Thermochimica Acta, 85 (1985) 267–270
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL METHODS OF ANALYSIS/DIFFERENTIAL SCANNING CALORIMETRY IN THEORY AND APPLICATION

H. WEBER-ANNELER[1] and R. W. ARNDT[2]
[1]Laboratorium für Bionik, CH-5412 Gebenstorf (Switzerland)
[2]Mettler Instrumente AG, CH-8606 Greifensee (Switzerland)

ABSTRACT

Two types of methods are commonly used in Differential Scanning Calorimetry (DSC), heat-flow DSC, formerly known as Quantitative Differential Thermal Analysis (QDTA) and power-compensated DSC. These two methods are widely believed to be fundamentally different. This is not generally true, on the contrary, both methods give the same physicochemical information depending merely on the quality of the instrument. This is shown on the firm ground of the theory of linear thermal systems. The equivalence of both methods becomes more clear from the viewpoint of linear filtering. From a discussion of current applications, new possibilities to overcome some of the limitations are outlined.

INTRODUCTION

More than half a century before H. Le Châtelier run the first thermoanalytical experiments, Jean-Baptiste Joseph Fourier wrote in his famous book on the analytical theory of heat:"My theory has been derived from very general and elementary principles and will find a large field of fruitful applications in many other fields as well and the instruments will be improved and experimental evidence multiplied." Has this statement of one of the greatest scientists of the 19th century been fulfilled? We know with certainty that Fourier's book contains the complete theory of modern thermoanalytical instruments.

THEORY OF LINEAR THERMAL SYSTEMS

Thermoanalytical methods make use of linear thermal systems. Such a system always consists of a furnace with a well designed measuring cell. It is most important that the thermal response of the system is a linear function of the thermal input. The difference of the two response-curves in fig. 1 is due to a slight asymmetry in the DSC-furnace- and cell-construction.

Figure 2 shows how the response of a thermal system to an arbitrary input IV can be synthesized from Dirac-response-signals. The essence of linearity of thermal systems is: proportionality of the amplitudes and invariance of the time scales. This principle is universal and inherent to all field-theories. Its mathematical implications have been thoroughly studied elsewhere (ref. 1).

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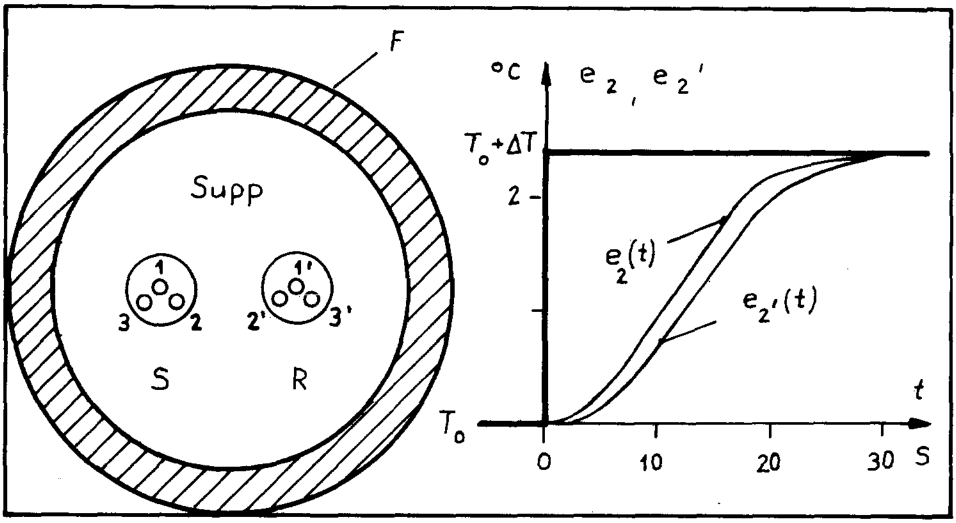

Fig. 1. DSC-Furnace and Step-Response from furnace temperature.

F: furnace, Supp: Heat conducting support, S: sample, R: reference
1: Heat input sample, 1': Heat input reference, 2: Temperature sensor sample, 2': Temperature sensor reference, 3: Electrical heater sample, 3': Electrical heater reference. $T_o \rightarrow T_o + \Delta T$: Input step, $e_2(t)$, $e_{2'}(t)$: Response signals.

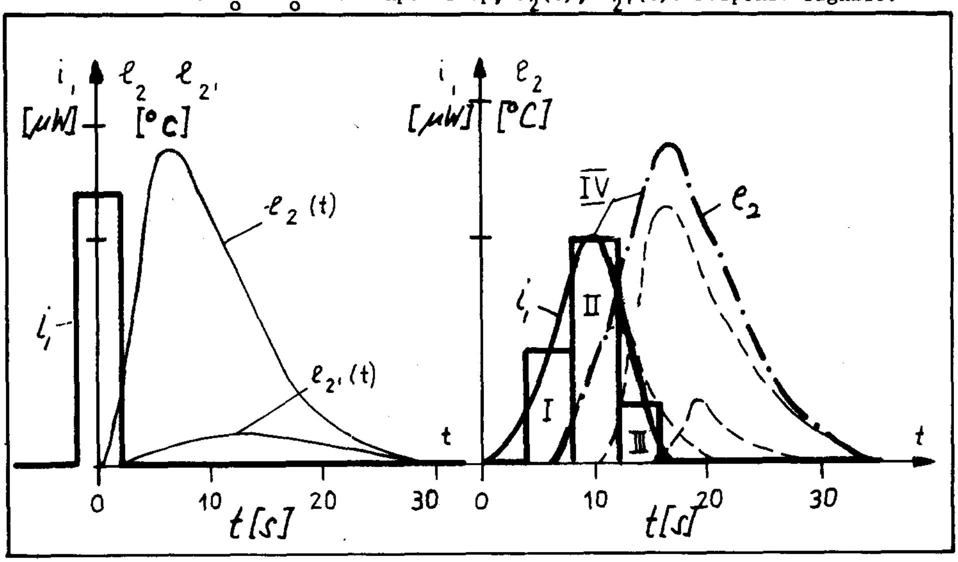

Fig. 2. Synthesis of thermal response signals

$e_2(t)=r_{2\ 1}(t)\cdot\Delta Q$: Response of sample, $e_{2'}(t)= r_{2'1}(t)\cdot\Delta Q$: Response of reference
i_1: Input ΔQ into sample, $r_{21}(t)$: Response function sample, $r_{2'1}(t)$: Response function reference, I, II, III: Input-Dirac-functions and their responses
IV: Resulting sample-signal.

ELECTRICAL REPRESENTATION OF THERMAL SYSTEMS

This universality can be used to represent thermal systems as electrical networks of completely analogous behaviour. Fig. 3 shows the electrical analog to a one-dimensional DSC-system.

There is a direct correspondance between this electrical lumped-element circuit of fig. 3 and a numerical approximation of the dynamics of thermal systems. The difference-equations obtained correspond to the laws of Kirchhoff for the circuit.

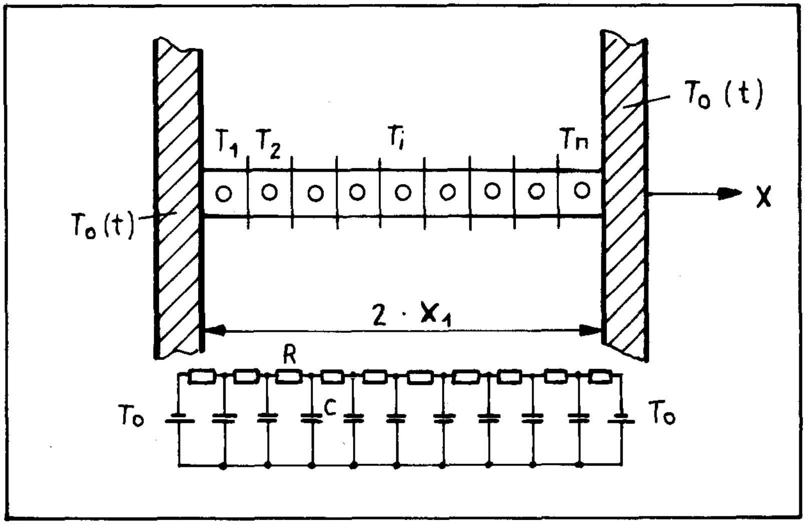

Fig. 3. Electrical representation of thermal system

R: electrical equivalent to thermal resistor
C: electrical equivalent to thermal capacitor

COMPENSATION AND DECONVOLUTION METHODS

In a compensated DSC-system, the calorimetric signal is transformed through a PID-controller into a differential power signal that is applied to the heaters 3 and 3'. The output of the PID-controller is proportional to the calorimetric power.

In a heat flow DSC the calorimetric signal is transformed using a deconvolution algorithm. Its effect is similar to the thermal feedback-loop in a compensated DSC, but the feedback-loop does not include the thermal system. When the signal processing is done by digital means, there is no principle difference between the two methods, although the construction of the two DSC-cells is not the same. The PID-controller is then replaced by a suitable linear filter (fig.4). Ref. 2 gives a good review over the calorimetric accuracy that can be reached.

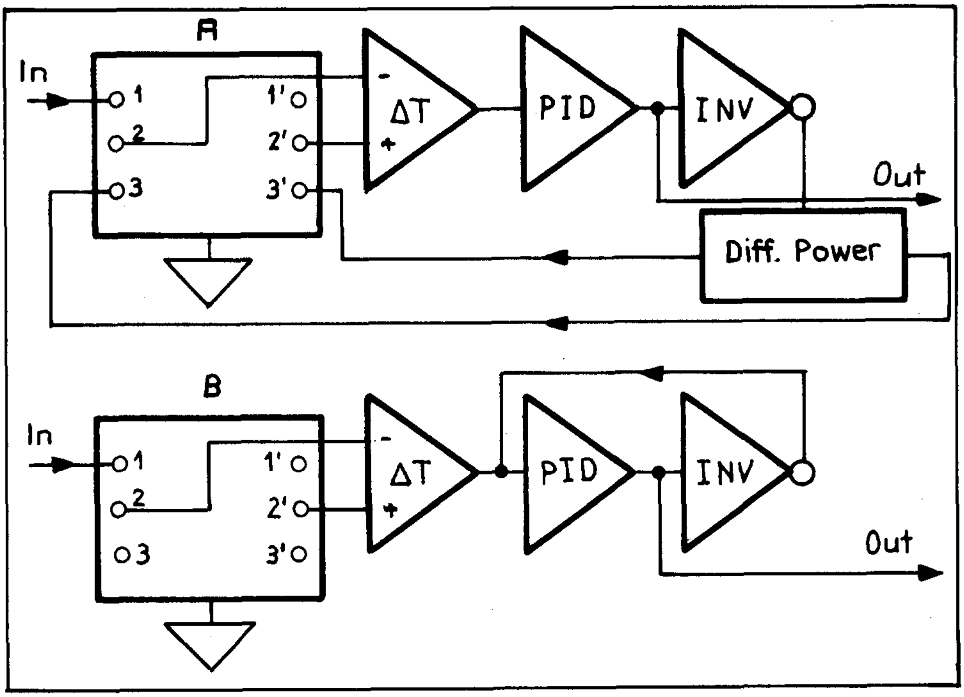

Fig. 4. A: Power-compensated DSC B: Heat-flow DSC

CURRENT AND FUTURE APPLICATIONS

There are a number of useful applications of DSC-systems for quality control of organic substances or as a research tool (e.g. artificial aging processes). The kinetics of chemical reactions can be investigated, but here DSC reaches its limits. Analysis of chemical reactions under process conditions is not possible. This limit can only be overcome by a real scanning calorimeter with a reaction vessel of a larger volume, where stirring and feeding of chemicals becomes possible. A further possibility could then be considered, namely the control of physico-chemical processes by suitable measurement conditions. When temperature and power are controlled in a specific manner, new materials can possibly be found. There is some incouraging work going on in this direction (ref. 3).

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