ABSOLUTE CHRONOAMPEROMETRIC DETERMINATION WITH CYLINDRICAL SEMIMICROELECTRODE

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An analytical application of chronoamperometry for determination of electroactive species not requiring standardization is described in this paper. It is based upon the separation of current component limited by the linear diffusion from that limited by cylindrical contribution to the total flux of determined substance to the cylindrical (wire) Pt-semimicroelectrode (radius 0.02 mm and length 15 mm). The absolute method of determination was verified with *o*-dianizidine, ferrocyanide, ascorbic acid and dopamine. The optimization of radius of the cylindrical electrode to minimize the determination error is also presented.

Amperometry has been traditionally used as a relative method of determination since the proportionality coefficient between current density and the flux of determined substance contains an unknown value of diffusion coefficient of the substance in the medium of sample.

In our previous papers[1,2] we proposed a chronoamperometric method of electroactive species determination avoiding the necessity of standardization. Electrochemical reduction on the mercury drop electrode hanging from the thin-wall capillary provided current–time dependence which could be evaluated in such a way that the current component caused by linear diffusion is separated from that caused by spherical contribution to the total current. Concentration of analyzed electroactive species was calculated from these components. Results of the analysis were accurate in the concentration range 10^{-3} to 10^{-4} mol l^{-1} and independent on temperature of analyzed solution.

In this paper we present the results in application of cylindrical semimicroelectrode made of Pt wire for analogous absolute determinations based upon electrode reactions (oxidations) requiring polarization of the electrode to more positive region than is the potential of Hg anodic dissolution.

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An approximate expression for chronoamperometric curves at stationary microcylinder electrodes was described by Aoki and co-workers[3] in the following form:

$$I = \frac{z F c D A}{r}\left(\frac{1}{\sqrt{\pi 0}} + 0.422 - 0.0675 \log 0 \pm 0.0058\{\log 0 - 1.47\}^2\right), \quad (1)$$

where $0 = Dt/r^2$, c the bulk concentration, D the diffusion coefficient and the upper sign holds for $\log 0 \geq 1.47$ and the lower sign for $\log 0 < 1.47$. This equation was in good agreement with the theoretically predicted curves measured at times ranging from 40 ms to 8 s (ref.[3]).

EXPERIMENTAL

Ascorbic acid and dopaminium chloratum were of chemical purity and other chemicals were of analytical grade purity. All of them were used without further purification. The stock solutions of *o*-dianizidine ($5 \cdot 10^{-3}$ mol l^{-1} in 1 M H_2SO_4), ferrocyanide ($5 \cdot 10^{-3}$ mol l^{-1} in 0.1 M KCl), ascorbic acid (0.1185 mol l^{-1} in acetate buffer, pH 4.7) and dopamine (0.2611 mol l^{-1} in phosphate buffer, pH 6.8) were analyzed coulometrically using the platinum Winkler's electrode (at the concentration level aproximately $5 \cdot 10^{-3}$ mol l^{-1}). Each analysis was repeated five times, the standard deviation was less than 1%. Coulometric results were regarded as the basis to judge the accuracy of results of absolute chronoamperometric analysis.

Working electrode was made of Pt-wire (radius 20 μm). The copper lead connecting the semimicroelectrodes with the electric circuit was bond with the Pt-wire by soldering. The adjusted located into a soft glass tube was fixed by the heating. The active area of electrode was calculated from known diameter and length of wire (15 mm). The area of cylindrical Pt-electrode was $1.89 \cdot 10^{-2}$ cm^2. The surface of electrode has been activated by fast cyclic voltammetry (scan rate 100 V s^{-1}) in medium of 1 M H_2SO_4 and 1 M HNO_3 (1 : 1, v/v) during 10 min. Standby potential was +1.0 V vs SCE and standby time 1 s. Polarization range from +1.0 to −0.1 V vs SCE. This procedure was repeated every day before the measurements were started. It was necessary for determination of dopamine and ascorbic acid. The electrode was rinsed with saturated solution of $K_2Cr_2O_7$ in concentrated H_2SO_4 and then with distilled watter after each measurement.

Chronoamperometric curves were measured using the multipurpose polarograph GWP 673 (Academy of Sciences, G.D.R.) This instrument "on line" with the microcomputer Compucorp 610 (Compucorp, U.S.A.) made it possible the registration of the chronoamperogram to the computer memory through the AD converter (Burr–Brown, U.S.A.) synchronized with the loading of working potential to the working electrode. Two-electrode arrangement was used with Pt-wire working semimicroelectrode and saturated calomel reference electrode (SCE).

RESULTS AND DISCUSSION

Evaluations of Chronoamperograms

Using of chronoamperograms for the determination of concentration of electroactive species is based on the equation of limiting current–time function for cylindrical electrode (Eq. (*1*)).

As noted in several papers[4 - 8], the microwire current reaches virtual steady state when $(Dt/r^2)^{1/2} > 10$. The current is then decreasing very slowly (logarithmically) with time.

In this paper we are using simplified Eq. (*1*) without logarithmical therms:

$$I = z F c D A \left(\frac{1}{\sqrt{\pi D t}} + \frac{0.422}{r} \right) . \qquad (2)$$

The difference in current calculated from Aoki equation and the simplified form does not exceed 3% in the interval $0.1 < Dt/r^2 < 2.5$. For typical value of $D = 1 . 10^{-9}$ m^2 s^{-1} and $r = 20$ μm this corresponds to the time interval $0.04 < t < 1$ s.

Registered chronoamperograms were transformed to the dependence of the chronoamperometric constant $(I\sqrt{t}/A)$ vs $\sqrt{t}$. It follows from Eq. (*2*) that the transformed dependence should be linear:

$$\frac{I\sqrt{t}}{A} = U + S\sqrt{t} \qquad (3)$$

with the slope S and the intercept U

$$S = \frac{0.422 z F D c}{r} ; \qquad U = \frac{z F D^{1/2} c}{\pi^{1/2}}$$

U and $(S\sqrt{t})$ being the components of chronoamperometric constant caused by linear and cylindrical contribution to the diffusion current, respectively. Values U and S determined from a single chronoamperometric experiment were used for calculating the concentration of the electroactive substance according to equation

$$c = \frac{U^2 \pi 0.422}{z F S r} . \qquad (4)$$

The chronoamperometric experiment and its evaluating are carried out with the following sequence of operations:

1. acquisition of *I–t* curve of the analyzed component; by the rule 1 000 points;

2. acquisition of *I–t* curve of the background (at the same working potential of the indication electrode);

3. correction of chronoamperogram of the analyzed component by subtracting the *I–t* background curve;

4. transformation of the corrected *I–t* curve to the form $I\sqrt{t}/A$ vs $\sqrt{t}$;

5. linear regression – calculation of U and S (inclusive standard deviations);
6. calculation of concentration (inclusive standard deviation).

Points 4. to 6. are offered by the program PROG2. The dependence $(I\sqrt{t}/A)$ vs $\sqrt{t}$ is loaded to the peripheral memory and it is registered on the XY recorder through DA converter. The transformed dependence is verified with regard to its linearity, the nonlinear (bent) dependences being set aside the next evaluation (approximately 15% of all measurements). The results of parallel determination are evaluated statistically with the elimination of outliers (approximately 5% of all measurements).

Verification of Evaluation Procedure

A prerequisit of successful analysis is absence of any transport of electroactive species other than diffusion in the time interval 0.04 to 1 s, proposed for the analysis. To prove that the convective transport contribution is negligable a chronoamperogram of *o*-dianizidine ($5 \cdot 10^{-4}$ mol l^{-1}) in H_2SO_4 (1 mol l^{-1}) was compared with the simulated curve calculated according to Eq. (*1*) for $z = 2$ and $D = 4.5 \cdot 10^{-6}$ cm^2 s^{-1}. In the time interval 0.04 to 1 s the current difference was less than 1%.

The simulated curves were also used to test that simplified Eq. (*2*) is suitable for absolute determination of concentration. Simulated curves were calculated according to Eq. (*1*) for $z = 2$, concentration $5 \cdot 10^{-4}$ mol l^{-1} *o*-dianizidine and D values ranging from $3 \cdot 10^{-6}$ to $6 \cdot 10^{-6}$ cm^2 s^{-1}. For different D the error in determined concentration did not exceed 5% of correct value $5 \cdot 10^{-4}$ mol l^{-1}.

Determinatiom of o-Dianizidine, Ferrocyanide, Ascorbic Acid and Dopamine

Applied electrochemical reactions was two electron oxidation of *o*-dianizidine, dopamine[9 - 11] and ascorbic acid[12] and one electron oxidation of ferrocyanide. In every analysis with given experimental arrangement it was necessary to determine optimum duration of chronoamperometric experiment to avoid convection influence caused by the density change in the diffusion layer as well as by the apparatus instability. This influence demonstrates itself by bending otherwise straight line $(I\sqrt{t}/A)$ vs $\sqrt{t}$ dependence towards higher $I\sqrt{t}/A$ values. All analyzed species were determined in medii indicated for their stock solutions (see Experimental). No electrochemical pretreatment of electrode surface was necessary for *o*-dianizidine and ferrocyanide.

Precision and accuracy of their absolute chronoamperometric analysis was tested within the concentration range 10^{-4} to 10^{-3} mol l^{-1} (this is the typical concentration range for polarographic analysis). The results are summarized in Tables I and II. The arithmetic mean does not differ statistically significantly from the value of *c(given)* at any of given concentrations of analyzed species. For the whole investigated range of concentrations in linear dependences $\bar{c}(found) = a + bc(given)$ the intercepts a do not

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TABLE I

Precision and accuracy of the chronoamperometric determination of $\bar{c} = \bar{c}(found)$ for *o*-dianizidine in 1 M H_2SO_4 (sample A) and ferrocyanide in 0.1 M KCl (sample B) at different concentrations $c = c(given)$. Current sampling interval 0.04 – 1 s after starting the electrolysis at the potential E = +0.6 V (sample A) or +1.1 V (sample B); prior to electrolysis is E = −0.2 V, all vs SCE. Working electrode Pt cylindrical semimicroelectrode, r = 20 μm and l = 15 mm; T = 298 K

Sample	$c \cdot 10^4$, mol l^{-1}	$\bar{c} \cdot 10^4$ [a], mol l^{-1}	Number of analyses [b]	$s \cdot 10^5$ [c], mol l^{-1}	S_r [d], %	95% Confidence limit	
						Δc, μmol l^{-1}	$(\bar{c} \pm \Delta c)/c$, %
A	1.00	1.08	5	1.2	11.1	14	108.0 ± 14.0
	2.50	2.46	5	1.3	5.3	16	98.4 ± 6.5
	5.00	5.11	5	1.8	3.5	21	102.2 ± 4.2
	7.50	7.55	5	2.2	2.9	26	100.7 ± 3.5
	10.00	10.10	5	2.6	2.6	31	101.0 ± 3.1
B	1.00	1.09	5	1.2	11.0	15	109.0 ± 15.0
	2.50	2.46	5	1.7	6.9	20	98.4 ± 8.0
	5.00	5.11	5	1.8	3.5	21	102.2 ± 4.2
	7.50	7.44	5	2.2	3.0	26	99.2 ± 3.5
	10.00	10.11	5	2.5	2.5	30	101.1 ± 3.0

[a] Mean value: second decimal place is insignificant with regard to confidence limit: $\bar{c} = 0.026 \cdot 10^{-4} + 1.01\,c$, $S_a = 0.05 \cdot 10^{-4}$, $S_b = 0.009$ (sample A) and $\bar{c} = 0.03 \cdot 10^{-4} + 1.00\,c$, $S_a = 0.08 \cdot 10^{-4}$, $S_b = 0.01$ (sample B); [b] without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs $\sqrt{t}$ dependence and without outliers; [c] standard deviation; [d] relative standard deviation.

TABLE II

Precision and accuracy of the chronoamperometric determination of $\bar{c} = \bar{c}(found)$ for ascorbic acid in acetate buffer (sample A) and dopamine in phosphate buffer (sample B) at different concentrations $c = c(given)$. Current sampling interval 0.04 – 1 s after starting the electrolysis at the potential E = 0.9 V; prior to electrolysis is E = 0.0 V, all vs SCE. Working electrode Pt cylindrical semimicroelectrode, r = 20 μm and l = 15 mm; T = 298 K

Sample	$c \cdot 10^4$, mol l^{-1}	$\bar{c} \cdot 10^4$ [a], mol l^{-1}	Number of analyses [b]	$s \cdot 10^5$ [c], mol l^{-1}	S_r [d], %	95% Confidence limit	
						Δc, μmol l^{-1}	$(\bar{c} \pm \Delta c)/c$, %
A	1.19	1.27	5	1.2	10.1	14	106.7 ± 11.8
	2.37	2.18	5	1.7	5.9	20	91.9 ± 8.4
	3.56	3.67	5	1.9	5.3	22	103.1 ± 6.2
	5.93	6.08	5	2.6	4.3	31	102.5 ± 5.2
	11.85	11.63	5	4.4	3.8	52	98.1 ± 4.4
B	2.61	2.85	5	1.8	6.3	21	109.2 ± 8.0
	5.22	5.27	5	2.2	4.2	26	100.9 ± 5.0
	7.83	7.65	5	3.1	4.0	37	97.7 ± 4.7
	10.45	10.51	5	4.0	3.8	47	100.6 ± 4.5

[a] Mean value: second decimal place is insignificant with regard to confidence limit: $\bar{c} = 0.08 \cdot 10^{-4} + 0.98\ c$, $S_a = 0.13 \cdot 10^{-4}$, $S_b = 0.02$ (sample A) and $\bar{c} = 0.2 \cdot 10^{-4} + 0.97\ c$, $S_a = 0.03 \cdot 10^{-4}$, $S_b = 0.03$ (sample B); [b] without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs $\sqrt{t}$ dependence and without outliers; [c] standard deviation; [d] relative standard deviation.

differ significantly from zero and the slopes b from unity (testing with the help of t-test and Lord's characteristics)[13].

From the principle of absolute chronoamperometric analysis it follows that the results of the analysis should not depend on the temperature of the analyte. This influence was investigated within the range 5 °C to 37 °C. The results of *o*-dianizidine sample are summarized in Table III. Testing the identity of arithmetic means it has been found that no pair of $\bar{c}$*(found)* for different temperatures is mutually significantly different. None of $\bar{c}$*(found)* values is an outlier with respect to their arithmetic mean ($10.09 \cdot 10^{-4}$ mol l^{-1}). Neither the arithmetic mean nor any of the $\bar{c}$*(found)* values are significantly different from the *c(given)*. From this it can be concluded that the temperature change does not influence significantly the result of chronoamperometric analysis. During the analysis, however, the temperature must be kept constant and equal in the whole analyte. It is not difficult to keep this condition due to short duration of the measurement (ca 1 s).

TABLE III

Influence of analyte temperature and H_2SO_4 and saccharose concentration on the precision and accuracy of *o*-dianizidine determination by absolute chronoamperometric analysis *c(given)* = $1.00 \cdot 10^{-3}$ mol dm^{-3} *o*-dianizidine; current sampling interval 0.04 – 1 s after starting the electrolysis at the potential +0.6 V vs SCE (potential prior to the electrolysis is −0.2 V vs SCE); working electrode Pt cylindrical semimicroelectrode, r = 20 μm and l = 15 mm

Temperature K	$c(H_2SO_4)$ mol l^{-1}	c(sacharose) %	$\bar{c}$*(found)* . 10^4 mol l^{-1}	Number of analyses[b]	95% Confidence limit	
					Δc μmol l^{-1}	$(\bar{c} \pm \Delta c)/c$ %
278	1.00	0	10.11	5	32	101.1 ± 3.2
288	1.00	0	10.10	5	33	101.0 ± 3.3
293.5	1.00	0	9.91	5	33	99.1 ± 3.3
298.2	1.00	0	10.06	5	31	100.6 ± 3.1
310	1.00	0	10.28	5	36	102.8 ± 3.6
298	0.10	0	10.13	5	35	101.3 ± 3.5
298	0.50	0	9.95	5	33	99.5 ± 3.3
298	1.00	0	10.07	5	32	100.7 ± 3.2
298	1.00	2	10.02	5	33	100.2 ± 3.3
298	1.00	5	10.11	5	40	101.1 ± 4.0
298	1.00	7	10.13	5	37	101.3 ± 3.7
298	1.00	10	10.15	5	41	101.5 ± 4.1

[a] The second decimal place is insignificant with regard to the value of limits of confidence; [b] without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs $\sqrt{t}$ dependence and without outliers.

Influence of electroinactive substances present in the analyte in high concentrations was also verified. By these substances both density and viscosity of the analyte can be changed substantially. The electroinactive electrolyte is to secure high electric conductivity and thus to suppress the migration component of the current of electroactive substance. Thus only solutions with the concentration of the electroinactive electrolyte higher than hundredfold of the concentration of determined substance were analyzed. From the electroinactive nonelectrolytes we investigated the saccharose influence on *o*-dianizidine determination. The results of the analyses are summarized in Table III.

The determined values of *o*-dianizidine concentration obviously do not depend either on the H_2SO_4 concentration (if this is higher than the hundredfold of *o*-dianizidine concentration), or on the concentration of the saccharose. This is attested by the fact, that none of the $\bar{c}$*(found)* values in Table III significantly differs from the arithmetic mean at the level of 95% probability. Neither $\bar{c}$*(found)* nor their mean value $10.08 \cdot 10^{-4}$ mol l^{-1} significantly differ from the value of *c(given)*.

The described and discussed results demonstrate that the chronoamperometric analysis with Pt cylindrical semimicroelectrode can be regarded as an absolute method of electroactive component determination, within the concentration range 10^{-3} to 10^{-4} mol l^{-1}. Proposed absolute method enables also to determine values of diffusion coefficient, if the concentration of electroactive species is in milimolar region. The accuracy and precision is comparable with that given for concentration.

The Optimization of Working Electrode Radius

Calculation of concentration is based upon the slope and intercept of $I\sqrt{t}/A$ vs $\sqrt{t}$ dependence obtained from a single chronoamperogram. The error of determination of the intercept, which is the linear component of chronoamperometric constant, will increase with decreasing radius of electrode since proportion of linear diffusion decreases. Analogically an increase of relative error of the slope with increasing radius is to be expected, since the proportion of the spherical component of the total flux will decrease. The error of concentration determination will thus increase both for very small and very large radii.

Relative error of determination aproximated as relative standard deviation was calculated for different electrode radii (routine PROG2) using simulated chronoamperograms charged by white noise with constant as well as proportional component. In our experimental conditions the amplitude of constant noise component was about 10 A m^{-2}. Amplitude of proportional noise component was estimated to 5% of limiting diffusion current. The values of relative standard deviations of found concentration for different radii are shown in Table IV together with the values of relative standard deviation of the slope and intercept.

The dependence of relative standard deviation of determined concentration on the radius of cylindrical electrode (Fig. 1) exhibits a minimum at 46 ± 2 μm radius for a common value of diffusion coefficient $1 \cdot 10^{-9}$ m^2 s^{-1} and time interval 0.04 to 1 s. For higher amplitudes of constant and proportional white noise the relative standard deviation of concentration increases, but the optimum radius retains its value. We have found out that this value is not very sensitive to the estimate of noise components.

It can be seen from the shape of dependence *1* on Fig. 1 that the cylindrical electrode used in this work enables the absolute determination with the relative error not significantly higher than the minimum value.

TABLE IV

Relative standard deviation of the slope (s_y/S), intercept (s_u/U) and found concentration (s_c/c) for cylindrical electrode of different radii[a]

Parameter	r, mm									
	0.001	0.005	0.01	0.02	0.03	0.05	0.1	0.5	1.0	5.0
$s_u/U \cdot 10^2$	14.280	2.916	1.450	0.713	0.493	0.299	0.167	0.088	0.087	0.086
$s_y/S \cdot 10^2$	0.344	0.466	0.503	0.586	0.625	0.655	0.873	1.718	2.139	4.167
$s_c/c \cdot 10^2$	48.05	19.12	11.23	5.50	2.21	1.83	3.32	14.28	22.11	41.15

[a] Curves simulated for: number of exchanged electrons 2; diffusion coefficient 10^{-9} m^2 s^{-1}; concentration 1 mol m^{-3}; electrode length 0.015 m; sampling interval 0.04 – 1 s (1 000 samples). White noise: constant component amplitude 10 A m^{-2}; proportional component amplitude 5% of diffusion current.

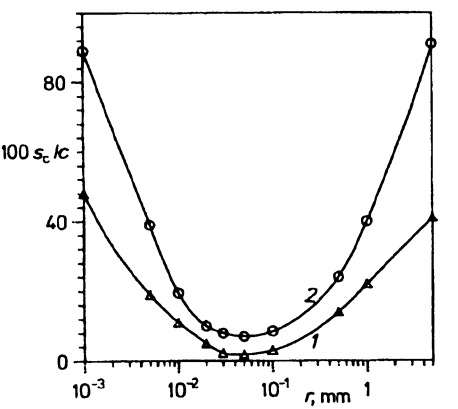

FIG. 1

Dependence of relative standard deviation of concentration determined by absolute chronoamperometry on the radius of cylindrical electrode: *1* simulation of chronoamperograms described in Table IV; *2* doubled amplitudes of white noise components

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