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MICROCOMPUTER-AIDED CONTROL SYSTEM FOR A PRECISION WATER BATH IN THE HEAT-EXCHANGE CALORIMETER

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ABSTRACT

In a heat-exchange calorimeter, the heat evolved in the sample vessel fixed in a water bath was exchanged freely with the ambient water. The stability of the observed baseline depended upon the thermal fluctuation and drift ranges of the water, which were determined from the temperature versus resistance characteristics of the thermistor pair used in the sample and reference vessels. A temperature-control system, in which the software took part in the fine control, in contrast to the simple hardware, was developed for practical use. Cooling water at lower than the set temperature was circulated. The difference between the temperature of the water bath and the set temperature was observed as a control deviation. Control was carried out by a heating element in order to minimize deviation. The direction of the temperature change was indicated from the last 10 data points including the latest deviation acquired in every second. An appropriate output value was calculated using a proportional, integral, and derivative (P, I, D) control expression modified by the authors and given to a heater circuit via a DAC as an output signal. Each parameter of P, I and D was selected by trial and error for speedy attainment and good efficiency to the set temperature. The optimum dynamic range for the input and output signals was switched in the program. The sufficient temperature range of $\pm 2 \times 10^{-4}$ °C was obtained by the proposed microcomputer-aided system for the precision water bath.

INTRODUCTION

In heat-exchange calorimetry [1], the sample and reference vessels are fixed differentially in a water bath. The heat evolved in the sample vessel is exchanged effectively with the ambient water. The thermal behaviour is described by the Newtonian cooling equation. The temperature in the sample vessel is measured via a thermistor placed within it against another thermistor in the reference vessel, and the reading is converted to an electric

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signal with a Wheatstone bridge. The total heat and the rate of heat evolution are estimated from analogue and/or digital treatment of the signals.

The bath temperature has special meaning in calorimetry. Since the bath water is a free exchanger of heat in vessels, a chemical reaction can be conducted at any temperature by controlling the bath temperature. However, the thermal fluctuation of the bath water must be kept within the range that is required for the minimum heat to be measured. In addition, the temperature drift may also be limited to a narrow range swayed by the resistance versus temperature characteristic of the thermistor pair used in the two vessels.

Several factors, including the stabilities of the bridge circuit and the amplifier, and uniformity of temperature in the bath, may be reflected in the measured baseline, and thereby in the estimated values. Therefore, temperature control of the water bath is necessary if the calorimeter is to be used in a non-air-conditioned laboratory, so that a small heat effect may be estimated with high accuracy and good precision.

In the present work, a temperature-control system for a precision water bath was developed, of which the primitive concept was reported previously [2]. Cooling water at a temperature slightly lower than the set temperature was circulated in the bath. The bath water was controlled so as to keep within the set temperature range by heating the requirement of which was indicated using a modified proportional, integral and derivative (PID) technique. The control deviation (the difference between the temperature of the bath water and the set temperature) was measured periodically by a thermistor placed in the bath and acquired into a microcomputer via an analogue-to-digital converter (ADC). The control input was calculated and output as a control signal to a power amplifier circuit via a digital-to-analogue converter (DAC). The sequence was continued. The hardware was minimized and simplified as much possible, and the fine control was carried out by the software. The optimum dynamic range of input and output signals was selected in the software.

EXPERIMENTAL

Apparatus

The temperature-control system used is shown in Fig. 1. A thermistor for measuring the temperature of the water, screws for a motor-driven stirrer, glass spiral tubing for the cooling water, and a heater element were included in the bath. The sample and reference vessels, and the titrant reservoir for the thermal equilibrium have been omitted in Fig. 1 for simplicity.

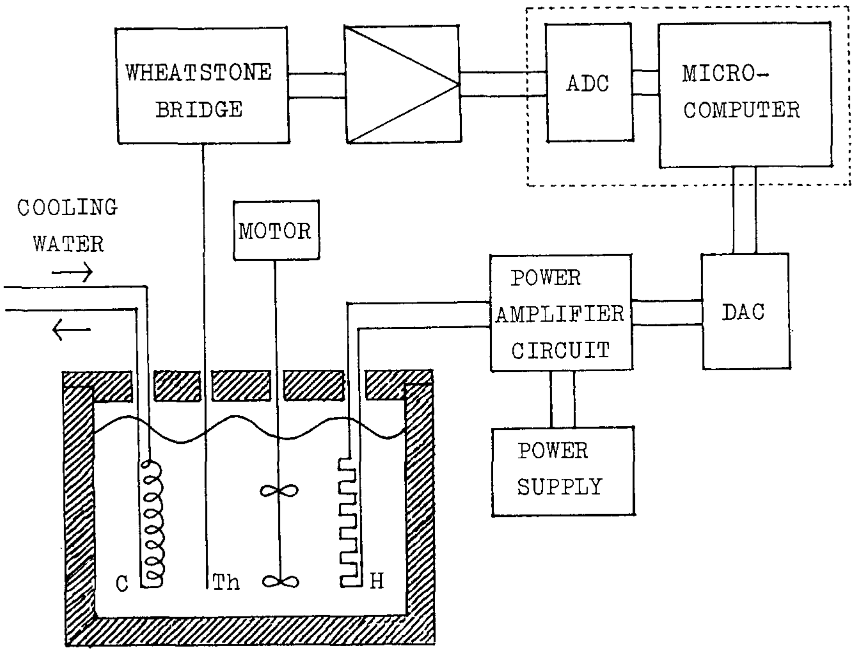

Fig. 1. Schematic diagram of the control system. Th, thermistor; H, heater; C, cooler.

A glass box of 23 × 30 × 27 cm in size, which was used as the bath, was covered with 3-cm thick Styrofoam insulator boards and was filled with 9 dm^3 of water.

The bath water was agitated with a motor-driven stirrer (35 W, PS-1, Yamato Kagaku, Tokyo). The temperature of the water, T_{bath}, was measured by a thermistor (NLB, Shibaura Denshi, Tokyo) assembled in an arm of a Wheatstone bridge. The B constant was observed to be 3199 K and the resistance 2.371 kΩ at 25 °C. A set temperature was indicated on the operation panel by two kinds of variable resistor assembled in the other arm. In the first step, the course temperature range was selected by a toggle switch from three groups: 10–25, 20–35 and 30–45 °C. In the second step, the fine set was given by a precision variable resistor (10 kΩ, 10-turn with a digital dial of 1000 divisions, Beckman). The relation of resistance versus temperature was calibrated by a commonly available standard thermometer. The unbalanced voltage corresponding to the deviation was adjusted to the input voltage of the ADC (from 0 to +5V in full scale) by a preamplifier (PM-17A, Toa Dempa, Tokyo). An 8-bit microcomputer (M100 ACE II, SORD, Tokyo, operated with a Z-80, Zilog) was used which included an 8-bit ADC with a conversion time of 8 ms. The deviation signal was acquired into the microcomputer every 1 s according to the built-in clock. A minus or plus sign was assigned to the deviation according to whether the temperature of the bath water was higher or lower than the set temperature, respectively.

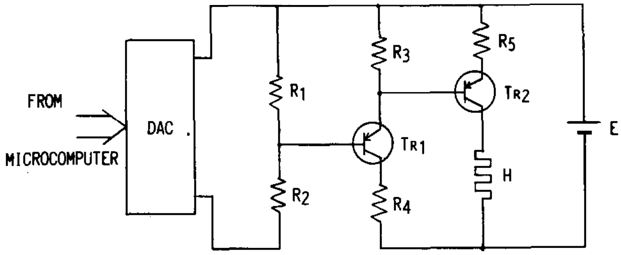

Fig. 2. The power amplification circuit of the heating element in the bath. E, power voltage; H, heating element in the bath; Tr_1, transistor, 2SB200; Tr_2, power transistor, 2SB250A; R_1 and R_2, 3 kΩ; R_3, 2 KΩ; R_4, 700 Ω; R_5, 1 Ω.

Running town water was used as cooling water, but for constant cooling during the summer season an electronic cooler (CTE-220 and CTR-220, Komatsu Electronics, Tokyo) was preferred. A control signal from the microcomputer was sent to DAC, and then to the heating element placed in the bath via a hand-made power amplifier circuit (see Fig. 2). DAC with a 3-digit resolution of voltage output type (4027, Teledyne Philbrick) (from 0 to −10 V DC at full scale, the written conversion time being 5 μs) was used.

A commercially available heater (500 W at a.c. 100 V, Hakko Denki Seisakusho, Tokyo) was used as a heating element. Delay of response of the heating element did not give rise to any essential problem. When 27.1 V of direct current were applied across the heating element, the maximum current was 1.43 A. The geometry of each element in the bath was decided from the direction of water flow by agitations.

The temperature of the bath water was monitored by an analogue *Y–t* recorder. The latest acquired control deviation, and each calculated parameter of PID output values were displayed on the monitor.

Software

Ten control deviations including the latest acquired data were used for calculating output terms of P, I and D. The latest data are written as $T(0)$, and n in $T(n)$ represents T acquired before n s. The constants of $K1$, $K2$, and $K3$ are coefficients of P, I and D, respectively, and selected from the progress of t, by trial and error. The output parameter, H, to be sent to the heater element via DAC was calculated as the sum of P, I and D, where $\mathrm{P} = T(0) \times K1$, $\mathrm{I} = M/K2$ and $\mathrm{D} = [T(0) - T(1)] \times K3$, and M is an integrated value of the control deviation.

A simplified flow chart of the programs is shown in Fig. 3. All programs were written in BASIC and amounted to 8 kbyte; the detailed flow charts are very complicated and have been reported separately [3].

Data acquired via an 8-bit ADC were within an accuracy of ±128 at full scale. When the control deviation was fairly large, the data were treated as

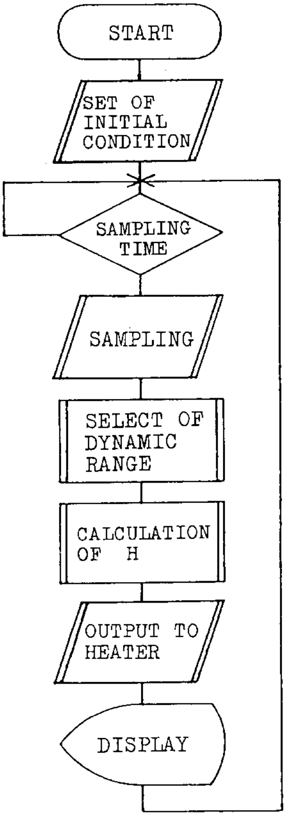

Fig. 3. A simplified flow chart of control programs.

± 178 at full scale. The calculated output parameter or control input, H, of 1000, instead of 1024, was correlated to 10 V at full scale of the control value. The term P showed a rapid approach of the temperature of bath water to the set temperature. The program flow was divided into three directions according to the relation of $T(0)$ and $T(4)$, and $K1$ was given depending upon $T(0)$. The summation, M, of the control deviation was used in term I to prevent the bath temperature from stabilizing at an off-set temperature.

When the control deviation, which was observed as the unbalanced voltage of a Wheatstone bridge including the thermistor, was large at a starting period of control, the output I sometimes did not work effectively to restore the drift due to a sudden increase or decrease in M. The same behaviour was sometimes observed when M was above an upper limit, provided that the temperature of the bath water drifted. M was replaced by a value less than the upper limit in order to obtain speedy response to T.

The output parameter D deals with any sudden change in the temperature. When the temperature is far from the set value, $K3$ was given only from comparison of $T(0)$ and $T(1)$. However, as the temperature gradually approached the set value, the progress of $T(3)$ and $T(5)$, which reflect the direction of the tangent and the extent of the difference, were also taken into consideration when determining $K3$. If there was no change in the temperature, a value of $K3$ instead of zero was given to D.

Procedure

The sample and reference vessels previously prepared for calorimetric measurement were fixed in the water bath of the heat-exchange calorimeter. The titrant reservoir was set for thermal equilibrium. The bath was filled with water of temperature near to the set temperature. Circulation of the cooling water and then execution of the program were started. The bath temperature was automatically maintained at the set temperature.

RESULTS AND DISCUSSION

The resistance R of the thermistors installed in the sample and reference vessels was measured over the temperature T range 10–45 °C. Plots of ln R versus $1/T$ for the two thermistors were linear. The constants B of the thermistors, obtained as the slope of the straight lines, were 3396 and 3342 K, and the resistances at 25 °C were 2.460 and 2.361 kΩ, respectively. As the heat evolved from the vessels was exchanged with the ambient water in the heat-exchange calorimeter, it was possible to keep the temperature in the vessels within the narrower fluctuation range of the bath water, when temperature control was carried out. Therefore, this experimental condition for measurement at a constant temperature may be better than that in an adiabatic calorimeter. In order to estimate the heat effect accurately to ± 0.1 J accuracy, a constancy of ca. $\pm 5 \times 10^{-4}$ °C was required in the temperature of bath water for a sample size of 50 cm^3. If the characteristics of the thermistor pair are similar, the required temperature range may be expanded widely. Therefore, the narrower fluctuation range may allow the measurement of a smaller heat effect. In the Japanese Industrial Standard, the temperature characteristic of the thermistor pair is adjusted by appropriate combinations of resistors. However, it is sometimes difficult to cover a wider range of temperature and it is also troublesome to adjust the resistance.

The PID technique is a very popular temperature-control method, in which three kinds of parameters (P, I, and D) selected empirically, are given before the start and usually remain unchanged during the operation [3]. On the other hand, the modified PID program including the fine conditional judgment was prepared in the present work; the detailed flow charts of this program have been presented separately [4]. The response time to the set temperature of control signals sent from microcomputer-aided modified PID programs should depend on the cooling and heating powers. When making such measurements heat exchange with the surroundings may be found. Heat conduction from a motor-driven stirrer for the bath and a magnetic stirrer for each vessel was also considered as a heating factor of the bath water. As the control deviation or the temperature of the bath water was measured periodically to calculate the control input, heat inflows and outflows were taken into consideration when heat was added from the heating element to keep the set temperature.

The control input to the water bath was linked to the power amplification circuit shown in Fig. 2 via a DAC from the microcomputer, to which 27.1 V d.c. were applied. The heating rate of the heating element was $+9.2 \times 10^{-4}\,^{\circ}\mathrm{C\ min^{-1}}$ in the water-bath system containing 9 $\mathrm{dm^3}$ of water. Heating effects, such as that of motors, reached an almost stationary state after a sufficient warming-up time and corresponded to $+4.5 \times 10^{-5}\,^{\circ}\mathrm{C\ min^{-1}}$ at room temperature (27 °C). For purposes such as that of the present study, running town water may be used as cooling water, even if the temperature changes are fairly large. However, in the summer, the temperature was higher than the set temperature and so the use of an electronic cooling device is recommended in this season. The cooling effect amounted to $-4.1 \times 10^{-4}\,^{\circ}\mathrm{C\ min^{-1}}$ when cooling water of 24 °C was circulated at a rate of 1.5 $\mathrm{dm^3\ min^{-1}}$.

The temperature profile of the bath controlled to the set temperature of 29.0 °C is shown in Fig. 4; running town water was used as cooling water and the thermal fluctuation was about $\pm 1\,^{\circ}\mathrm{C}$ or more. The temperature range of the controlled water was within about $\pm 4 \times 10^{-4}\,^{\circ}\mathrm{C}$ or less. Recovery from thermal disturbances (indicated by the two arrows in Fig. 4) was tested by adding about 40–50 $\mathrm{cm^3}$ of cool or hot water to the bath water

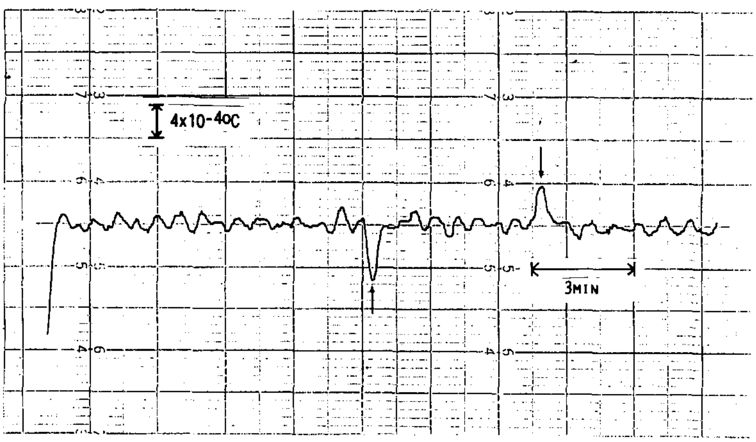

Fig. 4. The controlled temperature profile when using town water as coolant.

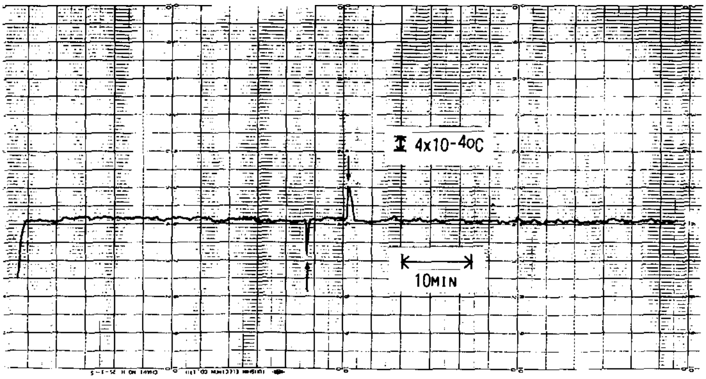

Fig. 5. The controlled temperature profile when using an electronic cooling device as coolant.

of 9 dm^3 which corresponds to a thermal change of about 100 J. The recovery time depended upon the heating and cooling power of the system, as stated before. The recovery time was measured as ca. 20 s in several runs, which was considered acceptable for practical use.

The same temperature control set at 25.0 °C was carried out by using an electronic device instead of town water as coolant; a typical profile is shown in Fig. 5. The temperature of cooling water was 22.5 ± 0.1 °C; the fluctuation was within $\pm 2 \times 10^{-4}$ °C, which is smaller than that with town water as coolant.

In the heat-exchange calorimeter, the control of the whole system and the calorimetric measurements were carried out by a host microcomputer. The temperature of the water bath was automatically controlled by a slave microcomputer which was started by a signal from the host computer.

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