

Determination of Aluminum(III) in Minerals, Sludges, Soils and Plant Extracts using 2-Hydroxy-3-Methoxybenzaldehyde-P-Hydroxybenzoic Hydrazone

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Abstract- Highly sensitive and selective direct and derivative spectrophotometric methods are proposed for the determination of aluminium in various materials. 2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone reacts with Al(III) forming yellow coloured soluble complex in aqueous dimethyl formamide which has a λ_{max} at 410 nm in the pH range 4.5 – 5.5. Sensitivity of the method has significantly increased in the presence of 0.02% of cetyl pyridinium chloride miscellar medium. The system obeyed Beer's law in the range 0.027 – 1.079 $\mu\text{g mL}^{-1}$ of Al(III). The molar absorptivity ($4.19 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), detection limit ($3.8 \times 10^{-3} \mu\text{g mL}^{-1}$) and determination limit ($1.16 \times 10^{-2} \mu\text{g mL}^{-1}$) indicate the sensitivity of the proposed method. The studies on effect of diverse ions showed almost all the anions (except F⁻) and majority of the cations do not interfere in more than 50 fold excess. The interference from Ni(II), Fe(III), Cu(II) and Ti(IV) was eliminated by using suitable masking agents. The direct method was applied for the determination of aluminium in silicate minerals, industrial sludges and in soils. The sensitivity and selectivity of the proposed method is further enhanced in the first to fourth order derivative spectrophotometric methods developed. Second order derivative method was applied for the determination of Al(III) in plant extracts, hair, tea and water samples.

I. INTRODUCTION

The industrial and biological applications of aluminium are quite abundant. 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 (osteopenia) resulting in growth retardation. Aluminium can cause neurotoxicity in very high doses which can alter the function of blood brain barrier¹. Aluminium increases estrogen related gene expression in human breast cancer cells grown in the laboratory². Mercury thermometers are not allowed on many airliners as it undergoes amalgamation with aluminium damaging protective oxide surface film on aluminium metal. Hence, determination of aluminium in trace quantities in various natural systems is an important task. Among the first reported spectrophotometric methods, the extraction method using 8-hydroxy quinoline is not sensitive but highly selective³. The proposed by Marzenko et

al⁴ Safavi⁵, and Ahmed *et al*⁶ are highly sensitive but they suffer from the interference of some diverse ions. The methods proposed by Nascimento *et al*⁷, are less sensitive. We are now reporting sensitive and reasonably selective direct and derivative spectrophotometric methods for the determination of aluminium in number of naturally occurring complex materials.

II. EXPERIMENTAL

The chromogenic reagent, 2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone was synthesized in the laboratory by condensing 2-hydroxy-3-methoxybenzaldehyde and p-hydroxybenzoic hydrazone. A DMF solution of the reagent in suitable concentrations was used in the studies.

0.01M stock solution of Al(III) was prepared by dissolving requisite amount of aluminium ammonium sulphate in distilled water and standardized volumetrically⁸. The working solutions were prepared by diluting the stock solutions with distilled water. Buffer solutions of pH 4.0 – 6.0 were prepared by mixing 0.2M CH₃ –COONa and 0.2M CH₃.COOH in suitable proportions and checking the pH by a pH meter. The miscellar medium, cetyl pyridinium chloride (1%) was prepared by dissolving 1 gram of salt (SRL Chemicals) in 100 ml of boiled distilled water.

The absorbance and derivative amplitude measurements were made on SCHIMADZU 160-A UV-visible spectrophotometer. The pH of the buffer solutions was measured by Elico pH meter (LI 610). All other chemicals used were of analytical or guaranteed reagent grade.

III. PROCEDURE

To 4 ml of buffer solution (pH 5.0) 1 ml of HMBABH (1 x 10⁻²M), 0.2 ml of c.p.c (1%) 1 ml of DMF taken in each of a set of 10 ml volumetric flasks, variable amounts of Al(III) were added and diluted to the volume with distilled water. The absorbance of these solutions was measured at 410 nm against reagent blank and plotted against the amount of aluminium. A straight line with a regression equation $A=1.5658 \epsilon (\mu\text{g mL}^{-1}) [\text{Al(III)}] - 0.0001$ was obtained in a specified concentration region of Al(III). For the derivative spectrophotometric determination of aluminium, first, second, third and fourth order derivative spectra were recorded in the wavelength region 350 – 600 nm with a scan speed of 2400 nm per minute and with 9 degrees of freedom. For the experimental solutions containing different amounts of the metal ion under optimal conditions and

the derivative amplitudes were measured at the suitable wavelengths and plotted against the amount of aluminium to evaluate the determinable ranges in various order derivative methods.

IV. RESULTS AND DISCUSSION

The absorption spectrum [Al(III) – HMBAHBH] complex showed maximum absorbance at 410 nm where the reagent showed negligible absorbance. The absorbance was found to be maximum and constant in the H range 4.5 – 5.5. Therefore, the analytical studies were carried out at pH 5.0. A 15 fold molar excess reagent was found to be necessary to obtain maximum colour intensity for a given amount of metal ion. The absorbance of the metal complex significantly increased in the presence of

cetyl pyridinium chloride and cetyl tri ammonium bromide cationic surfactants but slightly decreased in the presence of sodium dodecyl sulphate, polyvinyl alcohol and Triton-X-100. Between the two cationic surfactants cetyl pyridinium chloride gave maximum absorbance. Hence, the analysis was carried out in the presence of 0.02% c.p.c. The derivative spectra recorded in the wavelength region 350 – 600 nm for the experimental solutions showed maximum and proportional variable absorbances at 427 nm (1st order), at 444 nm (2nd order), at 424 nm and 457 nm (3rd order) and at 409 nm, 445 nm and 474 nm (4th order) as shown in Figures 1–4. The analytical results obtained in direct and first to fourth order derivative methods are tabulated in Table 1.

Table 1. Analytical characteristics of [Al(III) – HMBAHBH]

Parameter	Direct method	I derivative	II derivative	III derivative		IV derivative		
	410 nm	427 nm	444 nm	424 nm	457.5 nm	409 nm	445 nm	474 nm
Beer's law range ($\mu\text{g mL}^{-1}$)	0.027 to 1.079	0.0108 to 0.270	0.0054 to 0.270	0.0027 to 0.270	0.0053 to 0.270	0.0054 to 0.270	0.0054 to 0.270	0.0108 to 0.270
Molar absorptivity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	41,900	-	-	-	-	-	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.00064	-	-	-	-	-	-	-
Angular coefficient (m)	1.5658	1.1850	2.1208	4.9343	3.1079	1.9299	2.6169	1.0639
Y - intercept (b)	-0.00085	0.000012	-0.000457	-0.000149	-0.000565	-0.000057	0.00558	-0.000446
Correlation coefficient (r)	0.9999	0.9999	1.0000	1.0000	1.0000	1.0000	0.9999	0.9999
Relative standard deviation (%)	0.58	0.34	0.24	0.94	0.73	0.43	0.38	0.44
Detection limit ($\mu\text{g mL}^{-1}$)	0.0038	0.0011	0.0004	0.0007	0.0008	0.0008	0.0005	0.0013
Determination limit ($\mu\text{g mL}^{-1}$)	0.0116	0.0032	0.0012	0.0021	0.0025	0.0024	0.0016	0.0041
Composition (Metal : Ligand)	2 : 3	-	-	-	-	-	-	-
Stability constant	4.433×10^{19}	-	-	-	-	-	-	-

The molar absorptivity Beer's law ranges, detection limit, determination limit shown in the table indicate the high sensitivity of both the direct and derivative methods. However the derivative methods are found to be much more sensitive than the direct method. The effect of diverse ions on the absorbance of the experimental solution showed that all the anions tested (except F⁻) do not interfere in more than 100 fold excess. Fluoride is tolerable upto 45 fold excess. Among the cations Pb(II), La(III), Hg(II) and Th(IV) do not interfere in more than 100 fold excess. Y(III), Bi(III), Mo(VI) and Zr(IV) are tolerable upto 50 fold excess. The tolerance limits of other metal ions are 30 fold Cd(II), Se(IV), 26 fold (Au³⁺, Ru³⁺ and Zn²⁺, 20 fold

(Ti³⁺, Ag⁺, Mn³⁺, Cr⁶⁺, Ce⁴⁺) and 10 fold (Co²⁺, W⁶⁺, Pd²⁺). The tolerance limits of Ni²⁺, Fe³⁺, Cu²⁺, and Ti⁴⁺ which interfere seriously, are enhanced to more than 100 fold in the presence of EDTA or I as masking agents. The results presented in Table 2 reveal that in the 1st and 2nd derivative methods, the tolerance levels of number of metal ions which showed serious interference in zero order method are greatly increased. In the third and fourth derivative methods also the tolerance limits of some metal ions are found to be higher than in zero order method. This is an evidence of the greater selectivity of the derivative methods over zero order method.

Table. 2
Tolerance limits of Foreign ions
Amount of Al(III) taken = 0.270 $\mu\text{g mL}^{-1}$; pH = 5.0

Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Ascorbate	875	Pb(II)	104
EDTA	760	La(III)	70
Iodide	390	Hg(II)	40
Thio urea	380	Th(IV)	24
Tartrate	266	Y(III)	15
Phosphate	260	Bi(III)	15
Thio sulphate	250	Mo(VI)	10
Citrate	244	Zr(IV)	9
Sulphate	240	Cd(II)	8
Bromide	202	Se(IV)	8
Thiocyanate	154	Au(III)	7
Carbonate	140	Ru(III)	7
Nitrate	110	Zn(II)	7
Chloride	90	Tl(III)	6
Oxalate	74	Ag(I)	6
Fluoride	15	Mn(II)	6
		Cr(VI)	5
		Ce(IV)	5
		U(VI)	3
		Co(II)	3
		W(VI)	3
		Pd(II)	2
		Ni(II)	<1, 75 ^a
		Fe(III)	<1, 90 ^a
		Cu(II)	<1, 45 ^b
		Ti(IV)	<1, 60 ^a

Table.2.a. Tolerance limits of foreign ions

Foreign ion	Tolerance limits (in folds)							
	Zero Order	First derivative	Second derivative	Third derivative		Fourth derivative		
		427 nm	444 nm	424 nm	457.5 nm	409 nm	445 nm	474 nm
Cu(II)	< 1	26	30	interferes	interferes	25	30	38
Ni(II)	< 1	27	16	83	2	49	82	2

Y(III)	< 1	68	> 100	> 100	> 100	> 100	> 100	> 100
La(III)	< 1	> 100	> 100	> 100	> 100	> 100	> 100	> 100
V(V)	< 1	7	2	interferes	interferes	47	45	interferes
In(III)	< 1	10	15	interferes	interferes	interferes	interferes	interferes
Fe(II)	< 1	33	2	2	3	1	2	24
Ti(IV)	< 1	13	68	43	1	2	50	2
Ga(III)	< 1	17	22	interferes	interferes	interferes	interferes	interferes

Applications

The direct method was applied for the determination of aluminium in carbonate and silicate minerals, industrial sludges and soil samples. The sample solutions were prepared as per the recommended procedures for silicate minerals⁹, industrial sludges¹⁰. Variable aliquots of the sample solutions were treated with suitable amounts of HMBABH and c.p.c. (surfactant) under the prescribed conditions and the absorbances were measured at 410 nm. The amounts of aluminium present in these samples were computed from predetermined calibration plots and presented in Table 3, 4 and 5.

Table 3. Determination of Al(III) in carbonate and silicate minerals

Sample	Aluminum (%)		Relative Error (%)
	Certified Value	Found*	
Silica brick (NBS 102)	1.96	1.99 ± 0.006	+ 1.53
Glass frit (NBS 128)	1.80	1.78 ± 0.004	- 1.11
Optical glass (BSC 510/644)	0.75	0.76 ± 0.010	+ 1.33
Optical glass (NBS 128)	1.89	1.87 ± 0.014	- 1.05
Lime stone	0.39	0.40 ± 0.022	+ 2.56

* Average of four determinations ± S.D.

The results obtained in the present method with regard to sludges were compared with those obtained by flame atomic absorption spectrophotometric method and presented.

Table 4. Determination of aluminum in Sludge samples

Sludge sample	Amount of aluminum (mg/g)*
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	Present method	AAS method
1402 – 2	30.146 ± 0.032	30.428 ± 0.0028
1402 – 3	35.650 ± 0.018	35.460 ± 0.022
1402 – 4	32.870 ± 0.012	33.245 ± 0.014

* Average of four determinations ± S.D.

Table 5. Determination of aluminium in Soil samples

Sample	Amount of aluminium (µg mL ⁻¹)		Recovery (%)
	Added	Found*	
Garladinne (ground nut cultivation soil)	-	15.45 ± 0.008	-
Tadipatri (Bengal gram cultivation soil)	15.0	31.14 ± 0.011	102
Raphadu (Sunflower cultivation soil)	-	24.40 ± 0.012	-
	15.0	38.65 ± 0.016	98
	-	15.60 ± 0.006	-
	15.0	29.36 ± 0.014	96

*Average of four determinations ± S.D.

The second order derivative spectrophotometric method was employed for the determination of aluminium in plant extracts, human hair, tea and waste water samples. The solutions of plant, extract¹¹, human hair and tea¹² were prepared according to the recommended procedures and their aluminium content were determined by the proposed second order derivative method. The plant extract samples were also analysed by flame atomic absorption spectrophotometric method and compared with those of present method and IPE¹³ reported data. The results are presented in Table 6 and 7.

Table 6. Determination of aluminum in plant extracts

Sample	Amount of aluminium ($\mu\text{g mL}^{-1}$)		IPE reported ⁴³ data accepted range ^a (mg g^{-1})
	Present method*	AAS method*	
Rosa 119	58 ± 3	55 ± 4	42 – 99
Sprouts 599	97 ± 6	102 ± 5	67 – 128
Grass	298 ± 18	284 ± 12	252 – 658
Maize 638	126 ± 9	120 ± 14	109 – 237

* Average of five determinations

a = Samples from International Plant analytical exchange programme (I.P.E.)

Table.7. Determination of aluminium in human hair, tea and waste water

Sample	Amount of aluminium ($\mu\text{g mL}^{-1}$)				Reference ⁴⁴ Method	Relative error (%)
	Added	Found*	RSD (%)	Recovery (%)		
Tea ^a	-	215.0	1.6	-	217.5	+ 1.16
	5.0	221.4	1.2	100	218.5	- 1.30
Human hair	-	19.6	0.88	-	19.46	- 0.71
	5.0	25.4	0.96	103	25.90	+ 1.96
Waste water ^b	-	0.364	0.14	-	0.370	+ 1.65
	5.0	5.406	0.11	100	5.384	- 0.40

* Average of four determinations

a = Three roses tea sample, Brook Bond India Ltd.,

b = Domestic sewage water.

The proposed direct and derivative spectrophotometric methods are simple, sensitive, less tedious, reasonably selective and are applicable for the analysis of complex materials. The present direct method is found to be more sensitive than those proposed by Nemcova *et al*¹³, Zhong fang *et al*¹⁴, and Sergio *et al*¹⁵. The second derivative method was found to be more selective.

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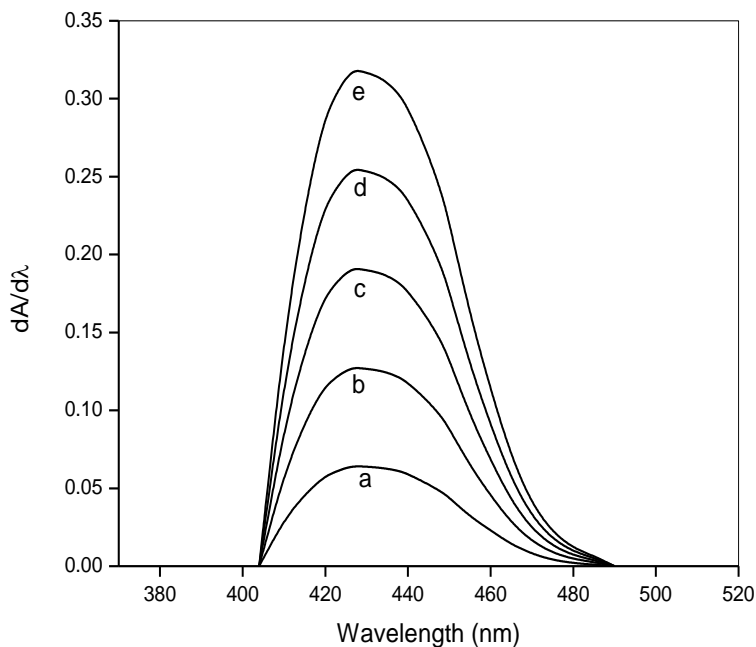


Fig. 1. First order derivative spectra of [Al(III) – HMBAHBH]
Amount of Al(III)($\mu\text{g mL}^{-1}$) ; a-0.054; b-0.108; c-0.162; d-0.216; e-0.270

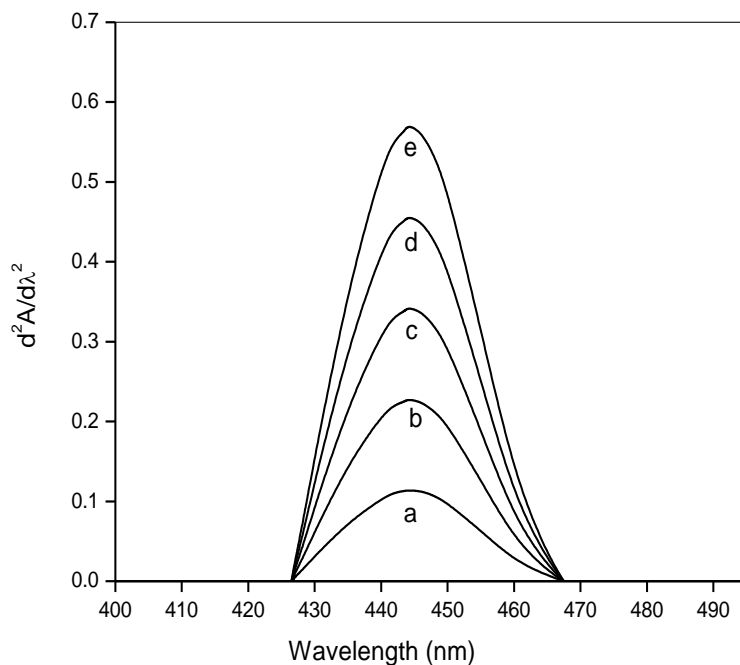


Fig. 2. Second order derivative spectra of [Al(III) – HMBAHBH]
Amount of Al(III)($\mu\text{g mL}^{-1}$) ; a-0.054; b-0.108; c-0.162; d-0.216; e-0.270

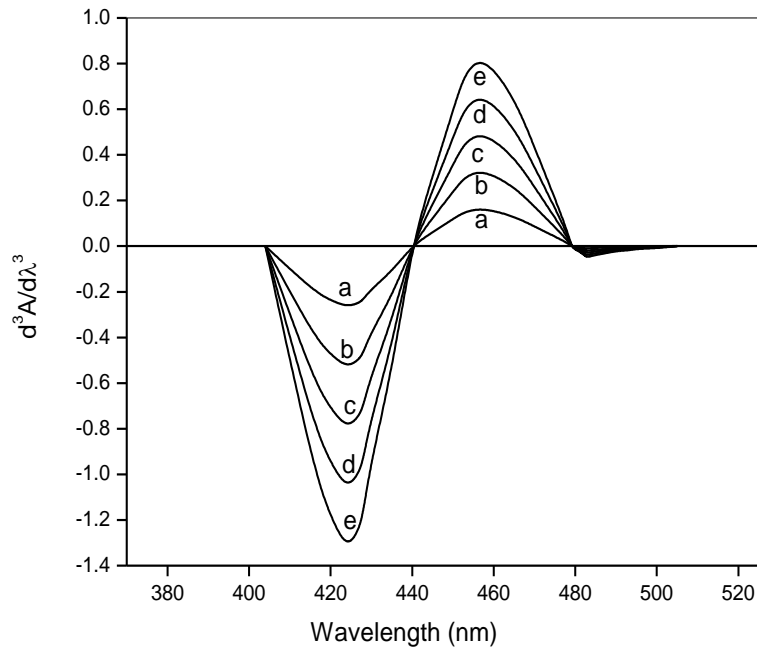


Fig. 3. Third order derivative spectra of [Al(III) – HMBAHBH]
Amount of Al(III)($\mu\text{g mL}^{-1}$) ; a-0.054; b-0.108; c-0.162; d-0.216; e-0.270

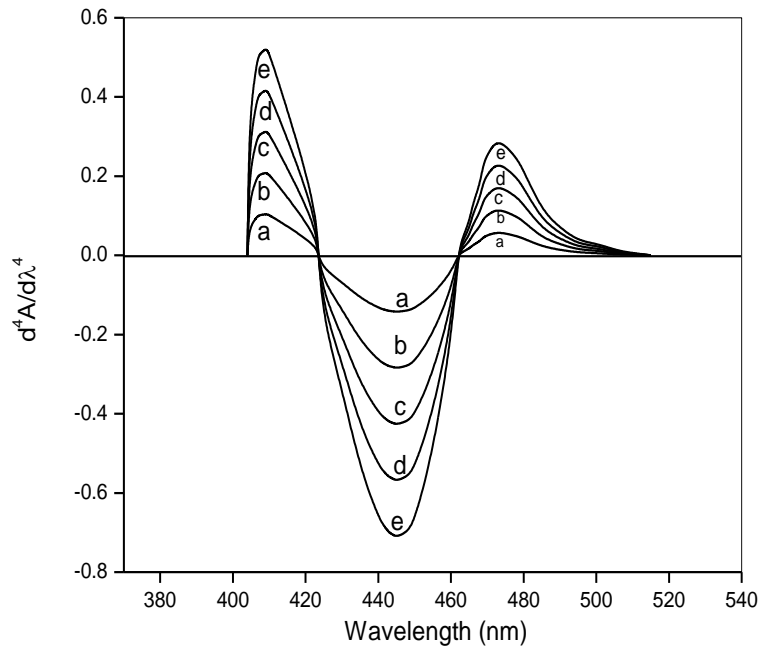


Fig. 4. Fourth order derivative spectra of [Al(III) – HMBAHBH]
Amount of Al(III)($\mu\text{g mL}^{-1}$) ; a-0.054; b-0.108; c-0.162; d-0.216; e-0.270