The application of microelectrodes for amperometric titrations

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The possibility of application of microelectrodes for the amperometric titrations with one or two indicating electrodes is described in this paper. Platinum and carbon microelectrodes with the radii 4 μm and 12.5 μm, respectively, have been used. The precision and accuracy of titrations of model samples are presented.

Recently microelectrodes with characteristic radius of *ca.* 20 μm are introduced as a novel element of instrumentation for modern electrochemical measurements [1]. In comparison with the electrodes of conventional size these have a whole lot of advantages which were published *e.g.* by *Dayton* [2] and *Ewing* [3].

From the viewpoint of electroanalytical chemistry the wave form of voltammograms following from the time independence of current also in nonstirred solutions may be considered to be the most advantageous property of microelectrodes. The time independence of current follows from the Cottrell equation corrected to the contribution of nonlinear diffusion

$$I = \frac{zFD^{1/2}Ac}{\pi^{1/2}t^{1/2}} + k\frac{zFDAc}{r\pi^{1/2}} = a + b$$

where a is the contribution of linear and b is the contribution of nonlinear diffusion to the limiting current, z is the number of exchanged electrons per particle for the analytically used electrode reaction, F the Faraday constant (C mol^{-1}), A electrode area (m^2), c concentration of the determined component (mol m^{-3}), D diffusion coefficient, r radius of disc electrode — of disc, sphere, cylinder, and k is the coefficient with the values $\pi^{1/2}$ for spherical electrode [4, 5]; 0.5 for cylindrical electrode [6, 7]. For the disc electrode the values 2.12 [8], 1.93 [9], and 1.7947 [10] are presented.

The less is the electrode radius r and its area A the less is proportion of the contribution of linear diffusion. The value of this is directly proportional to r^2 while the term b decreases linearly with r and thus its proportion in the limiting diffusion current increases. For the microelectrodes this is so high that the limiting diffusion current attains the time-independent value in a very short time.

Another important property of microelectrodes is that the very low current results in the beneficial effect of very low ohmic potential loss with a resulting tolerance for samples of low ionic strength [1].

Microelectrodes are mainly applied in the working procedures where constant substance flow is required, *e.g.* in stripping voltammetry [11, 12].

A typical application of voltammetry which requires the time-constant signal is the amperometric titration. In this field the application of microelectrodes has not been described till now in the literature. This paper deals with the use of microelectrodes in the field of amperometric titrations which can result in the possibility to simplify the experimental device preserving good precision and accuracy of titration results.

Experimental

All used chemicals were of anal. grade purity, water used for the preparation of solutions was deionized.

The measurements with the use of electrodes of conventional size were made with Polarograph OH-105 (Radelkis, Budapest). With the microelectrodes the Polarographic analyzer PA-3 (Laboratorní přístroje, Prague) and the XY-recorder ENDIM, 620.02 (Germany) which is more sensitive to current, have been used.

Working electrodes were made of carbon and platinum. The carbon electrode (SU Electrocarbon, Topoľčany) of disc shape with the radius 3 mm (I-C) was vacuum-impregnated with paraffin. Its active area $A = 0.234\ \text{cm}^2$ was determined chronoamperometrically with the help of standard 10^{-3} M *o*-dianisidine solution [13]. The platinum electrode was made of Pt-wire with the radius $r = 0.4$ mm (I-Pt). The active electrode area $A = 0.206\ \text{cm}^2$ was also determined chronoamperometrically. Indication microelectrodes of disc shape were made of Pt wires of $r = 12.5\ \mu\text{m}$ and carbon fibres of $r = 4\ \mu\text{m}$. The copper lead connecting the microelectrodes with the electric circuit was bound with the Pt or C microfibre by soldering or sticking with conductive Ag-epoxide. The adjusted microfibre located into a glass tube was fixed by the epoxide. After hardening of the epoxide the electrodes of disc shape were obtained by grinding of tubing face on fine abrasive paper. The active area of Pt and C disc was calculated from known diameters of fibres.

The area of the carbon disc microelectrode was $A = 5.2 \times 10^{-7}\ \text{cm}^2$ (II-C) and the area of the platinum microelectrode was $A = 4.9 \times 10^{-6}\ \text{cm}^2$ (II-Pt).

For the preparation of I_2 solution, solution of $KBrO_3$ ($c = 1.66 \times 10^{-4}$—$3.33 \times \times 10^{-3}\ \text{mol dm}^{-3}$) as a standard mixed with 4 M-HCl and 10 % KI in the volume ratio $\varphi_r = 1\ \ 5\ \ 5$ has been used. For the individual titrations with biamperometric indication 10 cm^3 resp. 1 cm^3 of the resulting solution were pipetted. With the electrodes of conventional size the volume of titrated solution was about 10 cm^3, with the microelectrodes the volume was 10 cm^3 and 1 cm^3 The polarization voltage for both kinds of electrodes was $\Delta E = 200$ mV 0.1 M- to 0.2 M-$Na_2S_2O_3\ \ 5H_2O$ solution was used as a titrant. It was standardized to $KBrO_3$ [14].

The Fe^{2+} stock solution was prepared by dissolution of an appropriate amount of $K_4[Fe(CN)_6]$ in 1 M-H_2SO_4. For the individual titrations 10 cm^3 resp. 1 cm^3 of Fe^{2+} stock solution with the concentrations 2×10^{-4} to 2×10^{-3} mol dm^{-3} were pipetted. 0.02 M- to 0.2 M-$Ce(SO_4)_2$ standardized to alkaline solution of As_2O_3 was used as a titrant. The equivalence point was determined biamperometrically with carbon electrodes of conventional size and with microelectrodes. The polarization voltage was always $\Delta E = 200$ mV [15].

The Bi^{3+} stock solution was prepared by the dissolution of an appropriate amount of $Bi(NO_3)_3$ in 2 M-HNO_3. 10 cm^3 resp. 1 cm^3 of the Bi^{3+} samples with the concentrations 1×10^{-4} to 1×10^{-3} mol dm^{-3} were titrated. Solution of Chelaton III (disodium salt of ethylenediaminetetraacetic acid) with the concentrations 1×10^{-2} to 1×10^{-1} mol dm^{-3} has been used as a titrant. The indication of equivalence point was made amperometrically with the indication platinum electrode polarized by the constant potential $E = -0.25$ V *vs.* SCE [16].

The statistically evaluated results of all titrations using both types of electrodes (I-C and II-C) are presented in Table 1.

Results and discussion

The procedures for amperometric titrations with one or two polarized electrodes were worked out and applied by many authors for the determinations of different substances. The indicating electrode was always of conventional size ($r = 1$ mm up to 1 cm) [14—16].

It was necessary to stir the solution uniformly during such titrations. The demand of a uniform stirring is disadvantageous from the standpoint of use of the method in the analytical practice. According to our experience the stabilization of current on the electrode I-C in the stirred I_2 solution in the course of its titration by thiosulfate lasted approximately 6 s. On the same electrode under the conditions of nonstirred solution the current signal was not constant even after 20 s. The time dependence of the current signal was registered chronoamperometrically. The measured $I—t$ curves were compared with the theoretical ones calculated from the corrected Cottrell equation for the given size of electrode and concentration of the solution. The rate of current stabilization $\Delta I/\Delta t$ was found to be even somewhat smaller than the calculated one presented in Table 2.

Similar measurement was made using microelectrode II-C with solution unstirred during the registration of the $I—t$ curve. The current was stabilized already after 4 s. The $I—t$ curves for individual extents of titration were similar to the theoretical $I—t$ curves calculated from the corrected Cottrell equation. The values of current stabilization rate are presented in Table 2.

Table 1

Statistical evaluation of the titrations

Electrode	m(taken)/mg	m(found)/mg	Number of determinations	Standard deviation/μg	Relative error/%	Confidence limits for 95 % probability/μg
			$I_2/Na_2S_2O_3$			
I-C	0.127	0.131	5	7	3.1	± 8
I-C	0.635	0.648	5	13	2.0	±16
I-C	1.270	1 294	4	18	1.8	±26
I-C	2.540	2.563	4	20	0.9	±30
II-C	0.127	0.130	5	4	2.9	± 5
II-C	0.635	0.650	5	14	2.3	±16
II-C	1.270	1.292	4	17	1.7	±25
II-C	2.540	2.568	4	20	1.1	±30
			Fe^{2+}/Ce^{4+}			
I-C	0.112	0.114	5	3	1.8	± 3
I-C	0.224	0.227	4	2	1.3	± 3
I-C	0.672	0.680	5	8	1.2	± 9
I-C	1.120	1.129	4	8	0.8	±12
II-C	0.112	0.114	5	2	1.8	± 2
II-C	0.224	0.227	4	3	1.5	± 5
II-C	0.672	0.678	5	7	1.0	± 9
II-C	1.120	1.131	4	7	1.0	±11

Table 1 (Continued)

Electrode	m(taken)/mg	m(found)/mg	Number of determinations	Standard deviation/μg	Relative error/%	Confidence limits for 95 % probability/μg
			Bi^{3+}/Chelaton III			
I-Pt	0.210	0.216	5	6	2.9	± 7
I-Pt	0.630	0.642	4	16	1.9	±23
I-Pt	1.050	1.065	4	14	1.4	±20
I-Pt	2.100	2.118	4	17	0.9	±25
II-Pt	0.210	0.217	5	5	3.2	±14
II-Pt	0.630	0.641	4	14	1.7	±21
II-Pt	1.050	1.065	4	13	1.4	±19
II-Pt	2.100	2.121	4	15	1.0	±21

The titration results have been evaluated statistically by the method of *Dean* and *Dixon* [17].

Table 2

Comparison of rate of the current stabilization response on the electrode of conventional size (I-C) and on the microelectrode (II-C) for the case of I_2 reduction

$\frac{t}{\text{s}}$	I-C electrode $(\Delta I/\Delta t)/(10^{-4}\ \text{A s}^{-1})$		II-C electrode $(\Delta I/\Delta t)/(10^{-8}\ \text{A s}^{-1})$	
	Calculated	Found	Calculated	Found
2	1.584	1.017	0.031	0.044
4	0.720	0.359	0.010	0.030
6	0.108	0.159	≈ 0	0.017
8	0.089	0.095		0.006
10	0.054	0.064		≈ 0
12	0.040	0.047		
14	0.027	0.037		
16	0.018	0.029		
18	≈ 0	0.025		
20		0.021		

From the I—t curves presented in Fig. 1 there is obvious a great difference of the electrode of conventional size and the microelectrode where the current signal after 4 s is practically unvariable.

The accuracy and precision of the procedures in the case of both electrodes are similar (Table 1).

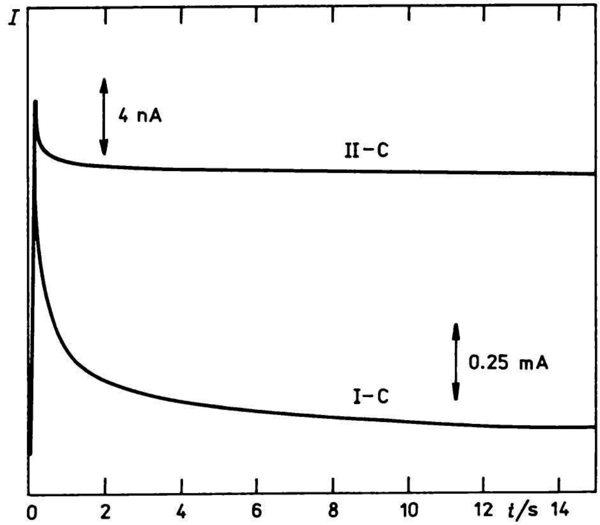

Fig. 1. I—t curves for I_2 reduction ($c = 2 \times 10^{-3}$ mol dm^{-3}, 10 cm^3) on the electrode of conventional size (I-C) and on the microelectrode (II-C).

The Fe^{2+} titration by Ce(IV) salt was made with two polarized carbon electrodes and the biamperometric indication of the equivalence point. Similar to the I_2 titration also in this case the I—t curves were registered for each extent of titration. No stable current signal has been obtained even after 20 s in the nonmixed solution using electrodes of conventional sizes (I-C). The I—t curves obtained for the individual titration extents with the polarized microelectrodes (II-C) showed the stable current signal already after 4 s.

The possibility to use the microelectrodes for amperometric titrations was also verified in chelatometric determination of Bi^{3+} ions with a single polarized electrode at the constant potential. Both Pt-microelectrode and Pt-electrode of the conventional size have been tested. The value of constant potential E_k was chosen 100 mV behind the current maximum of the voltammetric curve registered with the I-Pt electrode, resp. within the region of limiting current obtained with the II-Pt electrode. For both cases the optimum potential was $E_k = -0.25$ V *vs.* SCE.

The rate of current stabilization of I—t curves in nonmixed solution is approximately five times greater for the case of microelectrode than for the electrode of conventional surface size.

In the titration with microelectrodes the usual volume of the titrated solution 5—10 cm^3 can be reduced to 1 cm^3

On the basis of the results of described examples of titrations it can be stated that using microelectrodes in the function of one or two polarized electrodes simplifies the experimental arrangement. It is possible to leave out the uniform and time-stable stirring of the titrated solution or rotating the electrode. This also enables to decrease the volume of titrated solution. Herewith the precision and accuracy of determinations are similar with titrations using the electrodes of conventional surface size.

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