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Cloud Point Extraction as a Simple Preparation for Trace Amount of Aluminium by New Ligand 2-(3- indolyl) - 4,5 di Phenyl Imidazole(IDPI), after Determination by Flame Atomic Absorption Spectrometry in Real Samples

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ABSTRACT

2-(3- indolyl) - 4,5 di phynyl imidazole(IDPI), was used as a complexing agent in cloud point extraction for the first time and applied for selective pre-concentration of trace amounts of Aluminium. The method is based on the extraction of Aluminium at pH 3.5 by using non-ionic surfactant T-X114 and 2-(3- indolyl) - 4,5 di phenyl imidazole.(IDPI) as a chelating agent. The adopted concentrations for IDPI, Triton X-114 and HNO_3, bath temperature, centrifuge rate and time were optimized. Linearity for Al was obeyed in the range of Al^{3+} ion 0.2-20.0 ng mL^{-1}. The Detection Limit (n=10) 0.013(μg.mL^{-1}) for Aluminium ion, and along with enrichment factor of 37 for Aluminium ion, RSD % (n=5) 1.3(μg.mL^{-1}) for Aluminium ion was achieved. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated. The proposed method was successfully applied to the ultra-trace determination of aluminium in real samples.

Keywords: 2-(3- indolyl) - 4,5 di phenyl imidazole (IDPI), aluminium ion, cloud point extraction, flame atomic absorption spectrometry

INTRODUCTION

Aluminium(Al) is widespread throughout nature, air, water, plants and consequently in all the food chain [1]. Nevertheless, the excessive ingestion of aluminum can influence negatively the human organism disturbing calcium and phosphate metabolisms and thus damaging the bone system. Moreover, the accumulation of high amounts of aluminum in the brain is associated to Alzheimer disease, senescence symptoms and amnesia of young people [2]. Human beings are exposed to aluminum from several sources such as atmospheric air,

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cosmetics, foods, drinking water and medicines. A lot of papers devoted to the determination of aluminum in environmental samples, food, drugs, human body have appeared in the literature for years [3-5].

Several analytical techniques such as flame atomic absorption spectrometry (FAAS) [6], electrothermal atomic absorption spectrometry (ETAAS)[7], and inductively coupled plasma-optical emission spectrometry (ICP-OES)[8,9], and kinetic- Spectrophotometry [10] devoted to low-level metals determination, however, their present very high acquisition and operational costs. Spectrophotometry is a well-established analytical technique that provides low cost, simplicity and wide range of applications for aluminium determination in some food samples [11-13].

Cloud point extraction (CPE) is a separation and preconcentration method [14]. Cloud point extraction (CPE), employed in analytical chemistry to separate and preconcentrate organic compounds and metal ions, has been well reviewed [15], Cloud point extraction is the process in which the surfactant is added to the aqueous solution which containing the component or components that must be extracted [16].

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains either a water insoluble (or oil soluble) component and a water soluble component. The tail of most surfactants is consisting of a hydrocarbon chain which can be linear, branch or aromatic [17, 18]. Suitable amount of surfactant shall be added to provide the micelles in the solution. It means that the final concentration of the surfactant shall be exceeding from its CMC (Critical Micelle Concentration). Then for micelle or cloud solution formation, conditions (such as increase or decrease in temperature, increase in salt or other surfactants) are changed and with applying the suitable conditions, surfactant molecules form micelles. In order to speed up the separation of two phases, centrifugation can be used. Finally phase separation is done and a surfactant-rich phase and an aqueous phase will observe [19, 20].

In this work, a cloud-point preconcentration procedure was introduced for determination of Al^{3+} ion, after the formation of complex with 2-(3- indolyl) - 4,5 di phenyl imidazole (IDPI). The lipophilic IDPI-Al^{3+} complexe, completely extracted from aqueous solution to the concentrated micellar medium, and the analytes was ultimately analyzed by flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation

A Shimadzu AA-680 atomic absorption spectrometer equipped with deuterium background correction, Al hollow-cathode lamps as the radiation source, was used for absorbance measurements respectively. Shimadzu double beam UV-Vis spectrophotometer

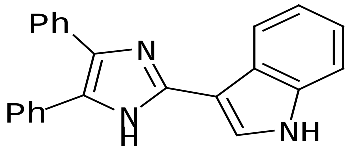
UV-1700 (Japan). A centrifuge (Shimifan) was used to accelerate the phase separation process. A Jenway model 3510 pH-meter was used for pH measurements.

Reagents

All solutions were prepared with deionized water. Analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck. All surfactants including. A 1.0% (w/v) Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of sodium dodecyl sulphate (SDS), Triton X-100, Triton X-114 cetyltrimethyl ammonium bromide (CTAB), were prepared by dissolving appropriate amount of each surfactant in DI water and make a final volume of 100 mL in volumetric flask. All chemicals obtained from commercial sources were of analytical grade unless otherwise stated. All aqueous solutions were prepared using doubly distilled water. The aluminum stock solution, 1000 μg L^{-1} was prepared from $Al(NO_3)3.9H2O$ in 10^{-3}M. The 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI) was synthesized, purified and characterized according to the literature [20].

Synthesis of Ligand 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI).

A mixture of benzil (1mmol), ammonium acetate (3mmol) and substituted benzaldehydes (1mmol), was added silica-bonded N-propylsulfamic acid (0.1 g) in solvent free condition at 80°C for the appropriate time, and heated at 80°C in an oil bath. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and remaining washed with warm ethanol (2-5 mL). After cooling, the corresponding 2,3-dihydroquinazolinone products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:3)] to give pure 2-(3-indolyl)-4,5 di phenyl imidazole.(IDPI) in 90% yield. (Scheme 1) was synthesized according to literature [21].



Scheme 1: 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI)

Mp: 302-305 °C

^{1}H-NMR (DMSO-d_6,400 Hz) δ: 7.05-7.16 (m, 3H), 7.23-7.28 (m, 3H), 7.37 (d, 3H, J=7.8 Hz), 7.44 (d, 2H, J=7.3 Hz), 7.56 (d, 2H, J=7.1 Hz), 7.93 (d, 1H, J=2.5 Hz), 8.40 (d, 1H, J=8.6 Hz), 11.29 (s, 1h), 12.20 (brs, 1H).

^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 106.8, 111.6, 119.7, 121.5, 121.8, 123.7, 125.1, 126.8, 128.1, 128.7, 136.2, 143.7, 145.3, 171.7.

IR(KBr) (cm^{-1}): 3412, 3055, 1621, 1598, 1491, 1451, 1336, 1208, 1182, 1049, 940, 854, 761, 749, 696.

Elemental analysis: C, 82.36; H, 5.11; N, 12.53.

Found: C, 82.17; H, 5.17; N, 12.29.

Procedure

Proposed procedure of cloud point extraction was tested by using model solution [Z]. For CPE, an aliquot of 15 mL of a solution containing Aluminium ion (0.05 µg mL^{-1}), 0.1 % Triton X-114 and 0.27 mM of IDPI was adjusted to pH 3.5 with HCl. The mixture was kept for 20 min in the thermostatic bath maintained at 50°C. The phase separation is accelerated by centrifuging at 4000 rpm for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 500 µL of 1.0 M HNO_3 in methanol and then the Aluminium ion content was readily evaluated by FAAS.

Preparation of Real Samples

Water samples

River water, natural mineral, Waste water (Hospital) and Spring water samples were collected in acid-leached polyethylene bottles. Al water samples was collected from (Bushehr, Iran), filtered through 0.45 µm Millipore cellulose acetate membrane filters to remove particles and diluted with distilled water to the ratio of 1:1. The samples were then adjusted to pH3.5 and immediately analyzed [22].

Baking powder sample

A sample of 100 g was dissolved in a mixture of 5 mL concentrated HNO_3 and 250 mL of distilled water. The solution was neutralized to pH 3.5 using 8.0 mol L^{-1} NaOH and then separation/preconcentration procedures given above were separately applied. The metal contents of the final solution were determined by flame AAS [23].

Soil samples

Accurately weighed 1.0 g of soil samples from near Bushehr petrochemical center (less than 200 meshes), dried at 110 °C were poured into a 250 mL beaker and 10 mL concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete drying, the mixture was cooled to room temperature. A second 10 mL portion of concentrated nitric acid was added and the procedure. Then 10 mL concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 mL of 1 M HCl and the solution was then filtered into a 100 mL calibrated flask, using a syringe filter (0.45 µm pore sized). The sample was

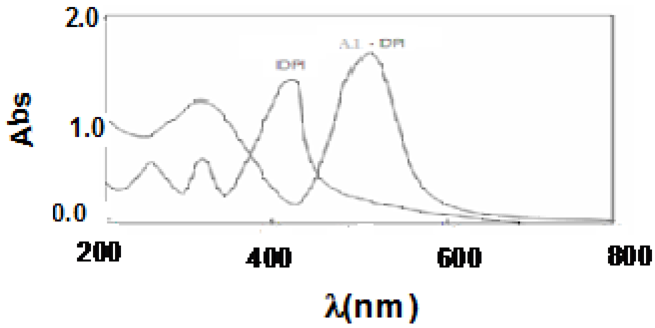


Figure 1. Absorption spectra of IDPI - Al complex. Conditions: 0.1% (w/v) Triton X-114, 0.27mM IDPI and 0.05 µg mL^{-1} Aluminium ion

neutralized by proper amounts of a 1 M NaOH solution and finally diluted to the mark with water [24].

RESULTS AND DISCUSSION

The aim of this work was to develop a simple, sensitive and available method for the preconcentration and determination of trace amounts of Al^{3+} ion in various real samples using flame atomic absorption spectrometry coupled with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and IDPI concentrations, heating time and temperature, centrifuge time and rate, as well as the effect of electrolyte on absorbance, were optimized. The complexation study yields important information about the interaction between the ligand and metal ions. Recently, we have used the spectrophotometric method for this purpose [25, 26], before using IDPI for the CPE of the metal ions.

Spectrophotometric Titrations

Atypical Cloud point experiment required the following steps: 25mL solution contain analyte ions, 0.1 % Triton X-114 for Al^{3+} ion and 0.27 mM IDPI was adjusted to related pH 3.5, was adjusted to related pH 3.5, the mixture shaken for 15 min and left to stand in a thermostated bath at 50°C for 20 min to Al^{3+} ion, high viscosity Cloud point formed ,the bulk aqueous phase was easily decanted .The remaining micellar phase was dissolved in ethanol and then the ion content was readily evaluated by UV-Vis spectrophotometry at λ_{max} for complex λ=539nm for Al^{3+} ion, as well as calculated distribution ratio values by spectrophotometric method[27]. With dependance on Calibration Curve **Figure 1**.

Effect of pH

A complex with sufficient hydrophobicity is required for separation of metal ions. The mentioned complex can be extracted in a small volume of surfactant-rich phase. The extraction efficiency is dependent on the pH at which complex formation occurs. Therefore, pH is the most important parameter affecting the extraction efficiency and it is necessary to choose the optimum pH at first [28-31]. The effects of pH on to extract metal complexes are given in **Figure**

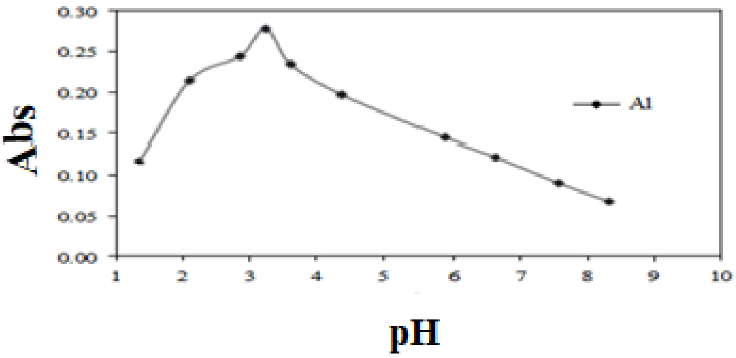


Figure 2. Effect of pH on the extraction recovery of Aluminium ion. Conditions: 0.05 µg mL^{-1}, 0.27 mM IDPI, 0.1% (w/v) Triton X-114. Other experimental conditions are described in Procedures

2. In the pH range of 1.0-8.5, extraction was quantitative. The decrease in recoveries at pH >3.5 is probably due to the precipitation of metal ions in the form of hydroxide, and at pH < 3.0 may be due to competition from hydronium ion toward ions for complexation with IDPI or decomposition of complex at pH <3.5, which led to the decrease in recoveries. In later experiments a pH of 3.5 was selected.

Effect of Ligand IDPI Concentration

In order to select the optimal concentration of ligand (at the fixed values of the other experimental parameters), the effect of the concentration of the chelating reagent on the extraction efficiency was evaluated over the range of 0.1-0.45 mM. The extraction recovery as a function of the IDPIconcentration is shown in Figure 3. At 0.27 mM IDPI, the recoveries of the ions were quantitative. Thus, 0.27 mM IDPI was chosen for subsequent experiments. The high concentration of IDPI with respect to the concentrations of the Aluminium ion makes it superior for analysis of real samples.

Effect of Surfactant on Sensitivity

The formation of Al-IDPI complexes are time consuming, requires rigid control of pH and temperature, and its sensitivity is not suitable for aluminium determination at trace levels. However, these disadvantages can be reduced by applying the cationic surfactant micelles to Al-IDPI complex [32]. Therefore, the effect of type of surfactant such as cationic(CTAB), anionic(SDS), nonionic(Triton X-100) and nonionic (Triton X-114) surfactants on spectra and sensitivity of the complexation of Al and IDPI reagent in acetate buffer pH 3.5 were investigated. It was found that the absorption spectrum of Al-IDPI in the presence of nonionic (Triton X-114) gave highest sensitivity Table 1. Therefore, nonionic (Triton X-114) was chosen as suitable surfactant for enhances the sensitivity of Al-IDPI.

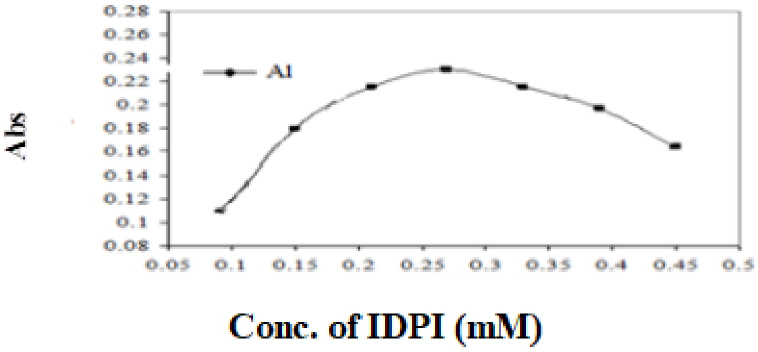


Figure 3. Effect of IDPI concentration on the extraction recovery of Aluminium ion. 0.05µg mL^{-1}, 0.1% Triton X-114, pH 3.5. Other experimental conditions are described in Procedures

Table 1. Effect of type of surfactant on sensitivity for 0.05 µg mL^{-1} of interest ion, pH 3.5, IDPI (0.27 mM) and 0.1 % (w/v) of each surfactant

Surfactant	Cd %
Triton X-100	48.7
Triton X-114	98.6
SDS	32.0
CTAB	27.4
No surfactant	15.9

Triton X-114 was used as extractant and the concentration of this surfactant affects both the extraction efficiency and the volume of the surfactant-rich phase. In order to obtain easy phase separation and maximum extraction efficiency the optimum amount of Triton X-114 should be determined [33]. The variation in absorbance of extracted Al^{3+} ion within the Triton X-114 concentration range of 0.01 - 0.15% (w/v) was examined and results shown in Figure 3. The results show that quantitative extraction was obtained with an optimum Triton X-114 concentration of 0.1% (w/v), at which the highest absorbance for extracted Al^{3+} ion was obtained. For concentrations lower than 0.1% (w/v), the preconcentration efficiency of the formed complexes was very low, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Al^{3+}ion. The decreasing of absorbance at a concentration higher than 0.1% (w/v) is due to the remaining of some part of Triton X-114 and IDPI in aqueous solution as this phase can compete with surfactant-rich phase to draw analyte ions.

Effect of Viscosity on the Analytical Signal and Centrifugation Time

As reported, the organic solvent increases the atomization temperature, whereas both the organic solvent and the surfactant can promote generation of small droplets during mobilization and lead to positive surface effects. The signal enhancement in the presence of organic solvents has been widely applied to increase sensitivity during the analysis of a variety of metallic ions [35, 35]. Solvents tested include acetone, ethanol, and methanol, and the best

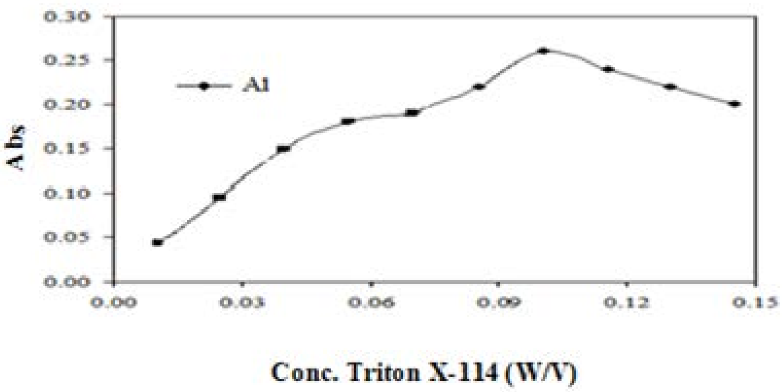


Figure 4. Effect of Triton X-114 on Aluminium ion Recovery, Condition: 15 mL 0.05 µg mL^{-1} Aluminium ion at various Triton X-114, 0.27 mM IDPI, pH=3.5, 0.2 % (w/v)KI, eluting solution 0.5ml of 1.0 M HNO3 in methanol

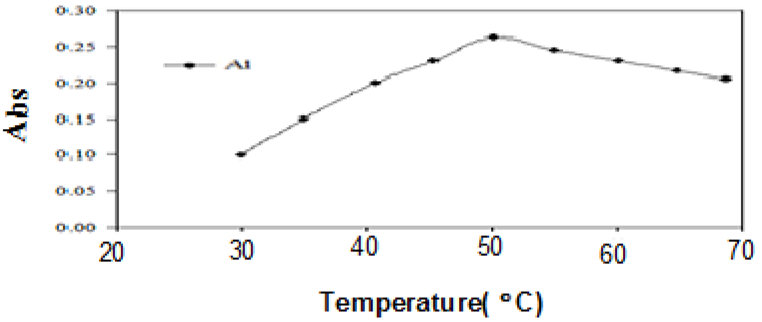


Figure 5. Effect of temperature on Aluminium ion recovery, Condition: 15 mL 0.05 µg mL^{-1} Aluminium ion at various temperature, 0.1% (w/v) Triton X-114, 0.27mM IDPI, pH=3.5, 0.2 % (w/v) KI, eluting solution 0.5mL of 1.0 M HNO_3 in methanol

results were obtained by using methanol; 0.5 mL 1.0 M nitric acid in methanol was used as the diluent. Under these conditions, maximum analytical signals were obtained.

Effect of Temperature and Equilibrium Time on CPE

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range 30-70 °C and 5-30 min were thoroughly optimized, respectively [36]. Holding the sample solutions for 25 min at 50 °C was found to be satisfactory to achieve a small volume of the surfactant-rich phase, quantitative extraction and experimental convenience.

Table 2. Optimum Conditions for the Presented CPE Method

Parameter	Optimum Value for ions
pH	3.5
IDPI concentration (mM)	0.27 mM
Triton X-114(w/v)	0.1 % (w/v)
Eluting agent	0.5 mL 1.0 mol L^{-1} HNO_3 in methanol
Bath temperature	50°C
Temperature time	20 min
Centrifuge time	15 min
Centrifuge rates	4000 rpm

Effect of KI Concentration

Addition of salt can cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Therefore, iodide was added to induce micelle growth and extraction of complex [2]. The effect of iodide concentration was studied in the range 0.05-0.8% (w/v). The absorbance for the sample increased by increasing in iodide concentration up to 0.2% (w/v) and remained constant at higher concentrations. Therefore, 0.2% (w/v) KI iodide was chosen as the optimum.

Effect of Centrifuge Time and Rates

Trace amounts of the Aluminium ion must be concentrated with high efficiency in a short time. Therefore, CPE was performed in a set of experiments with a 15 mL sample at pH 3.5, 0.27 mM IDPI, Al^{3+} ion (0.05 µg mL^{-1}), and 0. 2% (w/v) % KI by heating at 50°C, centrifuging at various rates, and further cooling for different times. The results indicate that the experiment with the optimized reagent concentration after heating for 20 min at 50°C, centrifuging for 20 min at 4000 rpm, and cooling for 15 min in an ice bath lead to high sensitivity of the metal ions in a short time.

Characteristics of the Method

Calibration curves were obtained by preconcentration of standard solutions under optimized extraction conditions. Because of very narrow of the linear calibration range for the elements, two different calibration curves were obtained. The dynamic range of calibration curves for studied element was in **Table 3**, [14]. Calibration graphs were obtained by preconcentrating 2.0 mL of standard solution in the presence of pH 3.5, 0.1% (w/v) Triton X-114, pH 3.5, 0.27 mM IDPI with 0.2% (w/v) KI, under the experimental conditions specified in the optimized procedure section. The solutions were introduced into the flame by conventional aspiration. The characteristics of the proposed method are shown in **Table 2**.

Table 3 gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also included [29, 37]. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS.

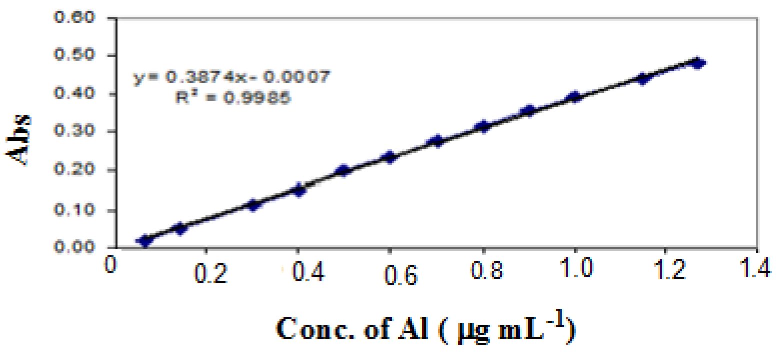


Figure 6. Calibration Curve by dithizone method for Al^{3+} ion

Table 3. Specification of Method at Optimum Conditions for Al^{3+} ion

Parameters	Ion
	Al
Linear Range (μg mL^{-1})	0/1-064/27
Correlation Coefficient	0/9985
Detection Limit (μg.mL^{-1}) (n =10)	0/013
Enrichment factor	37
Preconcentration factor	39
RSD % (n =5)	1/3
Recovery %	99

Effect of Diverse Ions on the Determinations

The extent of interferences from major anions and cations of natural waters and some metal ions were examined by measuring the absorbance of the solution preconcentration step [38]. Cations that may react with IDPI, and anions that may form complexes with the metal ions were studied [39]. The results were shown in Table 4. It was proved that Aluminium recoveries were almost quantitative in the presence of foreign cations.

Determination of Metal Ions in Real Samples

To validate the proposed method, the developed procedure was applied to the determination Aluminium ion in real samples. For this purpose, 15 mL of each of the samples were pre-concentrated with 0.1% (w/v) Triton X-114 and IDPI concentration of 0.27mM, following the proposed procedure. The results are shown in Table 5 and 6. In all cases the spike recoveries confirmed the reliability of the proposed method. Table 5 and 6 compares LODs and linear range for proposed method with other methods for determination of aluminum [22, 40].

Table 4. Effects of the matrix ions on the recoveries of the examined Al^{3+} ion (N=3)

Ions	Added As	Tolerance Limit, mg L^{-1}
Cl^-, K^+, Na^+,	KCl, NaCl, $MgCl_2$,	800
Zn^{2+}, Ba^{2+}	Nitrate salts	300
PO_4^{3-}	Na_3PO_4	800
Cu^{2+}, Ni^{2+}, Cr^{3+}, Hg^{2+}	Nitrate salts	200
Ca^{2+}, Mg^{2+}	Nitrate salts	50
Fe^{3+}	Nitrate salts	100
HCO_3^-	$NaHCO_3$	800

Table 5. Determination of Al^{3+} ion in Soil,Soda and Baking Powder

Ion	Soil				Soda			Baking Powder		
	Added (μg mL^{-1})	Found (μg mL^{-1})	RSD %	Recovery %	Found (μg mL^{-1})	RSD%	Recovery %	Found (μg mL^{-1})	RSD %	Recovery %
Al	0	0.90	1.4	-	1.23	0.9	-	0.04	1.2	-
	0.15	2.00	1.1	96	2.51	1.0	94	0. 11	1.3	101

Table 6. Determination of Al^{3+} ion in Waste water(Hospital), River water and Tap water

Ion	Waste water (Hospital)				River water			Spring water		
	Added (μg mL^{-1})	Found (μg mL^{-1})	RSD %	Recovery %	Found (μg mL^{-1})	RSD %	Recovery %	Found (μg mL^{-1})	RSD %	Recovery %
Al	0	2.38	1.1	-	0.95	1.2	-	4.5	1.3	-
	0.15	7.60	1.5	100.7	2.38	1.6	95.3	20.1	1.5	103

CONCLUSIONS

The combined advantages of the cloud point methodology and the use of 2-(3- indolyl) - 4,5 di phyeyl imidazole(IDPI), as a ligand for Aluminium were utilized for determination of Aluminium in real samples. The method is fairly selective, leading to an effective separation, and constitutes an inexpensive alternative to other pre-concentration methods. The method gives a low limit of detection, good R.S.D. and solvent-free extraction of the element from its initial matrix following a single step extraction procedure without interferences. Preconcentration factor of developed method is generally more than small the other study. The detection limits of method are comparable level with the works in literature including cloud point extraction, solid-phase extraction and coprecipitation [41-44]. Simultaneous separation and preconcentration of Aluminium is one of the important advantages. The proposed method has been applied different matrices.

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