ACHROMATIC SCREENING OF METALLOCHROMIC INDICATORS AS A CORRECTION METHOD FOR VISUAL END-POINT LOCATION*

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The method of calculation of composition of screened indicators suggested by Reilley and Flaschka has been applied successfully to modify the colour changes of metallochromic indicators in chelatometric titrations of metal ions. As examples of the screening, the indicators Eriochrome Blue SE and SNAZOXS used for titrations of zinc and copper(II), respectively, have been presented to show how the indicator colour change can be modified by a suitable choice of inert colour background to achieve an achromatic (grey) end-point colour. This technique of screening allows an easy shift of the visual end-point to the region of the steepest colour change of the indicator; thus, more precise results can be obtained. This correction of visual end-point helps also to diminish the difference from the chosen reference method.

The colour change of a metallochromic indicator, which was found to be less convenient in titrations of some metals, has often been modified empirically by addition of a suitable dyestuff. Although it was possible to improve somewhat the quality of colour change in number of cases (for examples see ref.[1]), the achromatic end-point was achieved only exceptionally. The solution being titrated can appear to be grey at the end-point only when the background colour is precisely complementary to that of the indicator under given illumination.

The objective way of preparation of screened chemical indicators suggested by Reilley, Flaschka and coworkers[2-4] is based on a relationship allowing (for dilute solutions only) a simple transformation between the x, y, z co-ordinates of the tristimulus CIE-xy system and the corresponding co-ordinates Q_x, Q_y, Q_z of the complementary colorimetric triangle. For example, it holds:

$$x = G_x - J(Q_x - G_x) = G_x - JV_x \,. \qquad (1)$$

Analogous equations relating the y and z (generally denoted by r) co-ordinates and the Q_y, Q_z (generally Q_r) co-ordinates can be written. The complementary co-ordinates G_r correspond to the achromatic (grey) point of the complementary system, the position of which depends on the choice of the particular standard source of light (usually C is used). Equation (*1*) can also be interpreted so that the two complementary colour points Q_r and G_r define the components of the vector $\boldsymbol{V}_r$. The chromaticity co-ordinates x, y also depend on the value of the optical

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concentration J, which is proportional to the product of the concentration c of the colour solute, and the thickness d of the absorbing layer,

$$J = Ecd, \qquad (2)$$

where the overall absorption coefficient E of the complementary system is a constant of proportionality. Complete definitions of all symbols[2] and methods for calculation of co-ordinates and necessary quantities[5] were discussed previously. When a dilute indicator solution is mixed with two apposite inert dyestuffs, the achromatic point can be reached only if all vector components $J_i \cdot V_{r,i}$ with respect to particular axes (Eq. (*1*)) are mutually compensated.

In one of our previous papers[6] we suggested a selection of inert dyestuffs suitable for screening colour background. With all screened acid-base indicators studied we realized that it is possible to calculate safely the optimum composition of a colour background for the required degree of the indicator colour change, even though validity of Eq. (*1*) is limited to only low concentrations of the colour components in the solution[5].

Colour Change Screening of Metallochromic Indicator

The screening of metallochromic indicators represents a rather complicated problem. The colours of their extreme forms and, hence, the quality of the whole colour change are affected by several factors. At the beginning of a direct chelatometric titration the colour of the solution titrated depends on the kind of the metal ion and the reaction conditions determining the contributions of individual indicator complex forms in the solution. The terminal colour corresponds to the free indicator and depends on the contributions of individual protonated indicator forms in an overtitrated solution at a given pH value. In spite of the fact that in some cases the equilibrium of an indicator colour change can be complicated, the indicator transition can be characterized by the photometric titration curve measured at a suitable wavelength. Objective determination of the chromaticity curve of a given colour change in the respective CIE colorimetric system is based on experimental family of transmittance curves in the visible. This method of investigation of colour changes of metallochromic indicators was described in our previous papers[7,8]. The experience gained by applying the theory of colour to the investigation of indicator colour changes is summarized in a recent article[9].

The calculation of the tristimulus values from spectrophotometric data is relatively laborious. This was probably the main reason that the abovementioned way of preparation of screened indicators had not found a wider application. Out of metallochromic indicators only PAN was modified in this way for the titration of copper(II) (ref.[2]). To verify the applicability of the calculation method for the preparation of screened metallochromic indicators, we chose (on the basis of former study) Eriochrome Blue SE and SNAZOXS for the titrations of zinc(II) and copper(II), re-

spectively. At the same time we also tried to point at two of the typical problems which can be solved in chemical analysis with the aid of metallochromic indicators.

Eriochrome Blue SE, disodium 4,5-dihydroxy-3-(5'-chloro-2'-hydroxyphenylazo)-2,7-naphthalenedisulfonate, is one of the indicators suited for visual chelatometric titration of zinc[8]. It has a marked colour change from purple to blue. The method of visual comparison of the end-point colour[10] gave very precise results[11], which were, however, subject to a systematic positive error when compared with the results of potentiometric titrations. We tried to eliminate this deviation from the chosen reference method by screening the colour change of Eriochrome Blue SE in such a way that the achromatic grey colour is attained exactly at the required point of the indicator transition.

SNAZOXS, disodium 8-hydroxy-7-(1'-naphthylazo)quinoline-4',5-disulfonate, giving a red solution in mildly acidic medium, forms yellow complexes with a number of metals. In titrations of copper(II) its colour change goes through orange hues, which makes it not very suitable for visual indication. The colour change is steepest about the middle part of the transition; thus placing of the end-point to the region of the terminal colour of the free indicator may lead to inaccurate results. It was also realized that the salt effect must be taken into account.

EXPERIMENTAL AND RESULTS

Solutions, Apparatus and Methods of Measurements

Zinc nitrate solution (10^{-2}M) was prepared by dissolving 2·9747 g of the hexahydrate salt (Analar grade, Lachema) and making up to 1000 ml. The cupric salt solution (10^{-3}M) was prepared by dissolving 0·0627 g of copper (99·98%) in 1 ml concd. HNO_3 and making up to 1000 ml after boiling off the nitrogen oxides. For use the solutions were adequately diluted. The titrant solutions of Chelaton 3 (10^{-2}M and $5 . 10^{-3}$M) were standardized by visual titration of recrystallized $PbCl_2$ using Xylenol Orange[12].

Ammoniacal buffer solution was prepared by adding dil. ammonia (1 + 4) to 50 ml 0·5M-NH_4Cl and making up to 100 ml with water. Acetate buffer solution was obtained by mixing 0·332M sodium acetate and 0·2M acetic acid. The required ionic strength was adjusted with solutions of NaCl, KNO_3 and Na_2SO_4, respectively.

The stock solution of Eriochrome Blue SE was prepared from 0·1945 g reagent (Lachema) per 250 ml solution. The reagent was dissolved with addition of little ammonia, and the solution was stabilized with hydroxylamine hydrochloride. The stock solution of the indicator SNAZOXS was prepared from 0·0755 g reagent (Spolana) per 100 ml water. For preparation of screened indicators the solutions of the following inert dyestuffs were prepared (see ref.[6]): Tartrazine (45·12 mg/250 ml), Phenosafranine (0·19 mg/250 ml), Alizarin Violanol R (8·308 mg / / 100 ml), Alizarin Pure Blue B (8·124 mg/100 ml), Methylene Blue (2·56 mg/500 ml).

Absorption spectra were measured within 380—770 nm with a VSU-2G spectrophotometer (Zeiss, Jena) in 50 mm cells. Photometric microtitrations were carried out with a Spekol spectrophotometer (Zeiss) equipped with a titration attachment[13]. The titration cell (d 50 mm, V 20 ml — type C, Zeiss) was filled with 3 ml of 10^{-3}M-$Zn(NO_3)_2$ (or 5 ml $3 . 10^{-4}$M-$Cu(NO_3)_2$), 2 ml

of ammoniacal (or acetate) buffer solution, 2 ml of $\sim 1{\cdot}5 \cdot 10^{-4}$M indicator solution, and the respective amount of salt solution to adjust the chosen ionic strength. After addition of water (to the total volume 20 ml) the solutions were titrated with 10^{-2}M (or $5 \cdot 10^{-3}$M)-EDTA. For photometric and visual microtitrations a syringe microburette of a total volume 434 µl was used.

Screening of Eriochrome Blue SE for the Titration of Zinc

The transition of Eriochrome Blue SE is sufficiently steep during the determination of zinc (Fig. 1) and is not affected significantly by pH within 8 to 10. In an ammoniacal buffer solution (pH 9) the indicator colour change proceeds from a purple colour of the zinc complex (λ_{max} 555 nm, curve *1* in Fig. 2) to a blue colour of the indicator free form (λ_{max} 600 nm, curve *3*). The isosbestic point at 582 nm indicates predominant formation of a simple complex (for its trichromatic specification see ref.[8]). The chromaticity curve of this colour change (curve *1*, Fig. 4) is only slightly bended, indicating a smooth transition between the two extreme colours without any marked trend to dichroism.

The results of visual titrations were precise[11] and agreed with the end-point evaluated by linear extrapolation of a photometric titration curve (Fig. 1). In order to get a better agreement with the results of potentiometric titrations, it was necessary to titrate to a point when the fraction of the free indicator form attained the following value: $\alpha = [\text{In}']/c_{\text{In}} = 0{\cdot}8$. The blended colour for such chosen visual end-point cannot be well remembered. However, by means of a suitable screening the visual end-point can be adjusted so that the solution being titrated becomes "colourless" at the given value of the fraction α, *i.e.* the colour change passes through a grey hue at that point.

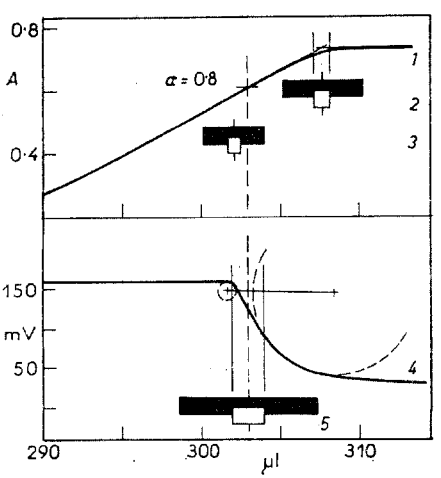

FIG. 1

Procedure for Screening of Eriochrome Blue SE

Photometric titration curve *1* with the statistically evaluated results obtained by visual end-point location with a comparison solution 2 and the titrations by memory using the screened indicator *3*; potentiometric titration curve 4 and the statistical evaluation of results *5*. Full rectangles give the interval $\bar{x} \pm 2s$, the empty ones give the reliability interval $\bar{x} \pm ts/\sqrt{n}$ (calculated for the significance level 0·05). Titration with 0·01M-EDTA solution.

The colour change of Eriochrome Blue SE can best be modified by addition of Tartrazine and Phenosafranine (for their tristimulus data see ref.[6]). For obtaining the achromatic hue of the titrated solution at $\alpha = 0{\cdot}8$ the ratio of the two inert

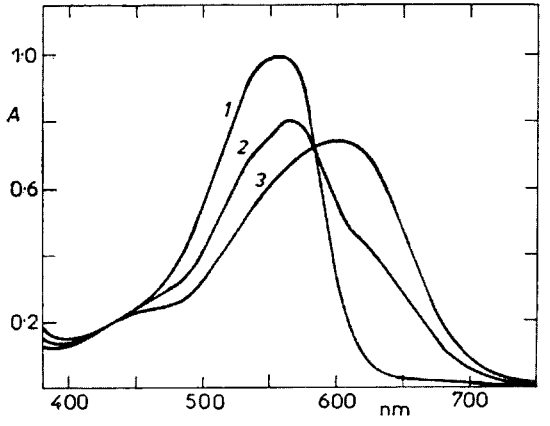

FIG. 2

Absorption Spectra of Solutions of Zinc(II) Titrated with 0·01M-EDTA using Eriochrome Blue SE as Indicator

$c_{Zn} = 1{\cdot}5 \cdot 10^{-4}$M; $c_{In} \sim 1{\cdot}5 \cdot 10^{-5}$M; pH 9·05; I 0·025; d 50 mm; additions of 0·01M-EDTA *1* 0·0; *2* 297·5; *3* 373·0 µl.

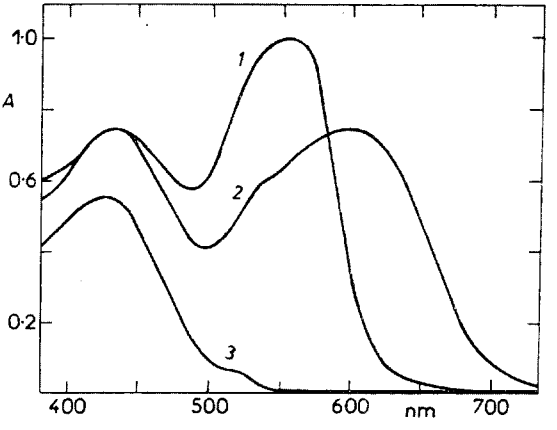

FIG. 3

Absorption Spectra for a Colour Change of Eriochrome Blue SE Screened for Chelatometric Titration of Zinc to the Value $\alpha = 0{\cdot}8$

1 The screened colour of the metal complex; *2* the screened colour of the free indicator; *3* the colour background formed by mixing Tartrazine and Phenosafranine.

dyestuffs and the indicator must be as follows: 1 mg Eriochrome Blue SE: 0·32 mg Tartrazine: 0·01 mg Phenosafranine (the Tartrazine solution has an almost complementary colour to that of the indicator at $\alpha = 0{\cdot}8$).

Absorbance curves of the titrated solution with the use of the screened Eriochrome Blue SE are given in Fig. 3. These photometric data were used for calculation of the tristimulus co-ordinates in the uniform chromaticity-scale diagram CIE-uv. The curve 2 in Fig. 4 confirms that the colour change of the screened indicator from pink to a bluish green hue passes through the achromatic point at the required phase of the indicator transition (for the CIE standard source C).

The screened Eriochrome Blue SE was used for a series of visual titrations arranged in the same way as with comparison microtirations[11]. However, the experimentator had no reference solution to compare the colours, and his task simply consisted in anouncing the end-point at the moment when the titrated solution appeared grey to him. Statistical evaluation (Fig. 1, Table IV) showed that the results of these titrations were equally precise as those based on end-point matching with a comparison solution. The deviations from the results of potentiometric titrations were only within the random experimental error (test t). On the contrary, the results of visual end-point location by memory ($\alpha = 0{\cdot}8$) using pure Eriochrome Blue SE were inaccurate, even though the indicator colour change was very steep. Accuracy of the results obtained with this type of screened indicator is determined mainly

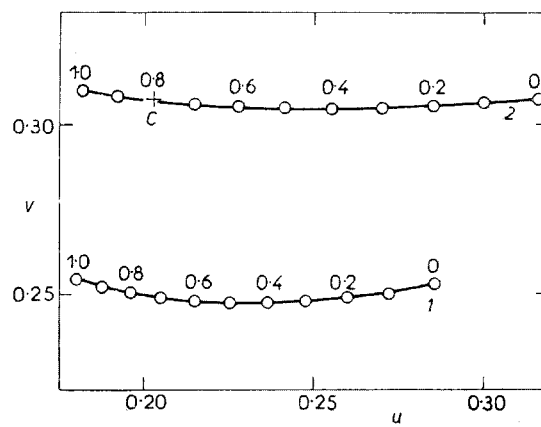

FIG. 4

The Curves of Eriochrome Blue SE Colour Change Represented in a Sector of the Uniform Chromaticity-Scale Diagram CIE-uv

1 The colour change of the indicator; *2* the colour change of the screened indicator; *C* the point of the standard source *C*; the numbers 0·0 to 1·0 denote the values of the fraction of the free indicator, $\alpha = [\mathrm{In}']/c_{\mathrm{In}}$.

by the ability of human eye to perceive slight colour changes in the region of the achromatic point which also can be well remembered. As it follows from the calculation[14] in the CIE-UVW space, there is a difference of 1·42 ΔE_{CIE} units between

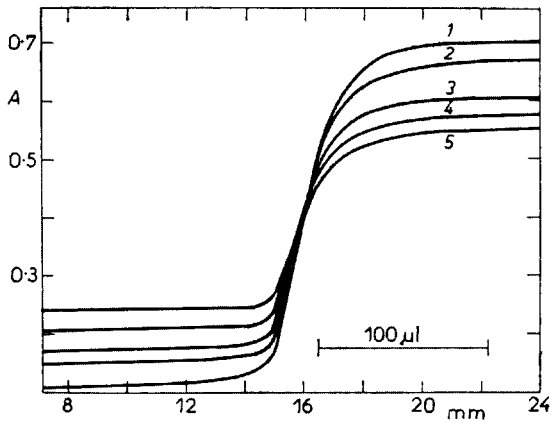

FIG. 5

Influence of Ionic Strength on the Shape of Photometric Titration Curves in-EDTA Titrations of Copper(II) using the Indicator SNAZOXS

$c_{Cu} = 7{\cdot}5 \cdot 10^{-5}$M; $c_{In} \sim 1{\cdot}5 : 10^{-5}$M; pH 5·9; *d* 50 mm; titration with 0·005M-EDTA; the ionic strength was adjusted with Na_2SO_4 to the following values *1* 0·03; *2* 0·108; *3* 0·182; *4* 0·332; *5* 0·632.

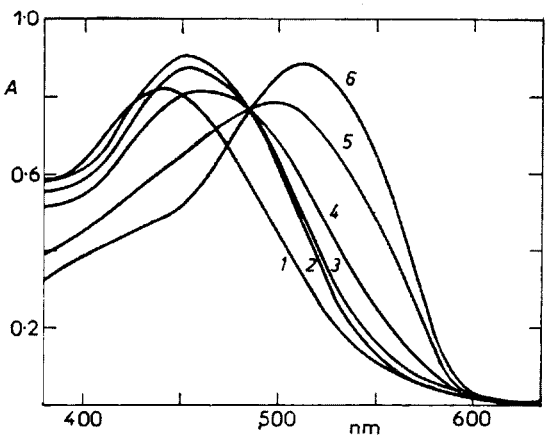

FIG. 6

Absorption Spectra of a Copper(II) Solution Titrated with EDTA using SNAZOXS as Indicator

$c_{Cu} = 7{\cdot}5 \cdot 10^{-5}$M; $c_{In} \sim 1{\cdot}5 \cdot 10^{-5}$M; pH 5·9; *d* 50 mm; *I* 0·03; additions of 0·005M-EDTA *1* 0·0; *2* 264·8; *3* 269·2; *4* 273·5; *5* 295·2; *6* 434·0 µl.

the colour of the screened Eriochrome Blue SE at $\alpha = 0{\cdot}8$ and the ideally achromatic hue having the same value of relative luminance. Such a slight difference in colour cannot be perceived by an average experimentator.

Screening of the Indicator SNAZOXS *for the Titration of Copper*(II)

The shape of photometric titration curves is affected considerably by the ionic strength of the titrated solution. Increasing concentration of indifferent salts brings about the bending in the final part of the curve so that the curve develops a distinct S-form (Fig. 5). Sodium sulphate and potassium nitrate affect the shape of the curve in the same way. Sodium chloride causes even more marked deformations of the titration curve. It can be seen form Fig. 5 that the indicator change is steepest in a narrow range of readings about the inflection points on the curves (about 285 µl), whereas in the following section it becomes more sluggish at higher ionic strength. If an abrupt colour change is desirable, it is advantageous to place the end-point just in this phase of the colour change and for this purpose the achromatic colour screening can again be used.

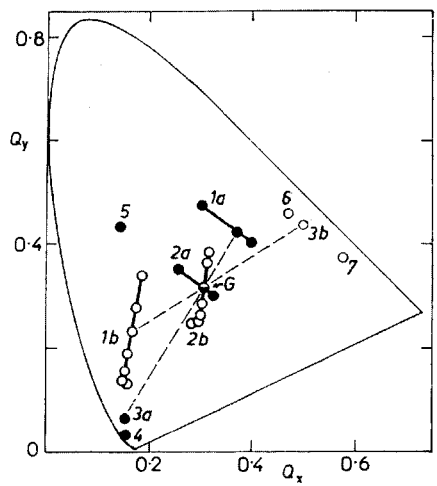

FIG. 7

Graphical Verification of Colour Changes of Screened Indicators in the Complementary Chromaticity Diagram Q_xQ_y

a Screening of Eriochrome Blue SE for titrations of zinc(II) (full points); $c_{Zn} = 1{\cdot}5 \cdot 10^{-4}$M; $c_{In} \sim 1{\cdot}5 \cdot 10^{-5}$M; pH 9·05; *I* 0·025; *b* screening of the indicator SNAZOXS for titration of copper(II) (empty points); $c_{Cu} = 7{\cdot}5 \cdot 10^{-5}$M; $c_{In} \sim 1{\cdot}5 \cdot 10^{-5}$M; pH 5·9; *I* 0·03; *d* 50 mm for all experiments. *1* The colour change of pure indicator; *2* the colour change of the screened indicator; *3* the mixture of inert dyestuffs forming the background of the screened indicator; complementary colour points *4* Tartrazine, *5* Phenosafranine, *6* Alizarin Pure Blue B, *7* Methylene Blue; *G* the achromatic point.

The absorption spectra of the solution measured during the titration of copper(II) (Fig. 6) indicate that a consecutive formation of complexes[3] takes part in the transition from the yellow complex indicator form (λ_{max} 440 nm, curve *1*) to red colour of the free indicator (λ_{max} 520 nm curve *6*).

The inert colour background modifying the indicator colour change to grey colour at the required end-point, lies on the straight line connecting the complementary colour point of the indicator at the given point of colour change and the achromatic point *G* (Fig. 7). This hue, which is complementary to the indicator colour at the end-point considered, can be adjusted by mixing two suitable inert dyestuffs at a proper ratio. From the recommended set[6] the best combinations were those in which Methylene Blue was mixed with Alizarin Pure Blue B or Alizarin Violanol R.

However, it was necessary to verify the influence of the salt effect on the absorption spectra of both the indicator in the considered range of the steep transition and the inert dyestuffs. From the spectrophotometric measurements and the calculation of the chromaticity co-ordinates it follows that the colour of solutions is affected especially by a higher salt concentration, the observed changes exceeding the experimental error[15]. Also the calculation of colour differences according to the CIE (1964) formula confirmed that the change in ionic strength is accompanied by a perceptible colour shift. When screened metallochromic indicators are prepared, it is thus advisable to base the calculation of mixture composition on the spectrophotometric data related to the ionic strength expected at the end-point. In Table I the calculated mixture compositions for individual ionic strength values are given. Changes in the weight proportions can be considered as significant. The composition

TABLE I

Examples of Colour Modifications of the Indicator SNAZOXS for the Titration of Copper(II) Weights of inert dyestuffs relate to 1·000 mg of the indicator.

Ionic strength	Variant I		Variant II	
	Methylene Blue mg	Alizarin Pure Blue B mg	Methylene Blue mg	Alizarin Violanol R mg
0·03	0·0969	1·0399	0·1712	0·5941
0·108	0·0939	0·9984	0·1597	0·5569
0·182	0·0988	0·8649	0·1612	0·3862
0·332	0·0687	1·1053	0·1364	0·6175
0·632	0·0557	1·2930	0·1321	0·6528
1·082	0·0420	1·4100	0·1268	0·7263

of the calculated mixtures (Fig. 7) was checked spectrophotometrically and by calculation of chromaticity co-ordinates.

Two combinations of screened indicators were further tested statistically using t and F tests[16] in a series of titrations with visual end-point estimation by memory. Two experimentators first titrated using the non-screened indicator SNAZOXS up to an orange hue corresponding to the end-point in the region of the steepest transition; this colour was shown to the experimentator before the titration series to be remembered. A second series of titrations in the same arrangement was carried out with the screened indicator. The end-point readings in the individual series differed within the random experimental error (Table II). When compared with results of titrations using the non-screened indicator, the determination of copper with screened indicators is not subject to any systematic error; however, the precision is far better. Thus the calculated mixtures of the screened SNAZOXS indicator can be recommended for a chelatometric determination of copper(II) in which a high precision is required.

TABLE II
Statistical Evaluation of Visual Titrations[a]

Indication	pH	I	n	$\bar{x}$ µl	s µl	t-Test		F-Test	
						t_{calc}	t_{crit}	F_{calc}	F_{crit}
				Zn^{2+}					
Eriochrome Blue SE[b]	9·05	0·025	28	307·7	1·2	9·565	2·013	1·47	1·90
Eriochrome Blue SE[c]	9·05	0·025	22	304·3	2·7	1·714	2·021	6·80	2·02
Screened Eriochrome Blue SE[c]	9·05	0·025	28	302·1	1·0	1·792	2·013	—	—
Potentiometric	5·35	0·03	20	302·9	2·1	—	—	4·37	2·09
				Cu^{2+}					
SNAZOXS[c]	5·9	0·03	20	284·9	9·9	0·524	2·025	59·35	2·21
Screened SNAZOXS[cd]	5·9	0·03	20	286·1	1·3	—	—	—	—
SNAZOXS[c]	5·9	0·332	10	284·7	5·4	0·553	2·101	145·0	2·97
Screened SNAZOXS[cd]	5·9	0·332	10	285·7	0·5	—	—	—	—

[a] Considered for the significance level $\alpha = 0{\cdot}05$; [b] comparison titration; [c] titration by memory; [d] variant I (Table I).

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