Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry
2016, 5 (1): 242-247
(International Peer Reviewed Journal)

Simultaneous Spectrophotometric Determination of Iron (II) And Gallium(III) In Micellar Media Using 2-Hydroxy-3-Methoxybenzaldehyde-Isonicotinoylhydrazone (HMBAINH)

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Accepted on 16th December 2015

ABSTRACT

*A simple and sensitive derivative spectrophotometric method for simultaneous determination of iron and gallium using 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone (HMBAINH**)** as a selective analytical reagent was developed. The complexes of metal ions with HMBAINH were formed immediately in acidic media at pH 5.0 in presence of aqueous solution of nonionic surfactant Triton-X100. The zero-crossing measurement technique was found suitable for the direct measurement of the second derivative value of [Fe(II)-HMBAINH] and [Ga(III)-HMBAINH] at 442 nm and 412 nm respectively. The concentration ranges applicable for the determination of Fe (II) and Ga (III) are 0.14-1.396 $\mu g\ mL^{-1}$ and 0.266-2.661 $\mu g\ mL^{-1}$ with detection limits 0.013 $\mu g\ mL^{-1}$ and 0.085 $\mu g\ mL^{-1}$ respectively. Analysis of synthetic samples of magnetic garnets showed that this method can be successfully used for simultaneous determination of iron and gallium in real samples.*

Keywords: Iron, Gallium, HMBAINH, Derivative spectrophotometry, Simultaneous determination.

INTRODUCTION

Iron and gallium exist together in iron - gallium alloys [1], iron meteorites [2], iron– gallium oxide catalyst [3], flux grown magnetic garnets [4] (R_1 R $_2$(Fe, Ga) $_5$ $O_{12,}$ where $R_{1,}$ R2 =Y, Eu, Gd), in red tinted calcites as iron and gallium porphirins, etc. Literature survey shows number of direct spectrophotometric methods [5-14] for the determination of these metals individually, but no simultaneous method has been reported so far. We are now reporting a simple, sensitive and rapid second order derivative spectrometric method for the simultaneous determination of iron and gallium in aqueous state without prior separation and without solving simultaneous equations.

MATERIALS AND METHODS

Apparatus: A Perkin Elmer (LAMBDA25) spectrophotometer controlled by a computer and equipped with a 1cm path length quartz cell was used for UV-Vis spectra acquisition. Spectra were acquired between 350- 600nm (1nm resolution). An ELICO model LI-120 pH-meter furnished with a combined glass electrode was used to measure pH of buffer solutions.

Reagents and solutions [15]: All chemicals used were of analytical-reagent grade. Doubly distilled water was used for preparing aqueous solutions. 0.01 M solution of Fe(II) and Ga(III) solutions were prepared by dissolving appropriate amounts of Mohr's salt (Sd. Fine) and gallium chloride (Sigma-Aldrich) in 100mL distilled water, solutions of lower concentrations were prepared by successive dilution of the stock solution.

Preparation of HMBAINH: Equimolar solutions of 2-hydroxy-3-methoxy benzaldehyde in methanol and isonicotinic acid hydrazide in water were refluxed for two hours on water bath and cooled. The light brownish yellow coloured solid obtained was then separated by filtration, washed and dried. The product was recrystallized from aqueous alcohol in the presence of norit. The product showed melting point of 224°C. Fig.1 shows the method of preparation and structure of HMBAINH. The reagent solution $1x10^{-2}$M of was prepared by dissolving 0.271 g in 100 mL of dimethylformamide (DMF). Working solutions were prepared by diluting the stock solution with DMF.

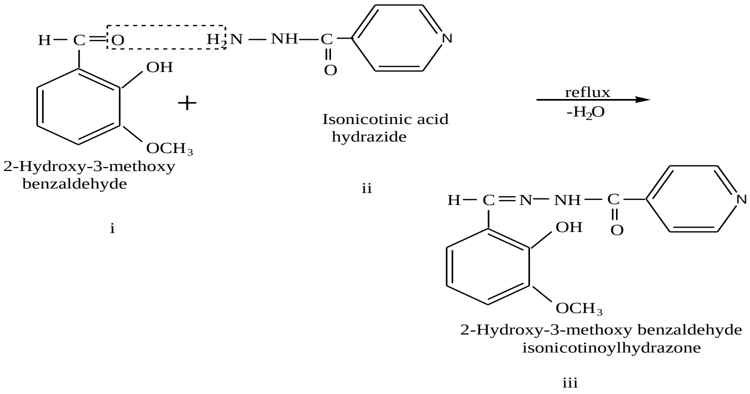


Fig. 1 Method of Preparation and Structure

Buffer solutions: Buffer solutions of various pH values were prepared by mixing the appropriate solutions in suitable ratios as shown below.

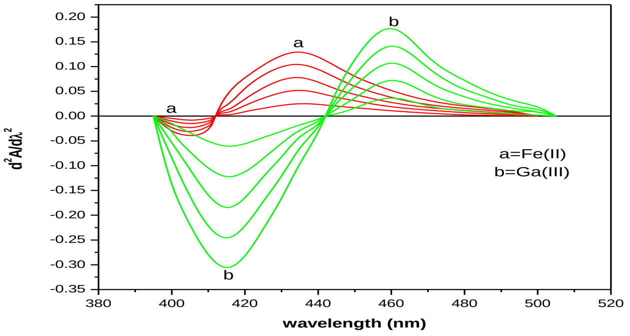
pH	**Constituents**
1.0 – 3.0	1 M of sodium acetate + 1 M hydrochloric acid
3.2– 6.0	0.2 M sodium acetate + 0.2 M acetic acid
7.0	1 M sodium acetate + 0.2 M acetic acid
8.0 – 11.0	2 M ammonium hydroxide + 2M ammonium chloride

Triton X-100 solution: A 1% solution was prepared by diluting 1.0 mL of Triton X-100 (AR Merk) to 100 mL with doubly distilled water.

RESULTS AND DISCUSSION

Determination of iron (II) and gallium (III) by zero order method: An aliquot of the solution containing iron (II) or gallium(III) in the analytical concentration range (Fe(II) = 0.140 – 1.396 µg mL^{-1}; Ga(III) = 0.266-2.661 µg mL^{-1}), 4 mL of buffer solution (pH = 5.0), 2mL of 1% Triton X-100 and 0.3 mL of HMBAINH ($1x10^{-2}$ M) were added in a 10mL volumetric flask and the contents were diluted to the mark with distilled water. The absorbance was measured at 385nm and 405 nm for Fe (II) and Ga (III) respectively. The measured absorbance was used to compute amount of metal ion from the respective calibration plot.

Simultaneous second order derivative spectrophotometric determination of mixture of iron and gallium: In a set of 10 mL volumetric flasks, different amounts of Fe (II) or Ga (III) were taken. 4 mL of buffer solution (pH 5.0), 0.3 mL of HMBAINH ($1x10^{-2}$ M) and 2mL of 1% triton x-100 were then added to each of these flasks and the contents were diluted to the mark with distilled water. The second order derivative spectra of [Fe(II)-HMBAINH] and [Ga(III)-HMBAINH] species were recorded in the wavelength region 350-600 nm against reagent blank. It can be seen from the fig.2 that at 442 nm, iron (II) species has considerably large derivative amplitude while Ga(III) species has zero amplitude. Similarly at 412nm Ga (III) species has large amplitude while Fe (II) species has zero amplitude. Therefore iron and gallium can be simultaneously determined in mixtures by measuring the second order derivative amplitudes at 412 nm for gallium and at 442 nm for iron without the need to solve the simultaneous equations.



Fe (II) (µg mL^{-1}): 0.279; 0.558; 0.837; 1.116; 1.396
Ga (III) (µg mL^{-1}): 0.279; 0.558; 0.836; 1.115; 1.394

Fig.2. Second order derivative spectra of (a) [Fe (II)-HMBAINH] and (b) [Ga (III)-HMBAINH]

Linearity: The calibration graph for the determination of Fe(II) ion was constructed by measuring the derivative amplitudes at the zero cross point of [Ga (III))-HMBAINH] species (442 nm) (Fig.3). In the same way, calibration graph was constructed for the determination of Ga (III) ion by measuring the derivative amplitudes at the zero cross point of [Fe (II)-HMBAINH] species (412 nm) (Fig.4). High values of correlation coefficient and the closeness of intercepts to zero (Table 1) show that the calibration plots are linear and obey Beer's law (Fig.3 and.4). The concentration ranges applicable for the determination of Fe (II) and Ga (III) are 0.140-1.396 µg mL^{-1} and 0.266-2.661 µg mL^{-1}respectively

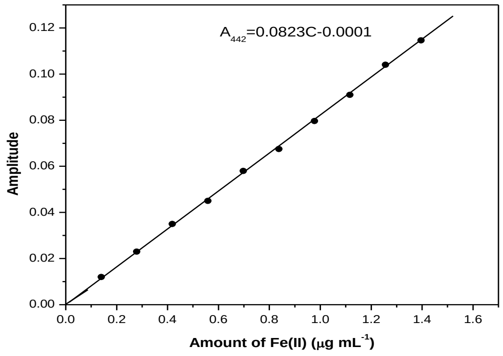


Fig.3. Beer's law plot of [Fe (II)-HMBAINH]

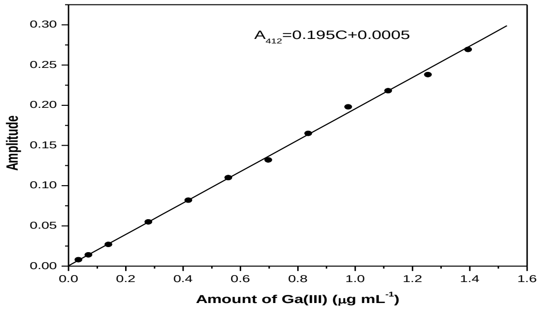


Fig.4. Beer's law plot of [Ga (III)-HMBAINH]

Interference analysis: The calibration plot of [Fe(II)-HMBAINH] constructed by measuring the derivative amplitudes at 442nm in the presence of 0.558 µg mL^{-1}of Ga(III) and the calibration plot of [Ga(III)-HMBAINH] at 412nm in the presence of 0.279 µg mL^{-1}of Fe(II) proves that there is no influence of Fe(II) on the derivative amplitude of Ga(III) species at 412nm and the amount of Ga(III) on Fe(II) species derivative amplitude at 442nm..The slopes, intercepts and correlation coefficients presented in table 1 confirm the mutual independency of Fe (II) and Ga (III) in the presence of each other. This allows the determination of Fe (II) and Ga (III) simultaneously by second order derivative method without any significant error and prior separation.

Table 1 Linear regression analysis of the determination of Fe(II) and Ga(III) in mixture by second derivative spectrophotometry.

Metal ion determined	Wave length (nm)	Other metal present (µg mL^{-1})		slope	Intercept	Correlation coefficient
		Fe(II)	Ga(III)			
Iron(II)	442			0.082	-1x10^{-4}	0.9996
			0.558	0.079	-0.9 x10^{-4}	0.9994
Gallium(III)	412			0.195	0.005	0.9999
		0.279		0.186	0.004	0.9997

Simultaneous determination of Fe (II) and Ga (III) in binary mixtures: The synthetic binary mixtures of Fe (II) and Ga (III) were prepared by mixing Fe (II) and Ga (III) in various proportions. The resultant mixtures were treated with suitable volume of HMBAINH (1X10^{-2}M) and 2mL of 1% triton-100 surfactant and a buffer solution of pH 5.0. The contents were finally diluted to the volume in 10mL volumetric flasks and the derivative amplitudes were measured at 412nm and 442nm for their second order derivative spectra. The amounts of Fe (II) and Ga (III) were evaluated from the measured derivative amplitudes and pre-determined calibration plots at 442nm and 412nm respectively. The results obtained along with the recovery percentages are presented in table.2.The relative error values calculated indicate the good acceptability of the proposed method for the simultaneous determination of Fe (II) and Ga (III) in the mixtures.

Table 2. Simultaneous second order derivative spectrophotometric determination of Fe II) and Ga (III)

Amount taken (µg mL^{-1})		Amount found* (µg mL^{-1}) (Recovery %)		Relative error (%)	
Fe(II)	Ga(III)	Fe(II)	Ga(III)	Fe(II)	Ga(III)
0.140	0.558	0.138 (98.6)	0.552 (98.9)	-1.43	-1.07
0.279	0.558	0.282 (101.1)	0.549 (98.4)	+1.07	-1.61
0.419	0.558	0.416 (99.3)	0.550 (98.6)	-0.72	-1.43
0.558	0.558	0.562 (100.7)	0.560 (100.4)	+0.71	+0.35
0.698	0.558	0.695 (99.6)	0.561 (100.53)	-0.43	+0.53
0.838	0.558	0.833 (99.4)	0.554(99.3)	-0.59	-0.72
0.279	0.139	0.277 (99.3)	0.140 (100.7)	-0.72	+0.72
0.279	0.279	0.280 (100.3)	0.269 (96.4)	+0.36	-0.36
0.279	0.558	0.275 (98.5)	0.560 (100.4)	-1.43	+0.35
0.279	0.836	0.282 (101.1)	0.838 (100.2)	+1.07	+0.23
0.279	1.115	0.281 (100.7)	1.111. (99.6)	+0.72	-0.35
0.279	1.394	0.278 (99.6)	1.390 (99.7)	-0.36	-0.28

*Average of four determinations

APPLICATIONS

The present second order derivative spectrophotometric method was applied for the determination of iron and gallium in flux grown magnetic garnets. Since, these natural samples were not available, synthetic mixtures of the garnetic samples containing yttrium, iron, gallium, europium and gadolinium were prepared by mixing these metal ions in suitable proportions. Appropriate volumes of these samples were treated with suitable amounts of HMBAINH reagent at pH 5.0 and the second order derivative spectra were recorded. The derivative amplitudes of the sample solutions measured at 412nm and 442nm were utilized for computation of the amounts of iron and gallium from pre- determined calibration plots. The results shown in table.3 indicate the applicability of the proposed simultaneous method for the analysis of real samples.

Table 3. Determination of iron and gallium in magnetic garnets

	Amount (µg mL^{-1})				Relative error	
Sample	Taken		Found(n=4)±SD		(%)	
(Composition)	Fe(II)	Ga(III)	Fe(II)	Ga(III)	Fe(II)	Ga(III)
Sample 1 (50 Fe;38 Ga ; 8 Y; 3.5 Eu; 0.5Gd)	1.50	3.60	1.48±0.04	3.68±0.03	1.30	2.20
	3.00	2.40	2.94±0.08	2.36±0.01	2.00	1.60
	5.50	4.60	5.64±0.30	4.48±0.50	2.50	2.60
Sample 2 (45 Fe ; 27 Ga ; 16 Y; 8 Eu ; 4 (Gd)	0.80	0.35	0.83±0.03	0.33±0.04	3.70	5.70
	2.40	1.70	2.52±0.05	1.73±0.03	5.00	1.70
	4.40	3.68	4.38±0.04	3.72±0.02	0.45	1.00

CONCLUSIONS

From the results of this study it can be concluded that the proposed second order derivative spectrophotometric method for simultaneous determination of iron and gallium using HMBAINH reagent is a simple, selective, rapid, reliable and inexpensive method. Analysis of synthetic mixtures showed that this method can be successfully used for simultaneous determination of Fe and Ga in real samples. So the recommended method can be easily and rapidly used in routine analysis.

REFERENCES

[1] R.A. Kellogg, A.M. Russell, T.A. Lograsso,\A.B. Flatau, A.E. Clark, M. Wun-Fogle, Tensile properties of magnetostrictive iron–gallium alloys, *Acta Materialia,* **2004**, 52(17), 5043–5050.

[2] Lovering, John F, Nichiporuk, Walter, Chodos, Arthur, Brown, Harrison, The distribution of gallium, germanium, cobalt, chromium, and copper in iron and stony-iron meteorites in relation to nickel content and structure, *Geochimica et Cosmochimica Acta,* **1957,** 11(4), 263-278.

[3] Zheng Wei Pan, Zu Rong Dai, Chris Ma and Zhong L. Wang, Molten gallium as a catalyst for the Large-scale growth of highly aligned silica nanowires, *J. Am. Chem Soc, 2*__002__, 124 (8) 1817–1822.

[4] Shin. Takasu, S. Shimanuki, Tunnel like defects of flux grown magnetic garnets, *Journal of Crystal Growth,* **1974**, 24–25, 641-645

[5] Q.K. Zhang, L.Z. Kong and L. Wang, Thiocyanate–phenanthroline– oil emulsifier OP spectrophoto metry of iron, *Fenxi Shiyanshi*, **2005**, 24(1), 77-79.

[6] P.K. Tarafder and R. Thakur, Amperometric methods for trace determination of Rhodium (III) and Ruthenium(III), *Microchem. J,* **2005**, 80(1), 39-43.

[7] P.K. Tarafder and R. Thakur, Surfactant-mediated extraction of iron and its spectrophotometric determination in rocks, minerals, soils, stream sediments and water samples, *Microchem. J,* **2005**, 80(1), 39-43.

[8] Battula Sreenivasa Rao, Gurrala Srinivasa Rao, B.V. Kiran and K.Siva Nagaraju, Effect of Nonionic Surfactant (Triton X–114) on the Spectrophotometric Determination of Selenium (IV) With Isonitriso p-Isopropyl Acetophenone Phenyl Hydrazone, *J. Applicable.chem,***2012**, 1(2), 232-238.

[9] Poonam P. Shevde, Sushama M. Lele, Mahesh D. Natikar, Determination of Iron in Spinach plants Grown in different areas by using HIMMI as a reagent, *J. Applicable.chem,* **2012**, 1(3), 392-396.

[10] F.G. Martins, J.F. Andrade, A.C. Pimenta, L.M. Lourenco, J.R.M. Casto and V.R. Balbo, Spectrophotometric study of iron oxidation in the iron(II)/thiocyanate/acetone system and some analytical applications, *Electica Quimica*, **2005**, 30(3), 63-71.

[11] K. Saraswathi and K. Madhavi, Spectrophotometric Determination of Cobalt in Water and Agricultural Samples, *J. Applicable. chem,* **2012,** 1(4), 500-504.

[12] J.M. Cano Pavon, A. Garcia de Torres, M.E.U. Pozo, Preconcentration of Cadmium, Cobalt, Copper, Nickel And Zinc By Solvent Extraction Into Methyl Isobutyl Ketone With 1,5-Bis [L-(2-Pyridyl) Ethylidene] Thiocarbonohydrazide And 1,5- Bis [Phenyl-(Zpyridyl) Methylene] Thio carbon hydrazide, *Talanta*, **1990**, 37(4), 385-391.

[13] V.K. Singh, N.K. Agnihotri, H.B. Singh and R.L. Sharma, Simultaneous determination of gallium (III) and indium(III) by derivative spectrophotometry, *Talanta.*, **2001**, 55(4), 799-806.

[14] Richard, Sample Pretreatment and Separation, *Wiley*., New York, **1987**, p.60.

[15] A.I. Vogel, Text Book of Quantitative Inorganic Analysis, 3rd Ed, Longman, London, **1972**.

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