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Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium ion

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Abstract

A simple and accurate spectrophotometric method for determination of trace and ultra-trace amounts of Al^{3+} ion in tap and wastewater sample has been described. Using the eriochrome cyanine R (ECR) in the presence of N,N-dodecyltrimethylammonium bromide (DTAB) as cationic surfactant spectrophotometric determination of Al^{3+} ion has been carried out. The Beer's law is obeyed over the concentration range of 4–400 ng mL^{-1} of Al^{3+} ion with the detection limits of 0.14 ng mL^{-1}, while the molar absorptivity of complexes is 1.19×10^5 L mol^{-1} cm^{-1}. The influence of type and amount of surfactant, pH, and amount of ligand on sensitivity of spectrophotometric method were optimized. The method has been successfully applied for Al^{3+} ion determination in real sample.
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1. Introduction

Aluminium compounds have anti-inflammatory and antibacterial activity and regulate lipid metabolism in the organism. It is recognized as an important toxic substance causing considerable morbidity and mortality, particularly in patients with chronic renal failure. Diseases that have been associated with aluminium include dialysis dementia, renal osteodystrophy and Alzheimer's disease, which have an effect on red blood cells, parathyroid glands and chromosomes.

The European Committee established that diluted dialysis fluids should not contain aluminium concentrations higher than $10 \mu g L^{-1}$ [1,2]. Aluminium was the most frequently investigated element due to its particular toxicity to patients with chronic renal failure, related to clinical disorders such as dematerializing osteodystrophy [3], dialysis encephalopathy [4] and aluminium-induced anemia [5].

GF-AAS and ICP-AES are accepted reference methods for determining total aluminium in natural waters. However, both methods suffer from serious matrix interferences. Moreover, the

equipment for GF-AAS or ICP-AES is much more expensive and the accurate determination of aluminium requires considerable expertise. Compared to ICP-MS, ICP-AES and Al-NMR methods, electrogravimetry and coulometric methods generally have moderate selectivity, sensitivity and speed, but strong buffering of some fixed pH is necessary to obtain reproducible data in polarography and voltammetric methods. Since the reduction of aluminium at the electrode in aqueous solutions is difficult, it cannot be easily determined by conventional voltammetry [6,7].

Nowadays, spectrophotometric methods due to advantages such as accuracy and good precision, low cost and simple operation have been applied for trace metal determination. Several reagents have been reported for the spectrophotometric determination of aluminium [8,9]. For this purpose, the widely used reagents are aluminon ($\varepsilon = 1.4 \times 10^4$ L mol^{-1} cm^{-1}), xylenol orange ($\varepsilon = 2.1 \times 10^4$ L mol^{-1} cm^{-1}), stilbazo ($\varepsilon = 1.8 \times 10^4$ L mol^{-1} cm^{-1}.), chlorophosphonazo I ($\varepsilon = 1.96 \times 10^4$ L mol^{-1} cm^{-1}.), and methylthymol blue ($\varepsilon = 1.9 \times 10^4$ L mol^{-1} cm^{-1}) [8]. These reagents do not have a high sensitivity. Although eriochrome cyanine R has high sensitivity ($\varepsilon = 6.5 \times 10^4$ L mol^{-1} cm^{-1}), it requires rigid control of pH and temperature [9]. In addition, for the reagents, such as chromeazurol S and pyrocatechol violet it is needed to use some surfactants for enhancement of selectivity and sensitivity

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Table 1
Characteristic performance of some reported spectrophotometric methods for aluminium determination

Ligand	I[a]	DL[b]	pH[c]	ε (L mol^{-1} cm^{-1})	λ_{max} (nm)	LR[d]	Reference
HNB	Cu^{2+}, Hg^{2+}, UO_2^{2+}, MO^{6+}, Co^{2+}, Ti^{4+}	–	5.5	1.66×10^4	569	0.03–1.6	[13]
CAS	–	5	5.7	1.34×10^5	625	0–0.4	[14]
PCV	–	3	–	–	–	3–10	[15]
PCV	–	–	–	6.4×10^4	710	–	[16]
PVP	NH_4^+, SO_4^{2-}, Bi^{2+}, Cu^{2+}, Fe^{3+}	–	4.75	1.70×10^4	510	–	[17]
BPR	–	1	–	–	623	0–0.3	[18]
PCV	–	3	5.5–10	8.9×10^4	587	–	[19]
CV	Be^{2+}, Cr^{3+}, V^{5+}, Zr^{4+}	–	–	1.50×10^3	615	0.27–54	[20]
				5.30×10^3	670		
VIAZ	–	0.5–3.5	5	1.27×10^4	375	–	[21]
AS	Be^{2+}, F^-, Zr^{4+}	–	–	2.15×10^4	567.5	0–1200	[22]
CPI	Zr^{4+}, Ti^{5+}	–	4–6	1.96×10^4	610	0.8	[8]
Morin	–	5.0	6.6–6.5	5.3×10^{-3}	421	0.01–5.0	[23]
TSN	Ni^{2+}, Zn^{2+}, Co^{2+}, Ga^{3+}, In^{3+}	4.0	54,600	479	0.005–1.079	–	[24]
ECR	No interferences	0.14	5	1.19×10^5	584	0.004–0.4	PW

PW: present work; HNB: hydroxynaphthol blue; CAS: chromeazurol S; CPI: chlorophosphonazo I; PVP: polyvinylpyrrolidone; CV: catechol violet; AS: azurol S; PCV: pyrocatechol violet; BPR: bromopyrogallol red; IAZ: 1-isonicotinoyl-2-salicylidenehydrazine; TSN: 2,2′,3,4-tetrahydroxy-3′-sulpho-5′-nitroazobenzene.

[a] Interference.
[b] Detection limit (ng mL^{-1}).
[c] Applicable pH range.
[d] Linear range (μg mL^{-1}).

of the methods [10,11]. Moreover, using reagents such as 8-hydroxyquinoline [10] and alizarin [9] some separation techniques like extraction are required. However, some of the problems of the method based on ECR are the serious interferences by Fe(III), Mn(II) and F$^-$, which widely exist in environment samples, and its sensitivity is not high enough to determine low concentrations of Al^{3+} ion. The characteristic performances of some spectrophotometric method for aluminium determination are presented in Table 1 [8,12–24].

Application of micelles in analytical chemistry involves the beneficial alteration of metal ion–ligand complex spectral properties via surfactant association. The surfactant has high capacity to solubilize an insoluble complex and/or ligands [25,26] by micellar solubilization or formation of ternary complexes containing surfactant monomers, which led to an improvement in sensitivity (molar absorptivity) and red shift (approximately 50–150 nm) [27,28] could be achieved.

The purpose of this work is to develop a sensitized and selective spectrophotometric method for trace and ultra-trace Al^{3+} ion determination in the presence of DTAB using ECR. The influence of some analytical parameters including pH, type and amount of surfactant, ligand concentration, and type of buffer were examined.

2. Experimental

2.1. Instrumentation

Absorbance measurements were carried out with a Perkin-Elmer UV–vis spectrophotometer EZ201. All pH measurements were made using pH meter Model 691 Metrohm and Titrionic model T23680 (SCHOTT Company) equipped with a combined glass–calomel.

2.2. Reagent and solution

All chemicals such as ECR, nitrate of Al^{3+}, hexamethylenetetramine buffer and other cations were of the analytical grade purchased from Merck Company. A 1% (w/v) solution of all surfactants (all from Merck) including sodium dodecyl sulphate (SDS), Triton X-100, Triton X-114, Brij 35, cetyltrimethylammonium bromide (CTAB), N,N-dodecyltrimethylammonium bromide (DTAB) was prepared by dissolving 1 g of surfactant in 100 mL volumetric flask while stirring.

2.3. Spectrophotometric titrations

Standard stock solutions of ligand (1.0×10^{-3} M) and the Al^{3+} ions (1.0×10^{-3} M) were prepared by dissolving appropriate and exactly weighed (with an accuracy of 0.0001 g) pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with deionized water. Working solutions were prepared by appropriate dilution of the stock solutions. According to the spectra reported in Fig. 1, titration of the ligand solution (9.1×10^{-5} M, 2.75 mL) at pH 5 (using hexamethylenetetramine buffer) was carried out by the addition of microliter amounts of a concentrated standard solution of the Al^{3+} ion solution (1.0×10^{-3} M) using a pre-calibrated microsyringe, followed by absorbance intensity reading at 25.0 °C at the related λ_{max}.

2.4. Potentiometric pH titrations

All potentiometric pH measurements were made on solutions in a 75-mL double-walled glass vessel using a Titrionic model T23680 equipped with a combined glass–calomel electrode. The temperature was controlled at 25.0 ± 0.1 °C by circulating water
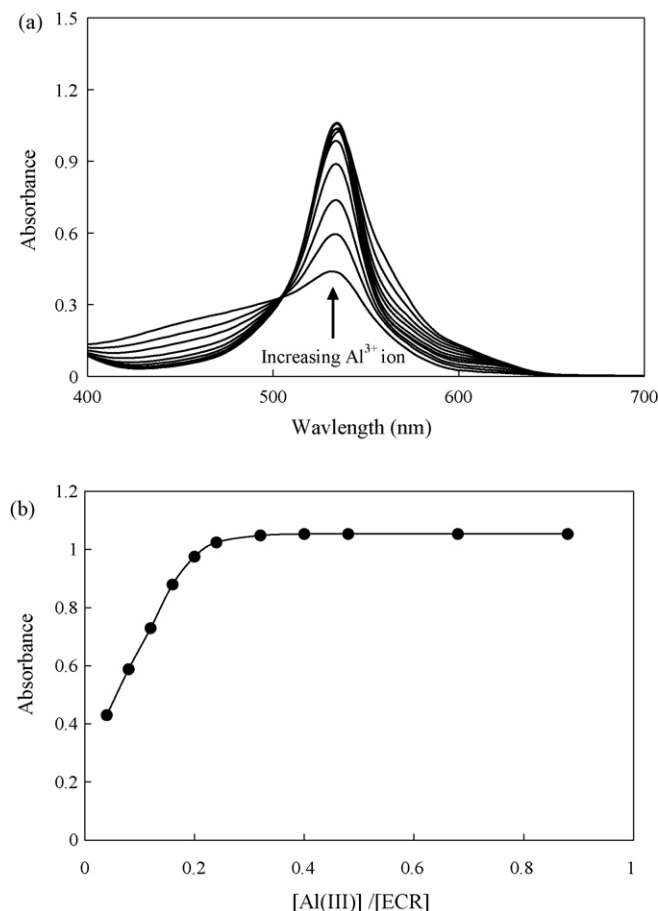
Fig. 1. (a) UV–vis spectra for titration of ECR (9.1×10^{-5} M, 2.75 mL) with Al^{3+} (1.0×10^{-3} M) in aqueous solution and adjust at pH 5.0 with hexamethylenetetramine buffer, $T = 25\,^{\circ}C$ and $I = 0.05$ M. (b) Corresponding mole ratio plot.

through the jacket, from a constant-temperature bath (homemade thermostat). The cell was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 20-mL capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. Atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. The concentrations of ECR were about 3.0×10^{-3} M, for the potentiometric pH titrations of ECR in the absence and presence of aluminium ions (1.0×10^{-3} M). A standard carbonate-free KOH solution (0.099 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KNO_3. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligands' protonation constants and their aluminium complexes, stability and hydrolysis constants were evaluated using the program BEST described by Martell and Motekaitis [29]. The value of $K_w = [H^+][OH^-]$ used in the calculations was $10^{-13.78}$ [30].

2.5. Pretreatment of real samples

Analysis of wastewater and spring water sample for determination of Al^{3+} ions content was done as follows: 250 mL of sample was poured in a beaker and 8 mL of 3 M HNO_3 solution

and 3 mL of H_2O_2 (30%) for elimination and decomposition of organic compound were added. While stirring, it heated to reach its volume to half. The organic content of sample was digested by illumination of sample for 1 h by a light pressure Hg lamp; after adjustment of sample's pH to the desired value, the spectrophotometric experiment was carried out. Amount of Al^{3+} ion in all of real and synthetic samples was found by standard addition method [31].

3. Results and discussion

3.1. Potentiometric study

According to our previous publications [32–34], the BEST program has been used for investigation of ECR–aluminium complexation system. It has been occurred to us that BEST program following potentiometric titration is an accurate and a powerful method for binary ligand–metal ions complexation [32–34]. In preliminary experiments, the fully protonated form of ECR was titrated with a standard KOH aqueous solution in order to obtain some information about their protonation constants.

The protonation constants ($K_n^H = [H_mL]/[H_{m-n}L][H^n]$, the charges are omitted for simplicity) were calculated by computer refinement of pH–volume data using the computer program BEST. The results are summarized in Table 2. ECR has both salicylic and p-quinomethide-2-carboxylic acid residues as potential coordination sites (called sites A and B, respectively). ECR has four acidic groups in aqueous solution. However, the zero proton level was chosen as the dicarboxylate (L) because of the very weak acidity of the salicylate –OH group. The phenolic proton in such systems usually has pK more than 12. As is obvious the most likely species in the case of ECR alone are LH (log $K_1 = 5.56$), LH_2 (log $K_2 = 2.85$) and LH_3 (log $K_3 = 2.15$).

In order to investigate the stoichiometry and the stability constant of the desired complex of Al^{3+} with ECR, known concentrations of ECR in the presence of the Al^{3+} ion (1:3 mole ratio) were titrated with a 0.099 M solution of KOH at a temperature of 25 °C and an ionic strength of 0.10 M maintained by KNO_3. The pH–volume data curves were used to calculate the equilibrium constants for the reactions between the Al^{3+} ion and ECR. The cumulative stability constant, β_{mlh}, is defined in Eq.

Table 2
Logarithm of overall stability constants assembling for the interaction of H^+ and Al^{3+} with the ECR at 25 °C and ionic strength of 0.1 M KNO_3

System	M	H	L	log β
LH	0	1	1	5.56
LH_2	0	2	1	8.41
LH_3	0	3	1	10.56
MLH	1	1	1	19.37
ML_2	1	0	2	20.56
ML_3	1	0	3	24.99
ML_3H	1	1	3	30.28
ML_3H_2	1	2	3	33.28
MLOH	1	−1	1	11.52
ML_2OH	1	−1	2	15.97

(1) (charges are omitted for simplicity):

$$mM + lL + hH \rightarrow M_m L_l H_h, \quad \beta_{mlh} = \frac{[M_m L_l H_h]}{[M]^m [L]^l [H]^h} \quad (1)$$
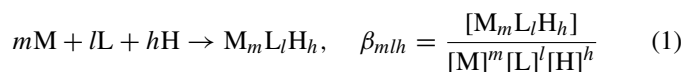
where M is the Al^{3+} ion, L the ECR, H the proton, and m, l and h are the respective stoichiometric coefficients. Since the ligands and complexes activity coefficients are unknown, the β_{mlh} values are defined in terms of concentrations. The errors are minimized by use of a high-constant ionic strength of 0.1 M and low ligand concentrations of 3.0×10^{-3} M. The results are shown in Table 2 and cumulative composition distribution curve are depicted in Fig. 1. In most species the cumulative stability ($\log \beta$) constants for the intersystem are MLH, ML_2, ML_3, ML_3H and ML_3H_2, ML(OH), ML_2(OH), 19.37, 20.56, 24.99, 30.28 and 33.28, 11.52, 15.97, respectively.

3.2. Spectrophotometric investigation

In the literature, it has been pointed out that the trivalent ions may substitute associatively as well as dissociatively as exemplified by iron-complexation, while the formation of a complex often is pictured as the substitution of coordinated water molecules by the incoming ligand by a dissociative process and the rate-determining step is rupture of the metal–water bond [35].

The ECR behaves as a bi-dentate (N, O–) univalent ligand to form chelates with several metal ions including Al^{3+} ions. The ECR is ionic and soluble in water at neutral pH. In preliminary experiments complexation between Al^{3+} ion and ECR was examined using spectrophotometric and potentiometric titration. A sensitive and sharp peak at about 535 nm (Fig. 1) indicates the strong interaction between the Al^{3+} and the ECR. The mole ratio plot was depicted in Fig. 1b. As it can be seen, a ML_3 complex could be formed which support the results represented earlier for Al–ECR system [36]. Our survey through literature revealed that the 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 1.19×10^5 L mol^{-1} cm^{-1} (584 nm) (Fig. 2).

Therefore, the addition of surfactant for increasing sensitivity is necessary. To confirm this idea, two similar solutions con-
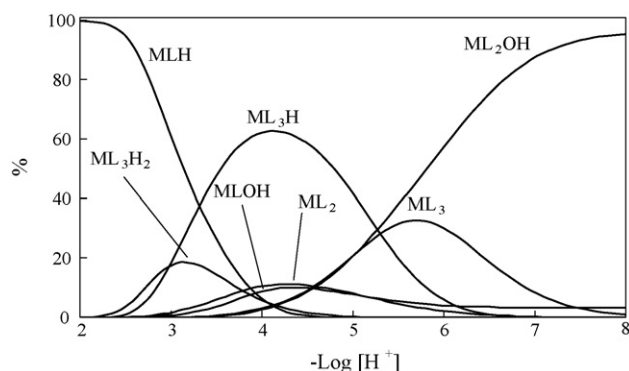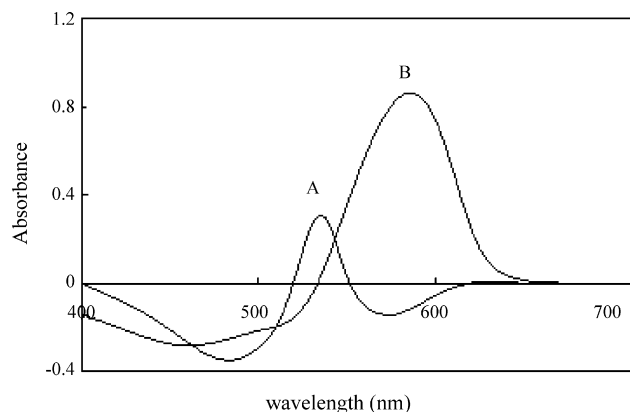

Fig. 3. Spectra of Al^{3+}–ECR complexes in the absence (A) and the presence (B) of DTAB. (A) 0.2 μg mL^{-1} Al^{3+}, 0.15 mM ECR, pH 5; (B) 0.2 μg mL^{-1} Al^{3+}, 0.15 mM ECR, 3.0 mM DTAB, pH 5.

taining 0.2 μg mL^{-1} Al^{3+} ion, 0.15 mM ECR in the presence and absence of 3.0 mM DTAB, which thier pH was adjusted with hexamethylenetetramine buffer (pH 5.0) has been performed. The respective spectra which are depicted in Fig. 3, indicate the experiment in surfactant media has higher sensitivity in short equilibrium time. It is mentioned that the system in the absence of surfactant at about 30 min reaches equilibrium, while by the addition of DTAB the system equilibrated less than 30 s.

3.3. Effect of pH on sensitivity

The variation of the absorbance of the aluminium–ECR–DTAB complex versus pH at 584 nm was investigated. The effect of pH on the determination of 2.0 μg of Al^{3+} (10 mL, 0.2 μg mL^{-1}) was studied by measuring the absorbance of desired complex in the pH range of 2.0–10.0 by introducing 0.15 mM of ECR in the 3.0 mM DTAB media. The results, which are presented in Fig. 4 display that Al(ECR)$_3$ in DTAB media complex showed the maximum absorption at pH 5. In higher pH, mixed complexes Al–ECR and OH$^-$ could be formed or due to probable hydroxide precipitation sensitivity will be decreased. On the other hand, at lower pH because of ligand protonation
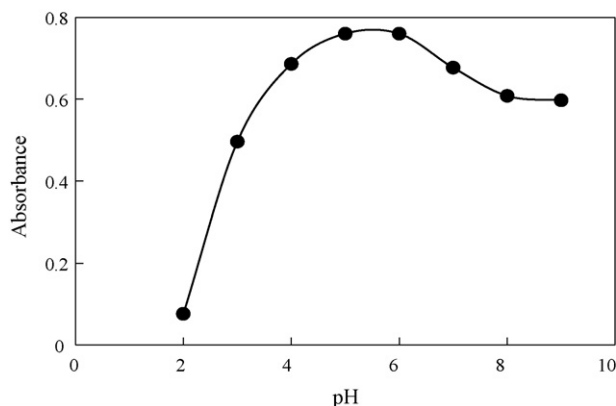

Fig. 2. Distribution curve of Al^{3+}–ECR system at 25 °C and μ = 0.1 M of KNO$_3$.

Fig. 4. Effect of pH on sensitivity of method (0.2 μg mL^{-1} Al^{3+}, 0.15 mM ECR and 3.0 mM DTAB in various pHs).

decrease in sensitivity will be observed. In subsequent work, pH 5 has been selected.

3.4. Effect of surfactant on sensitivity

Aluminium can be determined spectrophotometrically with ECR, but the method has several disadvantages including time consuming, need to rigid control of pH and temperature. On the other hand, the ECR shows considerable absorbance at the wavelength of maximum absorption of Al–ECR complex and the absorbance of complex varies considerably with pH, also the sensitivity of method is relatively low [37]. This disadvantage can be drastically reduced by addition of a cationic surfactant DTAB [38].

Cationic surfactants frequently shift the absorption peak of metal–dye complexes to longer wavelengths. The shift is usually accompanied by increase in molar absorptivity. The most widely accepted explanation for these effects is that positive charge on the surfactant micelles enhances the acid dissociation of the organic dyes, so that the formation of higher ligand:metal ratio complexes is made easier [39].

In the presence of $0.2\,\mu g\,mL^{-1}$ of Al^{3+} ion, $0.15\,mM$ of ECR and $3.0\,mM$ of (Brij 35 and Triton X-100 as nonionic, SDS as anionic surfactant, CTAB and DTAB as cationic surfactant), effect of type of surfactant on spectra and sensitivity were examined and results displayed in Table 3. For $3.0\,mM$ of DTAB media, the calibration curve with higher sensitivity and red shift could be constructed and its slope was more than other surfactants. In anionic surfactant a mentioned spectra for complexes could not be obtained. The higher sensitivity in the presence of cationic surfactant is an indication, that surfactant only led to aggregation of complexes and increase in sensitivity attributed to the electrostatic interaction. It seems that ECR combines with Al^{3+} ion to form a polar complex, which is extracted instantaneously into the local polar environment of micelle of cationic surfactant with a molar absorptivity of $1.19 \times 10^5\,L\,mol^{-1}\,cm^{-1}$ as ion pair formation and a ternary complex will be achieved. Since the concentration of the DTAB was somewhat less than micelle concentration, desired complex was homogenously dissolved in surfactant media.

A set of similar solution containing various concentrations of DTAB in the range of 1.62–3.89 mM adjusted at pH 5.0, were prepared and the absorbance of desired complex at concentration of $0.2\,\mu g\,mL^{-1}$ of Al^{3+} was investigated. The maximum absorbance was obtained when the concentration of DTAB was 3.0 mM.

Table 3
Effect of surfactant type on sensitivity of proposed method

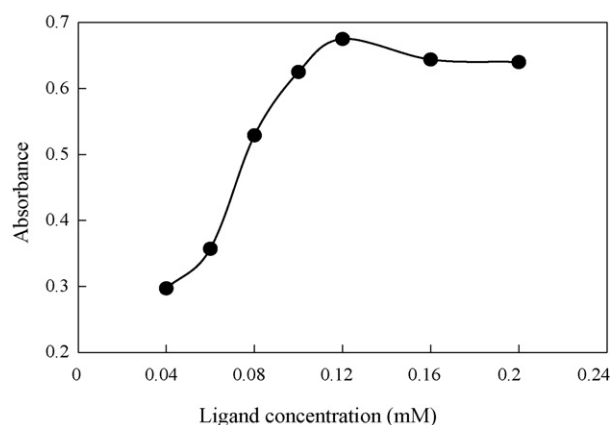| Surfactant	Absorbance	λ_{max} (nm)
No surfactant	0.31	535
CTAB	0.724	595
DTAB	0.798	584
Triton X-100	0.323	536
SDS	0.486	535
Triton X-114	0.414	535
Brij 35	0.412	535

Fig. 5. Effect of ECR concentration on sensitivity ($0.2\,\mu g\,mL^{-1}$ Al^{3+}, 3.0 mM DTAB, pH 5.0 and various concentrations of ECR).

3.5. Effect of ECR concentration on sensitivity

The concentration of ligand has a great effect on the absorbance of Al^{3+} as desired complex with ECR incorporated in the interior core of ad-micelle. It is known that Al^{3+} ion interact stoichiometrically with ECR to form a 1:3 complexes. Therefore, a set of similar experiments with various amounts of ECR at constant amount of DTAB and Al^{3+} ion were conducted and results are shown in Fig. 5. As it can be seen, in the case of the addition of the increased concentrations of ECR to aluminium solution, the absorbance of aluminium–ECR–DTAB complex increased and became constant in the ECR concentration up to 0.15 mM at 584 nm. For this reason, the present study was carried out with the 0.15 M of ECR concentration. Results display that ligand concentration must be exceed of Al^{3+} ion concentration to reach high sensitivity. Therefore, the ECR was added more than 200 times of Al^{3+} ion concentration to reduce fluctuation in measurement of absorbance. Order of addition of reactant is very important. This high amount of ligand with respect to Al^{3+} ion is an advantage of method for real sample analysis.

3.6. Calibration curve: an detection limit

A calibration curve was constructed at optimum conditions by conducting a set of similar experiment at various concentration of Al^{3+} ion and respective results are depicted in Fig. 6. The dynamic range of Al^{3+} ion was 4–$400\,ng\,mL^{-1}$, while the regression equation of correlation coefficient was 0.996. Based on the signals of 10 blank solutions and the slope of calibration curve, it was found that the detection limit was $0.14\,ng\,mL^{-1}$, which suitable the method for natural water sample with low level of aluminium ion.

In order to investigate reproducibility of the method, eight experiments under optimum conditions were carried out. The low R.S.D. of method (1.2%) is an indication of high reproducibility of proposed method. Consequently, the investigated method can be used for several times with high accuracy and precision.
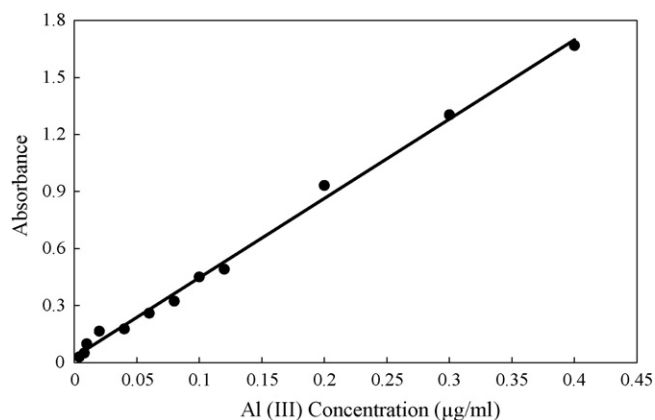
Fig. 6. Calibration curve of method at optimum conditions in 584 nm ($y = 4.173x + 0.029$, $R^2 = 0.996$).

3.7. Interference effect

The tolerance limit is defined as the ions concentration causing a relative error smaller than $\pm 5\%$ related to the absorbance of complex attributed to Al^{3+} ion. Therefore, various amounts of interfering ion were added to 0.2 $\mu g\,mL^{-1}$ of Al^{3+} ion solution at fixed optimized conditions of other variables and results are shown in Table 4. The determination of Al^{3+} ion was quantitatively with high accuracy and precision in the presence of large amount of alkaline and alkaline earth ions and some transition metal ions, which indicates method suitability for natural water analysis. Among the metal ions employed, Fe^{3+} and Cu^{2+} with a threshold concentration of 10-fold can cause increases of 5% in the signal of the Al–ECR–DTAB system, which successfully could be tolerated up to 500-fold after addition of 0.02 M ascorbic acid and 0.01 M L-histidine, respectively

3.8. Real samples—evaluation of method

We have explored the feasibility of the methodology using it for the determination of Al^{3+} ion in different matrices. To ensure that the method is valid and has reasonable accuracy and precision, recovery of the Al^{3+} ions in the wastewater, the tap water and synthetic sample were determined by these proposed techniques and the results which are shown in Table 5. The low relative standard deviations represent the high reproducibility in these measurements. Therefore, this proposed technique could be applied to the determination of $ng\,mL^{-1}$ level of Al^{3+} ion in real samples.

Table 4
Investigation of tolerance limit of interfering ions on proposed methods

Ion	Interfering ion/Al^{3+}ion
Co^{2+}, Zn^{2+}, Na^+, K^+, Pb^{2+}, Ba^{2+}, Mn^{2+}, Tl^+, Ca^{2+} Ni^{2+}, Mg^{2+}, Cr^{3+}, Ag^+, Hg^{2+}, Pd^{2+}, Cl^- Br^-, I^-, NO_3^-, PO_4^{3-}, CH_3COO^-, SO_4^{2-}	500
Fe^{3+} [a]	500
Cu^{2+} [b]	500

[a] After addition of 0.02 M ascorbic acid.
[b] After addition of 0.01 M L-histidine.

Table 5
Evaluating the accuracy and precision of method for analysis of real samples

Sample[a]	Added Al^{3+}	Founded Al^{3+}	R.S.D. (%)	Recovery (%)
Wastewater	0.0	12.2	0.8	–
	25.0	37.6	0.6	101.6
Tap water	0.0	5.2	0.9	–
	20.0	25.6	0.7	102.0

[a] Value is in $ng\,mL^{-1}$.

4. Conclusion

The spectrophotometric determination of Al^{3+} ion with ECR in surfactant media over other possibilities such as aluminon, quinolinol and eriochrome cyanine R has distinct advantages including rapid color development, sensitivity, use at room temperature, color stability, small consumption of material and simple experimental procedure. In addition to high selectivity, the studies with this reagent reported here relate to a general interest in developing field tests for rapid qualitative or semi-quantitative visual estimation of metal ions in natural samples such as soils and waters.

In comparison to the results presented in this paper with respect to other previously reported in Table 1, it can be seen that this method is superior to those in terms of selectivity [13,15,19,21], linear range [13,15,19,21], detection limit [14–16,22,23] and using the surfactant led to short equilibrium time.

It was demonstrated that the method could effectively be used with a simple UV–vis spectrophotometer, which allows a large number of samples to be generated on a day-to-day basis for environmental or industrial applications, such as soil analysis.

Acknowledgement

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