STRIPPING CHRONOPOTENTIOMETRY WITH A GLASSY CARBON DISC ELECTRODE: FUNDAMENTAL FACTORS AND COMPARISON WITH STRIPPING VOLTAMMETRY

L. LUONG and F. VYDRA

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 110 00 Prague 1

Received July 5th, 1974

Basic parameters of the chronopotentiometric (galvanostatic) indication in the electrochemical stripping analysis of trace amounts of metals or their mixtures on solid and mercury film electrodes were assessed. The most suitable electrode material is glassy carbon, which was used in the form of a stationary or rotating disc electrode. A comparison with stripping voltammetry showed that the chronopotentiometric indication is especially suitable in the analysis of trace metal mixtures or the determination of a trace amount of one metal in the presence of a large excess of another electroactive metal. The resolution is very good, about 40 mV difference in the dissolution potentials, which is comparable with the resolution of square-wave polarography of reversible systems.

A prevailing number of authors concerned with the electrochemical stripping analysis follows the dissolution process by d.c. polarography or voltammetry. The sensitivity of this method is limited by the charging current due to the electrode double layer and therefore also a.c. polarography and a.c. voltammetry have recently been used enabling an electronic compensation of the charging current. Also pulse polarography and its modifications find an increasingly broader application thanks to the modern instrumentation (operation amplifiers, *etc.*). Both latter methods of following the dissolution process enable to determine extremely small amounts of metals (of the order of p.p.b.), however the necessary equipment is relatively expensive and rather rarely used in analytical laboratories.

Other suitable electrochemical methods have been less widely explored. We proposed in a preliminary paper[1] the use of chronopotentiometry for the electrochemical stripping analysis on glassy carbon disc electrodes, and it turned out that this method is especially suitable for the analysis of metal mixtures (good resolution and well analysable curves even with mixtures of several metals), its sensitivity being equal to or somewhat lower than with the stripping voltammetry under equal conditions. For this reason we studied the chronopotentiometric method of following the dissolution process on disc and mercury film electrodes (both rotating and stationary) in more detail.

The present work deals with the fundamental effects and parameters to be observed in optimizing the conditions for determining trace amounts of metals and their mixtures.

EXPERIMENTAL

Apparatus. E–t and i–E curves were recorded on a Polarecord E 261 polarograph (Metrohm, Switzerland). The E–t curves were usually recorded at a chart speed of 2·4 s/cm and potential sensitivity of 80, 40 or 20 mV/cm. With higher chart speeds (1 or 0·5 s/cm), an X—Y recorder of the type Endim 620·10 (Meßapparatewerk, Schlottheim, GDR) was used. The acidity of solutions was measured with a PHM 26 type pH meter (Radiometer, Copenhagen). The graphite disc electrode was made of a GC 20 glassy carbon rod (Tokay Mgf. Co., Japan), 5 mm in diameter, pressed in a teflon holder of 15 mm in diameter. Similar electrodes were made of platinum and gold. The electrode was cleaned by polishing with a metallographic emery paper No 6 (SIA, Switzerland) during rotation before every experiment. The mechanical part of the electrode was manufactured in the workshop of this Institute and its rotation speed was variable. The speed of 2500 r.p.m. was used unless otherwise indicated. The counter electrode was a platinum foil (5 . 5 . 0·5 mm) sealed in glass. A saturated calomel electrode of a large surface area served as reference; it was connected with the electrolytic vessel by a salt bridge filled with saturated KCl (Merck, "Suprapur").

Chemicals. These were mostly of reagent grade. The metal salt solutions were prepared by dissolving the solid salts and their concentration was determined complexometrically. When working with extremely dilute solutions (10^{-8}M or less), the supporting electrolytes were purified by ion exchangers, or specially purified chemicals available on the market were used (Merck, "Suprapur", or BDH, "Aristar"). Water was distilled twice, once in a glass apparatus and for the second time in a quarz one (Purator, GDR). Nitrogen used to deaerate the solutions was purified by washing with an alkaline pyrogallol solution and distilled water.

Electric circuit. The electrolyses were carried out at constant potential with the aid of the polarograph as usual in stripping voltammetry, the dissolution with constant current (dry battery of a higher voltage and a series resistance) passing through the disc indicator and platinum counter electrode. The potential of the former against the reference electrode was recorded as a function of time on the polarograph (as a millivoltmeter) or on the X—Y recorder. The switching over from one circuit to the other was done manually (see below). The block diagram is shown in Fig. 1.

Experimental method. Solutions were prepared in calibrated 100 ml flasks (glass or quartz), transferred into the electrolytic vessel (transparent quartz for extremely dilute metal solutions) and deaerated for 15 min with nitrogen, which flowed over the solution during the analysis. After electrolysis at a constant potential the dissolution at a constant current took place and the E–t curve was recorded. The switching over from one circuit to another caused a certain time lag which should be minimized since it may sometimes cause a shortening of the dissolution time (An automatic change-over switch was not available.) To eliminate this undesirable effect, we proceeded as follows. After the electrolysis the electrode was polarized with a cathodic current of about 400 μA. Provided that the solution was not stirred, the 5—10 s electrolysis could be neglected and during this period the switching over to constant current electrolysis could be carried out. The unfavourable influence of the "rest period" was thus suppressed.

RESULTS

Electrolysis at Constant Potential

The chosen metal was accumulated by electrolysis at a constant potential while the electrode rotated at 2500 r.p.m. The dependence of the dissolution time, τ, on the potential of the electrolysis, E_e, is similar to the dependence of the peak current, i_p, on E_e in stripping voltammetry under the same conditions. The value of τ increases in most cases with the increasing negative value of E_e up to a certain limit and then does not change any more in a usually rather broad range of E_e values. The optimum values of E_e for the determination of certain metals on a graphite electrode are given in Table I. They correspond in substance to the limiting current on the polarographic or voltammetric curve of the metal in the same medium.

In stripping chronopotentiometry, the dependence of τ on the charge, Q, necessary for depositing the metal, or on the electrolysis time is linear in a broader range than the analogous dependence of i_p in stripping voltammetry (Fig. 2); for most metals it is linear for at least 10 min.

Indicator Electrodes

The most well-developed E–t dissolution curves were obtained with the glassy carbon electrode; they were symmetrical and enabled a precise determination of the dissolution time τ (Fig. 3). The platinum and gold electrodes proved unsatisfactory in determining the electronegative metals (Cd, Pb) which can be safely determined on the carbon electrode in a broad concentration range. This electrode, in contrast to the dropping mercury, enables the determination of the electropositive metals (Au, Ag, Hg), and it can be also coated with mercury. The assumed linear dependence of τ on the electrode surface area^2 was confirmed with carbon electrodes of different diameter.

Dissolution Current

It should be expected on the basis of elementary concepts that the charge, $Q = i_r\tau$, necessary for dissolving a constant amount of a metal, should be constant, or τ inversely proportional to the dissolution current, i_r:

$$\tau = Q/i_r\,. \qquad (1)$$

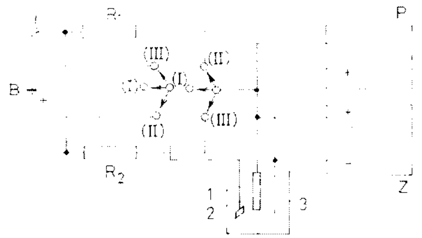

FIG. 1

Block Diagram for Stripping Chronopotentiometry

B 100 V battery, R_1 and R_2 resistances of the order of MΩ, P polarograph (for electrolysis), Z equipment for recording E–t curves, 1 auxiliary electrode, 2 disc electrode, 3 calomel electrode. Positions: I electrolysis, II "rest period", III dissolution.

However, in reality the relation between τ and i_r both on the rotating and stationary electrodes is more complicated. With electronegative metals, the product $i_r\tau$ decreases with decreasing i_r, whereas with electropositive metals it increases with decreasing i_r at constant amount of the deposited metal (Fig. 4).

The value of τ on a rotating electrode is usually shorter than on a stationary one, *i.e.*, the sensitivity of the determination is smaller. This difference is especially pronounced with small dissolution currents and depends on the kind of the metal.

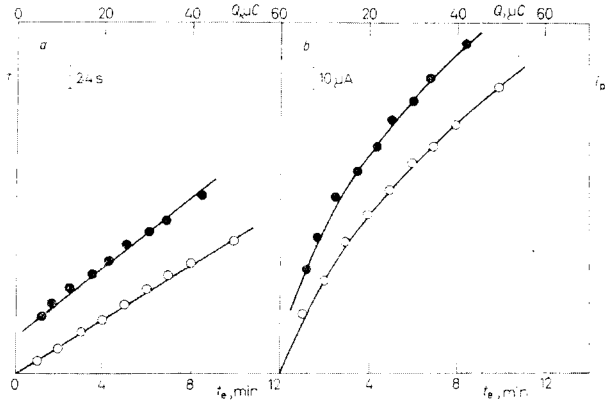

FIG. 2

Dependence of τ and i_p for Silver on the Consumed Charge Q and Electrolysis Time t_e
10^{-6}M-Ag^+ + 0·05M-KI; $E_e = -1·0$ V, $i_r = 21$ μA.

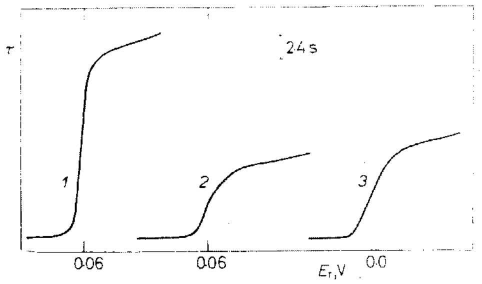

FIG. 3

E–τ Curves for Bismuth on Different Electrodes
5 . 10^{-6}M-Bi^{3+} + 0·1M-KSCN (pH = 2); $E_e = -1·0$ V, $t_e = 2·5$ min, $i_r = 11$ μA. *1* Glassy carbon; *2* platinum; *3* gold. Electrode diameter 3 mm.

It is negligible with gold and silver, which require larger dissolution currents, but considerable with lead, cadmium, tin, indium, and bismuth, where the dissolution time on the stationary electrode, τ_s, is $2-5$ times longer than on the rotating one, τ_r, at a small i_r (tens of μA), other conditions being the same (Figs 5 and 6).

The difference between τ_r and τ_s can be roughly attributed to different rates of transport of the metal on the rotating and stationary electrodes. The dependence of τ on the angular velocity ω can be expressed empirically as

$$\tau = k/\log \omega \,, \tag{2}$$

where the constant k depends on the kind of the metal and medium. It is important that the determination of metals can be up to five times more sensitive if the dissolution of the metal accumulated on the rotating electrode is carried out under stationary conditions.

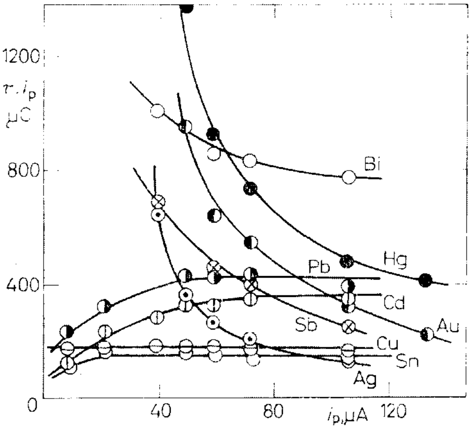

FIG. 4

Dependence of the Product τi_r on Dissolution Current i_r

Concentration of HCl: 1M-(Sn^{2+}); 0·5M-(Sb^{3+}); 0·1M-(Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Au^{3+}, Ag^{+}, Hg^{2+}). E_e: −1·25 V (Cd^{2+}, Sn^{2+}); −1·0 V (Pb^{2+}, Bi^{3+}, Hg^{2+}, Ag^{+}, Cu^{2+}); −0·65 V (Sb^{3+}); −0·5 V (Au^{3+}). t_e = 2·5 min; metal concentration always 10^{-5}M.

Influence of Idling of the Electrode

During the "rest period", necessary to switch over from electrolysis to dissolution, the value of τ decreases owing probably to some loss of the accumulated metal during this time. The most significant loss was observed with Cd, Pb, Sn, In, Co, Ni, and Bi; with the other metals it was substantially less pronounced. This effect is relatively smaller on a stationary electrode than on a rotating one. Also the composition of the supporting electrolyte plays a role. The undesirable loss of the metal, which could not be hitherto explained, can be eliminated as indicated above.

Dissolution Potential

In stripping chronopotentiometry, every metal is characterized by its dissolution potential, E_r, at which the accumulated metal dissolves; it can be read from the E–t curves similarly as $E_{1/2}$ in polarography and depends on the composition of the supporting electrolyte. It is shifted to more negative values by the addition of complexing agents similarly as E_p in stripping voltammetry (Table II). In some cases there is a linear dependence of E_r on the logarithm of the ligand concentration similarly as with E_p. It is seen from Table II that the values of E_r and E_p in the same solution are similar.

TABLE I

Optimum Values of Electrolysis Potentials for Several Metals in Different Media — Case of "Pure" Solutions

Ion	Medium	E_e, V
Au^{3+}	0·1M-HCl	−0·5
	0·1M-HCl + 0·01M-KBr	−0·5
	0·1M-HBr	−0·5
Ag^+	0·1M-KSCN (pH 2)	−1·0
	0·1M-KNO_3 (pH 2)	−0·75
	0·05M-KI (pH 2)	−1·0
Hg^{2+}	0·1M-HCl	−1·0
	0·05M-KI (pH 2)	−1·0
	0·1M-KSCN (pH 2)	−1·0
Cu^{2+}	0·1M-HCl	−1·0
	0·1M-NH_4NO_3 (pH 5, 7)	−1·0
	0·1M-KSCN (pH 2)	−1·0
Sb^{3+}	0·5M-HCl	−0·65
Bi^{3+}	0·1M-HCl	−1·0
	0·025M-KI (pH 2)	−1·0
	0·1M-KSCN (pH 2)	−1·0
Co^{2+}	0·1M-NH_4OH + 0·1M-NH_4Cl	−1·25
Ni^{2+}	0·2M-NH_4OH + 0·1M-NH_4Cl	−1·25
Sn^{2+}	1M-HCl	−1·25
Pb^{2+}	0·1M-HCl	−1·0
	0·1M-KSCN (pH 2)	−1·0
	0·05M-KI (pH 2)	−1·0
In^{3+}	0·1M-KBr (pH 3)	−1·25
Cd^{2+}	0·1M-HCl	−1·25
	0·1M-KSCN (pH 2)	−1·25
	0·0M-KBr (pH 2)	−1·25

To judge the selectivity of the method in the analysis of mixtures, it is important to know the dependence of E_r on the metal concentration in the solution.

For a mercury-plated graphite disc electrode in a reversible system, we derive this dependence by substituting $\tau/2$ for t (at the dissolution potential E_r) in the equation of the E–t curve[3]. After rearrangement we obtain

$$E_r = E_0 + (0{\cdot}059/n)\log\left[2l(\pi\tau D_{0x})^{-1/2}\right] - (0{\cdot}059/2n)\log(kC^0)\,, \qquad (3)$$

where k is a constant, C^0 concentration in solution, and l thickness of the mercury layer. In stripping voltammetry, the dependence of the peak potential (E_p) on C^0 is given by the equation[4]

$$E_p = E^0 + (0{\cdot}059/n)\log(f_{0x}C^0) - 0{\cdot}0218/n\,. \qquad (4)$$

TABLE II

Values of E_r and E_p for Several Metals in Selected Media

Ion	Conc., M	Medium	E_r, V	E_p, V
Au^{3+}	$5 . 10^{-6}$	0·1M-HCl	+0·72	+0·82
		0·1M-HCl + 0·01M-KBr	+0·64	—
		0·1M-HBr	+0·56	—
Ag^+	$3 . 10^{-6}$	0·1M-KSCN (pH 2)	−0·06	+0·06
		0·1M-KNO_3 (pH 2)	+0·26	+0·32
		0·05M-KI (pH 2)	−0·18	−0·12
Hg^{2+}	$3 . 10^{-6}$	0·1M-HCl	+0·11	+0·17
		0·05M-KI (pH 2)	−0·19	−0·12
		0·1M-KSCN (pH 2)	−0·05	+0·05
Bi^{3+}	$3 . 10^{-6}$	0·1M-HCl	−0·07	−0·03
		0·1M-KSCN (pH 2)	−0·05	+0·05
Cu^{2+}	$3 . 10^{-6}$	0·1M-HCl	−0·16	—
		0·1M-NH_4NO_3 (pH 5·7)	+0·02	+0·07
		0·1M-Na_2SO_4 (pH 2)	−0·06	—
		0·1M-KSCN (pH 2)	−0·32	−0·29
Sb^{3+}	$1 . 10^{-5}$	0·5M-HCl	−0·09	+0·07
Co^{2+}	$1 . 10^{-5}$	0·1M-NH_4OH + 0·1M-NH_4Cl	−0·41	−0·33
Ni^{2+}	$1 . 10^{-5}$	0·2M-NH_4OH + 0·1M-NH_4Cl	−0·44	−0·41
Sn^{2+}	$1 . 10^{-5}$	1M-HCl	−0·50	−0·45
Pb^{2+}	$1 . 10^{-6}$	0·1M-HCl	−0·48	−0·45
		0·1M-KSCN (pH 2)	−0·48	−0·45
		0·05M-KI (pH 2)	−0·53	—
In^{3+}	$1 . 10^{-5}$	0·1M-KBr (pH 3)	−0·64	−0·75
Cd^{2+}	$1 . 10^{-6}$	0·1M-HCl	−0·72	−0·77
		0·1M-$HClO_4$	−0·72	−0·75

It was found experimentally that in stripping chronopotentiometry on a disc electrode with or without a mercury layer the dissolution potential E_r is almost independent of C^0. Its shift does not exceed 50 mV in most cases if the concentration changes by a factor of $10^2 - 10^3$. In stripping voltammetry, however, the change of the peak potential E_p is subject to much larger changes with changing C^0 (Table III). This difference between both methods is important from the point of view of the electrochemical spectrum and analysis of mixtures, especially small amounts of one

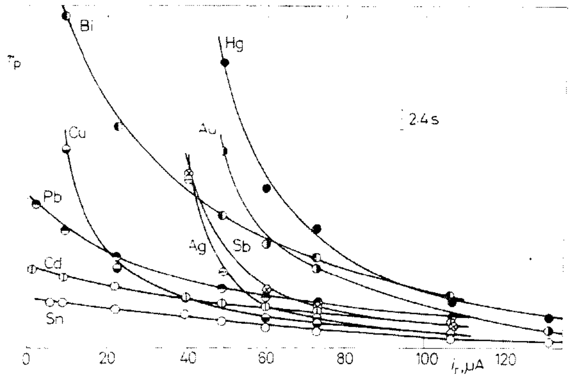

FIG. 5

Dependence of τ During Rotation of the Electrode on the Dissolution Current i_e
Same conditions as with Fig. 4.

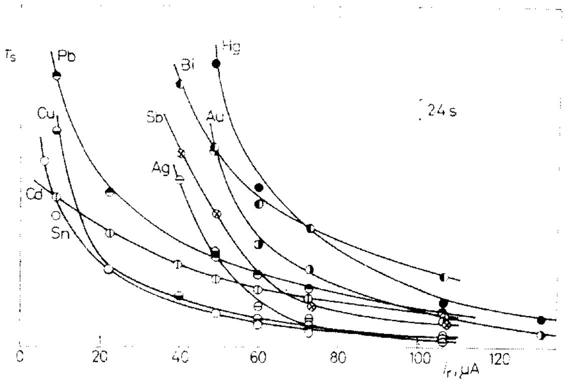

FIG. 6

Dependence of τ on i_r under Stationary Conditions
Same conditions as with Fig. 4.

metal in the presence of an excess of another, where on the voltammetric curve the peaks can overlap owing to the pronounced dependence of E_p on C^0. The value of E_r depends also on the dissolution current i_r, but this effect is in most cases negligibly small.

Simultaneous Deposition of Mercury with Another Metal on the Carbon Disc Electrode – Mercury Film Electrode in Stripping Chronopotentiometry

Carbon or graphite electrodes covered with a mercury layer have the following advantages in stripping voltammetry as compared to "pure" carbon or graphite[3-9] (disregarding the determination of precious metals and mercury): the sensitivity of the determination is in most cases higher, the reproducibility of the recorded curves is better, and interactions of two or more metals (solid solutions, intermetallic compounds) on the electrode surface are less frequent.

During the chronopotentiometric indication, the simultaneous deposition of mercury with the other metal influences also the *E–t* curves. With metals well soluble in mercury (Cd, Pb, In, Sn) the value of τ increases with the concentration of mercury in the solution (similarly as i_p in stripping voltammetry[10]) to a maximum usually at the ratio $[Hg^{2+}]/[Me^{n+}] \geqq 5$. The *E–t* curves are well developed. With metals sparingly soluble in mercury (Cu, Sb, Bi), the dissolution time τ decreases with in-

TABLE III

Shift of E_r and E_p with Changing Metal Concentration

Ion	Medium	Conc., M	E_r, V	ΔE_r, mV	E_p, V	ΔE_p, mV
In^{3+}	0·1M-KBr	10^{-5}	−0·62		−0·75	
	(pH 3)			10		270
		10^{-4}	−0·63		−0·48	
Pb^{2+}	0·1M-HCl	10^{-6}	−0·48		−0·45	
				20		400
		10^{-5}	−0·50		−0·17	
Cd^{2+}	0·1M-$HClO_4$	10^{-5}	−0·72		−0·75	
				0		580
		10^{-4}	−0·72		−0·17	
Sn^{2+}	1M-HCl	10^{-5}	−0·50		−0·45	
				20		260
		10^{-4}	−0·52		−0·19	
Sb^{3+}	0·5M-HCl	10^{-5}	−0·06		+0·07	
				40		300
		10^{-4}	−0·10		+0·37	

creasing concentration of mercury and the E–t curves become often distorted. With mercury film electrodes prepared by depositing mercury simultaneously with the metal the difference between the dissolution times τ_r and τ_s with and without rotation increases with concentration of mercury in the solution. For example, in the determination of Cu^{2+} or Sb^{3+} the difference $\tau_s - \tau_r$ is larger on a mercury film electrode than on a "pure" graphite electrode, hence a better sensitivity can be obtained.

With mercury film electrodes, the influence of the "rest period" on the value of τ is larger than in the absence of mercury, an evidence that the loss of the metal from the amalgam during the rest period is larger than the loss of the pure metal in the absence of mercury. This effect can be eliminated similarly as in the case of the "pure" graphite electrode.

Reproducibility, Sensitivity and Accuracy of the Determination

The glassy carbon electrodes have several advantages in comparison with other solid electrodes, including an easy preparation of a reproducible surface by polishing. The reproducibility of measurements in stripping voltammetry and especially in stripping chronopotentiometry is very good (Table IV).

The chronopotentiometric indication has been relatively little utilized in stripping analysis. The sensitivity of the determination of Hg^{2+}, Co^{2+}, and Cu^{2+} on a stationary impregnated graphite electrode was found[11] to be $5 \,.\, 10^{-7}$, $3{\cdot}4 \,.\, 10^{-7}$, and $1{\cdot}6 \,.\, 10^{-8}$M, respectively.

To obtain a maximum sensitivity, a small dissolution current, i_r, must be used. However, with very small i_r, the E–t curves are so distorted that no potential step can be distinguished on them. The sensitivity of the determination can be also in-

TABLE IV

Comparison of Reproducibility of τ and i_p in Determining Ag, Pb, and Bi at Equal Conditions

Conc., M	Compared quantities	τ (s) and $10^6 i_p$ (A) for curve No:				
		1	*2*	*3*	*4*	*5*
Ag^+	r	5·0	5·0	5·0	5·0	5·2
$3 \,.\, 10^{-6}$	i_p	38	41	42	42	43
Pb^{2+}	r	7·4	7·4	7·2	7·2	7·4
$3 \,.\, 10^{-6}$	s	28·9	26·9	25·7	24·5	24·5
	i_p	65	63	63	63	64
Bi^{3+}	r	12·2	12·7	12·2	12·2	12·2
$3 \,.\, 10^{-6}$	i_p	68	67	66	68	70

TABLE V

Relative Errors of Chronopotentiometric Stripping Analysis of Pb, Cd, and Bi

Ion	Given mg	Found mg	Rel. error %
Pb^{2+}	0·1035	0·120	+18
	0·207	0·190	− 6
	0·258	0·269	+ 4
	0·362	0·372	+ 2·8
	0·414	0·393	− 2·6
	0·621	0·621	± 0
	0·824	0·828	+ 3
Cd^{2+}	0·108	0·108	± 0
	0·162	0·1675	+ 4·6
	0·0216	0·0243	+12
	0·216	0·216	± 0
	0·0540	0·0567	± 5
Bi^{3+}	0·0418	0·0418	± 0
	0·0836	0·0778	− 4·9
	0·1254	0·1310	+ 4·8
	0·209	0·198	− 5
	0·627	0·595	− 5·1
	0·836	0·794	− 5·3
	1·045	1·043	− 1·0

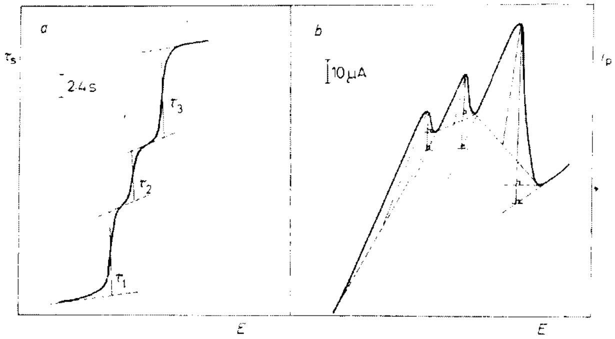

FIG. 7

Measurement of τ (*a*) and i_p (*b*) in Analysis of Mixtures

6 . 10^{-6}M-Cd^{2+}, In^{3+}, and Pb^{+2}, 0·1M-KBr (pH = 3); $E_e = -1·25$ V, $t_e = 2·5$ min, $i_r = 9$ μA.

creased by recording the E–t curves without rotation of the electrode and by a sufficiently rapid recording (higher chart speed) enabling to distinguish even very small τ values at optimum i_r. This is, of course, limited by the quality of the recorder.

The sensitivity achieved with the chronopotentiometric indication is comparable with that observed in stripping voltammetry. Of the studied metals, lead was determined with the highest sensitivity ($5 . 10^{-9}$M), others could be reliably determined at concentrations of $10^{-8}-10^{-7}$M. The chronopotentiometric stripping analysis enables to determine metals in a broader concentration range than stripping voltammetry. The dependence of τ on concentration is linear in the range $10^{-8}-10^{-4}$M (with a suitable duration of the electrolysis, t_e, and dissolution current, i_r).

In stripping analysis with chronopotentiometric indication, the measurement of the τ value is of basic importance. In the case where the solution contains only one metal, this value is simply determined in a similar manner as the limiting current in classical polarography.

The situation is different in the analysis of mixtures. In Fig. 7 are shown the stripping chronopotentiometric and stripping voltammetric curves obtained at equal condi-

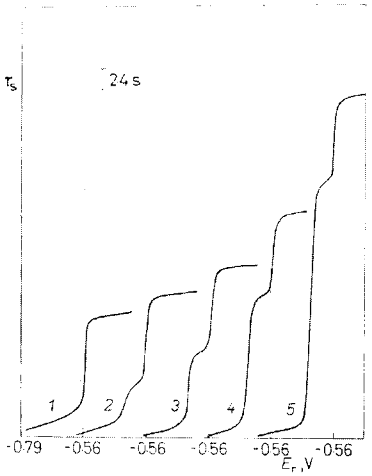

FIG. 8

Influence of Cadmium Concentration on the τ Value for Indium

10^{-5}M-In^{3+} + 0·1M-KBr (pH = 3) + + 10^{-4}M-Hg^{2+}; $E_e = -1·25$ V, $t_e = 2$ min, $i_r = 18$ μA. Concentration of Cd^{2+}: *1* 0; *2* $2 . 10^{-6}$M; *3* $5 . 10^{-6}$M; *4* 10^{-5}M; *5* $2 . 10^{-5}$M.

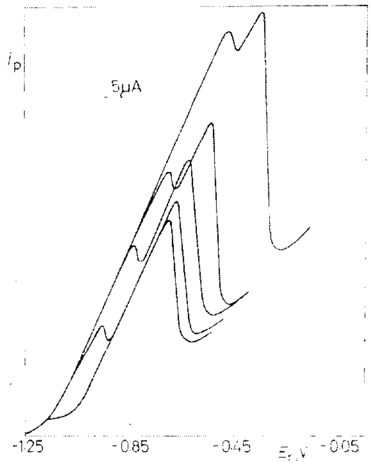

FIG. 9

Deformation of i–E Curves in Voltammetric Stripping Analysis of Cadmium–Indium Solutions with Increasing Cadmium Content

Same conditions as with Fig. 8.

tions and corresponding to a mixture of Cd^{2+}, In^{3+}, and Pb^{2+}. The i_p values obtained by different methods of measurement are considerably different, while the values of τ are determined simply and uniquely in the same way as in the case of a single metal, an obvious advantage of the chronopotentiometric stripping analysis. The mean relative error of the determination by this method was found to be $\pm 6\%$ in the concentration range $10^{-7} - 10^{-6}$M (Table V).

Selectivity of the Determination

The selectivity of the electrochemical stripping analysis depends on the method of following the dissolution process. In stripping voltammetry, the peak potential E_p is shifted to more positive values with increasing concentration of the metal ions, whereas in chronopotentiometry the E_r value is practically constant, an obvious evidence for a better selectivity of the latter method. Moreover, in stripping voltammetry the form of the curves changes with the concentration of the electroactive substances, whereas in stripping chronopotentiometry it is constant. This is shown in Figs 8 and 9, where the dependence of τ on the concentration of cadmium in the presence of a constant indium concentration is linear, the τ value for indium being constant. An analogous dependence could not be obtained from the stripping voltammetric curves.

The resolution of the chronopotentiometric method can be increased by using a higher sensitivity of the recorder on the potential axis as long as the curve does not become distorted (at several mV/cm). In stripping voltammetry the rate of the potential shift influenced the values of i_p and E_p under our experimental conditions, thus complicating the evaluation of the peaks in the analysis of mixtures.

With respect to the mentioned advantages, stripping chronopotentiometry gives satisfactory results in the analysis of solutions containing several metals. A sufficiently large difference in the E_r values, *e.g*, 200 mV in the case of lead and cadmium, enables to determine lead in the presence of a 1000 fold excess of cadmium. The values of τ corresponding to the ratios $[Cd^{2+}]/[Pb^{2+}] = 10, 100$, and 1000 are practically the same. In stripping voltammetry, cadmium interferes with lead even if their ratio is 10 : 1. Under optimum conditions it is possible to determine by stripping chronopotentiometry simultaneously two metals whose dissolution potentials differ by as little as 40 mV, which is comparable with the resolution of square wave polarography for reversible systems[12]. For example, in the simultaneous determination of bismuth and copper in 0·1M-HCl the τ values for bismuth remain constant at the ratio $[Cu^{2+}]$: : $[Bi^{3+}]$ varying from 1 to 50, whereas in stripping voltammetry the peaks of both metals are practically undistinguishable. The simultaneous determination of more than two metals is possible in favourable cases, and a mercury film electrode can be used often with advantage.

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Translated by K. Micka.