RAPID POLAROGRAPHY USING A VIBRATING MERCURY DROP ELECTRODE

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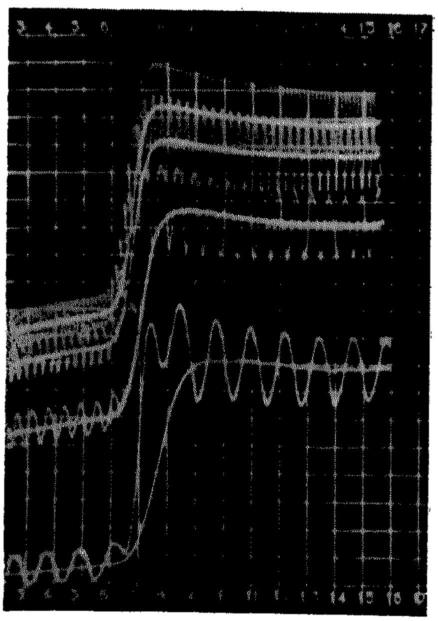
The authors suggest a vibrating mercury electrode and high-speed polarization for studying rapid processes. The time required for plotting a polarogram is reduced to a few tenths of a second.

Classical polarograms are plotted over "many" drops (50-200 drops over 1 V). Thus "rapid polarography," working with polarization rates of v = 0.03 V/sec instead of the normal 0.002-0.01 V/sec, requires quick-dropping electrodes with mechanical drop detachment, or Smoler electrodes [1, 2].

If a polarograph is to be used for recording rapid processes (for example, in kinetic measurements or as the detector in gas chromatography [3]) even "rapid polarography" is not fast enough. It is not always convenient to measure the oscillographic (i, E) curves at a given potential from one drop (with v of order several V/sec or even higher), owing to the complexity of treatment required for multi-step polarograms, the corrections required for variation in the electrode surface and the occurrence of "dead time." In this case, it may be useful to use classical polarography with a vibrating electrode and high polarization rates.



Rapid polarogram of ~ 10^{-3} M $CdCl_2$ in 0.1 N KCl at various polarization rates. t = 0.02 sec; v ≈ 0.5, 1.0, 2.0, and 4.0 V/sec; one division of the screen corresponds to 0.71 μA. The polarograms without oscillations are for the same v values and were obtained after connecting up a 50 cps filter.

There are several types of vibrating electrode, driven by electric motors, vibrators from vibro-mixers, etc. [4-6]. We are using a simple electrode with a vibrator unit made by the "Tochelektropribor" works; the dropping time is t = 0.02 sec. The vibrator is connected in circuit via an autotransformer, which enables us to vary the amplitude of vibration of the electrode.

The results obtained with this electrode are shown in the figure. The polarograms were recorded with a PO-5122 TsLA oscillographic polarograph with continuous scanning, with and without a filter with frequency cutoff at 50 cps.

Connecting up the filter completely removes the oscillations from the polarogram. When working with a vibrating electrode, the polarogram can be recorded with far fewer drops than usual. For example, the lower curve was obtained with 10 drops, over which the wave height remains practically unaltered. Clearly, convection as well as diffusion takes part in transporting the substance to the electrode in these conditions. However, this causes only a slight reduction of the limiting current when a vibrating electrode replaces a naturally dropping one. Thus in our experiments we could expect a three-fold decrease in i_{lim}; in fact, i_{lim} decreased only by ~ 40%.

With the dropping time given above, the whole polarogram can be plotted in a few tenths of a second.

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