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A new spectrophotometric method for fluoride based on its bleaching action on the color of aluminium (III) -gallacetophenone phenylhydrazone complex

D.Venkataramana Reddy[1,2]*, P.Jeevan Jyothi[1]

[1]Department of Chemistry, S.V.University, Tirupati, (INDIA)

[2]S.G.Govt.College, Piler-517 214, (INDIA)

E-mail : chemdvrr@yahoo.com

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ABSTRACT

A simple, sensitive, rapid and economical spectrophotometric method for the determination of fluoride is developed. The method is based on the bleaching action of fluoride on the intense yellow colour of Al (III)-GPPH complex with proportional decrease of absorbance. Therefore, in principle the decrease in colour intensity of the absorbing medium is proportional to the concentration of fluoride. At first, aluminium is determined spectrophotometrically by measuring the absorbance at 375nm. The system obeyed Beer's law upto 2.0ppm of Al. The molar absorptivity and Sandell's sensitivity of the Al (III) -GPPH complex are 1.34×10^{4}1. mole^{-1} cm^{-1}. and 0.002μg cm^{-2} respectively. The stoichiometry of the complex is found to be 1:1 by both Job's continuous variation and molar ratio methods. The stability constant of the complex is 3.197×10^{3} at 30°C. The effect of diverse ions has been studied. Based on the above principle, the method is employed for the determination of fluoride in water samples. The results of the proposed method are in close agreement with the values obtained from AAS.

KEYWORDS

Aluminium (III)-gallacetophenone phenylhydrazone complex;
Bleaching action;
Stoichiometry;
Indirect determination of fluoride.

INTRODUCTION

The use of hydrazones for the spectrophotometric determination of aluminium (III) is very limited. For example, hydrazones such as o-hydroxy benzaldehyde isonicotinoylhydrazone[1], pyridoxal salicyloyl hydrazone[2], gallacetophenone isonicotinoylhydrazone (GAPINH)[3] have been employed for the spectrophotometric determination of Al (III). The addition of fluoride ion to Al (III)-GAPINH complex causes proportional decrease in the absorbance and hence the bleaching of colour has been utilized for the indirect determination of fluoride. In the present investigation, gallacetophenone phenylhydrazone due to its good chromophoric properties has been introduced as an analytical reagent for both the spectrophotometric determination of Al (III) and the indirect determination of fluoride.

EXPERIMENTAL

Reagents

All the chemicals used are of AnalaR grade. Standard aluminium (III) solution-0.025M ammonium aluminium sulphate solution is prepared by weighing exactly about 2.834g of the salt. The solution is made upto 250ml and standardized by EDTA[4]. Sodium fluoride solution-0.025M sodium fluoride solution is prepared by dissolving 0.525g of the salt in 500ml. Gallacetophenone phenylhydrazone-It is prepared as per the standard procedure given by Blatt[5] and Curniss et al.[6]. The reagent solution (3.706×10^{-3}M) is prepared in 95% ethanol just before use. Sodium acetate-acetic acid buffer of pH 5.0 is prepared.

Apparatus

Recording spectrophotometer model SHIMADZU UV-240, Hitachi Atomic absorption/flame spectrophotometer model 170-30 and Elico digital pH meter model LI-120 are used in the present investigation.

Procedure

An aliquot of 2.0ml of 9.265×10^{-4}M aluminium (III) solution is transferred into a 20ml standard flask. 5.0ml of 3.706×10^{-3}M gallacetophenone phenylhydrazone solution and 5.0ml of sodium acetate-acetic acid buffer of pH 5.0 are added and the contents of the flask are made upto the mark with distilled water. The alcohol concentration is maintained at 25% v/v and then the spectrum of the complex is recorded against the reagent blank (Figure 1). It is observed that the complex has λ_{max} at 375nm. The absorbance of the reagent at this wavelength is minimum. Hence absorbance measurements of the complex are made at 375nm.

RESULTS AND DISCUSSIONS

Beer's law range, sensitity

A linear plot passing through the origin is obtained in the range 0.1 to 2.0μg/ml, thus obeying Beer's law. The Ringbom plot drawn between log C and (1-T) where C is concentration of Al(III) and T is transmittance has a sigmoid shape with a linear segment at intermediate concentration values 0.5-1.75g of Al/ml.

The method has a good reproducibility. For a set of ten measurements of 1.0μg/ml of Al(III), the standard deviation is 0.03μg/ml. The molar absorptivity of the complex is 1.34×10^{4}1.mole^{-1}.cm^{-1}. The Sandell's

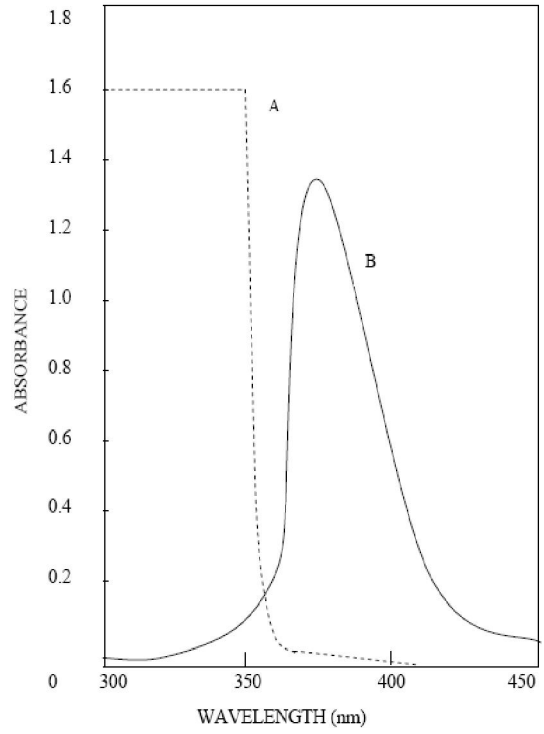

Figure 1 : A. Absorption spectra of GPPH and B. A1 (III)-GPPH complex

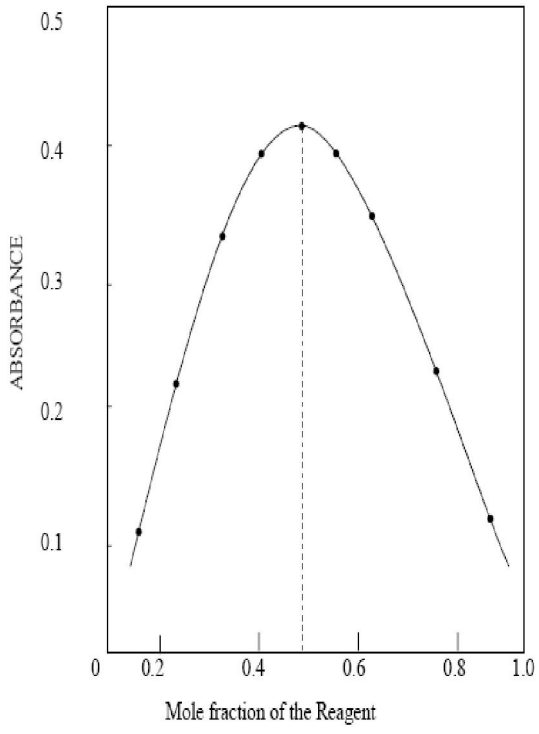

Figure 2 : Composition of A1 (III) – GPPH complex by Job's method

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TABLE 1 : Effect of foreign ions on the determination of 2.0µg of Al(III)

Ion added	Tolerance limit. µg/ml	Ion added	Tolerance limit. µg/ml
Be(II)	10	W(VI)	None
Ca(II)	100	Zn(II)	50
Cd(II)	50	Zr(IV)	None
Co(II)	50	Ascorbate	50
Cr(VI)	None	Br^-	100
Cu(II)	None	Cl^-	100
Fe(II)	None	Citrate	None
Fe(III)	None	$C_2O_4^{2-}$	None
Mg(II)	100	EDTA	None
Mn(II)	50	F^-	None
Mo(VI)	None	I^-	100
Ni(II)	50	$H_2PO_4^-$	None
Pb(II)	50	SCN^-	50
Ti(IV)	None	SO_4^{2-}	100
U(VI)	None	$S_2O_3^{2-}$	50
V(V)	None	Tartrate	None

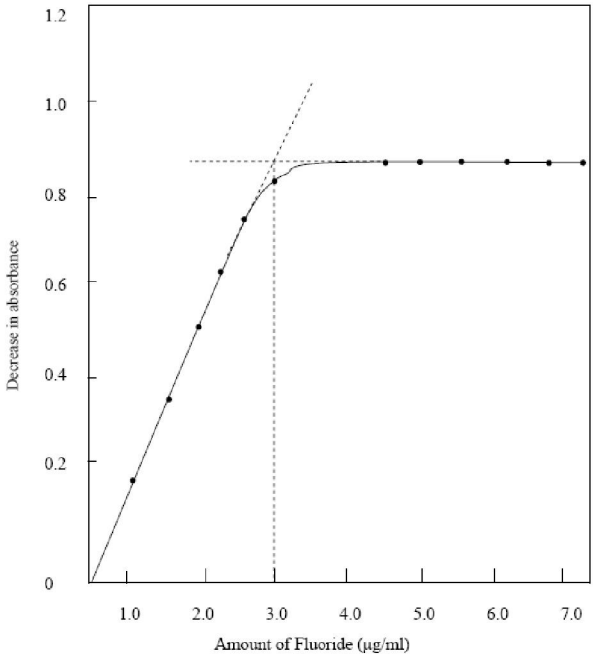

Figure 3 : Decrease in absorbance of Al (III) – GPPH complex vs amount of fluoride

sensitivity of the complex is found to be 0.002µg.cm^{-2}.

Composition of the complex

The composition of the Al(III)-GPPH complex is arrived at by Job's continuous variation and molar ratio methods. In Job's method, the graph (Figure 2) plotted between mole fraction of the reagent and absorbance shows that each mole of the metal ion reacts with one mole of the reagent. In molar ratio method a plot drawn between the molarity of the reagent and absorbance reveal the formation of 1:1 complex between Al(III) and GPPH which is in conformity with the above method. The stability constant of the complex calculated from Edmonds and Birnbaum's method is found to be 3.197×10^3 at 30°C.

TABLE 2 : Determination of fluroide in water samples

Sample Source	Fluoride determined (ppm)	
	Proposed method	AAS
Madanapalli	1.27	1.22
Thamballapalli	1.29	1.25
Somala	1.09	1.01
Kalikiri	1.15	1.16

Effect of foreign ions

The effect of foreign ions in the determination of 2.0µg/ml of Al(III) is studied. The tolerance limit is taken as the amount required to cause ±2% error in the absorbance. The tolerance limits of the ions are given in the TABLE 1.

A number of metal ions such as Mg(II), Ca(II), Ni(II), Mn(II), Cd(II) and Zn(II) do not interfere in the determination of Al(III), Be(II) does not interfere when present in 10-fold excess. However, Mo(VI), U(VI), V(V), W(VI), Ti(IV), Cr(VI), Fe(II), Fe(III) and Cu(II) interfere seriously. Titanium (IV) interferes in the determination of Al(III) where as Al(III) does not interfere in the determination of Ti(IV)[7], since it does not form a complex at lower pHs.

Among the anions tested fluoride, oxalate, citrate, tartrate, phosphate and EDTA interfere seriously in the determination of Al(III) by bleaching the color.

Indirect determination of fluoride

Addition of fluoride ions to the Al(III)-GPPH complex results in a proportional decrease of the absorbance. The bleaching action of fluoride has been utilized for its indirect spectrophotometric determination.

To 1.0ml portions of aluminium (1.48×10^{-3}M) solution taken in each of a set of 20ml volumetric flasks, 5.0ml of pH 5.0 buffer solution and 4.0ml reagent (3.706×10^{-3}M) solution are added. Known and varied amounts of fluoride (0.0-7.0µg/ml) are added to each of these flasks and the contents are made upto to mark

with distilled water. The absorbances of the solutions are measured at 375nm against the reagent blank. A plot (Figure 3) drawn between the amount of fluoride and decrease in absorbance revealed a linear decrease in the absorbance with increase of fluoride upto the inflexion point which corresponds to nearly 1:2 ratio (A1:F). On the basis of the stoichiometry, the following reaction is proposed for the bleaching action.

$$[Al\text{-}GPPH]^{2+} + 2F^- \rightarrow AlF_2^+ + GPPH^-$$

The method is useful in the determination of fluoride in water samples. This was used to determine fluoride in samples of drinking water collected from borewells in different parts of Chittoor District, A.P. The results obtained in the proposed method are in close agreement with the values derived from Atomic Absorption Spectroscopy as given in TABLE 2.

CONCLUSIONS

The spectrophotometric determination of Al(III) employing most of the organic reagents involves lake formation and then dissolution of precipitates in suitable solvents. On the other hand, the present method is a direct and rapid one. The sensitivity and selectivity of the method is well comparable with the other related hydrazones containing pyridine ring. The method is also useful in the indirect determination of fluoride present in water samples.

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