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SECOND ORDER DERIVATIVE VISIBLE SPECTROPHOTOMETRIC DETERMINATION OF AL (III) IN SOIL AND PLANT EXTRACT USING 5-BROMO-2-HYDROXY-3-METHOXYBENZALDEHYDE-P-HYDROXYBENZOIC HYDRAZONE

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Abstract: A second order derivative spectrophotometric method has been developed for the determination of Al (III) using 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone (5-BHMBHBH) in soil and plant extracts. Al (III) reacts with 5-BHMBHBH in acidic pH 2.0-6.0 to give a yellow colored complex. The complex has a broad absorption maximum around 390 nm. The second order derivative spectrum of the complex shows a peak at 427 nm, a valley at 406 nm and zero points at 415.8 nm and above 474 nm. The valley and peak amplitudes are found to vary linearly with concentration of Al (III) at pH 4.0. A fivefold excess of the reagent is sufficient to produce maximum amplitudes either at 427 or 406 nm. Linear plots are obtained between the amount of Al (III) and amplitudes either at 427 or 406 nm. They obey the equations $A_{427} = 157.263\ C + 0.0633$ and $A_{406} = 199.0469\ C + 0.2315$. Beers law is obeyed in the range 0.02 - 0.54 µg mL^{-1} both at 427 and 406 nm. The correlation coefficients are 0.99996 at 427 nm and 0.99995 at 406 nm. The standard deviation for eleven determinations is 0.2403 at 427 nm and 0.3594 at 406 nm. The effect of various diverse ions on the derivative amplitude is studied. In presence of EDTA the method is selective for determination of Al (III).The method is accurate, sensitive and precise. The method has been successfully applied for the determination of Al (III) in soil and plant extracts.
Keywords: Al (III), 5-BHMBHBH, Second order derivative spectrophotometry, soil and plant Extracts

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INTRODUCTION

The industrial and biological applications of aluminium are quite abundant. Today this cost – effective metal is widely available throughout and its alloys are widely used for adding strength and utility[1]. Aluminium is used for dialysis dementia [2].High amounts of aluminium is toxic for human beings[3]. However, its micro nutrient role is well recognized. Its applications range from aerospace industry, transportation, building and electrical transmission, packaging and water treatment. Certain aluminium salts serve as an immune response booster to allow the protein in vaccine to achieve sufficient potency as an immune stimulant. The other side of its effects is increased amounts of dietary aluminium reduced skeletal mineralization (osteophenia) resulting in growth retardation. Aluminium can cause neurotoxicity in very high doses which can alter the function of blood brain barrier[4]. Aluminium increases estrogen related gene expression in human breast cancer cells grown in the laboratory[5]. In keeping with its pervasiveness, aluminium is well tolerated by plants and animals .Owing to their prevalence ,potential beneficial biological roles of aluminium compounds are of continuing interest. Hence, accurate determination of aluminium in trace quantities in various natural systems is very important. Spectrophotometry is a good trace analysis technique. Recently several spectrophotometric methods[6-30]based on the use of various organic reagents are reported for the determination of aluminium. Some of these methods are not sensitive, some suffer from interference, some have limited applications, certain methods are used surfactants, some utilize solvent extraction and some are temperature dependent. The potential analytical applications of hydrazone derivatives by Singh et al[31].Krishnareddy et al[32] recently reported a sensitive method for the determination of aluminium, but it uses a surfactant.

Derivative spectrophotometry (DS) is an analytical technique of great utility for extracting both qualitative and quantitative information from spectral curves composed of unresolved bands. DS enhances the resolution of spectral bands allowing the detection and location of the wavelength of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation of active components, usually require in qualitative and quantitative spectrophotometric procedures, applied in the analysis of complex system is completely avoided. The simplicity, relatively quick and easy realization, increased selectivity and sensitivity in the analysis of minor components are the important reasons, why the interest in DS is constantly growing for practical application. DS have been used in pharmaceutical analysis , environmental analysis and finger print analysis of proteins but few data have been published on the determination of inorganic ions [33].

In view of the importance of DS and paucity of DS methods for the determination of Al (III) , the author reports a sensitive , highly selective and accurate second order derivative spectrophotometric method for the determination of Al (III) in soil and plant extracts.

MATERIALS AND METHODS:

Reagents

The reagent 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-P-hydroxybenzoic hydrazone was synthesized in our laboratory by condensing 5-Bromo-2-hydroxy-3-methoxybenzaldehyde and P-hydroxybenzoic hydrazide in methonal using a general procedure[34]. A 0.01 M solution in dimethyl formamide is used in the present studies.

A 0.01M stock solution of Al (III) was prepared by dissolving requisite amount of aluminium ammonium sulphate in distilled water and standardized volumetrically [35] .Working solutions were prepared daily by diluting the stock solutions to an appropriate volume .

For the preparation of buffer solutions , 1M HCl and 1 M sodium acetate (pH 1 to 3) and 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.2 to 7.0) were used.

Instruments

The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV – Visible spectrophotometer (Model UV-160 A) controlled by a computer fitted with 1 cm path length quartz cells and Elico digital pH meter (Model LI 613) respectively.

Procedure

In each of a set of different 10 ml standard flask , 5 ml of buffer solution (pH 4.0), various volumes of 4 x 10^{-4}M Al (III) solution, 1.5 ml of dimethyl formamide and 0.5 ml of 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-P-hydroxybenzoic hydrazone (1 x10^{-2} M) in DMF were added and made upto the mark with distilled water for these solutions. The second order derivative spectra were recorded in the wavelength region 360-600 nm. The derivative peak height and the valley height were measured by peak-zero and valley –zero method at 427 and 406 nm respectively. The peak amplitude was plotted against the amount of Al (III) at 427 nm and the valley amplitude at 406 nm was plotted against the amounts of Al (III) to obtain calibration curves at 427 and 406 nm. The plots are linear and follow the equations $A_{427} = 157.263\ C + 0.0633$ and $A_{406} = 199.0469\ C + 0.2315$.

RESULT AND DISCUSSION:

Second order derivative spectra

Al (III) reacts with 5-BHMBHBH to form a yellow colored complex in acidic pH. The second order derivative spectrum of Al (III)-5-BHMBHBH was recorded in the wavelength region 360-600 nm at pH 4.0 against the reagent blank and is shown in Fig . 1 .The spectrum shows a peak at 427 nm, a valley at 406 nm and zero points at 415.8 nm and above 474 nm.

pH effect

It is observed that the yellow colored complex between Al (III) and 5-BHMBHBH in the pH range 2.0-8.0. The study of effect of pH on color intensity of the reaction mixture showed that the color intensity is maximum in the pH range 3.0-7.0. Analytical studies were carried out at pH 4.0 as the interference due to foreign ions is at a minimum at this pH.

Effect of 5-BHMBHBH concentration

The studies revealed that a 5 fold molar excess of 5-BHMBHBH is essential for complete and constant color development. Excess of the reagent has no effect on the derivative amplitude of the complex.

Color and stability of the complex

The color reaction between Al (III) and 5-BHMBHBH was instantaneous at room temperature. The amplitude of the complex was found to constant for more than 48 hours.

Order of addition of reactants

It is observed that the intensity of the colored solutions is independent of the order of addition of the reactants. However the reagent was added after the addition of DMF to avoid precipitate formation.

Applicability of Beers law

The Beers law range along with regression characteristics, precision and accuracy of the proposed second order derivative method for the determination of Al (III) are given in table-1.The data in table-1 indicates the method is highly sensitive , accurate and precise.

Effect of foreign ions

The effect of various diverse ions on the determination of Al (III) was studied to find out the tolerance levels of these diverse ions in the present method . The tolerance limit of a foreign ion was taken as the amount of that ion that caused an error in the amplitude value by ± 2 % .The data are presented in table- 2. The data in table-2 indicates that all the anions expect fluoride do not interfere in more than 150 fold excess. Among the cations Pb (II), La(III), Hg (II) ,V (V) and Th (IV) do not interfere in more than 120 fold excess . Bi (III), Mo (VI), Zn (II) and Zr (IV) do not interfere even when present in 50 fold excess . 45 fold excess of Cd (II) Se (IV), 20 fold excess of Ru (III) ,Mn (II) , Ti (III) , Ag (II) , Cr(VI) , Ce (IV) and 10 fold excess of Au (III) ,W (VI) and Pd (II) do not interfere . Ni (II) , Co (II) , Fe (III) , Ti (IV), Cu (II) which interfere in the method are made tolerable to more than 80 fold excess in the presence of EDTA or iodide as masking agents.

Applications

I. **Determination of aluminium in soil samples**

The soil sample solutions were prepared as per the recommended procedure[36]. An aliquot of the sample was analyzed by the recommended general procedure. The results obtained were compared with those obtained from atomic absorption spectrophotometry and the data are presented in table-3

II. **Determination of aluminium in Tea, human hair and plant extract**

The solutions of plant extract[37], was prepared according to the recommended procedure. An aliquot of the sample was analysed for aluminium content by the general procedure. The results obtained were compared with those obtained from atomic absorption spectrophotometry and are presented in table-4.

CONCLUSIONS:

The second order derivative spectrophotometic method developed for the determination of Al (III) using 5-BHMBHBH is highly selective, sensitive , accurate and precise . The method is more sensitive than the direct spectrophotometric method reported by saritha etal [38]

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Table-1 Regression characteristics, precision and accuracy of the proposed method for Al (III)

Parameter	Peak	Valley
Analytical wavelength (nm)	427	406
Beer's law limits (μg mL^{-1})	0.02-0.54	0.02-0.54
Limits of detection (μg mL^{-1})	0.0046	0.0054
Regression equation (y = a + b x)		
Slope (b)	154.263	199.047
Intercept (a)	0.0633	0.2315
Correlation coefficient (γ)	0.99996	0.99995
Standard deviation (Sd)	0.2403	0.3594

Table-2 Tolerance limit of foreign ions Amount of Al (III) = 0.432 μg mL^{-1} , pH = 4.0

Ion	Tolerance Limit μg mL^{-1}	Ion	Tolerance Limit μg mL^{-1}
Ascorbate	2150	Pb(II)	305
EDTA	1195	La (III)	241
Iodide	996	Hg (II)	128
Thiourea	758	Th (IV)	90
Tartrate	636	Y (III)	65
Phosphate	468	Bi (III)	65
Thiosulphate	590	Mo (VI)	21
Citrate	588	Zr (IV)	35
Sulphate	600	Cd (II)	36
Bromide	550	Se(IV)	30
Thiocyanate	490	Au (III)	49
Carbonate	375	Ru (III)	22
Nitrate	350	Zn (II)	30
Chloride	300	Tl (III)	35
Oxalate	260	Ag(I)	36
Fluoride	Interferes	Mn(II)	55
Fe(III)	<1,46[a]	Cr (VI)	44
Cu(II)	<1,78[b]	Ce (IV)	36
Ti(IV)	<1,70[a]	U (VI)	15
Ni(II)	<1,95[a]	V(V)	66
Co (II)	<1,100[a]	W(VI)	50
		Pd(II)	10

a = Masked with EDTA ; b =Masked with iodide

Table-3 Determination of Al (III) in soil samples

Sample	Amount of aluminium (III) µg mL^{-1}			Error (%)
	Added	**Found***	**AAS method***	
Singanamala (ground nut cultivation soil)	-	20.40	20.38	0.98
	20.0	40.64	40.62	0.50
Gooty (Bengal gram cultivation soil)	-	25.50	25.30	0.81
	20.0	45.72	45.80	-0.17
Bathalapalli(Sunflower cultivation soil)	-	16.70	16.65	0.30
	20.0	36.66	36.64	0.05

* Average of five determinations± S.D

Table -4 Determination of Al (III) in plant extracts

Sample	Amount of Al (III) (µg mL^{-1})		Error (%)
	Present method*	**AAS method***	
Grass	287	286	0.35
Maize 638	136	137	0.73
Sprouts 599	99	101	-1.9

* Average of five determinations

Fig -1

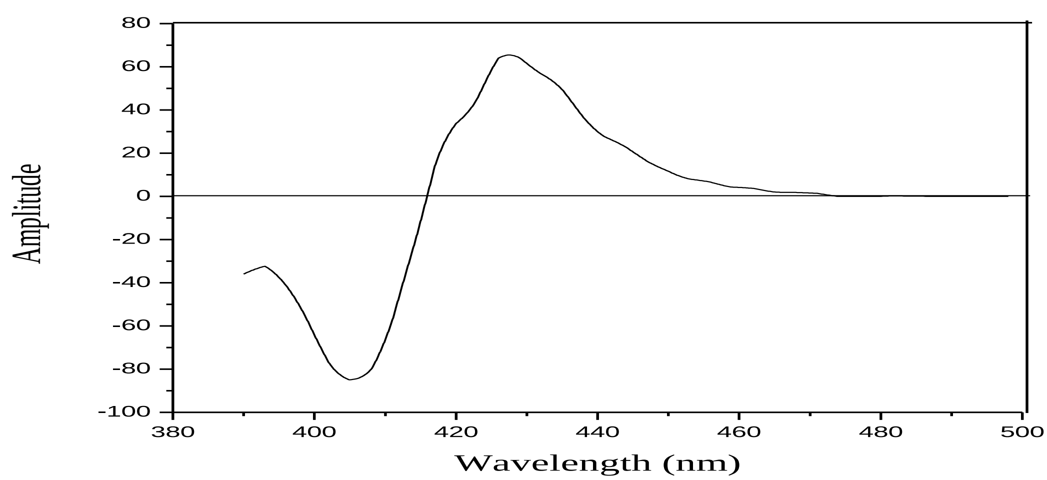

Fig .1 Second order derivative spectrum of Al (III) -5-BHMBHBH Vs reagent blank

[Al (III)] = 1.6 x10^{-5}

[5- BHMBHBH] = 5.0 x 10^{-3}, pH = 4.0

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