

## Simultaneous Second Order Derivative Spectrophotometric Determination Of Gallium (III) and Aluminium(III) using Diacetylmonoxime IsonicotinoylHydrazone

<sup>1</sup>P. Mallikarjuna, <sup>2</sup>K. Sreenivasulu, <sup>3</sup>M.V.N.V. Prasad Gupta, <sup>4</sup>G. Thippanna, <sup>5</sup>T. Mastanaiah, <sup>6</sup>V. Suryanarayana Rao

<sup>1-6</sup>Dept. of Chemistry Sri Krishnadeva University, Anantapur

<sup>1</sup>Dept. of Chemistry Brindavan Institute of Technology and Science, Kurnool.

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**Abstract:** Diacetylmonoxime Isonicotinoyl Hydrazone is new chromogenic reagent for the simultaneous determination of Gallium (III) and Aluminium(III). The reagent gives greenish yellow color in sodium acetate-acetic acid buffer medium with the metal ions. The maximum absorbance at 377 and 367 nm for Ga(III) and Al(III) respectively. The molar absorptivities of Al(III) and Ga(III) are  $2.69 \times 10^4$  and  $3.17 \times 10^4$  L.mol<sup>-1</sup>.cm<sup>-1</sup>, sandell's and sensitivities of Al(III) and Ga(III) are 0.00745 and 0.002002  $\mu\text{g.cm}^{-2}$  respectively. A few methods are available for simultaneous determination of Ga(III) and Al(III) by derivative spectrophotometric technique. Trace quantities of Ga(III) and Al(III) simultaneously determined in alloys and biological samples.

**Key Words:-** Gallium (III), Aluminium (III), Diacetylmonoxime IsonicotinoylHydrazone, simultaneous, alloys, biological samples, computed, second order derivative spectrophotometric.

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### I. Introduction

Hydrazones are usually named after the carbonyl compounds from which they are obtained. Isonicotinoyl hydrazones are the condensations products of isonicotinic acid hydrazide and the carbonyl components. Many of physically active hydrazones find application<sup>1</sup> in the treatment of diseases like tuberculosis, leprosy and mental disorders. Hydrazones also act as herbicides, nematocides, rodenticides, plant growth regulators, anti microbial, anti tuberculosis and anti tumor activities<sup>2, 3</sup>. Hydrazones act as chelating agents by forming colored complexes with metal ions. The potential applications of hydrazones derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh et.al<sup>4</sup>. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands that means it is resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using zero-crossing technique<sup>5, 6</sup>. In the absence of zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture<sup>7, 8</sup>. Derivative spectrophotometric analysis of two-component mixtures is also carried out without need to solve simultaneous equations<sup>9,10</sup>. Hydrazones reagents are widely used in our laboratories for the derivative spectrophotometric determination of metal ions<sup>8-11</sup>.

Gallium(III) and Aluminium(III) alloys are used as solid state electrolytes in fuel cells. An alloys of Al<sub>2</sub>O<sub>3</sub> (5%) and Ga<sub>2</sub>O<sub>3</sub> has high activity as a cracking catalyst for hydrocarbon oil. They also form a low melting eutectic alloy (M.P. 26.3°C). Here in we report the simultaneous second order derivative spectrophotometric determination of gallium (III) and aluminium (III) using Diacetyl monoxime Isonicotinoyl Hydrazone (DAMINH) in biological samples and alloys. The proposed simultaneous method involves the use of peak-to-base line measurement technique.

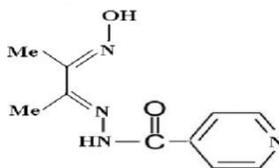
### II. Materials And Methods

#### Apparatus

Shimadzu 160A microcomputer based U.V - Visible spectrophotometer equipped with 1.0 cm quartz cells used for all absorbance studies and amplitude measurements in derivative spectrophotometry. An ELICO LI-120 digital pH meter was used in pH adjustments.

#### Reagents

All the reagents used were A.R grade unless and otherwise stated. All the solutions were prepared with doubly distilled water. Stock solutions (0.01 M) of gallium(III) and aluminium(III) were prepared by dissolving requisite quantity of gallium chloride (AR GSC) and aluminium sulphate (AR GSC) in 250 mL doubly distilled water respectively. The stock solutions were standardized and suitably diluted to obtain working solutions of metal ions.



**Figure 1:-** Structure of Diacetyl monoxime Isonicotinoyl Hydrazone (DAMINH)

The reagent was prepared by simple condensation of Diacetylmonoxime with IsonicotinoylHydrazide in 1:1 mole ratio and its structure is given above in figure 1. The reagent solution (0.01 M) was prepared by dissolving 0.22 mg of compound in 100 mL of dimethylformamide (DMF) and the solution was found to be stable for 48 hours.

**Triton X-100 solution**

A 5% solution was prepared by diluting 5.0 mL of Triton X-100 (AR Merk) to 100 mL with doubly distilled water.

**Buffer solutions**

Buffer solutions prepared by Hydrochloric acid (1.0 M) – Sodium acetate (1.0 M) (pH 0.5 - 3.5); Acetic acid (0.2 M) - Sodium acetate (0.2 M) (pH 4.0 - 6.5); Acetic acid (0.2 M) - Sodium acetate (1.0 M) (pH 7.0); Sodium tetraborate decahydrate (0.25 M) - Hydrochloric acid (0.1 M) (pH 8.0 – 9.1); Sodium tetraborate decahydrate (0.25 M) - sodium hydroxide (0.1 M) (pH 9.2 - 10.8) were used in the present study.

**Reaction with metal ions**

At different PH values some important metal ions were tested with DAMINH reagent. The samples were prepared in 25 ml volumetric flasks by adding 10ml of buffer, 1 ml of metal ion, 1 ml of 0.01 M DAMINH, 3 ml of DMF. The reaction mixture was diluted to the mark with distilled water. The absorbance was measured in 250 - 600 nm range against reagent blank. The results are computed in table 1 which indicates that the reagent is potential for the spectrophotometric determination of various metal ions.

**Table-1:**  
Analytical Characteristics of Diacetyl Monoxime Isonicotinoyl Hydrazone

Metal ion	pH	Color	$\lambda_{max}$ (nm)	Composition of the complex	Stability Constant	Molar absorptivity	Sandell's sensitivity	Range of determination ( $\mu\text{g/ml}$ )	Remarks Statistical data	
									S.D.	R.S.D (%)
Fe(II)	9	Yellow	355	1 : 1	$2.343 \times 10^5$	$3.83 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.002929	0.540 – 5.396	0.001194	0.138
V(V)	7	Greenish Yellow	356	1 : 1	$2.412 \times 10^7$	$2.65 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.008262	0.508 – 5.084	0.002649	0.579
Ga(III)	6	Greenish Yellow	362	1 : 1	$6.204 \times 10^6$	$3.17 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.002002	0.203 – 2.033	0.0149	2.899
Ni (II)	9	Brown	365	1 : 1	$3.21 \times 10^6$	$4.08 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.00219	0.188 – 1.886	0.478	0.00182
Ru (III)	10	Yellow	363	1 : 2	$8.620 \times 10^6$	$3.45 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.005024	0.470 – 4.695	0.003349	0.589
Al (III)	8	Golden Yellow	355	1 : 2	$1.01 \times 10^5$	$2.69 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.007526	0.785 – 7.588	0.00332	0.348
Hg (II)	6	Pale Yellow	364	1 : 1	$6.24 \times 10^7$	$5.06 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$	0.003240	0.942 -9.426	0.00174	0.302

**III. Recommended Procedures**

**(a). Determination of aluminium**

An aliquot of the solution containing 0.48 - 4.56  $\mu\text{g / mL}$  (ppm) of Al(III), 10 ml of  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  buffer solution (pH 8.0), 3 ml of DMF and 1 ml of 0.01 M DAMINH were combined in a 25 ml volumetric flasks and the resulting solution was diluted to the mark with distilled water. The absorbance of the solution was read at 355 nm against reagent blank. The measured absorbance is used to compute the amount of aluminium from predetermined calibration curve.

**(b). Determination of gallium**

An aliquot of the solution containing 0.2032 – 2.033  $\mu\text{g / mL}$  (ppm) of Ga(III), 10 ml of  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  buffer solution (pH 6.0), 3 ml of DMF and 1 ml of 0.01 M DAMINH were combined in a 25 ml volumetric flasks and the resulting solution was diluted to the mark with distilled water. The absorbance of the solution was read at 362 nm against reagent blank. The measured absorbance is used to compute the amount of aluminium from predetermined calibration curve.

**(c). Simultaneous determination of Aluminium and Gallium**

A known aliquot of a alloy containing 0.632 – 5.85 µg / mL Al(III) and 0.743 – 7.543 µg / mL of Ga(III), 3 ml of DMF and 1 ml of 0.01 M DAMINH were combined in a 25 volumetric flask and the resulting solution was diluted to the mark with distilled water. The absorbance was measured at 355 nm and 362 nm against reagent blank and the amounts of Aluminium (III) and Gallium (III) were respectively determined by solving the simultaneous equations.

**IV. Results And Discussion**

DiacetylmonoximeIsonicotinoylHydrazone is a new chromogenic reagent was not used for spectrophotometric simultaneous determination of Ga and Al so far. DAMINH reagent can easily prepared like any other Schiff base reagent. The reactions of some important metal ions with DAMINH are summarized in table1. The color reactions are mainly due to the complex formation of DAMINH with certain metal ions like Ni(II), Al(III), Ru(III), Fe(II), V(V), Hg(II), Ga(III) to give intense color complexes

**Simultaneous determination of Ga(III) and Al(III) in synthetic mixture**

The simultaneous spectrophotometric determination of aluminium(III) and gallium(III) in alloys and biological samples was carried out by employing the recommended procedure and the results are presented in the table

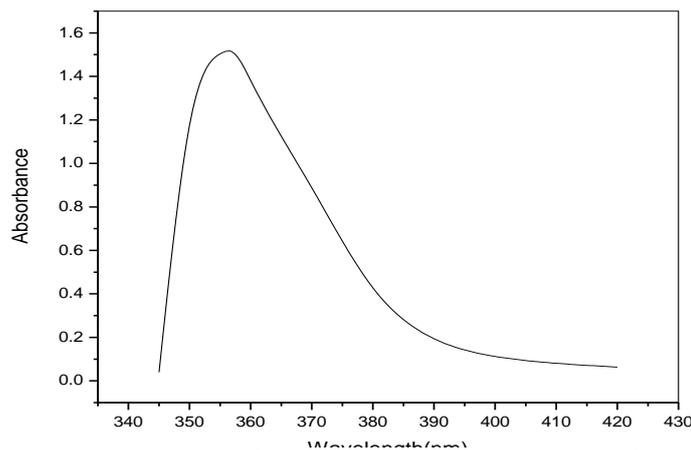
**Determination of aluminium (III) and gallium (III)**

Aluminium(III) and gallium (III) reacts with DAMINH neutral medium to give yellow colored complex. The color reactions are instantaneous even at room temperature at pH 7 range. The absorbents of yellow colored complexes remains stable for more than 10 hours in both cases. The maximum color intensity is observed at in the pH 5-6 and 7-8 range for Ga-DAMINH and Al-DAMINH complexes respectively. A 10 fold molar excess of reagent is sufficient for full color development in both systems. Addition of excess reagent has no adverse effect on the absorbance. The order of addition of metal ions, buffer, reagent and triton X-100 solutions has no adverse effect on the absorbance of complexes. Important analytical characteristics of Al-DAMINH and Ga-DAMINH complexes are computed in table2.

**Table 2: Important analytical characteristics of Al-DAMINH and Ga-DAMINH complexes**

Characteristics	Results	
	Al(III)-DAMINH	Ga(III)-DAMINH
$\lambda_{max}$ (nm)	355	362
Mole of reagent required per mole of metal ion for full colour development	5 - folds	10 – folds
Detection limit (µg/mL)	0.0735	0.0934
Limit of Quantization (µg/mL)	0.1454	0.1592
Molar absorptivity (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$2.69 \times 10^4$	$3.17 \times 10^4$
Sandell's sensitivity (µg.cm <sup>-2</sup> )	0.00745	0.002002
Beer's law validity range (µg/mL)	0.828 – 8.0	0.92 – 9.2
Optimum concentration range (µg/mL)	0.392 – 2.452	0.5352 -4.09
Slope (b)	0.224	0.195
Intercept (a)	0.045	0.048
Correlation coefficient	0.9891	0.8240
Specific absorptivity (ml.g <sup>-1</sup> .cm <sup>-1</sup> )	2.08	2.45
Relative standard deviation (%)	0.346	2.899
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1	1: 1

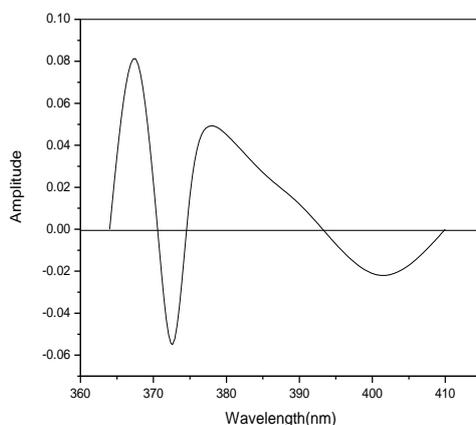
The direct and first order spectra of solutions of Al(III)-DAMINH and Ga(III)-DAMINH complexes in an aqueous neutral buffer medium (pH = 7) are shown in Figure 2. The absorption spectra overlap considerably and therefore direct and first order spectrophotometric determination of one metal in the presence of the other is not possible.



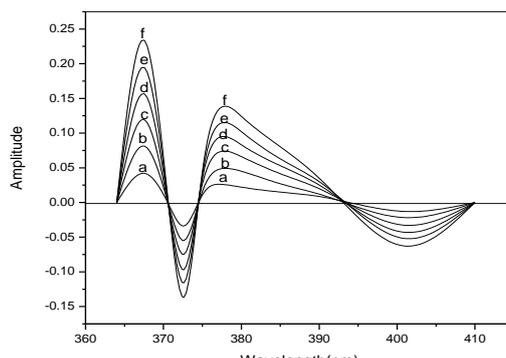
**Fig: 1** Zero order spectrum of Al(III) + Ga(III) in the presence of DAMINH  
 [Al(III)] =  $4 \times 10^{-5} \text{ M}$ ,  
 [Ga(III)] =  $1.6 \times 10^{-5} \text{ M}$ ;  
 [DAMINH] =  $5.6 \times 10^{-4} \text{ M}$  ;  
 pH = 7.0

**Derivative spectrophotometric determination of aluminium(III) and gallium(III)**

Second order derivative spectrophotometric is useful technique for simultaneous aluminium(III) and gallium(III) because it decreases the interference of adverse ions i.e., increase the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ions having overlapping spectra. The main reason why the interest in derivative spectra is due to simplicity, relatively quick, easy realization and increased analysis of minor components. The recommended derivative processor was employed for the simultaneous determination of aluminium(III) and gallium(III).



**Fig:2** Typical second order spectrum of Al(III) + Ga(III) in the presence of DAMINH  
 [Al(III)] =  $4 \times 10^{-5} \text{ M}$ ,  
 [Ga(III)] =  $1.6 \times 10^{-5} \text{ M}$ ;  
 [DAMINH] =  $5.6 \times 10^{-4} \text{ M}$  ;  
 pH = 7.0



**Fig: 3.13.5** Second order spectrum of Al(III) + Ga(III) in the presence of DAMINH

*Simultaneous Second Order Derivative Spectrophotometric Determination Of Gallium(III) And*

- [Al(III)] =  $4.0 \times 10^{-5}$  M;  
 [Ga(III)] =  $1.6 \times 10^{-5}$  M  
 [DAMINH] =  $5.6 \times 10^{-4}$  M ;pH = 7.0  
 a) 0.5 ml of Al(III) and Ga(III) each  
 b) 1.0 ml                    ,,  
 c) 1.5 ml                    ,,  
 d) 2.0 ml                    ,,  
 e) 2.5 ml                    ,,  
 f) 3.0 ml                    ,,

**Interference**

The selectivity of the derivative methods was tested by studying the effect of foreign ions which brings about change the amplitude by  $\pm 2$  % was taken as the tolerance limit. Interference of diverse ions which often accompany with Al(III) and Ga(III) has been studied in the determination of 1.3798  $\mu\text{g/mL}$  of Al(III) and 3.042  $\mu\text{g/mL}$  of Ga(III). The results are computed in table3.

**Table 3. Tolerance limit of foreign ions in the determination of 3.042  $\mu\text{g/mL}$  Ga(III) and 1.3798  $\mu\text{g/mL}$  of Al(III).**

Foreign ion	Tolerance limit ( $\mu\text{g/ml}$ )	Foreign ion	Tolerance limit ( $\mu\text{g/ml}$ )
Fluoride	217.12	Al (III)	24.1
Chloride	176.25	Pb (II)	1657.6
Iodide	507.60	W (VI)	73.54
Nitrate	992.04	Co (II)	7.04
Acetate	188.94	Se (IV)	30.08
Oxalate	20.0	Mn (II)	39.96
EDTA	78.0	La (III)	123.1
thiosulphate	19.72	Zn (II)	261.6
		Ru (III)	26.95
		Ni (II)	78.27
		Mo (VI)	5.69
		Hg (II)	5.29
		Pd (II)	0.59
		Ag (I)	1.68
		Mg (II)	1.793
		V (IV)	21.4
		V (V)	23.1

Al(III)- DAMINH			
Foreign ion	Tolerance limit ( $\mu\text{g/ml}$ )	Foreign ion	Tolerance limit ( $\mu\text{g/ml}$ )
Fluoride	20.54	U (VI)	82.80
Chloride	54.62	Ru (III)	13.26
iodide	253.8	W (VI)	63.95
nitrate	130.53	Co (II)	0.31
acetate	43.7	Mo (VI)	19.2
oxalate	8.85	Se (IV)	5.45
EDTA	1667	Pd (II)	0.12
thiosulphate	15.5	Mg (II)	32.41
		Cu (II)	0.45
		Sn (II)	14.84
		Ni (II)	0.612
		Zr (IV)	10.73
		Sr (II)	12.75
		La (III)	52.91
		Ti (IV)	6.96
		Al (III)	13.49
		Th (IV)	64.01
		Cd (II)	0.804
		Cr (VI)	5.19

**V. Applications**

The validity of the proposed method was tested by analyzing alloys sample and biological samples containing Al(III) and Ga (III). Satisfactory results were obtained for the recovery of both the metals indicating that the proposed method is effective for their simultaneous determination

**Analysis of Alloys and Biological samples:**

1 gm of alloy sample was digested in 10 mL of aqua-regia by warming and the solution was evaporated to dryness. The residue was dissolved in 20 mL of diluted HCl and resulting solution concentrated to 10.0 mL, diluted to 100 mL with doubly distilled water, filtered and made up to the mark in a 250-mL volumetric flask.

The simultaneous second order derivative spectrophotometric determination of Al(III) and Ga(III) in the biological samples, alloy samples were carried out by employing the recommended procedure. A known aliquot of the sample solution was taken in a 25-mL volumetric flask containing 10 mL buffer (pH = 7), 1.0 ml of Triton X-100 (5%) solution and 1.0 mL of DAMINH reagent (0.01 M) solutions. The contents in the flask were made up to the mark with doubly distilled water. The second derivative amplitudes of the reaction

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mixture were measured at 367 nm and 377 nm. The amount of aluminium(III) was computed from the pre-determined calibration plot at 367 nm. Similarly, the amount of gallium(III) was deduced from the pre-determined calibration plot at 377 nm. The results are computed in Table 4 and Table 5 respectively.

**Table 4: Simultaneous determination of Al(III) and Ga(III) in alloys**

Amount taken ( $\mu\text{g mL}^{-1}$ )		Amount found* ( $\mu\text{g mL}^{-1}$ ) (% of recovery)		Relative error (%)	
Al(III)	Ga(III)	Al(III)	Ga(III)	Al(III)	Ga(III)
0.050	0.432	0.049 (98.2)	0.425 (99)	-1.84	-1.10
0.100	0.432	0.101 (101.6)	0.428 (99.6)	+1.71	-0.54
0.150	0.432	0.148 (99.6)	0.439 (101.4)	-0.60	+1.30
0.200	0.432	0.197 (98.8)	0.430 (99.7)	-1.37	-0.36
0.250	0.432	0.248 (99.4)	0.428 (99.6)	-0.72	-1.49
0.300	0.432	0.303 (101.2)	0.441 (101.9)	+1.22	+1.68
0.100	0.216	0.101 (101.6)	0.215 (99.5)	+0.91	-1.49
0.100	0.432	0.098 (98.4)	0.430 (98.6)	-1.83	-1.30
0.100	0.648	0.099 (99.2)	0.646 (99.7)	-0.91	-0.49
0.100	0.864	0.100 (100)	0.866 (101)	0.00	+0.92
0.100	1.080	0.101 (101.96)	1.075 (99.4)	+0.92	+0.65
0.100	1.296	0.100 (100)	1.292 (99.4)	0.00	-0.42

\*average of four determinations

**Table 5: Simultaneous determination of Al(III) and Ga(III) in biological samples**

Sample	Ga(III) ( $\mu\text{g mL}^{-1}$ )		Al(III) ( $\mu\text{g mL}^{-1}$ )	
	Added	Found*	Added	Found*
Blood serum 1	0.250	0.254	0.135	0.133
Blood serum 2	0.620	0.622	0.075	0.078
Blood serum 3	1.250	1.254	0.230	0.233
Kidney	0.980	0.986	0.180	0.179
Brain	1.46	1.47	0.325	0.324

\*average of four determinations

## VI. Conclusions

DiacetylmonoximeIsonicotinoylHydrazone is a versatile chromogenic reagent used for the simultaneous determination of Ga(III) and Al(III) in neutral medium in microgram quantities. The present second order derivative spectrophotometric method is simple, rapid, sensitive and selective and do not involve heating or filtration or separation. Foreign ions do not interfere in the determinations. The method precise and accurate determinations can be made. Triton-X increases the stability of the complex. Hence simultaneous determination of Ga(III) and Al(III) can carried out by using DAMINH by the present method.

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