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# Variation of the noise levels in the baseline of an adsorption microcalorimeter

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**Abstract** This work shows the results obtained to determine the noise in the baseline of a specially designed Tian Calvet-Type adsorption microcalorimeter. The results show that noise levels vary from 0.5 to 10 μV, which were evaluated varying the electrical work and the micro calorimeter surrounding temperature. Relationships can be seen between the variables employed in the observation of stability, temperature, potency levels and generated noise.

**Keywords** Electrical signal · Noise · Calorimetry · Adsorption · Time constant

## Introduction

Calorimetry is defined as a science that involves the measurement of quantities of heat generated in different processes. The adsorption calorimetry is a sensitive and precise technique that can measure heats of the order of 100 mJ. For this reason, it is necessary to measure this quantity with extreme precision, avoiding errors that can distort the true signal. The most used sensors in adsorption calorimetry are thermo batteries that work under Seebeck effect and can give a signal of the electric potential as a response to a heat flow. However, they can introduce a certain error, which is due to small electrical signals generated by the unions or connections and imperfections in the electrical circuit used to obtain the thermoelectrical signal. In calorimetry, it is important to evaluate the noise level independently of the measured magnitude it should be compared to the measured thermal effect magnitude to quantify the possible error introduced in the measurements. Calorimetry has a wide field of action and nowadays it follows broadening its application possibilities to measure heats with good precision [1].

In this context, adsorption calorimetry is used in the characterization of porous materials, where its application is wide in basic sciences and industry. As an example, the necessity of a characterized catalyst can be mentioned, as their surface and chemical properties depend on their final application.

Among the methods to measure heat effects it is worth to mention: (a) the temperature change that is multiplied by a thermal equivalent; (b) the required potency to keep the isothermal insulation conditions with a power able to be supplied by a temperature electronic controller or by a change in the isothermal phase of a substance in contact with the calorimeter; (c) the temperature differences measured by means of fix thermal conductivity, which is determined in individual experiments of calibration [2, 3].

The calorimeter always has three components that directly affect the data quality: (a) the calorimetric cell, including the sensors employed to measure the thermal effect; (b) the surrounding that can be constituted by a thermo sized bath, a controlled temperature metallic block or the laboratory atmosphere; (c) a medium to initiate the

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reaction by a process that produces heat, which can be simplex or complex. The calorimeter can be twin-type where one of the cells acts as the reference and the other as the measure cell. The reference cell is used to rest estrange effects in the measurements [4–9]. The systems can be isoperibolic, $T$ and $p$ constant or adiabatic, controlled surroundings and the same temperature than the reaction cell. The start of reaction can be produced by a temperature, pressure or volume change, or by a change in the reactive concentrations.

To measure precisely the heat, various elements can be used. The thermometer can be very stable, but only by a period of time that exceeds the experiment. However, other sensors can be used, such as thermistors that are particularly useful for several reasons: high thermometric sensitivity; built with simple and inexpensive components; and at last, they have a small mass then, the time constant can be also small. The principal disadvantage is that the thermistor heats itself. Some electronic circuits are sometimes used when thermistors are employed to measure the temperature [1–3]. However, when a high sensitive system is required, like in calorimetric studies for the gas–solid interphase, a Calvet-type adsorption calorimeter is the chosen one. In these equipments the measuring system consists in a group of thermocouples in series that form the thermopiles, which is the measure thermoelement [10–13]. A thermopile works very well in theory, but errors are common in practice, which are attributed to small electrical signals generated by the unions, connections and imperfections in the electrical circuit employed in the laboratories to obtain the thermoelectrical signal. Within them it can be mentioned: (a) the length, thickness, polarity of the terminal wires in the thermo batteries; (b) the number of connections in the system; (c) the magnitude of the thermal gradients along the wires in the thermal elements.

Among the advantages of adsorption calorimetry we mention: in contrast to isosteric and chromatographic methods, the enthalpy does not emerge from experiments where the adsorption equilibrium must be guaranteed, thermal data can be obtained even at low pressure and, if the experiment is performed in a continuous way, the behavior of the change of enthalpy as a function of the amount adsorbed on the surface can be obtained [14].

Thermal noise (or Johnson)

Every kind of resistances generates by themselves and by their terminals a voltage with random fluctuations like thermal noise or Johnson, which is caused by the charge carrier random movement in conductor materials. It is always produced at temperatures above absolute zero (−273 °C or 0 K).

Shot noise

This kind of noise is related to the non-continuous nature of the electrical current, formed by a discrete charges flow that causes statistical fluctuations in the current. The shot noise, as well as the thermal noise, is a kind of white noise.

In this work, we studied the noise signal behavior generated in an adsorption microcalorimeter built in our laboratory, based in others built previously, respect to the applied potent and the temperature, to establish if the noise level can eventually affect the measures in the gas–solid interface [15].

In this work results are presented on the performance of a "twin-type" calorimeter with thermopile sensors constructed in our group, which is composed of a calorimetric unit and an adsorption unit for the simultaneous measurement of adsorbed quantities and heat generated during the adsorption. The estimation of electronic noise is important, given that the heats of adsorption in carbons are of the order of 10 to 18 kJ/mol, which are small values, and a baseline, which is stable at smaller values must be achieved in order to determine with accuracy the heat generated in the process [16].

## Methodology

The measurements are realized in a microcalorimeter designed in our laboratory, which basic scheme is shown in Fig. 1. I consist of basically in two parts: (a) adsorption

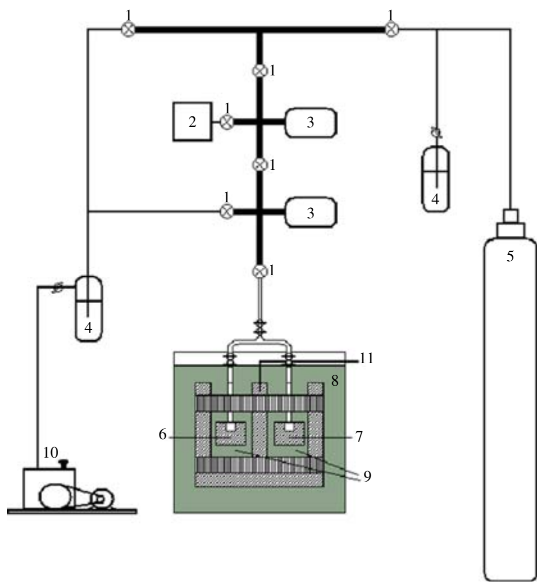


**Fig. 1** Adsorption Microcalorimeter. 1. Precision Valves 2. Calibration volume or storage. 3. Pressure Transducers. 4. Nitrogenous Traps 5. Adsorbate. 6. Reference Cell. 7. Reaction Cell. 8. Heat Storage. 9. 3D-Type Heat Sensors. 10. Vacuum System. 11. Temperature Control Sensor

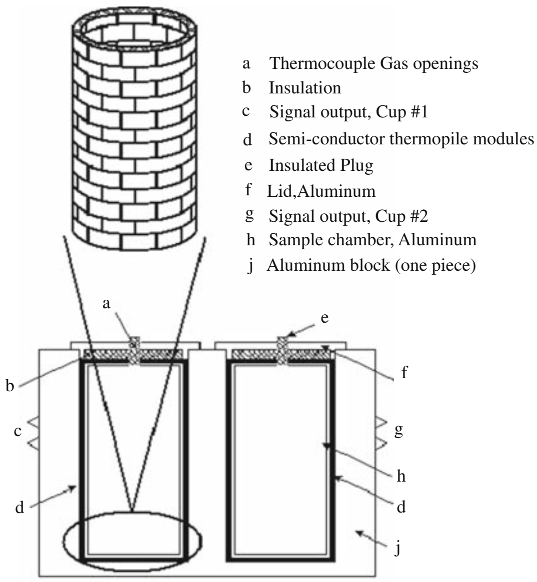


**Fig. 2** Calorimetric Cell in the adsorption microcalorimeter

part and (b) the micro calorimeter itself. Each one of these parts is detailed in the figure.

A part of the calorimetric cell is shown in Fig. 2. It consists of two calorimetric cells; one of them acts as the reference cell and the other as the measure cell. The 3D-Type heat sensors used are zoomed in the same figure.

The equipment is isolated from the surroundings to control the temperature by means of a plastic material with low thermal conductivity. The calorimeter has two resistances with the same magnitude, which value is about 698.32 kΩ. The measurements scheme is shown in Fig. 3; it is highlighted with an interrupted line, the external electrical connections between the adsorption micro calorimeter and the data entry system, which contribute to the noise in the signal measurements.

To determine the noise level, different signal potencies are applied by means of the electrical resistance with a fix electrical work at different temperatures and under experimental work conditions in the surroundings. It was also realized some essays at a fixed temperature and varying the electrical work level. A highly stabilized source Agilent$^{TM}$ E3649A Al model applies the potential and a multimeter

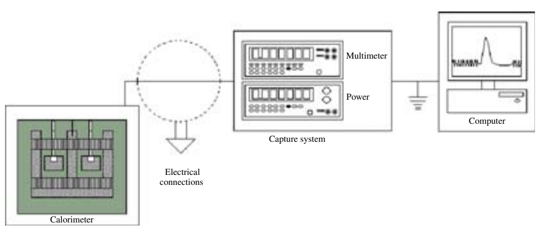


**Fig. 3** Data capture system

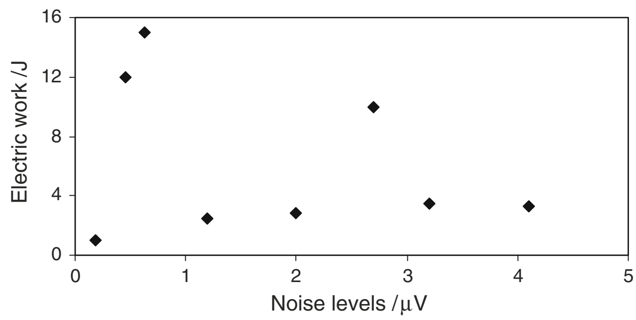


**Fig. 4** Peak to Peak Noise Level at 18 °C varying the Voltage Level

Agilent$^{TM}$ 34401 with 6½ numbers enters the data. This multimeter is connected to a PC by a GPIB interface, where the signals are evaluated.

## Analysis and results

The results shown in Fig. 4 are obtained at a constant temperature of 18 °C and varying the electrical work levels. The applied potential varied from 0.40 to 1.5 V, which correspond to electrical works from 0.19 to 4.10 J. Figure 4 shows that for values of electric work between 0.19 and 0.63 J the noise level of the baseline increases and reaches the maximum value of 15 µV. These values correspond to lower energies than those generated when a solid surface is put in contact with a gas or a liquid, which are around 15 kJ/mol [16]. For energy values higher than 1.0 J the noise level is close to 3 µV and still allows a calorimetric determination of the heat involved in the process without noise interference.

Although in specialized bibliography there are some studies about the noise level in calorimeters and/or in calorimetric measurements and different magnitude orders have been reported in different kind of calorimeters [17–22], this work focuses in the importance of determining in a precise way the signals that are not associated to what is under measure, like noises, which are due to the connections between the different parts of the equipment.

Figure 5 shows a calibration potentiogram for the constructed calorimeter with a zoom in the baseline signal part; it is clear that the noise level is insignificant respect to the signal with a noise value in this case of 0.5 µV for a dissipated electrical work of 0.42 J.

In this work it was studied if the time constant (τ) of the equipment could be affected by the noise level magnitude. It was established that it is not true obtaining repetitive values about 120 s, quite similar to commercial equipment like SETARAM$^{TM}$.

Figure 6 shows the behavior of the calorimetric system when is varied the temperature at a fix level of electrical

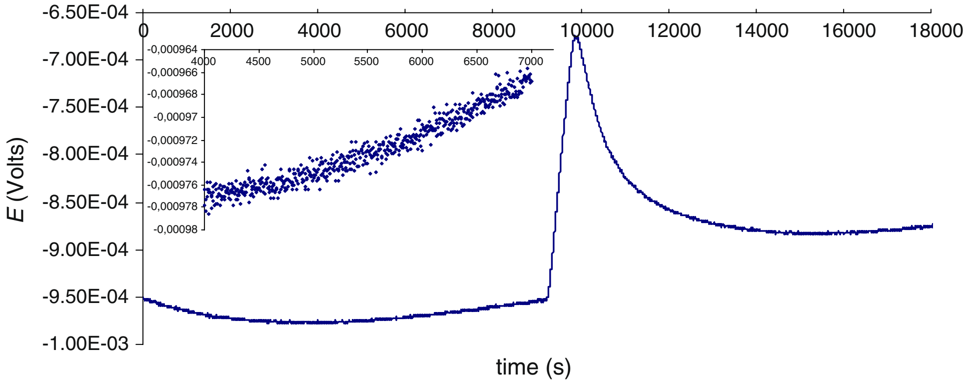


**Fig. 5** Potentiogram: Applied Work 0.42 Jules; Peak to Peak Noise 0.5 μV

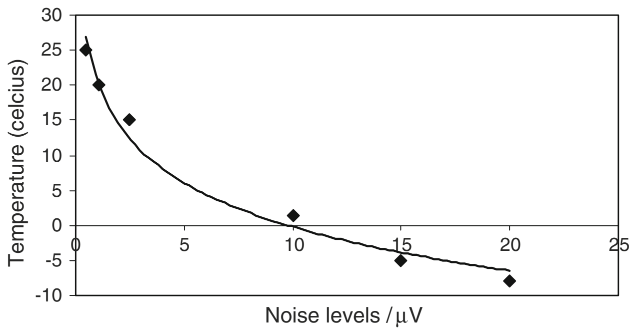


**Fig. 6** Peak to Peak Noise Level applying a 0.42 J Work

work (0.42 J). This essay is realized taking into account that the equipment was designed to work in a temperature range from −196 °C to 600 °C. The figure shows that near room temperature the signal noise level is about 0.5 μV, which permits without any doubt to carry out experiments with magnitudes about 5 mV with a good precision. At low temperatures the noise level increases up to about 20 μV. It must be taken into account that when the temperature decreases in the calorimeter a thermal gradient is generated between the heat sensor terminals inside the calorimeter and the ones connected to its external part causing a higher noise level in the signal. Certainly, it is observed here the thermal noise or Johnson that is present at temperatures higher than −273 °C, where the connections can be considered resistances that generate by means of their terminals a voltage with random fluctuations. This generates a random movement in the charge carrier in conducting materials. The resistance has a conduction band with electrons free that tends to move freely in any direction, the thermal energy of the surrounding provokes this random movement that at the same time increases the temperature.

In Fig. 7 the monitoring of the noise level can be seen keeping constant the temperature at 18 °C for more than 36 h.

It is noticed that the stability of the baseline is very important, when the noise level is under 0.5 μV; the scale is zoomed to a better visualization of the noise signal. It is important to recall that the electrical connections generate noises that can also be associated to the shot-type noise.

## Conclusions

The noise level in an adsorption micro calorimeter constructed in our lab was determined by varying the applied electrical work and the surrounding temperature. Noise was measured below 0.5 μV as the inferior limit and about 10 μV as the superior limit. The noise level is related to the surrounding temperature; at near room temperatures the noise level signals are lower than the signals obtained at under zero temperatures when the applied electrical work keeps constant. When the temperature keeps constant the noise signal is low for low levels of potency and increases when the potency increases, not reaching high values in comparison with the kind of measures that this equipment realize.

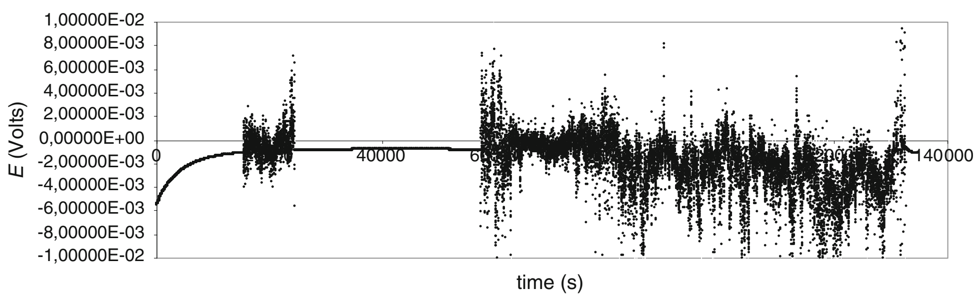


**Fig. 7** Noise Signal in the Calorimeter during 36 h

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