

by

R. Perla ^{1/} and E.R. LaChapelle ^{2/}INTRODUCTION

In his critique of methods for measuring liquid water in snow Colbeck (1978) resurrected a paper by Bader (1948) on alternatives to calorimetry. One of Bader's suggestions which we call the "dilution method" is especially attractive because of its speed and simplicity: an aqueous stock solution (at 0°C) containing a small (<1%) concentration of dissolved impurity is mixed thoroughly into a wet snow sample taking every possible precaution to maintain the mixture at 0°C. The mixture is decanted from the sample; the liquid water originally in the sample is computed from the impurity concentration ratio (mixture to stock). Bader proposed using a ~1/2% maltose stock solution and measuring the concentration ratio with a polarimeter. He did not have a chance for experiments, but believed the dilution method should be highly accurate.

DILUTION METHOD

Assume a 0°C stock solution of mass S and impurity concentration C_s is mixed thoroughly into a wet snow sample. C_s is small enough that the melting point depression of the mixture is small, but large enough to be well above the impurity concentration C_w of the liquid water in the sample. If the decanted mixture has an impurity concentration C_m , then the liquid W that was in the sample is computed from

$$(S + W)C_m = SC_s + WC_w \quad (1)$$

which can be rearranged as

$$W = S \left(1 - \frac{C_m}{C_s}\right) / \left(\frac{C_m}{C_s} - \frac{C_w}{C_s}\right) \quad (2)$$

Note that C_s , C_m , and C_w need not be determined since only ratios are required; this greatly simplifies the analytical chemistry. An accurate determination of C_m/C_s is crucial. The ratio C_w/C_s can be set very small ($\ll 1.0$) by selecting a suitable impurity.

STOCK-MASS RATIO

If we divide both sides of (2) by the sample mass M, we obtain

$$\frac{W}{M} = \frac{S}{M} \left(1 - \frac{C_m}{C_s}\right) / \left(\frac{C_m}{C_s} - \frac{C_w}{C_s}\right) \quad (3)$$

where W/M is the liquid water per unit mass, usually expressed as a percentage 100W/M, and typically in the range 0% to 30%. Note from (3) that increasing the ratio of stock solution to mass (S/M) in a measurement of fixed W/M drives C_m/C_s closer to unity, and hence increases the instrumentation accuracy needed to find W/M to its level of accuracy. Also the greater S/M, the greater the probability of phase change error during mixing since it is difficult to maintain the stock solution at precisely 0°C. Thus, it seems advantageous to keep S/M as small as possible. However, the larger S/M, the greater the probability that the stock solution will mix homogeneously with the sample liquid water, and if S/M is too small it is difficult to mix and decant.

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The optimum range of S/M probably depends on snow structure -- high surface area structures such as newly fallen snow probably require relatively high S/M. Using coarse grained snow, we found it difficult to mix and decant with $S/M < 1.0$, and obtained best results with $1.0 < S/M < 2.0$.

If $S/M = 2.0$ then C_m/C_s must be measured to accuracy about ± 0.01 if W/M is to be accurate to about ± 0.02 (i.e. 2g of liquid water in 100g of sample mass). If $S/M = 1.0$, a measurement of C_m/C_s to about ± 0.01 gives W/M to about ± 0.01 .

INSTRUMENTATION POSSIBILITIES

C_m/C_s can be measured using polarimetry on optically active solutions, as suggested by Bader; using spectrophotometry or fluorometry on dyes, as suggested in a recent paper by Davis and Dozier (in preparation); using differential refractometry; using interferometry; etc. With expensive and specialized instrumentation in a careful laboratory environment, C_m/C_s can be measured to accuracy ± 0.001 or better. However, the handling problem of mixing at precisely 0°C , and the problem of incomplete mixing limit the overall accuracy (to perhaps ± 0.01 or ± 0.02), irrespective of instrument sophistication.

ELECTROLYTIC CONDUCTIVITY

We selected the method of electrolytic conductivity to measure C_m/C_s and C_w/C_s . Digital conductance meters are available for 1/10th the cost of the above mentioned optical instruments with comparative resolution and repeatability. (We obtained poor results in terms of resolution and repeatability using low cost spectrophotometers and fluorometers). Moreover, a conductance measurement is relatively fast since the operator simply dips a cell into the mixture, whereas in most optical measurements one must carefully transfer the mixture into small tubes or cuvettes, and sacrifice the advantage of averaging over a large volume of the mixture in a single reading.

Our stock solution was 0.01 N HCl , which has a specific conductance of $\sim 4.1\text{ m}\Omega^{-1}/\text{cm}$ at 25°C , and a meltpoint depression of $< 0.05^\circ\text{C}$. The snowmelt of our samples had specific conductance $< 25\ \mu\Omega^{-1}/\text{cm}$, hence C_w/C_s was less than 0.01.

We corrected for the intrinsic nonlinear relationship between concentration and conductance using

$$(C_m/C_s) = (G_m/G_s)^q \quad (4)$$

where specific conductance of mixture and stock solutions are respectively G_m and G_s , and q is an empirical constant. For HCl in the concentration range 0.005 N to 0.01 N , interpolation from tables of equivalent conductance at $T = 25^\circ\text{C}$ (the "compensation temperature" of our meter) gave $q = 1.0133$.

In preliminary dilution tests using water and stock solution (no snow), we found that C_m/C_s could be measured with a resolution of ± 0.01 maximum error band.

SAMPLE PREPARATION

Dry snow samples were collected from 3 - 4 month old, coarse grained layers which were located 10 - 50 cm above soil in a 150 cm deep mountain snowpack in the Canadian Rockies. The snow was compacted into cylinders to densities in the range $400 - 500\text{ kg/m}^3$. At time of collection, snow temperatures were in the range -2°C to -5°C . The cylinders were transported in insulated boxes (filled with precooled snow) to a refrigerated laboratory, and then stored for several hours at $0^\circ\text{C} \pm 1^\circ\text{C}$ prior to testing. The mass of the "dry" snow sample M_d was determined to $\pm 0.1\text{ g}$. This measure was used to select the amount (W_a) of distilled water to be added to the sample, and the amount (S) of 0.01 N HCl stock solution. W_a and S were weighed to $\pm 0.1\text{ g}$ in polyethylene bottles, which were then stored in 0°C ice baths in the refrigerated laboratory.

A total of 172 samples were prepared in 17 runs performed from 28 January to 19 March 84. The left-hand columns of Table 1 list the number of samples per run N , the average dry snow mass \bar{M}_d in the run, the average stock solution-dry snow mass ratio S/\bar{M}_d , and the range of added water W_a .

Table 1. Sample data and errors.

Run	Samples in run N	Mean dry snow mass \bar{M}_d 1/ (g)	Mean stock to mass ratio S/\bar{M}_d (g/g)	Water added to samples W_a 1/ (g)	Water measured in samples W_m 1/ (g)	Error per 100 g of dry sample mass 2/		
						Mean of absolute 3/ (g/100 g)	Mean of algebraic 4/ (g/100 g)	Worst case 5/ (g/100 g)
1	15	88	2.28	0 to 45	1 to 43	2.65	+2.65	+8.74
2	15	105	0.95	0 to 45	1 to 35	3.89	-3.08	-12.76
3	15	117	1.51	0 to 47	4 to 36	3.95	+0.16	-9.71
4	15	108	1.75	0 to 47	2 to 44	2.03	-0.88	-5.37
5	15	112	2.01	0 to 46	4 to 47	2.21	+0.83	-4.22
6	15	112	1.74	0 to 43	-1 to 43	1.67	-1.41	-5.23
7	15	111	1.76	0 to 42	-1 to 39	1.25	-0.86	-3.12
8	15	109	1.74	0 to 43	1 to 43	0.65	-0.03	-2.29
9	7	474	1.75	0 to 152	4 to 165	2.53	+2.53	+3.51
10	7	451	1.49	0 to 149	5 to 158	1.16	+1.16	+1.98
11	7	440	1.26	0 to 149	1 to 155	0.88	+0.88	+1.53
12	7	445	1.26	0 to 150	1 to 158	0.81	+0.81	+1.69
13	6	887	1.25	0 to 256	8 to 273	1.65	+1.65	+1.85
14	6	863	1.26	0 to 252	3 to 214	2.18	-1.60	-4.54
15	4	1469	1.25	272 to 310	296 to 318	1.13	+0.89	+1.77
16	4	1920	1.24	369 to 415	360 to 412	0.59	-0.02	-1.06
17	4	1824	1.26	350 to 371	388 to 404	1.93	+1.93	+2.53

1/ Measurements were to nearest 0.1 g

$$2/ \text{ Error} = E_i = 100 \left[\frac{W_m^{(i)} - W_a^{(i)}}{\bar{M}_d^{(i)}} \right]$$

$$3/ \text{ Mean of absolute errors} = \left[\sum_{i=1}^N |E_i| \right] / N$$

$$4/ \text{ Mean of algebraic errors} = \left[\sum_{i=1}^N E_i \right] / N$$

5/ Worst of N sample errors

TEST PROCEDURES

The procedure for runs 1 - 8, which were restricted to relatively small M_d (~100 g) was to place each dry snow sample in a stainless steel beaker surrounded by a 0°C ice bath in a Dewar flask. The snow was disaggregated and stirred within the beaker to raise the snow temperature to 0°C from the initial storage temperature < 0°C. The distilled W_a was poured onto the snow, and as quickly as possible (to minimize phase change) the stock solution S was added to the wet snow ($M_d + W_a$) in the beaker. The mixture was stirred vigorously for at least one minute, then decanted into polyethylene bottles through coarse filter paper which withheld ice particles that floated in the mixture.

M_d was increased in runs 9 - 17 where mixing and sometimes vigorous shaking was performed in a variety of containers at the ambient laboratory temperature (0°C ± 1°C) without taking precaution to use an ice bath around the container.

In preliminary tests, we found accuracy improved if all the available mixture was decanted. The decanted mixture was stored for several hours until reaching room temperature, close to the compensation temperature (25°C) of our conductance meter. In order to further minimize the conductance variation with temperature, G_s and G_m were measured in rapid sequence:

$$G_s^{(1)}, G_m^{(1)}, G_s^{(2)}, G_m^{(2)}, \dots \text{etc.}$$

The ratio G_w/G_s was about 1/400, but could be a more significant factor depending on the ionic impurities in the snowmelt.

RESULTS

Errors for each run are shown in the right-hand columns of Table 1. The worst results occurred in the first three runs, and are probably due to inexperience with the method, -- the selections of S/M were not optimum, the mixing was probably too timid and incomplete, and full volume of the mixture was not decanted. The method seems to require a vigorous mixing and/or shaking for over a minute, although we cannot say when mixing is too prolonged in connection with phase change errors. All 172 sample points are plotted in Figure 1.

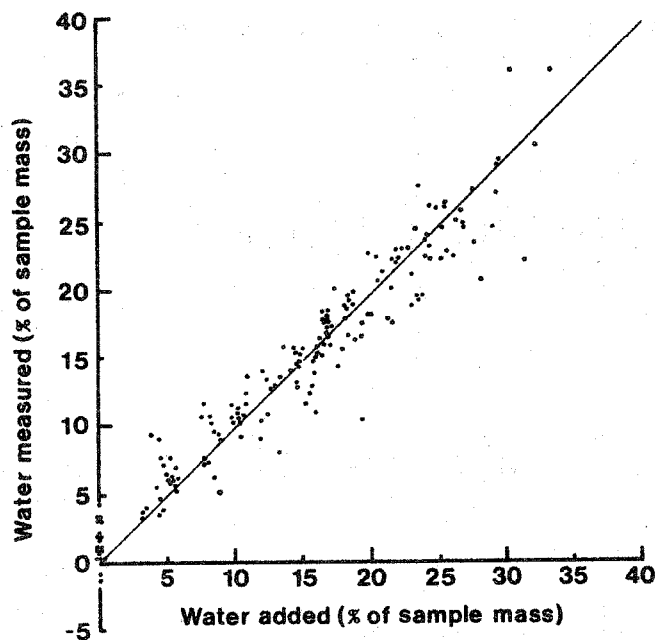


Figure 1. Dilution method results, 172 samples.

The ordinate represents the "measured water per unit mass", computed as

$$Y_i = 100\% W_m^{(i)} / (M_d^{(i)} + W_a^{(i)}) \quad (5)$$

and the abscissa represents the "added water per unit mass", computed as

$$X_i = 100\% W_a^{(i)} / (M_d^{(i)} + W_a^{(i)}) \quad (6)$$

If we define the "algebraic error" as $Y_i - X_i$ and the absolute error as $|Y_i - X_i|$, then for all 172 points:

- Mean algebraic error +0.1%
- Mean absolute error 1.7%
- Standard deviation of error 2.3%
- Worst positive error +6.1%
- Worst negative error -8.8%

These errors are somewhat less than errors shown in Table 1 because "per unit mass" is the total wet sample mass ($M_d + W_a$), whereas in Table 1, errors are computed per 100 g of dry sample mass.

COMPARISON WITH CALORIMETRY

Calorimetry may provide more accurate measurements, at least at small sample size and in a laboratory setting. Akitaya (1978) has achieved an average absolute error of about 1% using hot water calorimetry on 20 g to 50 g samples (Figure 2). According to Jones et al (1983), the error band of freezing calorimetry on 200 g samples is within $\pm 2\%$.

On the other hand, calorimetry error may increase with sample size, whereas dilution method errors do not appear to increase with increasing sample mass in the range 100 g to 2000 g. Moreover, the dilution method is much quicker and simple to use in the field.

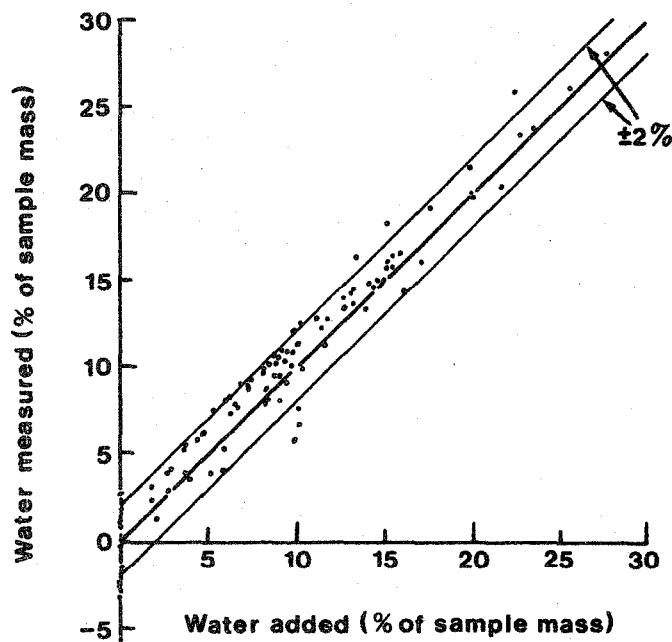


Figure 2. Akitaya's (1978) results using hot water calorimetry.

COMMENT

We have experimented with the dilution method, and although we cannot support Bader's claim for high accuracy, we found the method to be quick, simple, and applicable to a wide range of sample sizes. It should be given serious consideration as an alternative to freezing calorimetry for calibrating large scale dielectric measurements.

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