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Chromogenic Behaviour of Eriochrome Cyanine R.C. in the Spectrophotometric Determination of Scandium, Yttrium and Lanthanum*

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Sulphohydroxydimethyl fuchsone dicarboxylic acid (Eriochrome Cyanine R.C.) has been described as a reagent for the spectrophotometric determination of scandium, yttrium and lanthanum. The red coloured chelates formed have a composition 1 : 2 (metal : reagent) in all the cases. The colour of the dye changes with change in *p*H. The λ_{max} of scandium chelate is 535 mμ (at *p*H 5.0), of yttrium chelate is 530 mμ (at *p*H 6.0) and of lanthanum chelate 480 mμ (at *p*H 6.2). However the wavelength of study for lanthanum was selected at 500 mμ. A four fold excess of the reagent is required for full colour development. Other characteristics, i.e., range for adherence to Beer's law, range for effective photometric determination, *p*H range of stability and molecular extinction coefficient have also been determined.

Not many colour reactions of scandium, yttrium and lanthanum are known. Recently the use ot Alizarin Red S[1], Thoron[2], Chrome Azurol S[3], Chromotrope 2B[4] have been suggested as good reagents for the microdetermination of these elements.

This study was conducted to examine the possibility of carrying out the photometric determination of scandium, yttrium and lanthanum using sulphohydroxydimethyl fuchsone dicarboxylic acid (Eriochrome Cyanine R.C. ; abbreviated as ECRC), which has recently been suggested as a chromogenic reagent of metal ions[5-8].

EXPERIMENTAL

Absorbance and *p*H measurements were carried out as reported in earlier communications[4].

Johnson and Matthey samples of scandium, yttrium and lanthanum chlorides were dissolved in distilled water acidulated with HCl and the metal contents were estimated by the usual methods. An aqueous solution of ECRC was prepared by dissolving its known weight in distilled water. The ECRC was always freshly prepared as the colour of the reagent begins to fade after 90 minutes of its preparation.

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All experiments were performed in an air conditioned room at 25°. The total volume of all the mixtures was maintained at 25 ml and *p*H was adjusted by adding suitable amounts of NaOH and HCl solutions. The experiments were performed within 90 minutes of the preparation of the reagent.

RESULTS AND DISCUSSION

Complexex of Scandium, Yttrium and Lanthanum : Sc (III), Y (III) and La (III) react with ECRC to form red coloured water soluble chelates. The colour is stable only upto 90 minutes and after this the absorbance of the mixture decreases on standing.

The absorption spectra of the complexes were determined in presence of excess of metal ion. The solution contained 8×10^{-5}M ECRC and 2×10^{-4}M metal ion solution. The *p*H of the solutions were adjusted to 5.0 (for Sc), 6.0 (for Y) and 6.2 (for La). The absorbance was measured with reference to water. The absorption maxima for the chelates are 535 mμ for Sc, 530 mμ for Y and 480 mμ for La. The λ_{max} of the reagent at the respective *p*H are 500 mμ (at *p*H 5.0), 440 mμ (at *p*H 6.0 and 6.2). The wavelength of study chosen for lanthanum chelate is 500 mμ as the reagent absorbs little at this wavelength.

The molar ratio in the reactions of scandium, yttrium and lanthanum with ECRC was determined by the method of continuous variations as well as by the mole ratio method. For the former method, solutions of the metal ions and ECRC of the same concentrations were mixed in varying proportions and the absorbance of the solutions then measured. The composition of all the chelates was found to be 1 : 2 (metal : reagent). This composition was also supported by mole ratio method.

Conformity to Beer's Law : The linearity between the absorbance of the chelate and the metal concentration was tested by varying the metal ion concentration with a constant excess of ECRC (2×10^{-4}M in case of Sc and Y and 4×10^{-4}M in case of La) and measuring the absorbance. The range for adherence to Beer's law and range for effective photometric determination of each metal ion is given in Table I.

TABLE 1

Photometric Determination of Sc, Y and La with ECRC

Metal ion	*p*H of study	Wavelength of study (mμ)	Range for adherence to Beer's law (p.p.m.)	Range for effective photometric determination (p.p.m.)
Sc (III)	5 0	535	0.12 – 3.6	0.5 – 2.5
Y (III)	6.0	530	0.23 – 7.0	0.8 – 5.0
La (III)	6.2	500	0.37 – 18.0	0.1 – 12.0

Influence of pH : A series of solutions of each metals containing 4×10^{-5}M of $ScCl_3$ and YCl_3 and 8×10^{-5}M of ECRC and 8×10^{-5}M $LaCl_3$ and 1.6×10^{-4}M ECRC was prepared and *p*H adjusted to different values. The optimum *p*H range for the complexes for spectrophotometric determination was determined by plotting the absorbances of the complexes and the reagent separately at different *p*H values. The difference between the two curves showed the *p*H range of complex where the intensity of the complex remains the same. The results are given in Table II.

Stability of Colour at Room Temperature : Mixtures containing 4×10^{-5}M metal ion and 8×10^{-5}M ECRC at the *p*H of study retained colour intensity only upto 90 minutes. So every care was taken to use the reagent and finish the experiments within 90 minutes of the preparation of the mixtures.

Rate of Colour Formation : Colour formation is instantaneous but the mixtures should stand for half an hour for the equilibration.

Effect of Reagent Concentration : The absorbance values of different mixtures of the scandium, yttrium and lathanum solutions (4×10^{-5}M) with varying ratio of ECRC at the wavelength of study and at *p*H of study show that the maxium colour formation is only attained when the mixtures contain greater than 4-fold excess of the reagent with respect to metal ion.

Sensitivity : The sensitivity of colour reactions as defined by Sandell (based on an absorbance of 0·001 unit) for the metal ions was determined and the results are given in Table II.

Molar Absorption Coefficient : The molar absorption coefficient of the chelates was determined at the wavelength of study chosen. The solutions were prepared by taking a constant amount of the metal ion solution (2×10^{-5}M) and different amounts of excess of ECRC (15, 13 and 10 ml of 2×10^{-4}M reagent) were added. The average molar absorptivity calculated for each system is given in Table II.

TABLE II

Photometric Determination of Sc, Y and La with ECRC

System	*p*H	Wavelength (mμ)	Optimum *p*H range	Sensitivity (Sandell) $\mu g/cm^2$	Molar absorptivity
Sc–ECRC	5.0	535	4.8–6.0	0.018	23,000
Y –ECRC	6.0	530	5.8–6.5	0.045	15,000
La–ECRC	6 2	500	5.8–6.4	0.093	11,250

Interferences : The effects of some cations were studied under the conditions of study. Be (II), Al (III), Ga (III), In (III), Fe (III), Cr (III), Nb (V) and Pd (II) interfere at all concentrations whereas Zn (II), Co (II), Ni (II), Cd (II), Tl (III), Th (IV), U (VI), Mo (VI), Ca (II), Sr (II), Ba (II) and Mg (II)

do not interfere. Common anions like nitrate, sulphate and chloride show no interference.

To the metal ion solution containing between 0.5-2.5 p.p.m. of Sc, 0.8-5.0 p.p.m. of Y and 1.0-12.0 p.p.m. of La solution was added a 5-fold excess of the ECRC solution and the *p*H was adjusted to 5.0 (for Sc), 6.0 (for Y) and 6.2 (for La). The mixture was allowed to stand for 30 minutes for equilibration and then the absorbance was measured at 535, 530 and 500 mμ for Sc, Y and La respectively. The absorption value was then compared with the calibration curve.

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