AUTOMATIC DETERMINATION OF METALS BY SUBSTOICHIOMETRIC COULOMETRY

P. K. Agasyan, T. K. Khamrakulov, and A. I. Kordumov

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The theoretical basis for substoichiometric coulometry was outlined in a preceding paper with the example of silver and copper determination [1]. The method works as follows. Partial deposition of a substance is achieved on a solid electrode at certain values of the electrolysis current, i_e, and time, τ_e. After reversing the current, dissolution is conducted at a constant value of current, i_a, and the time required for dissolution, τ_a, is measured. This time is found, in absence of stirring, from the potential jump that begins when the function of the electrode changes.

The amounts of material deposited on the electrode and, consequently, of electricity, $Q_a = i_a \cdot \tau_a$, used for its dissolution are proportional to the concentration of the material, $C_{Me^{n+}}$, in the analyzed solution under the condition $i_e > i_d$ (i_d is the limiting current of the test material).

The content of test material is found from a calibration curve. If Q_a is determined with a coulometer or current integrator, then τ_a need not be measured, and i_a need not be kept strictly constant.

The problem has arisen to work out a technique for determining the components in binary and ternary alloys (Ag–Cu, Ag–Ni, Ag–Cu–Ni, Ag–Cu–Cd) and for automating the analysis. To this end the optimum conditions were studied for determining the components at upper and lower concentration limits, and an automatic instrument was assembled accordingly.

Reagents:

1. A solution of twice-recrystallized copper sulfate; the H_2SO_4 concentration in this solution was 0.1 N. The titer of the solution as calculated from the results of five parallel determinations by electrogravimetry and iodometry [2] was 0.1008 M.

2. A solution of silver sulfate prepared by carefully weighing in pure (99.999%) metallic silver and dissolving it in 0.1 N H_2SO_4 with a few drops of HNO_3 (1 : 1). After evaporation to dryness, the residue was dissolved and diluted with 0.1 N H_2SO_4 to the volume required to make the $AgSO_4$ concentration 0.1 N.

Solutions of lower concentrations of Cu^{2+} and Ag^+ were prepared by corresponding dilution. The base electrolyte was 0.1 N H_2SO_4 + 0.1 N K_2SO_4, prepared from chemically pure sulfuric acid and twice recrystallized potassium sulfate. Other reagents of "chemically pure" grade were additionally purified by recrystallizations. All solutions were prepared with distilled water that was pre-purified in an ion-exchanger column and distilled in presence of permanganate in a quartz vessel [3].

A platinum wire, ~ 4 cm^2, and a net having an apparent surface area of 12 cm^2 served as electrodes.

A 1 × 1 cm platinum sheet served as auxiliary electrode. The potential of the working electrode was measured relative to a saturated calomel electrode. The working electrode was treated with concentrated nitric and sulfuric acids and was in addition polarized anodically after each experiment for 20-25 sec.

From the theory of electrolysis we may conclude that for determining small concentrations it will be necessary to increase the surface area of the working electrode, to prolong the cathodic process, and to lower the anodic dissolution current. A series of experiments carried out previously [1] confirmed these rules. In the present work we have in addition studied the effect of other factors. The effect of temperature was studied between 20 and 70°C. Up to 40°C its effect on the slope of the calibrating line Q_a vs. $C_{Me^{n+}}$ is insignificant. At higher temperatures the dissolution time increases considerably; the slope of the calibrating lines increases correspondingly (Fig. 1). Passing nitrogen through the test solution has almost no effect on the results.

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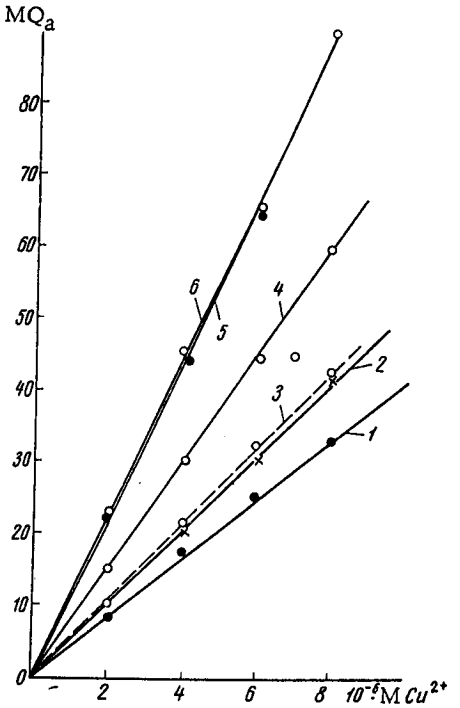

Fig. 1. Effect of temperature on the slope of the calibrating lines mQ_a against $C_{Me^{n+}}$. The curves 1-6 correspond to 20; 30; 40; 50; 60; and 70°C.

TABLE 1. Analytical Results for Copper-Silver Alloys

Weighed portion, mg	Cu content, %	Ag content, %	Cu found, %	Ag found, %	Error for Cu, %	Error for Ag, %
101,22	8,32	91,68	8,39	91,64	+0,07	−0,04
102,76	8,40	91,60	8,51	91,71	+0,11	+0,11
100,33	12,90	87,10	12,85	86,96	−0,05	−0,14
100,94	13,00	87,00	12,87	86,92	−0,13	−0,08
103,55	15,10	84,90	15,31	84,98	+0,21	+0,08
102,52	19,00	81,00	19,26	80,95	+0,26	−0,05
100,52	28,00	72,00	28,10	71,88	+0,10	−0,12

The effect of electrolytes (H_2SO_4, K_2SO_4, Na_2SO_4, KCL, NaCl, and KNO_3) was studied in more detail. Solutions with copper concentrations of $n \cdot 10^{-6}$ M were analyzed. 0.1 N H_2SO_4 + 0.1 N K_2SO_4 proved to be the best base electrolyte.

We have chosen the following working conditions: surface area of the Pt working electrode 4.0 cm^2, i_e = ~ 5 mA, i_a ~ 1 mA, τ_e ~ 300 sec, V = 50 ml, t ~ 25°C, base electrolyte 0.1 N H_2SO_4 + 0.1 N K_2SO_4.

Entirely analogous experiments carried out with pure Ag_2SO_4 solutions gave the same picture. However, in the anodic dissolution of silver deposited from solutions containing more than 10^{-4} M Ag^+, the formation of its peroxide on the electrode was often observed. This appears to be the reason for irreproducibility of the results.

In order to obtain compact deposits it was suggested [2] to add 2–3 g potassium persulfate per 100 ml solution. But in acid solutions at Ag^+ concentrations above $2 \cdot 10^{-3}$ M, such a quantity of persulfate causes precipitation of a dark Ag^{2+} deposit [4], especially when repeating the analysis of the same solution.

We have found that at Ag^+ concentrations below $2 \cdot 10^{-3}$ M, good reproducibility of the results is ascertained in presence of 2% $K_2S_2O_8$. If individual aliquots of the starting solution are analyzed, then the maximum admissible concentration $C_{Ag^+} \approx 10^{-2}$ M. With larger silver contents it is expedient to dilute the starting solution accordingly.

When Cu^{2+} and Ag^+ are present simultaneously, they can be determined together in the same solution sample only in absence of potassium persulfate and with $\leq 10^{-4}$ M Ag^+. With a larger silver concentration in the mixture, persulfate impedes copper deposition. Therefore, Cu^{2+} and Ag^+ are determined from two aliquot solution samples. In one of them silver is determined after addition of persulfate, in the other copper is determined in absence of persulfate. In this case no attention is paid to the partial deposition of silver since the copper deposited on the electrode will dissolve first. The lower limit for Cu^{2+} and Ag^+ determination is about 10^{-6} M.

All experiments and measurements were carried out with an automatic instrument assembled by us.

The instrument consists of four blocks (Fig. 2). Block I allows a constant current of 0.5-10 mA for cathodic and anodic reactions to be maintained. Block II is a mechanical timing relay that allows the duration of the cathodic process (up to 300 sec) to be controlled in steps, and a magnetic stirrer activated. After a given cathodic time, block II reverses the current with the aid of relay No. 3 and activates relay No. 1 in order to shut off the magnetic stirrer. The anodic reaction is carried out without solution stirring in order to increase the dissolution time. The relays No. 2, 4, and 5 are activated simultaneously to start blocks III and IV, and after a 40-sec delay the relay for the anodic dissolution current is also activated. Block III is a cathode follower with an automatic potentiometer ÉPP-09 for recording the $E_a - \tau_a$ curve. Block IV is a balanced tube bridge with electric timer used for automatically indicating the duration of the anodic process.

The cathodic process goes as follows. Switch K_1 is closed, and a current i_e flows into the cell. Simultaneously block II is activated setting the stirrer in motion. The magnitude of cathodic and anodic currents is checked by

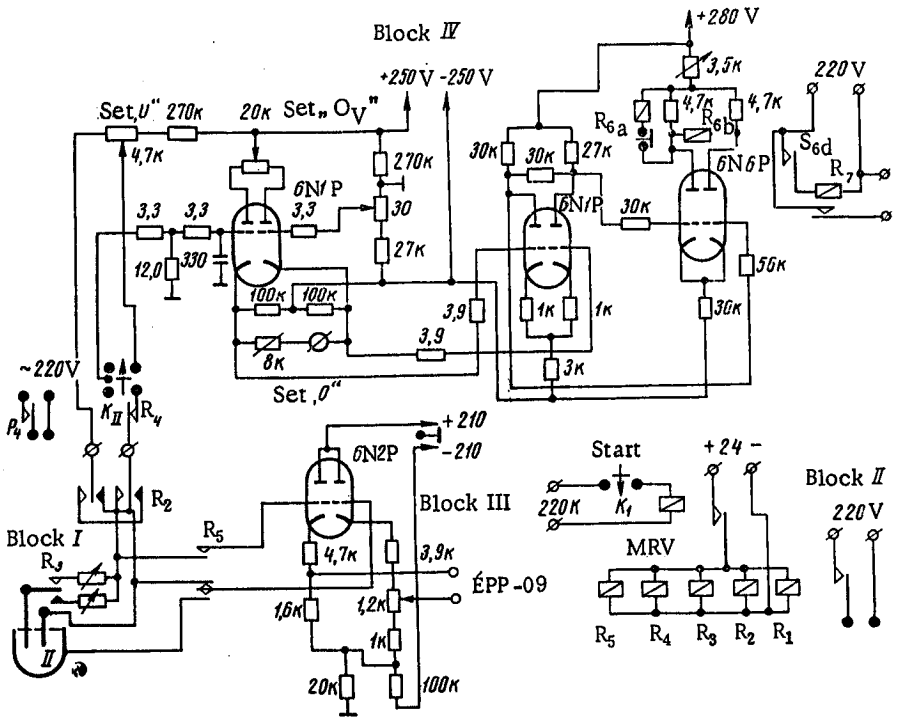

Fig. 2. Basic circuit of the instrument.

the millivolt-ammeter M-193. After a fixed time, a mechanical relay opens switch K and activates the relays No. 1-5. This brings about current reversal and establishes the required magnitude of the anodic current, activates blocks III and IV and the electric relay for starting the anodic current, and stops the stirring.

The anodic process goes as follows. After 40-sec relay No. 4 activates switch K_1, and the anodic dissolution of the deposited metal begins. Simultaneously a signal (the emf between working and reference electrode) is applied to blocks III and IV, and the electric timer is activated. After complete anodic dissolution, the anode potential changes sharply. When a preset electrode potential is reached, block IV closes R_7. Simultaneously the electric timer is switched off, and the signal to block III is discontinued. For a new measurement, after corresponding treatment of the working electrode, the instrument is returned to the starting position by resetting switch K_1.

In order to select the potential at which to shut off the instrument automatically, it suffices to carry out a blank experiment with the base electrolyte. The decomposition potential found for the base electrolyte serves as the parameter to be set on block IV. In a differentiating analysis of a multicomponent mixture, complete dissolution of each deposited element is determined from the dissolution curve $E_a - \tau_a$.

The calibration curves for Cu^{2+} and Ag^+ showed that the amount of electricity consumed in the anodic process is strictly proportional to concentrations up to 10^{-6} M.

For the analysis of binary alloys of silver and copper with high silver content, calibration curves were constructed under the above-mentioned optimum conditions. These characteristics are linear but do not go through the coordinate origin. This can be explained by the presence of impurities in the base electrolyte and the persulfate as well as by the transition time necessary for the working electrode to shift from its initial equilibrium potential to that of base electrolyte decomposition. However, this does not affect the analytical results since the calibration curves and the results for the analyzed materials are obtained under strictly identical conditions.

Results for the determination of alloy components are given in Table 1.

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