Determination of Trace Aluminum with Eriochrome Cyanine R after Cloud Point Extraction

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Abstract: Cloud point extraction (CPE) methodology and using surfactant cetyltrimethylammonium bromide (CTAB) as extractant was applied as a preconcentration step for determination of ultra-trace amounts of Al"" ion in tap and well water samples. Linearity for Al"" was obeyed in the range of 0.2-20.0 ng mL^-1. The detection limits for the determination of Al"" was 0.05 ng mL^-1. The interference effect of some anions and cations was also studied. The method was applied to the determination of Al"" in real samples.

Key words: Cloud point extraction · Al"" ion · Eriochrome cyanine R (ECR)

INTRODUCTION

Aluminium is recognised as an important toxic substance causing considerable morbidity and mortality, particularly in patients with chronic renal failure. The toxicity of aluminum is governed by its bioavailability [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, 3].

Human beings are exposed to aluminum from several sources such as atmospheric air, 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 [4-6].

Many methods for the assay of aluminum exist including atomic absorption spectrometry (AAS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], electro thermal atomic absorption spectrometry (ET-AAS) [9] and kinetic-Spectrophotometry [10]. However, AAS and ICP-AES are expensive and require skilled operators. Other methods either are time-consuming and labor intensive, or use hazardous chemicals such as chloroform, methyl isobutyl ketone which are harmful to humans and create waste disposal problems. In comparison, spectrophotometric determination has a great attraction for its simplicity, low cost, high sensitivity and sometimes its selectivity.

Cloud-point extraction (CPE), based on the clouding phenomena of surfactants, has become more and more attractive. In CPE, the selective separations can be achieved owing to the fact that the micellar aggregates have a size that prevents them from crossing certain ultrafiltration membranes. This, together with the capacity of micelles to solubilise different compounds, has been used for the separation of nitrates from underground water using cellulose membranes and the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) [11, 12]. CPE offers many advantages over traditional liquid-liquid extraction such as low cost, safety and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors [13]. Recently micelle-mediated phase preconcentration method for preconcentration of ultra-trace quantities of some cations as a prior step to its determination by spectrophotometry has been developed [14, 15].

The main goal of the present work is to propose a method for the spectrophotometric determination of aluminum after preconcentration in a simple cloud point extraction process. The method is based on the color reaction of aluminum with ECR and CTAB as extraction agent showed good sensitivity and selectivity.

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Experimental

Apparatus: A Jenway 6405 UV-Vis spectrophotometer was used for recording absorbance spectra. Absorption measurements at \( \lambda_{\text{max}} \) were performed with 1-cm quartz cell (750 \( \mu \)L). A Metrohm pH meter (model 713) with a combined glass electrode was used for pH measurements. A centrifuge with 10-mL calibrated tubes (Superior, Germany) was used to accelerate the phase separation process.

Reagents: Analytical-grade reagents and deionized doubly distilled water were used. A 1.000 g L\(^{-1}\) stock solution of Al\(^{3+}\) was prepared using Al(NO\(_3\))\(_3\)·3H\(_2\)O (Merck). Working standard solutions were obtained by appropriate dilution of the stock standard solution. A 4.0×10\(^{-4}\) mol L\(^{-1}\) ECR solution was prepared by dissolving an appropriate amount of ECR (Merck) in water. A 1.0 mol L\(^{-1}\) iodide solution in water was prepared. A 0.1% CTAB solution in water was prepared. Acetate buffer solution of pH 5.5 was prepared from 0.5 mol L\(^{-1}\) acetic acid and 0.5 mol L\(^{-1}\) sodium acetate solutions.

Procedure: An aliquot of the solution containing 2.0-200.0 ng of Al (III) ion was transferred into a 10 mL tube containing 0.1 mL of 1.2×10\(^{-4}\) mol L\(^{-1}\) ECR solution, 2.0 mL of pH 5.5 acetate buffer solution and 2.0 mL of 0.1% (w/v) CTAB solution. The solution was diluted to approximately 8 mL with water and allowed to stand for 10 min at room temperature. Then 2.0 mL of 1.0 mol L\(^{-1}\) KI solution was added and made up to the mark with water. Separation of two phases was accelerated by centrifuging for 5 min at 3000 rpm. The aqueous phase could be separated by inverting the tube. The surfactant-rich phase of this procedure was dissolved and diluted to 300\( \mu \)L with ethanol and transferred into a 750 \( \mu \)L quartz cell. The absorbance of the solution was measured at 595 nm. A blank solution was also prepared in the same way except that distilled water was used instead of aluminum solution. The blank solution was submitted to the same procedure and its absorbance was measured at 595 nm. The difference between the absorbance of the blank and sample solutions (\( \Delta \)A) was then calculated.

RESULTS AND DISCUSSION

ECR behaves as a bi-dentate (N, O) univalent ligand to form chelates with several metal ions including Al\(^{3+}\) ions. Molar absorptivity of ECR and Al-ECR systems are 2.06×10\(^4\) L mol\(^{-1}\) cm\(^{-1}\) (494 nm), 1.11×10\(^4\) L mol\(^{-1}\) cm\(^{-1}\) (533 nm) and 6.50×10\(^4\) L mol\(^{-1}\) cm\(^{-1}\) (533 nm) while molar absorptivity for Al-ECR complex in surfactant media is 1.19×10\(^4\) L mol\(^{-1}\) cm\(^{-1}\) (584 nm). Surfactants can interact with dye and/or the metal-dye complex as an individual molecule or aggregates. For example, cationic surfactants react by ion pair formation with the anionic Al (ECR), to form a ternary complex involving surfactant monomers [16]. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 595 nm.

Effect of pH: The effect of pH on the extraction of Al\(^{3+}\) complex is shown in Figure 1. It was found that in the pH range 2.5-8, extraction was quantitative. Complex shows the maximum absorption at pH 5.5. In higher pH due to probable hydroxide precipitation and at lower pH because of ligand protonation decrease in sensitivity will be observed. Therefore, pH 5.5 was chosen for subsequent experiments.
Fig. 3: Effect of CTAB concentration on signal of Al (III)-BPR complex Conditions: 5.0 ngmL⁻¹ Al (III); 0.2 mol L⁻¹ KI; 1.2×10⁻⁵ mol L⁻¹ ECR; pH=5.5.

Effect of Eriochrome Cyanine R Concentration: For this study, 10 ml of a solution containing 5.0 ng mL⁻¹ Al (III) in 0.02% (w/v) CTAB with various amounts of eriochrome cyanine R was subjected to the cloud point preconcentration process. The results showed (Figure 2) that the sensitivity of the method increased by increasing ECR concentration up to 1.00×10⁻⁴ mol L⁻¹ and remained constant at higher concentrations. Therefore, 1.20×10⁻³ mol L⁻¹ of ECR was used in our experiments.

Effect of CTAB Concentration: Effect of CTAB concentration on the extraction and determination of Al³⁺ was investigated in the range 0.003-0.03% (w/v). The results are shown in Figure 3. The amount of the absorbance for the sample increased by increasing CTAB concentration up to 0.02% (w/v) and remained constant at higher concentrations. Therefore, 0.02% (w/v) CTAB was chosen as the optimum.

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 0.0-0.8 mol L⁻¹. The absorbance for the sample increased by increasing in iodide concentration up to 0.1% (w/v) and remained constant at higher concentrations (Figure 4). Therefore, 0.2 mol L⁻¹ iodide was chosen as the optimum.

Interferences: In order to study the selectivity of the proposed method, we tested the effect of various cations and anions on the preconcentration and determination of 5.0 ngmL⁻¹ of Al³⁺ by the proposed method under the optimum conditions. Ca²⁺, Pb²⁺, Na⁺, Ba²⁺, Co²⁺, Ti⁴⁺, Mn²⁺, Zn²⁺, K⁺, Ni²⁺, Pd²⁺, Ag⁺, Cl⁻, Br⁻, I⁻, NO₃⁻, PO₄⁻ interfering in concentrations 500 times higher than the concentrations of Al(III). Interfering effect of Fe³⁺ and Cu²⁺ up to 500 ngmL⁻¹ was removed in the presence of 0.02 mol L⁻¹ ascorbic acid and 0.01 mol L⁻¹ L-histidine. The results are summarized in Table 1.

Characteristics of the Method: At the optimized conditions, the methodology was able to produce linear analytical fits in the concentrations ranging from 0.2 to 20.0 ng L⁻¹. This fit could be well represented by the following equation: A = 0.051 [Al(III) (ng L⁻¹)] + 0.006, r² = 0.9987. The limit of detection, estimated from three times the standard deviation of 10 measurements of the blank, was 0.05 ng L⁻¹. The RSD, calculated by taking 10 measurements of the 5.0 ng L⁻¹ Al (III) standard solution was 1.9%.

Table 1: Tolerance ratios of diverse ions on the determination of 5.0 ngmL⁻¹ of Al (III)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Tolerance limit(ng mL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺, Pb²⁺, Na⁺, Ba²⁺, Co²⁺, Ti⁴⁺, Mn²⁺, Zn²⁺, K⁺, Ni²⁺, Pd²⁺, Ag⁺, Cl⁻, Br⁻, I⁻, NO₃⁻, PO₄⁻</td>
<td>500</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>500</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>500</td>
</tr>
</tbody>
</table>

*After addition of 0.02 M ascorbic acid.
*After addition of 0.01 M L-histidine.
Table 2: Determination of Al⁺ in water samples by the proposed method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (mg/L)</th>
<th>Found (mg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>0.50</td>
<td>0.52</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>9.97</td>
<td>99.7</td>
</tr>
<tr>
<td>Well water</td>
<td>0.50</td>
<td>0.46</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>10.0</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3: Comparison of the proposed method with other techniques reported in the literature for determination of aluminum

<table>
<thead>
<tr>
<th>Determination technique</th>
<th>LOD (μg mL⁻¹)</th>
<th>Linear range (μg mL⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLLME-SFO-ICP</td>
<td>0.8</td>
<td>1.0-250.0</td>
<td>8</td>
</tr>
<tr>
<td>CHAPS-coated C18 column</td>
<td>0.74-0.83</td>
<td>5.0-10000</td>
<td>18</td>
</tr>
<tr>
<td>CPE-GFAAS</td>
<td>0.09</td>
<td>-</td>
<td>19</td>
</tr>
</tbody>
</table>

*Limit of detection; †Dispersive liquid-liquid microextraction based on solidification of floating organic drop

Analysis of Real Samples: Water samples are analysed in order to evaluate the analytical applicability of the proposed method. The results are given in Table 2. In all cases the spike recoveries confirmed the reliability of the proposed method.

Table 3 compares LODs and linear range for proposed method with other methods for determination of aluminum [17, 18].

CONCLUSION

The use of micellar systems for the separation and for preconcentration of trace metals from aqueous solutions is easy, safe, rapid and inexpensive. CTAB was chosen for the formation of surfactant-rich phase due to low cloud point temperature, high density of the surfactant-rich phase which easily facilitates phase separation by centrifugation, availability and relatively low price, the lack of electroactive groups in its molecule and low toxicity. Furthermore, it does not have any absorption at 559 nm.

On the other hand, in addition to simplicity and low cost this method is comparable with some sensitive methods such as ET-AAS and ICP-MS for Al⁺ determination.

REFERENCES


