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High Resolution Tritium Calorimetry Based on Inertial Temperature Control

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ABSTRACT

A reassessment of the basic equation governing calorimetry shows the crucial importance of temperature stability in the calorimeter environment. Following the principles derived, we have developed a new temperature control method^[1] and demonstrated it in a prototype calorimeter over a wide dynamic range (5 μ W to 2W). Temperature control is achieved by using a metal block of high thermal inertia, surrounded by heat flow sensing thermopile arrays, which is embedded in an isothermal environment. Any temperature fluctuations in this environment are detected by the heat flow sensors and can be corrected by conventional feedback control. The advantage of this method is its high sensitivity to temperature changes: whereas conventional thermometers typically provide signals in the order of $1 \times 10^{-3} \text{VK}^{-1}$, a correctly selected combination of inertial mass and thermopile arrays can provide signals in the order of 1VK^{-1} , thus permitting an improvement of temperature control by three orders of magnitude. A commercially available thermoelectric calorimeter in an isothermal environment controlled by the new method permitted to measure sample powers with $\pm 10 \mu\text{W}$ accuracy (long term, short term noise $\sim \pm 1 \mu\text{W}$), whereas in a conventional thermostatic bath (temperature stability $\pm 0.02 \text{Kh}^{-1}$) its resolution was limited to $\pm 3 \text{mW}$.

INTRODUCTION

Calorimetry, i.e. the accurate measurement of thermal energy released or absorbed by a sample, is used for studying a wide variety of processes in chemistry, biology and physics. Its main application in the specialised field of nuclear technology is the quantitative assay of radioactive isotopes for a variety of purposes, e.g. determinations of decay energy, half life and accountancy^[2]. Recent interest concentrates on the radioactive isotope tritium both for biomedical applications^[3] and for its application as a fuel in controlled thermonuclear reactors for energy production. In this case, tritium inventories are usually stored and transported on compact metal hydride beds and calorimetry represents the safest method of quantitative assay^[4, 5]. Tritium, a low-energy (max 18.6keV) β -emitter with a half life of 12.32 years and a decay heat of $0.324 \pm 0.001 \text{Wg}^{-1}$ ^[6] is well suited for calorimetry as virtually 100% of the β -energy released is adsorbed in the metal hydride itself and in the containment walls, while the simultaneously emitted neutrino does not deposit any measurable energy in the calorimeter.

The measurement of large quantities for accountancy purposes is relatively simple^[4, 5]. However, in the development of procedures for the handling and chemical processing of tritium and its compounds frequently rather small quantities are used both for reasons of expense and radiological hazard caused by its high specific activity ($\sim 3.6 \times 10^{14} \text{Bqg}^{-1}$) or larger batch sizes have to be accurately measured for the assessment of process performance. For this reason, it appeared desirable to develop calorimetric methods with $\sim 1 \mu\text{W}$ ($\sim 1 \times 10^9 \text{Bq}$) resolution. The major emphasis in this attempt is not to tighten the limits of accountancy, which are given by the accuracy of the decay heat to $\pm 0.3\%$ ^[6] and additional, usually unavoidable, systematic errors of experimental systems. High resolution calorimetry should be regarded primarily as a method to assess the relative merits of processes as a function of process parameters under otherwise identical conditions and to assist in calibration of other process sensors (e.g. ionisation chambers). In the following, we will recapitulate the basic principles of calorimetry showing that a major improvement in calorimeter performance can be achieved by employing the calorimetric method itself for temperature stabilisation by inertial feedback control and describe the design and performance of a thermoelectric calorimeter operated under these conditions.

BASIC PRINCIPLES OF CALORIMETRY

Thermoelectric calorimetry in the case of pure conductive heat transfer is governed by the general heat conduction equation^[7], which may be written as follows:

$$\rho c_p \frac{\partial \vartheta}{\partial t} = \nabla \cdot (\lambda \nabla \vartheta) + \sigma \quad (1)$$

This differential equation describes the volumetric heat balance for each volume element of a body.

$\rho(\vec{r}) c_p(\vec{r})$ is the heat capacity per unit volume, $\frac{\partial \vartheta}{\partial t}$ the partial derivative of temperature with respect to time. $\nabla \cdot (\lambda \nabla \vartheta)$, with the vector operator ∇ , the thermal conductivity $\lambda(\vec{r})$ and the temperature $\vartheta(\vec{r}, t)$ represents the heat flow through the surface of the volume element. $\sigma(\vec{r}, t)$ represents the heat generated in the volume element per unit volume, e.g. due to electrical heating or radioactive decay.

In a calorimeter, we intend to measure the heat generated in a relatively large volume V . This means that we observe the following integral quantities:

$$\int_V \rho c_p \frac{\partial \vartheta}{\partial t} dv = \int_A \nabla \cdot (\lambda \nabla \vartheta) da + \int_V \sigma dv \quad (2)$$

or
$$\Delta = \Pi + \Sigma \quad (2a)$$

The term on the left-hand side represents the total increase of thermal energy in the volume V per unit time. The first term on the right-hand side represents the total heat flow into the volume through its closed surface area A . The second term on the right-hand side is the quantity of interest, i.e. the sum of (or integral over) all heat generating sources σ contained in the volume.

The measurement of the source term Σ can be done by two methods:

1. Adiabatic Method

A calorimeter body of known heat capacity (including source and structural material)

$$\int_V \rho c_p dv = C_c \quad (3)$$

is ideally thermally insulated such that any heat flow Π through its surface is zero.

We obtain the source term:

$$\Sigma = C_c \cdot \dot{\Theta} \quad (4)$$

provided we can measure the heat capacity C_c and the temperature rise rate $\dot{\Theta}$ with sufficient accuracy. The method evidently find its limits (amongst other problems), when a small source in a body of large heat capacity gives a temperature rise rate in the order of temperature measurement accuracy and temperature stability of the environment, technically at best $\pm 1 \times 10^{-3} \text{Kh}^{-1}$.

2. Isothermal Method

This method places the calorimeter containing the source Σ in a temperature stabilised environment. Its surface A is enclosed by a heat flow sensing device (thermopile) which measures the (integrated) heat flow Π through the total surface A. Hence, the quantity measured is this heat flow, as given in equations (2) and (2a). Ideally, the environment is thermostatically controlled to the extent that all temperature derivatives with respect to time become negligibly small, i.e. in this ideal case, we obtain the quantity of interest

$$\Sigma = -\Pi \quad (5)$$

This method finds its limits again in technically feasible temperature control stability: in the presence of a temperature drift $\dot{\Theta}$ we measure a signal Π_m

$$\Pi_m = C_c \dot{\Theta} - \Sigma \quad (6)$$

Hence, the measurement yields the incorrect source term

$$\Sigma + \delta\Sigma = \Sigma - C_c \dot{\Theta} \quad (7)$$

with the error

$$\delta\Sigma = C_c \dot{\Theta} \quad (7a)$$

which is proportional to both the temperature drift $\dot{\Theta}$ and the total calorimeter volume heat capacity C_c (see figure 1). Presently used thermostats permit to control $\dot{\Theta}$ to $\pm 1 \times 10^{-2}$ (at best $\pm 1 \times 10^{-3}$) Kh^{-1} . To overcome this problem, state of the art calorimeters employ a differential method, where two identical calorimeters with (ideally) identical heat capacity, source distributions and sensors (one containing the unknown source, the other an electrical heater with accurately measurable power) permit to cancel the heat capacity effects and thereby the drift term $C_c \dot{\Theta}$. A wide variety of such devices called double-cup or twin calorimeters is described in the literature, some examples are given in [2, 3, 8].

These devices are still affected by imperfections in symmetry (heat capacity, response time, source distribution and coupling) and their performance could be substantially enhanced by improvements of thermostatic control.

The key to this improvement was the former Achilles heel of the isothermal calorimeter, ie its high sensitivity to temperature fluctuations, suggesting its use for temperature control.

THE INERTIAL THERMOSTAT

Consider a sensitive calorimeter containing a large heat capacity C_i , but no heat sources Σ_i , e.g. just a heavy block of metal, preferably with good thermal conductivity. We then obtain from equations (2) and (4)

$$\dot{\Theta} C_i = \Pi_i \quad (8)$$

This means, such a calorimeter will provide an output signal Π_i which is proportional to the heat capacity C_i of its internal (inertial) mass and the derivative $\dot{\Theta}$ of the ambient temperature Θ .

Referring to figure 1, we see that this calorimeter signal permits to control the temperature such that $\dot{\Theta} = 0$; the advantage of this method is its high sensitivity: whereas conventional thermometers such as e.g. platinum resistors typically provide electrical signals in the order of $1 \times 10^{-3} \text{VK}^{-1}$, a correctly selected combination of inertial mass and thermopile arrays can provide signals in the order of 1VK^{-1} and hence permit improvement of temperature stability (employing standard industrial control equipment) by three orders of magnitude.

Figure 2 shows schematically an assembly consisting of an inertial thermostat and a thermoelectric calorimeter. Both are integrated in a calorimeter body whose isothermal surface is coupled to an external thermostat through thermal insulation of suitable conductance and low thermal diffusivity. The isothermal surface is held at constant temperature by a heater whose standby power exceeds the power of samples to be inserted in the calorimeter. The control signal provided by the thermopile surrounding the inertial mass is used to control the calorimeter body to achieve $\dot{\Theta} = 0$.

EXPERIMENTAL SETUP

A slightly more complex version of a thermoelectric calorimeter with inertial thermostat is shown in figure 3. It uses a "double-cup" calorimeter^[8] suitable to exploit the advantages of a differential calorimeter or (alternatively) for

measuring two samples simultaneously. In addition to the simple schematic it features a multi-layer thermal insulation consisting of 40 alternating layers of 0.5mm aluminium sheet and 0.5mm ceramic fibre sheet. This insulation provides a well defined heat flow conductance ($\sim 1\text{WK}^{-1}$) and low thermal diffusivity in radial direction ($2 \times 10^{-7}\text{m}^2\text{s}^{-1}$) and is highly anisotropic ($\frac{\lambda_{\parallel}}{\lambda_{\perp}} \approx 1000$), thus helping to suppress any axial gradients. The inertial mass used for temperature control is a rectangular aluminium block of 6.7kg weight, coupled to the calorimeter body through flat thermopile arrays^[8].

Figure 4 shows a photograph of the inner assembly including the control heaters (constantan wire, one each of 100, 50 and 25 Ω resistance permitting use of a variety of controller outputs). The inertial mass with its heat flow sensors is located in a rectangular cut-out in the lower end of the assembly, the double cup calorimeter is located in the upper part as shown schematically in figure 3.

The size of the calorimeter cups (66.4mm ID \times 150mm height) was selected to accept tritium transport beds containing uranium getter material (Amersham MK IV, maximum capacity 5g T₂). The choice not to include the secondary containment for these transport beds was made in favour of measurement accuracy: as discussed earlier, any temperature fluctuation in the calorimeter environment will cause an error signal directly proportional to the heat capacity contained in the calorimeter, hence, inclusion of the secondary containment would reduce the achievable accuracy by one order of magnitude (increasing the calorimeter dead mass by a factor ~ 2 and the sample mass by a factor ~ 5).

The completed system was operated as follows:

An industrial thermostat (Julabo FC-30-HC) connected to the external cooling coil provided a basic temperature stabilisation to $\pm 0.02\text{Kh}^{-1}$ at 21°C. The bias/control heater on the calorimeter body was heated with constant power of $\sim 10\text{W}$ until equilibrium was nearly achieved ($\sim 50\text{h}$) and then feedback controlled for $\dot{\Theta} = 0$ using the inertial thermostat signal on an industrial controller (REX G9, TC Ltd) with a $\pm 10\text{mV}$ input range and standard PID autotuning capability. Both calorimeter cup thermopile signals were measured independently using a Keithley 182 Nanovolt meter with a 7001 Scanner system and a 7168 Nanovolt Scanner card. Electrical calibration heaters (390 Ω each) were fitted in both calorimeter cups. Power could be applied through a programmable Keithley 213 source with linear power amplifier and was measured via the voltage drop on

the heaters and on a 10Ω standard resistor in series. Data acquisition was performed by a PC interfaced with the measuring equipment via an IEEE 488 bus.

For low power measurements ranging from $5\mu\text{W}$ to 1mW , the bias power was reduced to 1W and the difference between Cup 1 (test power) and Cup 2 (zero power) was used for compensation of the remaining temperature fluctuations.

PERFORMANCE TEST RESULTS

The optimisation of temperature control proved rather simple thanks to the autotuning feature of the temperature controller used. Subsequently, the stability and reproducibility of the calorimeter signals was determined: the output signals of both calorimeters were stable with a standard deviation of $\sim\pm 1.2\mu\text{V}$ (long term, ie two weeks) returning to the same value within ~ 12 hours when the system was disturbed by opening and closing the calorimeter. Short-term stability ($\sim 20\text{min}$) and noise were in the order of $0.2\mu\text{V}$. After this basic stability test, the calorimeter was calibrated by raising the power in each cup from $5\mu\text{W}$ to 2W using 3 approximately equal steps (1-2-5) per decade. The result of this calibration is shown in figure 5a. The duration for each step was 3 hours, the last two hours of each step were used to derive the calibration constant for each cup. The figure 5b shows the actual response of the calorimeter for a single power step.

Subsequently, the data were processed forming the time average for the last two hours of each step and the calibration constant for each cup was calculated as the ratio of input power to output voltage. The result of this evaluation for one of the cups is shown in figure 6. It is important to note that the standard deviation is $\leq 1.5\mu\text{V}$ up to a power level of $\sim 10\text{mW}$ and then gradually increasing to $\pm 220\mu\text{V}$ at the 2 watt power level. This was found to be caused by the heater supply power amplifier which had only a basic stability of $\pm 10\text{mV}$ output voltage, a better power supply would have resulted in $\sim\pm 1.2\mu\text{V}$ standard deviation throughout the full range.

It should further be noted that this performance was achieved in an environment not particularly suited for calorimetry. The equipment was operated in a room without any air conditioning, all measurements being performed while ambient temperature fluctuated between 18°C (night) up to 26°C (day). When inertial feedback control was not used (i.e. controller operated

on "manual" with constant power output), the calorimeter signals varied by up to $\pm 300\mu\text{V}$ ($\underline{\Delta} \pm 2.3\text{mW}$) during a 24h period.

The short-term stability of the calorimeter is demonstrated in figure 7. A pocket watch with mechanical clockwork was inserted in Cup 1 and the data were evaluated by forming the difference between Cup 1 and the reference Cup 2. Although the sample power could not be measured in equilibrium due to long-term fluctuations in the order of $\pm 10\mu\text{W}$, the sudden drop in power when the clockwork stopped could be clearly distinguished. The step response shows the power dissipation ($7 \pm 1.5\mu\text{W}$) of this mechanical device. This may also serve as an example for applications of high resolution calorimetry in areas other than nuclear technology.

The inertial temperature feedback method permits not only temperature stabilisation ($\dot{\Theta} = 0$), but also ramping of the temperature ($\dot{\Theta} = \text{const}$), merely by selecting a setpoint $\neq 0$ on the feedback controller. By selecting a ramp rate which could be measured with sufficient accuracy by means of a platinum resistance thermometer on the calorimeter body ($\dot{\Theta} = 0.1\text{Kh}^{-1}$) we could determine the "ballast" heat capacity of the calorimeter from equation (8) to 550JK^{-1} . With this value, we find that a resolution of $\pm 10\mu\text{W}$ corresponds to a temperature stability of $\sim \pm 6 \times 10^{-5}\text{Kh}^{-1}$ and the short term stability of $\pm 1\mu\text{W}$ to a temperature stability of $\sim \pm 6 \times 10^{-6}\text{Kh}^{-1}$.

CONCLUSIONS

The test results have shown the high resolution ($\pm 10\mu\text{W}$) and the large dynamic range (6 decades) of a prototype thermoelectric calorimeter employing inertial feedback control. The temperature stability of $\pm 6 \times 10^{-5}\text{Kh}^{-1}$ can still be substantially improved: the calorimeter was assembled from available parts and, as a consequence, the control loop characteristics are far from ideal due to the large heat capacity ($\sim 2 \times 10^4\text{JK}^{-1}$) inserted between heater and sensor. A fully optimised device should be capable of exploiting the limit of available DC voltage measuring equipment ($\sim 1 \times 10^{-10}\text{V}$) with power resolution in the order of 1×10^{-9} to $1 \times 10^{-8}\text{W}$. It is, however, quite clear that many problems will have to be solved before achieving this goal. As a first step in this direction we are presently investigating an improvement of the external (industrial) thermostatic loop by cascading it with an inertial temperature control device^[1].

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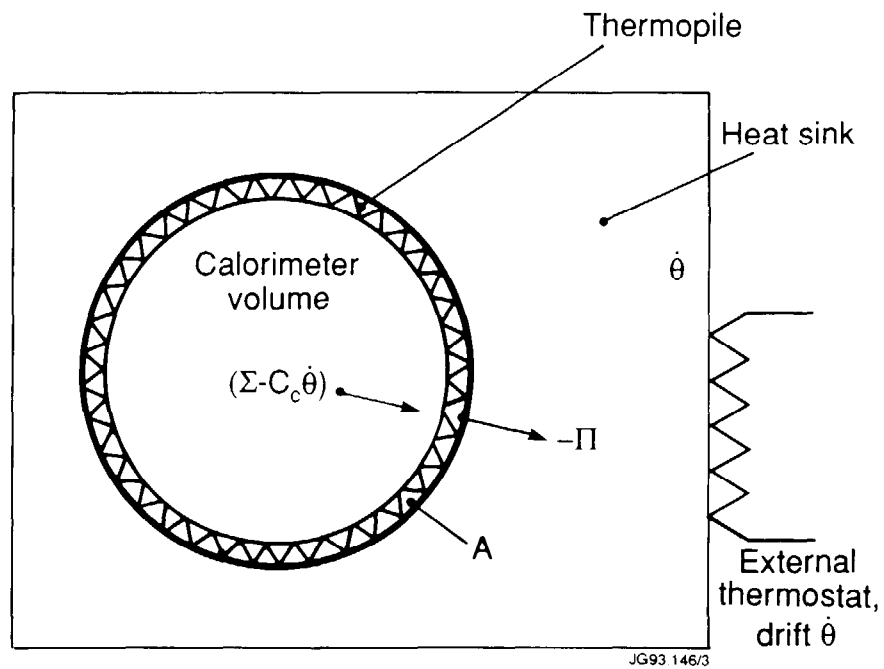


Fig.1. The basic problem of calorimetry: when a complete calorimeter assembly is subjected to a temperature drift $\dot{\theta}$ (caused by external thermostat imperfections or other external influences), the thermopile surrounding the calorimeter active volume measures the difference between the source term Σ and the additional heat flow through the surface area A due to the temperature drift.

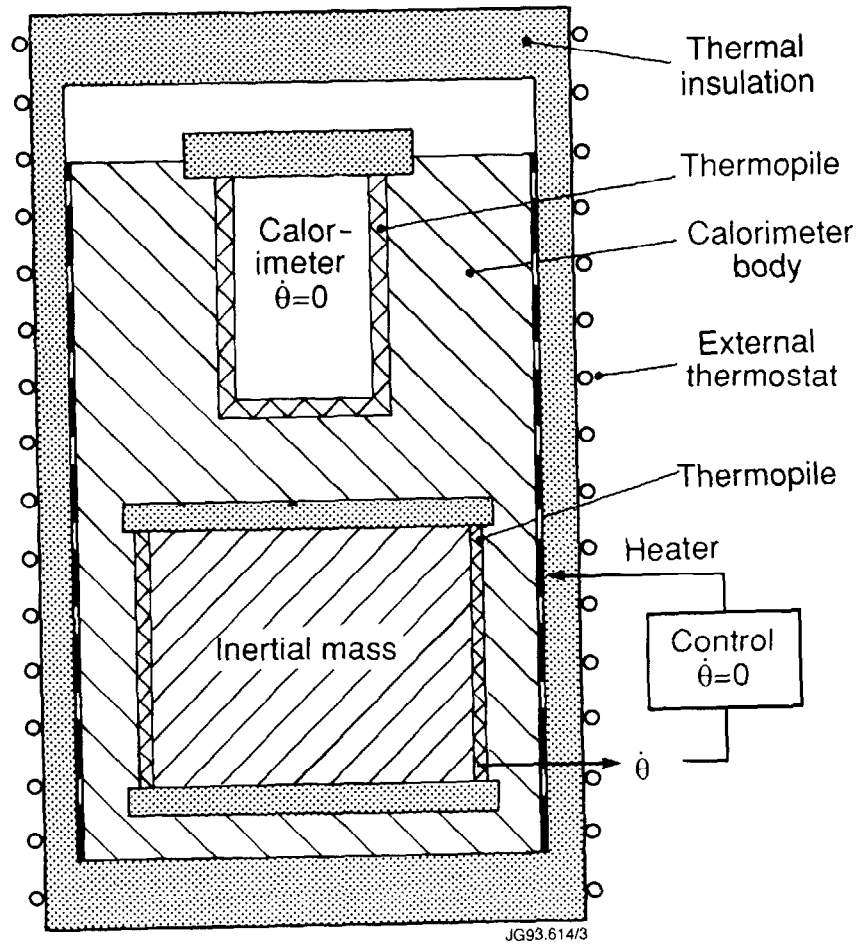


Fig.2. Calorimeter assembly integrated with inertial feedback control.

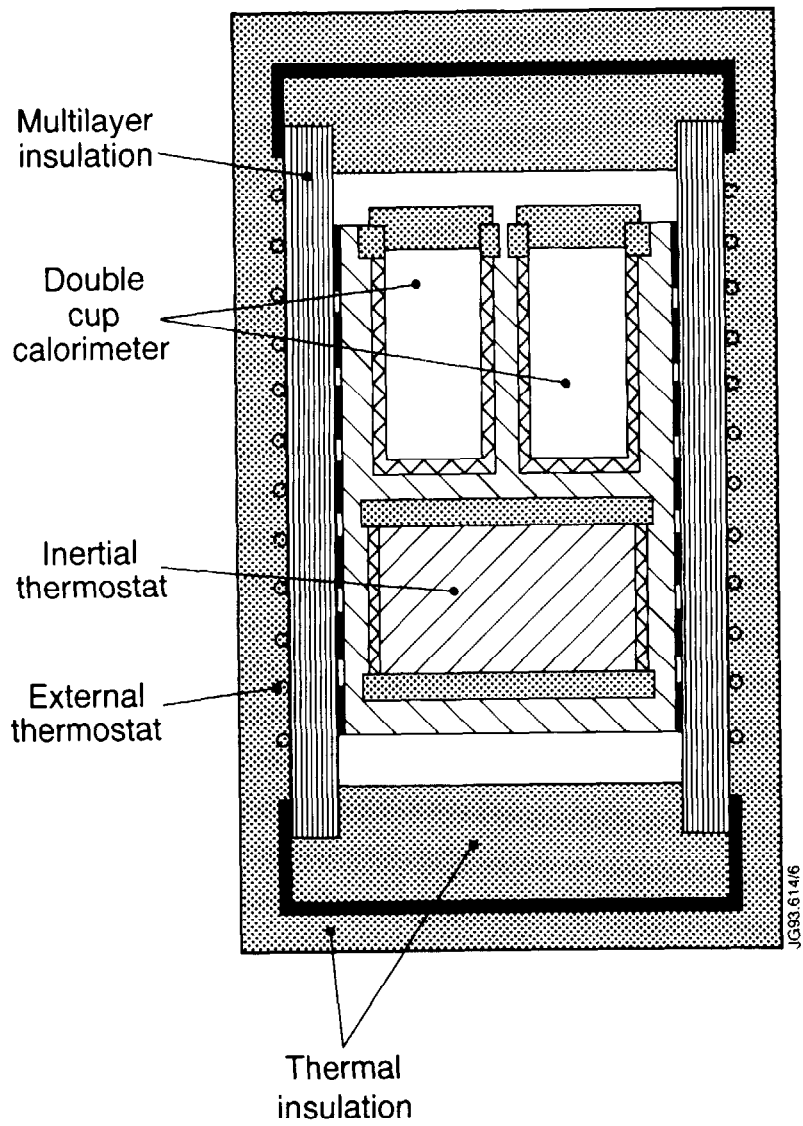


Fig.3. Schematic drawing of the double-cup calorimeter with integrated inertial feedback control used for prototype testing.

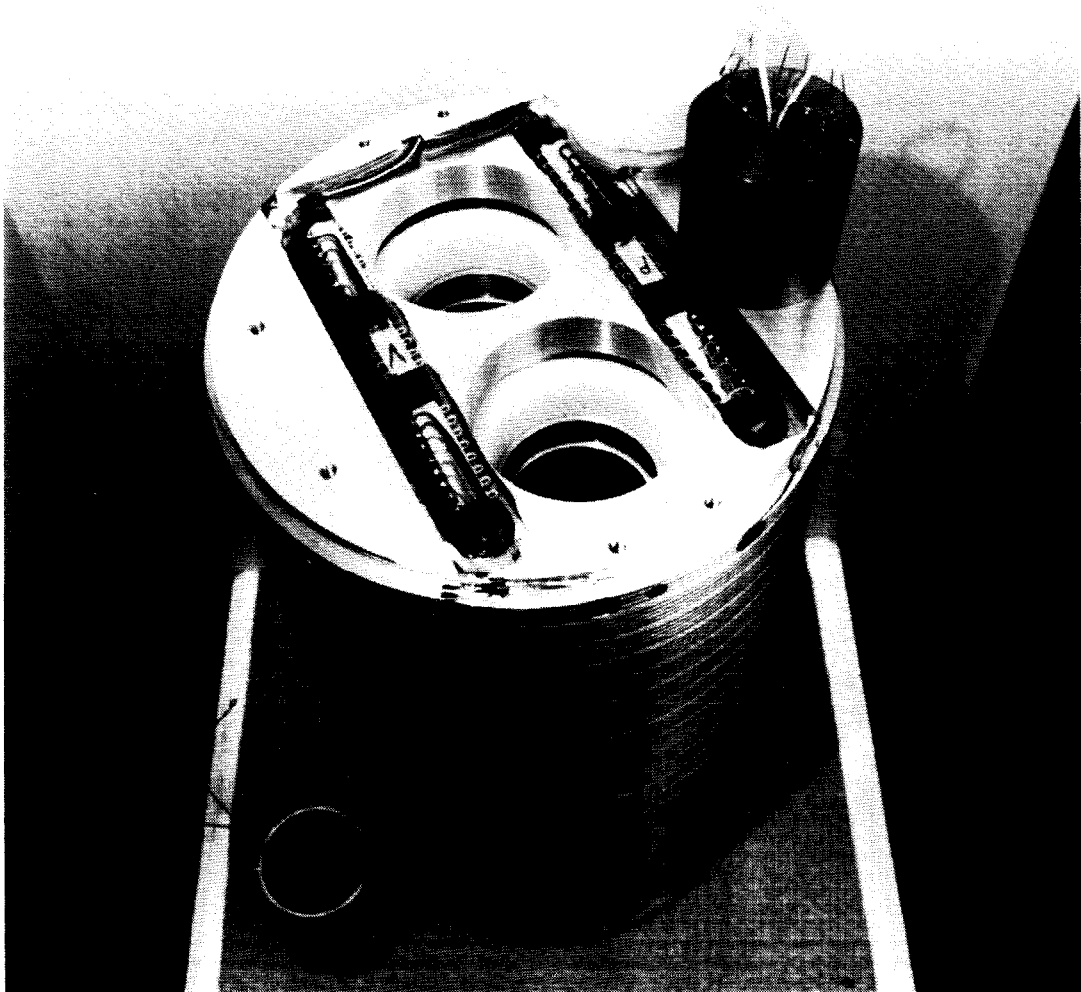


Fig.4. Photograph of inner assembly showing control heaters and the twin cups of the calorimeter with test lead connections and electrically heated calibration devices.

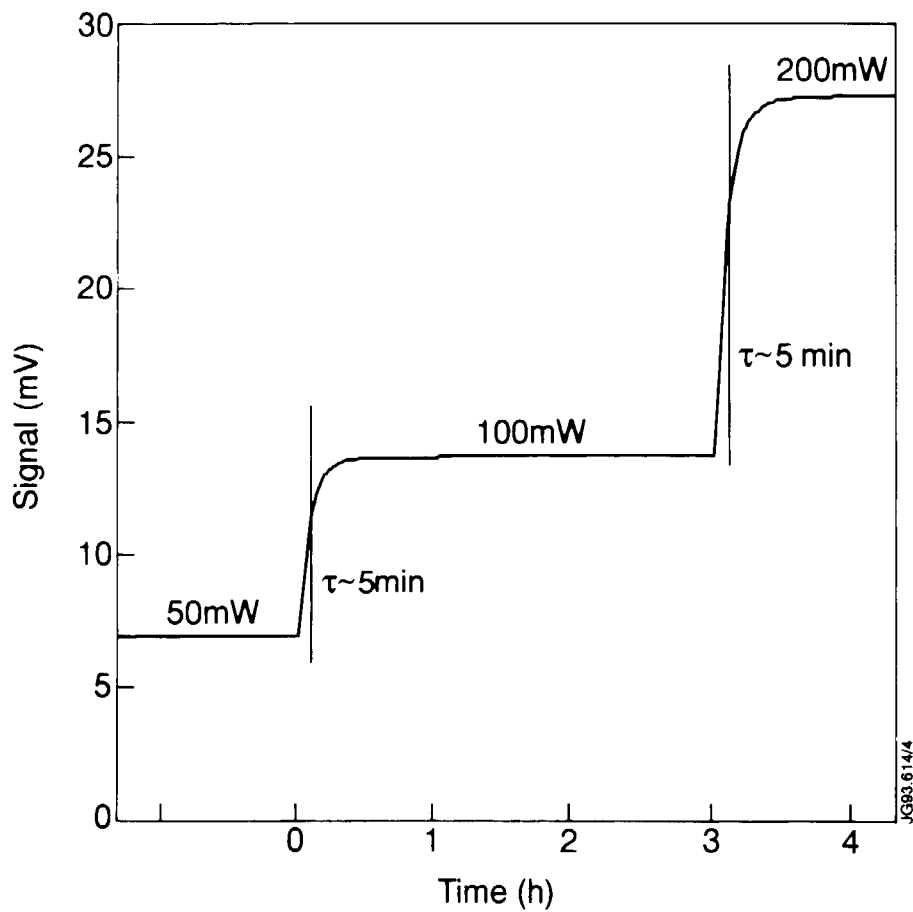
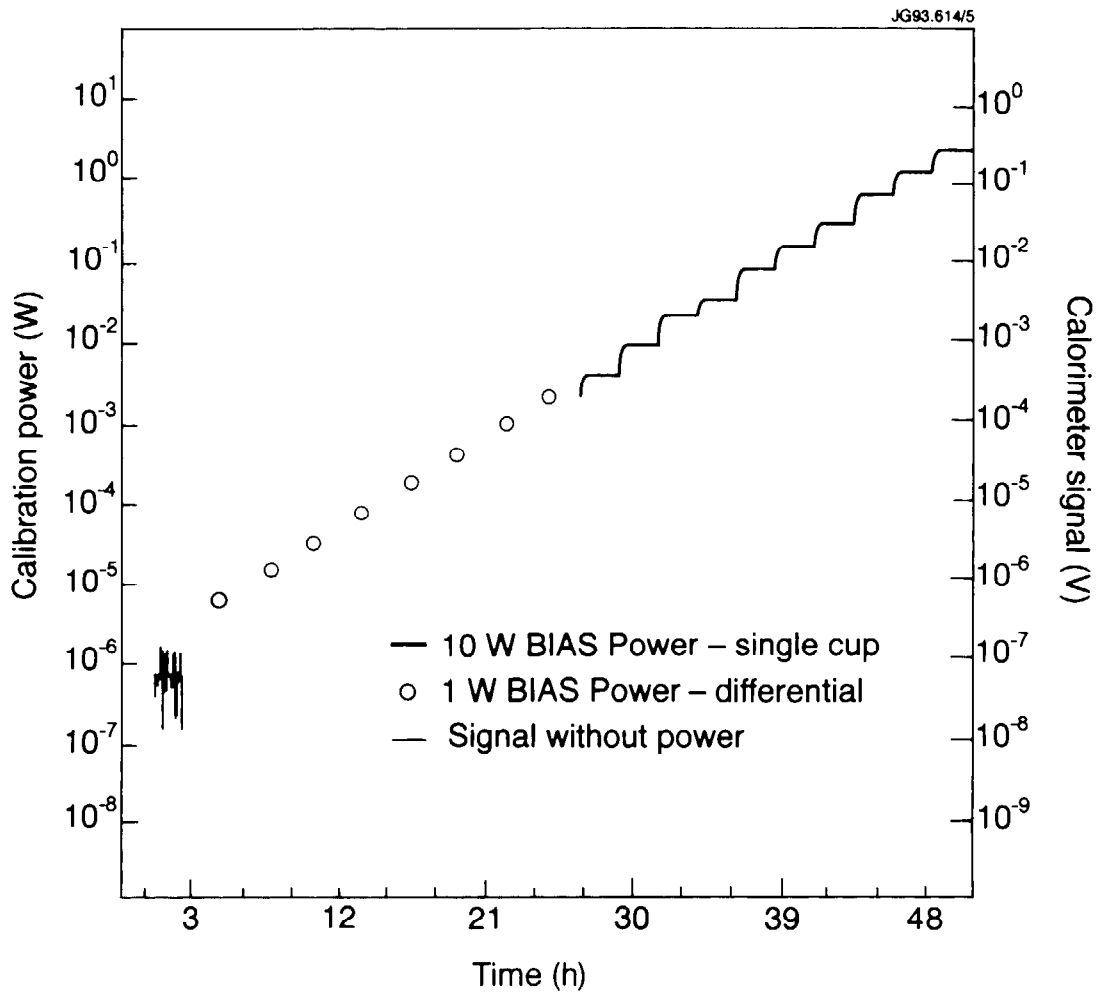


Fig.5. (a) Calibration run with power varied through six decades in three steps per decade - each step duration 3 hours. (b) Response for a single step change and the response time constant τ (raw data).

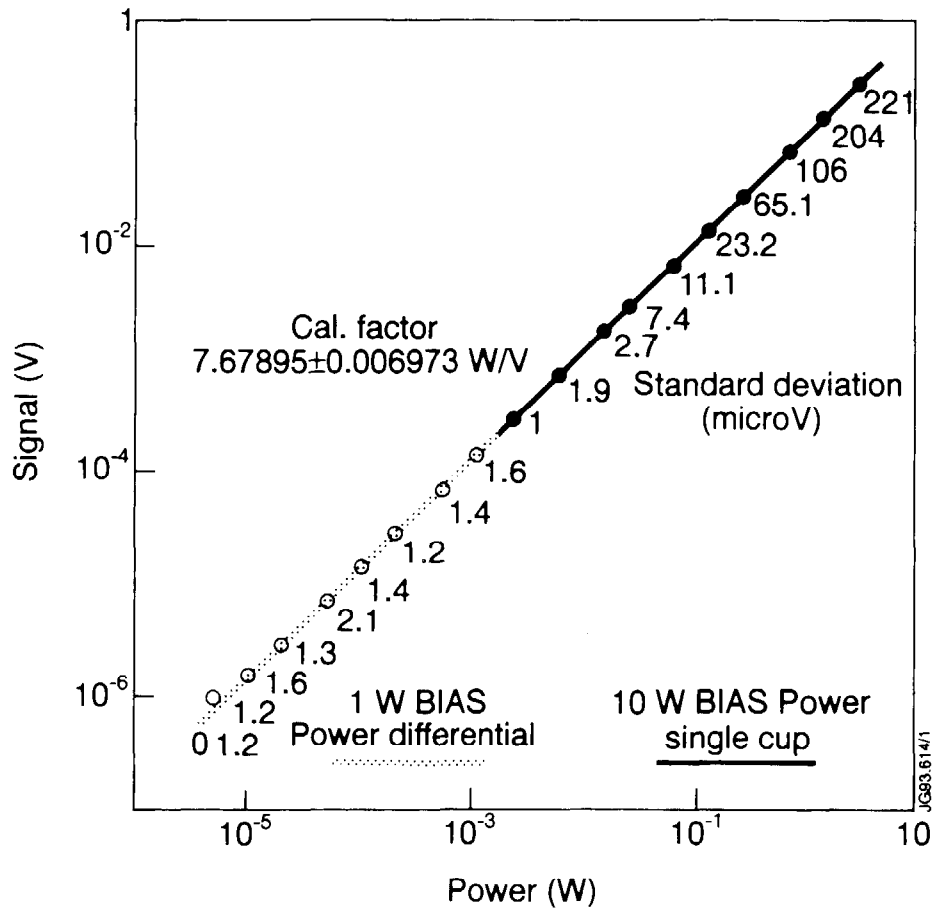


Fig.6. Calibration factor derived from data presented in Figure 5a.

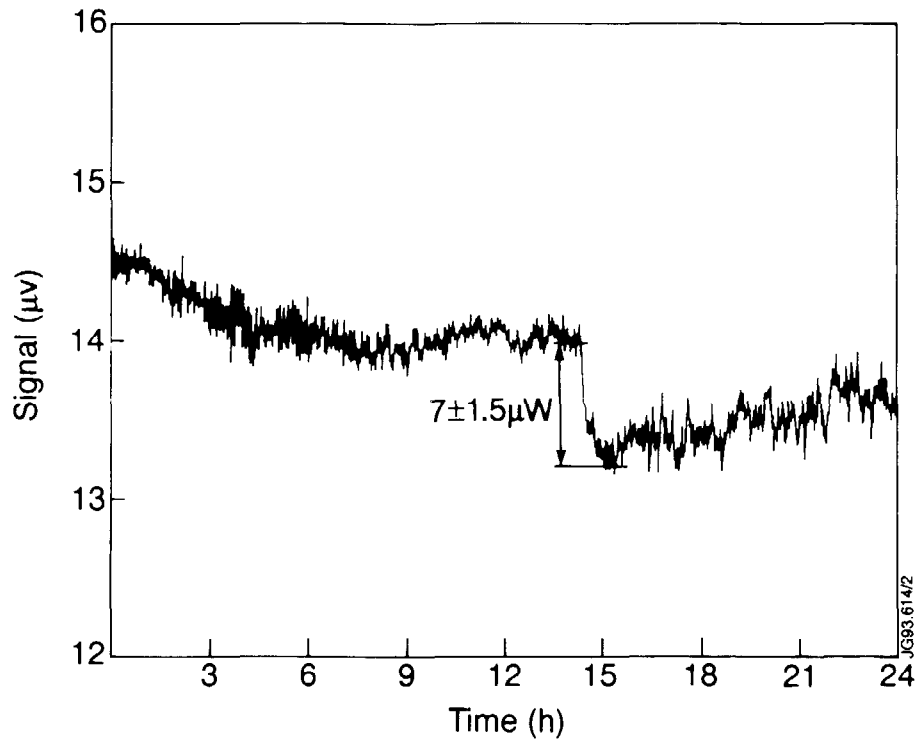


Fig.7. Measurement of the dissipation of a mechanical device (pocket watch clockwork). The short-term stability of $\pm 1.5 \mu\text{W}$ permitted to measure the clockwork power to $7 \pm 1.5 \mu\text{W}$ when the watch stopped.