

# Possibilities of absolute chronoamperometric determination II.\* Influence of parallel chemical reaction and shielding of the hanging mercury drop electrode

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Basis for application of chronoamperometry as an absolute determination method of electroactive substances is the separation of the signal component limited by the linear diffusion from that limited either by spherical or cylindrical contribution to the total flux of the determined substance to the hanging mercury drop electrode. Using the thick-wall capillary for its realization the results are loaded by proportional error following from electrode shielding by capillary wall.

The sufficient difference of half-wave potentials is a prerequisite in the case of application of chronoamperometry for absolute determination of two electroactive substances. The analysis of that reducing substance which is the second one in the order is performed after subtracting the current of the first species. Its result is by the rule less precise than with the analysis of one-component sample.

The absolute chronoamperometric determination is compared with the controlled potential coulometry. Apart from the greater rate of the analysis it seems to be more advantageous to use chronoamperometry in the cases (which are relatively often in the practice) when the analytically used electrode reaction is complicated by slow chemical processes.

Основой для применения хроноамперометрии в качестве абсолютного метода для определения содержания электроактивных веществ является отделение сигнального компонента, определяемого линейной диффузией, от компонента, определяемого сферическим или цилиндрическим вкладом, в общий ток определяемого вещества к висящему ртутному капельному электроду. При использовании толстостенных капилляров получаемые результаты включают пропорциональную ошибку, являющуюся следствием экранирования электрода стенкой капилляра.

Для возможности применения хроноамперометрии для абсолютного определения двух электроактивных веществ необходимо существенное различие в величинах их потенциалов полуволн. Анализ вос-

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\* For Part I see Ref. [1].

становливающего вещества, являющегося вторым по порядку, производится после вычитания величины тока, отвечающего первому веществу. Результат такого анализа, как правило, менее точен, чем при анализе однокомпонентного образца.

Проводится сравнение абсолютного хроноамперометрического определения и кулонометрии с постоянным потенциалом. Кроме более быстрого проведения анализа, применение хроноамперометрии, оказывается, обладает преимуществами по сравнению с кулонометрией и в случаях (относительно часто встречающихся на практике), когда используемая в аналитических целях электродная реакция усложнена медленными химическими процессами.

A possibility of absolute determination of  $Tl^+$  using its chronoamperometric reduction on the mercury drop electrode hanging from the thin-wall capillary was described in our previous paper [1]. The separation of the signal component caused by linear diffusion from that caused by spherical contribution to the total current of the determined component was the basis for this application. Computer evaluation of chronoamperometric experiment is based upon the transformation of chronoamperogram ( $I-t$  curve) to the dependence ( $I\sqrt{t}/A$ ) vs.  $\sqrt{t}$ . In the case of spherical shape of the indication electrode this dependence is a straight line with the slope  $S$  and with the intercept having the value  $U$ . In the sense of equation for current time dependence known from the literature [2, 3] the concentration  $c$  can be calculated from the experimentally known values  $U$  and  $S$  according to the relationship

$$c = \frac{U^2}{S} \frac{\pi}{zFr} \quad (1)$$

where  $r$  is the radius of mercury drop and  $z$  is the number of exchanged electrons in the used electrode reaction.

This paper is devoted to the investigation of possibility to use a thick-wall capillary for the realization of the hanging mercury drop electrode (HMDE) in connection with the absolute chronoamperometric analysis. The paper also deals with the possibility of application of the absolute method for determining two electroactive components and finally with the comparison of this new absolute method of analysis with the traditionally accepted one — with the coulometry.

## Experimental

### *Chemicals and solutions*

Commercially available chemicals used in this work were of anal. grade purity without further purification.  $K_3Cr(CN)_6$  was prepared and purified according to Ref. [4]. Its

purity was verified by the polarographic analysis [5]. The  $[\text{Cr}(\text{CN})_6]^{3-}$  concentration ( $0.01 \text{ mol dm}^{-3}$ ) in the stock aqueous solution of KCN ( $c = 1 \text{ mol dm}^{-3}$ ) was determined spectrophotometrically on the basis of Cr analysis after its oxidation to chromate by hydrogen peroxide [6]. Another way of determining the  $[\text{Cr}(\text{CN})_6]^{3-}$  in the stock solution was controlled potential coulometry using mercury pool electrode (surface area approximately  $14 \text{ cm}^2$ ). Evaluating the coulometric analysis of  $[\text{Cr}(\text{CN})_6]^{3-}$  the  $[\text{Cr}(\text{CN})_6]^{4-}$  reoxidation by water had to be considered [7]. Also the  $\text{Bi}^{3+}$  concentration ( $0.01 \text{ mol dm}^{-3}$ ) in the  $\text{HNO}_3$  stock aqueous solution ( $c(\text{HNO}_3) = 1 \text{ mol dm}^{-3}$ ) was determined coulometrically. Coulometric results were regarded as the basis to judge the accuracy of the results of the absolute chronoamperometric analysis.

### *Apparatus*

Kemula — type E 69 b (Radiometer, Copenhagen) hanging mercury drop electrode (HMDE) in the three-electrode arrangement was used as the indication electrode to measure the chronoamperograms. The electrochemical apparatus used “on line” with microcomputer is specified in Ref. [1], where also the procedure of the analysis is described in detail.

## **Results and discussion**

### *Application of thick-wall capillary for the absolute chronoamperometric determination*

The experimental work with thin-wall capillary HMDE (in Ref. [1] a glass capillary with the outer diameter approximately  $0.25 \text{ mm}$  was used) which excludes the shielding of the mercury drop by the glass of capillary tube, requires the higher care in manipulation. Possibility of application of the commercially available commonly used thick-wall capillaries with the diameter of *ca.*  $3 \text{ mm}$  was verified. The work with such a HMDE does not require any special care. The above-mentioned diameter, however, represents *ca.*  $2.5$  to  $4$  fold of the diameter of the mercury drop. The results of determinations using drops of two radii  $0.37 \text{ mm}$  and  $0.64 \text{ mm}$  are given in Table 1. Within this range the satisfactorily reproducible drop can be achieved using the specified type HMDE, the drop being resistant enough to the tearing from the capillary orifice. The verified  $\text{Tl}^+$  concentration range makes  $10^{-4}$  to  $10^{-3} \text{ mol dm}^{-3}$ , this being the typical concentration range of the polarographic analysis.

It can be seen from Table 1 that the variation of the current sampling interval has no statistically significant influence on the determination in any of the analyzed concentrations and in any investigated radius of the indication electrode. All 10 measurements for the given concentration can thus be regarded as a single set. The characteristics of linear dependence between the concentration

Table 1

Absolute chronoamperometric determination of  $Tl^+$  with the thick-wall capillary HMDE (*dca.* 3 mm);  $T = 298\text{ K}$ ;  $c(\text{KNO}_3) = 1\text{ mol dm}^{-3}$

$r = 0.37\text{ mm}$		Current sampled at the time interval 0.2 to 1 s			Current sampled at the time interval 0.2 to 5 s			
$10^4 c(\text{given})$ $\text{mol dm}^{-3}$	$10^4 \bar{c}(\text{found})$ $\text{mol dm}^{-3}$ (mean)*	Number of analyses**	Limits of confidence for 95 % probability		$10^4 \bar{c}(\text{found})$ $\text{mol dm}^{-3}$ (mean)*	Number of analyses**	Limits of confidence for 95 % probability	
			$\Delta c$ $\mu\text{mol dm}^{-3}$	$\bar{c}(\text{found}) \pm \Delta c$ $c(\text{given})$ / %			$\Delta c$ $\mu\text{mol dm}^{-3}$	$\bar{c}(\text{found}) \pm \Delta c$ $c(\text{given})$ / %
1.80	2.52	5	28	$140.0 \pm 11.1$	2.47	5	26	$137.2 \pm 10.5$
3.38	4.54	5	34	$134.3 \pm 7.5$	4.65	5	37	$137.6 \pm 8.0$
5.00	7.26	5	40	$152.0 \pm 5.5$	7.38	5	40	$147.6 \pm 5.4$
6.97	9.56	5	46	$141.5 \pm 4.8$	9.53	5	43	$136.7 \pm 4.5$
9.00	12.61	5	57	$140.1 \pm 4.5$	12.40	5	56	$137.8 \pm 4.5$
11.10	15.67	5	71	$141.2 \pm 4.5$	15.95	5	72	$143.7 \pm 4.5$

$c(\text{found}) = a + b c(\text{given})$ ; (together for both current sampling intervals — 10 analyses at each concentration)

$$a = -0.08 \times 10^{-4} \text{ mol dm}^{-3} \quad s_a = 0.11 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b = 1.42 \quad s_b = 0.02$$

Table 1 (Continued)

$r = 0.64 \text{ mm}$		Current sampled at the time interval 0.2 to 4 s			Current sampled at the time interval 0.2 to 10 s			
$10^4 c(\text{given})$	$10^4 \bar{c}(\text{found})$	Number of analyses**	Limits of confidence for 95 % probability		$10^4 \bar{c}(\text{found})$	Number of analyses**	Limits of confidence for 95 % probability	
$\text{mol dm}^{-3}$	$\text{mol dm}^{-3}$ (mean)*		$\frac{\Delta c}{\mu\text{mol dm}^3}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$			$\text{mol dm}^{-3}$ (mean)*	$\frac{\Delta c}{\mu\text{mol dm}^3}$
1.80	2.51	5	22	$138.9 \pm 8.8$	2.37	5	25	$131.6 \pm 10.5$
3.38	4.50	5	36	$133.1 \pm 8.0$	4.38	5	32	$130.4 \pm 7.3$
5.00	6.56	5	43	$131.2 \pm 6.6$	6.34	5	41	$126.0 \pm 6.5$
6.97	8.90	5	46	$127.7 \pm 5.2$	9.15	5	48	$131.3 \pm 5.2$
9.00	11.72	5	59	$130.2 \pm 5.0$	11.91	5	61	$132.3 \pm 5.1$
11.10	14.70	5	75	$132.4 \pm 5.1$	14.47	5	75	$130.4 \pm 5.2$

$c(\text{found}) = a + b c(\text{given})$ ; (together for both current sampling intervals — 10 analyses at each concentration)

$$a = 0.02 \times 10^{-4} \text{ mol dm}^{-3} \quad s_a = 0.11 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b = 1.31 \quad s_b = 0.02$$

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

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

determined by the absolute chronoamperometry  $c$  (found) and the known value of the concentration of testing solutions  $c$  (given)  $a$  and  $b$  are thus calculated for the whole sets (10 measurements for each concentration). The intercept of the linear dependence  $a$  does not statistically differ from zero but the slope  $b$  has values significantly differing from unity in both used drop radii. The limits of confidence in the case of thick-wall capillary do not differ distinctly from the value with thin-wall capillary but the results are higher in all analyzed concentrations. This difference is probably due to the shielding by the glass of the capillary supporting the drop. The accurate results corresponding to the value  $b = 1$  in Table 1 would be achieved if an "effective radius" were substituted to eqn (1) for the calculation of the concentration instead of the value of the geometrical radius. This is in coincidence with the results achieved by *Shain* and *Martin* [8] who describe the influence of shielding by glass support of the drop as a constant value current decrease preserving the trend of current time dependence. This change corresponds with the change of the drop radius value  $r$  in the equation of the limiting diffusion current *vs.* time dependence [2, 3]

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

from the geometrical to the so-called effective value. The effective value of the radius takes into account the fact that the diffusion layer becomes thicker on the place of glass support approaching the drop owing to which the diffusion becomes of hemispherical character. Comparing the values  $b$  for both used drop radii in Table 1 we can see that the shielding is more expressed in the case of smaller drop. It follows also from Fig. 1 where we see that the glass of thick-wall capillary takes greater portion of diffusion layer in the case of smaller drop than it is in the case of the drop with the greater radius. From the figure we can also see that using the thin-wall capillary the glass takes negligible portion of diffusion layer.

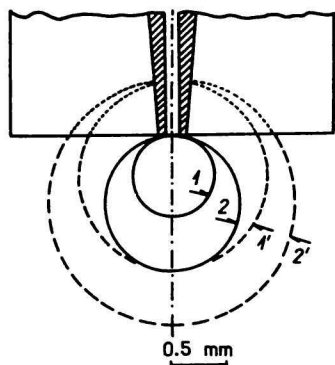


Fig. 1. Orifice of the thick-wall capillary tube,  $d = 3$  mm, (the orifice of the thin-wall capillary tube is hatched,  $d = 0.25$  mm) with drops  $r = 0.37$  mm (1) and  $r = 0.64$  mm (2). Broken lines represent the boundaries of diffusion layer with 1% exhaustion of the electroactive substance on the outer edge for  $t = 10$  s from the beginning of electrolysis, diffusion coefficient  $2 \times 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup> and drop 1 (boundary 1'), resp. 2 (boundary 2').

From the results summarized in Table 1 it follows that the HMDE with the thick-wall capillary can be on principle used for absolute determination. The possibility to use geometrical radius for the calculation of concentration from the relationship (1), however, is lost. It is necessary to determine the effective value of radius more or less different from geometrical and this should be done by calibration. The necessary calibration can, however, be done with the reference solution of any electroactive substance and is not restricted to the reference solution of analyzed species.

*Determination of two electroactive substances Bi<sup>3+</sup> and Tl<sup>+</sup> by chronoamperometry with thin-wall capillary HMDE*

The absolute chronoamperometric determination can be on principle applied also in the case of samples with two or more electroactive substances. A prerequisite of this is the sufficient difference of half-wave potentials. For the system with two electroactive substances the chronoamperogram is sampled at the potential of the limiting current of the reduction of the first substance — "1", inclusive the chronoamperogram of the background — "2". Similarly also the chronoamperogram is sampled at the potential of the limiting current of the reduction of the second substance — "3", inclusive chronoamperogram of the background — "4". The calculation of the concentration of the first reduced substance comes from the chronoamperogram obtained as a difference "1" — "2". The second reduced component is determined from the chronoamperogram of this component, obtained from the balance of currents: ["3" — "4" — ("1" — "2")]. Subtraction is made by computer using corresponding simple routines. Determination by the given procedure was tested on the example of Bi<sup>3+</sup> and Tl<sup>+</sup> analysis. The results are summarized in Table 2.

Statistical evaluation shows that the determination results of Bi<sup>3+</sup> are accurate and that the dependence  $c(\text{found})$  vs.  $c(\text{given})$  is linear with the intercept which does not differ statistically from zero and with the slope which does not statistically differ from unity. The same holds also for Tl<sup>+</sup> determination in the presence of Bi<sup>3+</sup>. The limits of confidence for 95 % probability, however, are substantially larger than in the case of Tl<sup>+</sup> determination in the solutions without Bi<sup>3+</sup> [1]. The reliability of determination will decrease with the growing Bi<sup>3+</sup> concentration. In this case the decrease of limits of confidence can be achieved by the repeated analysis.

The possible determination of the third and next electroactive components can be carried out analogously. The reliability of such an analysis will probably further decrease.

Table 2

Statistical evaluation of the results of the absolute determination of  $\text{Bi}^{3+}$  and  $\text{Tl}^+$ , in one analyte ( $c(\text{HNO}_3) = 1 \text{ mol dm}^{-3}$ )  
 Current sampling interval 0.2 s after starting the electrolysis at  $-0.3 \text{ V vs. SCE}$  ( $\text{Bi}^{3+}$  reduction) and  $-0.7 \text{ V}$  ( $\text{Tl}^+$  reduction); potential of  
 the indication electrode prior to the electrolysis is  $+0.1 \text{ V vs. SCE}$ ; indication electrode — stationary mercury drop,  $r = 0.44 \text{ mm}$  ( $A = 2.47 \text{ mm}^2$ );  
 diameter of capillary *ca.*  $0.25 \text{ mm}$ ;  $T = 298 \text{ K}$

$10^4 c(\text{Bi given})$ mol dm <sup>-3</sup>	$10^4 c(\text{Tl given})$ mol dm <sup>-3</sup>	$10^4 \bar{c}(\text{Bi found})$ mol dm <sup>-3</sup> (mean)*	$10^4 \bar{c}(\text{Tl found})$ mol dm <sup>-3</sup> (mean)*	Number of analyses***	Limits of confidence for 95 % probability	
					$\frac{\Delta c}{\mu\text{mol dm}^{-3}}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$
10.00	0	9.85	0	5	30	$98.5 \pm 3.0$
5.00	0	5.10	0	5	28	$102.0 \pm 5.6$
1.25	0	1.22	0	5	11	$97.6 \pm 8.5$
1.25	1.25	**	1.35	5	21	$108.0 \pm 17.0$
1.25	5.00	**	5.17	5	37	$103.4 \pm 7.4$
1.25	10.00	**	10.24	5	42	$102.4 \pm 4.2$

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

$$a(\text{Bi}) = 0.06 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b(\text{Bi}) = 0.98$$

$$a(\text{Tl}) = 0.08 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b(\text{Tl}) = 1.02$$

$$s_a(\text{Bi}) = 0.1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$s_b(\text{Bi}) = 0.02$$

$$s_a(\text{Tl}) = 0.12 \times 10^{-4} \text{ mol dm}^{-3}$$

$$s_b(\text{Tl}) = 0.02$$

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

\*\* Analyzed only the compound reduced at the more negative potential —  $\text{Tl}^+$

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



*Comparison of the method with the controlled potential coulometry*

Coulometry with the controlled potential of the working electrode is well recognized as an absolute method in analytical chemistry. This follows from the very high accuracy and precision of the value of the Faraday constant. The condition of such a use of coulometry in quantitative analysis is to secure the 100 % current efficiency. Controlled potential coulometry fulfils this condition by an appropriate choice of the potential of working electrode. Precision and accuracy are very good if the electrode reaction does not involve complications by chemical reactions. In the practice the case often occurs when the product of the electrode reaction B is slowly reoxidized to the initial substance A by an electroinactive substance Z (*e.g.* by solvent)



In such a case the current does not decrease to zero but to a time-independent steady state value  $I_{ss}$  and the reading of the electrical charge after the accomplished electrolysis, on which the coulometric analysis is usually based, cannot be used for the determination. The solution of such a problem consists in the introduction of some of the methods of the so-called predictive coulometry [9] which determines the total charge from the course of the electrolysis in its first phases using the experimentally known current or charge *vs.* time dependence. This can only be done when the complicating chemical reaction interferes negligibly. At higher values of  $k'$  the rate constant of the electrolysis  $p$  (limited by the substance transport) as well as the initial current  $I_0$  necessary for the calculation of the total charge ( $I_0/p$ ) could only be obtained applying the equations (1.44) and (1.45) in Ref. [7].

Such an analysis is based upon the time independence of the electrolysis rate constant  $p$ . Using the common laboratory electrolytic cell this condition is not fulfilled precisely due to different reasons. The dependence  $\log I$  *vs.*  $t$  deviates from the linearity also with the substance transport controlled processes. This involves the decrease in the precision and accuracy of the analysis.

As an example the  $\text{K}_3\text{Cr}(\text{CN})_6$  determination was investigated. The half-wave potential of the one-electron reversible reduction of  $[\text{Cr}(\text{CN})_6]^{3-}$  makes  $-1.38 \text{ V vs. SCE}$  [5]. The apparent rate constant of the electrode product reoxidation by water



has the value  $4.04 \times 10^{-4} \text{ s}^{-1}$  under the conditions of the analysis ( $c(\text{KCN}) = 1 \text{ mol dm}^{-3}$ ,  $T = 298 \text{ K}$ ). At the value  $p = 1.18 \times 10^{-3} \text{ s}^{-1}$  this caused a dis-

Table 3

Precision and accuracy of the chronoamperometric determination at different  $K_3Cr(CN)_6$  concentrations (in KCN solution,  $c = 1 \text{ mol dm}^{-3}$ )  
 Current sampling interval 0.2—5 s after starting the electrolysis at  $-1.5 \text{ V vs. SCE}$  (potential prior to the electrolysis kept at  $-0.9 \text{ V}$ ); the indication electrode—stationary mercury drop,  $r = 0.44 \text{ mm}$  ( $A = 2.47 \text{ mm}^2$ ); diameter of capillary *ca.*  $0.25 \text{ mm}$ ;  $T = 298 \text{ K}$

$10^4 c(\text{given})$ $\text{mol dm}^{-3}$	$10^4 \bar{c}(\text{found})$ $\text{mol dm}^{-3}$ (mean)*	Number of analyses**	Limits of confidence for 95 % probability	
			$\frac{\Delta c}{\mu\text{mol dm}^{-3}}$	$\frac{\bar{c}(\text{found}) \pm \Delta c}{c(\text{given})} / \%$
2.50	2.62	5	16	$104.8 \pm 6.4$
5.00	4.87	5	20	$97.4 \pm 4.0$
7.50	7.68	5	26	$102.4 \pm 3.5$
10.00	10.23	5	30	$102.3 \pm 3.0$

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

$$a = -0.06 \times 10^{-4} \text{ mol dm}^{-3}$$

$$b = 1.02$$

$$s_a = 0.11 \times 10^{-4} \text{ mol dm}^{-3}$$

$$s_b = 0.02$$

\* 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.

tinct deviation of the  $\log I$  vs.  $t$  dependence from the linearity already 1 min after starting the electrolysis which corresponds to only *ca.* 20 % of the electrolyzed substance. Determination of the accurate and precise  $p$  value meets with considerable difficulties.

The results of the absolute chronoamperometric determination of  $K_3Cr(CN)_6$  are, as demonstrated in Table 3, accurate and sufficiently precise at the concentration range typical for the classical polarography.

By the simulation of the influence of chemical reaction of the type (A) on the chronoamperometric analysis we have found that if the apparent rate constant of the reaction is not greater than  $0.1 \text{ s}^{-1}$  its influence on the determination can still be neglected. This means that in frequent cases when the kinetically uncomplicated electrochemical reaction cannot be found for electrochemical determination, the advantages of chronoamperometric absolute analysis can favour this method when the optimal method of determination is looked for.

A considerable advantage of the chronoamperometric analysis is the higher speed in comparison with the controlled potential coulometry. The duration of coulometric analysis is more than ten times longer even if a very effective mixing of solution is introduced. The measured current in chronoamperometry is well reproducible. In contrast to the coulometry it does not depend upon the further

surroundings of the electrode — on the form of electrolyzer and on the geometry of its arrangement.

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