التقدير الطيفي لايون السماريوم الثلاثي باستخدام كاشف 1 – (2- بنزواميدازولايل – ازو) – 2-هيدروكسي -3- حامض النفثويك

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الخلاصة

يتفاعل ايون السماريوم الثلاثي مع الكاشف 1 –(2- بنزوميدازولايل –ازو) -2- هيدروكسي -3-حامض النفثويك في المحيط القاعدي عند دالة حامضية مقدارها 8 مكونا معقدا ذا لون احمر برتقالي محمر عند طول موجي مقداره 550 نانوميتر ، وجد ان المعقد يكون مستقرا لاكثر من 48 ساعة عند الدالة الحامضية المثلى مع امتصاصية مولارية مقدارها 77، 7767 ل. مول $^{-1}$. سم$^{-1}$ مع مطاوعة لقانون بير لمدى من التراكيز بحدود (635 ، .* 10^{-5} – 35 ،6 * 10^{-5}) مولاري . تم تعيين تكافؤية المعقد من حيث نسبة الكاشف : فلز بطريقة النسبة المولية ووجد ان الارتباط يكون بنسبة 3 : 1 .

درس تأثير تداخل عدد الايونات الموجبة والسالبة عند التقدير الطيفي لايون السماريوم الثلاثي وتبين وجود تراكيز متباينة من الايونات المضافة تعطي نتائجا مختلفة على قيم الامتصاص .

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The Spectrophotometric Determination of Samarium (III) With (l-2(2-Benzoinidazoly-AZO)-2-Hydroxy-3-Naphthoic Acid

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Abstract

Samarium(III) ions react with (l-2(2-benzoinidazolyl-azo)-2-hydroxy-3-naphthoic acid in basic medium (pH = 8.0) forms a red-orange complex at A.$_{max}$ (550nm). The complex was found to be stable for at least 48 hrs. at the given pH. The apparent molar absorptivity is 7776.77 L.mol^{-1}.Cm^{-1} and a linear calibration curve is obtained in the range (0.639x 10^{-5}M - 6.350x 10 $^{-5}$M).

The stoichiometry of complex was confirmed by using mole ratio method which indicated that ratio of reagent to metal is 3:1.

The effects of the presence of different cations and anions as interferences in the determination of samarium(III) under the given conditions were investigated.

Introduction

A basic characteristic of the lanthanide group is the chemical similarity of the individual members. Consequently, data on the total lanthanide content often suffices in practical problems, particulary when all the lanthanides behave similarly, eg. in the production of alloy steels or when the ratio of the individual members is constant (e.g. in geochemistry).

In a search for new sensitive and selective reagents a wide variety of substituents and subgroups has been introduced on azobenzene and azonaphthalene derivatives in attempts to obtain more favorable metal-binding and colorimetric behavior for lanthanide elements, arsenazo-1, arsenazo(III) and dicarboxy-arsenazo(III) [1-3] have been widely used to determine total rare earth, but they are suffer from non selectivity.

Carboxynitrazo [4] and arsenazo-p-$N0_2$ [5-6] have been also reported to give sensitive colour reactions with cerium sub-group elements and to give no, or less sensitive reactions with yttrium subgroup elements, but have not been widely used.

Numerous spectrophotometric methods based on the use of molecules possess hydroxyl group, especially 0,0'- dihydroxy azo compound including erichrom black T [7], calmagite [8] and Xylenol orange[9], have been used to determine total rare earth but none of these procedures is very selective.

However atomic absorption, atomic emission and high performance liquid chromatography techniques are vastly superior to any of the spectrophotometric procedures described to data; so it is clear that further work is indicated.

The present paper reports aspectrophotometric determination of samarium(III) using a reagent (l-(2-benzoimidazolyI-azo)-2hydroxy-3-naphthoic) acid which was synthesized from 2-aminobenzimidazol and 2-hydroxy-3-napthoic acid as described previously [10], and the optimium reaction conditions are evaluated and excellent metal ion sensitivities are obtained.

Materials and Methods

Apparatus & Reagents: Spectrophotometric measurements were made with LKB-Bouch model NOVA SPEC, with pyrex cell of lOmm path length was used. The pH was measured on LP-56 pH-meter Aqueous solution of samarium (III) (4.42×10^{-6} M) was prepared by dissolving 0.0110 gm of ($Sm_2 0_3$) in 20 ml (5M) $HN0_3$ and then diluted to 100ml with deionized water.

An alcoholic (7.53×10^{-4} M) (1-2(2- benzo inidazolyl – azo) -2- hydroxyl -3-naphthoic acid reagent was prepared by dissolving 0.0625 gm of the reagent in 250 ml ethanol solution and kept in dark room.

Buffer solution (pH 4.0) was prepared by mixing 50 ml (0.2 M potassium hydrogen phthalate) with 0.4ml (0.2 M KOH) and then diluted to 200ml with deionized water(ll). The pH being adjusted with few drops of lM NaOH or lM HC1.

General Procedure: The test solution containing not more than 1.2 ug of samarium was taken in a 10ml volumetric flask; 1ml of buffer solution at pH 6.0 and 5ml of (7.53×10^{-4} M) reagent were added successively and mixed well. The solution was then diluted to the mark with water and the absorbance was measured at 550 nm against reagent blank solution.

Results and Discussion

Absorption Spectra: The absorption maximum of the reagent was at 490 nm [figl]. The complexes of Samarium have absorption maximum at 540nm at (pH 6.0), and there was no shift in the wavelength when the pH value varied from 5.0 to 8.0 under these conditions samarium forms a red-orange coloured complex. The formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately 60nm.

Effect of pH: The effect of pH on the absorption of the samarium complex was studied at 550nm with solution containing 4×10^{-7} M samarium and 1.12×10^{-4}M reagent. **A** plot of absorbance against pH [Fig 2] showed that the absorbance was increased gradually as the pH increased from 5.0 to 8.0 but decreased rapidly above pH 8.0. The increase in the absorbance under these condition may be explained by an increasing sensitivity of the reagents at this value of pH to word Samarium.

Reagent Concentration: The effect of the amount of reagent solution on the absorbance of a series of solutions containing known amount of Sm(III) solution buffered at pH 8.0 are shown in [Fig 3]. It was found that (3.76×10^{-4} M) of the reagent solution sufficed to complex (9.52×10^{-5} M) of Sm with large excess of reagent has deleterious effect on the absorbance.

Stoichiometery of Complex: The stiochiometery of the complex has been studied by the mole-ratio methods [fig 4], the method show that Sm(III) form as 1:3 complex (Metal : ligand) with reagents, this is in agreement with (Hamed) observation that reagent form a (1:3) complex with La^{+3} and Eu^{+3}.

Effect of Time: The stability of the complex was studied at laboratory temperature by measuring the absorbance of regular time intervals. The maximum absorbance was acheived after 5 min and no change was then observed for at least 48hr.

Beer᾿s Law and sensitivity : The absorbance of Sm(III) complex was found to be linear related to the concentration of metal, Beer's Law's was obyed in the concentration range (0.635×10^{-5} M - 6.35×10^{-5} M) with molar absorptivity of (7776.77 L. mol^{-1}.Cm^{-1}).

Effect of Forign Ions: The analytical method was applied to a fixed amount of Sm(lII) (6ug/ml) in the presence of various amounts of other ions.

The anions examined, chloride, nitrate, sulfate and chromate ions showed no interference at all concentration; fluoride, thiosulfate and citrate ions did not interfere in 50 fold molar amounts , or tartrate and phosphate ions in 20 fold amount.

The tolerance limits were taken of divalent and trivalent metal ions that caused an error are summarised in table (1) iron(III), nickel(II), Cerium(III), Zinc(II) and copper interfered seriously with determination in the (Sm-BIANA) system and their interference can be eleminated by addition (4mg) of ascorbic acid and 4 mg .Potassium cyanide, so that prior separation would be essential.

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Table (1) :Effect of foreign ions for the determination of 6ug/ml Samarium(III)

Ion	Amount ppm	Sm^{+3} Found (p.g)	Error %
Fe^{+3}	1.2	5.10	-15.0
Wi^{+2}	0.8	6.4	+6.6
Zn^{+i}	1.6	5.30	+ 11.6
Cu^{+1}	2	6.4	+6.60
Ce^{K1}	4	8.2	+36.6

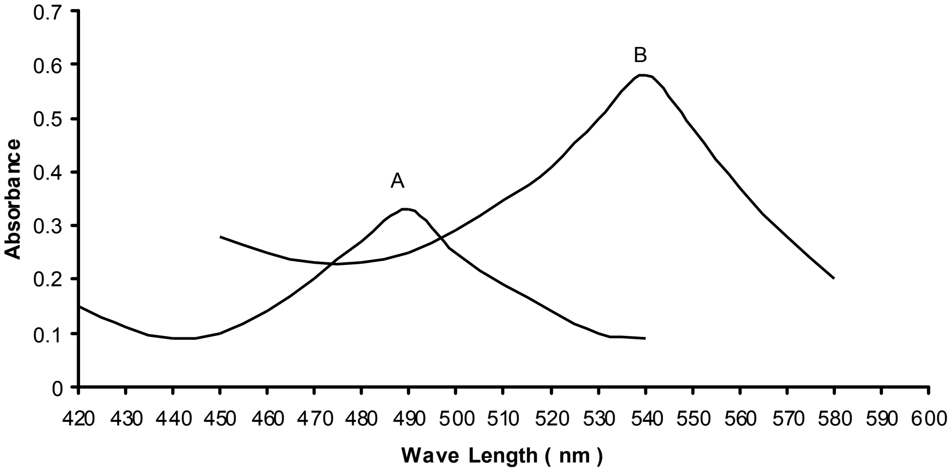

Fig (1) : Absorbance Spectra
A : Reagent blank measured against deionized water.
B : Samarium complex measured against reagent blank

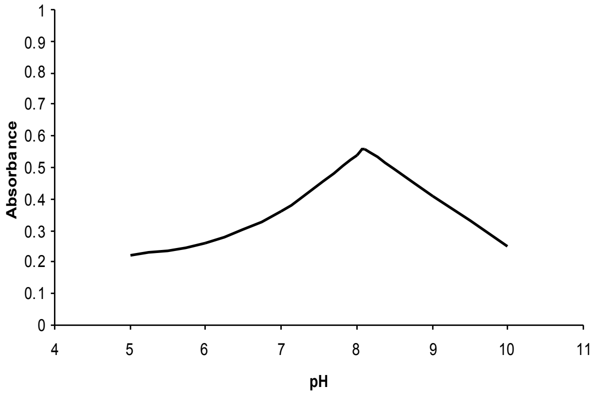

Fig .(2) : Effect of pH on absorbance measured at 550 nm.

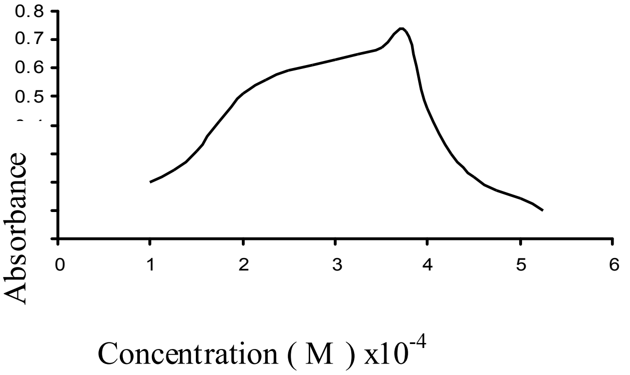

Fig. (3) : Effect of reagent concentration on the formation of Samarium (III) complex.

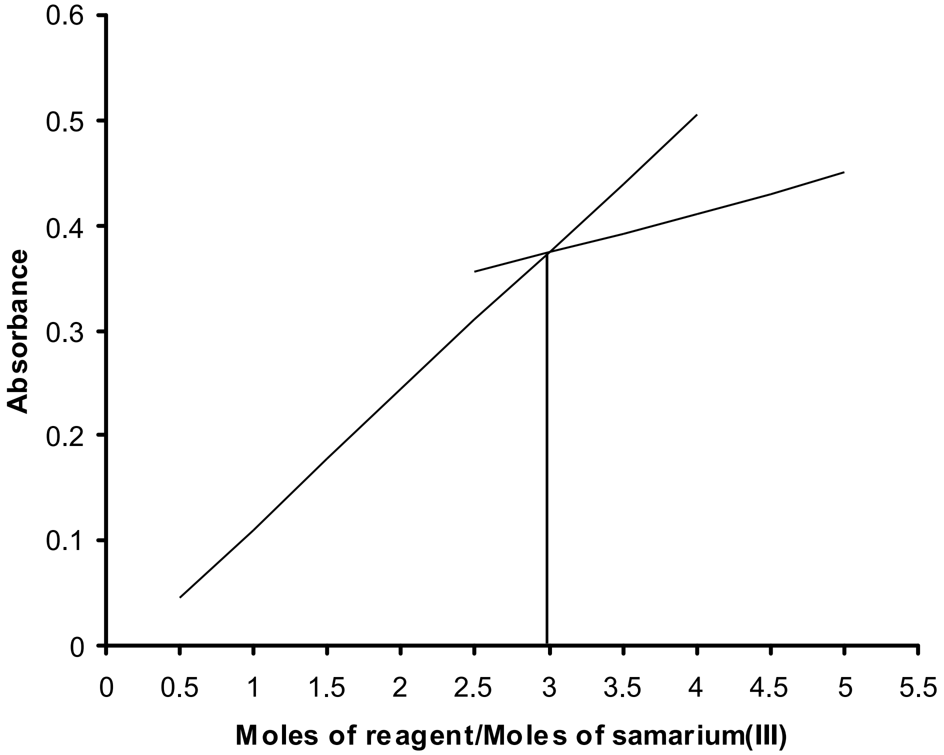

Fig. (4) : Mole Ratio