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Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Drop as an Efficient Preconcentration Method for Spectrophotometric Determination of Aluminium

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A rapid, simple, and sensitive dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME-SFOD) method coupled with UV-Vis spectrophotometry has been applied for the extraction and determination of trace amounts of aluminium. The aluminium was extracted from the aqueous media containing aluminon and cetyltrimethylammonium bromide (CTAB). After rapid injection of the 1-undecanol mixture as the extraction solvent and ethanol as the disperser solvent into the sample, a cloudy mixture was formed and the complex was extracted into 1-undecanol. After centrifugation and cooling in an ice bath, the solidified organic drop on top of the solution was transferred into a vial which was melted at room temperature. Then, the organic phase containing the metal complex was diluted with ethanol and was transferred into a microcell for quantification. The pink chelate exhibits maximum absorbance at 535.0 nm, and with a preconcentration factor of 100.0 obeys Beer's law over the concentration range of 1.0-15.0 $\mu\text{g l}^{-1}$ of aluminium. The limit of detection of 0.14 $\mu\text{g l}^{-1}$ and a relative standard deviation of 1.8% at 3.0 $\mu\text{g l}^{-1}$ ($n = 6$) were obtained. The procedure was successfully applied for the determination of aluminium in tea and water samples.

Keywords: Aluminium, Separation and preconcentration, DLLME-SFOD, Spectrophotometry

INTRODUCTION

Aluminium is the third most plentiful metallic element (8.1% by weight) on the earth's crust [1]. Aluminium is a useful element in human life and is used in medicine for dialyzes encephalopathy, in the aerospace industry, and packaging. Its compounds are used in various products such as antiperspirants, antacids, food additives, and its salts are usually used as coagulants in the water treatment process [2-4]. However, this element is unnecessary and even harmful to most living beings. In recent years, aluminum has attracted a lot of attention, due to its toxic effects on human life and the environment. Aluminium can enter the human body by drinking water, foods, medicine, cosmetics,

breathing and skin contact [5]. Probably aluminium cookware or storage containers are the most important entryway to the food, especially when the contents are acidic [6]. High dosage of aluminium and its accumulation in brain, has been considered as an interfering with normal activities of central nervous system and link with clinical disorders such as Alzheimer's disease (senile dementia), Parkinson, bone inflammation, renal osteodystrophy, and encephalopathy, though these connections have not been proven, yet [7,8].

International regulations has proposed 0.2 mg l^{-1} of aluminium as the maximum permissible level in drinking water [9]. Therefore, for human health and environmental safety, accurate separation and determination of trace amounts of Al(III) in real samples are necessary. The instrumental techniques such as flame atomic absorption

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spectrometry (FAAS) [10], electrothermal atomic absorption spectrometry (ET-AAS) [11], spectrofluorometry [12], chemiluminescence analysis [13], inductively coupled plasma optical emission spectrometry (ICP-OES) [14], and electrochemical methods [15] were used for the determination of aluminium in different samples. Among these techniques, spectrophotometry has the advantages of simplicity, availability, speed, precision, and adequate sensitivity making it appropriate for the analysis of the analyte. However, the direct determination of aluminium in real samples by this technique is difficult due to its low concentration and the possibility of matrix interferences, thus, a pretreatment step is generally required. Different sample preparation methods including solid phase extraction (SPE) [16], liquid-liquid extraction (LLE) [17], cloud point extraction (CPE) [18], supramolecular solvent based liquid-liquid microextraction [19], and dispersive liquid-liquid microextraction (DLLME) [20] have been used for the separation and preconcentration of aluminum prior to its spectrophotometric determination.

The traditional liquid-liquid extraction, the most versatile method for the separation and concentration of analytes from complex matrices, usually suffers from such disadvantages as the formation of the emulsion, the need of large quantities of sample and toxic organic solvents, high consumption of extraction time, and low enrichment factor [21]. The new trend in analytical chemistry is toward the development of simplified and miniaturized solvent extraction methods to make them more environmentally friendly and efficient sample preparation procedure. Liquid phase microextraction (LPME) methods such as single drop microextraction (SDME) [22], hollow fiber liquid phase microextraction (HF-LPME) [23], dispersive liquid-liquid microextraction (DLLME) [24], and dispersive liquid-liquid microextraction based on solidification of a floating organic drop (DLLME-SFO) [25] have overcome some of the disadvantages of the traditional liquid-liquid extraction. These methods are fast, simple, and use only a few microliters of extraction solvents [26].

Dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME-SFOD) is a novel LPME method which combines the advantages of both dispersive liquid-liquid microextraction (DLLME) and solidified floating organic drop microextraction (SFOD)

methods [27,28]. In DLLME-SFOD, the mass transfer is as fast as DLLME and does not need to use conical bottom glass tubes, which are easily damaged and hard to be cleaned. In this method, an appropriate mixture of the extraction and disperser solvents is rapidly injected into the aqueous sample. Thereby, a cloudy solution is formed and subsequently, the mixture would be centrifuged to separate the organic phase. After centrifugation, the organic phase containing the analyte is floated on top of the sample solution, solidified in an ice bath and is readily separated for quantification of the analyte. This technique in combination with ICP-OES had been used for determination of aluminium, however there is no report on its application with spectrophotometric technique [28].

The aim of the present study is to develop a new simple and sensitive DLLME-SFOD method combined with spectrophotometry for the extraction and determination of aluminium from real samples. The triammonium salt of the aurintricarboxylic acid (aluminon) was used as the chelating agent to form a sparingly soluble complex of Al(III)-aluminum in aqueous solution. Then, in the presence of cetyltrimethylammonium bromide (CTAB) the extraction of the complex into the fine droplets of 1-undecanol formed from rapid injection of a mixture of the extraction and disperser solvents was enhanced. After phase separation, the extracted analyte in the organic phase was quantified with the spectrophotometric method at 535 nm.

EXPERIMENTAL

Reagents

Aluminium nitrate (95%), aluminon (98%), 1-undecanol and other analytical grade chemicals were obtained from the Merck Company (Darmstadt, Germany). Doubly distilled water was used for the whole procedure. All glassware was kept in 10% (v/v) nitric acid for at least 24 h and then rinsed with distilled water before use. A 1000.0 mg l⁻¹ stock standard solution of aluminum was prepared by dissolving an appropriate amount of Al(NO₃)₃·9H₂O in distilled water. The working standard solutions were prepared daily by appropriate dilution of the stock solution. A 1.0 × 10⁻² M chelating agent (aluminon) stock solution was prepared by dissolving 0.1207 g of the compound in 25.0 ml of distilled water. A 1.0 × 10⁻² M cetyltrimethylammonium bromide

(CTAB) stock solution was prepared by dissolving 0.0911 g surfactant in 25.0 ml of distilled water.

Apparatus

A single-beam spectrophotometer model JENWAY-6300 (Jenway, Essex, UK) equipped with a 1 cm quartz microcell with 100 μl was used as the detection system for all the measurements. All the measurements were made against a reagent blank solution. The pH adjustments were carried out using a digital pH meter (Metrohm, model 827) equipped with a combined glass-calomel electrode. A centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was employed to accelerate the phase separation process.

Extraction Procedure

A 10.0 ml of the sample or the standard solution (pH = 3.5) containing 1.0-15.0 $\mu\text{g l}^{-1}$ of Al^{3+} , 25.0 μl of 0.01 M aluminon (as a chelating agent) and 25.0 μl of 0.01 M cationic surfactant CTAB solution was transferred into a centrifuge tube. Then, a mixture of 400.0 μl ethanol as the disperser solvent and 60.0 μl 1-undecanol as the extraction solvent was rapidly injected into the sample solution with a 1.0 ml syringe. In this step, a cloudy solution including the ultrafine droplets of 1-undecanol in the aqueous phase was formed and the pink colored complex was extracted into the organic phase in a few seconds. The mixture was centrifuged at 4000 rpm for 4 min. The extraction solvent droplets containing the analyte were floated on the top of the solution. Afterward, the test tube was placed in an ice bath for 10 min to solidify the organic phase including complex. In the next step, the solidified solvent was transferred into a small vial. After melting the solid droplet at room temperature, it was diluted with 45.0 μL of ethanol and transferred to a microcell (the volume of extraction solvent was $55 \pm 4 \mu\text{l}$). Finally, the absorbance was measured at 535 nm against a reagent blank.

PREPARATION OF REAL SAMPLES

Water Samples

Tap, well and mineral water samples were filtered through a 0.45 μm Millipore filter. Their pH values were adjusted to 3.5 and the concentration of Al(III) was determined according to the given extraction procedure.

Tea Samples

In order to analyze the tea sample, a proper amount of the dried and powdered tea leaves was decomposed at 500 $^{\circ}\text{C}$ for 60 min. Approximately 3 ml of aqua regia was added to the ash and heated at 100 $^{\circ}\text{C}$ for 5 min. The residue was diluted with distilled water to 250 ml in a volumetric flask and treated according to the recommended procedure [29].

RESULTS AND DISCUSSIONS

Aluminon is used widely as a selective chelating agent to form a colorful complex for spectrophotometric determination of aluminium in various matrices. This ligand forms a sparingly soluble complex with aluminium with an absorbance in the range of 515-530 nm (Figs. 1a and 1b). In the preliminary studies, it was found that addition of cationic surfactant enhances the solubility of aluminium-aluminon complex in 1-undecanol and sensitivity of measurement (Fig. 1c). Therefore, a DLLME-SFOD-spectrophotometric method was designed for separation/preconcentration and determination of trace amounts of aluminium in various samples and the effect of influential parameters on the formation of complex and extraction were optimized.

Effect of pH

The pH of the solution is the most important factor in the formation of the metal ion complex [28]. Moreover, it affects efficient hydrophobicity of the complex and its extraction into a small volume of the extractant phase. As the aluminium forms a stable pink complex with aluminon in the acidic medium (pH = 2.0-5.0), the influence of pH on the extraction of Al^{3+} from aqueous solutions was studied in the range of 2.0-5.5. The pH was adjusted by diluted solutions of HCl and NaOH while the other variables were kept constant during the extraction process. The results (Fig. 2) revealed that the maximum absorbance of the aluminium-aluminon occurs in the pH range of 3.0-4.0. The decrease in extraction efficiency at pH < 3 is probably due to competition between proton and the analyte for complex formation with aluminum. Moreover, the decrease in signal intensity at pH values above 4.0 can be related to the formation of aluminium hydroxide. Therefore, in order to

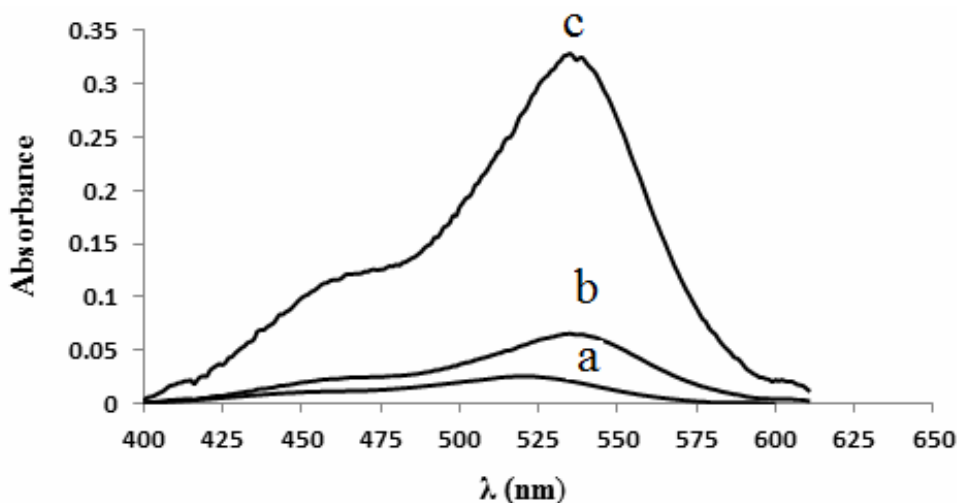


Fig. 1. Absorption spectra: a) aluminumon ligand, b) aluminum-aluminum complex, and c) aluminum-aluminum complex in the presence of surfactant in 1-undecanol.

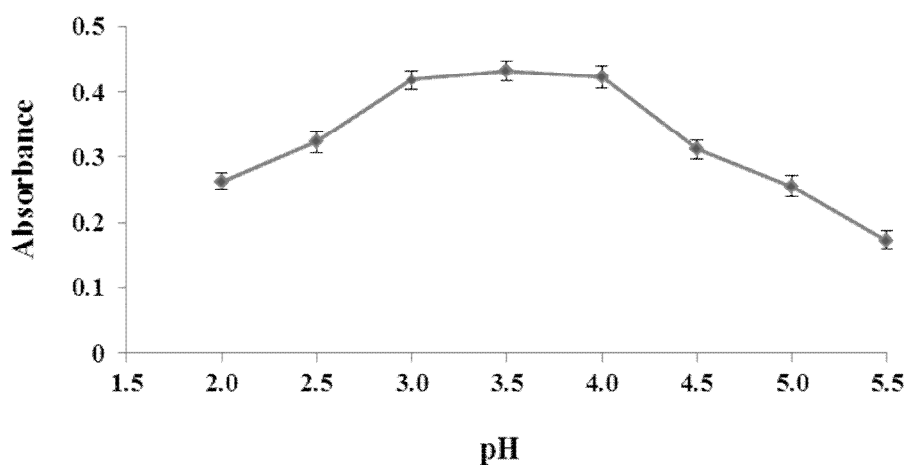


Fig. 2. The effect of pH on the extraction of $10 \mu\text{g l}^{-1}$ of aluminum. Extraction conditions: sample volume, 10.0 ml; extracting solvent, 40 μl of 1-undecanol; dispersive solvent, 450 μl ethanol; concentration of aluminumon, 2.0×10^{-5} M; concentration of surfactant (CPC), 2×10^{-5} M; $n = 3$.

achieve the highest extraction efficiency, a pH of 3.5 was chosen as the optimum pH for the subsequent studies.

Nature of the Extracting Solvent

The type of extraction solvent has an important role in the extraction and achievement of proper preconcentration factor of the analyte. The extraction solvent in DLLME-

SFOD process should have some specific features including good solubility in disperser solvent, low volatility, low toxicity, a melting point close to room temperature (in the range of 10-30 °C), and a density less than water to be easily floating on the water surface, and low solubility in water to have high extraction efficiency [25]. Based on these factors, several solvents including 1-undecanol (m. p.:

13-15 °C), n-hexadecane (m. p.: 18 °C), 1-dodecanol (m. p.: 22-24 °C), 1-bromohexadecane (m. p.: 17.3 °C), 1,10-dichlorodecane (m. p.: 14-16 °C) and 2-undecanol (m. p.: 15 °C) were investigated [32,33]. The maximum absorption was achieved with 1-undecanol as the extraction solvent (Fig. 3). The diffusion of the complex into the organic phase is directly related to the interfacial area between the two liquid phases. Since at room temperature the 2-dodecanol is relatively viscous, it cannot be dispersed properly in the aqueous solution which leads to the reduction in the interfacial area between two phases and consequently the extraction efficiency. Furthermore, the hydrophobicity of 1,10-dichlorodecane and 1-bromohexadecane is not sufficient for their complete collection from the aqueous phase and n-hexadecane cannot be dispersed properly due to its low solubility in ethanol. Based on these results, 1-undecanol was chosen as the best extracting solvent due to its high stability, low vapor pressure, low water solubility, more sensitivity, and the convenience of the drops collection from the surface.

Effect of Extraction Solvent Volume

The volume of the organic phase is an important factor affecting the extraction recovery and preconcentration factor. In order to optimize the volume of 1-undecanol, a series of experiments with different volumes of 1-undecanol (20 to 100 μl) was carried out. The extracted phase was diluted to 100.0 μl with ethanol and the absorption was measured. According to the results (Fig. 4), by increasing the volume of the organic phase up to 60.0 μl , the absorption signal increases which levels off at higher volume of extracting solvent. Thereby, an optimum volume of 60.0 μl of 1-undecanol was selected for further studies.

The Effect of Nature and Volume of Disperser Solvent

The most important factor for selecting a disperser solvent in the DLLME-SFOD method is its miscibility with both water and extraction solvent. In this respect, the effect of different solvents including ethanol, methanol, acetone, and acetonitrile on the extraction efficiency was considered. The results revealed that separation of the two phases was not possible with acetonitrile as the disperser solvent and so it was rolled out. Among other examined disperser solvents,

the recovery was higher with ethanol, probably due to the proximity of its dipole moment (1.69 D) to the water (1.85 D). Thus, ethanol was chosen as the most suitable disperser solvent.

Next, the effect of the volume of ethanol on the extraction efficiency was considered by performing several experiments with different volumes of ethanol (200.0 to 800.0 μl). It was observed that by increasing the volume of ethanol to 400.0 μl the absorbance reaches a maximum and then decreases slightly. At low volumes of ethanol, the extraction solvent was not completely dispersed in the aqueous phase whereas at a volume of higher than 400.0 μl the chelate solubility in aqueous solution was increased, resulting in a decrease in the extraction recovery. Thus, for quantitative extraction of the analyte, 400.0 μl of ethanol was chosen as the optimum volume of disperser solvent.

Effect of Nature and Amount of Surfactant

The effect of the presence of surfactants of CTAB, cetylpyridinium chloride (CPC), and Tetrabutylammonium chloride (TBAC) on the extraction efficiency of Al-aluminon complex was examined. The results (Fig. 5) implied that among the examined surfactants, the extraction efficiency was higher with CTAB as indicated by higher absorption of the extracted Al-aluminon at 535 nm. Then, the effect of the amount of CTAB on the absorption was investigated within the range of 1.0×10^{-5} - 3.5×10^{-5} M. The results showed that at a concentration of 2.5×10^{-5} M of CTAB, the absorption was maximum. So, this concentration (2.5×10^{-5}) was chosen as the optimum CTAB concentration.

Effect of Aluminon Concentration

In order to obtain the optimum concentration of the chelating agent, the concentration of aluminon in the aqueous phase was varied within the range of 1.5×10^{-5} - 4.0×10^{-5} M. As shown by the results, the absorption signal increased by increasing the aluminon concentration up to 2.5×10^{-5} M and then slightly decreased by a further increase in its concentration. The decrease in absorption can be related to the competition of excess amount of aluminon molecules with Al-aluminon complex for the extraction into the organic phase. Therefore, 2.5×10^{-5} M was chosen as the optimum concentration of aluminon.

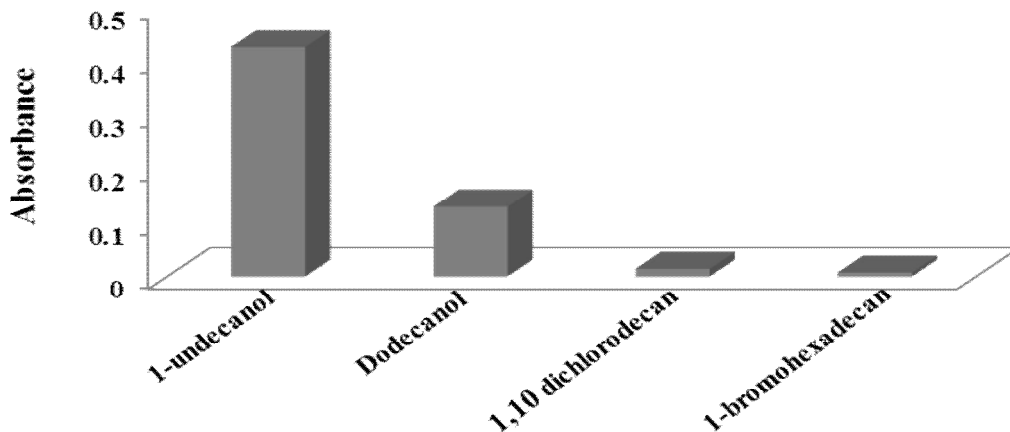


Fig. 3. The effect of extraction solvent on the extraction of $10 \mu\text{g l}^{-1}$ of aluminum. Extraction conditions: sample volume, 10.0 ml; pH ~ 3.5 ; extraction solvent, 40 μl ; dispersive solvent, 450 μl ethanol; concentration of aluminon, 2.0×10^{-5} M; concentration of surfactant (CPC), 2×10^{-5} M; n = 3.

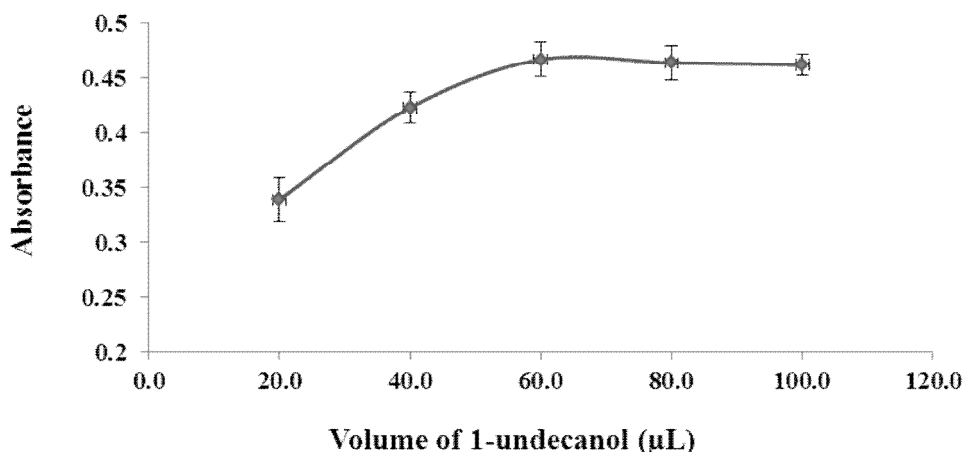


Fig. 4. The effect of volume of extraction solvent on the extraction of $10 \mu\text{g l}^{-1}$ aluminum. Extraction conditions: sample volume, 10.0 ml; pH ~ 3.5 ; dispersive solvent, 450 μl ethanol; concentration of aluminon, 2.0×10^{-5} M; concentration of surfactant (CPC), 2×10^{-5} M; n = 3.

Effect of Ionic Strength

The influence of ionic strength on the extraction efficiency of the analyte was examined by performing the procedure in the presence of various amounts of NaNO_3 (0.0-0.6 M). It was found that addition of salt up to 0.1 M has no significant effect on the extraction efficiency. However, a further increase in the salt concentration causes

a slight decrease in the analytical signal probably due to the change in the physical properties of Nernst diffusion layer resulting in a decrease in complex mass transfer from the aqueous solution into the organic drop. Thus, the method is suitable for the separation and preconcentration of aluminium from the solutions with salt concentration up to 0.1 M.

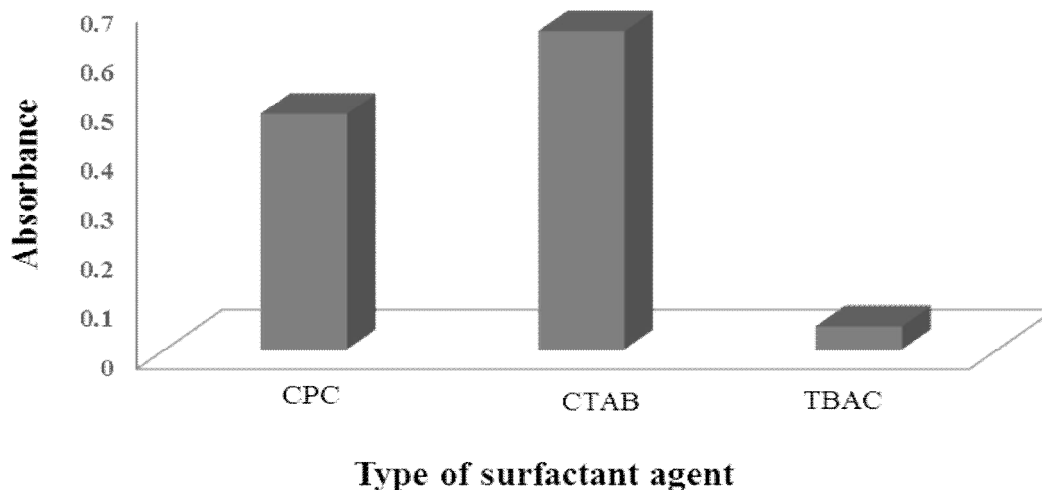


Fig. 5. The effect of surfactant on the extraction of $10 \mu\text{g l}^{-1}$ aluminum. Extraction conditions: sample volume, 10.0 ml; pH ~ 3.5 ; extraction solvent, 60 μl 1-undecanol; disperser solvent, 400 μl ethanol; concentration of surfactant, 2.0×10^{-5} M; concentration aluminum 2.0×10^{-5} M; $n = 3$.

Effect of Sample Volume

In the method development, the sample volume is a dominant factor in demonstrating the capability of the method in the extraction of the low amount of analyte from a high sample volume, as well as showing the preconcentration factor [30]. Several experiments were performed by employing different sample volumes (5.0 to 12.0 ml) containing 0.05 μg of aluminum. The results revealed that the extraction was quantitative in the range of 5.0-10.0 ml and then the extraction efficiency decreases with a further increase in the sample volume. Thus, the volume of 10.0 ml was selected as an optimum sample volume. Based on the final volumes of the organic phase (100.0 μl) and the aqueous phase (10.0 ml), an enrichment factor of 100.0 was calculated.

Interference Study

In order to investigate the selectivity of the method, the effect of common ions in real samples on aluminum extraction was studied. 10.0 ml of solutions containing 5.0 $\mu\text{g l}^{-1}$ of Al^{3+} and various amounts of coexisting ions with a mole ratio of 1000 were prepared and analyzed according to the developed method. The tolerance limit was defined as the maximum concentration of the ions causing a change of

less than 5% in the extraction efficiency. According to the results (Table 1), the extraction procedure was not affected by the presence of the cations and anions at the tested mole ratio which revealed high selectivity of the proposed method for separation/preconcentration of aluminium ions in presence of other ions.

Figures of Merit of the Method

The figures of merit of the developed method including detection limit, precision, and enhancement factor were determined by processing standard solution of Al^{3+} under optimum conditions, the results of which are tabulated in Table 2. The results (Table 2) revealed that the proposed method obeys Beer's law in the concentration range of 1.0-15.0 $\mu\text{g l}^{-1}$ of aluminium with the equation of calibration of $A = 0.0944C + 0.0106$ and correlation coefficient of 0.9998. In this equation, A is the absorbance value and C is the concentration of Al(III) ($\mu\text{g l}^{-1}$) in the sample solution. The limit of detection based on $3S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration graph) was found to be 0.14 $\mu\text{g l}^{-1}$. The relative standard deviation (RSD) at 3.0 $\mu\text{g l}^{-1}$ of Al^{3+} was 1.8% ($n = 6$). The enhancement factor defined as the ratio of the slope of the calibration curve with and without preconcentration was

Table 1. Tolerance Limits of Interfering Ions in the Determination of $5 \mu\text{g l}^{-1}$ of Al^{3+} in Optimization Conditions

Coexisting ions	Foreign ion to analyte (mol ratio)	Recovery (%)
Cd^{2+}	1000	104.8 ± 1.7
Ca^{2+}	1000	105.0 ± 3.0
Fe^{2+}	1000	103.1 ± 2.7
Mn^{2+}	1000	104.5 ± 2.4
Zn^{2+}	1000	101.8 ± 3.3
Mg^{2+}	1000	102.6 ± 4.3
K^{+}	1000	100.9 ± 1.6
Ag^{+}	500	99.5 ± 3.5
Cr^{3+}	500	103.3 ± 2.6
Pb^{2+}	500	105.0 ± 1.7
Ni^{2+}	500	105.0 ± 2.7
Cu^{2+}	200	106.3 ± 2.0
Co^{2+}	200	103.5 ± 4.0
Fe^{3+}	100	95.6 ± 2.1
Cl^{-}	1000	103.5 ± 2.3
CO_3^{2-}	700	104.7 ± 2.0
SO_4^{2-}	500	104.0 ± 3.0
F^{-}	40	96.5 ± 3.4

95.4 which is close to the preconcentration factor of 100 indicating that the extraction is quantitative (> 95).

Determination of Aluminum in Real Samples

In order to show the capability of the developed extraction method in the analysis of real samples, the concentration of Al^{3+} in well water, mineral water, tap water, black and green tea was determined (Tables 2 and 3). The accuracy of the method was determined through recovery experiments as well as comparing the results with

data obtained by independent analysis of electrothermal atomic absorption spectrometry (ETAAS). The results revealed that quantitative recovery of aluminum (95.0-103.3%) is possible with the samples type examined. The well agreement between the results of analysis by the developed method with those of ETAAS further confirmed the accuracy and reliability of the method.

Comparison with other Methods

The analytical performance of the developed method

Table 2. Determination of Aluminium in Water Samples

Sample	Added ($\mu\text{g l}^{-1}$)	Found ^a ($\mu\text{g l}^{-1}$)	Recovery (%)	GFAAS** ($\mu\text{g l}^{-1}$)
Mineral water	-	8.3 ± 0.1	-	8.4 ± 0.3
	3	11.2 ± 0.3	96.7	
	6	14.2 ± 0.2	98.3	
Tap water	-	3.5 ± 0.1	-	3.4 ± 0.1
	3	6.6 ± 0.2	103.3	
	6	9.6 ± 0.1	101.7	
Well water	-	4.6 ± 0.5	-	4.4 ± 0.2
	3	7.5 ± 0.6	96.7	
	6	10.3 ± 0.9	95.0	

^aMean and standard deviation relative to tree determination.

Table 3. Determination of Aluminium in tea Samples

Sample	Added ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$) ^a	Recovery (%)	GFAAS ($\mu\text{g g}^{-1}$)
Black tea	-	181 ± 4	-	179 ± 8
	50	230 ± 7	98.0	
	80	259 ± 6	97.5	
Green tea	-	243 ± 5	-	247 ± 9
	50	292 ± 3	98.0	
	80	322 ± 4	98.8	

^aMean and standard deviation of three independent analyses.

was compared with some previously reported extraction techniques for spectrophotometric determination of aluminum (Table 4). As it is observed, the developed method provides a higher enrichment factor and consequently lower limits of detection and quantification than other reported methods.

CONCLUSIONS

In this work, a simple, cheap, and fast DLLME–SFOD method combined with inexpensive spectrophotometry instrument was developed for the extraction and determination of ultra-trace amount of Al(III) in water and

Table 4. Comparison of the Developed Method with other Previously Reported Preconcentration Methods for Spectrophotometric Determination of Aluminium

Method	Chelating agent	LOD ($\mu\text{g l}^{-1}$)	RSD (%)	PF or IF	Ref.
SPE	Aluminon	0.52	2.65	83.3	[16]
CPE	Chrome Azurol S	0.52	2.85	40.3	[18]
Ss-LLME	8-Hydroxyquinoline	0.16	0.3	30	[19]
DLLME	Quercetin	2.0	0.2	26	[20]
UA-IL-ME	Quinalizarine	1.7	2.8	-	[30]
CPE	Chrome Azurol S	3.0	-	50	[31]
CPE	Eriochrome Cyanine R	10	2.2	7	[32]
This work	Aluminon	0.14	1.8	100	This work

LOD: preconcentration factor; RSD: relative standard deviation; PF: preconcentration factor; IF: Improvement factor; Ss-LLME: supramolecular solvent based liquid-liquid microextraction; SPE: solid phase extraction; DLLME: dispersive liquid-liquid microextraction; UA-IL-ME: ultrasound-assisted ionic liquid based microextraction.

tea samples. The main advantages of the developed method are low cost, an environmentally friendly process due to the low consumption of the organic solvent, high preconcentration factor, excellent precision and accuracy, high selectivity, and sensitivity with UV-Vis spectrophotometry apparatus. In addition, the employed method compared with all other separation/preconcentration methods for spectrophotometric determination of aluminum (Table 4) exhibits promoted preconcentration factor and detection limit.

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