DETERMINATION OF THE SPECIFIC HEAT OF AGRICULTURAL MATERIALS: PART I. CONTINUOUS ADIABATIC CALORIMETER

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A quantitative adiabatic calorimeter was designed to operate with continuous heating of the sample. By maintaining a constant power input to the sample and recording the temperature-time data, it is possible to obtain the complete enthalpy-temperature data. The apparatus and the calibration experiments are described. It was found that the experimentally determined specific heat values of aluminum, copper and ceramic catalyst pellets in the temperature range of 30-100°C were in excellent agreement with the literature values as long as the temperature gradient within the sample was less than 3°C.

NOMENCLATURE

\[ C_p = \text{specific heat, J/g°C} \]

\[ h = \text{specific enthalpy, J/g} \]

\[ H = \text{enthalpy, J} \]

\[ M = \text{mass, g} \]

\[ t = \text{time, min} \]

\[ T = \text{temperature, °C} \]

\[ q = \text{power input, J/min} \]

Subscripts

\[ c = \text{sample cell} \]

\[ f = \text{fluid} \]

\[ s = \text{sample material} \]

INTRODUCTION

Of all the thermal parameters of a material, the specific enthalpy or specific heat is probably the easiest property to measure accurately. All such measurements fall under the general heading of calorimetry and the equipment varies from the various forms of the drop calorimeter to the more sophisticated differential scanning calorimeters.

The drop calorimeter is based on the method of mixtures. It involves bringing a known amount of sample material to some equilibrium temperature, usually in a furnace, and keeping the insulated receiver, which is usually filled with an inert liquid, at a lower temperature. When both the sample and receiver have reached their respective steady-state temperatures, the sample is quickly transferred or dropped into the receiver. The temperature of the receiver is measured with respect to time before and after the drop. A complete plot of the receiver temperature history allows calculation of the enthalpy-temperature relation and hence the specific heat-temperature relation. Except for extremely sophisticated versions of the drop calorimeter, such as the Dynatech SHDW-R20® (Registered trademark, Dynatech R/D Company, Cambridge, Mass. 02139), most of these apparatuses suffer from errors introduced due to heat losses during transfer of the sample from the furnace to the receiver. One method used to circumvent this problem is to use a calibrated sample container with sufficiently thick walls to prevent the intermediate transients from penetrating the walls and sample. In this case a fictitious \( MC_p \) value is obtained for the container by performing an empty drop. This is in fact one of the features of the Dynatech SHDW-R20®.

The method of mixtures has so far been the conventional method of determining the specific heat of agricultural and food products. Pfalzner (1951) was probably the first person to measure specific heat of grain directly. He used the method of mixtures and a small cylindrical sample capsule to determine the specific heat of No. 1 grade Northern, hard wheat at moisture contents ranging from 0 to 15%. Subsequent workers discarded the sample capsule idea and poured the grain samples directly into the receiving medium. Thus, Disney (1954) used ice as the receiving medium and obtained \( C_p \) values of Manitoba wheat and Bersee hard wheat. More recently, Kazarian and Hall (1965) used a Dewar flask to measure the specific heat of yellow dent corn and of soft white wheat. They held the grain sample at room temperature and then dropped it into cooled water. To reduce the time required for the mixture to reach its final equilibrium temperature, the flask was agitated by shaking it by hand. This eliminated the use of a stirrer and hence a temperature increase due to the energy input by the stirrer.

The same method was used by Alam and Shove (1973) for soybeans. Watts and Bilanski (1970) used the same method but instead of water they used a liquid with a high thermal conductivity.

Although the sample and receiver liquid are immediately brought in excellent thermal contact, the initial temperature difference between the sample and the liquid is relatively small and any deviation from adiabatic conditions causes substantial errors in the final results. Another disadvantage of the drop calorimeter or method of mixtures is that only an average \( C_p \) value is obtained from the corresponding temperature range. If a complete \( C_p \) temperature relation is required, additional experiments must be run over different temperature ranges. This would involve use of a furnace and consequently the methods used by the various authors become unacceptable for accurate measurements because heat losses during sample transfer become significant. Watts and Bilanski (1970) reported on the problems of using soybeans at temperatures of 135°C and subsequent heat losses during transfer.

The differential scanning calorimeter (DSC) provides a rapid and dynamic method to determine the specific heats of solids and non-volatile liquids. The apparatus is designed to measure simultaneously increases in temperature and the power input to maintain that rate of temperature increase of the sample material. At the same time these measurements are compared with those of either an empty cell or a reference material. The additional power required is a direct function of the mass and specific heat of the sample. A comparison of the sample’s thermogram (rate of heat absorption versus temperature) with that of the reference material of known specific heat allows calculation of the sample’s specific heat. Brenner and O’Neill (1965) described a Perkin-Elmer model 880 DSC which uses sapphire as
the reference material in an external standardizing system.

Young and Whitaker (1973) used the DSC method to measure the specific heat of peanut kernels and hulls over the range of moisture contents and temperatures encountered during the drying process (32-57°C above room temperature). They found that the presence of moisture in biological materials required sealing the samples in air-tight containers to prevent weight losses during heating. This procedure required an extra thermogram to account for the container.

Although the DSC method is quite accurate and rapid, the apparatus is very expensive and in the case of biological materials, extra precautions have to be taken.

The term adiabatic calorimetry is reserved for a special type of calorimeter in which all heat losses are virtually eliminated. This instrument has long been very popular for the accurate determination of enthalpy and specific heats of materials by chemists and physicists. The majority of adiabatic calorimeters used in the past utilized an intermittent heating technique. With the intermittent heating method as described by West and Ginnings (1958), the sample cell and its adiabatic jacket are allowed to attain the same temperature while the initial sample temperature is also measured carefully. Then a constant power input is applied to the sample heater for a carefully measured time interval. During the heating period the adiabatic jacket is maintained at the same temperature as the sample, thus ensuring adiabatic conditions between the sample and the environment. At the end of the heating period, the sample and jacket temperatures are again allowed to equilibrate and the final sample temperature is again measured carefully. From the temperature change, the sample’s enthalpy-temperature relation or specific heat is calculated. The intermittent heating method is normally used for high accuracy work because the final and initial sample temperatures are taken when the sample is at a uniform temperature throughout. As described by Solomons and Ginnings (1964), a second method for operating an adiabatic calorimeter is to run the sample heater and adiabatic jacket heater continuously and record the sample temperature and power input as a function of time. This continuous method provides a complete set of enthalpy-temperature results over a wide temperature range in a relatively short time as compared with the much longer and tedious intermittent method.

The major disadvantage of the continuous method is the introduction of a thermal gradient within the sample. This gradient may become a source of significant error if not enough care is taken in the thermal design of the sample cell.

In this paper a continuous adiabatic calorimeter suitable for measuring enthalpy and specific heat data of agricultural and food products is described.

THE CONTINUOUS ADIABATIC CALORIMETER

A. Description

The schematic diagram of Fig. 1 shows the main features of the continuous adiabatic calorimeter. The copper sample cell is a cylinder 5 cm in diameter, 10 cm long, with a 1.575-mm wall thickness. The sample cavity has a volume of 185 cm³. The cell is equipped with a threaded copper lid (C) which hermetically seals the cavity after tightening. The sample is heated with a 0.8-mm diameter, 3.315 ohm, insulated nichrome heater which is placed inside a narrow, thin copper tube (D). The tube is wound and soldered onto the inside surface of the sample cell. The heater is powered by a regulated DC power supply (HP 6433B) which has an output stability of 0.15%.

The adiabatic or outer jacket (L) is a 10-cm inside diameter x 14.8-cm copper cylinder made of 0.6-cm thick material. The jacket is sealed with a 0.6-cm thick copper lid, a rubber gasket and six screws (O). The jacket and the lid are fitted with a 0.8-mm diameter nichrome heater (P). This heater is powered by another variable DC power supply (Harrison 6274A).

The adiabatic jacket is supported by three, 1-cm diameter, plastic rods. The rods are fastened to a wooden plate (S) which is placed on a styrofoam-covered wooden base. The whole system is enclosed in a styrofoam-lined wooden box (V).

Since the heat transfer between the sample cell and the surroundings must be as close to zero as possible, a number of steps were taken to ensure that this was the case. To reduce heat conduction between the cell and the jacket, the former was suspended from the jacket lid by two 1-mm diameter plastic rods (I). Furthermore, the heater and thermocouple leads from the cell are thermally grounded to reduce conduction through them. The space between the cell and the jacket is evacuated to 6 X 10⁻⁶ Pa with a Welch 1405H vacuum pump; this eliminates convective heat losses and reduces gas conduction. Radiant heat exchange is minimized by controlling the power input to the adiabatic jacket so that the temperature difference between the cell and jacket is as close to zero as possible.

B. Temperature and Power Measurements

The temperature of the cell cavity is measured with a protected thermocouple (B) placed at the center of the cavity. An ice bath is used as a reference source and the thermocouple output is displayed on a digital voltmeter (HP 3490A). The thermocouple is type K, chromel-alumel. It is covered with a metal sheath 1.524-mm o.d. and tightly compacted with a protective ceramic insulation.

The 28-gage, copper-constantan thermocouple used to sense the temperature difference between the sample cell and the adiabatic jacket is connected in a differential mode (X). During an experimental run, the power input to the adiabatic jacket is controlled manually by observing the output from the thermocouple using the HP 3490A digital voltmeter. As soon as the sample cell temperature exceeds the jacket temperature by 0.1°C (3 X 10⁻⁶ V), the power input to the jacket is increased. With a little practice it is possible to prevent overcorrection and keep the temperatures of the two containers within 0.2°C.

![Figure 1. Schematic diagram of the calorimetric apparatus. A. Copper sample cell; B. Protected thermocouple; C. Copper lid; D. Resistance heater; E. Plastic rods; L. Adiabatic jacket; M. Copper lid; G. Six screws; P. Resistance heater; S. Wooden plate; V. Styrofoam lined wooden box; Z. Differential thermocouple.](image-url)
The power input to the sample cell heater must be constant and carefully measured during an experimental run. To keep the power dissipation in the heater approximately constant while the heater resistance changes with temperature, the heater is connected in series with an equal value dummy resistor. This resistor is also made out of nichrome and is kept in an insulated box to simulate the sample heater environment.

The power dissipated in the heater is obtained by measuring the voltage across the heater with the digital voltmeter and then subtracting the voltage drop due to the leads. The current was measured by connecting a "1 ohm standard resistor" in-series with the dummy resistor and measuring the voltage across the standard resistor. The power was found to remain constant within ± 0.3% during an experimental time of about 90 min.

C. Theoretical Principles

The basic principle on which an adiabatic calorimeter operates is the First Law of Thermodynamics; that is, in adiabatic conditions the energy put into a system must equal the enthalpy gain of all the components of the system.

If the system consists of a heater and a sample cell with an inert fluid (used to promote heat transfer with granular samples), then the energy supplied by the heater during a time interval equal to the enthalpy rise of the components, or

\[ q = \Delta H_e(T) + \Delta H(T) \]  

The enthalpy change of a sample material is now readily obtained by repeating the experiments over the same temperature range and subtracting Eq. 1 from the results. Therefore,

\[ \Delta H(T) = \Delta H_{	ext{cell}}(T) - \Delta H(T) - \Delta H(T) \]  

The sample's specific enthalpy is

\[ h(T) = \Delta H(T)/M \]  

and its specific heat is then by definition:

\[ c_p(T) = (dh(T)/dT)_h \]  

which is the slope of the specific enthalpy-temperature plot.

In most cases we are only interested in the specific heat and it is determined more readily as follows. First, an experiment is performed with the calorimeter without a sample so that

\[ q = (MC_p)_h \]  

And then with a sample

\[ q = (MC_p)_h + (MC_p)_s + (MC_p)_h \]  

This approach allows determination of the cell MC_p versus temperature relationship for the cell, since the MC_p value of the finest fluid is known. Substitution of these values into Eq. 6 give the MC_p values for the sample. In both equations, \( dt/dt \) is obtained from either a strip chart recording or DVM readings and the appropriate thermocouple EMF-temperature reference tables. If the experimental temperature range is sufficiently large, the temperature-time plot will probably be non-linear. In that case values of \( dt/dt \) are obtained from the slope at enough discrete temperature points to obtain a smooth continuous curve for \( C_p \) versus temperature.

EXPERIMENTAL CONSIDERATIONS

A. Measuring \( (MC_p)_h \) of the Cell

In order to use Eq. 6 it is necessary to have a value for \( (MC_p)_c \). The most convenient method to obtain this value is to fill the cell with a liquid of known specific heat and run an experiment to measure the other parameters needed in Eq. 5. Water was selected as the reference material because of its availability in pure form and because of the many accurate measurements made of its heat capacity. Osborne et al. (1939) reported its specific heat in the range of 0–100°C to be 4.19 ± 0.0033 J/g°C.

Four experiments were performed to obtain a representative \( (MC_p)_h \) value. In each experiment the calorimeter was filled with 180.00 g of water, leaving a small air gap at the top of the cell for the thermal expansion of the water. The central temperature was recorded every 5 min. A typical temperature-time plot is shown in Fig. 2. The regression analysis described by Draper and Smith (1966) was used to obtain the best fits to the data. In all four cases the best fit was a straight line so that a single \( dt/dt \) value can be used for the experimental temperature range. The average \( (MC_p)_h \) value of the four experiments was calculated to be 209.50 J/°C with a standard deviation of 2.419 J/°C and a coefficient of variation of 1.15%.

B. Calibration of the Calorimeter

After obtaining the \( MC_p \) value of the cell and calibrating the various electrical components, it was considered desirable and necessary to check the overall performance of the cell by measuring the heat capacity of another pure material and comparing this value with the one obtained by other investigators. This check would provide proof of the reliability of the calorimetric measurements.

Since the calorimeter was to be used to obtain heat capacity values of granular materials, it was decided to obtain a calibration value using pure aluminum pellets of an accurately known specific heat and sufficient water to cover the material. In this case Eq. 6 was used and solved for \( (MC_p)_h \). The result is reported in Table I. It is felt that this approach is correct because the experimental conditions within the cell are more nearly equal to those encountered during actual runs. That is, heat is transported by convection of the liquid and conduction in the solid and liquid phases in both the calibration and sample runs. This should reduce the effect of varying temperature gradients within the cell which is one of the major potential sources of error in a continuous adiabatic calorimeter. The temperature gradient within the sample is a function of the effective thermal diffusivity of the sample material, the heating rate and the radial position. Since in most instances the thermal diffusivity changes with temperature, the temperature difference

![Figure 2. Typical temperature-time plot.](https://example.com/figure2.png)

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Amount of Al (g)</th>
<th>Heating power (l/min)</th>
<th>Heating rate (°C/min)</th>
<th>Linear regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>225.023</td>
<td>805.910</td>
<td>0.964</td>
<td>R² = 0.99995, Residual error = 0.02197, Max (abs (residual)) = 0.35735</td>
</tr>
<tr>
<td>2</td>
<td>224.742</td>
<td>810.000</td>
<td>0.964</td>
<td>R² = 0.99995, Residual error = 0.02197, Max (abs (residual)) = 0.35735</td>
</tr>
<tr>
<td>3</td>
<td>224.803</td>
<td>816.000</td>
<td>0.974</td>
<td>R² = 0.99995, Residual error = 0.02197, Max (abs (residual)) = 0.35735</td>
</tr>
<tr>
<td>4</td>
<td>224.787</td>
<td>816.000</td>
<td>0.974</td>
<td>R² = 0.99995, Residual error = 0.02197, Max (abs (residual)) = 0.35735</td>
</tr>
<tr>
<td>5</td>
<td>224.780</td>
<td>795.120</td>
<td>0.945</td>
<td>R² = 0.99995, Residual error = 0.02197, Max (abs (residual)) = 0.35735</td>
</tr>
</tbody>
</table>

TABLE 1. SPECIFIC HEAT OF ALUMINUM PELLETS
TABLE II. SPECIFIC HEAT OF SOME GRANULAR MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>( M_0 ) (g)</th>
<th>( M_1 ) (g)</th>
<th>( \frac{dT}{dt} ) (°C/min)</th>
<th>( C_p ) (J/g°C)</th>
<th>% difference</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>89.671</td>
<td>75.000</td>
<td>0.962</td>
<td>0.38</td>
<td>0.385</td>
<td>1.3</td>
</tr>
<tr>
<td>4-mm dia.</td>
<td>226.817</td>
<td>185.000</td>
<td>1.128</td>
<td>0.86</td>
<td>0.86</td>
<td>0</td>
</tr>
<tr>
<td>Ceramic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>North Co.</td>
</tr>
<tr>
<td>7.4-mm dia.</td>
<td>260.027</td>
<td>81.990</td>
<td>1.140</td>
<td>0.76</td>
<td>0.83</td>
<td>Bakeman, Ohio</td>
</tr>
<tr>
<td>Soda lime glass</td>
<td>33.949</td>
<td>82.000</td>
<td>1.441</td>
<td>1.23</td>
<td>1.46</td>
<td>15.8</td>
</tr>
<tr>
<td>4-mm dia.</td>
<td>242.445</td>
<td>80.000</td>
<td>1.153</td>
<td>0.79</td>
<td>0.83</td>
<td>4.8</td>
</tr>
<tr>
<td>Epoxy spheres (hollow)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Eaton &amp; Cummin</td>
</tr>
<tr>
<td>Borosilicate glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Corning Co.</td>
</tr>
<tr>
<td>Beads</td>
<td>3.9-mm dia.</td>
<td>116.160</td>
<td>81.000</td>
<td>1.153</td>
<td>1.63</td>
<td>1.47</td>
</tr>
</tbody>
</table>

D. Specific Heat of Some Granular Materials

Other materials such as copper, plastics, glass, and ceramic were also tested, thus covering various granular materials. These experiments were done to check further the ability of the calorimeter to provide reasonably accurate specific heat values. Water was used as an inert fluid. The results are compared with those from the literature measured within the same temperature range (30-90°C). (Table II).

The accuracy or exact source of the values reported by the manufacturers is not known. For example, the value supplied for soda-lime glass and borosilicate glass is the same; however, the Handbook of Applied Engineering Science (1970) shows that the specific heat of glass depends on its constituents and it gives different values for these types of glass.

The value of the ceramic catalyst support spheres is an experimental result obtained by North Corporation. The value is needed in reactor design and can be considered to be reasonably accurate.

CONCLUSIONS

Since the aluminum, copper and ceramic values compared favorably with experimental values reported in the literature, it was decided to use the calorimeter to determine the specific heat of granular agricultural products (Otten and Samaan 1980).

ACKNOWLEDGMENTS

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