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**Note on Polarographic Determination of Small Amounts of Lead\***

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The composition and characteristics of a new supporting electrolyte for the polarographic determination of small amounts of lead are described. The electrolyte is a 0.5 N aqueous solution of succinic acid containing 0.008% gelatine. The analysis of the results obtained with this electrolyte shows that it can be used even when concentrations of the order of  $10^{-6}$  M Pb (or 1  $\mu$ g Pb/ml.) are involved. It has been shown that the electrode reaction consists in a reversible cathodic reduction of bivalent lead ions to the uncharged metallic lead.

A number of supporting electrolytes for the polarographic determination

Solutions prepared in this way were transferred into polarographic cells and oxygen was displaced by bubbling hydrogen through the solution for 10 minutes prior to the polarographic determination. The hydrogen was purified with pyrogallol in sodium hydroxyde.

A Cambridge Polarograph, Pen Recording Type and standard polarographic cells of the same firm were used for recording polarographic waves. The sensitivity of the recorder was  $2.63 \times 10^{-9}$  A/mm. The wave heights were determined by measuring the increment in current between the extrapolation lines for the residual and diffusion current at the half-wave potential.

A capillary was used which at 50 cm. mercury column height and the potential of 380 mV had  $m$  and  $t$  values of 1.31 mg. of mercury per second and 3.05 seconds, respectively. The rate of mercury flow from capillary was measured by the method of Kolthoff and Lingane<sup>3</sup> using an experimental arrangement described by Filipović<sup>4</sup>.

The cell resistance was measured with a »Philoscop II« universal bridge (Philips-GM 4144) and an external current source. An Audio-frequency-generator (Philips-GM 2307) was used as the external current source and a valve voltmeter (Philips-GM 6005) was used for potential measurements. The potential difference on the potentiometer bridge was calibrated against a standard Weston cell.

The temperature was kept constant at  $25 \pm 0.1^\circ\text{C}$  by means of a water thermostat.

The statistical treatment of the results was performed in the usual way<sup>5</sup>.

The data for the estimation of the half-wave potential are given in Table 2. In this table the arithmetic means of the expression  $\log [i/(i_d-i)]$ , which were

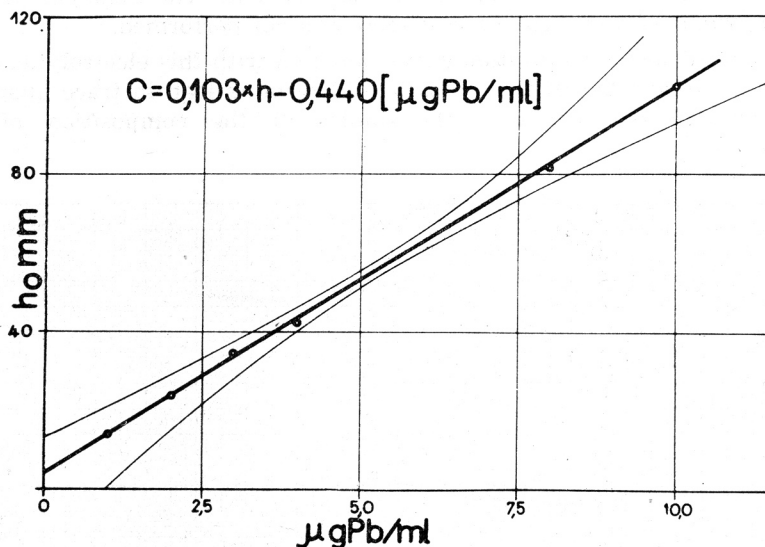


Fig. 1. Regression of  $c$  upon  $h$  and 95% confidence limits for predictions of  $c$  from measured values of  $h$ . The plotted points are mean values of  $h$  of two repeated measurements.  $h_0$  are polarographic wave heights expressed in terms of maximum sensitivity.

obtained from 6 independent determinations, are shown as a function of the applied potential of the dropping electrode.

TABLE II

$E_{d.e.}$ volts	0.325	0.350	0.375	0.400	0.425
$\log [i/(i_d-i)]$	-2.00804	-1.08522	-0.23308	0.52437	1.35981

The correction for the potential drop  $iR$  amounted to less than  $5 \times 10^{-4}$  volts, and was neglected. The values of the diffusion current  $i$  and the resistance  $R$  (for 3000 Hz) at the half-wave potential were  $194.62 \times 10^{-9}$  A and 2450 Ohms, respectively. Under these conditions the value of  $0.384 \pm 0.001$  volts vs. S. C. E. was obtained for the half-wave potential in this supporting electrolyte.

The coefficient  $RT/nFM$  in the Heyrowsky and Ilkovič equation<sup>8</sup> was estimated as 0.0299 volts with the standard error of 0.0009 volts.

A typical polarogram is shown in Fig. 2.

The new supporting electrolyte has proved satisfactory for the determination of small amounts of lead. The confidence limits for the prediction of lead concentrations from the measured polarographic wave heights are com-

paratively narrow. As seen from the calibration curve as well as from the equation (1) the regression line does not pass through the origin. This seems to be due to traces of lead contained in succinic acid. The removal of these impurities would be very troublesome, and was not performed.

The analysis of the calibration curve obtained with this electrolyte showed that it can be used when it is necessary to determine lead in trace quantities. It has been successfully used in the studies of the composition of lead dithizonate<sup>2</sup>.

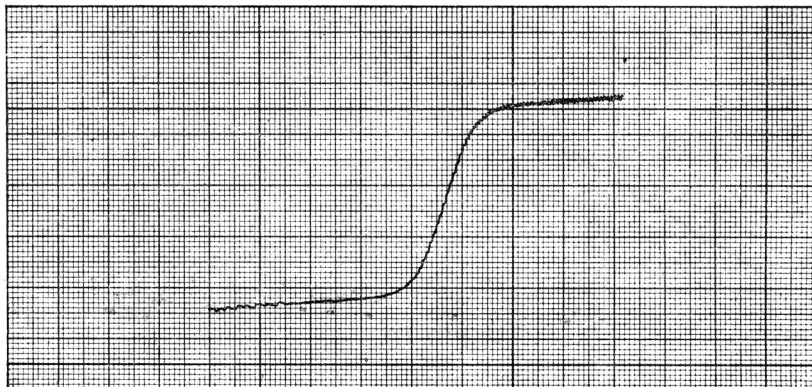
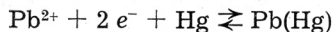


Fig. 2. Polarographic current voltage curve of +2 lead (8  $\mu\text{g}/\text{ml}$ .) in supporting electrolyte containing 0.5 N succinic acid and 0.008 percent gelatine. The curve begins at 0.150 volts v.s.S.C.E. Sensitivity of the recorder  $5.26 \times 10^{-9}$  A/mm, 1 mm. on the abscissa — 0.005 volts. Rate of recording: 3.75 mm. per min., damping 2.

The comparatively low value of the half-wave potential indicates that in the described electrolyte lead ions are present as simple ions which under these experimental conditions do not form complex compounds with succinic acid.

The value 0.2099 volts, which is our estimate of the coefficient  $RT/nFM$  is in very good agreement with the theoretical value of 0.0296 volts for a reduction process at 25°C involving 2 F of electricity per mole. It is therefore reasonable to assume that under such experimental conditions the electrode reaction may be described by the equation:



where Pb(Hg) symbolizes the amalgam formed at the surface of the mercury drops. The perfect agreement between the expected and the calculated value (the difference is smaller than the standard error) also indicates that the electrode reaction is reversible.

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### IZVOD

#### Prilog polarografskom određivanju malih količina olova

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Opisan je novi osnovni elektrolit za određivanje malih količina olova. Elektrolit se sastoji od 0.5 N jantarne kiseline i od 0.008% želatine. Statistička obradba dobivenih rezultata pokazala je, da je opisana metoda osjetljiva i dovoljno precizna za određivanje malih količina olova u otopini koncentracije reda veličine  $10^{-6}$  molova Pb/litru, odnosno 1  $\mu\text{g/ml}$ . Elektrodni se proces sastoji u reverzibilnoj katodnoj redukciji dvovalentnih olovnih iona u metalno olovo.

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