

A Device for a Vibrating Dropping Mercury Electrode

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A new device for a vibrating dropping mercury electrode is described. The applicability of the new electrode for the measurements of polarographic waves in the presence of a surface blocking substances is reported. The possibilities of the VDME for the speciation of certain metal ions in multiligand systems are discussed.

Experiments with a dropping mercury electrode (DME) are very often accompanied by several complications, such as plateau irregularities (maxima of the first and the second kind), an inhibition of the electrode reaction by the adsorption of some surface active substances, an appearance of the waves caused by the adsorption of depolarizer or product of the electrode reaction and the appearance of catalytic or kinetic waves which are not proportional to the bulk concentration of the depolarizer in a linear manner. In addition to this, the DME can not be used in stirred solutions because any stirring may cause an irregular mercury dropping as well as a change in the depth of the diffusion layer around the drop. A dropping rate is a very important regulator of the kinetic contribution to certain polarographic processes¹. The same effect may be achieved by changing the pulse duration or the frequency of a. c. polarography².

The vibrating dropping mercury electrode (VDME), with a drop lifetime of less than 0.5 seconds, although having a higher charging current and a smaller sensitivity than the DME³, can be successfully applied in cases when measurements with the DME are difficult to perform because of the complications stated above⁴. The first type of VDME, constructed by Berman and co-workers⁵, had 30 drops per second and was applied to continuously agitated systems. Wolf⁶ has developed the method of »rapid polarography« which consists of in the application of a high voltage scan rate to the VDME with the dropping rate of six drops per second. The sensitivity of the method was even higher than that of the classical polarography with current damping. Connery and co-workers⁷⁻¹⁰ have published a series of papers on VDME's in which they described the applications of a VDME to measurements when the maxima of the first or the second kind appear at the DME⁷ (for example, Cr(III) in a NaClO₄ medium and Cd(II) in a KCl medium), when the electrode surface blocking substances are present in the solution⁸ (for example, Cd(II) beside Triton-X-100), and to the analyses of quinine and quinoline reduction mechanisms^{9,10}.

The main disadvantages of devices for vibrating dropping mercury electrodes described in the literature are: a very complex construction and a

varying number of drops per second. A newly developed device for vibrating dropping mercury electrodes is shown in Fig. 1. The simplified mechanism improves the reproducibility of the dropping time. The capillary is 16 cm long with a diameter of 0.06 mm and a sharpened tip which does not allow the drop to be retained near the orifice after the shock is applied (1). The rubber O-ring (5) elastically holds the capillary in the universal voltammetric cell¹¹. The reproducibility of dropping is obtained by changing the altitude of a reservoir filled with mercury (for 75 drops per second this altitude is about

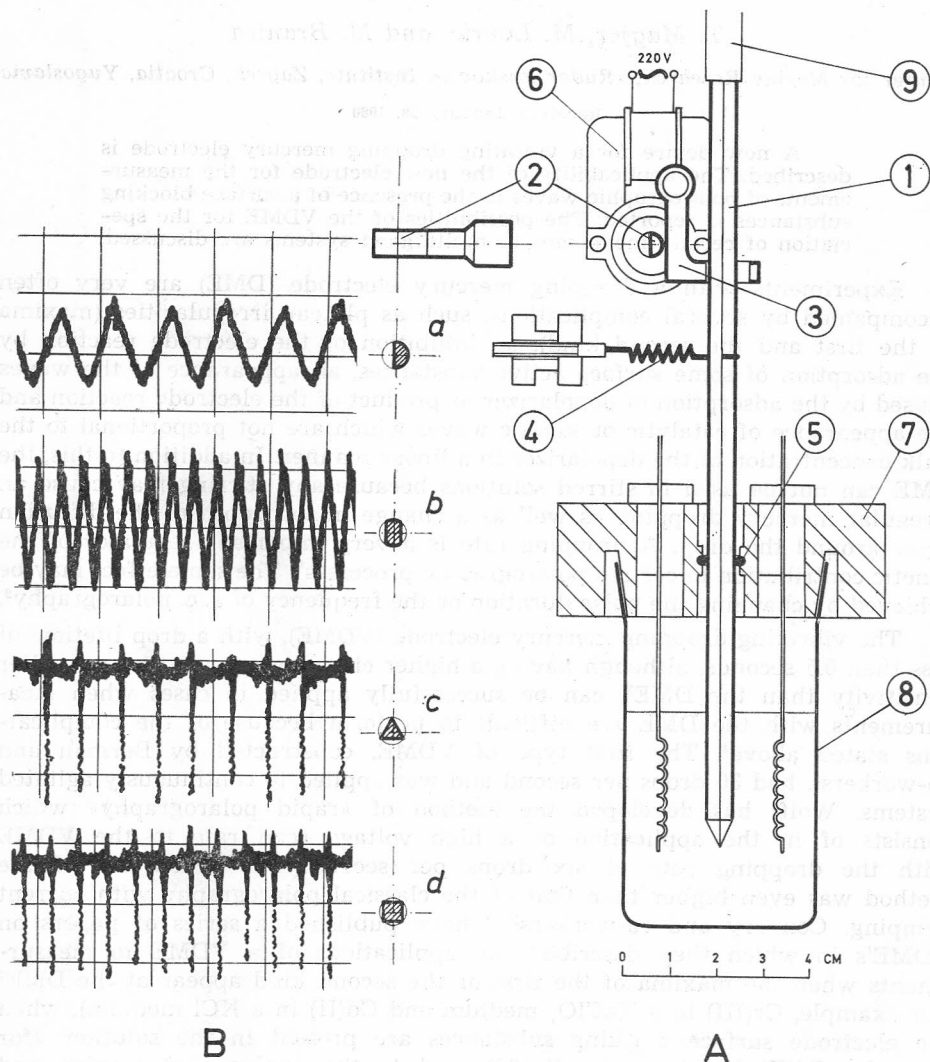


Figure 1. A) The scheme of the vibrating dropping mercury electrode
 1 — capillary; 2 — axle; 3 — plexy hammer; 4 — spring; 5 — rubber O-ring; 6 — electromotor;
 7 — plexiglass cover of the cell; 8 — polyethylene cell (100 ml); 9 — tygon tube.
 B) The oscillographic measurements of the reproducibility of the drop size and dropping rate
 a) 25 drops per second, b) 50 drops per second, c) 75 drops per second, d) 100 drops per second.

120 cm), by the proper distance between the vibrator and the rubber ring and, finally, by the right tension of the spring (4) which keeps the capillary tight to the vibrator. The vibrating device consists of a synchronic electromotor (6) with a rotation rate of 25 cycles per second and a set of axles (2), each of them with a different profile at the free end. Every time the sharp edge of the axle over the plexy hammer (3) hits the capillary, one drop is torn off. The number of edges on the profile of the axle determines the number of drops per second (the half-circle — 25 s^{-1} , profile b, Figure 1. — 50 s^{-1} , the triangle — 75 s^{-1} , and the square — 100 s^{-1} if the rotation rate of the motor is 25 s^{-1}). The altitude of the reservoir filled with mercury can be changed depending on the number of drops required. The high average flow rate of mercury makes the electrode work as a cut mercury stream electrode. Although very simple, the described electrode has a very exact dropping, which can be seen in Figure 1 for four different vibrating rates.

To illustrate the polarographic characteristics of the new electrode, a few typical experiments are presented.

The measurements of the oxygen reduction wave in the seawater polluted by Triton-X-100 (Figure 2) show that the adsorption of T-X-100 on the mercury surface can be avoided by the application of the VDME. This is confirmed by Cromer's results⁸.

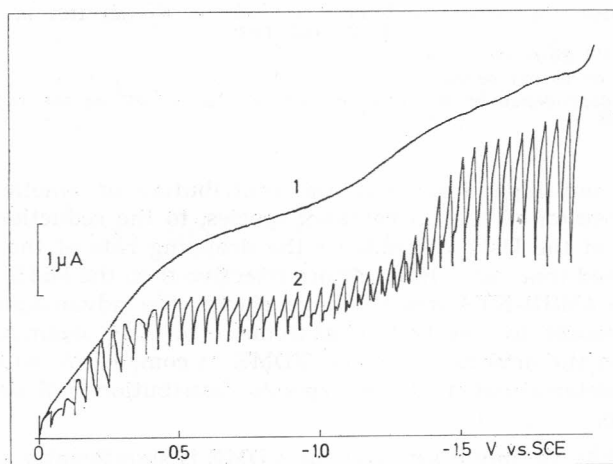


Figure 2. The oxygen polarographic reduction waves in seawater in the presence of $2.5 \cdot 10^{-3}\%$ Triton-X-100

- 1) VDME, 100 drops per second
- 2) DME, drop lifetime of 2 seconds

Determination of In(III) by the DME in the presence of tributylphosphate (TBP) is very difficult owing to the adsorption of TBP on the mercury surface. However, with a derivative d. c. polarography at the VDME we were able to detect Indium at the concentration level of 10^{-4} (M). In Figure 3, Indium peaks at the VDME and the DME are compared and the linear dependence of the peaks at the VDME on the bulk concentration of In(III) is presented.

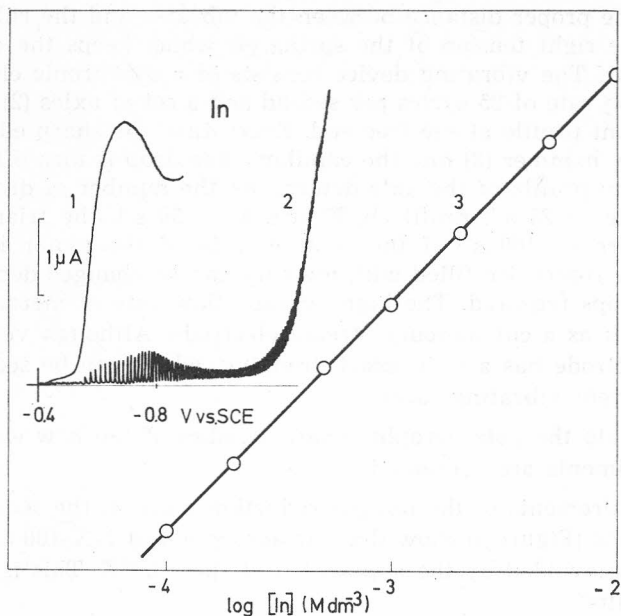


Figure 3. Derivative d.c. polarography of $5 \cdot 10^{-3}$ In^{3+} in 0.1 (M) HCl in the presence of $5 \cdot 10^{-4}$ (M) TBP

- 1) VDME, 100 drops per second
- 2) DME, 3 drops per second
- 3) Linear dependence of the peak current at the VDME on the bulk concentration of In(III) .

In certain multiligand systems, the contribution of kinetic current, due to the decomposition of several complex species, to the reduction current of a free metal ion at the DME depends on the dropping rate of the DME¹². Thus, it can be expected that the VDME is more selective than the DME. Experimental studies on the Cd(II)-NTA system have shown the advantages of the new device with respect to selective measurements of free cadmium ions (Cd^{2+}) only. Details on the application of the VDME in comparison with the DME in regard to the determination of ionic species distribution will be published in the near future.

In conclusion, we might say that the VDME is significantly superior to the DME for most analytical purposes where a study of a species in the bulk of a solution is needed. The inhibition of an electrode response by adsorption is avoided and the actual distribution of ionic species can be measured. The described VDME device is simple, with a good reproducibility and a constant number of drops per second. It can be easily obtained and is a useful tool in many electrochemical and analytical laboratories. The application of polarography with a very short drop lifetime is a significant advance in polarographic techniques.

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SAŽETAK

Nova konstrukcija otkidača kapi

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Opisana je nova konstrukcija otkidača kapi koji omogućuje da zašiljena kapilarna kapa brzinom od 100 kapi u sekundi. Pomoću sinhronog elektromotora brzine od 25 Hz koji nosi na sebi osovine različitih profila na slobodnom kraju mogu se postići brzine kapanja od 25 s^{-1} do 100 s^{-1} . Elektroda je primjenjiva za polarografska snimanja uz prisustvo raznih organskih supstanci koje adsorpcijom na površinu elektrode mogu blokirati prijenos elektrona.

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