

Kh. Z. Brainina, R. P. Lesunova,
and L. N. Serebryakova

UDC 543.257

One of the difficulties of the phase analysis of solids [1] is that a calibrating curve must be constructed in advance by use of standard samples. Moreover, the reproducibility depends on the degree of dispersion of the electroactive material, the uniformity of its distribution in the paste, often also its history and the presence of impurities.

It is the aim of the present investigation to provide quantitative analysis of a mixture of compounds of an element in various stages of oxidation without constructing a calibrating curve from standard samples.

A carbon paste electrode is used. The P-5827 potentiostat functions in the linear potential scan mode; a KSP-4 potentiometer records the current. Chemically pure metallic silver powder (average particle diameter from 0.0040 to 0.0050 cm) and silver oxides synthesized from chemically pure reagents served as the electroactive starting material. The material to be studied is incorporated into the carbon paste electrode [2]. Mercuric oxide electrodes serve as the reference electrode. All potentials are referred to this electrode. A 0.1 N potassium hydroxide solution prepared from analytically pure reagents serves as the electrolyte.

Figure 1 shows the cyclic polarization curve describing the electrochemical transformations of silver and its oxides. Silver is the electroactive starting material. The electrode was polarized anodically over the potential range from 0 to 0.9 V. The corresponding polarization curve exhibits currents for the oxidation of silver to Ag_2O and of Ag_2O to AgO . The higher silver oxide is provisionally described by the formula AgO , because in the literature opinion is divided as to its composition [3]. The direction of polarization was inverted without interrupting the polarization, and the cathodic currents for the reverse electrode reactions were recorded. One can select the potential limits of electrode polarization such that one of the electrode processes will occur alone.

Figure 2 shows a polarization curve describing the electrochemical transformations of lower silver oxide (Ag_2O) that was incorporated into a paste electrode. A potential of 0.6 V was selected as the starting potential. Here evidently only one electrode process, oxidation of the lower silver

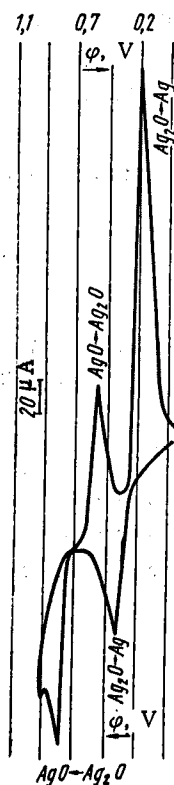


Fig. 1

Fig. 1. Cyclic polarization curve of the electrochemical transformations of silver incorporated into a paste electrode.

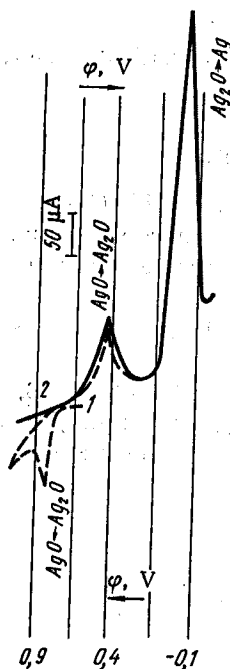


Fig. 2

Fig. 2. Polarization curves: 1 g of the paste contains 0.04 g Ag_2O (1) or AgO (2); $\phi_{\text{st}} = 0.6$ V (1) or 1.0 V (2).

TABLE 1. Results for Ag₂O Determination in Mixtures Ag₂O + AgO (%)

Ag ₂ O introduced in the mixture, %	Chemical method			Electrochemical method								
				from a calibrating curve [1]			from I_{aAgO}/I_{cAg_2O}			from I_{aAg_2O}/I_{cAgO}		
	n	$\bar{x}$	S_r	n	$\bar{x}$	S_r	n	$\bar{x}$	S_r	n	$\bar{x}$	S_r
30	3	30,5	0,02	5	32	0,10	5	30,0	0,18	—	—	—
20	5	20,0	0,04	11	20,0	0,10	11	20,0	0,09	11	19,6	0,06
10	5	10,5	0,05	11	10,0	0,09	17	10,0	0,04	16	9,8	0,10
7	5	7,0	0,12	13	7,4	0,12	19	6,6	0,08	15	7,0	0,12
5	5	6,0	0,07	15	5,0	0,10	17	5,1	0,20	10	5,0	0,11
1	5	2,0	0,07	15	0,9	0,12	7	0,8	0,15	16	1,0	0,09

Note. For the electrochemical measurements, a new paste was employed each time in three parallel determinations. The total silver concentration was determined by titration with ammonium thiocyanate solution in nitric acid medium in the presence of ammonium ferric alum, the AgO concentration with sodium iodide solution; the Ag₂O concentration was calculated from the difference of the results of these two determinations.

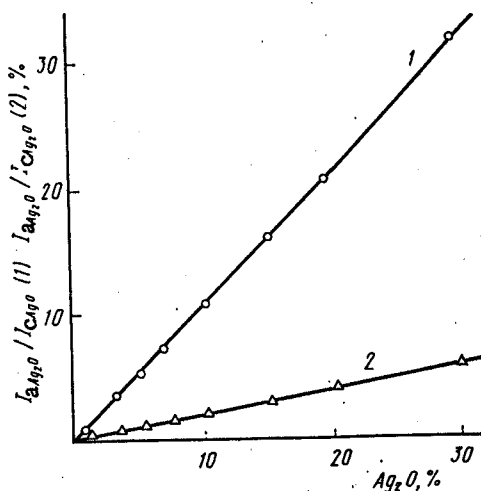


Fig. 3. The ratios I_{aAg_2O}/I_{cAgO} and I_{aAg_2O}/I_{cAg_2O} as functions of Ag₂O concentration in mixture of Ag₂O and AgO.

oxide, occurs in the potential range between 0.6 and 0.9 V. In the potential range between 0.6 and 0.3 V one observes reduction of the higher oxide which was produced in the anodic cycle (the dashed line). The cathodic polarization curve describes two stages of reduction of higher silver oxide (AgO) which was incorporated into the paste of the electrode in an amount such that its equivalent concentration equaled that of Ag₂O in the case of the first curve. The maximum cathodic currents for AgO → Ag₂O on the two polarization curves and the maximum current for the oxidation of the lower silver oxide are similar to one another. The current for the reduction of Ag₂O to Ag is several times larger than the other currents.

Figure 3 shows the ratios of currents I_{aAg_2O}/I_{cAgO} and I_{aAg_2O}/I_{cAg_2O} as functions of the concentration of lower silver oxide which was introduced into the paste as a mixture with the higher oxide (the suffices indicate anodic or cathodic process).

There is a linear relation between the ratio of experimentally measured currents and the argentous-oxide concentrations in the paste. Hence one can use this ratio as a source of information about the concentration of this oxide in a mixture being examined.

The product of the first electrode reaction (i.e., of the oxidation of the material being determined) and the appropriate compound added as second component of the mixture are electrochemically converted as a sum, the corresponding signal serving as standard signal. This sum represents the internal standard. The reduction currents for AgO → Ag₂O or Ag₂O → Ag can serve as the standard signals. The Ag₂O concentration in the mixture is determined from the relation $X = KY$, where X is the Ag₂O concentration in the mixture, in percent, and Y is the ratio I_{aAg_2O}/I_{cAgO} or I_{aAg_2O}/I_{cAg_2O} , in percent.

In the first case $K = 0.94$, which is close to the gram-equivalent ratio of the oxides being studied (0.93). Table 1 shows results of the analysis of silver oxide mixtures. Analysis was performed chemically and electrochemically with and without calibrating curves. The electrochemical methods give the more accurate results, especially when small quantities are to be determined. The reproducibility of the results is similar in the two cases, but can be attained in a much simpler way when the internal standard is used.

Analysis time is reduced to 5-10 min. The method can be used for control of the technical process, in phase analysis for determining the lower oxide of a metal in a mixture with higher oxide, as well as for determining metal in a mixture with its oxide.

In order to determine, e.g., Ag_2O in a mixture of Ag_2O and AgO , blend one volume part ($0.2\text{--}0.5\text{ cm}^3$) of the starting mixture, at any degree of dispersion, and possibly containing electroinactive components, with five volume parts of V-3 powdered charcoal, in form of a more finely divided fraction than the mixture being studied.

The mixture is stirred, one volume part of dibutylphthalate is added, and the mixture again stirred. The electrode paste obtained is placed into the holder, the electrode surface is leveled with filter paper, and the electrode is placed into the electrolyzer filled with 0.1 N KOH solution. The potential of the paste electrode is set between 0.55 and 0.65 V , and a linear anodic potential-time sweep is applied. The potential dependence of the oxidation current of Ag_2O to AgO is recorded, then the direction of polarization is inverted at potentials between 0.8 and 0.9 V , and the total reduction current of AgO is recorded (of the AgO introduced initially, and of the AgO produced in the oxidation step from Ag_2O). The concentration of wanted component in the sample is calculated from the formula.

LITERATURE CITED

1. Kh. Z. Brainina, R. P. Lesunova, and M. A. Evseeva, *Zavod. Lab.*, No. 12, 1414-1418 (1971).
2. V. G. Barikov, Z. B. Rozhdestvenskaya, and O. A. Songina, *Zavod. Lab.*, No. 7, 776-780 (1969).
3. D. MacMillan, *Uspekhi Khimii*, 23, No. 3, 334-359 (1964).