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Flotation-Spectrophotometric Determination of Traces of Lead Ion

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A simple, fast, reproducible and sensitive method for the flotation-spectrophotometric determination of Pb^{2+} is reported. The method is based on the ternary ion-association of Pb^{2+}, xylenol orange (XO) and cetyltrimethylammonium bromide (CTAB) which is floated at interface of aqueous phase and *n*-hexane by shaking the separating funnel. By discarding the aqueous solution (the more dense phase) the adsorbed ion associate (Pb^{2+}-XO)-CTA^+ on to the wall of a separatory funnel was extracted and dissolved in a small volume of methanol solvent and absorbance was measured at 583 nm. The apparent molar absorptivity (ε) of the ion associate was determined to be 6.13×10^4 mol^{-1} cm^{-1}. The calibration curve was linear in the concentration range of 0.2-5.0 μg mL^{-1} of Pb^{2+} with a correlation coefficient of 0.9996. The limit of detection (LOD) is 0.0427 μg mL^{-1}. The relative standard deviation (RSD) at 0.6 and 1.5 μg mL^{-1} of lead were 2.478 and 1.040 % (n = 8), respectively. The method was applied for measuring the amount of lead in blood and soil samples.

Key Words: Flotation-spectrophotometry, Lead, Xylenol orange, Cetyltrimethylammonium bromide, Ion associate.

INTRODUCTION

Ternary complexes in which the central ion reacts with two different ligands, have aroused considerable interest in the past two decades[1]. Flotation-spectrophotometry of such coloured ternary complexes probably provides the most sensitive, relatively simple and fast approach to trace metal analysis[2]. 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 solutions[1]. 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[3,4].

Different preconcentration-spectrophotometric[5-11] and electrochemical[12] methods are used for trace quantitative determination of Al^{3+}. Present paper shows a flotation-spectrophotometric method for (Pb^{2+}-XO)-CTA^+ ternary ion-associate in to the interface between aqueous and *n*-hexane phase by flotation method. The method proposed has been successfully applied for the determination of lead in different blood and soil 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 Pb^{2+} was prepared by dissolving 0.1598 g of $Pb(NO_3)_2$ (Merck) in freshly distilled water and diluting 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 were used in the concentration range of 0.001-0.100 mol L^{-1}.

Recommended procedure: Transfer an aliquot of a sample solution containing 2.5 mL of 10 μg mL^{-1} of Pb^{2+} into a 100 mL volumetric flask, 2.5 mL of 1×10^{-4} mol L^{-1} of XO, 2.5 mL of 1×10^{-3} mol L^{-1} of CTAB, 1.5 mL of 1×10^{-1} mol L^{-1} of NaCl, diluted to the mark with distilled water and left for 3 min. Then transfer the flask content to a 100 mL separatory funnel containing 10 mL of *n*-hexane and shake vigorously the mixture for 60 s and then allow standing for 15 min for separation of organic phase from aqueous phase. The (Pb^{2+}-XO)-CTA^+ ion associate (colour solid) floats on the interface. After discarding the aqueous phase (below layer) add 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 coloured ion associate was measured at 583 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 Pb^{2+} in blood and soil samples containing.

RESULTS AND DISCUSSION

The preliminary investigation indicated that interaction of Pb^{2+} with XO and CTAB can form a solid ion associate which is insoluble in aqueous and highly non-polar organic phases, but soluble in some polar organic solvent such as methanol. The absorption spectra of the dissolved (Pb^{2+}-XO)-CTA^+ ion associate in methanol showed a maximum absorbance at 583 nm. 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 1-25 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 Pb^{2+} at volumes more than 10 mL. So, 10 mL was used as optimum *n*-hexane volume. 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. 5 mL of methanol was used as optimum extracting solvent volume. The influence of pH on the flotation of (Pb^{2+}-XO)-CTA^+ ion associate was studied by varying the pH in the range of 1 to 12, before the organic phase addition (Fig. 1).

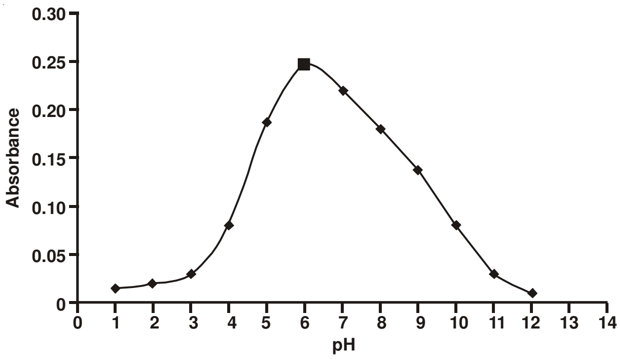

Fig. 1. Influence of pH on the flotation of (Pb^{2+}-XO)-CTA^+ ion associate; Conditions: Pb^{2+}: 1 μg mL^{-1}; XO: 2.5 × 10^{-5} mol L^{-1}; CTAB: 2.5 × 10^{-4} mol L^{-1}; $\lambda = 583$ nm

The pH was adjusted to the desired value using hydrochloric acid (0.001 mol L^{-1}). The maximum flotation was observed at 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 (Pb^{2+}-XO)-CTA^+ ion associate formation. The effect of XO dye concentration used for the flotation of Pb^{2+} was examined by varying the amounts of XO. The absorbance increased with increasing XO concentration up to 2.5 × 10^{-5} mol L^{-1} of XO in the final solution and concentrations more than 2.5 × 10^{-5} mol L^{-1} have no effect on the flotation of the ion associate.

The results are shown in Fig. 2 and so 2.5 × 10^{-5} mol L^{-1} of XO anionic dye for Pb^{2+} flotation process. The effect of CTAB concentration used for the flotation of Pb^{2+} was examined by varying the amounts of CTAB surfactant. The absorbance of ternary ion associate increased with increasing CTAB concentration up to 2.5 × 10^{-4} mol L^{-1} of CTAB in the final solution and decreases at more concentrations. 2.5 × 10^{-4} mol L^{-1} of CTAB in the final solution was chosen as the optimum concentration of CTAB for Pb^{2+} flotation process. The results are shown Fig. 3. It must be mentioned that higher concentration than 2.5 × 10^{-4} mol L^{-1} of CTAB in the final solution causes an increase in the blank absorbance and decreases the absorbance of ternary ion associate.

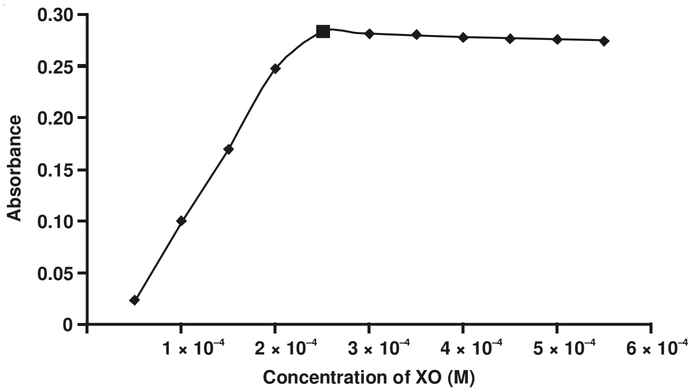

Fig. 2. Effect of XO dye concentration on the flotation of Pb^{2+};
Conditions: Pb^{2+}: 1 µg mL^{-1}; CTAB: 2.5 × 10^{-4} mol L^{-1}; pH = 6; λ = 583 nm

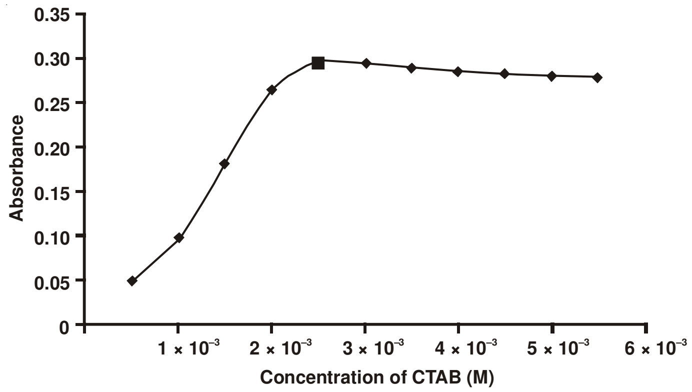

Fig. 3. Effect of CTAB concentration on the flotation of Pb^{2+}.
Conditions: Pb^{2+}: 1 µg mL^{-1}; XO: 2.5 × 10^{-5} mol L^{-1}; pH = 6; λ = 583 nm

The effect of time on the formation of (Pb^{2+}-XO)-CTA^+ ternary ion associate was studied over the time period 5-30 min for 1 µg mL^{-1} of Pb^{2+}, 2.5 × 10^{-5} mol L^{-1} of XO, 2.5 × 10^{-4} mol L^{-1} of CTAB and 6.0 × 10^{-3} mol L^{-1} of NaCl concentration at optimum pH (pH = 6) of solution and then by measuring the absorbance at 583 nm after flotation. The maximum absorbance was obtained at 15 min. The effect of electrolyte concentration on the formation of (Pb^{2+}-XO)-CTA^+ ternary ion associate was examined by various amounts of 0.1 mol L^{-1} of NaCl solution. The results showed that the absorbance of ion associate increases with increasing NaCl concentration up 6.0×10^{-3} mol L^{-1} in the final solution and remains constant at higher concentration of electrolyte (salting out). A constant concentration of 6.0×10^{-3} mol L^{-1} of NaCl was used throughout as optimum electrolyte concentration.

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. Maximum absorbance was obtained at 60 s shaking time. The stoichiometery of the ion pair was determined using the continuous variation method. The mol ratio of Pb^{2+}: XO: CTA^+: in the ion associate was 1:1:2.

Quantitative results: A calibration graph for the determination of Pb^{2+} was constructed under optimum experimental conditions described above. Beer's law was obeyed over the concentration range of 0.2-5.0 μg mL^{-1} of Pb^{2+} with a correlation coefficient of 0.9996 at 583 nm. The regression equation obtained by the least square method is $A = 0.236\ C_{Pb} + 0.0563$ for 0.2-5.0 μg mL^{-1} of Pb^{2+}, where A is the absorbance and C_{Pb} shows the concentration of Pb^{2+} in μg mL^{-1}. With regard to the preconcentration factor of the process (5 fold, *i.e.*, from 25 mL aqueous solution to 5 mL of methanol) and a path length of 1 cm, the conditional molar absorptivity was 6.130×10^4 L mol^{-1} cm^{-1} at the above wavelength. The relative standards deviation (RSD) for 0.6 and 1.5 μg mL^{-1} of Pb^{2+} were 2.478 and 1.040 % (n = 8), respectively. The limit of detection (LOD) was 0.0427 μg mL^{-1} based on $3S_b$[13]. The method exhibits a good reproducibility.

Effect of interferences: In order to study the influence of various cations and anions on the determination of Pb^{2+}, a fixed concentration of Pb^{2+}, 1 μg mL^{-1}, was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of ± 5 % with respect to the absorbance difference for the Pb^{2+} solution was considered tolerable. Telorance limits are as follows: Na^+, Cl^- (50 folds), Mn^{2+}, Li^+ (25 folds), NO_3^- (20 folds), Ba^{2+}, CH_3COO^- (15 folds), K^+, NH_4^+, Ag^+, Cu^{2+}, HCO_3^-, Br^-, HPO_4^{2-} (10 folds), $C_2O_4^{2-}$ (5 folds), Co^{2+}, Zn^{2+}, Cd^{2+} (2.5 folds), Sn^{2+}, Al^{3+} (0.5 folds).

Applications: The proposed method was applied to the determination of Pb^{2+} in blood and soil samples. The results are shown in Tables 1 and 2, respectively. The validity of the method is satisfactory.

TABLE-1
DETERMINATION OF Pb^{2+} IN BLOOD SAMPLES

Sample No.	Pb^{2+} (μg mL^{-1})*		Recovery (%)
	Added	Found	
1	–	0.099	–
2	0.1	0.198	99
3	0.2	0.297	98
4	0.3	0.395	96

*Average of three determinations.

TABLE-2
DETERMINATION OF Pb^{2+} IN SOIL SAMPLES AND TESTING THE VALIDITY OF THE METHOD BY STANDARD ADDITION METHOD

Sample No.	Pb^{2+} (μg mL^{-1})*		Recovery (%)
	Added	Found	
1	–	0.140	–
2	0.20	0.340	100
3	0.40	0.445	103
4	0.60	0.643	103

*Average of three determinations.

Conclusion

The proposed method is simple, rapid, reproducible and highly sensitive and can be applied for quality control of Pb^{2+} in blood 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 seems to be satisfactory.

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