Sulfonephthalein dyes. III.* Methylxylenol blue as a metallochromic indicator for direct visual chelatometric microtitrations of bivalent metals

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Methylxylenol blue proved to be a sensitive metallochromic indicator for chelatometric microdetermination of Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, and Mn^{2+} ions in mild acidic media buffered by acetate and urotropine solutions. The influence of pH and of the kind of buffer solution upon the slope of the colour changes of methylxylenol blue was studied *via* photometric microtitrations. Results of the visual comparative titrations using methylxylenol blue were statistically evaluated and compared with the results of other recommended methods. With a few exceptions only the determinations using methylxylenol blue are not laden with systematic errors with regard to the used methods of comparison and may be regarded as very accurate titration methods.

In the previous paper of this series [1], we reported results of the studies of protolytic equilibria of methylxylenol blue as well as the preliminary tests of the reactions of this dye with numerous cations. It was pointed out that methylxylenol blue can be applied not only as a reagent for spectrophotometric determinations of microgram amounts of metals (see references in [1]) but also as a sensitive metallochromic indicator for chelatometric titrations in suitably buffered media. In this communication we present our results of the studies of chelatometric microtitrations of bivalent metals in mild acidic media.

Experimental and results

Solutions, instruments, and measurements

A solution of methylxylenol blue (concentration *ca.* 1.5×10^{-4} M) was prepared from a purified [1] preparation. The sample of the dye was dissolved in a volumetric flask, then the solution was acidified with seven drops of 1 M-HNO_3 and the volume was made up to 50 ml by redistilled water. Solutions prepared in this way were stable for more than 10 days.

A 0.01 M solution of Chelatone 3 (Lachema, Brno) was prepared for chelatometric microtitrations. The used 0.001 M solutions of the salts of bivalent metals were obtained by diluting 0.01 M stock solutions prepared from differentially weighed samples of $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$,

* For Part II see Ref. [1].

$MnCl_2 \cdot 4H_2O$, and $SnCl_2 \cdot 2H_2O$, all of them anal. grade (Lachema, Brno). Recrystallized $PbCl_2$ [2] was used to prepare a standard solution of lead(II) salt. Solution of 1,10-phenanthroline was obtained from the preparation (0.03 g) dissolved in a small amount of ethanol and the volume was made up to 50 ml with water.

The common acetate and urotropine buffer solutions chosen for pH adjustments were prepared by mixing 0.2 M acetic acid with 0.2 M sodium acetate and 0.5 M nitric acid with 0.5 M urotropine, respectively.

A pH-meter OP-201/2 (Radelkis, Budapest) with glass and saturated calomel electrodes was employed for pH measurements. Photometric microtitrations were performed on a Spekol spectrophotometer (Zeiss, Jena), equipped with a special titration adapter [3]. The chelatone solution was measured by a piston microburette with a micrometer screw shifting the piston within the range of 25 mm. The microburette with total volume of *ca.* 500 μl was calibrated by weighed samples of water stratified with a layer of paraffin oil. The precision of measuring was given by the standard deviation $s_0 = 0.5$ μl.

Selection of optimum conditions for chelatometric titrations

The method of photometric microtitrations proved convenient for the study of the influence of the medium upon the slope of transitions of metallochromic indicators [4, 5]. A criterion for the selection of the optimum medium for the used indicator is the slope of photometric titrations curves, measured in the region of an absorption band of the free indicator or its metal chelate. The blue coloured solutions of metal chelates of methylxylenol blue exhibit absorption maxima in the range of wavelengths from 600 to 620 nm. Since mild acidic solutions of the free indicator show nearly no absorption of the radiation at such wavelengths, the greatest difference in the absorbance values is attained in this region.

The slope of the photometric titration curves was studied in the media of acetate and urotropine solutions, most often applied in chelatometric determinations of bivalent metals. The procedure was as follows: 0.001 M solution of metal salt (3 ml), buffer solution (2 ml), *ca.* 0.00015 M methylxylenol blue solution (2 ml), and water (13 ml) were measured in unaltered amounts for each titration into a cell with 50 mm path-length and volume 20 ml (type C, Zeiss, Jena). The cell was placed in the titration adapter and the solution titrated with 0.01 M chelatone. A set of photometric titration curves resulted from the titrations in various buffer solutions; an example of the titrations of lead(II) is seen in Fig. 1.

The optimum pH range of the titrated solutions is apparently given by the sharpest slope of the photometric titration curves before the end of the titration. In acidic solutions, where the apparent stability constant of chelatonate of the titrated metal decreases, the slope of the titration curve decreases too. On the other hand, pH of the solution must be adjusted to prevent the influence of the protolytic equilibria of the metallochromic indicator. For methylxylenol blue, pH should not exceed the upper limit 6.0 where the acid-base colour transition from yellow to blue, characterized by $pK_{a3} = 7.0$ [1], begins to take place.

It appears that the decisive factor for the optimum course of the photometric curve is not only to adjust a certain pH value but also to choose a suitable kind of buffer.

Our experience with the chelatometric determinations of the studied metals is thus summarized in the following paragraphs.

Determination of lead

Our study of the influence of pH on the shape of the titration curves revealed no substantial differences in the pH range 5.0—5.5 in urotropine solutions. The sensitivity

of methylxylenol blue decreased slightly when acetate buffer solutions were used. However, the difference in the course of titration curves disappeared when pH of the acetate solutions was increased by a half unit. Thus the sharpest slope of the colour change in the acetate

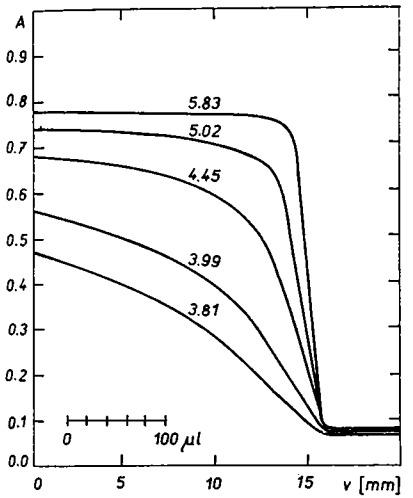

Fig. 1. The influence of pH on the shape of photometric titration curves corresponding to the determination of lead in acetate buffers.
$c_{Pb} \approx 1.4 \times 10^{-4}$ M, $c_I = 1.29 \times 10^{-5}$ M, $\lambda = 610$ nm, $d = 50$ mm.

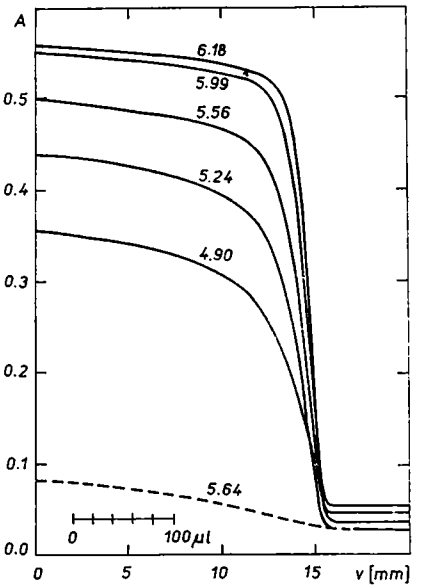

Fig. 2. The influence of pH on the shape of photometric titration curves corresponding to the determination of mercury in urotropine (full lines) and acetate (dashed line) buffers.
$c_{Hg} \approx 1.4 \times 10^{-4}$ M, $c_I = 1.20 \times 10^{-5}$ M, $\lambda = 600$ nm, $d = 50$ mm.

solutions was observed at pH 5.5—6.0. These conclusions quite agree with the results achieved in the study of titrations of lead(II) ions with methylthymol blue [5]. Many metals can be masked by addition of 1,10-phenanthroline [6] or cyanides [7], which increases the selectivity of the chelatometric determination of lead.

Determination of zinc

The sharpest colour change was achieved in the pH range 5.5—6.0 in both urotropine and acetate buffer solutions. In this medium the transition is also most colour-expressive while an acid-base transition begins at higher pH.

Determination of cadmium

Titrations of cadmium are usually reported [8] to be analogous to the zinc titrations. However, our study led us to a different conclusion. The titrations of cadmium(II) in urotropine buffer solutions showed the sharpest and the most expressive colour change at pH as high as 6.3 in spite of the beginning protolytic equilibrium of the indicator.

Determination of mercury

The sharpest and the most expressive colour change of methylxylenol blue occurred in the medium buffered by urotropine to pH 6.0 (Fig. 2). The acetate buffer solutions decreased considerably the apparent stability constant of the indicator chelate with metal, making thus impossible a microdetermination of mercury in the presence of acetate.

Determination of copper

Chelatometric determinations of copper(II) ions represent an interesting problem. A direct titration against xylenol orange or methylthymol blue is impossible since the chelates of these indicators with Cu^{2+} are more stable than copper(II) chelatonate. The same has been observed with methylxylenol blue [1]. Deblocking of the indicator transition is usually achieved by addition of 1,10-phenanthroline [9] or other complexing agent [10, 11]. Our study confirmed the advantageous use of the acetate buffer solutions for titrations with methylxylenol blue indicating the end point. The ratio of the apparent stability constants of the complexes of the indicator and chelatone was so changed that only a minimal addition of 1,10-phenanthroline was required to achieve a sharp colour transition (*ca.* 20 μl of 0.06% phenanthroline solution per 20 ml of titrated solution). The titrations in urotropine buffers required much greater addition of 1,10-phenanthroline bringing about systematic negative errors. As the most convenient medium we selected the acetate buffer with pH 5.6.

Determination of cobalt

In spite of the expectation, cobalt(II) ions could be very reliably determined by direct titration if the acidity of the titrated solution ranged from pH 5.4 to 5.7. At pH lower

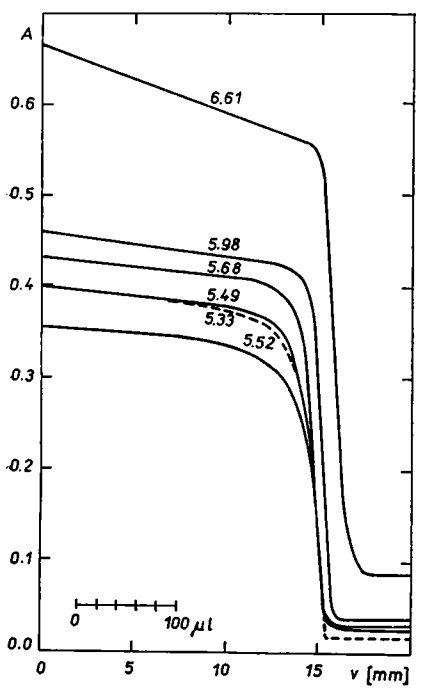

Fig. 3. The influence of pH on the shape of photometric titration curve corresponding to the determination of cobalt in urotropine (full lines) and acetate (dashed line) buffers.
$c_{Co} \approx 1.4 \times 10^{-4}$ M, $c_I = 1.22 \times 10^{-5}$ M, $\lambda = 610$ nm, $d = 50$ mm.

Symbol v in Figs. 1—3 stands for consumptions of 0.01 M volumetric solution of Chelatone 3. A segment plotted in each figure helps to convert the data in mm of the piston shift of microburette to μl of the Chelatone 3 consumed.

than 5.0, a marked decrease of the slope of titration curve was observed. When the pH exceeded the mentioned range, the time dependence of the measured absorbance values became evident. At pH 6.6 the absorbance values were unceasingly and slowly decreasing after each chelatone addition, thus making impossible any reliable recording of the titration curve (see Fig. 3). It should be noted that *Zimáková* [12] reported similar observations concerning titrations of the microgram amounts of cobalt using xylenol orange. Methylxylenol blue appeared to be convenient also for visual titrations of 0.01 M solutions of cobalt(II) salts while indications with pyrogallol red, pyrocatechol violet or even xylenol orange failed.

Determination of manganese

Methylxylenol blue forms a blue complex also with manganese(II) ions but the sharpest colour change was attained at pH as high as 6.3—6.4 in urotropine solutions. The titrations had to be carried out in the presence of a reducting agent (hydroxylamine, *etc.*) and the slope of titration curves was rather moderate.

Determination of tin

Only one macromethod for direct chelatometric determination of tin(II) has been described [21] till now, with methylthymol blue at pH 5—6. Our attempts at the analogous direct titration with methylxylenol blue were unsuccessful. Although we tried to eliminate the interfering oxidation by atmospheric oxygen, the absorbance values were unsteady for more than 5 min and the obtained photometric titration curves were unreproducible. Microdetermination of tin using methylxylenol blue was not possible.

Discussion

The precision and the accuracy of the visual microtitrations using methylxylenol blue were tested by comparison with common and recommended [8, 15] methods. All the titrations with the visual indication were carried out in a comparative arrangement [14] while the conditions (volume of the titrated solution, concentration of metal and reagent, concentration of chelatone in the volumetric solution, and the style of its measuring) remained the same as for the study of the photometric titration curves. Under this experimental arrangement we could evaluate statistically the results of titrations.

To compare the precision of two methods, the F test was used

$$F = s_A^2/s_B^2, \qquad s_A > s_B \tag{1}$$

and the mutual agreement of two different methods was verified by means of the t test

$$t = (|\bar{x}_A - \bar{x}_B|) \left[\frac{(n_A + n_B)\,(n_A\, s_A^2 + n_B\, s_B^2)}{n_A\, n_B (n_A + n_B - 2)} \right]^{-\frac{1}{2}} \tag{2}$$

In this formula, $\bar{x}_A$ and $\bar{x}_B$ are arithmetic means of the results of the methods A and B respectively, s_A and s_B estimates of standard deviations, n_A and n_B numbers of the parallel determinations.

The calculated F and t values were compared with tabulated values, F for the degrees of freedom $\nu_A = n_A - 1$ and $\nu_B = n_B - 1$ while t for the degree of freedom $\nu = n_A + n_B - 2$ [13]. Statistical evaluations of the results of the titration determinations are listed in Table 1.

Table 1

Statistical evaluation of the results of titration methods

Titrated metal ion	Indication and reference	pH	n	$\bar{x}$ 0.01 M-EDTA [μl]		Interval estimate μ [μl]	t Test		F Test	
							t_{calc}	t_{crit}	F_{calc}	F_{crit}
Pb^{2+}	Methylxylenol blue	5.2[a]	10	308.0	1.4	307.0–309.0	1.436	2.060	1.12	2.54
	Xylenol orange [14]	5.2[a]	17	308.9	1.3	308.1–309.4		—		—
Zn^{2+}	Methylxylenol blue	5.7[a]	14	298.8	1.2	298.1–299.4	0.197	2.055		—
	Zincon [16]	9.0[b]	14	298.9	1.7	297.9–300.0		—	1.82	2.57
Cd^{2+}	Methylxylenol blue	6.1[a]	13	293.4	1.6	292.4–294.4	1.291	2.074	1.57	2.91
	Eriochrome black T [17]	9.8[b]	11	294.3	1.3	293.4–295.2		—		—
	SNAZOXS [18]	5.5[a]	7	293.8	1.4	292.5–295.0	0.736	2.120	1.06	3.22
Hg^{2+}	Methylxylenol blue	6.0[a]	14	303.0	3.0	301.3–304.7	2.579	2.093	1.06	4.03
	Potentiometric [8]	5.2[a]	7	306.7	2.9	304.1–309.4		—		—
Cu^{2+}	Methylxylenol blue	5.6[c,d]	14	236.8	2.4	235.4–238.2	0.561	2.093		—
	Potentiometric [19]	4.8[c]	7	236.1	2.7	233.6–238.6		—	1.23	2.92
	PAN [20]	4.5[c,e]	14	244.9	4.9	242.0–247.7	4.165	2.093	4.10	2.57
Co^{2+}	Methylxylenol blue	5.4[a]	14	304.1	4.3	301.6–306.6	0.923	2.086	4.07	3.55
	Xylenol orange [12]	5.5[a]	8	305.7	2.2	303.9–307.5		—		—
Mn^{2+}	Methylxylenol blue	6.2[a]	10	302.9	5.8	298.7–307.0	3.481	2.074	5.26	2.72
	Eriochrome black T [8]	9.7[b]	14	309.2	2.5	307.8–310.6		—		—

a) Urotropine buffer solution; *b*) ammonia buffer; *c*) acetate buffer; *d*) with a minimum addition of 1,10-phenanthroline; *e*) titration in 50% EtOH exhibits the time dependence and is inconvenient for microgram amounts.

The results of the t test showed that in most cases the chelatometric titrations in the presence of methylxylenol blue are not laden with systematic errors in comparison with other recommended methods and also their precision is comparable (values of t_{crit} and F_{crit} are considered for the significance level $\alpha = 0.05$). Methylxylenol blue exhibits advantageous sharp colour transitions from the blue to yellow hues, *i.e.* nearly between the complementary colours. This introductory study thus makes possible to recognize methylxylenol blue as one of the most likely indicators for chelatometric determinations of cadmium(II), copper(II), mercury(II), zinc(II), and especially lead(II) ions in the mild acidic medium. Analogously we may expect future applications of this dye in chelatometric titration of microgram amounts of polyvalent metals and also in some indirect determinations.

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