A Calorimetric Method for Measuring Water Content of Hailstones

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ABSTRACT

A calorimetric method for measuring the liquid water content of hailstones has been developed. When parameters such as the radiative losses of the system and the changes in heat capacity of the apparatus are eliminated by performing all measurements under identical conditions, the temperature drop is linearly related to the mass of ice melted. For equal masses the temperature drop is smaller if water is present, and there is a linear relationship between the changes in temperature drop and the amount of water present. The water content of hailstones can then be determined from a calibration plot of the changes in temperature drop as a function of the water content of ice.

1. Introduction

Cloud physicists are divided in their opinions on the subject of the presence or the absence of water in hailstones. Some accounts of the presence of water are found in the literature. Weickmann (1953) mentions an observation of Brooks in 1943 of hail which consisted of only a hollow shell and of one stone "that had the unfrozen water still in it, for the bubbles moved about as it was tilted." He also mentions a similar observation by Arenberg in 1941 for a smaller stone. According to Weickmann, Floegel in 1872 observed stones about 10 mm in length under the microscope and found the "upper part composed of many small cells which contained spherical spaces still filled with water." Browning (1963), referring to spongy hailstone growth, writes that "embryos re-entering the updraft at a lower level may grow persistently wet, being unable to lose heat sufficiently rapidly to freeze immediately all the accreted droplets."

List (1961) comments that the major difficulty in studying hailstones arises from the fact that they have to be transported and stored before examination at temperatures below 0C. Consequently, phase transitions occur and freeze the "liquid water often contained in the system of capillaries within the ice particles. Since at present there is no known method for detecting subsequently in the frozen state whether such a transition has taken place, an attempt has to be made at measuring any such liquid water content directly ⋯ . What is also urgently called for is that due importance be attached to this factor and the necessary apparatus prepared for establishing the presence of liquid water in hailstones."

Radar measurements offer support to the model of hail with a large water content at 15,000 to 30,000 ft (Atlas *et al.*, 1964). However, the amount of freezing which takes place before the hail reaches the ground is not known.

2. Theory

The water content of hailstones was determined experimentally in a calorimeter. Since the calorimeter operates adiabatically, the heat lost by the contents of the calorimeter must equal the heat gained by the ice sample; therefore, the final temperature of the melted ice and calorimeter bath are the same. The heat lost by the water is manifested by the temperature drop of the water in the calorimeter. The heat gained by the ice is equal to the heat necessary to melt the ice at 0C and then to raise the temperature of the melted ice to the final equilibrium temperature of the calorimeter. For a sample of pure ice at 0C, these relationships can be expressed mathematically in the following form where the right hand side of the equation is the heat lost by the calorimeter bath, while the left hand side is the heat gained by the ice, i.e.,

$$g_i(L_f+C_{p_w}t_f)=(K+MC_{p_w})\Delta t, \qquad (1)$$

where

g_i = grams of ice,
L_f = heat of fusion of ice (cal gm^{-1}),
t_i = initial temperature of bath before ice is introduced (°C),
t_f = final equilibrium temperature after the ice is melted (°C),
$\Delta t = t_i - t_f$,
K = heat capacity of apparatus [cal(°C)$^{-1}$],
M = total mass of water initially in the calorimeter (gm),
C_{p_w} = heat capacity of water [cal gm^{-1}(°C)$^{-1}$].

Solving for g_i, we have

$$g_i=\frac{(K+MC_{p_w})}{(L_f+C_{p_w}t_f)}\Delta t. \qquad (2)$$

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A plot of the grams of ice versus the temperature drop of the calorimeter should be linear with slope $(K+MC_{p_w})/(L_f+C_{p_w}t_f)$. For pure ice this plot will be referred to as the baseline.

For the slope of this plot to be constant, it is seen that K, M and t_f must remain constant along with the physical quantities L_f and C_{p_w}. K is kept constant by making t_i constant. C_{p_w} is strictly a function of temperature and can more accurately be represented by a polynomial of the form $a+bt+ct^2$, but over the small temperature ranges covered by the method presented here it can be considered as constant.

For the amount of ice weighed in these experiments (between 2 and 15 gm) Δt varies between 0.50 and 3.00, a maximum difference in t_f of 2.5C. The term $C_{p_w}t_f$ is small in comparison to L_f, and a variance of t_f of 2.5 results in a maximum error of less than 1 per cent.

If a sample is made up of g_i gm of ice and g_w gm of water at 0C, the heat balance becomes

$$g_iL_f+(g_i+g_w)C_{p_w}t_f=(K+MC_{p_w})\Delta t, \quad (3)$$

which can be rearranged to give

$$(g_i+g_w)=\frac{(K+MC_{p_w})}{(L_f+C_{p_w}t_f)}\Delta t+\frac{g_w}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}. \quad (4)$$

It can be seen that a plot of the grams of ice plus the grams of water in the hailstone sample versus the temperature drop of the calorimeter has the same slope as a plot of Eq. (2). The plots for water and ice (lines B and C, Fig. 1) are parallel to the plot for pure ice (line A, Fig. 1) since the slope is the same. In order for the slope to be constant, the same conditions apply as for ice alone. As the amount of water g_w in the hailstone is increased, the intercept

$$g_w\Big/\left(1+\frac{C_{p_w}t_f}{L_f}\right)$$

increases. The grams of water in the sample can be determined in the following manner.

Eq. (4) can be written in the form

$$(g_i+g_w)=(S\Delta t)+a_0, \quad (5)$$

where S is the slope and a_0 is the intercept when $\Delta t=0$.

If we let

$$\alpha=\frac{C_{p_w}t_f}{L_f},$$

then

$$g_w=a_0(1+\alpha). \quad (6)$$

For any given sample containing water and ice, the experimental point obtained will lie above the baseline on a plot of (g_i+g_w) vs. Δt. The water in the sample can be found by drawing a line through the point parallel to the baseline. The grams of water in this sample can be found by multiplying the intercept $(\Delta t=0)$ by the dimensionless parameter $(1+\alpha)$.

A second method of obtaining the water content of the hailstone can be developed in the following manner. Eq. (4) will be written for two samples A and B (Fig. 1) as

$$(g_i+g_w)_{\rm A}=\frac{\left(\dfrac{K+MC_{p_w}}{L_f}\right)}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}(-\Delta t_{\rm A})+\frac{g_{w\rm A}}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}, \quad (7)$$

$$(g_i+g_w)_{\rm B}=\frac{\left(\dfrac{K+MC_{p_w}}{L_f}\right)}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}(-\Delta t_{\rm B})+\frac{g_{w\rm B}}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}. \quad (8)$$

Subtracting (7) from (8),

$$(g_i+g_w)_{\rm A}-(g_i+g_w)_{\rm B}$$

$$=\frac{\left(\dfrac{K+MC_{p_w}}{L_f}\right)}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}[(-\Delta t_{\rm A})-(-\Delta t_{\rm B})]+\frac{(g_{w\rm A}-g_{w\rm B})}{\left(1+\dfrac{C_{p_w}t_f}{L_f}\right)}. \quad (9)$$

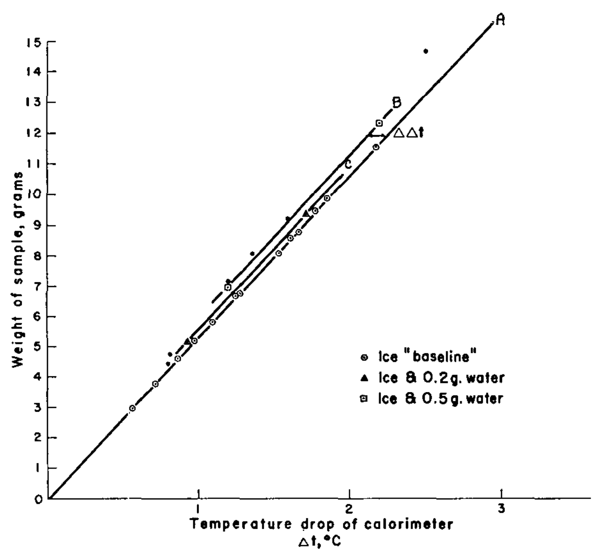

FIG. 1. Calibration curve for ice cubes and ice cubes with water. From this plot $\Delta\Delta t$ can be obtained and the water content of the sample then read from Fig. 2.

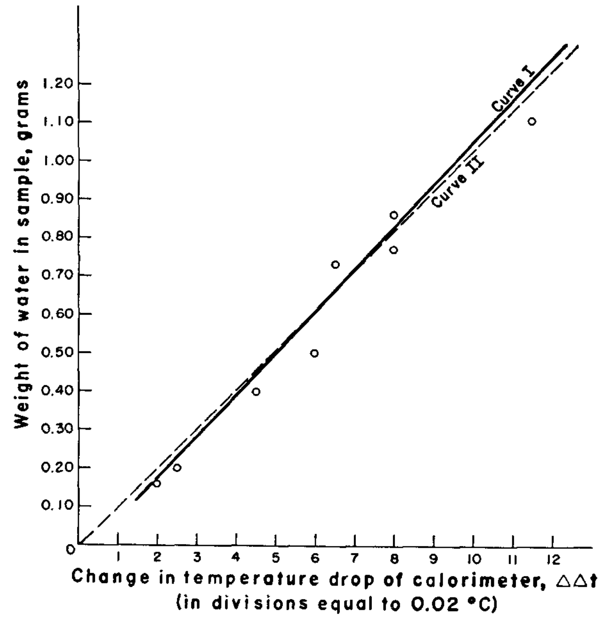

FIG. 2. Curve I: experimental. Water content in cavities drilled in ice cubes vs. $\Delta t_{\text{ice}} - \Delta t_{\text{ice+water}} = \Delta\Delta t$. Curve II: theoretical.

If we let

$$\alpha = \frac{C_{p_w} t_f}{L_f},$$

$$\beta = \frac{K + MC_{p_w}}{L_f},$$

then

$$(g_i + g_w)_A - (g_i + g_w)_B = \frac{\beta}{(1+\alpha)} (\Delta t_B - \Delta t_A) + \frac{(g_{w_A} - g_{w_B})}{(1+\alpha)}. \quad (10)$$

If A is the baseline for ice, then $g_{w_A} = 0$ and

$$(g_i + g_w)_A - (g_i + g_w)_B = g_{i_A} - (g_i + g_w)_B.$$

If values of $(g_i + g_w)_B$ and Δt are plotted on Fig. 1, the horizontal distance between an experimental point and the baseline is precisely $\Delta\Delta t$ where $\Delta\Delta t = \Delta t_B - \Delta t_A$. Along this horizontal line, $g_{i_A} - (g_i + g_w)_B = 0$, i.e.,

$$g_{i_A} - (g_i + g_w)_B = 0 = \frac{\beta}{(1+\alpha)} \Delta\Delta t - \frac{g_w}{(1+\alpha)}. \quad (11)$$

Therefore,

$$g_{w_B} = \beta \Delta\Delta t. \quad (12)$$

As can be seen from Eq. (12), a plot of the grams of water vs. $\Delta\Delta t$ will be linear with slope β. This plot is shown in Fig. 2. By obtaining $\Delta\Delta t$ for each sample of known water content g_w, one can obtain a calibration plot of g_w versus $\Delta\Delta t$. Once this calibration has been obtained, the amount of water in a sample of unknown water content can readily be determined. The weight of the sample and the temperature drop of the calorimeter are plotted on Fig. 1. From this point, $\Delta\Delta t$ can be determined and the water content of the sample can then be evaluated from Fig. 2 from the intersection of $\Delta\Delta t$ with the calibration curve.

3. Apparatus

Calorimeter. The calorimeter (Fig. 3) consists of a Dewar flask (A) within a stainless steel flask surrounded by thick, evacuated walls (B). The jacket (C), between the two flasks, is filled with water maintained at ambient temperature, i.e., the initial temperature of the distilled water inside the Dewar. A styrofoam ring (D) minimizes the losses by evaporation and radiation from the jacket. The top is sealed with a cork lid (E), held tightly in place by wing nuts.

The temperature is read from a Model 19400 Beckmann thermometer (F) graduated to cover 6C with readings within 0.001–0.002C. The immersible heater (G) is an infrared coil encased in quartz and connected in parallel, through a rectifier, to a voltmeter and in series with an ammeter. The voltage is regulated with a variac. The total electrical input used is 23.25 W. The stirrer (H) consists of a glass rod set in a Teflon bushing to prevent heating from the motor; it has three paddles at different levels and is driven by a dc servo-motor controlled by means of a transistorized

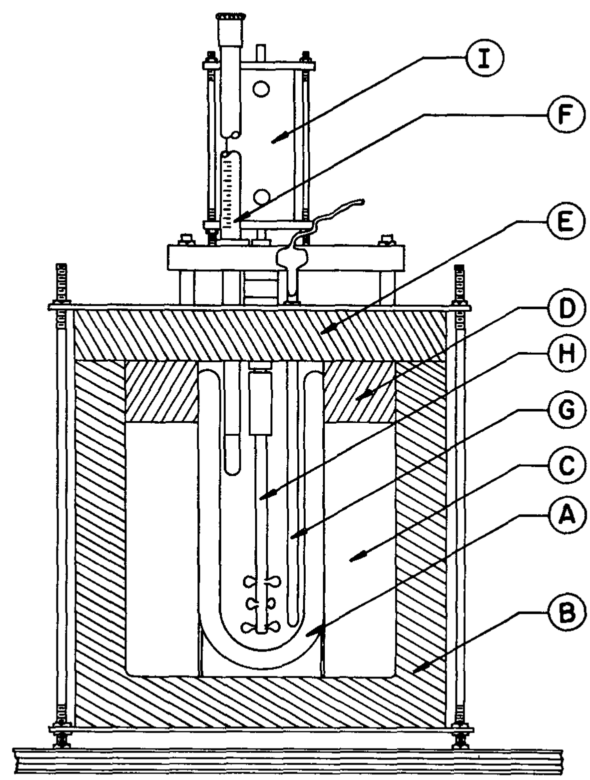

FIG. 3. Schematic drawing of the apparatus. See text for details.

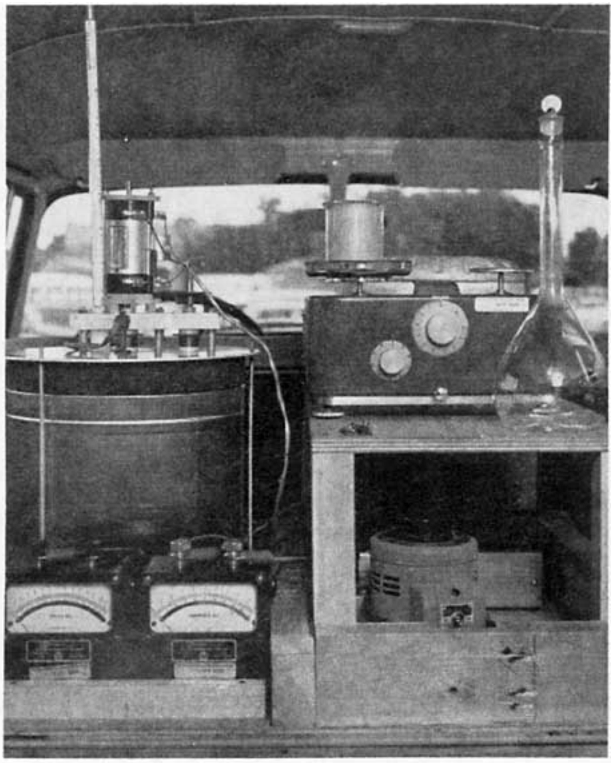

FIG. 4. Equipment in the truck.

unit. The scale used was a torsion balance damped for rapid weighing to within ±0.05 gm.

A refrigerator, set at slightly less than 0C was used to prevent the hailstones for calibration from melting and to allow them to reach a temperature near 0C. The hailstones were placed on a plastic screen.

Field equipment. The equipment for field work was transported in a Dodge Power Wagon equipped with a 110V power supply. The calorimeter was clamped to a table fastened to the floorboard (Fig. 4).

A citizens-band transmitter-receiver was used to obtain from the New Raymer radar site operated by Colorado State University information on weather conditions for an area of about 100-mile radius from the location of the radar. When a cloud had a high top on the radar screen, hail was assumed probable and the truck operators were alerted and directed to the general storm area. In three cases, 2, 9 and 10 July 1965, the radar operator directed the truck to the center of the storm as hail was beginning to fall, and these storms supplied the hailstones for the experiments.

4. Procedure

Distilled water at ambient temperature was poured into the jacket and 500 gm were poured into the Dewar. Preliminary measurements indicated that the system reached equilibrium within a few minutes. The temperature inside the Dewar was measured, the apparatus covered, the stirrer turned on, and the water in the Dewar heated to about 4C above the measured temperature. This initial temperature was the same for each run. After the Beckmann thermometer reached a steady reading, the initial temperature was recorded. The hailstones were put in beakers lined with blotting paper to absorb the water on the surface and weighed by difference and then immediately introduced into the calorimeter. When the Beckmann thermometer again reached a steady temperature, this temperature was recorded and the temperature drop Δt evaluated. The water content of the hailstones was then read from Fig. 2. The assumption that the hailstones were at 0C when they were put into the calorimeter is justified in Section 7.

If several runs are desired, the hailstones can be collected in insulated containers and put on a screen in a refrigerator kept 1–2C above 0C. This would prevent freezing if any water is contained in the hailstone, and the amount of melting which takes place at the surface is small.

5. Calibration

Calibration with ice cubes. Ice cubes were used to calibrate the calorimeter, and a straight line plot of grams of ice vs. temperature depression was obtained (Fig. 1, baseline).

The ice, kept at −25C in the refrigerator, was left in a 0C water-ice bath to reach equilibrium. Measurements made with a thermocouple frozen inside a $4\times3\times2.2$ cm^3 ice cube indicate that one-half hour is required for the center of the cube to reach 0C, without stirring. All cubes were left in the bath at least one-half hour. A similar calibration was carried out for ice containing water. The procedure was to drill a hole in the ice cube, weigh it, introduce water at 0C, and weigh the total mass of ice plus water. Lines parallel to the ice baseline were obtained with ice cubes containing 0.2, 0.4 and 0.5 gm water (Fig. 1).

Calibration with hailstones. No difference was observed between the calibrations with hailstones and with ice cubes when the frozen hailstones were kept at 1 to 2C for 15 min on a screen in the refrigerator and then left at room temperature for 3 or 4 min to insure a temperature of 0C at the center of the stone. Since it is obvious (Fig. 5) that milky hailstones soak up water into their network of connected chambers, this procedure was preferred to that of soaking the stones in a water-ice bath.

The hailstones with clear outer shells do not absorb water, as can be seen from Fig. 5.

6. Precision

The best fit to points in Figs. 1 and 2 was obtained by the least square line method. The standard deviation method indicates that the error in the grams of water read from Fig. 2 is ±0.1. It follows that a

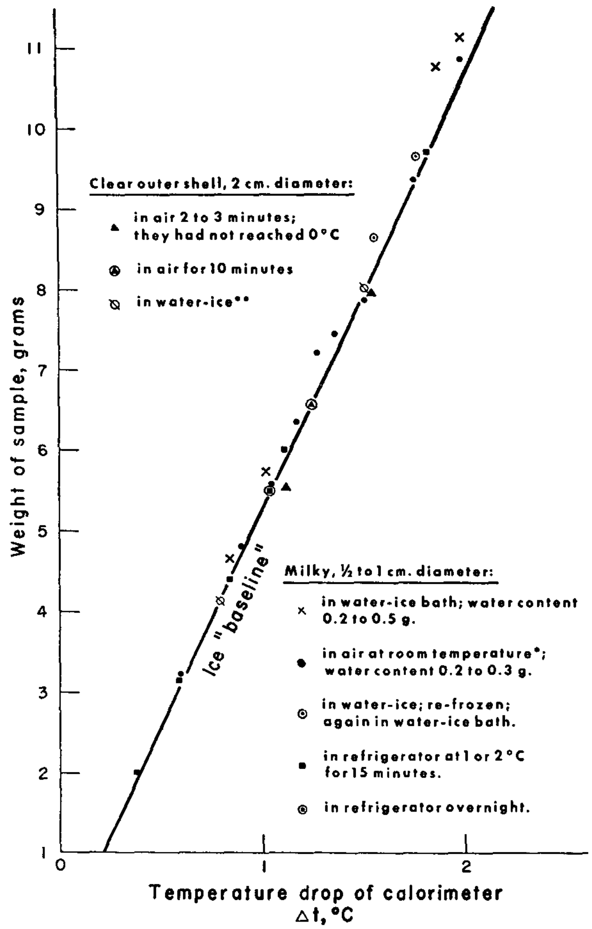

Fig. 5. Laboratory calibration with hailstones.

* There was much wetting and this water may have entered the channels.

** There was no absorption of water from bath.

deviation of ± 0.1 gm of water is within experimental error, and that by this method one should be able to detect 0.2 gm of water with confidence.

Since the time for each run is short and approximately the same for all runs, the error from radiative losses of the system cancel out.

Evaporation was small enough not to affect the measurements because the amount of water in the Dewar is large in comparison to that of ice. The heating effect of stirring was determined to be negligible. The rate at which the system reached thermal equilibrium was determined by measuring, with thermocouples and recording on a Honeywell Electronik 19 Recorder, the temperature at three levels in the calorimeter. The stirring was found to be adequate.

The heat capacity of the apparatus was kept a constant by heating the system to the same initial temperature for all runs. The weight of the water in the Dewar was kept to ± 1 gm. A difference of 1 gm in weighing produces, for 14 gm of ice and $t_i = 30$C, a change of 0.4 per cent in Δt, which is within experimental error. The weighing of the hailstones was within ± 0.05 gm which would produce a Δt of 0.01C, well below the experimental error. For errors due to changes in t_f it should be borne in mind that to a certain increment in t_i (Δt_i) corresponds an increment in t_f (Δt_f) which is equal to Δt_i for the same amount of ice provided the increment is not large (2 or 3C). If measurements have been carried out at different values of Δt_i, one of them will have to be chosen as the "baseline" and a correction made to the other values using Eq. (2). For a calibration t_i equal to 27C:

$$K + MC_{p_w} = 564.96, \qquad \left(\frac{564.96}{80+27}\right) = 5.28,$$

$$t_i + \Delta t_i = Z,$$

$$\frac{K + MC_{p_w}}{80+Z} = \frac{564.96}{80+Z} = \text{slope},$$

$$\text{slope} \times \Delta t = \text{grams of ice},$$

$$5.28 \times \Delta t - \text{slope} \times \Delta t = \text{correction}.$$

7. Discussion of results

Evaluation of the measurements. The values of the calibration carried out in the field using hailstones from the 2 and 9 July storms are shown in Fig. 6. These hailstones were previously frozen in dry ice and then put in plastic bags in a water-ice bath. Fig. 6 shows that the points of this calibration (solid dots) and those of the laboratory calibration (solid triangles) correspond to hailstones which contain approximately the same amount of water trapped in the cavities. This water was absorbed from the bath. Larger stones can absorb more water and the slope becomes steeper with increasing size.

The values obtained with the fresh hailstones sampled from the 2, 9 and 10 July storms, and equilibrated in plastic bags in a water-ice bath are also shown in Fig. 6. In general, the water content of these fresh hailstones is slightly higher than that of the calibration stones. The average depression per gram for the calibration samples is 0.176C and for the fresh ones is 0.170C. This indicates that the fresh stones contained some water upon reaching the ground. However, the test is not conclusive because of the water-ice bath used to bring the temperature of the sampled stones to zero. For future measurements this uncertainty can be removed by keeping the hailstones at 1 or 2C on a rack in a refrigerator to prevent freezing of the water present, if any, as discussed in Section 5. If we assume that the small amounts of water shown on Fig. 6 are real then the interconnected cavities and canals were almost empty when the stones reached the ground or they shed most of their water on impact. The latter alternative appears improbable since there was no evidence of water oozing out of the stones

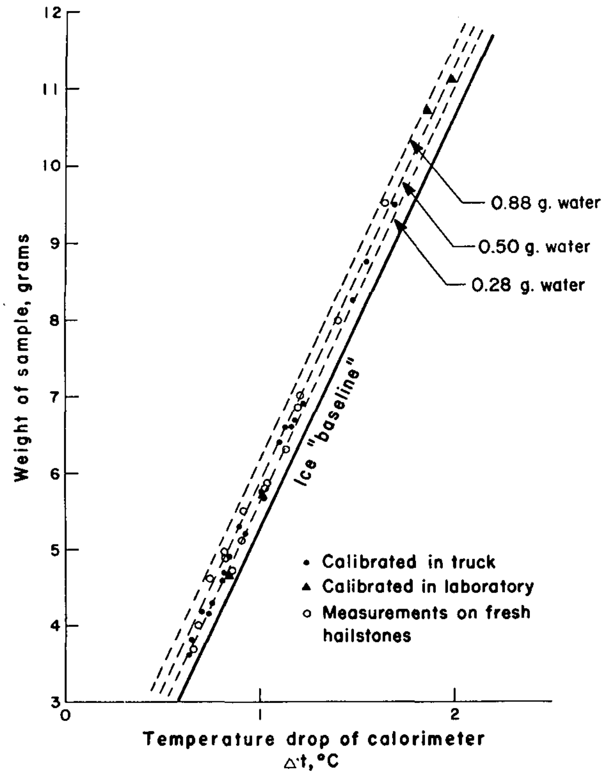

FIG. 6. Calibration points of frozen hailstones (solid dots and solid triangles) and measurements on fresh hailstones (open circles).

	Average Δt	Average $\Delta\Delta t$	Average water content per gram	Per cent
For fresh hailstones	0.170	0.018	0.08	8
For calibration hailstones	0.176	0.012	0.06	6

after collection nor of appreciable cracking in the collected stones.

The small difference in Δt per gram (0.006C) between fresh and frozen hailstones reveals, if real, a theoretical water content of 0.08 gm per gram of fresh hailstone and 0.06 gm per gram of calibration hailstones, or 8 and 6 per cent respectively. The difference, 2 per cent, would then correspond to the water content of the fresh hailstones.

In conclusion, the hailstones which fell near New Raymer, Colo., on 2, 9 and 10 July of 1965 contained, at the most, less than the 0.2 gm of water which can be detected confidently by the present method. Moreover, all evidence suggests that the network of capillaries contained no water but only air.

Evaluation of the method. From the considerations presented above, the conclusion can be drawn that the method can easily detect 0.2-0.3 gm of water in a hailstone of any size. The reliability of this method depends on two main assumptions.

1) The hailstones are at 0C when they are put into the calorimeter. The ideal situation is where the hailstones can be introduced into the calorimeter immediately upon reaching the ground. This means that the hailstones have to be at 0C when they reach the ground. If the freezing level is higher than 3 km above ground this is a reasonable assumption according to Stauder and Hitschfeld (1965), who treated the problem of thermal gradients in, as well as surface temperatures of, hailstones.

Fig. 7 shows that when the freezing level is at 3 km, a hailstone of 0.48 cm radius reaches a surface temperature of 0C at 2 km above ground, one of 0.79 cm radius at 1.3 km, and one of 1.1 cm radius at 0.8 km.

If the hailstones have to be stored for one-half to one hour to allow time for making several successive runs, the fresh hailstones can be kept in a constant temperature air bath as near 0C as possible to prevent all but slight melting at the surface but not below 0C to prevent freezing of water, if present. Presumably there will be no shedding from the cavities nor any incorporation into the cavities of water from melting.

2) The hailstones do not shed any other water than that from superficial melting. Further studies are warranted to establish conclusively whether water is shed upon impact with the ground or during collection and storing and to develop a method to distinguish between water from surface melting and water shed by the cavities.

Since the calibration with hailstones of clear ice outer shell indicates that water does not permeate the

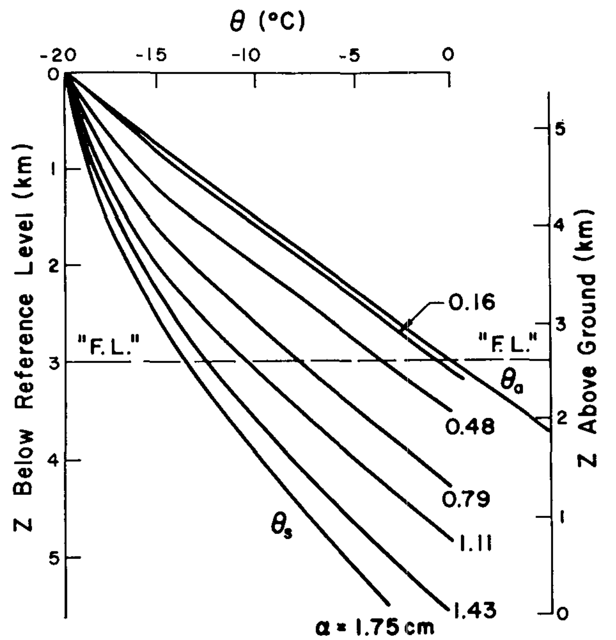

FIG. 7. Surface temperature of hailstones of different radii as a function of distance fallen through clear air. Air temperature θ_a is shown. (No updraft or evaporation are considered.) From Stauder and Hitschfeld (1965).

cavities of the milky core, it is valid to assume that no water can filter out through the clear layers. Consequently, they can be stored at 0C without fear of water draining from the cavities. These hailstones then make ideal test samples.

8. Temperature measurement of hailstones below 0C

Cubes that were introduced into the calorimeter directly from a dry ice bucket show an appreciably larger depression due to the greater amount of heat extracted from the calorimeter to heat the ice to 0C before fusion can begin.

This could be used to determine the average temperature of hailstones below 0C. However, a calibration would have to be carried out with ice at known temperatures below 0C and a curve of grams of ice at a certain temperature vs. $\Delta\Delta t$ be plotted.

9. Conclusions

a) The method described is sufficiently accurate to detect liquid water contents of hailstones, or of any ice samples, as small as 0.2 gm.

b) The experimental calibrations with pure ice or with frozen hailstones agree with theoretical calculations.

c) Although the results are of a preliminary nature, they show that the 15 samples of fresh hailstones sampled in northeastern Colorado contained less than 0.2 gm of liquid water, i.e., about 2 per cent by weight.

Further measurements, incorporating the refinements discussed above, are being planned for the next hail season in the High Plains and for next spring in East Africa.

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