

Possibilities of absolute chronoamperometric determination. I

D. BUSTIN

*Department of Analytical Chemistry, Slovak Technical University,
CS-812 37 Bratislava*

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A new analytical application of chronoamperometry as an absolute method of determination of the electroactive substances is described in this paper. Basis of such a determination not requiring standardization is separation of the signal component caused by linear diffusion from that caused by either spherical or cylindrical contribution to the total diffusion current of the determined substance. From the suitable indication electrodes of small sizes the use of hanging mercury drop electrode has been verified within the concentration range of the analyzed Tl^+ 10^{-3} to 10^{-4} mol dm^{-3} . Results of the analysis were accurate and independent of the temperature of the analyzed solution within the range 5—37°C (with the necessity to keep the temperature constant during several seconds of duration of the chronoamperometric determination). It has also been shown that the result of the analysis does depend neither on the radius of mercury drop within the range 0.37 to 0.63 mm nor upon the concentration of the electroinactive substances influencing the density and viscosity of the analyzed solution. The significance of this possibility to use chronoamperometric determination without necessity of standardization follows from the lack of reference samples for standardization which is often observed in the practice.

В работе описывается новое аналитическое применение хроноамперометрии как абсолютного метода определения содержания электроактивных веществ. Основой для подобного определения, не нуждающегося в стандартизации, является отделение сигнального компонента, вызываемого линейной диффузией, от компонента, вызываемого сферическим или цилиндрическим вкладом в общий ток диффузии определяемого вещества. Из числа подходящих индикаторных электродов небольших размеров был испытан висячий ртутный капельный электрод в диапазоне концентраций анализируемых ионов Tl^+ от 10^{-3} до 10^{-4} моль $дм^{-3}$. Результаты определения были правильны и не зависели от температуры анализируемого раствора в промежутке 5—37°C (необходимо поддерживать температуру постоянной в течение нескольких секунд продолжительности хроноамперометрического определения). Было также показано, что результаты анализа не зависят ни от радиуса ртутной капли в промежутке 0,37—0,63 мм, ни от концентрации электронеактивных веществ, влияющих на плотность и вязкость анализируемого раствора.

Значение такой возможности применения хроноамперометрического определения без необходимости стандартизации вытекает из частого отсутствия на практике образцов сравнения, нужных для стандартизации.

Electrochemical methods with the small indication electrode (voltammetry, polarography, chronopotentiometry, chronoamperometry) are used in the quantitative analysis in such a way that the signal of the sample (*e.g.* limiting diffusion current, transition time, *etc.*) is compared with the signal of reference material, *e.g.* of the solution with known concentration of determined component. The necessity of such a procedure follows from the fact that the parameters of the used indication electrode (surface area, geometry of electrode — solution phase boundary) as well as the values of the diffusion coefficient in the medium of analyzed solution are unknown. Whilst the parameters of the indication electrode can be relatively easily determined by physical measurement, the value of the diffusion coefficient of the determined component is always difficultly accessible. The tabulated values have mostly no importance for the calculation of concentration from theoretical equations. The value of diffusion coefficient for the given medium of analyte has to be known. It can be determined only using the signal of reference sample with known concentration of the analyzed component.

This paper presents an attempt to use chronoamperometric measurements for determination of electroactive substances without necessity to compare the signal of the analyzed and reference samples (standardization). Because of generally observed lack of reference samples this approach would increase the significance of chronoamperometry in analytical practice.

The basis for chronoamperometric determination without standardization is the separation of signal component caused by linear diffusion from that caused by spherical or cylindrical contribution to the total diffusion flux of determined substance to the indication electrode of small size. Only indication electrodes of simple geometry, *e.g.* spherical, cylindrical or disc electrodes, could be possibly used, for which the equations of current—time functions are known. If the value of the constant potential of indication electrode is sufficiently higher than the value of half-wave potential (this being the condition of the limiting diffusion current), the current *vs.* time dependence has the following form

$$I = zFcA \left(\frac{D}{\pi t} \right)^{1/2} \left[1 + N \left(\frac{Dt}{r^2} \right)^{1/2} \right] \quad (1)$$

where z is the number of exchanged electrons,
 F — the Faraday constant (A s mol^{-1}),
 A — electrode area (m^2),

- c — concentration of determined substance (mol m^{-3}),
 D — diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
 r — radius of disc, sphere or cylinder surface, which forms the electrode (m^2)

and N is the coefficient with the value $\sqrt{\pi}$ for the spherical electrode [1, 2]; 0.5 for cylindrical electrode [2—4]; for disc electrode the following values are given: 2.12 [5], 1.93 [6], 1.7947 [7].

In the case of the expanding spherical electrode used in polarography (the dropping mercury electrode) the equation of limiting diffusion current *vs.* time dependence has the form [8, 9]

$$I = k \cdot zFcD^{1/2}m_{\tau}^{2/3}t^{1/6} \left[1 + k' \frac{D^{1/2}t^{1/6}}{m_{\tau}^{1/3}} + k'' \left(\frac{D^{1/2}t^{1/6}}{m_{\tau}^{1/3}} \right)^2 \right] \quad (2)$$

where m_{τ} is the mercury flow rate (kg s^{-1}),

$$k = 7.32 \times 10^{-3} \text{ m}^2 \text{ kg}^{-2/3},$$

$$k' = 39 \text{ kg}^{1/3} \text{ m}^{-1},$$

$$k'' = 150 \text{ kg}^{2/3} \text{ m}^{-2}.$$

The substantial difference of these equations from the simple equation for current limited by semi-infinite linear diffusion (Cottrell's equation) is that their right-hand side contains besides the Cottrell's term with the exponent of diffusion coefficient 1/2 one term more, containing the diffusion coefficient in the first power (eqn (2) also the term with $D^{3/2}$). From this fact it follows that minimally two measurements of current in two different times of the electrode polarization can be used to make up two equations of the type (1) or (2), with two unknowns (D and c), which can be calculated if number of exchanged electrons z , electrode radius r , and mercury flow rate m_{τ} are known. This enables to use the chronoamperometry for quantitative analysis without the necessity to determine the diffusion coefficient by independent measurement, *i.e.* by standardization. Preference of chronoamperometry to other voltammetric methods with the indication electrode of small size for using in absolute determination follows from the possibility of a simple correction of measurement to the residual current the capacity component of which is negligible shortly after switching on the working potential.

Experimental

Chemicals and solutions

All chemicals were of anal. grade purity and were used without further purification. The stock solution ($c(\text{Tl}^+) = 0.01 \text{ nmol dm}^{-3}$) in solution of KNO_3 ($c = 1 \text{ mol dm}^{-3}$) or

HNO_3 ($c = 1 \text{ mol dm}^{-3}$) was analyzed coulometrically using the mercury pool electrode (surface area approximately 14 cm^2). The 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.

Choice of the indication electrode

Electrodes of the above-mentioned simple geometry (sphere, disc, cylinder) can be fabricated from solid metallic materials, carbon or mercury. Solid electrode materials have several disadvantages of which especially the difficulty of the reproducible preparation of well defined electrode surface (surface activity, oxide films, etc.) is to be mentioned. In comparison with the mercury electrodes they have, if they are made of noble metals or carbon, the advantage of possibility to reach substantially more positive potentials than $+0.4 \text{ V vs. SCE}$, at which potential anodic oxidation of the material of the mercury electrode proceeds also in noncomplexing media. If the more negative potential range is used in the analysis, the mercury capillary electrodes are preferred due to the simplicity of their preparation and manipulation as well as due to their well defined and reproducible surface.

The mercury capillary electrode can have the form of cylinder, sphere or expanding sphere. The cylinder form can be achieved by the streaming electrode. Because of great consumption of purified mercury the use of this electrode for measurements is impractical.

The use of dropping mercury electrode, which has been applied with great success in the polarography, for absolute determination is hindered by the factors causing deviations of real measurements from the values calculated from eqn (2). The solution stirring caused by falling drops is demonstrated especially in the early phases of the growth of the next drop by convection contribution to the transport of electroactive component. The current maxima of the second kind [10] are connected with the convection caused by high linear mercury flow rate in the capillary. The depletion by preceding polarization of the solution in the vicinity at the beginning of the drop life [11] usually causes the current decrease compared with the theory. Derivation of the relationship (2) counts with the constant mercury flow rate. In fact, however, the mercury flow rate changes during the growth of the drop [12] as the back-pressure is changed which is opposed to hydrostatic pressure of the mercury column. If the thick-wall capillary is used for mercury drop electrode it comes also to the deviations caused by shielding of the drop by its support [9].

Most of the above-mentioned problems disappear if the stationary mercury electrode is used realized e.g. as the mercury drop hanging at the capillary orifice (HMDE) or on the metal conductor electric contact sealed in glass. The last mentioned construction was used by *Shain* and *Martin* [13] who experimentally verified the validity of eqn (1). The reports of Japanese authors [14, 15] make use of stationary drop forced out from the thin-wall capillary tube for chronoamperometric measurements for determination of diffusion coefficients. From the standpoint of the solution of our problem the most important result of the mentioned papers lies in the statement that eqn (1) for current

limited by diffusion towards the spherical electrode holds for the stationary mercury drop electrode. Using the thin-wall capillary as the drop "support" the shielding is negligible and the deviations from the validity of eqn (1), if any, can be ascribed to the convection.

In Ref. [13] the change of drop shape is described due to the change of surface tension switching-over the potential of the indication electrode from the initial to the working value. The range of deformation of the sphere depends on the mercury surface tension. The sudden potential change causes the change of surface tension resulting in a slight change of drop shape. The movement of drop surface forces the movement of the surrounding solution and thus the convection transport. According to Ref. [13] this convection is significant especially in the case of drops with larger diameters and causes the growth of current in the early phase of electrolysis (according to the authors' estimation up to the fourth second). In the later phase of the chronoamperometric experiment another positive deviation of current is mentioned due to the convection caused by changes of electrolyte density in the diffusion layer (*e.g.* depletion of electroactive species by electrolysis). According to Ref. [14] this convection must be taken into account for the electrolysis times longer than 10 s.

Chronoamperometric measurements

Chronoamperometric curves were measured using the multipurpose polarograph GWP 673 (Academy of Sciences, GDR). This instrument "on line" with the microcomputer Compucorp 610 (Compucorp, USA) made possible registration of the chronoamperogram to the computer memory through the AD converter (Burr-Brown, USA) synchronized with the loading of working potential to the indication electrode (program IN 1). Standard three-electrode arrangement was used with the Kemula — type E 69 b (Radiometer, Copenhagen) hanging mercury drop indication electrode (HMDE). The thin-wall capillary tube was prepared from soft glass by drawing out to the outer diameter 0.25 mm. The wall thickness was *ca.* 0.1 mm and the diameter of capillary tube orifice *ca.* 0.05 mm.

Results and discussion

Calculation of concentration

The registered chronoamperogram is transformed to the dependence of the so-called chronoamperometric constant ($I\sqrt{t}/A$) *vs.* \sqrt{t} . From the adapted eqn (1) for the case of spherical electrode

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

$$U = zFc\sqrt{\frac{D}{\pi}}; \quad S = \frac{zFcD}{r}$$

it can be seen that this dependence should be linear, the straight line being determined by the intercept U and the slope S . Both U and $(S\sqrt{t})$ are the components of the so-called chronoamperometric constant caused by linear and spherical contribution to the diffusion current.

The values U and S determined from a single chronoamperometric experiment can be used for calculating the concentration of the electroactive substance according to the relationship

$$c = \frac{U^2}{S} \frac{\pi}{zFr} \quad (4)$$

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

1. Acquisition of $I-t$ curve of the analyzed component; by the rule 1000 points (maximum 2000 points) — program IN 1;
2. acquisition of the $I-t$ curve of the background (at the same working potential of the indication electrode) — program IN 1;
3. correction of chronoamperogram of the analyzed component by subtracting the $I-t$ background curve — the program SUCET;
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 PROG 2. The dependence $(I\sqrt{t}/A)$ vs. \sqrt{t} is loaded to the peripheral memory (floppy disc) and it is registered by the program OUT 2 on the XY recorder through the 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) [16].

The absolute chronoamperometric Tl⁺ analysis with the thin-wall capillary HMDE

The applied electrochemical reaction is the cathodic reduction of Tl⁺ by one electron ($z = 1$) under the formation of Tl amalgam.

In every analysis with given experimental arrangement it is necessary to determine the maximum duration of the chronoamperometric experiment where the convection caused by density change in the diffusion layer as well as by the apparatus instability is still not expressed. The determination is carried out after the chronoamperogram transformation to the $(I\sqrt{t}/A)$ vs. \sqrt{t} dependence. The

convection influence demonstrates itself by bending this otherwise straight line dependence towards higher $(I\sqrt{t}/A)$ values.

The convection in first phases of electrolysis reported in Ref. [13] was not observed in any of our experiments. We assume that the positive error reported in Ref. [13] can be connected with the slowness of used registration apparatus. Though the $(I\sqrt{t}/A)$ vs. \sqrt{t} dependence with the Tl^+ analysis using the thin-wall capillary was the straight line for at least 10 s (6 experiments) the chronoamperogram was evaluated only in the interval 0.2 to 5 s.

Precision and accuracy of the absolute chronoamperometric analysis was tested within the concentration range 10^{-4} to 10^{-3} mol dm $^{-3}$ (this being the typical concentration range for polarographic analysis). The results are summarized in Table 1. The arithmetic mean does not differ statistically significantly from the value of $c(\text{given})$ at any of the given Tl^+ concentrations. For the whole investigated range of concentrations in the linear dependence $c(\text{found}) = a + b c(\text{given})$ the intercept a does not differ significantly from zero and the slope b from unity (testing with the help of t -test and Lord's characteristics).

From the principle of absolute chronoamperometric analysis it follows that the result 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 are summarized in Table 2.

Testing the identity of arithmetic means it has been found that no pair of $\bar{c}(\text{found})$ for different temperatures is mutually significantly different. None of $\bar{c}(\text{found})$ values is an outlier with respect to their arithmetic mean (10.09×10^{-4} mol dm $^{-3}$). Neither the arithmetic mean nor any of the $\bar{c}(\text{found})$ values are significantly different from the $c(\text{given})$. From this we can conclude 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.* 5 s).

In the case of ideal spherical electrode the determination of concentration does not depend on its radius. The mercury drop hanging on the thin-wall capillary, however, only approaches the spherical shape. The deviation from the "ideal" spherical symmetry can be caused by deformation of the drop, and by the shielding by the capillary tube walls. The influence of these factors was verified with the changes of drop size within the range of drop radius 0.37 to 0.63 mm. Maximum value was limited by drop stability at the orifice and the minimum value by the achievable sufficient precision on the specified HMDE. The influence of drop size was tested analyzing Tl^+ in the optimal concentration *ca.* 10^{-3} mol dm $^{-3}$. The results summarized in Table 2 show that the drop size does not influence the accuracy of absolute determination (none from the values of $\bar{c}(\text{found})$ is the outlier). The influences of shielding (minimalized using the

Table 1

Precision and accuracy of the absolute chronoamperometric determination at different Tl^+ concentrations; current sampling interval 0.2–5 s after starting the electrolysis at the potential -0.9 V vs. SCE (potential prior to the electrolysis is -0.2 V vs. SCE), indication electrode — stationary mercury drop, $r = 0.44$ mm; outer diameter of capillary orifice *ca.* 0.25 mm; $c(KNO_3) = 1$ mol dm^{-3} ; $T = 298$ K

$\frac{10^4 c(\text{given})}{\text{mol dm}^{-3}}$	$\frac{10^4 \bar{c}(\text{found})}{\text{mol dm}^{-3}}$ (mean)*	Number of analyses**	Standard deviation $\frac{s \cdot 10^5}{\text{mol dm}^{-3}}$	Relative standard deviation $s_r/\%$	Limits of confidence for 95 % probability	
					$\frac{\Delta c}{\mu\text{mol dm}^{-3}}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$
1.25	1.26	5	1.4	11.1	16	100.8 ± 13.1
2.50	2.42	5	1.4	5.7	17	96.8 ± 6.7
5.00	5.12	5	1.6	3.2	19	102.4 ± 3.8
7.50	7.40	5	2.2	2.9	26	98.7 ± 3.5
10.00	10.18	5	2.8	2.8	33	101.8 ± 3.5

$$\bar{c}(\text{found}) = a + b c(\text{given})$$

$$a = -0.05 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b = 1.02$$

$$s_a = 0.08 \times 10^{-4} \text{ mol dm}^{-3}$$

$$s_b = 0.01$$

* The second decimal place is insignificant with regard to the value of limits of confidence.

** Without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs. \sqrt{t} dependence and without outliers.

Table 2

Influence of analyte temperature and hanging drop size on the precision and accuracy of Tl^+ determination
by absolute chronoamperometric analysis

$c(KNO_3) = 1 \text{ mol dm}^{-3}$; current sampling interval 0.2–5 s after starting the electrolysis at the potential -0.9 V vs. SCE (potential prior to the electrolysis is -0.2 V vs. SCE); outer diameter of capillary orifice *ca.* 0.25 mm

T/K	Drop radius r/mm	$10^4 c(\text{given})$ mol dm ⁻³	$10^4 \bar{c}(\text{found})$ mol dm ⁻³ (mean)*	Number of analyses**	Limits of confidence for 95 % probability	
					$\frac{\Delta c}{\mu\text{mol dm}^{-3}}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$
278	0.44	10.00	10.07	5	32	100.7 ± 3.2
288.2	0.44	10.00	10.10	5	31	101.0 ± 3.1
291.4	0.44	10.00	10.11	5	36	101.1 ± 3.6
296.9	0.44	10.00	9.89	5	33	98.9 ± 3.3
310.0	0.44	10.00	10.30	5	37	103.0 ± 3.7
298	0.37	9.55	9.75	5	71	102.1 ± 7.4
298	0.44	9.55	9.57	5	28	100.2 ± 3.0
298	0.53	9.55	9.66	5	35	101.2 ± 3.6
298	0.63	9.55	9.31	5	46	97.5 ± 4.9

* The second decimal place is insignificant with regard to the value of limits of confidence.

** Without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs. \sqrt{t} dependence and without outliers.

Table 3

Influence of KNO_3 and saccharose concentration on the precision and accuracy of Tl^+ determination by absolute chronoamperometric analysis $c(\text{given}) = 1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ TlNO}_3$; current sampling interval 0.2–5 s after starting the electrolysis at the potential -0.9 V vs. SCE (potential prior to the electrolysis is -0.2 V vs. SCE); indication electrode — stationary mercury drop, $r = 0.44 \text{ mm}$ ($A = 2.47 \text{ mm}^2$); outer diameter of capillary orifice *ca.* 0.25 mm; $T = 298 \text{ K}$

$\frac{c(\text{KNO}_3)}{\text{mol dm}^{-3}}$	$\frac{c(\text{saccharose})}{\%}$	$\frac{10^4 \bar{c}(\text{found})}{\text{mol dm}^{-3}}$ (mean)*	Number of analyses**	Limits of confidence for 95 % probability	
				$\frac{\Delta c}{\mu\text{mol dm}^{-3}}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$
0.1	0	10.13	5	37	101.3 ± 3.7
0.5	0	9.89	5	33	98.9 ± 3.3
1.0	0	10.02	5	33	101.2 ± 3.3
1.0	5	10.14	5	59	101.4 ± 5.9
1.0	10	10.15	5	51	101.5 ± 5.1

* The second decimal place is insignificant with regard to the value of limits of confidence.

** Without analyses set aside because of nonlinearity of the $I\sqrt{t}/A$ vs. \sqrt{t} dependence and without outliers.

thin-wall capillary) and that of the drop shape deformation are thus either negligible or they are mutually compensated. The limits of confidence for 95 % probability seem to be significantly higher for small drop, this being probably connected with the reproducibility of small drop preparation. The minimal standard deviation occurs when measuring with the drop the area of which takes *ca.* 2.5 mm².

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 Tl⁺ determination. The results of the analyses are summarized in Table 3.

The determined values of Tl⁺ concentration obviously do not depend either on the KNO₃ concentration (if this is higher than the hundredfold of Tl⁺ concentration) or on the concentration of the saccharose. This is attested by the fact, that none of the \bar{c} (found) values in Table 3 significantly differs from the arithmetic mean at the level of 95 % probability. Neither \bar{c} (found) nor their mean value $10.07 \times 10^{-4} \text{ mol dm}^{-3}$ significantly differs from the accurate value. The addition of saccharose to the analyzed solutions seems to cause little increase of limits of confidence of the result of analysis.

The described and discussed results demonstrate the fact that the chronoamperometric analysis with the thin-wall capillary HMDE can be regarded as an absolute method of electroactive component determination, within the concentration range 10^{-3} to $10^{-4} \text{ mol dm}^{-3}$

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