POLAROGRAPHIC DETERMINATION OF GOLD ON A ROTATING MICRODISC PLATINUM ELECTRODE

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Polarographic determination of gold on a dropping mercury electrode is difficult because of the chemical interaction of many gold compounds with mercury metal. Usually complexing agents are used which form compounds with gold which are stable to mercury metal [1-10].

The behavior of gold toward reduction on solid electrodes has not hitherto been studied in detail, although there are individual references to the possibility of using such electrodes for the polarographic determination of gold [11, 12]. Ezerskaya [6] using a rotating platinum wire electrode, obtained a gold wave which is not clearly defined enough for direct quantitative polarographic determination. This author has, however, successfully titrated gold amperometrically. While investigating the properties of a rotating wire electrode, the back part of which was screened with a ceresin coating, Ferret and Phillips [13], in addition to other metals, determined gold polarographically.

We studied the reduction of gold on a platinum microdisc electrode, and also the possibility of using the latter for the polarographic determination of gold.

A M7-2000 visual polarograph of the Gorky Institute of Chemistry was used in conjunction with a GZS-47 mirror galvanometer which had a maximum sensitivity of 10^{-9} amp/mm.

An electrode (Fig. 1) which could be called a microdisc electrode was used. It was in the form of a platinum wire fused into a glass tube. The bottom part of the tube and the platinum were carefully polished. Contact was established through mercury in which a copper wire was immersed. The surface area of the platinum cathode was 0.78 mm^2.

A platinum plate with an area of 400 mm^2 was used as the anode, as well as an external anode – a saturated calomel element plus mercury with sufficiently large area.

The rotational speed of the electrode was kept constant at 800 rpm. A vessel described previously [14] was used as the electrolyzer.

A standard gold solution was prepared from commercial chloroauric acid. The concentration of the standard solution was determined gravimetrically [15, 16]; it was found to be 0.0103 g/ml. More dilute solutions were prepared by diluting the standard solution.

Experiments showed that in a supporting electrolyte of 0.1 M $NaNO_3$ or KCl from which oxygen had been removed by passing nitrogen through the solution, the gold from the solution of chloroauric acid is reduced on a platinum microdisc rotating electrode, and gives a clear cut polarogram with two diffusion regions (Fig. 2, Curve 3). The first break on the curve, at a potential of + 0.6 v (relative to the saturated calomel electrode) is accompanied by deposition of metallic gold on the electrode, and corresponds to the process $[AuCl_4]^- + 3e \rightarrow Au^0 + 4Cl^-$. The second break on the curve, as in the case of the reduction of chloroplatinic acid [17], corresponds to electrical reduction of hydrogen ions.

Oxygen which is dissolved in water, since it is reduced on a platinum microelectrode, gives a distinct wave and interferes with the determination of many ions. Bearing in mind that gold is reduced at a more positive

potential (+0.6 v with respect to the saturated calomel electrode) than oxygen (+0.2 v) it should be possible to omit the removal of oxygen which is necessary in other cases [14, 17]. It is clear from Fig. 2 that in the given test solution, oxygen does not affect the gold wave.

Distinct polarograms are obtained for gold in the following supporting electrolytes: 0.1 M solutions of the chlorides of potassium, sodium, lithium, ammonium, and in 0.1 M solutions of sodium nitrate, sodium perchlorate, hydrochloric, sulfuric, nitric, and perchloric acids. The nature of the ions tested has no effect on the reduction potential of gold.

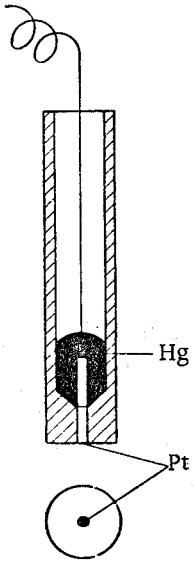

Fig. 1. Microdisc platinum electrode.

In a supporting electrolyte of 0.1 M sodium acetate, the height of the gold wave was depressed somewhat; in a supporting electrolyte of ethylamine hydrochloride the rise on the curve was steeper than in the preceding cases. A gradual drop in the wave height was observed when gold was polarographed in a supporting electrolyte of sodium tartrate. During this process, the solution acquired a violet color, presumably because of the chemical reduction of gold. A similar state of affairs was observed when Complexon III was used as a supporting electrolyte.

Changing the concentration of the supporting electrolyte from 10^{-5} to 1-2 M (as was done in the case of KCl and $NaNO_3$) while the solutions were thermostatted, has no essential effect on the wave height and on the reduction potential of gold. Some of the increase in the limiting current corresponds to the reduction of anions on the cathode [19]. In subsequent experiments the supporting electrolyte used was 0.1 and 1 M KCl.

Of particular importance in carrying out polarographic determinations with solid electrodes is the question of the repeatability of waves when successive polarograms are taken. In the case of other noble metals which we have studied [14, 18], it was shown that under certain conditions it is possible to obtain reproducible results. The definition and the reproducibility of the gold wave depends to a significant extent on the state of the surface of the microdisc electrode. The first one or two polarograms taken with a freshly prepared electrode do not appear to be sufficiently characteristic for a given gold concentration. They differ in that they have a more negative reduction potential, the shape of the wave is less distinct, and the wave height is less. The third and succeeding polarograms exhibit good reproducibility, and preserve their shape and height in the course of 15-20 polarograms.

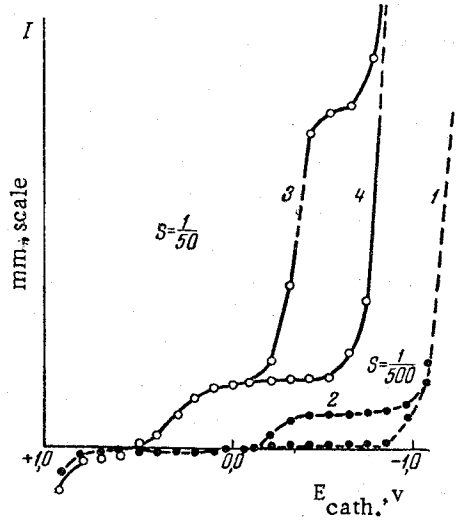

Fig. 2. Effect of oxygen on the gold wave: 1 and 2) Supporting electrolyte 0.1 M KCl before and after removal of oxygen; 3 and 4) solution containing 0.43 mg of gold in 25 ml, before and after removal of oxygen.

After a large number of gold polarograms have been taken, they become somewhat distorted, probably as a result of the considerable increase in the electrode surface because of deposition of gold on it. In such cases, the electrode is treated with aqua regia or is polished with fine emery cloth. The design of the microdisc electrode permits the latter technique, which is the simplest method, to be used. Before the electrode is used it is carefully washed with distilled water, and two or three polarograms are taken which are not used for quantitative measurements. After these two or three polarograms have been taken, reproducible waves can be obtained which are suitable for analytical purposes.

In order to get sharply defined polarograms for gold, and to get constant reduction potentials, it is also essential to choose conditions which will ensure that there is hardly any polarization of the platinum anode. As is evident from Fig. 4, it is only when the anode surface is large enough that its potential remains constant during the whole time that polarograms are being taken, i. e., an anode that is similar to other nonpolarizable anodes.

As shown in Fig. 5, there is a direct proportionality between the wave height of gold and the concentration of the latter in solution over a fairly wide interval of 2×10^{-4} to 3×10^{-6} M/liter.

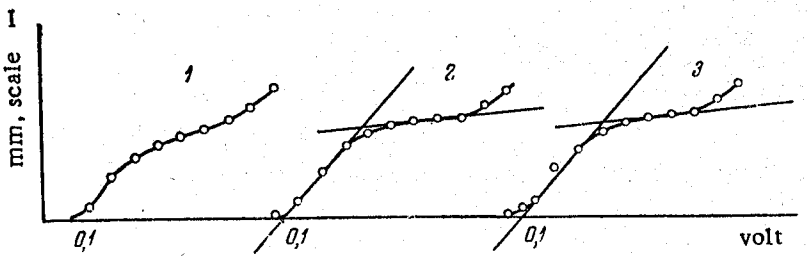

Fig. 3. Repeatability of the gold wave in successive polarograms: 1) After cleaning the microelectrode; 2) after gilding the microelectrode; 3) the tenth polarogram.

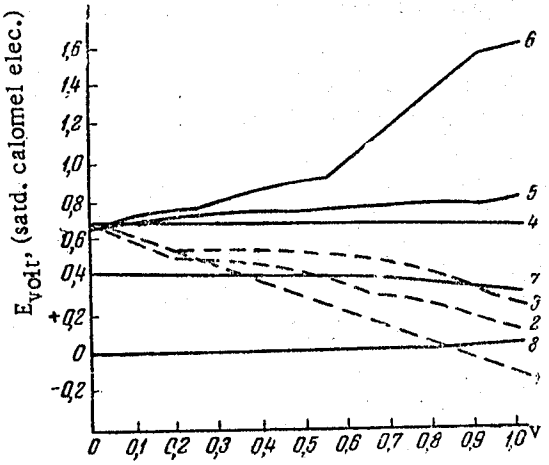

Fig. 4. Change in electrode potentials during polarographic determinations of gold: 1,2,3,) of cathode (microdisc platinum rotating electrode); 4,5,6) of anode – platinum disc with surface area of 400, 120, and 60 mm^2 respectively; 7 and 8) of anode – mercury, saturated calomel electrode.

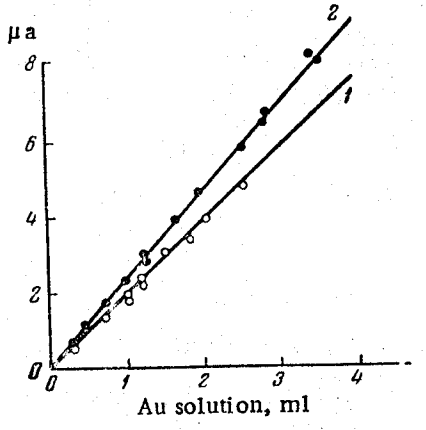

Fig. 5. Relation between the diffusion current and gold concentration when a rotating microdisc platinum cathode is used: 1) Anode – saturated calomel electrode; 2) anode – platinum disc area 400 mm^2. T_{Au} = 0.00043 g/ml.

Determination of Gold

Au taken, $g \cdot 10^{-6}$/ml	Wave ht. mm of scale**	Au found, $g \cdot 10^{-6}$ per ml	Error abs.	Error rel. %	Au taken $g \cdot 10^{-6}$/ml	Wave ht. mm of scale**	Au found, $g \cdot 10^{-6}$/ml	Error abs.	Error rel., %
4,3	5,2	4,04*	—0,26	—6	16,2	20,3	16,0*	—0,2	—1,2
4,3	5,5	4,2*	—0,1	—2,3	21,5	27,7	22,2	+0,7	+3,3
6,0	8,8	6,3*	+0,3	+5	21,5	27,6	21,7	+0,2	+0,9
8,6	10,6	8,43	—0,17	—2	22,4	28	22,4	0,0	0,0
10,3	13	10,3	0,0	0,0	22,4	27,9	22,3*	—0,1	—0,4
12,0	14,8	11,87	—0,13	—1,1	25,8	32,5	25,8	0,0	0,0
14,6	18	14,7*	+0,1	+0,7	26,7	33,8	27,26*	+0,56	+2,1
16,2	20,5	16,2	0,0	0,0					

* Determined by the method of additions.

** Mean of three determinations.

Unknown amounts of gold were determined by means of a calibration curve and also by the method of additions. Results of such determinations are given in the Table.

The method which has been developed for the polarographic determination of gold by means of a rotating microdisc electrode is characterized by a fully satisfactory reproducibility with an average accuracy of ± 2%.

In conclusion we should like to thank Yu. S. Lyalikov for his interest in the work.

SUMMARY

Conditions for the polarographic determination of gold solutions by means of a solid platinum microdisc rotating electrode have been studied.

It has been established that gold from chloroauric acid gives a clearly defined polarogram in various supporting electrolytes; the wave is a result of the reduction of Au^{III} to Au^{0}; polarographic determinations can be carried out without resorting to preliminary removal of dissolved oxygen.

There is a linear relation between gold concentration and the diffusion current over the gold concentration range of 2×10^{-4} to 3×10^{-6} M/liter.

Within the concentration range indicated, unknown amounts of gold can be determined either by means of a calibration curve, or by the method of additions, with an accuracy of about ± 2-3%.

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