SPECTROPHOTOMETRIC DETERMINATION OF THORIUM USING CHRYSIN

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Not many organic reagents have been employed for the colorimetric estimation of thorium. Among the reagents which have been used are morin,[1] quinalizarin,[2] naphthazarin,[3] and morellin.[4] Kanno[5] has reported the formation, at different pH values, of two yellow coloured chelates with quercetin sulphonic acid. Rutin[6] has also been used for the spectrophotometric determination of thorium. It has now been found that chrysin forms a yellow coloured complex with thorium, which can be utilised for the spectrophotometric determination of this metal. All the observations have been carried out in 40% alcoholic medium. Beer's law is obeyed between 2 and 36 p.p.m. of thorium and the complex has been found to have the molar composition of 1 : 1. About 2·5 to 3 times the amount of chrysin is sufficient for full colour development.

The reagent can be easily prepared and possesses the advantage of forming a very stable complex with thorium. The complex is soluble in 40% alcohol and in this respect it differs from the complexes formed by some other well-known reagents which are insoluble and form lakes. The colour intensity is also very high and very small amounts of thorium can be conveniently estimated.

Experimental

Chrysin was prepared by the method of Rao, Rao and Seshadri.[7] Thorium nitrate (A.R., B.D.H.) was used for preparing standard thorium solution. 0·254 gm. of chrysin was dissolved in one litre of alcohol. The absorption spectrum of chrysin was taken using Perkin-Elmer spectracord. All other spectrophotometric measurements were made using Coleman spectrophotometer, Model 14. All pH measurements were made with the help of a Metrohm pH-meter, type E 350.

Region of Maximum Absorption.—The absorption spectrum of chrysin was taken in the ultra-violet as well as in the visible region. Maximum

absorption was observed at 270 mμ and 315 mμ. No absorption maximum was observed in the visible region. The thorium-chrysin complex was found to have its absorption at 380 mμ. This wavelength was, therefore, chosen in the subsequent investigations. The absorption spectra of the complex were also studied at various pH values (from 2·0 to 4·8) and the maximum was always found to be at 380 mμ in all these cases (Fig. 1).

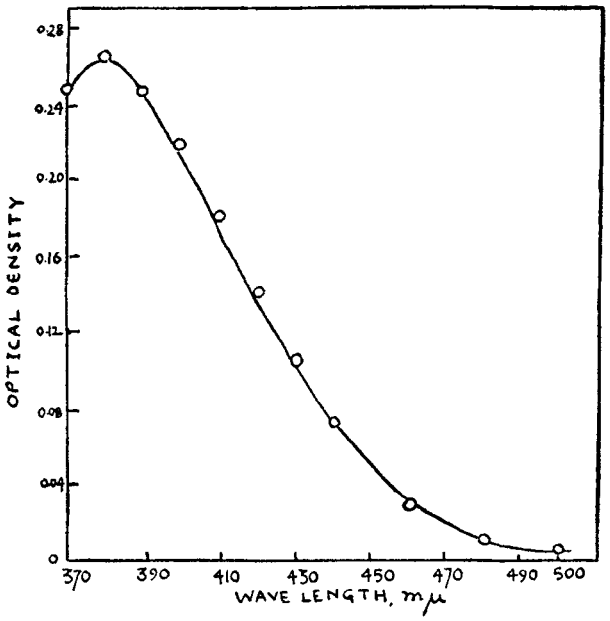

FIG. 1. Absorption Spectrum of Thorium-Chrysin Complex.

Minimum Amount of the Reagent Needed.—The optical densities of a series of solutions containing chrysin and thorium in the molar ratio of 1:2 to 10:2 were observed at 380 mμ. Results of these observations are summarized in Fig. 2, from which it can be seen that at least 2·5 moles of chrysin are needed for full colour development. However, in the subsequent studies, the molar ratio of chrysin to thorium was maintained at 5.

Effect of pH on Thorium-Chrysin Complex.—The effect of pH on the complex was studied and it was found that the absorption by the complex is maximum at pH 2·8, and it is less at other pH values (Fig. 3).

The decrease in colour intensity at low pH may be accounted for by the competition of hydrogen ions with thorium ions for chrysin, while the effect at high pH is probably due to the tendency of thorium ions to combine hydroxyl ions. The pH of the solutions was adjusted by the addition of very dilute solutions of hydrochloric acid and sodium hydroxide.

Stability of the Complex.—The complex was found to be quite stable and no change in colour was observed even on keeping it for several hours.

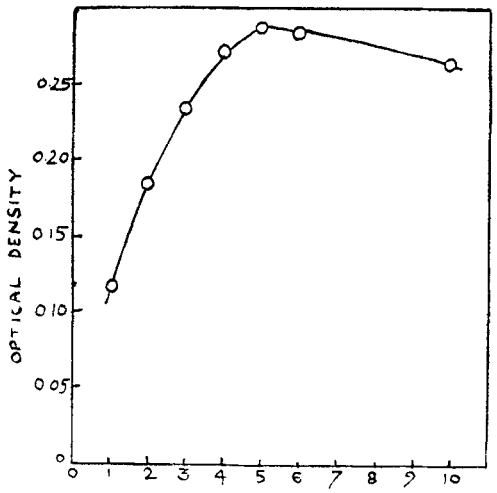

FIG. 2. Moles of Chrysin added to two Moles of Thorium.

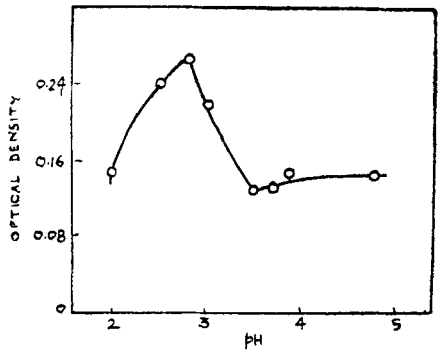

FIG. 3. Effect of pH on the Complex.

Beer-Lambert's Law.—The complex was found to obey the Beer-Lambert's law between 2 and 36 p.p.m. of thorium concentration at pH 2·8 (Fig. 4).

Molar Composition of the Complex.—Job's[8] method of continuous variations, as modified by Vosburgh and Cooper,[9] was employed for determination of the composition of the complex. Optical densities of the following two solutions prepared by mixing (*a*) x ml. of 1×10^{-3} M chrysin solution with $(10 - x)$ ml. of 1×10^{-3} M thorium solution and finally diluting

to 25 ml. and (*b*) x ml. of $0{\cdot}5\times10^{-3}$ M chrysin solution with $(10-x)$ ml. of $0{\cdot}5\times10^{-3}$ M thorium solution and finally diluting to 25 ml. (where x was varied from 1 to 9) were determined at 380 mμ employing chrysin solution of the corresponding strength as refernece solution. The absorption due to thorium salt and chrysin is negligible at 380 mμ. Hence the function, defined as the difference between the optical density observed for a given mixture of

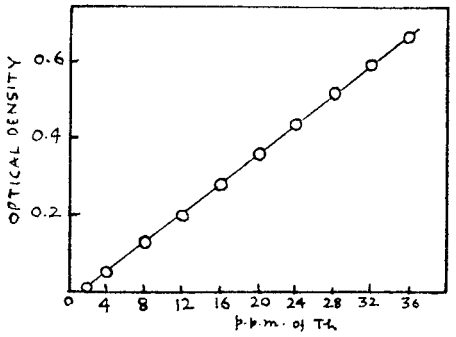

FIG. 4. Beer-Lambert's Law

the constituents and the corresponding optical densities of the respective components for no reaction, was taken in the present case as the observed optical density of the complex solution. The values of y are plotted against x (Fig. 5). The peak in the curve occurs when the molar ratio of chrysin to

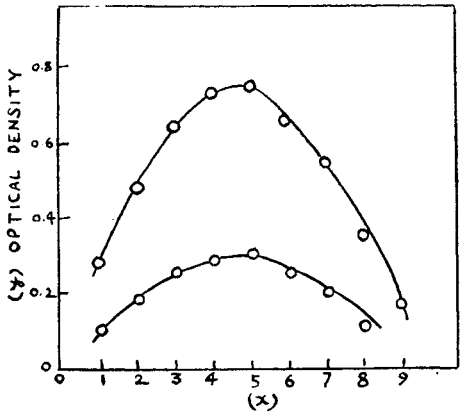

FIG. 5. Composition of the Complex (Job's Method of Continuous Variations)

thorium ions is 1 : 1. The complex, therefore, has the molar composition Th M where M is a molecule of chrysin.

The molar composition of the thorium-chrysin complex was also verified by the slope ratio method of Harvey and Manning.[10] For this purpose

two series of solutions were prepared employing 1×10^{-3} M solutions of chrysin and that of thorium. In one series concentration of thorium was varied maintaining that of chrysin constant and in sufficient excess. In the other series chrysin concentration was varied maintaining that of thorium constant and in sufficient excess. The optical densities of the solutions of both series were determined at 380 mμ with aqueous alcohol as reference. Two parallel curves are obtained showing that the composition of the complex is 1 : 1.

Summary

Chrysin forms a yellow coloured complex with thorium. This colour reaction has been investigated and utilised for spectrophotometric determination of thorium. The colour has maximum intensity at pH 2·8. It obeys Beer-Lambert's law at 380 mμ between the concentration limits of 2 and 36 p.p.m. of thorium. The molar composition of the complex has been found to be 1 : 1.

Acknowledgement

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