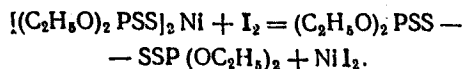


Analysis Procedure

The alloy sample, weighing from 0.2 to 0.5 g, depending on the amount of cadmium contained in it, is dissolved with heating in 15 ml of sulfuric acid (1:5), several drops of nitric acid (1:1) are added to obtain a better solution of the cadmium, and if the alloy contains a large amount of zirconium, the further addition of 2-3 ml of nitric acid is made. After cooling, the solution of the alloy is treated with 15 ml of 0.05 N nickel diethyldithiophosphate solution, the whole mixed well, allowed to stand for an hour, and then suction-filtered through a weighed No. 3 glass filter. The precipitate on the filter is washed 5-6 times with small portions of saturated aqueous cadmium diethyldithiophosphate solution, and then dried to constant weight. The factor for converting the weight of precipitate to cadmium is 0.2328. With this method it is possible to determine as little as 0.05% Cd.

For all practical purposes, the anion of diethyldithiophosphoric acid [2] is oxidized quantitatively by iodine in acid medium, according to the equation:



On the basis of this reaction, we worked out a volumetric method for the iodometric determination of cadmium in magnesium alloys.

A 0.05 N solution of pure, recrystallized nickel diethyldithiophosphate is used to precipitate the cadmium; the precipitate is filtered through fine filter paper, washed on the filter 4-5 times with saturated cadmium diethyldithiophosphate solution, then transferred to an Erlenmeyer flask with a stream of water, dissolved by the addition of small portions of ammonia, neutralized with pure hydrochloric acid to methyl orange until the color is pink, and then another 1 ml of acid is added in excess. After this the solution is titrated with 0.05 N iodine solution in the presence of starch until the blue color remains constant. Near the end point the titration must be made slowly with vigorous mixing.

The same conditions are used to standardize the nickel diethyldithiophosphate solution against the iodine solution; in the calculations the theoretical titer of the nickel diethyldithiophosphate solution with respect to cadmium is used.

The volumetric method is considerably faster than the gravimetric, and the operating technique is simpler; the analysis accuracy is the same for both methods (Table 2).

LITERATURE CITED

- [1] A. I. Busev and M. I. Ivanyutin, J. Anal. Chem. (USSR) 13, 312 (1958).
- [2] A. I. Busev and M. I. Ivanyutin, J. Anal. Chem. (USSR) 11, 523 (1956).

THE ROLE OF TRIVALENT IRON IN PULSE POLAROGRAPHY

B. Ya. Kaplan

Chemical Laboratory of the Geological Administration of the
Central Districts

When large amounts of ferric oxide are present in a solution, the pulse-polarographic peaks [1] are shifted upward and to the right, i.e., toward negative potentials. Shifts in the peaks make a rapid pulse-polarographic determination of various components difficult, and require special operations for the removal or reduction of the iron.

Horizontal shifts of the pulse-polarographic peaks are caused by a decrease in the direct component of the

voltage in the electrolyzer circuit, linked with a large value for the direct component of the diffusion current for the reduction of iron [1]. We set ourselves the task of determining the reason for the vertical shifts of the pulse-polarographic peaks. Of especial interest was the fact that such shifts are not observed using the Barker pulse polarograph [2].

In order to determine whether these peaks are due to an actual increase in the condenser current, linked with an increase in the charge of the cations in the double electrical layer, we investigated the relation between the period of cutting off the condenser current and the relative magnitude of the vertical shift of the peak. To change the period of "cutoff" of the pulse polarometer PVPP [3], we varied the capacity of the integrating condenser, connected to the thyatron grid of the apparatus. Changing the cutoff period from 2.7 to 8.0 msec was practically without effect on the relative magnitude of the vertical shift for the peak of 2 mg of In in a liter of HCl (1:7) solution, containing 1 g of Fe^{3+} . Consequently, the experimental facts contradict the accepted postulation.

The postulation that a high area of the pulse-polarographic curve appears as a nearly horizontal "tail" of the iron (or mercury, see below) peak also proved invalid. In this case a slight decrease in this effect should be observed in going to more negative potentials. However, we were unable to detect such a phenomenon.

In seeking other reasons for the vertical shifts of the pulse-polarographic peaks, we came to make a detailed oscillographic study of the voltages at the control grids of all of the bulbs of the PVPP when operating with different solutions.

It was established that in hydrochloric acid solutions, at high Fe^{3+} concentrations, a gradual change in the polarization voltage leads to a very sharp change in the conductance of the dropping-mercury electrode. Its highest conductance is observed in a certain narrow region of the potential. In 1.5 M HCl solution, containing 2.5 g of Fe^{3+} per liter, a high conductance of the electrode is observed in the range from minus several hundredths to -0.5 v (relative to the saturated calomel electrode), with a smooth change in the direct component of the polarization voltage toward negative potentials. When the change in the voltage is in the opposite direction, the dropping-mercury electrode shows a high conductance at a considerably higher positive potential (-0.4 and even -0.3 v, relative to the saturated calomel electrode). The limits of the region of a high conductance lack good reproducibility. Reducing the amount of Fe^{3+} in the solution narrows the region of a high conductance for the electrode. In a solution, containing 0.7-0.8 g of Fe^{3+} per liter, the region of a high conductance is no longer observed.

A sharp change in the polarization voltage in order to shift the dropping-mercury electrode from the region of a high conductance to that of a normal conductance gives the corresponding effect only after the separation of the next drop of mercury. The drop, formed in the region of a high conductance, remains a good conductor even after a sharp change in its potential.

The addition of 6-9 ml of a 1% gelatin solution per liter completely removes the effect of a high conductance. Small amounts of gelatin narrow the region of a high conductance from both sides. High concentrations of H_3PO_4 (1 mole/liter) function in the same manner.

In the limits of the region of a high conductance either a sharp increase or decrease is observed in both the alternating and direct components of the current in the electrolyzer circuit.

The existence of a high conductance region is not mentioned in the literature, possibly for the reason that the need of investigating electrolyte solutions with such a high Fe^{3+} content had failed to arise up to now.

In sufficiently concentrated mercuric chloride and V^{V} solutions exactly the same region of a high conductance was observed as in trivalent iron solutions. Both mercuric chloride and V^{V} , the same as Fe^{3+} , oxidize mercury metal at a zero potential relative to the saturated calomel electrode.

The creation of a region of high conductance is linked either with adsorption phenomena or with hydrodynamic phenomena, similar to polarographic maxima. In both cases we are dealing with a qualitatively new fact. In all solutions that have been studied up to now, the polarographic maxima were not detected using the pulse-polarographic technique, while the adsorption phenomena were detected only as tensometric peaks, determined by the reversible adsorption-desorption phenomena of surface-active substances [4]. We believe that the region of a high conductance is linked with the peculiar structure of the calomel adsorption layer; the nucleus

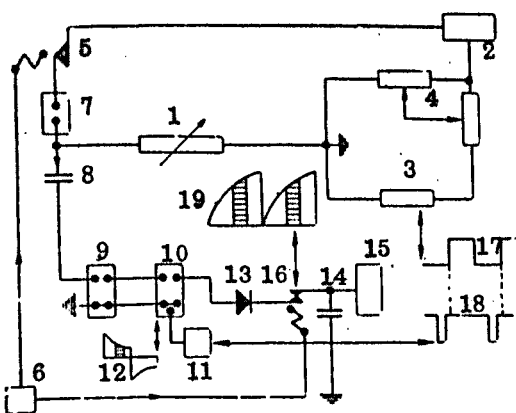


Fig. 1. Functional scheme of the peak pulse-polarograph PP.

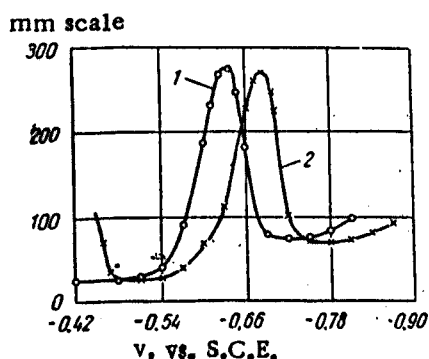


Fig. 2. Visual pulse-polarograms on a support of 1.5 M HCl: 1) 10 mg Cd/liter; 2) 10 mg Cd + 1 g Fe/liter.

of large Fe^{3+} concentrations can lead to a closing of one of the bulbs of the booster and to a large distortion in its mode of operation.

In the Barker pulse polarograph the measuring apparatus is turned off at the initial moment of existence of the mercury drop, and consequently the effect of the fluctuations of the direct component of the current caused by drop formation is not recorded by this apparatus [2]. Other investigators failed to encounter the indicated phenomenon only for the reason that they did not study the pulse-polarographic behavior of solutions with a very high content of electropositive elements.

To confirm the results of the indicated oscillographic observations, and to liquidate the effect of the vertical shift of the pulse-polarographic peaks, we constructed a peak pulse-polarograph PP, the functional scheme of which is shown in Fig. 1.

To the circuit of electrolyzer 1 is connected the direct component of the polarization voltage from source 2 and the alternating square component of the voltage (oscillogram 17) from generator 3 through divider 4. Separation of the mercury drop is induced by electromagnetic hammer 5, operated by a special relay-thyratron assembly 6.

The alternating component of the voltage drop at resistance gauge 7 is filtered off by condenser 8, amplified by booster 9, and fed to the electronic commutator 10, securing the effect of cutting off the condenser current [1, 3].

As a commutator in the apparatus we used a pentode, closed by a positive shift at the cathode. The

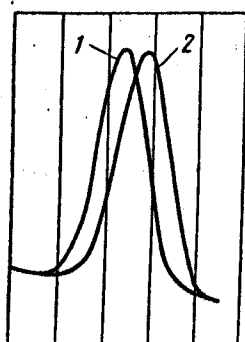
of this structure is retained in the first moment after the drop breaks away, and this determines the hysteresis effect characteristic for the discussed phenomenon.

At the Moscow Electrochemical Seminary the theory was expressed by Academician A. N. Frumkin that a high conductance is determined by anodic oxidation of the mercury and is caused by a shift of the electrode potential as the result of intensified tangential movements on the drop surface, responsible for the large ohmic drop of the voltage in the solution.

In practical pulse-polarographic analysis it is essential to avoid creating a high conductance of the dropping-mercury electrode.

Fluctuations of the direct component of the current in the electrolyzer circuit caused by drop formation are not filtered off by the inlet condenser of the PVPP booster, and are recorded by the apparatus. The magnitude of these fluctuations, which depends on the diffusion current of the electropositive elements in the solution, determines the vertical shift of the pulse-polarographic peaks. Attempts to filter off these fluctuations by a more complex system of R-C filters proved unsuccessful, since the indicated fluctuations of the current are characterized by a broad frequency spectrum.

In the PVPP the separation of the drop induces a positive voltage impulse at the inlet side of the booster. In its sign this impulse coincides with that of the half-period of the alternating current in the electrolyzer circuit, measured by the apparatus, and for this reason the presence of large amounts of Fe^{3+} is recorded by the apparatus as an increase, and not a decrease, of the open-circuit current. The separation of the drop in the presence



0.30-0.36-0.42-0.48-0.54-0.60
V, vs. S.C.E.

Fig. 3. Pulse-polarograms on a support of 1M $H_3PO_4 + HCl$: 1) 5 mg Pb/liter; 2) 5 mg Pb + 500 mg Sn + 2.5 g Fe/liter.

Verification of the Method for the Determination of Lead on a Support of $H_3PO_4 + HCl$ in the Presence of Bivalent Tin, Oxidized with Iron

Amount of Pb in sample, mg	Amount of Sn added, mg	Found Pb, mg
1.0	50.0	1.05
1.0	100.0	1.0
2.0	200.0	1.9
2.0	300.0	2.0
5.0	300.0	5.1
5.0	500.0	5.0

commutator is opened periodically by the commutating negative voltage impulses (oscillogram 18), entering from special generator 11.

On the oscillogram of the alternating component of the current in the electrolyzer circuit 12 the portion of the current that is filtered off by the commutator is shown crosshatched, and can be measured using a peak lamp voltmeter, consisting of diode 13, memory condenser 14 and electronic measuring bridge 15. Either visual or recording measuring devices can be attached to the diagonal of the bridge. Relay 16, operated by the same relay-thyratron assembly as the electromagnetic hammer, disconnects the measuring bridge from the booster of the apparatus during the initial period (period of rapid increase in the surface area) of forming the mercury drop; the memory condenser, connected to the control grid of one of the tubes in the bridge, assures a constant reading of the apparatus during the entire period. On the oscillogram of the voltage at the inlet side of the measuring bridge 19 the portion of the voltage that corresponds to the period of connecting the bridge to the booster of the pulse polarograph is shown crosshatched.

The first experiments with the pulse polarograph revealed that the effect of a vertical shift of the pulse-polarographic peaks in the presence of large concentrations of Fe^{3+} is sharply suppressed in this apparatus even in the absence of voltage feed to the relay-thyratron assembly. The point is that the peak voltmeter of the pulse polarograph registers the peaks of the negative voltage impulses at the inlet side of the booster, while the large time constant of the voltmeter makes it insensitive to the positive voltage impulses caused by separation of the drop.

The relay-thyratron assembly increases the sensitivity of the pulse polarograph (practically twofold) and reduces the oscillation caused by drop formation.

The pulse polarogram of cadmium, obtained in the presence of Fe^{3+} , shows a horizontal shift caused by a decrease in the direct component of the voltage in the electrolyzer circuit and a slight vertical shift downward. In the presence of large concentrations of Fe^{3+} , an apparent decrease in the condenser current is observed on the pulse polarograph, but not an increase, since the apparatus measures not a positive, but a negative voltage half-period at the inlet side of the booster. Figure 2 was taken with the relay-thyratron assembly disconnected; it should be mentioned that the vertical shift of the peaks is even less pronounced when this assembly is connected.

In conclusion, we will give a practical example of using the pulse-polarographic method of analysis in the presence of excess Fe^{3+} .

Sn^{2+} interferes in either the pulse-polarographic or polarographic determination of lead in chloride solutions. A method has been proposed [6] for the separation of these two elements based on the polarographic determination of lead in the presence of tin using a citrate support. Milner and Slee [5] established the pulse-polarographic inactivity of Sn^{2+} on a support of 1 M H_3PO_4 . However, traces of chlorides lead to the appearance of the tin peak on this support, and for this reason the British authors recommend not using hydrochloric acid to decompose tin-containing samples when it is desired to determine lead in them by the pulse-polarographic technique. Not using HCl for the decomposition is not always convenient, since chlorides facilitate the complete dissolution of lead, especially in those cases where the ore contains sulfates, or where the latter are formed in the process of decomposing the sample.

We found that Sn^{4+} gives pulse-polarographic peaks in hydrochloric acid solutions, but phosphoric acid suppresses these peaks. In 1 M H_3PO_4 + HCl solution, tetravalent tin is firmly bound as a phosphate complex and does not give peaks. From Fig. 3 it follows that, after oxidation with trivalent iron, a 100 fold excess of tin does not interfere with the determination of lead on this support.

On the basis of the above, we worked out a method for the determination of lead in ores that contain acid-soluble tin.

A 0.1-2.0 g sample is treated with 15 ml of dilute hydrochloric acid (1:1) and the mixture boiled in a 200 ml volumetric flask for 15 min, after which 30 ml of a solution, containing 15 ml of HCl (1:1) and 500 mg of Fe^{3+} , is added. In 10 min 25 ml of conc. phosphoric acid is added to the flask, the solution made up to volume with water, shaken, allowed to settle, and then pulse-polarographed.

The method was checked on ore samples free of tin, to which known amounts of stannous chloride solution were added during decomposition. The results obtained are given in the table.

Despite the high concentrations of Fe^{3+} in solution, regions of a high conductivity were not observed on the pulse polarograms because phosphoric acid was present. The proposed method, in which iron is used to oxidize stannous tin, cannot be duplicated in classical polarography.

SUMMARY

1. The effects of both a horizontal and a vertical shift of the pulse-polarographic peaks in the presence of high concentrations of ferric oxide were investigated and explained.
2. A peak pulse-polarograph, which excluded the effect of a vertical shift of the pulse-polarographic peaks, was built.
3. It was shown that the dropping-mercury electrode exhibits a high conductivity in the presence of very high concentrations of ferric oxide.
4. A method was developed for the pulse-polarographic determination of lead in ores, containing acid-soluble tin.

LITERATURE CITED

- [1] B. Ya. Kaplan, *Indust. Lab. (USSR)* **20**, 771 (1957).
- [2] D. J. Ferret and G. W. C. Milner, *Analyst* **81**, 193 (1956).
- [3] B. Ya. Kaplan and E. N. Ulanovskii, *Indust. Lab. (USSR)* **24**, 11 (1958). [See English translation.]
- [4] B. Breyer and S. Hacobian, *Australian J. Sci. Research* **A5**, 500 (1952).
- [5] G. W. C. Milner and L. J. Slee, *Analyst* **82**, 139 (1957).

POLAROGRAPHIC DETERMINATION OF TELLURIUM IN COPPER ALLOYS

I. E. Bykov and L. S. Gorshkova

Institute of Metallurgy of the Ural Branch of the Academy of
Sciences of the USSR

The problem of reducing tetravalent tellurium at the dropping-mercury electrode in alkaline cyanide solutions, containing large amounts of copper [1], and of working out a method for the rapid determination of tellurium in copper alloys without removal of the copper, possesses practical interest.