

Sulfonephthalein dyes. IV.*

Methylxylenol blue as a metallochromic indicator for chelatometric microtitrations of rare earth metals

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The possibility of using methylxylenol blue as a metallochromic indicator for the chelatometric determination of Sc^{3+} , La^{3+} , Ce^{3+} , Sm^{3+} , and Er^{3+} ions was examined by the method of photometric and visual comparison microtitration. The influence of the kind of buffer solution and of pH upon the steepness of the colour changes of methylxylenol blue was investigated. Lanthanum, samarium, and erbium can be titrated in the medium of urotropine or acetate buffer solutions, while for the titration of cerium(III) ions the acetate buffer solutions are better suited. Scandium is to be titrated in the medium of dilute nitric acid (pH 2–3) or formate buffer solutions. It is also possible to use methylxylenol blue for consecutive determination of scandium and lanthanoids in a mixture.

Методом фотометрического и визуального сравнительного микротитрования были изучены возможности использования метилксиленолового синего в качестве металлохромного индикатора при комплексонометрическом определении ионов Sc^{3+} , La^{3+} , Ce^{3+} , Sm^{3+} и Er^{3+} . Было исследовано влияние pH и разных буферных растворов на крутизну изменений цвета метилксиленолового синего. Лантан, самарий и эрбий можно титровать в среде уксуснокислых и уротропиновых буферных растворов, для титрования ионов церия более подходящие уксуснокислые буферные растворы. Скандий можно титровать в среде разбавленной азотной кислоты (pH 2–3) или в муравьинокислом буферном растворе. Метилксиленоловый синий может быть использован тоже для последовательного определения скандия и лантаноида находящихся в одном растворе.

Methylxylenol blue was found [1] to be a sensitive metallochromic indicator for chelatometric microdeterminations of bivalent metals. These determinations and the study of protolytic equilibria of methylxylenol blue [2] indicated that this indicator is analogous to methylthymol blue, which implies a possibility of further analytical applications of this dyestuff. Therefore we aimed our attention at the problems of chelatometric microdetermination of rare earth metals for which methylthymol blue as well as methylxylenol blue have been suggested only once as indicators. *Körbl* and *Pribil* refer in their introductory communication on methylthymol blue [3] to the

* For Part III see Ref. [1].

titration of scandium and lanthanum in a pure solution of particular nitrate with an addition of a drop of pyridine for Sc(III) or a urotropine buffer solution for La(III). *Mori* and *Enoki* [4] mention the titrations of trivalent cerium employing methylxylol blue in a medium buffered with urotropine. In this paper we present the results of a more detailed study based on the method of photometric and visual microtitration.

Experimental

Solutions, instruments, and methods of measurement

For chelatometric microtitrations a 0.01 M standard solution of Chelaton 3 (Lachema, Brno) was prepared. The 0.01 M stock solutions of rare earth metals were prepared from differentially weighed samples of $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, all of them anal. grade (Lachema, Brno). The stock solution of cerium(III) nitrate was stabilized by an addition of hydrogen peroxide (about ten drops of 30% H_2O_2 per 100 ml of solution). All stock solutions of metals were acidified with nitric acid (about 5 drops of 65% HNO_3 per 100 ml) in order to prevent hydrolysis. The approximate concentration of the solutions of methylxylol blue was 1.5×10^{-4} M [1]. Acetate and urotropine buffer solutions, prepared from 0.2 M acetic acid and sodium acetate or 0.5 M nitric acid and urotropine, were chosen for the adjustment of pH. The titrations of scandium were studied in formate buffer solutions obtained by mixing from 0.2 M formic acid and sodium formate as well as in the medium of dilute formic and nitric acids.

A pH-meter OP-201/2 (Radelkis, Budapest) with a glass and saturated calomel electrode was used for pH measurements. The photometric microtitrations were performed on a Spekol spectrophotometer (Zeiss, Jena) equipped with a special titration attachment [1]. A syringe microburette was used for titrations; the total volume of the microburette was 400 μl , the accuracy of delivery being $\pm 0.2 \mu\text{l}$.

Selection of optimum conditions and the visual microtitrations

The procedure used in the investigation of the influence of the reaction medium on the sharpness of the colour changes of methylxylol blue, employing the method of photometric microtitrations, was described in detail in a preceding paper [1]. The steepness of photometric titration curves was measured in the region of absorption maxima of the metal chelates of methylxylol blue in the range from 590 to 610 nm. For each titration with 0.01 M chelaton 0.001 M solution of metal salt (3 ml), buffer solution (2 ml), 0.00015 M methylxylol blue solution (2 ml), and water (13 ml) were measured into a cell with a 50 mm path-length and a volume of 20 ml (type C, Zeiss, Jena). Equal amounts of all components were used for visual comparison titrations [5]. Only for the titrations of scandium in the medium of dilute nitric acid, instead of a buffer solution (2 ml) we pipetted an equal volume of 1 M- KNO_3 and a corresponding amount of nitric acid calculated for the chosen ionic strength ($I = 0.1$) according to an empirical formula [6]. The summary of the results is presented in subsequent paragraphs.

Determination of lanthanum

We did not observe any substantial differences in the course of photometric titration curves determined in different buffer solutions. The colour transition from blue to yellow

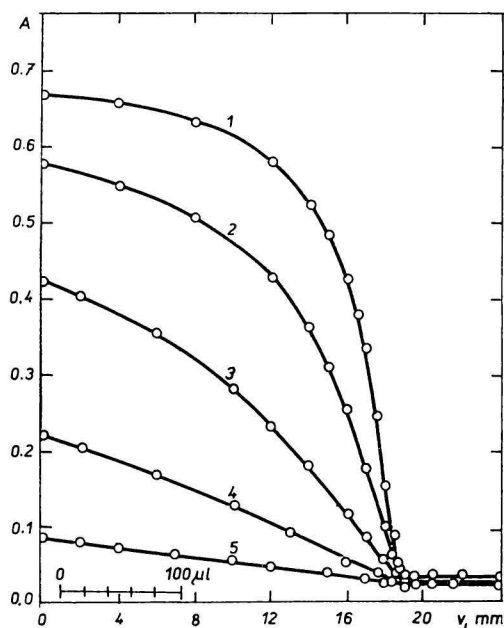


Fig. 1. Influence of pH on the shape of photometric titration curves corresponding to the determination of lanthanum in acetate buffer solutions.

$c_{La} \approx 1.5 \times 10^{-4}$ M, $c_I \approx 1.5 \times 10^{-5}$ M, $c_{HOAc} \approx 0.02$ M, $\lambda = 610$ nm, $d = 50$ nm.

Titrated with 0.01 M chelatorone at pH 5.45 (1), pH 5.02 (2), pH 4.70 (3), pH 4.33 (4), and pH 3.90 (5).

Symbol v in Figs. 1–3 stands for the consumption of the volumetric solution of chelatorone in terms of the micrometer readings [in mm] on the microburette. The conversion to the data in microliters can be made with the aid of a relative scale shown in the figures.

exhibits the sharpest change in the pH range from 5.2 to 6.0 in both acetate and urotropine buffer solutions. A decrease of pH causes a decrease in the sharpness of colour change. The photometric titration at $pH < 4$ was not possible (Fig. 1).

Determination of cerium

In urotropine buffer solutions recommended for the titration of cerium(III) ions by Mori and Enoki [4] the oxidation by atmospheric oxygen has an unfavourable effect at $pH > 5$ manifested on the photometric titration curves by a shift of the end-points towards lower consumptions. On the other hand, the end-points are located at higher absorbance values, because a part of methylxyleneol blue is blocked by the cerium(IV) ions formed. No improvement was achieved by the use of a reduction agent, such as ascorbic acid or hydroxylamine. The values of absorbance during titration depended on the time of reading and the photometric titration curves were poorly reproducible. However, we did not observe these phenomena in the medium of acetate buffer solutions

and therefore we chose pH 5.0–5.5 as the most suited for visual titrations. Oxidation by atmospheric oxygen has no unfavourable effect in solutions buffered with acetate and so it is possible to achieve a sharp and distinct colour change of the indicator.

Determination of samarium and erbium

Samarium and erbium can be titrated in both acetate and urotropine buffer solutions to a fairly sharp and conspicuous colour change of the indicator. The optimum pH range is 5.0–5.5 for the titration of samarium and 4.5–5.5 for the titration of erbium. An increase in acidity of the titrated solution results in a reduction of the sharpness of the colour change.

Determination of scandium

A medium with the pH values ranging from 2.5 to 3.2 is convenient for the visual chelatometric determination of scandium with methylxylenol blue as indicator. The titrations may be carried out either in a formate buffer or in the presence of dilute nitric acid. In more acid solutions the steepness of the colour change decreases, but it was

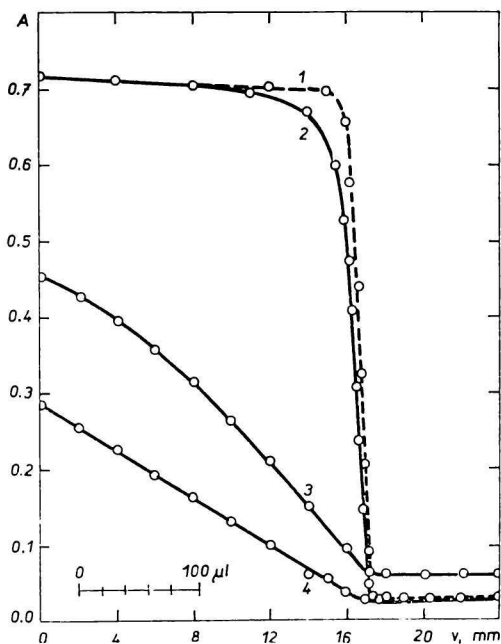


Fig. 2. Influence of pH on the shape of photometric titration curves corresponding to the determination of scandium in dilute solutions of formic acid (full lines) and formate buffer solution (dashed line).

$$c_{Sc} \approx 1.5 \times 10^{-4} \text{ M}, c_I \approx 1.5 \times 10^{-5} \text{ M}, \lambda = 590 \text{ nm}, d = 50 \text{ mm.}$$

Titrated with 0.01 M chelator at pH 2.65 (HCOOH/HCOONa) (1) or in the medium of 0.5% (2), 3.5% (3), and 5% HCOOH (4).

possible to obtain a photometric curve even for titrations in 5% formic acid (Fig. 2). The acetate or urotropine solutions are not convenient though they were frequently recommended. The reaction equilibrium is slowly attained in these solutions, which prevents reproducible recording of the photometric titration curve.

The results and the statistical evaluation of visual comparison microtitrations of all metals studied are presented in Table 1.

Table 1

Statistical evaluation of visual comparison chelatometric microtitrations of rare earth metals with methylxylenol blue as indicator

Titrated metal ion	pH		\bar{x} μl 0.01 M-EDTA	<i>s</i>	Interval of 95% reliability
Sc ³⁺	2.50 ^a	14	277.3	0.4	277.1—277.5
La ³⁺	5.67 ^c	14	300.8	0.7	300.4—301.3
Ce ³⁺	5.18 ^b	9	274.2	1.2	273.3—275.1
Sm ³⁺	5.25 ^c	14	300.3	0.7	299.9—300.8
Er ³⁺	5.66 ^c	10	305.1	0.4	304.8—305.3

a) Formate, b) acetate, c) urotropine buffer solution.

Consecutive determination of scandium and lanthanoides

For the chelatometric titration of lanthanum it was necessary to adjust the pH value within the range 5.2—6.0 in order to achieve a sharp colour change of the indicator. For erbium the optimum pH range is shifted to lower values of pH, while scandium can best be titrated in the medium of a dilute nitric acid. These experimental results are in a good agreement with the theory, since the stability of the chelatonates of the rare earth metals studied increases in the following sequence: La (15.50), Ce (15.98), Sm (17.14), Er (18.85), and Sc (23.10); the values of $\log \beta_{MY}$ in parentheses are taken from [7]. The difference between the values for scandium(III) chelatonate and lanthanoide chelatonates indicates the possibility of a consecutive determination of scandium and a lanthanoide metal ion or a sum of lanthanoides. Such consecutive titration is usually used for the analysis of mixtures containing a trivalent and a bivalent metal ion (*e.g.* the determination of Bi³⁺ and Pb²⁺ [6]), but it has also been suggested for a mixture of thorium and rare earth metals with xylenol orange as indicator [8]. Our intention was to verify whether methylxylenol blue could also be used as an indicator for the visual titration of scandium and lanthanoides in a mixture.

The titration solution was prepared by transferring 0.001 M solution of Sc(NO₃)₃ (1.5 ml), 0.001 M solution of particular lanthanoide (1.5 ml), about 0.00015 M solution of methylxylenol blue (2 ml), 1 M-KNO₃ (1.7 ml), and 0.1 M-HNO₃ (3.7 ml) in a titration vessel, and the volume was made up to 17 ml by water. This solution of pH about 2.1 was titrated with 0.01 M chelatonate photometrically or visually to the colour change from blue to yellow. When the titration of scandium was completed, the acidity of the titration solution was adjusted to pH about 5.3 by adding 0.5 M urotropine (2.5 ml) and the titration was continued to a further colour change. The following mixtures were investigated: Sc³⁺—La³⁺ (Fig. 3), Sc³⁺—Sm³⁺, and Sc³⁺—Er³⁺ and for all cases good results were obtained.

Discussion

Methylxlenol blue proved to be a very sensitive metallochromic indicator for chelatometric titrations of rare earth metals. Very accurate results can be obtained in titrations accompanied by sharp colour changes from blue to yellow. With the exception of the titration of cerium(III) no difficulties are encountered.

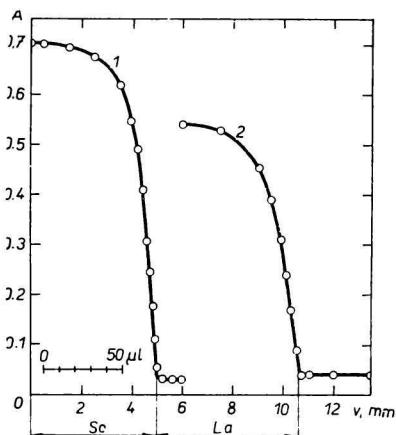


Fig. 3. Consecutive photometric microtitration of scandium and lanthanum.

$c_{Sc} = 454 \mu\text{g}$, $c_{La} = 650 \mu\text{g}$, $c_I \approx 1.5 \times 10^{-5} \text{ M}$,
 $\lambda = 600 \text{ nm}$, $d = 50 \text{ mm}$.

Titrated with 0.01 M chelatonate at pH 2.15 (HNO_3) (1) and pH 5.00 (HNO_3 /urotropine) (2).

For the titrations of scandium and lanthanum the results were compared with the aid of the t test with a reference method for which xlenol orange was chosen as indicator. This reference method has been recommended on the basis of a thorough study [9] for its reliable and accurate results. For both methods tested the difference in results can only be ascribed to random errors and since the titrations of cerium, samarium, and erbium are analogous, the results of the titrations of these metal may also be assumed to be correct.

The different stability of the chelatonates of scandium and the lanthanoids makes possible to determine these cations in a mixture. Before titration, the acidity of the solution containing scandium and some lanthanoid is adjusted by dilute nitric acid to the pH value of about 2. When the end-point for scandium is reached, the solution is adjusted to the pH value of about 5.5 by an addition of urotropine or a saturated solution of sodium acetate and the titration is continued to a next colour change of the indicator. From the difference in the consumption between the first and second end-point the concentration of the lanthanoid present can be determined. No significant differences in the results of these consecutive titrations were observed with respect to those obtained for individual metals. Some differences become evident only in the determinations of very low concentrations of metal ions (about 10^{-5} M) titrated with 10^{-3} M chelatonate [10].

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