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Application of a deconvolution method to kinetic studies with conduction type microcalorimeters [α]

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Abstract

A deconvolution method has been developed using a microcomputer to correct the inevitable thermal inertia of a heat conduction type calorimeter.

The numerical algorithms based on fast Fourier transform (FFT) were designed and constructed assuming that the convolution equation holds for the artificial stepwise heat evolution curve. This heat was generated electrically by a resistor inserted into the sample cell of the calorimeter. The algorithms reproduced correctly the original rectangular heat evolution curve, i.e. the curve without thermal inertia. However, the Tian–Calvet equation which was also tried, failed to reproduce the curve.

The value of the activation energy for the alkaline hydrolysis of ethyl acetate obtained by the new deconvolution method is in good agreement with that in the literature obtained by chemical titration.

INTRODUCTION

A conduction type microcalorimeter is known to be a useful tool with which to measure small amounts of thermal energy. However, this instrument has an inevitable large thermal inertia which renders the measured thermal curves delayed from the real rate of enthalpy change for a chemical reaction occurring in the vessel. Therefore, if this distorted curve is applied directly to kinetic studies, some errors occur and wrong conclusions may be drawn. Some equations, such as the Tian–Calvet equation [1], have been proposed to correct the delayed curve and to reproduce the real rate of enthalpy change. However, those equations seem too simple, especially for fast chemical reactions, to reproduce the real rate of enthalpy change, as will be exemplified below.

Deconvolution, one of the theories of control engineering, is known to be available for correcting the thermal lag of a calorimeter [2]. A discussion of

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the various numerical methods for deconvolution is given by Tachoire et al. [3]. Randzio and Suuskuusk [4] and Zielenkiewicz [5]. We have developed a generalized deconvolution procedure using a personal computer recently developed to facilitate digital data processing, and have applied the procedure to kinetic studies of the alkaline hydrolysis of ethyl acetate.

BASIC PRINCIPLES

Assuming a linear heat flow between the wall of the sample vessel in a heat conduction type calorimeter and that of its constant temperature surroundings, the signal $\theta(t)$ which the calorimeter records as a function of time t is expressed in the following form:

$$\theta(t)=\int_0^t v(\eta)g(t-\eta)\,\mathrm{d}\eta \tag{1}$$

where $v(t)$ is the rate of enthalpy change in the calorimeter, $g(t)$ is the impulse response of the calorimeter and η is a parameter. The impulse response $g(t)$ is the output signal for the power

$$P_{\text{impulse}}(t)=\delta(t) \tag{2}$$

where $\delta(t)$ is the delta function of time t. Equation (1) indicates that the measured signal $\theta(t)$ is a convolution of the true signal $v(t)$ with the impulse response $g(t)$.

If a conduction type calorimeter is of the first-order delay system, its impulse response $g(t)$ is given by

$$g(t)=\exp(-ht/C)/C \tag{3}$$

where parameters C and h are the heat capacity and the heat transfer coefficient of the calorimeter, respectively. Substituting eqn. (3) into eqn. (1), eqn. (1) can be solved in the form

$$v(t)=C\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}+h\theta(t) \tag{4}$$

Equation (4) is called the Tian–Calvet equation. The parameter h can be determined by

$$h=S/Q \tag{5}$$

where Q is the electric energy supplied to the calibration heater and S is the recorded peak area. Parameter C was determined so that the output signal might fit eqn. (6) using the least-squares method after the energy supply had ceased at time:

$$\theta=\theta_0\exp\{-h(t-t_0)/C\} \tag{6}$$

Now that parameters C and h have been determined, $v(t)$ can be obtained from $\theta(t)$ using the Tian–Calvet equation (eqn. (4)) (the Tian–Calvet

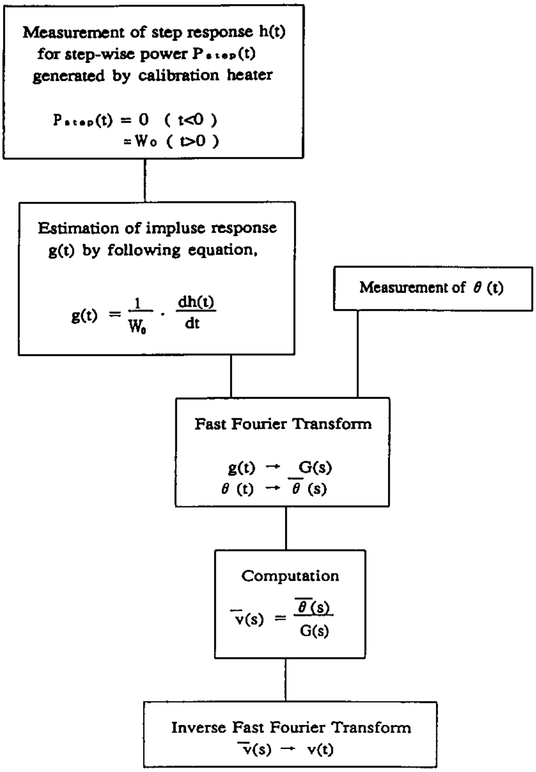

Fig. 1. Block diagram of the procedure for the deconvolution method by fast Fourier transform.

method). This method often gives a false rate of enthalpy change because the impulse response $g(t)$ is not usually as simple as eqn. (3) implies.

Equation (1) can also be solved numerically taking advantage of fast Fourier transform (FFT). Taking the Fourier transform of eqn. (1) with respect to t, we get

$$\theta(s) = v(s)G(s) \tag{7}$$

where $v(s)$, $G(s)$ and $\theta(s)$ are the Fourier transforms of $v(t)$, $G(t)$ and $\theta(t)$ respectively and s is the parameter. From eqn. (7) we obtain the following relation:

$$v(s) = \theta(s)/G(s) \tag{8}$$

Taking the inverse Fourier transform of eqn. (8), we obtain the rate of the enthalpy change $v(t)$ occurring in the calorimeter (deconvolution method). Figure 1 shows the numerical algorithms of the deconvolution method. The impulse response $g(t)$ can be determined experimentally by differentiating the step response $h(t)$ with respect to time t, where $h(t)$ is the signal intensity when the electrical power $P_{step}(t)$ is generated in the vessel by the calibration heater in such a way that

$$\begin{aligned} P_{step} &= 0 \qquad (t<0) \\ &= W_0 \qquad (t>0) \end{aligned} \tag{9}$$

DATA PROCESSING SYSTEM

The output signal from the calorimeter was amplified and measured with a 4(1/2)-digit A/D converter (Takeda Riken Inc., TR6841). The 2048 digital data points were stored and numerical computation was carried out continuously using a personal computer (NEC, PC-9801). The program was written in C-language.

EXPERIMENTAL VERIFICATION OF THE ALGORITHM

The algorithm described above has been tested on two types of twin-vessel Calvet-type conduction microcalorimeters, the MMC-5111 (Tokyo Riko Inc.) and the C-80 (Setaram), by supplying them with artificially generated heat. Table 1 shows the specifications of the calorimeters. They have built-in sensitivity calibration heaters which can generate heat in an arbitrary manner.

Figures 2 and 3 show the step response $h(t)$ of the MMC-5111 and C-80 instruments, respectively. The initial part of the $h(t)$ curve gives the time constant of the calorimeter (see Table 1). Figure 4 shows the impulse responses, $g(t)$, of the MMC-5111 given by differentiation of step response $h(t)$ (Fig. 2) with respect to time t. Figure 5 shows the output signal from the MMC-5111 when a Joule heat pulse of 120 min (broken curve) was generated in the calorimeter. The recorded output signal increases towards

TABLE 1

Specifications of calorimeters

	MMC-5111	C-80
Temperature	Constant, 5–60 ° C	Constant or scanned (max 2 ° C min^{-1}), ambient–300 ° C
Detectors	Thermomodule	Thermopile
Detection limit in power	1 μW	10 μW
Time constant	800 s	250 s
Vessel capacity	Approx. 30 cm^3	Approx. 10 cm^3

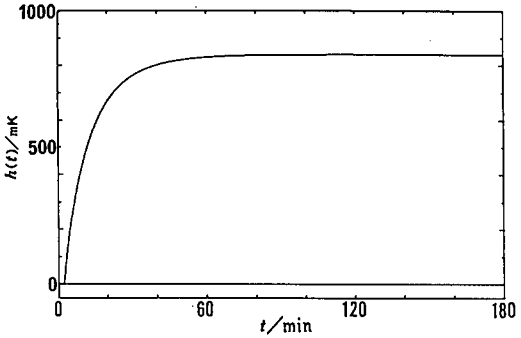

Fig. 2. Step response $h(t)$ of the MMC-5111 calorimeter.

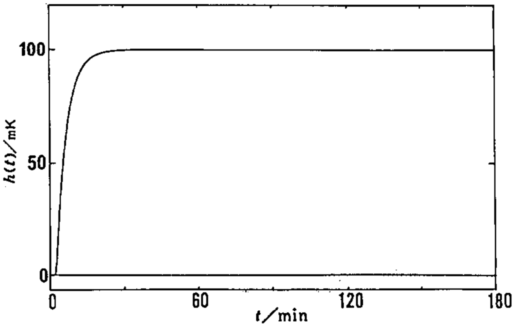

Fig. 3. Step response $h(t)$ of the C-80 calorimeter.

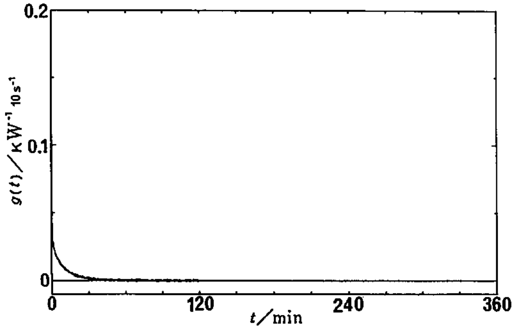

Fig. 4. Impulse response $g(t)$ of the MMC-5111 calorimeter.

the equilibrium level and decreases towards the baseline with inertia, obviously differing from the broken curve.

Figure 6 shows the rate curve of the enthalpy change in the reaction vessel of the MMC-5111 obtained by applying our deconvolution method to the solid curve in Fig. 5. It is obvious that the method reproduces a precise rectangular heat-evolution curve of exactly the same shape as the broken line in Fig. 5.

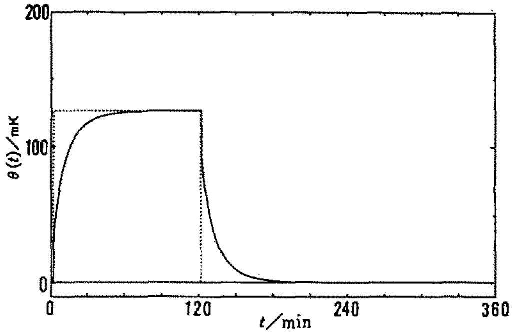

Fig. 5. Output signal from the MMC-5111 calorimeter (solid line) plotted against time t for a 120 min Joule heat pulse generation (broken line).

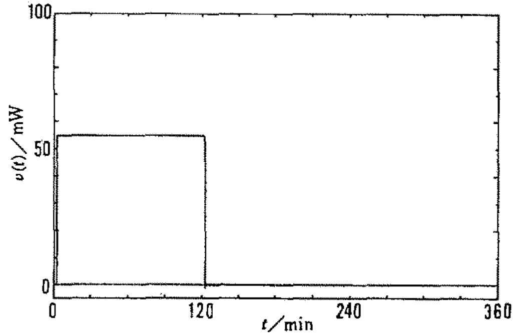

Fig. 6. Reconstructed signal from the MMC-5111 calorimeter obtained by the deconvolution method.

Figure 7 shows an output signal from the C-80 calorimeter when a Joule heat pulse of 60 min (broken curve) was generated. Figure 8 shows the deconvoluted rate curve of the enthalpy change. Figures 6 and 8 show that

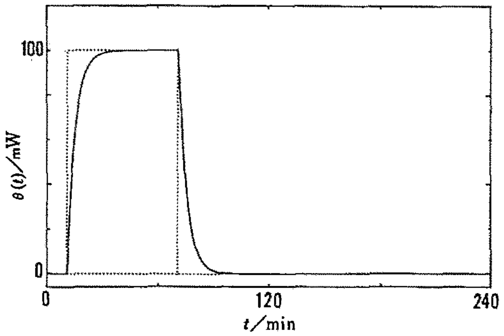

Fig. 7. Output signal from the C-80 calorimeter (solid line) plotted against time t for a 60 min Joule heat pulse generation (broken line).

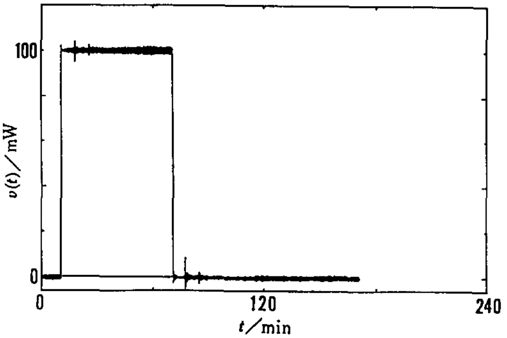

Fig. 8. Reconstructed signal from the C-80 calorimeter obtained by the deconvolution method.

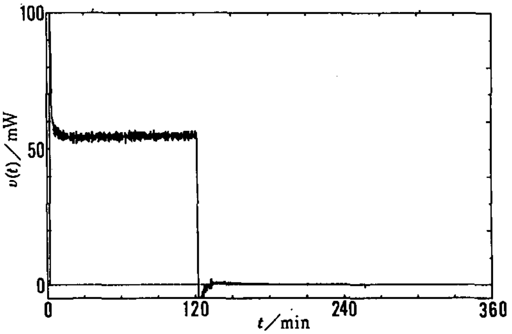

Fig. 9. Reconstructed signal from the MMC-5111 calorimeter obtained by the Tian–Calvet method (cf. Fig. 6).

our deconvolution method can reproduce real heat-evolution curves, regardless of the value of the time constants of the calorimeters.

Figure 9 shows the rate curve of the enthalpy change in the MMC-5111 vessel reproduced by the Tian–Calvet method for comparison, where parameter C was determined so that the output signal from 125 to 142 min in Fig. 5 would fit eqn. (5) using the least-squares method. Figure 9 indicates that the Tian–Calvet method yields only a noisy curve which does not reproduce the strictly rectangular heat evolution.

APPLICATION TO CHEMICAL REACTION

We applied our deconvolution procedure to the alkaline hydrolysis of ethyl acetate. Experiments were carried out on the MMC-5111 equipped with a glass ampoule module. The hydrolysis was started by breaking the glass ampoule fitted with ethyl acetate in the presence of sodium hydroxide solution.

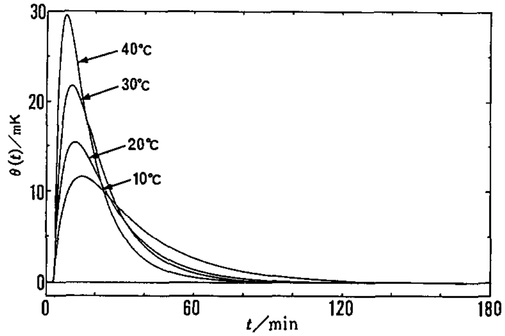

Fig. 10. Output signal from the MMC-5111 calorimeter plotted against time t for the alkaline hydrolysis of 2% ethyl acetate at 10, 20, 30 and 40 °C.

Figure 10 shows the original output signal from the calorimeter when 2% ethyl acetate (1 g) was hydrolysed by 0.025 N sodium hydroxide solution (20 cm^3) at 10, 20, 30 and 40 °C in the vessel.

Figure 11 shows the rate curves reconstructed by applying our deconvolution method to the curves in Fig. 10 and introducing the following additional modifications: (i) an electrical heater for the determination of the impulse response $g(t)$ was immersed in water in the sample vessel to generate a heat flow similar to that of the chemical reaction; and (ii) a window function was adopted to remove the statistical noise above 20 mHz.

A rate constant k for the alkaline hydrolysis of ethyl acetate can be determined by the equation

$$\frac{1}{b-a}\ln\left\{\frac{(b/a-\xi)a}{(1-\xi)b}\right\}=kt \tag{10}$$

where a and b are the initial concentrations of sodium hydroxide and ethyl acetate respectively, and ξ is the extent of the reaction estimated by integrating the peak area.

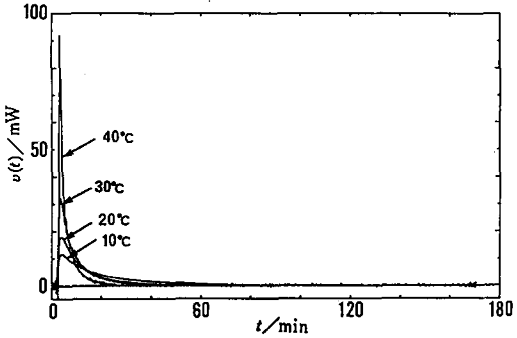

Fig. 11. The rate curves of the enthalpy change in the vessel plotted against time t for the alkaline hydrolysis of 2% ethyl acetate at 10, 20, 30 and 40 °C (after deconvolution of the curves in Fig. 10).

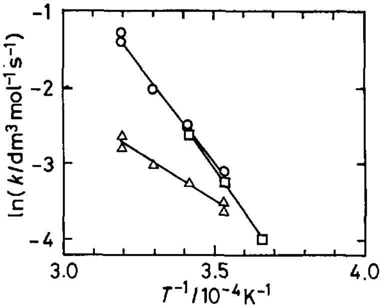

Fig. 12. The temperature dependence of the rate constant k for the alkaline hydrolysis of ethyl acetate: ○, calorimetric method (after deconvolution); △, calorimetric method (before deconvolution); and □, chemical titration [6].

Figure 12 shows the temperature dependence of the rate constant k obtained with the three methods described in the caption. Table 2 lists the values of the activation energy obtained from the slopes of the straight lines in Fig. 12. From Fig. 12 and Table 2, it can be seen that the value of E obtained by our deconvolution method is in good agreement with that obtained by chemical titration [6].

TABLE 2

Activation energies of the alkaline hydrolysis of ethyl acetate

	T (°C) [a]	Frequency factor ln A	Activation energy E (kJ mol^{-1})
Original curve	10, 20, 30, 40	4.5	18.1
Reconstructed curve	10, 20, 30, 40	15.4	43.8
Chemical titration	0.0, 9.8, 19.1	17.2	48.1

[a] Reaction temperatures.

TABLE 3

Enthalpy changes for the alkaline hydrolysis of ethyl acetate

T (°C)	Run	$-\Delta H$ (kJ mol^{-1})	
		Original curve	Reconstructed curve
10	1	52.3	53.1
	2	50.7	51.8
20	1	52.9	54.4
	2	53.0	54.6
30	1	55.0	54.3
	2	52.7	53.9
40	1	50.7	53.8
	2	52.2	54.6

Table 3 lists the heats of hydrolysis determined by the integration of each curve in Figs. 10 and 11. A good agreement between the enthalpy changes from the original curves and those from the reproduced curves reinforces the validity of our deconvolution method, because this fact satisfies the general condition that any correction methods should never affect the measured enthalpy change itself.

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