CHAPTER V.

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

1. SUMMARY

A critical examination of the Sr\(^{2+}\)-2,3,4-trihydroxyacetophenone system in an aqueous medium is presented. This system showed a broad absorption maximum at 560 nm \((\varepsilon_{560} = 3.05 \times 10^3)\); the procedure for the spectrophotometric determination of Sr\(^{2+}\) included the following experimental conditions: pH range, 11.6 to 12.2 units; concentration range for the maximum accuracy (corresponding to the absorbance range 0.2 to 0.7 units at 560 nm) 6 ppm to 20 ppm of Sr\(^{2+}\); concentration of 2,3,4-trihydroxyacetophenone, 15 ml. of \(8 \times 10^{-3}\) M reagent in a total volume of 25 ml of the experimental solution; absorption measurements to be taken within the time interval of 15 minutes to 50 minutes. Beer's law was obeyed over the concentration range of 6 ppm to 40 ppm of Sr\(^{2+}\). Among the commonly occurring ions with strontium the following ions were found to cause an error of +2 per cent when Sr\(^{2+}\) concentration was 40 ppm: V(IV), Cr(VI), Mn(II), UO\(_2^{2+}\) (5 ppm); error from Mg\(^{2+}\) due to a partial precipitation of Sr\(^{2+}\) with magnesium hydroxide; an appreciable error from Ca\(^{2+}\), Ba\(^{2+}\) and Fe(III).
2. INTRODUCTION.

Among a few colorimetric reagents reported for the spectrophotometric determination of strontium the promising reagents are chloranilic acid, murexide, nitroorthanilics, chlorophosphonazo III. One of the limitations in the use of last three reagents was that the absorption spectra of the reagent and its strontium complex were not well separated; the method with using chloranilic acid might be considered to be indirect procedure. During the study of spot tests of Ca²⁺, Sr²⁺, Ba²⁺ with 2,3,4-trihydroxyacetophenone (THAP) it was observed that THAP gave the characteristic colour-reactions in the basic medium. The results of the systematic study of the Sr²⁺-THAP system are summarized in this chapter.

3. STOCK SOLUTIONS.

For the preparation of the standard solution of strontium 5.332 g of strontium chloride 6-hydrate (AR) were dissolved in distilled water to make 1 litre volume. The strontium content was checked by the potentiometric EDTA titration using the mercury electrode. The stock solution thus prepared was $2 \times 10^{-2}$ M.

The stock solution of THAP was $8 \times 10^{-3}$ M in water.

4. ANALYTICAL PROCEDURE

Order of Addition of Reagents. In the visual colour reaction of Sr²⁺ with THAP in an alkaline medium, the order
FIG. 1 ABSORPTION SPECTRUM OF $\text{Sr}^{2+}$ (3 ml of $2 \times 10^{-3}$ M)–THAP (5 ml of $8 \times 10^{-3}$ M) SYSTEM AT pH 11.8 (TOTAL VOLUME 25 ml)

FIG. 2 VARIATION IN ABSORBANCE WITH TIME OF $\text{Sr}^{2+}$ (3 ml of $2 \times 10^{-3}$ M)–THAP (5 ml of $8 \times 10^{-3}$ M) SYSTEM AT pH 11.8 (TOTAL VOLUME 25 ml)
of addition of reagents was not specific. In the spectro-
photometric determination of strontium the following order
of addition of reagents was recommended to have the precision
measurements of absorbance: add an appropriate concentration
of THAP to Sr\(^{2+}\) solution and then adjust the pH with a rapid
mixing of the final solution.

The reverse addition of the reagents sometimes gave a
little higher absorbance reading probably due to the formation
of a colloidal suspension.

**Absorption Spectrum.** The pH of the solution containing 3 ml
of Sr\(^{2+}\) (2 x 10\(^{-3}\) M) and 5 ml of THAP (8 x 10\(^{-3}\) M) was
adjusted to 11.8 and the total volume was made to 25 ml with
water. An appropriate blank was prepared in a similar manner
except that water was used in place of Sr\(^{2+}\) solution. Absorption
measurements were taken in the wavelength region 480 nm to
650 nm within the time interval 15 minutes and 45 minutes after
adjusting the pH of the solution. A strong absorption due to
THAP was observed below 480 nm. The Sr\(^{2+}\)-THAP complex showed
a broad absorption band at 560 nm (Fig. 1) with the molar
absorptivity of 3.05 x 10\(^{3}\).

**Rate of Reaction and Stability.** Absorption measurements at
560 nm and 620 nm made on a solution of pH 11.8 containing
3 ml of Sr\(^{2+}\) (2 x 10\(^{-3}\) M) and 5 ml of THAP (8 x 10\(^{-3}\) M) in a
total volume of 25 ml showed no change during the time
interval between 15 minutes and 50 minutes; within the first
FIG. 3 VARIATION IN ABSORBANCE WITH THE VARIATION IN pH OF Sr$^{2+}$ (3 ml OF $2 \times 10^{-3}$ M)-THAP (5 ml OF $8 \times 10^{-3}$ M) SYSTEM (TOTAL VOLUME 25 ml)
FIG. 4 JOBS METHOD OF CONTINUOUS VARIATIONS FOR Sr$^{2+}$—THAP SYSTEM
AT pH 11.8 (TOTAL VOLUME 25 ml)
FIG. 5 MOLE RATIO METHOD FOR Sr$^{2+}$ (3 ml of $2 \times 10^{-3}$ M)–THAP SYSTEM AT pH 11.8 (TOTAL VOLUME 25 ml)
12 minutes and after 50 minutes there was a decrease in absorbance (Fig. 2). During the recommended time interval between 15 minutes and 50 minutes, the absorbance changed by less than 0.4 per cent. Absorbance measurements reported in the further sets of experiments were done at 20 minutes after the adjustment of pH. Absorbance of a solution stored in a stoppered flask in dark at 0° to 5° remained constant for about twenty-four hours.

**Effect of pH.** Absorbance measurements were made at 560 nm and 620 nm on a series of solutions containing 3 ml of Sr^{2+} (2 x 10^{-3} M) and 5 ml of THAP (8 x 10^{-3} M) in a total volume of 25 ml adjusted to the various pH values in the range 10.0 to 12.5 (Fig. 3). The variations in absorbance in the pH range 11.6 to 12.2 were less than 0.4 per cent.

**Mole Ratio Studies.** An empirical formula of the predominant Sr^{2+}-THAP complex in a solution was established by two independent techniques: the continuous variations method of Job and the mole ratio method of Yoe and Jones. The results (Fig. 4 and Fig. 5) indicated that the predominant complex in a solution was formed by one mole of Sr^{2+} reacting with one mole of THAP (R), giving the empirical formula as SrR. The shape of the curves indicated the probable presence of another complex species in equilibrium of the empirical formula SrR_2.

It was concluded from the results of the mole ratio method that a solution containing 3 ml of Sr solution
FIG. 6 BEER'S LAW FOR Sr$^{2+}$-THAP (5 ml of 8 x 10$^{-3}$ M) SYSTEM AT pH 11.8
(TOTAL VOLUME 25 ml)
(2 \times 10^{-3} \text{ M}) \text{ required at least 2.0 ml of THAP (8 \times 10^{-3} \text{ M}) to give the constant values of absorbance. Absorbance was constant upto 6 ml of THAP (8 \times 10^{-3} \text{ M}).}

**Conformity to Beer's Law.** A number of solutions of pH 11.9 ± 0.2 containing the varying amounts of Sr^{2+} and 5 ml of THAP (8 \times 10^{-3} \text{ M}) in a total volume of 25 ml were prepared to determine whether the colour system conforms to Beer's law (Fig. 6). Beer's law was obeyed over the concentration range 6 to 40 ppm of strontium; outside this concentration range an appreciable deviation from the Beer's law was observed.

**Sensitivity.** The optimum range for absorbance measurements is between 0.2 and 0.7 units for the best precision with a spectrophotometer. This range of absorbance at 560 nm was corresponding to a concentration range from 6 ppm to 20 ppm of strontium; this concentration range is narrow because the Beer's law showed deviation below absorbance of 0.3. Absorbance measurements were reproducible within 0.003 unit corresponding to a sensitivity of 1 part of strontium in 10 million parts of solution.

**Effect of Diverse Ions.** In order to determine the effect of different inorganic and organic ions which might reasonably be encountered in strontium analysis, the solutions of pH 11.9 ± 0.2 were prepared containing 40 ppm strontium, 5 ml of THAP (8 \times 10^{-3} \text{ M}) and the varying concentrations of each
ion to be tested in a total volume of 25 ml. The solutions containing as low as 1 ppm of Ca\(^{2+}\), Ba\(^{2+}\), Fe\(^{3+}\) gave an appreciable error. An error observed for a solution containing magnesium with about more than ten times of strontium concentration showed an appreciable error probably due to the precipitation of strontium. The ions V(IV), Cr(VI), Mn(II), UO\(^{2+}\) with the concentrations of 5 ppm gave about +2 per cent error in strontium concentration; the error of the same magnitude was given by 30 ppm of Mo(V), Zr(IV), Th(IV).

5. DISCUSSION.

The new reagent, THAP is one of the few reagents which are used for the direct spectrophotometric determination of strontium. The molar absorptivity of Sr\(^{2+}\)-THAP is reasonably high and the absorption maximum of the complex is well separated from that of the free ligand. Absorbance of the Sr\(^{2+}\)-THAP system in an aqueous medium under the appropriate experimental conditions is reasonably constant during the time interval between 15 minutes and 50 minutes after the preparation of the solutions; this time interval is sufficient for most of the analytical work.

Only a few metal ions remain in solution at the high pH recommended for the colour development. Calcium and barium gave colour-reactions similar to that of strontium. Although magnesium does not react with THAP, strontium precipitates readily in the presence of even the small amounts of magnesium and the determination of strontium will be in an error.
The reversibility of the colour reaction which is an essential condition for most of the colorimetric determinations is satisfied for the reactions studied in the present work. The mole ratio studies show the predominance of the complex with the empirical formula SrR. From the nature of the curves of the mole ratio studies the formation of SrR₂ is also indicated; the stability for SrR₂ may not be too different from that for SrR.

The molar absorptivity of strontium complex decreases in the presence of alkali halides. The separate experiments were carried out to test the validity of the Beer's law for strontium in the presence of the definite concentration of alkali halides; the plots of Beer's law were straight lines over a limited concentration of strontium and passed through the origin. When the concentration of alkali halide is known, it is possible to determine the concentration of strontium by using the appropriate value of the molar absorptivity.

6. REFERENCES.


8. Present work, p. 166.