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EFFECT OF MOISTURE CONTENT AND TEMPERATURE ON SPECIFIC HEAT OF WHEAT

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ABSTRACT

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EFFECT OF MOISTURE CONTENT AND TEMPERATURE ON

SPECIFIC HEAT OF WHEAT

Major Professor: Dr. W. E. Muir

The specific heat of hard red spring wheat from three different years of harvest was measured by using a calorimetric method of mixtures. Three series of tests were conducted with wheat containing moisture ranging from 0 to 42% dry basis in different temperature ranges between -35 C and +20 C.

The specific heat of wheat was found to be linearly dependent on the moisture content up to 30% dry basis. The regression equations relating specific heat to moisture content were determined for the various temperature ranges tested. The average specific heat of dry wheat was 0.270 cal $g^{-1}C^{-1}$. Wheat containing moisture contents less than 30% dry basis did not appear to freeze or give up its latent heat of fusion at any distinct temperature within the temperature range investigated. Wheat containing higher than 30% moisture appeared to have a wide freezing range, rather than a fixed freezing point.

There was no difference in the specific heat of wheat obtained from different years of harvest.

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NOMENCLATURE

α	=	thermal diffusivity, $cm^2\ sec^{-1}$
c	=	specific heat, cal $g^{-1}C^{-1}$
d.b.	=	dry basis
E	=	water equivalent of calorimeter, g
k	=	thermal conductivity, cal $C^{-1}cm^{-1}sec^{-1}$
M	=	moisture content, % wet basis
M_D	=	moisture content, % dry basis
ω	=	uncertainty
Q	=	quantity of heat, cal
r	=	correlation coefficient
ρ	=	density, g cm^{-3}
s	=	standard deviation
T	=	temperature, C
w.b.	=	wet basis
X	=	moisture content, g water/g dry mass

Unit

BTU	=	British Thermal Unit
C	=	degree centigrade
cal	=	calorie
cm	=	centimeter
F	=	degree Fahrenheit
g	=	gram
min	=	minute
ml	=	milliliter
mv	=	millivolt
sec	=	second

1. INTRODUCTION

Wheat is considered the most important grain grown in Canada, the United States and other parts of the world. Western Canadian farmers have been storing their harvested grain in farm bins for a considerable period of time before delivering it to country elevators. A survey taken by the Canadian Wheat Board indicated that 465 million bushels of wheat were stored in farm bins at the end of the 1969-70 crop year (The Western Producer, September 3, 1970). Due to infestations of insects and mites and growth of fungi a large quantity of stored grain is lost each year. The rate of deterioration of the stored grain can be controlled by a number of factors; the primary factor being temperature control. To rationally design and control operations to combat grain storage problems, grain temperature must be predicted. One of the physical properties required to predict grain temperature is the specific heat of the grain. Knowledge of the specific heat is also useful in estimating the rate of heating or cooling of the grain and may help to clarify the relative influence of biological factors such as insects and fungi on respiration and heating.

Specific heat is defined as the quantity of heat required to change the temperature of a unit mass of a substance one degree. The unit of measurement is cal $g^{-1}C^{-1}$ or BTU $lb.^{-1}F^{-1}$. The numerical value for specific heat in either system of units is the same

The specific heat of a hygroscopic material is influenced by several factors including temperature and moisture content. Several investigators (Babbitt 1945; Pfalzner 1951; Moote 1953; Disney 1954 and Kazarian 1962) have shown the effect of moisture content on the specific heat of wheat at or near room temperature. So far the effect of low temperature on specific heat of wheat has not been determined. Therefore, in this investigation the combined effect of moisture content and low temperature on specific heat of wheat was determined using the calorimetric method known as the "method of mixtures".

The main objectives of this investigation were:

(1) To determine the specific heat of wheat at different moisture contents ranging from 0 to 40 percent dry basis and at temperatures ranging from -35 C to +20 C.

(2) To study whether or not the specific heat is different among the samples from different years of harvest.

(3) To study whether or not moisture adsorbed in grain underwent a freezing process at low temperatures.

2. LITERATURE REVIEW

Values of the specific heat of unmilled wheat have been reported by several investigators since 1945. Generally the published data show considerable variation. Due to the lack of a standard method and technique in testing, it is difficult to compare these values. In many cases the same method has been used but the variation in test conditions yielded diverse results.

In 1945 Babbitt calculated a value for the specific heat of Marquis wheat from the measured values of thermal conductivity (k), thermal diffusivity (α) and density (ρ). Wheat containing 9.2% (dry basis) moisture with a bulk density of 0.85 g cm^{-3} was enclosed in a galvanized steel cylinder. The measured value of the thermal conductivity was 0.00036 cal $C^{-1}cm^{-1}sec^{-1}$ and the thermal diffusivity 0.00115 cm^2sec^{-1}. The specific heat calculated from the relationship $c = k/\alpha\rho$ was 0.370 cal $g^{-1}C^{-1}$. The temperature of the wheat varied from 26.1 C (79F) to 48.9 C (120F) during the experiment.

Pfalzner (1951) measured the specific heat of wheat at moisture contents ranging from 0% to about 15% wet basis. The method of mixtures was used with a 5-g sample of wheat enclosed in a small cylindrical copper capsule dropped into water in a calorimeter. The calorimeter was cooled to about 1 C by introducing ice water. The wheat was held at room temperature before it was dropped into the calorimeter. The temperature was read on a Beckmann thermometer at one minute intervals during the tests. Three samples from different lots of wheat were tested. Sample A and B were from the same year and sample C from a different year. The specific heat was linearly dependent on moisture content and the results were expressed as:

Sample A $c = 0.283 + 0.00724\ M,$

Sample B $c = 0.301 + 0.00733\ M,$

Sample C $c = 0.288 + 0.00828\ M,$

where c is the specific heat, cal $g^{-1}C^{-1}$, and M is the moisture content, per cent wet basis. Pfalzner concluded that the apparent specific heat of bound water does not differ appreciably from that of free water over the range of moisture and temperature investigated.

Moote (1953), following the same method used by Babbitt, studied the effect of moisture on the thermal properties of wheat. Two lots of No. 1 Northern Manitoba wheat were tested. The first lot of wheat was initially dried and then moisture was gradually added during the test. The second lot was dried in steps with tests made between the drying periods. The calculated values of the specific heat of wheat containing various amounts of moisture from 1.4% to 13.7% wet basis were reported. The specific heat values for high moisture wheat were considerably affected by the migration of moisture during the tests. At very low moisture content there was no significant movement of moisture so the values of specific heat were presumably correct. The specific heat of dry wheat were 0.314 and 0.310 cal $g^{-1}C^{-1}$ for No. 1 Northern Manitoba wheat.

In 1954 Disney measured the specific heat of Manitoba and Bersee hard wheat with a modified Bunsen ice calorimeter. The method consisted of dropping a measured amount of wheat at room temperature into the ice calorimeter and measuring the amount of ice that melted. The specific heat of No. 1 Northern Manitoba wheat was measured at seven different moisture contents ranging from 1.29 to 17.5% wet basis. Values of the specific heat reported, ranged from 0.310 cal $g^{-1}C^{-1}$ at 1.29% moisture content to 0.447 cal $g^{-1}C^{-1}$ at 17.5% moisture content. Specific heat measurements of twenty different moisture contents were reported for Bersee wheat. Fifteen of the tests were conducted at moisture contents obtained by intermittently drying the wheat from 33.6 to 0.14% wet basis. Five tests were performed after the moisture content of the sample was changed from 1.99 to 18.2% by the addition of water. The specific heat determination after conditioning the wheat by desorption varied from 0.582 cal $g^{-1}C^{-1}$ at 33.6% moisture content to 0.307 cal $g^{-1}C^{-1}$ at 0.14% moisture. Conditioning the wheat by adsorption produced specific heat values ranging from 0.306 cal $g^{-1}C^{-1}$ at 1.99% moisture content to 0.457 cal $g^{-1}C^{-1}$ at 18.2%. Disney concluded that there was very little difference between the specific heat of the two varieties of wheat over the range of moisture contents investigated.

Kazarian (1962) measured the specific heat of soft white wheat at five different moisture contents by using the method of mixtures. The grain samples were held at room temperature and then dropped directly into the calorimeter water. In each test about 60 g of wheat and 40 g of water were used. The temperature of the sample and the water were measured and recorded with a 30-gauge copper-constantan thermocouple and recording potentiometer. The first series of tests were done over a temperature range of 10.7 C to 31.7 C (51.2 F to 89.0 F). The specific heat reported, ranged from 0.347 cal $g^{-1}C^{-1}$ at 0.68% moisture content to 0.522 cal $g^{-1}C^{-1}$ at 20.3% moisture content. A second series of specific heat measurements were conducted over a temperature range of 25 C to 46.2 C (77 F to 115.1 F). The values obtained at the higher temperatures ranged from 0.323 cal $g^{-1}C^{-1}$ at 0.68% moisture content to 0.532 cal $g^{-1}C^{-1}$ at 20.3% moisture content. The test results at the higher temperatures appeared to be consistently lower than the data obtained at the lower temperatures. Kazarian concluded that the specific heat of soft white wheat is a linear function of moisture content and could be expressed by the equations,

$c = 0.334 + 0.00977\ M$ at mean temperature 21.2 C (70.1 F),

and $c = 0.311 + 0.0112\ M$ at mean temperature 33.9 C (93.1 F).

where c = specific heat, cal $g^{-1}C^{-1}$, M = moisture content, per cent wet basis.

Wheelock and Lancaster (1970) derived an equation for the specific heat of wheat flour from the pooled data gathered on soft white winter wheat flour and unmilled wheat. The equation obtained was expressed as,

$$c = 0.295 + 5.51\ (10)^{-4}\ T + 0.441\ X + 1.144\ X^2,$$

where c = specific heat, cal $g^{-1}C^{-1}$,

T = temperature, C,

X = moisture content, g water/g dry flour

This equation could be used for determining the specific heat of wheat flour with a moisture content up to 20% (X = 0.25) and over a temperature range of 0 C to 60 C.

The published values for the specific heat of wheat are summarized in Table 2.1.

TABLE 2.1

Reported data for specific heat of wheat

Kind of Grain	Moisture Content (% wet basis)	Temperature Range	Mean Temperature	Specific Heat (cal $g^{-1}C^{-1}$)	Reference
Wheat, Marquis	8.4	26.1 to 48.9 C	27.5 C	0.370	Babbitt (1945)
Wheat, Manitoba No. 1	1.4	32 to 60 C	46 C	0.319	Moote (1953)
	2.2			0.339	Moote
	3.5			0.354	Moote
	4.5			0.373	Moote
	7.4			0.403	Moote
	10.9			0.440	Moote
	13.7			0.460	Moote
Wheat, Manitoba No. 1	1.29	0 to 18 C	9 C	0.310	Disney (1954)
	4.9			0.333	Disney
	10.1			0.367	Disney
	17.5			0.447	Disney
Wheat, Bersee	0.1	0 to 18 C	9 C	0.307	Disney
	4.2			0.322	Disney
	13.7			0.405	Disney
	19.9			0.475	Disney
	25.8			0.525	Disney
	33.6			0.582	Disney

TABLE 2.1

Reported data for specific heat of wheat

(continuation)

Kind of Grain	Moisture Content (% wet basis)	Temperature Range	Mean Temperature	Specific Heat (cal $g^{-1}C^{-1}$)	Reference
Wheat, Soft White	0.68	10.7 to 31.7 C	21.2 C	0.347	Kazarian (1962)
	5.5			0.375	Kazarian
	10.3			0.428	Kazarian
	14.4			0.500	Kazarian
	20.3			0.522	Kazarian
Wheat, Soft White	0.68	25 to 46.2 C	33.9 C	0.323	Kazarian
	5.5			0.366	Kazarian
	10.3			0.418	Kazarian
	14.4			0.490	Kazarian
	20.3			0.532	Kazarian

3. METHOD AND APPARATUS

3.1 Introduction

In all experimental determinations of specific heat, the amount of heat added to or removed from a body must be measured. The theory and practice of making measurements of quantities of heat is generally classed as calorimetry. Numerous calorimetric methods for conducting these measurements have been proposed. In this investigation a standard calorimetric method known as the "method of mixtures" was employed. The method of mixtures consists essentially of adding a known mass of material at a high temperature to a known mass of water at a lower temperature, or vice versa, and measuring the equilibrium temperature that results. The specific heat is then calculated using the heat capacity of the calorimeter and the measured temperature change.

3.2 Development of Test Apparatus

The test apparatus used in this study was modified from the ASTM Standard Method of Test for Mean Specific Heat of Thermal Insulation (American Society for Testing and Materials). The test apparatus was less complex than those generally used in scientific calorimetry but it provided sufficient precision and accuracy. The test apparatus, as shown in Figures 3.1a and 3.1b, consisted essentially of the calorimeter and the temperature measurement instruments. The test apparatus will be described in detail in the subsequent sections.

3.2.1 Calorimeter

The calorimeter was an Isotherm Dewar flask with a capacity of 1000 ml. The metal jacket was removed from the flask since it prevented the use of a magnetic stirrer. The flask was then insulated with one and a half inches of fiber-glass insulation to minimize the heat exchange with the surroundings. An insulating cover was used for covering the flask during the experiment. The cover was divided into two parts in order to facilitate the temperature measurement of the calorimeter water and to reduce the size of the opening while transferring the sample into the calorimeter. A glass rod five inches long was connected to the smaller part of the cover so that it protruded into the calorimeter flask. A thermocouple fixed at the end of this rod measured the temperature of the calorimeter water at the same location throughout the tests (Figure 3.2). A magnetic stirrer was used to stir the calorimeter water to maintain a constant temperature throughout the flask.

3.2.2 Temperature Measurement Instruments

The temperature of the calorimeter water was measured with a 36-gauge (Brown and Sharpe) Copper-constantan thermocouple connected to a potentiometer type strip chart recorder (Electronik 124*). The temperature of the grain sample was measured and recorded using a 24-gauge (Brown and Sharpe) Copper-constantan thermocouple and a SuperMite* manual indicating potentiometer. A water-ice reference chamber (Model 136 Air cooled Frigister*) provided a reference temperature for the thermocouples which was maintained at 0 C $\pm$ 0.01 C.

A Philadelphia* differential thermometer having a range of 5 C with 0.01-C divisions was employed to calibrate the calorimeter water thermocouple. Two precision-type thermometers, ASTM number 62 C and 63 C with 0.1-C divisions were used to calibrate the thermocouple which was located in the grain sample.

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* Trade name

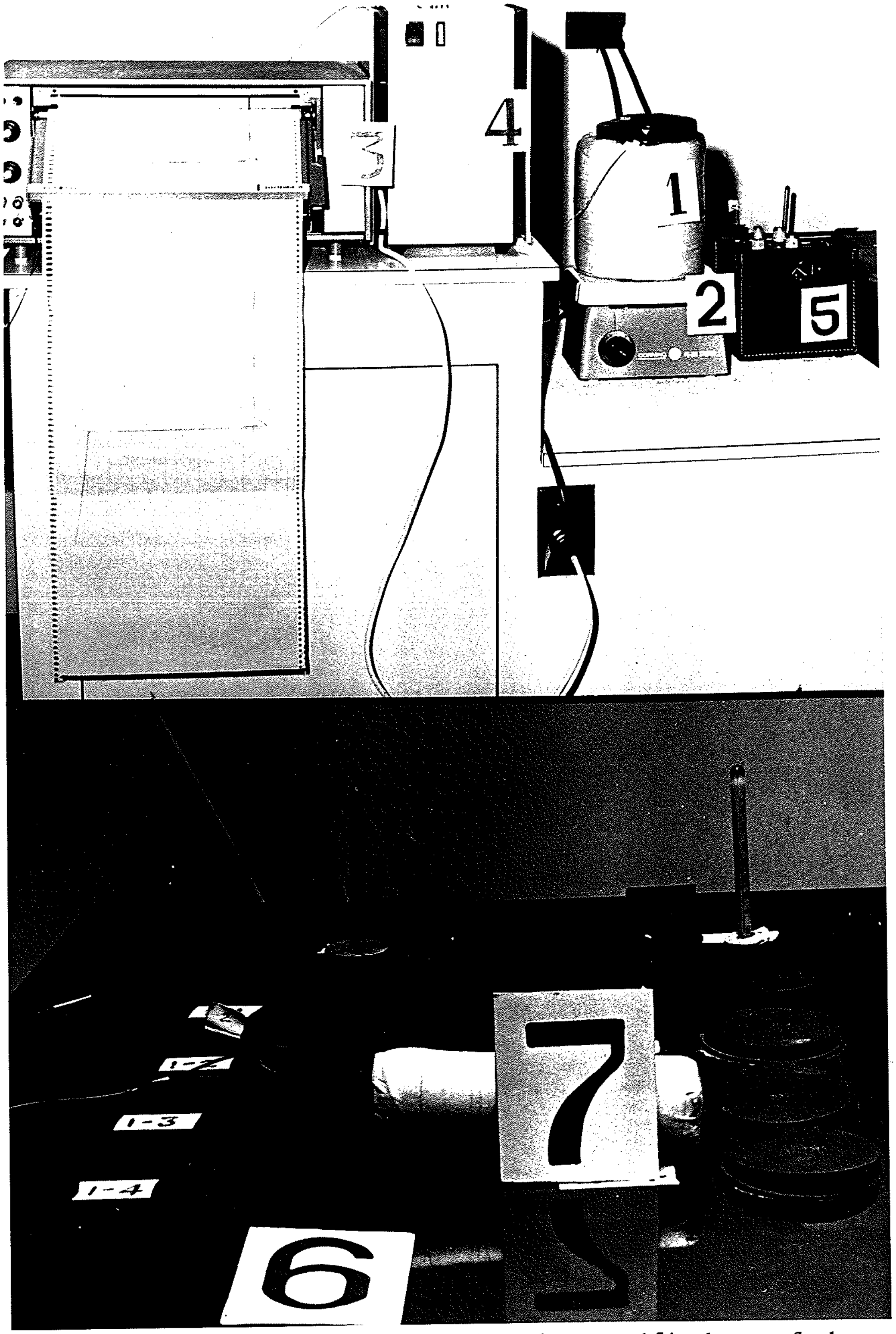

Figure 3.1a Apparatus for determining the specific heat of wheat:

1. calorimeter
2. magnetic stirrer
3. strip chart recorder potentiometer
4. water-ice reference chamber
5. manual indicating potentiometer
6. cooling bath
7. insulated glass tube

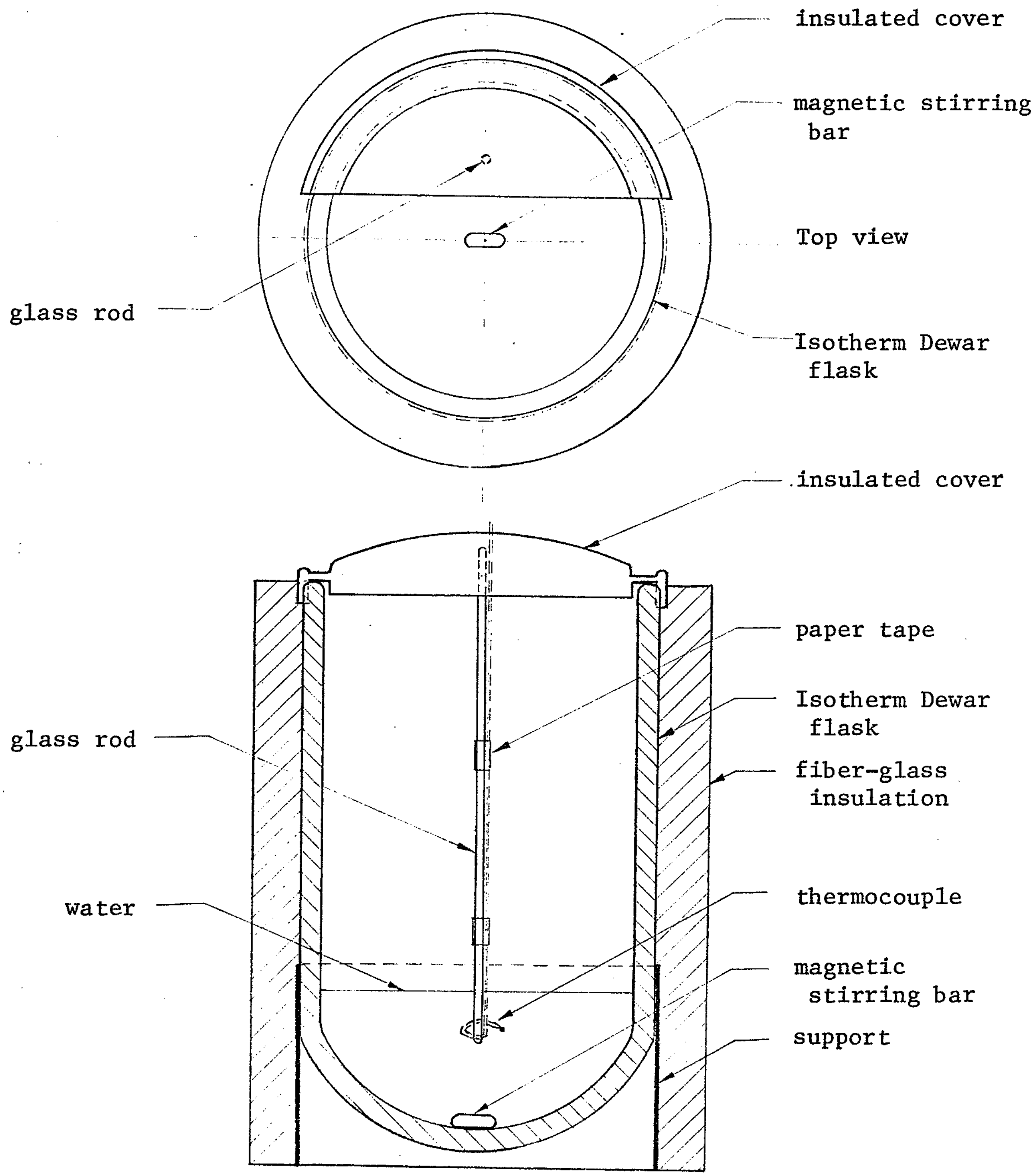

Figure 3.1b Schematic diagram of calorimeter.

Figure 3.2 Calorimeter flask and cover.

Figure 3.3 Dropping the grain sample into the calorimeter.

3.2.3. Auxiliary Equipment

Other equipment consisted of a liquid cooling bath for cooling the grain sample to the desired temperature. A 25-ml glass tube, insulated with fiber-glass, was used for containing the grain sample. The insulated glass tube assisted in producing a uniform temperature throughout the sample while it was being cooled and reduced heat transfer while the tube was being moved from the cooling bath to the calorimeter. A Mettler* K4 balance, accurate to 0.1 g, was used for weighing the calorimeter water. A Mettler* H10T balance, accurate to 0.0001g, was used for weighing the grain sample and the specific heat standard. An electrically operated drying oven was used for determining the moisture content of the grain sample.

3.3 Specific Heat Standard

A specific heat standard is a material of accurately known specific heat. In this study granular aluminum was employed as a specific heat standard for calibrating the calorimeter. Granular copper was used to check the reliability of the equipment and the procedure employed.

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* Trade name

4. PROCEDURES

4.1 Grain Sample

The grain samples used in this test were obtained from three different lots of Manitou No. 2 grade Hard Red Spring wheat, harvested during the fall of 1967, 1968 and 1969. Initial moisture and protein contents of the wheat are shown in Table 4.1.

TABLE 4.1

Initial moisture and protein contents of Manitou wheat.

Year Harvested	Moisture Content		Protein Content*
	(% dry basis)	(% wet basis)	%
Fall 1967	12.9	11.4	11.6
Fall 1968	11.9	10.6	13.2
Fall 1969	13.8	12.1	13.3

* Protein content based on 13.5% moisture content (wet basis) and using a nitrogen to protein conversion factor of 5.7.

Before conditioning to different moisture contents the wheat was cleaned by using a 10-mesh-per-inch screen. Moisture contents below the initial moisture were obtained by drying in an oven at 100 C. High moisture contents were obtained by the addition of calculated amounts of distilled water and allowing the samples to stand for 5 to 7 days to assure an even distribution of adsorbed water. Low moisture content grain samples were kept at room temperature in plastic bags, high moisture content samples were put in plastic bags and kept in a refrigerator at a temperature about 0 C to prevent mold and fungi growth. The moisture contents of the grain samples used for determining the specific heat are given in Table 4.2.

TABLE 4.2

Moisture content of grain samples used for determining the specific heat.

Grain Sample	Moisture Content (% dry basis)	Moisture Content (% wet basis)
1967, cleaned wheat	2.4	2.3
	12.9	11.4
	21.1	17.4
1968, cleaned wheat	3.5	3.4
	11.9	10.6
	20.2	16.8
1969, cleaned wheat	0.9	0.9
	9.6	8.8
	13.8	12.1
	16.8	14.4
	23.5	19.0
	30.5	23.4
	42.0	29.6
1969, uncleaned wheat (contained 1.5% dockage)	2.1	2.1
	12.1	10.8
	20.6	17.1

4.2 Moisture Content Determination

The moisture contents of the grain samples were determined by an oven drying method. Three duplicate samples of about 20 to 25 g were weighed to 0.0001 g and dried in a ventilated oven at 100 C for 4 days and then reweighed. Moisture contents were calculated from the difference between initial and final weights and expressed in percentage of initial weight, i.e. per cent wet basis (M) as the following:

$$M = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100\% \quad - - - - - - - - 4.1$$

and percentage of final weight, i.e. per cent dry basis (M_D) as the following:

$$M_D = \frac{\text{initial weight} - \text{final weight}}{\text{final weight}} \times 100\% \quad - - - - - - - 4.2$$

4.3 Temperature Measurement

The accuracy of the specific heat determination is dependent on the measurement of (1) the initial temperature of the calorimeter water, (2) the initial temperature of the grain sample, and (3) the temperature of the mixture. The temperature of the calorimeter water was measured and recorded with a 36-gauge (Brown and Sharpe) Copper-constantan thermocouple and a recording potentiometer. The small diameter was chosen in order to reduce temperature measurement errors due to heat conduction along the wire. The thermocouple was calibrated with a differential thermometer in the temperature range of 20 to 25 C. A graph of temperature versus electrical potential was prepared for converting the recorded electrical potential of the thermocouple circuit into temperature accurate to $\pm$ 0.005 C. A 24-gauge (Brown and Sharpe) Copper-constantan thermocouple was used in measuring the temperature of the grain sample. The thermocouple was calibrated by comparison with the ASTM number 62 C and 63 C precision thermometers over the temperature range +10 C to -40 C. The calibration curve prepared for converting the measured electrical potential into temperature was accurate to $\pm$ 0.05 C.

4.4 Specific Heat Determination

The sample of wheat whose specific heat was to be determined was weighed and placed into an insulated glass tube. About 20 g of wheat were used in each test and the sample was weighed accurate to $\pm$ 0.0001 g with a Mettler H 10 T balance. The glass tube containing the grain sample was covered with a rubber stopper which had a 24-gauge Copper-constantan thermocouple inserted through the center to measure the temperature of the sample. The glass tube with the contents was inserted into a copper cup in a cooling bath. The temperature of the cooling bath was adjusted to the required temperature. When the grain samples were in thermal equilibrium in the cooling bath, the temperature varied with time less than $\pm$ 0.5 C. The grain samples were cooled 8 to 10 hours.

The procedure for obtaining measurements was as follows: The calorimeter flask was filled with 200 $\pm$ 5 g of distilled water at a temperature approximately 23 C. The exact weight of water was determined to the nearest $\pm$ 0.1 g, as the difference between the weight of the flask with water and the weight of the empty flask. The magnetic stirring bar was put into the calorimeter and the stirrer was set in motion. The same stirrer speed was used during all tests. The calorimeter flask was covered at all times except when the sample was actually being dropped into the flask. The recording potentiometer was set to record the temperature of the calorimeter water at a chart speed of 1 inch min^{-1} with a 0.1-mv span (approximately 2.5 degrees centrigrade). When the rate of change of the temperature of the calorimeter water became constant for about 5 to 6 min the sample was dropped into the calorimeter water. The temperature of the sample was recorded prior to transferring from the cooling bath. The time required to transfer the sample from the cooling bath into the calorimeter water was approximately 3 or 4 sec. In this short period of time, the quantity of heat exchange with the surroundings was relatively small since the sample was contained in the insulated glass tube. The grain sample was poured from the glass tube directly into the calorimeter water and thermal equilibrium was established in approximately 30 to 40 sec. The temperature of the calorimeter water was continuously recorded for about 10 min after thermal equilibrium of the mixtures was established.

A typical time-electrical potential curve of the calorimeter water is shown in Figure 4.1.

The value of temperature of the mixture (T_m) was determined by extrapolating the straight line portion of the time-electrical potential curve to the "transient time" as illustrated in Figure 4.1. The term transient time is used to define the time at which the sample was dropped into the calorimeter water. Then, by equating the heat lost to the heat gained, we have:

$$c_s M_s \; (T_m - T_s) = (M_w + E) \; c_w \; (T_c - T_m) \qquad \text{- - - - - - - - -} \; 4.3$$

where c_s = mean specific heat of the sample, cal $g^{-1}C^{-1}$,

c_w = mean specific heat of calorimeter water, cal $g^{-1}C^{-1}$

M_s = mass of the sample, g,

M_w = mass of the calorimeter water, g,

T_c = initial temperature of the calorimeter water at transient time, C,

T_s = initial temperature of the sample, C,

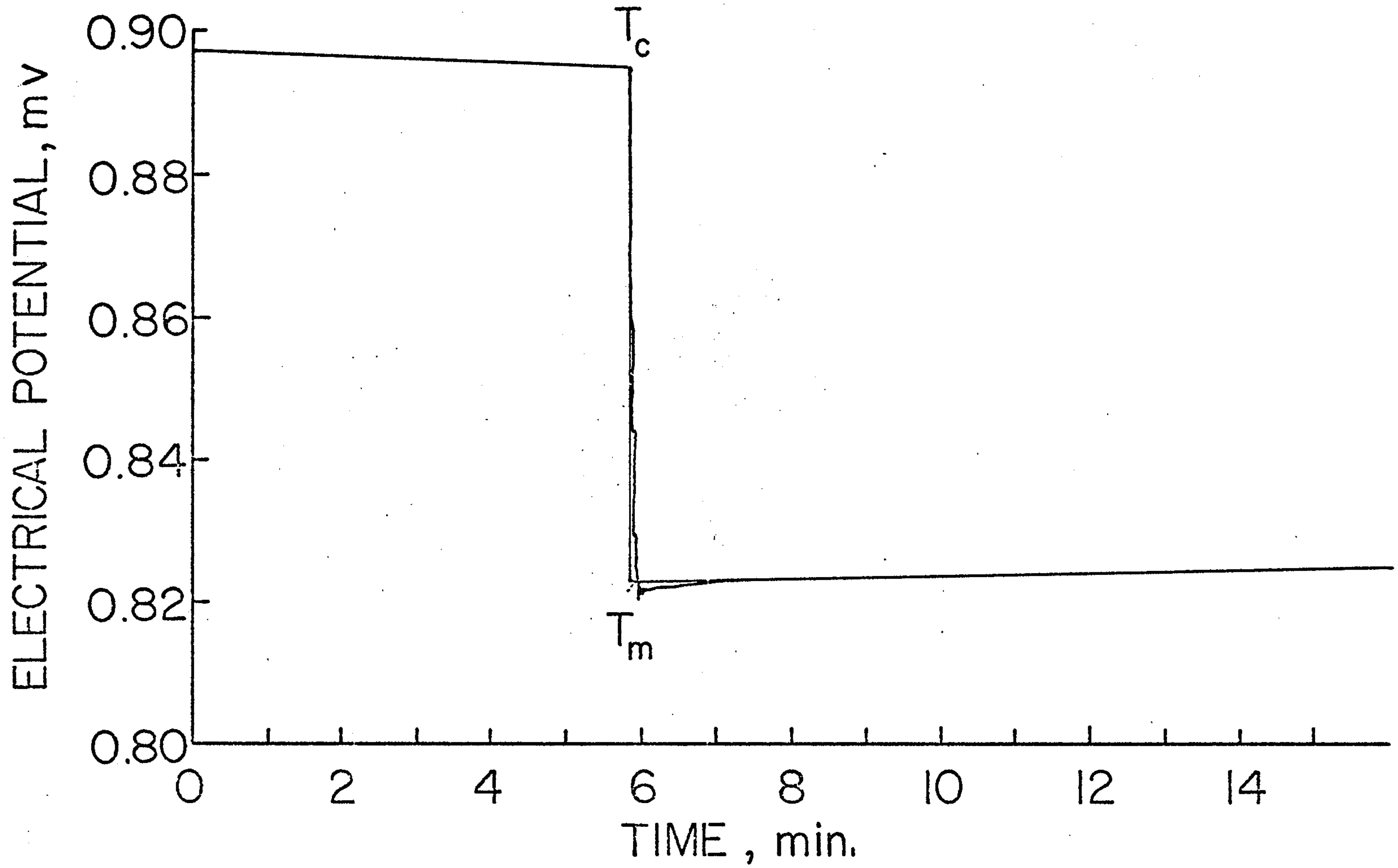

Figure 4.1 A typical time-electrical potential curve from calorimetric test in determining the specific heat of wheat.

T_m = temperature of the mixture extrapolated at transient time, C,

E = water equivalent of calorimeter and its accessories, g.

Rearranging, the specific heat of the sample is calculated as follows:

$$c_s = \frac{(M_w+E)\ c_w\ (T_c-T_m)}{M_s\ (T_m-T_s)} \quad \text{-------------} \quad 4.4$$

The mean specific heat of water (c_w) used in all calculations is 0.999 cal $g^{-1}C^{-1}$ at temperature 20 to 23 C. (CRC Handbook of Chemistry and Physics, 49th Ed. 1969).

4.5 Calibration of the Calorimeter

The calorimeter was calibrated using the same procedure described in section 4.4, except to substitute the specific heat standard (aluminum) for the grain sample. The water equivalent of the calorimeter (E) was then calculated using the equation:

$$E = \frac{M_s c_s\ (T_m-T_s)}{c_w(T_c-T_m)} - M_w \quad \text{-------------} \quad 4.5$$

where M_s = mass of the specific heat standard, g,

c_s = mean specific heat of specific heat standard, cal $g^{-1}C^{-1}$.

The water equivalent of a body is defined as the mass of water that requires the same amount of heat as the given body in order to change its temperature by an equal amount.

The water equivalent of the calorimeter obtained from the average of sixteen determinations was 24.40 g with a standard deviation of 2.86 g.

4.6 Accuracy of the Experiment

The accuracy of the experiment in determining the specific heat was within 3.93% uncertainty (see Appendix C).

To check the accuracy and precision of the experimental apparatus and the technique employed, the specific heat of pure granular copper was determined in the temperature range of -22.1 C to +21.6 C. The value of specific heat of copper as obtained from an average of eight determinations was 0.0937 cal $g^{-1}C^{-1}$ with a standard deviation 0.00151 cal $g^{-1}C^{-1}$. When compared to the published value for specific heat of copper at 0 C, the experimental value was 2.9% greater (Specific heat of copper at 0 C is 0.091 cal $g^{-1}C^{-1}$, Heat Transfer Engineering, Prentice Hall 1961). However the error was within the limit of the experimental uncertainty.

To check whether dropping the grain directly into water would affect the specific heat, a series of tests was conducted with wheat enclosed in a polyethylene bag. The wheat contained 0.9% moisture (dry basis) and the temperature range tested was -33.5 C to +20.8 C. The specific heat value obtained by dropping the grain directly into water for the average of eight tests was 0.281 cal $g^{-1}C^{-1}$ with a standard deviation 0.0047 cal $g^{-1}C^{-1}$. For wheat contained in a polyethylene bag, the specific heat value obtained from the average of eight determinations was 0.275 cal $g^{-1}C^{-1}$ with a standard deviation 0.0120 cal $g^{-1}C^{-1}$. Analysis of variance showed that there was no significant difference between the two means at the 5% level.

Since it was found that the method of dropping the grain directly into the calorimeter water did not affect the specific heat value, the procedure described was used to determine the specific heat of wheat at various moisture contents and temperature ranges.

5. RESULTS

The test results of the determination of specific heat of wheat are divided into three series. The first series of determinations was conducted with wheat, harvested during the fall of 1969. The mean specific heat was determined over five temperature ranges of -33.5 to +20.8 C, -21.4 to +21.0 C, -10.8 to +21.2 C, +0.6 to +21.1 C and +8.9 to +21.8 C, with moisture contents ranging from 0.9% to 21.4% (dry basis). The mean values of specific heat obtained in this series of tests are summarized in Tables 5.1 to 5.5.

Linear regression equations relating specific heat to moisture content were determined for each of the five temperature ranges (Figures 5.1 to 5.5). The mean regression equation for all five test temperature ranges was:

$$c = 0.270 + 0.00878\, M_D \qquad \text{- - - - - - - - - - -} \quad (5.1)$$

$$r = 0.99, \; s = 0.0099$$

where c = specific heat, cal $g^{-1}C^{-1}$,

M_D = moisture content, % dry basis,

r = correlation coefficient,

s = standard deviation of the regression equation, cal $g^{-1}C^{-1}$.

The standard deviation of the regression equations is based on the means of eight determinations for each moisture content.

The regression equations of small temperature intervals between -33.5 to -21.4 C, -21.4 to -10.8 C, -10.8 to +0.6 C and +0.6 to +8.9 C were calculated by using the equations given in Figures 5.1 to 5.5 (see Appendix B). Figure 5.6 shows the four computed equations and the equation described in Figure 5.5 in the temperature range of +8.9 to +21.8 C.

Substituting the values of moisture content into those equations (Figure 5.6), the specific heats in the respective temperature intervals were calculated for wheat containing 5, 10, 15, 20 and 25% moisture (dry basis). Figure 5.7 shows the plot of the computed specific heat versus temperature at the midpoint of each temperature interval.

In the second series of tests, the specific heats of clean wheat harvested in 1967 and 1968 and unclean wheat harvested in 1969 (wheat from the same bulk tested in the first series of tests) were measured in the temperature range -21.5 to +21.0 C and +1.3 to +21.6 C (see Tables 5.6, 5.7, Figures 5.2, 5.4). The specific heat of these three different wheat samples was not significantly different at the 1% level from those for the clean, 1969 wheat.

The third series of specific heat determinations were conducted with 1969 wheat containing 30.5 and 42 percent moisture (dry basis). The purpose of this series of tests was to determine whether or not the high moisture adsorbed in wheat underwent a freezing process at low temperatures. The tests were performed at eight different temperature ranges for wheat containing 30.5% moisture (Table 5.8, Figure 5.8) and nine temperature ranges for wheat containing 42% of moisture (Table 5.9, Figure 5.8). Calculations for the specific heats in the small temperature intervals (Figure 5.8) were performed as for Figure 5.7.

Table 5.10 shows the heat capacities per gram of 10, 20, 30.5 and 42% adsorbed water calculated between the corresponding temperature and +21 C, taken as 0 at +21 C. Two assumptions were made in calculating the heat capacity of adsorbed water. First it was assumed that the wheat kernels were composed of a mixture of water and solid matter and that the heat capacity of each is independent of the other. The second assumption was that the specific heat of solid matter was independent of temperature and the value of 0.270 cal $g^{-1}C^{-1}$ (Equation 5.1) was used in calculating the heat capacity of solid matter. The heat capacity of adsorbed water was obtained by subtracting the heat capacity of the solid matter from the heat capacity of wheat (solid matter plus adsorbed water), and recalculated on the basis of 1 g of adsorbed water. Figure 5.9 shows the curves of heat capacity of adsorbed water against the temperature in comparison with the heat capacity of free water.

TABLE 5.1

Specific heat of wheat in the temperature range -33.5 to +20.8 C

Moisture content		Specific heat*	Standard deviation
(% dry basis)	(% wet basis)	(cal g^{-1} C^{-1})	(cal $g^{-1}C^{-1}$)
0.9	0.9	0.281	0.0047
9.4	8.6	0.338	0.0070
13.4	11.8	0.375	0.0067
16.4	14.1	0.397	0.0081
22.7	18.5	0.452	0.0089

* Mean of 8 tests.

TABLE 5.2

Specific heat of wheat in the temperature range -21.4 to +21.0 C

Moisture content		Specific heat*	Standard deviation
(% dry basis)	(% wet basis)	(cal g^{-1} C^{-1})	(cal $g^{-1}C^{-1}$)
1.1	1.1	0.286	0.0037
9.4	8.6	0.346	0.0022
13.3	11.7	0.382	0.0039
16.4	14.1	0.409	0.0042
22.7	18.5	0.457	0.0040

* Mean of 8 tests.

TABLE 5.3

Specific heat of wheat in the temperature range -10.8 to +21.2 C

Moisture content (% dry basis)	Moisture content (% wet basis)	Specific heat* (cal g^{-1} C^{-1})	Standard deviation (cal $g^{-1}C^{-1}$)
1.1	1.1	0.285	0.0046
9.4	8.6	0.355	0.0069
13.3	11.7	0.388	0.0058
16.4	14.1	0.420	0.0040
22.5	18.4	0.471	0.0056

* Mean of 8 tests.

TABLE 5.4

Specific heat of wheat in the temperature range +0.6 to +21.1 C

Moisture Content (% dry basis)	Moisture Content (% wet basis)	Specific heat* (cal g^{-1} C^{-1})	Standard deviation (cal $g^{-1}C^{-1}$)
0.9	0.9	0.271	0.0040
9.6	8.8	0.352	0.0021
13.8	12.1	0.398	0.0051
16.8	14.4	0.423	0.0045
23.5	19.0	0.489	0.0040

* Mean of 8 tests.

TABLE 5.5

Specific heat of wheat in the temperature range +8.9 to +21.8 C

Moisture Content		Specific heat*	Standard deviation
(% dry basis)	(% wet basis)	(cal g^{-1} C^{-1})	(cal $g^{-1}C^{-1}$)
2.9	2.8	0.300	0.0082
9.5	8.7	0.362	0.0058
13.8	12.1	0.401	0.0068
17.4	14.8	0.435	0.0069
24.1	19.4	0.498	0.0056

* Mean of 8 tests.

TABLE 5.6

Specific heat of wheat from different years of harvest, temperature range -21.5 to +21.0 C

Moisture content		Specific heat*	Standard deviation
(% dry basis)	(% wet basis)	(cal g^{-1} C^{-1})	(cal $g^{-1}C^{-1}$)
Manitou wheat, harvested fall 1967, cleaned			
2.4	2.3	0.299	0.0033
12.9	11.4	0.374	0.0048
21.1	17.4	0.446	0.0063
Manitou wheat, harvested fall 1968, cleaned			
3.5	3.4	0.301	0.0032
11.9	10.6	0.362	0.0050
20.2	16.8	0.437	0.0047
Manitou wheat, harvested fall 1969, uncleaned			
2.14	2.1	0.290	0.0021
12.1	10.8	0.366	0.0055
20.6	17.1	0.442	0.0042

*Mean of 4 tests.

TABLE 5.7

Specific heat of wheat from different years of harvest, temperature range +1.3 to +21.6 C

Moisture content (% dry basis)	Moisture content (% wet basis)	Specific heat* (cal g^{-1} C^{-1})	Standard deviation (cal $g^{-1}C^{-1}$)
Manitou wheat, harvested fall 1967, cleaned			
2.4	2.3	0.282	0.0049
12.9	11.4	0.387	0.0074
21.1	17.4	0.463	0.0032
Manitou wheat, harvested fall 1968, cleaned			
3.5	3.4	0.288	0.0021
11.9	10.6	0.371	0.0010
20.2	16.8	0.453	0.0022
Manitou wheat, harvested fall 1969, uncleaned			
2.4	2.1	0.281	0.0081
12.1	10.8	0.380	0.0021
20.6	17.1	0.467	0.0016

* Mean of 4 tests.

TABLE 5.8

Specific heat of wheat in the different temperature ranges, moisture content 30.5% dry basis (23.4% w.b.)

Temperature range	Specific heat* (cal g^{-1} C^{-1})	Standard deviation (cal $g^{-1}C^{-1}$)
-35.6 to +20.7 C	0.526	0.0072
-26.2 to +20.7 C	0.534	0.0024
-21.0 to +20.8 C	0.534	0.0053
-16.3 to +20.7 C	0.534	0.0045
-11.8 to +21.0 C	0.532	0.0052
- 6.6 to +21.1 C	0.533	0.0033
+ 0.5 to +21.4 C	0.543	0.0066
+ 5.9 to +21.7 C	0.551	0.0017

* Mean of 4 tests.

TABLE 5.9

Specific heat of wheat in the different temperature ranges, moisture content 42.0% dry basis (29.6% w.b.)

Temperature range	Specific heat* (cal g^{-1} C^{-1})	Standard deviation (cal $g^{-1}C^{-1}$)
-35.5 to +20.7 C	0.640	0.0081
-30.5 to +20.7 C	0.660	0.0048
-26.2 to +20.8 C	0.681	0.0057
-21.3 to +20.4 C	0.702	0.0080
-16.5 to +20.8 C	0.688	0.0075
-10.9 to +20.5 C	0.688	0.0056
- 5.9 to +21.0 C	0.632	0.0044
+ 1.1 to +21.4 C	0.584	0.0088
+ 5.1 to +21.3 C	0.590	0.0111

* Mean of 4 tests.

TABLE 5.10

Heat capacity per gram of adsorbed water in wheat between the corresponding temperature and +21 C.

10% adsorbed		20% adsorbed		30.5% adsorbed		42% adsorbed	
Temperature (C)	Heat Capacity (cal)	Temperature (C)	Heat Capacity (cal)	Temperature (C)	Heat Capacity (cal)	Temperature (C)	Heat Capacity (cal)
+21	0	+21	0	+21	0	+21	0
+ 8.9	-16.04	+ 8.9	-17.06	+ 5.9	-22.23	+ 5.1	-21.50
+ 0.6	-25.48	+ 0.6	-28.15	+ 0.5	-29.48	+ 1.1	-26.50
-10.8	-40.45	-10.8	-42.74	- 6.6	-38.51	- 5.9	-40.19
-21.4	-51.09	-21.4	-53.42	-11.8	-45.63	-10.9	-53.70
-33.5	-62.07	-33.5	-66.38	-16.3	-52.20	-16.5	-63.12
				-21.0	-58.78	-21.3	-73.20
				-26.2	-66.06	-26.2	-78.33
				-35.6	-77.28	-30.5	-81.81
						-35.5	-85.93

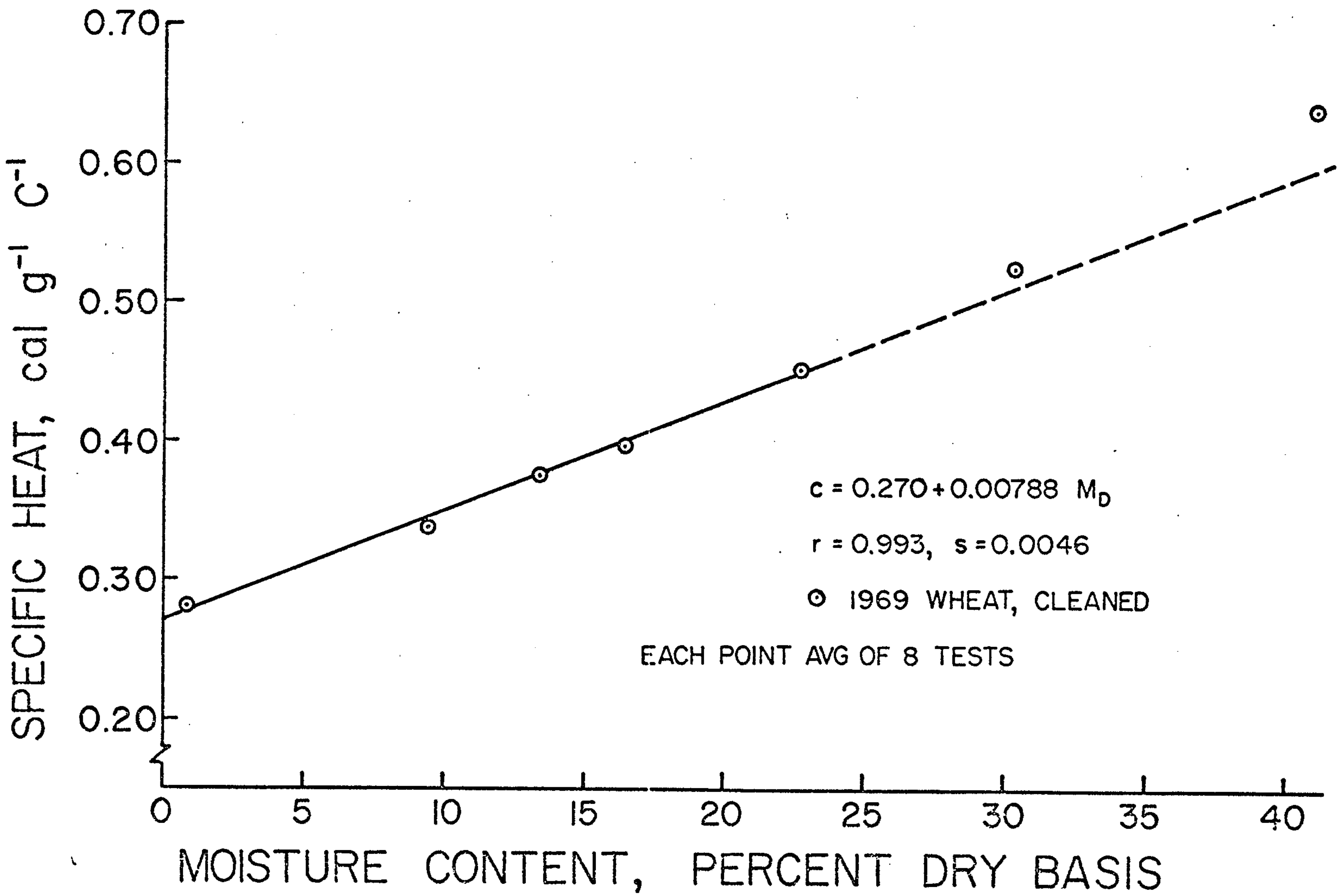

Figure 5.1 Effect of moisture content on specific heat of wheat in the temperature range -33.5 to 20.8 C.

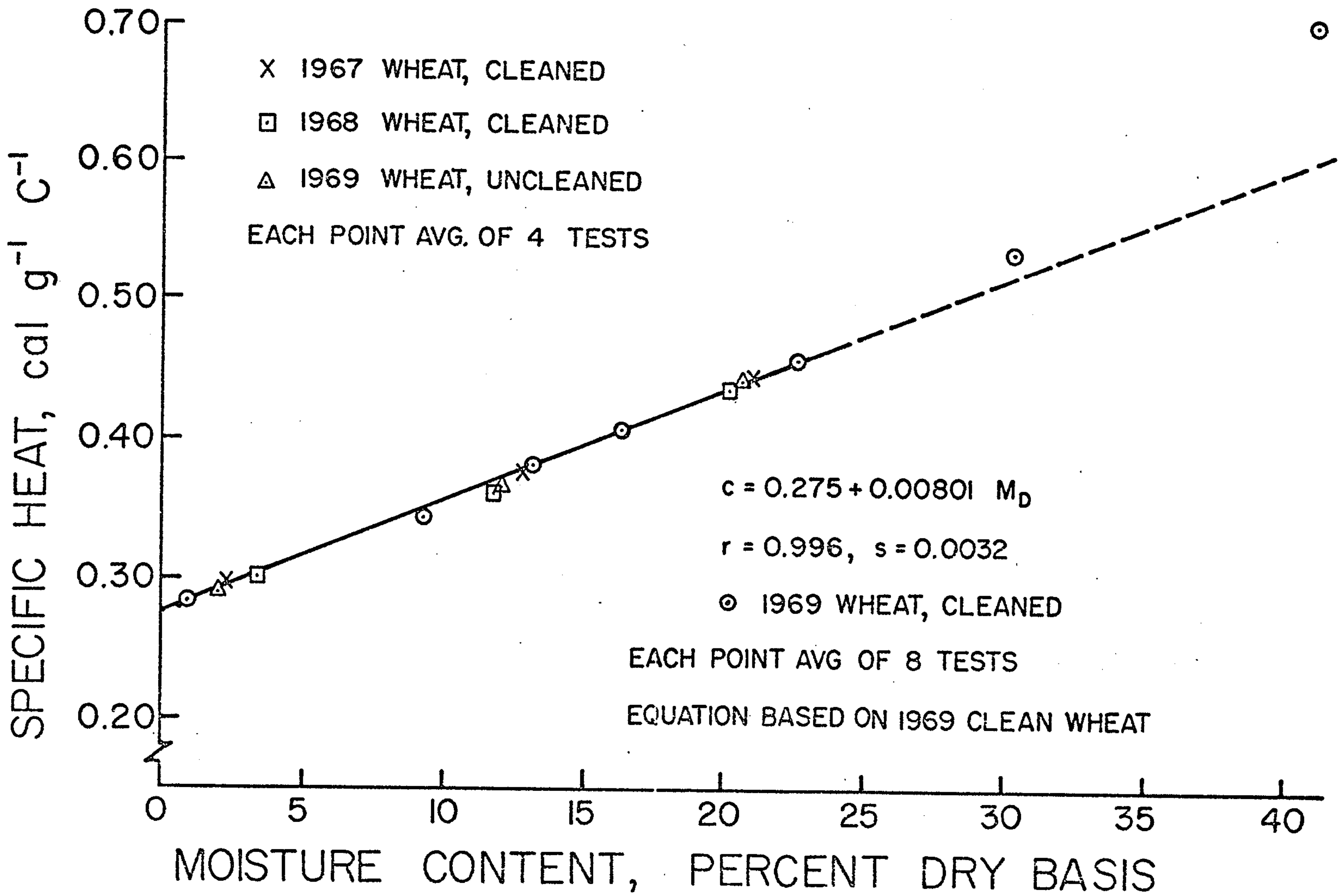

Figure 5.2 Effect of moisture content on specific heat of wheat in the temperature range -21.4 to 21.0 C.

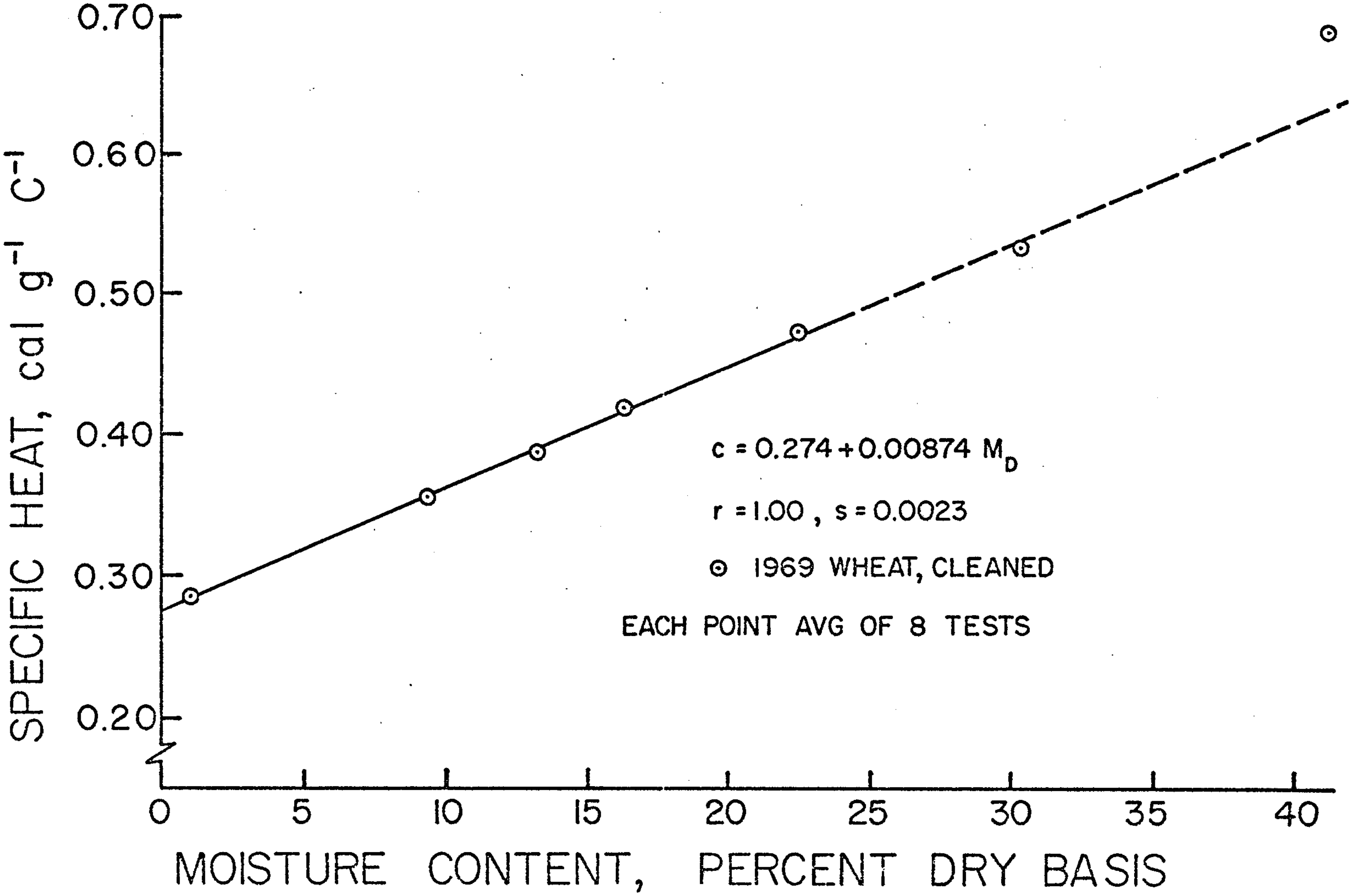

Figure 5.3 Effect of moisture content on specific heat of wheat in the temperature range -10.8 to 21.2 C.

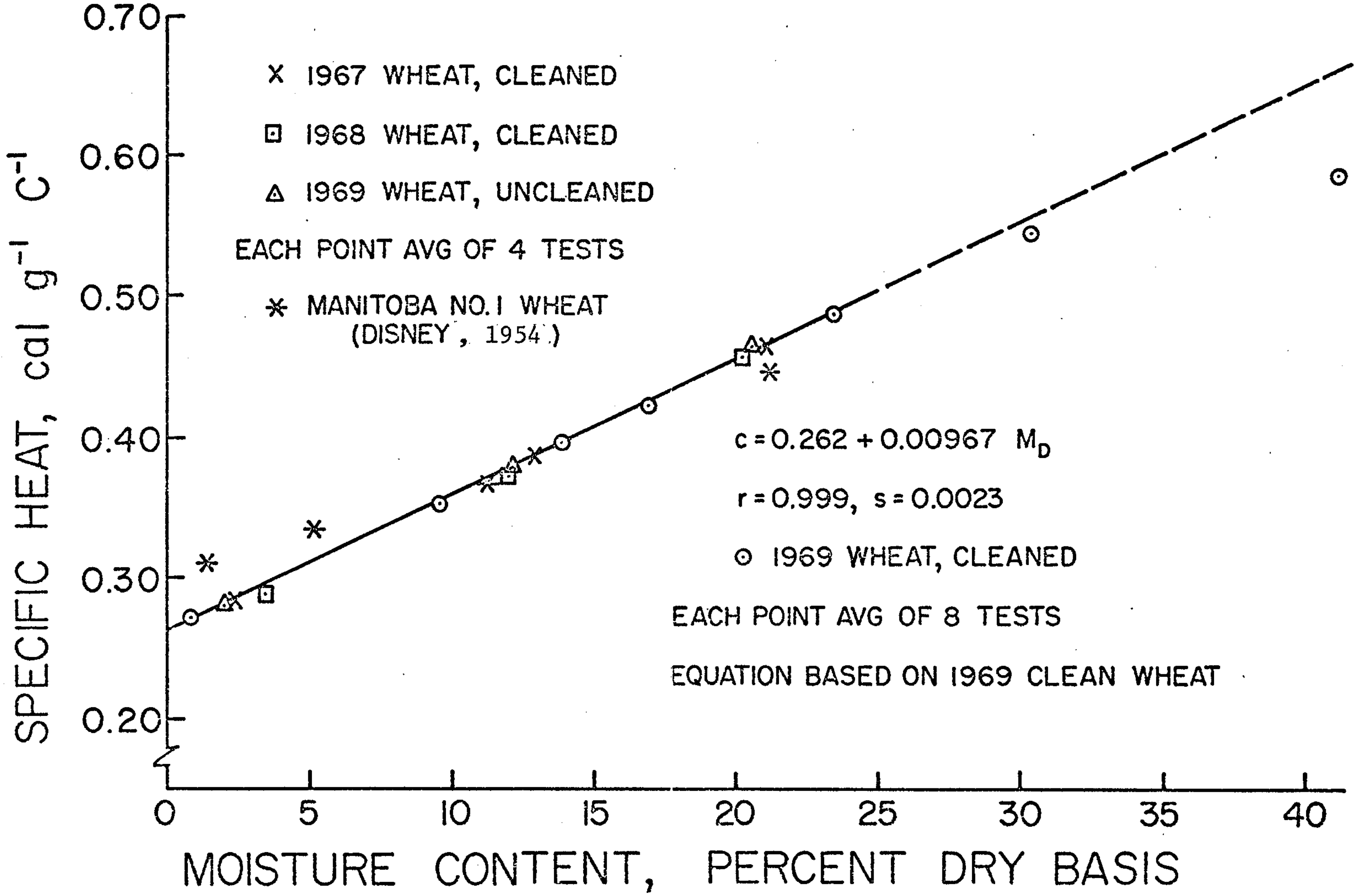

Figure 5.4 Effect of moisture content on specific heat of wheat in the temperature range 0.6 to 21.1 C.

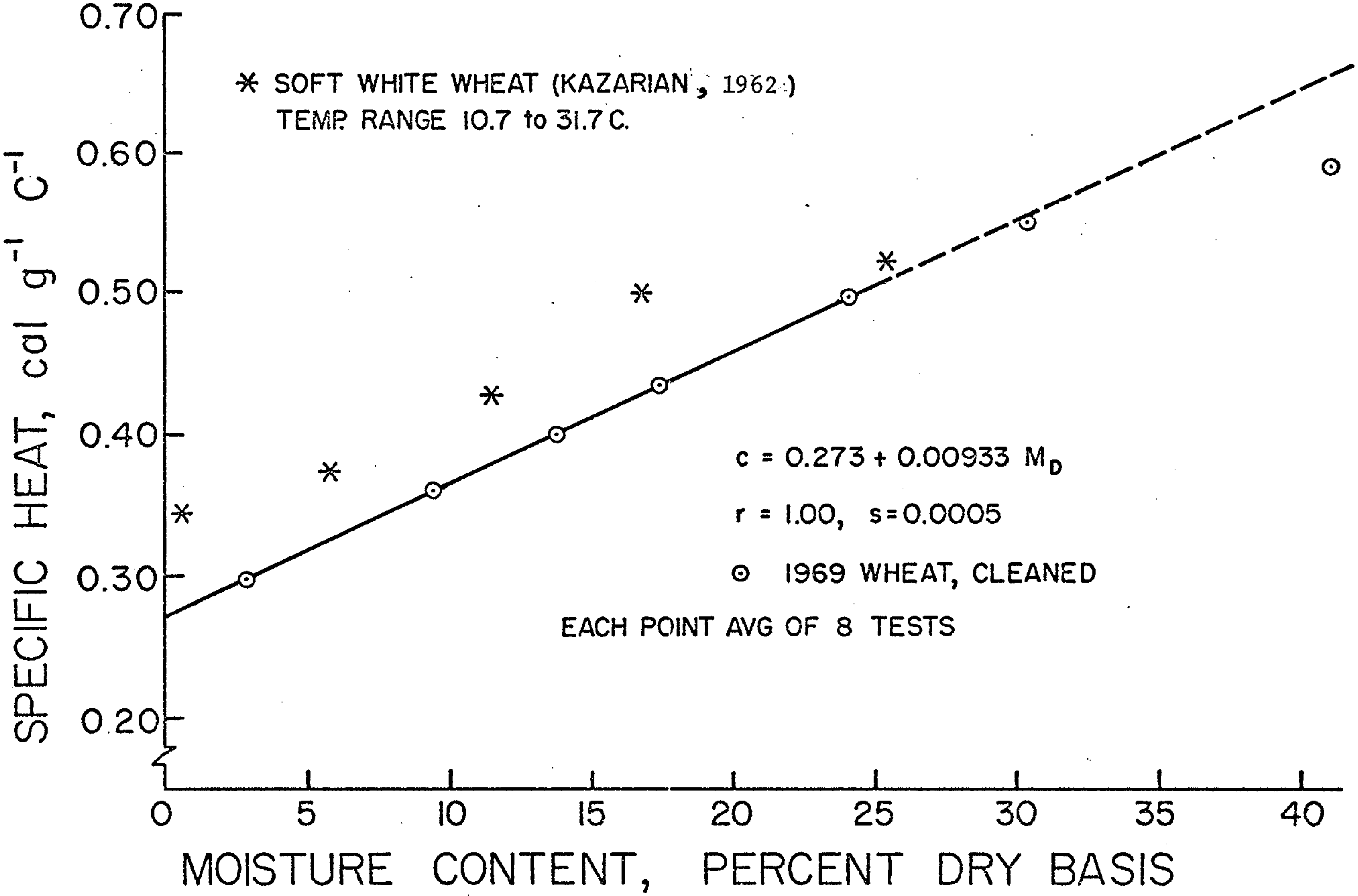

Figure 5.5 Effect of moisture content on specific heat of wheat in the temperature range 8.9 to 21.8 C.

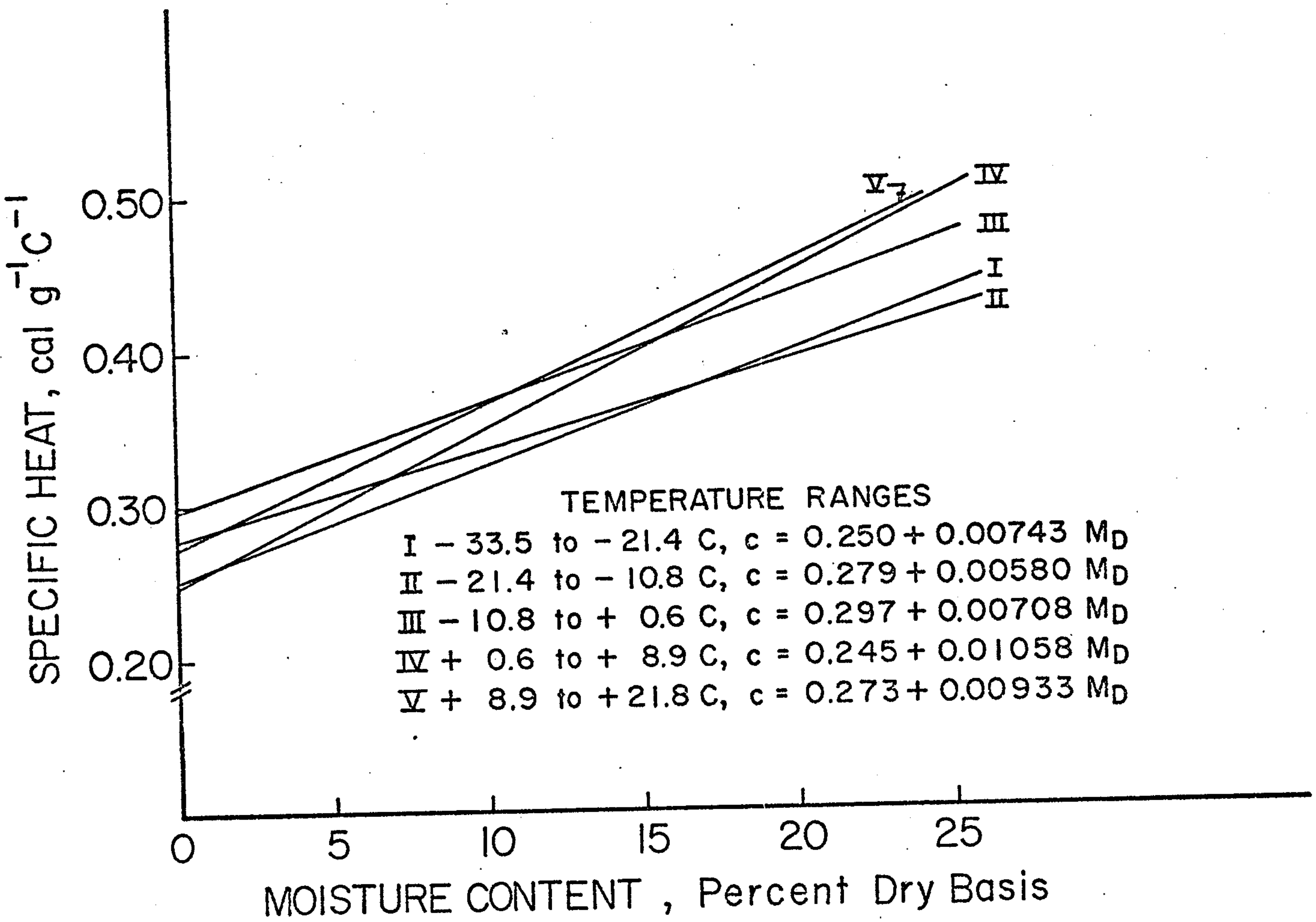

Figure 5.6 Effect of moisture content on specific heat of wheat in different temperature ranges

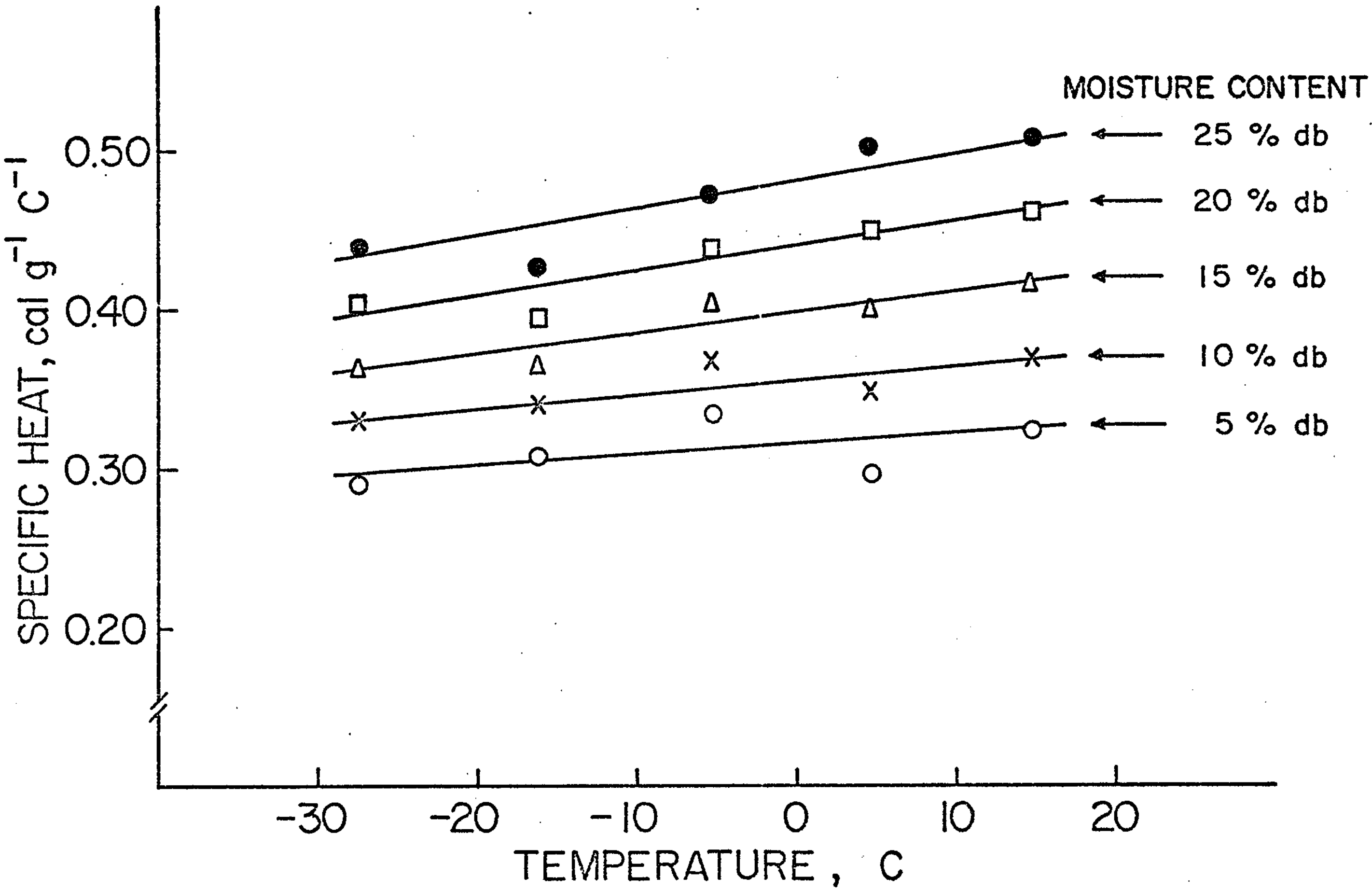

Figure 5.7 Effect of temperature on specific heat of wheat

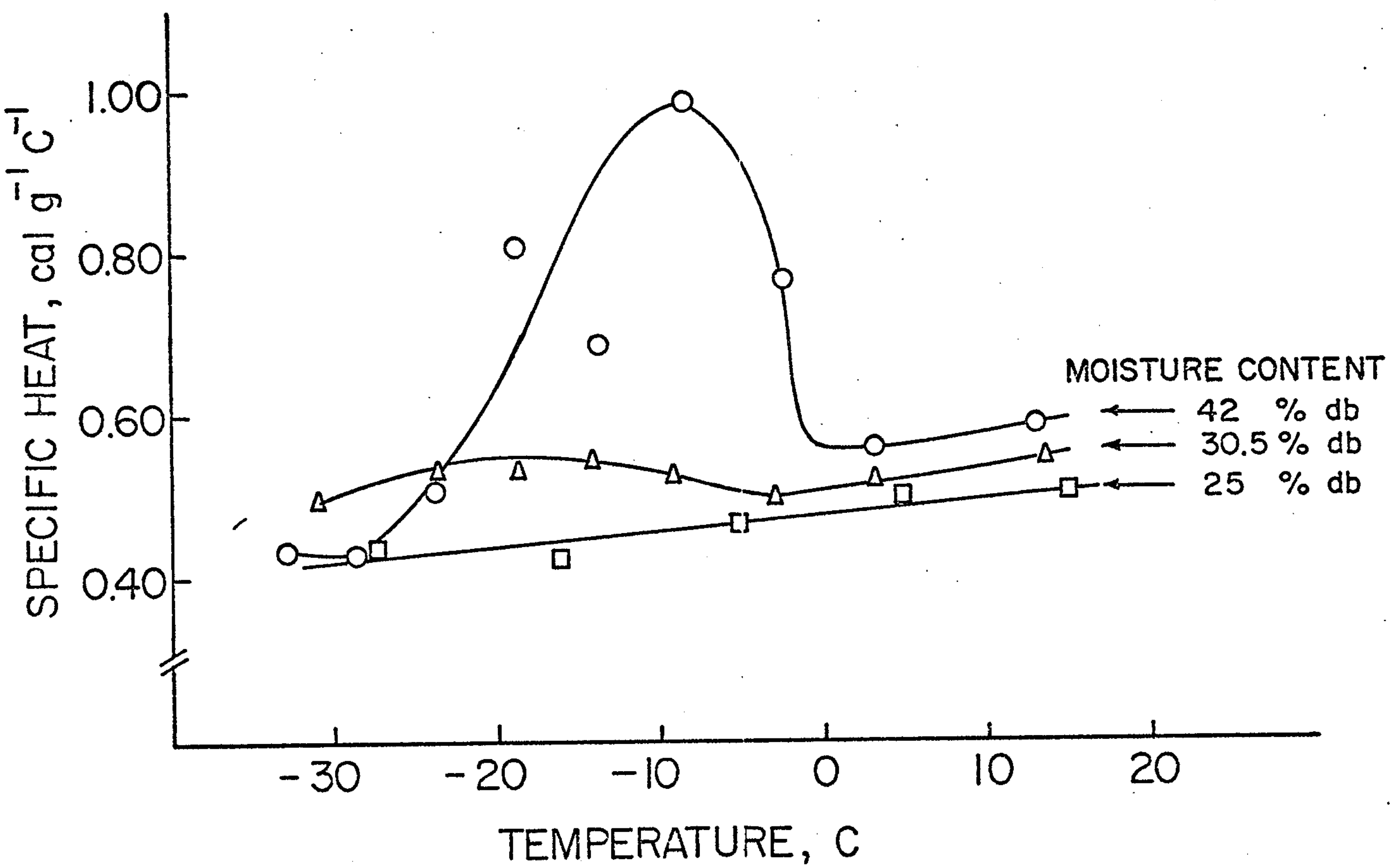

Figure 5.8 Effect of temperature on specific heat of wheat.

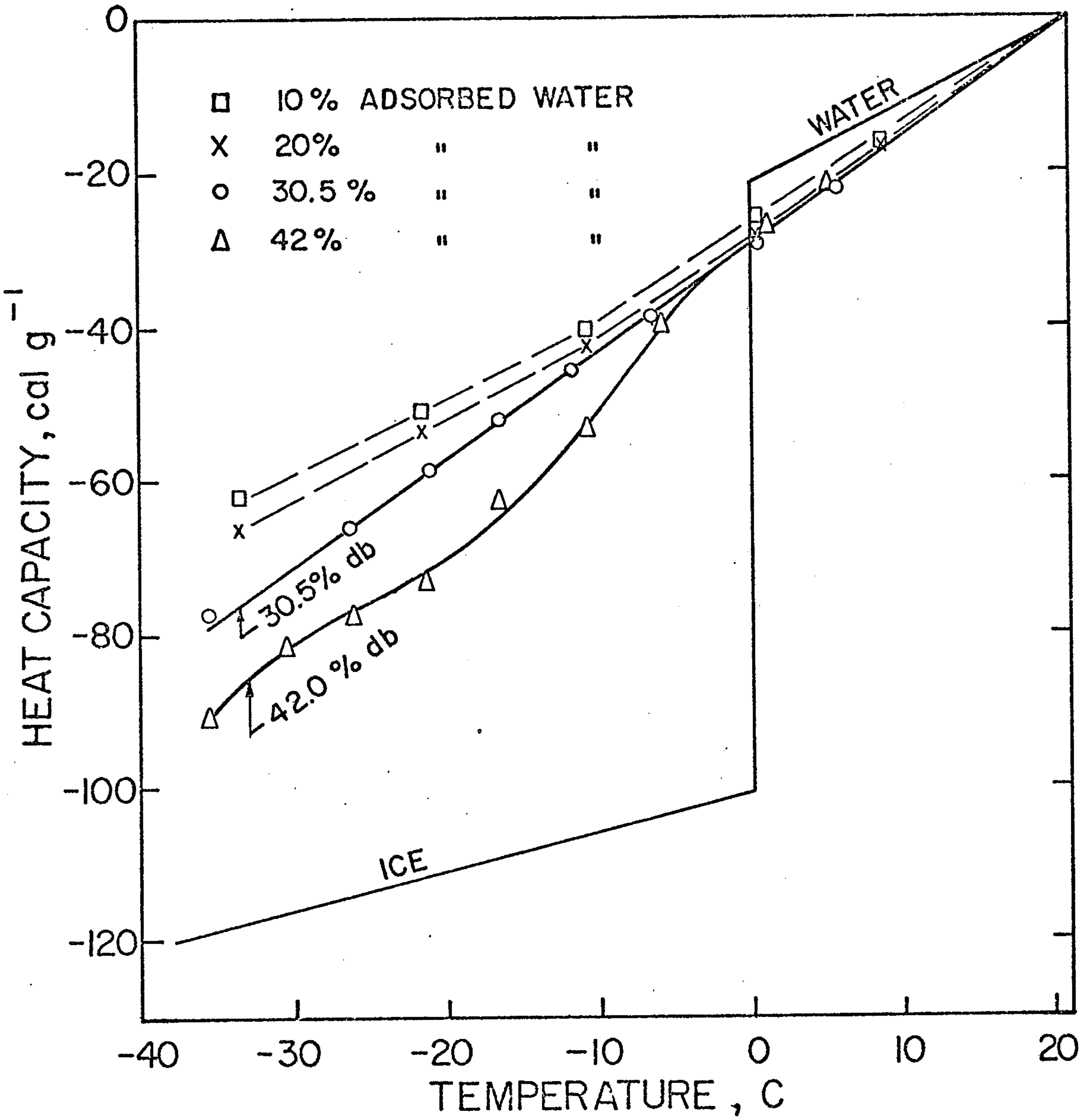

Figure 5.9 Heat capacity of adsorbed water between +21 C and lower temperature.(taken as 0 at +21 C)

6. DISCUSSION

Specific heat of wheat appears to be a linear function of moisture content up to a moisture content of 30% dry basis. A similar conclusion was also reported by Pfalzner, 1951; Disney, 1954, and Kazarian, 1962. It was found that an increase of one percent in the moisture content of wheat resulted in an average increase of 3.25% in the specific heat (Equation 5.1). Evidently in the temperature range above 0 C, the effect of moisture content at a level higher than 30% dry basis was decreased (Figures 5.4, 5.5) as was also shown by Disney (1954). On the contrary the effect of moisture contents above 30% increased the specific heat as the temperature of the sample was decreased below 0 C (Figures 5.1 to 5.3).

The effect of temperature was less at low moisture content but increased with increasing moisture content. For wheat containing less than 30% moisture there was a linear increase in specific heat with increasing temperature. The specific heat of wheat containing more than 30% moisture increased considerably at low temperature (Figure 5.8). The effect of low temperature on high moisture wheat could be expected if the latent heat of fusion was released. From the heat capacity curves (Figure 5.9), it is apparent that the freezing process certainly occurs in wheat containing 42% moisture (dry basis). This is indicated by the definite break in the heat capacity curve which occurs at -1 C. Evidently this sharp break is due to the latent heat of fusion of the adsorbed water as it freezes. This curve is similar in appearance to the heat capacity curve for gelatin-water mixtures described by Hampton and Mennie in 1934. The curves (Figures 5.8, 5.9) show no definite freezing point of wheat but rather a freezing range. The freezing range for wheat containing 42% moisture lies between -1 C and -29 C. This freezing range can be readily explained if we consider the wheat to be a mixture of water and organic chemical compounds (i.e. starch and protein) which have the effect of lowering the freezing point of the mixture. When the initial freezing point of the solution is reached, a portion of the water changes phase. This results in an increase in the concentration of the remaining solution and a corresponding decrease in freezing point. The temperature again decreases until this new freezing point is reached and more liquid solidifies. This explains the reason for the freezing temperature range indicated by the curve (Figure 5.9) rather than a sharp freezing point that occurs with water. Wheat containing moisture contents less than 30% dry basis did not appear to freeze or give up latent heat at any distinct temperature (Figure 5.9). Also since specific heats below 0 C do not increase with decreasing temperature, there does not appear to be a wide freezing range for wheat below 30% moisture content; that is, the wheat does not release any latent heat.

The results obtained for 1967, 1968 and 1969 (uncleaned wheat) compared with the regression lines (Figures 5.2, 5.4) shows that there is no significant difference between different samples tested. That is the dockage in grain and years of harvest did not affect specific heat.

In general the data obtained from this investigation agree with the data of Disney (1953) for Manitoba No. 1 wheat in the corresponding temperature range (Figure 5.4). When compared to the data for soft white wheat (Kazarian, 1962), the specific heat of soft white wheat is considerably higher than that of hard red spring wheat (Figure 5.5). This difference in results may be due to the higher temperature range under which the soft wheat was tested or the difference in the technique and procedures employed in testing or possibly due to a varietal difference of wheat.

7. CONCLUSIONS

Conclusions that can be drawn from the experimental results are as follows:

1. The specific heat of hard red spring wheat is a linear function of moisture content up to 30% dry basis. The mean regression equation was $c = 0.270 + 0.00878\ M_D$ cal $g^{-1}C^{-1}$ over a temperature range of -33.5 C to +21.8 C.

2. The effect of temperature on specific heat of wheat increased with increasing moisture contents.

3. Wheat containing moisture contents less than 30% did not appear to freeze or give up the latent heat of fusion at any distinct temperature within the range of temperature investigated.

4. The freezing process appeared to occur in a wide temperature range below the freezing point of water for wheat containing moisture contents greater than 30% dry basis.

5. Dockage in grain and the year of harvest did not affect specific heat.

8. RECOMMENDATIONS FOR FURTHER STUDY

1. The effect of temperature on the other thermal properties of grain such as thermal conductivity and thermal diffusivity should be investigated.

2. The effect of mould and fungi on the thermal properties of grain should also be studied.

3. The specific heat of the supercooled unfrozen water absorbed in grain should be more thoroughly investigated.

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APPENDIX A

Sample calculation for specific heat of wheat

The equation for calculating specific heat is;

$$c_s = \frac{(M_w+E)\ c_w(T_c-T_m)}{M_s(T_m-T_s)} \quad . \ . \ . \ . \ A\ 1.1$$

For test No. 1 for wheat at a moisture content of 0.9% dry basis and a temperature range of -33.5 to +20.8 C.

c_s = mean specific heat of wheat, cal $g^{-1}C^{-1}$

c_w = mean specific heat of calorimeter water, 0.999 cal $g^{-1}C^{-1}$

M_s = mass of wheat, 20.0569 g

M_w = mass of calorimeter water, 202.5 g

T_c = initial temperature of calorimeter water, 22.13 C

T_s = initial temperature of wheat, -33.11 C

T_m = temperature of the mixture, 20.78 C

E = water equivalent of the calorimeter, 24.4 g

Substituting into Eq. A 1.1:

$$c_s = \frac{(202.5 + 24.4)(0.999)(22.13 - 20.78)}{(20.0569)[20.78 - (-33.11)]}$$

$$= \frac{(226.9)(0.999)(1.35)}{(20.0569)(53.89)}$$

$$= 0.283 \quad \text{cal } g^{-1}C^{-1}$$

The average value for 8 tests

$$= 1/8(0.283 + 0.276 + 0.276 + 0.287 + 0.276 + 0.282 + 0.287 + 0.279)$$

$$= 0.281 \quad \text{cal } g^{-1}C^{-1}$$

Standard deviation = 0.0047 cal $g^{-1}C^{-1}$

APPENDIX B

Sample calculation for regression equation for specific heat of wheat in small temperature intervals.

From the definition of specific heat, the following equation was obtained:

$Q = mc\Delta T$ . . . . A 2.1

Let Q = quantity of heat required to raise the temperature of 1 g of wheat from -33.5 to -21.4 C, cal

c = mean specific heat of wheat in the temperature range -33.5 to -21.4 C, cal $g^{-1}C^{-1}$

$\therefore Q = (1)(c)[-21.4 - (-33.5)]$

$= 12.1\,c$ . . . . . . A 2.2

Let Q_1 = quantity of heat required to raise the temperature of 1 g of wheat from -33.5 to +21 C, cal

c_1 = mean specific heat of wheat in the corresponding temperature range, cal $g^{-1}C^{-1}$

$= 0.270 + 0.00788\,M_D$ (From Figure 5.1)

$\therefore Q_1 = (0.270 + 0.00788\,M_D)\,[21 - (-33.5)]$

$= (0.270 + 0.00788\,M_D)(54.5)$ . . . . A 2.3

Let Q_2 = quantity of heat required to raise the temperature of 1 g of wheat from -21.4 to +21 C, cal

c_2 = mean specific heat of wheat in the corresponding temperature range, cal $g^{-1}C^{-1}$

$= 0.275 + 0.00801\,M_D$ (From Figure 5.2)

$\therefore Q_2 = (0.275 + 0.00801\,M_D)\,[21 - (-21.4)]$

$= (0.275 + 0.00801\,M_D)\,(42.4)$ . . . . . A 2.4

Since $Q_1 = Q + Q_2$ . . . . A 2.5

Substituting the value of Q, Q_1 and Q_2 in Eq. A 2.5, the following was obtained:

$$(0.270 + 0.00788\ M_D)\ (54.5) = 12.1\ c + (0.275 + 0.00801\ M_D)\ (42.4)$$

Solving for c;

$$c = 0.250 + 0.00743\ M_D\ \text{cal g}^{-1}\text{C}^{-1}$$

APPENDIX C

Calculation of experimental uncertainty

The equation of specific heat is

$$c_s = \frac{(M_w + E)\, c_w \Delta T_w}{M_s \Delta T_s} \qquad \text{------------- A 3.1}$$

The uncertainty of the specific heat of a sample can be calculated by using the method described by Kline and McClintock (1953).

$$\left(\frac{\omega c_s}{c_s}\right)^2 = \left(\frac{\omega(M_w+E)}{M_w+E}\right)^2 + \left(\frac{\omega c_w}{c_w}\right)^2 + \left(\frac{\omega \Delta T_w}{\Delta T_w}\right)^2 + \left(\frac{\omega M_s}{M_s}\right)^2 + \left(\frac{\omega \Delta T_s}{\Delta T_s}\right)^2 \qquad \text{---- A 3.2}$$

where ω = the uncertainty of individual measurements, (20 to 1)

ΔT_w = the measured temperature change of the calorimeter water, C

ΔT_s = the measured temperature change of the sample, C.

The quantity of the measured values and their uncertainties are shown in the Table below.

Quantity	Minimum Value	Uncertainty	% Uncertainty
ΔT_w	0.35 C	$\pm$0.01 C	2.86
ΔT_s	12.9 C	$\pm$0.1 C	0.78
M_w+E	225 g	$\pm$5.8 g	2.58
c_w	0.999 cal $g^{-1}C^{-1}$	$\pm$0.001 cal $g^{-1}C^{-1}$	0.10
M_s	20 g	$\pm$0.0001 g	0.0005

By substituting the above values into Equation A 3.2, produced

$$\left(\frac{\omega c_s}{c_s}\right)^2 = (2.58)^2 + (0.10)^2 + (2.86)^2 + (0.0005)^2 + (0.78)^2$$

$$\frac{\omega_{c_s}}{c_s} = (15.45)^{\frac{1}{2}}$$

$$= \pm 3.93\%$$

Therefore the specific heat values obtained from the experiment are within $\pm$ 3.93% uncertainty.