Separation and preconcentration of aluminium by float precipitate formation/flocculation and determination with flame atomic absorption spectroscopy

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ABSTRACT

In this study a new method based on formation of complex of aluminium with 1,2,5,8-tetrahydroxy anthraquinone, which is not water soluble. The insoluble precipitate was separated by filtering, then dissolved in acid and determined by atomic absorption spectrometry. The important variables such as pH, type, concentration and volume of acid, volume of ligand, foreign ions and volume of flocculent were optimized. In this method to obtain enrichment factor of 60, we can preconcentrate 200 mL of sample solution to 3 mL. The limit of detection for aluminium was 0.020 mg L^{-1} and standard deviation was below 7%. The proposed method was applied to the determination of trace aluminium in real environmental tap and well water samples with satisfactory results. In comparison with inductively coupled plasma optical emission spectrometry (ICP-OES), the result obtained shows that the method is accurate and gives good recoveries.
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INTRODUCTION

Aluminium is a ubiquitous element, widely distributed and constitutes approximately 8.8% of the earth's crust. Exposure is unavoidable because of the wide use of this element in industry and due to its toxic effects on plants, animals and humans it has been attended[1]. Aluminum is present in many manufactured foods and is also added to drinking water for purification purposes. Aluminium is a metal with considerable biological, environmental and industrial significance and, hence, sensitive, selective and precise methods are required for its determination in various matrices[2].

High aluminium amounts limit the input and the transport of the nutriments and influence negatively the cell division and cell-walls of the plants. The chronical effect of aluminum compounds is often connected with mortality of some animals and Alzheimer's disease, Parkinson's disease, Parkinson–Guam's disease, amyotrophic lateral sclerosis, diabetes and cancer[3]. Due to its low solubility in a solution under neutral conditions, Al was regarded for a long time as a nontoxic element and its environmental and biological effects were not investigated. When you fill a glass with water from your tap, you expect to drink water that is safe and pure but most water sources may be contaminated with pesti-

cides, and heavy metals.

Aluminium is in category of Secondary Drinking Water Standards, and its contamination level in drinking water is in the range of 0.05-0.20 mg L^{-1} (Secondary Standards are guidelines for water treatment plant operators and state governments attempting to provide communities with the best quality water possible)[4]. While determination of high Al concentrations can be realized with no serious problem, reliable determination of its trace and ultratrace concentrations requires the development of advanced techniques for improving both, selectivity and also sensitivity for this analyte.

Analytical methods used for the determination of trace levels of aluminum include spectrophotometric determination[5,6], voltammetry[7], fluorimetry[8] atomic absorption spectrometry (AAS)[9,10], high performance liquid chromatographic[11,12] inductively coupled plasma optical emission spectrometry (ICP-OES)[13]. Despite the using advance instrumental techniques, trace quantities of metals analysis most often requires some form of separation and preconcentration methods to remove interfering matrices and to make ensure the level of analyte is detectable. However, these methods have the disadvantages of high cost of instruments and matrix interference.

The aim of the present work was the development of a new method based on precipitation/coagulation for the aluminium preconcntration and determination with atomic absorption spectrosccopy in water samples.

EXPERIMENTAL

Apparatus

In this study, a model 55B flame atomic absorption spectrometer (Varian, Australia) is used for the measurements of Al equipped with a hallow cathode lamp at a wavelength of 307.6 nm using an N$_2$O–acetylene flame. Determination of Al^{3+} ions was performed using a sequential inductively coupled plasma optical emission spectrometry (ICP-OES) model Vista PRO from Varian Company (Varian, Australia) coupled to V-groove nebulizer and equipped with a charge coupled device (CCD) detector. The pH was determined with a model MP230 TOLEDO METTLER, pH meter with a combined glass–calomel electrode. Filter paper No. 40 (pore size 8.0 micrometer) was prepared from Whatman (England).

Reagents

All experiments are performed with high-purity grade chemicals and solvents. HCl, HNO3, CH3COOH, H2SO4 and reagent grade 1,2,5,8-tetrahydroxy anthraquinone (quinalizarine) prepared from Merck (Darmstadt, Germany) and was used as received. An appropriate of quinalizarine was dissolved in acetone to obtain a solution of 1000 mg L^{-1}. A standard solution of Al^{3+} (1000 ppm) and nitrate or chloride salts of other cations were prepared from Merck. Flocculent AN2 was prepared from NASCO (USA, Washington DC)

General procedure

To 50 mL of solution containing 2.0 mg L^{-1} aluminium ion, 0.7 mL of quinalizarine (except otherwise stated) at pH = 6.0 (except otherwise stated) was added. The resultant solution heat on a water-bath at 60 ℃ for one hour. At this time, aluminium precipitates and floats on surface of vessel. Then 0.5 mL of flocculent was added and solution was cooled in room temperature and filtered with filter paper No. 40. After filtration, precipitate was dissolved in 5 mL of acid and determined with FAAS.

RESULTS AND DISCUSSION

Quinalizarine has extractive properties and has frequently been used as a reagent for liquid–liquid extraction and spectrophotometric determination of cations. Quinalizarin is a hydroxyl anthraquinone reagent which has been used as a colorimetric reagent for determination of Be, Al, Mg, Cu and B. Some primary experiment shows that Al^{3+} precipitate with quinalizarine and can dissolve in acidic medium after separation. We used flocculent for coagulation of precipitate (Flocculation is used to describe the removal of a sediment from a fluid and flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles). Some parameters that affect precipitation/coagulation process were investigated.

The effect of type, concentration and volume of acid

According to chemical structure of aluminium-quinalizarin, for dissolvation of Al^{3+} precipitate HCl, HNO$_3$, CH$_3$COOH and H$_2$SO$_4$ were investigated. The

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results show that 5 mL of 1.0 M HNO_3 can release Al^{3+}, quantitatively and other acids can not release Al^{3+} quantitatively. Thus 1.0 M HNO_3 used for further experiments (Figure 1). Due to the volume of HNO_3 has influence on preconcentration factor, the volume of the eluent must be as low as possible to achieve the highest enrichment factor. For this purpose, precipitate obtained from 50 mL of solution containing 2.0 mg L^{-1} of Al^{3+} element at pH = 6.0 dissolved with 1-5 mL 1.0 M HNO_3, separately. The results are seen in the Figure 2. As you can see, at least 3 mL of 1.0 M HNO_3 is need to dissolved precipitate, completely.
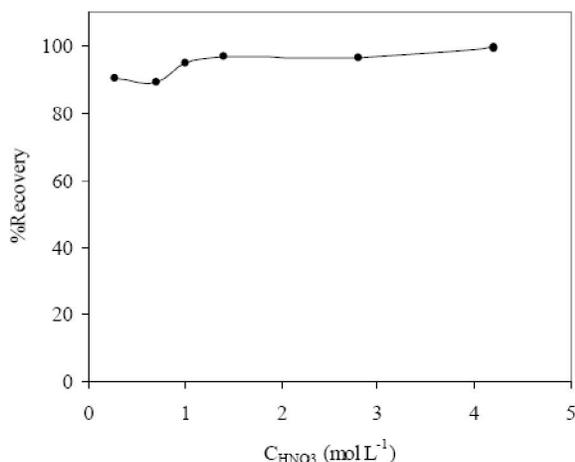

Figure 1 : Effect of concentration of HNO_3 on recovery of Al^{3+} ions. Conditions: 50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions precipítate with 0.7 mL of 1000 mg L^{-1} quinalizarine at pH = 6.0 and redissolved in 5 mL of HNO_3.
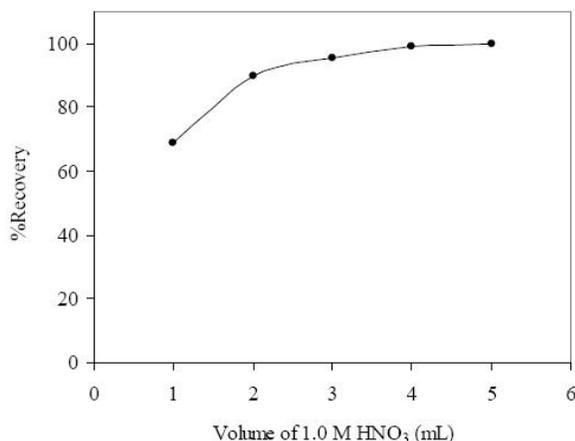

Figure 2 : Effect of volume of 1.0 mol L^{-1} HNO_3 on recovery of Al^{3+} ions. Conditions: 50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions precipítate with 0.7 mL of 1000 mg L^{-1} quinalizarine at pH = 6.0 and redissolved in 1.0 mol L^{-1} HNO_3.

Effect of pH

The effect of pH on separation process (precipita-

tion/coagulation) was investigated in the range of 1-9. As you can seen from Figure 3, the precipitate formed only in the range of 4-6.5, and maximum recovery for aluminium obtained at pH = 6-6.5 and aluminium–quinalizarine precipitate was not formed at lower pH (< 6) and higher pH (>6.5). Quinalizarin exhibits an acid-base indicator behavior—orange in acidic form (neutral), blue in mild base (deprotonation of one hydroxyl group occurs) and purple in strong base (deprotonation of two hydroxyl groups occur). In acidic solution, aluminium can not formed precipitate due to proton competition and in alkaline solution deprotonation of hydroxyl groups cause to dissolve Quinalizarin and precipitate was not formed.
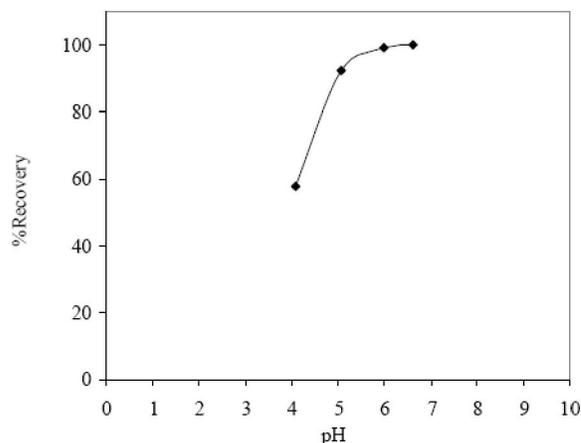

Figure 3 : Effect of pH on recovery of Al^{3+} ions. Conditions: 50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions precipítate with 0.7 mL of 1000 mg L^{-1} quinalizarine in appropriate pH and redissolved in 5.0 mL of 1.0 mol L^{-1} HNO_3.

Effect of amount of ligand

According to Loshatle–law it is necessary to use excess reagent in equilibrium reaction. For this purpose amount of quinalizarine varied from 0.2-2 mL of solution containing 1000 mg L^{-1} for precipitation of 50 mL of solution containing 2.0 mg L^{-1} of Al^{3+}. The results shown aluminium ion precipitation is complete in studied range of quinalizarine (Figure 4). For precipitation of an aluminium the multiplication of aluminium and quinalizarine must be higher than precipitation constant. This results show the concentration of quinalizarine must be above the concentration need to precipitation constant.

Effect of amount of flocculent

According to the IUPAC definition, flocculation is "a process of contact and adhesion whereby the par-

ticles of dispersion form larger-size clusters." Flocculation is synonymous with agglomeration and coagulation. In colloid chemistry, flocculation refers to the process by which fine particulates are caused to clump together into floc. The floc may then float to the top of the liquid, settle to the bottom of the liquid, or can be readily filtered from the liquid. The precipitate formed from Al^{3+} and quinalizarine is colloidal and must be aggregate. By using as flocculent these colloids form large size precipitate and float on surface of solution. For study of this effect we add different volume of flocculent to solution following precipitate formation. The results show flocculent has no effect on recovery of Al^{3+} and only facile coagulation (Figure 5).
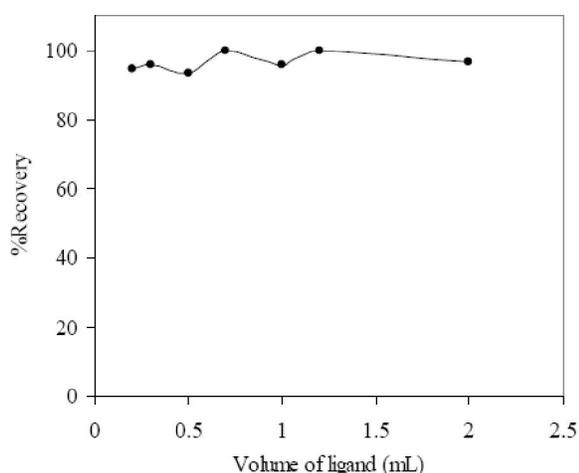

Figure 4 : Effect of ligand volume on recovery of Al^{3+} ions. 50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions precipítate with quinalizarine at pH = 6.0 and redissolved in 5.0 mL of 1.0 mol L^{-1} HNO_3.
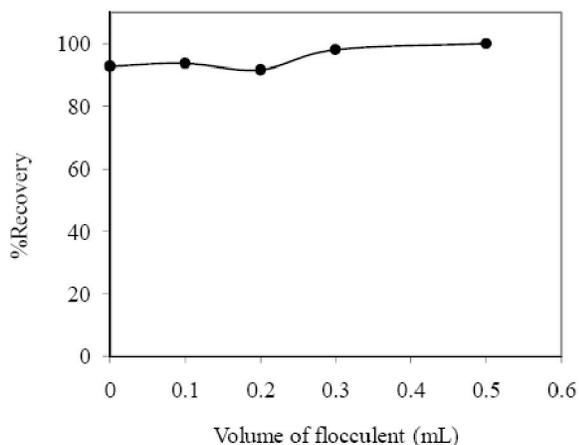

Figure 5 : Effect of amount of flocculent on recovery of Al^{3+} ions. 50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions precipítate with 0.7 mL of 1000 mg L^{-1} quinalizarine at pH = 6.0 and redissolved in 5.0 mL of 1.0 mol L^{-1} HNO_3.

Interference effect and analytical performance

To confirm that major matrix components of natural water an interference study was carried out by quantifying the effect of the presence of several metal ions on percentage recovery of Al^{3+}. To perform this study, 50 mL solution containing 2.0 mg L^{-1} of Al^{3+} and interfering ions at 50 mg L^{-1} level were subjected to the complete procedure. The results obtained showed that presence of other ions cannot affect precipitation of Al^{3+}, significantly (TABLE 1) and we can use this method for preconcentration of Al^{3+} in aqueous samples. The calibration graph using the preconcentration system for Al^{3+} was linear with a correlation coefficient of 1.0000 at 0.06–5 mg L^{-1}. The limit of detection (LOD) and the limit of quantification (LOQ) was 0.020 and 0.060 mg L^{-1}, respectively, with at least a preconcentration factor of 60 (200 mL sample used and preconcentrated to 3 mL with proposed method) and a relative standard deviation (R.S.D.) lower than 7%. The limit of detection for aluminium was 0.020 mg L^{-1} and standard deviation was below 7%. The proposed method was applied to the determination of trace aluminium in real environmental tap and well water samples with satisfactory results. In order to evaluate the validity of analytical data, known amounts of Al were added to known volume of samples (add-found method). The results given in TABLE 2 are in good agreement with those obtained by ICP–OES and add-found method.

TABLE 1 : Effect of interference ions on determination of Al^{3+} ions with proposed method. (50 mL of sample solution containing 2.0 mg L^{-1} of Al^{3+} ions and 50 mg L^{-1} of other ions was taken).

Foreign ion	Ratio of foreign ion to Al^{3+} ion (w/w)	% Recovery
Cu (II)	25	95
Zn (II)	25	98
Co (II)	25	97
Mn (II)	25	93
Ni (II)	25	97
Pb (II)	25	95
Ca (II)	25	98
Cr (II)	25	97
Fe (III)	25	91
Na (I)	25	93
K (I)	25	96

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TABLE 2 : Determination of Al^{3+} ion in water samples (100 mL) with the proposed method.

Sample	Amount of Al^{3+} (μg L^{-1})		
	Added	Found	Detected by ICP-OES
Tap Water (Tehran)	-	244	255
	500	735	750
Well Water (Tehran)	-	321	330
	404	710	725
Well Water (Gillan)	-	336	341
	420	750	742
Well Water (Gazvin)	-	270	264
	300	550	555

CONCLUSION

In this study, the method was found a simple, inexpensive, easy to operate for separation/preconcentration and determination of trace amount of aluminium with satisfactory results. The method use Quinalizarin as a selective precipitating agent for Al^{3+} preconcentration and flame atomic absorption for detection.

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