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A Cell for Continuous Analysis in Flowing Solutions with the Rapidly Dropping Mercury Electrode

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IN THE LAST DECADES, there have been several polarographic approaches to the problem of continuous analysis in flowing solutions (*1–15*). For this purpose, both the conventional dropping mercury electrode (DME) (*2–8, 11, 12, 14, 15*) and the rapidly dropping mercury electrode (RDME) (*9, 10, 13*) have been used. The RDME differs from the DME in the shorter dropping time (t = 1.5–0.1 sec). It can be obtained with L-shaped capillaries (*16*), horizontally placed capillaries (*9*), or large bore capillaries (*10*). In conjunction with the use of DME and RDME as detectors in flowing solutions, special cells have been developed (*2, 3, 5–8, 10, 12, 13*).

The fundamental characteristics of a detector in flowing solutions have been described by some authors (*e.g.*, Buchanan and Bacon (*14*)): rapid response; high sensitivity; specificity; linear response with respect to concentration; reliability over long periods of operation; and little processing of solutions.

This paper describes a cell for the RDME and an application for accurate measurements of small signals over high background currents.

The cell possesses a low holdup time and volume and a low flushout time and volume, which ensure rapid response. This cell does not require dismantling or cleaning for a long time, even when the investigated system is changed.

The RDME has been obtained with horizontally placed capillaries with: t, 0.1–0.35 sec; capillary length, 5–8 cm; capillary radius, 35–45 μ; mercury flow, 4–12 mg/sec; size of detaching drop, 1–2 mg, 0.50–0.65 mm in diameter.

The functional characteristics of the RDME (obtained with L-shaped capillaries) in experimental conditions close to those described here, but in static solutions, have been investigated and reported (*17*).

The polarographic current obtainable with the described apparatus possesses very low oscillations and very low noise. As a consequence, high sensitivity is achievable, even in the presence of high background current. This property can be useful in eliminating processing, when the investigated solution contains a variable minor component and an invariable major component, both polarographically active; or when small concentration variations must be detected in flowing solutions.

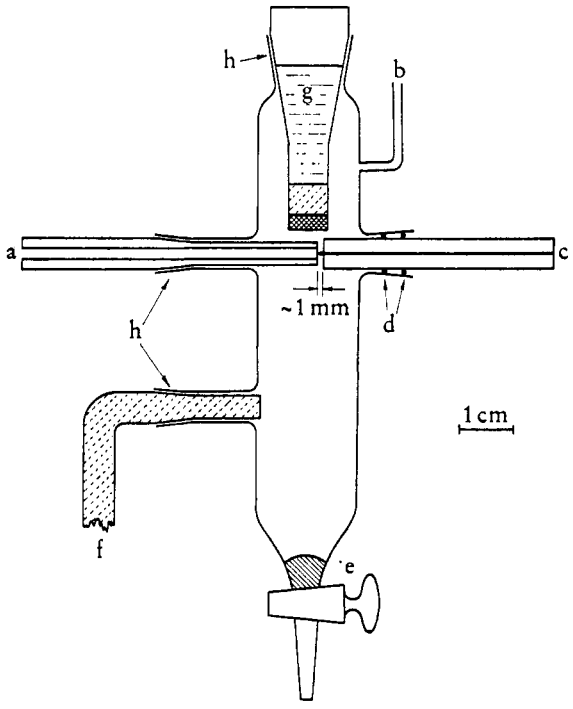

Figure 1. The cell

a. **Solution inlet (i.d. 2 mm), connected to the 2-way stopcock**
b. **Solution outlet, connected to the narrow glass tube**
c. **RDME, hold in position by means of a rigid support**
d. **O-rings, which make solution tight seal**
e. **Mercury outlet**
f. **Agar bridge, connecting to counterelectrode (a large SCE)**
g. **Reference SCE compartment, with low porosity sintered glass disk, agar plug, and 1*M* KCl solution**
h. **Greased ground glass joints, held in position by means of springs**

EXPERIMENTAL

The base solution was 1*M* KCl and $10^{-3}M$ HCl. The other solutions were a little more concentrated in HCl. The difference in HCl concentration in comparison with the base solution (ΔC) ranged from 3×10^{-6} to $3 \times 10^{-4}M$. Solutions were kept in 2-liter glass bottles, connected by means of latex rubber tubing (i.d. 2 mm) to a 2-way stopcock, which was connected with the cell (Figure 1). The changing of the solution flowing through the cell was achieved by turning the 2-way stopcock. The changing from one solution set to another was achieved by substituting the bottles.

Solution flow was determined by hydrostatic pressure. Its value was fixed by the length of a narrow glass tube connected to the solution outlet of the cell. To have the same flow for each solution and experiment, as well as during an experiment, the same hydrostatic pressure (within 2 mm H_2O) was maintained, employing the Mariotte-flask principle. The solution flow ranged from 1 to 10 ml/min, corresponding to a

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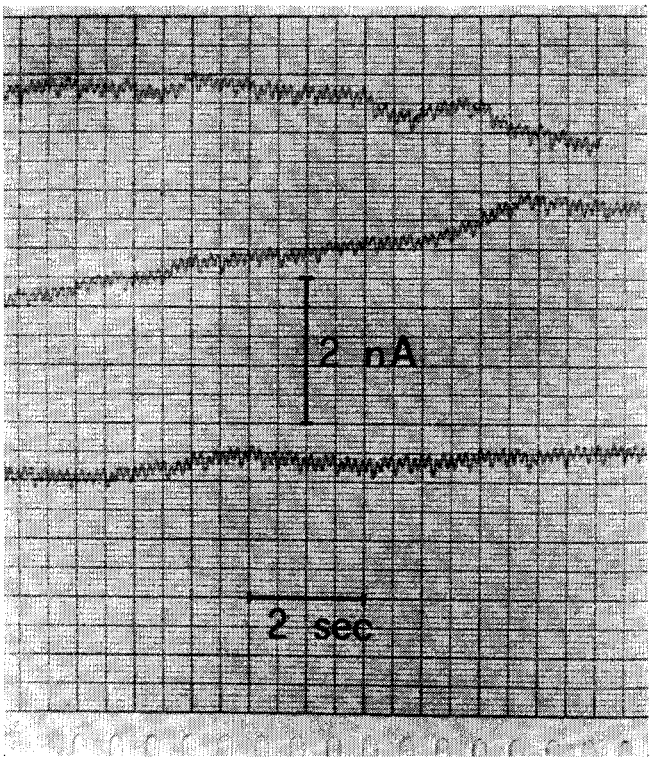

Figure 2. Current oscillations and noise

R = 24.7 kΩ; t = 0.128 sec; recorder chart speed = 60 cm/min; recorder scale = 0.5 mV; solution flow rate = 2 ml/min

linear flow rate of about 32–320 cm/min inside the solution inlet tube (2 mm wide). Measurements were made with not deoxygenated solutions (*17*), at room temperature, in a place well protected from drafts and thermic convection of the air.

The current was measured with a 1019 Beckman pH meter, across a resistor R (1 or 24.7 kΩ) connected in series with the cell. Small variations of the current were registered on 0.5, 1, or 10 mV scales of a Bausch and Lomb VOM 7 Recorder, which was connected by means of a 5 mV Beckman Recorder Connection Adapter to the pH meter set at high or full scale sensitivity. In this case, the current was to a great extent suppressed by means of the pH meter. The RDME potential was read with the pH meter and fixed at a potential in the middle of the hydrogen plateau, *e.g.*, at −1820 ± 0.1 mV *vs.* SCE.

Particular care was taken to use well cleaned mercury. Dirty capillaries were cleaned as previously described (*17*). Care was taken also to avoid heat transfer to the solutions and the cell, especially in handling the 2-way stopcock.

After measurements were taken, the cell was not dismounted. Solution and mercury flows were just stopped with stopcocks, leaving the cell filled with solution. For new measurements it sufficed to let mercury and solution flow again. Even after long periods of non-operation (up to 20 days), the apparatus performed well on startup. We followed this procedure for months with satisfactory results. Indeed it would be better to avoid dismounting, because each new assembling of cell and capillary was followed by some hours of troublesome measurements (see below).

RESULTS AND DISCUSSION

Oscillations of the current depended on t; the smaller t, the smaller oscillations. Oscillation amplitude ranged from 3 to 0.3 nA, and from 0.02 to 0.001% of the total current. Current noise was of the same order (Figure 2). Greater values of current noise were due to:

Table I. Current Dependence on Solution Flow Rate

Base solution; R = 1 kΩ; E_{RDME} = −1820 mV *vs.* SCE; t = 0.115 sec; current measurements made with the Beckman pH meter

Solution flow		
ml/min	cm/sec	i, μA
0	0	30.6[a]
0.6	0.32	29.4
0.9	0.48	29.5
1.3	0.69	29.6
1.4	0.74	29.7
1.9	1.01	29.8
2.7	1.40	30.2
5.6	3.00	31.2
6.3	3.30	31.6
7.4	3.90	33.2

[a] Not stable.

Table II. $\Delta i = K\Delta C$

R = 1 kΩ; E_{RDME} = −1820 mV *vs.* SCE; t = 0.115 sec; background current = 31.4 μA; solution flow = 2 ml/min.

Recorder scale, mV	ΔC, M	Δi, div	K, div/M 10^6
0.5	3.2×10^{-6}	28.0	8.8
	7.0×10^{-6}	60.0	8.6
	10.0×10^{-6}	89.0	8.9
1	7.0×10^{-6}	34.0	4.9
	10.0×10^{-6}	48.0	4.8
	20.0×10^{-6}	96.0	4.8
10	2.0×10^{-5}	9.5	0.48
	6.0×10^{-5}	30.0	0.50
	10.3×10^{-5}	50.0	0.48

Defective capillary (*17*) (sometimes a diminution of current noise was obtainable by turning the capillary around its axis; for each capillary, indeed, positions of minimum noise exist).

Penetration of solution inside the capillary during periods of non-operation (penetration was avoided by placing the stopcock for the mercury as near as possible to the capillary).

Strong vibrations or shocks (turning the 2-way stopcock resulted in a transient variation of the current (Figure 3): but if hydrostatic pressure varies, a permanent variation results).

Irregular thermic variations.

Irregularities in the solution flow (*e.g.*, those due to gas bubbles entrapped in tubing and cell).

Because of the smallness of oscillations and current noise:

The RDME potential could be fixed and maintained constant with great precision (within the readability of the pH-meter).

High sensitivity recorder scales could be used.

Variations of room temperature resulted in a drift of the base line when the current was registered.

The flow of the solution introduced a convective component in the current, which was dependent on the flow rate (Table I), but had little or no influence on t.

The linear response of the current with respect to variation of concentration was satisfactory (Table II), taking into account the poor control on temperature and the high background current.

The current variation with changing of flowing solution is shown in Figure 3. The base solution and a more acid solution were alternatively substituted to each other. The transient variations of the current, due to the turning of the 2-way stopcock, are visible in Figure 3, as small marks before the

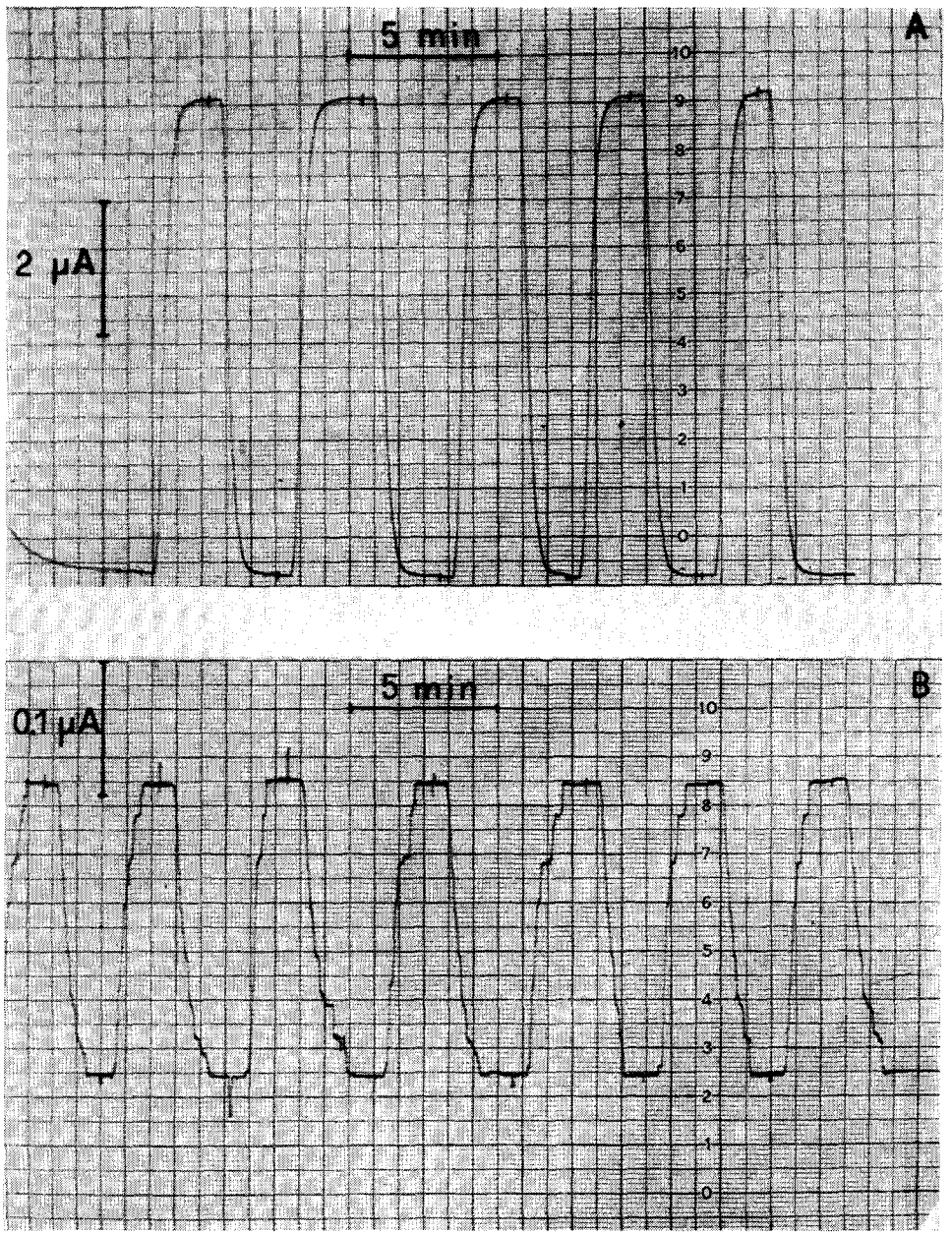

Figure 3. Current variations due to changes in composition of the flowing solution

R = 1 kΩ; t = 0.115 sec; background current = 31.4 μA; solution flow = 2 ml/min. Solutions: (*A*) base solution and a solution with ΔC = $2.3 \times 10^{-4}M$; (*B*) base solution and a solution with ΔC = $7 \times 10^{-6}M$

current jumps. From Figure 3 the holdup time (*i.e.*, the time elapsed from the mark to the beginning of the current jump), the flushout time (*i.e.*, the time elapsed from the beginning of the current jump to the achievement of stable current after the jump) and the corresponding volumes can be calculated. Mean approximate values are, respectively: 30 sec, 80 sec, 1 ml, and 2.5 ml. From Figure 3, also reproducibility in measurement of current difference between two solutions can be calculated (the % standard deviation resulted (*A*) 0.7 and (*B*) 0.9).

The unique feature of the described cell is that the composition of the filling solutions does not need to be renewed in order to obtain the signal corresponding to the flowing solution. In fact, because of the design of the cell, the mercury drop is always surrounded by the solution coming from the inlet tube. Therefore, the presence of a different solution into the bulk of the cell is of no consequence.

The cell is also convenient for mercury flow measurements. After all it is very convenient from a practical point of view, because it is always ready for use, and it is not necessary to dismount and clean when different solutions are to be examined.

Analysis time is short, 2–3 min (Figure 3). The absolute quantity of substance necessary for analysis is in the nmole range (*e.g.*, 20 nmole, with ΔC = $10^{-5}M$). The limit of determination deducible from the current noise is about $10^{-7}M$, with background concentration 10^4 times higher.

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