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Medicinal and Analytical Chemistry International Journal
ISSN: 2639-2534

Spectrophotometric Determination of Lanthanum (III) and Some Rare Earths with Xylenol Orange

Primo A*

Environmental Chemistry, Tishreen University, Syria

***Corresponding author:** Abdullah Primo, Environmental Chemistry, Higher Institute for Environmental Research, Tishreen University, Lattakia, Syria, Tel: 00963936904542; Email: abdullah.Primo@tishreen.edu.sy

Research Article
Volume 8 Issue 2
Received Date: May 29, 2024
Published Date: July 03, 2024
DOI: 10.23880/macij-16000196

Abstract

Xylenol orange reagent was used to complex lanthanum cations in aqueous solutions, where the solution was colourless before complexing, and when adding Xylenol orange, it turned violet at a wavelength of 578 μm at a pH of about 6, where it was adjusted using a buffer solution composed of acetic acid and sodium acetate. Between the lanthanum cation and the indicator in a ratio of 1:1, the resulting complex is very stable for a time of up to 180 minutes at a room temperature of approximately 25 °C. Sulphate ions, chlorides and nitrates did not affect the absorbance of the solution at different concentrations, while fluorides, oxalates and tartrate negatively affected in high quantities, and the presence of EDTA and NTA negatively affects complex formation and stability.

Keywords: Xylenol Orange; Lanthanum Complexing Spectrophotometric Titrations

Introduction

Since xylenol orange was first prepared by KSrbl and others [1-3] 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; Cheng [4-8], and recently bitsmuth, by Onishi and Ishiwatari [9,10], have thus determined zirconium, hafnium, iron and bismuth. 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 lanthanum- (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 (lanthanum, Cerium, neodymium and yttrium) and were standardized by EDTA titration, using xylenol orange as an indicator [10-12]. About 10-3M of a xylenol orange solution was prepared by dissolving Dottie XO reagent (Dojindo & Co., Kumamoto) in distilled water. According to Ueno [12,13], this solution is stable for several months [14,15].

Apparatus

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

Procedure

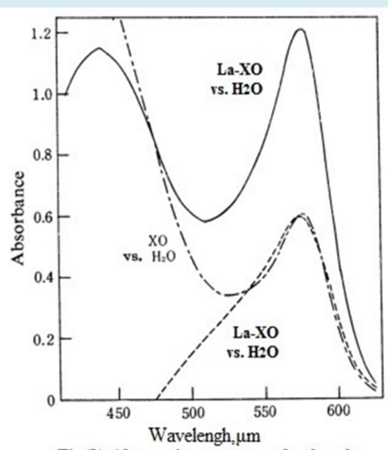
From zero to 100 ppm. Of one of the rare earths was transferred to a 25ml volumetric flask. (When lanthanum was to be determined, 1ml of a 0.5% solution of ascorbic acid was added to prevent oxidation of the lanthanum(III) to the ceric state).

Three to four milliliters of a xylenol orange solution and 15ml. of an acetate buffer solution (pH 6.1±0.1, 0.17M 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 lanthanum complex at a pH of 6.1. Both the reagent and the complex have an absorption maximum at about 580 µm. When a correction for the reagent blank is applied, an absorption peak of the complex is found at 575 µm. A wavelength of 575µm, therefbre, has beenadopted in the determination of lanthanum. (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 lanthanum complex. Their absorption peaks are found at 576 µm for lanthanum and 578 µm for neodymium and yttrium.



Fig(1) Absorption spectra of xylenol orange and its lanthanum complex.
La: 1.9×10^{-5} M XO: 1.2×10^{-4} M

Effect of pH

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

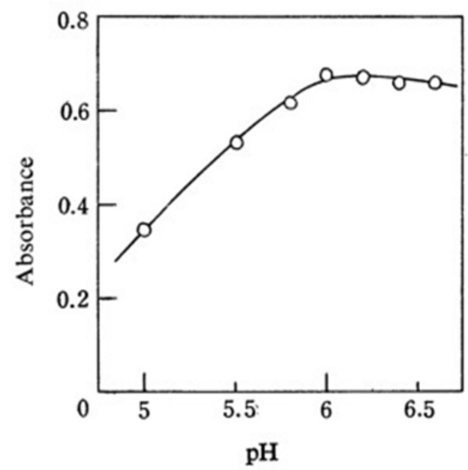


Fig. 2. Effect of pH on color development.
La : 65 ppm

Effect of Xylenol Orange

A practically constant absorbance is obtained by adding 3 to 5ml. of a 1×10-3M xylenol orange solution (Figure 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.

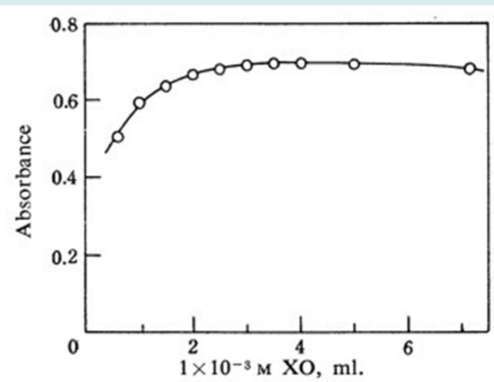


Fig. 3. Effect of addition of xylenol orange.
La: 65 ppm

Stability of Complex

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

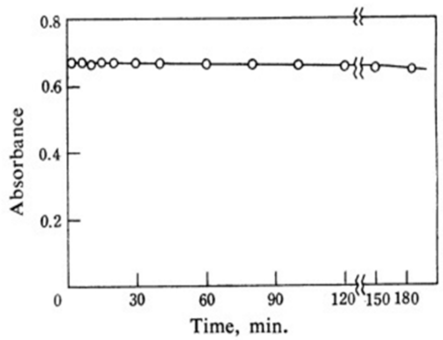


Fig (4) Stability of La-XO complex
La : 65 ppm

Calibration Curve

As is shown in Figure 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 ppm lanthanum. 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 most convenient reagent for spectrophotometric determination of trace amounts of rare earths.

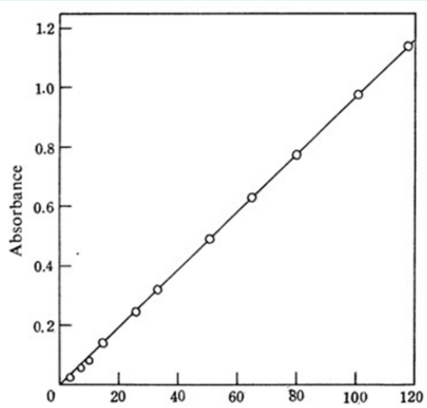


Fig (5) Calibration curve

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 Figures 6,7 it is evident that lanthanum forms a 1:1 complex with xylenol orange. The formation constant was calculated from the curves shown in Figure 7, based on the method described by Cheng [5] and et al. It was found to be 3×105 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 7×105, 1×106 and 3×105 respectively. These values are slightly lower than those of zirconium (5), hafnium (6) and bismuth-xylenol orange (8,9) complexes.

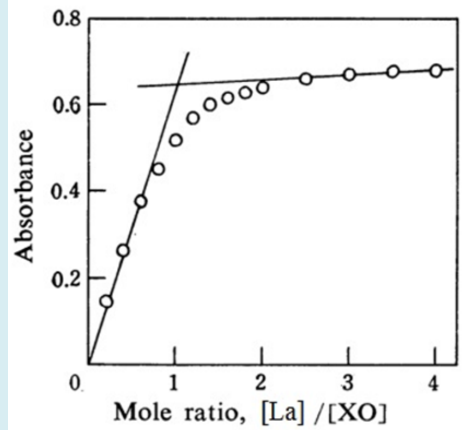


Fig. 6. Mole ratio method.
XO : 2×10^{-5} M

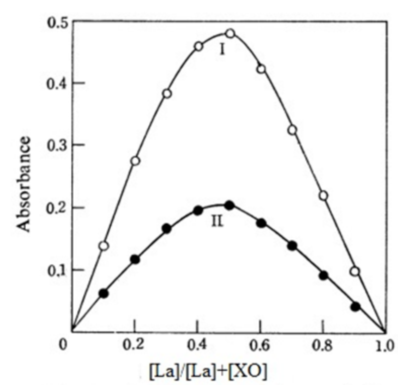


Fig. 7. Continuous variation method.
I : [La] + [XO] = 4×10^{-5} M
II : [La] + [XO] = 2×10^{-5} M

Effect of Anions

Table 1 indicates the effect of anions on the determination of lanthanum. Chloride, nitrate, sulfate and thiosulfate do not interfere. Large amounts of fluoride, oxalate, tartrate and citrate decrease the absorbance considerably. NTA (nitrilotriaceticacid) and EDTA, which may form a stable complex with the rare earths, seriously inhibit the color development of the complex.

Anions		Lanthanum	
Present	Added (μ mole)	Taken (μ gram)	Found (μ gram)
Chloride	200	98.3	98.3
	400	98.3	98
Fluoride	2	95.5	90.3
	6	95.5	81.7
	10	95.5	70.1
Nitrate	200	98.3	98
	400	98.3	98.3
Sulfate	200	98.3	98.3
	400	98.3	98.3
Oxalate	2	96	83.1
	6	96	75.2
Phosphate	2	96	55.3
	4	96	30.9
	6	96	12.1
Tartrate	10	96	87.6
NTA	0.5	95	90.4
	1	95	79.9
	1.5	95	54.5
EDTA	0.01	95	78.6
	0.05	95	42.3
	0.1	95	16.7
	0.2	95	1.2

Table 1: Effect of anions on Lanthanum determination.

Summary

A method has been described for the spectrophotometric determination of 20 to 100 ppm. of a rare earth element using xylenol orange. The complexes of lanthanum (III), cerium (III), neodymium(III) and yttrium(III) with xylenol orange have an absorption maximum at 575 to 578 μm vs. the reagent blank. Each of them is a 1:1 complex and has a formation constant of approximately 105 under the conditions studied. Anions such as NTA and EDTA inhibit the color development of the complexes.

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