Journal of Thermal Analysis, Vol. 52 (1998) 663–681

CONDUCTION CALORIMETERS[*]
Heat transmission systems with uncertainties

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Abstract

A critical reading of early papers on heat flux or conduction calorimetry (1920–1965) reveals the original kinetic aims of the developed instrumentation and the progressive appearance of the intrinsic difficulties. An analysis of current publications demonstrates biased applications/results relating to equivalent problems. Modelling of the systems by the RC analogy of heat transfer equations establishes the problems connected with the structure of the apparatus and also the experimental conditions to be fulfilled. Analysis of the equations highlights several possibilities that are used in part today. For instance, the reduction of noise and drift on the calorimeter output by a software approach and the conditions to be attained with crucibles for increased accuracy.

Keywords: accuracy, conduction calorimeter, modelling

Introduction

Around 1960, the company D.A.M. began to market the Tian-Calvet Microcalorimeter, supplying a complete measurement system involving calorimeter, calibration system, temperature control and auxiliary elements. The commercialization was based on the book written by Calvet and Prat [1]. The exhaustive text of this book contains technical data on the construction and on operative methodologies, and a large number of examples of physicochemical and biological applications. In 1965, Calvet organized an international colloquium in Marseilles [2], which can be regarded as the final element in this early cycle (Calvet died in 1966). Progressively, new apparatus appeared and conduction calorimetry and thermal analysis became standard methods in material characterization and in the study of biochemical and biological systems.

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1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The year 1965 was the starting point for the standardization of the processes used in calorimetric techniques, and for their generalization as methods of characterization. Different manufacturers progressively constructed complete equipment, operating over large temperature domains and providing standard routines for the treatment of observations and the elaboration of the results. Calorimetry and thermal analysis thereby became customary techniques used in university and industrial laboratories that could purchase complete operative equipment. At the beginning of 1980, the systems were progressively computerized, leading to the present state of the art: completely automated measurement systems controlled by the software provided with the equipment.

In this survey we present selected extracts from the papers published by Tian, Calvet and Laville up to the Marseilles colloquium in 1965. These reveal the inherent kinetic aims of their activities, and the advantages of the differential systems, together with the dynamic problems observed in the measurement of the dissipated heat power and/or energy. Study of the conduction calorimeters developed by Tian, together with the improvements introduced by Calvet, is very illuminating. Further, an analysis of recent references demonstrates that the criteria used in some cases are still uncertain. This is particularly the case for the introduction and systematic use of computer resources, perhaps without sufficient critical analysis; these techniques are especially tempting, as they are capable of furnishing series of simple measurements and frequently apparently excellent results, but which may nevertheless sometimes be of doubtful validity. From several recent references, aspects of constan interest relating to dynamics have been selected: the kinetic goals of the instrumentation, the integration of the heat flux produced in the laboratory cell, the disturbances associated with the external surroundigs and, in general, the reliability of the results relating to differences between accuracy and reproducibility. The use of an adequate mathematical model allows an analysis of the calorimetric and, possibly, thermal analysis systems and clarification of the possibilities available, e.g. the reduction of noise and drift on the calorimeter output signal when a temperature-controlled system is used, and the formal conditions needed in the calorimetric cell.

The early period (1920-1965) in heat flux or conduction calorimetry: from Tian to Calvet

In 1933, Tian published a book [3] summarizing his calorimetric investigations, in which he stated: 'A calorimeter which has a rapid cooling rate disposes of a new property: it can also function as a thermal oscilloscope. The system allows measurement of the total amount of heat released during the experiment and ... one can follow the instantaneous heat power...'. Amongst his objectives (mainly isothermal measurements and a dynamic approach), it is necessary to highlight the conversion of thermal measurements into electrical measurements, thereby allowing compensation for the higher part of the signal with the objective of obtaining the maximum resolution possible on the residual part of the signal* or 'thermogram' [4]. The capability of the experimental system was limited by the detector system: the full scale did not surpass 2000 points (today, the full scale of voltmeters overcomes 5 or 6 significant figures). In December 1922, Tian presented the conduction calorimeter to the Société Chimique de France and stated that: 'one of the most appropriate ways to determine the rate of chemical reactions consists in determining the amount of heat released in each unit of time' [5] and indicates: 'the value of compensation calorimeters in measurements of the amounts of heat released by slow reactions'. This first Tian calorimeter was surrounded by several shells [6, 7]. The device contained two iron-constantan thermocouple groups. One was used to compensate the dissipation (by hand control) by means of the Peltier effect or an auxiliary Joule effect. The other group acted as a null detector by means of a galvanometer. The correct performance of the compensation and the invariance of the temperature of the reagents were therefore guaranteed in this way. the reaction was not affected by the change in temperature associated with the dissipation of the reaction. The performance of measurements using Joule or Peltier compensation requires continuous care of the experimental system in experiments covering several hours. In general, the emphasis placed on the Peltier effect was much larger than its subsequent applications. The parasitic effects of the Joule effect were decisive as concerns its limited practical applicability.

Measurement of the heat power and/or the dissipated energies was one of the main subjects: '... I resolved to use it as a calorimetric oscillograph ... its application as an integrator calorimeter has been studied (and) this use seems to me to be the most important'[3]. In this description, we find the coexistence of two actions. One is the decisive contribution of the evaluation of the process kinetics to the development of the equipment. The other is the tendency to use a calorimeter to measure total dissipated energies. Today, the measurement of dissipated energies is a main subject in both isothermal and programmed temperature applications (as in DSC) [8]. From the experimental output signals, the instantaneous dissipated power may be found via the Tian equation. However, his aim was to make 'oscillographic' equipment, i.e. a fast system appropriate for furnishing directly the dissipation $W(t)$:'... equipment that merits the name oscillograph must furnish directly a curve ... that represents the dissipation W'. Additionally it may

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* The compensation is adequate to ensure the constancy of temperature before and after the experiment and to maintain it within a reduced margin of fluctuation during the measurements.This situation is independent of parasitical effects related with the location of energetic dissipations in the laboratory cell. In Tian's calorimeter, the detector system is not a perfectly integrated sphere, nor is it a closed surface around the cell. This working hypotheses, repeatedly used by Calvet, is intrinsically incorrect, although it provides satisfactory results via an adequate calibration for each type of measurement.

be deduced from the Tian equation that the dissipated energy can be obtained by integration of the associated calorimeter output signal. The Tian equation was the first formal approach to the actual dissipated power or thermogenesis, or in other words: a deconvolution method (see, for instance, [9, 10] and related references).

Calvet started his doctoral thesis under the direction of Tian in 1926. His work centred on a kinetic study of the hydrolysis of amides, the aim being an estimation of the process kinetics. Kinetic study always seems to have been the main goal behind the ideas of Tian and Calvet. Twenty years later (1946), Calvet introduced [11] the differential system, through the association of two Tian calorimeters in a single thermostatic bath: 'We have built a new calorimetric device that will be able to work at all temperatures up to nearly 80°C, with a higher resolution and with a measurement time that is practically unlimited for each experiment'. Reference [8] gives the basic reasons for this modification relative to the Tian device: 'The origin of the baseline drift ... The changes in temperature of the ... (floor of the deep room) ... Thomson effects that appear between different parts having non-uniform temperature ... It is very difficult to perform suitable experiments lasting more than a day'. The system design started from the association of two identical calorimeters connected in opposition [12], with increases in the symmetry, in the number of thermocouples (from 42 to 800) and in the resolution (from 50 to 0.2μW) '... we have associated two identical calorimeters in opposition. These two calorimeters, including galvanometer and switch,... are placed inside a large block of copper in an appropriate way. This latter is placed in a thermostat, the temperature of which can be changed as desired.' In his 1956 book, Calvet [1] confirmed his unwavering interest in estimations of process kinetics by means of conduction calorimetry: 'We believe that the majority of physico-chemical investigations should start from a curve representing exactly the energetic dissipation against time.' (page 139), and 'Thermokinetic is becoming a basic analysis method ...'(page 277).

The equipment that came onto the market in 1960 was generalized for different temperature domains, laboratory cell volumes, temperature rates, and so on. The system with two groups of thermocouples (and two Peltier possibilities) directly afforded three sensitivities, through use of the smaller group, the bigger group or the two groups connected in series. In fact, the Peltier possibilities were practically unused. The Tian equation remained the basis for the modelling of behaviour until 1955. The papers published by Laville [13,14] provided a partial generalization of the Tian equation, starting from the Fourier heat transfer equation and the Laplace transform, with the same limitations as for the Tian equation [13]: 'The Calvet microcalorimeter is essentially a volume conductor (for instance, the calorimetric vessel), which receives from one part of this area (S_1) a heat flux $\varphi(t)$. From another part (S_2), the heat is transmitted towards the exterior, which is carefully thermostatized.' The equation used implies a heat balance, the area detector S_2 being the only boundary for the heat losses from the working space (crucible). It is implicitly considered that a laboratory cell absorbs energy from a dissipation element (for instance, a resistance inside S_1) and simultaneously transmits energy to the thermostat via the detector system (surface S_2). The Laville work permits the first formalism of the thermostat fluctuations acting on S_2: 'The fluctuations (of the thermostat temperature) produce a zero drift which, due to the linearity of the equation, superimposes the output signal which would be obtained without any disturbances'.

The model used is that established from the Tian equation and generalized by Laville: 'I. A Schematic description of Calvet's microcalorimeters. ... 3. Two thermoelectric batteries ... which completely surround the cell, establishing the thermal link with the external space ... The *e.m.f.* of the detector battery is proportional to the heat flux which escapes from the cell independently of the temperature distribution at the surface or inside the cell.' Laville's paper justifies the methods described in previous publications by Calvet, which constitute a basis (explicit or implicit) for the modellization described in 'Microcalorimétrie' and establishes five relevant ideas: a) the system is linear; b) there is a complete integration of the heat flux away from the cell (or the sensitivity is constant); c) the series of time constants is identical in the dissipation of interest, as with the calibration (only one series exists); d) the output signal and baseline drift can be obtained by convolution using in each case an appropriate Dirac or Heaviside input signal; e) two exponentials yield an appropriate representation of the output signal corresponding to the Dirac input [13, 14]. The five ideas originate from: a) the linearity of the heat transport equation and the invariant values of the parameters; b) the Tian equation, but the calorific flux is only partially detected; c) a consequence of the Fourier equation in an invariant and bounded system; d) the output signal originates from two convolutions (two independent input signals and only one output. The first is the dissipation of interest and the second is the effect of the surrounding temperature; two transference functions should be provided and also output signal and the environmental temperature; e) it is probably related to the poor resolution attainable and the difficulties of graphic calculation. Hypothesis b), also used by Tian, is only an approach, and today induces to misunderstandings, with a resulting reduction in the accuracy of the results.

In reference [15], the goals are perfectly clearly set out:'II. Situation of the problem: the search for the thermogenesis starting from the output signal ... III. Solution ... This theory ..., simultaneously solves the following two problems: a) obtaining, via the output signal, the amount of heat $q(t)$ dissipated, and b) correction of the baseline drift.': In current language, part of the analysis assumes that the output signal response only has poles in the transference function. It also takes into consideration the case when: 'As we approach the thermal source or when the cell is very conductive, the output signal presents a sharper maximum which, to be correctly represented, needs at least three exponentials ... the first two exponential terms have positive coefficients and the last is negative.'

There are no indications of a change in sensitivity when the content of the cell is modified (on going from one to another substance), but the shape of the response depends on the content: 'When the cells contain liquids or solids of relatively low thermal conductivity, the impulsive curve is correctly represented by two exponentials ... When the laboratory cell is full of material which is a good conductor ... the impulsive curve is only correctly represented by the sum of three exponentials'. It is evident that analysis of the curves and its treatment was extremely difficult in 1958. For this reason, one of the final observations is surprising, but understandable: '3. Last remark ... one can deduce an apparent paradox in our experiments: it is not appropriate that the thermocouple detectors are close to the thermal dissipation. ... An experimental system producing smoothed output signals is more convenient. ... the curve can be analysed by means of two exponentials ... Perhaps it would be more convenient to insert a thermal insulator between the dissipation and the thermocouples.' The last remark relates with the zeros in the transference function and with the overshoot (an apparent artifact) induced by the limited filtering possibilities available. But the introduction of only one thermal insulator is highly inappropriate: it induces changes in the transference function, without any increase in accuracy.

The colloquium Proceedings [2] permitted a survey of previous work and also showed the appearance of new features. Firstly, Tian's remarks (page 17 in ref. [2]) illustrate the progress introduced around 1922: 'I constructed the microcalorimeters myself ... The tube which contained the laboratory cell was made of copper, it was surrounded by an insulating fabric (silk) onto which the thermocouples were fixed ... With this system, Mlle Béranger confirmed that the heat generated from the esterification of acetic acid and alcohol was positive and not negative as believed earlier. By carrying out the experiment inversely, ... she found the same value, and the heat of hydrolysis was negative.' A difficult and painstaking construction provided new and decisive results. In general, high reproducibility is a necessary condition, but is not equivalent to a guaranteed level of accuracy.

Let us concentrate our attention on the problems relating to the 'invariant' value of the sensitivity [16]*. The experimental development of a reliable measuring system for reaction enthalpies [16] searched for a parallelism between conduction and adiabatic (or isoperibol) calorimetry with the international standards based on benzoic acid. The measurements implied very fast dissipations in the core of the laboratory cell and divergences of the sensitivity values: 'it is necessary for the standard energy and the measured energy to dissipate in a similar manner in the interior of the laboratory cell. ... Despite the fact that the distribution of the thermal flux is not identical in measurement and in calibration ...' In the discussion, we find: 'Why do you not believe that the calibration using the

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[*] Other interesting subjects at the colloquium were the problems associated with thermogenesis evaluation [17, 18], the appearance of semiconductor detectors [19] using only one flat surface, and a suggestion for computerization [20].

Joule effect is not totally satisfactory? According to M. Calvet's book, all the phenomena that occur within the interior of the calorimeter cell can be measured with this type of calibration, independently of the type of spatial distribution of the thermal flow'; '...in calorimetry, it is advisable to carry out comparative measurements. It is necessary in all cases that the standard thermal flows and the measurements being studied have the same geometric distribution and the same intensity...', 'Why? In accordance with M. Calvet's theory, an excellent calibration is obtained independently of the type of flow distribution in the cell...' Calvet continues: 'The same total area will always be obtained, independently of the type of output signal or the distortions occasioned by the variations in the position in the cell's interior, ... what changes is the form according to the position of the thermal source within the interior of the cell. The effect is important in thermokinetics, but in calorimetry it is irrelevant...'. The last remark emphasizes the change in sensitivity. 'But when the contents... have a similar volume, ... the calibration coefficient (sensitivity) sometimes depends on the geometric distribution of the thermal flow: it cannot be considered that the laboratory cell is a perfectly closed space...' In fact, the partial covering of the detector system induces sensitivities that change with the content and internal distribution of heat production in the interior of the cell. Table 1 (adapted form ref. [21]) illustrates the dependence of the sensitivity on the content and the position of the heating resistance in a 100 cm^3 Tian-Calvet calorimeter. The reproducibility is excellent, but the divergencies between positions and/or contents exceed 2.5% and can be increased in a flash reaction such as combustion. The sensitivity variancy is a recurrent problem with no easy solution. Through the use of relatively sophisticated calorimetric models, it is possible to elucidate experimental conditions which give a sensitivity independent of the process involved. For this, an adapted laboratory cell constructed as a multi-shell system with thermal protection seems appropriate (see below, in models).

The thermogenesis evaluation [17, 18] gave rise to similar remarks relating to a differentiation between analysis measurements (i.e. several forms of Joule ef-

Table 1 Sensitivity (mV/*W*) in a standard Tian-Calvet calorimeter (100 cm^3 laboratory cell) [21] at 293 K

Contents	A	B	C
Hg	41.78	41.96	42.07
Hg(*)	41.88	42.04	42.16
Cu	42.35	42.41	42.57
Fe	42.70	42.81	42.78
Al	41.07	41.45	41.74

(*) unloading and reloading the same laboratoy cell; A: heater (resistance) in the cell axis; B: coaxial in the middle position; C: coaxial near the cell wall fects on the same resistance) and unknown measurements: '... when it is not known where the dissipations occur ... in what way can corrections be applied;' 'The problem consists in finding an experimental calibration method which produces an identical response to the response generated from the phenomenon ... In some cases, it will be very difficult to obtain usable practical systems'. In one comment by Calvet, he appears to agree with some variation in the sensitivity with regard to the content: 'From an external point of view, it is possible to obtain almost perfect identity of the differential elements. It is necessary to put the same elements in both cells and to know perfectly how to carry out the calibration required'.

Remarks on the more recent literature

By the end of 1965, differential equipment was available (baseline drift corrected by 'hardware') in which reliable behaviour and high resolution had been progressively introduced into the current automated systems. In particular, an important part of the analysis was based on a deep knowledge of the experimental equipment (calorimeter and measurement system), and a slight systematic misunderstanding. In fact, the models used were based on an implicit working hypothesis: the dissipation produced during the calibration procedures and that associated with an unknown process were considered to be identical. This means that the thermocouple system constitutes an 'integrant sphere' or, otherwise, that it always detects a constant fraction of the total heat flux. The current marketing and use of a 'standard calibration system' (for instance, involving a Joule effect on resistance or melting standards) are a partial consequence of this working hypothesis. After 1965, heat flux or conduction calorimetry was progressively developed in standard analytical methods using provided software package. Several improvements resulted from new insight into the applications, but the theoretical basis of the quantitative measurements was related with isothermal calorimetry. Today, however, just as in the past, several papers indicate that the old questions remain unsolved.

Three examples will be provided. The first is connected with an unchanging goal: the capability of the calorimeter to produce kinetic information and, as a first result, accurate measurements of dissipated energy. The results obtained from the study of slow phenomena are satisfactory, e.g. the use of calorimeter output signals associated with isothermal measurements over several days, as in Ref. [22]: 'The kinetics and even the mechanism of the reaction of cement with water can be successfully investigated by the use of microcalorimetry'. The kinetic goal [23] does not avoid several difficulties relating to the apparent ease of energetic mea-surements. For instance, a preliminary result [24] with a Calvet calorimeter yields a stepwise curve for the mixing enthalpy measurements on a binary without a miscibility gap. The use of variable-temperature systems increases the difficulties and several results are qualitative, but the comparison of output signals furnishes reliable information [25 ,26]. Quantitative evaluation of the experimental curves is a more difficult and not completely solved task. Modelling with insufficient complexity leads to a thermal description that is unable to characterize the main features of instrumentation and for inexperienced users induces an illusory level of accuracy [27]: 'A general mathematical treatment is given which relates the techniques of classical DTA, power-compensated DSC and heat-flux DSC. An idealized system, representative of almost any type ... for the idealized system ... there are no other losses in the simplified system.' With the use of only four heat capacities in a differential system, a relevant lack of accuracy can be expected. From an energetic point of view, the proposed model is similar to the Tian and Calvet representation of calorimeters. In fact, the heat flux is completely integrated without parasitic and evolutive losses. At the end of the paper, a minor comment suggests the potential appearance of difficulties: 'the ... (thermal) resistance between the sample pan and the sample itself, which was ignored in the simple analysis given ...'. General and idealized or simple? That is the question. An exceedingly simplified model is probably an optimistic and incorrect approach. The reliability in the experimental result is related with the appropriate complexity of the equations describing the behaviour of the apparatus.

The second example centres around the reliability of the software package. The equipment usually works as a black box system. For instance, reference [28] indicates that 'Enthalpy changes are evaluated by a ... (provided) ... software package', or in reference [29]: 'Data analysis ... was performed ... with ... provided software'. The difficulties are intrinsic [30], even in standard and fundamental melting processes. In reference [31], Callanan explains the main difficulties encountered in temperature determination and in fusion enthalpy measurements. At a heating rate of 10 K min^{-1}, the measured melting temperature of Al differs by around 10 K from the thermodynamic value (933.61 K). The fusion enthalpy is scattered from 312.4 to 326.3 J g^{-1}. The standard value is 370.0 J g^{-1}. The generalized application of provided software produces a low level of accuracy: '... the difference between the observed transition temperature and the value accepted for it is determined for one material; the same correction is then applied ... For enthalpy, a correction factor is derived for one material and applied to all ... the results obtained in this study showed that this procedure does not give results as reliable as ...'. Achieved results with high accuracy is a problem which has received constant attention, and the standard software seems unsatisfactory [32]: '... operation manuals only explain how to handle the computer and the software, suggesting that the software will fix every problem. ... It follows from experience that this holds for routine measurements, but that precision measurements need a more particular knowledge of the peculiarities ...', or in [33]: 'It should be borne in mind that for the definition of the temperature scale static methods are used which in a scanning calorimeter can always be realized only approximately. Furthermore, the location of temperature measurement in the calorimeter is never the location of the sample. In dynamic measurements, this leads to a systematic error which is a function of the test parameters'. Systematic error is temperature and temperature rate-dependent, with a particular dependence on the cell contents and internal distribution: the software does not fix any of the new problems.

The third example relates to the difficulties associated with interpretation of the fitting results. The obtaining of results from calorimeter output signals involves a margin of uncertainty, which is relatively higher when the curves are to be identified with the models. The accuracy of physical parameters determined by fitting (from experimental output signals) displays a high level of uncertainty [34]: 'A method is suggested for obtaining polynomials from experimental data. ... A number of procedures have been reported for calculating the non-isothermal kinetic parameters. ... Merely obtaining a correlation coefficient of one or nearly one for a chosen polynomial does not mean that the polynomial represents a given function in all respects. When approximating a given function $f(x)$ by a polynomial function, $\varphi(x)$, one may ask: how should the closeness of the approximation be measured?; and what are the criteria for the best polynomial approximation to the function?'. Increase of the mathematical tools available at the mouse touch-and-go furnishes a highly powerful possibility, but the multiple choice need rigorous criteria as concerns accuracy, applicability and physical relevance of the fitted parameters. With regard to the assessment of kinetic parameters, the series of papers published by Šesták and co-workers are of fundamental interest and permit an overview of the kinetic state of the art (see [35, 36] and related references). In general, enhancement of the touch-and-go analysis does not automatically increase the physical relevance and accuracy of the results.

The early book by Hemminger and Höhne [37] contains remarks that remain fully valid: The same problems to be answered persist today: 'Without up-to-date textbooks and courses ... With education usually restricted to equilibrium thermodynamics, the irreversible, time-dependent nature of calorimetry is frequently not appreciated. All this has led to a growth in the quantity of calorimetry, often without an accompanying growth in quality.' Sixty years after Tian's work, the standard calibration is often a proprietary method unavailable to the customers. In fact, a recent E-mail (June 1996) stored in the authors' records explains: 'The Joule-effect calibration was conducted by XXXX. They have not shared their raw data with me. I will ask their sales representative if that information is available.'

Calorimetric models

The calorimetric system [38, 39] comprises several shells of materials with three-dimensional complicated structures, from cell contents to detectors and external isothermal or programmable heat sinks. The formulation via the Fourier equation requires mathematical models in three dimensions and associated equations (heat flux and temperature) for boundary surfaces. In the analysis-limited systems with constant coefficients (isothermal conditions), the calculated output signal related to a Dirac pulse is represented by an infinite series of exponentials with decreasing time constants (τ_l).

The experimental requirements relating to the sampling (Δt) and the signal-to-noise ratio ($s/n \approx 10^L$) reduce the number of parameters and the complexity of the model. The value of Δt bounds the infinite series of terms. The contribution of the terms with $\tau_l \ll \Delta t$ is irrelevant. The effect of s/n is much more restrictive. The number N of terms in the series satisfies the phenomenological relation $L \approx N-M$. The physical separation between the dissipation (heater or physico-chemical reaction inside the cell) and the detection (thermocouples) leads to $0 \leq M < N$. The impulsive response is represented by the sensitivity (S), N poles and M zeros, and the complexity of the model is reduced to a very limited number of parameters. In the experimental output signals, $L \leq 5$ is achieved and usually $M \leq 2$. The numbers of parameters to determine ($N+M+1$) satisfy the inequality: $N+M+1 \leq 10$. The available signal-to-noise ratio (or s/n) suggests the construction of simplified models with N heat capacities ($N \leq 10$) containing, if possible, the main features of the actual calorimeter.

In classical RC analogy with N heat capacities and several thermal couplings between them, the instantaneous carried energy provides a system with N differential equations. With the heat power dissipations $W_j(t)$, the heat capacities C_j and the thermal resistances $R_{jk}(P_{jk} \equiv 1/R_{jk})$, the energetic equilibrium reads

$$W_j = C_j\frac{dT_j}{dt} + \sum_{k \neq j} P_{jk}(T_j - T_k) + \sum_n P_{jn}(T_j - T_n^*); \quad j = 1, 2, \ldots, N \tag{1}$$

Each temperature $T_j = T_j(t)$ is deduced from the initial values ($T_j(t=0)$), the dissipations $W_j(t)$ and, eventually, the environmental temperature fluctuations (laboratory, thermostat, ...) $T_n^*(t)$. Equation (1) with only one element ($N=1$) furnishes the Tian equation. Calvet's standard modellization with two time constants needs only two heat capacities. Perfect differential systems have $N+N$ elements, but symmetric conditions reduces this to N elements. If the elements are similar, but not exactly equal, the complete complexity of $N+N$ elements partially remains. The situation is more complex when temperature programming is carried out. Several temperatures $T_n^*(t)$ usually participate in the differential equations (relating to room temperature, furnaces and/or cooling devices).

If the system works with only one and constant environmental temperature T^*, the general equations can be reformulated, using T^* as a temperature reference ($\Theta_j = T_j - T^*$), to

$$W_j = C_j\frac{d\Theta_j}{dt} + \sum_{k \neq j} P_{jk}(\Theta_j - \Theta_k) + P_j\Theta_j \tag{2}$$

If the coefficients C_j and P_{jk} are constants, Laplace transform determines the functions $\Theta_j(p)$. In particular, the response in the m-th element $\Theta_m^{W_k}$ associated with an arbitrary dissipation $W_k(t)$ in the k-th element can be deduced from a convolution of $\Theta_m^{W_k^{(\delta)}}$ related to a Dirac pulse $W_k(\delta)$ with the associated conditions $\Theta_j(t=0)=0$. In other words, $\Theta_m^{W_k^{(\delta)}}$ is the transference function $TF_{m,k}$ associated with the m-th temperature and the k-th dissipation:

$$\Theta_m^{W_k^{(\delta)}} \equiv \Theta_m(W_1(\delta)\equiv 0,\ W_2(\delta)\equiv 0,\ldots,\ W_k(\delta)\neq 0,\ldots,\ W_N(\delta)\equiv 0) \equiv TF_{m,k} \qquad (3)$$

From the previous conditions, we can establish

$$\Theta_{m,k}(p) = W_k(p)\Theta_m^{W_k^{(\delta)}} = W_k(p)TF_{m,k}(p) \qquad (4)$$

The $TF_{m,k}$ derived from the differential equation systems is, in Laplace coordinates, a ratio between two polynomials $(P(p)/Q(p))$. $Q(p)$ relates only to the thermal parameters and the geometric structure of the model. $P(p)$ of degree $M(M<N)$ as a function of the m and k values affords

$$TF_{m,k}(p) = \frac{P_{m,k}(p)}{Q(p)} = \frac{\sum\limits_{j=0}^{M(m,k)} b_j(m,k)p^j}{\sum\limits_{i=0}^{N} c_i p^i} = S_{m,k}\frac{\prod\limits_{j=1}^{M(m,k)}(\tau_j^*(m,k)p+1)}{\prod\limits_{i=1}^{N}(\tau_i p+1)} =$$

$$= \sum_{i=1}^{N}\frac{a_i(m,k)}{p+\omega_i} \qquad (5)$$

with

$$\tau_i = 1/\omega_i,\quad M(m,k)<N \quad \text{and} \quad S_{m,k} = \sum_{i=1}^{N} a_i(m,k)\tau_i \qquad (6)$$

If energy is dissipated in several elements, the macroscopic temperature $\Theta_m(t)$ is the sum of independent contributions:

$$\Theta_m(t) = \sum_k \Theta_{m,k}(t) \qquad (7)$$

The output signal $s(t)$ can be determined by using the appropriate Seebeck coefficient (α) and adding every related thermocouple temperature. If m and m' are the pointers of the related warmer and colder temperatures, the output signal (in Laplace coordinates) reads

$$s(p) = \alpha \sum_{m} (\Theta_m(p) - \Theta_{m'}(p)) \tag{8}$$

When dissipation occurs in only one element or when there is proportional dissipation in all of them (a distributed dissipation, but with maintenance of a proportional relation as $W_1(t) = c_1 W_k(t)$, we can extract $W_k(t)$, and obtain

$$s(p) = W_k S \frac{\prod_{j=1}^{M} (\tau_j^* p + 1)}{\prod_{i=1}^{N} (\tau_i p + 1)} = W_k \sum_{i=1}^{N} \frac{a_1}{p + \omega_i} = W_k TF(p); \ (M < N) \tag{9}$$

The a_i values are derived from $a_i(m,k)$ and include the Seebeck coefficient. The particular sensitivity of the overall system includes the detector type, the cell contents and the heat position:

$$S = \sum_{i=1}^{N} a_i \tau_1 \tag{10}$$

The associated transference function in p (Laplace) or t (time) coordinates reads

$$TF(p) = S \frac{\prod_{j=1}^{M} (\tau_j^* p + 1)}{\prod_{i=1}^{N} (\tau_i p + 1)} = \sum_{i=1}^{N} \frac{a_1}{p + \omega_i}; \ TF(t) = \sum_{i=1}^{N} a_1 e^{-t/\tau_i} \tag{11}$$

By convolution of the temperatures $\Theta_j^{W,(\delta)}(t)$ derived from the model, we can determine $s(t)$ for any type of dissipation $W(t)$ via $TF(t)$ if the experimental conditions are identical to the theoretical conditions established in the model:

$$s(t) = \int_0^t W(t^*) TF(t - t^*) \mathrm{d}t^* \tag{12}$$

The output signal $s(t)$ depends on the position of the dissipation. If the position or the spatial distribution of the dissipation changes, the transference function $TF(t)$ changes and the output signals are different: accurate deconvolution al ways needs the appropriate *TF*. The changes in *TF* are related to the heater or reaction position (sensitivity and zeros in the transference function) and the cell contents and distribution (sensitivity, poles and zeros).

The linearity of the differential equations establishes the equivalence between the Dirac pulse and the Heaviside step. Because of this:

$$S=\sum_{i=1}^{N}a_i\tau_i-\left(\frac{\text{signal surface}}{\text{dissipated energy}}\right)_{\text{Dirac pulse}}-\left(\frac{\text{steady signal}}{\text{dissipated heat power}}\right)_{\text{Heaviside step}} \quad (13)$$

The experimental linearity [40], determined from the sum of the signals from diverse amplitudes (Fig. 1), allows the use of signal-processing resources to allow the identification of the experimental system and the performance of the deconvolution of the output signals and derivation of the actual energetic dissipation. This is an ill-determined and complex process. The noise cuts the greater frequencies. If the accuracy is the label required, it is always necessary that the transference function corresponds strictly to the same conditions of measurements.

If the whole heat flux produced inside the cell (or an invariant percentage) crosses the detector system, the sensitivity is always invariant. This is only a 'theoretical' situation without experimental counterpart, but, even in recent papers, it is implicitly regarded as the basis in the models used [39]: 'A model of the heat conduction calorimeter as shown schematically ... It consists of three concentric and symmetrical domains.' The heater position only influences the zeros of the transference function; the sensitivity and the time constants are invariant. In this particular case, the change of localization of the dissipation merely changes the amplitudes a_i, maintaining S constant:

$$S=\left(\sum_{i=1}^{N}a_i^{(1)}\tau_i\right)_{\text{position 1}}=\left(\sum_{i=1}^{N}a_i^{(2)}\tau_i\right)_{\text{position 2}}=\left(\sum_{i=1}^{N}a_i^{(3)}\tau_i\right)_{\text{position 3}}=\ldots. \quad (14)$$

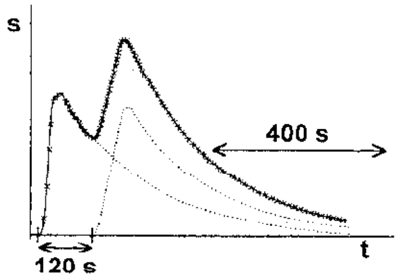

Fig. 1 Linearity of conduction calorimeters: addition of input signals and associated output signal; ···· obtained with independent input signals; — experimental measurement obtained with the same, but delayed, inputs; x x x calculated values, applying linearity

In this particular situation (concentric domains), if the contents change, the time constants also change, but not the sensitivity: their value is only a function of the thermal resistance between the warm and cold junctions.

In a steady state (with only partial heat flux detection, as usual), the distribution of the temperature depends only on the coefficients P_{ij}. Linearity indicates that the sensitivity depends only on the coefficient values of P_{ij} and the structure of the model used. When the content of the laboratory cell is modified, the evolution of one or more coefficients P_{ij} changes the sensitivity. The values of sensitivity for several contents and positions of the heating resistance in a Tian-Calvet calorimeter are to be found in Table 1. In this particular case, the higher thermal conductivity of the metals used relative to the thermal resistance of the system detector allows a sensitivity fluctuation level of approximately 2%. With other contents or with much faster processes (combustion calorimetry), it is possible to obtain repetitive values when carrying out a series of measurements (near 0.2%), but with the greatest error bars around 10%. Experimental changes in sensitivity are of critical significance. In fact, the calorimeter measures only a variable percentage of the overall heat flux. For instance, in a Tian-Calvet calorimeter, the thermocouple width approaches 2 cm and the equalization time t (disappearence of a Dirac pulse) is around 4000 s. An elementary approach ($x^2 \approx 2Dt$) indicates a low value of mean thermal diffusivity D of around $0.5 \cdot 10^{-7}$ m^2 s^{-1} near ordinary concrete ($5 \cdot 10^{-7}$ m^2 s^{-1}). If semiconductor thermobatteries are used, the equalization time is around 50 s, the distance reduces to 3 mm, and D approaches $1 \cdot 10^{-7}$ m^2 s^{-1}. The heat flux transmitted by the detector system is only part of the overall heat flux and similar problems are expected.

An approach to accuracy via the calorimetric cell

To minimize the positional effect, very small reactive masses should be used together with miniaturization of the equipment. The process is basically a scaling increasing the dynamic characteristics, but the positional effect remains. To smooth the parasitic effects of the sample and the positions of the thermal heaters, two conditions need to be fullfilled. The first is that dissipation can be produced in only one specific domain (always the same), and the second is that the changes in internal contents and thermal contacts need to be minimized.

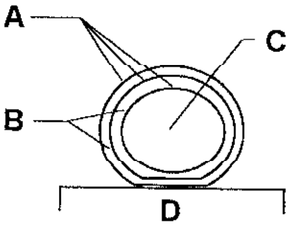

Fig. 2 Schematic representation of a multishell (protected) crucible. A: conductor shells; B: isolated shells; C: cell contents; D: detector

The experimental conditions seem to be met with a crucible constructed in a multishell system (onion type as *A-B* in Fig. 2) of insulating/conducting layers. If the thermal diffusivity of the contents exceeds the mean diffusivity of the shells, the heater position and the contents are irrelevant. The calorimeter output will be smoothed, but the internal structure of the cell contents *C* is indistinguishable with the detector *D*. Obviously, the increase in potential accuracy reduces the dynamic availability of the system.

Temperature-varying effects: noise reduction by independent input-output analysis

The external temperature generates perturbations in the output signals. During operation under isothermal conditions, the thermostat fluctuation in temperature T^* produces equivalent effects on the supplementary dissipations. From the general equation (1), the corresponding system of equations is

$$W_j = C_j \frac{dT_j}{dt} + \sum_{k\neq j} P_{jk}(T_j - T_k) + P_j(T_j - (T^* + \delta T^*)); \ j = 1, 2, \ldots, N \qquad (15)$$

Defining $\Theta_j = T_j - T^*$ we have

$$W_j + P_j\delta T^* \equiv W_j^{T^*} = C_j \frac{d\Theta_j}{dt} + \sum_{k\neq j} P_{jk}(\Theta_j - \Theta_k) + P_j\Theta_j; \ \ j = 1, 2, \ldots, N \qquad (16)$$

In any case, a new dissipation term independent of the value of standard heat production by the heater or reaction W_j, appears in element j ($P_j\delta T^*$), related to the temperature fluctuation of the thermostat. The temperature fluctuation is equivalent to a positive dissipation in the whole elements relating to the thermostat. If the system is subjected to the actions of two or more external temperatures, the complexity of the dissipations relating to perturbations increases. To be able to eliminate the effect of the disturbances, it is necessary to have access to information regarding its causes. With this approach, the representative model of the complete calorimetric system appears divided into at least two parts or 'partial models': The first is the classical transference function between heater and output signal (the model from the cell to the detector) [41]. The second is the model between the external thermal perturbation and the output signal [42].

For programmable temperature systems, the Peltier effect [43] allows for control and programming of the temperature with an accuracy near 0.003 K. The control produces fluctuations in the intensity of the Peltier current which affects the output signal. In order to eliminate these disturbances, one should establish a functional relationship between the impulses derived from the intensity δI and the fluctuation associated with the output signal. This identification should be

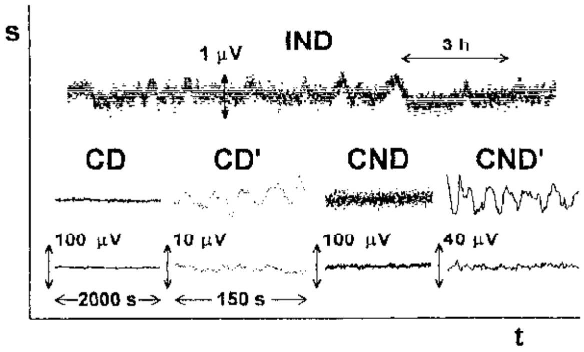

Fig. 3 Baseline *vs.* time: noise in differential and non-differential calorimeters at 298.15 K; top: IND: isothermal, low-priced, non-differential system [44]; middle and bottom: differential calorimeter similar to that described in Ref. [43]; CD and CD': programmed differential system; upper: baseline; bottom: after correction of the control actions; CND and CND': using only one plate as a non-differential system

carried out by using several temperatures within the working temperature domain. From the intensity of the current used, its average value and its fluctuation values (δI) can be derived. On subtraction of the numerical convolution of the perturbations, the output signal fluctuations are reduced by 80%. With a PC-486, 66 MHz or higher, the complete process needs only a few seconds of computer time. Figure 3 compares the standard and the corrected baseline with those for a cheaper and isothermal non-differential system [44].

The physical image models built to connect the output signal with the process carried out inside the cell yield excellent results in mass-varying systems [41, 45]. In general, it appears possible to establish a modellization of the experimental system based on two complementary aspects. One is the relationship between the energetic dissipation (or thermogenesis) and the calorimeter output signal [46–48]. It is the classical transference function in invariant systems and their generalized form or functional connection in non-invariant systems. The other aspect is to relate the effects of the programming and control with the output signal. The suppression or reduction of the disturbances produced by the surroundings starting from an adequate identification is one way of increasing the effective resolution of the calorimetric systems, i.e. by using some other transference function or functional connection determined separately [42]. Increased accuracy needs a powerful link between the experimental systems and representative models explaining the actual complexity of the apparatus.

Conclusions

An analysis of the literature from Tian up to the present indicates that several problems still exist in connection with conduction calorimeters and are ill-determined: only a high similarity between standard calibration procedures and actual measurements ensures satisfactory accuracy in energetic and/or kinetic studies.

The physical image models built to connect the output signal with the process carried out inside the cell seem to be the tools for enhanced measurements. Suggestions are given for improved measurements using multishielded crucibles or calorimetric cells and a way to reduce baseline fluctuations via independent signal processing relating to the perturbation detection: a software improvement of the hardware-based differential system.

Recent results indicate how the improved accuracy approach needs (as in the early works) a permanent critical analysis of the complete system: the experimental system, the applied thermodynamic formalism, the representative model and the transference function used in energetic measurements or in deconvolution procedures, and also the available mathematical tools.

* * *

This research was carried out in the frame of contracts ERASMUS/SOCRATES ICP-D-4054/13, NATO 920452 and DGICYT HF 1996-0010. V. T. acknowledges partial support from Dir. Pol. Terr. (Generalitat of Catalonia).

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