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Spectrophotometric Determination of Scandium (III) with Eriochrome Cyanine R and Cetylpyridinium Chloride – Application to Waters and Synthetic Alloys*

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ABSTRACT

The detailed investigation of a sensitive and selective spectrophotometric method for the trace amounts of scandium is described. The method is based on the reaction of scandium with eriochrome cyanine R reagent in the presence of cetylpyridinium chloride surfactant at pH 4.1, to form a violet-blue ternary chelate which exhibits maximum absorption at 595nm. Beer's law is obeyed over the range 0.1-3.0 µg\25ml, i.e., 0.004-0.12 ppm, with a molar absorptivity of 1.3×10^{5} $\mathrm{l.mol^{-1}.cm^{-1}}$, (r=0.9991), Sandell's sensitivity index of 0.45 $\mathrm{ng.cm^{-2}}$, a relative error of 0.0-0.4% and a relative standard deviation of ±0.6 to ±6.1 %, depending on the concentration level.

The method has been applied successfully to determine, scandium in various samples of water and synthetic alloy.

التقدير الطيفي للسكانديوم مع كاشف الايريوكروم سيانين- R وسياتل بريدينيوم كلوريد- التطبيق بالماء و السبائك المصنعة

الملخص

لقد تم تطوير طريقة طيفية حساسة وانتقائية لتقدير كميات متناهية في الصغر من السكانديوم وتعتمد الطريقة على مفاعلة السكانديوم مع كاشف اريوكروم سيانين R وبوجود CPC عند دالة حامضية 4.1 لتكوين معقد بنفسجي – مزرق في الوسط المائي الذي يعطي أعلى شدة امتصاص عند الطول الموجي 595 نانوميتر.

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*تم إلقاءه في المؤتمر العلمي الأول للكيمياء المنعقد بتاريخ 22-23 نيسان 2008 فى قسم الكيمياء / كلية العلوم/ جامعة الموصل

كانت حدود قانون بير بين 0.1 و3.0 مايكروغرام من السكانديوم في حجم نهائي 25 ملتر (0.12-0.04 جزء/ مليون) وبمعامل ارتباط 0.9991 والامتصاصية المولارية 1.3×10^5 لتر. مول$^{-1}$.سم$^{-1}$ ودلالة ساندل للحساسية 0.45 نانوغرام /سم^2 والخطأ النسبي بين (0.0-0.4)% والانحراف القياسي النسبي بين ±0.6 و ±6.1% اعتماداً على مستوى التركيز.

تم تطبيق الطريقة وبنجاح لتقدير السكانديوم في نماذج مختلفة من الماء وكذلك في السبائك المصنعة.

INTRODUCTION

Scandium (l.Scandia, Scandanavia) ; the element was discovered by Nilson in 1876 (Weast *et al.*,1986-1987), in which he summarized his results on gadolinite analysis and the isolation of a newly discovered element. This element, answering Mendeleev's prediction and description (Horovitz, 1999-2000). Nilson succeeded in isolating from 10 kg euxenite several grams scandium and ytterium oxides of a higher purity grade.

Scandium is never found as the free metal. Scandium is apparently a much more abundant element in the sun and certain stars than on earth. It is widely distributed in living matter, and highly positive or negative correlations with many other elements are found (Horovits, 2002).

An artificial radioactive isotope of scandium has been used in tracer studies and leak detection, and there are some applications in the semi-conductor field (Hawley,1981).

Because of importance of scandium in the different fields, numerous methods have been proposed for its determination.

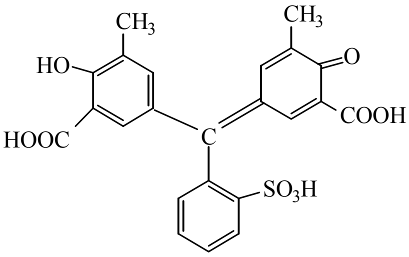
The gravimetric determination of scandium is accomplished by di-(2-ethylhexyl) phosphate (DEHPA) as a precipitant and the mole ratio of Sc-DEHPA precipitate obtained in ethanol medium have been investigated and found as 1: 2 (Sc : DEHPA) (Cha and Jeong, 1994).

The scandium ion is titrated with a 0.01 M EDTA at pH 2.4 using semi-xylenol orange (SXO) as metallochromic indicator. A comparison of SXO and xylenol orange indicators for the scandium is carried out (Sirirak, *et al.*,1990).

Scandium has been preconcentrated from a large volume of its aqueous solution after solid phase extraction of its 1-(2-thiazolylazo)-2-naphthol chelate onto ammonium tetraphenylborate naphthalene absorbent in the pH range 4.0-5.8. The solid mass, consisting of metal complex along with the absorbent, was dissolved in 5 ml of DMF and quantified by second derivative spectrophotometry. The calibration graph is linear in the concentration range 0.08-2.8 $\mu g.ml^{-1}$ with a correlation coefficient of 0.9998. Nine replicate determinations of 7.0 µg of scandium in 5 ml of final DMF solution give a relative standard deviation of 0.92% (Bhalotra and Puri, 2000).

Analytical procedures have been developed for the reliable determination of 19 trace elements (one of them Sc) in a polar ice core at pgg^{-1} and fgg^{-1} concentrations using ICP-spectro field mass spectrometry. The accuracy of the results is carefully evaluated using the certified water reference material SLRS-4(Krachler *et al.,* 2005).

The present article is devoted to the development of a spectrophotometric method for the determination scandium using the ECR which is 5-[α-(3-carboxy -5-methyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2-sulphobenzyl-3-methyl salicylic acid] reagent in the presence of cetylpyridinium chloride.



Eriochrome Cyanine R (ECR)

EXPERIMENTAL

Apparatus

Spectral and absorbance measurements are carried out using Cintra 5, GBC scientific equipment and Cecil EE 1021 1000 SERIES, using 1-cm plastic cells. The pH measurements are carried out using Philips PW 9420 pH meter.

Reagents

All chemicals used are of the highest purity available.

Stock (500 µg\ml) Scandium(III) solutions. This is prepared by dissolving 1.3511 g of scandium sulphate hexahydrate (Fluka AG) in distilled water and the volume is completed to 500 ml with distilled water in a volumetric flask. The less concentrated (2 µg/ml) working solution has been prepared by a suitable dilution of the stock scandium (500 µg/ml)_ solution.

ECR reagent solution, 5×10^{-4}M.

Prepared by dissolving 0.0268 g of ECR (trisodium salt, Fluka) in distilled water and the solution is diluted to 100 ml in a volumetric flask. The solution is transferred to a brown bottle and remains stable for only 48 hr.

Cetylpyridinium chloride (CPC) solution, (1×10^{-3}M).

Prepared by dissolving 0.179 g of CPC (Koch-light) in distilled water and the solution is diluted to 500 ml in a volumetric flask.

Buffer solution (pH 4.1).

This solution is prepared by mixing 17.4 ml of 1M formic acid with 12.5 ml of 1M NaOH and diluting the volume to 250 ml with distilled water in a volumetric flask (Perrin and Dempsey, 1974).

Synthetic sea water.

It is prepared as described (Herkinson, 1965) by dissolving 2.2 g NaCl, 9.7 g $MgCl_2.6H_2O$, 3.7 g anhydrous Na_2SO_4, 1g $CaCl_2$, 0.65 g KCl, 0.17 g $NaHCO_3$ and 0.023 g H_3BO_3 in about 500 ml of distilled water, then the solution is diluted to 1 l with distilled water in a volumetric flask.

RESULTS AND DISCUSSION

Preliminary study

During the preliminary study, it has been observed that when scandium ion and ECR reagent are present in the same solution, they react to form a colour, encouraging subsequent investigation of this colour reaction by spectrophotometry.

Effect of pH

The effect of pH on colour intensity of the complex has been examined in the pH range 3.44-11.16. To series of solutions containing 2 µg scandium(III), 1ml of 5×10^{-4}M ECR reagent, 1ml of 1×10^{-3}M CPC solutions and various volumes of 0.005M HCl and 0.005M NaOH are added. The absorbance of each coloured solution against its corresponding reagent blank and the final pH of the reaction mixture are both measured at 601nm. The results obtained are given in Table 1.

Table 1: Effect of HCl and NaOH on absorbance

Ml of 0.005M HCl	**Absorbance**	**Final pH**	**Ml of 0.005M NaOH**	**Absorbance**	**Final pH**
0.0	0.232	5.62	0.0	0.256	5.66
0.1	0.234	5.11	0.1	0.265	6.25
0.2	0.201	4.67	0.2	0.253	6.71
0.3	0.214	4.57	0.3	0.244	6.85
0.4	0.217	4.36	0.4	0.190	7.32
0.5	0.213	4.28	0.5	0.158	7.61
0.6	0.233	4.20	0.6	0.162	7.75
0.7	0.251	4.11	0.7	0.147	9.33
0.8	0.238	4.09	0.8	0.147	9.63
0.9	0.227	4.00	0.9	0.136	9.94
1.0	0.217	3.96	1.0	0.130	10.20
2.0	0.175	3.64	2.0	0.143	11.12
3.0	0.134	3.44	3.0	0.198	11.16

From the results shown in Table 1, it can be observed that the colour reaction reaches maximum intensity experimentally when the final pH of the reaction mixture is 4.11 which is selected for the study of the effect of buffer solution in the subsequent investigation.

Effect of Buffer

The effect of different buffers having pH 4.1 on the colour intensity of the scandium complex and the blank has then been examined. Tartaric acid-NaOH (B_1), citric acid-NaOH (B_2), potassium hydrogen phthalate (B_3) formic acid-sodium format (B_4) and acetic acid-sodium acetate (B_5) have been selected for their pH effect on the colour reaction under study. The results are given in Table 2.

Table 2: Effect of buffers on absorbance

Ml of buffer solution	**Absorbance/ ml of buffer added**				
	B_1	**B_2**	**B_3**	**B_4**	**B_5**
0.1	0.000	-0.002	0.202	0.233	0.239
0.3	-0.011	0.000	0.197	0.222	0.208
0.5	-0.005	-0.002	0.187	0.228	0.193
0.7	-0.007	-0.002	0.163	0.202	0.159
1.0	-0.007	-0.001	0.141	0.217	0.156
2.0	-0.002	-0.003	0.069	0.225	0.138
3.0	-0.005	0.000	0.050	0.209	0.132
4.0	-0.002	0.005	0.026	0.215	0.023
5.0	0.017	0.045	0.020	0.212	0.008
Final pH of the reaction mixture	3.76-4.06	4.90-5.18	4.13-4.68	4.19-4.90	4.13-4.27

It can be noticed (table 2) that B_4 is only useful from the analytical point of view. The other buffers show an un-encouraging results. For the subsequent work, a 2 ml of buffer (B_4) solution has been chosen because it gives the highest sensitivity and lower blank value (0.006) and good colour contrast.

Effect of Surfactants

The effect of the presence of cationic surfactants (CPC and CTAB), anionic surfactant (SDS) and non-ionic surfactant (Triton X-100) on the colour intensity of the complex is examined (Table 3).

Table 3: Effect of different surfactants

Surfactant 1×10^{-3}M solution	**Absorbance/ml of surfactant solution**						**Final pH of the reaction mixture**
	0	1	2	3	4	5	
CPC	0.184	0.208	0.175	0.172	0.157	0.155	4.04-4.15
CTAB		0.000	0.008	0.008	0.009	0.008	4.18-4.21
SDS		0.185	0.181	0.169	0.128	0.099	4.19-4.2
Triton X-100 1%		0.012	0.012	0.012	0.015	0.015	4.20-4.22

The experimental data (Table 3) reveal that the presence of CPC surfactant gives a useful effect, mainly the stronger colour contrast. Since the colour, in the absence of CPC surfactant, shows maximum absorption at 525 nm and 0.184 absorbance unit, while in its presence, maximum absorption occurs at 601 and 0.208 absorbance unit. And since 1 ml of 10^{-3} M CPC solution has given the lowest blank value (0.008), it has been used through out the subsequent work.

Effect of Masking Agents

It is well known that organic chelating reagents are most often unselective. Therefore, to increase the selectivity of their colour reaction generally, the study of the effect of masking agents has been performed. The results are summarized in Table 4.

Table 4: Effect of masking agents on absorbance

Ml of 0.01M solution of masking agents	**Ml of reagent**	**Absorbance*/ml of masking agent added**											
		T.A.	**pH**	**C.A.**	**pH**	**Ox.A.**	**pH**	**Asc.A**	**pH**	**NaF**	**pH**	**5-SSA**	**pH**
0.5	0.5	0.016	4.15	0.002	4.27	0.003	4.26	0.228	4.24	0.007	4.65	0.176	4.26
1.0		0.008	4.18	0.004	4.26	0.004	4.25	0.194	4.24	0.002	4.63	0.154	4.24
2.0		0.006	4.19	0.005	4.26	0.004	4.25	0.180	4.24	0.006	4.55	0.125	4.23
0.5	1.0	0.050	4.21	0.001	4.26	0.002	4.25	0.196	4.25	0.006	4.50	0.169	4.23
1.0		0.030	4.22	0.003	4.25	0.001	4.25	0.199	4.25	0.006	4.45	0.254	4.22
2.0		0.020	4.24	0.006	4.26	0.001	4.25	0.184	4.24	0.007	4.39	0.223	4.21
0.5	1.5	0.158	2.24	0.006	4.25	0.002	4.26	0.184	4.23	0.006	4.37	0.282	4.22
1.0		0.043	2.25	0.005	4.27	0.009	4.26	0.214	4.25	0006	4.33	Slightly turbid	4.21
2.0		0.013	2.26	0.004	4.26	0.007	4.28	0.216	4.25	-0.001	4.29	Slightly turbid	4.21

* Measured at λ 601nm.

In the above table, it can be noticed that tartaric acid, citric acid, oxalic acid and NaF cause masking for scandium, while other complexones have no effect. Therefore, a composite masking solution containing 0.01M of each of 5-sulphosalicylic acid and ascorbic acid is prepared and the effect of different volumes of this solution on the absorbance of Sc(III)-ECR-CPC at buffer pH 4.1 complex is then examined. However, the results obtained are not satisfactory as to further use this composite masking solution in the subsequent experiments. Therefore, it has been omitted.

Effect of ECR Reagent Amount

The investigation of the effect of ECR amount on the formation of the ternary complex ScIII-ECR-CPC has been carried out at pH 4.1 . Experimentally, it has been found that over 1.5 ml of 5×10^{-4}M ECR reagent solution, a turbidity has been observed. A 1 ml of the prescribed concentration has been selected due to lowest blank value and r value is excellent. The results are shown in Table 5.

Table 5: Effect of the reagent amount on absorbance

µg of scandium (III)	**Absorbance*/ml of reagent Solution 1×10^{-3}M**		
	0.5	**1.0**	**1.5**
0.5	0.054	0.042	0.059
1.0	0.110	0.098	0.093
2.0	0.233	0.213	0.201
3.0	0.287	0.357	0.341
5.0	0.311	0.587	0.639
7.0	0.323	0.623	0.830
9.0	0.327	0.340	0.942
10.0	0.330	0.643	0.932
20.0	0.365	0.654	0.893
r* (1-5)	0.8802	0.9991	0.9979

* correlation coefficient

Effect of Order of Addition

The effect of the order of addition of reagents on the absorbance is investigated by mixing the metal ion (M), surfactant (S), the reagent (R) and buffer solution (B) in various orders. The absorbance of each order against its corresponding blank is measured. The results (Table 6) indicate that order VI**:**metal + surfactant + buffer + reagent gives the highest absorbance and the lowest blank values, so it is selected for the next investigation.

Table 6: Effect of order addition on absorbance

Reaction components	**Order number**	**Absorbance**
M+R+S+B	I	0.229
M+R+B+S	II	0.224
M+B+R+S	III	0.254
M+S+R+B	IV	0.227
M+B+S+R	V	0.226
M+S+B+R	VI	0.258

Effect of Time

The optimum time for full colour development of ternary complex Sc-ECR-CPC, at pH 4.1 is then examined. Under the optimum conditions obtained, complete colour formation occurs immediately and the absorbance of the complex remains essentially the same for at least 1 hour [except for the 4 µg level of scandium (III) ion]. The results are shown in Table 7.

Table 7: Effect of time on absorbance

Time (min)	**Absorbance/µg of Sc(III) present**			
	0.5	**1.0**	**2.5**	**4.0**
ADTTM*	0.030	0.107	0.287	0.443
5	0.030	0.107	0.288	0.442
10	0.030	0.106	0.290	0.444
15	0.030	0.105	0.295	0.438
20	0.030	0.104	0.296	0.448
25	0.030	0.102	0.281	0.430
30	0.030	0.102	0.284	0.427
35	0.030	0.102	0.288	0.433
40	0.030	0.102	0.287	0.423
45	0.030	0.102	0.289	0.416
50	0.030	0.102	0.291	0.417
55	0.030	0.102	0.285	0.403
60	0.030	0.105	0.286	0.402

*after dilution to the mark immediately.

Final Absorption Spectra

Scandium ions form a violet water-soluble ternary complex with ECR reagent and CPC at pH 4.1. The ternary complex shows a single maximum absorption at 595 nm (Fig. 1), while the reagent blank shows maximum absorption at 503 nm.

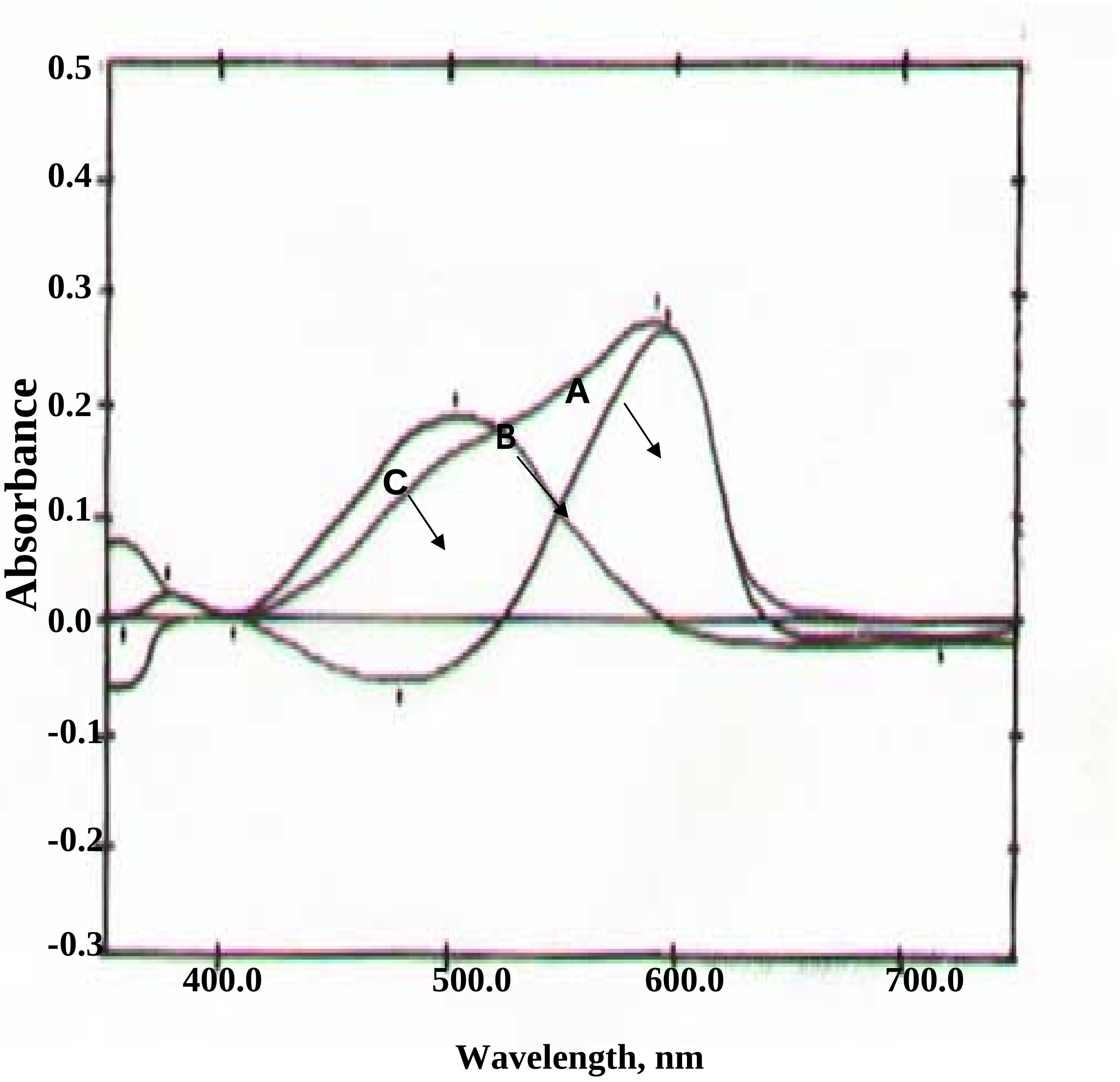


Fig. 1: Absorption spectra of 2 µg Sc(III) / 25 ml measured against (A) blank, (B) distilled water and (C) blank against distilled water.

Recommended Procedure and Calibration Graph

Increasing volumes of working Sc(III) solution are transferred to a series of 25-ml calibrated flasks to cover the range of 0.1-3 µg Sc, 1 ml of (1×10^{-3}M) CPC, 2 ml of buffer pH 4.1 and 1 ml of (5×10^{-4}M) Eriochrome Cyanine R reagent are then added and volumes are made to the mark with distilled water. The reaction mixtures are mixed and the absorbances are measured at 595 nm, against the reagent blank prepared in the same manner but without Sc(III). A plot of absorbance versus determinand concentration (Fig. 2) shows that Beer's law is obeyed over the range of (0.004-0.12) ppm. The molar absorptivity being 1.3×10^5 $l.mol^{-1}.cm^{-1}$ and the Sandell sensitivity is 0.45 $ng.cm^{-2}$. At higher Sc(III) concentrations, a negative deviation occurs.

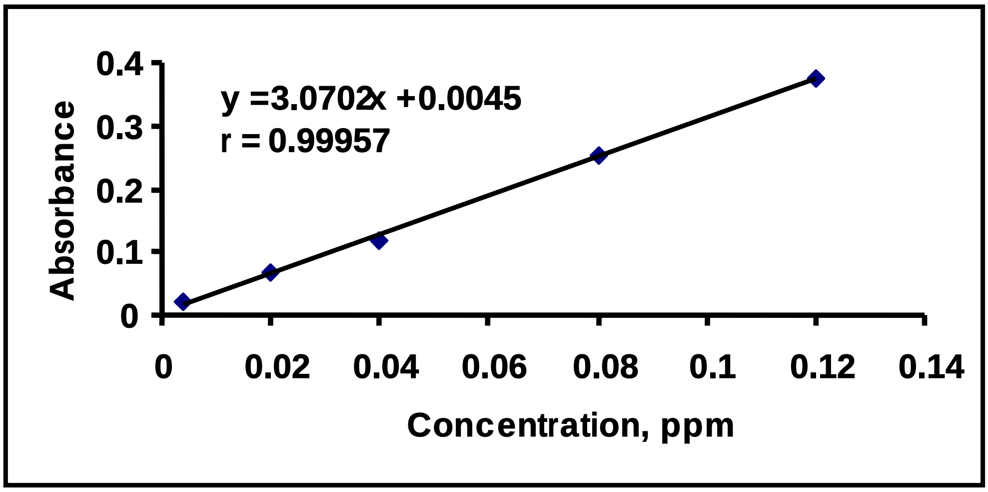


Fig. 2: Calibration graph for scandium determination with EC

Accuracy and Precision of the Method

To check the accuracy and precision of the method, scandium (III) is determined at five different concentrations, the results shown in Table 8 indicate that the method is satisfactory.

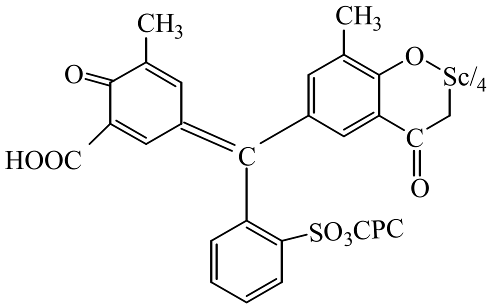
Table 8: Accuracy and precision

Sc(III) taken, (μg)	**Recovery, %***	**Relative standard deviation,%**
0.3	100.0	±6.1
0.5	100.0	0.0
1.0	100.0	±0.75
2.0	104.0	±0.6
3.0	100.0	±1.1

* Five determinations

Nature of the Complex

A study of the composition by Job's method of continuous variations at the wavelength of the maximum absorption (595 nm) reveals that the components react in a ratio of 1:4 scandium to ECR reagent. (Fig. 3). The molar ratio of Sc(III) to ECR also confirms this stoichiometric ratio as represented in Fig. 4. The proportion of CPC in the complex is determined by measuring the absorbance of the mixtures containing Sc(III) and ECR in a 1:4 ratio and



increasing amount of CPC Fig. 5. reveals that one fold molar ratio of CPC to complex is required. Therefore, the empirical formula of the chelate can be written as follows:

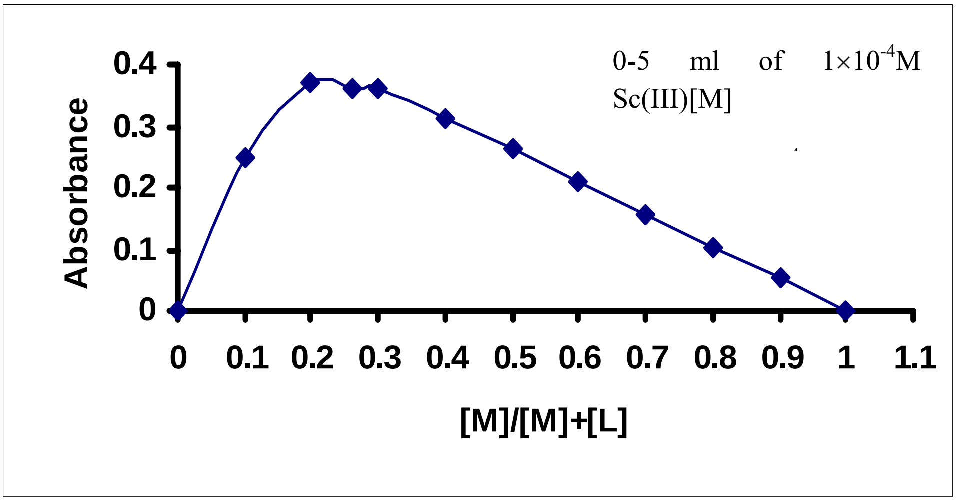


Fig. 3: Continuos-variations plot for Sc(III)-ECR-CPC chelate

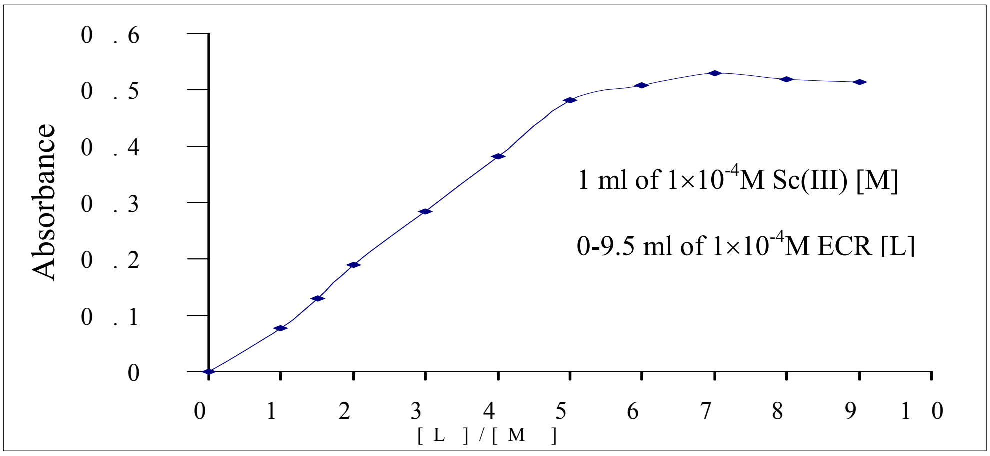


Fig. 4: Mole-ratio plot for the Sc(III)-ECR-chelate

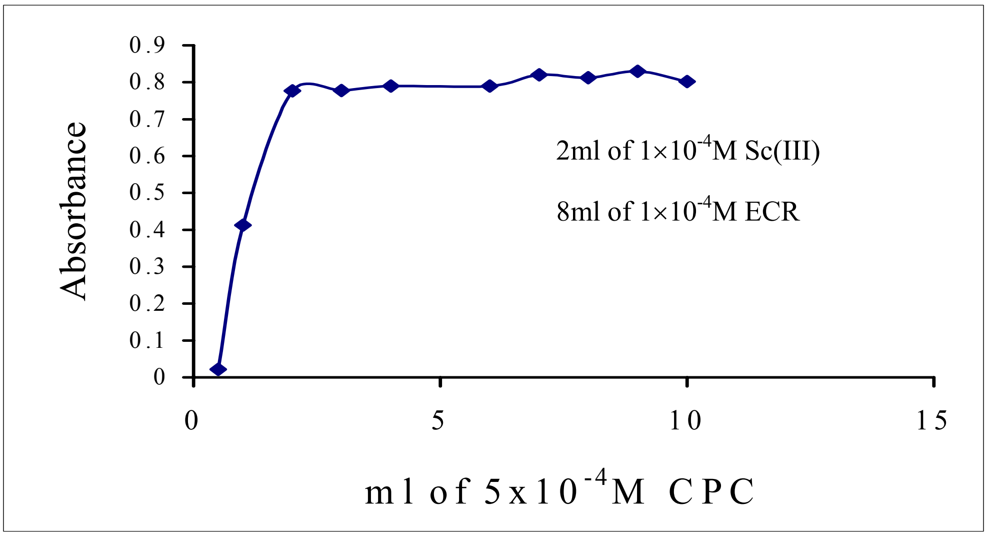


Fig. 5: Mole-ratio plot for the Sc(III)-ECR-CPC-chelate

Solutions are prepared to contain exactly one proportion of scandium (III) to four of the ECR reagent. The interaction between the metal (M) and ligand (L) proceeds according to:

$$\begin{array}{ccccc} M & + & 4L & \rightleftharpoons & ML_4 \\ \alpha C & & 4\alpha C & & C(1-\alpha) \end{array}$$

Then it is possible to write the stability constant as:

$$K = \frac{[ML_4]}{[M]\,[4L]^4}$$

If α is the degree of dissociation and C the final concentration of the complex, the above equation can be written as:

$$K = \frac{[C(1-\alpha)]}{[\alpha C][4\alpha C]^4} = \frac{1-\alpha}{256\alpha^5 C^4}$$

Knowing the value of α from the equation:

$$\alpha = \frac{A_m - As}{A_m}$$

Where A_m is the absorbance of the solution containing excess amount of ligand and A_s is the absorbance of the solution containing stoichiometric amounts of ligand and metal. C is essentially the concentration of Sc(III) ion (Al-Gabsha, 1975).

The apparent or conditional stability constant of the 1:4 (Sc(III)-ECR) coloured complex is calculated using the suitable equation (Al-Hadidi, 1997 and Khalil, 1993).

The results of estimation of the stability constant are given in Table 9.

Table 9: Stability constant of Sc(III)-ECR chelate

ml of 1×10^{-4} M Sc(III) /25 ml	Absorbance		α	K $l^4.mol^{-4}$
	A_s	A_m		
0.5	0.177	0.255	0.3059	6.3265×10^{22}
0.7	0.255	0.349	0.2693	3.2785×10^{22}

The value of the stability constant indicates that the complex is highly stable.

Effect of Organic Solvents

Different organic solvents are examined to evaluate their effects on the spectrum of the resulting chelate and the results are given in Table 10 and Fig. 6.

Table 10: Effect of organic solvents

Solvent	λ_{max}, nm	ε, $l.mol^{-1}.cm^{-1}$
Acetic acid	461	1.5×10^4
Acetone	613	1.7×10^3
Dimethyl sulphoxide	610	4.5×10^3
Ethanol	565	6.8×10^3
Formic acid	558	1.1×10^3
Methanol	608	1.7×10^4
n-Propanol	560	1.8×10^4
Pyridine	584	3.9×10^3
Tetrahydrofuran	563	1.8×10^3
Water	597	1.3×10^5

Water is still chosen in the subsequent experiments because of availability, non-toxicity and cheap as well as being a suitable medium from the sensitivity (being highest) point of view.

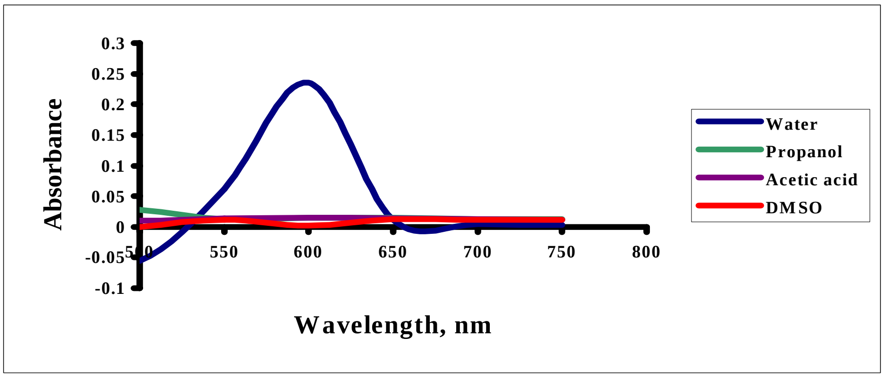


Fig. 6: Effect of solvents on spectral properties of ECR-Sc chelate

Interferences:

The effect of amounts of foreign compounds on the determination of Sc(III) is examined (Table 11).

Table 11: Effect of organic solvents

Foreign ion	**Form added**	**Amount added µg**	**Interferences%**
Al^{3+}	$AlCl_3.6H_2O$	5.0	-0.4
B^{3+}	H_3BO_3	7.0	-0.4
Ba^{2+}	$BaCl_2.2H_2O$	7.0	-1.3
Be^{2+}	$BeSO_4.4H_2O$	10.0	+3.0
Bi^{3+}	$Bi(NO_3)_3.5H_2O$	10.0	-3.4
Cd^{2+}	$Cd(CH_3COO)_2.2H_2O$	5.0	+3.1
Ce^{4+}	$Ce(SO_4)_2.2H_2O$	5.0	+5.1
Co^{2+}	$Co(NO_3)_2.6H_2O$	5.0	+2.1
Cr^{3+}	$CrCl_3$	5.0	-4.5
Cr^{6+}	K_2CrO_4	10.0	-1.3
Cs^{1+}	$CsNO_3$	2.0	0.0
Cu^{2+}	$CuSO_4$	0.5	(-4.2)[a]
Hg^{2+}	$Hg(NO_3)_2$	5.0	0.0
Ho^{3+}	Ho_2O_3	5.0	-2.6
K^{+}	KCl	7.0	+4.5
La^{3+}	$LaCl_3$	1.0	+4.3
Li^{+}	$Li_2SO_4.\ H_2O$	10.0	+3.6
Mg^{2+}	$MgCl_2.6H_2O$	10.0	-4.7
Mn^{2+}	$MnCl_2$	7.0	+2.7
Mo^{6+}	$(NH4)_6Mo_7O_{24}.4H_2O$	10.0	+2.1
Na^{1+}	NaCl	7.0	+0.9
Ni^{2+}	$NiCl_2.6H_2O$	7.0	-1.3
Pb^{2+}	$Pb(NO_3)_2$	2.0	+4.4
Pd^{2+}	$PdCl_2$	1.0	(+4.5)[b]
Sn^{2+}	$SnCl_2$	7.0	-2.2
Sr^{2+}	$SrCl_2$	5.0	-0.4
Th^{4+}	$Th(NO_3)_4.6H_2O$	7.0	+2.1
U^{6+}	$UO_2(NO_3)_2.6H_2O$	1.0	(+4.5)[b]
V^{5+}	NH_4VO_3	7.0	-3.4
Zn^{2+}	$ZnSO_4$	10.0	-1.3
BO_3^{3-}	H_3BO_3	5.0	(-0.9)[b]
Cl^{1-}	KCl	5.0	-2.6
CO_3^{2-}	Na_2CO_3	7.0	-1.3
HCO_3^{1-}	$NaHCO_3$	7.0	-1.3
I^{1-}	NaI	7.0	-1.3
NO_2^{1-}	$NaNO_2$	7.0	(0.0)[c]
SO_3^{2-}	Na_2SO_3	7.0	-4.7
SO_4^{2-}	Na_2SO_4	7.0	-3.7
$S_2O_3^{2-}$	$Na_2S_2O_3.5H_2O$	10.0	-2.8

a : in the presence of 1 ml (0.01 M) 5-sulfosalicylic acid.
b : in the presence of 1 ml (0.01 M) ascorbic acid.
c : in the presence of 1 ml (0.01 M) sulfamic acid.

It appears that the method can not applied to ores unless preceeded by a step separation for scandium, which is a subject of future work.

Application of the Method

The proposed method has been applied to the determination of scandium (III) in synthetic alloys, different types of water, the results are shown in Tables 12&13, and blood but it has not been successful which suggests the preliminary separation of scandium from blood before determination by this method.

Table 12: Determination of scandium (III) in synthetic alloys

Ion	**Relative error, %**
0.5 µg Al, 0.5 µg Mg, 0.5 µg Zr, 2.0 µg Sc	1.4
2.0 µg Al, 2.0 µg Mg, 2.0 µg Zr, 2.0 µg Sc	3.7
5.0 µg Al, 5.0 µg Mg, 5.0 µg Zr, 2.0 µg Sc	7.8

The results in the above table indicate that the method can be applied satisfactorily except when the amount of Zr exceeds 2 µg. And this is not unexpected since Sc and Zr have very similar chemical properties.

Table 13: Determination of scandium (III) in water samples

Sample	Ml of sample	Sc(III) added, µg	Recovery, %
Spring water (Alemadia water)	1	1	94.1
		3	94.3
		5	95.0
	3	1	94.0
		3	94.4
		5	96.5
	5	1	102.3
		3	105.6
		5	106.8
Well water	1	1	105.0
		3	98.0
		5	98.0
	3	1	106.4
		3	104.7
		5	102.1
	5	1	100.4
		3	98.8
		5	94.3
Tigris river water	1	1	103.9
		3	103.9
		5	105.0
	3	1	100.4
		3	103.5
		5	105.1
	5	1	98.3
		3	103.7
		5	105.1
Sea water*	1	1	100.0
		3	103.0
		5	106.0
	3	1	95.0
		3	99.0
		5	103.0
	5	1	94.7
		3	100.2
		5	105.0

* The composition of sea water (which is prepared in the laboratory) is given in (Henriksen, 1965).

The above results indicate that scandium may be determined in waters, since some errors are relatively high.

Comparison of Method

Table 14 shows the comparison between the analytical variables of the present method with those of another method (Park and Cha, 1999).

Table 14: Comparison of methods

Analytical parameter	Present method	Literature method(Park and cha, 1999)
pH	4.1	6.5
λ_{max} (nm)	595	610
Amount of reagent	1 ml of 5×10^{-4} M	5 ml of 1×10^{-3}M
Amount of surfactant	CPC, 1ml of 1×10^{-3} M	CTMAB, 10 ml of 2.0×10^{-4}M
Range of scandium determination, (ppm)	0.004-0.12	0.004-0.13
Molar absorptivity, ($l.mol^{-1}.cm^{-1}$)	1.3×10^{5}	5.6×10^{5}
Error, (%)	0.0-4.0	-
RSD, (%)	±0.6 to ±6.1	-
Correlation coefficient, (r)	0.9991	-
K ,($l^4.mol^{-4}$)	0.5×10^{23}	-
Nature of complex	1:4	1:1
Application of the method	Synthetic alloys, and four types of water	Monazite

The present method is sensitive and is applicable to more different samples than the literature one.

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