

APPLICATION OF THE CRYTUR 20—15 Ca^{2+} -SELECTIVE ELECTRODE IN VOLUMETRIC ANALYSIS

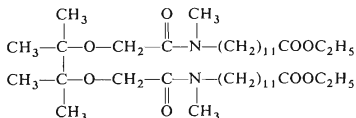
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Some possibilities have been studied of application of the Crytur 20—15 Ca^{2+} -selective electrode in volumetric analysis especially for determination of the compounds which react with calcium(II) salts to form precipitates or complexes. Titrations with standard calcium(II) nitrate solution have particularly proved useful for determination of aminocarboxylic acids, but sufficiently developed potentiometric titration curves have also been obtained in titrations of fluoride, oxalate and higher carboxylic acid anions (soaps). Also reliable results have been obtained in titrations of Ca^{2+} besides Mg^{2+} with standard EGTA solution.

Application of Ca^{2+} -selective electrodes in analytical chemistry is dealt with in several reviews and monographs, *e.g.*¹⁻⁵. Usually these electrodes are constructed as sensors with liquid membrane, the electroactive compounds used being alkyl (or alkyl aryl) phosphates or specially synthesized neutral carriers (for a review see⁶). As shown by Simon and coworkers⁷, the electrodes whose membranes contain the neutral carriers exhibit usually a more distinct selectivity and can be used in a broader concentration range. Recently an electrode has been developed⁸ in Monokrystaly Turnov for determination of Ca^{2+} ions whose membrane contains 38·64% high-molecular PVC, 60·10% plasticizer (2-nitro- or, more recently, 2,4-dinitrophenyl *n*-octyl ether), 0·43% sodium tetraphenylborate, and 0·83% carrier (similar to the ligand prepared by Simon and coworkers⁷) of the following structure:



The membrane potential is measured by means of internal electrolyte (0·1M- CaCl_2) and inner reference electrode (Ag/AgCl). In the studies of application possibilities of this electrode we preferred the method of potentiometric titration to the direct potentiometric measurement which is usually less correct and less accurate; in ad-

dition, the chosen method has the advantage that the electrode response need be neither Nernstian nor reproducible. The only important value is the consumption of reagent at which the titration curve exhibits a potential jump whose inflexion point can be well evaluated. The results are presented in this communication.

EXPERIMENTAL

Reagents, Apparatus and Measurement Methods

Calcium(II) nitrate solution (c_{Ca} about 0.05 mol l^{-1}) was prepared from an Analar substance (Lachema) and standardized chelatometrically in ammonia buffer medium with Eriochrome Black T as indicator (in the presence of Mg-EDTA complex). The used standard EDTA solution (c_{EDTA} about 0.05 mol l^{-1}) was standardized with lead(II) nitrate in urotropine buffer medium with Xylenol Orange as indicator (for the both methods see ref.⁹). Standard solution of 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide (S) (c_S about 0.05 mol l^{-1}) was prepared from Septonex (Slovakofarma, Hlohovec). Its titre was determined by potentiometric titration¹⁰ of a sodium tetraphenylborate solution (Analar, Jenapharm-Laborchemie Apolda) standardized with thallium(I) nitrate as standard¹¹.

Stock solutions of other reagents and titrated compounds were prepared from available chemicals, their concentration was about 0.05 mol l^{-1} . The following chemicals were used: nitrilotriacetic acid (NTA), 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA), oxalic acid, disodium salt of ethylenediaminetetraacetic acid (EDTA), potassium fluoride, and magnesium sulphate of the Analar grade, stearic, palmitic, oleic and lauric acids "pure" (all Lachema), sodium lauryl sulphate "puriss" (Fluka). Purity was not declared with ethyleneglycol-bis(2-aminoethyl ether) tetraacetic acid (EGTA) and N-(2-hydroxyethyl)ethylenediamine-N,N',N'-tri-acetic acid (HEDTA).

The titrations were carried out in non-buffered media or with addition of borate-stock solution containing $9.5 \text{ g Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$ (Analar, Lachema) in 500 ml. The higher carboxylic acids were converted into sodium salts by addition of NaOH, oxalic acid was titrated in the presence of slight excess of ammonia. The potentiometric measurements were carried out with a Universal pH-Meter OP-204 (Radelkis, Budapest) using a cell composed of the Ca^{2+} -selective electrode Crytur 20-15 (Monokrystaly, Turnov)⁸ and saturated calomel electrode (S.C.E.). In the titrations of anionactive tensides and soaps, the cell composed of a coated-wire electrode with PVC membrane plasticized with 2-nitrophenyl n-octyl ether (code 180A) on aluminium conductor¹² vs S.C.E. was used. The potentiometric titrations were carried out in usual way.

RESULTS AND DISCUSSION

Determination of Aminocarboxylic Acids and Chelatometric Titration of Ca^{2+} besides Mg^{2+}

It was evident that the Ca^{2+} -selective electrode Crytur 20-15 could be used for indication of chelatometric titrations of calcium(II) salts. This fact was also verified by the reverse procedure, *i.e.* titration of aqueous solutions of aminocarboxylic acids with standard solution of calcium(II) nitrate in borate buffer medium of pH 9. Except for NTA ($\log \beta_{CaL} = 6.3$), Ca^{2+} ions give sufficiently stable complexes

($\log \beta_{\text{CaL}}$ for EDTA 10.7; DCTA 12.5; HEDTA 8.0; EGTA 11.0; see ref.¹³), so the titration curves exhibit steep and sufficiently distinct potential jump.

For practical purposes it is more interesting to investigate the determination of calcium in the presence of magnesium. If EDTA is used for titration of salt mixtures of these two elements ($\log \beta_{\text{MgI}} = 8.6$), the obtained potentiometric curves show two potential jumps. The reading at the inflexion point of the first jump corresponds to the added amount of Ca^{2+} salt, but evaluation of the end-point is not reliable. Overall consumption can be read with sufficient accuracy. A substantially steeper course of the potential change in the titration of Ca^{2+} in the presence of Mg^{2+} is obtained with standard solution of EGTA ($\log \beta_{\text{MgI}} = 5.2$). This reagent enables reliable determination of calcium, whereas determination of the overall consumption is inaccurate (Fig. 1).

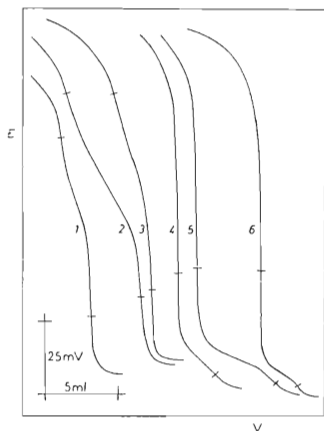


FIG. 1

Chelatometric titration of Ca^{2+} in the presence of Mg^{2+} . Standard solution of EDTA (1–3) or EGTA (4–6) (both 0.05 mol l^{-1}) were used as titrants; concentration ratio $c_{\text{Ca}}/c_{\text{Mg}}$ 1 : 1 (1, 4), 1 : 2 (2, 5), and 2 : 1 (3, 6); pH 9 (borate buffer); readings for the individual cations are indicated on the curves

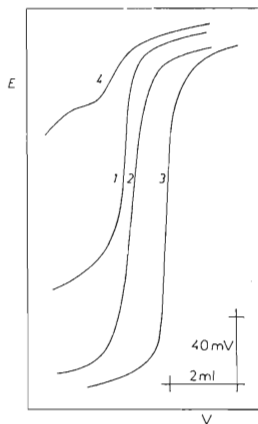


FIG. 2

Titration of soaps and a tenside by calcium(II) salt. Oleic acid 1, palmitic acid 2, stearic acid 3 (pH 10), sodium lauryl sulphate 4 (pH 6). The solutions contained about 0.25 mmol of the titrated substance; $c_{\text{Ca}} = 0.05 \text{ mol l}^{-1}$

TABLE I
Statistical evaluation of the titration results of solutions of the studied compounds and characteristic data of the potentiometric titration curves

| The compound determined | Rel. M_r molecular mass | Given mg | Found ^a | | | Lord test ^b μ_0 | Titration curve | |
|---|------------------------------|-------------|--------------------|-----------|-------------------------------|--------------------------------------|---|-------|
| | | | \bar{x} mg | s mg | ΔE_{pot} mV | | $(\Delta E/\Delta V)_{\text{ind}}$ mV/0.1 ml | |
| The titration with Ca^{2+} salt solution | | | | | | | | |
| NTA | 191.14 | 48.22 | 5 | 47.27 | 0.82 | 0.50 | 110–120 | 3–5 |
| EDTA ^c | 372.24 | 88.78 | 5 | 87.47 | 1.21 | 0.47 | 110–125 | 55–60 |
| DCTA ^d | 364.35 | 84.00 | 5 | 83.46 | 0.70 | 0.33 | 100–115 | 54–60 |
| HEDTA ^e | 380.24 | 68.86 | 5 | 68.16 | 0.90 | 0.33 | 100–120 | 16–20 |
| EGTA | 380.35 | 92.92 | 5 | 92.15 | 1.06 | 0.31 | 105–115 | 35–50 |
| Oxalic acid ^f | 126.07 | 31.19 | 5 | 30.88 | 0.68 | 0.20 | 90–100 | 7–10 |
| Potassium fluoride | 58.10 | 335.60 | 5 | 334.22 | 3.42 | 0.17 | 75–85 | 6–8 |
| Palmitic acid | 256.43 | 61.53 | 5 | 44.10 | 2.76 | 2.72 | 190–200 | 20–25 |
| Stearic acid | 284.49 | 68.25 | 5 | 65.41 | 1.22 | 1.00 | 200–210 | 30–40 |
| Oleic acid | 282.47 | 67.78 | 5 | 63.54 | 2.43 | 0.75 | 155–165 | 20–30 |
| Sodium lauryl sulphate | 288.49 | 68.26 | 5 | 65.09 | 1.24 | 1.10 | 60–65 | 3–4 |
| The titration with standard Septonex solution | | | | | | | | |
| Palmitic acid | 256.43 | 64.54 | 5 | 62.82 | 1.52 | 0.49 | 460–480 | 18–25 |
| Stearic acid | 284.49 | 67.82 | 5 | 66.83 | 1.22 | 0.35 | 470–480 | 80–90 |
| Oleic acid | 282.47 | 68.97 | 5 | 67.78 | 1.82 | 0.28 | 580–600 | 40–50 |
| Lauric acid | 200.32 | 23.12 | 3 | 22.22 | 0.58 | 0.91 | 30–35 | 3–5 |
| Sodium lauryl sulphate | 288.49 | 66.68 | 5 | 65.82 | 1.39 | 0.27 | 190–210 | 15–25 |

^a n Number of the measurements, \bar{x} the arithmetic mean, s standard deviation; ^b evaluated for the significance level $\alpha = 0.05$ (95% probability); critical value $\mu_0 = 0.51$ for $n = 5$ and $\mu_0 = 1.3$ for $n = 3$. The substance was weighed as ^c dihydrate of disodium salt; ^d monohydrate; ^e dihydrate of trisodium salt; ^f dihydrate.

Determination of Fluorides and Oxalates

The titrations of fluorides (each added amount 1 mmol KF) were carried out in non-buffered medium; a slight excess of ammonia was added to oxalic acid. The both anions, which form precipitates with Ca^{2+} ions, can be determined with sufficient reliability. Potential is adjusted rapidly in the titrations, the curves have typical S-shape.

Determination of Soaps

Sodium salts of higher carboxylic acids (soaps) were titrated at enhanced temperature (about 60°C) at pH 10. The titration curves (Fig. 2) had favourable course, the potential was adjusted almost immediately. Limited solubility of the salts, however, made the dosing of samples difficult, which made itself felt in the results, too (Table I).

As any other electrode with plasticized membrane the Crytur 20-15 electrode can be used for indication of titrations based on formation of ionic pairs (e.g. it was used for determination of arenediazonium salts with sodium tetraphenylborate¹⁵). Being univalent anions of carboxylic acids, soaps can be titrated by a reagent of opposite charge^{16,17}; we used Septonex for comparison in this work. As shape of the titration curves depends, first of all, on the used plastic and plasticizer¹⁴, we made use of the electrode of coated-wire type with a PVC membrane plasticized with the

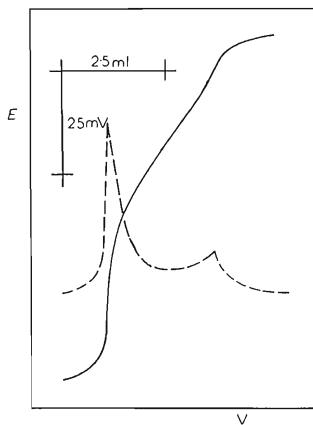


FIG. 3

Potentiometric titration of a mixture of soap and tenside with calcium(II) salt. Given about 0.125 mmol stearic acid and about 0.25 mmol sodium lauryl sulphate; pH 10. The dashed line denotes the derivation curve

same plasticizer. The potential jump near the equivalence point is much greater which, however, has no significant effect on accuracy of the results due to the above-mentioned difficulties with dosing of samples.

Titrations of Mixtures of Soaps and Tensides

Interfering effect of anionic tensides on function of Ca^{2+} -selective electrodes is treated in a number of papers¹⁸⁻²⁰, but their determination by the method of direct potentiometric titration with Ca^{2+} salts gives titration curves with small potential changes (Fig. 2). Cationic reagents are much more suitable for determination of these substances¹⁰.

Anghel and coworkers¹⁶ showed that mixtures of soaps with cationic tensides can also be titrated with the use of a suitable reagent (*e.g.* cetyldimethylbenzylammonium chloride). In acid medium (pH 2 to 5) only the tensides with strongly acidic group are determined, the second titration in alkaline medium (pH 10 to 13) gives the overall consumption, and the soap content is calculated from difference of the two readings. We reproduced²¹ this procedure but with not too much convincing results. The errors were obviously due to bad solubility of soaps in acid media: the soaps precipitated even in the presence of auxiliary solvents as *e.g.* propanol, the consumption in alkaline medium corresponded to the overall composition of the mixture. Content of a soap in a mixture with tenside can be better determined, if the mixture is titrated with standard solution of Ca^{2+} salt (for various prepared mixtures of stearate or palmitate with sodium lauryl sulphate, evaluation of the inflexion point gave always the expected consumption of the reagent). In the potentiometric titration curve recorded with the Crytur 20-15 electrode, the consumption of Ca^{2+} salt corresponding to the soap content is determined by the first distinct potential jump, whereas the end-point reading for the tenside is doubtful (Fig. 3).

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