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Technical Report

73-12-PR

AN EXPERIMENTAL STUDY OF THE FREEZE-DRYING OF RAW BEEF

by

Malcolm N. Pilsworth, Jr.

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October 1972

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760



PIONEERING RESEARCH LABORATORY

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FOREWORD

A cooperative program between the Food Laboratory and the Pioneering Research Laboratory was begun in the fall of 1969. The FL representatives were Dr. Maxwell C. Brockmann and Mr. John Swift; the PRL representatives were those whose names appear as authors on the present report. The work now being described was completed in 1970, and the present report is being prepared from research records and from an informal report written at that time.

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ABSTRACT

Freeze-drying curves for small sticks of beef are presented and it was found that in many cases the specimen weight was accurately represented by a quadratic function of the time. In many runs the drying was interrupted and the cross-section of the ice core was measured, after which freeze-drying was completed. A graph showing ice-core diameter versus percent of water (including ice) remaining in the specimen is given, showing that the ice core does not disappear until the water content has been reduced to about 1% of the original weight (about 4% of the dry weight). It is therefore impractical to stop the freeze-drying process at a higher water content in order to permit compression without crumbling. The required moisture could be left in the meat but it will not be uniformly distributed; the wet core will affect product quality adversely.

An Experimental Study of the Freeze-Drying of Raw Beef

1. Introduction

The Armed Services are interested in reducing the weight of foods and also in reducing their bulk. Freeze-drying reduces the weight, and it has been shown that freeze-dried foods can be compressed, which reduces the bulk also. Freeze-dried foods will crumble and shatter when they are compressed, however, unless part of the moisture removed by freeze-drying is restored to them before they are compressed. The partial rehydration is a time-consuming process that adds significantly to the cost of the food, and it would be highly desirable to eliminate it. Specifically, if freeze-drying could be stopped while the proper amount of moisture remained in the food, the rehydration would be unnecessary.

Published results did not make it clear whether it was practical to avoid the rehydration step by stopping the freeze-drying at the appropriate moisture content or not. It is known that after the subliming ice-front passes, the cold layer of food contains bound water which gradually vaporizes as the temperature of the dried food rises. The measurements of Kan [1] on beef indicated that when the last ice disappeared, the remaining moisture amounted to no more than 2 or 3% of the initial weight (8 to 12% of the dry weight). Other authors spoke of considerably more water that came off after the ice was removed. There appeared to be a definite possibility that if freeze-drying were stopped just as the ice cores disappeared, there would be enough moisture remaining to "plasticize" the dried product and permit it to be compressed without crumbling.

In view of this possibility it was decided to make new measurements of the remaining water content as a function of ice-core diameter as raw beef was freeze-dried. Then, if the remaining water was sufficient to serve the plasticizing function an attempt would be made to develop electronic equipment to detect ice and adsorbed water as drying proceeded, so that freeze-drying could

be stopped at just the right water content. According to Kan [1] if any ice cores remained when drying was stopped, they would discolor and toughen the product. However we knew that drying would have to be stopped very soon after the ice cores were gone if sufficient water for plasticizing was to be retained.

2. Samples

The Food Laboratory purchases fresh unfrozen U. S. Choice top round of beef at intervals of 1 month or somewhat more, several cuts at a time, for experimental purposes. Initially the cuts contain about 18 to 22% of fat, but about 1/3 of the fat is trimmed off when the cuts are received. Each cut is wrapped in 2 layers of paper, after which all the cuts are frozen in a blast freezer, which cools them to about -25 F (-32C) (estimated) in 4 or 5 hours. The cuts are then transferred to a freezer held at 0 F (-18 C) where they are stored until needed.

One of the cuts from the freezer was removed and quickly sawed on a band saw into pieces 0.5 x 0.5 x 1 inch in size; about 160 specimens were prepared, all from the same cut. The pieces were quickly canned under nitrogen and immediately cooled to -10 F (-23 C). At no time were the specimens allowed to rise above the freezing point; there was no evidence of surface melting. A few days later the specimens at -10 F (-23 C) were transferred to a refrigerated room held at 4 F (-16 C), located nearer to the laboratory where measurements were to be made. When specimens were required, a can of pieces was placed in dry ice and taken to the laboratory. At the end of the day unused specimens were returned to the cold room.

3. Apparatus

The apparatus used for the majority of the measurements is shown in Fig. 1. The specimen to be freeze-dried is suspended from a vitreous-silica spring inside an evacuated pyrex-glass drying chamber. The lower part of the chamber has a water jacket through which a fluid (water or ethylene glycol) was circulated to produce the desired wall temperature while drying took place.

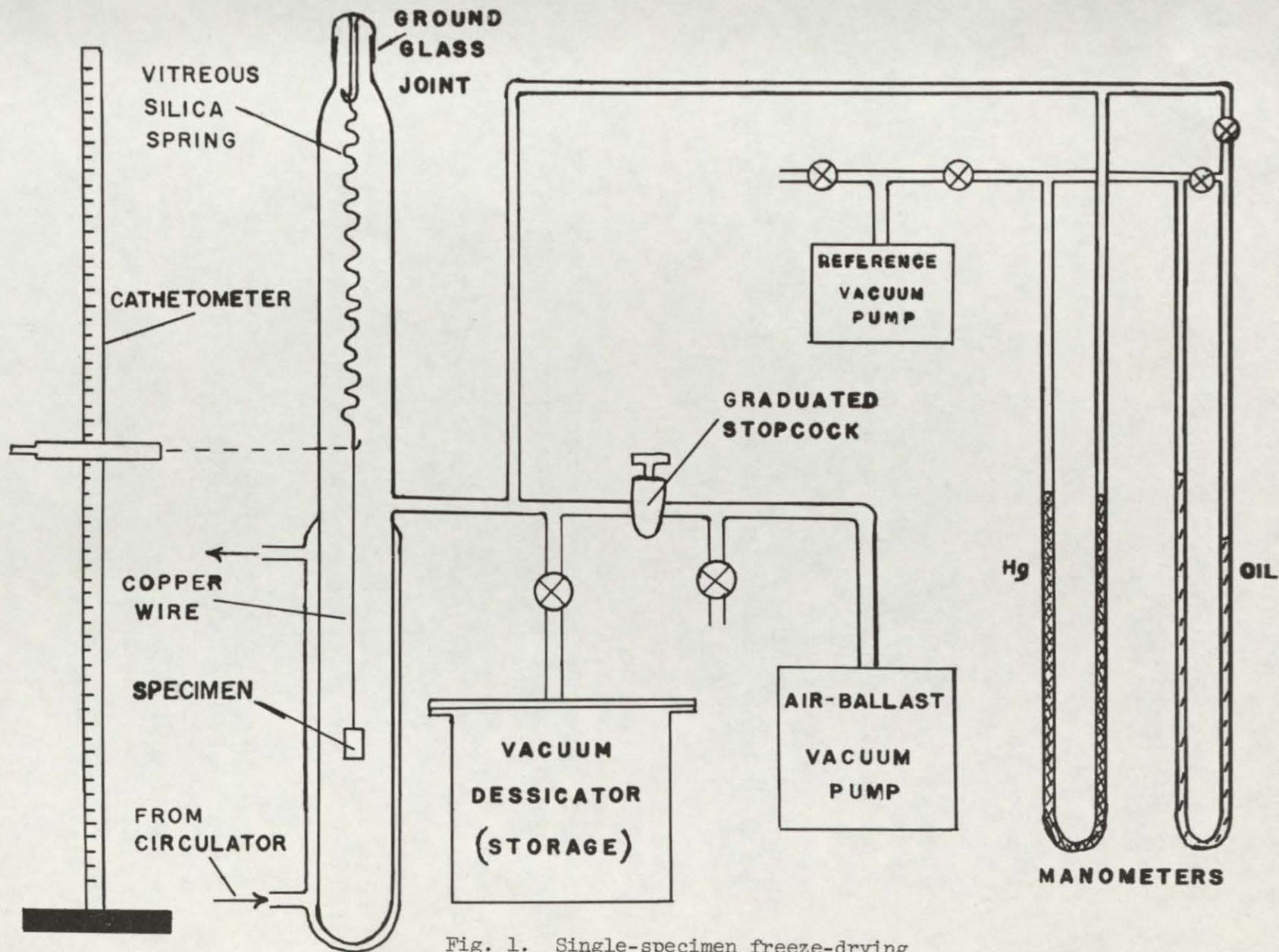


Fig. 1. Single-specimen freeze-drying apparatus, with provision for continuous observation of weight and pressure.

Freeze-drying was produced by a Leybold 2-stage mechanical vacuum pump of 3.3 CFM capacity. The pump had provision to admit gas ballast between stages when pumping water vapor, but it was not necessary to use this feature to keep the pump-oil dry enough for good operation. Only one specimen was freeze-dried at a time, and a rough estimate indicates that the rate of pumping was never over about 1.4 g of water vapor per hour. There was no condenser to remove water vapor by freezing it.

The pyrex shut-off valve between the drying chamber and the pump had O-ring packings and an O-ring seat. It was very convenient for accurate control; when desired, the pressure of water vapor in the chamber could easily be set to the required level with an accuracy of better than 0.1 torr. The pressure could be maintained manually near a desired value by adjusting the valve occasionally. This was done in 2 runs; normally the valve was left wide open.

Pressures in^{the} drying chamber were read on the mercury manometer or on the oil manometer. The oil density was 0.0644 that of mercury; this value was found by comparison of manometer readings made at room temperature. Both manometers were absolute. The two arms of the oil manometer were connected together and to the reference vacuum until the chamber pressure was low enough for the measuring arm to be connected to the chamber. The reference vacuum for both manometers was furnished by a Welch 2-stage mechanical pump.

Completely dried specimens of beef were stored in the dessicator, which was kept evacuated except when it was opened to insert or remove a sample.

The specimen being dried was attached to the spring with a 40 cm length of AWG 32 nylon-coated copper wire, having a diameter overall of 0.24 mm. Each wire was previously weighed and was used with only one specimen; it was kept with the specimen after drying was completed. The vitreous-silica spring was calibrated in place by hanging known weights from it. Its constant is 0.1612 g/cm. Calibration was performed in place, at room

temperature. A few calibrations were made with the spring in the lower part of the vacuum chamber, where its temperature could be controlled by the water jacket. It was more difficult to measure the extensions accurately here because of curvature of the glass jacket; but enough readings were obtained to show that, to the accuracy required in the present work, the spring constant could be considered independent of temperature. Note that the spring is normally entirely contained in the upper, unjacketed part of the drying chamber, where it is only slightly heated by the water jacket. Observed weights are estimated to be correct to ± 2 mg or better.

A Stokes laboratory-size freeze-dryer, Model 2003F-2, having a tray area of 4 sq ft, was used in some of the measurements, to obtain data rapidly on ice-core diameter as a function of moisture content. Pressures and temperatures could be controlled and measured in this apparatus but weights could be determined only before and after the specimens were put in the dryer, and when they had been removed specifically for the purpose of weighing. Specimens were placed on two sheets of hardware cloth for convenient insertion in and removal from the drying chamber. The hardware cloth also permitted easy escape of vapor from the lower surface of the specimens.

4. Procedures

A specimen of frozen beef was removed from the dewar flask containing dry ice and its 3 dimensions were immediately measured, normally with a traveling microscope. The copper suspension wire was then attached and the specimen was hung from the spring (not yet in the drying chamber) with its long axis vertical. During these operations the specimen was returned to the dry-ice flask from time to time to keep it cold. With the specimen hanging from the spring and surrounded by the flask, the initial weight (m_0) of the specimen was determined, after which the spring and specimen were inserted in the drying chamber and the tapered joint was seated. Pumping was immediately begun, and the timing clock was started at about the time the pressure reached 4 torr. Readings of the specimen weight were begun as soon as possible, but it was

impossible to install the specimen without setting up oscillations. Since the vitreous-silica spring is highly elastic and the surrounding pressure was low, there was very little damping; about 10 minutes was required for the oscillations to die down enough to permit good readings to be made with the cathetometer.

Readings of spring extension and chamber pressure were made at suitable intervals as freeze-drying progressed. Near the beginning and end of the actual freeze-drying, readings were made every 10 minutes or oftener, but during the intervening time the intervals between readings were longer. When the ice had all sublimed and the final (finishing) period was in progress, the interval between readings was also lengthened.

In all except three runs, the freeze-drying was interrupted at some suitable time so that the cross-section of the core of ice remaining in the specimens could be measured. The vacuum was broken; the specimen was removed and cut into two equal parts. Usually the cut was perpendicular to the long axis, yielding two nominally 0.5-inch (1.27 cm) cubes, but in some cases the cut contained the long axis, yielding two pieces, each nominally 0.25 x 0.5 x 1 inch (0.635 x 1.27 x 2.54 cm). Two measurements of the core diameter were made with the traveling microscope on each freshly-exposed cut surface; normally the two measured diameters on each piece were at right angles to each other. The 4 readings were averaged to give the core diameter. In many cases the cross section of the core was nearly circular but in others it was far from it.

As soon as the core had been measured, the two parts of the specimen were put back together in their original configuration, fastened together by the copper suspension-wire originally used, and returned to the freeze-drying apparatus. Freeze-drying was resumed at once. By working rapidly it was possible to keep the time from breaking of the vacuum to restoring it down to about 8 min, on the average. There was some melting of the exposed ice cores at the cut surfaces, but it is believed that the ice surfaces that were fully insulated by freeze-dried material probably did not rise to 0 C.

The majority of the runs were completed in one working day. Under our usual operating conditions the ice cores disappeared after about 4.30 hours of freeze-drying, and complete drying was achieved by continuing for 2 or 3 hours beyond this time. Subsequent loss of weight was quite small; more information on this point is given later.

As the standard conditions for freeze-drying in the present experiments we adopted a wall (water jacket) temperature of 65 C (149 F) and a chamber pressure as low as the freeze-drying pump would maintain with the throttling valve wide open. This pressure was about 0.5 torr at the beginning of a run and fell gradually to less than 0.03 torr when substantially all the water had been removed. These pressures would be somewhat different if a pump of a different size were used, or if larger or smaller specimens or more than one specimen at a time were dried.

All pieces freeze-dried in the single-specimen apparatus were dried at our standard conditions except Specimens 9 and 10, which were freeze-dried at standard temperature but at 1 and 3 torr, respectively; and Specimens 24 and 25, which were freeze-dried at standard pressures but at a wall temperature of 45 C (113 F). We attempted in the Stokes dryer to match our standard conditions but succeeded only partially. The pressures were probably not far from those typically attained in the single-specimen apparatus, but they are not accurately known because they were read on a McLeod gage in which some condensation of water vapor may have occurred during pressure readings. The observed values were < 0.1 torr. The wall temperatures were too low on the average. Starting at 48 C (118 F) the wall temperature gradually rose to the desired value of 65 C during a period of 1.67 hr; we are not able to raise the temperature more rapidly. After 3.83 hr of freeze-drying (including the time while the temperature was rising), the specimens were removed from the Stokes dryer to be weighed, cut open, and to have their core diameters measured.

When the Stokes apparatus was used so that many specimens could be dried at once, it was necessary to weigh the specimens in addition to getting their dimensions before they were put in the dryer. After weighing, the specimens were freeze-dried until it

was judged (on the basis of experience with the other apparatus) that some would be completely dry, and most of the rest would have water contents ranging up to 10 or 12%. At this time the specimens were removed, weighed again, cut open, and the cores were measured. The specimens were then returned to the Stokes dryer and dried for an additional 18 hours, when it was assumed that the dry weights had been reached. The specimens were removed, weighed a third time, and stored at atmospheric pressure and temperature.

5. Results

Fourteen pieces of frozen raw beef were separately freeze-dried in the apparatus shown in Fig. 1. Twelve additional pieces were dried as a batch in the Stokes dryer. Table 1 contains information on all of the specimens that were studied, giving initial and dry weight, drying time, measured ice-core diameter and corresponding water content, and other properties.

Drying curves (weight versus time) for two typical specimens are shown in Fig. 2 where each plotted point represents a weight determined from cathetometer readings. The smooth curves drawn to represent the points are parabolas, about which more will be said later. Note that all of the weights referring to Specimen 1 have been increased by 0.5 g so that the data for the two specimens would not overlap and become confused. The drying process may be conveniently divided into two parts. The first part, which extends from the beginning of drying until the vertex of the parabola is reached, will be referred to as the freeze-drying regime. The remainder to the process will be referred to as the finishing regime. Substantially all of the water is lost in the first regime.

The time at which the freeze-drying regime ends and the finishing regime begins is taken as the drying time. The method of determining the drying time that we have subsequently adopted as standard is somewhat simpler than the method used in the research now being reported, which required the equations of parabolas to be derived and the vertices of the parabolas to be located. Our later,

Table 1. Freeze-drying data. m_0 = weight just before freeze-drying, m_d weight after freeze-drying, initial %H₂O = 100 [1 - (W_d/W₀)], ρ_0 = initial density, wall T = temperature of water jacket of specimen chamber, pressure = pressure in the freeze-drying chamber, t_v = time corresponding to the vertex of the drying parabola (the drying time), m_v = weight corresponding to the vertex of the drying parabola, t_i = time at which the specimen was inspected for an ice core, %H₂O (inspection) = amount of water present at time of inspection, core d. = diameter of ice core when inspection took place.

Specimen	m_0 g	m_d g	Initial %H ₂ O	ρ_0 g/cm ³	Freeze-Drying				Inspection			Specimen
					Wall T, °C	Pressure torr	t_v hr	$m_v - m_d$ mg	t_i hr	% H ₂ O	core d. mm.	
1	4.072	1.084	73.4	0.981	65	<0.5	4.18	-7	-	-	-	1
2	4.282	1.208	71.8	.939	65	"	5.13	+15	-	-	-	2
3	3.758	0.868	76.9	.958	65	"	4.27	-49	3.01	18.7	5.3	3
4	4.124	1.112	73.0	.991	65	"	4.22	+36	4.27	0.5	0	4
5	4.114	0.975	76.3	.963	65	"	4.67	+46	3.68	15.5	4.4	5
6	4.025	1.032	74.4	.976	65	"	4.38	+12	4.02	3.2	1.3	6
7	3.746	1.017	72.8	.944	65	"	4.33	+19	3.68	7.1	4.8	7
8	4.174	1.116	73.3	.976	65	"	4.37	-2	3.60	9.0	5.3	8
9	4.257	1.197	71.9	.980	65	1	4.50	+19	4.01	3.9	2.4	9
10	4.016	1.032	74.3	.970	65	3	4.78	+32	3.68	14.1	4.6	10
11	4.269	1.149	73.1	1.001	48-65	<0.1?	-	-	3.83	14.3	5.5	11
12	4.074	1.066	73.8	1.003	48-65	"	-	-	"	9.7	5.2	12
13	4.227	1.051	75.1	0.991	48-65	"	-	-	"	20.3	7.1	13
14	4.231	1.146	72.9	.993	48-65	"	-	-	"	20.9	5.1	14
15	4.215	1.061	74.8	.968	48-65	"	-	-	"	18.6	5.1	15
16	3.929	1.000	74.6	.978	48-65	"	-	-	"	10.4	3.5	16
17	4.289	1.122	73.8	1.006	48-65	"	-	-	"	14.0	4.9	17
18	3.978	1.023	74.3	0.946	48-65	"	-	-	"	20.5	5.9	18
19	3.873	0.987	74.5	1.015	48-65	"	-	-	"	14.7	4.4	19
20	4.247	1.111	73.8	1.005	48-65	"	-	-	"	22.0	6.1	20
21	4.144	1.183	71.4	1.002	48-65	"	-	-	"	8.6	2.7	21
22	3.667	1.001	72.7	0.978	48-65	"	-	-	"	9.9	3.9	22
23	4.060	1.095	73.0	.993	65	<.5	4.40	-1	4.26	1.3	0	23
24	4.194	1.093	73.9	.917	45	"	6.13	+8	5.68	2.8	0	24
25	4.067	1.041	74.4	.995	45	"	6.33	-32	5.26	7.6	2.9	25
26	4.066	1.051	74.2	.943	65	"	4.25	+1	-	-	-	26

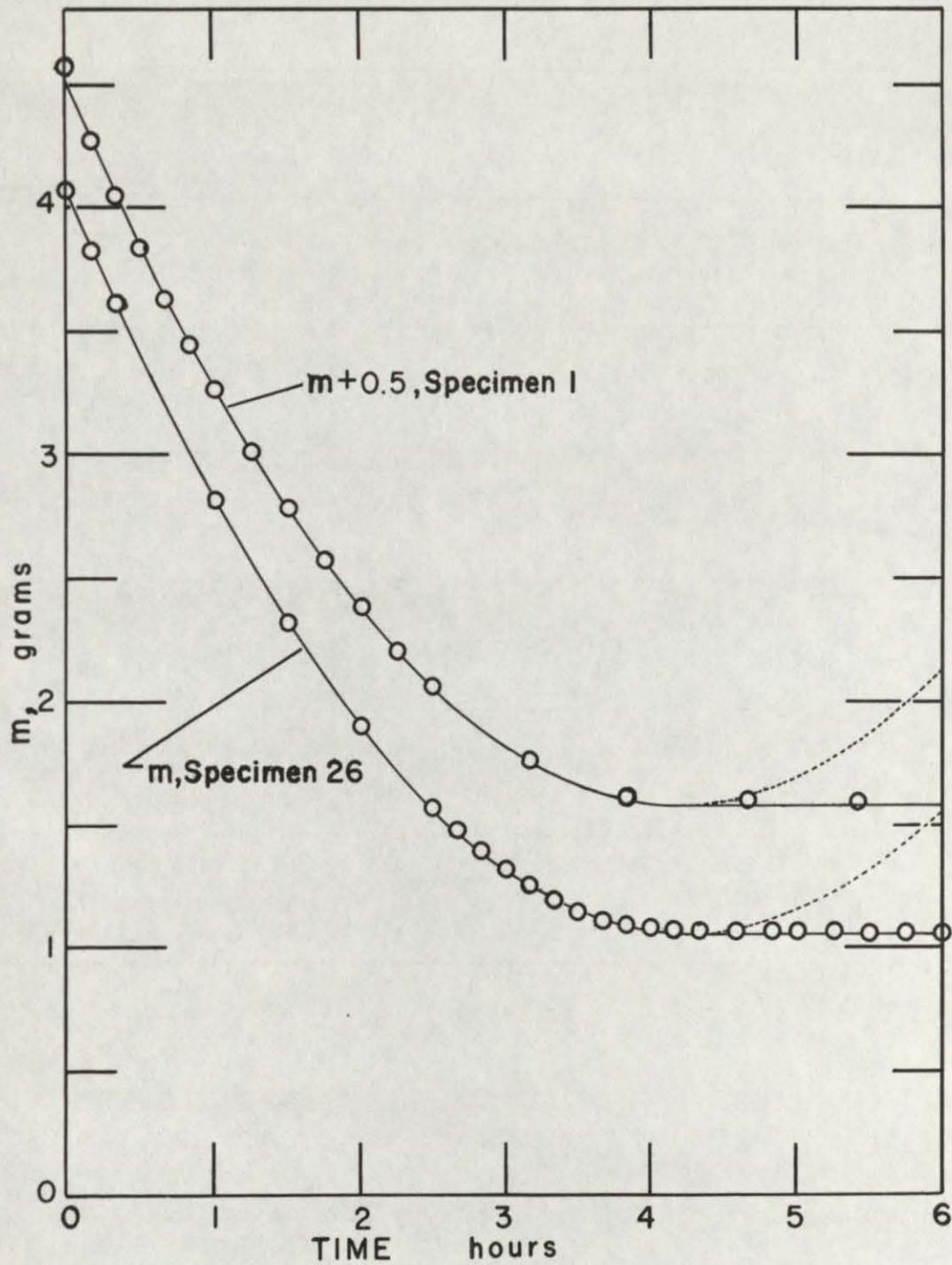


Fig. 2. Freeze-drying curves for beef specimens 1 and 26, showing how data may be represented by parabolas.

simpler method involves only the calculating and plotting of the derivatives of the drying curves; it does not require the equations of the drying curves actually to be derived. Derivatives of the drying curves are calculated from the equation

$$\dot{m}_i = \left(\frac{dm}{dt} \right)_i = \frac{1}{2\tau} (m_{i+1} - m_{i-1}) \quad (1)$$

where τ is a uniform increment of time (10 minutes in the present case) and the subscripts $i-1$, i , and $i+1$ are used to designate any three successive sets of values of m and \dot{m} , determined at intervals of τ . Whenever the experimental measurements of m were not made at uniform, 10-minute intervals it was necessary to plot m versus time and read off values at 10-minute intervals before eq (1) could be used.

The results of applying eq (1) to the data shown in Fig. 2 are the values of \dot{m} shown in Fig. 3. The values of \dot{m} for each specimen are satisfactorily represented by two straight lines, one for the freeze-drying regime and one for the finishing regime. The drying time was found from the intersection of the two straight lines, taking the equation in the finishing regime to be $\dot{m} = 0$. As in Fig. 2, the ordinates for specimen 1 have all been increased by a constant amount to separate the two sets of data. Clearly, a much more accurate and reproducible estimate of drying time can be made from a graph of \dot{m} versus time (Fig. 3) than from a graph of m versus time (Fig. 2).

The ice cores within the drying specimens disappear at or slightly before the end of the freeze-drying regime. After the last ice disappears, the material that was nearest the core is still cold and can perhaps give off water vapor rapidly for a short time, but it is unlikely that this process can persist more than a few minutes.

The accepted dry state. It had been decided to continue each finishing regime for 2 hours or more and to take the last observed weight as the dry weight of the specimen. In reaching this decision,

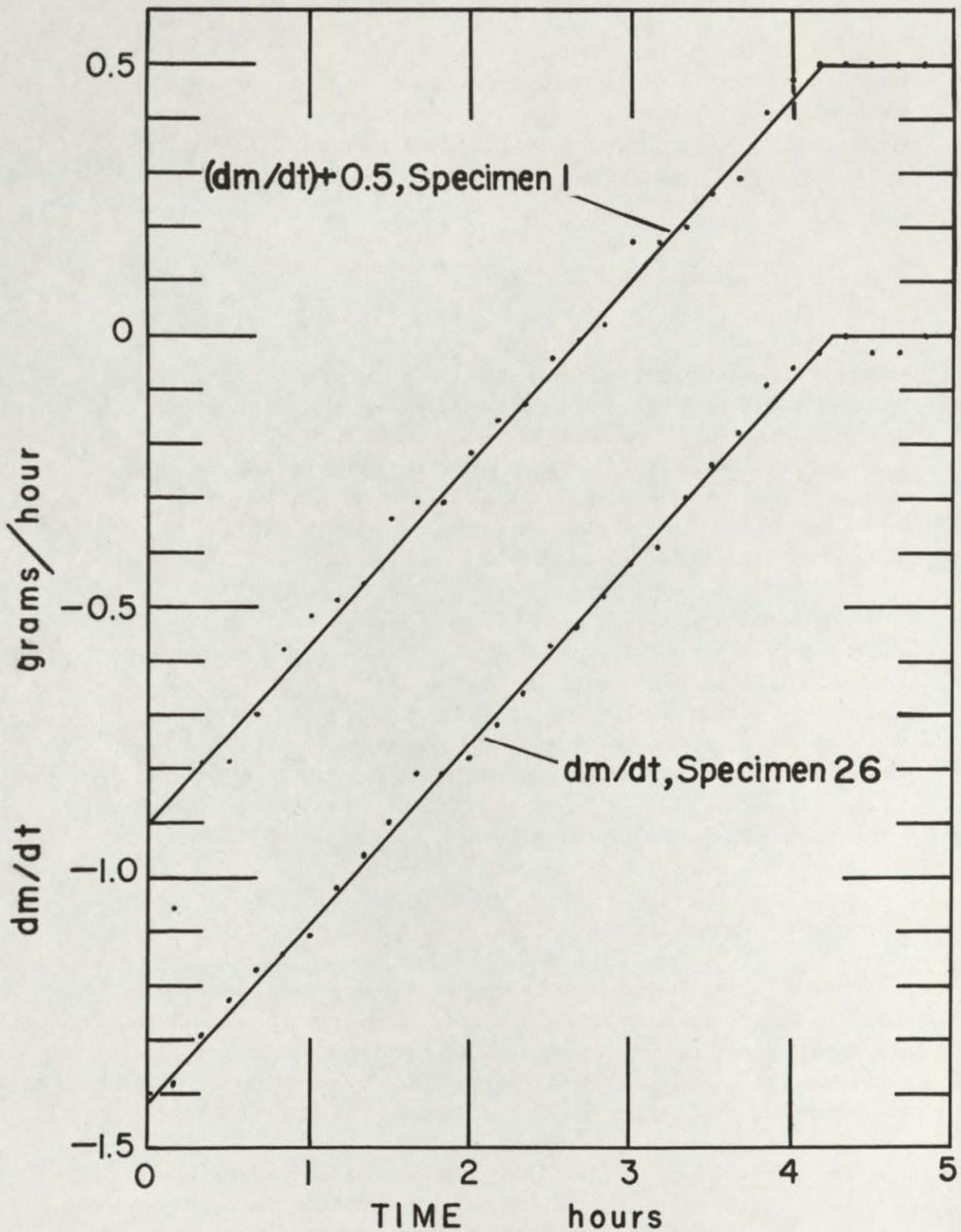


Fig. 3. Graphs showing that the derivative dm/dt is a linear function of time, for beef specimens 1 and 26.

two specimens (1 and 26) were studied intensively in the finishing regime. Specimen 1 was finished for 6 hours. Its weight at the beginning of finishing was 1.102 g; it lost 8 mg during the first hour of finishing and 9 mg more during the remaining 5 hours. This loss is only 1.6% of the dry weight. Specimen 26 was finished for 10.8 hours in 2 stages. The first stage was 0.7 hr at 65 C. The initial weight of 1.071 g was reduced by 7 mg in this stage. The temperature was then raised to 97.5 C (207.5 F) where in 2.4 hr 11 mg was lost. Continuing at this temperature for 7.7 additional hours, the weight loss was 2 more mg. The total weight loss of 20 mg amounted to 1.9% of the dry weight.

The finishing of specimen 26 at 97.5 C was an adaptation of Method 23.002 of the Association of Official Agricultural Chemists [2], for determining moisture. The description of this method is brief and will be quoted in full, "Dry quantity of sample representing ca 2 g dry material to const. wt. at 95-100° under pressure not > 100 torr (ca 5 hr). Use covered Al dish at least 50 mm diam. and not > 40 mm deep. Report loss in wt as moisture." It was decided that the more important of these conditions could be achieved in our apparatus (Fig. 1) by simply raising the temperature of the freeze-drying chamber to 97.5 C, and drying for about 5 hours at the lowest pressure that the drying pump would maintain (< 0.03 torr). Our samples were about half the recommended weight, and we used no dish. Otherwise we met the conditions of the method. We concluded that finishing for 2 hours or more at 65 C would be adequate for our purposes and would drive off nearly as much water as would be lost at 97.5 C.

It is of course possible that bound water is still present, comprising part of what we accept as the dry weight. It seems unlikely that such tightly-bound water could make up any significant percentage of the "dry" weight, but if it did our experiments and general conclusions would still be valid. We would simply be referring our water contents to a displaced zero.

Ice cores and water content. As freeze-drying progresses, the core of ice recedes from the surface of the specimen. In an idealized piece, homogeneous and isotropic, the ice would at first

be a rectangular parallelepiped coincident in shape with the specimen, but as freeze-drying proceeded the ice would shrink, and the edges and corners of the core would very soon become rounded. For an idealized piece 0.5 x 0.5 x 1.0 inch (1.27 x 1.27 x 2.54 cm), which was the initial size of the pieces used in the present experiments, the core would shrink until, shortly before it disappeared, it approximated a circular cylinder with hemispherical ends, with a length of about 0.5 inch (1.27 cm). Actual beef is non-homogeneous whenever fat or other non-muscle tissue is present. It is non-isotropic because of the grain (muscle-fiber direction). However, we may expect the actual ice cores to behave very roughly as described above.

All of the specimens studied except specimens 1, 2, and 26, were examined for ice cores at some time judged appropriate during the freeze-drying process. In a few cases the ice had already disappeared. If an ice core was present, it was measured as described earlier. The time of examination, core diameter, and corresponding water content of each specimen are given in Table 1. Core diameter as a function of water content is shown in Fig. 4. Data for Specimens 3-10 and 23, which were freeze-dried in the single-specimen apparatus (Fig. 1), are plotted as open circles. Data for Specimens 11-22, which were freeze-dried as a single batch in the Stokes dryer, are plotted as solid circles. The average water content when the specimens were removed from the Stokes dryer for examination was 15% of the original weight. This was slightly larger than desired because we had made insufficient allowance for the low initial wall temperature of the dryer.

A smooth curve has been drawn in Fig. 4 to represent the ice-core data. The data scatter more than we would like, but even so we can see that ice cores persist down to a relatively low water content. The curve has been drawn to cut the axis of abscissas at 1% water content. It could be drawn to cut the axis at any point between 0.5% and 1.5% without doing violence to the data, but curves that cut the axis above 2% begin to look unreasonable. This is the important point. We see that if freeze-drying is stopped when there is 2% of water remaining (8% on a dry-weight basis) the meat will contain ice cores. Since we believe that ice cores

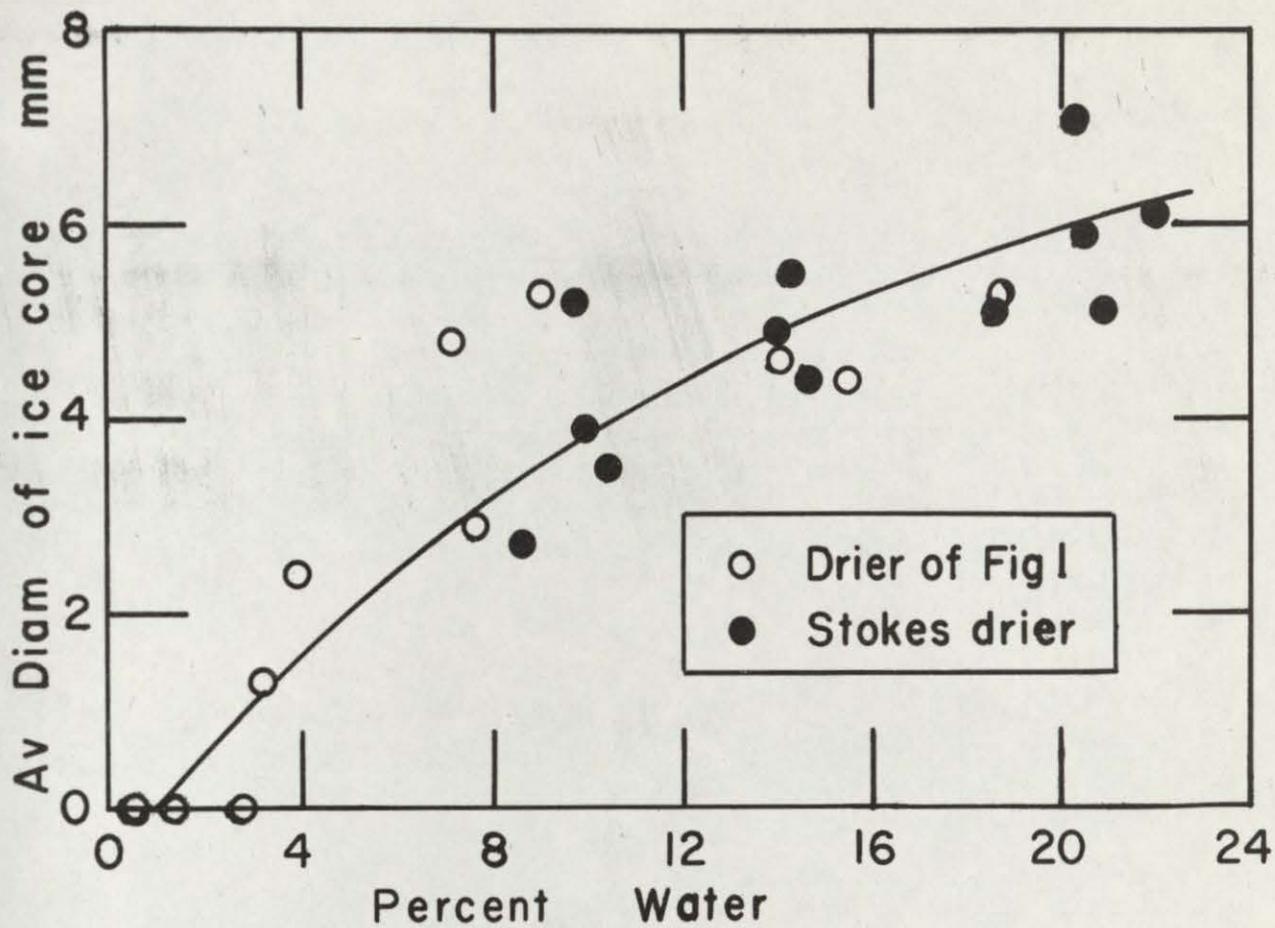


Fig. 4. Diameters of ice cores of beef specimens as a function of water (including ice) content.

will give a product of inferior quality, we cannot stop freeze-drying in this region.

Effect of wall temperature on drying time. Many observers have noted that wall temperature (sometimes called shelf temperature or platen temperature) has an important influence on freeze-drying time, whereas the pressure maintained in the drying chamber has a much smaller effect, at least within the acceptable-pressure limits. Our data confirm these findings.

Two specimens (Specimens 24 and 25) were freeze-dried under standard pressure conditions but with a wall temperature of 45 C instead of the standard 65 C. The freeze-drying times (t_v) were 6.13 hr for Specimen 24 and 6.33 hr for Specimen 25. The 7 normal specimens dried under standard conditions had an average t_v of 4.30 hr. The average drying time at 45 C was 45% greater. This confirms the well-known fact that freeze-drying should be performed with the highest wall temperature that does not harm the product.

Effect of pressure on drying time. Two specimens (Nos. 9 and 10) were freeze-dried at standard wall temperature but at non-standard drying-chamber pressures. Specimen 9, dried at 1 torr, required 4.50 hr; Specimen 10, dried at 3 torr required 4.78 hr. For comparison, 7 normal specimens dried at standard pressure conditions (ranging downward from 0.5 torr) required an average drying time of 4.30 hr. We do not know whether these differences are significant or not. The increased pressure has two effects: it increases the thermal conductivity of the dried layer and it raises the temperature of the ice core. The first of these tends to speed up freeze-drying and the second tends to slow it down. Most of the evidence we have indicates that the first effect predominates, except in the early stages of freeze-drying, and that drying should be more rapid at 1 or 2 torr than at pressures below 0.5 torr.

Shrinkage. It is often stated that materials do not shrink when they are freeze-dried. It is true that the shrinkage is very much less than it would be in ordinary drying. However, our experience

shows that beef can undergo substantial shrinkage during freeze-drying and finishing. Specimens 1, 2, and 26, which were completely freeze-dried without being cut open or examined, were measured both before and after the process. The results are given in Table 2. The volume shrinkage of the 3 specimens ranged from 18.0 to 25.4%. There is some evidence, partially contradictory, that shrinkage across the grain is greater than shrinkage along the grain. The greater shrinkage of Specimen 26, as compared with the other two, is probably due to the higher temperature to which it was exposed during most of the finishing period. The longer finishing period might also increase the shrinkage of this piece.

6. Parabolic Drying Curves and Abrupt Changes in Drying Rate.

In Section 5 of this report it was mentioned that the curves of specimen weight versus time were found to be parabolas. Two examples are shown in Fig. 2, and similar quadratic relations were found to hold for most of the other specimens for which data were obtained. The equations of the parabolas shown are, for Specimen 1

$$m = 4.006 - 1.400 t + 0.1673t^2 \quad (2)$$

and for Specimen 26

$$m = 4.069 - 1.420t + 0.1671t^2 \quad (3)$$

where m is in grams and t is in hours. The derivatives of these equations are the slanting straight lines shown in Fig. 3.

In a few cases (3 out of 14) a single quadratic equation did not fit the experimental drying data. An example of one of these cases is shown in Fig. 5. Here the data are well represented by using two parabolas for the same specimen. The equations and their regions of validity are

$$\left. \begin{aligned} m &= 4.286 - 1.420t + 0.1779t^2 \\ 0 &\leq t \leq 2.87 \text{ hr} \end{aligned} \right\} \quad (4)$$

Table 2. Shrinkage during freeze-drying

Specimen		1	2	26
Wall T, °C		65	65	65-97.5
a, cm with grain	before	1.270	1.308	1.300
	after	1.214	1.251	1.171
	% change	-4.41	-4.36	-9.92
b, cm across grain	before	1.270	1.339	1.302
	after	1.161	1.198	1.167
	% change	-8.58	-10.53	-10.37
c, cm across grain	before	2.573	2.604	2.549
	after	2.413	2.477	2.354
	% change	-6.22	-4.88	-7.65
volume cm ³	before	4.150	4.561	4.314
	after	3.401	3.712	3.217
	% change	-18.05	-18.61	-25.43

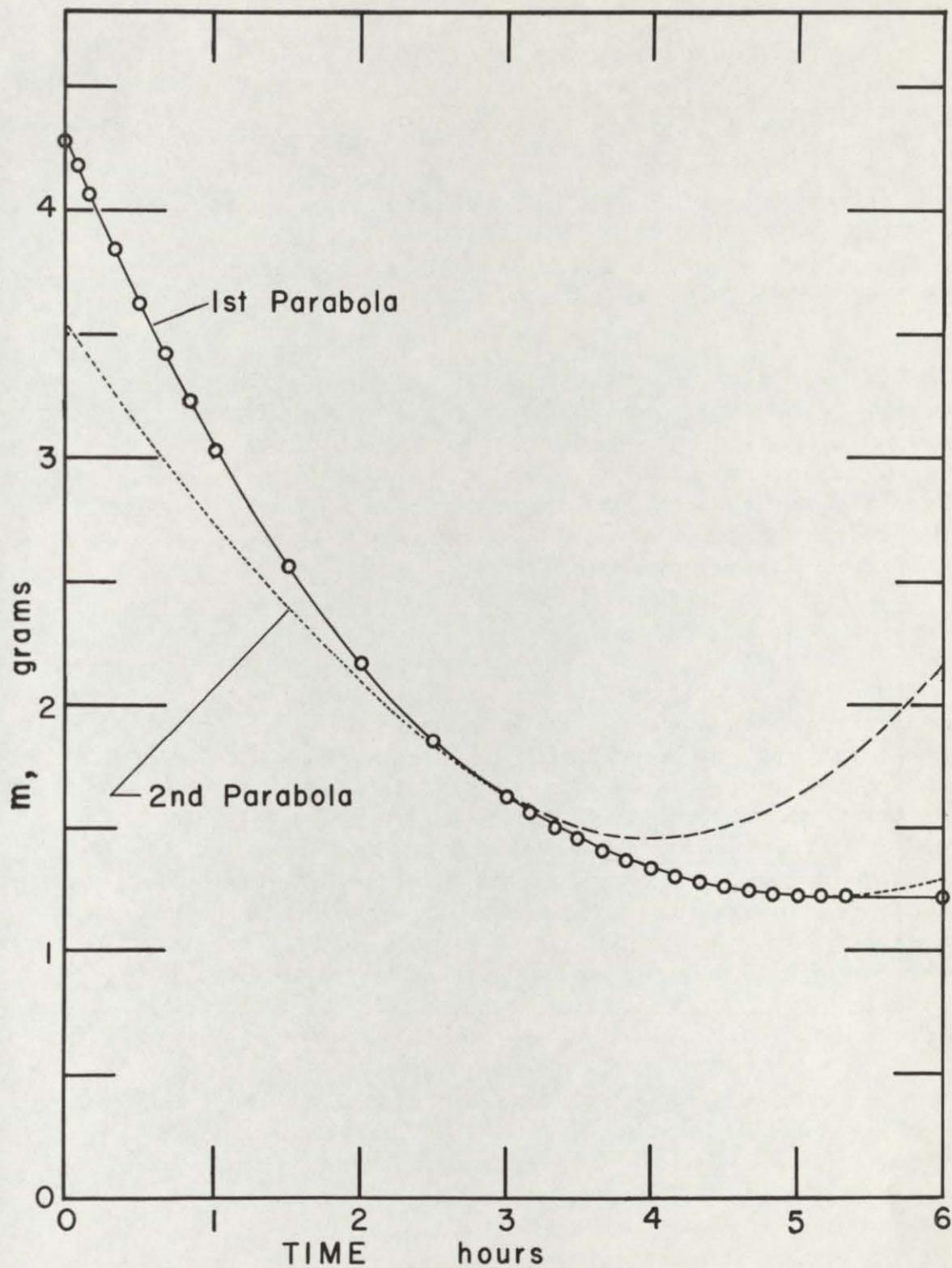


Fig. 5. Freeze-drying curve for specimen 2, showing that the data may be represented by two parabolas.

$$\begin{array}{l}
 m = 3.550 - 0.906t + 0.0882t^2 \\
 2.87 \leq t \leq 5.13 \text{ hr.}
 \end{array}
 \left. \vphantom{\begin{array}{l} m = 3.550 - 0.906t + 0.0882t^2 \\ 2.87 \leq t \leq 5.13 \text{ hr.} \end{array}} \right\} \quad (5)$$

Note that the constants in eqs (2), (3), and (4) are quite similar, whereas those in eq (5) differ from the other three considerably. It appears that Specimen 2 behaved normally for 2.87 hours and then began to freeze-dry in an abnormal way.

For those who may be skeptical (as we were at first) that the data for Specimen 2 are sufficient to define two different parabolas, Fig. 6 is presented. The two straight lines are the slopes of eqs (4) and (5). The plotted points come directly from the experimental data, by the use of eq (1). The two straight lines represent the data very well. The other abnormal specimens were Nos. (5) and (7). They give slopes similar to those shown in Fig. 6 but with the changes in slope not quite so striking.

It seems likely that the abnormal drying of samples such as Specimen 2 is associated with variations in structure, perhaps associated with layers of fat or connective tissue. Tissue and fat, the latter especially, may be expected to be much better thermal conductors than freeze-dried muscle, but they probably hinder the flow of water vapor. Models can be constructed that will explain some of the observed abnormal freeze-drying behavior. For example, a homogeneous specimen or one with many closely-spaced layers of fat would behave normally, whereas a specimen with fewer, more-widely-spaced layers of fat would dry normally so long as the ice core made contact with one or more layers, but would dry more slowly after this contact was lost.

The existence of abnormal, slow-drying beef such as Specimen 2 is of considerable importance in commercial freeze-drying. If, as seems likely, any batch of beef contains some pieces or parts of pieces that are slow-drying, these slow-drying pieces will determine the required total drying time. In our experience, seven normal specimens required an average freeze-drying time

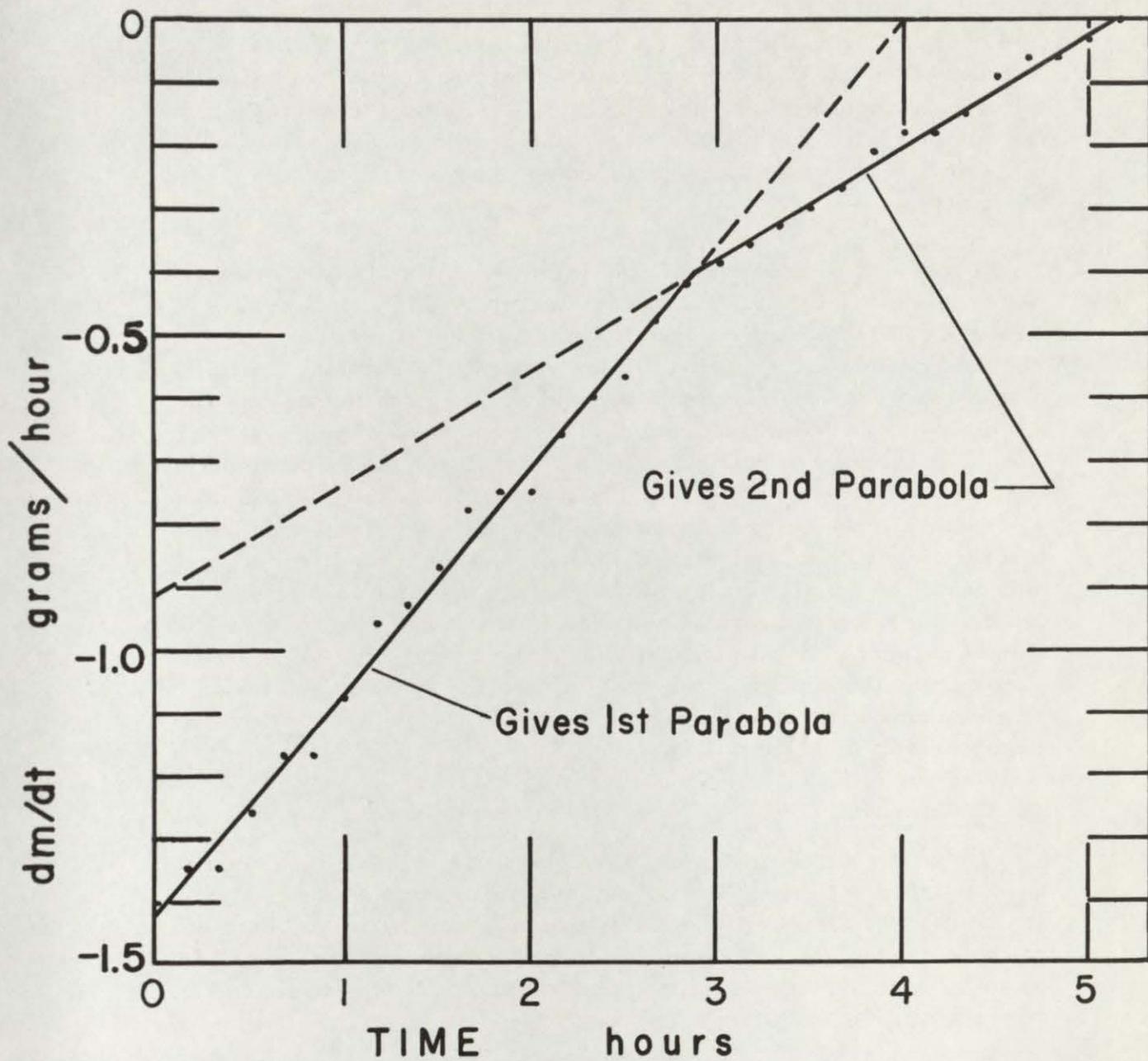


Fig. 6. Graph showing that two straight lines, rather than a single line, are required to represent dm/dt of specimen 2.

of 4.30 hr. Each of the three abnormal specimens required a longer-than-average drying time: Specimen 2, the most abnormal, required 5.13 hr, which is 19% above the average, Specimen 5 was 9% above average, and Specimen 7 was only 1% above. The extra time required by Specimen 2 was 50 minutes.

When the measurements now being reported were first made, and it was found that all our drying curves could be well represented by parabolas, we began to wonder if the parabolas resulted from some fundamental properties of the drying meat. However, we have since found that specimens of different geometry (spheres, cubes, and slabs) do not necessarily give parabolic drying curves. On the basis of all the evidence obtained to date, we find that sticks (typically 0.5 x 0.5 x 1.0 inch; 1.27 x 1.27 x 2.54 cm) nearly always give parabolic drying curves and that other shapes (spheres, cubes, and slabs) seldom do. Our tentative conclusion is that when the derivative ^{is} plotted against the time the normal behavior is for sticks to give straight lines (corresponding to parabolic drying curves), for slabs to give curves that are concave upward, and for spheres and cubes to give curves that are concave downward. There were a few exceptions to this pattern, however.

7. Conclusions

The study shows that when specimens of raw beef have been freeze-dried until their ice cores disappear, their water content is about 1% of their initial weight, which is equivalent to about 4% of their dry weight. This amount of water is much less than the 10 or 12% of the dry weight required to plasticize the beef and prevent crumbling during compression.

It was also shown that there is a substantial difference in the drying times of similar specimens. Data obtained on 10 similar specimens dried under standard conditions showed drying times ranging from 4.18 to 5.13 hours, which is a spread of 23%. Three of the 10 specimens were abnormal in that they showed abrupt changes in freeze-drying rate while drying was in progress. Excluding the abnormal specimens, the drying times ranged from 4.18 to 4.40 hours, a spread of 5%.

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13. ABSTRACT Freeze-drying curves for small sticks of beef are presented and it was found that in many cases the specimen weight was accurately represented by a quadratic function of the time. In many runs the drying was interrupted and the cross-section of the ice core was measured, after which the freeze-drying was completed. A graph showing ice-core diameter versus percent of water (including ice) remaining in the specimen is given, showing that the ice core does not disappear until the water content has been reduced to about 1% of the original weight (about 4% of the dry weight). It is therefore impractical to stop the freeze-drying process at a higher water content in order to permit compression without crumbling. The required moisture could be left in the meat but it will not be uniformly distributed; the wet core will affect product quality adversely.			

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	REFRIGERATING	8		6			
	LYOPHILIZATION	8		6			
	COLLOIDING	8		6			
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