TABLE 2. Analytical Results for Artificial Mixtures of Nitric and α-Hydroxyisobutyric Acids by Two Methods (I—Titration in methyl ethyl ketone with 0.1 N tetraethylammonium hydroxide, II—titration in acetone with 0.1 N sodium hydroxide in aqueous acetone)

Ratio taken of nitric acid to α-hydroxy-isobutyric acid, g-eq	Method I			Method II		
	taken, g	found, g	relative error, %	taken, g	found, g	relative error, %
1:1	0.0233 0.0373	0.0234 0.0376	+0.4 +0.8	0.0441 0.0738	0.0440 0.0742	—0.2 +0.5
1:5	0.00464 0.0413	0.00461 0.0415	—0.6 +0.5	0.0126 0.1036	0.0126 0.1030	0.0 —0.5
1:10	0.00331 0.00664	0.00330 0.0668	—0.3 +0.6	0.00630 0.0995	0.00627 0.0999	—0.4 +0.4

TABLE 3. Analytical Results for Production Mixtures of Nitric and α-Hydroxyisobutyric Acids

Content of acids in mixture, %		Ratio found for nitric to α-hydroxyisobutyric acids (g-eq) in mixture analyzed
I	II	
9.1 83.4	9.1 83.3	1:5
6.5 85.3	6.5 85.2	1:8
4.7 77.0	4.7 77.0	1:10

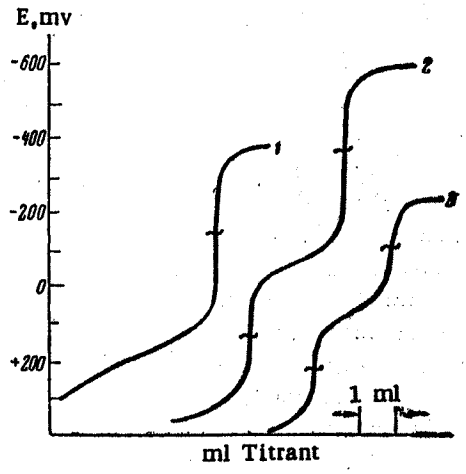

Fig. 2. Titration curves for mixtures of nitric and α-hydroxyisobutyric acids: 1) 0.1 N aqueous NaOH in a water medium; 2) 0.1 N $(C_2H_5)_4NOH$ in benzene-methanol in a methyl ethyl ketone medium; 3) 0.1 N NaOH in aqueous acetone in an acetone medium.

THE REPRODUCIBILITY OF A STATIONARY MERCURY DROP FOR DETERMINING ULTRAMICROIMPURITIES

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It has been found possible to make repeated determination of microconcentrations (10^{-7}M) of Pb, Zn, and Cu by the method of additions, using the same mercury drop suspended from platinum. This eliminates the need for producing drops of uniform dimensions, shortens the time of analysis, and simplifies its performance.

In recent years, the determination of ultramicroimpurities (10^{-5}% and less) in specially pure and semiconducting materials has been carried out by the method of amalgam polarography, using a stationary electrode in the form of a suspended mercury drop [1-9]. Calibration is normally by the method of additions. As a rule, all authors up to now have used a fresh mercury drop for each anodic peak. The reproducibility of repeat determinations therefore depends on reproducing drops with precisely the same dimensions. This difficulty suggested the possibility of carrying out the analysis by making additions to a single mercury drop. Such a procedure would avoid the difficulties associated with the production of precisely uniform drops and would also shorten the time for analysis.

We have found that it is possible to carry out repeat analyses with a single drop, obtained by electrolysis on to a platinum wire.

The work was carried out with a Hungarian photorecording polarograph M-103. Since there was no reverse drive to the potentiometric drum, it was necessary to reverse the connections to obtain anodic polarograms.

Because of this, the change in potential from positive to more negative was from right to left in the polarogram. The electrolyzer arrangement was as described previously [2]. A 25 ml volume of solution was used. The mercury drop was produced by electrolysis of a saturated mercurous nitrate solution, using a 31 ma current for 1 min, on a platinum wire 0.2 mm in diameter and 0.1 mm long. The diameter of the mercury drop was 0.080 cm.

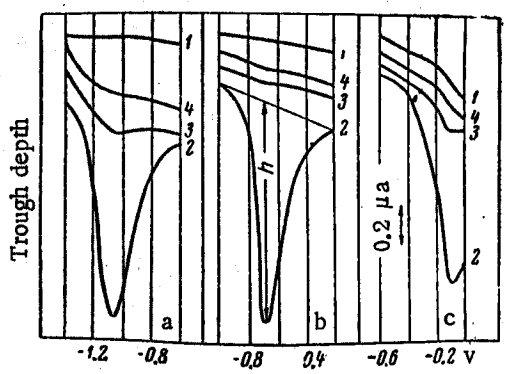

Fig. 1. Anodic polarograms: 1) Supporting electrolyte 0.1 N KOH 2)–a) 5×10^{-6}M Zn^{2+} τ = 30 min; b) 2×10^{-7}M Pb^{2+}, τ = 80 min; c) 10^{-6}M Cu^{2+}, τ = 30 min. 3 and 4) After depolarization of electrode for 5 and 10 min. Scale: 1 mm = 0.0112 μa (sensitivity setting 1:1). The electrolysis time is τ.

Reproducibility of Results for the Same Drop (Electrolysis Time 20 Minutes, Depolarization Time 10 Minutes)

Trough depth,mm			Trough depth,mm		
Zn	Pb	Cu	Zn	Pb	Cu
22	29	38	24.5	32.5	40
25	33	36	24.5	32	39
25	31	38	25	29	—
24.5	33	40	25.5	27	—

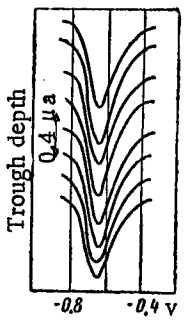

Fig. 2. Anodic polarogram for lead (7×10^{-7} M), obtained by repetitions with the same mercury drop. The electrolysis time was 20 min, and the depolarization time was 10 min; 1 mm of scale = 0.021 μa (sensitivity setting 1:2).

We investigated 10^{-7} to 10^{-6} M solutions of zinc, lead, and copper. The supporting electrolyte was 0.1 N caustic potash. The electrolyte was stirred by magnetic stirrer in a nitrogen stream. The technique for carrying out an experiment was as follows: The magnetic stirrer was started up, the nitrogen stream was turned on, and electrolysis was continued for a definite time at constant potential, -1.4 v (vs S.C.E.) with zinc, -1.0 v with lead, and -0.6 v with copper. A delay of 30 sec was allowed after the electrolysis; then the potentiometer drum was switched on, and the potential dropped gradually to -1.0, -0.6, and -0.02 v (vs S.C.E.) respectively. The change in current was recorded on the photographic paper. The element under investigation could then be removed from the mercury drop by depolarizing the electrode at -0.02 v (vs S.C.E.). After depolarization for a definite time, the potential was changed back to the polarizing value and a second polarogram was recorded. The depolarization was repeated if this second polarogram showed any trough.

It is clear from Fig. 1 that , for all three elements investigated, there was no trough corresponding to the element in the second polarogram after the electrode had been depolarized for 10 min at -0.02 v (vs S.C.E.).

Fig. 2 shows repeats of the trough for lead, all obtained with the same mercury drop. Similar polarograms were obtained with zinc and copper.

It is clear from the table that the reproducibility of the results for repeated measurements with the same mercury drop, for solutions of zinc (1.5×10^{-6} M), lead (7×10^{-7} M), and copper (5×10^{-6} M), corresponded to a devia-

tion of 8-12% from the mean value. This lies within the limits of precision required for determination of micro-impurities (15-20%).

Kemula [10] carried out experiments with a platinum sphere (diameter 1-2 mm), coated electrically with a very thin mercury film, and showed that there was a reduction in the anode trough for zinc and certain other metals. He attributed this to the formation of intermetallic compounds between the metals, platinum, and mercury*. However, this effect was not observed in our experiments, since the small surface of the platinum wire face was covered by a drop and not merely a film of mercury.

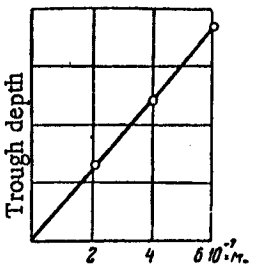

Fig. 3. Calibration curve for lead. The time for preliminary electrolysis was 20 min; 1 mm of scale = 0.021 μa (sensitivity setting 1:2).

We use the same mercury drop to obtain polarograms of zinc, lead, and copper at different concentrations. A further addition of standard solution was made after each depolarization following a polarogram, and the measurements were repeated with the same drop. In this way we constructed calibration curves; the trough depth for lead (Fig. 3) was proportional to the concentration of lead ion in solution. Similar results were obtained for zinc and copper.

The results obtained in this paper show that the same stationary mercury electrode can be used for determining microconcentrations of lead, zinc, and copper by the method of amalgam polarography, using the method of additions without changing the drop.

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THE POLAROGRAPHIC DETERMINATION OF TITANIUM AND IRON IN TITANIUM-ZIRCONIUM AND IRON ORES

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A polarographic method is proposed for the determination of high contents of titanium and iron, using 5 M H_3PO_4 and M H_2SO_4 as supporting electrolyte. The determination is not affected by Zr, Nb, or Ta.

* The fading of zinc troughs under the conditions of Kemula's experiments may not have been due to formation of intermediate compounds, but to hydrogen evolution at sites on the platinum sphere not covered by mercury, since the hydrogen overvoltage on platinum is considerably less (by about 1 v) than on mercury.