The Spectrophotometric Determination of Fluorine with a PAC-Th Complex

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In the course of our studies of the thorium complex formed with ortho-substituted phenylazochromotropic acid, it was found that the thorium complex of PAC, [2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxy acetic acid],[1] can be used in the spectrophotometric determination of microgram quantities of fluoride ions, and that the sensitivity of the thorium complex towards fluoride ions was almost twice that of the thorium Neo-thorin complex.[2]

The principle of the determination of fluoride ions with the thorium complex was the same as the case of the thorium Neo-thorin complex; it was based on the bleaching effect of the fluoride ions on the thorium complex.

Figure 1 shows the absorption spectra of the reagent and its thorium complex. The color of the reagent is pink, while the thorium complex is a bluish violet.

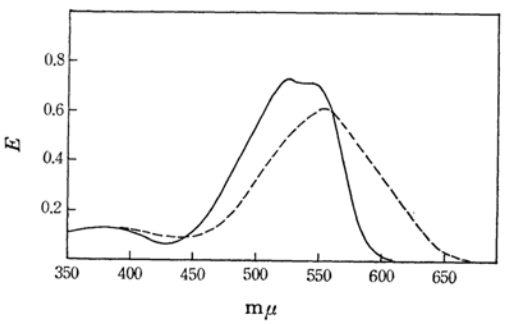

Fig. 1. Absorption spectra of the reagent and its thorium complex (broken line) at pH 2.7.
—— 2.0×10^{-5} M
---- Thorium concn. to the reagent concn. =0.68 : 1

Figure 2 shows the effect of pH on the absorbances of the thorum complex and the reagnet at 610 mμ. The absorbance of the thorium complex remains constant between the pH values of 2.5 and 4.0.

According to the mole ratio method, the thorium complex in the pH range was a 1 : 1 complex[1] formed completely by adding less than 0.75 mol. thorium to one mole of the reagent in the molar ratio cited. Therefore, the reagent used in the present experiment was composed of a 0.68 : 1 mixture of thorium and PAC (on the molar basis).

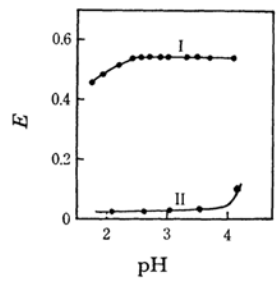

Fig. 2. Effect of pH on the absorbance of the thorium complex at 610 mμ.
I The thorium complex (the reagent concn.=4.0×10^{-5} M)
II The reagent

Figure 3 shows the calibration curve of fluoride ions: Five milliliters of the reagent (2×10^{-4} M), 0.3 ml. of the thorium nitrate solution (2.27×10^{-3} M), varying amounts (0—1.2 ml.) of the standard sodium fluoride solution (1.91×10^{-3} M) and 0.2 ml. of a 0.2 N perchloric acid solution were mixed in order to adjust the pH and then diluted to 25 ml. with distilled water. The absorbance was measured at 610 mμ in a 1 cm. cell against a water blank.

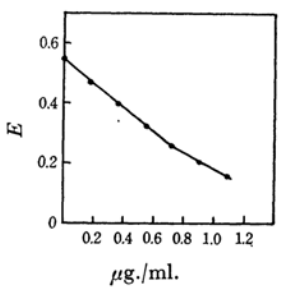

Fig. 3. Calibration curve of fluoride ion.

Beer's law is obeyed over the range from 0 to 0.6 μg. per ml. of fluoride ions.

Further, detailed studies are now in progress.

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1) K. Tōei, H. Miyata, T. Shibata and S. Miyamura, This Bulletin, **38**, 334 (1965).

2) K. Emi and T. Hayami, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **76**, 1291 (1955).