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## Recent improvements in conduction calorimetry. Application to the martensitic transformations in shape memory alloys<sup>☆</sup>

H. Tachoire<sup>a,\*</sup>, V. Torra<sup>b</sup>

<sup>a</sup> *LPCM/Thermochimie, Université de Provence, F-13331 Marseille CEDEX 03, France*

<sup>b</sup> *CIRG-DFEA-ETSECCPB-UPC, C/. Gran Capità s/n, Campus Nord, B-4,  
E-08034 Barcelona, Spain*

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### Abstract

A critical reading of the work of Tian and Calvet and the actual state of the art in thermostats, temperature control and the modelling of differential conduction calorimeters suggest a backwards evolution to non-differential calorimeters. An elementary design shows increased performances at constant temperature; the sensitivity is  $700 \text{ mV W}^{-1}$  at room temperature, the short-term noise around  $200 \text{ nV} \approx 0.3 \text{ } \mu\text{W}$ , and the baseline fluctuations around  $1 \text{ } \mu\text{V} \approx 1 \text{ } \mu\text{W}$ .

Measurements of the dissipated heat power, indicative of the internal processes after a heat treatment (different types of quench) were realised for a Cu–Zn–Al shape memory alloy. The experimental results established that the dissipated heat evolves in time for at least 2 or 3 days. At least two time constants were detected and, as expected, the values are dependent on the quench type and sample mass.

*Keywords:* Alloy; Calorimetry; Martensitic transformation

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### 1. Introduction

Heat flux conduction calorimetry using thermocouples as detectors started in the 1920s with the work of Albert Tian in Marseilles [1–5]. The experimental system

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\* Corresponding author.

<sup>☆</sup> Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday. His contributions to phase transition studies are a reference for all workers in experimental thermodynamics.

developed initially to study the reactions kinetics allows the evaluation of the dissipated power and, by integration, the measurement of the total energy. The device, operating on the maximum sensitivity, had baseline drift related to fluctuations in the ambient temperature [3–6] or, if present, in the control thermostat. Starting in 1946 [7], Edouard Calvet created the differential calorimeter to compensate the baseline drift by the addition of two identical “Tian calorimeters” [8]. In this system, an “identical” calorimetric element is used to compensate for environmental effects. In this way, an experiment can last days or even weeks, exploiting all the sensitivity of the device. In fact, all the current calorimeters which work on a constant or programmed temperature use the same principle: two “identical” elements, with the calorimeter vessel and the reference cell situated in opposition to neutralize the effects of room temperature.

Conduction differential calorimetry has provided interesting results in materials science. In the field of smart materials and particularly with the martensitic transformations of shape memory alloys, it is able to produce information about transition temperatures, enthalpy changes, associated frictional effects, etc. Moreover, correlations have been established between the change in entropy production and the dislocations created in the material [9–11]. To attain this, the evolution of the thermograms produced on submitting the material to a series of thermal cycles is analysed. Results have also been obtained on the dissipations associated with the evolving processes that take place when a single phase evolves after quenching due to the internal changes associated with the atomic ordering processes [12–14]. In fact, the technological application of these materials needs a high level of reliability. This implies the need to know the characteristics of the evolving material when submitted to heat treatment.

Current instrumental conditions are very different from those available more than 50 years ago. The thermostats have a high reliability and resolution level and the digital voltmeters can give directly a resolution equivalent to the best galvanometers used by Tian and Calvet [5, 15]. They also allow measurements to be made on a wider scale than that available on a galvanometer. This suggests that the use of a differential system is probably superfluous in most applications. Suppression of the differential elements occurs in different instrumental fields as the digital systems allow reliable corrections to be made. For example, Ref. [16] discusses a single-beam (non-differential) spectrophotometer in a chromatographic system. In a recent bibliography, there has been a suggestion that analysis from models indicates the possibility of operating in non-differential systems [17]. Recently, some preliminary results on non-differential calorimetric devices [18] have been described [19], obtained [20] or, for instance, constructed using new pyroelectric sensors [21].

The process stimulating the introduction of differential systems is described in this paper, in particular the necessary device sensitivity, the surrounding environmental conditions and the possibilities of the instrumentation used. Starting from the operative experimental conditions and from the possibilities of the current instrumentation, a very simple non-differential system was built, with sufficient baseline stability to make accurate measurements over several days, specifically to analyse the quenching process in shape memory alloys in order to evaluate the internal atomic ordering processes. The

observations allow the evaluation of the more relevant time constants of the heat power dissipated in the process.

## 2. Critical approach to differential calorimeters: from Tian to Calvet calorimeters

It is appropriate to consider, as a start of the conduction calorimetry activities of Albert Tian, a series of experiments about the characteristics of the thermostats in order to “perfectionner et de simplifier les thermostats actuels en vue d’expériences de longue durée”<sup>1</sup> [1, 2], in this case, the kinetic study of salt hydrolysis which is a slow process. Tian then designed, built and operated a conduction calorimeter which was presented to the Société Chimique de France in December, 1922 [3]. From his experience, he stated that: “une des manières les plus rationnelles de mesurer la vitesse des réactions chimiques consiste à déterminer la quantité de chaleur dégagée par unité de temps”<sup>2</sup> and indicated “l’intérêt des calorimètres à compensation pour la mesure des quantités de chaleur dégagées par les réactions lentes”<sup>3</sup>. This description provides the basic aim of the device: to attain the dynamic characteristic of a reaction. In modern parlance, this means to supply the numerical elements and correct formulae to deduce the released power at each time by eliminating the internal transfer function and, if required, to establish the respective kinetic laws.

This first Tian calorimeter was surrounded by a thermostat with several shells. The device contained two iron–constantan thermopiles. One was used to compensate the dissipation (by a hand-made control) by means of the Peltier effect or, eventually, by an auxiliary Joule effect. The other thermopile acted as a null detector by means of a galvanometer. Therefore, the correct performance of the compensation and the invariance of the temperature of the reactives were guaranteed. In this way, the reaction was not affected by the changes in temperature associated with the dissipation of the reaction.

When operating a galvanometer, if high resolution is to be maintained, the maximal amplitude of the signals that have to be observed is lower. The detection of the relevant dissipations implies a reduction in the detection system resolution. To obtain high resolution, Tian proposed to compensate totally or partially the dissipation produced. Without compensation or with partial compensation, the galvanometer recording is named “the thermogram”. From Tian’s analysis of the chemical reactions kinetics, a total compensation is needed to keep the working temperature constant. However, in an experiment in 1924 [4] when the dissipations were relatively fast and high, he stated that “... il est utile de combiner les deux méthodes: la majeure partie de la chaleur est compensée et le surplus, positif ou négatif, est enregistré.”<sup>4</sup> In this way, you can use the full resolution of the calorimeter even with high dissipations.

<sup>1</sup> “Improve and simplify the current thermostats to be able to perform long-period experiments”

<sup>2</sup> “One of the most appropriate ways to determine the rate of chemical reactions consists of the determination of the amount of heat released in each unit of time”

<sup>3</sup> “The interest in compensation calorimeters in the measurements of amounts of heat released by slow reactions”

<sup>4</sup> “It is useful to combine both methods: most of the heat is compensated and the residual value, positive or negative, is recorded”

In the same experiments, Tian emphasized the relevant difficulties due to the electrical noise and drift produced by the instabilities of the temperature: “l’exactitude des mesures est surtout limitée par l’effet suivant: si la température de la salle est mal distribuée, il s’établit dans le circuit du galvanomètre, hors de l’appareil, des forces électromotrices thermo-électriques accidentelles.”<sup>5</sup>

The same research into calorimetric systems is described in his book published in 1933 [5]: “...j’ai envisagé son utilisation en oscillographe calorifique... On a surtout étudié son fonctionnement en calorimètre intégrateur, cette utilisation paraissant être néanmoins la plus importante”.<sup>6</sup> From this description, we discover two themes: one is the decisive contribution of the evaluation of the process kinetics to the development of the equipment, and the other is the tendency to use the calorimeter to measure total dissipated energies. The measurement of the dissipated energies is still a recurring subject in isothermal as well as in differential scanning calorimetry (DSC) [22].

In the same reference, the Tian equation was introduced. The dissipated power at each moment was determined from the experimental thermograms. The aim, however, was to make an “oscillograph” equipment, i.e. a fast system that could give the dissipation directly: “... un appareil méritant vraiment le nom d’oscillographe doit donner directement une courbe ... qui puisse représenter la quantité  $W$ ”.<sup>7</sup> It can be deduced from the Tian equation that the dissipated energy can be obtained from the integration of the associated thermogram. The Tian equation was the first formalism to approach the actual dissipated power or thermogenesis, in other words, a deconvolution method (see, for examples, Refs. [23, 24] and related references).

### 3. The Tian calorimeter

The experimental results produced a progressive evolution of the device with the aim of stabilizing the external temperatures [4]. Starting in 1926, the Tian laboratory was installed in a deep underground room of the Faculty of Sciences in Marseilles and the calorimeter was placed in a hole in the ground. The mean temperature was 17°C (maximum 18.7°C in October and minimum 15.6°C in April, 1927). The operating conditions were particularly favourable in April and October. Actually, in a 10 h interval, the temperature fluctuations did not exceed 0.01°C [5].

The calorimeter (Fig. 1) contained a 70 mm high and 14 mm diameter laboratory cell. The detector was formed of 42 iron–constantan thermocouples connected to a Kipp-type Zc (Zernicke) galvanometer and the signal was recorded continuously with a photographic device over 120 mm width paper. If needed, the energetic dissipations

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<sup>5</sup>“The accuracy of the measurements is mostly limited by the following effect: if the temperature of the room is wrongly distributed, unexpected electromotive and thermoelectric forces appear on the galvanometer circuit”

<sup>6</sup>“... I resolved myself to use it as a calorimetric oscillograph ... Basically, its operation as an integrator calorimeter has been studied; overall, this seems to me to be the most important application”

<sup>7</sup>“... An equipment that merits the name of oscillograph must furnish directly a curve ... that represents the dissipation  $W$ ”

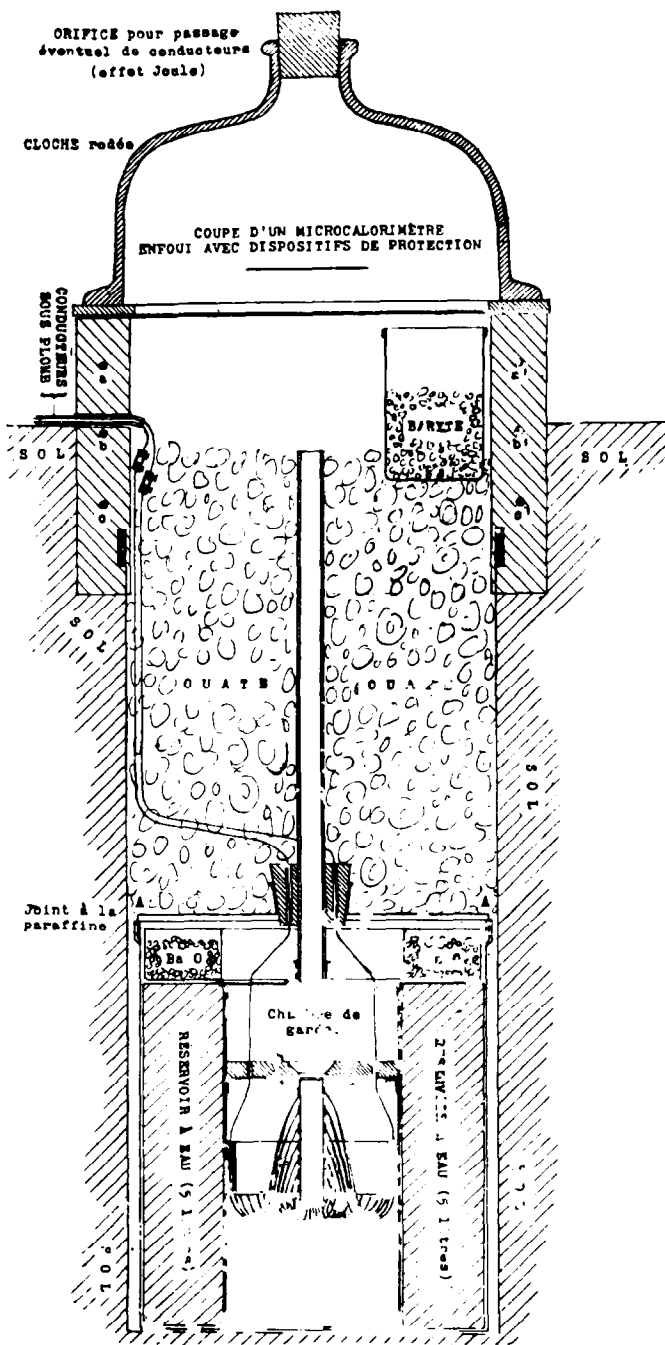


Fig. 1. The Tian calorimeter (from Ref. [5]).

were compensated by means of the Joule effect or by the Peltier effect produced by a second group of 7 thermocouples.

#### 4. The Calvet calorimeter

Edouard Calvet, under the direction of Tian, started his doctoral thesis in 1926 working on a Tian calorimeter situated in the cellar of the Town Hall in Avignon and, afterwards (starting in 1928), in the Tian laboratory in Marseilles. His study was centred on the kinetics of the hydrolysis of amides. The experimental system used the same kind of thermostat and environment and the aim was the estimation of the process kinetics, this being the main target of Tian and Calvet's research.

Calvet's investigations with the Tian system, up till 1946, enabled him to gain complete experience on the effects of the environment on the devices. This suggested [7] the differential system which he presented in 1946: "Nous construisons un nouvel appareil calorimétrique qui pourra fonctionner à toutes températures jusqu'à 80° environ, de sensibilité encore accrue et dont la durée d'utilisation sera pratiquement illimitée pour chaque expérience".<sup>8</sup> In Ref. [8], where he presented the differential system, the basic reasons for this modification are described. In particular, the duration of the measurements that could be done effectively using the Tian device: "*Causes des variations du zéro expérimental des microcalorimètres ... Les variations de la température de l'enceinte thermostatique du calorimètre (sol d'une cave) ... des effets Thomson qui apparaissent entre les différentes portions du circuit dont la température n'est pas uniforme ... Il n'est guère possible de suivre fidèlement une expérience pendant plus d'un jour*".<sup>9</sup>

The system design (Fig. 2) began with two identical calorimeters [8] increasing the number of thermocouples up to 144, constructed using chromel–constantan wire (Peltier effect, 16 couples; detection, 128 couples). They are distributed with precise symmetry and both elements are connected in opposition: "... nous avons associé deux calorimètres identiques en disposant leurs couples en opposition. Ces deux calorimètres, ainsi que le galvanomètre et le commutateur ... se trouvent placés au sein d'un gros bloc de cuivre de forme convenable. Celui-ci est lui-même disposé dans un thermostat dont on peut faire varier la température à volonté".<sup>10</sup> The difference between the "identical and independent" and the "coupled" elements is discussed at the end.

Resolution of the differential calorimeter using the Kipp-type Zc (Zernicke) galvanometer allows the detection of  $0.001 \text{ cal h}^{-1}$  when the galvanometer shift is 1 mm in

<sup>8</sup> "We built a new calorimetric device that will be able to work at all temperatures up to nearly 80°C, with a higher resolution and a practically unlimited experimental time for each application"

<sup>9</sup> "THE ORIGIN OF THE BASELINE DRIFT ... The temperature evolution of the thermostated external shell of the calorimeter (the ground of the cellar) ... the Thomson effects that appear between different parts that have non-uniform temperatures ... It is very difficult to conduct suitable experiments lasting more than a day"

<sup>10</sup> "... We have constructed two identical calorimeters in opposition. These two calorimeters, including galvanometer and switch ... are placed inside a huge block of cooper in an exact manner. One is itself placed in a thermostat, the temperature of which can be changed as desired"

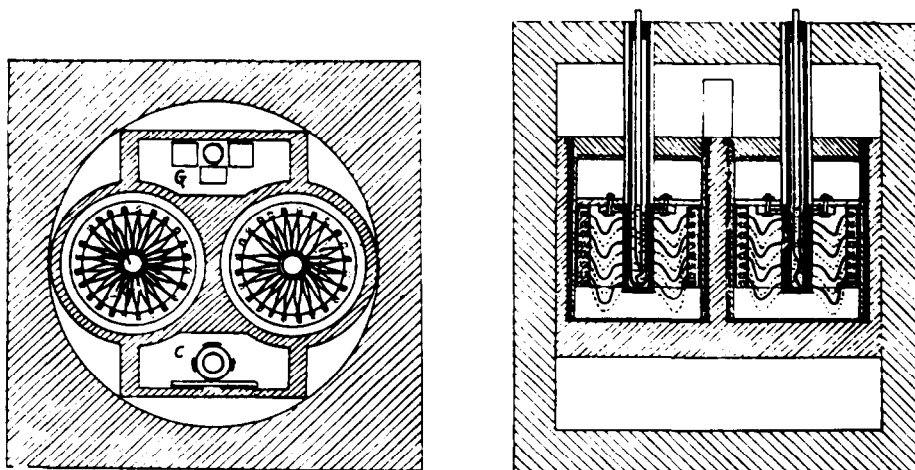


Fig. 2. The first differential conduction calorimeter constructed by Calvet [8].

a scale set at 1 m. In present units, this represents a resolution of  $\approx 1 \mu\text{W}$ . The photographic paper used (120 mm width) allowed a full scale of  $\approx 120 \mu\text{W}$ .

Starting in 1950, the detecting system increased the number of thermocouples to nearly 400. The calorimetric block was protected by using a system of many shells to obtain an increased reduction in the external thermostat temperature fluctuations. The entire equipment was marketed in 1960 (Fig. 3), becoming generalized for different temperature domains, laboratory cell volumes, temperature programs, etc. In fact, the Peltier devices were used less and less. The system, having two groups of thermocouples, provided directly three sensitivities, using the smaller group, the larger group, or both connected in series.

In his 1956 book, Edouard Calvet [15] confirmed his lasting interest in the estimation of process kinetics by means of conduction calorimetry: on page 139: “Nous pensons que la plupart des recherches physico-chimiques devraient débiter par l’étude d’un enregistrement fidèle de la puissance calorifique produite par la réaction en fonction du temps”<sup>11</sup> and on page 277: “La thermocinétique devient une méthode d’étude fondamentale ... ”.<sup>12</sup>

## 5. Sensitivity, resolution and baseline stability

To compare with the current equipment, it is necessary to estimate the characteristics of the devices, and to make an elementary evaluation of the sensitivity as a function of

<sup>11</sup> We believe that the majority of the physico-chemical investigations should start from a curve representing exactly the energetic dissipation against time.

<sup>12</sup> Thermokinetics becomes a basic analysis method.

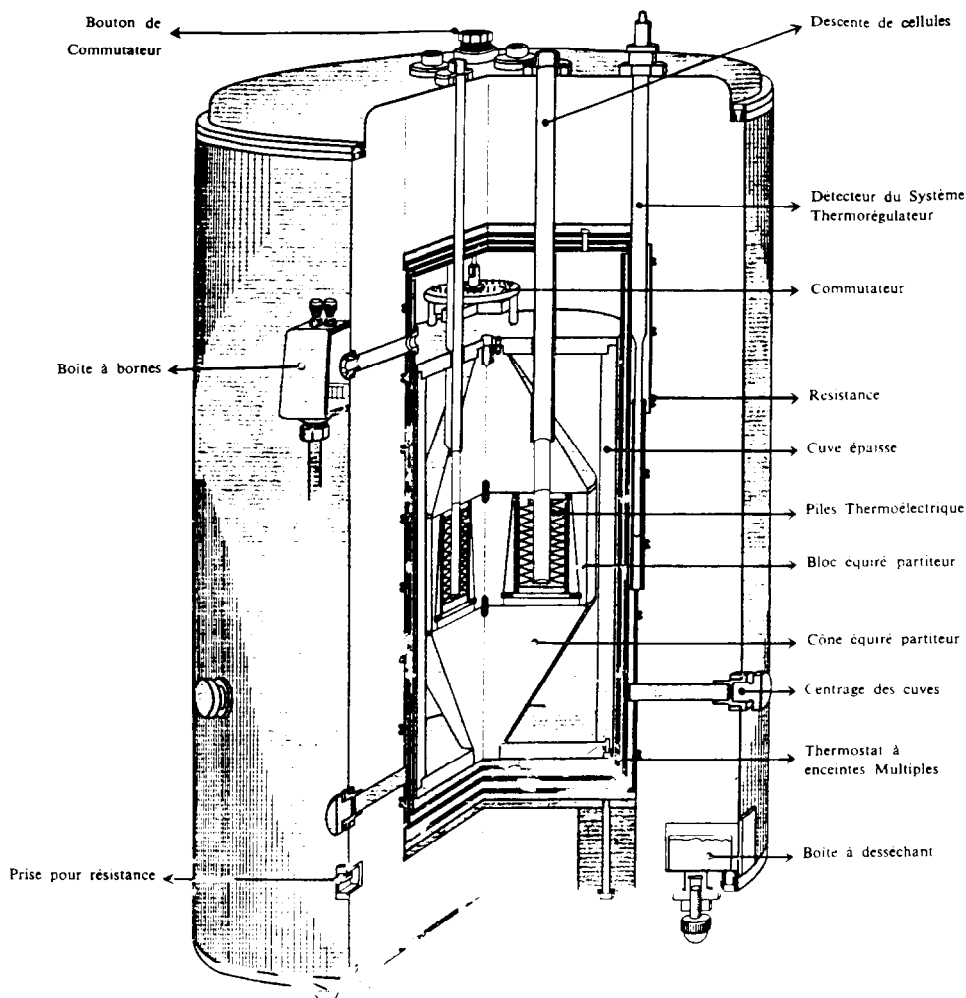


Fig. 3. Standard Tian-Calvet differential heat conduction calorimeter (DAM constructeur, Lyon).

the number of thermocouples and of the characteristics of the Seebeck effect of the wires used in the detecting system (Table 1). Table 1 gives the power resolution in the steady state and/or the energy resolution associated with the pulse signals. The galvanometer initially used by Tian (resistance  $21 \Omega$ ) had a  $5 \text{ nA mm}^{-1}$  resolution with the scale at 1.50 m [5]. The Kipp galvanometer, with the same resistance, had a resolution of  $0.5 \text{ nA mm}^{-1}$  at 1 m. The resistance of the group of thermocouples stayed between 22 [5] and  $50 \Omega$  and the galvanometers operated up to 1 Hz. The associated Johnson noise (thermal parasitic e.m.f.) was approximately 5 nV. This e.m.f. produces fluctuations on the galvanometer equivalent to a 0.2 m shift; this is the threshold of the system resolution. The Tian and Calvet equipment supplied the maximum resolution avail-



Table 1

Relative sensitivity and resolution from the literature; galvanometer spot deviation 1 mm; the heat power resolution corresponds to a steady state, the energy resolution to a pulse response. The relative sensitivity was evaluated from the Seebeck effect and the number of thermocouples. The volume of the Tian cell approaches 7 ml; in the Calvet cell, the volume was near 16 ml

	Tian 1922 [5]	Calvet 1947 [8]	Calvet 1956 [15]
Number of thermocouples	42 (+ 7 Peltier)	128 (+ 16 Peltier)	800 (+ 200 Peltier)
Alloys used	Iron–constantan	Chromel–constantan	Chromel–constantan
Relative sensitivity	1.0	3.6	22.8
Resolution	$\approx 50 \mu\text{W}$ $\approx 400 \mu\text{J}$	$\approx 1 \mu\text{W}$	$\approx 0.5 \mu\text{W}$ $\approx 700 \mu\text{J}$

able. Actually, the resolution is intrinsically limited by the Johnson noise which increases with the number of thermocouples (increasing the resistance) and, moreover, with the maximum frequency being accessible, is determined by the expected oscillographic characteristics of the equipment. To reduce the Johnson e.m.f. ( $\varepsilon$ ) and to improve the resolution, the accessible frequency ( $\nu$ ) must be reduced. In fact, both magnitudes are related by

$$\varepsilon \sim \sqrt{\nu}$$

For different types of measurements [5], the lengths of time for the experimental measurement are lower than 36,000 s. They were recorded photographically and go up to  $\pm 300 \mu\text{W}$  (full scale  $600 \mu\text{W}$ ). Actually, the recording system would digitalize with less than 1000 points. The drift effects are included in the height of the thermogram which is why it can be considered equivalent to the equipment resolution ( $\approx 1$  mm high).

In the differential calorimetric systems built by Calvet towards 1960, the resolution was of  $\approx 2 \mu\text{W}$  (the standard Calvet systems have nearly 400 thermocouples). The drift was irrelevant. Using air conditioning and a highly controlled room temperature, the resolution level approaches  $\leq 1 \mu\text{W}$ . If we assume that an extremely careful construction of the differential mounted elements compensated to 99%, the drift would be included in the Johnson noise. The resolution level under 1 Hz frequency, i.e. 0.1 Hz, would stay near  $0.1 \mu\text{W}$  and the recorders used (full-scale 250 mm) would digitalize with fewer than 2500 points. In practice, full scale (for the Tian and Calvet calorimeter) is under 2000 points.

## 6. An application of the non-differential calorimeter

The best calorimeters that can be bought provide, at a constant temperature, practical resolution between 0.1 and  $1 \mu\text{W}$  and ordinarily between 1 and  $10 \mu\text{W}$ . The calorimeters operating on a programmable temperature basis have a resolution between 10 and  $30 \mu\text{W}$ . The prices stay between US \$ 50000 and 100 000.

Currently, the thermostats (see, for instance, the Lauda or Haake thermostats, US \$ 10 000) generally have stability and resolution higher than 0.01 K. The data capture systems are digitalized by means of DMMs. The cheaper ones (US \$ 1000) allow resolution of 100 nV. The full scale is 100 mV and the sampling is around 1 s (or less). Other voltmeters allow 10 nV and a full scale near 1 V. This puts the resolution on the best conditions of a galvanometer, i.e. the Kipp type used by Tian and Calvet, but with a reading that attains directly 1 000 000 points or more. The systems can operate directly without reducing resolution and without compensating the introduced dissipation.

The drift is associated with the environmental effects (external temperature fluctuations) and the differential system was introduced to obtain full resolution during long time phenomena. *If the thermostat is stable enough* (or the temperature rate in a temperature program), *the use of the differential system does not seem necessary at all* except, may be, to allow observation when operating near the resolution limit imposed by the Johnson noise.

A preliminary experimental analysis of the current possibilities has been performed with a non-differential calorimeter using semiconductor detectors, like the one described in Refs. [14, 23]. The calorimeter (Fig. 4) is protected with a multilayer system (external diameter, near 10 cm) and submerged in a Lauda type RLS 6-D thermostat. The calorimeter sensitivity is about  $680 \text{ mV W}^{-1}$  at 298 K and its first time constant, determined by Joule calibration is 19 s (dependent of the heater type used). Using DMMs with 100 nV resolution, the baseline drift over a long time ( $\approx 24 \text{ h}$ ) is around  $1 \mu\text{V}$ . In Fig. 5A, the baseline of this system is shown; those obtained in a classical differential calorimeter are shown in Fig. 5B. The “noise and drift” in the example used (Arion Electronique BCP type [25]) is around  $1 \mu\text{V}$  (near  $0.5 \mu\text{V}$ ), due to room temperature fluctuations. Fig. 5A and B show that the effective noise and drift are equivalent in both experimental systems.

The thermograms in Fig. 6 belong to different types of quenching of a Cu–16.06 at% Zn–15.97 at% Al sample (mass 1.304 g, electronic concentration 1.48 e/a). The time constants associated with the atomic ordering processes related to each quenching can be determined from the experimental curves (Table 2). The mathematical conditions relating the time constants of the calorimeter and the time constants of the phenomena analysed are discussed below (Section 8).

The results are reproducible for “identical” heat treatments performed for the same samples. The dependence on the type of quenching is clearly shown in Fig. 6A and B, including the effect of introducing the sample or the reference effect. Two curves are presented for each heat treatment to show the reproducibility of the measurements. Obviously, a supplementary effect can be associated with the mass of the sample. In fact, its volume has an effect on the cooling rate and, therefore, over its initial ordering status.

## 7. Conclusion

Analysis of the original works by Tian and Calvet highlights the effects of the changing environmental temperature around the calorimeter as the reason behind the

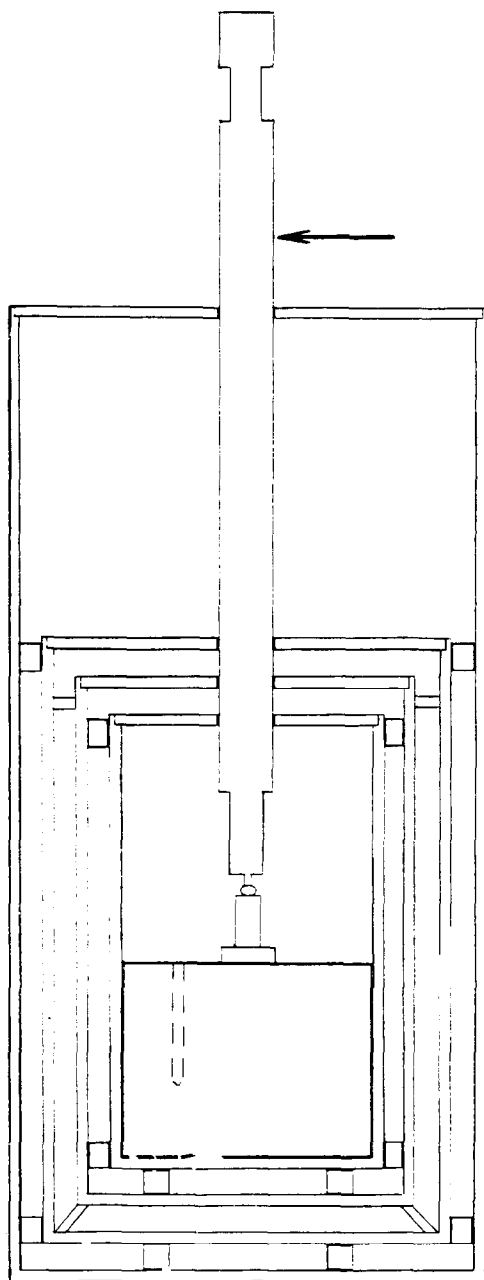


Fig. 4. Schematic representation of the non-differential calorimeter; the arrow indicates the “handler” used for the introduction of the sample.

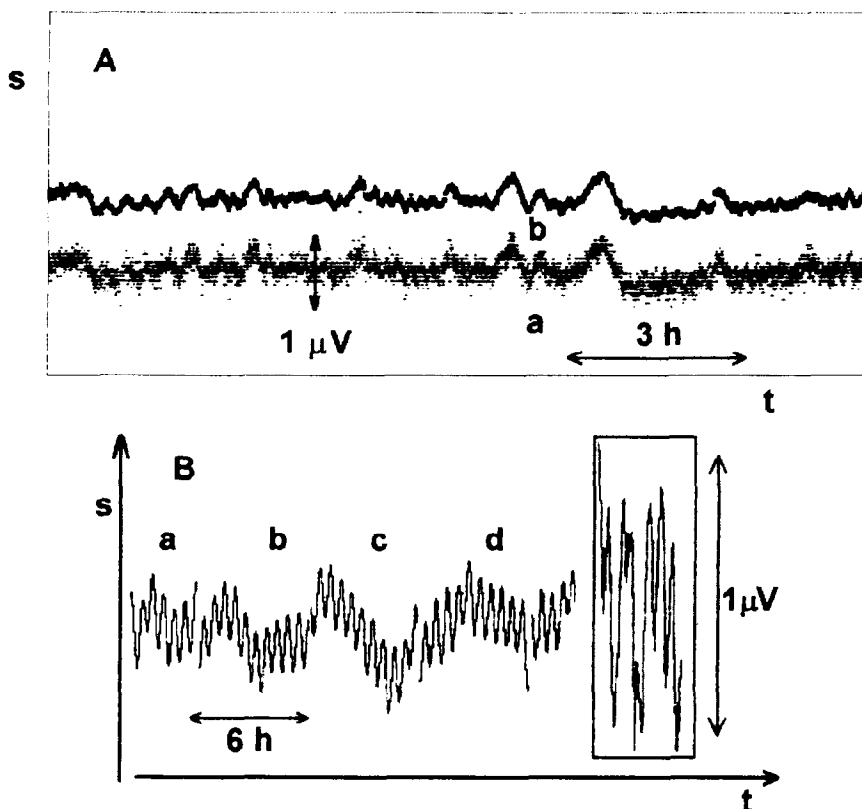


Fig. 5. Baseline noise and drift against time. A. Non-differential calorimeter: curve a, sampling, 1.2 s; curve b, smoothed curve, equivalent sampling, 20.4 s. B. Differential calorimeter (Arion Electronique BCP type used in liquid mixtures analysis [25]): left, a, b, c, d consecutive files, without stirring action; right, with typical stirring action.

introduction of the differential system. The resolution of the equipment was around  $1 \mu\text{W}$ , which is equivalent or higher than the current commercial calorimeters. The galvanometric detecting systems operated to a full scale of  $\leq 2000$  points, which implied compensation of the dissipations obtained or operation at a lower resolution.

The use of 0.01 K magnitude resolution and a stability thermostat allows the construction of non-differential calorimetric systems that, with a resolution and baseline drift of around  $1 \mu\text{W}$ , have a full scale of 1 000 000 points available. This is why it seems natural to suggest that, in the technological development of conduction calorimeters, the systematic use of differential systems must be reconsidered. In general, it seems possible to use non-differential devices that have a higher symmetry and a more simple construction.

The use of a preliminary non-differential system with a Seebeck element (bismuth telluride) semiconductor has yielded information about the time constants associated

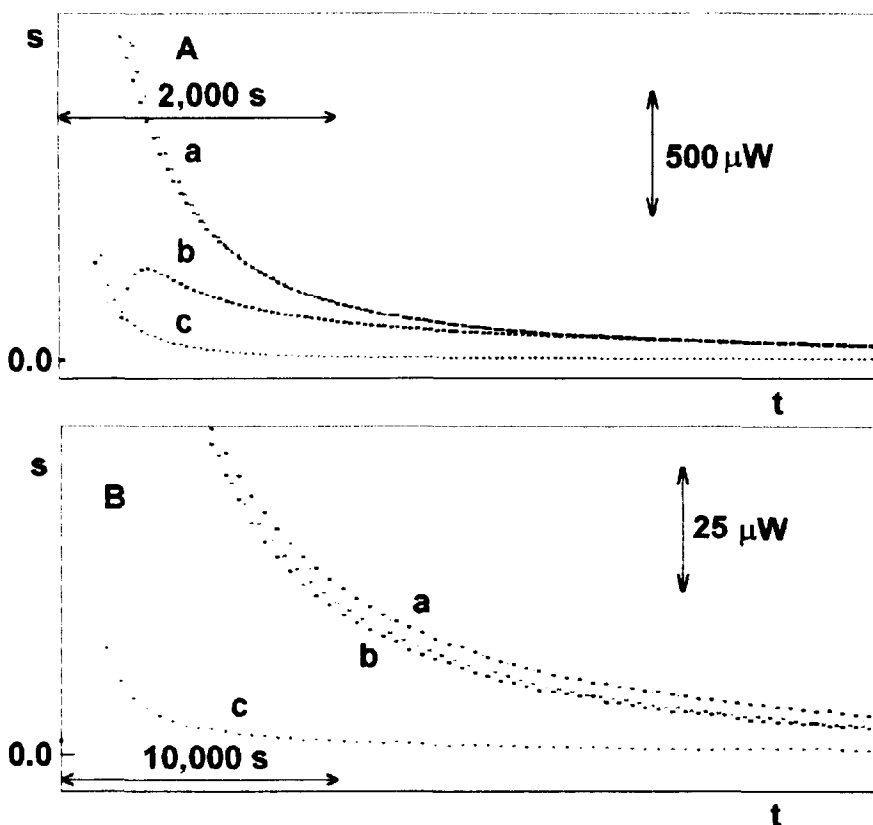


Fig. 6. Power ( $\mu\text{W}$ ) against time (s). A. Initial part of the thermograms for: a, water quenching; b, air quenching; c, reference effect. B. Later part of thermograms for: a, air quenching; b, water quenching; c, reference effect.

with ordering process dynamics on shape memory alloys (Cu–Zn–Al) in measurements lasting 2 or more days.

## 8. Additional remarks

### 8.1. From the thermogram to the time constants $\tau_k^W$ of the ordering processes

If the heat power  $W(t)$  supplied to the calorimeter has the form

$$W(t) = \sum_k a_k^W e^{-t/\tau_k^W}$$

the classical transfer function can be represented by

$$TF(t) = \sum_j a_j e^{-t/\tau_j}$$

Table 2  
Time constants obtained from a fitting of the thermograms

	$\tau_2^W/s$	$\tau_1^W/s$	$\tau_2/s$	$\tau_1/s$
A	–	–	1.700	10.000
B	4.200	17.000	1.700	10.000
C	7.200	40.000	1.700	10.000

A, values for “reference” measurements; B, water quenching; C, air quenching.

The thermogram  $s(t)$  can be obtained by convolution of  $W(t)$  using the transfer function  $TF(t)$  by

$$s(t) = \int_0^t W(t-u) TF(u) du$$

If the two conditions

$$\tau_k^W \ll \tau_j \text{ for the complete set of } k \text{ and } j \text{ values}$$

and

$$t \gg \tau_j \text{ for all } j \text{ values}$$

are satisfied, the convolution formula ( $S$  parameter represents the sensitivity) reduces to

$$s(t) \Rightarrow SW(t)$$

and the thermogram approaches, directly, the power dissipated. If the conditions do not hold, deconvolution procedures are to be used for the evaluation of  $W(t)$ .

## 8.2. Non-differential, differential and coupled calorimeters

If the calorimetric system can be represented by an RC-analogy, the heat transfer equation reads

$$W_j(t) = C_j \frac{dT_j}{dt} + P_{j0}(T_j - T_0) + \sum_{l \neq j} P_{jl}(T_j - T_l)$$

where  $W_j(t)$ ,  $C_j$ ,  $P_{j0}$ ,  $P_{jl}$  are, respectively, the power dissipated in the  $j$ th element (at  $T_j$ ), the heat capacity, the thermal coupling with the thermostat (at  $T_0$ ) and couplings with the neighbouring elements.

In Fig. 7, a model of a four-element calorimeter with explicit couplings is schematized to analyse the particular behaviour of the non-differential, differential or coupled calorimeters. Obviously, more complex models have the same mathematical behaviour. If no coupling exists between the two parts ( $P_{jj} = 0$ ), the overall system of the 8 elements can be differential by “appropriate” electrical links. For  $P_{jj} \neq 0$ , the system is a “coupled calorimeter” as, for instance, in standard DSC systems.

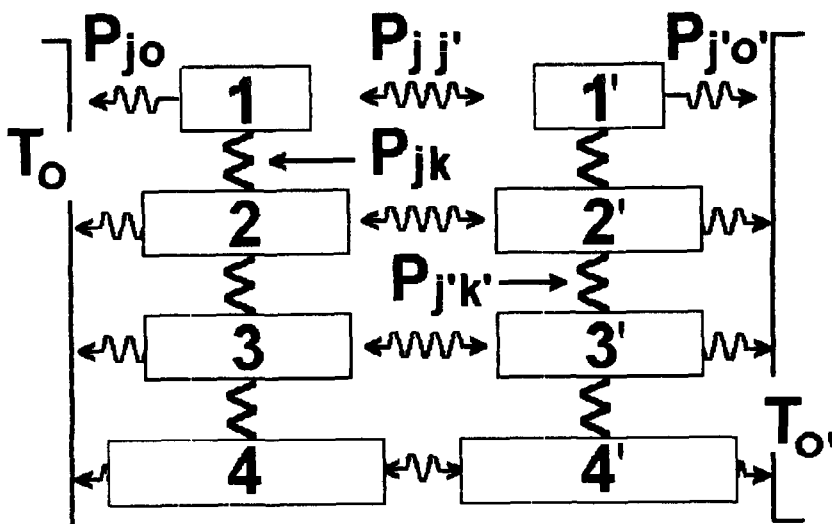


Fig. 7. Schematic conduction calorimeter: 1, calorimetric vessel; 2 and 3, thermocouple (“warm” and “cold” junctions); 4, calorimetric block;  $T_0$ , thermostat and thermostat temperature;  $P_{jk}$ , thermal couplings; primed values correspond to the “reference” or differential element.

The representative equations, for elements 1–4 of Fig. 7 reads

$$W_1(t) = C_1 \frac{dT_1}{dt} + P_{10}(T_1 - T_0) + P_{12}(T_1 - T_2)$$

$$P_{12}(T_1 - T_2) = C_2 \frac{dT_2}{dt} + P_{20}(T_2 - T_0) + P_{23}(T_2 - T_3)$$

$$P_{23}(T_2 - T_3) = C_3 \frac{dT_3}{dt} + P_{30}(T_3 - T_0) + P_{34}(T_3 - T_4)$$

$$P_{34}(T_3 - T_4) = C_4 \frac{dT_4}{dt} + P_{40}(T_4 - T_0)$$

The “thermogram”  $s(t)$  corresponding to this non-differential system can be defined by

$$s(t) = k(T_2 - T_3)$$

and the transfer function reads

$$TF(t) = k \sum_{j=1}^4 a_j^* e^{-t/\tau_j}$$

The fluctuations on the thermostat temperature

$$T_0 \Rightarrow T_0 + \delta T_0$$

produce perturbations on the thermogram. For instance, the first equation of the system becomes

$$W_1(t) = C_1 \frac{dT_1}{dt} + P_{10}(T_1 - (T_0 + \delta T_0)) + P_{12}(T_1 - T_2)$$

that is

$$W_1(t) + P_{10}\delta T_0 = C_1 \frac{dT_1}{dt} + P_{10}(T_1 - T_0) + P_{12}(T_1 - T_2)$$

The effect of the external temperature disturbances acts as an unknown power over the actual thermogram in this “non-differential situation”.

The second set of equations for elements 1', 2', 3', and 4' reads

$$W_{1'}(t) = C_{1'} \frac{dT_{1'}}{dt} + P_{1'0}(T_{1'} - T_0) + P_{1'2}(T_{1'} - T_2)$$

$$P_{1'2}(T_{1'} - T_2) = C_{2'} \frac{dT_{2'}}{dt} + P_{2'0}(T_{2'} - T_0) + P_{2'3}(T_{2'} - T_3)$$

$$P_{2'3}(T_{2'} - T_3) = C_{3'} \frac{dT_{3'}}{dt} + P_{3'0}(T_{3'} - T_0) + P_{3'4}(T_{3'} - T_4)$$

$$P_{3'4}(T_{3'} - T_4) = C_{4'} \frac{dT_{4'}}{dt} + P_{4'0}(T_{4'} - T_0)$$

The associated thermogram is defined by

$$s'(t) = k'(T_{2'} - T_{3'})$$

and the transfer function associated with this set of elements reads

$$TF'(t) = k' \sum_{j=1}^4 a_j^* e^{-t/\tau_j}$$

If thermal perturbations act over the two subsystems and, also, if primed and uprimed magnitudes are strictly equal, the introduction of the differential system deletes completely the effect of thermostat fluctuations.

The thermogram for an arbitrary differential system reads

$$s^{\text{DIF}}(t) = s(t) - s'(t) = k(T_2 - T_3) - k'(T_{2'} - T_{3'})$$

and, in perfectly differential conditions, the effects of the  $\delta T$  parameters are strictly compensated. The equal perturbations  $\delta T$  and  $\delta T'$  cancel out by subtraction

$$s^{\text{DIF}}(t) = k((T_2 - T_3) - (T_{2'} - T_{3'}))$$

The dynamic response (for instance, the time constant values) of the differential system is the same as for the non-differential one. For a non-strictly differential system, the two complete series of time constants for each element remain in the output thermogram and in the transfer function.



If couplings exist between the two systems ( $P_{jj} \neq 0$ ), the representative equations of the whole system read

$$W_1(t) = C_1 \frac{dT_1}{dt} + P_{10}(T_1 - T_0) + P_{12}(T_1 - T_2) + P_{11'}(T_1 - T_{1'})$$

$$P_{12}(T_1 - T_2) = C_2 \frac{dT_2}{dt} + P_{20}(T_2 - T_0) + P_{23}(T_2 - T_3) + P_{22'}(T_2 - T_{2'})$$

$$P_{23}(T_2 - T_3) = C_3 \frac{dT_3}{dt} + P_{30}(T_3 - T_0) + P_{34}(T_3 - T_4) + P_{33'}(T_3 - T_{3'})$$

$$P_{34}(T_3 - T_4) = C_4 \frac{dT_4}{dt} + P_{40}(T_4 - T_0) + P_{44'}(T_4 - T_{4'})$$

$$P_{11'}(T_1 - T_{1'}) = C_{1'} \frac{dT_{1'}}{dt} + P_{1'0}(T_{1'} - T_0) + P_{1'2'}(T_{1'} - T_{2'})$$

The undifferential transfer function includes all the elements of the whole system and, obviously, the complete series of time constants. In this example, there are eight time constants. If the system is perfectly differential, the choice of a set of new variables

$$\Theta_j^{\text{DIF}} = T_j - T_{j'}$$

reduces the differential equation system from eight to four equations. The transfer function is then defined by only four time constants corresponding to the non-differential system without couplings.

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