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THE THORIUM – APANS COMPLEX
A SPECTROPHOTOMETRIC STUDY

by

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Abstract

The analytically useful complex formed by thorium and APANS [1–(o–arsonophenylazo)–2–naphthol– 3:6 disulphonic acid] has been studied by a spectrophotometric method. The complex is shown to be of the 1:2 type and its equilibrium constant measured.

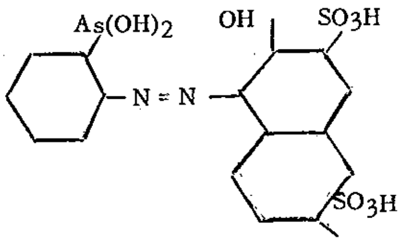
Sydney, February, 1958.

CONTENTS

1. INTRODUCTION

The reagent 1–(o–arsonophenylazo) – 2 – naphthol – 3:6 disulphonic acid was first introduced by Kuznetsov (1), (2) in 1941 for the detection of thorium. Thomason, Perry and Byerly[3] used this reagent to develop a method for the determination of microgram quantities of thorium. Recently, Foreman, Riley and Smith[4] have used the reagent to estimate microgram amounts of quadrivalent uranium.

The reagent is known by various trivial names; thoron, thorin, thoronol, naphtharson and APANS. All names refer to the same material whose structural formula may be written:–



The reagent is available commercially in the form of its disodium salt. In this communication, the trivial name APANS will be used for the reagent.

2. EXPERIMENTAL

Reagents:–

(i) APANS solution:– 0.2611 g of the disodium salt (as supplied by B.D.H.) was dissolved in water and diluted to 1 litre. This gave a solution 4.53×10^{-4}M.

(ii) Thorium solution:– A solution prepared by dissolving A.R. thorium nitrate in water was standardised by precipitating the thorium as the hydroxide and igniting to constant weight. The solution thus prepared was 4.53×10^{-2}M. A solution 4.53×10^{-4}M was prepared by dilution.

Absorption measurements were made with a Hilger "Uvispek" Spectrophotometer using 1cm or 4cm matched glass cells. The light source was a tungsten lamp.

3. THE THORIUM – APANS COMPLEX

The structure of the Thorium–APANS complex has been studied previously by Byrd and Banks(5) and Clinch(6). Byrd and Banks find that the complex is predominantly 2 moles of thorium to 3 moles of APANS. They state, however, that the results are inconclusive; although titration experiments also suggest a formula Th_2R_3.

Clinch (6) states that spectrophotometric analyses indicate that the complex is formed from one atom of thorium and two molecules of APANS. In view of this discrepancy, it was decided to reinvestigate this system.

Figure 1 shows the spectra of the APANS reagent and the thorium – APANS complex. The addition of the reagent causes a shift to longer wavelengths. If the density of the complex is measured using a reagent solution as reference; a curve showing maximum density at 545 mu is obtained.

The empirical formula of the thorium -- APANS complex was investigated by the method of continuous variations [7], [8], [9] and by the slope ratio method [10], [11]. For the continuous variations method, equimolar solutions (4.53×10^{-4}M) of thorium and APANS were mixed in the proportions of x to 10-x ml, and made up to 100 ml. The pH of the final solution was adjusted to approximately 1 by the addition of appropriate quantities of nitric acid. Typical plots of corrected optical density against the parameter x are shown in Figure 2.

The maxima in the curves correspond to the addition of 3.33 ml. of thorium to 6.67 ml of APANS, and since equimolar solutions are used it is evident that the complex contains 2 molecules of APANS to one of thorium. The correspondence of the curves at different wavelengths suggests the formation of only one complex. For the uranium IV - APANS complex, Foreman et al (4) find that the complex contains two molecules of APANS to one of uranium IV.

The formula ThR_2 is also suggested by the evidence obtained by the slope ratio method. In this method, the optical densities versus the concentration of the variable component are plotted from two origins at either end of the X axis. Typical plots are shown in Figure 3. It is seen that the two curves intersect at a point corresponding to a mol ratio of thorium to APANS of 1:2.

The molar optical density of the complex may be measured by preparing solutions containing an excess of reagent corresponding to the plateau in Figure 4.

If the value of the molar optical density of the pure reagent is known; then provided the solutions obey Beers Law, the apparent stability constant K of the complex may be calculated[12] assuming that the formation is in accordance with the following equation

$$Th + 2R = ThR_2$$

where R represents the molecule of APANS

$$\text{Hence } K = \frac{[ThR_2]}{[Th]\,[R]^2}$$

Application of this method to several solutions gave a value of $K = 1.4 \pm 0.1 \times 10^{10}$

4. DISCUSSION

In the absence of information as to its charge, it is not possible to assign a structure to the complex. The sharp peak of the curves in Job's procedure and the modified molar ratio method substantiate the high value of the stability constant.

No evidence was obtained for the stepwise formation of the complex, Job's method giving similar results at the three wavelengths employed. The high value for the stability constant of the complex is further supported by dilution experiments. Varying amounts of thorium solution were mixed with equal amounts of APANS of the same molarity and diluted always to the same volume. In this way the concentration of the complex was varied ten fold in a series of experiments. Plots of optical density versus volume were linear.

5. SUMMARY

The compound formed from thorium and APANS has been studied by the spectrophotometric methods and shown to contain thorium and reagent in the ratio 1:2. The apparent stability constant of this complex has been measured as $1.4 \pm 0.1 \times 1010$.

6. REFERENCES

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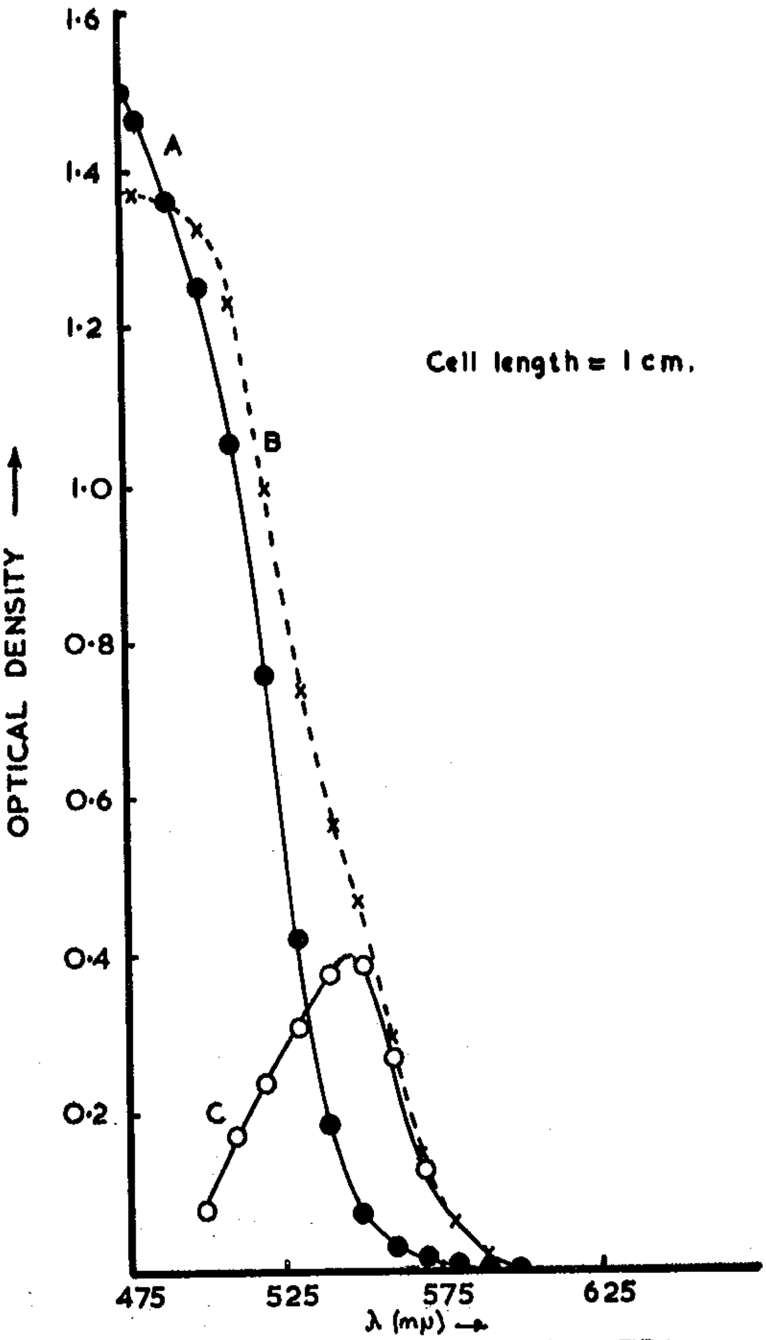

FIGURE 1. ABSORPTION SPECTRA.

A. Reagent vs. water.

B. Complex vs. water.

C. Complex vs. reagent.

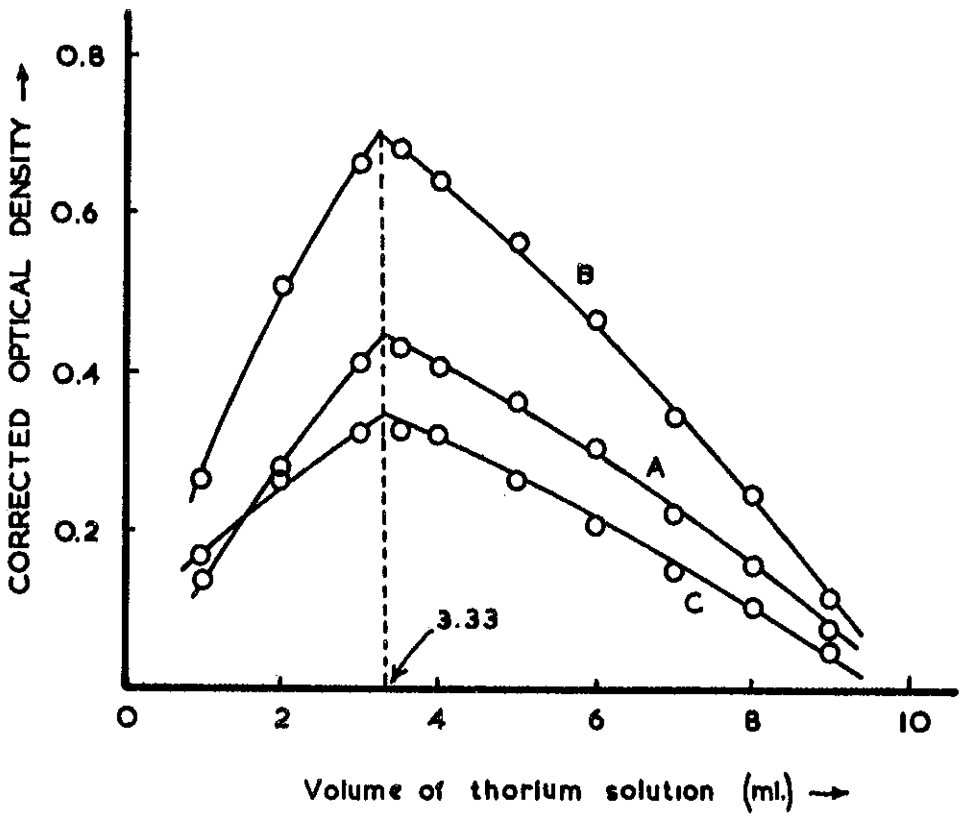

FIGURE 2. JOB'S METHOD.

A = 500 mμ, B = 530 mμ, C = 560 mμ.

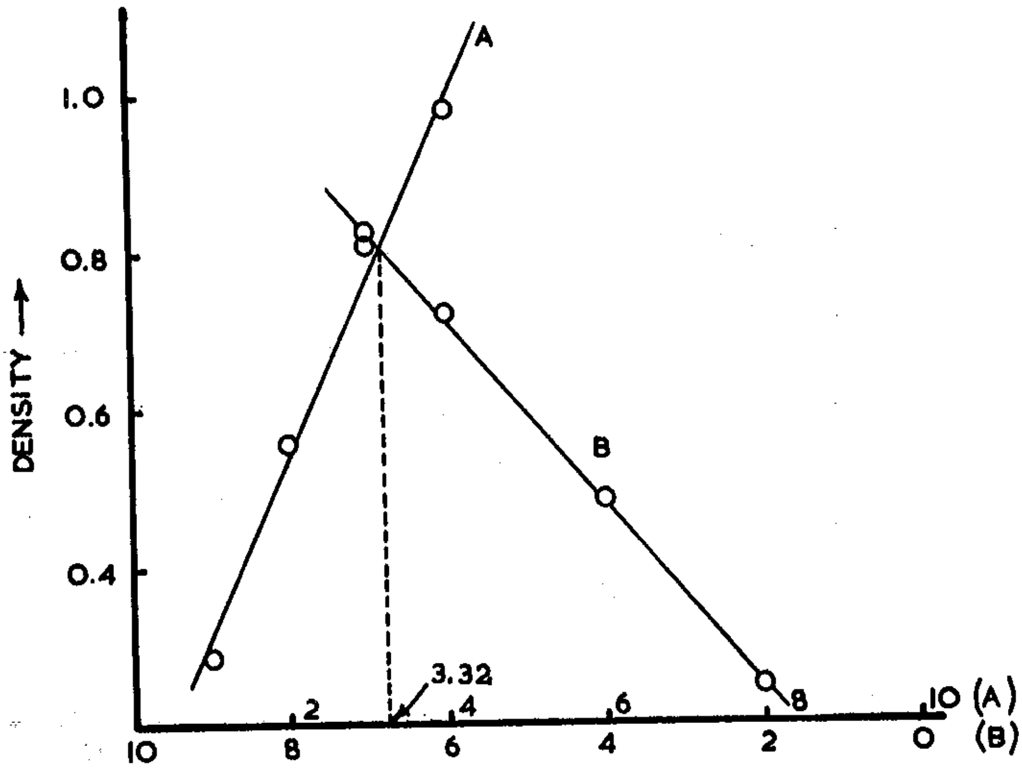

FIGURE 3.

MODIFIED SLOPE RATIO METHOD

530 mμ

A. Mls. of thorium for 10 ml. reagent.

B. Mls of reagent for 10 ml. thorium.

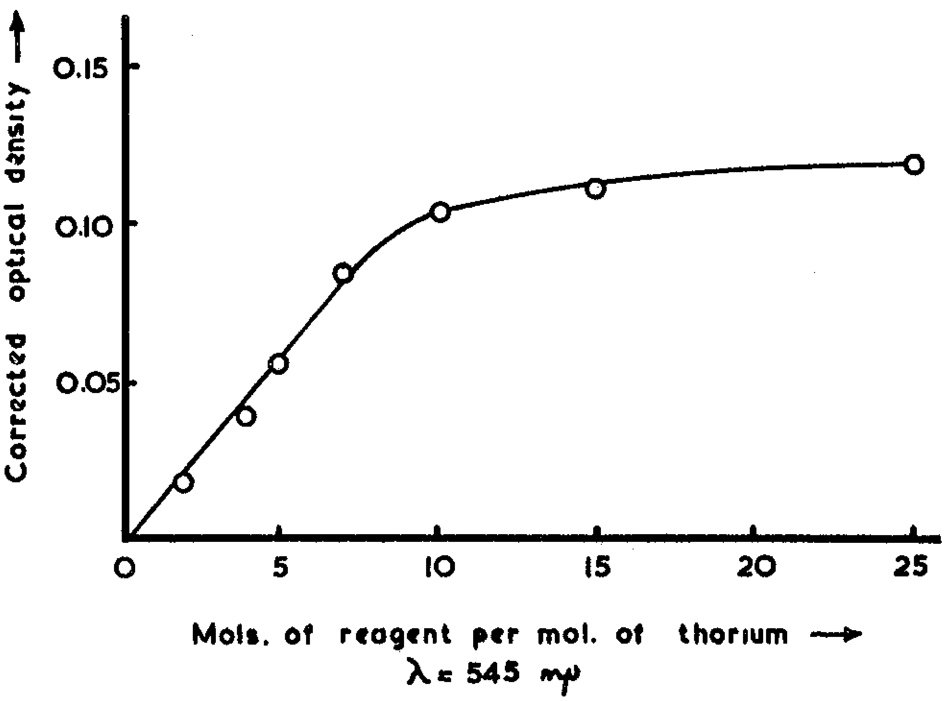
Corrected optical density →
0.15
0.10
0.05
0
5
10
15
20
25
Mols. of reagent per mol. of thorium →
λ = 545 mμ

FIGURE 4.