FREEING POLAROGRAPHIC SOLUTIONS FROM OXYGEN

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A. G. Stomberg and Yu. N. Zhikharev

Tomsk Polytechnic Institute
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The authors find the optimum conditions for freeing polarographic solutions from oxygen by the combined action of copper shavings and divalent vanadium. The residual current and degree of purification are judged by the coefficient $P = i_{res}/i_{cap}$.

One of the factors which affect the sensitivity of cumulative amalgam polarography (CAP) is the residual current. As shown theoretically in [1], by reducing the residual current to the value of the capacitive current, it would be possible to determine 10^{-9}-10^{-10}% impurities. As the residual current depends on the presence of dissolved oxygen, it is very important to remove the latter as completely as possible.

To remove oxygen from the nitrogen used to blow out the solutions, the gas can be passed through a tube furnace containing copper shavings at high temperature, a solution of vanadous sulfate, or a layer of finely divided copper precipitated on silica gel, or purified by various other means.

We recommend a combination of these methods, and have selected the optimum conditions for the operation of the purifying system.

For rough purification we used copper shavings of size 3-5 mm. These are first degreased with 10-15% alkali solution and then treated with 10-20% nitric acid, after which they are placed in a quartz tube of diam. 30 mm and length 400 mm, insulated by glazing at both ends. The tube is tightly sealed and heated in a current of hydrogen at 300-400°C. The completion of reduction is assessed by the color change of the copper shavings from brown to light red.

The finely-divided copper on silica gel was prepared as described in [2]. The granules were placed in a tube and heated in a current of hydrogen until fully reduced.

In the next purification stage of nitrogen we used a 0.1 M solution of vanadous sulfate. 6-8 ml H_2SO_4 (1.8) were added to 600 ml of this solution. The vanadic ions were reduced with zinc amalgam at the bottom of the washing vessel. To each 100 ml vanadium (II) solution were added ~100 g amalgam, prepared as follows: the granulated zinc was pickled in 10% HCl and then washed with distilled water, and 1 ml Hg added per 100 g Zn. Three Drechsel bottles were connected in series, and 200 ml solution placed in each. After the zinc amalgam is added to the vanadium solution, a certain time is required for the reduction to take place. If the entire system, in the non-operative state, is placed in an atmosphere of nitrogen, the optimum conditions are reached after 30 min. An excess pressure of 20-30 mm can be obtained by means of a nitrogen-filled cushion.

The degree of freedom from oxygen is assessed by means of the coefficient P [1],

$$P = \frac{i_{res}}{S \cdot C_y \cdot W},$$

where i_{res} = residual current in amp, S = electrode surface in cm^2, C_y = 20 $\mu F/cm^2$ = double layer capacity at mercury-solution interface, and $W = 6.7 \cdot 10^{-3}$ V/sec = rate of change of potential. The residual current was registered at −0.7 V (relative to saturated calomel electrode). The coefficient P shows by what factor the residual current exceeds the apparent capacitive current.

Values of P for Various Methods of Purifying Nitrogen from Oxygen and Various Durations of Purification

Method of nitrogen purification	Time of passing nitrogen		
	10 min	20 min	30 min
Unpurified nitrogen	26.0	24.0	20.5
Copper shavings at 450-500°C	10.5	10.5	9.7
	9.5	9.0	8.2
Pyrogallol	12.0		11.0
	13.0	11.4	10.2
Vanadous sulfate (II)	12	12.4	11.6
	9.7	7.5	6.7
Copper shavings + vanadous sulfate	6.7	3.7	2.2
(II)	6.0	3.7	3.2
Copper shavings + finely divided	4.8	3.7	3.7
copper on silica gel	4.5	3.0	2.2
Copper shavings + finely divided copper on silica gel + vanadous	4.8	3.0	3.0
ion solution (II)	4.2	2.8	1.5

As electrode we used a stationary mercury drop, electrodeposited on to a platinum contact from a saturated $Hg(NO_3)_2$ solution by a 30 mA current acting for 45-60 sec. The surface of such an electrode is 0.013-0.015 cm^2. The electrolyte was 0.1 M KOH.

In our experiments with various electrodes, we observed the different residual currents. For each electrode this current is constant for identical working conditions and electrode preparation methods. In our opinion, the differing residual currents observed with different electrodes are explained by the different qualities of the platinum contacts [3, 4]. At the boundary between the platinum wire and the glass to which it is glued, there are microfissures which are difficult to amalgamate. A high residual current is explained by the presence of parts of the platinum not covered with mercury, where the hydrogen and oxygen overvoltages are lower.

For residual current determinations in solutions not freed from oxygen, P varies from 185 to 260. On passing nitrogen not purified from oxygen, P declines to 24-26 after 10 min and 19-22 after 20 min. These P values correspond to $\sim 2\%$ O_2 in the nitrogen and about $1 \cdot 10^{-5}$ mole/l O_2 in the solution. Most of the reduction in P takes place during the first ten minutes of nitrogen passage.

From the results (see the table) it follows that the best purification of the solution—P = 2.2—is attained by the combined use of copper shavings and vanadous ion solution or copper shavings and finely divided copper on silica gel. We recommend the first variant, as the purifying system lasts longer. For 6-8 hours' work per day, the copper shavings need regenerating every fortnight by passing hydrogen at 300-400°C for 3-4 h. The working life of the vadadium solution is $\sim$ 2 months.

LITERATURE CITED

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