Photometric microtitrations. VII.*
Chelatometric determination of scandium and lanthanides by direct and successive titration using Methylxylenol Blue

S. KOTRLÝ, V. MACH, and K. VYTŘAS

*Department of Analytical Chemistry, University of Chemical Technology,
532 10 Pardubice*

The precision and accuracy attainable in direct titrations of the Sc^{3+}, La^{3+} or Er^{3+} ion with a 0.001 M solution of the disodium salt of ethylenediaminetetraacetic acid using Methylxylenol Blue as a metallochromic indicator has been studied.

For linear extrapolation of the end-point in titrations of the Sc^{3+} and Er^{3+} ions with a solution of the disodium salt of ethylenediaminetetraacetic acid it is convenient to measure the titration curve at 560 nm (in case of La^{3+} at 570 nm) and to adjust the concentration of indicator in the titrated solution to 1—2×10^{-5} M. For the microtitration of Sc^{3+} the pH range 2—3 is obtained by adding the chloroacetate buffer while for the titration of lanthanides the optimum pH value (pH 5.4 for Er^{3+} and pH 5.9 for La^{3+}) is adjusted with the hexamethylenetetramine buffer solution. The influence of the blank titration on accuracy of results was eliminated by successive titration: the analyzed solution was measured and introduced into a solution immediately after completing a preliminary titration of the ion being determined.

In repeated determinations of these metals in very dilute solutions ($c_M \approx 10^{-5}$ M) the relative random error does not exceed 1% and the systematic error 0.8—1.5% (referred to the most accurate visual titration performed at concentrations higher at least by one numerical order). Accurate results may also be achieved by a successive titration. The Sc^{3+} ion is titrated at pH 2.5; then the pH value is adjusted to 5.4—5.9 by adding the hexamethylenetetramine buffer solution and the La^{3+} ion (or Er^{3+} ion) is titrated.

Была изучена точность и правильность, достигаемая при прямом титровании ионов Sc^{3+} или La^{3+} и Er^{3+} с 0,001 М раствором двухзамещенной натриевой соли этилендиаминтетрауксусной кислоты с использованием метилксиленолового синего в качестве металлохромного индикатора.

Для линейного экстраполирования окончания титрования подходит измерение кривой титрования при 560 нм в случае Sc^{3+} и Er^{3+} и при 570 нм

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* For Part VI see Ref. [1].

в случае La³⁺, концентрацию индикатора в титруемом растворе выбирают 1—2 10⁻⁵ M. Для микротитрования Sc³⁺ можно ограничить диапазон pH 2—3 добавкой хлоруксусного буферного раствора, для титрования лантанидов оптимальное pH 5,4 (Er³⁺) до pH 5,9 (La³⁺) достигается гекса-метилентетрааминовым буферным раствором.

Влияние холостого опыта на правильность результатов было исключено постепенным титрованием, причем испытуемый раствор прибавлялся к раствору, в котором уже предварительно оттитрован определяемый ион.

При повторном определении этих металлов в очень разбавленных растворах ($c_M \approx 10^{-5}$ M) относительная случайная ошибка не превышает 1% и систематическая ошибка 0,8—1,5% по отношению к наиболее точному визуальному титрованию при концентрациях по меньшей мере на порядок выше. Точных результатов можно добиться и при постепенном титровании, при котором ион Sc³⁺ титруется при pH 2,5 и затем La³⁺ или Er³⁺ после изменения pH до 5,4—5,9 прибавлением гексаметилентетра-аминового буферного раствора.

It has been shown in our previous publications [1—3] that the photometric indication of chelatometric titration with the use of a metallochromic indicator provides very accurate results in the region of microgram concentrations. The Methylxylenol Blue proved to be a sensitive metallochromic indicator suited for visual titrations of some bivalent metals [4] in mildly acid medium of the acetate or urotropine buffer solution. This medium was also evaluated as the optimum for visual and photometric microtitrations of rare earth metals [5] with a 0.01 M solution of the disodium salt of ethylenediaminetetraacetic acid. Since a scandium salt may be titrated in a solution adjusted to pH 2—3 by adding nitric acid or a formate buffer, it was also possible to perform a successive titration of scandium and some lanthanide in mixture. This procedure ensures accurate results [5] in titrations with a 0.01 M solution of Chelatone 3 while a photometric indication does not practically deviate from visual estimate in the attainable level of accuracy, especially if a reference solution is used [6, 7], because the colour change of indicator is distinct and sharp. A higher accuracy of photometric indication usually appears in the concentration range lower by one numerical order [8]; however, the accuracy of end-point location should be verified for the particular conditions [2]. In this paper, the results are presented for the study of precision and accuracy of the photometric indication with the use of Methylxylenol Blue for the determination of microgram amounts of rare earth metals either by direct titration of individual Sc³⁺, La³⁺, and Er³⁺ ions or by successive titration of the Sc³⁺ and La³⁺ ions and of the Sc³⁺ and Er³⁺ ions.

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Experimental

Solutions, instruments, and measuring methods

0.01 M and 0.001 M solutions of Chelatone 3 (disodium salt of ethylenediaminetetraacetic acid, Lachema, Brno) were prepared for visual and photometric titration, respectively. The titre of these solutions was verified by visual titration with Pb^{2+} using Xylenol Orange as indicator [8]. Recrystallized and dried lead dichloride was used as a standard. The titre of the 0.01 M solution was determined with the use of solutions prepared by difference weighing of $PbCl_2$ $(s_r$ $(\%) = 0.1$ for $n = 4$; relative error referred to weighed amount of Chelatone 3 was e $(\%) = +0.5)$. The results obtained in repeated titrations with the 0.001 M solution of Chelatone 3 by means of two different standard solutions of $PbCl_2$ were insomuch identical that they could not be statistically evaluated $(e$ $(\%) = -0.05)$.

Standard 0.01 M solutions of the rare earth metals were prepared by weighing the dried anal. grade salts $(Sc(NO_3)_3 \cdot 4H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Er(NO_3)_3 \cdot 6H_2O$; Lachema, Brno) and dissolving them in dilute nitric acid the resulting concentration of which was approximately 0.01 M. These solutions were standardized by visual titration with 0.01 M Chelatone 3 using Xylenol Orange and chloroacetate (for Sc^{3+}) or urotropine solution. The results obtained were very accurate and practically identical $(n = 4)$. They may also be considered sufficiently correct [9].

The purified preparations of indicators were used for preparing 0.01% stock solutions of Xylenol Orange (xo) and Methylxylenol Blue (mxb) [10]. These solutions were stabilized by acidifying with nitric acid $(c_{HNO_3} \approx 0.001$ M).

The chloroacetate buffer solution of pH 3 was prepared by mixing 2 M-$CH_2ClCOOH$ and 1 M-CH_3COONa and controlled by means of a pH-meter. Similarly, the urotropine solutions of pH 5.2 and pH 6 were prepared by mixing 0.5 M solutions of hexamethylenetetramine and nitric acid.

A pH-meter OP-201/2 (Radelkis, Budapest) with a cell consisting of   electrode and saturated calomel electrode was used for pH measurements.

The photometric microtitrations were carried out with the aid of a   ctometer Spekol (Zeiss, Jena) which was equipped with a photoelectric head, an a.np ., and other special accessories (titration adapter [11] and microburette with glass piston) which were made in the development workshop of the University of Chemical Technology. The microburette was calibrated and tested by a new gravimetric and titration method [12]: for the measurement of the total volume of 566.1 µl the estimate of standard deviation was 0.4 µl $(n = 7)$.

Selection of optimum conditions for the direct titration of scandium and lanthanides

The estimate of optimum conditions for titrations of individual metals in pure solutions could be based on the knowledge obtained in titrations with 0.01 M Chelatone 3 [5]. However, the determination in a very dilute solution depends more on the selection of conditions for titration and the experimental arrangement.

The reliability of linear extrapolation of the titration end-point in the photometric titrations with 0.001 M Chelatone 3 is significantly affected by the choice of wavelength if stepwise complexes of indicator with the titrated metal exist in equilibrium in the course of the indicator transition. In this respect, Methylxylenol Blue resembles Xylenol Orange (*cf.* [8]). Therefore it was necessary, in the first place, to investigate the influence of wavelength on the shape of titration curve in full detail.

Fig. 1 shows the parts of titration curves in the region of equivalence, which are important for linear extrapolation of the titration end-point for La^{3+} A change in wavelength affects the extent of curvature and the length of linear section on the oblique branch of titration curve. Thus the number of experimental points which may be used for drawing the extrapolation line is limited. Therefore the form of titration curve predetermines magnitude and sign of the deviation of the extrapolated end-point from the equivalence point the position of which is marked by arrows in Fig. 1. So the curve corresponding to 570 nm was found to be suitable for microtitration of the La^{3+} ion while the optimum wavelength for Sc^{3+} and Er^{3+} was 560 nm.

The study of photometric microtitrations confirmed that the chloroacetate medium ($pH \approx 2.5$) was convenient for the determination of Sc^{3+} while the hexamethylenetetramine buffer solution was the most suitable medium for the titrations of the rare earth ions (pH 5.4 for Er^{3+} and pH 5.9 for La^{3+}). The concentration of indicator in the titrated solution was in the range 1×10^{-5}—$2 \times \times 10^{-5}$ M.

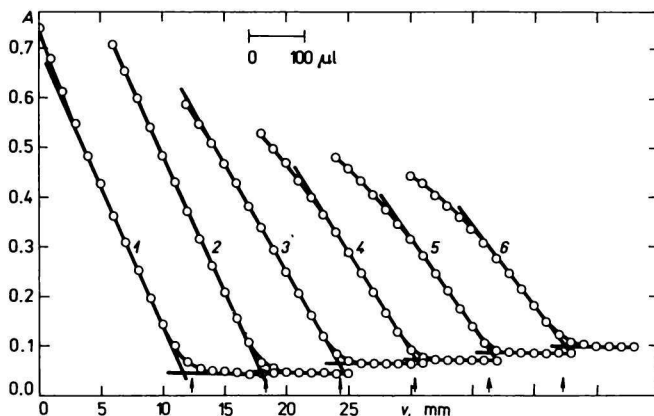The results of statistical evaluation of titration series presented in Table 1 show

Fig. 1. Photometric microtitration of lanthanum using Methylxylenol Blue at different wavelengths.
$c_{La^{3+}} = 8.67 \times 10^{-6}$ M; $c_{In} = 2.3 \times 10^{-5}$ M; pH 5.88.
λ (nm): *1.* 610; *2.* 590; *3.* 570; *4.* 560; *5.* 550; *6.* 540.
Curves *2*—*6* are gradually shifted to the right side on the *x* axis by 6 units.

Table 1

Statistical evaluation of series of the photometric microtitrations with 0.001 M Chelatone 3 using Methylxylenol Blue as indicator

| Titrated ion | 0.001 M Chelatone 3, µl | | | | s_r (%) |
	c_M, mol l^{-1}	$\bar{x}$	s	Interval of reliability	
Sc^{3+}	1.30×10^{-5}	266.9^a	2.26	$\bar{x} \pm 2.0$	0.85
	6.38×10^{-6}	130.2^a	0.84	$\bar{x} \pm 0.7$	0.64
	3.68×10^{-6}	76.5^a	1.09	$\bar{x} \pm 1.0$	1.42
La^{3+}	1.42×10^{-5}	281.9^b	1.17	$\bar{x} \pm 1.0$	0.42
	8.67×10^{-6}	167.5^b	1.68	$\bar{x} \pm 1.5$	1.00
	5.72×10^{-6}	113.9^b	0.54	$\bar{x} \pm 0.5$	0.47
Er^{3+}	1.30×10^{-5}	254.2^c	1.42	$\bar{x} \pm 1.3$	0.56
	7.95×10^{-6}	154.4^c	1.84	$\bar{x} \pm 1.6$	1.19
	5.40×10^{-6}	99.6^c	3.77	$\bar{x} \pm 3.4$	3.78

The titrations were performed at the wavelength: *a*) 560 nm; *b*) 570 nm; *c*) 560 nm in the volume of 20 ml and for cuvette length 50 mm.

$c_{mxb} = 2.2 \times 10^{-5}$ M; pH: *a*) 2.8—2.9; *b*) 5.8—5.9; *c*) 5.3—5.5.

The number of titrations in a series $n = 7$; level of significance $\alpha = 0.05$.

that sufficient accuracy may be achieved under the above-given optimum conditions even for micromolar concentrations of scandium and lanthanides.

Elimination of the influence of blank titration by the method of successive determination

The accuracy of the determination of metal in very dilute solutions may be considerably affected by the value of blank titration which, however, may frequently be low, outside the region where this method gives reliable results. In order to eliminate the influence of blank titration, we used the principle of successive titration. Before the actual determination, the conditions were adjusted and a small amount of the metal to be titrated (*e.g.* 1 ml of 5×10^{-5} M standard solution) was added. This addition as well as the trace amounts of other interfering elements were titrated together in the first titration. A certain volume, *e.g.* 5 ml, of the solution to be taken for the actual titration, was precisely measured and transferred into the somewhat overtitrated solution and the titration was continued to the second titration end-point. A titration curve for such titration is represented in Fig. 2. The results of three typical series of successive titrations are listed in Table 2. The accuracy achieved in these titrations was practically equal to the accuracy of simple direct titrations. The systematic error referred to the results of the visual titrations using 0.01 M Chelatone 3 and Xylenol Orange at higher concentrations of the titrated metals (*ca.* 5×10^{-4} M) was 0.8—1.5%. The

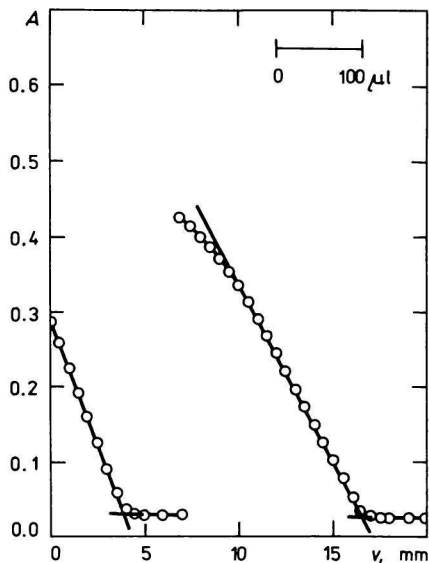*Fig. 2.* Successive photometric titration of lanthanum using Methylxylenol Blue and involving elimination of blank experiment. $c_{La^{3+}} = 1.7 \times 10^{-5}$ M; $c_{mxb} = 1.3 \times 10^{-5}$ M; pH 5.7; $\lambda = 570$ nm.

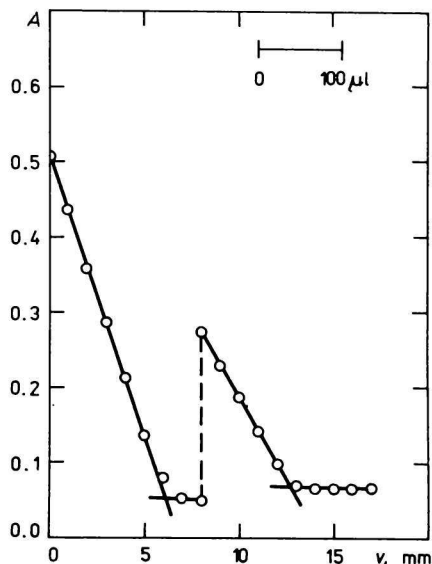*Fig. 3.* Successive photometric titration of scandium at pH 2.3 and erbium at pH 5.2 using Methylxylenol Blue. $c_{Sc^{3+}} = 6.38 \times 10^{-6}$ M; $c_{Er^{3+}} = 7.95 \times 10^{-6}$ M; $c_{mxb} = 2.1 \times 10^{-5}$ M; $\lambda = 560$ nm.

Table 2

Statistical evaluation of precision and accuracy for the determination involving elimination of blank experiment by successive titration

c_M at the end of successive titration	Sc^{3+} 1.16×10^{-5} M	La^{3+} 1.70×10^{-5} M	Er^{3+} 1.58×10^{-5} M
Given, µg	8.72	39.3	44.2
$\bar{x}$, µl	195.6[a]	287.1[b]	267.8[c]
s, µl	1.2	2.7	2.9
s_r (%)	0.6	1.0	1.1
Interval of reliability	$\bar{x} \pm 1.4$	$\bar{x} \pm 3.2$	$\bar{x} \pm 3.5$
Found, µg	8.79	39.9	44.8
u_0	0.60	0.61	0.57
e (%)	+0.8	+1.4	+1.5

It was titrated with 0.001 M Chelatone 3 at pH: *a*) 2.6; *b*) 5.7; *c*) 5.4.

The number of titrations in a series $n = 5$; other data are given in Table 1. Level of significance $\alpha = 0.05$; critical value of Lord's characteristic $u_0 = 0.51$.

calculated value of Lord's characteristic u_0 for all three series is higher than the critical tabulated value for the level of significance 0.05, which means that the observed differences are statistically significant. In comparison with usual errors incurred in other types of indication in titrations in very dilute solutions, the level of precision and accuracy achieved in the series listed in Table 2 may be considered to be satisfactory.

Successive microtitration of scandium and lanthanum or scandium and erbium

As already shown in paper [5], it is possible to titrate first scandium in the nitrate medium of pH 2.5 and after pH adjustment by adding hexamethylenetetramine buffer the titration may be continued to determine rare earth metals. The possibility of this successive determination was thoroughly studied in the region of microgram concentrations. Fig. 3 represents a photometric titration curve for the combination of Sc^{3+} and Er^{3+} In this case the titrated solution should be acidified up to the lower limit of the above pH range, otherwise the values of absorbance get settled slowly during the titration. After the titration of scandium was completed, the pH value of the solution was adjusted to pH 4.9—5.4 by adding 2 ml of the hexamethylenetetramine buffer solution and the titration of Er^{3+} succeeded. As can be seen from Fig. 3, there are no difficulties in the end-point evaluation for both metals.

Table 3

Statistical evaluation of series of the successive photometric microtitrations of Sc^{3+} and La^{3+} or Sc^{3+} and Er^{3+} with 0.001 M Chelatone 3 using Methylxylenol Blue as indicator

| Series | Titrated concentration of metal c_M, mol l^{-1} | 0.001 M Chelatone 3, µl | | | s_r (%) |
		$\bar{x}$	s	Interval of reliability	
1	1.30×10^{-5} M-Sc^{3+}	271.9^b	1.07	$\bar{x} \pm 2.4$	0.39
	5.72×10^{-6} M-La^{3+}	117.7^c	4.55	$\bar{x} \pm 10.0$	3.86
2	6.38×10^{-6} M-Sc^{3+}	135.8^b	0.14	$\bar{x} \pm 0.3$	0.10
	8.67×10^{-6} M-La^{3+}	170.2^c	2.01	$\bar{x} \pm 4.4$	1.18
3	3.68×10^{-6} M-Sc^{3+}	82.2^b	0.67	$\bar{x} \pm 1.5$	0.82
	1.42×10^{-5} M-La^{3+}	283.7^c	0.67	$\bar{x} \pm 1.5$	0.24
4	1.30×10^{-5} M-Sc^{3+}	271.0^a	0.53	$\bar{x} \pm 1.2$	0.20
	5.40×10^{-6} M-Er^{3+}	103.9^d	1.34	$\bar{x} \pm 2.9$	1.29
5	6.38×10^{-6} M-Sc^{3+}	137.6^a	1.74	$\bar{x} \pm 3.8$	1.26
	7.95×10^{-6} M-Er^{3+}	153.0^d	4.55	$\bar{x} \pm 10.0$	2.97
6	3.68×10^{-6} M-Sc^{3+}	81.5^a	2.13	$\bar{x} \pm 4.7$	2.61
	1.30×10^{-5} M-Er^{3+}	253.1^d	1.20	$\bar{x} \pm 2.6$	0.47

It was titrated at pH: *a*) 2.3; *b*) 2.4—2.6; *c*) 5.3—5.5; *d*) 4.9—5.4.
The number of titrations in a series $n = 3$; other data are given in Table 1.

The results of titration series of three parallel determinations are given in Table 3. The statistical evaluation shows that the determination of the ion Sc^{3+} titrated first is a little more precise than the determination of the rare earth ion. If two ions are titrated successively in a mixture, it is, however, necessary to determine the value of blank titration separately for the two pH values. It is worth to notice that analogous successive titrations of two metals have been described in literature, but they were only seldom studied in detail, especially from the view-point of attainable precision and accuracy. Further knowledge in this field could contribute to elucidation of the potential sources of errors in practical applications of chelatometric titrations.

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