

THE POSSIBILITY OF RAISING THE SENSITIVITY OF STRIPPING VOLTAMMETRY OF METALS

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We have shown in previous communications [1-3] that difficulties in the electrocrystallization of microquantities of metals on the surface of graphite electrodes represent an important limitation for the sensitivity of stripping voltammetry. The sensitivity is sharply increased when there is on the electrode (or when there forms during the deposition of the metal being determined) a small amount of mercury. It can be hypothesized that a similar effect should also be exhibited by other metals which, while they deposit on the electrode, are capable of serving as sites of electrocrystallization for the element being determined. This hypothesis is strengthened by previous observations of enhanced sensitivity in the determination of iron when it was electrodeposited on a copper base [4], and in that of arsenic in the presence of gold [5].

In the present work new data are presented which confirm the above hypothesis, and recommendations are given concerning its practical use. The experimental technique has been described before [1].

Figure 1 presents stripping voltammetric curves for a solution containing traces of lead ($2 \cdot 10^{-9}$ g-ion/liter) and copper ($2 \cdot 10^{-8}$ g-ion/liter); $\tau_{el} = 10$ min, $v_{scan} = 3$ V/min. Such amounts of impurities are readily determined in the presence of mercury (curve 3). With the usual graphite electrode they are hard to detect (one must increase the electrolysis potential to -1.5 V*) and yield negligible electrodisolution currents. However, an increase in the Pb(II) concentration in solution leads, not only to an increase of its own peak but also to an increase in the peak of codeposited copper, and also to a decrease in the deposition potential of the two metals. Deposition of lead on an electrode thus promotes the electrodeposition of copper. Copper probably has the same effect upon the electrodeposition of lead. Both metals when depositing on the electrode markedly raise the sensitivity of the determination of mercury and arsenic in a base electrolyte of 0.1 N HCl at $\phi_{el} = -1.2$ V and $\tau_{el} = 10$ min (Fig. 2) or $\phi_{el} = -0.7$ V and $\tau_{el} = 5$ min (Fig. 3). A similar effect is also observed when mercury is deposited simultaneously with cadmium.

The data presented show that during the electrolysis of highly dilute solutions, many metals are deposited on graphite electrodes in considerably larger quantities when another metal is simultaneously electrodeposited.[†] In the best case the quantity of the metal being determined then becomes proportional to the amount obtained during electrolysis of its considerably more concentrated solutions under ordinary conditions. The effect discovered can be called "the effect of base metal." It should evidently be observed also on other indifferent solid electrodes. There is also every reason to believe that the method of increasing the sensitivity with the aid of a mercury-graphite or of amalgamated electrodes is a special case of utilization of the above effect.

In the determination of elements which form amalgams, it will be most appropriate to use mercury as the base metal, but other metals can be used as well. With mercury one attains maximum sensitivity of the determination, and one also eliminates the interaction between simultaneously deposited solid metals which in many cases leads to a distortion of the voltammetric curves for their electrodisolution [6]. The use of solid metals as base metals is necessary, however, in order to raise the sensitivity toward elements not forming amalgams, and toward

*The potentials are reported relative to the sce.

[†]In a number of cases it can be deposited in advance.

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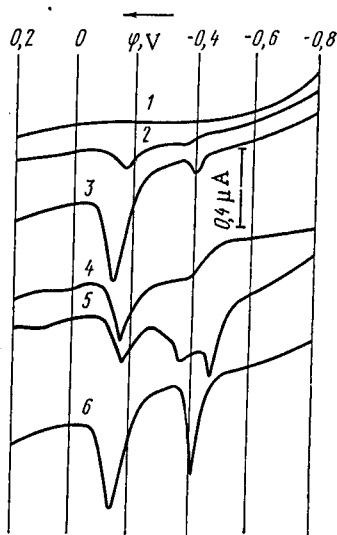


Fig. 1. Voltammetric curves for solutions containing lead(II) and copper(II): $[Pb(II)] = 2 \cdot 10^{-9}$ (1-3) and $1.2 \cdot 10^{-8}$ (4-6), $[Cu(II)] = 2 \cdot 10^{-8}$ (1-6) g-ion/liter. Base electrolyte 0.1N HCl (1, 2, 4, 5) or 0.1N HCl + $5 \cdot 10^{-5}$ g-ion/liter Hg(II) (3, 6); $\varphi_{el} = -1.0$ V (1, 3, 4, 6) and -1.5 V (2, 5).

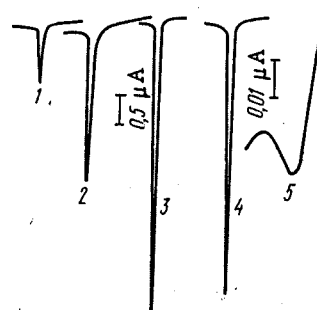


Fig. 2. Voltammetric curves for the electrodisolution of mercury deposited under the usual conditions (1) and simultaneously with lead (2), copper (3), cadmium (4), and gold (5): $[Hg(II)] = 1 \cdot 10^{-6}$, $[Pb(II)] = 1 \cdot 10^{-5}$, $[Cu(II)] = 1 \cdot 10^{-6}$, $[Cd(II)] = 5 \cdot 10^{-6}$, $[Au(III)] = 5 \cdot 10^{-6}$ g-ion/liter.

mercury itself. Joint electrodeposition with copper makes it possible to raise the sensitivity of arsenic determination by more than two orders of magnitude [7]. The same effect was obtained in the determination of mercury on a base of cadmium [8].

It is convenient to select as base element a metal forming solid solutions or intermetallic compounds with the element being determined. The latter should be the more electropositive element, because it could be demonstrated previously [6, 9] that in such cases, the polarograms of the electrodisolution of the more electronegative metal are distorted. Otherwise a negative effect of base metal can be observed. It can be seen from Fig. 2 that the peak of mercury deposited in the presence of gold decreases by a factor of approximately 50 and becomes broader. The disturbing influence of gold on mercury determination has been noted before [10].

The optimum concentration of base metals for the determination of elements over a wide range is $5 \cdot 10^{-6}$ – $5 \cdot 10^{-5}$ g-ion/liter. When electronegative elements are used as base metals, the metal being determined and the auxiliary metal must be deposited simultaneously. Electrodisolution of the electronegative base metal also can cause removal from the electrode of the element being determined if the base has been formed in advance and forms a film adhering to the electrode. Moreover, interaction between the metals "in the instant of deposition" is stronger. This leads to an increase in the amount of the metal being determined at the electrode.

It is evidently for this reason that the sensitivity of arsenic determination on a preformed copper film is markedly lower than that during simultaneous electrodeposition of the elements. Determinations of copper in the presence of lead and cadmium, of gold in the presence of mercury, of arsenic in the presence of lead and copper have demonstrated that electrodisolution of the more electronegative element from deposits formed simultaneously will not decrease the amount of metal remaining on the electrode. The requirement of a simultaneous deposition of the metals combines with the practical convenience in carrying out the analysis, because in order to make use of the effect of base metals it suffices to introduce into the test solution ions of the auxiliary metal, and to carry out electrolysis at a more negative potential than usual. In some cases the deposit of the metal being determined is not formed right from the start of electrolysis, but this is not a drawback (Fig. 4).

The effect of base metals can also arise spontaneously. Figure 5 shows the peak of arsenic ($6.6 \cdot 10^{-6}$ g-ion/liter As(III)) as obtained during electrolysis of a solution prepared with ordinary distilled water. This peak is not detected when twice distilled water is used. This is due to the presence of traces of copper in distilled water. It follows that the effect of base metals may also appear in the usual form for stripping voltammetry when uncontrolled impurities are present in the base electrolytes and test products.

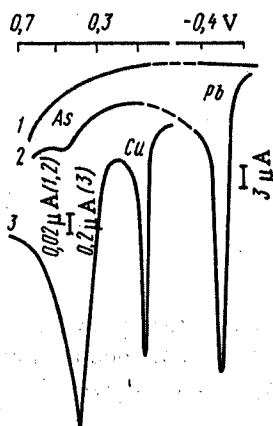


Fig. 3

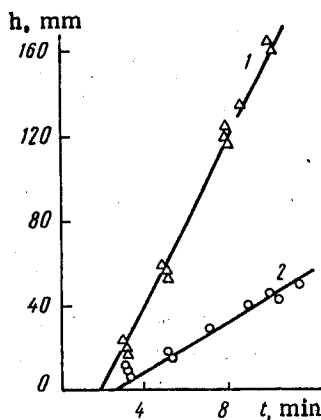


Fig. 4

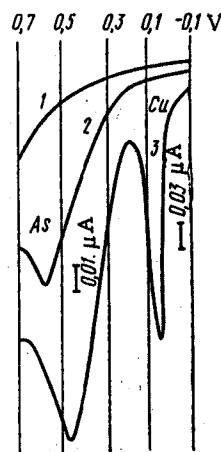


Fig. 5

Fig. 3. Voltammetric curves for solutions containing arsenic (III) (1-3), lead (II) (2), and copper (II) (3): $[As(III)] = 5 \cdot 10^{-6}$, $[Pb(II)] = 5 \cdot 10^{-5}$, and $[Cu(II)] = 3 \cdot 10^{-5}$ g-ion/liter.

Fig. 4. The maximum current of arsenic electrooxidation as a function of the duration of electrolysis in the presence of Cu(II) (1) and in its absence (2): $[As(III)] = 2 \cdot 10^{-6}$ (1, 2), $[Cu(II)] = 2 \cdot 10^{-6}$ (1) g-ion/liter.

Fig. 5. Voltammetric curves for solutions containing As(III): 1, 2) 1 N HCl prepared with twice distilled water; 3) 1 N HCl prepared with ordinary distilled water. $[As(III)] = 6.6 \cdot 10^{-6}$ (1, 3) and $2 \cdot 10^{-5}$ g-ion/liter (2).

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