p-Nitrobenzene Azochromotropic Acid (Chromotrope 2B) as a Colorimetric Reagent for Thorium

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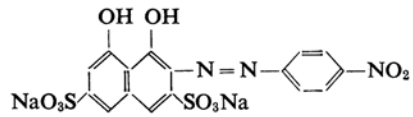
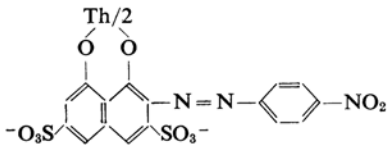
Metal chelates of *p*-nitrobenzene azochromotropic acid (disodium salt), (Chromotrope 2 B, abbreviated as CTB) with copper,[1] thorium,[2] lanthanum[3] and rare earths have been extensively studied in these laboratories. Chromotrope 2 B has also been recommended as a metalochromic indicator in the EDTA titration of thorium.[4] The structure of the reagent is as follows:



The possibility of chelation with metals in the ligand is at 1 : 8 hydroxy groups; hence, the structure of the metal chelate of Chromotrope 2 B may be assigned as:



The composition of the thorium - Chromotrope 2 B chelate (λ_{max} 550 mμ), as reported by Banerji and Dey,[2] is 1 : 2. This communication report the results of the spectrophotometric determination of thorium using Chromotrope 2 B as a chromogenic reagent.

Experimental

Instruments.—A Unicam SP 500 spectrophotometer operated by a Doran mains unit was employed for the absorbance measurements. The measuring glass cells, 1 cm. thick, were those supplied with the instrument.

A Leeds and Northrup direct reading pH indicator was employed for the adjustment of the hydrogen ion concentration.

Reagents.—Stock solutions of thorium chloride (B. D. H. AnalaR) and *p*-nitrobenzene azochromotropic acid (disodium salt) were prepared in distilled water and standardised by the usual methods. Solutions of various concentrations were obtained by suitable dilution. The other reagents used were also of the AnalaR grade.

Results and Discussion

The Rate of Colour Formation.—The colour formation is almost immediate; it takes less than five minutes to assume the full colour intensity.

The Influence of pH Value.—Full coloration is obtained between pH 3.0 and 6.5 (Fig. 1).

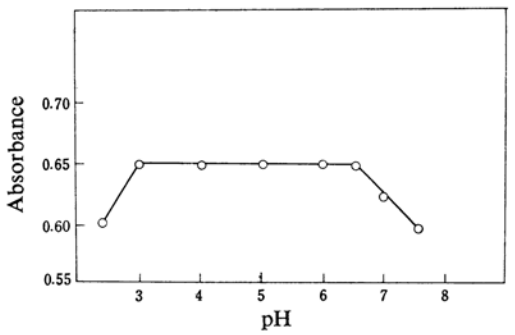


Fig. 1. The Effect of pH on the intensity of the colour.
CTB $2.0 \cdot 10^{-4}$ M
Thorium chloride 4.0×10^{-5} M, 580 mμ

The Effect of the Temperature.—The absorbance value of a mixture containing (2.0×10^{-4} M) Chromotrope 2 B and (8.0×10^{-5} M) thorium chloride was found to be constant, i. e., 0.820 at 580 mμ, at temperatures from 5 to 95°C.

Beer's Law.—Varying quantities (1 ,2, 3, ..., 8, 9 ml.) of thorium chloride were added to an excess of the reagent and the volume was raised to 25 ml. after the pH had been adjusted to 3.5. The colour instensity was measured with a Unicam SP 500 spectrophotometer at 580 mμ. It was found that the system adheres to Beer's law in the range from 0.74 p. p. m. to 16.6 p. p. m. of thorium (Fig. 2).

Sensitivity.—The sensitivity as defined by Sandell[5] was found to be 0.232 γ/cm^2. The practical sensitivity based upon an absorbance

1) S. P. Sangal and A. K. Dey, *Ind. J. Chem.*, **1**, 870 (1963).
2) S. K. Banerji and A. K. Dey, *J. Indian Chem. Soc.*, **38**, 139 (1961).
3) S. P. Sangal and A. K. Dey, ibid., **40**, 273 (1963); S. P. Sangal, *J. prakt. Chem.*, in press.
4) S. P. Sangal and A. K. Dey, *Z. anal. Chem.*, **183**, 178 (1961).
5) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd Ed., Inter. Sci., New York (1950).

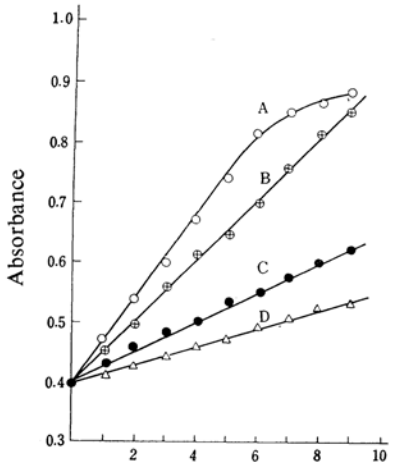


Fig. 2. Adherence to Beer's law.
(Total volume 25 ml.), pH 3~5, 580 mμ
Curve A 5 ml. (1.0×10^{-3} M) CTB + x ml. (4.0×10^{-4} M) $ThCl_4$ + $(20-x)$ml. H_2O
Curve B 5 ml. (1.0×10^{-3} M) CTB + x ml. (2.0×10^{-4} M) $ThCl_4$ + $(20-x)$ml. H_2O
Curve C 5 ml. (1.0×10^{-3} M) CTB + x ml. (1.0×10^{-4} M) $ThCl_4$ + $(20-x)$ml. H_2O
Curve D 5 ml. (1.0×10^{-3} M) CTB + x ml. (8.0×10^{-5} M) $ThCl_4$ + $(20-x)$ ml. H_2O

of 0.01 unit was found to be 2.32 γ/cm^2 at 580 mμ.

Interference Due to Foreign Ions.—The effect of various cations and anions was studied; it was found that silver, copper, beryllium, cadmium, titanium, zirconium, hafnium, tungsten, scandium, yttrium, lanthanum and rare earths, uranium, tartrate, oxalate, citrate, acetate and fluoride interfere.

Recommended Procedure.—For the determination of thorium from this method, the interfering substances must be removed. The pure solution of thorium chloride should then be added to an excess of the reagent and the pH adjusted to 3.5. The colour intensity is then measured by a spectrophotometer at 580 mμ.

Summary

A method for the colorimetric determination of thorium with Chromotrope 2 B has been described. The composition of the coloured chelate (λ_{max} 550 mμ) is $Th(Ke)_2$. The system adheres to Beer's law from 074 p. p. m. to 16.6 p. p. m. of thorium between pH 3.0 and 6.5 at all temperatures from 5 to 95°C. The sensitivities are 0.232 γ/cm^2 (Sandell) and 2.32 γ/cm^2 (practical) based on an absorbance of 0.01 unit at 580 mμ. The interference of some cations and anions has also been reported.

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