

SPECTROPHOTOMETRIC DETERMINATION OF HOLMIUM (III) WITH SOLOCHROME BLACK T REAGENT

التقدير الطيفي لأيون الهولميوم الثلاثي باستخدام الكاشف
Solochrome Black T

Alaa F.Hussain , Baker A. Joda and Muneer A.AL-Daamy
Dept.of Chem. College of Science Univ.of Kerbala

Abstract:

Solochrome Black T reagent product a violet complex with Holmium(III)in aqueous solution media at (pH=5).The complex was found to be stable at the given pH.Beer's law is obeyed in the concentration range(6.06×10^{-7} - 54.56×10^{-7} M) with molar absorptivity of ($14432 \text{ L.mole}^{-1} \cdot \text{cm}^{-1}$).The stoichiometry of complex was confirmed by using mole ratio method which indicated the ratio of reagent to metal is 2:1.The effect of the presence of different cations and anions as interference in the determination of Holmium (III) under the given condition were investigated .The proposal method was applied for the determination of Holmium in standard rock sample by direct methods and a satisfactory results were obtained.

الخلاصة:

يكون الكاشف (Solochrome Black T) معقد ذو لون بنفسجي مع أيون الهولميوم الثلاثي عند دالة حامضية مقدارها (5) ووجد أن هذا المعقد يكون مستقرا عند الدالة الحامضية المثلى مع مطاوعة لقانون بير-لامبرت في مدى من التراكيز يتراوح بين (6.06×10^{-5} - 54.56×10^{-5} M) مع قيمة امتصاصية مولارية مقدارها $14432 \text{ L.mol}^{-1} \cdot \text{cm}^{-1}$. تم تعيين تكافؤية المعقد من حيث نسبة الكاشف - فلز بطريقة النسب المولية وطريقة مولارد فوجد أن الارتباط في المعقد يكون بنسبة 1:2. تمت دراسة تأثير تداخل وجود عدد من الأيونات الموجبة والسالبة عند التقدير الطيفي لأيون الهولميوم. طبقت الطريقة المقترحة لتقدير الهولميوم في نموذج صخري قياسي باستخدام الطريقة المباشرة وتم الحصول على نتائج مقنعة.

Introduction:

A basic characteristic of the Lanthanide group is the chemical similarity of individual members. Consequently, data on the total Lanthanide content often suffices in practical problems, particularly when all the Lanthanides behave similarly, eg-in the production of alloy steel or when the ratio of the individual member is constant. Among the numerous spectrophotometric reagent for the determination of Lanthanides azobenzene and azonaphthalene derivatives were applied to obtain more favorable metal-binding but they are suffers from non selectivity⁽¹⁻³⁾.Hydroxy naphthol blue alone⁽⁴⁾ and in conjugation with EDTA⁽⁵⁾ was used for the spectrophotometric micro-determination of alkaline earth and lanthanides. Although this complex are instable in basic solution and tendency to bind to many different metal ions weaken its effectiveness.Several spectrophotometric methods based on the use of molecules posses hydroxyl group, especially O, O-dihydroxy azo compound including xylenol orange⁽⁶⁾ and calmagite⁽⁷⁾ have been used to determine total veare earth elements but none of these procedures is very selective. However atomic absorption, atomic emission and high performance liquid chromatography technique are vastly superior to my of the spectrophotometric procedures described to data, so it is clear that further work is indicated. The formation of ternary complexes often improves the sensitivity and selectivity of an analytical method. During studies on the sensitizing effects of colloid particle of cationic surfactants on the reaction of chromogenic reagent with various metal ion^(8,9,10).The present paper presents introduces a spectrophotometric method for the determination of Holmium(III) ions by binding with solochrome Black T and the optimum reaction

conditions are evaluated and excellent metal ion sensitivities may be obtained and the proposed method was applied for the determination of Holmium(III) in standard rock sample namely JG-1(Granodiorite).

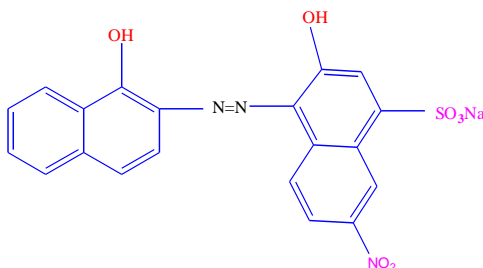


Fig (1): Solochrome Black T

Experimental:

- Apparatus:

Spectrophotometric measurement were made with a LKB-Bouch UV visible spectrophotometry model NOVA SPEC, with Pyrex cell of 10 nm path length was used. pH values were measured with a digital pH/mv/Temp./pH-meter model 470 universal.

-Reagents:

All chemicals used were of analytical grade unless stated otherwise and all solution were prepared using distilled water.

1-A stock solution of Holmium (III) $6.06 \times 10^{-3} \text{M}$ was prepared by dissolving 0.1145 gm of Holmium oxide Ho_2O_3 in 100ml of demonized water.

2-Solochrome Black T (SBT) reagent ($1.08 \times 10^{-2} \text{M}$) was prepared by dissolving 0.5 gm of reagent in 100 ml deionized water . The pH being adjusted with few drops of (1M) Sodium hydroxide or (1M) Hydrochloric acid.

Unvaried optimization

-Procedure:

The test solution containing not more than $20 \mu\text{g}$ Holmium was taken in 10 ml volumetric flask, 5ml of $1.08 \times 10^{-3} \text{M}$ reagent, 1ml of buffer solution at (pH=5). The solution was then diluted to the mark with deionized water allow the solution to stand for 2 min and then the absorbance was measured at (570)nm against the reagent violet solution .

Results and Discussion:

-Absorption spectra:

The absorption spectra of the reagent and its Holmium (III) complex at (pH=5) are shown in fig. (2).

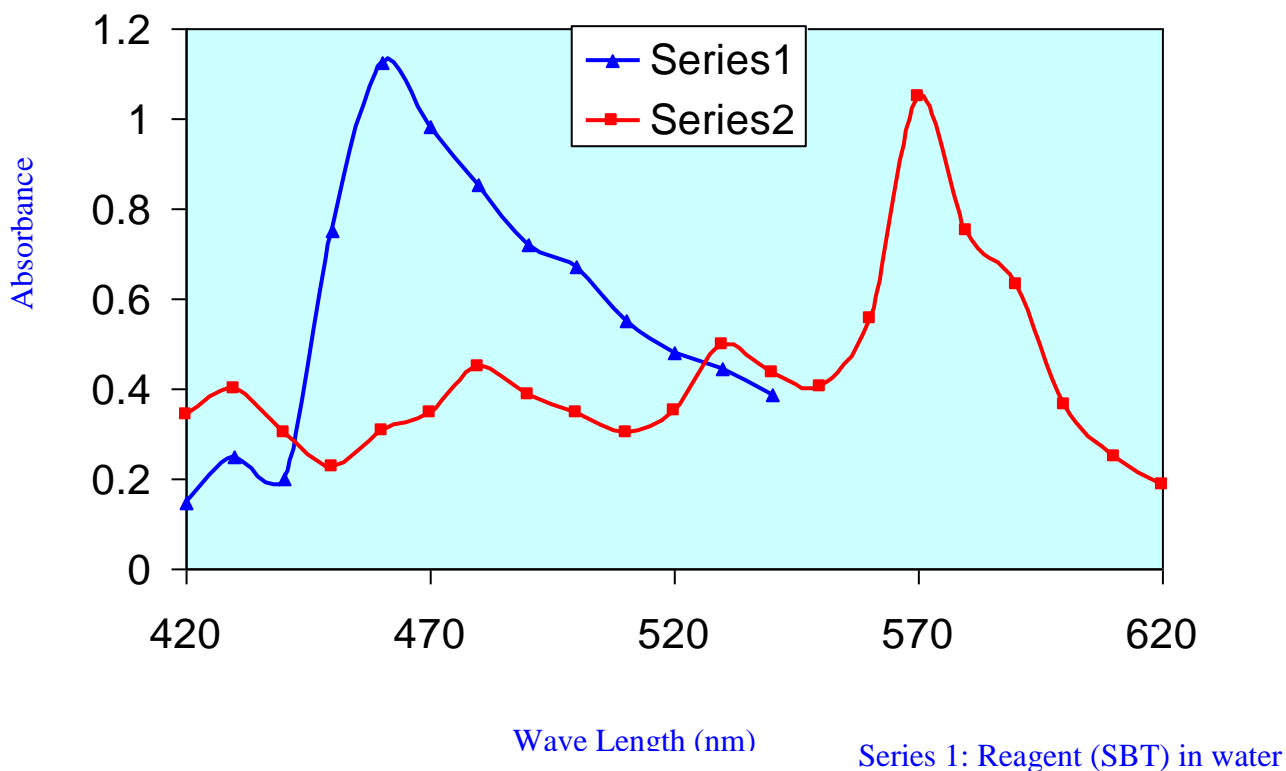


Fig. (2): Absorption Spectra

Included for comparison is the spectrum of the binary Holmium (III) complex formed at (pH=5).The ternary complex has an absorption maximum at (570) nm and is stable for at least several hours, under these conditions Holmium (III) ions forms a pure violet colored complex, the formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately 90 nm optimization of variables.

Effect of pH:

Standard amount of Holmium (III) and SBT solution were buffered at varying pH-value (range from 1 to 10). The final pH of each solution was measured with a pH-meter and the absorbance measured at (570)nm .A plot of absorbance against pH are shown in (Fig.3) and showed that the absorbance was increased gradually as the pH increased from 1.0 to 5.0 ,but decreased rapidly above pH 5.The increase in the SBT complex solution absorbance under these conditions may be explained by an increasing the sensitivity of the reagent at this value of pH toward Holmium.

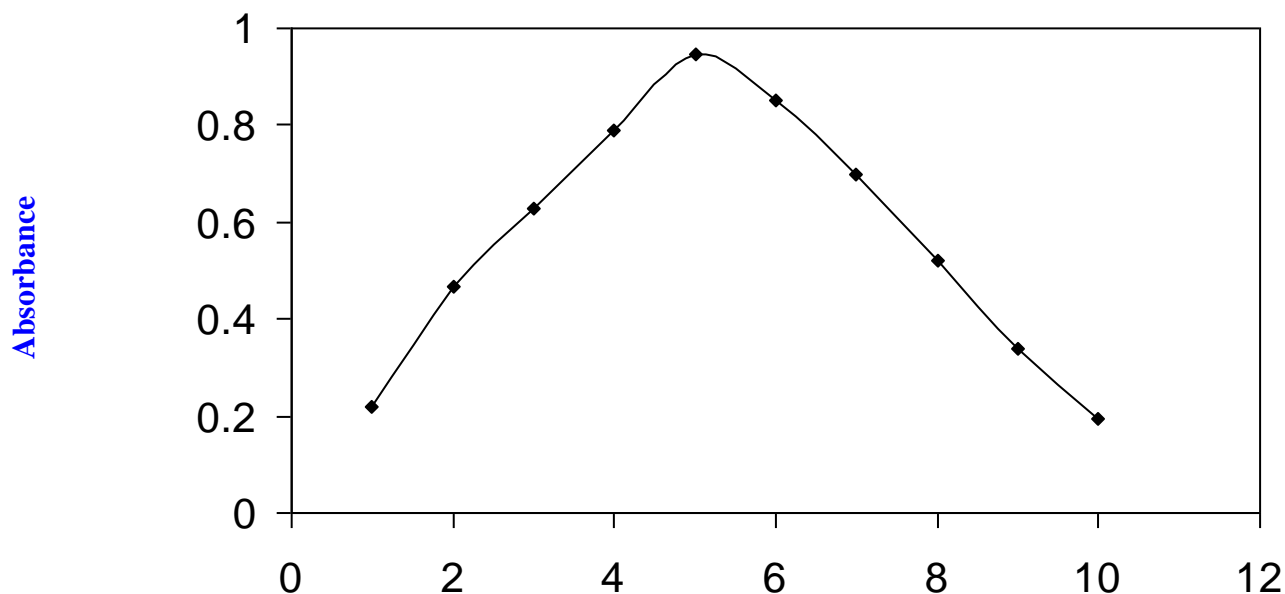


Fig.(3):Effect of PH on absorbance measured

Reagent Concentration:

The influence of excess reagent concentration on the absorbance of the complex illustrated in Fig. (4), where the absorbance of $1.21 \times 10^{-5} \text{M}$ Ho(III) solution at (pH=5) is plotted against reagent concentration in the range ($0.22 \times 10^{-4} \text{M}$ to $1.73 \times 10^{-4} \text{M}$). It is found that the absorbance increases with an increasing in the reagent concentration and $0.76 \times 10^{-4} \text{M}$ metal ion concentration were chosen for 10 ml sample volumes.

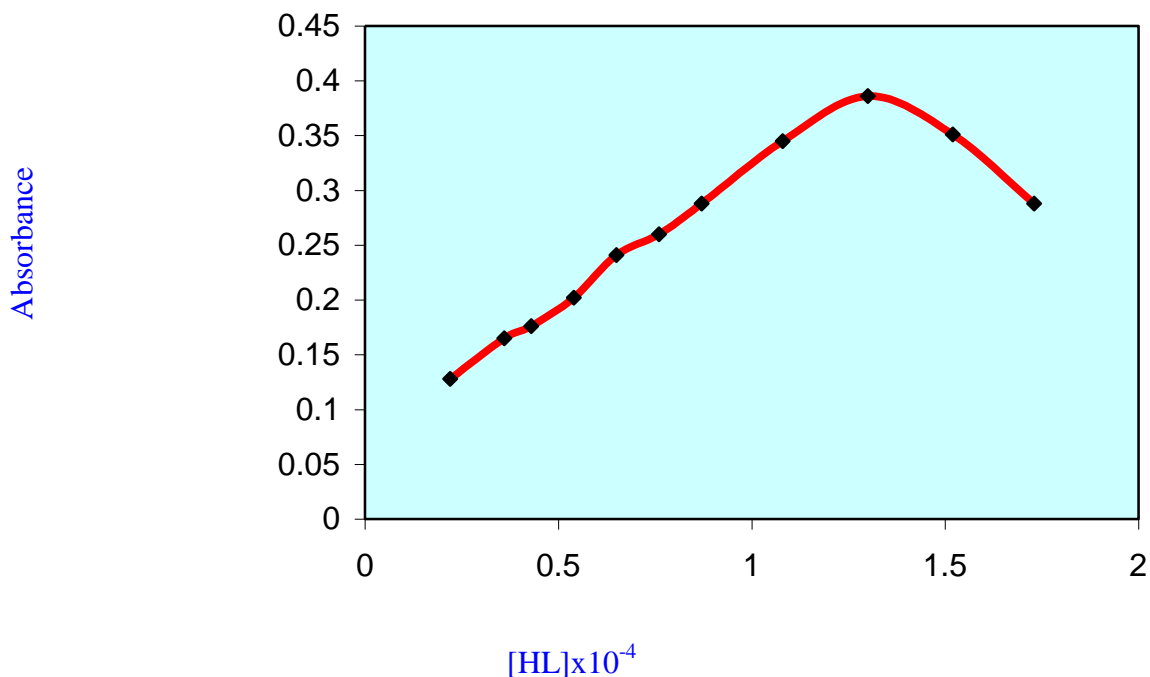


Fig.(4):Effect of reagent concentration on the absorbance of the Ho-SBT

Effect of Time:

The stability of complex was checked by measuring the absorbance of the solution at different time of intervals. The absorbance reached its maximum value within (2) min. The complex was found to be stable until 35 hr.

Stoichiometry of complex:

The stoichiometry of the complex has been studied by the mole –ratio method (Fig 5) .The method shows that Holmium (III) forms a 1:2 complex (metal:ligand) (M-L) with SBT reagent. This results is in agreement with other papers indicated reagent forms 1:2 complex with $Ni^{+2(11)}$, $Pb^{+2(12)}$. The formation constant calculated by applied procedure ⁽¹³⁾ was found to be $3.38 \times 10^{12} L^2 \cdot mol^{-2}$.

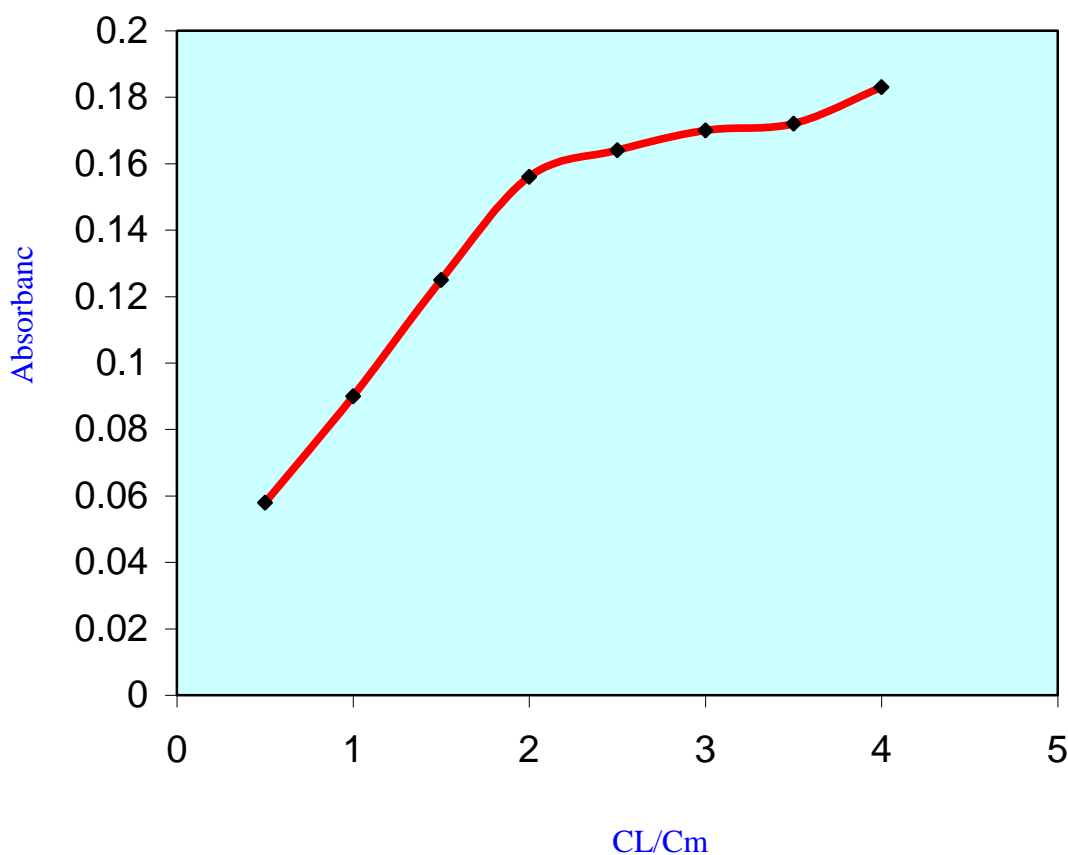
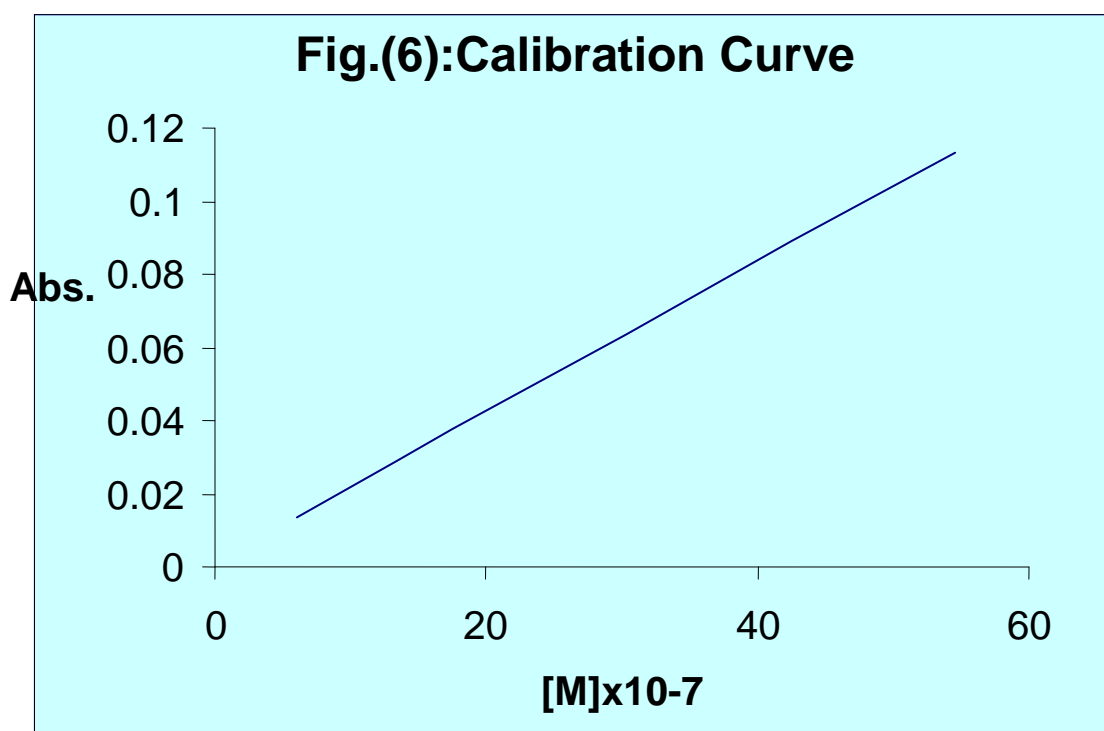


Fig (5): Mole-Ratio Method

Beer's law and sensitivity:

The absorbance of Holmium complex was found to be linear depending on the concentration of metal. Beer's law was obeyed in the concentration range ($6.06 \times 10^{-7}M$ - $54.5 \times 10^{-7}M$) with molar absorptivity of $14432 L \cdot mol^{-1} \cdot cm^{-1}$. Fig.(6) shown the calibration curve of Holmium ion.



Effect of foreign ions:

The selectivity of the proposed methods was investigated by the determination (2mg/ml) of Holmium (III) in the presence of a series of cations and anions (Table 1). The results show the tolerance limit was taken as the amount that caused an concentration error of + 4.2% in the absorbance .The most anions added have no effect at the given of Holmium studies.

The greatest interference was caused by Iron (III), Nickel (II) and Copper (II). However their interference can be eliminated by the addition 3ml of (5%) potassium cyanide. So that this method becomes one of the most selective available method for the determination of Holmium (Table 2). Zn⁺²,Mn⁺² ions can not be masked by cyanide ion and should be separated before attempting to determine the concentration of Holmium ion with the reagent . Oxalic acid EDTA and Ascorbic acid solution can not be used as a masking agent because of there interferences.

Table (1): Determination of 2 mg/ml of Holmium (III) in the presence of foreign cations and anions.

Foreign ions	Amount added (mg/ml)	Error %
Zn ⁺²	10	0.00±
	40	+0.90
Mn ⁺²	10	0.00±
	30	+0.50
Ni ⁺²	5	-0.00
	20	+1.30
Hg ⁺²	20	0.00±
	80	+2.71
Fe ⁺³	5	+0.00
	20	+4.20
Cr ⁺³	5	0.00±
	20	+2.20
C ₄ H ₄ O ₆ ⁼	40	0.00±
	80	-0.80
NO ₃ ⁻	30	0.00±
	90	+3.11
CH ₃ COO ⁻	60	0.00±
	120	-2.91
CO ₃ ⁻²	10	0.00±
	35	-0.11

Table (2): Determination of (2mg/ml) of Holmium (III) in the presence of foreign cations with cyanide reagents.

Foreign ion	Amount added	Error %
Ni ⁺²	20	0.00±
	80	+2.01
Cu ⁺²	o	0.00±
	v.	-1.10
Fe ⁺³	15	0.00±
	120	+0.63

Application to the determination of Holmium in rock:

One sample provided by the geological survey of Japan (1-1-3) (Higashi, Yatabe, Ibaraki, 303 Japan) was analyzed in order to check the validity of the method. The preparation of the sample solution is as follows.

Transfer 0.5gm of a sample in Teflon vessel and decomposed in 5ml of concentrated hydrofluoric acid plus 0.5 ml of concentrated perchloric acid. The mixture was carefully heated on a hotplate until its volume was residue in 10 ml of 1N hydrochloric acid and diluted to 25 ml with deionized water. Lanthanides were separated on a column (100 cm long and 2 cm internal diameter) containing 25 ml amberlite IR-120 action exchanger treated with 2M HCl).The sample solution was allowed to drain in to the column, then the column was washed twice with deionized water . Followed by the addition of 300ml of 1.85M HCl to elute the sample impurities. Lanthoids were eluted with 400ml of 4M HCl and the elute was reduced by heating on a hotplate and the volume was made up to 10 ml with deionized water. (Table 3) show the results obtained for the analysis of certified sample.

Table (3): Results for the analysis of certified sample rock (JG-1 Granodiorik) certified.

Certified concentration 1.68 µg/g Ho	
Con.	1.83
	2.06
	1.91
RSD	1.12
Relative Error E /	+8.35

References:

- 1-Zymunt, Marzenko, Spectrophotometric Determination of elements, John whiley and sonc.Ine. (1971).
- 2-Savvin, S.B., Zawod.Lab, 29(1963)131. 3-Savvin, S.B., Petrova, T.V.and Romanon, P, N, Talanta, 19(1972)1437
- 4-Brittain, H.G, The use of hydroxynaphthol blue in the ultramicrodetermination of alkaline earth and lanthanide elements: An improved method. Analytical chemica Acta.96 (1978)165-170.
- 5-Brittain H.G, Effect of EDTA amount on the determination of rare earth elements. Analytica. Chemica. 49(1977)969.
- 6-Svoboda, V and Chomy, V"Spectrophotometric determination of minute amounts of Lanthanum with xylenol orange."Talanta 13(1966)237.
- 7-Brittain, H.G"Spectrophotometric determination of Lanthanides with calmagite ."Analytica. Chemica Acta, 106(1979)401.
- 8-Zhao .S,Xia.X and Hu,Q"Complex formation of the new reagent 5(6-methoxyl-2-benzothiazoleazo)-8-aminoquioline with cobalt and nickel for their sensitive spectrophotometric detection-Analatic Chimica.Acta,391(3)(1999),365-371.
- 9-Ferreyra.R,Camina,J,and Luco J.M. Simultaneos spectrophotometric determination of La, Ho, Mn , J. of Analytical Chemistry 363(6)(2000),595-600.
- 10-Yadvendra, K and Panavelil, T, Analyst, 112(1987)1015.
- 11-Ahmed, R.K.Thesis.M.Sc.University of Baghdad (2000).
- 12-Almurab, S.H., Al-Kubasy, R.K, and Hessian A.F, Ibn-Al-Haitham J for pure and Appl SCI 15(2002)32.
- 13-Job ,M.A, Ann.Chem.9(1928)113.