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Ambient perturbation reduction in microsized calorimetric systems

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Abstract

To avoid thermostatting effort in a calorimeter the influence of ambient temperature perturbations on the output signal can be reduced by predicting and correcting the perturbation part of the output signal of the calorimeter. The prediction can be verified by measuring the temperature perturbations and simulating the corresponding output signal. Using a dynamical model of the calorimeter, simple methods for the solution of this problem are shown and tested experimentally. © 1997 Elsevier Science B.V.

Keywords: Dynamic model; Heat-flow calorimeter; Model identification; Thermopile chip

1. Introduction

For actual applications it is necessary to perform dynamic calorimetric measurements of heat power dissipation with improved resolution and accuracy. Recently, new microsystems based on conduction calorimetry have been developed allowing the use of small quantities of the substance for the measurement. Such calorimeters have been applied as thermochemical sensors [1]. To improve the resolution it implies to solve two fundamental problems in calorimetric measurements: (a) the appropriate calibration avoiding the perturbation effects due to the localization of the thermic sources and (b) the reduction of perturbations on the base line.

Conduction calorimeters can be viewed as multi input-single output systems. The inputs correspond to different points of dissipation, the external room temperature and the temperature control actions. The output is the measured signal. Deconvolution is indeterminate and only approximations can be used in order to obtain satisfactory results. Ideal differential systems allow 'hardware suppression' of the perturbation effects from temperature control and thermostatting. However, in practice, such systems are far from being perfect. The identity between the measured system and the differential element is only approximate at least because the contents of the calorimetric vessels are different. In fact, thermostat fluctuations induce an independent input signal on the calorimetric system. In other words, the experimental system has two independent inputs and only one output with a mixture of signals.

Recent studies have shown that with good thermostatting it is possible to use non-differential systems at constant temperature (see Ref. [2] and related references). The design of systems operating under hard

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conditions requires a high capacity to reduce the effect of external perturbations. In temperature-controlled systems, partial causal perturbation reduction can be achieved via software using the theory of systems and an appropriate identification. In Ref. [3], the control effect on the measured signal is divided by five. In this paper, we will show how appropriate modelling and identification can be used to reduce external causal perturbations in the measurement in a micro-sized non-differential calorimeter without thermostatting. The developed procedure needs an independent measurement of the external temperature and is useful to avoid thermostatting effort; this is meaningful for strong miniaturized calorimeters.

2. Perturbation reduction

The goal is to reduce perturbations in the measured signal produced by external variables as ambient temperature fluctuations and effects of thermostatting. In all the cases, we will study the causal connection between the perturbation and the measured signal.

In order to reduce the effect of perturbation signals in the measured signal, two things are necessary: (a) to have an independent way for measuring perturbation and (b) to know the connection between the perturbations and the system's response. We add to the classical calorimeter a new input measurement (the perturbation) and a new identification (the causal connection between perturbation and measured signal). In that situation we can estimate which part of the measured signal is due to perturbation signals and, then, we will be able to reduce this effect.

In general, perturbations can be interpreted as changes in the boundary conditions of our system. With a good modelling of the system, temperature fluctuations in the system which are due to external sources can be calculated if we know the boundary conditions. That means, we must know the temperature in a surface which is not possible in practice. In fact, we can only measure a finite number of points that represent the temperature in the external surface.

Usually, in order to model a calorimetric system, we use the *RC* analogy [2,4]: the calorimetric system is decomposed into N elements, characterized by a thermal capacity (C_i) and connected among themselves by Newton coupling, characterized by the

Fig. I. Fraction of an *RC* model with non-homogeneous ambient temperature.

coefficient (P_{ik}) . This kind of model gives a system of N differential equations. Each equation describes the connection between one element and its neighbours. For the element i , we will have the following equation:

$$
q_i(t) = C_i \frac{dT_i}{dt} + \sum_{k \neq 1} P_{ik}(T_i - T_k) + \sum_l P_{il}^0 (T_i - T_l^0);
$$

(k = 1, 2, ..., N; l = 1, 2, ..., M). (1)

The function $q_i(t)$ is the dissipation in element i and M the number of external temperatures. External temperatures have a pattern that is independent of the system behaviour. In Fig. 1, the fraction of an *RC* network is shown in which the considered element $i = 3$ is connected to three elements in the neighbourhood and three different ambient temperatures $(N=3, M=3)$.

Perturbations can be of two types: heat power sources as those used for temperature control like Peltier and/or Joule effect (denoted as terms q_i), and one or more temperature fluctuations like thermostat/external temperatures T_t^0 . In our case, only one thermostat temperature is considered (T^0) .

This linear model allows us to use the techniques of the theory of linear systems. Eventually with slowly

Fig. 2. General model of the system using linear system theory.

(ad hoc) time dependent coefficients. Whatever the case, we can characterize the connection using a transfer function (or impulse response). Fig. 2 shows the transfer function approach. Then, the measured signal (system's output) can be determined from the inputs as

$$
v(t) = v_T(t) + v_q(t) = \mathbf{h}_T(t)^* \mathbf{T}(t) + h_q(t)^* q(t)
$$
\n(2)

where $\mathbf{T}(t)$ is the vector of perturbations, $\mathbf{h}_T(t)$ the vector of impulse responses connecting output and perturbations, $h_a(t)$ the impulsive response connecting the power dissipation of the measurement and the output, $q(t)$ the heat power of reaction, $v_T(t)$ the part of the output due to the perturbations, $v_q(t)$ the part of the output due to the signal that is being measured and $v(t)$ the measured signal.

The goal of measurements is to extract the signal $q(t)$. Two problems are presented: (a) reduction of the perturbating term $v_T(t)$ and (b) deconvolution in order to obtain the heat power dissipation $q(t)$ from the measured signal $v(t)$. Here, we focus on the problem of reduction of the term $v_T(t)$. That can be done by calculating

$$
v'(t) = v(t) - v'_T(t) = v(t) - h'_T(t)^*T(t).
$$
 (3)

 $v'_T(t)$ being the estimation of the perturbating term and $h'_T(t)$ the estimation of the connection between perturbations and measured signal. Then, the problem reduces to making a good measurement of $T(t)$ and in estimating $h_T(t)$. The problems discussed above are present in all the calorimeters but the kind of solution adopted here will be highly influenced by the system analyzed.

In this paper, we will show an approach to the problem of reduction of external temperature fluctuations and we apply it to a specific system.

2.1. Perturbation measurement

In practice, the border conditions are measured as a finite set of temperatures. Measuring several points will complicate the experimental arrangement and the identification of the vector $\mathbf{h}_T(t)$ can be highly complicated. In our simplified system, only one external temperature $T⁰$ is considered (in a general formalism their action appears in one or more heat transfer equations).

As an approach it should be possible to use the measurement at only one point, if it represents the perturbation signal. This point must be located so that the connection between the temperature and the output of the system is independent of the origin of perturbation. This is correct in the following cases:

- The part of the system which is in contact with the ambient has a high thermal conductivity. Thus, one can consider that there is no gradient of temperature and the temperature of any single point is sufficient for describing the border conditions.
- The system can be considered as composed of two parts: an outer part in contact with the ambient and an inner part where the experiment will be carried out. If the inner part is in contact with the outer part at one point, then, this point can be considered as the border conditions for the inner part.

In these two cases, one can consider that the perturbation source is outside the calorimetric system.

2.2. Parametric model for a continuous system

The output (measured signal) of the system can be calculated for the simplified case of a homogeneous ambient temperature from Eq. (2) and using the Laplace transformation:

$$
V(s) = V_T(s) + V_Q(s) = H_T(s)T(s) + H_Q(s)Q(s)
$$
\n(4)

The aim of the correction is to eliminate the term $V_T(s)$ corresponding to the perturbations. Therefore, we must estimate the function $H_T(s)$. This function describes the causal connection between the measured signal and the perturbations. The calorimetric system can be modelled using *RC* analogy with an appropriate number of heat capacities (m) . With this experimentally derived model, we can write the transfer function $H_T(s)$ as a Pade form (quotient of two polynomials):

$$
H(s) = \frac{a_n s^n + \dots + a_0}{b_m s^m + \dots + 1}
$$
 (5)

Using this representation, the coefficient a_0 represents the sensitivity. The experimental conditions, mainly the signal-to-noise ratio, will determine the model's complexity, which is possible to analyze [5]. We can build an *RC* model which takes account of the entire system but depending on the signal-to-noise ratio only a few elements will represent the system's connection between input and output. Once we have chosen the order of the function, we must estimate the coefficients.

The output due to the perturbation signal $T(s)$ is:

$$
V_T(s) = H_T(s)T(s). \tag{6}
$$

Using, for $H_T(s)$, the same general form given above and applying the inverse Laplace transform, the connection between perturbations and measured signal can be written as

$$
b_m \frac{d^m v_T}{dt^m} + \cdots + v_T = a_n \frac{d^n T}{dt^n} + \cdots + a_0 T.
$$
\n(7)

Defining the vectors

$$
\theta = [a_n, \ldots, a_0, b_m, \ldots, b_1]^t \tag{8}
$$

and

$$
\varphi(t) = \left[\frac{\mathrm{d}^n T}{\mathrm{d}t^n}, \dots, T, -\frac{\mathrm{d}^m v_T}{\mathrm{d}t^m}, \dots, -\frac{\mathrm{d} v_T}{\mathrm{d}t}\right]^t, \tag{9}
$$

the differential equation can be written as

$$
\nu_T(t) = \varphi^t(t)\theta. \tag{10}
$$

2.3. Parameter estimation methods

For performing the identification of the model, one must work in conditions in which the output of the system is given from the perturbation signals only. Then:

$$
v(t) = v_T(t). \tag{11}
$$

The input for the identification algorithm are the signals $T(t)$ and $v(t)$. The signal $T(t)$ can be generated by noisy artificial perturbation (see Section 3). In practice, signals $T(t)$ and $v(t)$ are discrete ones. The task is now to solve the system equation for θ in

$$
\nu_T(t) = \varphi^t(t)\theta \tag{12}
$$

within the sampling interval $t_0 < t < t_1$. Because the system is over determinated, no solution exists in general. Therefore, the search of a parameter vector is necessary to minimize the quadratic criterion

$$
F_{t_0,t_1}(\theta) = \frac{1}{t_1-t_0} \sum_{t=t_0}^{t=t_1} (\nu_T(t) - \varphi^t(t)\theta)^2.
$$
 (13)

This is a standard engineering problem and a lot of methods for solving it are known [6]. The basic equations of the *instrumental-variable method* which we have applied in this work are given in Appendix A. Also comfortably usable computer programs are available for quite some time (e.g. MATLAB [8] includes an enormous number of powerful toolboxes for these purposes). To demonstrate the ease of use of such computer programs, a short sequence of MATLAB instructions including identification and prediction is also given in the Appendix A. After the successful approximation of θ , the prediction of $v'_T(t)$ is a simple system simulation procedure.

3. Experimental

The heat-flow calorimeter which we have used for testing the perturbation reduction procedure is shown in Fig. 3. For more details see Ref. [1]. The equipment consists of two axial connected cylindrical aluminium blocks. In the centre of the arrangement a silicon thermopile chip is located, embedded in a ceramic carrier. On the 'hot zone' of the thermopile, drops of glycerol are placed. The ceramic carrier is thermally connected with the lower aluminium cylinder via metallic pins. At the lower face of this block a heater is attached due to generate temperature fluctuations within the block. The temperature fluctuations are measured using a platinum resistance thermometer

Fig. 3. Scheme of the calorimeter used for testing the perturbation reduction procedure.

(Pt 1000) placed at the edge of the ceramic carrier. Because the thermal conductivity of the ceramic material is rather high, the measured temperature at this point is a satisfactory approach for the temperature fluctuations in the surroundings of the thermopile. The aim of the investigation is to analyze the influence of the temperature fluctuations on the output voltage of the thermopile. The resistance of the platinum thermometer and the generated heat-flow signals are monitored with the help of a commercial data acquisition system (DaisyLab/DAP-Interface [7]). Stochastic heat power is produced by numerical generation of gaussian white noise and output via a digital-analogue converter and amplifier. For each experiment data, files are collected after disappearance of the transient effects caused by switching on of the heating source.

4. Results and discussion

4.1. Model selection

In order to perform the identification of the system, we have to select the model on which the identification

Fig. 4. Simplified model of the calorimeter.

and correction algorithms are based. The physical characteristics of the system should be taken into account. We can start with a second-order model as shown in Fig. 4. In this model the chip carrier is modelled by two elements (two heat capacities of the RC model), first (T) wherein the perturbation measurement is done and second (T_c) coupled with the sample (T_s) . This system is described by

$$
\begin{bmatrix} \tau_c s + 1 + \varrho & -\varrho \\ -1 & \tau_s s + 1 \end{bmatrix} \begin{bmatrix} T_c \\ T_s \end{bmatrix} = \begin{bmatrix} T \\ 0 \end{bmatrix} \qquad (14)
$$

with

 $\tau_c = RC_c$, time constant of the chip carrier; $\tau_s = R_{cs}C_s$, time constant of the reaction zone ('hot zone') and $\rho = R/R_{\text{cs}}$, ratio of the heat transfer resistances.

For the output in the Laplace region, we obtain:

$$
V'(s) = K(T_c(s) - T_s(s))
$$

= $K \frac{\tau_s s}{(\tau_c s + 1)(\tau_s s + 1) + \varrho \tau_s s} T(s)$ (15)

with the scaling factor K which depends on the units of measurement. $V'(s)$ represents the estimated output to the perturbation and $T(s)$ represents the perturbation measurement. This expression can be simplified assuming $\rho \ll 1$:

$$
H(s) = \frac{V(s)}{T(s)} = K \frac{\tau_s s}{(\tau_c s + 1)(\tau_s s + 1)}
$$
(16)

In practice $\tau_s < \tau_c$. Because perturbations have a low-frequency variation, we can consider that only the biggest time constant is affecting the measurement. Therefore, we can approximate Eq. (16) by a first order one:

$$
H(s) = \frac{V(s)}{T(s)} = K \frac{\tau_s s}{(\tau_c s + 1)}
$$
 (17)

This is a high pass filter for the perturbation signal. The model is described by two parameters. We can write this function in a more general way as:

$$
H(s) = \frac{as}{1 + bs}.
$$
 (18)

The parameter vector is

 $\theta = [a, b].$

Therefore, the differential equation can be written as:

$$
v(t) = \varphi^t(t)\theta \tag{19}
$$

with

$$
\varphi(t) = \left[\frac{\mathrm{d}T_{\rm c}}{\mathrm{d}t}, -\frac{\mathrm{d}v}{\mathrm{d}t}\right]^t.
$$
 (20)

4.2. Identification and perturbation reduction

Examples for input (temperature) and output (heat flow) signals which are used for the identification are shown in Fig. 5. The sampling period was 1 s. For the identification both signals were filtered in the same

Fig. 5. Input (temperature, a) and output (measured signal, b) signals used for the identification.

way by a butterworth band-pass filter. The parameters in the model have been identified using the instrumental-variable method (Section 2.3). Calculations were carried out by the help of programs written in a MATLAB programming environment [8]. The coefficients obtained for different measurements are presented in Table 1. For the perturbation reduction, it is necessary to perform a prediction of the output by simulating the system with the measured temperature as input. The corrected output was obtained by subtracting the measured and the predicted outputs. As a measure of perturbation reduction, the following parameter can be defined:

$$
\text{reduction} = \frac{E[|v - v_{\text{simulated}}|]}{E[|v|]} \times 100 \tag{21}
$$

Fig. 6 shows the filtered heat flow, the predicted signal and the predicting error (difference between experimental output and predicted outputs). The identification has been done using data in the interval (500, 1500 s). As it is seen from this figure, the prediction is also good outside the identification interval. This means that the parametric model used for the identification gives a good description of the real system. In Fig. 7, the model was tested by a pulse perturbation. The upper part of the figure shows the temperature response of the heating pulse. In the lower part, the measured and predicted heat-flow signals can be seen. The prediction was made with the help of averaged parameters from Table 1. The low influence of the perturbation on the error signals confirms the quality of the identification and the stability of the system, respectively.

In order to test the dependence of the parameters of the sample mass, the mass used in the Experiment 5 was doubled. As seen from Table 1, parameter a was also doubled as expected from the model. But parameter b was also affected by the sample mass. That means, the approximations made are too coarse. It can

Fig. 6. Results of the identification and prediction: The curves of the measured output and predicted measured signal are almost the same. The error curve is the difference of both curves.

Fig. 7. Pertubation reduction: The temperature curve (a) is caused by a heat power impulse. With earlier obtained parameters of the system the measured signal is predicted (b). Subtracting the predicted signal from the measured signal provides the corrected curve.

be shown [9] that Eq. (16) can be approximated more accurately by

$$
H(s) = \frac{V(s)}{T(s)} = K \frac{\tau_s s}{(\tau_{cs} s + 1)}
$$
 (22)

where

$$
\tau_{\rm cs}^2 = \tau_{\rm c}^2 + \tau_{\rm s}^2.
$$
 (23)

The time constant τ_{cs} in Eq. (22) now depends on the thermal properties of the chip carrier as well as on the sample mass. Tbis is in good agreement with the experimental results. A second-order model has been tested but no improvement has been observed in the results.

5. Conclusion

To avoid thermostatting effort in a calorimeter, the influence of ambient temperature perturbation on the output signal can be reduced by predicting and correcting the perturbation part of the signal. In the same way, perturbations produced by temperature control with Peltier and/or Joule effect can be reduced. The perturbation can be reduced by measuring the temperature perturbations and simulating the corresponding output signal. This procedure is useful for measurements of temperature at any one point that must be representative of the perturbations. If that is the case, it is easy to analyze the calorimeter in order to obtain a dynamic model which is necessary for the prediction by standard system identification methods like the instrument-variable method. Stochastic excitations seems preferable for the identification procedure. If the signal-to-noise ratio of the temperature measurements is high enough, natural fluctuations of the ambient temperature could be used during the identification runs. Under such conditions, an adaptive system identification should be possible. Furthermore, the method seems appropriate in differential as in nondifferential systems.

6. List of symbols

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Appendix A

A. 1 The instrumental-variable method (IVM)

The aim of the parameter estimation is to solve Eq. (12) by minimizing Eq. (13). The solution of this problem using the least-square method (LSM) is [6]:

$$
\hat{\theta}_{t_0,t_1}^{\text{LS}} = \left[\sum_{t=t_0}^{t=t_1} \varphi(t) \varphi^t(t) \right]^{-1} \left[\sum_{t=t_0}^{t=t_1} \varphi(t) v_T(t) \right]
$$
\n(A.1)

In the presence of noise,

$$
\nu_T(t) = \varphi^t(t)\theta_0 + n(t), \qquad (A.2)
$$

where θ_0 is the true parameter vector and $n(t)$ is a zeromean noise, we obtain

$$
\hat{\theta}_{t_0,t_1}^{\text{LS}} = \theta_0 + \left[\sum_{t=t_0}^{t=t_1} \varphi(t) \varphi'(t) \right]^{-1} \left[\sum_{t=t_0}^{t=t_1} \varphi(t) n(t) \right]. \tag{A.3}
$$

If the noise is not white noise, some correlation will exist between the noise and the vector $\varphi(t)$ and the estimation will not converge to the true parameters. Therefore, the instrumental-variable method should be applied. This method gives a solution for the noise problem in the LSM. The LSM corresponds to the solution of the equation

$$
\hat{\theta}_{t_0,t_1}^{\text{LS}} = \text{solution}\left\{\frac{1}{t_1 - t_0} \sum_{t=t_0}^{t=t_1} \varphi(t) [v_T(t)] - \varphi'(t)\theta] = 0\right\}
$$
\n(A.4)

That means, the method tries to decorrelate the vector $\varphi^{t}(t)$ with the prediction error. When the noise is not white, the vector $\varphi^{t}(t)$ will be correlated with the noise and then the solution will be incorrect. In the last equation we can try to decorrelate the prediction error with another vector $\zeta(t)$ not influenced by the noise $n(t)$. This method is called instrumental-variable method and the elements of $\zeta(t)$ are called instruments. The solution is similar to that of the LS method:

$$
\hat{\theta}_{t_0,t_1}^{\mathbf{IV}} = \left[\sum_{t=t_0}^{t=t_1} \zeta(t)\varphi'(t)\right]^{-1} \left[\sum_{t=t_0}^{t=t_1} \zeta(t)v_T(t)\right].
$$
\n(A.5)

The question is how to generate the instrument vector so that it will be uncorrelated with the noise and correlated with the output of the system. One possibility is to first use the LS method and then the parameter obtained to generate the instruments. That is:

$$
\zeta(t) = \left[\frac{\mathrm{d}^n T}{\mathrm{d}t^n}, \dots, T, -\frac{\mathrm{d}^m y}{\mathrm{d}t^m}, \dots, -\frac{\mathrm{d}y}{\mathrm{d}t}\right]^t \quad \text{(A.6)}
$$

where $y(t)$ is the simulated output for the system using the parameters obtained from the LS method. Then, the vector $\zeta(t)$ will not be influenced by the noise $n(t)$.

A.2 MATLAB examples

The following sequence of MATLAB instructions can be applied to perform the identification and the correction procedures.

Identification:

% Input data:

% v l - vector of measured heat flow signal

% T1 - vector of measured temperature

% perturbation

% Output data:

- *% num- numerator polynom of the transfer % function*
- *% den denominator polynom of the transfer % function*
- *% err error information*
- *% vs simulated heat flow signal %*
- *vf = idfilt(vl,3,[O.O04 0.04]);*
- *% filtering of vl and T1 using a third order Tf = idfilt(T1,3,[O.O04 0.04]);*
- *% band-pass butterworth filter, the pass % band is from 0.004 Hz to 0.04 Hz %*

[num, den, vs, err] =
$$
idvar([time \text{ vf } Tf], 0, 0, 2)
$$
;

% identification procedure for % 2nd order model

Correction:

- *% Input data:*
- *% v2 vector of measured heat flow signal*
- *% T2 vector of measured temperature*
- *% perturbation*

% num - numerator polynom of the transfer

% function

%

- *% den denominator polynom of the transfer*
- *% function*
- *% Output data:*
- *% vc corrected heat flow signal*
	-
- *vf = idfilt(v2,3,[O.O04 0.04]);*
- *% filtering of v2 and T2 using a third order*
- *Tf = idfilt(T2,3,[O.O04 0.04]);*
- *% band-pass butterworth filter, the pass*
- *% band is from O. 004 Hz to O. 04 Hz*
- $vT = lsim(num, den, Tf, time); %$ *simulation of the % system with Tf*
- *% vT is the predicted signal due to Tf* $vc = v - vT$; % correction

The instructions *idfilt, idvar* and *lsim are* build-in procedures of the MATLAB toolboxes IDENTIFICA-TION, IDCON and CONTROL [8].

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