

## SPECIFIC HEAT CAPACITY OF SOILS AND MINERALS AS DETERMINED WITH A RADIATION CALORIMETER

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To solve soil problems involving heat capacity and heat flow, soil specific heat capacities must be known. In the past, most reported soil specific heat capacities were determined by the "method of mixtures" (3, 4, 5, 6). Briefly, this method consists of heating a substance to a particular temperature and quickly mixing it into a liquid medium of known temperature and known specific heat. Ideally, from the law of conservation of energy, the heat lost by the substance must equal the heat gained by the liquid. By knowing the masses involved, the changes in temperatures, and the specific heat of the liquid, the unknown specific heat may be easily computed.

While the theory is relatively simple, accurate measurements are quite complex. Difficulties arise in accounting for such factors as thermal leakage of the calorimeter, heat generated by the stirrer, and evaporation of liquids. In addition, the heat absorbed by the calorimeter and accessories must be considered. For colloidal materials, such as soils, the measurements become more difficult because of the "heat of hydration."

Many early investigators of soil and soil mineral specific heats (4, 5, 6) reported values to the third and fourth decimal place. Calorimetry of this precision is costly, time-consuming, and requires extensive training and experience. In view of the variation in most soils, such precision may be unwarranted. Thus, the purpose of this investigation was to find a method to measure soil specific heat that demanded less training, time, and expense and yet gave results sufficiently accurate for most soils work.

### THEORY

The radiation method of measuring specific heats is based on "Newton's Law of Cooling,"

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which states that the rate at which a body cools is directly proportional to the temperature difference between the body and its surroundings, providing this difference is small. This relationship is easily derived from the Stefan-Boltzmann radiation law and Prevost's law as follows: The Stefan-Boltzmann law states that for a "black body"

$$R = \sigma T^4. \quad [1]$$

Prevost's law states

$$\frac{dQ}{dt} = A(R_1 - R_2). \quad [2]$$

By substitution

$$\frac{dQ}{dt} = \sigma A(T_1^4 - T_2^4). \quad [3]$$

For a "non-black body"

$$\frac{dQ}{dt} = \epsilon \sigma A(T_1^4 - T_2^4) = kA(T_1^4 - T_2^4) \quad [4]$$

$$\frac{dQ}{dt} = kA(T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3) \quad [5]$$

Assume that  $T_1$  is the absolute temperature of cooling body and that  $T_2$  is the absolute temperature of its surroundings, a large heat reservoir the temperature of which remains constant during heat exchange. Further assume that  $T_1 - T_2$  is small compared with both  $T_1$  and  $T_2$ . Then equation [5] reduces to the following approximation:

$$\frac{dQ}{dt} \doteq 4kAT_2^3(T_1 - T_2) = K(T_1 - T_2) \quad [6]$$

where

$$\frac{dQ}{dt} = \text{net rate of radiant energy loss}$$

$$R_1 = \text{rate of radiant energy loss per unit area}$$

$$R_2 = \text{rate of radiant energy gain per unit area}$$

- $\sigma$  = Stefan-Boltzmann constant  
 $\epsilon$  = emissivity of cooling body  
 $k$  = radiation constant of cooling body  
 $A$  = surface area of cooling body  
 $T_1$  = temperature °K of cooling body  
 $T_2$  = temperature °K of surroundings  
 $K$  = proportionality constant.

If the temperature change of the cooling body is sufficiently small for its specific heat to be considered constant, the relation between net rate of energy loss and the rate of temperature change is as follows:

$$Q = mcT \quad [7]$$

$$\frac{dQ}{dt} = \frac{mcdT}{dt} \quad [8]$$

where

- $Q$  = thermal capacity of cooling body  
 $\frac{dQ}{dt}$  = net rate of energy loss  
 $\frac{dT}{dt}$  = rate of temperature change  
 $T$  = temperature of cooling body  
 $m$  = mass of cooling body  
 $c$  = specific heat of cooling body.

Equations [6] and [8] are the basis of the radiation calorimeter.

Figures 1 and 2 show a radiation calorimeter both disassembled and assembled. Since the two chromed brass cups were so constructed that their sizes, finishes, and masses were almost identical, they may be considered identical emitters. Since for each cup the surface area  $A$

is the same, the radiation constant  $k$  is the same, and the temperature of the surrounding water is the same and almost constant, then from equations [4] to [6] when the two cups have the same temperatures (not necessarily simultaneously) their net rates of energy loss are equal. Therefore

$$\frac{dQ_A}{dt_A} = \frac{dQ_B}{dt_B} \quad [9]$$

Since the above method is only an approximation, finite differences may be used in equation [9]. Thus

$$\frac{\Delta Q_A}{\Delta t_A} = \frac{\Delta Q_B}{\Delta t_B} \quad [10]$$

Customarily this procedure is used to determine the specific heat of liquids. In doing so, one cup is filled with distilled water, the other with the liquid being tested. Both are heated to the same temperature and then placed in radiation calorimeters and allowed to cool. By comparing the cooling curves, one easily computes the specific heat. A detailed description of the complete procedure is given by Weber (7) and in Cenco's selected experiments in physics (1).

Because of the simplicity of operation, the ease of computation, and commercial availability of the radiation calorimeter, it was decided to adapt it to soil specific heat determinations.

#### PROCEDURE

A soil-water or mineral-water mixture was placed in one of the cups; distilled water was placed in the other. All soils and minerals were ground, screened, and oven-dried at 50°C. The

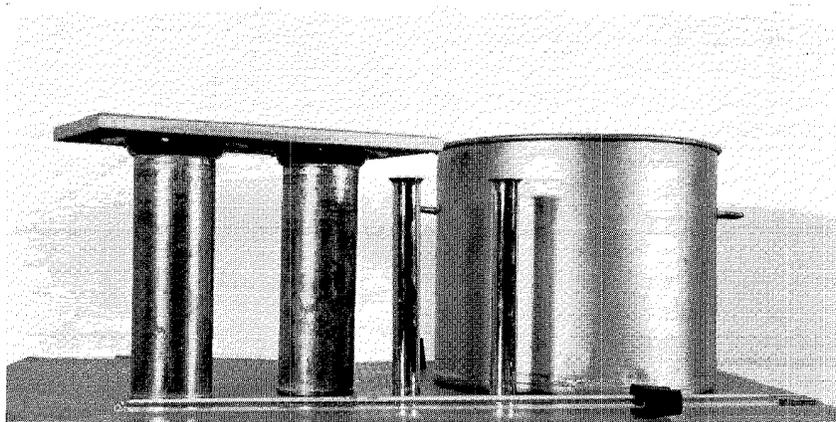


FIG. 1. Disassembled radiation calorimeter, showing water bath, thermometers and stoppers, evacuated tubes, and radiation cups.

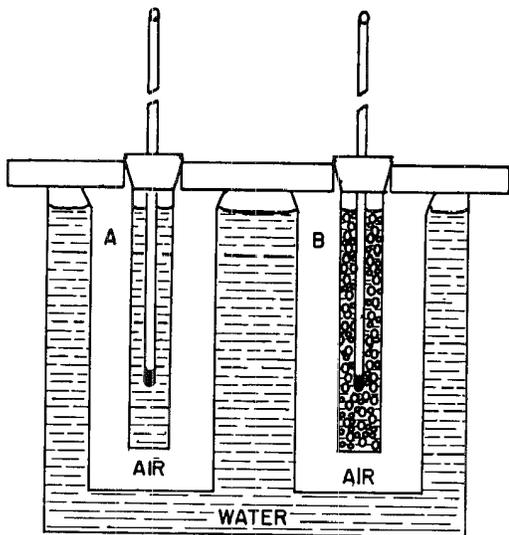


FIG. 2. Radiation calorimeter in use. Cup *A* contains water; cup *B* contains a soil-water mixture.

dry materials were placed in the calorimeter cup; distilled water was added until saturation was reached. It was necessary to soak the fine-textured soils overnight.

Both cups were filled to the same level, about four-fifths full. Rubber stoppers and thermometers were then inserted. The thermometers were submerged to about two-thirds the depth of the cup. The cups were then partially submerged in boiling water until the thermometers both read about 50°C. Then the cups were removed and, after all water was quickly wiped from their surfaces, were placed in the calorimeter.

While they cooled in the calorimeter, each thermometer was read at 1-minute intervals for a 1-hour period. Stem magnifiers were used to facilitate readings. From these readings cooling curves were established for each cup (fig. 3).  $\Delta T$  was arbitrarily chosen from 37° C. to 29° C. and from the cooling curves the time  $\Delta t$  it took each cup to drop through that interval was found.

Once the above procedure was completed, soil specific heat was computed as follows:

From equation [8] it is evident that

$$\frac{\Delta Q_A}{\Delta t_A} = (C_A + c_w m_{wA}) \frac{\Delta T}{\Delta t_A} \quad [11]$$

$$\frac{\Delta Q_B}{\Delta t_B} = (C_B + c_s m_s + c_w m_{wB}) \frac{\Delta T}{\Delta t_B} \quad [12]$$

From equation [10] it follows that

$$(C_B + c_s m_s + c_w m_{wB}) \frac{\Delta T}{\Delta t_B} = (C_A + c_w m_{wA}) \frac{\Delta T}{\Delta t_A} \quad [13]$$

$$c_s = \frac{(C_A + c_w m_{wA}) \Delta t_B - (C_B + c_w m_{wB}) \Delta t_A}{m_s \Delta t_A} \quad [14]$$

where

$\Delta T$  = temperature drop in °C. for cups *A* and *B*

$\Delta t_A$  = time in minutes for cup *B* and contents to drop  $\Delta T$

$\Delta t_B$  = time in minutes for cup *A* and contents to drop  $\Delta T$

$m_{wA}$  = grams of water in cup *A*

$m_{wB}$  = grams of water in cup *B*

$m_s$  = grams of soil

$c_w$  = specific heat of water in cal./g. °C

$c_s$  = specific heat of soil in cal./g. °C.

$C_A$  = thermal capacity of cup *A* and thermometer in cal./°C.

$C_B$  = thermal capacity of cup *B* and thermometer in cal./°C.

and

$$C(A \text{ or } B) = (V_{Th}) (0.46 \text{ cal./cm.}^3 \text{ °C.}) + (m_c) (0.090 \text{ cal./g. °C.})$$

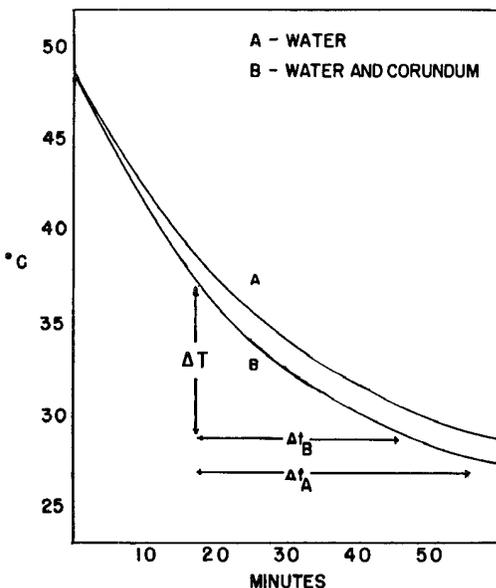


FIG. 3. Cooling curves for corundum and water mixture (*B*) and water (*A*).  $\Delta t_a$  is the time necessary for curve *A* to drop  $\Delta T$ ;  $\Delta t_b$  is the time which it took curve *B* to drop  $\Delta T$ .

TABLE I

Soil and mineral specific heats as determined with a radiation calorimeter and their comparison with values determined by the "method of mixtures"

Materials	Radiation Method									Method of Mixtures				
	37°C to 29°C									Av.	Lang	Ulrich approx. 100°C	White 0 to 100°C	Patten approx. 100°C.
Derby loamy sand..	0.22	0.20	0.23	0.18	0.20					0.21				
Cass loam.....	0.23	0.20	0.21	0.21						0.21				
Solomon clay.....	0.28	0.22	0.26	0.24	0.31	0.32	0.24	0.26		0.27				
Sutphen silty clay..	0.26	0.27	0.26	0.25						0.26				
Sarpy fine sandy loam.....	0.21	0.22	0.22	0.22						0.22				
Coarse quartz sand..	0.18	0.20	0.19	0.20	0.18					0.19	0.198	0.191	0.1868	0.1901
Hematite.....	0.17	0.15	0.16	0.18						0.16	0.163	0.165		
Apatite.....	0.20	0.19	0.22	0.22						0.21		0.183		
Albite.....	0.22	0.24	0.24	0.18						0.22			0.1948	
Microlite.....	0.21	0.21	0.21							0.21			0.1871	
Lithographic limestone.....	0.23	0.22	0.21							0.22	0.206*	0.208*		
Dolomite.....	0.23	0.22	0.23							0.23		0.222		
Corundum.....	0.19	0.18	0.18	0.21	0.19	0.20	0.20	0.18	0.19	0.19				

\* Values for CaCO<sub>3</sub>.

where

(*V<sub>th</sub>*) = volume of submerged portion of thermometer in cm.<sup>3</sup>

*m<sub>c</sub>* = mass of cup in grams

0.46 cal./cm.<sup>3</sup> = thermal capacity of thermometer

0.090 cal./g. °C. = specific heat of brass cups

The thermometers used in this experiment were of laboratory grade with a range of 0° to 51°C. Subdivisions were marked in 0.1°C. intervals. Arbitrarily one was chosen as correct; the other was corrected to it by a calibration curve. This curve was established by submerging the two thermometers in distilled water heated to 50°C. and reading each as the stirred water cooled to 25°C. The thermometers were submerged to the same depth as in the cups.

The volumes of that portion of the thermometer submerged in the cups were determined by submerging them to the same depth in a water-filled buret tube and noting the displacement.

RESULTS

One set of cooling curves is shown in figure 3. All materials gave curves of the same general shape.

Table 1 gives the specific heat results for several soils and minerals. These results are compared with those reported by earlier investigators who used the "method of mixtures" (4, 5, 6, 8).

As shown in table 1, there is considerable variation in specific heat values for any one material when determined with a radiation calorimeter. The average of several values did, however compare favorably with values determined by the "method of mixtures." Among the minerals this was especially true for quartz sand, hematite, dolomite, and corundum; the other minerals varied by less than 0.03 cal./g. °C. In the above comparisons it should be recognized that the specific heat of a mineral will vary slightly in the interval 37°C. to 100°C.

Of special interest is the average value of corundum. Corundum has been recommended by the calorimetry conference as the standard reference for heat capacity measurements from 14°K. to 1200°K. Values for this range are reported by Ginning and Furukawa (2). At 310°K. (36.84°C.) the specific heat capacity of corundum is 0.1912 cal./g. °C. This agrees very closely with the average value for corundum found by the radiation method.

Since there are no reported values with which to exactly compare the soil specific heats, no

definite conclusions can be made regarding the accuracy of this method with soils. Patten (5), however, did report the specific heats of some similarly textured soils as follows: Podunk fine sandy loam, 0.1850 cal./g.°C.; Leonardtown silt loam, 0.2374 cal./g.°C.; Hagerstown loam, 0.2004 cal./g.°C.; and Galveston clay, 0.2307 cal./g.°C. Thus, using Patten's work as a reference, it appears that the values for Solomon clay and Sutphen silty clay may be high.

In view of the assumptions made in developing the radiation method, all values determined with the radiation calorimeter must be considered approximate. The suitability of this method can be judged only in reference to the standards and goals set by the experimenter.

#### SUMMARY

The theory and method of making specific heat capacity determinations with a radiation calorimeter are given.

Approximate soil and mineral specific heat capacities are easily and quickly determined with the radiation calorimeter. A minimum of instruction is needed to make these determinations.

The average of several determinations gave values closely approximating the known specific

heat capacities for several minerals. Corundum, a calorimetric reference, was especially close.

Values for fine-textured soils appeared high compared with the values for similarly textured soils reported by Patten.

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