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Note

A SIMPLE MICROCALORIMETRIC ANALYTICAL CELL

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A microcalorimetric cell for routine analysis, operating jointly with a Bioactivity Monitor LKB-2277, has been designed. Our aim was a simple (as compared to a commercially available perfusion cell [1]) and sensitive cell applicable to analytical microcalorimetric experiments with an accuracy of ~ 1%.

RESULTS AND DISCUSSION

Figure 1 shows the cell. It is a rod 325 mm in length with alternating copper cylinders (A) having good thermal contact with the inner surface of the Bioactivity Monitor (diameter 14 mm) [2] and with polymer cylinders of poor heat conductivity (B) (diameter 10 mm). The bottom of the rod accommodates a metal reaction vessel (C) (diameter 14 mm) charged with the solution (2–2.5 ml). An electric motor (D) driving a mixer (H) (2 rpm) is fastened to the top of the rod. The mixer is a polyethylene tube (diameter 2 mm), the lower end of which is hermetically sealed with silicon rubber (RS components, limited stock N 555-588). The frictional heat of the mixer is ~ 5 μW with a heat noise of 0.3–0.5 μW.

The titrating solution is fed into the vessel (C) along a teflon tube (E) having good heat contact with the copper cylinders (A). The heat contact is improved by a heat-sink compound (Dow Corning 340).

The titrating solution is administered by a syringe (F); its plunger is manually moved by a screw (G). The accuracy of a screw turn is 5–6 deg, i.e. less than 1% (at two turns of the screw).

The syringe was calibrated by the chemical method. 0.2 N NaOH (2–2.5 ml) was placed in the reaction vessel and 0.1 N titrated HCl (2 ml) was placed in the syringe (F) which was attached to the Teflon tube (E). The screw (G) was turned several times to provide the HCl to the reaction vessel (C). After reaching thermal equilibrium, the HCl solution was added (one portion every 20–30 min) to the vessel.

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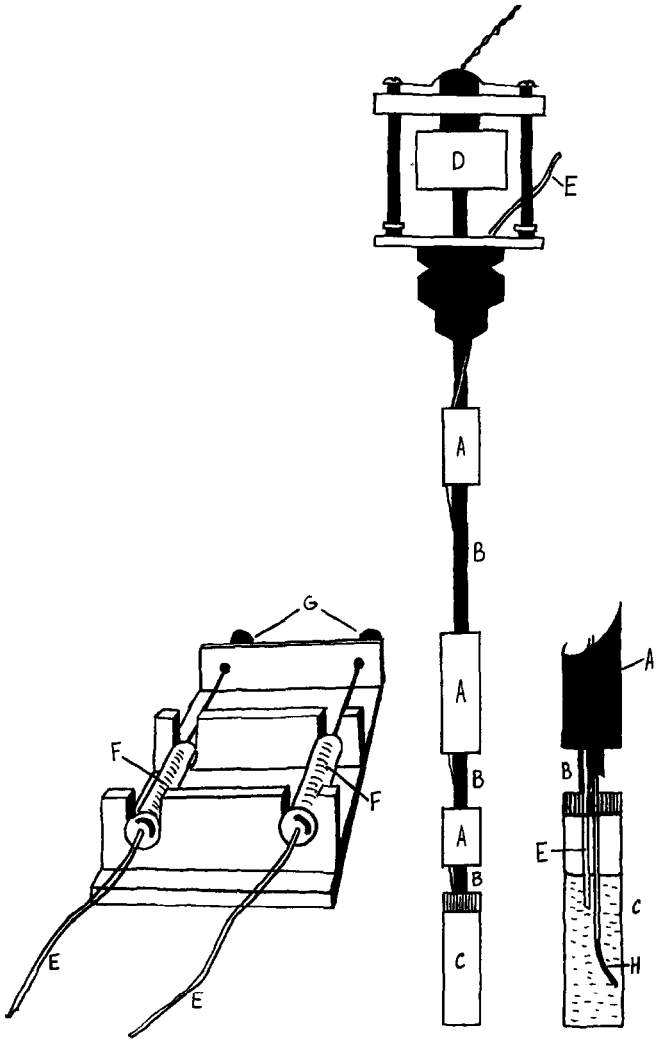

Fig. 1. Analytical cell for calorimetric titration: A, copper cylinder; B, polymer cylinder; C, reaction vessel; D, electric motor; E, Teflon tube; F, feeder syringe; G, screw; H, mixer.

In several series of experiments (fifteen in all) the portion volume was measured: two full screw turns allow passage of 0.1257 ± 0.0009 ml of the solution into the vessel, the error being the standard deviation from the average.

For electrical calibration, we have made a special cell. Its appearance and the materials used are practically identical to those of the analytical cell described above (Fig. 1). The cell for electric calibration lacks the teflon tube (E) and the mixer (H) is replaced by four electric wires with resistance (0.8 kΩ) burned-on at their ends. These four wires are used for potentiometric measurements of the electrical power supply of the cell. The resistance

(0.8 kΩ) is placed into the vessel (C) filled with oil. The measurement scheme includes a digital voltmeter (accuracy class 0.05), resistance boxes (accuracy class 0.02) and a source of direct current (battery 1.4 V).

It should be noted that the similar design and identical materials for the electric cell and the calibration cell were chosen to ensure equal heat loss.

The analytical cell operation was verified by determination of the glutamine ionization enthalpy. The reaction vessel contained 2–2.5 ml 0.3 N glutamine solution (pH 9.6–8.7) and the syringe contained 2 ml 0.1 N titrated HCl solution. Analogous experiments were carried out in parallel using a titration accessory for the batch microcalorimeter LKB-2107-III [4]. In the first case the glutamine ionization enthalpy is $\Delta H_i = -41.9 \pm 0.3$ kJ mol^{-1} (14 experiments) and in the second, $\Delta H_i = -41.7 \pm 0.6$ kJ mol^{-1} (17 experiments). These values are in good agreement. The analytical cell operates with an accuracy twice that of the batch cell, mainly due to the error in evaluating the portion volume of the titrating solution in the accessory of the LKB-2107-III batch microcalorimeter.

The correction for the mixing heat is ~ 6–7% of the heat released in the test using the titration accessory of the batch microcalorimeter, and 0.1–0.2% with the analytical cell. Thus, when using the analytical cell, no correction for the solvent mixing is necessary if the desired accuracy is 1%. This, in turn, facilitates the experiment and simplifies the calculations.

Thus, the simple analytical cell we propose for calorimetric titration has approximately the same parameters (heat noise, reagent mixing heat, accuracy of analytical detection, etc.) as the perfusion cell [1] of more complicated design. Our cell is designed for titration only and is not for perfusion applications.

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