DETERMINATION OF SOME METALS AND THEIR MIXTURES BY STRIPPING CHRONOPOTENTIOMETRY ON A GLASSY CARBON ROTATING DISK ELECTRODE

L.LUONG and F.VYDRA

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

The optimum conditions for the determination of Au, Ag, Hg, Cu, Bi, Sb, Pb, In, Cd, Ni, Co, Sn and several mixtures are given. The mixtures were selected in order to illustrate the potentialities of stripping chronopotentiometry. Simple combinations (large ΔE_s values) are not discussed.

In a previous paper[1], the basic parameters of the method were studied in detail in order to facilitate the determination of the optimum conditions for the stripping chronopotentiometric determination of various metals. In this paper, the results of the determinations of several metals and of analysis for several metals in a single sample are given. The recommended pre-electrolysis potentials (E_e) and stripping potentials (E_s) were tabulated in the previous communication[1] for the given metals in various media; the precision of these determinations is also given there. The optimum values of the stripping current (i_s) and the other conditions are discussed.

EXPERIMENTAL AND RESULTS

Determination of Individual Metals

Silver. Several papers have been devoted to the stripping voltammetry of silver on solid electrodes[2-5]. The determination can be effected in various media $(H_2SO_4,$ $KNO_3,$ $NH_4OH + NH_4NO_3,$ KSCN, *etc.*). The best-shaped E–t curves in the chronopotentiometric determination were obtained in 0·05M-KI (pH 2), but the best reproducibility was attained in 0·1M-KSCN. Suitable values of the stripping current and the pre-electrolysis time for various concentration ranges in several media are given for silver and other metals in Table I.

The concentration dependence is linear from 10^{-4} to 10^{-8}M. Silver can be reliably determined (*i.e.* with a relative error not exceeding $\pm 5\%$) at concentrations down to 10^{-8}M; this is a slightly poorer sensitivity than that attained in stripping voltammetry.

Table I

Recommended t_e and i_s Values for the Determination of a Number of Metals

Me^{n+}	Medium	Concentration range	t_e min	i_s μA
Au^{3+}	0·1M-HCl	10^{-5}—10^{-6}	2·5	100
		10^{-6}—10^{-7}	15	100
Ag^+	0·05M-KI (pH 2)	10^{-6}—10^{-7}	5	20
		10^{-7}—10^{-8}	20	20
Hg^{2+}	0·1M-KSCN (pH 2)	10^{-6}—10^{-7}	5	50
	0·1M-KSCN (pH 2)	10^{-5}—10^{-6}	2·5	30
		10^{-6}—10^{-7}	10	30
Cu^{2+}	0·05M-KI (pH 2)	10^{-5}—10^{-6}	5	20
	0·1M-NH_4NO_3 (pH 5, 7)	10^{-5}—10^{-6}	2·5	20
	0·1M-Na_2SO_4; 0·1M-KSCN	10^{-5}—10^{-6}	2·5	20
		10^{-6}—10^{-7}	5	20
		10^{-7}—10^{-8}	20	20
Sb^{3+}	0·5M-HCl	10^{-4}—10^{-5}	1	100
		10^{-5}—10^{-6}	2·5	50
		10^{-6}—10^{-7}	15	50
Ni^{2+}	0·1M-NH_4Cl + 0·2M-NH_4OH	10^{-4}—10^{-5}	1	100
		10^{-5}—10^{-6}	2·5	50
		10^{-6}—10^{-7}	20	50
Co^{2+}	0·1M-NH_4Cl + 0·1M-NH_4OH	10^{-4}—10^{-5}	2	100
		10^{-5}—10^{-6}	2·5	50
		10^{-6}—10^{-7}	10	50
Bi^{3+}	0·1M-HCl	10^{-5}—10^{-6}	2·5	50
		10^{-6}—10^{-7}	5	50
		10^{-7}—5.10^{-8}	20	50
Sn^{2+}	1M-HCl	10^{-4}—10^{-5}	0·5	50
		10^{-5}—10^{-6}	2·5	10
		10^{-6}—10^{-7}	10	10
Pb^{2+}	0·1M-HCl; 0·1M-KSCN (pH 2)	10^{-4}—10^{-5}	0·5	100
	0·1M-KBr (pH 2); 0·1M-$HClO_4$	10^{-5}—10^{-6}	2·5	10
	0·05M-KI (pH 2)	10^{-6}—10^{-7}	5	10
		10^{-7}—10^{-8}	20	1·5
In^{3+}	0·1M-KBr (pH 3)	10^{-4}—10^{-5}	2	20
		10^{-5}—10^{-6}	5	20
		10^{-6}—10^{-7}	10	20
Cd^{2+}	0·1M-HCl; 0·1M-$HClO_4$	10^{-4}—10^{-5}	1	100
	0·1M-KBr (pH 2)	10^{-5}—10^{-6}	2·5	10
		10^{-6}—10^{-7}	10	1·5

Gold. This metal was determined *e.g.* in ores[6] or in films on metals[5], using stripping voltammetry on a graphite electrode. The manner in which the $E-t$ curves are recorded is important in chronopotentiometric stripping of a gold deposit. If it is recorded using the procedure described in the experimental part of ref.[1], the curves obtained are difficult to evaluate and accurate τ values are not easy to obtain. The following procedure has been found to be satisfactory: after the constant potential pre-electrolysis, the potential is instantaneously changed to $+0.5$ V and maintained for 30 seconds at this value; then the $E-t$ curve is recorded from this value. The most suitable medium is 0.1M-HCl. However, $E-t$ curves can be recorded in a broader potential range $(40-20$ mV/cm$)$ in bromide media, owing to the suitable shape of the upper parts of the curves. A linear dependence of τ on the pre-electrolysis time is obeyed in an interval of $1-15$ min. The τ *vs* concentration dependence is linear from 10^{-4} to 10^{-7}M. After a 30 minute pre-electrolysis, gold can be reliably determined[1] under the given experimental conditions in 10^{-7}M solutions; this result is comparable with the values obtained using stripping voltammetry[6].

Mercury. Stripping voltammetry[6,7-9] generally permits the determination of mercury down to 10^{-9}M solutions[9]. Using second harmonic a.c. voltammetry[9], a somewhat higher sensitivity has been achieved on a glassy carbon electrode $(5 \cdot 10^{-10}$M$)$. Chronopotentiometry was utilized[10] for the determination of mercury in a KI medium; $5 \cdot 10^{-7}$M mercury solutions were determined after a 60 minute electrolysis. The results obtained indicate that, in both cases, 0.1M-KSCN at pH 2 is the optimum medium for the determination, in agreement with the optimum conditions specified in refs[6,7]. In KI media, satisfactory results were obtained only in mercury solutions with concentrations above 10^{-6}M. The effect of the "rest period" on the τ value is marked in KI medium, while it is very small in KSCN. The dependence of τ on the concentration is linear in a range from $1 \cdot 10^{-5}$ to $5 \cdot 10^{-7}$M. In a 0.1M-KSCN medium after a 30 minute pre-electrolysis, satisfactory results can be obtained in analysis of solutions with concentrations down to $5 \cdot 10^{-8}$M-Hg $($ref.[1]$)$.

Bismuth. Stripping voltammetric determinations of bismuth were carried out using a graphite electrode and a mercury-coated graphite electrode[11-13]. HCl media are usually employed. However, chronopotentiometric indication yields good results even in acidic solutions of KSCN, KBr and KI. The choice of medium depends in practice on the selectivity requirements. The dependence of τ on the concentration is linear for concentrations of $10^{-4}-10^{-7}$M; recording of the $E-t$ curves under stationary conditions leads to an increase in the sensitivity by about 50%. Simultaneous deposition of mercury with bismuth on a graphite disk electrode causes a decrease in τ, but the presence of mercury is advantageous in analysis of mixtures, as it improves the selectivity of the determination of bismuth. After a 20 minute electrolysis, bismuth can be determined at concentrations down to $5 \cdot 10^{-8}$M $($ref.[1]$)$.

Copper. The voltammetric determination of copper using graphite, glassy carbon

and mercury-coated electrodes has been reported[2,10,13−15]. The chronopotentio-metric technique using an impregnated graphite electrode permitted the determina-tion[8] of concentrations down to $1 \cdot 6 \cdot 10^{-8}$M. Very similar E–t curves were obtained in determinations in various supporting electrolytes in the absence of complexing agents. E_s shifts to more negative values in the presence of complexing agents. In NH_4NO_3, τ and E_s are shifted to more negative values with increasing pH (pH 2: $-0 \cdot 02$ V, pH $7 \cdot 6$: $-0 \cdot 16$ V) and at a pH of about 9 the wave of copper disappears, which agrees with results obtained during the stripping voltammetric determination of copper[2]. Similarly as with bismuth, simultaneous deposition of Hg leads to a de-crease in the τ value, but the shape of the E–t curves is improved and the difference between the τ_s and τ_r values increases[1]. The simultaneous deposition of mercury leads to an increase in the selectivity of the determination. After a 20 minute electro-lysis, copper can be reliably determined in concentrations down to $5 \cdot 10^{-8}$M.

Antimony. Small amounts of antimony have been determined by stripping voltammetry in a wide range of materials, for example[15−18]. For the determination of antimony by electrochemical stripping methods, hydrochloric acid is the most convenient medium. The τ and E_s values depend on the HCl concentration; the τ values increase with increasing concentration and become constant in $1-2$M-HCl. E_s depends linearly on the logarithm of the HCl concentration. In this medium, E_s depends linearly on the logarithm of the stripping current. τ attains a maximum value in a narrow electrolysis potential interval $(-0 \cdot 6$ to $-0 \cdot 7$ V$)$. The simultaneous deposition of mercury on the electrode surface has a similar effect on the values and shape of the E–t curve as for copper. τ is linearly dependent on the antimony concentration in $10^{-4}-10^{-7}$M solutions.

Nickel. The voltammetric stripping determination of nickel on a graphite electrode has not been extensively studied and the determination has a relatively low sensitiv-ity[15,19,20] (10^{-7}M). The determination has been carried out in a number of media $(Na_2HPO_4, KSCN, KCl, NH_4OH + NH_4Cl, etc.)$. From the results thus obtained on a graphite electrode[21], it follows that the determination can be carried out satis-factorily in $0 \cdot 2$M-$NH_4OH + 0 \cdot 1$M-NH_4Cl medium (pH 10). Our results were identi-cal for the chronopotentiometric method, indicating a linear dependence of E_s on the logarithm of the stripping current in this medium. Divalent mercury has an un-favourable effect[21] (due to formation of the intermetallic compound, HgNi). τ is linearly dependent on the concentration in the range, $10^{-4}-10^{-6}$M. The determina-tion can be extended to $5 \cdot 10^{-7}$M by employing long electrolysis times.

Cobalt. This element has been determined in a number of materials using stripping voltammetry, for example[15,22,23]. Chronopotentiometric indication was used in the work[10] where cobalt was determined in $3 \cdot 4 \cdot 10^{-7}$M solutions. The determination of trace amounts of cobalt has been studied in a number of complexing media and non-complexing media; here $NH_4OH + NH_4Cl$ was found most favourable. The

concentration of NH_4Cl has a marked effect on the shape of the E–t curves and the τ value (Fig. 1a); pH $8-9$ is optimal (0.1M-NH_4OH + 0.1M-NH_4Cl). The determination can also be carried out in KSCN medium (Fig. 1b); the most useful curves are obtained in 0.01M-0.02M-KSCN base electrolyte. τ is linearly dependent on the concentration in $10^{-4}-10^{-7}$M cobalt solutions.

Indium. This metal has been determined using both stripping polarography on a hanging mercury drop electrode[24] and stripping voltammetry on an impregnated graphite electrode[25]. Solutions of chloride, bromide and iodide or mixtures thereof are most frequently used as base electrolytes. Bromide and iodide give the best results for chronopotentiometric stripping analysis. The value of τ depends markedly on the base electrolyte concentration (complexing ability) and on the pH. The highest τ value was found in 0.1M-KI at pH $3-3.5$ (Fig. 2a, b); under these conditions, E_s depends linearly on the KI concentration. There is a marked difference between τ_s
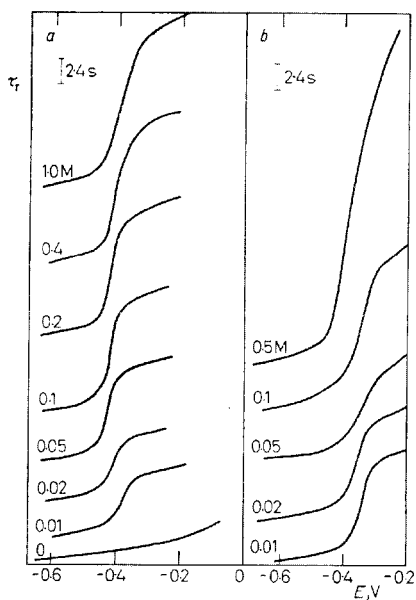

FIG. 1

Effect of the Concentration of a NH_4Cl and b KCNS on the Shape of the E–t Curves and the τ Values for Cobalt

a $1 . 10^{-5}$M-Co^{2+}, 0.15M-NH_3, E_e -1.25 V, t_e 2.5 min, i_s $49 \mu A$; b $1 . 10^{-5}$M-Co^{2+}, E_e -1.25, t_e 2.5 min, i_s $49 \mu A$.
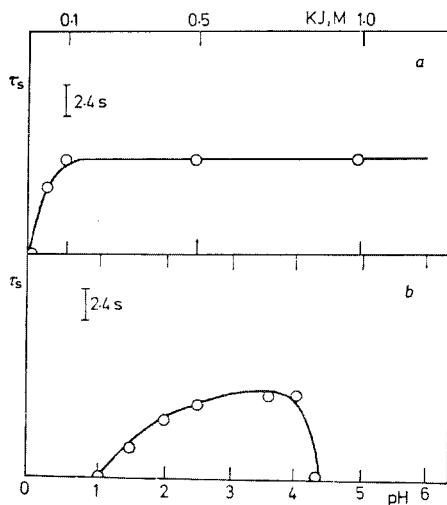
FIG. 2

Effect of the Concentration of KI and of the pH on the τ Values for Indium

a $2 . 10^{-5}$M-In^{3+}, E_e -1.25 V, t_e 2.5 min, i_s $22.5 \mu A$, pH 3; b $2 . 10^{-5}$M-In^{3+}, E_e -1.25 V, t_e 2.5 min, i_s $22.5 \mu A$, 0.1M-KI.

and τ_r (ref.[1]) so that registration of $E-t$ curves under stationary conditions leads to a $2-3$ times increase in the sensitivity compared to a rotated electrode. The value of τ is increased slightly when mercury is deposited simultaneously with indium on the graphite electrode surface (ref.[1]), so that the sensitivity is also increased. The value of τ depends linearly on the concentration in the range $10^{-4}-10^{-7}$M and the curve obtained for 10^{-7}M-I^{3+} can be evaluated much better than the corresponding curve obtained by stripping voltammetry.

Tin. Stripping voltammetry has been carried out on various electrodes[22,26,27]. The analysis is usually carried out in HCl medium and the τ and E_s values are strongly dependent on its concentration; the largest τ values were obtained in $1-2\cdot5$M-HCl. E_s is linearly dependent on the logarithm of the HCl concentration. The use of small stripping currents (less than $10\,\mu$A) enables the determination of small amounts of tin using reasonable electrolysis times. The sensitivity can be further increased by registering the $E-t$ curves under stationary conditions[1]. The τ value is increased by the simultaneous deposition of mercury and the reproducibility is improved. Tin can be determined by this method in concentrations down to 10^{-7}M (10 minute electrolysis). τ is linearly dependent on the concentration in $10^{-4}-10^{-7}$M solutions.

Lead. Polarography and voltammetry were employed most frequently for following the stripping process, *e.g.*[25,27-34]. Stripping chronopotentiometry was studied only on a hanging mercury drop electrode[35], at lead concentrations down to 10^{-10}M. The determination was generally carried out in mineral acids and their salts and only rarely in complexing agents as base electrolytes (iodide, bromide, thiocyanate, *etc.*). In the absence of complexing agents, the chronopotentiometric stripping curves are very simple and similar and E_s has a value of about $-0\cdot45$ to $-0\cdot55$ V. The difference between τ_s and τ_r is large, so that lead can be determined under optimum conditions (especially employing long electrolysis times) at concentrations down to $5 . 10^{-9}$M. The τ value is increased only very slightly by the simultaneous deposition of mercury. Under normal conditions, τ is linearly dependent on the concentration in the range $10^{-4}-10^{-8}$M.

Cadmium. A number of works have been published, for example[11-14,34-36]. Using a.c. polarography, cadmium was determined at concentrations down to 10^{-10}M (ref.[36]). The chronopotentiometric stripping determination was carried out on a hanging mercury drop electrode and the authors state that they were able to determine 10^{-10} g of Cd in 5 ml solution[35]. A number of base electrolytes can be employed (KCl, KNO_3, K_2SO_4, HCl, *etc.*) in which the $E-t$ curves are practically identical, as are the τ and E_s values. Small current values can be used (below $10\,\mu$A) and the difference between the τ_s and τ_r values is quite large. The presence of mercuric ions increases the τ value and improves the reproducibility of the curves[1]. Under optimum conditions, cadmium can be determined down to 10^{-8}M. Under normal conditions, τ is linearly dependent on the concentration in the range $10^{-4}-5 . 10^{-8}$M.

Analysis of Mixtures of Metals

In the previous communication[1], we mentioned the advantages of chronopotentio-metry for the analysis of mixtures of trace amounts of metals. Here, for the sake of illustration, a few other concrete mixtures which can be determined by the described method were studied. In some cases, the determination is compared with stripping voltammetry.

Bismuth–mercury. According to ref.[37], no interfering effects occur during simul-taneous deposition of the metals on solid electrodes, but the stripping potentials, E_s (and the peak potentials in voltammetry) are very similar: ΔE_s and ΔE_p in 0·1M-KSCN are equal to 0 V and 10 mV, in 0·1M-HCl to 190 mV and 200 mV and in 0·1M-KBr to 40 mV and 60 mV, respectively (the differences are given for identical Bi^{3+} and Hg^{2+} concentrations of $3 . 10^{-6}M$). Thus the simultaneous determination of bismuth and mercury in KSCN is impossible both voltammetrically and chronopotentio-metrically due to the small differences in E_p and E_s. In HCl, both metals can be de-termined by stripping voltammetry only up to Bi^{3+}/Hg^{2+} ratios of 1 : 5 or 5 : 1 (ref.[21]) while using chronopotentiometry the two metals can be determined simul-taneously in this medium at ratios of 1 : 20 to 20 : 1. In 0·1M-KBr (pH 2) the simultane-ous determination of the two metals by stripping voltammetry is impossible (Table II, Fig. 3a). Under the same conditions, chronopotentiometry gives satisfactory results. In Fig. 3b it can be seen that the τ and E_s values for mercury practically do not change at Bi^{3+}/Hg^{2+} concentrations of 0 to 10 and τ remains proportional to the concentration. Thus, under optimum conditions, small amounts of bismuth (*e.g.* 4·5 μg) can be determined in the presence of large amounts of mercury (about 0·8 mg) and, on the other hand, small amounts of mercury (*e.g.* 4·0 μg) can be determined in the presence of an excess of bismuth (about 4·0 mg) in 0·1M-HCl and 0·1M-KBr (pH 2) media.

Bismuth–copper. In the absence of complexing materials, these two metals have similar E_p and E_s values. From chronopotentiometry it follows that the interference of these two metals is not due to the similarity in their stripping potentials alone, but is more complicated. In 0·1M-HCl, the E_s value for bismuth is $-0·09$ V and that of copper equals $-0·16$ V. In the presence of bismuth, the copper wave disappears, leaving that of bismuth alone. The reverse effect of copper on the determination of bismuth is less pronounced. The simultaneous deposition of mercury completely eliminates the effect of copper on the determination of bismuth[1]. However, the effect of bismuth on the determination of copper remains practically the same. The most favourable medium is then 0·1M-KSCN (pH 2) in the presence of mercury; only the wave of copper appears and can be easily evaluated. The τ value for copper is constant at Bi^{3+}/Cu^{2+} ratios from 0 to 10. From these and other results[1], it follows that, with simultaneous deposition of mercury, small amounts of bismuth (*e.g.* 40 μg) can be determined in the presence of excess copper (about 630 μg) in 0·1M-HCl

medium and, on the other hand, small amounts of copper (about 12 µg) can be determined in the presence of excess bismuth (about 400 µg) in 0·1M-KSCN medium (pH 2).

Cadmium–lead–indium. In some materials it is necessary to determine trace amounts of all three metals simultaneously. Their mutual interferences were studied using stripping polarography[24] and voltammetry on an impregnated graphite electrode[25]. The results indicate that the determination can be carried out only with marked limitations. Initial results suggest that chronopotentiometric indication provides much better results.

The interactions of indium and cadmium. In 0·1M-HCl medium, ΔE_s is 80 mV for these metals. In this medium the sensitivity of the determination of indium is very low (concentrations down to 10^{-4}M can be determined) so that its interference

FIG. 3
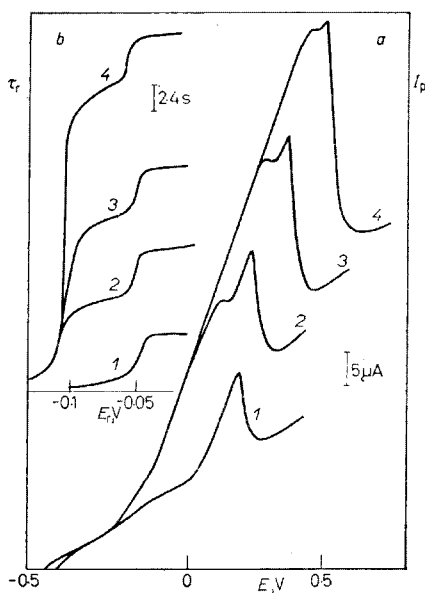
Effect of Bismuth *a* on i_p Values and on the Shape of the *i–E* curve for Mercury and *b* on the τ Values and the Shape of the *E–t* Curve for Mercury $2 \cdot 10^{-6}$M-Hg^{2+}, E_e $-1\cdot0$ V, t_e 2 min, i_s 40 µA. The concentration of Bi^{3+} (for *a* and *b*): *1* 0; *2* $2 \cdot 10^{-6}$M; *3* $5 \cdot 10^{-6}$M; *4* $1 \cdot 10^{-5}$M.
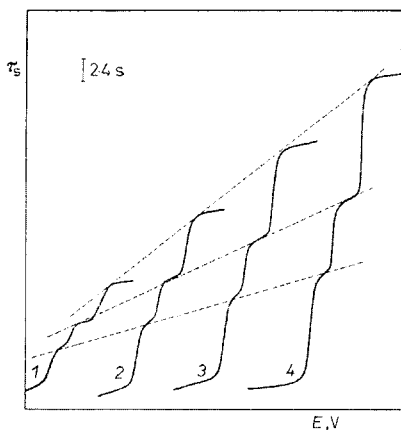

FIG. 4

E–t Curves Recorded During Analysis of Mixtures of Cd, In, and Pb

0·1M-KBr (pH 3), $1 \cdot 10^{-4}$M-Hg^{2+}, E_e $-1\cdot25$ V, t_e 2 min, i_s 9 µA. The concentrations of all three ions in one sample are identical: *1* $2 \cdot 10^{-6}$M; *2* $4 \cdot 10^{-6}$M; *3* $6 \cdot 10^{-6}$M; *4* $8 \cdot 10^{-6}$M.

in the determination of cadmium is negligible. The results of the determination of cadmium in the absence of indium and in, for example, a 50 times excess, are practically identical. As was mentioned under the determination of indium, $0.1M$-KI or $0.1M$-KBr (pH 3) electrolytes are favourable media. The effect of cadmium on the determination of indium in these media was studied and can be removed by simultaneous deposition of mercury; the value obtained for indium $(10^{-5}M)$ is then constant for cadmium concentrations up to $10^{-4}M$ and is about 10% lower than the τ value for indium alone. $0.1M$-HCl is a very favourable medium, in which cadmium (c.55 μg) can be determined in the presence of excess indium (c. 2.75 mg) and, on the other hand, in $0.1M$-KI or KBr (pH 3) with simultaneous deposition of mercury, indium (e.g. 55 μg) can be determined in the presence of excess cadmium (c. 550 μg).

The interactions of indium and lead. In $0.1M$-HCl (and similarly for $0.1M$-KI and KBr) the τ value for lead is practically the same for analysis of a pure solution and in the presence of a 50 times excess of indium. In $0.1M$-KI and $0.1M$-KBr (pH 3) the effect of lead on the determination of indium is the same. The dependence of the τ value for indium on the lead concentration passes through a maximum. This interference of lead in the determination of indium can be removed by simultaneous deposition of mercury. As in the simultaneous analysis of mixtures of cadmium and indium, for example, 20 μg of lead can be determined in the presence of excess indium (c. 550 μg) in $0.1M$-HCl. $0.1M$-KBr or $0.1M$-KI (pH 3) can be used with equal success and indium at the c. 50 μg level can be determined in the presence of 1 mg of lead, employing simultaneous deposition of mercury.

The interactions of cadmium and lead. In non-complexing base electrolytes, the E_s values for cadmium and lead are quite different (ΔE_s approx. 200 mV) and thus a small amount of one metal can be determined in the presence of large amounts of the other[1].

The mutual interferences are thus minimal in $0.1M$-KBr medium (pH 3) in a rather wide concentration interval. The dependence of the τ values on the concentration of the three metals remains linear in approximately $10^{-6}M$ solutions. The E–t curves for the three metals are given in Fig. 4. At very low concentrations (of the order of $10^{-8}M$) dependable results were obtained for analysis of mixtures, provided maximum concentration ratios were not exceeded.

REFERENCES

1. Luong L., Vydra F.: This Journal *40*, 1490 (1975).
2. Kopanica M., Vydra F.: J. Electroanal. Chem. *31*, 175 (1971).
3. Chulkina L. C., Sinyakova C. I.: Zh. Anal. Khim. *24*, 247 (1969).
4. Miwa T., Oki S., Mizuika A.: Japan Analyst *17*, 819 (1968).
5. Brainina Kh. Z., Dolgopolova E. A., Neyman A. E.: Zavod. Lab. *36*, 7 (1970).
6. Peták P.: *The Use of Modern Electroanalytical Methods for the Determination of Low Concentrations of Metals and in Minerals.* Ore Research Institute, Prague 1971.

7. Perone S. P., Kretlow W. J.: Anal. Chem. *37*, 968 (1965).

8. Kolpakova N. A., Nemtinova G. M., Kaplin A. A.: Zavod. Lab. *35*, 529 (1969).

9. Štulíková M., Vydra F.: J. Electroanal. Chem. *42*, 127 (1973).

10. Ranev G. G., Volkova B. S.: Zh. Anal. Khim. *27*, 651 (1972).

11. Neyman E. A., Brainina Kh. Z., Trukhacheva L. N.: Zavod. Lab. *38*, 1 (1972).

12. Neyman E. A., Dolgopolova G. M., Trukhacheva L. N., Dmitriev K. G.: Zavod. Lab. *36*, 683 (1970).

13. Malkov E. M., Fedisyeyeva A. G.: Zavod. Lab. *36*, 912 (1970).

14. Neyman E. A., Dolgopolova G. M., Trukhacheva L. N.: Elektrokhimiya *31*, 123 (1970).

15. Brainina Kh. Z., Raizenblat E. M., Bietivskaya V. B., Kiva N. K., Fomicheba T. I.: Zavod. Lab. *33*, 274 (1967).

16. Vasos B. H., Mark H. B.: J. Electroanal. Chem. *13*, 1 (1967).

17. Brainina Kh. Z., Sapozhnikova E. A.: Zh. Anal. Khim. *21*, 807 (1968).

18. Neyman E. A., Brainina Kh. Z., Trukhacheva L. N.: Zavod. Lab. *37*, 16 (1971).

19. Nicholson M. M.: Anal. Chem. *32*, 1058 (1960).

20. Brainina Kh. Z., Sapozhnikova E. A.: Zh. Anal. Khim. *23*, 232 (1968).

21. Luong L., Vydra F.: J. Electroanal. Chem. *50*, 379 (1974).

22. Brainina Kh. Z., Krapivkina T. A.: Zh. Anal. Khim. *22*, 74 (1967).

23. Krapivkina T. A., Brainina Kh. Z.: Zavod. Lab. *33*, 400 (1967).

24. Neeb R., Dessantes J.: Fresenius' Z. Anal. Chem. *224*, 376 (1967).

25. Neyman E. A., Ponomarenko G. B.: Zh. Anal. Khim. *28*, 1485 (1973).

26. Philips S. P., Shain J.: Anal. Chem. *34*, 282 (1962).

27. Olson C., Adams R. N.: Anal. Chim. Acta *29*, 358 (1963).

28. Kalvoda R.: This Journal *22*, 1390 (1957).

29. Neeb R.: Fresenius' Z. Anal. Chem. *171*, 321 (1959).

30. Roe D. K., Atoni J. E.: Anal. Chem. *37*, 1503 (1965).

31. Matson W. R., Roe D. K.: Anal. Chem. *37*, 1594 (1965).

32. Brainina Kh. Z., Kiva N. K.: Zavod. *29*, 526 (1963).

33. Marple T. L., Rogers L. B.: Anal. Chim. Acta *11*, 574 (1954).

34. de Algaro S. R., Kalvoda R.: Proc. Anal. Chem. Conference, Budapest 1966, p. 126.

35. Cincent H. A., Wise E. N.: J. Electroanal. Chem. *11*, 54 (1966).

36. Underkoffler W. L., Shain J.: Anal. Chem. *37*, 390 (1965).

37. Galus Z., Kemula W., Sacha S.: J. Polarog. Soc. *14*, 59 (1968).

Translated by M. Štulíková.