the error within the concentration range of $5 \cdot 10^{-6} - 1 \cdot 10^{-6}$ M does not exceed 5-8%. A certain difference in the composition of the solutions does not hinder the determination.

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POLAROGRAPHIC DETERMINATION OF ALUMINUM

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The polarographic determination of aluminum is one of the difficult problems in polarography of metal ions. Aluminum salts are easily hydrolyzed in solutions with pH > 4 and the resulting diffusion current does not express the actual concentration of aluminum. In solutions with pH < 3.2 near the reduction potential of aluminum (− 1.7 v on the background of magnesium chloride) there appears a hydrogen wave which hinders the determination of the true wave height of aluminum.

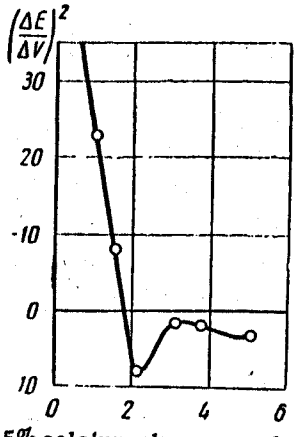

Fig. 1. Change of $\Delta^2 pH/\Delta v^2$ (expressed as $\Delta^2 E/\Delta v^2$) of solution of aluminum sulfate after addition of calcium gluconate.

The polarographic methods of aluminum determination which have been described in the literature are mainly indirect ones.

For the development of a method of aluminum determination we used buffer solutions with pH = 3.5-4, having a large buffer capacity and, also, we used the ability of aluminum to form complex compounds with a number of organic acids [1].

The use of the buffer solution of Walpole type with pH = 4.1, containing 75 ml of 0.2N acetic acid and 80 ml of 0.2 N sodium acetate failed to give satisfactory results. The complexes formed by aluminum with tartaric, citric and lactic acids have a high stability constant, the separation potential of aluminum moves strongly in the negative direction and the aluminum wave cannot be seen, owing to the beginning of reduction of the background electrolyte. Weak complex − formers (glucose, glycerol, salicylic acid) generally do not retain aluminum in solution [2].

Similar results were obtained by us with the backgrounds of sodium oxalate and lithium citrate.

It was most satisfactory to use gluconic acid [3-5] in the form of its calcium salt. The appearance of a weak yellow-green color after the addition of a solution of calcium gluconate to the colorless solution of aluminum sulfate or aluminum potassium alum serves as a proof of the formation of a complex

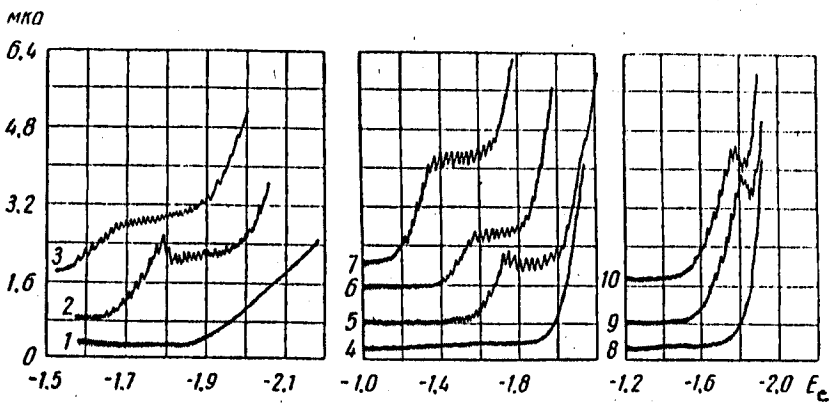

Fig. 2. Polarographic waves of aluminum on the background of calcium gluconate at the various concentrations of the latter. 1) 0.2% calcium gluconate (10 ml); 2) 0.5 ml of 2% $Al_2(SO_4)_3$ added; 3) 0.1% agar added; 4) background: 2% calcium gluconate (10 ml); 5) 0.5 ml of 2% $Al_2(SO_4)_3$ added; 6) 0.1% agar added; 7) 1 ml of 2% $Al_2(SO_4)_3$ added; 8) background: 10% calcium gluconate (10 ml); 9) 1 ml of 2% $Al_2(SO_4)_3$ added; 10) 0.1% agar added. E_c for all curves is measured against the internal anode.

Results of Determination of Aluminum Sulfate in Mixtures with Zinc Sulfate and Boric Acid

Taken g. per 100 ml of solution			Determined by the polarographic method	
$Al_2(SO_4)_3$	$ZnSO_4$	H_3BO_3	$Al_2(SO_4)_3$	$ZnSO_4$
0.500	0.500	2.0	0.487	0.495
0.500	0.500	2.0	0.483	0.495
0.350	0.500	3.0	0.332	0.501
0.350	0.500	3.0	0.333	0.498

compound between the simple aluminum salt and gluconic acid. Addition of a few drops of sulfuric or other strong acid to this mixture causes the disappearance of the color which may be gradually restored by careful addition of sodium hydroxide. In addition to this, alkali added to a mixture of aluminum sulfate and calcium gluconate does not produce precipitates even at pH > 5.5, the same being true for NaH_2PO_4. The precipitate appears, after the addition of the phosphate only with a large excess of sodium phosphate, evidently because of the rise in pH.

A fall in pH is observed after mixing of a solution of aluminum sulfate with a solution of calcium gluconate. Thus, for example, a fall in pH down to 2.99 is observed in the mixture after mixing 4.5 ml of 2.8% aluminum sulfate solution (pH = 3.13) with 2.25 ml of 5% calcium gluconate solution (pH = 6.95).

The acidity of the aluminum sulfate solution increases with the addition of a calcium gluconate solution, and addition of phosphate ions does not bring about an appearance of a precipitate. This allows us to suggest the following chemistry for the interaction* of aluminum with calcium gluconate:

$$3\,[C_6H_6(OH)_4OHCOO]_2Ca + 2Al^{3+} \rightleftarrows 2\left\{\left[C_6H_6(OH)_4\begin{array}{c}O\\ \diagup\diagdown\\ COO\end{array}\right]_3Al\right\}^{3-} + 3Ca^{2+} + 6H^+.$$

*The possibility is not excluded, of course, that complexes with other compositions may form, especially with change of the medium for the reaction.

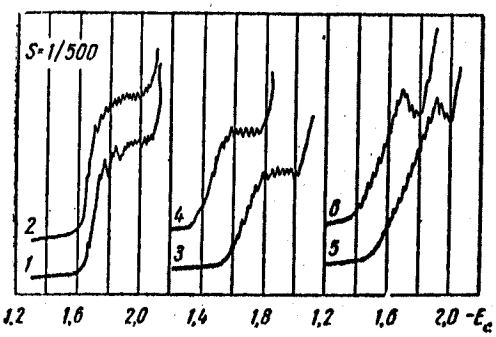

Fig. 3. The effect of the proportion of calcium gluconate and calcium chloride in the background composition on the aluminum wave (0.2 ml of 5% $AlCl_3$ in 10 ml of background electrolyte): 1) 6% $CaCl_2$; 2) 6% $CaCl_2$ + 0.5 ml of 1% agar; 3) 3% $CaCl_2$ containing 5% calcium gluconate; 4) same + 0.5 ml of 1% agar; 5) 10% calcium gluconate; 6) same + 0.5 ml of 1% agar.

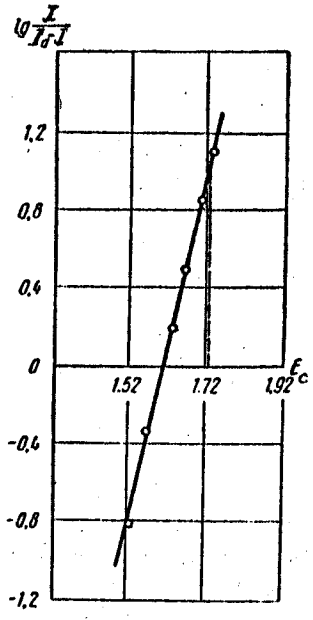

Fig. 4. The dependence of $\log(I/I_d - I)$ on E for aluminum with the background of 5% calcium gluconate containing 5% calcium chloride.

A similar scheme is suggested by Babko and Rychkova [1] in describing the character of the reaction between the aluminum ion and salicylic acid. The stoichiometric relationship between calcium gluconate and aluminum sulfate was established and the composition of the complex was studied. For this purpose we prepared 5% solutions of calcium gluconate and 2.77% solutions of aluminum sulfate. The variation of pH of the aluminum sulfate solution after addition of calcium gluconate with constant volumes of the mixtures was determined potentiometrically with the quinhydrone electrode. The pH should drop during complex formation in accordance with the above equation and this may be utilized for the determination of the composition of the complex.

The equivalence point is clearly seen during the drawing of the curve using as coordinates $\Delta^2E/\Delta v^2 - v$ (Fig. 1). The inflection point lies at 1.65 ml of the calcium gluconate solution and the resulting proportion confirms the formula of the complex formed and, consequently, the suggested scheme of complex formation.

This complex compound was used by us for the polarographic determination of aluminum (capillary characteristic: m = 2.63 mg/sec, temperature 17°).

The appearance of the polarographic curves with aluminum waves, which were obtained at different concentrations of calcium gluconate are shown in Fig. 2; the best wave is obtained with the background concentration of 2%. However, even under these conditions the wave is accompanied by a maximum which has to be suppressed with agar.

The effect of pH on the character and the height of the aluminum wave was studied. It follows from the resulting data that the wave height for aluminum remains practically constant after alteration of the pH from 4.7 to 3.5. In a solution with pH = 3.32 (S = 1/500) there is seen the formation of the hydrogen wave which distorts the actual height of the aluminum wave. For this reason, the determination with this background is best run at pH = 3.5-5. The addition of calcium chloride to the calcium gluconate solution does not interfere with the polarographic determination and allows one to use more concentrated gluconate solutions for the background, these having larger buffer capacities, a fact very important for stabilization of the pH.

The results of polarography of aluminum, using mixtures with various proportions of $CaCl_2$ and the gluconate as the background electrolyte, showed that the best background is a mixture of 5% calcium gluconate and 3-5% $CaCl_2$. The halfwave potential with this background: $E_{1/2}$ = 1.57-1.60 v (relative to a saturated calomel half-cell). The aluminum wave is distinct and is easily measured (Fig. 3). The wave height rises linearly with the alteration of aluminum concentration. The change of $CaCl_2$ concentration almost does not affect the wave height. Small amount of K^+ or Na^+ ions also does not affect the result. The presence of ferrous iron in the solution does not allow for a determination of aluminum since the iron wave shifts toward potentials which are close to the aluminum separation potentials, evidently owing to the formation of a complex compound of iron with the gluconic acid.

The slope of the resulting curve is < 1, as shown by the graph of $E - \log(I/I_d - I)$ (Fig. 4), which indicates an irreversible reduction of aluminum in the complex with the calcium gluconate. The temperature coefficient of the halfwave potential was determined by us to be 2.5-3 mv per degree (instead of 0.7-1 mv/degree according to theory), which also confirms the presence of irreversibility of the process under our consideration.

The resulting aluminum wave was used by us for quantitative determination of aluminum in a series of mixtures of aluminum salts with zinc salts. A calibration curve was constructed for this purpose; if the zinc concentration in the mixtures changes considerably, it is better to use the method of additions, since the height of the aluminum wave decreases with the addition of zinc ions.

A considerable positive error was obtained in the results when the background, which had been selected by us – 5% $CaCl_2$ + 5% calcium gluconate – was used for the determination of aluminum in mixtures containing boric acid. A special test showed that the height of the aluminum wave rises after an addition of boric acid, but small amounts of lime water lower this noticeably. This circumstance indicates that the effect of boric acid is caused by the increase of hydrogen ion concentration. This is explained by the formation of a complex compound between boric and gluconic acids which has a greater dissociation constant than does boric acid. Similar phenomena which had been often observed with hydroxy compounds and boric acid have been described in the literature in detail [6]. Hence, in a determination of aluminum in mixtures with gluconic acid, it is necessary to perform a preliminary neutralization of the resulting H+ ions by means of calcium hydroxide. Bromphenol blue is best used for the indicator. A small excess of $Ca(OH)_2$ does not interfere since aluminum is retained in calcium gluconate solution even at pH = 5.5.

The results of aluminum determinations in its mixtures with zinc sulfate and boric acid are shown in the table.

Aluminum was also determined in the so-called Burov liquid [7].

For this purpose we took 1 ml of the liquid and placed it in a 25 ml volumetric flask; to this was added 12.5 ml of 10% calcium gluconate, 2.5 ml of 50% calcium chloride and 8-9 ml of 0.1% agar solution, after which the solution was brought to the mark with water and, after passage of hydrogen, the solution was polarographed. A calibration curve was used for the estimation in this case. The results obtained in this instance were readily reproducible; the time for the determination did not exceed 25 min.

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