) were highly purified reagents produced in Merck Co. (Darmstadt, Germany). 1-Hexyl-3-methylimidazolium hexafluorophosphate (CAS 304680-35-1) [Hmim] $[\text{PF}_6]$ ionic liquid was produced and achieved from Sigma-Aldrich (USA). Deionized water (1-10 $\text{M}\Omega\text{ cm}$) achieved from a Labconco system (Labconco Co., Kansas City, USA) was applied throughout all studies. A solution of 100 mg mL^{-1} NaPF_6 was prepared by dissolving appropriate amount of NaPF_6 in water. The handling of IL was difficult and their viscosity was high, so working solution ($[\text{Hmim}][\text{PF}_6]$, 0.8 mg L^{-1}) was prepared in acetone. The vessels were kept in 10% HNO_3 for about one day and subsequently washed with water.

2-Amino-4-(m-tolyazo) pyridine-3-ol (ATAP) was prepared using conventional diazotization and coupling methods [43]. A solution of 2.0×10^{-3} M of ATAP was prepared by dissolving an appropriate amount of the reagent in ethanol. A buffer solution (0.1 M) was prepared by dissolving the appropriate weights of sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) (Merck) in water and adjusted to pH 6.0 by adding dilute HNO_3 solutions.

General procedure

Standard or sample solution containing Al (III) in a volume of 40 mL, adjusted to pH 6.0 using phosphate buffer, was moved to a 50 mL conical-bottom glass centrifuge tube. Then, 100 μL 0.4 % m/v NaNO_3 , 2.5 mL of a mixture (2.0×10^{-3} M of ATAP, 0.06% v/v Triton X-114, 45 mg of IL ($[\text{Hmim}][\text{PF}_6]$) as extraction solvent) and 50 μL of the solution containing NaPF_6 applying a Hamilton syringe were fastly injected into the above aqueous sample solution. It was kept in a thermostatic bath at 50°C for 5.0 min, after shaking. In an ice bath, the tube was then cooled for 5.0 min and a cloudy solution was formed. The cloudy solution was subsequently centrifuged for 5.0 min at a centrifugation rate of 4000 rpm. The fine droplets of IL settled at the bottom of the tube was observed. With a microsyringe, the upper aqueous phase was removed, and the IL phase was dissolved in 100 μL of ethanol and moved to quartz microcell. The absorbance of the formed complex was measured at λ_{max} 642 nm.

Optimization of the CIAME sample preparation method

In the present article, to achieve higher selectivity, sensitivity and precision of aluminum detection, the CIAME procedure coupled with spectrophotometer technique was optimized, after selecting the λ_{max} of aluminum complex. The influence of various factors (as the concentration of ionic liquid, sample ionic strength, pH, chelating agent concentration, and time of extraction), was established and optimized.

The precision of the procedure was reported after calculation and as the RSD of 10 independent measurements, carried out for $150 \mu\text{g L}^{-1}$ Al (III). To detect the Linear Dynamic Range (LDR) of the procedure, eight sample solutions of Al (III) with different amounts were extracted under the optimized experimental conditions. The IL phase was dissolved in $100 \mu\text{L}$ of ethanol, after extraction, and absorbance was recorded at λ_{max} of the complex formed. The enhancement factor (EF) is reported as the ratio of the slope of preconcentrated samples using CIAME to that achieved without preconcentration. The detection limit is evaluated as $3S_b/m$ (where S_b is standard deviation of the blank and m is the slope of the calibration graph).

Optimum conditions

A solution of (40 mL, $0.15 \mu\text{g mL}^{-1}$ of Al (III), pH 6.0) was examined for extraction with ATAP in ethanol (2.0 mL, 2.0×10^{-3} M), to achieve the λ_{max} of the Al (III) formed complex. Absorption spectra corresponding to the complex in ethanol in the wavelength between 350-750nm were investigated.

Among sample acidity, which was detected by the pH of the sample solution, chemical variables, played an important role in the overall performance of the solvent extraction and influenced the extraction efficiency and complex formation. The effect of pH on the absorbance was reported in pH's of 2.0-12 by adjusting it in Al (III) solution with phosphate buffer media. In addition, the effect of ATAP level on the extraction in the range of 10^{-3} – 10^{-5} M was illustrated.

The effect of extraction ([Hmim] [PF₆]) amount, solutions containing various amounts of [Hmim] [PF₆] were examined. The experimental conditions were included and fixed the various amounts of [Hmim][PF₆] in the range of 20-100 mg. In addition, to illustrate the effect of common ion, similar experiments were made in their presents. A common ion is any ion presented in the solution that is common to the ionic liquid being dissolved. In this investigation, NaPF₆ was applied as a common ion source and the effect of this agent on the analytical responses was established.

The influence of Triton X-114, as an anti-sticking agent, was recommended in order to overcome the adherence of the IL-phase on the wall of the centrifuge tube in the range of 0.00–0.10% (v/v). The influence of the ionic strength on the CIAME performance was investigated. Many experiments were made with different amounts of NaCl. Due to high solubility of NaNO₃, salt effect was investigated till 30% (m/v).

Temperature affects the solubility of ILs in water and the partition coefficient of analytes. The solubility of ILs in water also increases, as the temperature increases. So, the chosen of optimum extraction temperature is important factor. To illustrate, aluminum samples in water bath with various temperature (20-75°C) were extracted while other conditions were kept constant. Centrifugation is an important step to achieve two distinguishable phases in the extraction tubes. The effect of time of the centrifugation on the extraction efficiency was recorded in the range of 5000-4750 rpm.

Determination of aluminum in biological samples

Human blood (2.0–5.0 mL) and urine (20-30 mL) human gallstone (0.1-0.5 g) was gathered in polyethane bottles from the affected persons. Once after gathering, they were stored in a salt-ice mixture and kept at -20°C . The samples were moved

to a 100 mL micro-Kjeldahl flask. Glass bead and 10 mL of concentrated HNO₃ were transferred and the flask was put on the digester under gentle heating. The solution was removed and cooled following a method reported [50]. When the initial brisk reaction was over. A 1.0 mL volume of concentrated H₂SO₄ was supplemented carefully, followed by 2.0 mL of concentrated HF, and heating was continued for at least 0.5 hr and then cooled. The content was then neutralized with diluted NH₄OH solution. The resultant solution was then transferred quantitatively into a 10 mL measuring flask and made up to the mark with water.

Aliquot (1.0-2.0 mL) of the final solution was pipetted into a 10 mL measuring flask and the aluminum content was detected as described above employing 1,10 phenanthroline as masking agent. The results of biological analyses were in a good agreement with those applying ICP-AES.

Determination of aluminum in environmental water sample

Evaporated nearly to dryness, each filtered environment water sample (500 mL) [through a Whatman no. 40 filter paper] with a mixture of 1.5 mL HCl and 5.0 mL concentrated HNO₃ in a fume cupboard, then a method recommended [51] was followed and heated with 10 mL of water to dissolve the salts. The solution was cooled and neutralized with dilute NH₄OH. It was carried into 50 mL measuring flask and diluted up to the mark with water. A 1.0 mL of the final solution was pipetted into a 10 mL measuring flask and the Al content was defined as described in general above procedure, employing 1,10 phenanthroline as a masking agent.

Determination of aluminum in soil samples

An accurately weighed amount (100 g) of air-dried soil sample was taken and placed in a 100 mL micro-kjeldahl flask. The sample was digested as the method recommended [52]. The contents of the flask were filtered via a Whatman no. 40 filter paper into 25 mL measuring flask neutralized with dilute NH₄OH and diluted to the volume with water. Aliquots (1.0-2.0 mL) were brought to a 10 mL measuring flask and the evaluated amount of 5×10^{-4} M H₂SO₄ required to give a final acidity, followed by 1.0 mL of 1,10 phenanthroline (0.1%) solution. Al content was then detected as mentioned in the above procedure.

Food sample preparation

A 10 g of rice flour, wheat flour, tomato, onion, cabbage, squash and potato samples were first carbonized each, and then burned in the furnace at 700°C for 3-4 h. After each residue was cooled to $25 \pm 2^\circ\text{C}$, it was extracted by heating in 1.0 mL of 6.0 M HCl, filtered into a 100 mL measuring flask [33]. This solution was treated under the above general procedure. Six replicate measurements were performed for each sample. The recovery tests were also performed by taking known concentrations of aluminum solution to the samples. The percent recovery was calculated from the added and found values.

Results and discussion

Spectrophotometric study

The complex formed represented highly absorbance at λ_{max} 642 nm while further experiments showed that ATAP did not have any absorption band at this wavelength in ethanol, so this wavelength was selected for the subsequent experiments.

Optimization of the system

The extraction efficiency of Al (III) achieves a maximum in the pH ranges of 5.5-6.5. At pH < 4.5, a decrease in metal extraction recovery is due to the low formation of the complex. At pH more than 8.0, the analyte is mainly present as hydroxide species, which do not form complex with the ATAP. Thus, a buffer media of pH 6.0 was optimal for all subsequent experiments. The recovery of metal extraction as a function of the ATAP level is represented in Figure 1. The results represented that the extraction efficiency increased by increasing ATAP up to 8×10^{-5} M and remained nearly constant at higher concentrations. Therefore, this concentration was selected as the best for all subsequent investigations.

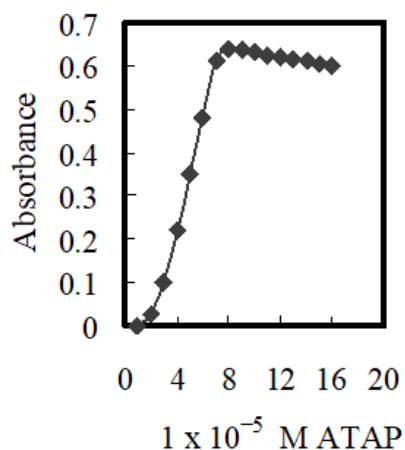


Figure 1: Effect of 1×10^{-5} M ATAP on complexation of 150 ng mL^{-1} Al (III).

Figure 2 records the effect of ionic liquid level in the presence and absence of NaPF_6 as a common ion source. As represented, in the absence of NaPF_6 , minimum level of ionic liquid applied to achieve maximum absorbance was 80 mg. In the presence of constant NaPF_6 (50 μL), this level reduced to 45 mg. Naturally, the solubility of the ionic liquid increases, in the presence of excess concentration of salt. According to common ion effect, solubility decreases in the presence of IL with common ion and lower level of ionic liquid is consumed. So, 45 mg of IL and 50 μL of NaPF_6 were selected for the next steps.

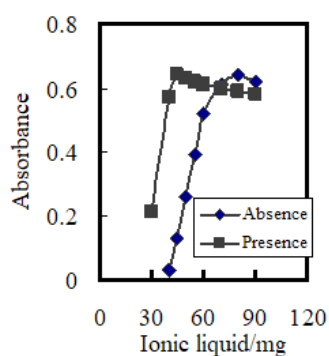


Figure 2: Effect of 1×10^{-5} M ATAP on complexation of 150 ng mL^{-1} Al (III).

The absorbance increased up to 0.06% (v/v), in the presence of Triton X-100, as represented in (Figure 3), and then remains approximately constant. Hence, 0.06% (v/v) was chosen for the rest of the investigation.

In the presence of high medium salt content, the solubility of ILs increases and the phase separation does not occur. But

according to the common ion influence, solubility decreases in the presence of NaPF_6 . NaNO_3 was selected to illustrate the salt influence. The successfully occurred phase separation was recorded in the presence of NaPF_6 . As a result of salting out influence, Absorbance was increased slightly. A concentration of 0.4 % NaNO_3 was selected for all subsequent experiments to increase the recovery.

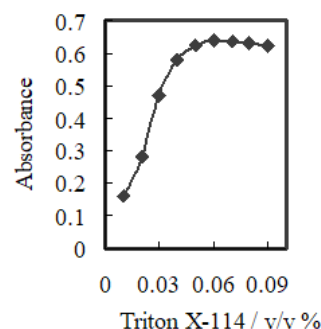


Figure 3: Effect of Triton X-114 on the complexation of 150 ng mL^{-1} Al (III) at the optimum conditions.

The experimental data defined (Figure 4) that in the temperature of 20-45°C the absorbance increased due to increasing of analyte partition coefficient, whereas, at temperatures higher than 55 °C, absorbance slightly decreased due to ionic liquid solubility. In the range of 45-55°C, absorbance was stable, and constant. Therefore, a temperature of 50°C was selected for the rest of the work.

It was recorded that over 3750 rpm, IL-phase completely settled, so the rate of 4000 rpm was represented as the best point. At the best rate, the absorbance was illustrated as a function of time of centrifugation. The maximum absorption band was achieved after 5.0 min, and no significant variation was indicated when the time exceeded 5.0 min. Therefore, a 5.0 min was chosen as best centrifugation time for all subsequent studies.

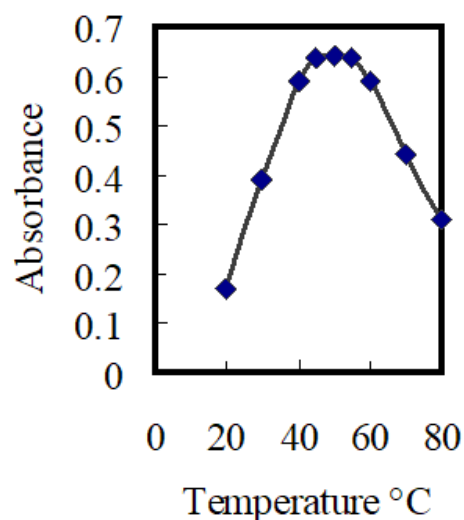


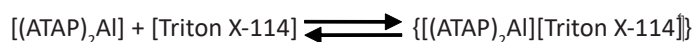
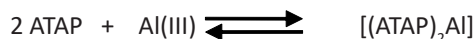
Figure 4: Effect of temperature on the absorbance of the complex of 150 ng mL^{-1} Al (III) under optimum conditions.

Stoichiometric ratio

The nature of the complex was illustrated at the optimum conditions reported above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of ATAP to Al (III), achieved by varying the ATAP concentration, represented inflection at molar ratio 2.0, defining presence of two ATAP molecules in the complex formed. Moreover,

the Job method indicated a ratio of DMPAHPD to Al (III) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2:1) [ATAP:Al]. The conditional formation constant (log K), evaluated applying Harvey and Manning equation using the data achieved from the above methods, was found to be 5.87, whereas the true constant was 6.02.

For ternary complexes of Al-ATAP-Triton X-114, the stoichiometric ratio as achieved from molar ratio represented the formation of 1:1 for [(ATAP)₂Al] : [Triton X-114]; therefore, the conjectured ternary complex [(ATAP)₂Al] [Triton X-114] is formed in the system. The suggested structure of which is probably as represented follows:



Interferences

After choosing the optimum experimental conditions, influence of common coexisting ions on the recovery of aluminum were illustrated by spiking appropriate level of the relative ions to solutions containing 150 ng mL⁻¹ Al (III), treated according to the above procedure. More than 50 cations, anions and complexing agents were reported individually to study their influence on the detection of 150 ng mL⁻¹. The criterion for interference was an absorbance value varying by $\pm 5.0\%$ from the expected value for Al alone [53]. There was no interference from the following: 12000-fold levels of nitrate, chloride, thiocyanide, phosphate, azide, ammonium, alkali metals or acetate; 10000-fold levels of bromide or iodide. 8000-fold levels of arsenic (III&V) cerium (IV), magnesium (II), barium (II), sulfide, tin (II and IV), silver (I), cadmium (II), manganese (II), bismuth, chromium (VI), calcium (II), mercury (II), tungsten (VI), lead (II), 1,10-phenanthroline, ascorbic acid, sulphate, dimethylglyoxime (DMG), strontium (II), selenium (IV&VI), arsenic (III), uranium (VI). 5000 fold level of tellurium, oxine and cyanide, molybdenum (VI), 3500-fold level of EDTA, fluoride, tartrate. 1, 10-phenanthroline prevented the interference from a 300-fold levels of iron (II&III), zinc (II), nickel (II), copper (II), cobalt (II &III). 100-fold EDTA prevented the interference from a 120-fold amount of Vanadium (V). During the interference investigations, if a precipitate was formed, it was removed by centrifugation. The amount mentioned is not the tolerance limit but the actual level studied. However, for those ions whose tolerance limit has been investigated, their tolerance ratios are mentioned in (Table 1). The tolerance ratio was evaluated by X /Al i.e. fold level of foreign ion / fold level of Al.

Analytical performance

The performance of the procedure was defined under the best experimental conditions (Table 2). Excellent linearity was obtained over the concentration range of 3.0-230 ng mL⁻¹ for Al(III) with favorable coefficient of correlation (r^2) 0.9992. Enrichment factor of aluminum was as high as 500. The repeatability studies were carried out by extracting spiked water samples at 150 ng mL⁻¹ Al (III), and RSD was 1.79% (n = 10). The detection limit (LOD) [54], depended on 3σ of standard deviation of absorbance of blank, was 0.87 ng mL⁻¹. These results confirmed that the procedure is sensitive, stable, and facilitate the analysis of aluminum at ultra-trace levels. The improvement factor, detected as the ratio of the slope of the calibration graph for the CIAME procedure to that of the calibration graph in micellar

media without CIAME, was 850.

The proposed method characteristics have been compared with those of other methods. Table 3 compares analytical quality parameters of the proposed method with those reported previously for Al (III) determination [55-59].

It was represented that the proposed method is comparable in limit of detection to the reported works. Therefore, CIAME combined with spectral study is a very simple and sensitive procedure for the preconcentration and detection of Al (III).

Taking into account that all samples were simultaneously processed, the frequency of analysis was six samples per hour approximately, being the total sampling time controlled using step heating [60].

The analytical characteristics of proposed method to detect Al³⁺ was compared with previously reported preconcentration methods of Al³⁺ in various matrixes (Table 4). The enhancement factor achieved in this work are comparable with literature reported [61-65]. The recommended data illustrated that the various analytical parameters, detection limit and enhancement factors are superior to those of instrumental techniques. The evaluated detection limit was sufficiently low as to be valuable for determining Al³⁺ in various samples.

Analytical applications

There have been no reports demonstrating the viability of performing a CIAME technique for aluminum extraction from non-invasive biological samples as urine, blood and human gallstone. Therefore, the obtained results after urine, blood and human gallstone analysis are illustrated in Table 5. The proposed procedure was applied to six portions of urine, blood and human gallstone matrices and the average levels of Al (III) were taken as base values. A 10-160 ng mL⁻¹ Al (III) was then, added to samples and the same method was followed. The recoveries for the addition of Al (III) to all samples were in the range of 98.82-101.63%. The results obtained with the proposed method were in good agreement with those reported previously applying ICP-AES, while Al (III) recoveries were highly satisfactory for all cases.

The performance of the reported method was assessed by evaluation of the t- value (for accuracy) and F- test (for precision) compared with ICP-AES ones. The mean values were achieved at 95% confidence limits for five degrees of freedom [66]. The results represented that the reported values did not exceed the theoretical values. A wider range of detection, higher accuracy, more stability and less time consuming, indicates the advantage of the reported method over other ones.

The reported method has been used to determine Al (III) in waters (tap, well, river and bottled mineral) samples using the standard addition procedure. The mean value (six determinations) of the Al(III) evaluated in the analysis for 50 mL sample system (taking into account the dilution factor) was 54.5 \pm 0.011 ng mL⁻¹ for tap water, 6.20 \pm 0.008 ng mL⁻¹ for mineral water, 36.0 \pm 0.07 ng mL⁻¹ for well water and 21.0 \pm 0.014 ng mL⁻¹ for river water samples. The performance of the reported method was assessed by evaluation of the t- value (for accuracy) and F- test (for precision) compared with ICP-AES method. The mean values were achieved in a Student's t- and F- tests at 95% confidence limits for five degrees of freedom [66]. The results represented that the calculated values (Table 6) did not exceed the theoretical once. Reasonable agreement between the proposed and ICP-AES methods was evaluated.

The proposed procedure was used to determine Al (III) in environmental samples; soil, and food samples. These samples were treated to preconcentration and Al (III) determination using the reported method. The results are given in (Table 7). The percentage recovery was evaluated by using the equation: $R = \{100(C_m - C_0)/m\}$, where C_m is a value of metal in a spiked sample, C_0 is a value of metal in a sample and m is the amount of metal spiked. The calculated recoveries were reasonable for ultra-trace Al (III) analysis in soil, and food matrices, in a range of 98.36-101.47 %. These results confirm the validity of the proposed procedure. A wider range of determination, higher accuracy, more stability and less time consuming, represents the advantage of the proposed procedure over other methods. Also, there is no need for extraction or heating in the reported method.

Table 1: Table of tolerance limits of foreign ions.

Species x	Tolerance ratio [Species (x)/Al (w/w)]	Species x	Tolerance ratio [Species (x)/Al (w/w)]
Acetate	12000	Lead(II)	8000
Iron(II)	5000 ^{d,e}	Magnesium(II)	8000
Ammonium(I)	12000	Manganese(II)	8000
Arsenic(III)	8000	Mercury(II)	8000
Arsenic(V), (VI)	8000	Molybdenum	5000 ^b
Azide	12000	Nitrate	12000
Ascorbic acid	8000	Nickel(II)	3500 ^c
Barium	8000	Phosphate	12000
Beryllium(II)	8000	Potassium	10000
Bromide	10000	Selenium(IV)	8000
Calcium(II)	8000	Silver	8000
Cadmium(II)	8000	Selenium(VI)	8000
Cesium(II)	8000	Sodium	12000
Chromium (III)	8000	Tartrate	3500
Chloride	12000	Strontium	8000
Copper (II)	3500 ^{d,f}	Thiocyanate	12000
Chromium(VI)	8000	Tellurium	5000
Cyanide	5000	Tin (II and IV)	8000 ^a
EDTA	3500	Tungsten(VI)	8000
Fluoride	3500	Vanadium(V)	3500 ^b
Iodide	10000	Zinc(II)	3500 ^d

^aTolerance limit was defined as ratio that causes ± 5.0 % interference with 10 mg L⁻¹ EDTA

^bwith 10 mg L⁻¹ DMG (dimethylglyoxime)

^cwith 10 mg L⁻¹ 1,10-phenantroline

^dwith 10 mg L⁻¹ SCN

^ewith 10 mg L⁻¹ Oxine

Table 2: Analytical features of the proposed method.

Parameters	CIAME method	Without CIAME
Amount of ethanol, μ L	100	---
pH	6.0	6.0
Optimum [ATAP]	8×10^{-5}	8×10^{-3}
Reaction time (min)	5.0	5.0
Stirring time (min)	5.0	----
Beer's range (ng mL ⁻¹)	3.0 – 230	9000 – 50000
Ringbom range (ng mL ⁻¹)	15 – 215	1500 – 46000
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	1.15×10^5	1.35×10^3
Sandell sensitivity (ng cm ⁻²)	0.024	2000
Intercept		
Slope (ng mL ⁻¹)	4.27	0.005
intercept	- 0.008	+ 0.02
Correlation coefficient (r)	0.9992	0.9850
RSD ^a (%)	1.79	3.85
Detection limits (ng mL ⁻¹)	0.87	2850
Quantification limits (ng mL ⁻¹)	2.98	8800
Enrichment factor	500	
Improvement factor	850	

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

Surfactants	Detection	Comments	Ref.
Triton X-114	GFAAS	LOD = 0.09 ng mL ⁻¹ RSD = 4.7% $r^2 = 0.9981$ Samples: biological fluids and water samples	[1]
Triton X-114	GFAAS	LOD = 0.06 ng mL ⁻¹ RSD = 3.6% Samples: human albumin	[49]
PONPE 7.5	ICP-OES	LOD = 0.25 ng mL ⁻¹ $r^2 = 0.9997$ Samples: parenteral solutions	[56]
Triton X-114	Spectrofluorimetry	LOD = 0.79 ng mL ⁻¹ $r^2 = 0.998$ Samples: tap water, mineral water and food samples	[57]
Tween-20	Spectrofluorimetry	LOD = 3 ng mL ⁻¹ RSD = 2.9% $r^2 = 0.986$ Samples: natural water	[58]
CTAB, NaC and PONPE 5.0	Spectrofluorimetry	LOD = 0.281 ng mL ⁻¹ LOQ = 0.853 ng mL ⁻¹ Samples: tap and beverage water, serum, plasma and urine	[59]
CTAB and Triton X-114	Spectrophotometry	LOD = 0.52 ng mL ⁻¹ Linearity = 3–100 ng mL ⁻¹ Samples: water	[18]
CIAME and Triton X-114	Spectrophotometry	LOD = 0.87 ng mL ⁻¹ LOQ = 2.98 ng mL ⁻¹ Samples: Food, water and biological samples	This work

Table 4: Comparative data of analytical characteristics of the proposed with previous reported preconcentration techniques.

Method	Reagent	Surfactant/solvent	Technique	Sample	EF ^a	LOD ^b ng L ⁻¹	Refs.
DLLME	Morin	1-Undecanol	ICP-OES	Water	128	0.8	[29]
DLLME	Oxine	Chloroform + acetonitrile	GFAAS	Urine		0.3	[61]
(IL-DLLME)	Oxine	[Hpy] [PF6] ionic liquid	SFS	Water, fruit juice and food	100	0.05	[62]
TIL-DLLME	Oxine	[C4mim] [PF6]	FAAS	Scalp hair	85	0.56	[63]
CPE	PAN	Triton X-114	GFAAS	Human albumin	34.8	0.06	[57]
CPE	PMBP	Triton X-114	GFAAS	Biological and water	37	0.09	[1]
CPE	ECR	Triton X-114	ETAAS spectrophotometry	Water		0.03 0.01	[64]
CPE	Xylidyl Blue	Triton X-114	FAAS	Water	50	1.43	[65]
CIAME	ATAP	Triton X-114	spectrophotometry	Water, Food and biological	500	0.87	This work

DLLME: Dispersive Liquid–Liquid Microextraction; ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry; Eriochrome ECR: Cyanine R; CPE: Cloud Point Extraction; FAAS: Flame Atomic Absorption Spectrometry; ETAAS: Electrothermal Atomic Absorption Spectrometry; PMBP: 1-Phenyl-3-Methyl-4-Benzoyl-5-Pyrazolone; PAN: 1-(2-Pyridylazo)-2-Naphthol; IL-based DLLME: Ionic Liquid-Based Dispersive Liquid–Liquid Micro-Extraction; SFS: Stopped-Flow Spectrofluorometry; oxine: 8-hydroxyquinoline; [Hpy][PF6]: 1-Hexylpyridinium Hexafluorophosphate; [C4mim][PF6]: Ionic Liquid 1-Butyl-3-Methylimidazolium Hexafluorophosphate.

^a Enhancement factor. ^b Limit of detection.

Table 5: Concentration of aluminum in human blood, urine and gallstone samples.

Sample source ^a	Sample	Added ng mL ⁻¹	Proposed method		ICP–AES method		t-test ^b	F-test ^c
			Found ^a	Recovery %	Found ^a	Recovery %		
Normal adult (Male)	Blood	--	122.0	--	123.2	---		
		10	133.2 ± 0.41	100.91	132.8 ± 1.66	99.70	0.89	2.22
		20	141.8 ± 0.39	99.86	144.2 ± 0.67	100.70	0.81	2.16
		40	163.7 ± 0.47	101.05	165.1 ± 0.52	101.16	0.88	2.20
Urine		--	41.8	---	42.3	---		
		30	72.3 ± 0.42	100.70	70.8 ± 1.67	97.92	1.16	2.95
		60	100.6 ± 0.56	98.82	103.6 ± 0.45	101.27	0.79	2.11
		120	162.7 ± 0.83	100.56	164.4 ± 0.29	101.29	1.23	3.00
Cancer patient (Leukemia)	Blood	--	315	---	313.5	---		
		25	338.7 ± 0.37	99.62	327.4 ± 1.97	99.67	1.02	2.61
		50	366.6 ± 0.52	100.44	361.3 ± 1.42	99.39	0.84	2.15
		100	416.3 ± 0.47	100.31	414.9 ± 1.48	100.34	0.74	2.02
Urine		--	130	---	129.2	---		
		15	145.9 ± 0.36	100.62	145.7 ± 1.84	101.04	0.91	2.29
		30	158.7 ± 0.42	99.19	157.9 ± 1.43	99.18	0.77	2.08
		60	192.6 ± 0.21	101.37	193.4 ± 1.29	102.22	0.92	2.29
Lung cancer (Male)	Blood	--	265	---	267.5	---		
		20	283.3 ± 0.57	99.40	289.7 ± 1.33	100.77	0.81	2.10
		40	208.1 ± 0.31	101.46	304.9 ± 1.45	99.15	0.99	2.37
		60	323.5 ± 0.38	99.54	325.8 ± 1.38	99.48	0.78	2.05

	Urine		111.5	---	113.0	---		
		17.5	129.6 ± 0.44	100.47	129.4 ± 1.17	99.16	0.93	2.32
		35	145.8 ± 0.63	99.52	150.8 ± 0.91	101.89	1.13	2.76
		70	183.2 ± 0.39	100.94	181.8 ± 0.81	99.34	1.31	3.09
Gallstone patient (Male)	Human gallstone	--	30.3	---	29.7			
		35	66.0 ± 0.46	101.07	165.4 ± 0.57	101.80	1.23	2.68
		70	99.6 ± 0.89	99.30	98.8 ± 1.29	99.10	0.99	2.34
		105	137.5 ± 0.67	101.63	136.9 ± 0.89	101.63	1.16	2.83

^aMean ± Relative Standard Deviation (n= 5);

^bTabulated t-value for five degrees of freedom at P (0.95) is 2.57;

^cTabulated F-value at P (0.95) is 5.05.

Table 6: Determination and recovery studies of aluminum in water samples using the proposed method.

Sample	Added ng mL ⁻¹	Proposed method			ICP–AES method			t-test ^b	F-value ^b
		Found ^a ng mL ⁻¹	Recovery (%)	RSD (%)	Found ^a ng mL ⁻¹	Recovery (%)	RSD (%)		
Tap water	0	54.5	-	1.24	55.0	-	1.37		
	25	80.3	101.01	1.08	81.1	101.38	1.15	1.63	1.13
	50	103.8	99.33	0.96	103.8	98.85	1.70	0.61	3.14
	75	127.4	98.38	0.84	132.5	101.92	1.32	1.20	2.47
Mineral water	0	6.2	-	1.07	6.0	-	1.05		
	40	46.7	101.08	1.39	45.4	98.70	1.40	0.37	1.01
	80	85.8	99.54	1.25	87.5	101.74	1.82	1.01	2.12
	160	167.2	100.60	1.71	164.7	99.22	1.30	0.12	1.73
Well water	0	36.0	-	0.93	35.5	-	1.02		
	30	65.4	99.09	1.16	66.3	101.22	1.28	0.18	1.22
	60	97.2	101.25	1.29	94.7	99.16	1.42	0.72	1.21
	120	155.3	99.55	0.99	157.3	101.16	1.10	0.39	1.23
River water	0	21.0	-	0.86	21.4	-	1.11		
	20	41.7	101.71	1.50	42.2	101.93	1.62	0.31	1.17
	40	60.8	99.67	1.37	62.7	102.12	1.51	0.23	1.21
	80	100.5	99.50	1.68	100.2	98.82	1.74	0.22	1.07

^aAverage of six determinations.

^bTheoretical values for t- and F-values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.

Table 7: Determination and recovery of Al (III) in soil, and food samples using the proposed procedure.

Sample	Added (µg g ⁻¹)	Proposed method		ICP–AES method	
		Found ^a (µg g ⁻¹) ± RSD (%)	Recovery (%)	Found ^a (µg g ⁻¹) ± RSD (%)	Recovery (%)
Agriculture soil	00	9.6 ± 1.83	-	9.5 ± 2.34	-
	25	35.1 ± 1.17	101.45	34.3 ± 2.21	99.42
	50	59.1 ± 1.08	99.16	60.5 ± 2.50	101.68
Industrial soil	00	17.0 ± 0.37	-	16.7 ± 2.65	-
	50	65.9 ± 0.51	98.36	65.8 ± 2.51	98.65
	100	116.2 ± 0.68	99.32	117.8 ± 2.34	100.94

Tomato	00	14.0 ± 0.78	-	14.1 ± 1.87	-
	50	63.8 ± 0.83	99.69	64.5 ± 1.65	100.62
	100	114.7 ± 1.42	100.61	113.6 ± 2.02	99.56
Onion	0.0	29.0 ± 0.60	-	28.8 ± 1.45	-
	50	78.20 ± 0.84	98.98	77.5 ± 1.77	98.35
	100	128.0 ± 1.21	99.22	129.4 ± 2.11	100.47
Cabbage	00	45.0 ± 2.30	-	45.4 ± 3.12	-
	50	96.4 ± 2.54	101.47	96.2 ± 3.25	100.84
	100	144.4 ± 2.70	99.59	143.5 ± 3.45	98.69
Squash	0	34.0 ± 1.10	-	35.0 ± 2.10	-
	50	85.5 ± 1.0	101.79	86.5 ± 1.96	101.76
	100	133.6 ± 1.34	99.70	136.3 ± 2.22	100.96
Rice flour	00	27.0 ± 1.80	-	26.5 ± 3.10	-
	50	76.5 ± 2.07	99.35	75.4 ± 2.85	98.56
	100	127.9 ± 2.72	100.71	127.8 ± 3.65	101.03
Wheat flour	00	25.0 ± 1.95	-	24.5 ± 1.80	-
	50	75.8 ± 2.38	101.07	76.1 ± 1.10	102.15
	100	123.8 ± 2.47	99.04	125.8 ± 2.54	101.4

^aAverage of six determinations.

Conclusions

In the reported method, IL-CIAME procedure combined with spectrophotometry was used to determine Al (III) in environmental, and biological. The procedure has a high enhancement factor, acceptable accuracy and precision, good repeatability, and a wide dynamic range to determine Al (III). Comparison with other procedures, the reported method decreases the exposure danger of the toxic solvents, applied to extract and pre-concentrate in conventional extraction methods, it also needs a lower time of extraction. The detection limit applying only 50 mL of sample is better than that of other procedures and is robust against high medium salt content.

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