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CHANGES IN THE TRANSFER FUNCTION OF A FLOW MICROCALORIMETER

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Abstract

Flow microcalorimeters are used to determine thermodynamic properties of liquid mixtures, the accuracy of these measures depends on the right calibration of the instrument. In this work the system is identified by means of the transfer functions of the two poles, it is proven that the first time constant and the sensitivity change with the value of $\rho c_p f$ of the injected liquids (ρ – density, c_p – heat capacity, f – injection flow), and that the sensitivities obtained in the electrical and chemical calibrations are different for the same value of $\rho c_p f$ because the dissipation in each case does not occur in the same place. As a summary of the calibration carried out, it is proposed a sensitivity value of 313±4 mV W^{-1} for $\rho c_p f$<15 mW K^{-1} that permits to make thermal measures with an uncertainty of 3%.

Keywords: conduction calorimeter, flow microcalorimeter, liquid mixtures, modelling, signal processing, thermal measurement, transfer function

Introduction

This work is about the calibration of an isothermal flow microcalorimeter TAM 2277-204 by Thermometric AB [1] used to measure the energy taken place when mixing two liquids. This type of calorimeter is frequently used nowadays to determine thermodynamic properties of liquid mixtures [2–4].

Due to the inherent characteristics of performance of these calorimeters, the users of these instruments base the calibration on the calculation of the sensitivity [5–7]. The simultaneous injection of two liquids in the mixture area of a flow microcalorimeter provides an output of the detecting system that reaches the stationary state when the mixture is homogeneous; in this stationary situation the power dissipated by the mixture is proportional to the experimental output, the proportionality constant is the sensitivity in V W^{-1}. The sensitivity explains the static performance of the system but, in order to understand the dynamic operation, it is necessary to know the transfer function (TF) of the instrument. It is clear that we will be able to speak of the transfer function only if the instrument is working in a linear and invariable situation.

Starting from thermal models of the calorimeter, a functional relationship can be established among the dissipated powers inside the calorimeter and the output of the

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detecting system [8–9]; generally, this relationship is linear but it is not always invariable as in the case of the titration microcalorimeter in which the mass of the laboratory cell increases during the injection [9–10].

Nowadays the determination of the transfer function of the calorimeters remains being of interest since it allows to make measures that also include the dynamics of the process under study [11]. Besides, to improve the experimental systems it is necessary to model them, and the first model that is calculated is the one provided by the transfer function of the device; there are many applications for this, Velázquez–Campoy *et al*. [12–13] whose purpose is to reduce the main time constant of the calorimeter from 80 to 20 s. Lerchner *et al*. [14] are able to reduce the interference of the ambient temperature in a microsized calorimetric system using a model of two poles. Löwen *et al*. [15] determine the heat capacity of some substances starting from the calculation of the time constants of the TF.

Each calorimetric instrument has its own characteristics. In a previous work we analyzed the micro-effects of two types of injection calorimeters: titration microcalorimeters and flow microcalorimeters [16]; in a later work [17] we proposed a model with physical image that acceptably represented the performance of a flow microcalorimeter providing an expression of the sensitivity according to $\rho c_p f$ (ρ is the density, c_p is the heat capacity and f is the flow of the injected liquid), but this model was obtained from electrical calibrations and it does not represent the results of the chemical calibrations sufficiently well, mainly because the mixture does not take place in the same area where the electrical resistance of calibration is located.

In this work the main changes of the transfer function of a flow microcalorimeter are evaluated. The modification of the parameters of the TF of the instrument happens when some of the following factors change: 1) the injection flow, 2) the heat capacity of the injected liquids, 3) the dissipation place and 4) the mixture type. These changes are unavoidable in the ordinary use of the instrument, for this reason a careful study of the effects produced by the four mentioned factors is made; there have been carried out enough experimental measures for this study which correspond to electrical and chemical calibrations.

The selected order to present this work is the following one: a brief description of the experimental equipment and of the measures carried out for the calibration is firstly made, then the model and the identification method of the parameters of the model are exposed, and finally an analysis of the obtained results is made.

Experimental system and calibration measures

The studied flow microcalorimeter has been designed to work at constant temperature, this is the reason why the calorimetric cylinder is submerged in a thermostatic bath TAM2277 by Thermometric. All the measures carried out in this work have been made with a temperature of the thermostat T_0=298.15 K, this bath maintains the temperature constant with an accuracy of ±0.001 K in stationary state.

The calorimetric cylinder 204 by Thermometric contains a detecting system and a mixture area (in Fig. 1 the capsule and the mixture coil). The calorimetric output is directly digitized by a Hewlett Packard HP3457A multimeter (10 nV of resolution). The electrical calibration is made by the dissipation of a known power in a resistance of 50 Ω located inside the calorimeter, the resistance is connected to a source HP6284A/HP59501B. The system is controlled through the bus GPIB by a PC and the readings are stored for a subsequent analysis. The sampling interval used is $\Delta t \approx 1.0989$ s.

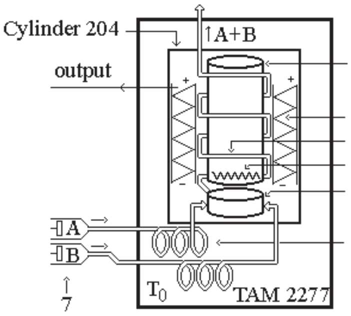

Fig. 1 Scheme of the TAM 2277-204 flow microcalorimeter by Thermometric (only the mixture cell is represented, the reference cell is not represented). 1 – cell-holder; 2 – thermocouple detector; 3 – mixture coil; 4 – electrical calibration resistance; 5 – flow-mix cell; 6 – heat exchanger; 7 – Hamilton syringes of 50 cm^3; T_0 – thermostat

The injection system is made up of two Hamilton syringes of 50 cm^3 pushed by a stepper motor MT-160-250 by Microcontrole producing an injection of 0.0184 mm^3 per step. The desired injection flow is obtained by programming the number of steps in every sampling period.

The selected working models for the chemical calibration are the liquid mixtures cyclohexane+hexane, cyclohexane+benzene and water+methanol. In all the experimental measures the two syringes inject at the same injection flow ($f_A=f_B$), this is the reason why the concentration and the enthalpy per mole of mixture is the same, although the total injection flow changes. The reference enthalpies for 298.15 K, and for a concentration in which $f_A=f_B$, are the following ones:

Cyclohexane (A)+hexane (B): H^E_{ref}= 220.3 J mol^{-1}; x_A=0.5472 [18]

Cyclohexane (A)+benzene (B): H^E_{ref}=796.2 J mol^{-1}; x_A=0.4527 [19]

Water (A)+methanol (B): H^E_{ref}=875.0 J mol^{-1}; x_A=0.6926 [20]

The volumetric heat capacities (ρc_p) of every liquid for 298.15 K, are as follow [21]:

Water: 4.18 J cm^{-3} K^{-1}
Methanol: 2.01 J cm^{-3} K^{-1}
Benzene: 1.52 J cm^{-3} K^{-1}
Hexane: 1.49 J cm^{-3} K^{-1}
Cyclohexane: 1.41 J cm^{-3} K^{-1}

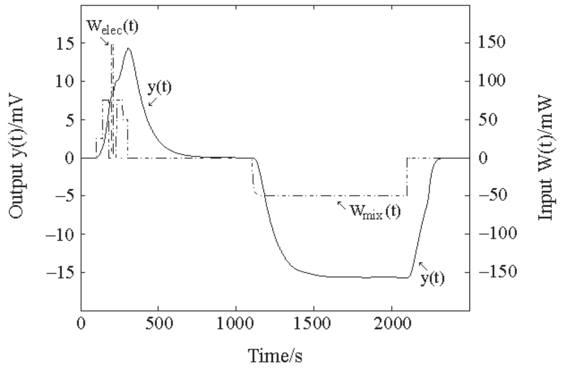

Fig. 2 Input (W_{elec} and W_{mix}) and output (y) curves corresponding to the electrical and chemical calibrations. The curve $W_{\mathrm{mix}}(t)$ corresponds to cyclohexane(A)+benzene(B) mixture for $f_A=f_B=3.03$ mm^3 s^{-1} and $W_{\mathrm{ref}}=49.51$ mW

In order to study the injection effect, different flows have been tested in each syringe: from 0.756 to 8.318 mm^3 s^{-1}. As the experimental output to the mixture process reaches the stationary state, we can suppose that a homogeneous mixture is obtained (Fig. 2). The homogeneity of the mixture is not reached instantly and, due to this fact, we cannot associate the mixture power (input of the system) to a Heaviside type signal. As a first approach, we suppose that the input power (W_{mix}) follows an exponential function with a time constant (τ_{mix}) that will depend on the injection flow and the mixture process itself [22–23]:

$$W_{\mathrm{mix}}(t)=W_{\mathrm{ref}}[1-\exp(-(t-\Delta_{\mathrm{mix}})/\tau_{\mathrm{mix}})] \tag{1}$$

Δ_{mix} is a time lag in the carrying out of the mixture due to the relative situation of the pure liquids inside the injection tubes. The reference power is proportional to the injection flow, and we can express it according to the molar enthalpy of reference with the following expression:

$$W_{\mathrm{ref}}=H^{\mathrm{E}}_{\mathrm{ref}}(\dot{n}_{\mathrm{A}}+\dot{n}_{\mathrm{B}}) \tag{2}$$

The input signal used for the electrical calibration consists of a sequence of pulses of different power and duration (Fig. 2). During the measurement (before, during and after the electrical dissipation) the same pure liquid is injected in every tube. The measures are made for different flows: from 0 to 8.318 mm^3 s^{-1} and the injection flow of every syringe is the same ($f_A=f_B$). The liquids are the same that were used in the chemical calibration: cyclohexane (Sigma-Aldrich, 99.9% HPLC grade), benzene (Sigma-Aldrich, 99.9% HPLC grade), *n*-hexane (Merck, 99%) and methanol (Fluka, 99.8% HPLC grade).

Model and identification

In order to model the instrument we have considered a system with two possible inputs and an output. The first possible input is the power developed when mixing the two injected liquids and the possible second input is the power dissipated in the electrical resistance of calibration. The output is the one provided by the thermocouple detecting system. In the case of measures resulting from electrical calibrations the input power is previously programmed and it is measured at every moment during the measurement itself. But, if it is a chemical calibration, the input will be given by the Eq. (1) and the reference power by Eq. (2) where we suppose a known reference enthalpy $H_{\mathrm{ref}}^{\mathrm{E}}$ for the concentration that results from the injected flows of each liquid.

We make the primary study of the system using a very simple empirical model of two poles, the transfer function $H(s)$ is given by:

$$H(s)=\frac{K}{(1+s\tau_1)(1+s\tau_2)} \tag{3}$$

s is the Laplace variable, K is the sensitivity or static gain, τ_1 and τ_2 are the time constants.

To determine the parameters of the transference functions we use a non-linear adjustment method by minimal squares based on the Marquardt's algorithm [24] making use of the mrqmin routines obtained from numerical recipes in Fortran [25]. The calculated output y_{cal} is obtained by a convolution integral between the input $W(t)$ and the corresponding impulsional output $h(t)$, this is carried out by using the following expressions:

$$\begin{gathered} y_{\mathrm{cal}}(t)=\int_0^{\mathrm{t}} h(t-\tau)W(\tau)\mathrm{d}\tau \\ h(t)=\frac{K}{\tau_1+\tau_2}[\exp(-t/\tau_1)-\exp(-t/\tau_2)] \end{gathered} \tag{4}$$

Results

A model with two time-constants has been chosen because the relationship signal/noise of the experimental curves does not allow to identify more than two time-constants. The relationship signal/noise of the curves corresponding to the electrical calibration is of 75 dB and in the curves corresponding to the mixtures varies between 32 and 50 dB according to the cases.

The noise of the baseline is ±1 μV, but in the mixture measures, during the process of injection of liquids, it appears a low frequency superimposed noise (0.01 Hz) which depends on the value that the outpus signal in stationary state reaches; for example, in output signals with an amplitude in stationary state of 1 mV the noise is ±20 μV, while in output signals with an amplitude of 132 mV the noise increase to ±250 μV.

In the adjustments carried out over the curves of electrical calibration the standard deviation (σ_{d}) has been less than 25 μV, and in the curves of mixtures the standard deviation depends on the amplitude of the signal, but its value relative to the maximum value of the curve has not surpassed 1%, that is to say: $100\sigma_{\mathrm{d}}/y_{\mathrm{max}}<1$. The standard deviation is defined by:

$$\sigma_{\mathrm{d}}=\sqrt{\sum_{\mathrm{k=1}}^{\mathrm{N}}(y_{\mathrm{exp}}[k]-y_{\mathrm{cal}}[k])^2/(N-1)} \qquad (5)$$

where $y_{\mathrm{exp}}[k]$ represents the values of the experimental curve in each point, $y_{\mathrm{cal}}[k]$ are the calculated values, and N is the number of points used in the adjustment, in this case N=1000.

When using the curves of electrical calibration, it is obtained a good approximation of the value of the time constants (τ_1 and τ_2) and of the sensitivity (K) for each case. When the injection flow is zero, the first time constant depends on the heat capacity of the liquid that floods the mixture coil, so τ_1 varies from 110.4 s for water to 99.8 s for hexane, this variation (≈10%) is small due to the fact that the mass of the liquid inside the calorimeter is small with regard to its mass. Figure 3 represents the variation of τ_1 according to the parameter $\rho c_{\mathrm{p}}f$ for each type of injected liquid. The parameter $\rho c_{\mathrm{p}}f$ represents the volumetric heat capacity per time unit of the two injected liquids, that is to say:

$$\rho c_{\mathrm{p}}f=(\rho c_{\mathrm{p}}f)_{\mathrm{A}}+(\rho c_{\mathrm{p}}f)_{\mathrm{B}} \qquad (6)$$

In the figure mentioned above it is observed how τ_1 diminishes when the injection flow increases. The second time constant remains invariable for every kind of fluid, injection flow and mixture carried out: τ_2≈24 s.

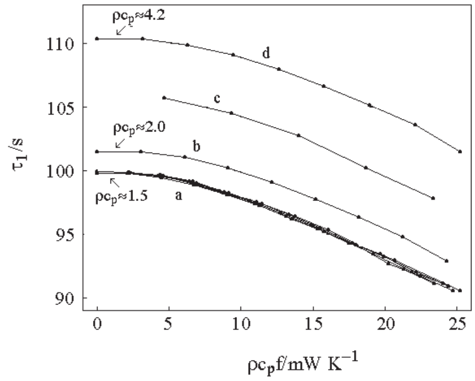

Fig. 3 First time constant (τ_1) of the transfer function as function of $\rho c_{\mathrm{p}}f$. Calibration results in the following cases: injection of benzene, cyclohexane or hexane (points in curve a); methanol injection (points in curve b); simultaneous injection of water and methanol (points in curve c); water injection (points in curve d). ρc_{p} is the volumetric heat capacity of every injected pure liquid in J cm^{-3} K^{-1}

The sensitivity obtained in the measures of electrical calibration varies from 315 to 297 mW V^{-1}, the results are represented in Fig. 4 according to the parameter $\rho c_{\mathrm{p}}f$ for different flows and injected liquids. The electrical sensitivity depends mainly on the parameter $\rho c_{\mathrm{p}}f$ but the results show a slight dispersion of values that we consider that is due to other physical properties of the used liquids (thermal conductivity, viscosity, etc.). In the same Fig. 4 it is shown the variation of the sensitivity obtained in

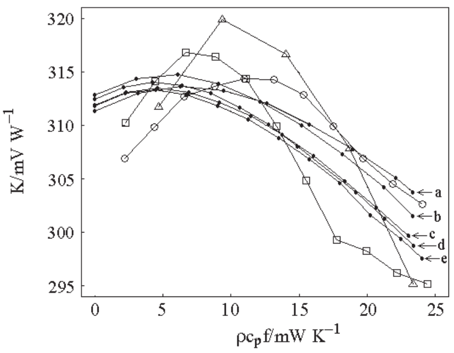

Fig. 4 Sensitivity (*K*) as function of $\rho c_p f$. Results of electrical calibrations in the cases: a – water injection, b – methanol injection, c – benzene injection, d – hexane injection, e – cyclohexane injection. Results of chemical calibrations in the cases: water+methanol mixture (triangles), benzene+cyclohexane mixture (squares), cyclohexane+hexane mixture (circles)

the chemical calibrations for each type of mixture. The clear difference between the sensitivity values obtained in the electrical and chemical calibration for the same value of the parameter $\rho c_p f$ is mainly due to the different location in which the dissipation occurs. Even for every mixture there are also sensitivity differences for the same value of $\rho c_p f$ because the three mixtures have a different behaviour and the dissipation of the mixture is carried out in a spatial zone more or less long and more or less near the detectors. The different behaviour of each mixture can also be observed in the results obtained for the time constant τ_{mix} (Eq. (3)), it can be seen how the mixture water + methanol has a τ_{mix} greater than the two others (Fig. 5).

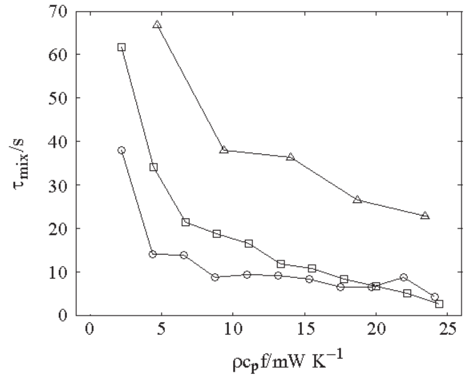

Fig. 5 Time constant (τ_{mix}) as function of $\rho c_p f$. Results of the chemical calibrations in the cases: water+methanol mixture (triangles), benzene+cyclohexane mixture (squares), cyclohexane+hexane mixture (circles)

The impossibility of foreseeing accurately the dynamic behaviour of each mixture and the need of proposing a sensitivity value that could be used for a wide range of substances with different behaviours in mixtures are the reasons why it is proposed an only sensitivity value. Considering the range of sensitivity defined by the maximum and minimum values obtained in the chemical calibrations where $\rho c_p f<15$ mW K^{-1} (Fig. 5), we take as a sensitivity value the center of the limits, and if we consider to calculate the uncertainty a rectangular distribution, we have: $K=313\pm4$ mV W^{-1} for $\rho c_p f<15$ mW K^{-1}. Besides, taking into account a coverage factor equal to 2, we can say that the instrument permits to obtain thermal measures with an uncertainty of 3% [26].

Conclusions

For the studied cases we check that the poles of the transfer function only depend on the value of $\rho c_p f$ of the injected liquids (ρc_p is the volumetric heat capacity and f is the injection flow) although the sensitivity depends on the value $\rho c_p f$ of the injected liquids and the dissipation place.

The results of the calibration are the following ones: τ_1 varies from 110 to 90 s (Fig. 3 permits to obtain an approximation of τ_1); $\tau_2\approx24$ s; $K=313\pm4$ mV W^{-1} for $\rho c_p f<15$ mW K^{-1}, we think that the parameter $\rho c_p f$ defines adequately the validity space of the calibration carried out. That calibration is valid for the studied instrument and the procedure used is applicable to other similar thermal measuring instruments. The solution of the calculated energy results will be directly related to the calibration carried out within its validity range; in this case and with the final model obtained, the instrument allows to obtain thermal measures with an uncertainty of 3%.

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