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PERFORMANCE OF A NEW DIFFERENTIAL SCANNING CALORIMETER CELL

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A calorimeter cell has been developed utilizing a geometry which optimizes dynamic gas flow and quantitative heat transfer to each sensing thermocouple. The basis of the cell is a sensitive thin form differential thermocouple which is symmetrically and rigidly positioned, containing a center port. The thin form differential thermocouple serves as a sample and sample container support as well as a differential detector. The dynamic gas enters through the center port permitting good contact with the sample and sample pan adjacent to it. The theoretical aspects are discussed and the necessity of having a high thermal resistance between the heat source and sample and a low thermal resistance between the sample and detecting thermocouple is demonstrated. Applications which show both qualitative and quantitative capabilities are presented.

Thermal systems capable of providing quantitative data using dynamic calorimetric techniques are often classified as differential scanning calorimeters in order to differentiate these devices from those that provide only qualitative data. Two types are recognized, one of which is based on power as the ordinate readout and the other of which is based on differential temperature as the ordinate readout.

For the latter types which are based on the differential temperature readout technique, a number of theoretical treatments have appeared which discussed and demonstrated aspects of quantitative capability [1 – 12]. In every instance in which area measurements were made on a peak produced as a result of an enthalpic change within a sample, the area was found to be proportional to the enthalpic effect. The number of calories involved is determined by multiplying the peak area by the heat transfer coefficient for the particular device, taking into account such parameters as chart speed and attenuation.

Two such treatments used air as the reference material and showed that the calorimetric peak value is independent of the specific heat of the sample [7, 9]. Another study demonstrated the dependence of specific heat only on ΔT and heating rate and reconfirmed the independence of phase transition heats of specific heat and heating rate in various environments when using a time base recording system [11]. Berg and Egunov have shown that a number of factors such as specific heat, thermal conductivity, bulk density, etc., need not be taken into account (within limits) for solid phase invariant processes [10].

In the quantitative studies mentioned above, attention was devoted only to the effect of experimental conditions on peak area quantitation. Usually, the heat transfer coefficient is treated as a lumped parameter and the instrument design problems which limit sensitivity and response are not discussed.

One study has specifically addressed itself to this problem, and the effects of thermal resistance on system response and sensitivity have been pointed out [13]. While this study analyzed the problem correctly, it is believed that the thermal resistance, R, used in this study is in reality a simplification of the thermal resistances encountered normally. The final equation, however, is identical to those of other studies [7].

Theoretical background and design considerations

In any consideration of the effects of design or instrument performance, the possible paths of heat flow and the effect of each individual thermal resistance affecting heat flow must be considered.

In any experiment involving heat flow, heat will be absorbed or evolved by the sample or lost to the surroundings. If heat is lost to the surroundings, the sample temperature will be unaffected except for the rise due to scanning rate. For sam-

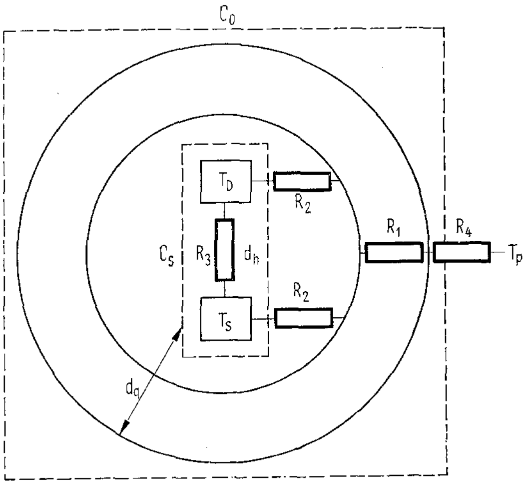

Fig. 1. Schematic diagram of a thermal analysis cell. R_1 = thermal resistance across wall of sample container; *small* in value; R_2 = thermal resistance between wall of sample container and sample, reference, or detector; *large* in value; R_3 = thermal resistance between sample or reference and detector; *small* in value; R_4 = thermal resistance between heat source and walls of the sample container; *small* in value; T_p = heat source generator, *very large* in value; C_s = thermal capacity of sample, *small* in value; C_0 = thermal capacity of entire sample holder, *small* in value; T_s = temperature of sample; T_D = temperature of detector; dh = heat generated by the sample; dq = heat flow from the thermal source

ples that exotherm or evolve heat, the sample temperature is either raised or heat is lost due to the surroundings. Thus, we have:

$$\mathrm{d}h = C_s \mathrm{d}T_s - \mathrm{d}q \tag{1}$$

The rate of heat loss is determined by the thermal resistance and the temperature difference between the sample and surroundings and is similar to the way in which current flow across a resistor is controlled by the potential difference across it. The thermal analog of Ohm's law is:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{T_p - T_s}{R} \tag{2}$$

where T_p is the temperature of the thermal supply, T_s is the temperature of the sample, and R is the thermal resistance of the path from the heat generator to the sample. However, this is a much too simplified consideration of what is actually encountered.

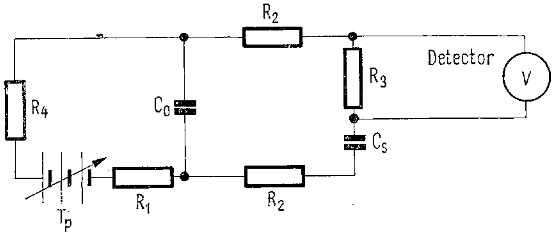

Fig. 2. Electrical analog of thermal analysis cell

For the purpose of a more explicit representation of the heat transfer within a thermal analysis cell, we use the cell and resistors shown in Fig. 1. The electrical analog of this cell is illustrated in Fig. 2.

Redefining dh in terms of the rate of heat loss $\frac{\mathrm{d}h}{\mathrm{d}t}$, and $\frac{\mathrm{d}q}{\mathrm{d}t}$ and $\frac{\mathrm{d}h}{\mathrm{d}t}$ in more precise terms of the electrical analog, we obtain:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{C_s \mathrm{d}T_s}{\mathrm{d}t} + \frac{C_0 \mathrm{d}T_0}{\mathrm{d}t} - \frac{\mathrm{d}q}{\mathrm{d}t} \tag{3}$$

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{T_p - T_{W_0}}{R_4} + \frac{T_{W_0} - T_{WI}}{R_1} + \frac{T_{WI} - T_s}{R_2} + \frac{T_D - T_s}{R_3} + \frac{T_{WI} - T_D}{R_2} \tag{4}$$

where:

T_0 = temperature of the entire cell
T_p = heat source generator

T_{w_0} = temperature of the outside wall
T_{wI} = temperature of the inside wall
T_s = temperature of the sample
T_D = temperature of the detector.

Other terms are defined in Fig. 1.

Substituting for $\frac{\mathrm{d}q}{\mathrm{d}t}$ in Eq. (3) for the equivalent form in Eq. (4), we have:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{C_s \, \mathrm{d}T_s}{\mathrm{d}t} + \frac{C_0 \, \mathrm{d}T_0}{\mathrm{d}t} + \frac{T_{w_0} - T_p}{R_4} + \frac{T_{wI} - T_{w_0}}{R_1} + \frac{T_s - T_{wI}}{R_2} + \\ + \frac{T_s - T_D}{R_3} + \frac{T_D - T_{wI}}{R_2} \tag{5}$$

for the reference cell $\frac{\mathrm{d}h}{\mathrm{d}t} = 0$ and we can write:

$$0 = \frac{C_R \, \mathrm{d}T_R}{\mathrm{d}t} + \frac{C_0 \, \mathrm{d}T_0}{\mathrm{d}t} + \frac{T_{w_0} - T_p}{R_4} + \frac{T_{wI} - T_{w_0}}{R_1} + \frac{T_R - T_{wI}}{R_2} + \\ + \frac{T_R - T_D}{R_3} + \frac{T_R - T_{wI}}{R_2} \tag{6}$$

Subtracting Eq. (6) from Eq. (5) and rearranging, we obtain an expression for the instantaneous heat generation by the sample:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{C_s \, \mathrm{d}T_s}{\mathrm{d}t} - \frac{C_R \, \mathrm{d}T_R}{\mathrm{d}t} + \frac{T_s - T_R}{R_2} + \frac{T_s - T_R}{R_3} \tag{7}$$

It is interesting to observe that the remaining thermal resistors R_2 and R_3 largely determine "sample" performance from the standpoint of sensitivity and response. A large R_2 will provide good sensitivity since heat leakage will be minimized. A small R_3 will enhance this condition and at the same time provide rapid response. The sample heat capacity C_s also determines "sample" performance, as Figs 1 and 2 show, but not to the same extent as R_2 and R_3. In any event, this is not a serious limitation since the system under consideration will generally utilize milligram quantities of undiluted samples.

The cancelled terms, R_1, R_4, and C_0, will determine "cell" performance primarily, and only secondarily will "sample" performance be controlled by these parameters. The cell itself may be slow to heat and cool but the sensitivity and response of the detectors (thermocouples) need not necessarily be degraded since the effect of these parameters on both sample and reference detector is identical. Similar arguments also apply to T_p. However, if T_p is made sufficiently large in comparison to R_2, the result will be to minimize the effect of a large R_2 and provide a fast instrument response.

From the above, it appears that optimum performance will result when:

1. T_p is sufficiently large so that an appreciable current (heat) will flow across R_2 even though R_2 is large. The heat source should be completely uniform with respect to the cell and have a heating capacity orders of magnitude greater than that required normally.
2. R_2 must be large to provide small heat losses and correspondingly high sensitivities.
3. R_3 must be exceedingly small compared to R_1 and R_2. This will permit the heat generated by the sample to be efficiently transferred to the detecting thermocouple. As a consequence, high sensitivity and little reduction in response time should be occasioned by the high values of R_1 and R_2.
4. R_4 must be small to ensure rapid response in both heating and cooling modes. Thus heat can be introduced or extracted rapidly across R_1 and R_2.
5. R_1 is normally small but sufficiently large to ensure even heat transfer to the sample and detectors.

With a proper combination and optimization of the above parameters, good performance can be expected.

Cell design

A sample cell design that attempts to take into consideration many of the parameters mentioned previously is shown in Fig. 3. This particular DSC cell is relatively small in diameter (~2.5 cm) and wall thickness in order to provide rapid response. Close coupling to the heat source is achieved by maintaining a small furnace opening of 3.75 cm.

The differential thermocouple is of a new thin form design that is isolated from the cell walls and cell bottom to provide high sensitivity. The thin form thermocouple consists of a sheet of negative Platinel II type thermocouple alloy while the leads are positive Platinel II thermocouple alloy [14]. This type of thermocouple material is utilized because (1) it is more resistant to oxidation than chromel-alumel [14], (2) the thermal stability is excellent being $\pm 0.75\%$ for 1000 hours of exposure to air 1204° [14], (3) it has a relatively high thermal emf being comparable to chromel-alumel thermocouples, (4) it covers wide temperature ranges, usually usable from ambient to 1200°, and (5) good constancy of calibration has been reported [14] and experienced by us. A differential thermocouple of this design takes advantage of the fact that (1) flat sample pans can be utilized, (2) a third interconnecting lead between one of the thermocouple legs does not have to be made extraneous to the primary thermal zone as is often the case, and (3) the thin form thermocouple can be made and positioned with a great deal of uniformity, thus providing good baseline stability.

The sensitivity of the differential thermocouple is governed by the thickness and values of R_2 and R_3. The thermocouple is maintained sufficiently thick so as to provide a rigid stable platform for the sample cups and at the same time be rigidly fixed in order that reproducible results can be obtained. The thin form design takes advantage of the rapid response attributes of the thin film thermocouple [15] and the high sensitivity of the conventional DTA thermocouple.

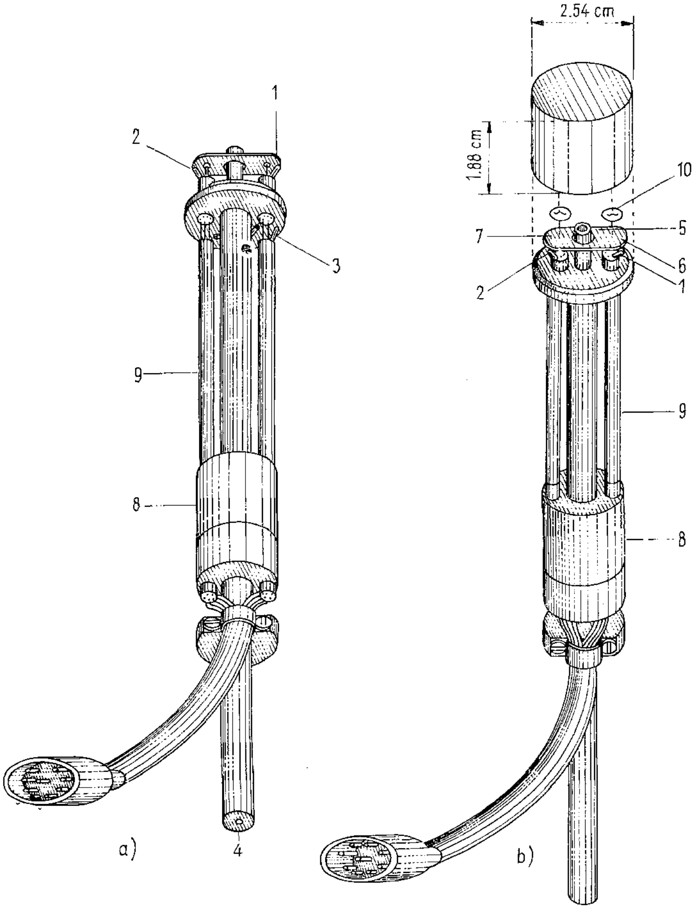

Fig. 3. Differential scanning calorimeter cell. a) Bottom view; b) Top view

1. Thermocouple for x-axis or system temperature readout. 2. Limit switch thermocouple. 3. Programming or furnace thermocouple. 4. Dynamic gas port entry. 5. Dynamic gas port exit. 6. Sample side of differential thermocouple. 7. Reference side of differential thermocouple. 8. Ceramic thermal insulator. 9. Ceramic support rods. 10. Sample pans

The use of a thin form thermocouple with a center port permits the dynamic gas to enter the cell immediately adjacent to the sample through the gas port entry. This feature ensures good contact of sample with the dynamic gas.

The size and placement of the thin form differential thermocouple along with the cell size have been found to influence the problem of providing uniform heat transfer to each side of the differential couple. Performance criteria influenced the design of a cell in which the differential couple was symmetrically placed but yet was not so rigidly fixed that minor adjustments could not be made to provide an instrument baseline of good quality.

There are two additional thermocouples present for measuring absolute temperature. Each one is positioned under one side of the differential thermocouple as Fig. 3 shows. One is used to activate a limit switch while the other one measures furnace temperature in the immediate vicinity of the sample. A third thermocouple which is positioned below the cell bottom place is used as the programming or furnace thermocouple.

Cell performance

A Stone-Premco Model 150 Thermal Analyzer along with a DSC-100-2 Calorimeter Cell were used for all experiments. The upper temperature limit of this cell is 1000°. An H-P Model 7100B time base recorder was used for signal readout with this system.

In order to examine the calorimetric response of the cell, a number of ACS Reagent Grade metals were utilized. These materials have known temperatures of transition and heats of fusion so that they are usable as standards. A scanning rate of 10°C/minute was used for all runs. All calibration results are the average of duplicate determinations.

The response of this cell was determined by measuring the area produced by the fusion of each metal from which the heat transfer coefficient of the cell was calculated as described previously [11]:

$$K = \frac{\Delta H_f \text{ of Std (cal/g)} \times \text{chart speed (in/min)}}{\dfrac{\text{area}}{\text{sample wt.}}\left(\dfrac{\text{in.}^2}{\text{g}}\right) \times \text{attenuation}\left(\dfrac{{}^\circ\text{C}}{\text{in}}\right)} = \frac{\text{cal}}{\text{minute} \times {}^\circ\text{C}}$$

The heat transfer coefficients were calculated using the actual thermocouple output (°C/in.) in the transition temperature region. In similar systems, it has been shown that $\Delta H = K \int_{t}^{t_0} \Delta T \mathrm{d}t$ [7, 11]. The K factor is a lumped parameter model that includes the size of the thermocouple wire, geometry of the sample holder furnace design, heat capacity of the thermocouples, sample containers, etc. [11]. This approach is acceptable in a fixed system.

The heat transfer coefficients (K) were then plotted as a function of temperature using the first deviation from the baseline as the transition temperature. In a system such as this which utilizes furnace temperature as the readout, the first deviation is the true transition temperature [16]. A dynamic gas flow of 0.04 SCFH nitrogen was used. The resulting calibration curve is shown in Fig. 4.

The sensitivity of this cell differs from that reported previously as is evidenced by the K factors [11]. The unique feature of the calibration curve of this cell is the demonstrated linearity over the temperature range examined. The completely linear response permits easy calculation of the K factor at the transition temperature of an unknown substance either directly from the curve or from the equation of the curve. From these values, the heat involved in an unknown transition is calculated according to:

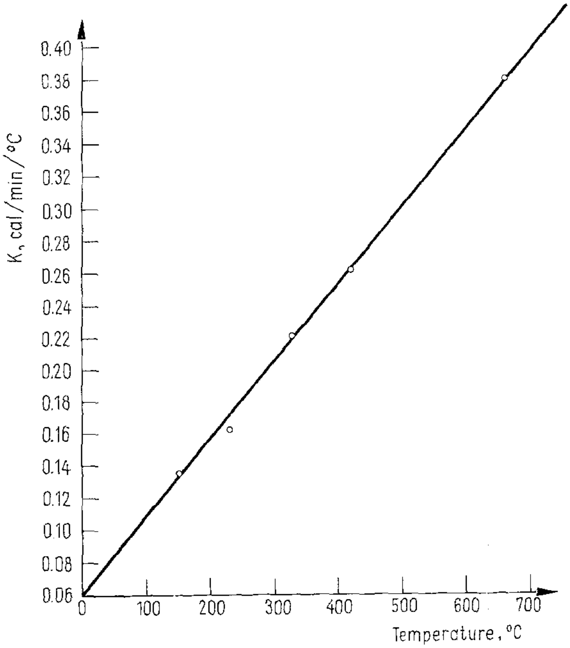

Fig. 4. Heat transfer coefficient (K) vs. temperature

$$\text{cal} = K\,(\text{cal/min/°C}) \times \text{area}\,(\text{in}^2) \times \text{Att}\left(\frac{\text{°C}}{\text{in}}\right) \times \text{chart speed}\left(\frac{\text{min}}{\text{in}}\right)$$

$$\frac{\text{cal}}{\text{sample weight}} = \frac{\text{cal}}{\text{g}}$$

A least squares calculation for the calibration curve was performed and the equation of the line was found to be:

$$K = 4.94 \times 10^{-4} \times T + 0.0558$$

Although K is not independent of temperature as in the type of differential scanning calorimeter which utilizes power as the ordinate readout, this type of dynamic calorimeter based upon the differential thermocouple detector has been found to provide quantitative enthalpic measurements within ±2% error. The error was checked by comparing the heats of fusion and specific heats determined with this cell with known values on such materials as polyurethane, polycarbonate, aluminium, and potassium nitrate.

Effect of scanning rate

The effect of scanning rate on the quantitative calorimetric response was determined at three different heating rates. These results are shown in Table 1 and indicate that the calorimetric values determined are within the expected deviation mentioned above and are independent of heating rate.

Table 1

Effect of scanning rate on calorimetric response

Sample	Scanning rate, °C/min.	ΔH_f determined, cal/g.
Tin	5	14.0
Tin	5	13.9
Tin	10	13.8
Tin	10	13.5
Tin	25	13.5
Tin	25	13.5

This is not the case when an X-Y Recorder is used. A previous study in which identical findings were reported attributed the independence of heating rate to good heat transfer and lack of thermal gradients within the sample [11]. However, this is only true when small undiluted samples are used.

Resolution and response

The resolution of the 100-2 DSC Cell was evaluated using *n*-dotriacontane. Approximately 1 mg was placed in a sample pan weighing 3 mg and scanned at a rate of 10°C/min. The thermogram shown in Fig. 5a is a re-run that was obtained on a sample which had been heated previously through the melting transition and cooled. At a scanning rate of 10°C/min, good resolution is evidenced between the chain rotational transition and melting as compared to previously published thermograms of this material [15, 17].

The thermogram shown in Fig. 5b is a run of precisely the same sample, sample pan, and reference pan as in 5a except that in this case a 0.0037 cm sheet of polyethylene was placed between the thin form thermocouple and the sample pans. In this instance, the resolution is degraded because of the thermal resistance. For any system, a thermal resistance can be visualized that is sufficiently large so that no signal at all will be seen across it.

This would seem to lend credence to the theoretical contention that R_3 is the thermal resistor that limits performance. The thermal resistors R_1, R_2, and R_4 also limit performance but only in the sense that instrument performance is limited, that is, scanning rates, temperature stability, etc., will be limited. However, only within these bounds is sample performance limited and then only by R_3, or detector design.

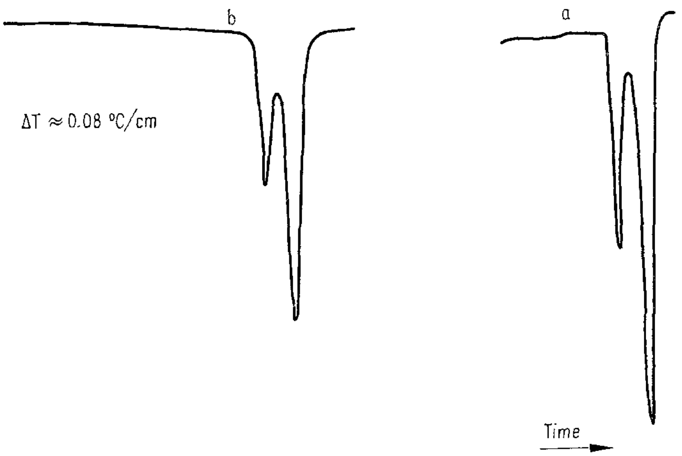

Fig. 5. DTA curves of *n*-dotriacontane showing resolution and the effect of thermal resistance. *a)* Sample run as is. *b)* Re-run of same sample with sheet of polyethylene between sample dish and thermocouple

The actual area measurements for thermograms 5a and 5b are 0.76 and 0.69 square inches respectively. The small percentage difference between the areas of thermograms 5a and 5b was expected to be larger and is probably kept to a minimum by a large R_2. Thus, the heat source which completely surrounds the entire cell maintains a uniform temperature which minimizes the heat losses except to the detectors.

In any event, R_3 is very small compared to R_1, R_2, and R_4 because the flat surface of the thin form thermocouple detector, flat sample pan, thermocouple mass tend to optimize the heat transfer to the thermocouple. As further evidence for the overriding effect of R_3, we have observed that cells and furnaces of identical design except for the differential thermocouple and/or sample container have provided widely varying responses.

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RÉSUMÉ — On a mis au point une cellule calorimétrique dont la conception est favorable à la circulation d'un courant gazeux et au transfert quantitatif de la chaleur vers chaque thermocouple détecteur. Le fond de la cellule est constitué par un thermocouple différentiel fin et sensible, disposé symétriquement et d'une manière rigide, et dont le centre est muni d'un orifice. Ce fin thermocouple différentiel sert de support d'échantillon et de détecteur différentiel. La circulation du gaz s'effectue par l'orifice central qui permet un bon contact avec l'échantillon et le support d'échantillon qui lui est adjacent. Les aspects théoriques sont discutés et l'on montre la nécessité d'une résistance thermique élevée entre la source de chaleur et l'échantillon et faible entre l'échantillon et le thermocouple détecteur. Des applications illustrent les possibilités qualitatives et quantitatives de ce dispositif.

ZUSAMMENFASSUNG — Es wird über eine kalorimetrische Zelle mit einer Geometrie, die einen optimalen Gasstrom und quantitative Wärmeübermittlung zu jedem Thermoelement ermöglicht, berichtet. Die Zelle besteht aus einem empfindlichen dünnen Thermoelement, das symmetrisch und fest angelagert ist und eine Öffnung in der Mitte besitzt. Das dünne Thermoelement dient zum Halten der Probe, des Probebehälters und als Differentialdetektor. Das dynamische Gas tritt durch die Öffnung ein, wodurch eine gute Berührung mit Probe und umgebendem Probebehälter ermöglicht wurde. Die theoretischen Aspekte werden erörtert und es wird bewiesen, daß zwischen der Wärmequelle und der Probe ein hoher, zwischen dem messenden Thermoelement und der Probe ein niedriger thermischer Widerstand nötig ist. Anwendungen informieren über die qualitativen und quantitativen Fähigkeiten der Zelle.

Резюме — Сконструирована калориметрическая ячейка, обладающая геометрией для оптимализации динамического потока газа и количественного перехода теплоты к каждой чувствительной термопаре. Основание ячейки является чувствительной дифференциальной термопарой, помещенной симметрично и неподвижно, и, таким образом, содержит вход в центре. Дифференциальная термопара служит подставкой для контейнера образца, а также дифференциальным детектором. Поток газа проходит через центральный вход, что создает хороший контакт образца с чашкой, содержащей образец. Обсуждены теоретические аспекты и обусловлена необходимость высокого термического сопротивления между образцом и детектирующей термопарой. Показаны некоторые пути применения ячейки с возможностью качественных и количественных измерений.