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AN AUTOMATIC ADIABATIC CALORIMETER FOR INTERMEDIATE AND HIGH TEMPERATURES

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Abstract

A fully automated adiabatic calorimeter for a temperature range from 20 K to 670 K has been constructed. The system is used for specific heat measurements on solid state phase transitions with an absolute accuracy of 0.4 %. Usual temperature increments are 0.2 K or less per measuring cycle. The sample temperature is determined by thermistors or diodes with a resolution of 0.1 mK. The whole measuring process is computer controlled; all received data are stored on data tape so that they can be easily evaluated. The performance of the apparatus is illustrated by results obtained on a sapphire sample.

Basic principles

Adiabatic pulse heating calorimeters can be used for high precision specific heat measurements on wide temperature ranges. The pulse heating method is directly derived from the classical definition of the thermal capacity:

$$C(T) = \lim_{\Delta T \to 0} (Q/\Delta T)$$

According to this equation, a heat pulse Q is applied to the sample, and the temperature increment is measured. Usually, we use heat pulses of 10 minutes

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duration and temperature increments of 0.2 K or less.

A typical measurement cycle, which gives a single specific heat value at a certain temperature, can be separated into three stages, as shown in Fig. 1.

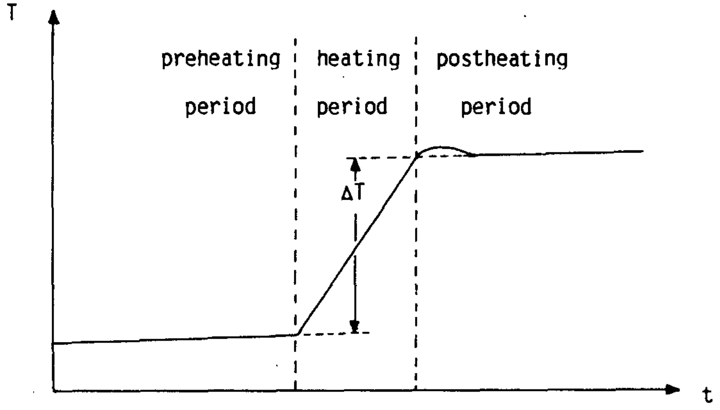

Fig. 1: Typical temperature vs. time cycle, schematically

During the preheating period, temperature and time are monitored, and we determine the constants of a linear polynomial by an interpolation algorithm. During the heating period, an electrical heater applies the energy Q to the sample. The postheating period starts with a waiting cycle. During this waiting cycle, thermal equilibrium between the sample and the sample support should appear; then temperature and time are again monitored and the constants of the linear postheating polynomial are determined. By an extrapolation of these two polynomials to the middle of the heating period the temperature increment is calculated.

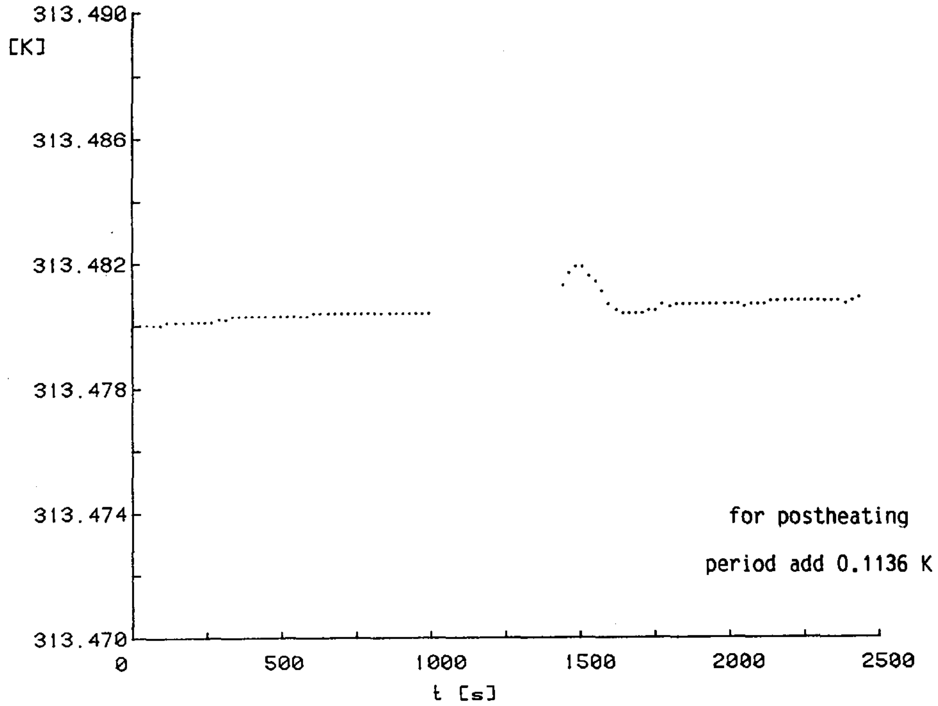

Fig. 2: Typical temperature vs. time cycle, recorded during the specific heat measurement of a sapphire sample

Fig. 2 shows a typical measurement cycle, recorded during the test of our calorimeter with a 4.027 g sapphire sample. From the temperatures of the postheating period, the increment of 0.1136 K in this case must be sustracted in order to get an appropriate temperature resolution in this picture.

For samples with small thermal diffusivities (e.g. 10^{-3} cm^2/s in the case of some polymeres), the time for one measurement cycle may increase up to more than one hour. These long cycle times and the possibility to use modern data reducing techniques were some reasons to automate the calorimeter. Such computer controlled systems are described respectively cited by Gmelin[1]. Our computer is a BASIC programmed ROHDE & SCHWARZ PPC desk top computer, which is derived from the CBM 3032; the data flow between the measuring instruments and the computer runs via IEEE - 488 bus.

The calorimeter

The calorimeter consists of the vacuum recipient, the cooling equipment, two heated adiabatic shields and the sample holder. Two stainless steel tanks, on which copper cylinders are soldered, build up the cooling equipment; the lids of these cooling shields are screwed on. The two tanks can be filled from outside with LN_2, or, in the case of measurements below 80 K, the outer one with LN_2 and the inner one with LHe. The temperatures of the bottoms of the tanks can be controlled by platinum resistances, which show to the operator when the tanks have to be refilled.

Fig. 3 is a view of the adiabatic shields containing a sample holder. These shields are double walled in order to reduce temperature gradients along their walls. The NiCr heaters are embedded into grooves. The temperature difference between the sample support and the inner adiabatic shield (IAS) is measured by thermocouples; a nanovoltmeter amplifies the signal, and a PID regulator with a DC power amplifier supplies the heaters. The zero control of the nanovoltmeter allows to adjust the temperature drift of the sample at the beginning of a measurement cycle; an external 12 bit DAC enables the computer to minimize the drift to values as 10^{-6} K/s. A second pair of thermocouples receives the temperature difference between the IAS and the outer adiabatic shield (OAS). The OAS temperature is controlled by a similar system with a more powerful DC amplifier. The zero control of this regulator makes it possible to adjust the temperature difference between the IAS and the OAS to a negative value, so that a constant thermal current flows from the IAS outwards. The choosen temperature difference was 3 K for low respectively 0.5 K for high temperatures.

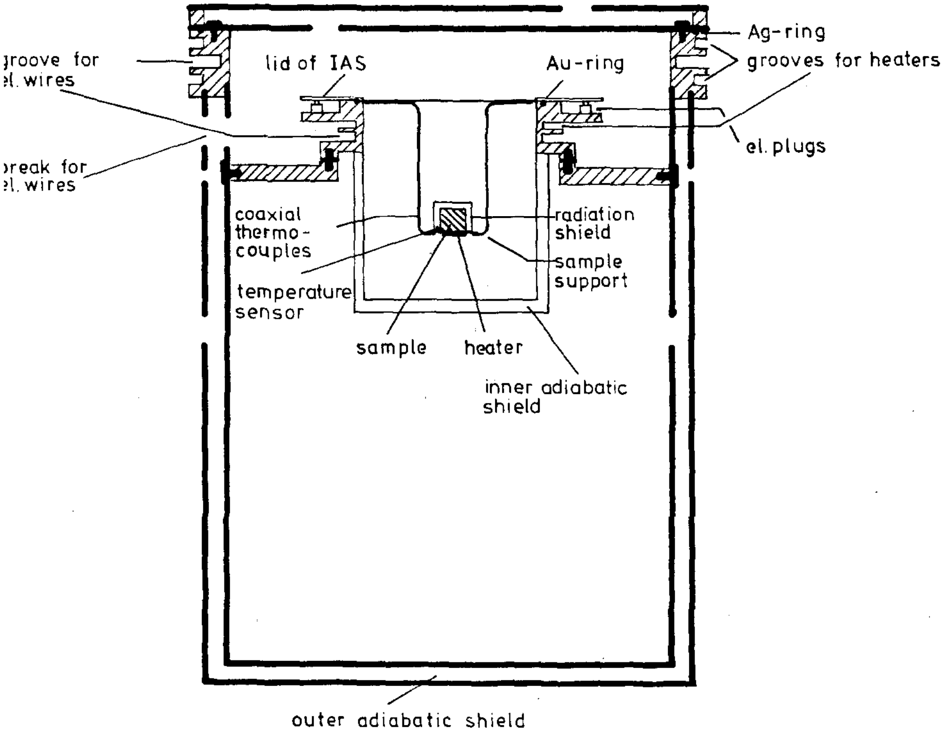

Fig. 3: View of the adiabatic shields containing a sample holder

The sample holder consists of the lid of the inner adiabatic shield, the sample support and a plate with the temperature sensor. The IAS carries on its upper periphery 15 electrical female contacts. The male contacts are mounted on the lid of the IAS, so that the complete sample holder can be easily removed. The sample support is a 15 * 15 mm^2 silver plate which is fixed at the lid by the coaxial thermocouples. The sample heater is an equal coaxial thermoelement which is soldered at the bottom side of the sample support. The plate with the temperature sensor can be easily changed; it is pasted onto the sample support, and the electric wires are plugged into the contacts of the IAS; all other wires are soldered at the male contacts of the sample holder. The sample itself is pasted onto the plate with the temperature sensor. As paste APIEZON N or H for low respectively high temperatures is used. A folded metal foil serves as radiation shield.

The measuring problem

The temperature is determined by a DC four wire resistance measurement, carried out by a 7 1/2 digit DATRON 1071 digital multimeter; the measuring current usually is choosen between 100 nA and 1000 nA. GaAs or Si diodes, thermistors or platinum resistances serve as sensors.

Fig. 4 shows the program flow of the temperature measuring subroutine; it is typical for any measuring subroutine and includes a programmed digital filter.

First the error counter F is reset. Passing the routine, the temperature is measured two times running. The maximum allowed difference ΔT between these two values is set to 0.02 K for pre- and postheating periods; this limit is obtained by experience. At the beginning, the instrument is switched on average mode, which gives the last digit after about 8 seconds. Then the resistance value is read, and the average mode is switched off. The temperature is calculated by a stored algorithm or calibration table. Sometimes, there occurs an error with the IEEE - 488 data transfer; then the temperature calculation

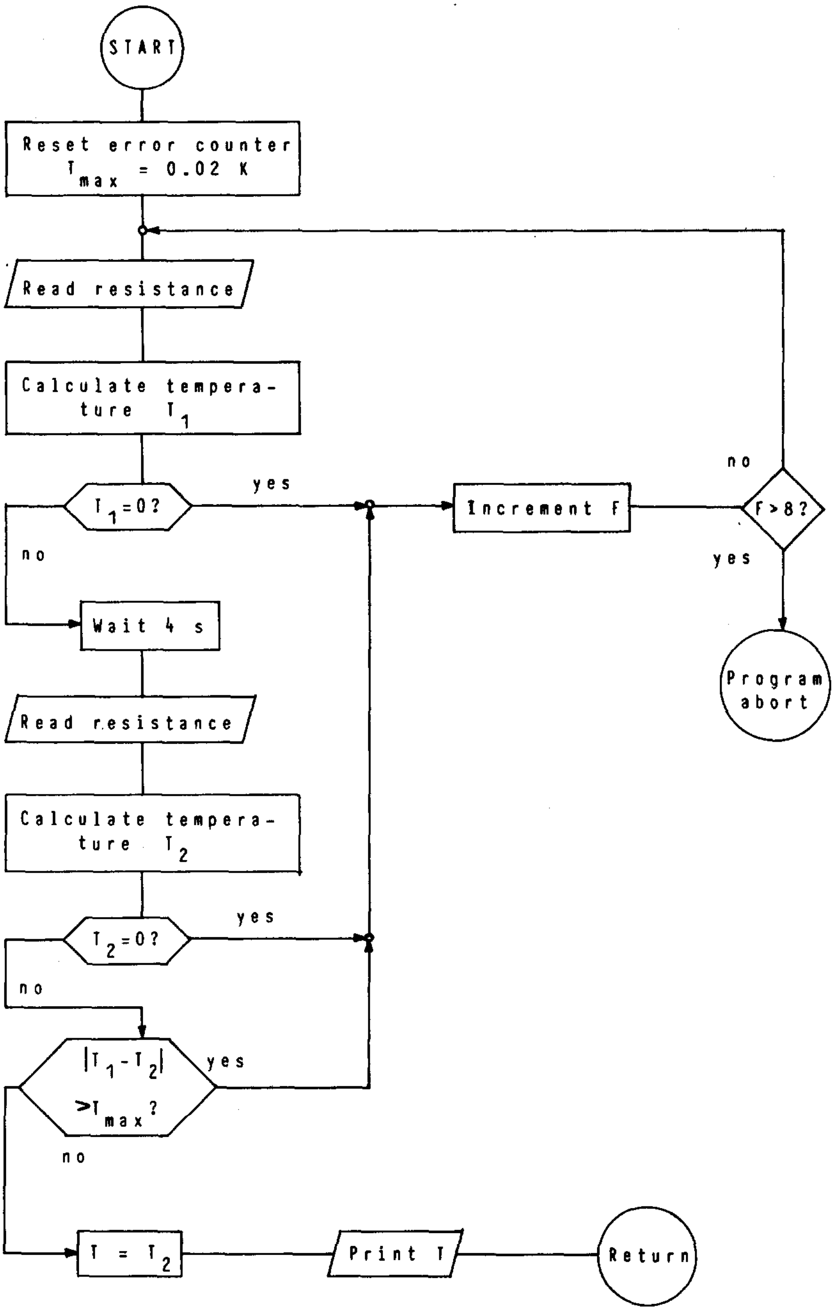

Fig. 4: Temperature measurement cycle

can give zero. In this case, the error counter is incremented, and, if it is less or equal 8, the measuring cycle starts from the beginning. If F is greater than 8, the program is aborted and the operator is informed; the calorimeter is set to a waiting position and can be easily restarted. If the result of the temperature calculation was unequal zero, a new resistance measurement is started after 4 seconds waiting; it runs like already shown. Again the corresponding temperature is calculated, and the difference between the two values is compared to the allowed maximum. If it is less, the last measured temperature is defined as the actual one, printed, and the subroutine ends with RETURN. Because of measuring or data transfer errors it may happen that the difference between the two measured temperatures is greater than the allowed limit; then the error counter is incremented, and, if $F \leqslant 8$, a complete new cycle is started. This routine guarantees a reasonable certainty of the measured value; other used measurement routines are organized similarly.

Temperature errors can be caused by instrument errors, calibration errors, and the heating of the temperature sensor itself by the measuring current. The instrument error gives for usual thermistors an absolute temperature deviation of less than 4 mK; the calibration errors are held below 20 mK (calibrated against a standard platinum resistance thermometer). The heating of the temperature sensor by the measuring current produces a typical power between 1 μW and 10 μW; the maximum resulting deviation of the absolute temperature is less than 5 mK. This permanent heating must be compensated by lowering the IAS temperature. The variation of the thermistor resistance during a usual heating period gives only a neglectible variation of the thermistor heating power. The temperature errors mainly give a shift of the absolute temperature and only small errors in the measured value of the specific heat compared to the later discussed errors which are caused by small deviations from the adiabatic conditions and other small heat leaks.

The measurement of the heating energy is separated into heating voltage, current and time measurement. Alternating during the whole heating period, voltage and current are determined by a 5 1/2 digit DATRON 1051 digital voltmeter. For the switching we use special bistable relays, which are computer controlled. Finally the power values are averaged.

The heating time is determined by the program. The computer sets a 4 digit clock and gives a start signal; the clock turns on the sample heating and turns it off at the end of the heating time. A flag shows to the computer the active state of the clock. The accuracy of the energy determination for a typical heating time of 600 s and a heating power of 0.5 mW is better than 0.03 %. The main part of this error is caused by the power measurement.

The program

The whole program is written in BASIC, which is possible because there are no time problems. Fig. 5 shows the main program flow chart.

The program is started with the preparations. The data tape is initialized, sample designation, date and time are stored, and the instruments ranged and tested. Then the menu is called. At its beginning it gives an acoustical sign; during the next 5 seconds, the program can be interrupted by pressing any key of the computer, which is never else possible. If no key is pressed, the output "measurement" of the menu is used; in the other case, the operator can call special subroutines like one which allows to heat the sample automatically to a programmable start temperature. All these specials go back to the menu at the end. A flag decides, if a preheating period is necessary. If the drift during the last gone postheating period was small enough, this postheating period is used as the preheating period of the following measurement cycle in order to save time. The program continues with a

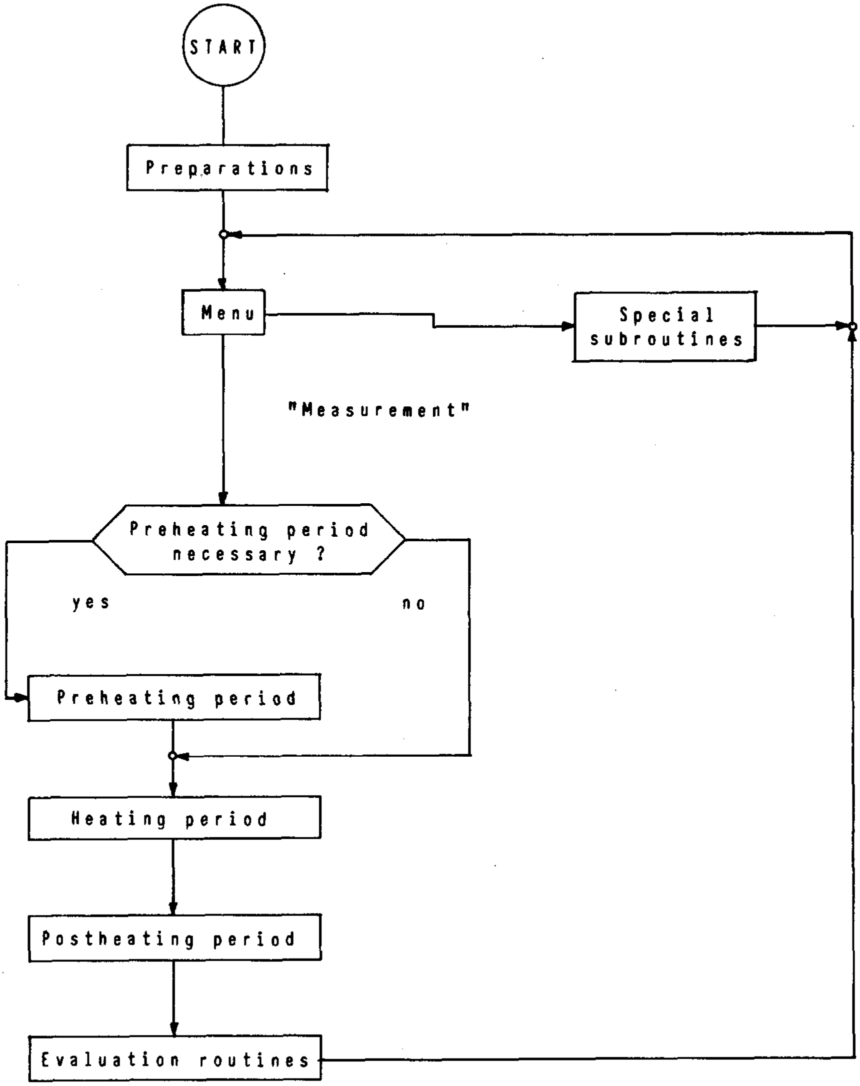

Fig. 5: Main program flow

preheating period or with a heating period. Then the postheating period follows, and the experiment can be evaluated by the drift extrapolations; at the end, the program goes back to the menu.

Every preheating period starts with the automatic drift correcture subroutine; Fig. 6 is the flow chart. 15 pairs of temperature / time values are read, and an interpolation algorithm determines the constants of the quadric polynomial

$$T(t) = A*t^2 + B*t + C$$

The coefficient A of the quadric term is destinated by unsteady thermal currents and shows the deviation from the equilibrium state. The coefficient B of the linear term corresponds to the thermal drift.

If $|A|$ is not greater than the allowed maximum A_{max}, the drift coefficient B determines if a drift correction is carried out or not. The case that $|B|$ is less than B_{max}, is the only correct exit of this routine. If $|B|$ is greater or equal than B_{max} the computer calculates a value for the zero correction of the IAS nanovoltmeter. The calculation algorithm is linear and given by experience. If the calculated value is out of the DAC limits, there is no correction possible; the program goes to a waiting position and requests service. Otherwise, the correction is made, and, after a waiting cycle, which is inserted to return to equilibrium, the automatic drift correcture is restarted.

If $|A|$ was greater than A_{max}, the reduced constants $|A|/A_{max}$ and $|B|/B_{max}$ are compared. If $|A|/A_{max}$ is less than $|B|/B_{max}$, a drift correction is carried out like already shown; if not, the automatic drift correcture is restarted after a waiting cycle during which thermal equilibrium should occur.

Only if $|A| < A_{max}$ and $|B| < B_{max}$ the preheating period continues moni-

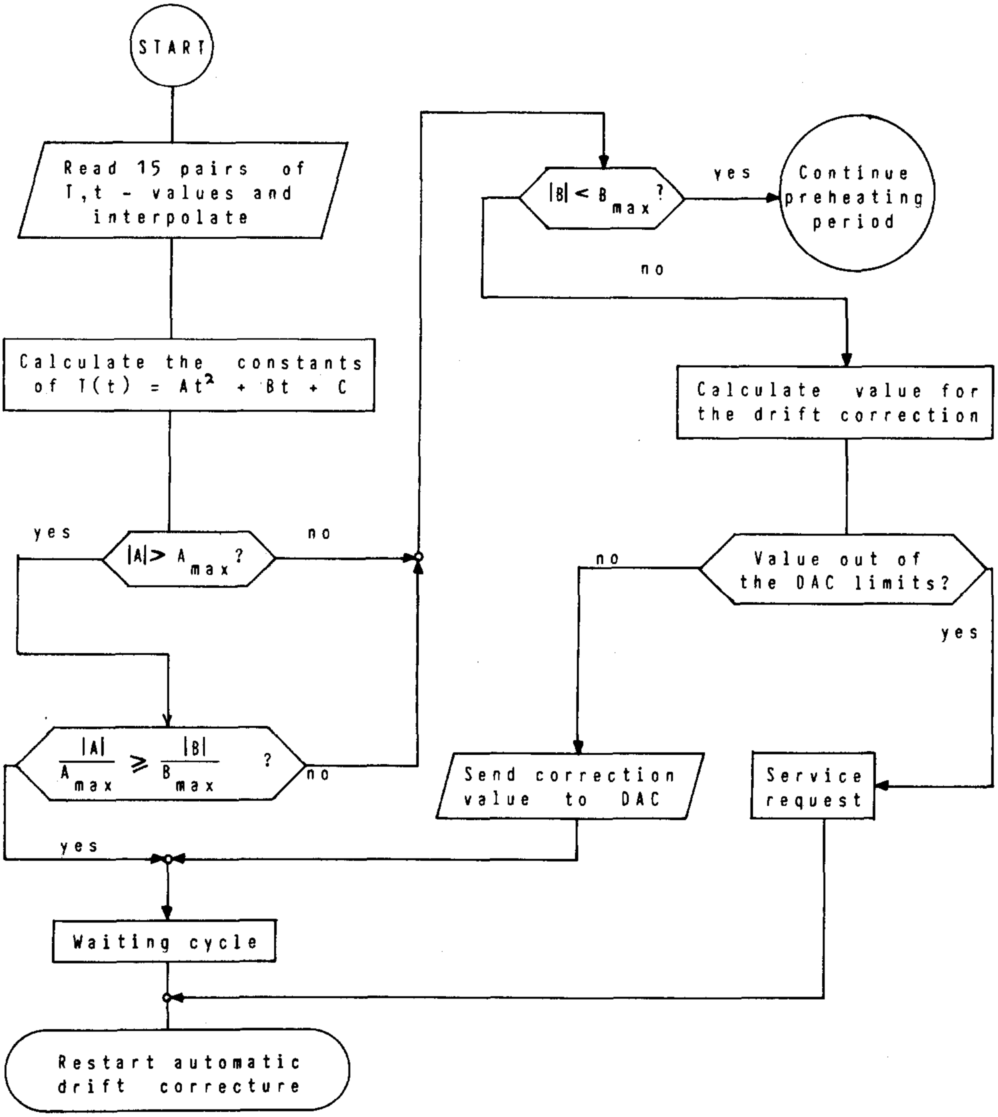

Fig. 6: Automatic drift correcture

toring T(t), followed by the heating period and the postheating period. During the two latter periods, no drift correction is allowed.

In the postheating period, the constants of the quadric postheating polynomial are determined. If one of these constants is greater or equal than its allowed maximum, a new preheating period is necessary; a flag is set for the correct branching in Fig. 5. In the other case, the flag is reset.

The program was written with particular respect to reliability, because it runs without supervision by an operator. Any measurement disorders, bus errors, or power supply perturbations are perceived by the program with great certainty; so any breakdowns could not be observed. During the program flow, all data of interest like temperatures and times, polynomial coefficients, heating powers, and the calculated temperature increments and heat capacities are stored on data tape. In the menu, a special subroutine allows the operator to change the data tape, so that a partial evaluation of the experiment is possible with a second computer during the measurement goes on. This evaluation is mostly automated; as computer a TEKTRONIX 4052 is used because of its graphic features. T(t) plots like shown in Fig. 2 are drawn for each measurement cycle; C(T) plots and lists are also possible.

Performance

As already shown, the specific heat errors caused by the measuring instruments are limited to very small values. More significant errors result from small deviations from the adiabatic conditions. These deviations produce a small heat exchange between the sample and the inner adiabatic shield by thermal conduction and radiation. A further heat leak is that part of the heating power produced by the sample heater which does not flow to the sample but flows off through the electric connections.

As an example for our proceeding the specific heat measurement of a 4.027 g sapphire sample is discussed. After the sample measurement, the heat capacity of the empty sample holder was measured and substracted from the total heat capacity. Comparing our specific heat values with those of the NBS[2], the difference between the two measurements can be well fitted by the derivation of a Stefan - Boltzmann law with an additional constant term:

$$F(T)/\% = -8.156*10^{-8}*T^{3} + 2.75$$

The T^3 - term gives the heat exchange by radiation between the sample and the IAS at a constant temperature difference; the thermal conduction can be neglected. The additional constant term corresponds to the heat flow through the electric connections of the sample heater, which was in according to the value appraized from data of the heating construction.

Fig. 7 shows the results of our test measurement on the sapphire sample; the values are corrected by the above denoted F(T) - law. The remaining errors are less than 0.4 % of the absolute specific heat value. The reproducibility was 0.25 %.

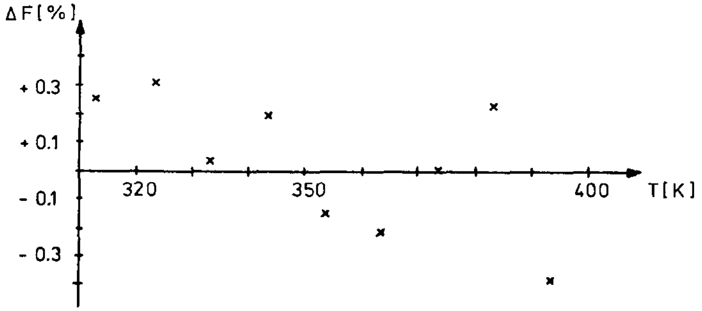

Fig. 7: Error of our measured specific heat values compared to the values of the NBS (4.027 g sapphire sample)

For the specific heat determination of an unknown sample the heat capacity of the sample support with temperature sensor and radiation shield must be well known like already mentioned. These data can be got by measuring the heat capacity of the empty sample holder. However, these measuring conditions are very different from those of a sample measurement, and this fact results in different deviations from the adiabatic conditions. In order to minimize the remaining errors we measure a reference sample e.g. sapphire of similar heat capacity instead of the empty sample holder to reach comparable measuring conditions. The total errors do not exceed the size of the specified value of 0.4 %, because these data were obtained by measuring the empty sample holder. The reproducibility remains 0.25 %.

Acknowledgement

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