Spectrophotometric Determination of Cerium(III) and Some Rare Earths with Xylenol Orange[1)]

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(Received July 9, 1962)

Since xylenol orange was first prepared by Körbl and others[2,3)] as a metallochromic indicator of the "complexone type", this reagent has widely been used by a number of investigators in complexometric titrations. However, only a few workers have applied this reagent to the spectrophotometric determination of metals; zirconium, hafnium, iron and bismuth have been thus determined by Cheng[4-8)], and recently bitsmuth, by Onishi and Ishiwatari[9)].

The present investigation was undertaken to evaluate the applicability of xylenol orange as a spectrophotometric reagent for various metal cations. From the results, a new spectrophotometric method for the determination of cerium(III) and of some rare earth elements is proposed. As in the other cases[4-9)], the molar ratio of the complex between rare earth and this reagent is also 1:1.

Experimental

Reagents. — Stock solutions of rare earths were prepared separately by dissolving the purified oxide of rare earths (cerium, lanthanum, neodymium and yttrium) and were standardized by EDTA titration, using xylenol orange as an indicator[10)].

About 10^{-3} M of a xylenol orange solution was prepared by dissolving Dotite XO reagent Dôjindô) & Co., Kumamoto) in distilled water. According to Ueno[11)], this solution is stable for several months.

Apparatus. — All the absorption measurements were made with a Hitachi model EPU-2A spectrophotometer, using 1 cm. cells.

Procedure. — From 0 to 100 μg. of one of the rare earths was transferred to a 25 ml. volumetric flask. (When cerium was to be determined, 1 ml. of a 0.5% solution of ascorbic acid was added to prevent oxidation of the cerium(III) to the ceric state). Three to four milliliters of a xylenol orange solution and 15 ml. of an acetate buffer solution (pH 6.1 ± 0.1, 0.17 M as acetate ions) were then added. After the mixture had been diluted to the mark with water and mixed, the absorbance of the solution was measured at the wavelengths mentioned below.

Results and Discussion

Absorption Spectra. — Figure 1 shows the absorption spectra of xylenol orange and its cerium complex at a pH of 6.1. Both the reagent and the complex have an absorption maximum at about 580 mμ. When a correction for the reagent blank is applied, an absorption peak of the complex is found at 575 mμ. A wavelength of 575 mμ, therefore, has been

1) Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.
2) J. Körbl, R. Pribil and A. Emr, *Collection Czech. Chem. Communs.*, **22**, 961 (1957).
3) J. Körbl and R. Pribil, *Chemist Analyst*, **46**, 102 (1956).
4) K. L. Cheng, *Talanta*, **2**, 61 (1959).
5) K. L. Cheng, ibid., **2**, 266 (1959).
6) K. L. Cheng, ibid., **3**, 81 (1959).
7) K. L. Cheng, ibid., **3**, 147 (1959).
8) K. L. Cheng, ibid., **5**, 254 (1960).
9) H. Ônishi and N. Ishiwatari, This Bulletin, **33**, 1581 (1960).
10) K. Ueno, "Chelate Titration", Nankôdô, Tokyo (1960), p. 328.
11) Ibid., p. 125.

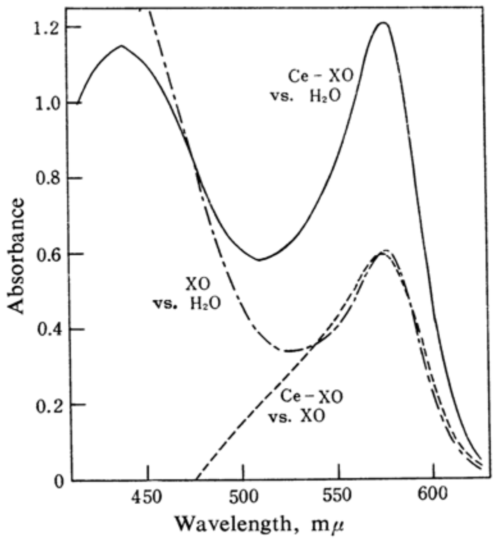

Fig. 1. Absorption spectra of xylenol orange and its cerium complex.

Ce: 1.9×10^{-5} M XO: 1.2×10^{-4} M

adopted in the determination of cerium. (At this wavelength the absorbance of the complex is about six times that of the reagent itself.) The complexes of lanthanum, neodymium and yttrium exhibit similar tendencies with the cerium complex. Their absorption peaks are found at 576 mμ for lanthanum and 578 mμ for neodymium and yttrium.

Effect of pH.—The effect of pH on the color development of the cerium complex was studied with solutions varying in pH value from 4 to

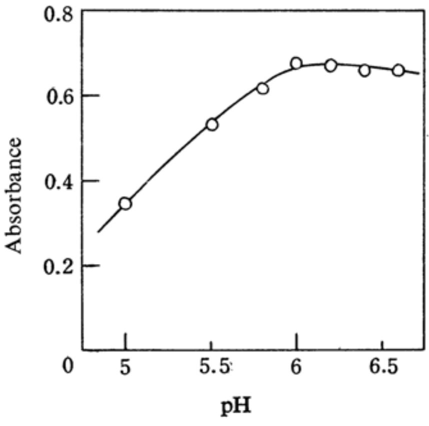

Fig. 2. Effect of pH on color development. Ce: 65 μg.

7. Figure 2 shows that the maximum color development is obtained over the pH range of 6.0 to 6.5. Similar results are also obtained for the other rare earths.

Effect of Xylenol Orange. — A practically constant absorbance is obtained by adding 3

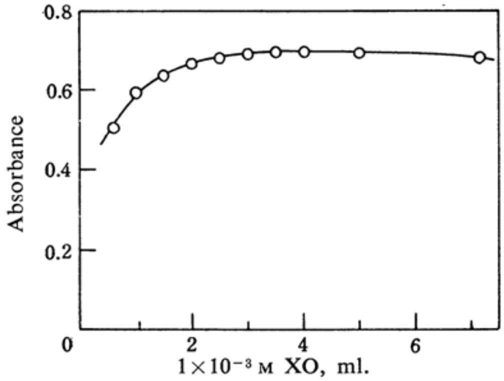

Fig. 3. Effect of addition of xylenol orange. Ce: 65 μg.

to 5 ml. of a 1×10^{-3} M xylenol orange solution (Fig. 3). Too large amounts of the dye tend to decrease the absorbance. It seems, therefore, that in the presence of a large excess of the dye, these rare earths may form a complex other than a 1 : 1 complex.

Stability of Complex.—Figure 4 shows the stability of the colored complex of cerium. Since the color is stable at room temperature for at least 2 hr., no particular attention need be paid to the time of standing.

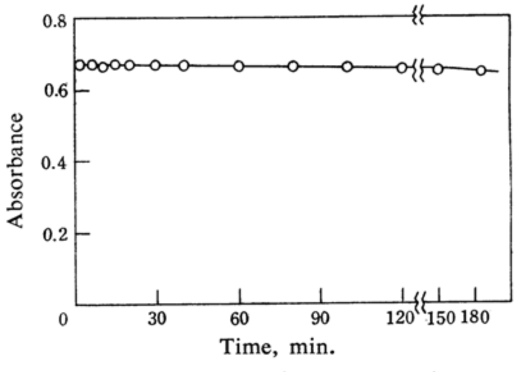

Fig. 4. Stability of Ce-XO complex. Ce: 65 μg.

Calibration Curve. — As is shown in Fig. 5, a linear relationship exists between the absorbance and the rare earth concentration over the range investigated. The optimum concentration range was then determined by Ringbom's procedure[12] and was found to lie between 20 to 100 μg. cerium. At the measured wavelength, the molar extinction coefficients of the xylenol orange complexes of lanthanum, cerium, neodymium and yttrium are 32000, 31000, 38000 and 48000 respectively. From these high sensitivities, xylenol orange is found to be the

12) A. Ringdom, *Z. anal. Chem.*, **115**, 332 (1938/9).

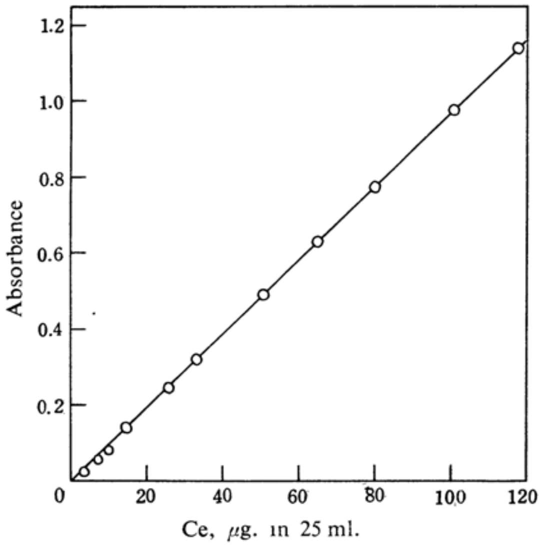

Fig. 5. Calibration curve.

most convenient reagent for spectrophotometric determination of trace amounts of rare earths.

Formation Constant.—The mole ratio method and the continuous variation method (Job's method) were applied to establish the mole ratio of the complex in solution. From Figs. 6 and 7, it is evident that cerium forms a 1 : 1 complex with xylenol orange. The formation constant was calculated from the curves shown in Fig. 7, based on the method described by Cheng[5] and et al. It was found to be 3×10^5 at 25°C. Because of its low formation constant, it is easily understood why xylenol orange has been successfully used as an indicator in the EDTA titration of rare earths. Lanthanum, neodymium and yttrium also form a 1 : 1 complex with xylenol orange; their formation constants are calculated to be 7×10^5, 1×10^6 and 3×10^5 respectively. These values are slightly lower than those of zirconium-[5],

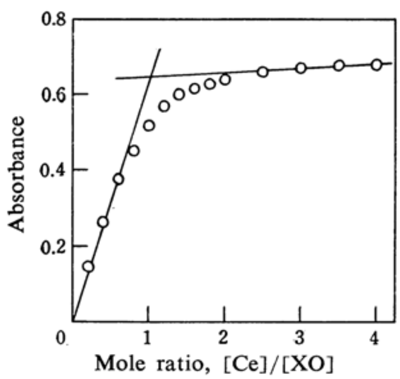

Fig. 6. Mole ratio method.
XO: 2×10^{-5} M

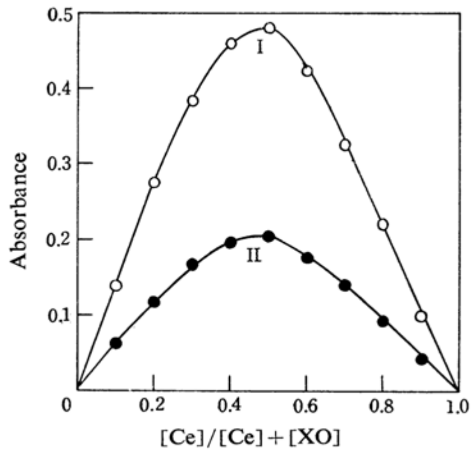

Fig. 7. Continuous variation method.
I: $[Ce]+[XO]=4\times10^{-5}$ M
II: $[Ce]+[XO]=2\times10^{-5}$ M

TABLE I. EFFECT OF ANIONS ON CERIUM DETERMINATION

Anion		Cerium	
Present	Added μ mol.	Taken μg.	Found μg.
Chloride	250	98.1	98.1
	500		97.0
Fluoride	1	92.5	88.4
	5		74.1
	10		46.5
Nitrate	250	98.1	96.6
	500		99.5
Sulfate	250		100.3
	500		99.7
Thiosulfate	8	97.4	96.3
	20		93.3
Oxalate	2.5		88.3
	5		82.2
Phosphate	1	98.1	43.5
	2.5		15.5
	5		5.2
Tartrate	5	97.4	91.9
Citrate	0.2		91.7
	1		88.0
NTA	0.5	92.5	92.3
	1.5		81.9
EDTA	0.01		73.0
	0.05		2.0
	0.2		1.0

hafnium-[6] and bismuth-xylenol orange[8,9] complexes.

Effect of Anions.—Table I indicates the effect of anions on the determination of cerium. Chloride, nitrate, sulfate and thiosulfate do not interfere. Large amounts of fluoride, oxalate, tartrate and citrate decrease the absorbance considerably. NTA (nitrilotriacetic acid) and EDTA, which may form a stable complex with the rare earths, seriously inhibit the color development of the complex.

Summary

A method has been described for the spectrophotometric determination of 20 to 100 μg. of a rare earth element using xylenol orange. The complexes of cerium(III), lanthanum-(III), neodymium(III) and yttrium(III) with xylenol orange have an absorption maximum at 575 to 578 mμ vs. the reagent blank. Each of them is a 1 : 1 complex and has a formation constant of approximately 10^5 under the conditions studied. Anions such as NTA and EDTA inhibit the color development of the complexes.

The authors wish to express their thanks to Miss Iku Mizuki for her assistance in the measurements.

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