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DETERMINATION OF THE TRANSFER FUNCTION OF TEMPERATURE-SCANNING CALORIMETERS

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ABSTRACT

The removal of instrumental distortion from the thermokinetic data recorded by means of a temperature-scanning calorimeter requires the determination of the instrument transfer function and of its changes in the course of the experiments. The present study, carried out with a simulated first-order calorimeter, indicates that pseudo-random binary sequences of thermal pulses, generated by a computer system on-line with the calorimeter, can be conveniently used for this purpose. The intensity of the calibration pulses can be decreased so as not to perturb the thermal phenomenon under study. Transfer-function determinations can be automatically repeated at frequent time intervals. The method also allows simultaneous measurement of the calorimeter sensitivity.

INTRODUCTION

Calorimeters can be considered as linear systems, under normal conditions of operation [1,2]. The distortion, due to thermal lag, which inevitably affects the calorimeter response, may therefore be alleviated by application of the general equation of linear systems

$$G(p) = H(p) . F(p) \tag{1}$$

where G(p) and F(p) are the Laplace transforms of, respectively, the calorimeter response and the input, i.e. the thermal phenomenon under study. Resolution of the equation requires the determination of H(p), the calorimeter transfer function. This may be achieved by the analysis of the calorimeter response to known inputs, e.g. Dirac pulses or steps. In previous studies [3], it has been shown that, when a calorimeter is operated in a constant-temperature mode, the transfer function, determined by preliminary calibration, can be used to "reconstruct" calorimetric curves.

When a calorimeter is operated in a temperature-scanning mode, thermal contact resistances and/or the heat content of the cell change in the course of the experiment. The calorimeter may be still considered as a linear system, but its transfer function changes during the experiment in a way that generally cannot be simulated in preliminary calibration eperiments. Therefore, reconstruction of the calorimetric data then requires the frequent determination of the instrument transfer function in the course of the experiment itself. As in the case of constant-temperature calorimeters, this may be achieved by generating, generally by Joule heating, known thermal inputs into the calorimeter cell but, in a temperature-scanning calorimeter, the calibration inputs must be selected so they can be (i) eventually superimposed on the thermal effect produced by the phenomenon under study, and (ii) regularly repeated during the whole experiment. The essential requirement that these calibration inputs must meet is not to perturb the experiment under study. For this reason, Dirac pulses (theoretically of an infinite intensity) cannot be utilized. The quality of the data reconstruction, its "resolution", very much depends on the frequency of the heat-transfer determinations. Therefore, long-lasting calibration inputs, like thermal steps, are not recommended. Moreover, the calibration inputs should allow a convenient and accurate determination of the calorimeter sensitivity, in order not only to reconstruct the kinetic events but also to quantitatively measure heat production or absorption.

The object of this study was to test the possibility of using a pseudo-random binary sequence (PRBS) of thermal pulses as calibration input in temperature-scanning calorimetry. The derivation of the pulse response of a linear system from its response to a PRBS has already been described [4]. In the present paper, we attempt to show the advantages and limitations of this method, by means of simulated experiments with a first-order calorimeter.

EXPERIMENTAL

A computing system was used to generate the PRBS, to collect and analyze the experimental data. This system, which has been previously described [5], is based on a Z80 microprocessor. It includes both erasable-programmable-read-only memories (4K) and random-access memories (4K), an arithmetic unit which directly provides all classical functions, a clock and a number of interfaces for the acquisition and production of analog data, the entry of parameters and/or instructions from a keyboard, the display of messages and results on a printer. This computing system may be interfaced with the data acquisition line of a calorimeter so that all calculations can be achieved on-line.

For the sake of convenience, however, the calorimeter was, in the present experiments, replaced by an RC circuit. Provided that all components are selected with some care, the relation between the input and output current in an RC circuit is indeed identical to the simple Tian equation, relating thermal input and calorimetric curve in a first-order calorimeter [6], i.e., a calorimeter whose response to a pulse is a single exponential

$$f(t) = g(t) + \tau \frac{dg(t)}{dt} \tag{2}$$

$f(t)$ and $g(t)$ are, respectively, the input and output functions, τ, the time constant, is the exponential exponent. In the case of the first-order calorimeter, τ is defined as the ratio of the heat capacity of the calorimetric cell and of its content to the heat-transfer coefficient between the cell and its surroundings. In the case of an RC circuit, τ is defined as the product of the circuit resistance, R, to its capacity, C. The value of the parameters, R and C, can be easily modified. It is therefore easier to vary the time constant of an RC circuit in a known and reproducible way than the time constant of a calorimeter and, for this reason, an RC circuit was used to simulate the calorimeter in all the following experiments.

The experimental arrangement is schematically represented in Fig. 1. Connections between the RC circuit and the computing system have been provided for (i) recording and analyzing the response, (ii) activating three independent relays, used respectively to generate the PRBS of electrical pulses, a constant current and variable electrical inputs to simulate calorimeter experiments.

Several methods are available for generating a PRBS [4]. The method

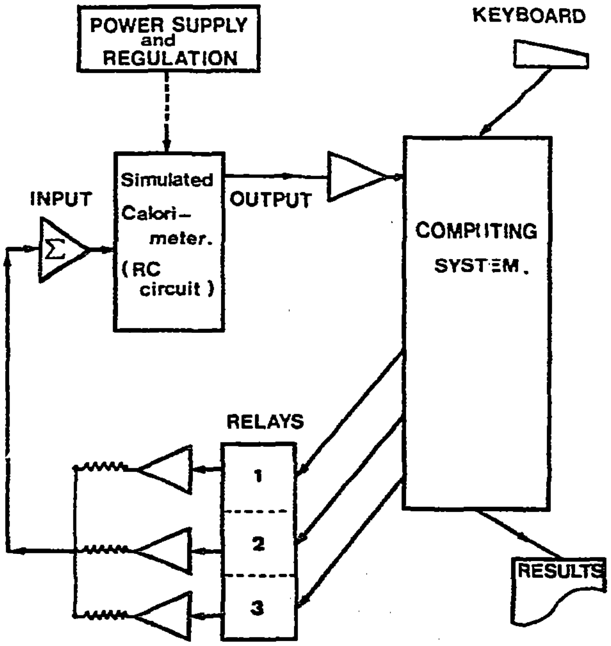

Fig. 1. Schematic representation of the experimental arrangement.

selected in the present study is particularly simple and convenient since the corresponding program is limited to four instructions in the Z80 assembler language [7]. With an 8-bit word, 255 random binary values are generated (1–255). In the present study, however, only bit 7 is maintained so that a series of pseudo-random pulses is obtained

bit 7 = 1 → 1 pulse (relay: on)

bit 7 = 0 → no pulse (relay: off)

All pulses have a constant width (equal to T, the sampling period) and height, which can be directly indicated on the computing-system keyboard.

Five other computer programs were used in this study.

(1) Reconstruction of the pulse response: the calorimeter (or RC circuit) pulse response is obtained from the vectorial product of the response samples with a binary matrix whose elements may be calculated from the reciprocal of the polynomial generating the PRBS [8].

(2) Subtraction of a constant (thermal or electrical) power (see below).

(3) Subtraction of a variable (thermal or electrical) power (see below).

(4) Determination of the time constant, by means of an exponential regression routine, from the reconstructed pulse response.

(5) Data-smoothing programs are available and can be used whenever needed.

RESULTS AND DISCUSSION

The object of the first series of preliminary experiments was to determine the rules for selecting T, the sampling period. In agreement with previous results [8], we observed that, in order to correctly reconstruct the pulse response, the length of the PRBS should be larger than that of the pulse response itself. In the following experiments, the PRBS was so constructed that its length would always be equal to or exceed 3 τ. This rule, in turn, determines a lower limit for the sampling period T, since each value in the PRBS corresponds to one sample. Thus $255\ T \geqslant 3\ \tau$; when the time constant of the RC circuit was set at ~7 s, for instance, the sampling period could be adjusted to 0.1 or 0.2 s.

It is only before and after the thermal process under study that, in an actual calorimeter experiment, the PRBS is generated in the calorimeter cell in the absence of other heat production or absorption. At any other time, the PRBS is superimposed on other heat-exchanging phenomena. In order to reconstruct the calorimeter pulse response, it is therefore necessary to eliminate, from the recorded data, all but the relevant information. In a series of experiments we tested the possibility of reconstructing the pulse response from the PRBS recorded in the presence of a constant heat production in the calorimeter (simulated by a constant electrical current in

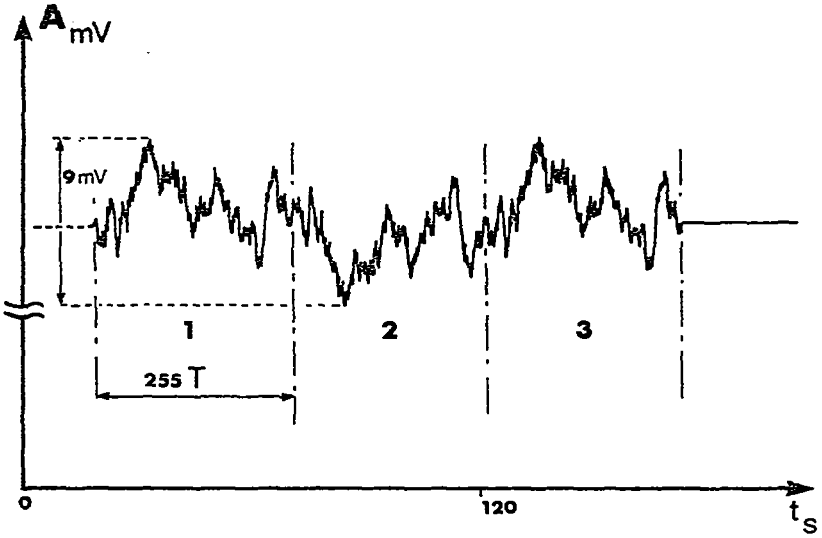

Fig. 2. Analog response of the RC circuit to a series of three, successively direct, inverse and direct, pseudo-random binary sequences of 255 values. Sequence 1 for initiating the reconstruction of the pulse response; sequences 2 and 3 for substracting any constant power, superimposed on the PRBS ($T=0.2$ s).

the RC circuit). The most efficient method [8] consists of producing, successively, direct and inverse PRBS, elimination of the constant power being achieved by the subtraction of two successive sequences (y_1-y_2, Fig. 2). In all the following experiments, the PRBS was therefore generated continuously, so that direct and inverse sequences were successively injected in the RC circuit in order to eliminate any eventual constant deflection from the base-line.

However, it is very seldom that, in actual experiments with a temperature-scanning calorimeter, the record shows a stable heat production. In most cases, heat production or absorption varies with time. In order to remove variable heat production, hereafter called base-line shift, from the data, a program based on the comparison of two successive identical PRBS was added to subtract the base-line shift, supposed to be linear, from the record of the PRBS. In the case of regularly changing thermal (or electrical) power, the program was shown to be efficient, the pulse responses reconstructed in the presence or absence of the external effect being identical (Fig. 3). A program based on a parabolic approximation of the base-line shift should probably be preferred in the case of more complex thermal or electrical processes. It is evident, however, that any abrupt kinetic change taking place during a single PRBS would not be correctly accommodated by these simple base-line shift correction programs.

In order to conveniently select and check the preceding programs, the intensity of the electrical pulses in the PRBS was set at a rather large value (generally 1 V). In actual calorimetric experiments, intense heat pulses gener-

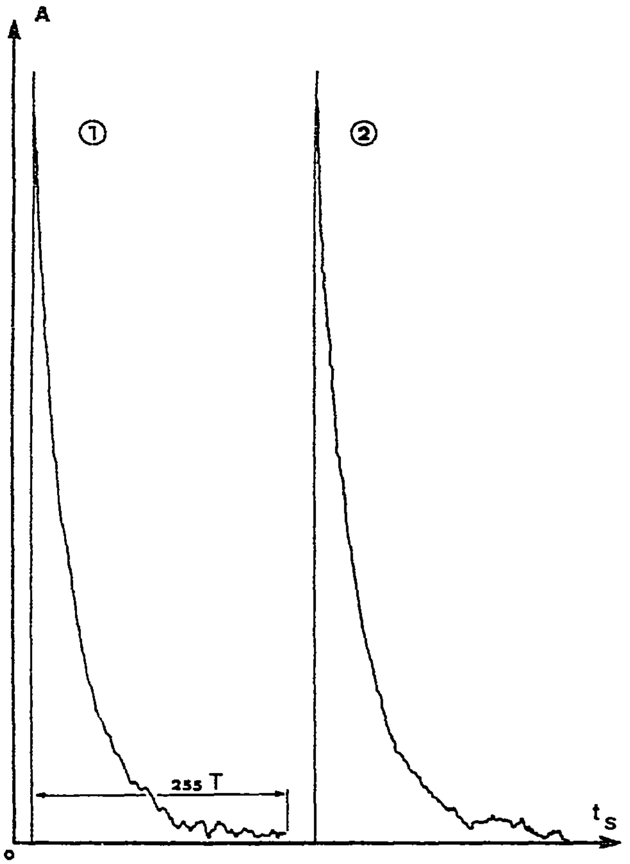

Fig. 3. Pulse response of the RC circuit, reconstructed by means of a PRBS of electrical pulses, superimposed on a time-dependent potential (10 mV s^{-1}, curve 2) and, for comparison, pulse response of the same RC circuit in the absence of a time-dependent potential (curve 1) ($T = 0.2$ s; $\tau = 7.3$ s).

ated in the calorimeter cell would perturb the thermal phenomenon under study. The object of the following series of experiments was therefore to determine the minimal intensity of the pulses in the PRBS which could still be utilized to accurately reconstruct the pulse response of the RC circuit. After several runs it was concluded that pulses of 50 mV still yield acceptable information. The circuit response to a PRBS with these pulses vary within 8 digits (corresponding to 9 mV, Fig. 2) over a full-scale possibility of 2048 digits. On an analog record, the response to the PRBS would correspond to a 1 mm thick base-line on a 250 mm wide recording paper. Therefore, it can be estimated that the heat that such a PRBS produces in the calorimetric cell will not significantly modify the course of most thermal processes under investigation. However, Fig. 4 shows that the pulse response that can be reconstructed from a PRBS of low-intensity pulses contains a rather high noise level, particularly for the lowest values of the response. The noise can easily be abated by smoothing procedures, as illustrated on curve 2

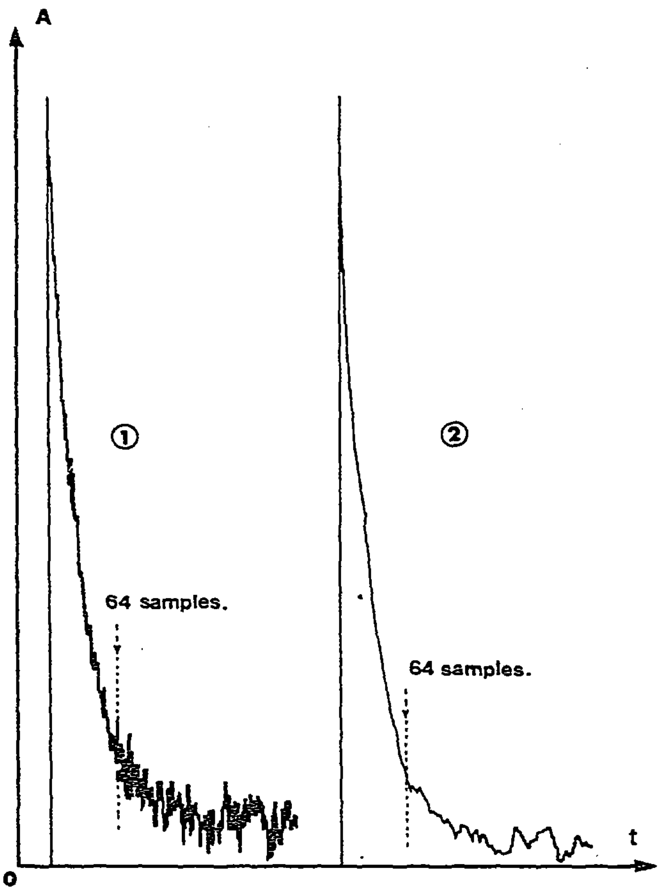

Fig. 4. Pulse response of the RC circuit, reconstructed by means of a PRBS of low-intensity electrical pulses (pulse response: 8 digits; 0.4% full-scale deflection: 2048 digits, $T = 0.2$ s; $\tau = 6.8$ s). Curve 1, raw data; curve 2, smoothed data.

of Fig. 4, and the analysis of the smoothed response curves yields acceptable values. Reproducibility of the calculated results is still improved if the exponential regression program is only applied to the first part (64 samples, Fig. 4) of the reconstructed pulse response and not to these samples for which, in the raw data, the noise-to-signal ratio is excessive. For instance, in one particular series of experiments when the theoretical value of the circuit time constant was 7.4 s, 26 experimental determinations gave an average value of 7.33 s with a 0.09 s standard deviation.

In order to test the quality of the pulse response reconstruction during a continuous operation of the calorimeter (or RC circuit), a program was written which includes (i) the continuous generation of direct and inverse PRBS, (ii) the reconstruction of the pulse response of the system and the calculation of the corresponding time constant for every third PRBS. The computer program also allows recording of the intensity of the calorimeter (or RC circuit) response to pulses in the PRBS, from which the calorimeter (or RC circuit) sensitivity may be calculated.

Figure 5 illustrates the application of the program in the case of an experiment during which a time-dependent potential was applied to the RC circuit (stages 2–4) whose time constant was moreover slightly modified during stage 3.

The sampling period was set at 0.2 s and pulse response determinations were, therefore, automatically repeated every 2.55 min. The results demonstrate that the time constant can indeed be determined, at regular time intervals, in the absence or in the presence of a base-line shift. As discussed earlier, however, the change in the base-line shift occurring at the end of stage 4, which took place during a PRBS, cannot be corrected by the present program and yields an erroneous value for the time constant (Fig. 5, circled point). The results also show that changes in the value of the time constant can be accurately detected within two successive determinations and that a variation of 0.7 s is readily measured.

More demanding tests of the program were also carried out and are summarized in Figs. 6 and 7. In a first series of tests (Fig. 6), the potential applied to the RC circuit was kept constant and the circuit resistance was changed linearly with time. The resulting linear change of the time constant is correctly detected from the analysis of the circuit response to successive PRBS of electrical pulses of low intensity (0.4% full-scale). The standard deviation of the experimental values from the expected ones is 0.35 s during stage 2 of the experiment reported in Fig. 6.

In a second series of tests (Fig. 7), the potential applied to the RC circuit and the circuit resistance were changed linearly with time. This simulates the

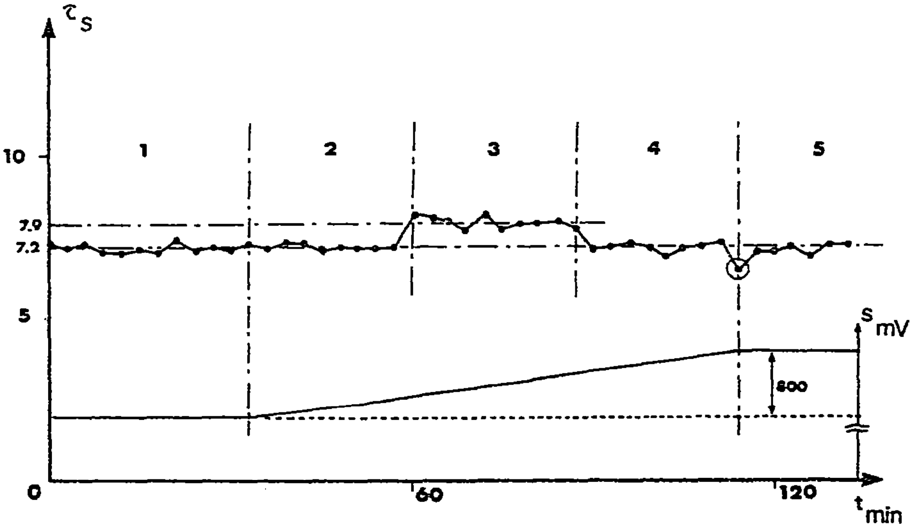

Fig. 5. Evolution of the time constant of the RC circuit as a function of time. The simultaneous evolution of the potential applied to the circuit is presented in the lower part of the figure (PRBS=50 mV; T=0.2 s).

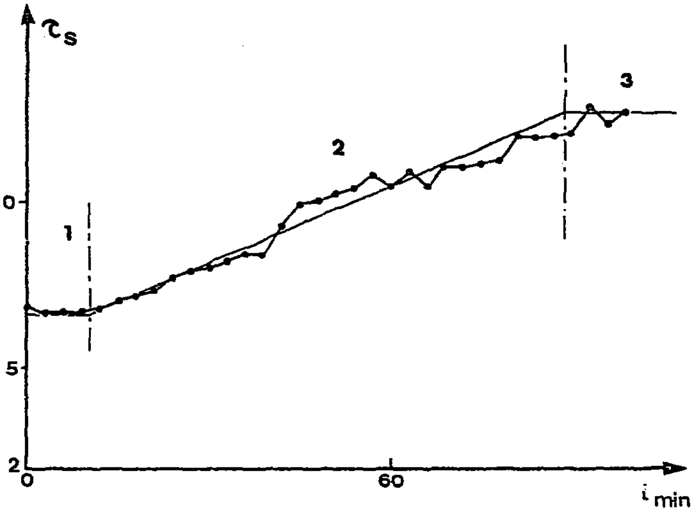

Fig. 6. Evolution of the time constant of the RC circuit as a function of time. ●, Experimental values calculated from the reconstructed pulse response; ————, theoretical values (PRBS =50 mV; T=0.2 s; stable base-line).

case, often encountered in actual temperature-scanning calorimetric experiments, in which the heat content and/or the heat transfer characteristics of the calorimetric cell change in the course of the experiment while, simultaneously, heat produced or absorbed by the process under study also varies. The results are summarized in Fig. 7. The standard deviation of the experimental values from the expected ones is somewhat larger in this case than in the preceding experiments and attains 0.55 s (part of the increased scatter

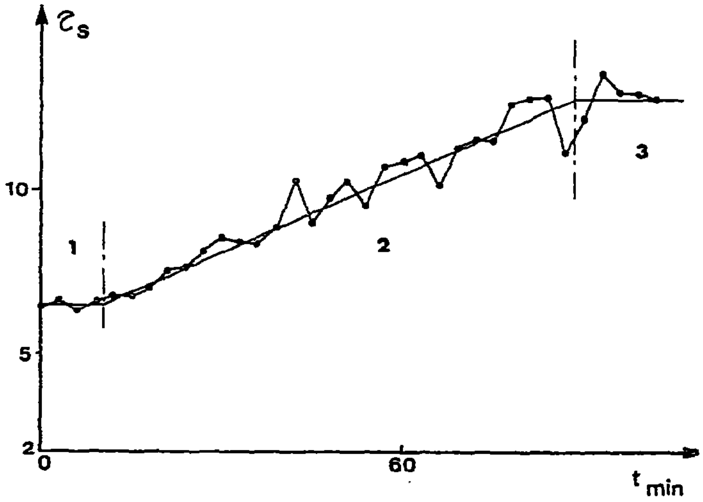

Fig. 7. Evolution of the time constant of the RC circuit as a function of time (●, Experimental values calculated from the reconstructed pulse response; ————, theoretical values (PRBS=50 mV; T=0.2 s; base-line shift=10 mV s^{-1}).

may be due to imperfections in the experimental arrangement for simultaneously increasing the resistance and the applied potential). However, the computer program still allows reconstruction of the pulse response of the system from successive PRBS of low-intensity electrical pulses and there is no systematic error in the experimentally determined time constants.

CONCLUSIONS

The experiments with a simulated first-order calorimeter reported in the present article have demonstrated that pseudo-random binary sequences of thermal pulses can be employed as calibration inputs to determine the calorimeter transfer function and to follow its changes in the course of an actual experiment. The programs which have been written for the computing system on-line with the calorimeter (elimination of constant and/or variable base-line shifts) are still in a preliminary stage and do not allow, for instance, to accurately perform the system identification when rapid kinetic changes take place in the calorimeter cell. Nevertheless, they indicate that, in most cases, it is possible to remove all but the relevant information. It has been shown, moreover, that the intensity of the thermal pulses in the PRBS can be decreased (down to $\sim 0.5\%$ of a full-scale response) so as not to significantly perturb the thermal phenomenon under study. The time constant of the first-order system can be determined at regular time intervals in the course of the experiments. With the present program determinations are repeated every third PRBS. However, the time lag between two determinations can be decreased to $3\,\tau$, τ being the time constant of the calorimeter. The computer program also allows determination of the calorimeter sensitivity at regular time intervals. All the information needed to quantitatively reconstruct kinetic data is therefore available and, thus, in situ calibration by means of pseudo-random sequences of thermal pulses appears to be a realistic method for removing data distortion in the case of temperature-scanning calorimeters.

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