CHAPTER XI.

USE OF 2,3,4-TRIHYDROXYACETOPHENONE IN THE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM.

1. SUMMARY.

A critical examination of the thorium (IV) -2,3,4-trihydroxyacetophenone system in an aqueous medium is presented. This complex shows an absorption maximum at 405 nm ($405 = 2.9 \times 10^3$); the procedure for the spectrophotometric determination of Th(IV) included the following experimental conditions: pH range, 2.3 to 3.1 units; concentration range for the maximum accuracy (corresponding to the absorbance range 0.2 to 0.7 units at 405 nm) 16 ppm to 57 ppm of Th(IV); concentration of 2,3,4-trihydroxyacetophenone, 8 ml of $8 \times 10^{-3}$ M reagent in a total volume of 25 ml of the experimental solution; absorption measurements were taken within the time interval of 90 minutes after adjusting the pH of the solutions. Beer's law was obeyed up to 110 ppm. Among the commonly occurring ions with thorium, the following ions were found to cause an error of +2 per cent when Th(IV) concentration was 30 ppm: Zr(IV) (1 ppm); V(IV) (4 ppm); $\text{UO}_2^{2+}$ (9 ppm); Bi$^{3+}$ (16 ppm); W(VI) (18 ppm); even
0.1 ppm of Fe(III) and Cr(VI) showed an appreciable error; there was negligible error due to Be, Mg, Al, Cd, Mn(II), Co(II), Ni(II).

2. INTRODUCTION.

A large number of colorimetric reagents are reported in the literature for the spectrophotometric determination of thorium.\(^1\) The recent review\(^2\) on the light absorption methods include the use of bromopyrogallol red, heteropoly blue of Th-molybdophosphoric acid and quinalizarine for the determination of thorium. The reduced heteropoly complex\(^3\) is a sensitive, but not a selective reagent. The most widely used reagent for the determination of the small quantities of thorium is thoron;\(^4\) however, the anions which are commonly present with thorium in the working solution, like sulphate and phosphate, do seriously interfere the determination of thorium using thoron. One of the most sensitive chromogenic reagent for thorium is morin;\(^5\) there is a serious interference of zirconium, aluminium, ferric iron and ferrous iron in this procedure. The use of arsenazo\(^6\) is recommended in the spectrophotometric determination of uranium and thorium: the interfering elements like zirconium and iron are also extracted with thorium and uranium using mesityl oxide.

The bonding in the morin-thorium complex is proposed\(^5\) through a phenolate ion and a keto group. These groups are favourably situated in 2,3,4-trihydroxyacetophenone (THAP) also. Thus it is expected that thorium will form stable
**Fig. 1** Absorption Spectrum of Th(IV) (4 ml of 1 x 10^{-3} M) - THAP (2.5 ml of 8 x 10^{-3} M) System at pH 2.7 (Total Volume 25 ml)

**Fig. 2** Variation in Absorbance with Time of Th(IV) (4 ml of 1 x 10^{-3} M) - THAP (2.5 ml of 8 x 10^{-3} M) System at pH 2.7 (Total Volume 25 ml)
complex with THAP in an acidic medium. The results on thorium-THAP system are reported in this CHAPTER.

3. STOCK SOLUTIONS.

A stock solution of thorium was prepared by dissolving 6.0 g of thorium nitrate hydrate (Th(NO₃)₄·xH₂O) in 1 litre of 3 per cent nitric acid. The stock solution was standardized by precipitating thorium as thorium sebacate and weighing it as thorium dioxide. The concentration of the final stock solution was adjusted to 1 x 10⁻² M.

The stock solution of THAP was 8 x 10⁻³ in water.

4. ANALYTICAL PROCEDURE.

Order of Addition of Reagents. Although the absorbance of the system under study did not depend on the order of the addition of the reagents, the following scheme was used to have the identical experimental conditions: add an appropriate concentration of THAP to Th(IV) solution and then make the volume by using the appropriate buffer.

Absorption Spectrum. The pH of the solution containing 4 ml of Th(IV) (1 x 10⁻³ M) and 2.5 ml of THAP (8 x 10⁻³ M) was adjusted to 2.7 and the total volume was made to 25 ml. An appropriate blank was prepared in a similar manner except that water was used in place of Th(IV) solution. Absorption measurements were
FIG. 3 VARIATION IN ABSORBANCE WITH THE VARIATIONS IN pH OF Th(IV) (4 ml OF $1 \times 10^{-3}$ M) - THAP (2.5 ml OF $8 \times 10^{-3}$ M) SYSTEM (TOTAL VOLUME 25 ml)

FIG. 4 JOB'S METHOD OF CONTINUOUS VARIATIONS FOR Th(IV) - THAP SYSTEM AT pH 2.7 (TOTAL VOLUME 25 ml)
FIG. 5  MOLE RATIO METHOD FOR Th(IV) (4 ml of 1 x 10^{-3} M) - THAP SYSTEM AT pH 2.7 (TOTAL VOLUME 25 ml)
taken in the wavelength region of 360 nm to 500 nm within the
time interval of 1 hour after the adjustment of pH of the
solution. A strong absorption of THAP at pH 2.7 was observed
at 290 nm. The Th(IV)-THAP complex showed an absorption band
at 405 nm (Fig. 1) with the molar absorptivity of $2.9 \times 10^3$.

Rate of Reaction and Stability. Absorption measurements at
405 nm and 440 nm made on a solution of pH 2.7 containing 4 ml
of Th(IV) ($1 \times 10^{-3}$ M) and 2.5 ml of THAP ($8 \times 10^{-3}$ M) in a
total volume of 25 ml showed less than 0.4 per cent change in
absorbance during 90 minutes after adjusting the pH of the
solution. There was a very gradual decrease in absorbance of
the solution with time (Fig. 2). Absorption measurements
reported in the further sets of experiments were done at
20 minutes after adjusting the pH of the solution. Absorbance
of a solution stored in a stoppered flask in dark at 0° to 5°
remained constant for more than three days.

Effect of pH. Absorption measurements were made at 405 nm
and 440 nm on a series of solutions containing 4 ml of Th(IV)
($1 \times 10^{-3}$ M) and 2.5 ml of THAP ($8 \times 10^{-3}$ M) in a total volume
of 25 ml adjusted to the various pH values in the range 1.2 to
3.5 (Fig. 3). The variations in absorbance in the pH range
2.3 to 3.1 were less than 0.5 per cent.

More Ratio Studies. An empirical formula of the predominant
Th(IV)-THAP complex in a solution was established by two
FIG. 6  BEER’S LAW FOR Th(IV)–THAP (8 ml OF 8 x 10^{-3} M) SYSTEM AT pH 2.7 (TOTAL VOLUME 25 ml)
independent techniques: the continuous variations method of Job\textsuperscript{8} and the mole ratio method of Yoe and Jones\textsuperscript{9}. The results (Fig. 4 and Fig. 5) indicated that the predominant complex in a solution was formed by one mole of Th(IV) reacting with one mole of THAP (R), giving the empirical formula as ThR. The shapes of the curves (Fig. 4 and Fig. 5) indicated that the complexes with other empirical formulae had a negligible concentration in equilibrium.

It was concluded from the results of the mole ratio method that a solution (25 ml) containing 4 ml of Th(IV) solution (1 x 10\textsuperscript{-3} M) and 2 ml to 8 ml of THAP (8 x 10\textsuperscript{-3} M) showed 0.5 percent variation in absorbance; a steady increase in absorbance was observed with the increase of the ligand concentration in the range 2 ml to 10 ml of THAP (8 x 10\textsuperscript{-3} M).

Conformity to Beer's Law. A number of solutions of pH 2.7 ± 0.1 containing the varying amounts of Th(IV) and 8 ml of THAP (8 x 10\textsuperscript{-3} M) in a total volume of 25 ml were prepared to determine whether the colour system conformed to Beer's law (Fig. 6). Beer's law was obeyed up to 110 ppm. For the solutions with concentrations below 1.5 ppm the absorbance reading were less than 0.03 (path length 1 cm).

Sensitivity. The optimum range for absorbance measurements is between 0.2 to 0.7 units for the best precision with a spectrophotometer. This range of absorbance at 405 nm was corresponding to a concentration range from 16 ppm to 57 ppm.
of thorium. Absorption measurements were reproducible within 0.003 unit corresponding to a sensitivity of 1 part of thorium in 7 million parts of solution.

**Effect of Diverse Ions.** In order to determine the effect of the different inorganic and organic ions which might reasonably be encountered in the thorium analysis, the solutions of pH 2.7 ± 0.1 were prepared containing 30 ppm of thorium, 8 ml of THAP (8 x 10^{-3} M) and the varying concentrations of each ion to be tested in a total volume of 25 ml. The absorption measurements showed an appreciable error for solutions containing even 0.1 ppm of Fe(III). The absorption measurements were 2 per cent higher for the solutions containing 1 ppm of Zr(IV), 4 ppm of V(IV), 9 ppm of UO_2^{2+}, 16 ppm of Bi^{3+}, 18 ppm of W(VI), 60 ppm of Ca^{2+}, 90 ppm of Sr^{2+} and 40 ppm of Ba^{2+}. The error due to the presence of Cr(VI) was much higher than that due to the presence of Fe(III). There was a negligible error due to Be^{2+}, Mg^{2+}, Al^{3+}, Cd^{2+}, Mn(II), Co(II), Ni(II) and Cu(II). Phosphate ions have a serious error on the determination of Th(IV).

5. DISCUSSION.

The absorbance of Th(IV)-THAP system in an aqueous medium under the appropriate experimental conditions was constant during the time interval of 90 minutes from the preparation of solutions; this time interval was more than
sufficient for the routine analysis. The absorption maxima of THAP and thorium complex with THAP are well separated (by \( \lambda 115 \) nm) unlike with most of the other reagents reported in the literature. Although the molar absorbance of Th(IV)-THAP complex is about one-tenth that of Th(IV-Thorium complex), THAP is in some respect superior as sulphate do not interfere in the colour reaction of THAP with Th(IV). The determination of Th(IV) will be in error when the other ions like Fe(III), Cr(VI) and \( UO_2^{2+} \) are present; however, it may be possible to device a procedure for the simultaneous determinations of these elements when these are present in the semimicro concentration range.

The colour-reaction studied in the present work was reversible which was an essential condition for most of the colorimetric determinations. The mole ratio studies showed the predominance of the complex with the empirical formula ThR.

6. REFERENCES.


