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Microcomputer-aided optimal selection of control input for the precision water bath of a heat exchange calorimeter

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Abstract

In heat exchange calorimetry, sample and reference vessels are fixed differentially in a water bath. The heat evolved in the sample vessel is exchanged freely with the ambient water. The accuracy and precision of the calorimetry depend on the temperature range of the drift and fluctuation in the bath water. In the present report, a simple temperature-control system with no empirical factors is proposed for the precision water bath. The heat exchange between the inside of the vessels and the ambient water is expressed by a differential equation or a Newtonian cooling equation. Similarly, the thermal behaviour of a water bath placed in a non-air-conditioned laboratory was also considered to be expressed by the same equation. The heat exchanged with the surroundings, the non-stationary heat flow from warm stirrer motors, and other thermal factors were considered to be part of the heat sources. Cooling water about 2°C lower than the set temperature was circulated in the water bath. The difference between the set temperature and the observed temperature was fed into a microcomputer every second. The latest four data points were used to fit a modified Newtonian equation by the common method of least-squares. The control input to the bath was calculated and given to the heater circuit after power amplification. The program written in BASIC was about 3.3 kbyte. The controlled range of drift and fluctuation was almost the same, or better, as that previously reported.

INTRODUCTION

In heat exchange calorimetry [1], sample and reference vessels are fixed differentially in a water bath whose temperature is controlled precisely. The heat evolved in the sample vessel by chemical reactions or electrical heating is exchanged freely with the ambient water. Any measuring temperature may be readily selected by changing the temperature of the bath water. The thermal behaviour is expressed by a simple differential equation or Newtonian cooling equation. A thermistor used as a temperature sensor was installed in each vessel, and incorporated in two arms of a Wheatstone bridge. The temperature change in the sample vessel was detected as an

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electrical signal and compared with that in the reference vessel. The rate of heat evolution and the total heat were estimated from the signal by analogue treatments and/or digital computations.

For estimating the rate of heat evolution, analogue differentiation is recommended for simplicity, rather than digital calculations. However, a water bath whose temperature fluctuation is controlled within a narrow range is necessary in order to estimate it precisely, because noisy input signals may not result in practice in the case of the analogue differentiation. On the other hand, because the calorimeter is generally required to operate in a non-air-conditioned room, a simple temperature-control system is also indispensable for the water bath, so that a change in room temperature will not affect the calorimeter. In addition the temperature range of the drift and fluctuation of the bath water may not only decide the precision of the estimated thermal data, but also affect the minimum temperature difference or the minimum heat effect to be estimated. The extent of drift should be restricted within the narrow range governed by the behaviour with temperature of the electrical resistance of the thermistor pair used in the vessels [2].

Heat exchange calorimetry is also sufficiently sensitive to respond to sudden thermal changes [3]. For this reason, a modified PID (proportional, integral and differential, respectively) control was applied to the calorimeter [4]. In this way, thermal constancy can be virtually maintained, even if external disturbances are imposed. However, each P, I and D constant should be adjusted empirically by such experimental conditions as the volume and set temperature of the bath water, etc.

In the present report, a general control system which is not affected by empirical factors was developed. The fundamental concept of heat exchange calorimetry was applied to construct the temperature-control system for the bath water. The heat flowing into and out of the water bath to the surroundings is considered to be expressed adequately by the Newtonian equation. Cooling water, slightly lower in temperature than the set temperature, was circulated in the water bath. The deviation between the observed temperature and the set temperature of the bath water was fed into a microcomputer every second. The subsequent optimal control input to the water bath was calculated and the heater circuit was adjusted accordingly, so that the deviation became minimum or zero. The sequence was repeated.

GENERAL CONSIDERATIONS

According to the fundamental concept of heat exchange calorimetry, a water bath system may be considered as a large vessel which is allowed to exchange heat freely with the surroundings. The thermal phenomena are expressed by the Newtonian differential equation

$$\mathrm{d}T_{\mathrm{bath}}/\mathrm{d}t = q/C - \alpha T_{\mathrm{bath}} \tag{1}$$

where T_{bath} is the temperature of the bath water, t the time, q the rate of heat evolution, C the effective heat capacity and α a constant which gives the extent of the heat exchange with the surroundings. If q/C is not constant, eqn. (1) cannot be resolved mathematically. Within a short time-range and small temperature change, q/C is assumed to be constant in order to solve eqn. (1) mathematically. Then

$$T_{bath} = q(1 - \exp(-\alpha t))/(\alpha C) \tag{2}$$

Every second, the deviation, T_{dev}, is fed into a microcomputer as $T_{set} - T_{bath}$ which is obtained as the output of a Wheatstone bridge.

$$T_{dev} = T_{set} - T_{bath} \tag{3}$$

where T_{set} is the set temperature.

The heat input from the warmed-up motors of the agitators and magnetic stirrers to the water bath was considered to be a part of the heat supply or heating effect, whose sign depends on the relation between the room temperature and T_{set}. As the bath water to be controlled was cooled by circulating cooling water or coolant, any cooling effect, such as a heat leak, was also considered to be a part of the cooling. Therefore, insufficient heat for minimising T_{dev} or the difference between T_{set} and T_{bath} was supplied to the water bath from the heater element via the microcomputer.

As a general expression, eqn. (4) may be obtained from eqns. (2) and (3).

$$y = a\ \exp(bt) + c \tag{4}$$

where $y = T_{dev}$, $a = q/\alpha C$, $b = -\alpha$ and $c = T_{set} - q/\alpha C$. Because α is physically positive, b is always negative. From eqn. (4), y approaches c at high values of t, regardless of the sign of a. When T_{bath} is equal to T_{set}, T_{dev} may be zero. Therefore, if $c = 0$, eqn. (4) may be used to calculate the control input; eqn. (5) is obtained from the logarithmic calculation of eqn. (4):

$$\ln\ y = \ln\ a + bt \tag{5}$$

The constants, ln a and b, are calculated, as usual, using the method of

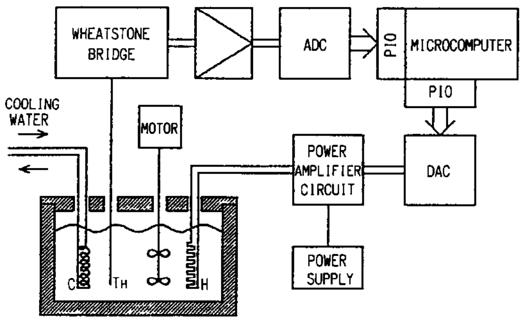

Fig. 1. Schematic diagram of the control system. Th, thermistor, H, heater; C, cooler

least-squares by using n sets of observed data: $(t_0, y_0), \ldots, (t_{n-1}, y_{n-1})$. Then the value of y_n obtained is the deviation expected at t_n. A control input on the basis of the calculated y_n was given to the bath water via the heater circuit. In the following sampling interval of T_{dev}, a new set of t_{n-1} and y_{n-1} values was acquired and the oldest set of (t_0, y_0) was deleted. Calculations of eqn. (5) were repeated until temperature control of the water bath was not required.

EXPERIMENTAL

Apparatus

The heat exchange calorimeter and the temperature control system for the bath water were assembled as shown in Fig. 1, the essential parts of which are similar to those reported previously [4]. In Fig. 1, the sample and reference vessels, the magnetic stirrers fixed to each vessel, the aluminium frame used to fix both vessels and stirrers, and the titrant reservoirs for thermal equilibrium were omitted for simplicity.

The T_{bath} was measured by a thermistor (NLB, Shibaura Denshi Co., Tokyo) with a resistance, R, of 2.371 kΩ at 25 °C and a B constant (defined as $R = A \exp(B/T)$) of 3199 K [4]. The thermistor comprised one arm of a Wheatstone bridge. The T_{set} was given on the operation panel by two kinds of variable resistors, which comprised another arm of the bridge. Details of the resistor assembly were reported previously [4]. The relationship of the temperature to the resistance was calibrated by a commercially available standard thermometer. The unbalanced voltage corresponding to the deviation was adjusted to a maximum of ± 2 V by a preamplifier (PM-17A, Toa Dempa Co., Tokyo) for the subsequent electronic treatments. The electrical voltage corresponding to the deviation was fed every second into a small microcomputer (M5, SORD Co., Tokyo, operated with Z-80A, Zilog) as parallel signals via an analogue-to-digital converter (ADC) (AD-80-12, Analog Devices) and a programmable parallel input–output (PIO) (i8255, Intel). A temperature change in the bath water of 1.5×10^{-5} °C corresponded to 1 digit. Optimal signal inputs to the bath were calculated from the acquired data using the expression proposed in this report, and were passed to a power amplifier circuit via a digital-to-analogue converter (DAC) (DAC-80-12, MicroNetwork).

Three types of water bath were used for comparison in the present report. The first type, shown as 1 in Fig. 2, was a plastic box $27 \times 47 \times 28$ cm^3 in size, of which all of six surfaces were covered with 3-cm thick Styrofoam insulator boards and filled with 28 dm^3 of water. Two motor-driven stirrers (35 W, PS-1, Yamato Kagaku Co., Tokyo) were used for agitation of the bath water. The second type, shown as 2 in Fig. 2, was a glass box $23 \times 30 \times 27$ cm^3 in size, covered with 5-cm thick Styrofoam insulator

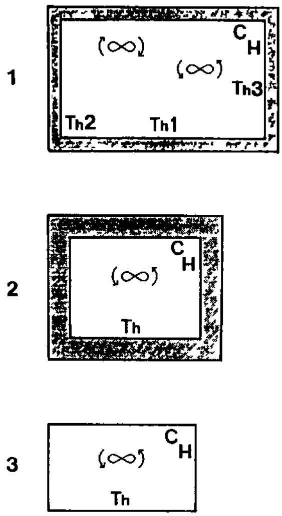

Fig 2 Water baths examined From Th_1 to Th_3, thermistor; H, heater, C, cooler A pair of arrows indicates the direction of the rotation.

boards and filled with 12 dm^3 of water, which was agitated by the same type of motor-driven stirrer as the first type. A plastic box $20 \times 34 \times 21$ cm^3 in size was used as the third type of water bath without any cover boards, shown as 3 in Fig. 2, and filled with 10 dm^3 of water. Water baths of types 1 and 2, of which the shaded area in Fig. 2 represents thermal insulation, were used in typical calorimetric measurements.

A hand-made heater element, which was reported previously [2] and shown as H in Fig. 2, was used in the water baths. The resistance was about 20 Ω. A direct current voltage of about 30 V maximum was applied across the heater element from a stabilised power supply (532B, Metronix Co., Tokyo). The output signals from the microcomputer were passed to the power amplifier circuit via a DAC which controlled the current running through the heater element.

The cooling water which was kept automatically 2 °C lower than the given T_{set} with an electronic cooler (CTE-200 and CTR-220, Komatsu Electronics Co., Tokyo), was circulated in the water bath using glass spiral tubing, at a flow rate of 1.5 dm^3 min^{-1}. The temperature range of the cooling water was within ± 0.2 °C, but such a narrow range was not necessary in practice.

Software

When T_{bath} is equal to T_{set}, T_{dev} or y is zero, and ln y cannot be calculated. However, the use of eqn. (5) may be desirable in spite of any temperature change in the bath water. According to the T_{dev} fed into the microcomputer, ln y was treated as zero for $y = 0$, and $-\ln(-y)$ or

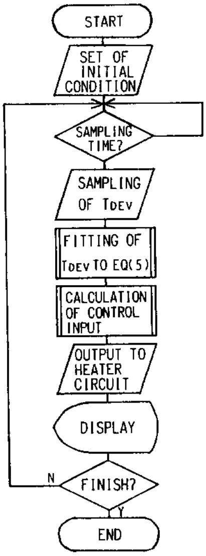

Fig 3. A simplified flow chart of the control programs.

$-\ln|y|$ was calculated for $y<0$ in the programs. Then, if positive and negative signs coexist for several values of y acquired, to be used in a single calculation, $-\ln a$ was used for $y<0$ and $\ln a$ or $-\ln a$ was selected for $y=0$, according to the sign of $\ln a$ obtained in the previous calculation group.

A simplified flow chart of the program is shown in Fig. 3. All the programs were written in BASIC and amounted to 3.3 kbyte, much shorter than the 8 kbyte of the modified PID method [4].

Procedure

The sample and reference vessels, each holding 50.0 g of water, were fixed differentially in the frame and placed in the water bath of the heat exchange calorimeter. The T_{set} was adjusted on the operation panel by means of two steps; a coarse setting via a toggle switch and a fine setting via a 10-turn precision potentiometer with a digital dial. The water bath to be controlled was filled with water at a temperature within about 1° C of the set temperature although this was not essential for effective control. The magnetic stirrers beneath each vessel were turned on. Then the cooling water was circulated and the motor-driven stirrers and the heater circuit were started. Sampling of T_{dev} was started and the temperature-control system operated by the microcomputer began to run. The T_{dev} acquired from the bath and the calculated control input to the bath were displayed on the monitor. From eqn. (3), T_{dev} was considered to correspond to T_{bath} because T_{set} is constant. T_{dev} was also recorded on a strip-chart recorder.

RESULTS AND DISCUSSION

The thermal behaviour of a water bath placed in a non-air-conditioned laboratory was simulated by the fundamental concept of heat exchange calorimetry. The heat evolved in the sample vessel was exchanged with the ambient water, the efficiency being expressed by the constant α in eqn. (1). However, in calorimetry, the temperature θ observed via a thermistor used as a sensor should include the delay in response and be distinguished strictly from the temperature T in the sample vessel. The relation between θ and T can also be expressed by a simple differential equation

$$d\theta/dt = \beta(T - \theta) \qquad (6)$$

where β is a constant showing the delay in response. At time t after a heat-evolving period of t^*, the following equation may be obtained from eqns. (1) and (6)

$$\theta = A \exp(-\alpha(t - t^*)) \qquad (7)$$

where A is a constant. At two points, θ_1 and θ_2 at t_1 and t_2, respectively, on the θ versus t curve, α was obtained from eqn. (8) derived from eqn. (7):

$$\alpha = \ln(\theta_1/\theta_2)/(t_2 - t_1) \qquad (8)$$

In practice, α was estimated from several pairs of θ values on the curve. It was also affected by experimental conditions, such as the material of the vessels and their contents. In vessels typically used in calorimetry, α was $(7.3 \pm 0.3) \times 10^{-3}$ s^{-1}. However, in the analogue computation circuit to convert from θ to total heat, the time constants of the circuit were adjusted to be reversely equal to α and β values of the calorimeter [1]: time constants almost equal to α were obtained, within error, by the two methods.

In the present work, the water bath to be controlled was considered as the vessel of the heat exchange calorimeter, of which α was estimated from each cooling curve of T_{bath} versus t, according to eqn. (8). In a non-air-conditioned laboratory at 20 °C, α of the glass box shown as 2 in Fig. 2 with no covers was 1.73×10^{-4} s^{-1}, while it was $(7.6 \pm 0.5) \times 10^{-6}$ s^{-1} after each surface was covered by insulator boards. The heat flow from the stirrer motors corresponded to 5.1×10^{-6} K s^{-1} dm^{-3}, the α being $(2.6 \pm 0.7) \times 10^{-5}$ s^{-1} under those conditions. When cooling water of 23 ± 0.2 °C was circulated at almost the same rate as in practical runs, α was 3.45×10^{-4} s^{-1}. A complete adiabatic state may be obtained at $\alpha = 0$. With the proposed control, an effective adiabatic state was fulfilled as reported below.

Optimal data numbers for calculation of the control input were examined. In a stationary controlled state, the number of data sets (n) used for fitting T_{dev} to eqn. (5) was 3, 5, 7 and 10, the traces of T_{dev} or deviation (solid lines) and the estimated control input (dotted lines) being a, b, c and d, as shown in Fig. 4, respectively. The use of too many data sets resulted in a large delay

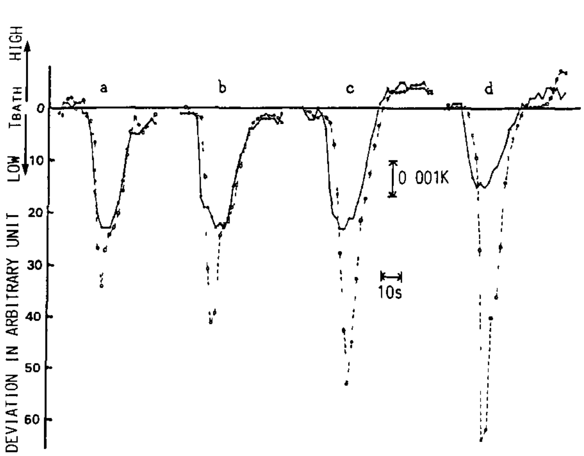

Fig 4 Effect of the number of data sets used to fit the observed T_{dev} to eqn. (5). Symbols a, b, c and d correspond to 3, 5, 7 and 10 sets, respectively T_{dev} is shown as a solid line, and the estimated control input as a dotted line

in the response of the control input and a lowering of T_{bath}. The situation was indicated by a large deviation in c and d in Fig. 4. Therefore, in the present report, four data sets were selected from the power balance of cooling and heating in the system used.

The T_{bath}, i.e. the T_{dev} being controlled by the proposed method, was monitored in the water baths shown in Fig. 2 and the corresponding traces are shown in Figs. 5–7. The controlled system was subjected to thermal disturbances by adding hot or cold water, as shown by arrows in Figs. 5 and 6, and the recovery was tested. The exaggerated difference between the addition and the disturbance peak corresponds to the time necessary for

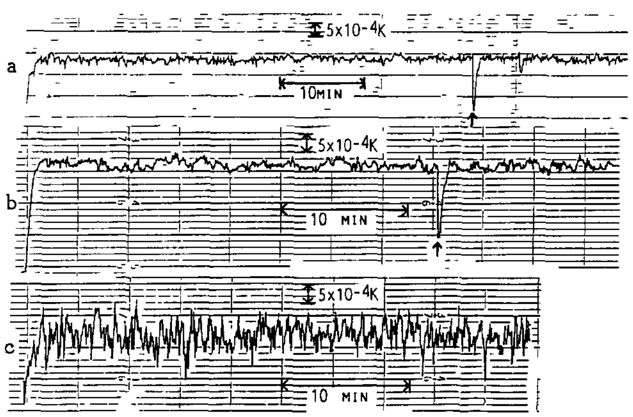

Fig 5 Traces of T_{dev} in the water bath shown as 1 in Fig. 2

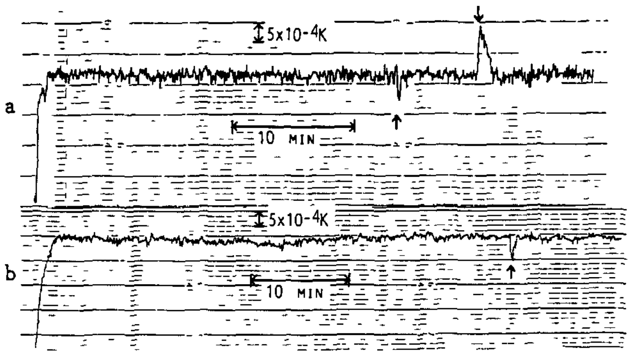

Fig. 6. Traces of T_{dev} in the water bath shown as 2 in Fig 2.

mixing; it was negligibly small in practice. The response speed may depend on the power of the heater or cooler.

The progress of T_{dev} was assessed at three points from Th_1 to Th_3 shown in Fig. 2 and the observed traces are shown as a, b and c, respectively, in Fig. 5. As expected, in spite of intense agitation of the bath water, fairly large differences in the fluctuation range were observed owing to the geometry of the bath. In practice, an appropriate area in the bath after adequate mixing should be selected from Fig. 5.

In the second water bath, as shown in Fig. 6, the water was controlled at T_{set} values of 25.0 and 37.0 °C, and the traces are shown in a and b, respectively. The temperature of the cooling water was 2 °C lower than each T_{set}, and the temperature range was within ± 0.2 °C. Cold water was added at the arrow positions, and the recovery was confirmed. The fluctuation range observed in both cases was sufficiently small for use in the heat exchange calorimeter.

The third water bath, as shown in Fig. 7, was controlled to 25.0 °C of T_{set} in the non-air-conditioned laboratory at a room temperature of 29 ± 0.1 °C. The cooling water of 23 ± 0.3 °C was circulated whilst being controlled. The fluctuation range was estimated to be less than about $\pm 1 \times 10^{-3}$ K.

Use of the proposed control system composed of simple, available instruments is recommended for the versatile control of a precision water bath, as well as for the water bath of a heat exchange calorimeter.

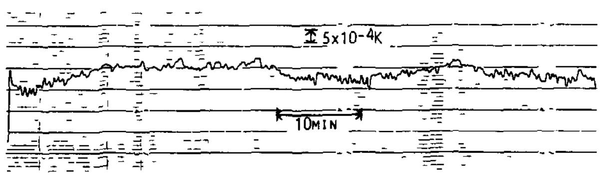

Fig 7 Trace of T_{dev} in the water bath shown as 3 in Fig. 2

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