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(54) Title: DIFFERENTIAL ADIABATIC SCANNING CALORIMETER

(57) Abstract: The present invention generally relates to a differential adiabatic scanning calorimeter (dASC) for simultaneous measurements of the temperature dependence of heat capacity and enthalpy of an unknown sample (liquid or solid) from a comparison with the heat capacity and enthalpy of another known sample (liquid or solid). In particular, the invention allows the determination of small differences in heat capacity and enthalpy of an unknown sample and of a known very similar reference sample. Moreover, the invention allows for an accurate separation between pre-transitional enthalpy variations and true latent heats at first- order or weakly first-order phase transitions of the unknown sample. In addition, the invention relates to calorimeters for controlling temperature differences and heat fluxes in different modes of operation.

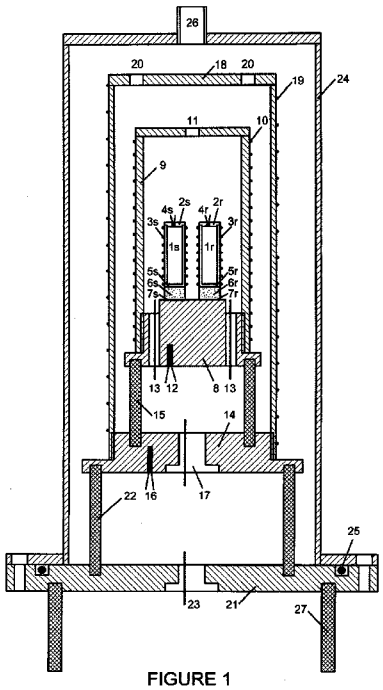

FIGURE 1

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DIFFERENTIAL ADIABATIC SCANNING CALORIMETER

Background of the invention

A. Field of the invention

The present invention generally relates to a differential adiabatic scanning calorimeter (dASC) for simultaneous measurements of the temperature dependence of heat capacity and enthalpy of an unknown sample (liquid or solid) from a comparison with the heat capacity and enthalpy of another known sample (liquid or solid). In particular, the invention allows the determination of small differences in heat capacity and enthalpy of an unknown sample and of a known very similar reference sample. Moreover, the invention allows for an accurate separation between pre-transitional enthalpy variations and true latent heats at first-order or weakly first-order phase transitions of the unknown sample. In addition, the invention relates to calorimeters for controlling temperature differences and heat fluxes in different modes of operation.

B. Description of the related art

Measurements of the heat capacity and enthalpy changes play an important role in monitoring the energy content of condensed matter systems. As such calorimetry is an indispensable technique for many scientific fields. Depending on the application envisioned several different technical approaches with varying degrees of accuracy and precision have been developed. Over wide temperature ranges generally the classical Nernst heat pulse method is used.[1] During the last 50 years several new approaches, supported to a large extent by novel developments in electronic measurements instrumentation, have emerged, e.g. differential scanning calorimetry (DSC),[2,3] scanning transitiometry[4-6] and modulation techniques like ac calorimetry[7,8], the 3ω method[9] and more recently photoacoustic and photopyroelectric techniques,[10] Peltier ac and Peltier tip calorimetry,[11,12] Peltier heat-flow and modulated bath ac calorimetry.[13,14]

A novel development beyond classical adiabatic heat pulse calorimetry, took place at the end of the 1960s when Australian scientists[15-17] imposed a very slow constant heating (or cooling) rate on the thermal shield (in a classical type adiabatic calorimeter) surrounding the sample cell and the cell was forced to follow with the same rate. By measuring the imposed rate and the power applied (heating) to or extracted (cooling) from the cell, the heat capacity C is readily obtained from

$$C = T\frac{dS}{dT} = \frac{dQ}{dT} = \frac{dQ/dt}{dT/dt} = P/\dot{T}, \qquad (1)$$

with S the entropy, T the temperature, dQ the supplied heat, t the time, P the supplied power and $\dot{T}$ the temperature scanning rate. If one considers the shield (forced to change its temperature at constant $\dot{T}$) as the reference 'sample', the setup is conceptually identical to the (power compensated) differential scanning calorimeter. There are, however, basic differences in design principles and area of applications. The DSC is very useful for many (material science) applications when the (total) energy change of a transition is of greater interest than the detailed form of the specific heat or enthalpy curve (near phase transitions). A commercial DSC (or modulated DSC) generally does not yield accurate absolute values of

specific heat and by using high scanning rates (typically above 0.2 Ks^{-1} to have a reasonable sensitivity) quite often operate out of thermodynamic equilibrium, in particular near fluctuations dominated phase transitions. Moreover, with DSC it is often not possible to discriminate between second-order (continuous) phase transitions and (weakly) first-order ones.[18] Many of the limitations of DSCs have been eliminated in scanning transitiometry by imposing very slow constant scanning rates in a high precision differential concept[4-6]. However, imposing constant rates in this approach remains a basic problem for high-resolution work at and near (weakly) first-order transitions. Buckingham and coworkers called their apparatus a high precision scanning ratio calorimeter (for use near phase transitions).[17] In order to cope with the critical slowing down near the investigated liquid-gas critical point, they imposed constant scanning rates as low as 10^{-6} Ks^{-1}. In the mid 1970s a group at the Catholic University of Leuven (Belgium) built a four stage scanning calorimeter to measure with high resolution the heat capacity (at constant pressure) near critical (consolute) points of binary and ternary liquid mixtures.[19-22] The construction of that calorimeter was such that in addition to different scanning modes it could also be used as a classical step calorimeter. It was also realized that near phase transitions and critical points it would be much easier to cope with the critical slowing down and the large increase of the heat capacity and possible latent heats, by imposing a constant heating or cooling power to the sample and determine the rate instead of imposing a constant heating or cooling rate as was done before, i.e. keeping P constant and not $\dot{T}$ in Equation (1).[20,21] In fact, this change in operation mode is essential for the proper investigation of (weakly) first-order phase transtions.[23,24] It is quite straightforward to show that the direct experimental results of the (constant) power P and the temperature $T(t)$ of the sample as a function of the time t (since the start of the run at $T(t_0)$) yields the temperature dependence of the enthalpy (including a value of the latent heat when present) by

$$H(T) = H(T_0) + P(t - t_0) \tag{2}$$

Around that time, calorimeters similar to the Leuven adiabatic scanning type calorimeter were developed by other groups as well. In 1980 Würz and Grubić[25] described a three-stages adiabatic calorimeter of the scanning ratio type and did measurements at constant scanning rates of 128.8 and 6.98 μKs^{-1} near a liquid-liquid critical point. Junod[25] described a setup with a continuous adiabatic (scanning) method for the graphical recording of the heat capacity of solids over the temperature range between 80 K to 320 K at moderate to fast scanning rates (typically, around 10 mKs^{-1}). A microcomputer controlled ASC type apparatus for solid samples was described in a paper of 1981.[27] After the introduction of adiabatic scanning calorimetry (ASC) for first-order and second-order phase transition studies in liquid crystals[23,24] it was also used for liquid crystal studies by Anisimov and coworkers.[28] Bessergenev et al. used different ASC modes of operation to study first-order and second-order transitions in rear earth metals.[29] Lysek et al. described a scanning ratio calorimeter (at rates of about 1 mKs^{-1}) for use in adsorption studies.[30] An ASC technique similar to the Leuven one was used by Sirota to study phase transitions and super-cooling of normal alkanes.[31,32] Schnelle and Gmelin introduced a high resolution ASC for small (solid) samples.[33] Moon and Yeong proposed, in 1996, a so-called rate-scanning modified adiabatic calorimeter (MAC) (with scanning rates between 0.2 mKs^{-1} and 30 mKs^{-1}).[34,35] However, their setup is operationally the same as the previously well-established standard ASCs as used by several other groups. An ASC similar to the Leuven one for the study of liquid-liquid critical points was built by Jacobs and collaborators.[36]

An essential requirement of a high-resolution adiabatic calorimeter operating in the heating mode is the equality (better than one mK) of the temperatures of the sample and the surrounding thermal shield. For operations in the cooling mode a constant preset temperature difference between the sample and the shield has to be maintained within the same stability limits. This is presently achieved using thermistors as highly sensitive resistance thermometers placed on the sample and on the shield. Before these sensors can be used, time consuming extensive calibrations (against reference thermometers) have to be executed. Moreover, the temperature coefficients of the resistance of two thermistors do never perfectly match. Via hardware adaptations in the measuring circuits[23] or in software modifications of the calibration curves, one can partly correct for it. In a previous invention[37]these problems are completely eliminated by inserting between the sample and the shield a very sensitive (of the order of 0.1V/K) semi-conductor materials based Peltier element (PE), either a Peltier cooler or Peltier thermogenerator, which are commercially available. The μK sensitivity of the PE for temperature differences allows in combination with proper servo-systems (hardware or software) to maintain almost perfect equality of the sample and shield temperatures in the heating mode. For the cooling mode a preset temperature difference between sample and shield can be kept constant with equal resolution.

Summary of the invention

The present invention builds on and extends the solutions of the previous invention[37] to the problems of the related art by introducing a differential adiabatic scanning calorimeter (dASC) for simultaneous measurements and comparison of heat capacity and enthalpy of an unknown (liquid or solid) sample from a comparison with the heat capacity and enthalpy of another known reference sample (liquid or solid) over broad temperature ranges (typically 100K) in accurately controlled scanning modes by introducing sensitive Peltier elements in the temperature and scanning rate control of the different samples and stages in the calorimeter. In particular, the invention allows the determination of small differences in heat capacity and enthalpy between an unknown sample and a known very similar reference sample. In its major operational modes the dASC imposes a constant (heating or cooling) power P_s on the sample (s) and imposes (using sensitive Peltier elements) equality of the (changing) rates $\dot{T}_s$ and $\dot{T}_r$ of the unknown sample (s) and of the reference (r) by adjusting the power P_r to the reference. This is exactly the opposite of what is done in transitiometry or DSC calorimetry, whether or not in an adiabatic environment for the sample and reference cells[38]. This can for the heat capacity C be easily seen from Eq. (1) for the sample (index s) and the reference (index r):

$$C_s = \frac{P_s}{\dot{T}_s}, \tag{3}$$

$$C_r = \frac{P_r}{\dot{T}_r}. \tag{4}$$

Imposing a known constant power P_s to the sample modify (and measure) P_r in such a way that at all times $\dot{T}_r = \dot{T}_s$ results in:

$$C_s = \frac{P_s}{P_r} C_r. \tag{5}$$

Thus from the imposed and known P_s and the measured P_r the temperature dependence of $C_s(T)$ is obtained from the known temperature dependence $C_r(T)$ of the reference. An

analoguous expression for the enthalpy can be derived from Eq. (2). By choosing $H(T_0)$=0 at t_0 =0 one has:

$$H_s(T) = \int_0^{t(T)} P_s(t)dt \quad (6)$$

$$H_r(T) = \int_0^{t(T)} P_r(t)dt \quad (7)$$

Since $T(t)$, P_s (imposed constant) and P_r can be measured at the same time, one has:

$$H_s(T) = H_r(T)t(T)P_s / \int_0^{t(T)} P_r(t)dt \quad (8)$$

In accordance with the purpose of the invention, as embodied and broadly described herein, the invention is broadly drawn to eliminate problems with keeping temperature differences between an investigated sample material and a reference sample and a surrounding thermal (adiabatic) shield zero or at a preset fixed value during temperature scanning over broad ranges without approximations and lengthy sensor calibrations with the previous art. Moreover, since the heat capacity and enthalpy of the sample are at each temperature directly linked to the same quantities of the reference sample via the measurement of P_s and P_r, there is no need for high-resolution determination of the rate $\dot{T}_s$ (or $\dot{T}_r$). However, these rates can be obtained and if desired used for control purposes.

In one aspect of the invention it is possible in the two principal (heating or cooling) scanning modes of operation of the calorimeter to simultaneously arrive at accurate and detailed information on the temperature dependence of the heat capacity and enthalpy of an unknown sample by delivering constant heating or cooling power to the sample and by adjusting and measuring the changing power to a reference sample and by Peltier element based control of the temperature of the thermal shield and of the reference sample. The thus operated calorimeter allows for a clear separation of pretransitional enthalpy increases and true latent heats at (weakly) first-order transitions and precise characterization of heat capacity anomalies at second-order phase transitions in a sample from comparison with a reference sample.

Another aspect of the calorimeter is the possibility to operate, besides in the above mentioned principal modes, in several other more conventional or unconventional ways, as e.g. in DSC-like constant heating or cooling rate modes, as a classical (Nernst-type) heat pulse step calorimeter. Still another aspect of the invention is the versatility in arranging the sample (liquid or solid) and the reference configurations to adapt to the chosen scanning modes.

In still another aspect of the invention, the full implementation of programmable electronic measurement and control equipment connected to a personal computer allows full software choice of operational modes, long term independent operation and extensive data analysis.

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this

detailed description. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention.

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Detailed description of embodiments of the invention

The following detailed description of the invention refers to the accompanying drawings. The same reference numbers in different drawings identify the same or similar elements. Also, the following detailed description does not limit the invention. Instead, the scope of the invention is defined by the appended claims and equivalents thereof.

Legend to the graphics of the application

Figure 1 shows diagrammatically an elevational front view of an exemplary embodiment of a Peltier elements based differential adiabatic scanning calorimeter (dASC) for simultaneous measurements of the heat capacity and enthalpy of an unknown sample (liquid or solid) from a comparison with a reference sample (liquid or solid). Separate elements have been numbered and the numbers have been identified hereunder in the description.

Figure 2 represents in the top part diagrammatically an enlarged elevational front view of part of the calorimeter with the (typically liquid) sample [1s], sample holder [2s], heater [3s], temperature sensor [4s] on the sample holder [2s], Peltier element [6s], top [5s] and bottom [7s] plates of the Peltier element [6s], and part of the shield bottom [8] with shield temperature sensor [12]. The bottom part of figure 2 gives diagrammatically an enlarged elevational front view of part of the calorimeter with the (typically liquid) reference sample [1r], reference sample holder [2r], heater [3r], temperature sensor [4r] on the reference sample holder [2r], Peltier element [6r], top [5r] and bottom [7r] plates of the Peltier element [6r], and part of the shield bottom [8] with shield temperature sensor [12].

Figure 3 represents in the top part diagrammatically an enlarged elevational front view of part of the calorimeter with a solid sample [1s], (film) heater [3s] on the sample [1s], (surface) temperature sensor [4s] on the sample [1s], Peltier element [6s], top [5s] and bottom [7s] plates of the Peltier element [6s], and part of the shield bottom [8] with shield temperature sensor [12]. The bottom part of figure 3 diagrammatically gives an enlarged elevational front view of part of the calorimeter with a solid reference sample [1r], heater [3r] on the reference sample [1r], temperature sensor [4r] on the reference sample [1r], Peltier element [6r], top [5r] and bottom [7] plates of the Peltier element [6r], and part of the shield bottom [8] with shield temperature sensor [12].

Figure 4 represents in the top part diagrammatically an enlarged elevational front view of part of the calorimeter with the (liquid or solid) sample [1s], sample holder [2s], adapter piece [28s] with heater [3s] and temperature sensor [4s], Peltier element [6s], top [5s] and bottom [7s] plates of the Peltier element [6s], and part of the shield bottom [8] with shield temperature sensor [12]. The bottom part of figure 4 represents diagrammatically an enlarged elevational front view of part of the calorimeter with the (liquid or solid) reference sample [1r], sample holder [2r], adapter piece [28r] with heater [3r] and temperature sensor [4r], Peltier element [6r], top [5r] and bottom [7r] plates of the Peltier element [6r], and part of the shield bottom [8] with shield temperature sensor [12].

Figure 5 gives in a schematic representation of the different building blocks used for the proper implementation of the different exemplary modes of operation and of the measurements of the necessary parameters to arrive at the calculation of the temperature dependence of the heat capacity and enthalpy via equations (5) to (8).

Description of a preferred exemplary embodiment

Referring now specifically to the drawings, a Peltier elements based differential adiabatic scanning calorimeter for simultaneous measurements and comparison of heat capacity and enthalpy of an unknown sample (liquid or solid) and of a reference sample (liquid or solid) according to a preferred exemplary embodiment of the present invention is illustrated in figure 1, and partly in figure 2. In one part (on the left in the drawing) of the middle of the calorimeter a sample [1s] is contained in a good thermal conducting (e.g. metal) sample holder [2s] containing a heating element [3s] (e.g. heating wire or thin-film heater) and a sensitive temperature sensor [4s] (e.g. a thermistor or a platinum resistance thermometer). A Peltier element is arranged to geometrically position between said at least one plate that contacts the sample holder and at least one plate that contacts the shield for instance the shield bottom [8]. Depending upon the orientation and position, in a logical special orientation of the apparatus as displayed in the figures 1 to 4 (hereby not limiting the invention to a certain special position and proposing the position of the entire apparatus to be exemplary only), the sample holder [2s] is positioned in good thermal contact with the top plate [5s] of the Peltier element [6s]. Good thermal contact can e.g. be achieved by soldering, with good thermal conductive varnish, epoxy or paste. For ease of removal of the sample holder thermal paste can preferentially be used. The base plate [7s] of the Peltier element is also positioned in good thermal contact with the shield bottom [8]. Good thermal contact can e.g. be achieved by soldering, with good thermal conductive varnish, epoxy or paste. In another part (on the right in the drawing) of the middle of the calorimeter a reference sample [1r] is contained in a good thermal conducting (e.g. metal) sample holder [2r] containing a heating element [3r] (e.g. a heating wire or a thin-film heater) and a sensitive temperature sensor [4r] (e.g. a thermistor or a platinum resistance thermometer). A Peltier element is arranged to geometrically position between said at least one plate that contacts the sample holder and at least one plate that contacts the shield for instance the shield bottom [8]. Depending upon the orientation and position, in a logical special orientation of the apparatus as displayed in the figures 1 to 4 (hereby not limiting the invention to a certain special position and proposing the position of the entire apparatus to be exemplary only), the sample holder [2r] is positioned in good thermal contact with the top plate [5r] of the Peltier element [6r]. Good thermal contact can e.g. be achieved by soldering, with good thermal conductive varnish, epoxy or paste. For ease of removal of the sample holder thermal paste can preferentially be used. The base plate [7r] of the Peltier element is also positioned in good thermal contact with the shield bottom [8]. Good thermal contact can e.g. be achieved by soldering, with good thermal conductive varnish, epoxy or paste. As examples of Peltier elements, but not exclusively or limiting, commercially available Peltier Elements of Thermion Company (Odessa, Ukraine) and thin Film Peltier Coolers or thin Film Thermogenerators of Micropelt (Freiburg, Germany) can be and have been used. The shield top [9] around the central part of the calorimeter is in very good thermal contact with the shield bottom [8] by a sufficiently long screw thread. The shield top [9] has a heater [10] incorporated in the wall. A small hole [11] in the shield is present for possible evacuation or as inert gas inlet. The shield also has its own temperature sensor [12]. The shield bottom also has the necessary electrical feed-troughs [13]. The first shield bottom [8] rests on the bottom [14] of a second shield and is thermally insulated by typically three thin rods or tubes [15]

with very high thermal resistances. The second shield bottom [14] contains also a temperature sensor [16] and (multipin) electrical feed-troughs [17]. In the top part of the second shield [18] a heater [19] is also incorporated. In the shield wall there are also a few holes [20] for evacuation, or for inert gas inlet. The top [18] and bottom [14] of the second shield are in very good thermal contact by means of a sufficiently long screw thread. The second shield bottom rests on the bottom [21] of a third shield (outer can) and is thermally insulated by typically three thin rods or tubes [22] with very high thermal resistances. The third shield bottom [21] contains vacuum-tight multipin electrical feed-troughs [23]. The top [24] of the third outer shield and bottom [21] can be vacuum-tightly closed by means of screws and an O-ring [25] in a groove of the bottom [21]. The third shield top [24] (or alternatively shield bottom [21]) contains a connecting tube [26] to a vacuum pumping system or to an inert gas inlet system. The bottom of the third (outer) shield [21] is supported by typically three thin rods or tubes [27] with very high thermal resistance. This allows the calorimeter to be place on a table top and if desired surrounded with insulating material. In an alternative exemplary setup the calorimeter is placed in a temperature controlled chamber (stability around ±0.1 K) equipped with heating and cooling units allowing measurements between -60 °C and 150 °C. Lower cryogenic temperatures (e. g. to -200 °C) can be achieved by minor design changes and incorporation of the calorimeter in a Dewar system. Proper choice of Peltier elements allows temperatures up to above 200 °C.

Figure 2 gives in the top part a more detailed view of a possible sample cell [2s] with heater [3s] and temperature sensor [4s] and with inside a sample [1s] (typically a liquid), on top of the top plate [5s] of the Peltier element [6s]. The bottom plate [7s] of the Peltier element [6s] is placed on top of (part of) the bottom [8] of the first shield with the temperature sensor [12] also indicated. The bottom part of figure 2 gives a more detailed view of a possible (nearly identical) reference cell [2r] with heater [3r] and temperature sensor [4r] and with inside a reference sample [1r] (typically a liquid), on top of the top plate [5r] of the Peltier element [6r]. The bottom plate [7r] of the Peltier element [6s] is placed on top of (part of) the bottom [8] of the first shield with the temperature sensor [12] also indicated.

Figure 3 gives in the top part a more detailed view of an alternative embodiment for a solid sample [1s] directly placed on top of the top plate [5s] of the Peltier element [6s]. A heater [3s] and a temperature sensor [4s] are directly attached to the sample [1s]. The bottom plate [7s] of the Peltier element [6s] is placed on top of (part of) the bottom [8] of the first shield with the temperature sensor [12] also indicated.The bottom part of figure 3 gives a more detailed view of an alternative embodiment for a solid reference sample [1r] directly placed on top of the top plate [5r] of the Peltier element [6r]. A heater [3r] and a temperature sensor [4r] are directly attached to the reference sample [1r]. The bottom plate [7r] of the Peltier element [6r] is placed on top of (part of) the bottom [8] of the first shield with the temperature sensor [12] also indicated.

Figure 4 gives in the top part a more detailed view of an alternative embodiment for easy sample [1s] and sample holder [2s] replacement and no need for heater [3s] or sensor [4s] removal. On the top plate [5s] of the Peltier element [6s] an adapter piece [28s] of a highly thermal conducting material (e. g. aluminium, silver, copper) is fixed. This adapter piece contains an (embedded) temperature sensor [4s] and a (thin film) heater [3s]. The sample [1s] (solid or liquid) is contained in a (thin) small sample holder [2s] consisting of a cup [29s] and a lid [30s] made of thin (soft) metal sheet. The cup [29s] and the lid can be pressure closed. The sample holder cup [29s] fits tightly in the cavity [31s] of the adapter piece [28s]. Thermal contact between the sample holder cup [29s] and the adapter piece

[28s] can be further improved by using (a minute quantity of) thermal conducting paste. The bottom part of figure 4 gives a more detailed view of an alternative embodiment for easy reference sample [1r] and sample holder [2r] replacement and no need for heater [3r] or sensor [4r] removal. On the top plate [5r] of the Peltier element [6r] an adapter piece [28r] of a highly thermal conducting material (e. g. aluminium, silver, copper) is fixed. This adapter piece contains an (embedded) temperature sensor [4r] and a (thin film) heater [3r]. The reference sample [1r] (solid or liquid) is contained in a (thin) small sample holder [2r] consisting of a cup [29r] and a lid [30r] made of thin (soft) metal sheet. The cup [29r] and the lid can be pressure closed. The sample holder cup [29r] fits tightly in the cavity [31r] of the adapter piece [28r]. Thermal contact between the sample holder cup [29r] and the adapter piece [28r] can be further improved by using (a minute quantity of) thermal conducting paste.

Description of the exemplary operational modes and measurement control.

In this part we refer, in addition to the drawings of figures 1 to 4, also to the drawings of figure 5. The same reference numbers in the different drawings of the different figures identify the same or similar elements. The modes 1 and 2 below are the principal operational modes but several other operational modes are possible and described.

Mode 1) A first mode of operation of the calorimeter is at (known) constant heating power P_s delivered to the heater [3s] on the sample holder [2s] (in figures 1 and 2), or directly on the sample [1s] (in figure 3), or on the adapter piece [28s] (in figure 4), while a zero or negligibly temperature difference with the bottom [8] and top [9] of the first shield is implemented. The desired power is delivered by a DC current source [32s] under the control, via a GPIB link [33] or equivalent, of a software program implemented on a personal computer (PC) [34]. The accurate value of the power P_s is measured by voltage measurements over the resistive heater [3s] and over a reference resistor [35s] in series with the heater by means of a high-resolution digital multimeter (DMM) [36] equipped with a multiplexer [37]. The negligible temperature difference between sample and first shield is achieved by a software PID control program unit on the PC [34] directing (via the GPIB link [33] or equivalent) the programmable power supply [38] to deliver the necessary heating power to the shield heater [10] in order to keep the output voltage of the Pelier element [6s], measured with the DMM [36], always zero during the (scanning) heating run. For stability reasons a different PID control program unit on the PC [34] directs a different programmable power supply [39] to deliver the necessary power to the heater [19] in order to keep the temperature of the second shield top [18] and bottom [14] a few tenths of a degree below that of the first shield [8] and [9]. The temperature difference is obtained from the resistance measurements, with the DMM [36], of the calibrated temperature sensors [12] and [16]. For very high resolution and stability of a run the whole calorimeter is placed in a closed chamber [40] equipped with an externally addressable (by the PC [34] via the GPIB link [33]) temperature controlling unit. The temperature of the chamber is controlled in such a way that a fixed temperature difference of a few degrees is maintained between the temperature of the second shield [14], [19] and the temperature of the outer (third) shield [24]. During the whole run the resistance of the calibrated temperature sensor [4s] (in good thermal contact with the sample [1]) is measured almost continuously every few seconds with the commercial high resolution digital multimeter [34] (typically 7 or 8 digits resolution). The measured resistance data are converted to temperature and stored together with the measured heating power values. During the entire run the voltage output of the Peltier element [6r], measured with the DMM [36], is kept zero by applying the appropriate

heating power P_r to the heater [3r] on the reference sample holder [2r] (in figures 1 and 2), or directly on the reference sample [1r] (in figure 3), or on the adapter piece [28r] (in figure 4). This ensures at all times $T_r(t) = T_s(t)$ and $\dot{T}_r = \dot{T}_s$. The desired power is delivered by a DC current source [32r] under the control, via a GPIB link [33] or equivalent, of a software program implemented on a personal computer [34]. The accurate value of P_r as a function of time is measured by voltage measurements over the resistive heater [3r] and over a reference resistor [35r] in series with the heater, by means of a high-resolution, digital multimeter (DMM) [36] equipped with a multiplexer [37]. The recorded data of $T_r(t) = T_s(t)$, $P_s(t)$ and $P_r(t)$ allow with equation (5) to derive $C_s(T)$ of the sample as a function of $C_r(T)$ of the reference. Likewise equations (7) and (8) allow one to derive $H_s(T)$ of the sample as a function to $H_r(T)$ of the reference.

Mode 2) A second mode of operation of the calorimeter is at constant cooling power P_s. This is achieved by starting at a desired high temperature and setting and keeping the temperature of the first shield top [9] and bottom [8] always a chosen ΔT (depending on the desired cooling rate) below that of the sample holder [2s] and/or sample [1s]. The sample holder and/or sample will cool down mainly by thermal conduction through the Peltier element [6s] and also by heat exchange with the first shield through radiation and gas conduction (when present). Keeping ΔT between sample and first shield constant by a given negative output voltage of the Peltier element [6s] by the software PID control program unit on the PC [34] (controlling the temperature of the first shield) results (with proper calibration) in constant cooling power runs. The temperatures of the second and third shield are controlled in the same way as for the constant heating power mode. The heaters on the sample [1s] or the holder [2s] or adapter piece are not in use in this cooling mode 2. During the whole run the resistance of the temperature calibrated temperature sensor [4s] (in good thermal contact with the sample [1s]) is measured almost continuously every few seconds with the commercial high resolution digital multimeter [36] (typically 7 or 8 digits resolution). The measured resistance data are converted to temperature and stored by the PC [34]. During the entire run the voltage output of the (identical) Peltier element [6r], measured with the DMM [36], is kept at the same value as set for the Peltier element [6s] by applying the appropriate heating power P_r to the heater [3r] on the reference sample holder [2r] (in figures 1 and 2), or directly on the reference sample [1r] (in figure 3), or on the adapter piece [28r] (in figure 4). This ensures at all times $T_r(t) = T_s(t)$ and $\dot{T}_r = \dot{T}_s$. The desired power is delivered by a DC current source [32r] under the control, via a GPIB link [33] or equivalent, of a software program implemented on a personal computer [34]. The accurate value of P_r as a function of time is measured by voltage measurements over the resistive heater [3r] and over a reference resistor [35r] in series with the heater, by means of a high-resolution, digital multimeter (DMM) [36] equipped with a multiplexer [37]. The recorded data of $T_r(t) = T_s(t)$, $P_s(t)$ and $P_r(t)$ allow with equation (5) to derive $C_s(T)$ of the sample as a function of $C_r(T)$ of the reference. Likewise equations (7) and (8) allow one to derive $H_s(T)$ of the sample as a function to $H_r(T)$ of the reference.

Mode 3) Instead of carrying out heating runs with constant heating power (mode 1) it is also possible to do runs at constant (or nearly constant) heating rate $\dot{T}_r = \dot{T}_s$. (as in a heating run in a DSC). In this mode, a constant power P_r is delivered by the power supply [32r] to the heater [3r] on the reference sample holder [2r] (figures 1 and 2), or directly on the reference sample [1r] (in figure 3), or on the adapter piece [28r] (in figure 4). The temperature difference between the sample, the reference and the first shield is kept zero by controlling the voltage output of the Peltier element [6r] to zero at all times by adjusting the current

delivered by the power supply [38] to the heater [10]. The settings for the second shield and for the T-controlled chamber [40] containing the calorimeter are as for mode 1. During the entire run the voltage output of the Peltier element [6s], measured with the DMM [36], is kept zero by applying the appropriate heating power P_s to the heater [3s] on the sample holder [2s] (in figures 1 and 2), or directly on the sample [1s] (in figure 3), or on the adapter piece [28s] (in figure 4). This ensures at all times $T_r(t) = T_s(t)$ and $\dot{T}_r = \dot{T}_s$. The desired power is delivered by a DC current source [32s] under the control, via a GPIB link [33] or equivalent, of a software program implemented on a personal computer [34]. The accurate value of P_s as a function of time is measured by voltage measurements over the resistive heater [3s] and over a reference resistor [35s] in series with the heater, by means of a high-resolution, digital multimeter (DMM) [36] equipped with a multiplexer [37]. The recorded data of $T_r(t) = T_s(t)$, $P_s(t)$ and $P_r(t)$ allow with equation (5) to derive $C_s(T)$ of the sample as a function of $C_r(T)$ of the reference. Likewise equations (7) and (8) allow one to derive $H_s(T)$ of the sample as a function to $H_r(T)$ of the reference.

Mode 4) Instead of carrying out cooling runs with constant cooling power (mode 2) it is also possible to do runs at a constant cooling rate $\dot{T}$ (similar to a cooling run in a DSC). In this mode the temperature of the second shield is kept at a fixed difference below that of the first one. The temperature of the (cooling) reference is maintained a constant value ΔT above that of the first shield by controlling the voltage output of the Peltier element [6r] to a chosen fixed value at all times by adjusting the current delivered by the DC current source [32r] to the heater [3r]. The settings of the T-controlled chamber [40] containing the calorimeter are as for mode 2. During the entire run the voltage output of the (identical) Peltier element [6s], measured with the DMM [36], is kept at the same value as set for the Peltier element [6r] by applying the appropriate heating power P_s to the heater [3s] on the sample holder [2s] (in figures 1 and 2), or directly on the sample [1s] (in figure 3), or on the adapter piece [28s] (in figure 4). This ensures at all times $T_r(t) = T_s(t)$ and $\dot{T}_r = \dot{T}_s$. The desired power is delivered by a DC current source [32s] under the control, via a GPIB link [33] or equivalent, of a software program implemented on a personal computer [34]. The accurate value of P_s as a function of time is measured by voltage measurements over the resistive heater [3s] and over a reference resistor [35s] in series with the heater, by means of a high-resolution, digital multimeter (DMM) [36] equipped with a multiplexer [37]. The recorded data of $T_r(t) = T_s(t)$, $P_s(t)$ and $P_r(t)$ allow with equation (5) to derive $C_s(T)$ of the sample as a function of $C_r(T)$ of the reference. Likewise equations (7) and (8) allow one to derive $H_s(T)$ of the sample as a function to $H_r(T)$ of the reference.

It will be apparent to those skilled in the art that various modifications and variations can be made in *the choice of the type and numbers of Peltier elements and in its implementation in the calorimeter and in using different numbers of shields and their temperature measurements and control approaches* of the present invention and in construction of the system and method without departing from the scope or spirit of the invention. Examples of such modifications have been previously provided.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

DIFFERENTIAL ADIABATIC SCANNING CALORIMETER

Claims

1. A differential adiabatic scanning calorimeter apparatus comprising a Peltier element [6s] and a sample [1s] on the sample holder [2s], a heater [3s], and another Peltier element [6r] and a reference sample [1r] on the reference sample holder [2r], another heater [3r], at least one thermal or adiabatic shield [24] surrounding the sample [1s] (or sample holder [2s]) and the reference sample [1r] (or the reference sample holder [2r]).

characterized in that

the differential adiabatic scanning calorimeter is adapted for simultaneous measurements of the temperature dependence of heat capacity and enthalpy of solid or liquid samples [1s] and phase transitions therein by a Peltier element [6s], used as a differential thermometer, which is placed between the sample or sample holder and the shield and makes mechanical and thermal contacts with the sample or sample holder and the shield so that a constant preset temperature difference (e.g. fixed temperature difference of a few tenths of a degree) or a zero difference between the sample or sample holder and the shield is maintained and another Peltier element [6r], used as a differential thermometer, which is placed between the reference sample or reference sample holder and the shield and makes mechanical and thermal contacts with the reference sample or reference sample holder and the shield so that a constant pre-set temperature difference (e.g. fixed temperature difference of a few tenths of a degree) or a zero difference between the reference sample or reference sample holder and the shield is maintained.

2. The apparatus of claim 1, whereby the Peltier element [6s] is arranged to geometrically position between said at least one plate that contacts the sample [1s] or sample holder [2s] or adaptor piece [28s] and at least one plate that contacts the shield [24] for instance the shield bottom [8], and whereby the Peltier element [6r] is arranged to geometrically position between said at least one plate that contacts the reference sample [1r] or reference sample holder [2r] or adaptor piece [28r] and at least one plate that contacts the shield [24] for instance the shield bottom [8].
3. The apparatus of claim 1, whereby the sample holder [2s] is positioned in thermal conductive contact with a top plate [5s] of the Peltier element [6s] and the base plate [7s] of the Peltier element [6s] is also positioned in thermal contact with the shield bottom [8], and whereby the reference sample holder [2r] is positioned in thermal conductive contact with a top plate [5r] of the Peltier element [6r] and the base plate [7r] of the Peltier element [6r] is also positioned in thermal contact with the shield bottom [8].
4. The apparatus of any of the claims 1 to 3, whereby the Peltier elements, when in operation, act as a differential thermometer for controlling the temperature and the scanning rate of the different stages in the calorimeter.
5. The apparatus of any of the claims 1 to 4, whereby a sample holder [2s] comprises at least one temperature sensor [4s] on the sample holder [2s] and whereby a reference sample holder [2r] comprises at least one temperature sensor [4r] on the reference sample holder [2r].
6. The apparatus of any of the claims 1 to 4, whereby at least one thermal or adiabatic shield [24] surrounding a sample or sample holder and a reference sample and reference sample holder comprises at least one temperature sensor [12] on the shield [24].

7. The apparatus of any of the previous claims, whereby the shield sensor is in the shield or shield bottom [8].
8. The apparatus of any of the previous claims, which is a differential adiabatic scanning type calorimeter (ASC).
9. The apparatus of any of the previous claims 1 to 8, whereby the active devices are differential detector thermocouples.
10. The apparatus of claim 9, whereby the Peltier elements or Peltier diodes are provided with either cooler or thermogenerator function.
11. The apparatus of claim 9, whereby the Peltier elements or Peltier diodes or thermopiles are zero instruments.
12. The apparatus of any of the previous claims, whereby the mechanical contact is for heat transfer.
13. The apparatus of any of the previous claims, whereby the temperature sensors are thermistors.
14. The apparatus of any of the previous claims, whereby the temperature sensors are Platinum resistance thermometers.
15. The apparatus of any of the previous claims, whereby at least one temperature sensor is placed on an adaptor piece and on the shield.
16. The apparatus of any of the previous claims, where the sample is a liquid in a sample holder.
17. The apparatus of any of the previous claims, where the reference sample is a liquid in a reference sample holder.
18. The apparatus of any of the previous claims, where the sample is a solid in a sample holder or in direct thermal contact with the Peltier element.
19. The apparatus of any of the previous claims, where the reference sample is a solid in a reference sample holder or in direct thermal contact with the Peltier element.
20. The apparatus of any of the previous claims, where the sample holder is placed in an adaptor piece.
21. The apparatus of any of the previous claims, where the reference sample holder is placed in an adaptor piece.
22. The apparatus of any of the previous claims, whereby the apparatus is provided with a controller with servo systems (hardware or software) to maintain almost perfect equality of the sample, the reference sample and shield temperatures in the heating mode based on the readings of the Peltier elements.
23. The apparatus of any of the previous claims, whereby when operational the controller and the Peltier element keep the temperature differences between an investigated sample (or a reference sample) and a surrounding thermal or adiabatic shield zero or at a preset fixed value during temperature scanning over broad ranges without the need to rely on approximations and calibrations of the separate temperature sensors.
24. The apparatus of any of the previous claims, whereby the temperature difference between sample and shield can be kept constant.
25. The apparatus of any of the previous claims, whereby the temperature difference between reference sample and shield can be kept constant.
26. The apparatus of the previous claims, whereby when operational a Peltier element keeps the temperature difference between the shield and the sample that is analyzed on zero or at a constant temperature difference during the whole temperature range.
27. The apparatus of the previous claims, whereby when operational a Peltier element keeps the temperature difference between the shield and the reference sample at zero or at a constant temperature difference during the whole temperature range.

28. The apparatus of any of the previous claims, whereby the apparatus when operational in the heating mode maintains equality of the temperatures of the sample, the reference sample and the surrounding thermal shield.
29. The apparatus of any of the previous claims, where the sample, the reference sample and adiabatic shield are surrounded by additional thermal shields, each with temperature sensors and heaters under the control of a servo system on a processor.
30. The apparatus of any of the previous claims, where the number of thermal shields or Peltier elements is varied.
31. The use of the apparatus of any of the previous claims 1 to 30, where a constant heating power is delivered to the sample and/or to the sample holder.
32. The use of the apparatus of any of the previous claims 1 to 30 where a constant cooling power is delivered to the sample and/or to the sample holder.
33. The use of the apparatus of any of the previous claims 1 to 30, where a constant heating power is delivered to the reference sample and/or to the reference sample holder.
34. The use of the apparatus of any of the previous claims 1 to 30, where a constant cooling power is delivered to the sample and/or to the sample holder.
35. The use of the apparatus of any of the previous claims 1 to 34, where the calorimeter can be evacuated.
36. The use of the apparatus of any of the previous claims 1 to 34, where the calorimeter can be filled with a chosen gas.
37. The use of the apparatus of any of the previous claims 1 to 36, for simultaneously in one scan measuring in a thermodynamic equilibrium the heat capacity and enthalpy of phase transition of a sample.
38. The use of the apparatus of any of the previous claims 1 to 36, for simultaneous measurements of heat capacity and enthalpy of phase transitions by an operation in thermodynamic equilibrium, in particular near fluctuations dominated phase transitions.
39. The use of the apparatus of any of the previous claims 1 to 36, for separation between pretransitional enthalpy of transition variations and true latent heats at first-order or weakly first-order phase transitions.
40. The use of the apparatus of any of the previous claims 1 to 36, which operates in thermodynamic equilibrium for simultaneously in one scan measuring heat capacity and enthalpy of phase transitions of a sample.
41. The use of the apparatus of any of the previous claims 1 to 36, to yield accurate absolute values of specific heat of a sample by using slow scanning rates, in particular below 0.2 Ks^{-1}.
42. The use of the apparatus of any of the previous claims 1 to 36, to discriminate between second-order (continuous) phase transitions and (weakly) first-order phase transition of a sample.
43. The use of the apparatus of any of the previous claims 36, for in one scan defining or characterizing of a phase transition of a material as influence of a production process.
44. The use of the apparatus of any of the previous claims 1 to 36, for in one scan defining or characterizing of a phase transition in liquid crystals.
45. The use of the apparatus of any of the previous claims 1 to 36, for in one scan defining or characterizing of a phase transition on biological systems.
46. The use of the apparatus of any of the previous claims 1 to 36, for in one scan defining or characterizing of a phase transition in cell membranes.

47. The use of the apparatus of any of the previous claims 1 to 36, for in one scan defining a suitable material for a defined property.
48. The use of the apparatus of any of the previous claims 1 to 36, for in one scan selecting a suitable material for a use.
49. The use of the apparatus of any of the previous claims 1 to 36, for monitoring the energy content of a condensed matter sample by quantifying in one scan in thermodynamic equilibrium simultaneously the temperature dependence of the heat capacity and of enthalpy of a sample and of phase transitions therein, the method involving 1) delivering constant heating or cooling power to the sample and by a Peltier element keeping temperature differences between an investigated sample and a reference sample and its surrounding thermal shield zero or at a preset fixed value during temperature scanning over broad ranges without approximations.

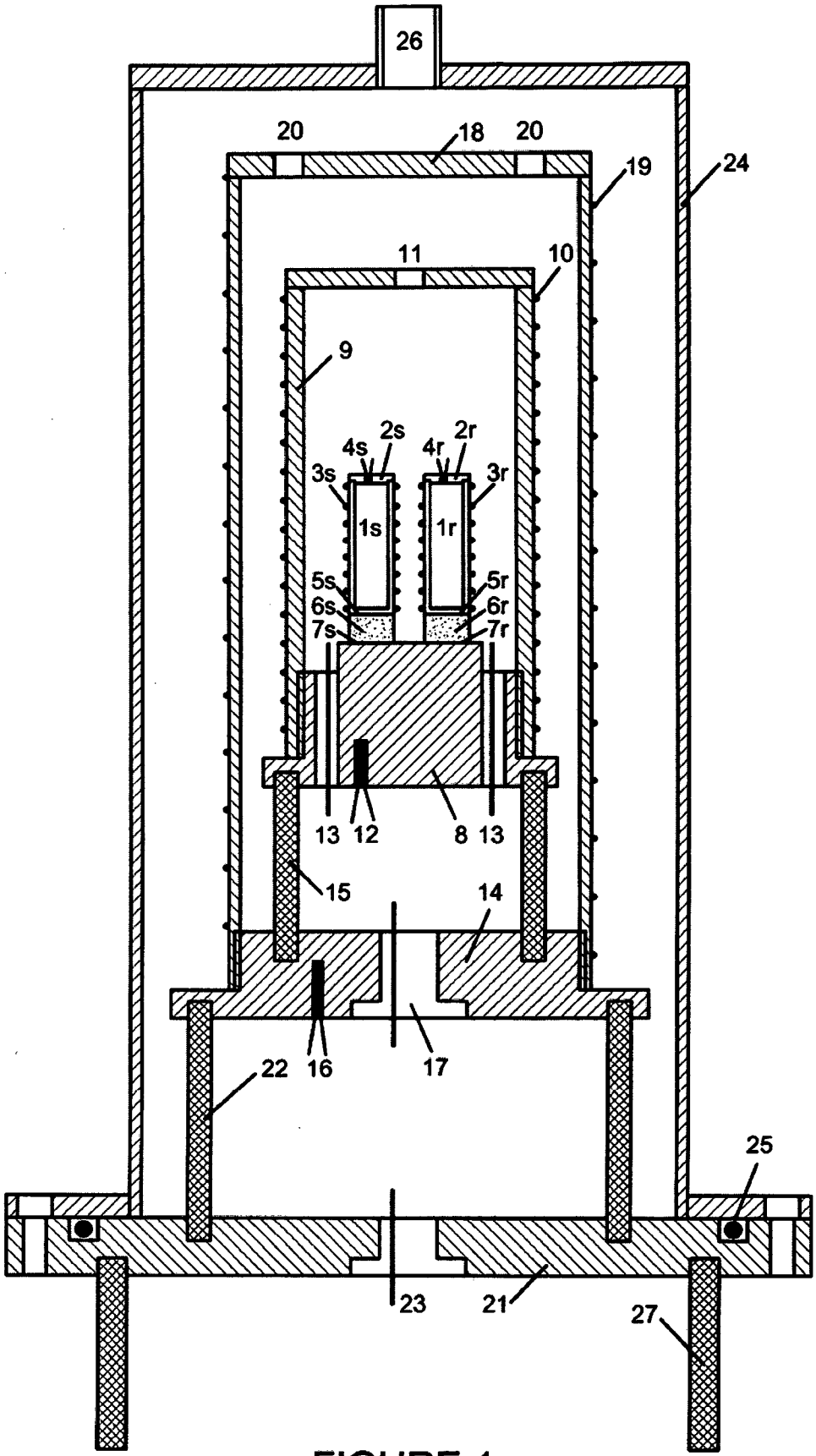
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FIGURE 1

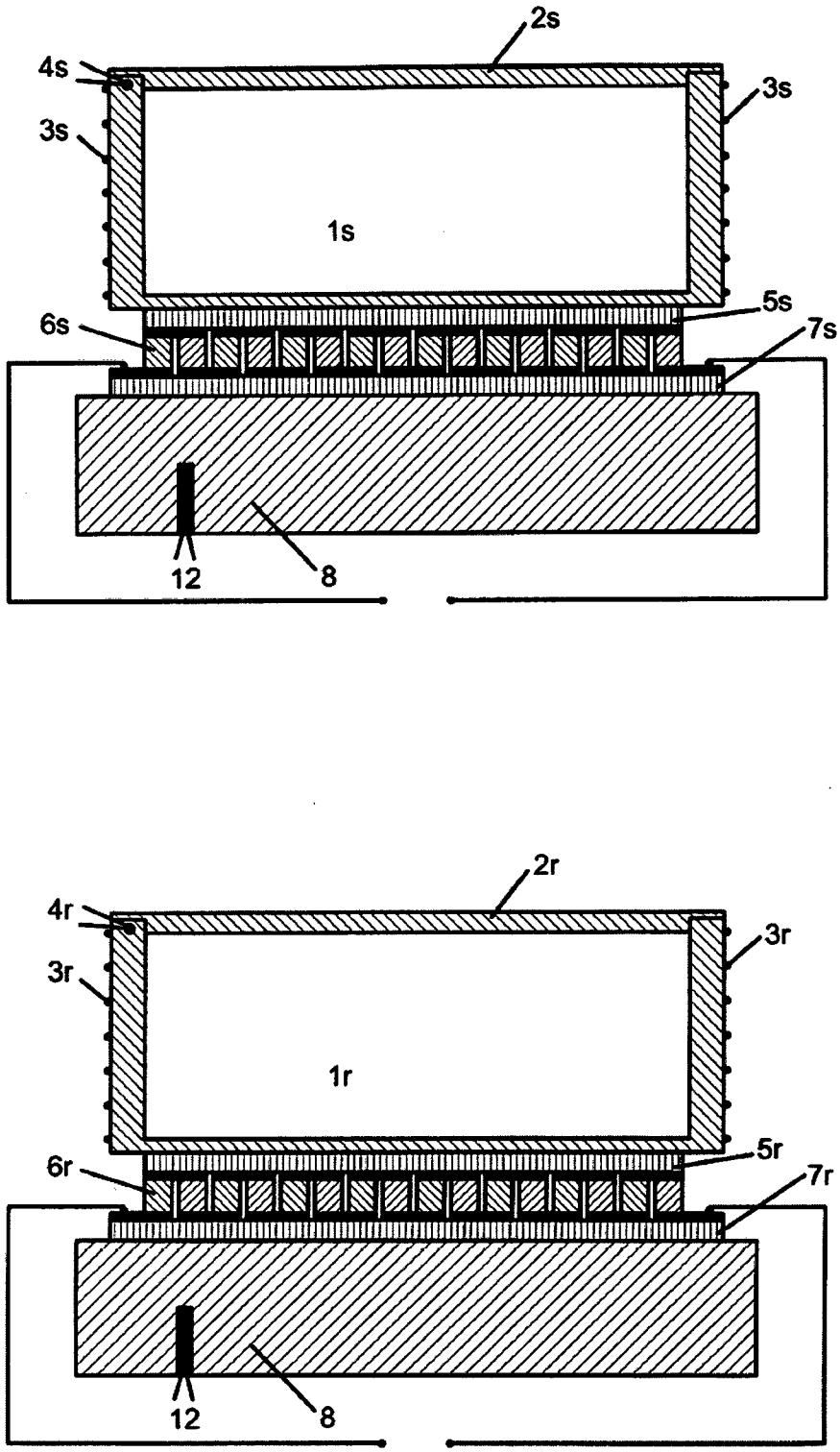


FIGURE 2

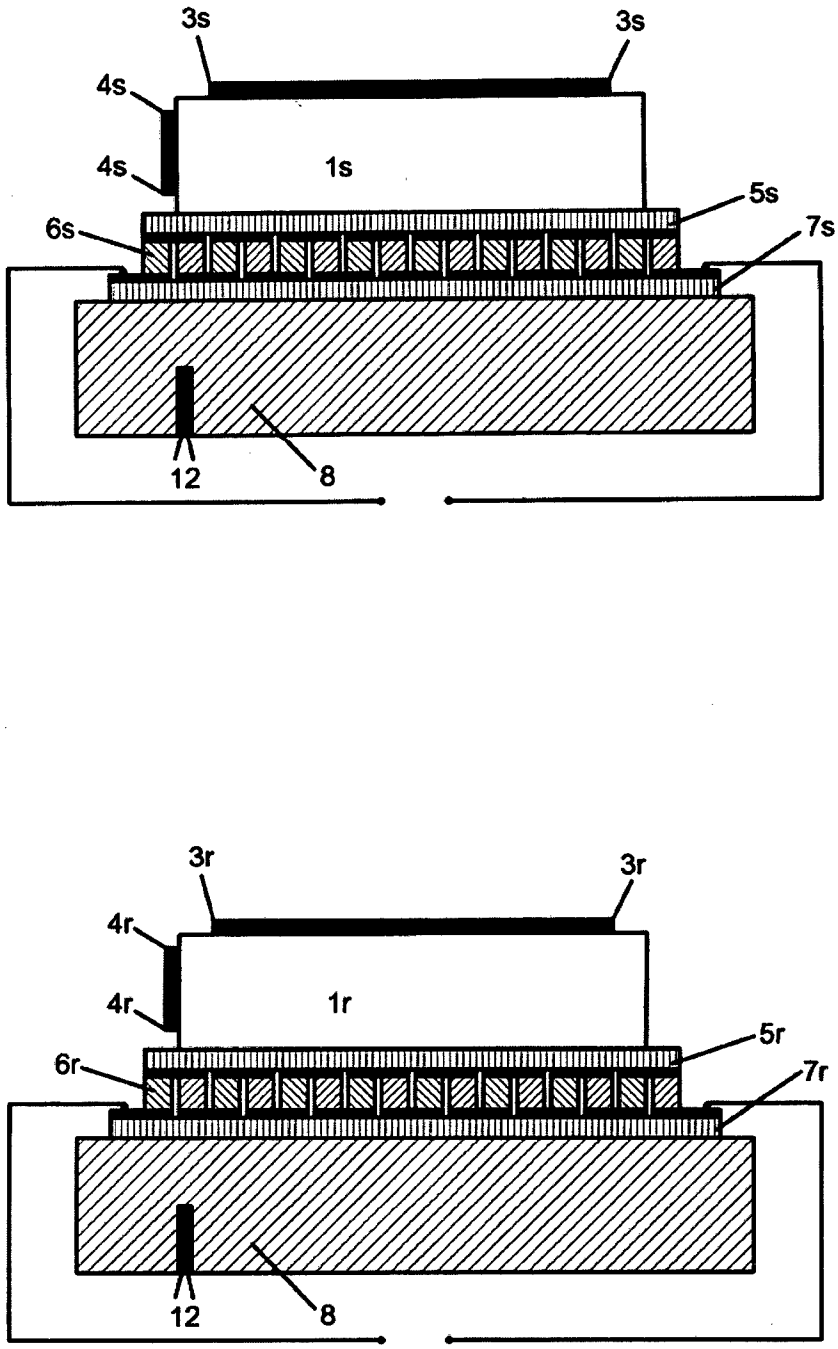
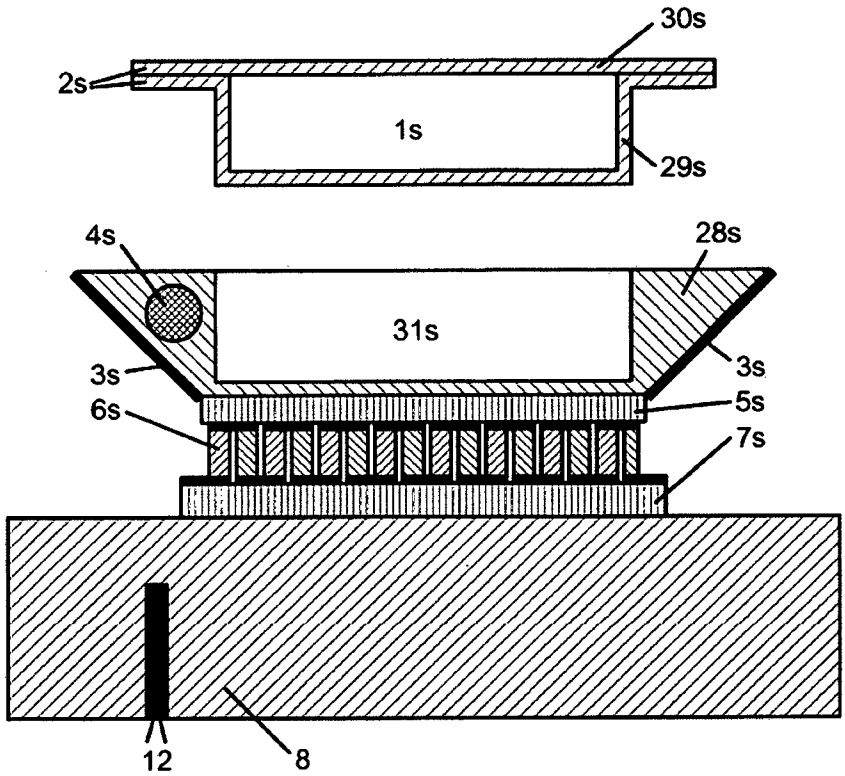


FIGURE 3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31s
3s
3s
6s
5s
7s
12
8

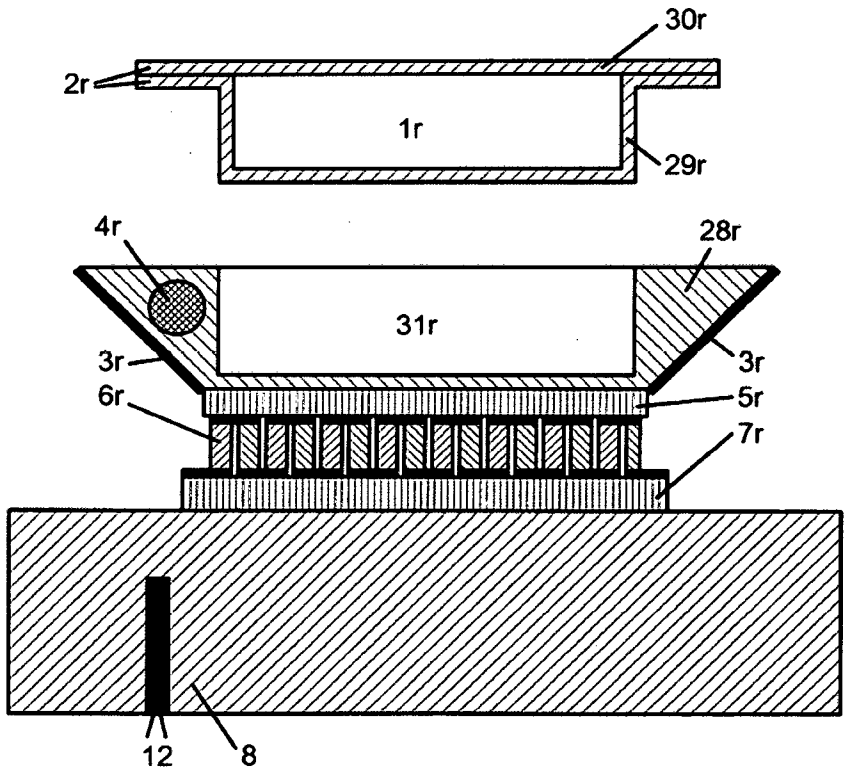
30r
2r
1r
29r
4r
28r
31r
3r
3r
6r
5r
7r
12
8

FIGURE 4

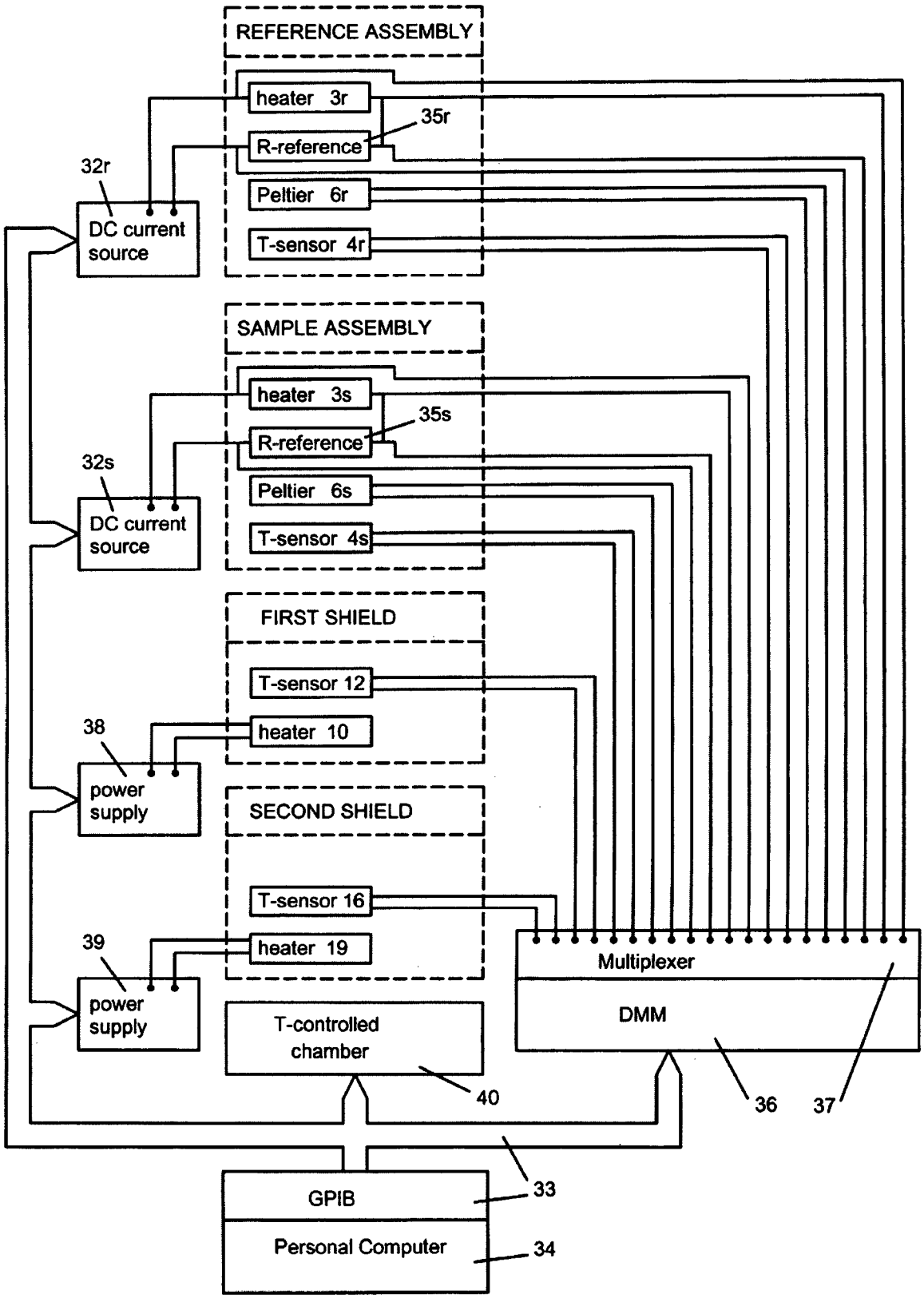
REFERENCE ASSEMBLY
heater 3r
R-reference
35r
32r
DC current source
Peltier 6r
T-sensor 4r
SAMPLE ASSEMBLY
heater 3s
R-reference
35s
32s
DC current source
Peltier 6s
T-sensor 4s
FIRST SHIELD
T-sensor 12
heater 10
38
power supply
SECOND SHIELD
T-sensor 16
heater 19
39
power supply
T-controlled chamber
40
Multiplexer
DMM
36
37
GPIB
33
Personal Computer
34

FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/BE2012/000002

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N25/48 G01K17/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N G01K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 059 471 A (CALVET EDOUARD J P) 23 October 1962 (1962-10-23) column 4, line 60 - column 6, line 47 column 7, lines 5-54 column 8, lines 66-68 column 10, lines 49-52 column 12, lines 3-49 -----	1-49
X	US 4 255 961 A (BILTONEN RODNEY L ET AL) 17 March 1981 (1981-03-17) abstract column 1, lines 22-51 column 2, line 61 - column 3, line 16 column 3, line 64 - column 4, line 22 ----- -/--	1

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 June 2012	14/06/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Filipas, Alin

INTERNATIONAL SEARCH REPORT

International application No
PCT/BE2012/000002

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PRIVALOV P L ET AL: "Three generations of scanning microcalorimeters for liquids", THERMOCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 139, 1 March 1989 (1989-03-01), pages 257-277, XP026536554, ISSN: 0040-6031, DOI: 10.1016/0040-6031(89)87027-3 [retrieved on 1989-03-01] cited in the application page 258 - page 262 page 265	1
A	YUN Y ET AL: "Peltier tip calorimeter", REVIEW OF SCIENTIFIC INSTRUMENTS, AIP, MELVILLE, NY, US, vol. 77, no. 6, 8 June 2006 (2006-06-08), pages 64901-064901, XP012093130, ISSN: 0034-6748, DOI: 10.1063/1.2204584 cited in the application abstract	1
A	DE 43 20 781 A1 (PRAESSL WENDL MARIA THERESIA [DE]; GOENNER WINFRIED KARL [DE]) 3 March 1994 (1994-03-03) the whole document	1
A	KLUMP HORST ET AL: "SCANNING CALORIMETRY AS AN ANALYTICAL TOOL TO CHARACTERIZE DNAs", BERICHTE DER BUNSEN-GESELLSCHAFT FUR PHYSIKALISCHE CHEMIE, VERLAG CHEMIE. WEINHEIM, DE, vol. 88, no. 1, 1 January 1984 (1984-01-01), pages 20-24, XP009159921, ISSN: 0005-9021 page 20, paragraph Calorimetry	45

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/BE2012/000002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 4255961 A	17-03-1981	EP 0020545 A1	07-01-1981
		US 4255961 A	17-03-1981
		WO 8000878 A1	01-05-1980
DE 4320781 A1	03-03-1994	NONE	