



Flotation-Spectrophotometric Method for the Determination of Aluminium ion Using Xylenol Orange

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Abstract: A simple, fast, reproducible and sensitive method for the flotation-spectrophotometric determination of Al^{3+} is reported. The apparent molar absorptivity (ϵ) of the ion associate was determined to be $8.35 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The calibration curve was linear in the concentration range of $1.0\text{-}50 \text{ ng mL}^{-1}$ of Al^{3+} with a correlation coefficient of 0.9997. The limit of detection (LOD) was 0.621 ng mL^{-1} . The relative standard deviation (RSD) at 10 and 30 ng mL^{-1} of aluminium were 1.580 and 2.410% ($n=7$) respectively. The method was applied for measuring the amount of aluminium in water samples.

Keywords: Flotation-spectrophotometric, Aluminium, Xylenol orange, Cetyltrimethylammonium bromide, Ion associate

Introduction

Aluminium has long been considered as virtually non-toxic and non-absorbable from the gastrointestinal tract. More recent studies on humans, however, expose its acute toxicity¹, including impaired memory, convulsions, characteristic EEG changes, uremia, shaver's disease (lung)², alzheimer's disease (brain)³ and also increased risks of cancer⁴ of the lung and pancreas and leukaemia. Aluminium at trace and sub-trace levels in the water used for dialysis can cause brain damage, bone disease and anaemia⁵. All these findings cause alarming concern in public health, demanding accurate determination of this metal ion at trace and sub-trace levels. Ternary complexes in which the central ion reacts with two different ligands, have aroused considerable interest in the past two decades⁶. Flotation-spectrophotometry of such colored ternary complexes probably provides the most sensitive, relatively simple and fast approach to trace metal analysis⁷. Ion association systems, in general way, could be said to result from the interaction of charged particles such as metal cations or complexes with oppositely charged ions. When quaternary ammonium containing

compounds are used, the primary complex produced is a cation, possessing the same charge as that of a metal. Such complexes were made to associate with anionic dyes in order to be extractable from aqueous solutions⁶. It should be mentioned that the term "flotation-spectrophotometric" is based on the fact that some ion associations are not soluble in polar organic solvents. Once both phases have been separated the precipitate is dissolved in an appropriate solvent and the corresponding measurements have been made by spectrophotometric methods^{8,9}.

Different preconcentration-spectrophotometric¹⁰⁻¹⁶ and electrochemical¹⁷ methods are used for trace quantitative determination of Al³⁺. Present paper shows a flotation-spectrophotometric method for (Al³⁺-XO)-CTA⁺ ternary ion-associate in to the interface between aqueous and *n*-hexane phase by flotation method. The effect of standing time, concentrations of surfactant, xylenol orange and salt on the flotation-spectrophotometric of aluminium has been studied in order to establish optimum conditions. The method proposed has been successfully applied for the determination of Al cation in different water samples.

Experimental

The absorption spectra were recorded on a Shimadzu model 160A UV-Vis. A Metrohm model 691 pH meter with a combined glass electrode was for pH measurements. Unless otherwise stated, all commercial reagents used were of analytical grades without further purification.

1000 µg mL⁻¹ stock solution of Al³⁺ was prepared by dissolving 3.4757 g of Al(NO₃)₃·9H₂O (Merck) in freshly distilled water and diluted to the mark in a 100 mL volumetric flask.

Stock solution of XO (1×10⁻⁴ mol L⁻¹) was prepared by dissolving 0.0067 g of XO (Fluka) in distilled water and diluting to 100 mL in a flask.

Stock solution of CTAB (1×10⁻³ mol L⁻¹) was prepared by dissolving 0.0364 g of CTAB (Merck) in distilled water and diluting to 100 mL in a flask.

Stock solution of NaCl (1×10⁻¹ mol L⁻¹) was prepared by dissolving 0.584 g NaCl in distilled water and diluting to 100 mL in a flask.

Phosphate buffer solution in the pH range of 6 was made by mixing 250 mL of 0.1 mol L⁻¹ solution of acid or salt with appropriate volumes of 0.1 mol L⁻¹ solution of sodium hydroxide. Different concentrations of hydrochloric acid and sodium hydroxide in the concentration range of 0.001-0.100 mol L⁻¹.

Recommended procedure

Transfer an aliquot of a sample solution containing 3 mL of 1 µg mL⁻¹ of Al³⁺ into a 100 mL volumetric flask, 6.0 mL of 1×10⁻⁴ mol L⁻¹ of XO, 3.0 mL of 1×10⁻³ mol L⁻¹ of CTAB, 2.0 mL of 1×10⁻¹ mol L⁻¹ of NaCl, diluted to the mark with distilled water, let stand for 3 min. Then transfer the flask content to a 100 mL separatory funnel containing 15 mL of *n*-hexane and shake vigorously the mixture for 50 s and then allow standing for 10 min for separation of organic phase from aqueous phase. The (Al³⁺-XO)-CTA⁺ ion associate (color solid) floats on the interface. After discarding the aqueous phase (below layer) add 2.5 mL of methanol to *n*-hexane solution containing adsorbed ion associate. The methanol phase extracts the solid ion associate from *n*-hexane phase and dissolves it completely. The absorbance of extracted colored ion associate was measured at 536 nm in 1 cm cells against a reagent blank. All the experiments were carried out at room temperature. The proposed procedure has been applied to the determination of Al³⁺ in water samples containing.

Quantitative results

A calibration graph for the determination of Al^{3+} was constructed under optimum experimental conditions described above. Beer's law was obeyed over the concentration range of 1.0-50 ng mL^{-1} of Al^{3+} with a correlation coefficient of 0.9997 at 536 nm. The regression equation obtained by the least square method is $A = 4.30 \times 10^{-3} C_{\text{Al}} + 0.0476$ for 1.0-5.0 ng mL^{-1} of Al^{3+} , where A is the absorbance and C_{Al} shows the concentration of Al^{3+} in ng mL^{-1} . With regard to the preconcentration factor of the process (40 fold, *i.e.*, from 100 mL aqueous solution to 2.5 mL of methanol) and a path length of 1 cm, the conditional molar absorptivity was $8.350 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the above wavelength. The relative standards deviation (RSD) for 10 and 30 ng mL^{-1} of Al^{3+} were 1.580 and 2.410% ($n = 7$), respectively. The limit of detection (LOD) was 0.621 ng mL^{-1} based on $3S_b$ ¹⁸. The method exhibits a good reproducibility. The stoichiometry of the ion pair was determined using the continuous variation method. The mol ratio of Al^{3+} : XO: CTA^+ in the ion associate was 1:1:1.

Results and Discussion

The preliminary investigation indicated that interaction of Al^{3+} with XO and CTAB can form a solid ion associate which is insoluble in aqueous and highly nonpolar organic phases, but soluble in some polar organic solvent such as methanol. The absorption spectra of the dissolved $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate in methanol showed a maximum absorbance at 536 nm.

Effect of pH

The influence of pH on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate was studied by varying the pH in the range of 2 to 11, before the organic phase addition. The pH was adjusted to the desired value using hydrochloric acid (0.001 mol L^{-1}). The maximum flotation was observed at $\text{pH}=6$, using phosphate buffer but decrease the absorbance of ternary ion associate. It must be mentioned that protonation of phosphate groups of the dye in pH values lower than 6 cause low $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate formation. The results are shown in Figure 1.

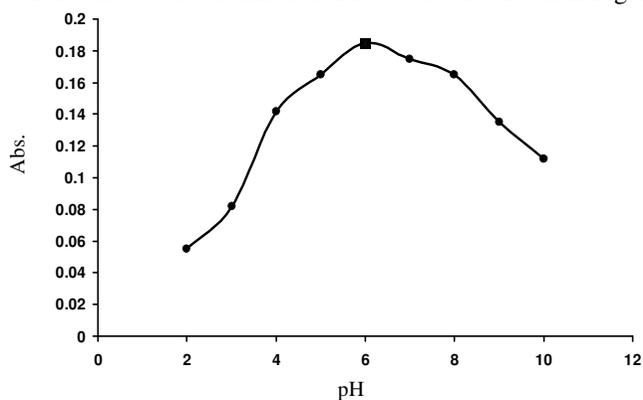


Figure 1. The effect of pH on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate. Conditions: 30 ng mL^{-1} Al^{3+} ; $6.0 \times 10^{-6} \text{ mol L}^{-1}$ XO; 3.0×10^{-5} CTAB; $\lambda_{\text{max}} = 536 \text{ nm}$

Effect of xylenol orange concentration

The effect of XO dye concentration used for the flotation of Al^{3+} was examined by varying the amounts of XO. The absorbance increased with increasing XO concentration up to $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of XO in the final solution and concentrations more than $6.0 \times 10^{-6} \text{ mol L}^{-1}$ have no effect on the flotation of the ion associate. The results are shown in Figure 2 and so $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of XO anionic dye for Al^{3+} flotation process.

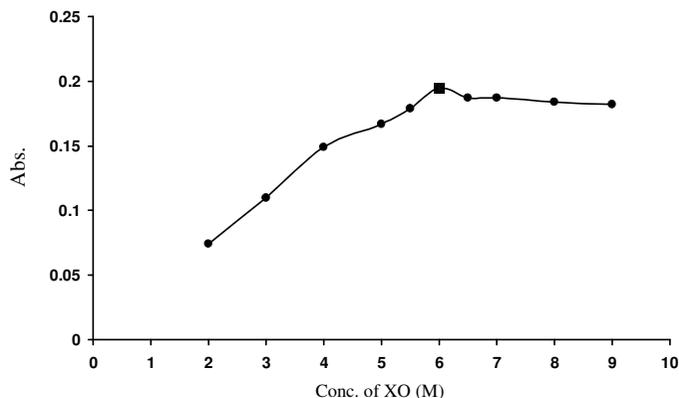


Figure 2. The effect of XO (1×10^{-6} M) dye concentration on the flotation of Al^{3+} Conditions: 30 ng mL^{-1} Al^{3+} ; 3.0×10^{-5} CTAB; $\text{pH} = 6$; $\lambda_{\text{max}} = 536 \text{ nm}$

Effect of CTAB concentration

The effect of CTAB concentration used for the flotation of Al^{3+} was examined by varying the amounts of CTAB surfactant. The absorbance of ternary ion associate increased with increasing CTAB concentration up to $3.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution and decreases at more concentrations. $3.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution was chosen as the optimum concentration of CTAB for Al^{3+} flotation process. The results are shown in Figure 3. It must be mentioned that higher concentration than $3.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution causes an increase in the blank absorbance and decreases the absorbance of ternary ion associate.

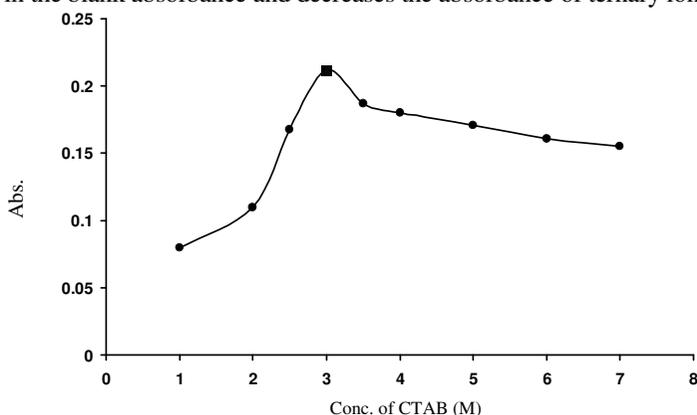


Figure 3. The effect of CTAB (1×10^{-5} M) concentration on the flotation of Al^{3+} (Conditions: 30 ng mL^{-1} Al^{3+} ; $6.0 \times 10^{-6} \text{ mol L}^{-1}$ XO; $\text{pH} = 6$; $\lambda_{\text{max}} = 536 \text{ nm}$).

Effect of NaCl concentration

The effect of electrolyte concentration on the formation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ternary ion associate was examined by various amounts of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of NaCl solution. The results showed that the absorbance of ion associate increases with increasing NaCl concentration up to $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of NaCl in the final solution and remains constant at higher concentration of electrolyte (salting out). A constant concentration of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of NaCl was used throughout as optimum electrolyte concentration. The results are shown Figure 4.

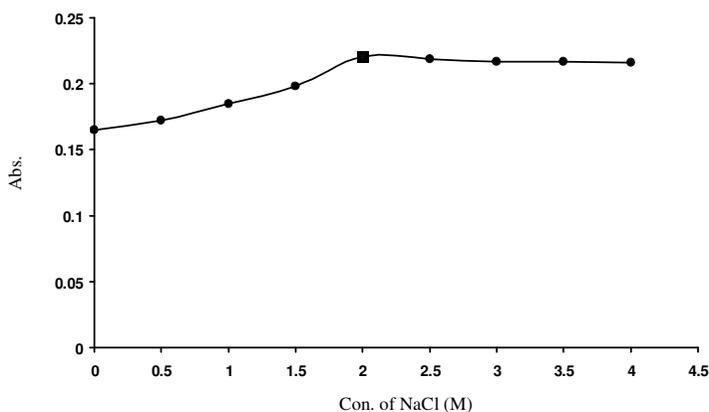


Figure 4. The effect of NaCl (1×10^{-3} M) concentration on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate (Conditions: $30 \text{ ng mL}^{-1} \text{ Al}^{3+}$; $6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ XO}$; $3.0 \times 10^{-5} \text{ CTAB}$; $\lambda_{\text{max}} = 536 \text{ nm}$).

Effect of n-hexane volume

Among organic solvents tested (cyclohexane, carbon tetrachloride, dimethylformamide, methyl ethyl ketone and *n*-hexane), *n*-hexane showed good characteristics as a flotation dissolvent. Since the ion associated solid floats at the *n*-hexane-water interface and adheres on the funnel wall, the aqueous phase can be easily discarded completely and the *n*-hexane in the separation funnel can be immediately used cyclically without any treatment.

The volume effect of the *n*-hexane on the flotation process was examined in the range of 5-30 mL and the results showed that by increasing the volume of *n*-hexane the flotation process proceeds more effectively and have no effect on the flotation of Al^{3+} at volumes more than 15 mL. So, 15 mL was used as optimum *n*-hexane volume. The results are shown Figure 5.

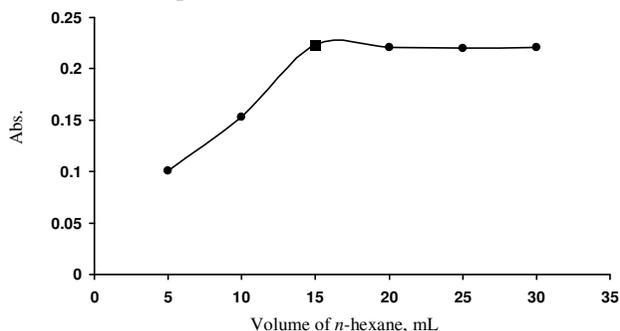


Figure 5. The Effect of *n*-hexane volume on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate Conditions: $30 \text{ ng mL}^{-1} \text{ Al}^{3+}$; $6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ XO}$; $3.0 \times 10^{-5} \text{ CTAB}$; $\lambda_{\text{max}} = 536 \text{ nm}$

Among organic solvents (Acetone, ethanol, methyl ethyl ketone, THF and methanol) examined to extract and dissolve the adhered ion associates from the wall of the separating funnel, dissolution of the ion associate with methanol is almost perfect.

Effect of shaking and standing time

The effect of standing time on the formation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ternary ion associate was studied over the time period 5-20 min for 30 ng mL^{-1} of Al^{3+} , $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of XO, $3.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB and $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of NaCl concentration at optimum pH (pH=6)

of solution and then by measuring the absorbance at 536 nm after flotation. The maximum absorbance was obtained at 10 min. The results are shown Figure 6. The standing time required in the proposed method is only 10 min while the standing time required for other procedures are higher¹⁹.

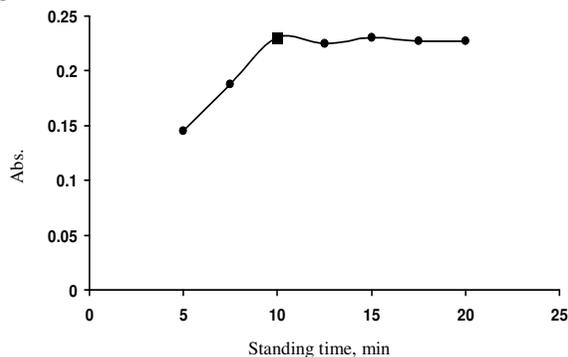


Figure 6. The Effect of standing time on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate
Conditions: $30 \text{ ng mL}^{-1} \text{ Al}^{3+}$; $6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ XO}$; $3.0 \times 10^{-5} \text{ CTAB}$; $\lambda_{\text{max}} = 536 \text{ nm}$

The flotation of the ion associate may also be influenced by the shaking time, because of increase in the active surface of the gas-liquid interface. It was studied for a time interval of 5-60 s. Maximum absorbance was obtained at 50 s shaking time. The results are shown Figure 7.

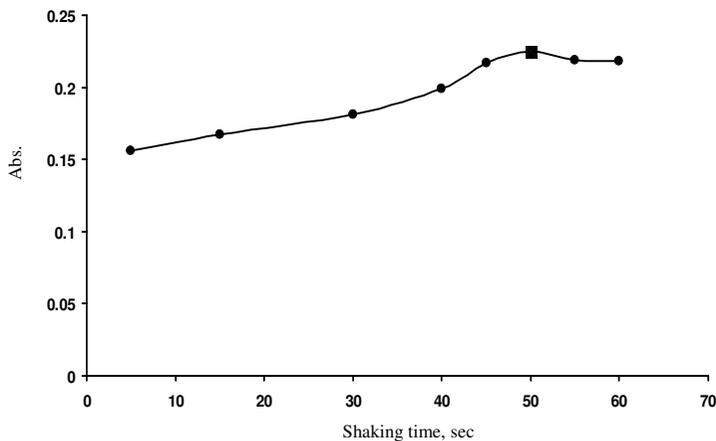


Figure 7. The Effect of shaking time on the flotation of $(\text{Al}^{3+}\text{-XO})\text{-CTA}^+$ ion associate
Conditions: $30 \text{ ng mL}^{-1} \text{ Al}^{3+}$; $6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ XO}$; $3.0 \times 10^{-5} \text{ CTAB}$; $\lambda_{\text{max}} = 536 \text{ nm}$

Effect of interferences

In order to study the influence of various cations and anions on the determination of Al^{3+} , a fixed concentration of Al^{3+} , 50 ng mL^{-1} , was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of $\pm 5\%$ with respect to the absorbance difference for the Al^{3+} solution was considered tolerable. Tolerance limits are as follows: Na^+ , Cl^- (600 folds), Mn^{2+} , Li^+ (300 folds), NO_3^- (250 folds), Ba^{2+} , CH_3COO^- (150 folds), K^+ , NH_4^+ , Ag^+ , Cu^{2+} , HCO_3^- , Br^- , HPO_4^{2-} (100 folds), $\text{C}_2\text{O}_4^{2-}$ (50 folds), Co^{2+} , Zn^{2+} , Cd^{2+} (25 folds), Sn^{2+} (10 folds).

Application

We have explored the feasibility of the methodology using it for the determination of Al^{3+} in mineral and river water samples. For this purpose, 15 mL of each of the samples was treated under the general procedure. Spiking aluminium to the samples performed the validity of the procedure. The results presented in Table 1. The validity of the method is good.

Table 1. Determination of Al^{3+} in water samples

Sample	Spiked	Found ^a	Recovery, %
River water ^b	-	14.30±0.36	-
	15	29.60±0.67	102
	20	34.0±0.84	99
	25	39.50±0.99	101
Mineral water ^b	10	9.50±0.25	95
	20	20.6±0.60	103

^a Average of four determinations ± standard deviation. ^b Spiked and found as ng mL^{-1}

Conclusion

The proposed method is simple, rapid, reproducible and highly sensitive and can be applied for quality control of Al^{3+} in water samples. Method shows good sensitivity due to high molar absorptivity character of XO dye and gave a wide linear dynamic range with respect to reported methods. The limit of detection of the proposed method is better than some of the previously reported methods²⁰⁻²⁷.

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