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Spectrophotometric Determination of Fluorine with the PAC-Th Complex

Yasuaki SHIMOISHI

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

and Tadashi HAYAMI

Liberal Arts and Science, Okayama University, Tsushima, Okayama

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The method of determining micro amounts of fluorine is based on the bleaching of the thorium complex of 2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid (PAC) by fluoride ions, which are strongly coordinated to the thorium in the complex and with thus liberate the free PAC. The complex is composed of thorium and PAC in a 1 : 1 molar ratio. PAC has an absorption maximum at 525 mμ, while the thorium complex shows a maximum at 555 mμ. The determination is based on the decrease in the absorbance at 610 mμ. Beer's law holds up to 30 μg fluoride ions per 25 m*l*. The optimum pH range is from 2.5 to 3.5. The apparent molar extinction coefficient is calculated to be 20000.

The reagent, PAC (2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid), was first prepared in our laboratory.1,2) It was found that the PAC-Th complex could be used in the spectrophotometric determination of micro amounts of fluoride ions. The proposed method is very sensitive; its sensitivity is higher than that of the Neothorin-Th complex method.3)

Experimental

Reagents. *3.00×10^{-4} M PAC Solution:* Dissolve 162.7 mg of PAC (disodium salt) in distilled water and dilute to 1 *l*.

2.38×10^{-2} M Standard Sodium Fluoride Solution: This solution was prepared by dissolving 100 mg of sodium fluoride in distilled water in a 100-m*l* volumetric flask and then storing the mixture in a polyethylene bottle. Working solutions of fluoride were then prepared by diluting the standard solution with distilled water.

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

2) K. Toei, T. Hayami, H. Miyata and Y. Shimoishi, *ibid.*, **39**, 638 (1966).

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

2.20×10^{-2} M Thorium Nitrate Solution: 12.1 g of reagent-grade thorium nitrate ($Th(NO_3)_4\cdot4H_2O$) were dissolved in distilled water and dilute to 1 *l*. The solution was standardized by the oxalate method.[4]

Perchloric Acid: 1 N and 0.2 N.

Apparatus. A Hitachi spectrophotometer, Model EPU-2A, and Hitachi recording spectrophotometer, Model EPS-2, were used for all the absorbance measurements, using 1-cm glass cells. A Toa Denpa glass electrode pH meter, Model HM-5A, was used for all the determinations.

All the experiments were carried out at 25°C.

Procedure. Place an aliquot containing not more than 30 μg of fluoride ions in a 25-m*l* volumetric flask. Add 5 m*l* of a PAC solution (3.00×10^{-4} M) and 0.5 m*l* of a thorium nitrate solution (2.20×10^{-3} M). Adjust the pH to between 2.5 and 3.5 with 0.2 N perchloric acid, and dilute to the mark with distilled water. Measure the absorbance at 610 mμ against water.

Results and Discussion

Absorption Spectra. The absorption spectra of PAC and the thorium complex are shown in Fig. 1. The absorption maximum of the reagent is at 525 mμ, and that of the PAC-Th complex, at 555 mμ.

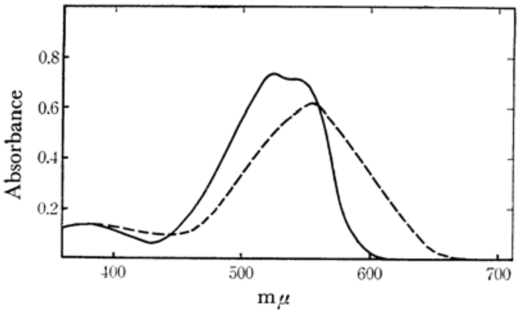

Fig. 1. Absorption spectra of the reagent (full line) and thorium complex (broken line) at pH 2.7.
5 m*l* of 2.0×10^{-4} M PAC soln. in 50 m*l*
5 m*l* of 2.0×10^{-4} M PAC soln. and 0.3 m*l* of 2.2×10^{-3} M $Th(NO_3)_4$ soln. in 50 m*l*

Effect of pH. Figure 2 shows the effect of the pH on the absorbances of PAC and PAC-Th at 600, 605, 610, 615, and 620 mμ. The decreasing order of the difference of the absorbances between PAC and PAC-Th (ΔAbs) is as follows:

$$\Delta\mathrm{Abs}_{(600)}>\Delta\mathrm{Abs}_{(605)}>\Delta\mathrm{Abs}_{(610)}>\Delta\mathrm{Abs}_{(615)}<\Delta\mathrm{Abs}_{(620)}$$

On the contrary, the effect of the pH change on the ΔAbs increases with wavelength. The most favorite wavelength for the measurement is 610 mμ, which gives a comparatively large and constant ΔAbs value over the pH range between 2.5 and 3.5.

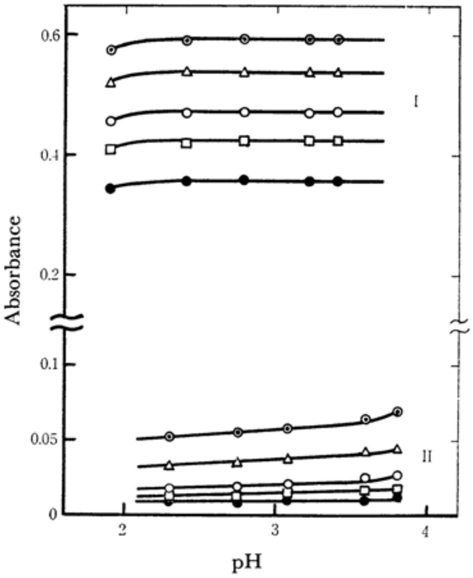

Fig. 2. The effect of pH on the absorbances of the reagent and the thorium complex.
I, The thorium complex (thorium concn. to the reagent concn. = 0.73 : 1)
II, The reagent (3.0×10^{-5} M) at ⊙ 600 mμ, △ 605 mμ, ○ 610 mμ, □ 615 mμ, ● 620 mμ

Mole-ratio Method. Figure 3 shows that the mole ratio of thorium to PAC is 1 : 1, and that the complex is slightly dissociated at that point. To determine fluoride ions by use of the PAC-Th complex, the amount of the thorium should be less than that of PAC.

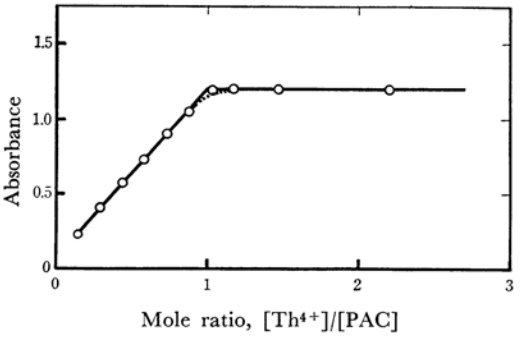

Fig. 3. Mole ratio method.
The reagent: 6.0×10^{-5} M, pH 2.7 at 610 mμ

From Fig. 3, it can be seen that the complex formation is virtually completed when less than 0.75 mol of thorium is added to 1 mol of PAC. Therefore, the colorimetric reagent for fluoride used in this experiment was composed of a 0.73 : 1 mixture of thorium and PAC (on the molar basis). The molar extinction coefficient of the complex was calculated to be about 20000 at 610 mμ.

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[4] W. W. Scott, "Standard Methods of Chemical Analysis," D. van Nostrand Co., Inc., New York, N. Y. (1939), p. 593.

Calibration Curve. The calibration curve (Fig. 4) follows Beer's law up to 30 μg of fluoride ions.

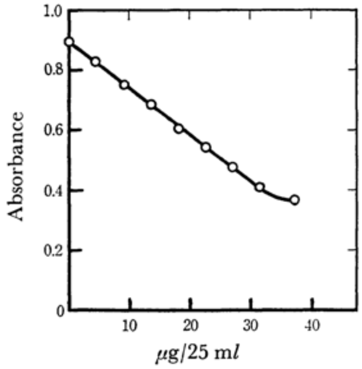

Fig. 4. Calibration curve of fluoride ion (at 610 mμ).

Stability of the Color. The color development between thorium and PAC occurs instantaneously at room temperature. The color intensity of the solution remains constant for at least 1.5 hr at pH 2.7.

Effects of Diverse Ions. The effects of diverse ions are summarized in Table 1. 13.6 μg of fluoride ions were added to aqueous solutions containing diverse ions. Chloride and nitrate ions did not interfere under the described conditions. Aluminum and iron(III) gave negative errors. Sulfate, posphate, aluminum and iron(III) interfere seriously, however, even when present in trace amounts.

TABLE 1. THE EFFECT OF DIVERSE IONS (13.6 μg F^-, 610 mμ, pH 2.7)

Ions	Added as	Amounts of ions added μg/25 ml	Absorbance
None			0.699
			0.686
Cl^-	NaCl	10000	0.678
SO_4^{2-}	Na_2SO_4	30	0.693
PO_4^{3-}	Na_2HPO_4	7.5	0.674
Ca^{2+}	$CaCl_2$	600	0.674
Mg^{2+}	$Mg(NO_3)_2$	250	0.676
Al^{3+}	$Al(NO_3)_3$	2.5	0.728
Fe^{3+}	$FeCl_3$	5	0.712

Reproducibility after Steam Distillation.[2,5] In order to check the recovery of the steam distillation of fluoride from a sulfuric acid medium in the presence of silica, the absorbance decrease with a known amount of fluoride added was measured. The recovery is quantitative; the average error is 2 per cent with 22.6 μg of fluoride.

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5) A. D. Horton, P. F. Thomason and F. T. Miller, *Anal. Chem.*, **25**, 548 (1952).