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METHOD OF SEPARATING THE SENSITIVE VOLUME OF CALORIMETRIC CELLS IN A DIFFERENTIAL TITRATION CALORIMETER

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Abstract

A scientific and technical solution of capillary calorimetric unit design is described based on a method of separating the sensitive volume of calorimetric cells with a heat-conducting bridge in a differential titration calorimeter.

The design of the calorimetric cells as thin capillary tubes allowed to minimize the dimension of the heat-conducting bridges and to separate with high accuracy the sensitive volume of the calorimetric cells which is of 78.5 μl. Due to high calorimeter power sensitivity (10 nW) a modern level of requirements for measuring minimum specific heat of processes is provided.

The adopted design of the calorimetric cells permits to possess the cells located horizontally and to simplify the solution of the problem of equalizing components concentration along the volume of the calorimetric cells.

Keywords: differential titration calorimeter, heat-conducting bridge, sensitive volumes of calorimetric cells

Introduction

The method of separating sensitive volumes with a heat-conducting bridge for a capillary cells adiabatic scanning calorimeter [1, 2] was improved and studied to apply to the development of a differential titration calorimeter. The use of such calorimetric cells for building a new instrument proved to be promising in combined solution of several interdependent problems determining the main user's parameters of the calorimeter such as power sensitivity, working volume of cells, accuracy of separating the sensitive volume, mixing of components, etc. The present paper pays attention to the solution of the problem of accurate separation of the sensitive volume in elongated calorimetric cells. The sensitive volume of calorimetric cells is the main user's parameter serving to determine the amounts of reagents involved in an experiment and to calculate measured parameters such as enthalpy change, heat power, etc.

In this paper we present in detail theoretical analysis of the method of sensitive volume separation with a heat-conducting bridge and the results of the first experiments supporting the theoretical calculations.

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The development of the new titration calorimeter was carried out based on the state-of art level of the best (in our opinion) titration calorimetric instruments, described in [7, 8, 12].

Setup design

The technical requirements for developing a new titration calorimeter with capillary calorimetric cells were formulated on the base of an analysis of similar instruments developed earlier. Table 1 presents the performance of the most successful titration calorimeters developed. To compare these data we have proposed a method of comparing the titration calorimeters depending on their capacity to measure minimum specific energy of heat processes. This method is based on the method of comparing scanning calorimeters first proposed in [14]. In our case, for titration calorimeters the comparison is performed on the base of the cell volume/noise ratio which characterizes the signal/noise ratio of the instrument. An instrument having a higher cell volume/noise ratio enables to register the specific heat of measured processes more precisely. For example, at the study of heat power of interaction between the same components using the setup of Wiseman [7] and El Harrous [6] at constant 'additive amount/working volume' ratio according to the performance of these instruments, the real signal/noise ratio for the Wiseman instrument [7] will be 14-fold better.

The method of comparing instruments in terms of minimum heat level [6, 7] registered by the instrument is often used as characteristic of instrument capacities. In our point of view, this method does not permit to evaluate the level of the instruments accurately due to the drawbacks of the common method for determining minimum energy level registered in titration calorimeters.

We present in Table 1 the noise level of the titration calorimeters on the base of experimental data from the mentioned papers.

Figure 1 presents a technical solution of a calorimeter with a titration unit design and comprises the main elements differentiating our instrument from existing analogs. The calorimetric unit comprises two calorimetric cells designed as capillary tubes with an internal diameter of 1.2 mm. The total volume of one cell is 122 and the sensitive volume is 78.5 μl. To separate the sensitive volume an active and a passive heat-conducting bridges are used. The main elements of the thermostatic control in the calorimetric cells are a constant-temperature shield and a thermopile-based thermostat. The housing of the instrument represents the load-carrying structure bearing a calorimetric unit and a titration unit. The titration unit consists of two syringes located in a common case. The pistons of the dispensing syringes are joined together by means of a connecting bar. To perform the titrant injection process in the calorimetric cells, the case of the syringes is tied to a first screw mechanism, the bar being tied to a second screw mechanism. The screw mechanisms are actuated by stepping motors. The control system has no conceptual differences from analogous control circuits [6, 7, 9, 11]. The presented structure provides for computer control of the calorimeter, data acquisition and processing, etc.

Table 1 Main technical characteristics of modern titration calorimeters

Reference	Noise level/ nW	Mixing	Thermostatic control	Volume/ μl	Ratio/ $\mu l(nW)^{-1}$
Gorman Nordmark *et al.,* [5]	1000	mechanical, impeller	water thermostat and a high-mass equalizing sink	1000	1
Spokane *et al.,* [11]	1000	mechanical, blade in one cell	water thermostat and two internal shields with automatic temperature control	1000	1
McKinnon *et al.,* [10]	50	mechanical, blade in one cell	water thermostat with an internal shield and a high-mass equalizing sink	200	4
Wiseman *et al.,* [7]	50	mechanical, impeller	adiabatic shield, cooling agent circulation to get temperature lower than room temperature	1400	28
Freire *et al.,* [8]	100	mechanical, impeller in both cells	water thermostat and a high-mass equalizing sink	1400	14
El Harrous *et al.,* [6]	100	mechanical	water thermostat and a high-mass equalizing sink	200	2
Garcia-Fuentes *et al.,* [9]	1000	mechanical, impeller	water thermostat and a high-mass equalizing sink	2900	2.9
CSC 6200, [12]	±15	hydraulic impulse stirring	adiabatic shield located in a thermopile-based thermostat	330	11
CSC 6150, [12]	±15	hydraulic impulse stirring	adiabatic shield located in a thermopile-based thermostat	330	11
Kotelnikov *et al.,* [13]	10	diffusion mixing; diffusion mixing combined with oscillating needle mixing	isothermal jacket, thermopile-based thermostat	78.5	7.8

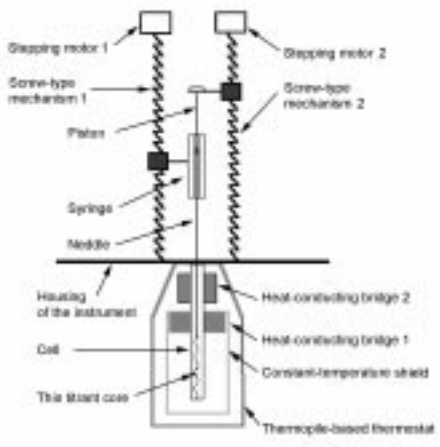

Fig. 1 Calorimetric unit with a titration unit

The sensitive volume of the calorimetric cells is represented by the volume of the portion of the tubes located below the passive heat-conducting bridge and is 50 mm long. A titrant dose is injected in the sensitive volume as a thin core equally distributed along its length. This is provided as a result of a simultaneous translation of the case of the syringes and of the bar joining the pistons. The dose volume depends on the translation value of these elements. In case of an equal translation of these elements the dose is equal to 0. When the translations are not equal the volume of the dose changes from 0 to the maximum. We used the 10-μl Hamilton syringes, the dose volume was changed from 0.1 to 10 μl. The system of thermostatic control provides for precise isothermal conditions, the temperature of the isothermal shield being maintained at a noise level of less than 10^{-5}°C by the automatic control system and has practically no longitudinal temperature difference. Due to the use of a zero-position-error system in the heat power measuring system, the temperatures of the sample cell and of the reference cell are equal to each other in all the modes of the calorimeter operation. The heat-conducting bridge 2 is designed to prevent heat exchange of the calorimetric cell sensitive volume and the heat-conducting bridge 1 with the environment through the outlet part of the capillary tubes. An analysis of the heat-conducting bridge 1 operation is described later.

The parameters we set in the design allowed to build a new titration calorimeter having a modern level as to the main user's parameters given in Table 1. The present instrument solves the problem of an accurate separation of the sensitive volume in the calorimetric cells the volume of which is determined by the volume of the calorimetric cells located below the heat-conducting bridge for the first time for titration calorimeters. The volume of the calorimetric cells is determined by the geometry of the calorimetric cells and its value is known with accuracy near one percent. Moreover, the advantages of the instrument are the small volume of the calorimetric cells and high sensitivity. An important advantage of the capillary calorimetric cells is as well the fact that the value of the sensitive volume is unchangeable for any position of the

cells which enables to locate the cells horizontally and to simplify the solution of the problem of equalizing components concentration throughout the volume of the calorimetric cells. High-accuracy knowledge of the sensitive volume prevents practically the need of experimental and theoretical operations to get the optimal value as described, for example, by El Harrous [6]. The use of elongated thin capillaries enabled to have space-saving heat-conducting bridges but demanded to build a particular system for thermostatic control of the cells since the capillary length of the sensitive volume is of 50 mm.

Evaluation of the accuracy of separating the sensitive volume of a calorimetric cell in a differential titration calorimeter

To evaluate theoretically the accuracy of the sensitive volume separation of a calorimetric cell in a differential titration calorimeter a thermal model (Fig. 2) for one calorimetric cell (the measuring thermocouple and the second calorimetric cell not shown in Fig. 2) was examined.

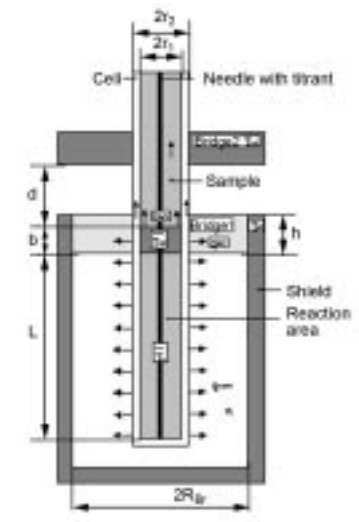

Fig. 2 Schematic drawing of the calorimetric unit with heat bridges 1 and 2

The calorimetric cell has ideal thermal contact with heat-conducting bridges 1 and 2 providing for separation of sensitive volumes of the cells. The heat-conducting bridge 1 has ideal thermal contact with an isothermal shield whose temperature is maintained constant and is T_{sh}. The temperature of the bridge 1 at the surface of contact with the shield ($R=R_{br}$) is equal to T_{sh}. A control system maintains the temperature of the bridge 2 equal to that of the isothermal shield T_{sh}.

The volume of the reaction area where a thermal effect occurs while dispensing with a dispenser needle moving up $V=V_c+V_{br}$ where the sensitive volume of a calorimetric cell $V_c=\pi r_1^2 L$, r_1 being the internal radius of a calorimetric cell and L being the

height of the sensitive volume, and the volume of the calorimetric cell adjoining its sensitive volume where a heat reaction occurs $V_{br}=\pi r_1^2 b$, b being the height of heat evolution area outside the sensitive volume.

The thermal effect arising in the sensitive volume of a calorimetric cell V_c:

$$Q_{sv}=Q_{sp}V_c\rho_{liq}$$

where Q_{sp} is specific thermal effect of a reaction, ρ_{liq} is the density of the liquid.

The thermal effect arising in the volume V_{br} adjoining the sensitive volume V_c:

$$Q_{br}=Q_{sp}V_{br}\rho_{liq}$$

The thermal effect of the reaction recorded by the calorimeter is determined as follows:

$$Q_{rec}=Q_{sv}+KQ_{br}=Q_{sp}\rho_{liq}\,(V_c+KV_{br})$$

where K is a factor of influence of the thermal effect in the area of the volume V_{br} on the thermal effect recorded in the sensitive volume of the calorimetric cell V_c.

The accuracy of separating the sensitive volume of the calorimetric cell in a differential isothermal titration calorimeter is determined by the error of measuring thermal effect in the sensitive volume of the calorimetric cell depending on the influence of the thermal effect in the volume V_{br} adjoining the sensitive volume of the calorimetric cell.

The error of measuring thermal effect in the sensitive volume of the calorimetric cell V_c depending on the influence of the thermal effect in the volume V_{br}:

$$\delta=\frac{Q_{rec}-Q_{sv}}{Q_{sv}}100\%=K\frac{b}{L}100\% \quad (0\le b\le h) \tag{1}$$

where h represents the height of the bridge 1.

To determine the factor of influence K the arguments as follows can be taken into consideration. We believe that constant power P is released only in the volume V_{br} (stationary mode). In this case:

$$P=q_{br1}+q_{br2}+q_{conv} \tag{2}$$

where q_{br1} is heat flow carried away from the volume V_{br} through the bridge 1 to the shield at fixed temperature T_{sh}; q_{br2} is heat flow carried away from the volume V_{br} through the cell and the sample to the bridge 2 at fixed temperature T_{sh}; q_{conv} is heat flow carried away from the volume V_{br} to the sensitive volume V_c and by convection from the last to the shield at fixed temperature T_{sh}.

The factor of K influence can be expressed as ratio of the heat flow q_{conv} coming into the sensitive volume of a calorimetric cell and recorded by the microcalorimeter to the sum of the heat flows $q_{br1}+q_{br2}$ non-measured by the instrument:

$$K=\frac{q_{conv}}{q_{br1}+q_{br2}} \tag{3}$$

The heat flow carried away by convection from the sensitive volume of the calorimetric cell [4]:

$$q_{\text{conv}} = 2\pi r_2 L\alpha (\overline{T}_{\text{c}} - T_{\text{sh}}) \tag{4}$$

where r_2 is the outer radius of the calorimetric cell; α is convective heat exchange factor; $\overline{T}_{\text{c}}$ is volume-averaged temperature of the sensitive volume of the calorimetric cell.

The heat flow carried away from the volume V_{br} through the cylindrical bridge 1 to the shield [4]:

$$q_{\text{br1}} = \frac{2\pi\lambda_{\text{br}} h(\overline{T}_{\text{br}} - T_{\text{sh}})}{\ln\dfrac{R_{\text{br}}}{r_2}} \tag{5}$$

where λ_{br} is thermal diffusivity of the material of the bridge; $\overline{T}_{\text{br}}$ is volume-averaged temperature of the cell containing a sample of volume V_{br}.

The heat flow carried away from the volume V_{br} to the heat-conducting bridge 2:

$$q_{\text{br2}} = q_{\text{cw1}} + q_{\text{liq1}} \tag{6}$$

where q_{cw1} is heat flow at the calorimetric cell wall from the volume V_{br} to the bridge 2; q_{liq1} is heat flow at the sample from the volume V_{br} to the heat-conducting bridge 2.

$$q_{\text{cw1}} = \frac{\pi(r_2^2 - r_1^2)\lambda_{\text{c}} (\overline{T}_{\text{br}} - T_{\text{sh}})}{d} \tag{7}$$

where λ_{c} is thermal diffusivity of the cell material; d is the distance between the volume V_{vr} and the bridge;

$$q_{\text{liq1}} \approx \frac{\pi r_1^2 \lambda_{\text{liq}} (\overline{T}_{\text{br}} - T_{\text{sh}})}{d} \tag{8}$$

where λ_{liq} is thermal diffusivity of the liquid.

Since the radius r_1 of the capillary is small, the heat transfer in the liquid by convection is not taken into consideration in the capillary.

Substituting Eqs (7) and (8) in (6) we obtain:

$$q_{\text{br2}} = \frac{\pi(\overline{T}_{\text{br}} - T_{\text{sh}})}{d}[(r_2^2 - r_1^2)\lambda_{\text{c}} + r_1^2 \lambda_{\text{liq}}] \tag{9}$$

Substituting Eqs (4), (5) and (9) in (3) we obtain:

$$K = \left[\frac{2r_2 L\alpha}{\dfrac{2\lambda_{\text{br}} h}{\ln\dfrac{R_{\text{br}}}{r_2}} + \dfrac{(r_2^2 - r_1^2)\lambda_{\text{c}} + r_1^2 \lambda_{\text{liq}}}{d}} \right] \frac{(\overline{T}_{\text{c}} - T_{\text{sh}})}{(\overline{T}_{\text{br}} - T_{\text{sh}})} \tag{10}$$

The relation of temperatures $\frac{(\overline{T}_c - T_{sh})}{(\overline{T}_{br} - T_{sh})}$ is evaluated taking into consideration the following reasons. Let us suppose in the first approximation that the temperature is distributed linearly along the sensitive volume of the calorimetric cell. In stationary mode, the heat flow carried away by convection from the working surface of the calorimetric cell is equal, at every moment, to the heat flow coming from the volume V_{br} into the sensitive volume of the calorimetric cell via the cell walls and the liquid sample, i.e.:

$$q_{conv} = q_{cw2} + q_{liq2} \tag{11}$$

where q_{cw2} represents the heat flow carried away from the volume V_{br} to the wall of the calorimetric cell through the sensitive volume V_c; q_{liq2} stands for the heat flow carried away from the volume V_{br} through the liquid sample to the sensitive volume V_c.

$$q_{cw2} \approx \frac{\pi(r_2^2 - r_1^2)\lambda_c(\overline{T}_{br} - \overline{T}_c)}{\frac{L}{2}} \tag{12}$$

$$q_{liq2} \approx \frac{\pi r_1^2 \lambda_{liq}(\overline{T}_{br} - \overline{T}_c)}{\frac{L}{2}} \tag{13}$$

Substituting Eqs (12) and (13) in (11) one obtains:

$$q_{conv} \approx \frac{2\pi(\overline{T}_{br} - T_c)}{L}[(r_2^2 - r_1^2)\lambda_c + r_1^2\lambda_{liq}] \tag{14}$$

Making Eqs (4) and (14) equal gives:

$$[(r_2^2 - r_1^2)\lambda_c + r_1^2\lambda_{liq}](\overline{T}_{br} - \overline{T}_c) = \alpha L^2 r_2(\overline{T}_c - T_{sh})$$

Transforming this equation one obtains:

$$\frac{(\overline{T}_c - T_{sh})}{(\overline{T}_{br} - T_{sh})} \approx \frac{1}{1 + \frac{\alpha L^2 r_2}{(r_2^2 - r_1^2)\lambda_c + r_1^2\lambda_{liq}}} \tag{15}$$

Substituting Eq. (15) in (10) gives a final formula for approximate estimation of K:

$$K \approx \left[\frac{2\alpha L r_2}{\frac{2\lambda_{br}h}{\ln\frac{R_{br}}{r_2}} + \frac{(r_2^2 - r_1^2)\lambda_c + r_1^2\lambda_{liq}}{d}}\right]\left[\frac{1}{1 + \frac{\alpha L^2 r_2}{(r_2^2 - r_1^2)\lambda_c + r_1^2\lambda_{liq}}}\right] \tag{16}$$

Substituting numerical values in Eq. (16): $\alpha \approx 2 \cdot 10^{-5}$ W mm^{-2} K^{-1} [4]; L=50 mm; h=8 mm; R_{br}=20 mm; r_2=0.6 mm; r_1=0.5 mm; λ_c=0.07 W mm^{-1} K^{-1} (platinum); λ_{br}=0.39 W mm^{-1} K^{-1} (copper); λ_{liq}=0.65 W mm^{-1} K^{-1} (water), one obtains the numerical value of $K \approx 1.4 \cdot 10^{-4}$.

Then we estimate the value of the factor K taking into consideration heat dissipation from the cell through the thermopile to the second cell and assuming its temperature equal to that of the shield T_{sh} (maximum heat dissipation).

In this case

$$q_{conv} \approx \alpha (\bar{T}_c - T_{sh}) 2L\pi r_2 + \frac{\pi r_{wire}^2 (\lambda_{const} + \lambda_{cop}) n (\bar{T}_c - T_{sh})}{l_{wire}} \tag{17}$$

where n stands for the number of branches of a copper-constantan measuring thermopile coupled between the cells; r_{wire} represents the wire radius of thermocouple branches; l_{wire} is the length of each thermopile branch; λ_{const} is Constantan thermal diffusivity; λ_{cop} is copper thermal diffusivity.

Making Eqs (14) and (17) equal, one obtains after transformation:

$$\frac{(\bar{T}_c - T_{sh})}{(\bar{T}_{br} - T_{sh})} = \frac{1}{1 + \dfrac{2l_{wire}\alpha L^2 r_2 + r_{wire}^2 (\lambda_{const} + \lambda_{cop}) nL}{2l_{wire}[(r_2^2 - r_1^2)\lambda_c + r_1^2 \lambda_{liq}]}} \tag{18}$$

Substituting Eqs (5), (9), (17), (18) in (3), one obtains after transformation:

$$K = \left[\frac{2\alpha L r_2 + \dfrac{n r_{wire}^2 (\lambda_{const} + \lambda_{cop})}{l_{np}}}{\dfrac{2\lambda_{br} h}{\ln \dfrac{R_{br}}{r_2}} + \dfrac{(r_2^2 - r_1^2)\lambda_c + r_1^2 \lambda_{liq}}{d}} \right] \left[\frac{1}{1 + \dfrac{2l_{wire}\alpha L^2 r_2 + nL r_{wire}^2 (\lambda_{const} + \lambda_{cop})}{2l_{wire}[(r_2^2 - r_1^2)\lambda_c + r_1^2 \lambda_{liq}]}} \right] \tag{19}$$

Substituting the above given numerical values in (19) as well as n=100; l_{wire}=6 mm; r_{wire}=0.025 mm; λ_{const} =0.021 W mm^{-1} K^{-1}; λ_{cop}=0.396 W mm^{-1} K^{-1}, one obtains the numerical value of $K \approx 1.7 \cdot 10^{-4} \approx 2 \cdot 10^{-4}$.

So, at L=50 mm, b=h=8 mm, using (1) one estimates the error of measuring thermal effect in the sensitive volume of the calorimetric cell V_c depending on the influence of the thermal effect in the volume V_{br}:

$$\delta \approx 2 \cdot 10^{-4} \frac{8}{50} 100\% \approx 0.003\%$$

Experimental

Figure 3 shows experimental data obtained after injecting a 2 μl dose of 5% C_2H_5OH aqueous solution into the working cell. The dispensing is performed by inserting the dispenser needle into the cell from its upper end. When translating the needle along the cell portion surrounded by the system heat-conducting bridges, energy released as a result of interaction between the titrant and the sample is not registered. After the needle attains the sensitive volume the calorimeter starts registering heat power the value of which increases as the needle penetrates the sensitive volume. The dispensing stops when the needle gets to the bottom of the calorimetric cell after which heat power becomes equal to zero. The upper curve obtained by differentiation of the lower curve allows to register with more accuracy the moment of commencement of heat power registration by the calorimeter. This moment corresponds to that of enter-

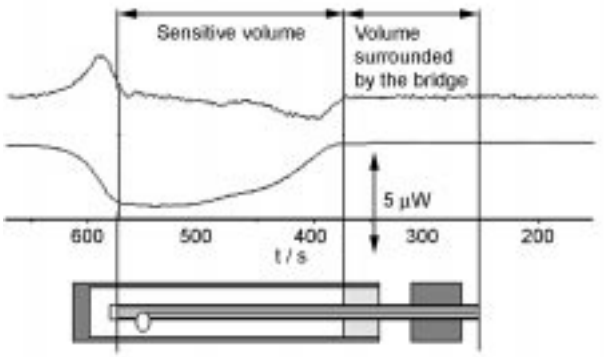

Fig. 3 Measured curve of heat power for interaction C_2H_5OH–water (higher curve represents a derivative of heat power curve; cell geometry is shown below)

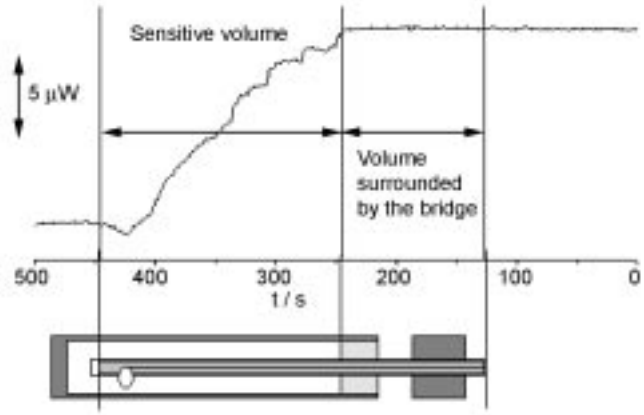

Fig. 4 Measured curve of heat power produced by a vibrating dispensing needle into the calorimetric cell (cell the geometry is shown below)

ing the sensitive volume by the needle. The fact of entering the sensitive volume by the needle is confirmed at a given moment by the translation value of the dispenser.

Figure 4 shows experimental data obtained after inserting a stirrer into one of the cells. This stirrer is represented by the needle itself of the dispenser. The needle performs induced oscillations at a frequency of the master oscillator. 10 Hz frequency is used in this experiment. This experiment repeats the technique of the above described experiment with C_2H_5OH. The data obtained confirm as well the fact of separating the calorimetric cell sensitive volume from the edge of the heat-conducting bridge 1 on the cell.

Results and discussion

The experimental results support the calculated value of the sensitive volume with an error of near one percent. The experimental results obtained should be considered as a first stage of experimental verification for the method described in the paper and we are planning to complete the experiments in future. We want to use for this most exact standard specimens as to the energy value in order to compare calculated and experimental values of the sensitive volume value on the base of energy value registered by the calorimeter. We believe as well we will be able to improve the accuracy of the methods applied at present and to improve essentially the accuracy of evaluating the sensitive volume.

Conclusions

A prototype of the differential titration calorimeter developed which implements the method of separating the sensitive volume in the calorimetric cells by means of heat-conducting bridges corroborated good prospects of this method. The calorimetric cells presented as thin capillary tubes allowed to have reduced size of heat-conducting bridges and to separate with high accuracy the sensitive volume in calorimetric cells of 78.5 μl. The calorimeter has modern level as to the main parameters.

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