GENERATION OF THE COULOMETRIC TITRANT Pb (II) BY THE CURRENT OF INTERNAL ELECTROLYSIS FROM LEAD AMALGAM

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An active lead electrode for the generation of Pb (II), with the object of coulometric titration of chromate, oxalate, molybdate, tungstate and ferrocyanide ions, has been used by Tutundzhich and Stoikovich [1]. The end point of the titration was determined amperometrically with a dropping mercury electrode.

There have been few papers published on the use of metallic amalgams as generator electrodes. An electrochemical investigation was carried out on tin amalgam for electrogeneration of the titrant Pb (II) and determination of the ions Cr (VI), V(V), Fe (III), and $[Fe(CN)_6]^{3-}$, with biamperometric and potentiometric determination of the end point [2]. The same method has been used for determining iron in wood pulp [3].

We now propose an internal electrolysis method for the external generation of Pb (II) from lead amalgam. This possesses known advantages, inherent in the method of using two active electrodes [4]. The use of lead amalgam as a generator electrode eliminates the effect of anodic disintegration of the lead [5].

In this work we used an apparatus [6] for external electrogeneration of titrants with a metal amalgam galvanic cell. The active generator electrode consisted of lead amalgam, prepared directly by contacting lead turnings with mercury, under a layer of 1 : 1 acetic solution, with heating to 60 to 70°C on a water bath. The auxiliary electrode

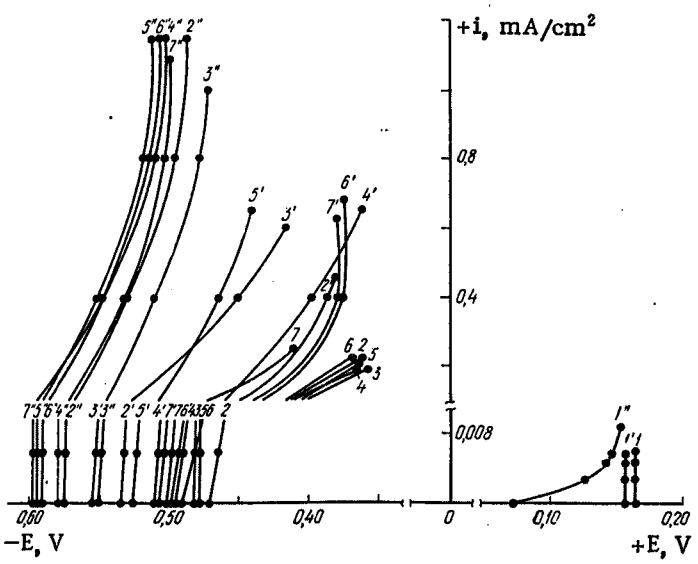

Fig. 1. Voltage–current curves for mercury and lead amalgam: 1, 1', and 1") for mercury in the supporting electrolytes 0.1, 1.0, and 2 M CH_3CO_2Na; 2, 2', and 2") to 7, 7', and 7") for 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0% lead amalgams with the same supporting electrolytes.

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TABLE 1. The Coulometric Determination of Anions with Freshly Generated Pb (II) (n = 5)

Anion titrated	Taken, mg	$\bar{x}$	s	s_r
SO_4^{2-}	0,480	0,45	0,035	0,078
	2,400	2,6	0,200	0,077
	4,800	4,8	0,121	0,024
PO_4^{3-}	0,162	0,170	0,001	0,006
	0,324	0,378	0,003	0,008
	0,972	1,00	0,014	0,014
MoO_4^{3-}	0,398	0,41	0,010	0,025
	0,796	0,79	0,012	0,015
	3,985	4,00	0,050	0,013
WO_4^{2-}	1,237	1,24	0,026	0,021
	3,718	3,69	0,025	0,007

was of platinized platinum [5], immersed in a cathode chamber containing the indifferent electrolyte saturated KCl in 0.5 M HNO_3. In this case the nitric acid played the part of a depolarizer.

The supporting electrolyte was fed from a flask, the tubulure of which was fitted with a bung and a glass tube, through a rubber hose to the inlet of the anodic chamber of the electrolyzer. The rate of flow of the electrolyte through the cell (about 0.05 ml/sec) was controlled by a Hofmann clamp, and for interruption of the flow of electrolyte we used a Mohr clip.

For amperometric determination of the end point, the indicator current for oxidation of Pb (II) at a platinum rotating microelectrode, at E = + 1.07 V against a saturated calomel electrode [7], was recorded on the chart of an ON-101 polarograph, with coordinates indicator current i and generation time τ.

We used the apparatus described above to carry out an electrochemical investigation of lead amalgam. It was found that the internal electrolysis current for a 0.5 to 3.0% Pb amalgam remained constant for 3 h or more in solutions of CH_3CO_2H, HCl, $NaNO_3$, and CH_3CO_2Na, and also when the above named salts were added to these acids. The maximum currents were obtained in solutions of the electrolytes 4 to 6 M HCl, 0.1 to 1 M KNO_3, 0.1 to 2 M CH_3CO_2Na, and 0.1 M HCl + 0.01 to 1 M KNO_3. These currents were approximately 2.0-2.7, 0.1-0.2, 0.2-1.2, and 0.5-0.7 mA/cm^2 respectively.

We investigated the conditions for the electrical generation of Pb (II) from lead amalgam by means of a polarization curve. The commutator method was used to construct curves of $E = f(i)$ for mercury and lead amalgams, containing 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0% of depolarizer, for all the above-mentioned supporting electrolytes. Figure 1 shows, as an example, the results obtained with 0.1 to 2 M solutions of CH_3CO_2Na. Under these conditions a 100% yield of Pb (II) with respect to current was secured at current densities from 0.001 to 1.2 mA/cm^2.

Since the effective valency may decrease if heterogeneous amalgams are used [8], the best prospects are for working with amalgams in which the depolarizer concentration is 1.0 to 1.5%, i.e., close to the solubility of lead in mercury (1.2%), with 2 M CH_3CO_2Na as supporting electrolyte. The same conditions ensured that coulometric titration, by the precipitation method, could be carried out with an adequate internal electrolysis current ($i \sim 1.2$ mA/cm^2). The yield of Pb (II) with respect to current, from a 1.5% Pb amalgam, was additionally checked as follows: Pb (II) was generated for a definite time, with 2 M CH_3CO_2Na as supporting electrolyte, at current densities 0.440 and 0.880 mA/cm^2. This was titrated with a standard solution of potassium bichromate by the precipitation method with amperometric determination of the end point.

With n = 4 the mean values of the Pb (II) yields with respect to current at the stated current densities were 101.7% (S = 3.3) and 99.4% (S = 1.4) respectively.

The reproducibility of the values of the current efficiency, calculated from the results of the titrimetric determination of the generation product, reflected the acceptable precision of the method for the determination of very small amounts of material.

The optimum conditions found provided a basis for the coulometric titration of model solutions of the ions: WO_4^{2-}, MoO_4^{2-}, PO_4^{3-}, and SO_4^{2-}. The solutions to be titrated were prepared as previously described [9].

In order to achieve quantitative precipitation, 50 ml of acetone was added to the solution before titration. Table 1 shows some results.

The total sulfur content of a technological sulfite lye was determined after oxidation of the sulfur-containing compounds to sulfate [10]. For this purpose 100 ml of lye was placed in a 300-ml heat-resistant beaker, treated with 10 ml of concentrated nitric acid, saturated with potassium chlorate, and heated until the reaction mixture became clear. The product was evaporated to dryness. The dry residue was twice treated with 5 ml of HCl (1.19) and again evaporated to dryness.

The residue was dissolved in water, transferred quantitatively to a 100-ml graduated flask, and made up to the mark. A 2-ml aliquot of this solution was then transferred to the titration cell, treated with 50 ml of acetone, and titrated. The sulfur contents of samples were determined gravimetrically [11] and coulometrically (n = 4). The results agreed well: 1.35 (S = 0.07) and 1.30 (S = 0.04) mg of SO_4^{2-} per liter respectively.

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