Analytical Applications of Semixylenol Purple : A Sensitive Photometric Reagent for Thorium

Analytical Applications of Semixylenol Purple : A Sensitive Photometric Reagent for Thorium

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Summary

A reagent of the sulfophthalein nitrilodiacetate type, Semixylenol Purple (SXP), was synthesized, purified, and applied to the spectrophotometric determination of thorium. SXP reacts with thorium to form a water-soluble reddish-violet complex. The optimum pH range for the color development is 2.8-3.6 and the maximum absorption of the colored solution lies at 541-545 nm. Beer's law is held up to 2.0 $\mu g\ cm^{-3}$ of thorium. The sensitivity of the determination and the molar absorptivity of the complex are 3.5×10^{-3} $\mu g\ cm^{-2}$ of thorium for 0.001 of absorbance and 6.61×10^4, respectively. As a result of the investigation of the composition of the complex by the continuous variation method, the mole ratio of thorium and SXP was estimated to be 1 : 1. The recommended procedure for the determination of thorium is as follows.

A sample solution containing up to 50 μg of thorium is taken into a 25 cm^3 of volumetric flask. Then, 3 cm^3 of 0.05% SXP solution and 10 cm^3 of 0.1 mol dm^{-3} glycine-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} hydrochloric acid buffer solution are added. After making up the volume to 25 cm^3 (the final pH : 3.0), the absorbance is measured at 544 nm against reagent blank as a reference.

Among the seventeen diverse ions examined, aluminum, lead, zinc, yttrium, iron(III), cobalt, and nickel interfere with the determination, but the effect of iron(III) could be eliminated by the addition of ascorbic acid.

SXP also reacts with some other ions than thorium to form water-soluble stable complexes. So, it seems that it is possible to use this reagent for the spectrophotometric determinations of these ions.

Introduction

Up until now, a lot of organic compounds have been proposed as the indicators for the complexometric titrations and as the spectrophotometric reagents for the determination of metals. In those compounds, the sulfophthalein derivatives are the most useful ones, and Xylenol Orange, Methylxylenol Blue, and Methylthymol Blue, the representative compounds of the derivatives, have been widely used for these purposes, because they can form complexes

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with metal ions which exhibit sharp color transitions and high molar extinction coefficients. As a part of the investigation of the methods for the photometric determinations of metal ions with sulfophthalein derivatives, the author newly synthesized Semixylenol Purple, 3-[N-(carboxymethyl)methylaminomethyl]-*m*-cresolsulfophthalein, from Metacresol Purple and iminodiacetic acid by the Mannich condensation,[1] purified it by cellulose column, and examined the color reaction with thorium. It was found that Semixylenol Purple (SXP) is a suitable spectrophotometric reagent for this ion in respect to sensitivity and can be applied to the determination up to 2.0 μg cm^{-3} of thorium. Comparing the sensitivity of the present method for thorium with ones of other methods which use reagents with structures similar to that of SXP, SXP is less sensitive than Xylenol Orange,[2] but more sensitive than Methylthymol Blue[2] and Semimethylxylenol Blue.[3] Further, SXP is more sensitive than Thorin,[4] Neo-Thorin,[5,6] Chlorphosphonazo III,[7,8] Chromazurol S,[9] Eriochrome Black T,[10] Carboxyarsenazo,[11] Quercetin,[12] Quercetinsulfonic acid,[13] Flavonol-2'-sulfonic acid,[14] Tropolone-sulfonic acid,[15] 4-(2-thiazolylazo)-resorcinol,[16] Bromopyrogallol Red,[17] Dibromoarsenazo II,[18] sodium 4, 5-dihydroxy-3-(4-sulphophenylazo)naphthalene-2,7-disulphonate,[19] and phenylthiazolylazo-chromotropic acid,[20] however, it is less sensitive than Arsenazo III[21-23] and Chromazurol S and cetyltrimethylammonium chloride.[24,25] It was also found that SXP reacts with some other ions than thorium such as beryllium, aluminum, gallium, indium, lead, copper, zinc, cadmium, scandium, yttrium, lanthanum, cerium, samarium, zirconium, vanadium(V), manganese(II), cobalt, nickel, and palladium to form water-soluble stable complexes. In every case, the color developments occurred instantaneously at room temperature and it seems that these colorations are available to the spectrophotometric determinations of these metal ions.

This paper describes the fundamental conditions for the spectrophotometric determination of thorium with SXP and the color reactions of SXP with some metal ions.

Reagents and Apparatus

A solution containing about 1 mg cm^{-3} of thorium was prepared by dissolving guaranteed reagent grade thorium nitrate in a small amount of nitric acid and diluting with distilled water. The solution was standardized by the complexometric titration using Xylenol Orange as an indicator. This solution was diluted as required. A 0.05% SXP solution was prepared by dissolving in distilled water a weighed amount of SXP. The SXP was synthesized by the Mannich condensation.[1] One gram (2.6×10^{-3} mol) of Metacresol Purple, 2.6×10^{-3} mol of iminodiacetic acid, and 0.6 g of sodium hydroxide were dissolved in 50 cm^3 of distilled water at 50°C. After the water was distilled off, the mixture was dissolved in 40 cm^3 glacial acetic acid followed by adding 1 cm^3 of 37% formaldehyde and was kept at 50°C for 2 hrs. with stirring. The solvent was, then, distilled off under reduced pressure. The SXP was separated from the reaction mixture on a cellulose column by 1-butanol saturated with 10% acetic acid, which was one of the most suitable eluents among examined ones to separate the SXP from other materials. The SXP obtained was passed through a column of strongly acidic ion-exchange resin, Duolite C-20, to make it the free acid form, and finally, the free acid form of SXP was again chromatographed to remove iminodiacetic acid completely using 1-butanol saturated with 10% acetic acid as the eluent. The SXP obtained as the orange compound had m.p. 191-200°C (decomp.). The purity of this compound was checked by the paper chromatography, and only one spot was observed. The result of the elemental analysis was as follows. Found : C, 56.29% ; H, 4.41% ; N, 2.36%. Calcd for $C_{26}H_{25}O_9NS \cdot 2H_2O$: C, 59.20% ; H, 4.78% ; N, 2.66%. The absorption spectra of this reagent by measuring 8 μg cm^{-3} SXP solution in various pH are shown in Fig. 1. The SXP solution colors orange at pH 1. The color of the solution changes to yellow with increase in pH, but, over the pH range from about 2 to 6, there is no color change and the solutions show the almost same absorption curves which have an absorption maximum at 438-441 nm. By further increase of pH value, however, the color of the solution changes again, and it becomes yellow-green at pH 7.0, and violet at pH 8-12. According to these color changes, the absorption maximum of 438-441 nm decreases, accompanied with the increase of that of 577-581 nm. 0.01 mol dm^{-3} cetyltrimethylammonium chloride (CTMAC) solution was prepared by dissolving in 20% ethanol a weighed amount of the reagent (Nakarai Chemicals). For the pH adjustment, 1 mol dm^{-3} hydrochloric acid-1 mol dm^{-3} sodium acetate and 0.1 mol dm^{-3} hydrochloric acid-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} glycine buffer solutions were used. All the other reagents used were of guaranteed reagent grade. For the absorbance and the pH measurements, a Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells and a Hitachi-Horiba model M-5 glass electrode pH meter were used, respectively.

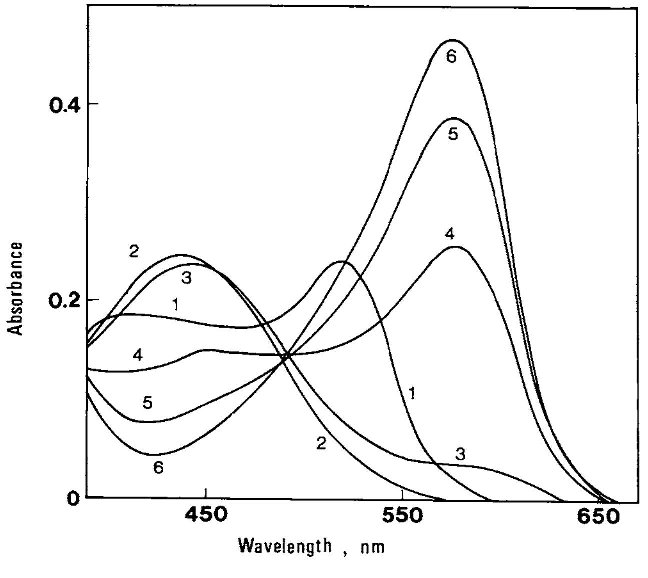

Fig. 1. Absorption spectra of SXP in a 25 cm^3 aqueous solution containing 1 cm^3 of 0.02% SXP solution at pH 1.0 (1), pH 2.0 (2), pH 7.0 (3), pH 8.2 (4), pH 9.0 (5), or pH 12.0 (6). The absorbances were measured against water as a reference.

Results and Discussion

Absorption Curves of Thorium Complex: The absorption spectra of the thorium complex were measured. A solution containing 20 μg of thorium and 3 cm^3 of 0.05% SXP were taken into a 25 cm^3 volumetric flask. Then, 10 cm^3 of 0.1 mol dm^{-3} glycine-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} hydrochloric acid buffer solution were added for pH adjustment and the volume was made to 25 cm^3 with water. The absorption spectrum of the colored solution was measured against the reagent blank as a reference. The results obtained at various pH are shown in Fig. 2. The colored solution of the thorium complex has an absorption maximum at 541-545 nm. This maximum wavelength does not shift with the change of the pH of the solution over the range from pH 2.0-4.0 and the shapes of the absorption curves also do not change over this pH range. So, in this experiment, the wavelength of 544 nm is used for the measurements of absorbances.

Optimum Conditions for Color Development: The effect of pH on the color development of the complex was examined at 544 nm by measuring the absorbance of colored solution containing 20 μg of thorium and 3 cm^3 of 0.05% SXP at different pH values from 2.0-4.0. The results obtained are shown in Fig. 3. The range in which the maximum and nearly constant absorbance is obtained are pH 2.8-3.6. So, the pH of the solution was adjusted at 3.0 for the color development in further experiments. The necessary amount of the reagent for the complete color development was studied with the solutions containing 20 μg of thorium and various amounts of 0.05% SXP solution. The absorbances were measured at 544 nm. As the results are shown in Fig. 4, the maximum and almost constant absorbances were obtained by adding from 2-5 cm^3 of SXP solution. The effect of the amount of 0.1 mol dm^{-3} glycine-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} hydrochloric acid buffer solution on the thorium

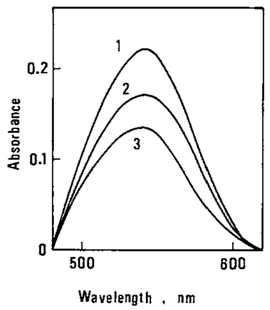

Fig. 2. Absorption spectra of thorium-SXP complex in a 25 cm^3 aqueous solution containing 20 μg of thorium and 3 cm^3 of 0.05% SXP solution at pH 3.0 (1), pH 4.0 (2), or pH 2.4 (3). The absorbances were measured against reagent blanks as references.

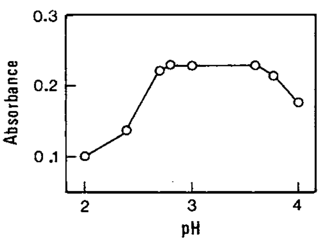

Fig. 3. Effect of pH on the absorbance of thorium-SXP complex examined with a 25 cm^3 solution containing 20 μg of thorium and 3 cm^3 of 0.05% SXP solution. The absorbances were measured at 544 nm against reagent blanks as references.

complex was examined. The absorbance of the colored solution was measured by varying the amounts of the buffer solution, but keeping the pH of the solution constant. The results indicated that the addition from 2 to 15 cm^3 of the buffer solution had no effect on the color intensity of the thorium complex (Fig. 5). The color development for the thorium complex occurs instantaneously at room temperature, and its intensity was not affected with heating in 30-90°C water bath for at least 15 minutes. The color, once developed, was very stable, and the absorbance remained almost constant for at least three hours. On the complex formations of the sulfophthalein derivatives with metal ions, it has been well known that the presence of the cationic surface active agents makes the molar absorptivities of the complexes higher than the case of the absence of it. So, in this experiment, the effect of the addition of the cationic surface active agent, CTMAC, was studied. However, no increase of the absorbance of the complex was recognized by the addition of the CTMAC. The relationship between the absorbance of the thorium complex and the concentration of thorium was examined by being colored various amounts of thorium with 3 cm^3 of 0.05% SXP solution at pH 3.0 and by measuring the absorbances at the wavelength of 544 nm. The calibration curve for thorium obtained are shown in Fig. 6. Beer's law is obeyed up to 2.0 $\mu g\ cm^{-3}$ of thorium. The molar absorptivity of the complex calculated from the curve and the sensitivity of the determination are 6.61×10^4 and 3.5×10^{-3} $\mu g\ cm^{-2}$ of thorium for $\log(I_0/I)=0.001$, respectively. When the sensitivity of this method is compared with those of other reagents, SXP is lower than that of Xylenol Orange,[2] Chromazurol S and cetyltrimethylammonium chloride,[24,25] or Arsenazo III[21-23] which is representative spectrophotometric reagent for thorium, but SXP is more sensitive than many other reagents.[2-20] The reproducibility of this method, expressed by the relative standard deviation of the absorbances which were obtained from five repeat determinations, was 2.8%. The composition of the thorium-SXP complex was examined at pH 3.0 by the continuous variation method, measuring the absorbance at the wavelength of 544 nm. In this experiment, the total mole of thorium and SXP was held at 2.2×10^{-5} mol dm^{-3}. As the

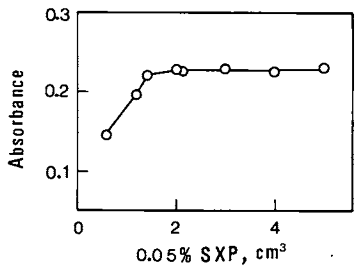

Fig. 4. Effect of SXP concentration on the absorbance of thorium-SXP complex examined with a 25 cm^3 solution containing 20 μg of thorium at pH 3.0. The absorbances were measured at 544 nm against reagent blanks as references.

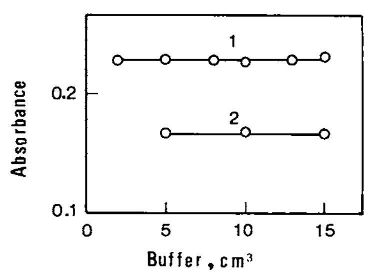

Fig. 5. Effect of the amount of buffer solution on the absorbance of thorium-SXP complex examined with a 25 cm^3 solution containing 20 μg of thorium and 3 cm^3 of 0.05% SXP solution at pH 3.0. The absorbances were measured at 544 nm (1) and 570 nm (2) against reagent blanks as references.

result is shown in Fig. 7, the maximum point of the absorbance in the continuous variation method indicated that the mole ratio between thorium and SXP is 1 : 1.

Recommended Procedure for Thorium Determination : Based on the results obtained from above experiments, the following method is recommended for the spectrophotometric determination of thorium with SXP.

A sample solution containing up to 50 μg of thorium is taken into a 25 cm^3 volumetric flask. Then, 3 cm^3 of 0.05% SXP solution and 10 cm^3 of 0.1 mol dm^{-3} glycine-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} hydrochloric acid buffer solution are added. After making up the volume to 25 cm^3 (the final pH : 3.0), the absorbance is measured at 544 nm against reagent blank as a reference.

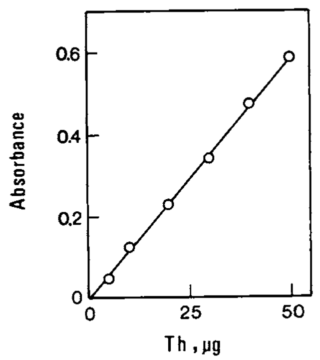

Fig. 6. Calibration curve of thorium in a 25 cm^3 aqueous solution containing 3 cm^3 of 0.05% of SXP solution at pH 3.0. The absorbances of the thorium-SXP complex were measured at 544 nm against reagent blanks as references.

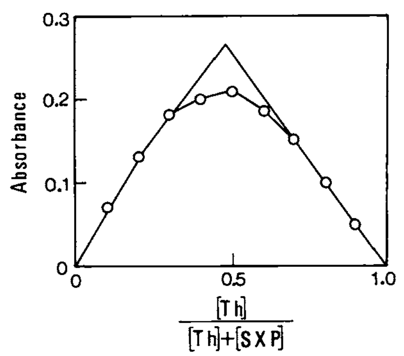

Fig. 7. The continuous variation method examined with solutions in which the total mole of thorium and SXP was held at 2.2×10^{-5} mol dm^{-3} at pH 3.0. The absorbances were measured at 544 nm against reagent blanks as references.

Interferences : The effect of seventeen diverse ions on the determination of 20 μg of thorium has been examined by measuring the absorbance at 544 nm. The results obtained are summarized in Table 1. Thorium can be determined within 5% errors in the presence of 1 mg each of potassium, magnesium, calcium, strontium, barium, cadmium, chromium(III), chromium(VI), and manganese(II) and 100 μg of copper. Aluminum, lead, zinc, yttrium, iron(III), cobalt, and nickel interfere with the determination, but the effect of iron(III) could be eliminated by the addition of ascorbic acid.

Reactions of SXP with Some Other Ions : The color reaction between SXP and some other ions than thorium were investigated. The metal ions which gave colors are summarized in Table 2. A lot of ions react with SXP and give water-soluble colored complexes. In every case, the color developments occurred instantaneously at room temperature and the complexes formed were stable. At pH 3.0, scandium forms a red complex with SXP which has an

Table 1. Effect of diverse ions on the determination of thorium

Ion	Amount added (μg)	Thorium found (μg)	Ion	Amount added (μg)	Thorium found (μg)
K^+	1000	20.0	Cu^{2+}	100	20.9
Mg^{2+}	1000	20.2	Ni^{2+}	20	24.9
Ca^{2+}	1000	20.3	Al^{3+}	20	25.2
Sr^{2+}	1000	19.9	Pb^{2+}	20	23.5
Ba^{2+}	1000	19.8	Zn^{2+}	20	21.5
Cd^{2+}	1000	20.8	Y^{3+}	20	22.2
Cr(VI)	1000	20.8	Fe^{3+}	20	27.6
Cr^{3+}	1000	20.7	〃 a)	1000	20.1
Mn^{2+}	1000	20.1	Co^{2+}	20	23.0

Twenty micrograms of thorium was taken.
a) One cm^3 of 5% ascorbic acid solution was added.

Table 2. Reactions of SXP with metal ions

Ion	pH	Color of Complex
Be^{2+}	6-8	Orange-red
Al^{3+}	2-4	Reddish-pink
Ga^{3+}	1-3	Reddish-pink
In^{3+}	5-8	Orange-red
Pb^{2+}	6-10	Reddish-violet
Cu^{2+}	6-8	Reddish-violet
Zn^{2+}	6-8	Reddish-yellow
Cd^{2+}	8-10	Reddish-violet
Sc^{3+}	2-4	Red
Y^{3+}	8-10	Reddish-violet
La^{3+}	6-8	Orange-red
Ce^{3+}	8-9	Reddish-violet
Sm^{3+}	8-10	Violet
Zr^{4+}	1-3	Reddish-pink
V(V)	2-5	Orange-red
Mn^{2+}	6-8	Reddish-violet
Co^{2+}	6-8	Orange-red
Ni^{2+}	6-8	Orange-red
Pd^{2+}	2-3	Pink

absorption maximum at 536-538 nm. Zinc and lanthanum also react with SXP at pH 3.0 to form reddish-yellow complexes which have absorption maxima at 445-449 nm and 440-442 nm, respectively. At pH 9.5, samarium forms a violet complex showing an absorption maximum at 617-619 nm. Concerning other elements, aluminum, gallium, zirconium, and vanadium(V) form reddish complexes in acidic solution and beryllium, indium, lead, copper, cadmium, yttrium, cerium, manganese(II), cobalt, nickel, and palladium form reddish-violet complexes in neutral or alkali solution. These complexes may probably be utilized for the spectrophotometric determination of these metal ions.

Conclusions

From this study, SXP is recommended as a spectrophotometric reagent for thorium, because of its excellent complex formation ability. The method proposed here has a high sensitivity and a good precision. The molar absorptivity of the complex and the reproducibility of this method, expressed by the relative standard deviation of the absorbances which were obtained from five repeat determinations, were 6.61×10^4 and 2.8%, respectively. The optimum concentration range for the determination is 0.2-2.0 $\mu g\ cm^{-3}$ of thorium. From the investigation of the coloration of SXP with various metal ions, it seems that this reagent is also available for the spectrophotometric determinations of some other ions than thorium.

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