Sulfonephthalein dyes. V.*
Characterization of the colour changes of methylxylenol blue in chelatometric titrations

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The colour changes of methylxylenol blue in the chelatometric titrations of Cd^{2+}, Ce^{3+}, Co^{2+}, Cu^{2+}, Er^{3+}, Hg^{2+}, La^{3+}, Mn^{2+}, Pb^{2+}, Sc^{3+}, Sm^{3+}, and Zn^{2+} were studied spectrophotometrically. The absorption spectra of the titrated solutions were used for the calculation of the course of colour change curves in the colorimetric $CIE—xy$ triangle and the complementary $Q_x Q_y$ diagram. On the basis of this objective valuation the accuracy of visual titrimetric determinations was characterized by the indices of perceptibility of the colour change of methylxylenol blue at the end-point $(\Delta v/\Delta E)_{a \to 1}$

Спектрофотометрическим методом были изучены изменения окраски метилксиленолового синего при хелатометрическом титровании Cd^{2+}, Ce^{3+}, Co^{2+}, Cu^{2+}, Er^{3+}, Hg^{2+}, La^{3+}, Mn^{2+}, Pb^{2+}, Sc^{3+}, Sm^{3+} и Zn^{2+} Из спектров поглощения титрованных растворов был рассчитан ход кривых перехода окраски в колориметрическом треугольнике $CIE—xy$ и дополнительной диаграмме $Q_x Q_y$. На основании этого объективного рассмотрения была оценена точность визуального титрования при помощи показателей наблюдаемости изменения окраски метилксиленолового синего в конце титрования $(\Delta v/\Delta E)_{a \to 1}$.

In the preceding communications [1—3] we paid attention to the chromogenic reactions of methylxylenol blue. The optimum medium for the chelatometric determinations of bivalent metals [2] and rare earth metals [3] was established by the method of photometric titration using methylxylenol blue as a metallochromic indicator. The photometric titration curves describe the steepness of the colour change. The values of transmittance or absorbance measured in the range of indicator change in the region of visible radiation (380—770 nm) are basic data for the specification of the colour hues of the titrated solutions. By processing these sets of data on a computer [4] the values of trichromatic components and coordinates in the CIE systems and the complementary $Q_x Q_y$ triangle are to be obtained (the methods of calculation were discussed earlier [5]). The colour change of indicator is thus objectively characterized by the chromaticity curve of the

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transition in the *CIE—xy* or *CIE—uv* triangle and the corresponding change in relative luminance. This objective method of the characterization of indicator changes proved already earlier to be well suited for a comparative study of the suitability of different metallochromic indicators for the titration of lead [6] and zinc [7]. However, for the time being there is a lack of systematic data for a certain indicator under specified conditions.

Experimental and results

Solutions, instruments, and methods of measurement

The preparation of the solutions of metal ions (approximately 10^{-3} M), volumetric EDTA (10^{-2} M) solution, methylxylenol blue solution (1.5×10^{-4} M), and buffer solutions was described in preceding communications [2, 3]. The instruments used for photometric microtitrations and pH measurements were also described in the cited papers.

The absorption spectra of the titrated solutions were preliminarily measured on a recording spectrophotometer Specord UV VIS (Zeiss, Jena). For more precise measurements from the view-point of colour specification [8] spectrophotometers VSU-1 and VSU-2G were used. These instruments were tested by means of standard solutions of K_2CrO_4, $(NH_4)_2Co(SO_4)_2$, and $CuSO_4$ [9]. The composition of the titrated solutions was the same as in photometric and visual titrations [2, 3] and the results of spectrophotometric measurements are quoted for equal width of the absorbing layer (50 mm).

Chromaticity curves of the change of methylxylenol blue in colorimetric systems

The results of the spectrophotometric measurements are illustrated by an example (Fig. 1) which embraces the absorption spectra of methylxylenol blue in the chelatometric titration of cadmium. At the beginning of the titration the concentration of metal c_M is tenfold with respect to the concentration of indicator c_i. The absorption maximum of the blue indicator complex ($a = [I']/c_i = 0$) decreases in the course of titration and simultaneously the maximum in the region of absorption of the free form of indicator (440—450 nm, $a = 1$) increases. The position of the absorption maximum of metal chelates of methylxylenol blue varies only slightly. The following values of λ_{max} (in parentheses, nm) were determined for individual metals: Cd^{2+} (613), Ce^{3+} (606), Co^{2+} (618), Cu^{2+} (598), Er^{3+} (602), Hg^{2+} (622), La^{3+} (607), Mn^{2+} (620), Pb^{2+} (614), Sc^{3+} (588), Sm^{3+} (604), and Zn^{2+} (600). In no case do the absorption spectra of the titrated solutions intersect in isosbestic point, which indicates that the individual partial equilibria are not negligible in the formation and decomposition of indicator complexes. It follows that the colour changes of methylxylenol blue in chelatometric titrations cannot be calculated from the absorption spectra of the limiting forms of indicator (see [7]) without knowledge of the equilibrium constants of individual partial reactions. The specification of colour shade is therefore quoted in the range of the whole colour change in Table 1.

In chelatometric titrations of more concentrated solutions of the metals the hydrated ions or chelatonates of which are coloured a mixing of colours takes place. For instance, Fig. 2 illustrates the superposition of the absorption spectrum of copper(II) chelatonate on the spectrum of methylxylenol blue in the proximity of equivalence.

The course of the chromaticity curves of the colour change of methylxylenol blue for some systems

Table 1

Colour changes of methylxylenol blue in chelatometric titrations

Titrated metal ion M^{n+}	pH	Consumption 0.01 M-EDTA µl	A_λ	System *CIE*			Complementary system		
				Y	x	y	Q_x	Q_y	J
Cd^{2+}	6.33[a]	0.0	0.625[f]	43.0	0.255	0.274	0.396	0.370	0.756
		252.1	0.471	48.8	0.280	0.301	0.360	0.339	0.685
		282.8	0.346	54.9	0.307	0.327	0.316	0.300	0.636
		302.1	0.174	67.0	0.345	0.360	0.247	0.233	0.553
		370.8	0.055	80.3	0.370	0.385	0.182	0.155	0.475
Ce^{3+}	5.18[b]	0.0	0.609[e]	43.8	0.255	0.264	0.402	0.389	0.709
		232.1	0.432	51.0	0.286	0.295	0.355	0.350	0.621
		257.7	0.266	60.2	0.321	0.328	0.292	0.295	0.549
		267.3	0.156	68.3	0.344	0.350	0.243	0.244	0.499
		320.1	0.020	87.1	0.365	0.382	0.163	0.124	0.380
Co^{2+}	5.47[a]	0.0	0.677[g]	42.2	0.250	0.274	0.403	0.367	0.780
		267.0	0.520	46.6	0.275	0.298	0.366	0.341	0.727
		281.8	0.351	53.5	0.308	0.325	0.315	0.303	0.657
		291.1	0.173	64.2	0.346	0.356	0.249	0.244	0.582
		370.8	0.032	80.3	0.375	0.386	0.174	0.154	0.484
Cu^{2+}	5.68[b]	0.0	0.557[e]	36.9	0.280	0.271	0.350	0.368	0.874
		264.2	0.429	43.3	0.303	0.303	0.321	0.333	0.802
		278.1	0.246	56.1	0.342	0.348	0.266	0.267	0.690
		287.3	0.142	66.9	0.366	0.377	0.220	0.208	0.628
		370.8	0.040	81.6	0.381	0.404	0.173	0.130	0.546
Er^{3+}	5.66[a]	0.0	0.674[e]	43.8	0.240	0.247	0.436	0.419	0.680
		288.1	0.450	51.0	0.274	0.275	0.382	0.388	0.568
		296.1	0.189	66.4	0.326	0.326	0.276	0.292	0.466
		300.9	0.060	81.4	0.353	0.363	0.195	0.180	0.373
		336.1	0.025	87.3	0.360	0.377	0.168	0.129	0.354
Hg^{2+}	6.04[a]	0.0	0.658[g]	44.1	0.253	0.284	0.400	0.357	0.760
		255.8	0.502	48.4	0.275	0.302	0.366	0.336	0.698
		270.6	0.340	56.0	0.308	0.329	0.314	0.296	0.623
		280.0	0.182	65.3	0.340	0.353	0.255	0.247	0.552
		370.8	0.052	80.0	0.366	0.382	0.188	0.159	0.500
La^{3+}	5.67[a]	0.0	0.611[f]	46.8	0.249	0.264	0.423	0.395	0.648
		276.9	0.422	53.5	0.280	0.292	0.371	0.359	0.564
		289.7	0.250	62.1	0.315	0.321	0.302	0.306	0.491
		294.5	0.107	75.1	0.344	0.354	0.229	0.221	0.416
		328.1	0.018	88.0	0.360	0.376	0.163	0.126	0.346

Table 1 (Continued)

Titrated metal ion M^{n+}	pH	Consumption 0.01 M-EDTA μl	A_λ	System *CIE*			Complementary system		
				Y	x	y	Q_x	Q_y	J
Mn^{2+}	6.30^a	0.0	0.826^g	34.4	0.249	0.289	0.383	0.342	1.044
		139.1	0.658	38.9	0.275	0.317	0.353	0.317	0.972
		222.4	0.422	48.2	0.325	0.355	0.293	0.270	0.862
		268.8	0.214	60.5	0.366	0.387	0.235	0.214	0.764
		370.8	0.061	74.4	0.394	0.410	0.180	0.149	0.681
Pb^{2+}	5.83^b	0.0	0.870^f	28.0	0.230	0.237	0.400	0.386	1.107
		273.4	0.640	33.7	0.269	0.273	0.358	0.359	0.980
		282.8	0.398	43.3	0.319	0.319	0.302	0.312	0.852
		292.0	0.192	56.4	0.363	0.361	0.241	0.249	0.744
		370.8	0.048	78.0	0.392	0.410	0.172	0.137	0.633
Sc^{3+}	2.50^c	0.0	0.776^d	38.6	0.250	0.235	0.409	0.430	0.787
		259.3	0.478	48.6	0.290	0.283	0.350	0.371	0.643
		268.9	0.200	65.7	0.339	0.336	0.255	0.272	0.495
		274.5	0.079	77.7	0.359	0.364	0.197	0.194	0.426
		304.1	0.019	87.7	0.367	0.384	0.158	0.118	0.382
Sm^{3+}	5.25^a	0.0	0.639^e	43.0	0.249	0.255	0.414	0.403	0.707
		283.3	0.439	50.0	0.284	0.289	0.359	0.359	0.625
		292.1	0.205	64.2	0.329	0.330	0.275	0.287	0.492
		294.5	0.078	77.8	0.355	0.363	0.204	0.194	0.420
		328.1	0.021	87.2	0.364	0.381	0.164	0.124	0.374
Zn^{2+}	5.80^b	0.0	0.742^e	31.5	0.252	0.245	0.381	0.388	0.990
		276.2	0.530	38.6	0.293	0.291	0.334	0.344	0.887
		287.3	0.360	47.3	0.330	0.328	0.289	0.300	0.797
		297.6	0.200	60.0	0.362	0.368	0.237	0.235	0.702
		370.8	0.050	78.8	0.391	0.406	0.170	0.138	0.603

For the definition of the trichromatic quantities Y, x, y or Q_x, Q_y, J see Ref. [5]. Measured in the medium of urotropine (*a*), acetate (*b*), formate buffer solution (*c*). The values of absorbance A_λ are quoted for the wavelengths λ 590 (*d*), 600 (*e*), 610 (*f*), 620 nm (*g*); concentration of metal $c_M \approx 1.5 \times 10^{-4}$ M; concentration of indicator $c_i \approx 1.5 \times 10^{-5}$ M; $d = 50$ mm.

studied is shown in Fig. 3. The curves pass closely by the point of the standard source and some of them even pass through it (*e.g.* in titrations of La^{3+} and Ce^{3+}). This fact demonstrates that the colours of the limiting forms of indicator are practically complementary. The colour change from blue to yellow shows therefore an achromatic medium part, which contributes to the achievement of accurate results even at visual observation of the end-point [2, 3]. In this line a change in the values of relative luminance manifests itself significantly.

Perceptibility of colour change

The reliability of the results of chelatometric titrations in the range of microgram concentrations depends considerably on the way in which the colour hue of the titrated solution changes immediately before the end of titration while the titration usually continues until all indicator bonded in the complexes with the titrated metal is released, *i.e.* to the values $\alpha \rightarrow 1$. We recommended [10] to introduce the perceptibility of the colour change which was defined as an addition of the volumetric solution of chelatone (Δv) necessary for a unit change in colour $(\Delta v/\Delta E)_{\alpha \rightarrow 1}$ for the criterion of accuracy of chelatometric titrations. The values of the index of perceptibility of colour change are given in Table 2.

Table 2

Evaluation of the steepness and perceptibility of the colour change
of methylxylenol blue before the end-point $(\alpha \rightarrow 1)$

Titrated metal ion M^{n+}	ΔA_λ	ΔE^a	$\Delta v/\Delta A_\lambda$ μl	$\Delta v/\Delta E$ μl
Cd^{2+}	0.127^c	17.2	117.9	0.872
Ce^{3+}	0.127^d	18.6	79.1	0.540
Co^{2+}	0.143^d	20.2	52.7	0.373
Cu^{2+}	0.102^c	14.8	73.2	0.504
Er^{3+}	0.035^c	7.0	32.2	0.161
Hg^{2+}	0.113^c	18.3	64.2	0.396
La^{3+}	0.089^d	13.3	36.9	0.247
Mn^{2+}	0.142^c	18.7	300.1	2.283
Pb^{2+}	0.144^d	25.3	41.9	0.239
Sc^{3+}	0.060^b	10.7	24.4	0.137
Sm^{3+}	0.057^c	9.5	35.2	0.210
Zn^{2+}	0.150^c	22.0	58.0	0.396

a) The colour differences ΔE were calculated according to the formula CIE (1964). The differences between the values of absorbance ΔA_λ were read at wavelengths λ 590 (b), 600 (c), 610 (d) nm.

Discussion

The study of the colour change of methylxylenol blue involving the application of colorimetric systems showed the virtues of this metallochromic indicator in visual chelatometric determinations of the salts of the metals studied. The index of perceptibility of the colour change of indicator before the end-point $(\Delta v/\Delta E)_{\alpha \rightarrow 1}$ comprises both criteria significant of the attainable accuracy of determination, *i.e.* steepness and colour quality of the indicator change. The values of perceptibility of a colour change may be correlated with the estimates of standard deviations in visual comparative titrations [10]. Of course, the dosing accuracy of titration agent
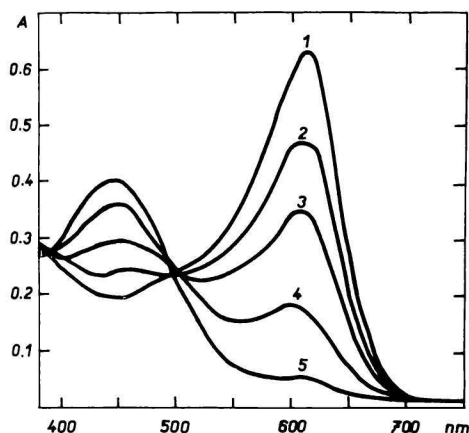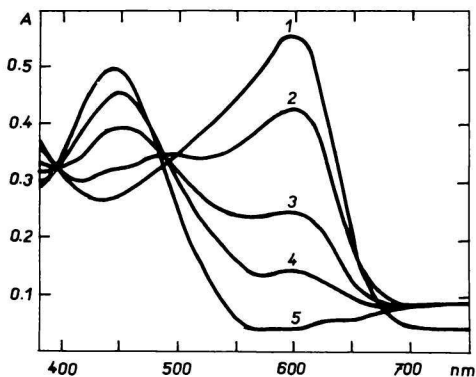
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Fig. 1. Absorption spectra of a solution of Cd(II) salt titrated with a 0.01 M solution of EDTA using methylxylenol blue as an indicator.

$c_{Cd} \approx 1.5 \times 10^{-4}$ M; $c_i = 1.2 \times 10^{-5}$ M; pH = 6.33; $d = 50$ mm; recorded for the consumption (*1*) 0.0; (*2*) 252.1; (*3*) 282.8; (*4*) 302.1; (*5*) 370.8 μl.
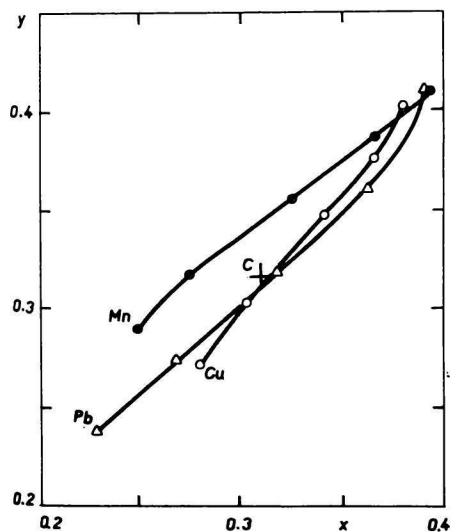

Fig. 2. Absorption spectra of a solution of Cu(II) salt titrated with a 0.01 M solution of EDTA using methylxylenol blue as an indicator.

$c_{Cu} \approx 1.5 \times 10^{-4}$ M; $c_i = 1.5 \times 10^{-5}$ M; pH = 5.68; $d = 50$ mm; recorded for the consumption (*1*) 0.0; (*2*) 264.2; (*3*) 278.1; (*4*) 287.3; (*5*) 370.8 μl.

Fig. 3. Course of the chromaticity curves of the methylxylenol blue change in the chelatometric titrations of Mn^{2+}, Pb^{2+}, and Cu^{2+} represented in a sector of the colorimetric *CIE—xy* triangle. *C* — Achromatic point for the *CIE* standard source *C*.
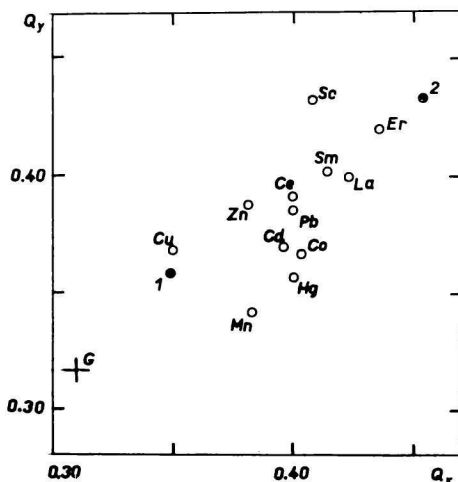

Fig. 4. Position of the complementary colour points of the complexes of methylxylenol blue in a sector of the $Q_x Q_y$ triangle.

Black points correspond to symmetric structures of the indicator at pH 8.94 (point *1*, H_2I^{4-}), or H— 14.40 (point *2*, I^{6-}); *G* — achromatic "grey" point.

(kind of microburette) must be taken into account. Moreover, if the results of the determinations of different cations are compared, the individual differences in the behaviour of these cations in dilute solutions may also manifest themselves.

The solutions of methylxylenol blue show distinct absorption bands at about 600 nm in the presence of metal ions and are coloured similarly as the solutions of some of their protonated particles with a symmetric resonance structure. In general, it is assumed [11] that the solutions of metal chelates of a metallochromic indicator show the same colour as the solution of its fully deprotonated anion. This comparison may be performed objectively by using the positions of complementary points in the Q_xQ_y triangle which are plotted in Fig. 4 for methylxylenol blue. The colour hue of metal chelates usually more resembles that of the free indicator form H_2I if the proton of the second hydroxy group has been split off (see [1]).

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