Convolution denoising of a large volume Seebeck calorimeter

Wu-Shu Zhang
Institute of Chemistry, CAS, Beijing 100190, China. E-mail: wszhang@iccas.ac.cn

Calorimetry has been a crucial issue and debated all the time since the discovery of cold fusion in 1989. Seebeck envelope calorimeters (SECs) are widely used in this community for the benefit of large measuring room, high range and easy to operate. However, the thermal background noise of SEC (e.g. peak-peak signal is 0.1 W in Ref. [1]) is much greater than the microcalorimeter (e.g. 10 nW to 1 μW for Calvet microcalorimeters of TA and Setaram) due to large volume and worse temperature stability. Therefore, the low excess heat and its slight changes cannot be detected by present SECs. The reason is that the requirement of high thermal power measurement has to be satisfied by rapid heat transfer and thus the temperature stability is limited by the circulating bath matched. The multilevel thermostatic baths used in the Calvet calorimeter cannot be applied here.

In this paper, a new technique of denoising for SEC is reported. Its principle is as follows, thermal power noise of SEC mainly comes from temperature fluctuations of cooling fluid, our goal is to measure the fluctuation and eliminate it. Firstly, a reference vessel, which is a small size of SEC, is made. Its outer fluid pipe for thermostating is among the outlet of circulating bath and the outer fluid pipe of sample vessel. This design can ensure the thermal signal change of reference vessel induced by fluctuation of fluid temperature being prior to the response of sample vessel of SEC (see the left picture of Figure 1). Before regular calorimetry, a temperature step is applied on purpose, two thermal pluses of reference vessel and sample vessel occur successively. Deconvoluting these two pluses and obtain the response function of the calorimeter. In practical calorimetry, the waveform of convolution of thermal signal of reference vessel is much like the signal of sample vessel induced by fluctuation of fluid temperature as shown in the right picture of Figure 1. The sample vessel's signal minus the convolution signal can eliminate most of thermal noise.

As shown in the Figure 1, the preliminary test shows that the noise can be reduced by more than 2 orders of magnitude, which is physically equivalent to the water bath temperature stability changing from 0.005°C to better than 0.000035°C. At the same time, the detection limit of the large volume calorimeter is extended from order of 0.1 W to order of mW, and the measurement sensitivity and accuracy are greatly improved. This calorimeter can be used widely in cold fusion studies.

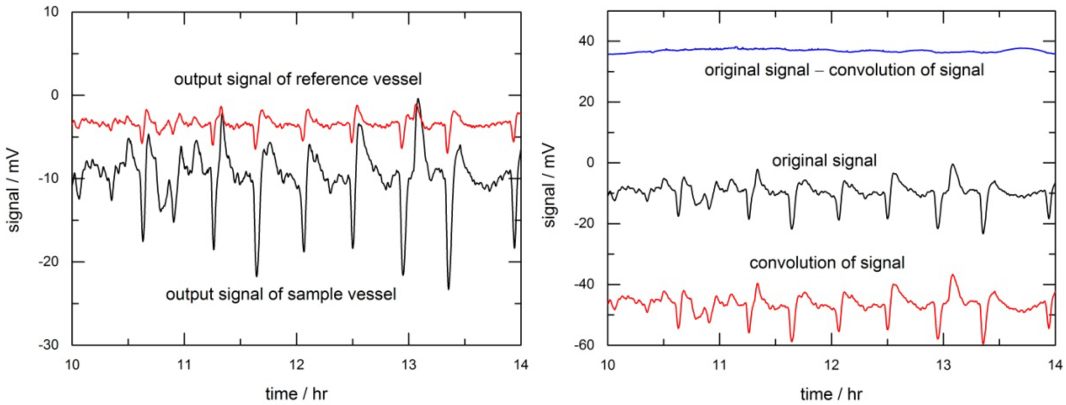

Fig. 1. Preliminary application of convolution denoising. The left picture is the output signals of the reference vessel and the sample vessel; The right picture is the convolution of the output signal of the reference cell and the difference between the two. It can be seen that after convolution processing, the reference cell signal can mostly cancel with the sample cell signal (for example, the peak-peak near 13 hr is 21 mV or 280 mW, after processing, it becomes 0.14 mV or 1.8 mW, only 0.7% of the former).

References:

[1] W. S. Zhang, Thermochim. Acta 499 (2010) 128.
[2] W. S. Zhang, China Invention Patent No. 201810191597.0.