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Color Reaction among Pyrogallol Red, Thorium(IV) and Samarium(III), and Its Application to the Determination of These Metals

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Synopsis. The color reactions between Pyrogallol Red(PR) and thorium(IV), and also those among PR, thorium(IV) and samarium(III) were studied. Simple and sensitive spectrophotometric determinations of these ions were newly carried out in the range for 1—22 μg/10 cm^3 of thorium (IV) and 0.5—10 μg/10 cm^3 of samarium(III) at 635 nm by using the PR-Th-Sm ternary complex.

Although Pyrogallol Red(PR) has already been used for chelatometric titration and spectrophotometric determination of various metal ions,[1—5] the studies on the color reactions between PR and thorium(IV) or PR and rare earth elements such as samarium(III), lanthanum(III), etc. were comparatively few. We have found that the color reaction between PR and thorium(IV) or PR and samarium(III) was catalyzed by the coexistence of small amounts of samarium(III) or thorium(IV), respectively, and that the color was caused by a ternary complex system.

In this paper, the color reaction among PR, thorium(IV) and samarium(III) in the presence of a nonionic surfactant was studied, and the spectrophotometric determination of these ions using the PR-Th-Sm ternary complex was proposed.

Experimental

Apparatus and Reagents. Spectrophotometric determination was done on Shimadzu model UV-240 and 260 recording spectrophotometers with 1.0-cm fused quartz cells. The Hitachi-Horiba M-5 and F-7AD glass electrode pH meters were used for the pH measurements.

A 1.0×10^{-3} mol dm^{-3} solution of PR was prepared by dissolving PR (Tokyo Kasei Kogyo Co., Ltd.) in methanol. A stock solution (1.0×10^{-2} mol dm^{-3}) of thorium(IV) was prepared by dissolving of thorium nitrate in water. A stock solution (1.0×10^{-2} mol dm^{-3}) of samarium(III) was prepared by dissolving 360 mg of Sm_2O_3 in 3 cm^3 of concd. hydrochloric acid, and it was diluted to 100 cm^3 with water. The concentrations of the stock solutions of thorium(IV) and samarium(III) were determined by chelatometric titration,[4] and then the working solutions (5.0×10^{-4} mol dm^{-3}) were prepared by dilution of these stock solutions. A 1.0% of poly(vinyl alcohol) (PVA) solution was prepared by dissolving PVA (n=2000) in water. A 2.0×10^{-1} mol dm^{-3} sodium acetate-acetic acid buffer solution (Walpole buffer) was used for the pH adjustment. All the other reagents and materials were of analytical grade. Doubly-distilled water was used.

Determination of Thorium(IV): To a solution containing 1—22 μg thorium(IV) in a 10 cm^3 volumetric flask were added 2.0 cm^3 of a Walpole buffer solution (pH 4.5), 2.0 cm^3 of a 1.0% PVA solution, 1.0 cm^3 of a 1.0×10^{-4} mol dm^{-3} samarium(III) solution, and 1.5 cm^3 of 1.0×10^{-3} mol dm^{-3} PR solution. The mixture was diluted to 10 cm^3 with water, and the solution was kept at 60 °C for 30 min. After the mixture was cooled in water for 10 min, the absorbance of the PR-Sm-Th solution (Solution D) was measured at 635 nm against the PR-Sm solution (Solution C).

Determination of Samarium(III): A solution containing 0.5—10 μg samarium(III) was placed in a 10 cm^3 volumetric flask. To this solution 2.0 cm^3 of 1.0% PVA and buffer solutions, 1.0 cm^3 of a 5.0×10^{-4} mol dm^{-3} thorium(IV) solution, and 1.5 cm^3 of 1.0×10^{-3} mol dm^{-3} PR solution were added. The mixture was diluted to the mark with water, and heated at 60 °C for 30 min. After the mixture was cooled in water for 10 min, the absorbance of Solution D was measured at 635 nm against the PR-Th solution (Solution B).

Results and Discussion

Figure 1 shows the absorption spectra of PR solution (Solution A), PR-Th solution (Solution B), PR-Sm solution (Solution C) and PR-Th-Sm complex solution (Solution D) in the presence of PVA, respectively. Solution D gave a larger absorbance

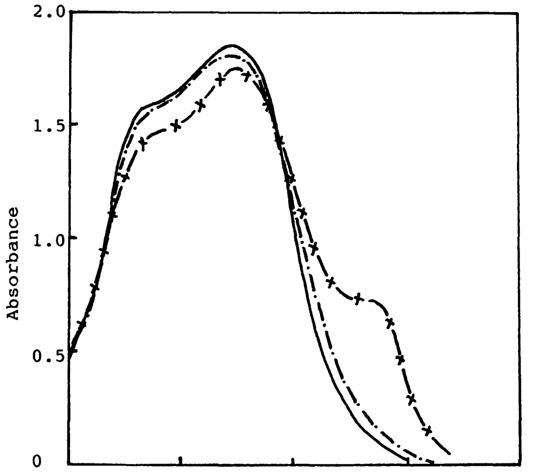

Fig. 1. Absorption spectra of PR-Th-Sm solution, PR-Th solution, PR-Sm solution and PR solution at pH 4.5 in the presence of PVA.

Thorium(IV): 5.0×10^{-6} mol dm^{-3}; Samarium(III): 1.0×10^{-5} mol dm^{-3}; PR: 1.5×10^{-4} mol dm^{-3}; PVA: 2.0 cm^3 of 1.0% PVA solution/10 cm^3; Reference: water.

—×—: PR-Th-Sm solution=Solution D, ----: PR-Th solution=Solution B, ——: PR-Sm solution=Solution C and PR solution=Solution A.

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Table 1. Effects of Some Surfactants

Surfactants		Absorbance at	max λ nm
PVA,	Poly(vinyl alcohol)		
(2000)		0.470	635
(500)		0.450	635
PVP,	Poly(*N*-vinyl-2-pyrrolidone)	0.328	620
Tween 20	Poly(oxyethylene) sorbitan monolaurate	0.338	620
HTAC,	Hexadecyltrimethylammonium chloride	0.126	630
SDS	Sodium dodecyl sulfate	0.272	625

PR, 1.5×10^{-4} mol dm^{-3}; Thorium(IV), 5.0×10^{-6} mol dm^{-3}; Samarium(III), 1.0×10^{-5} mol dm^{-3}; Surfactant, 2.0 cm^3 of 1.0% surfactant/10 cm^3; pH 4.5; Reference, PR-Sm solution=Solution C

Table 2. Effects of Foreign Ions for the Determination of Thorium(IV)

Foreign ion	Added as	Added µg/ 10 cm^3	Absorbance at 635 nm	Tolerance molar ratio*
—	—	—	0.470	—
Bi(III)	Nitrate	0.03	0.369	1/400
Zr(IV)	Nitrate	68.4	0.694	5
Sn(IV)	Sulfate	0.4	0.400	1/100
Al(III)	Nitrate	1.4	0.533	1/20
Fe(III)	Sulfate	0.6	0.519	1/10
Ni(II)	Nitrate	596.9	0.430	50
Cu(II)	Nitrate	47.7	0.693	10
Cd(II)	Nitrate	112.4	0.503	10
Zn(II)	Nitrate	16.3	0.512	20
Co(II)	Nitrate	294.7	0.500	10
Mg(II)	Nitrate	243.1	0.470	300
Tartrate	Acid	370.2	0.398	25
Citrate	Acid	9.5	0.402	1/2
Oxalate	Sodium	7.1	0.402	1
Sulfite	Sodium	9.6	0.491	10
Sulfide	Sodium	15.0	0.355	10
TEA	—	4.9	0.470	1
NTA	Sodium	225.0	0.405	10

Thorium(IV) taken, 11.6 µg/10 cm^3; PR, 1.5×10^{-4} mol dm^{-3}; Samarium(III), 1.0×10^{-5} mol dm^{-3}: pH, 4.5; PVA, 2.0 cm^3 of 1.0% PVA solution/10 cm^3; Reference, PR-Sm solution=Solution C

* foreign ion/thorium(IV)

and was more stable than Solution B or C, and its absorbance was proportional to the concentration of thorium(IV) or samarium(III). The similar phenomena were observed in this reaction system, when rare earth elements such as lanthanum(III) were used instead of samarium(III), and hafnium(IV) or zirconium(IV) instead of thorium(IV).

The effect of pH on the reaction systems was examined. The maximum and constant absorbance was obtained in the pH range of 4.2 to 5.2 with 2.0 cm^3 of 2.0×10^{-1} mol dm^{-3} buffer solution. The reproducibilities of color development of Solutions B, C, and D without a surfactant were poor. As a dispersion agent, PVA was the most effective one among nonionic surfactants and these solutions gave the stable and the highest sensitivity as shown in Table 1.

The use of samarium(III) among the various rare earth elements tested-lanthanum(III), cerium(III), praseodymium(III), gadolinium(III), dysprosium(III), etc. was the most effective in terms of sensitivity.

The maximum and almost constant absorbance was obtained by using of 0.8—1.4×10^{-5} mol dm^{-3} samarium(III) for the determination of thorium(IV), and 3.75—7.5×10^{-5} mol dm^{-3} thorium(IV) solution for the determination of samarium(III) in the final concentration, respectively. The recommended volume of PR was 1.5 cm^3 of a 1.0×10^{-3} mol dm^{-3} solution in the final 10 cm^3.

Consequently, all further work was carried out with 1.0×10^{-5} mol dm^{-3} samarium(III) and 1.5×10^{-4} mol dm^{-3} PR solution for thorium(IV), and 1.5×10^{-4} mol dm^{-3} PR and 5.0×10^{-5} mol dm^{-3} thorium(IV) in the final concentration for the determination of samarium(III), respectively. A nearly constant absorbance of Solution D against Solution B or C was obtained after aging for 5 h at room temperature, or after 30 min at 60 °C. The absorbance was almost constant for at least 32 h at room temperature.

The calibration curves covered the range of 1—22 µg/10 cm^3 thorium(IV) and 0.5—10 µg/10 cm^3 samarium(III). The sensitivities of Sandell's scale were 0.0028 µg cm^{-2} for thorium(IV) and 0.0015 µg cm^{-2} for samarium(III), and the apparent molar absorption coefficients were 8.2×10^4 dm^3 mol^{-1} cm^{-1} for thorium(IV) and 1.0×10^5 dm^3 mol^{-1} cm^{-1} for samarium(III), respectively. The reproducibilities for thorium(IV)(11.6 µg) and samarium(III)(5 µg) were 1.4% and 1.5% (8 experiments).

The effects of foreign ions on the determination of thorium(IV) and samarium(III) were examined. The coexistence of sulfate, chloride, nitrate, nitrite, nickel(II), magnesium(II), calcium(II), etc. did not interfere in 100—200 fold mole excess over thorium(IV) or samarium(III), and thiosulfate, sulfite, triethanolamine(TEA), L-ascorbic acid, copper(II), iron(III), zinc(II), cadmium(II), etc. in 2—10 fold mole excess over thorium(IV) or samarium(III). The tolerance limits were taken as the amount causing 2% error in the absorbance. Meanwhile, the coexistence of bismuth(III), tin(IV), etc. seriously interfered, and these interfering ions must be separated by suitable procedures. Interference by copper(II), iron(III) or zinc(II) can be prevented by addition of a sodium thiosulfate, TEA or L-ascorbic acid solution. The results for the determination of thorium(IV) are shown in Table 2.

The molar ratios of thorium(IV) to PR in the presence of large amounts of samarium(III), and those of samarium(III) to PR in the presence of thorium(IV) were estimated by the molar-ratio and continuous-variation methods, and these molar ratios were found to be 1:2. On the other hand, the molar ratio of thorium(IV) to PR in the absence of samarium(III) was 2:3. Although further investigation is necessary, the coloring formed among PR, thorium(IV) and samarium(III) in the presence of PVA as a nonionic surfactant may be regarded as the ternary complex system.

In conclusion, the color reactions among PR, thorium(IV) and samarium(III) in the presence of PVA as a nonionic surfactant were discussed. The ternary complex system, PR–Th-rare earth elements such as samarium(III), was more stable and gave higher absorbance than the PR–Th system or PR–Sm system (Slution C)(=PR solution). Thus, simple, rapid and sensitive spectrophotometric determinations for thorium(IV) and samarium(III) by using the ternary complex (thorium(IV) 1:samarium(III) 1:PR 2) were established. The present method was 2—10 fold more sensitive than other methods[1–9] utilizing xanthene dyes (for example, Xylenol Orange(XO), Methylthymol Blue(MTB), PR) alone, and it was simple and rapid.

Although further investigation is necessary, the color reaction among various xanthene dyes (for example, gallein, XO, MTB, etc.), thorium(IV) and rare earth elements such as samarium(III) may be used as a new color reaction system in analytical chemistry like the reactions reported previously[10].

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