EFFECT OF THE INJECTION VELOCITY ON THE SPATIAL LOCALIZATION OF THE MIXTURE DISSIPATION IN A FLOW MICROCALORIMETER

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The effect of the injection velocity in the chemical calibration of a flow microcalorimeter is studied in this article. The experimental measures show a parabolic variation of the sensitivity in terms of the injection flow. The considered hypothesis is that the maximum of the sensitivity curve is produced when the spatial area in which the mixture dissipation takes place is centred with regard to the detector system. When increasing the injection flow, this mixture zone moves till it goes out of the detection area making the sensitivity diminish. It has been defined a time constant $\tau_{\text{mix}}$ which is related to the establishment time of the homogeneous mixture and with the length occupied by the mixture dissipation. A study has been carried out with three liquid mixtures that have different behaviours; within these mixtures, $\tau_{\text{mix}}$ has been determined in terms of the injection flow and the considered hypothesis has been confirmed.

Keywords: chemical calibration, flow microcalorimeter, injection calorimeter, isothermal conduction calorimeter, liquid mixtures, sensitivity

Introduction

Flow microcalorimeters are isothermal heat conduction calorimeters that are used to determine the energy developed in a liquid mixture process [1]. The basic principle of operation consists in injecting two liquids continuously in a mixture zone; when the mixture is homogeneous, the experimental response reaches the stationary state. In this situation the power developed by the mixture is equal to the experimental output divided by the sensitivity of the calorimeter. The concentration of the mixture is determined from the injection flows, new mixture concentrations are obtained by changing the injection flows. The improvement of the instruments and, above all, their automation have facilitated their handling, these are the reasons why their use have increased considerably in the last years.

Among the most interesting works within the large bibliography about the calibration of these instruments, we want to point out the articles by Monk and Wadsö and Harsted and Thomsen [2, 3] in which they propose empirical expressions about the sensitivity in terms of the injection flow, and the work by Tanaka et al. [4] in which he adds the dependence of the heat capacity of the injected liquids in the sensitivity. Subsequently, a methodology of calibration has been established for these instruments [5–7] with the help of some models that try to explain their static and dynamic operation. In these last works, a clear difference between the sensitivity obtained in the electrical calibrations and the one obtained in the chemical calibrations can be observed; besides, these differences are also extensive to the different chemical calibrations. This uncertainty in the sensitivity is justified because the energetic dissipation does not always happen in the same place. Faced with the impossibility of establishing a sensitivity function that could be applied for any kind of mixture, it is proposed to establish, after a thorough experimental study, a validity domain of the calibration carried out; this domain is defined with the parameter $\rho_{\text{cf}}$ ($\rho_{\text{cp}}$: volumetric heat capacity, $f$: injection flow). Thus, for the established domain, a sensitivity value is proposed with an uncertainty that has to be calculated in the calibration.

In this article, the causes by which the distinct chemical calibrations of a flow microcalorimeter provide different sensitivity values will be studied. The preliminary working hypothesis is that these differences are due to the fact that the mixture dissipation does not always occur in the same area and that each mixture shows a different behaviour. The need for a thorough study is increased because, nowadays, very small new devices [8] whose operating principle is similar and, probably, with the same calibration problems are being developed.

This work will be exposed according to the following order: firstly, the experimental system and the experimental measures will be briefly described; secondly, our work will centre upon the study of the sensitivity in terms of $\rho_{\text{cf}}$ and the injection flow, also de-
fining, the time constant $\tau_{mix}$, and finally, it will take place a final discussion presenting the hypothesis about how the mixture dissipation is produced in each one of the three studied mixtures.

**Device and experimental**

The utilized experimental system is a flow microcalorimeter TAM 2277-204 by Thermometric AB. The detector system of thermopairs provides the experimental output that is directly read by a Hewlett Packard HP3457A multimeter (10 nV of resolution). The system is controlled through the bus GPIB by a PC and the readings are stored for the subsequent analysis. The sampling interval used is $\Delta t=1.0989$ s. The injection system is composed of two Hamilton syringes of 50 cm$^3$ pushed by a stepper motor MT-160-250 by Microcontrole producing an injection of 0.0831 µL per step of the motor; the desired injection flow is obtained by programming the number of steps in every sampling period [5, 6].

For this study, it has been used the measures of chemical calibration provided by the liquid mixtures water+methanol, cyclohexane+benezene and cyclohexane+hexane. Different injection flows have been tested: from 2.075 to 2.825 µL s$^{-1}$ and, in all cases, both mixed liquids are injected with the same flow ($f_1=f_2$). As a consequence, the concentration and the enthalpy per mol of mixture is the same although the total injection flow was changed. The enthalpies of reference for the working temperature $T_0=298.15$ K and for the concentration in which $f_1=f_2$, are the following ones:

<table>
<thead>
<tr>
<th>Liquid mixture</th>
<th>$H^E_{mol}$ [J mol$^{-1}$]</th>
<th>$x_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water(1)+methanol(2)</td>
<td>$875.0$</td>
<td>0.6926 [9]</td>
</tr>
<tr>
<td>cyclohexane(1)+benzene(2)</td>
<td>$796.2$</td>
<td>0.4527 [10]</td>
</tr>
<tr>
<td>cyclohexane(1)+hexane(2)</td>
<td>$220.3$</td>
<td>0.5472 [11]</td>
</tr>
</tbody>
</table>

As a sample of the measures utilized in this work, the experimental outputs corresponding to the mixture of cyclohexane+benezene for three different injection flows are shown in Fig. 1: 2.075, 2.1.5 and 2.2.25 µL s$^{-1}$; the powers developed in each case are $-12.379$, $-24.758$ and $-37.137$ mW, respectively. Although the noise of the baseline is of ±1 µV, when the mixture dissipation begins, it appears some low frequency oscillation ($\approx 0.01$ Hz) that makes the relationship signal/noise of these curves be between 40 and 500 (32 and 54 dB, respectively).

The measures of electrical calibration consist in the dissipation of a known power in the calibration resistance when the same pure liquid is being injected for each pipe; the liquids and flows used in the electrical calibration are the same used in the chemical calibration, in these curves the relationship signal/noise is of 5600 ($\approx 75$ dB).

**Sensitivity of the calorimeter vs. $\rho c_p f$**

To model the device, it is necessary to calibrate the system with dissipations of the Joule type in order to obtain results that permit to determine the size and complexity of the model required by the calorimeter. The measures of electrical calibration carried out on this system [5, 6] show that the system remains well identified with a transference function (TF) of two poles:

$$TF(s)=\frac{Y(s)}{W(s)}=\frac{K}{(1+s\tau_1)(1+s\tau_2)}$$

where $s$ is the Laplace variable, $Y(s)$ is the output Laplace transform or curve, $W(s)$ is the input Laplace transform or developed power, $K$ is the sensitivity, $\tau_1$ and $\tau_2$ are the time constants. These parameters have been evaluated and it has been checked that the sensitivity changes with the heat capacity and with the injection flow of the injected liquids [2–7] and that the main time constant, $\tau_1$, increases with the heat capacity of the liquids and decreases with the injection flow [5–7].

An analysis of all the calibration measures carried out suggests to impose a maximum limit in the injection flow that guarantees that the injected liquids have acquired, through the homogeniser coil, the thermostat temperature before arriving at the mixture zone. The limit chosen for our calorimeter is of a maximum volumetric flow, for each pipe, 7 µL s$^{-1}$ and a flow in heat capacity units, for each pipe, $\rho c_p f<12.5$ mW K$^{-1}$ ($\rho c_p$ is the volumetric heat capacity and $f$ is the injection flow). With these limits, the measures of chemical calibration used in this study have dissipations that goe