STANDARDIZATION OF DILUTE SOLUTIONS OF EDTA BY PHOTOMETRIC TITRATION WITH STANDARD TETRAAMMINECOPPER(II) TITRANT

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Direct photometric titration (without an added indicator) using a standard ammoniacal solution of copper(II) prepared from pure copper metal as a primary standard is recommended as a reliable method for the standardization of Na_2H_2(edta) in $10^{-3}-5 . 10^{-4}$M solutions. The technique of photometric microtitration (720 nm, 50 mm cell) with an increased precision of transmittance reading ($s \approx 10^{-2}\%$, $n > 7$) and in optimum medium of pH 4·7 ± 0·4 (acetate buffer) can yield precise results in assays of EDTA ($s_r \leqq 10^{-1}\%$, $n = 6-9$).

The accuracy attainable in chelometric titrations, which are often used to check standard metal solutions needed for calibrations of instrumental methods (e.g. AAS), is much affected by standardizing EDTA. This is even more evident with a dilute solution of EDTA (e.g. 10^{-3} mol l^{-1}) the concentration of which decreases with time[1] and should be controlled as necessary.

An overview of substances useful as standards for chelometry is available in basic monographs[2,3]. There are several previous contributions deserving further attention, namely the studies by Vřešťál et al.[4], Espersen and Jensen[5], and the critical survey by Chalmers[6] with an inspiring discussion of all problems involved. In authoritative studies presenting results from several laboratories bismuth[7] and zinc[8] were recommended as useful metal standards. In a paper inspired by previous work by Sweetser and Bricker[9] and by Underwood[10] Huldén and Harju[11] described a precise direct photometric titration of copper(II) with 0·05M-Na_2H_2(edta) (λ = 700 nm) at pH 5 (acetate buffer). Copper metal was recommended as a useful standard substance which is easily available in a high purity (99·999%). The end-point was calculated as intersection of two straight lines obtained by linear regression of particular sets of several points before and after the equivalence. Thus a relative standard deviation of 0·08% was obtained for one series of titrations (n = 7)[11]. As confirmed by our experiments, this procedure can be used for standardization of EDTA solutions within the concentration range 0·05–0·01 mol l^{-1}.

More dilute EDTA solutions are usually prepared by an appropriate dilution of such a stock EDTA solution – and this procedure may incur a systematic error. In order to achieve a level of accuracy required for instrumental microtitrations of microgram amounts of metals we found it necessary to investigate in some detail the conditions for a reliable standardization of EDTA solutions within the concentration range $1-0{\cdot}5$ mmol l^{-1}.

Our approach to standardization of such dilute EDTA titrant is based on exchange of the two reactants, using copper(II) solution as titrant. Direct photometric titration of copper(II)[9–11] can be based on the prevailing absorption of the increasing concentration of the chelate $[Cu(edta)]^{2-}$ which has an absorption maximum in the red region of the visible. Practically the same changes in absorbance can be obtained if a dilute EDTA solution to be standardized is titrated with approx. 80-times more concentrated solution of copper(II). When a pure copper metal is dissolved in nitric acid, a certain amount of the acid remains in excess and its is not easy to remove it just to the level required. The resulting solution should remain acidic in order to prevent hydrolysis of Cu(II). Thus after appropriate treatment and dilution to volume, a copper(II) solution of pH about 1 is obtained. With such titrant a common buffer will not prevent a decrease in pH, which may cause a curvature of the initial part of the titration curve.

As shown in our experiments, it is possible to maintain an optimum pH region more easily if an ammoniacal copper(II) titrant is used. Our attention was focused, therefore, on the development of a reliable procedure for the preparation of a standard tetraamminecopper(II) solution and on verification of its stability. Besides, it was necessary to find optimum conditions for its application in direct photometric microtitrations of dilute solutions of EDTA.

EXPERIMENTAL

Apparatus

For photometric titrations a single-beam spectrophotometer Spekol (Carl Zeiss, Jena) was equipped with a special titration adapter[12] which makes easy to change the cells for adjusting and controlling the reference signal. A higher precision of the transmittance readings was achieved with the use of a precise digital millivoltmeter (type OP 208, Radelkis, Budapest) and a regulated power supply for the whole instrumental arrangement. Thus it was possible to take a reading with an error in tenths of millivolt (for a reference value of about 1 000 mV). The titrations were performed in a 50 mm glass cell (type C, Carl Zeiss, Jena) of a total volume approx. 22 ml.

A micrometer glass syringe burette was used for the titrations. The polyethylene capillary tip of the microburette was dipped into the titrated solution. A new design of the microburette was realized in the Central workshop of our Institute[13]. For the calibration a modification of the method of weighing measured volumes of distilled water was developed. For example, for 5 successive calibrations the volume corresponding to a full displacement (25 mm) of the glass piston was $486{\cdot}11 \pm 0{\cdot}10$ µl (20°C, $s_r = 0{\cdot}018\%$). Pipettes were also calibrated.

A Radelkis OP 201/2 pH-meter with a combined glass electrode (type OP-0808, Radelkis, Budapest) was calibrated with buffer solutions of the operational pH-scale[14].

Proper function of an analytical balance (type WA-33, Zaklady mechaniki precyzyjnej, Gdańsk, Poland; attainable precision ±0·05 mg) was checked.

Reagents and Solutions

A selected batch of analytical-grade disodium dihydrogen ethylenediaminetetraacetate dihydrate, $Na_2H_2(edta).2\,H_2O$ (Chelatone III, Lachema, Brno) was used to prepare 1—0·5 mmol l^{-1} solutions by dissolving an appropriate amount of the reagent in redistilled water and by dilution to volume in a graduated flask.

As the end-point of an instrumental titration may be affected by the presence of nitrilotriacetic acid (NTA)[15], the content of this component in Chelatone III used in this work was determined by isotachophoresis[16]. A two-column isotachophoretic analyser (ÚRVJT, Spišská Nová Ves, Czechoslovakia) was used (inside diameter of the columns: 0·8 and 0·3 mm). The driving currents were 250 and 50 μA for the pre-separating and main separating steps, respectively. A 30 μl sample of 0·01M solution of Chelatone III was injected per run of the analysis. A solution of 0·01M-HCl adjusted with solid 6-aminocaproic acid to pH 4·25 was used as the leading electrolyte, with 0·01M benzoic acid buffered with TRIS [2-amino-2-(hydroxymethyl)-1,3-propanediol] to pH 5·0 as the terminating electrolyte. On comparison with a sample containing a standard addition of NTA [$c(\text{NTA}) = 10^{-5}$ mol l^{-1}, i.e. $n(\text{NTA}) : n(\text{EDTA}) = 1 : 1\,000$] the isotachopherogram for the solution of Chelatone III only showed a corresponding zone but actually on the limit of detection. Thus the content of disodium hydrogen nitrilotriacetate in Chelatone III of analytical reagent quality was about 0·01 wt. %. The effect of NTA on the results of precise microtitrations can, therefore, be taken as negligible.

Acetate buffers were prepared by mixing 1M stock solutions of acetic acid and sodium acetate. All reagents should be of the highest purity available; e.g. semiconductor-grade HNO_3 (Lachema, Neratovice Plant, Czechoslovakia) was used.

Standard Copper Metal

Copper Metal 99·995% pure (batch Cu-IXB-252 EG, Research Institute of Metals, Panenské Břežany, Czechoslovakia) was selected as a standard substance. Copper shavings were degreased first; then to remove the surface oxides they were heated to red glow and poured into redistilled methanol. After drying at laboratory temperature lustrous red-pink copper was obtained.

Recommended Procedures

Preparation of a standard tetraamminecopper(II) *solution.* A differential weighing of pure copper metal, e.g. for a 0·04M standard solution, was dissolved in a tall-form silica beaker in 36·2 ml of dilute nitric acid (1 : 1). This amount of acid, added in appropriate excess, corresponds to $n(HNO_3) \approx 0{\cdot}26$ mol. After short boiling to expel oxides of nitrogen the solution was transferred into a 1 000 ml graduated flask and treated with 375 ml of 2M ammonia [$n(NH_3) \approx 0{\cdot}75$ mol]. In this manner a clear solution of tetraamminecopper(II) complex was obtained with pH about 9·9. For dilution to the mark redistilled water adjusted with ammonia to pH 9·9 was used in order to prevent hydrolysis. A standard 0·08M tetraamminecopper(II) solution was prepared similarly using appropriate amounts of nitric acid and ammonia.

Standard tetraamminecopper(II) solutions with pH about 9·9 were found to be very stable (up to one year). At pH lower than 9·6 a hydrolytic precipitate may be formed after some time.

Photometric microtitration. A 20 ml aliquot of the EDTA solution to be standardized was transferred into a 50 mm spectrophotometric cell and adjusted with 2 ml of acetate buffer to pH 4·7 ± 0·4. The 100% transmittance reading was adjusted at 720 nm against water in the reference cell. For the titration of 0·001M-EDTA a standard 0·08M solution of $[Cu(NH_3)_4]^{2+}$ was used, whereas for 5 . 10^{-4}M-EDTA the concentration of the titrant was 0·04 mol l^{-1}. In this manner it was possible to obtain the extrapolated end-point approximately at half of the total volume of the microburette. The increments of the titrant (≈ 20 μl) should allow a sufficient number (>7) of experimental points to be obtained on both branches of the titration curve. It should be noted that the arrangement of the two experimental sets might affect the end-point evaluation.

Transmittance readings were converted to absorbance and corrected for dilution caused by the titrant. Two modes of end-point evaluation were used: a graphical extrapolation to the point of intersection of the two straight lines drawn to fit best the points on the titration curve, or more precisely, with the aid of a least-squares program and a personal computer[17].

RESULTS AND DISCUSSION

A relatively wide pH range suitable for the titration of copper(II) with EDTA (cf. refs[9,10]) corresponds to a considerable stability of the chelate $[Cu(edta)]^{2-}$ ($\log \beta = 18{\cdot}70$, 25°C, $I = 0{\cdot}1$ mol l^{-1})[18]. A marked dissociation of the chelate due to protonation of EDTA takes place in a rather acidic medium (pH < 2). However, this equilibrium is also influenced by formation of a mixed proton-complex $[CuHedta]^-$; at pH 4·0 $[CuHedta]/[Cu(edta)] = 0{\cdot}1$. If the pH value is low, a greater contribution of the proton-complex causes a bend of the initial part of the titration curve. Contrarily, at pH higher than 4 this part of the titration curve before the equivalence is truly linear. In preliminary experiments acetate buffer medium was found as suitable. As shown in Fig. 1, the absorption maximum of the copper(II) chelate ($\lambda_{max} \approx 730$ nm) grows higher in the pH region 3·7–4·7; no change is observed further on. Similarly, at the end of the red region a flat absorption maximum of acetato-complexes is enhanced due to increasing concentration of the acetate ion.

The family of curves in Fig. 1 illustrates both the possibilities and limitations of a direct photometric titration based on this relatively simple equilibrium system. Thus at the wavelength 720 nm it is possible to reach a maximum change in absorbance; accordingly, a suitable shape of the titration curve is obtained. It is also evident that the buffer system should be safe enough: hydrogen ions liberated in formation of the chelate $[Cu(edta)]^{2-}$ should not bring about such decrease in pH which might cause a curvature of the titration curve before equivalence. At pH 4·7 ± 0·4 the titration curve consists of two linear parts (Fig. 2). An evident advantage of the ammoniacal copper(II) titrant is that this optimum pH range can easily be maintained during the titration. As there is a small excess of ammonia in the tetraamminecopper(II) titrant, more than enough for the neutralization during a titration, a small increase in pH (about 0·2) may be observed when the titration is finished; this has no significant effect on the end-point evaluation.

Our study of the titration curves for the reaction system EDTA–Cu(II) indicated that the standardization against copper metal is applicable even for a very dilute

TABLE I

Results of standardization at low concentrations of EDTA

Series[a] No.	Number of determinations	End-point[b] V µl	s µl	Found[c] c(EDTA) $L_{1,2}$ mmol l^{-1}	s_r %	$Na_2H_2(edta).2\,H_2O$ content, %
I	7	255·43[d]	0·79	1·0321 ± 0·0030	0·31	99·47 ± 0·28
II	7	257·20[d]	0·80	1·0393 ± 0·0030	0·31	99·39 ± 0·29
III	6	255·22[e]	0·01	1·01608 ± 0·00006	0·005	99·419 ± 0·005
IV	6	255·42[f]	0·94	0·5166 ± 0·0020	0·37	99·48 ± 0·39
V	7	245·22[f]	0·67	0·4960 ± 0·0012	0·27	99·41 ± 0·25
VI	9	262·90[g]	0·26	0·53760 ± 0·00041	0·098	99·516 ± 0·075

[a] For each series of titrations a fresh solution was prepared by weighing out a sample of Chelatone III; [b] in series III, IV, and VI each, one value was omitted as result of Grubbs' test ($\alpha = 0{\cdot}05$); [c] arithmetic mean with a confidence interval $L_{1,2}$; $c([Cu(NH_3)_4]^{2+})$, mmol l^{-1}: [d] 80·703; [e] 79·513; [f] 40·398; [g] 40·840.

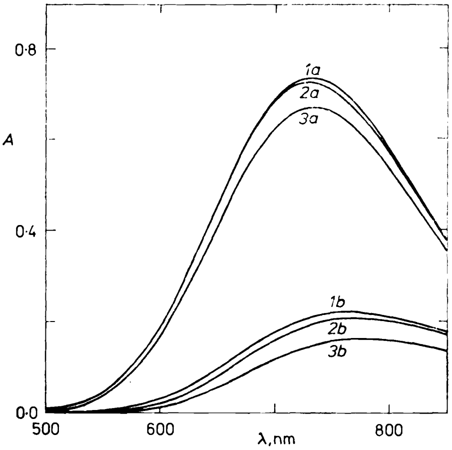

FIG. 1

pH-Dependence of the absorption spectra of copper(II) complexes [$c(Cu^{2+})$ = = 1·6 mmol l^{-1}] in medium of acetate: *a* with H_2edta^{2-} in excess, $c(Na_2H_2edta)$ = = 2 mmol l^{-1}; *b* acetato-complexes only, pH: *1* 5·85, *2* 4·7, *3* 3·9

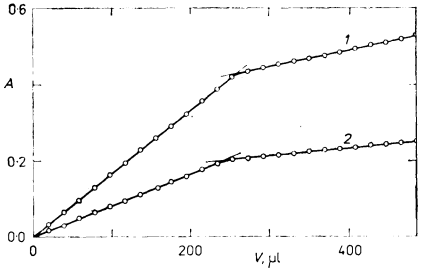

FIG. 2

Photometric microtitration of dilute solutions of Na_2H_2(edta) (pH 4·7 ± 0·4; λ = = 720 nm); *1* $c(Na_2H_2edta)$ = 1·05 mmol . l^{-1}, titrant 0·08M-$[Cu(NH_3)_4]^{2+}$; *2* $c(Na_2H_2edta)$ = 0·5 mmol l^{-1}, titrant 0·04M-$[Cu(NH_3)_4]^{2+}$

solution of EDTA if the sample solution of EDTA is transferred into the titration cell and titrated with an 80-times more concentrated ammoniacal copper(II). Curve 2 in Fig. 2 for $5 \, . \, 10^{-4}$M-Na_2H_2(edta) represents evidently a limiting case for a safe end-point evaluation. The angle between the two extrapolation straight lines is becoming too obtuse in a further dilution.

For a graphical end-point extrapolation a large-scale graph is necessary. This procedure is time-consuming and may be influenced by a subjective approach of the analyst. The precision of the end-point is increased if the point of intersection is evaluated by linear regression analysis of both linear branches of the titration curve. A new algorithm was developed allowing to divide the whole set of experimental points into sub-sets corresponding to the two linear parts of the titration curve prior to the least-squares treatment. This numerical approach was realized in a program KJM89 for a personal computer[17].

The results of several series of standardization titrations are listed in Table I together with the statistical evaluation. It is evident that an adequate level of precision can be achieved even for the assay of EDTA in a $5 \, . \, 10^{-4}$M solution.

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