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CALIBRATION STUDIES WITH THE LKB-SORPTION CALORIMETER, FLOW TYPE

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Summary:
The usual calibration with the built-in calibration heater is compared with an electrical simulation of a calorimetric experiment. The detector sensitivity was about 11% smaller in the latter.

In order to get reproducible quantitative data in experiments with immobilized enzymes we considered it very important that the heat for calibration is produced at the same place and under the same conditions as in the following experiment, namely within the glass cylinder of the flow cell.

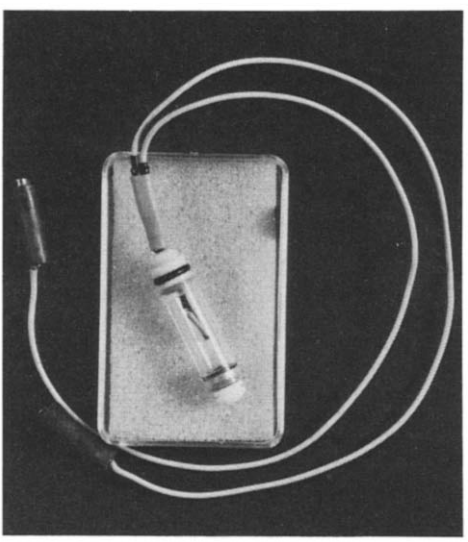

Fig. 1: Calibration heater designed to be installed within the glass vessel.

For this purpose a resistor of known magnitude was introduced into the flow sorption vessel (Fig. 1). The vessel was closed at the bottom by putting a rubber plate over the stopper, and than filled with paraffin oil. The wires of the

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resistor were connected with the plugs for the current of the reference cell through the connection tube at the upper end of the cell. By this arrangement the built-in heater can be compared with the calibration heater in the mounting block of the sorption vessel. The results are shown in the following table:

TABLE I

Difference of calibration constants depending on the location of the calibration heater.

CELL	LOCATION OF HEATER	RESISTANCE [ ]	CURRENT [mA]	HEAT EFFECT [/uWatt]	CALORIMETRIC RESPONSE [/uV]	DETECTOR SENSITIVITY /uV//uW
1	a	49.974	2.0	199.9	10.9	0.0543
1	b	47.4	2.0	189.6	9.25	0.0485 = 89%
2	a	49.968	2.0	199.87	12.4	0.0620
2	b	47.4	2.0	189.6	10.3	0.054 = 88%

[a] Calibration heater in the mounting block: "external calibration".

[b] Calibration heater inside the glass cylinder: "internal calibration".

The detector sensitivity using the internal calibration was about 11% smaller than that using the external calibration. As an explanation we suppose that the heat transition from the inner volume of the cell through the glass cylinder to the heat sink is not absolutely isothermal. For quantitative evaluation of the reaction enthalpy of biological experiments we suggest to multiply the sensitivity measured with the calibration heater attached to the cell housing and under the working conditions (flow rate etc.) by the factor 0.89.

That this explanation is very probable could be shown in parallel experiments with the flow calorimeter, mixing type. Here the reaction heat is directly transferred from the gold capillary to the heat sink. The neutralization heat of NaOH (10^{-3} till 10^{-2} M) with HNO_3 (10^{-2} M) measured by means of the commercial calibration of the calorimeter was in excellent agreement with the calculation regarding the concentrations and the flow-through rate till the HNO_3 was completely neutralized.

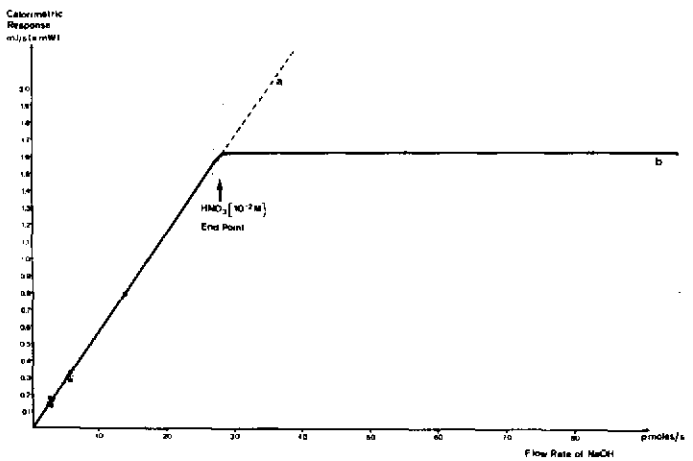

Fig. 2: Heat of neutralization between NaOH and HNO_3

a) ---- : Calculated using a molar neutralization enthalpy of 52 Joule per mmol NaOH.

b) —— : Determined by calorimetric measurement using the built-in calibration for calculation.