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VIEWS

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Simultaneous Determination Of Aluminium (Iii) And Gallium (Iii) By Second Order Derivative Spectrophotometry Using 2-Hydroxy-1-Naphthaldehyde-P-Hydroxy Benzoichydrazone

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ABSTRACT

A highly sensitive and selective second order derivative spectrophotometric method is proposed for the simultaneous determination of aluminium and gallium. Al(III) and Ga(III) react with 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH) at pH 6.0 forming lemon yellow coloured and yellow coloured solutions with λ_{max} at 445 nm and 455nm respectively. Both the metal ions were simultaneous determined by measuring the second derivative amplitudes at 476.5 nm and 449.5 nm (zero cross method) against the reagent blank and plotting against the amount of the corresponding metal ion. Beer's law was obeyed in the range 0.013-0.256 µg mL^{-1} and 0.017-1.324 µg mL^{-1} for Al(III) and Ga(III) respectively. No interference from associated anions and cations was observed. The method was applied for the determination of Al(III) and Ga(III) in standard reference materials and biological samples.

***Key words**:* Simultaneous determination, derivative spectrophotometry, Al (III) and Ga(III), 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone

INTRODUCTION

Determination of trace amounts of aluminium and gallium has become significant in recent years due to their physiological distribution in biological systems. Some gallium compounds exhibit antitumour activity,[1-3] but at the same time certain levels of gallium show appreciable toxicity. Aluminium, which was consider to be non-toxic till recently, is now found to be responsible for various clinical disorders in patients leading to renal failure. The adverse effects of aluminium were demonstrated in patients suffering from dialysis dementia.[4,5] Aluminium toxicity is also associated with osteodistrophy,[6] anaemia,[7] gastrointestinal symptoms[8] and also probably cardio toxicity.[9] The most important source of aluminium in patients appears to be the water
used for dilution of the dialysis solution.[10]

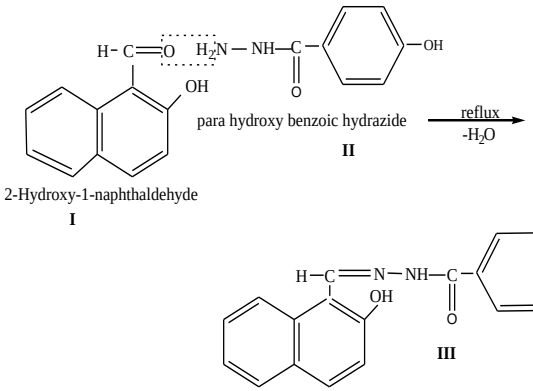
Gallium and aluminium alloys are used as solid state electrolytes in fuel cells. An alloy of Al_2O_3 (5%) and Ga_2O_3 has high activity as a cracking catalyst for hydrocarbon oil. They also form a low melting eutectic alloy (m.p. 26.3^0C). Determination of aluminium and gallium in these alloys and electrolytes without separation is important in characterizing these alloy materials. Singh et al[11] and Agnihotri and his co-workers[12] developed derivative spectrophotometric methods for the simultaneous determination of Ga(III) and In(III). Agnihotri et al[13] determined Ga(III) and Th(III) simultaneously in binary mixtures by derivative spectrophotometry. The literature survey reveled that no method is reported for the
simultaneous determination of Ga(III) and Al(III). We are now proposing second derivative spectrophotometric method for the simultaneous determination of Al(III) and Ga(III) by zero cross method without the need for solving simultaneous equations.

MATERIALS AND METHODS

2.1. Reagents

2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH)

The reagent was synthesized by condensing equimolar solutions of 2-hydroxy-1-naphthaldehyde and parahydroxybenzoichydrazide adopting the described procedure [14] (m.p.272-274^{0}c). The stock solution of the reagent (1×10^{-2} M) was prepared by dissolving 0.3100 g in 100 ml of dimethyl formamide (DMF). Working solutions were prepared by diluting the stock solution appropriately with DMF.



Scheme: I

The structure of the yellow coloured product was established by IR and NMR spectral analysis. The IR peaks at 3185 cm^{-1} (–OH), 3292 cm^{-1} (–NH), 1735 cm^{-1} (>C=O), 1635cm^{-1} (>C=N-) and 1383 cm^{-1} (>C=N-) and NMR peaks at δ 12.10 ppm, (–OH), δ 10.50 ppm (–NH) and δ 9.49 ppm (–CH) confirm the structure of hydrazone formed as shown in (III).

1×10^{-2} M solution of the reagent was prepared by dissolving 0.3100 g in 100 ml of dimethyl formamide (DMF). Working solutions were prepared by diluting the stock solution with DMF.

Aluminium (III)

0.4533 g of aluminium ammonium sulphate (AR, BDH) was dissolved in 100 ml distilled water to get 0.01 M solution. The solution was standardized volumetrically[15] and appropriately diluted with distilled water to get the working solution.

Gallium (III)

0.1254 g of gallium chloride (Sigma-Aldrich) was taken in an air tight weighing bottle, weighed and transferred into a 250 ml volumetric flask. This was dissolved in distilled water containing few ml of hydrochloric acid and made upto the mark with distilled water to get 1×10^{-2} M solution. The solution was standardized[6] and diluted as required.

Cityltrimethyl ammoniumbromide

A 1% solution of cityltrimethyl ammoniumbromide (Sigma chemicals) was prepared by dissolving 1 g in hot distilled water and diluting to the volume in a 100 ml volumetric flask.

Buffer solutions

Buffer solutions of various pH values were prepared by mixing 1 M HCl and 1 M of CH_3COONa (pH 1.0-3.0), 0.2 M CH_3COOH and 0.2 M CH_3COONa (pH 3.5-7.0), 0.2 M CH_3COOH and 1 M CH_3COONa (pH 7.0) and 2M NH_4Cl and 2 M NH_4OH (pH8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter.

2.2. Sample preparation

Standard reference material

0.5 grams of carbon steel (JSS, 061-2) was treated with 30 ml of dilute HCl. 3 ml of 30% H_2O_2 were added and then the excess peroxide was decomposed by boiling to near dryness. The residue was dissolved in minimum volume of 2% HCl and cooled. The solution was filtered and diluted to 100 ml with distilled water. Known amounts of gallium were added to the samples during the mineralization.

Biological sample

The kidney and brain samples collected from Nizam Institute of medical sciences, Hyderabad were digested with a mixture of conc. HNO_3 (10 ml) and 30% H_2O_2 (3 ml) in a reflux apparatus. The mixture was heated till a clear solution was obtained. Known amounts of gallium were added to these solutions and evaporated to a small volume. They were then neutralized with NaOH and finally diluted to 50 ml in a volumetric flask with distilled water.

2.3. Instrumentation

Shimadzu UV-visible spectrophotometer (160A) fitted with 1 cm Quartz cells and ELICO digital pH meter models (LI–120) were used for absorbance and pH measurements respectively.

2.4. Procedure

Variable amounts of aluminium (0.054-0.270 µg mL^{-1}) and gallium (0.069-0.698 µg mL^{-1}) were mixed in 10 ml volumetric flasks and treated with 4 ml buffer(pH 6.0), HNAHBH (1×10^{-2} M, 0.9 ml) and Cityl trimethyl ammoniumbromide solution (1%, 0.5ml) and made upto the mark with distilled water. The second order derivative spectra were recorded in the wavelength region 350-600 nm and derivative amplitudes were measured at 476.5 nm and 449.5 nm. The amounts of aluminium and gallium present in the binary mixtures were evaluated from the measured derivative amplitudes and pre-determination calibration plots.

RESULTS AND DISCUSSION

The second order derivative spectra recorded for the various solutions containing different amounts of aluminium (III) or gallium (III) are shown in figure 1. The [Al(III)-HNAHBH] solution showed large amplitude at 476.5 nm where the [Ga(III) - HNAHBH]solution showed zero amplitude. Similarly the [Ga(III)-HNAHBH] species showed almost maximum amplitude at 449.5 nm where the Al(III) complex showed zero amplitude.

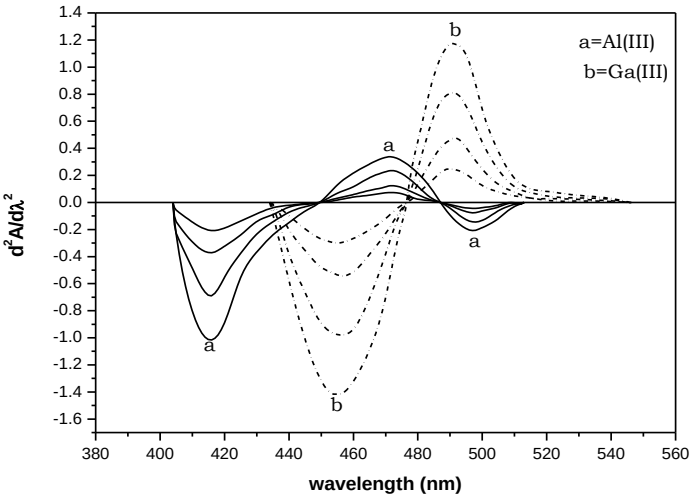


Fig. 1 Second order derivative spectra of

(a) Al(III) – HNAHBH and (b) Ga(III) – HNAHBH

Al(III) (µg mL^{-1}): 0.054; 0.094; 0.175; 0.256.

Ga(III) (µg mL^{-1}): 0.278; 0.487; 0.906; 1.324.

The simultaneous determination of Al(III) and Ga(III)was carried out by measuring the second derivative amplitudes at 476.5 nm and 449.5 nm respectively. The plots constructed between the derivative amplitudes measured and the amount of Al(III) or Ga(III) showed that the Beer's law was obeyed in the range 0.013-0.256 µg mL^{-1} of Al(III) and 0.017-1.324 µg mL^{-1} of Ga(III) respectively. Since no amplitude was observed for Ga(III)complex at 476.5nm where the Al(III) complex showed considerable amplitude and no derivative amplitude was noticed for Al(III) complex at 449.5 nm where the Ga(III) complex has maximum amplitude, the zero cross method was adopted for the simultaneous determination of Al(III) and Ga(III) in the binary synthetic mixtures by measuring their derivative amplitudes at 476.5 nm and 449.5 nm respectively. The results obtained along with recovery percentages are shown in table 1. The relative errors obtained in these determinations indicate the suitability of the proposed method for the simultaneous determination of Al(III)and Ga(III). The study on the effect of diverse ions on the derivative amplitudes showed that the presence of large number of anions and cations have no effect on the derivative amplitudes at the said wavelengths. Only Y(III) interferes when present in more than 3-fold excess.

Table.1
Simultaneous second derivative spectrophotometric determination of Al (III) and Ga (III)

Amount taken (µg mL^{-1})		Amount found* (µg mL^{-1}) (Recovery %)		Relative error (%)	
Al(III)	**Ga(III)**	**Al(III)**	**Ga(III)**	**Al(III)**	**Ga(III)**
0.054	0.279	0.053(98.15)	0.275(98.57)	-1.48	-1.43
0.108	0.279	0.110(101.85)	0.282(101.07)	+1.85	+1.07
0.162	0.279	0.160(98.76)	0.274(98.20)	-1.23	-1.79
0.216	0.279	0.219(101.39)	0.281(100.72)	+1.39	+0.72
0.270	0.279	0.268(99.26)	0.276(98.92)	-0.74	-1.07
0.176	0.069	0.179(101.70)	0.070(101.45)	+1.70	+1.43
0.176	0.139	0.173(98.29)	0.137(98.56)	-1.70	-1.43
0.176	0.279	0.177(100.57)	0.281(100.72)	+0.57	+0.72
0.176	0.418	0.177(100.57)	0.423(103.35)	+0.57	+1.19
0.176	0.557	0.175(99.45)	0.554(99.46)	-0.57	-0.54
0.176	0.698	0.177(100.57)	0.701(100.43)	+0.57	+0.43

*Average of four determinations

3.1. Applications

The proposed simultaneous method was applied for the determination of Al (III) and Ga(III) in standard reference materials and biological samples.

Known aliquots of the sample solutions were taken and the amounts of aluminium and gallium were evaluated by the proposed simultaneous method by measuring the second derivative amplitudes at 476.5 nm and 449.5 nm. The results are presented in tables 2 and 3.

The proposed method is simple, accurate and does not require the solving of simultaneous equations. The applicability of the method is evident from the recovery percentages of the metal ions and the relative errors noticed in the simultaneous determination of Al(III) and Ga(III) (tables 2 and 3).

Table. 2
Determination of aluminium and gallium in standard reference materials**:**

Sample	Aluminium content (μg mL^{-1})		Gallium content (μg mL^{-1})	
	Taken	Found*	Added	Found*
Carbon steel[a]	0.086	0.085 ± 0.006	0.415	0.413 ± 0.004
	0.172	0.174 ± 0.005	0.604	0.607 ± 0.002

*Average of five determinations ± SD

a-(%): Al: 0.034, C: 0.64, Cu: 0.011, Cr: 0.019, Si: 0.260, S: 0.012,
Ni: 0.019, N: 0.0038 P: 0.010, Mn: 0.490.

Table .3
Determination of aluminium and gallium in biological sample solutions**:**

Sample	Aluminium content (μg mL^{-1})		Gallium content (μg mL^{-1})	
	Added	Found*	Added	Found*
Kidney	-	0.014 ± 0.005	0.012	0.013 ± 0.003
	-	0.016 ± 0.002	0.034	0.033 ± 0.004
Brain	-	0.017 ± 0.003	0.024	0.024 ± 0.004
	0.005	0.023 ± 0.005	0.048	0.047 ± 0.006

*Average of four determinations ± SD

CONCLUSION: The present method is successfully applied for the simultaneous determination of Al and Ga in its trivalent state in various standard reference materials and biological samples and the result obtained are quite encouraging.

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REFERENCES

1. Hart M.M., Adamson R.H., *Proc.Natl.Acad.Sci.U.S.A.*1971, **68**, 1623–1626.
2. Hayes R.C., *J. Nucl.Med.*1970, **18**, 740–742.
3. Zweidinger R.A., Barnett R.L., *Anal.Chem.*1973, **45**, 1565–1566.
4. Dunea G., Mahurkar S.D., *N.Engl.J.Med.*1978, **88**, 502-510
5. Davison A.M., Oli H., Walker G.S.,. Lewins A.M, *Lancet.*1982, **ii,** 785–787.
6. Wills M.R., *Clin.Chem.*1985, **31**, 5–13.
7. Fernandez Soto I., Allende M.T., Diaz de Grena M.C., Machos M., Diaz Lopez B., Cannata J.B., *Nefrologia*. 1986, ***6,*** 71–74.
8. Siderman S., Manor D., *Nephron.*1982, ***31***, 71-77.
9. Andreoli S.P., Bergstein J.M., Sherrard D.J., *N.Engl.J.Med.*1984, **310**, 1079–1084.
10. Rodriguez Suarez C., Serrano M., Rodriguez Roza R., Peral V., Cannata J.B., *Nefrologia.*1986, ***6,*** 75–78.
11. Singh V.K., Agnihotri N.K., Singh H.B., Talanta, 2001, **55,** 799.
12. Agnihotri N.K., Ratnani S., Singh V.K., Singh H.B., Anal. Sci 2003,**19**, 1297-1301.
13. Agnihotri N.K., Ratnani S., Singh V.K., Shukla S.K., Parashar G.K., Anal.Lett, 2004, **37**(12), 2515-2529.
14. Brown E.V., Caglioti L., Paoluca G., Sucrow W., Hydrazones and hydrazones, In: Methodicum chemicum, C-N compounds, Academic Press, New York, 1975, pp. 6.
15. Vogel A.I., 'A Text book of Quantitative Analysis' 4th edn, Longmans, London, 389(1978).
16. Kolthoff I.M., and Elving P.J., "Treatise on Analytical Chemistry", Part II, Vol.2, p.85. Interscience, New York, (1962).