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DETERMINATION OF FREEZABLE WATER CONTENT OF BEEF SEMIMEMBRANOUS MUSCLE DSC study

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Abstract

The freezable water contents of samples obtained from previously chilled semimembranous muscle of middle-aged beef carcasses after a 24 h cooling period a room at in 5±1°C were determined by differential scanning calorimetry (DSC) at −5, −10, −15, −20, −30, −40, −50 and −65°C. This was accomplished by freezing the samples at the above-mentioned temperatures, followed by thawing to 35°C, and measuring the melting peaks of freezable water. The areas of these peaks were determined by using the peak integration method programs through a computer linked to the DSC, and they were then used to determine the latent heat of melting (ΔH_m) in kJ kg^{-1} at each freezing temperature. The resultant latent heat of melting per sample was divided by the latent heat for pure water to determine the amount of freezable water present in these samples. This amount of freezable water was divided by the total water content of the meat sample to determine the percentage of freezable water in the sample. The percentage of freezable water was subtracted from 100 to determine the percentage of bound water present in the sample.

Keywords: DSC, freezable water, muscle water

Introduction

The contents and proportions of the different fractions of water play a significant role in various features of meat: its appearance; its texture and tenderness; its taste and aroma; its processing to different products and its freezability; its packaging requirements and the resultant microbial growth; and also the storage and shelf-life requirements [1, 2]. Protein is the water-binding macromolecule in animal tissues [2–4]. The myofibrillar proteins have the greatest effect on the water-holding capacity of meat, while the fibrous proteins have the least effect [1, 2]. Ockerman [1], Ross [5] and Roos [6] categorize the total water content of meats as free and bound water from a technological perspective, while Price and Schweigert [3] and Judge *et al.* [4] distinguish it from biochemical aspects into three groups: bound, immobile and free water groups. Chou and Morr [7] and Fennema [8] have further classified the biochemical identified groups by taking the lower of these subgroups into

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consideration. Chou and Morr [7] identified these subgroups as structural, monolayer, unfreezable, hydrophobic, imbibitation, and capillary and hydrodynamic hydration, i.e. a total of six subgroups. Fennema [8], on the other hand, categorized the total water content in five groups: structural, visual, multilayer, entrapped and free water.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are two recently-developed techniques available to the food industry for multi-purpose uses. DTA was used by Duckworth [9], Parducci and Duckworth [10] and Bushuk and Mehrotra [11, 12], while Ross [5], Karmas and Chen [13], Muffet and Snyder [14], Kumagai *et al.* [15], Roos [6, 16, 17], Lovric *et al.* [18], Heinevetter *et al.* [19], Roos and Karel [20] and Wang and Kolbe [21] applied DSC to determine the free and bound water contents of different food products and biological materials.

In light of the above studies, the main aim of the present work was to apply DSC to determine the freezable and non-freezable water (bound water) contents of a sample obtained from the semimembranous muscle of a middle-aged beef carcass, at the following temperatures: –5, –10, –15, –20, –30, –40, –50 and –65°C.

Materials and methods

The meat sample used for determination of the freezable and non-freezable water contents was obtained from the semimembranous muscle of a middle-aged beef carcass. The meat was obtained from a major slaughter-house in Erzurum, Turkey. The beef sample was chilled for 24 h in a cooling room (5±1°C). Following the chilling process, all trimmable fat and connective tissue were removed. The lean meat was then ground once through a 3 mm plate prior to initiating the experiment. The total water contents of samples were determined by holding them in an oven [105±2°C) for 18 h, and then determining the mass loss of each sample.

The freezable water contents of the meat samples were determined by using the DSC-50 (Shimadzu Corporation, Kyoto, Japan), which was linked to a temperature and heat transfer controller (TA-50I, Shimadzu Corporation, Kyoto, Japan), together with an IBM-compatible 80486-DX computer (Excell brand) with built-in programs provided by the Shimadzu Corporation. Approximately 20–25 mg of lean meat samples (all trimmable fat and connective tissue removed) were measured into aluminum hermetic cups (Shimadzu 201-53090), which have a resistance of 294.2 kPa. These cells were individually sealed with their own lids, one empty cell being sealed for use as a reference. Liquid nitrogen was used to freeze the cells: 99.9% pure liquid nitrogen at a flow rate of 30 ml min^{-1} was injected to block water condensation in the cells. The same procedure was followed during equipment calibration and analysis. Indium (Mettler standard) with a melting point of 156.6°C and a latent heat of melting (ΔH_m) of 28.45 kJ kg^{-1}, together with triply distilled pure water (mp: 0°C, ΔH_m: 333.2 kJ kg^{-1}), were used for heat transfer and temperature calibration. The experiment was conducted at a heating rate of 5°C min^{-1}. The melting peaks of the meat samples were determined by freezing the samples at –5

to −65°C, followed by heating to 35°C, to establish complete thawing. The experiment was repeated three times for each treatment.

As can be seen from Fig. 1, the latent heats of melting and the initial temperatures of thawing of the samples were determined by using the technique developed by Roos [6, 16]. ΔH_m of the samples were determined with the methodology developed by Ross [5], and were then used to determine the bound water contents of the meat samples. Due to the deviation from the baseline, calculations were based on a latent heat of 350 kJ kg^{-1}, which was determined during the calibration runs by using pure water, instead of the latent heat of 333.20 kJ kg^{-1} for pure water. The determined 350 kJ kg^{-1} is based on the results obtained during calibration runs that were repeated a total of 6 times and the average was taken (standard deviation, $Sd=1.94$). These same problems were encountered by Roos [6, 16], and Lovric *et al.* [18].

Results and discussion

The total water contents of the two different bulk samples were determined as 75.0 and 76.0% (Table 1). The initial temperature of thawing and the latent heat of each sample were determined from the melting curves by using the methods described by Roos [6, 16], and are presented in Table 1. The DSC curves for samples frozen to −5, −30 and −65°C and thawed to 35°C are presented as examples in Fig. 2. The initial thawing temperatures of these samples (−0.9, −2.3 and −2.7°C), determined by the same methodology as described above, are also presented in Fig. 2.

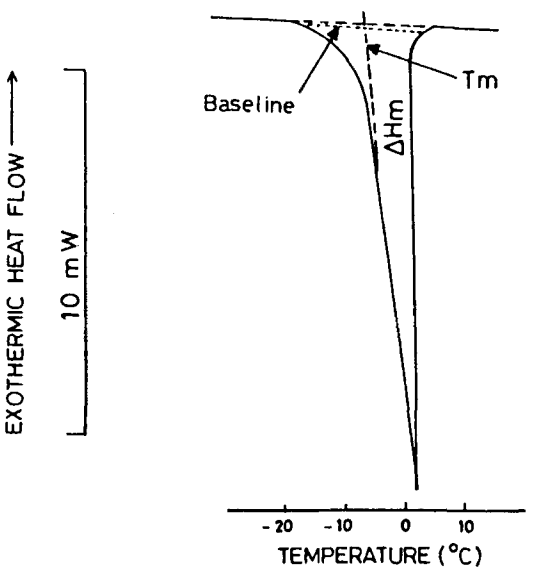

Fig. 1 Determination of latent heat of melting and initial temperature of melting from DSC curves

Table 1 Average values of total water content, initial temperature of thawing and latent heat of melting of meat samples, with standard deviation (*Sd*)

DSC temp./	*Total water	Initial temp. of thawing		Latent heat of melting	
°C	content/%	°C	*Sd*	kJ kg^{-1}	*Sd*
–5	76.0	–0.9	0.12	135.4	0.32
–10	"	–1.2	0.03	149.2	1.49
–15	"	–1.9	0.12	185.0	1.68
–20	"	–1.9	0.09	197.6	1.06
–30	75.0	–2.3	0.09	185.0	3.54
–40	"	–2.6	0.10	175.8	1.26
–50	"	–2.8	0.15	188.2	2.71
–65	"	–2.7	0.18	184.9	0.97

* Due to the experimental design, experimental samples were taken from two bulk samples.

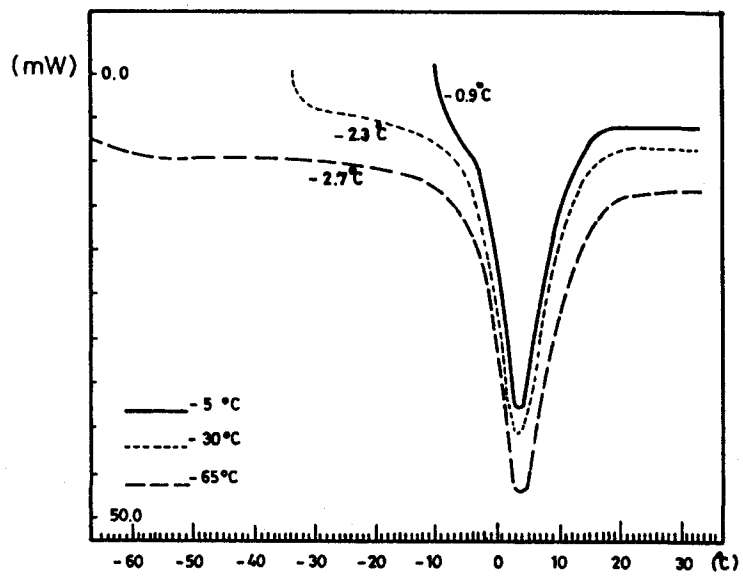

Fig. 2 Thawing peaks of samples frozen at –5, –30 and –65°C, as determined by DSC

As can be seen from Table 1, the lower the DSC temperature, the lower the initial temperature of thawing becomes. This drop in the initial temperature of thawing may be due to the relative increase in the concentration of dissolved matter present in the bound water. The same phenomenon was found in the studies of Heldman [22] and Evranuz and Çataltaş [23], where it was shown that an increase in the dissolvable matter concentration results in a decrease in the freezing point of a given sample.

It is also seen from Table 1 that the initial of thawing almost stabilizes after the temperature of original freezing reaches –40°C. This condition may be due to the fact that the total fraction of freezable water in the meat samples is mostly frozen at this temperature; in other words, this temperature of –40°C may be assumed to be the critical temperature, where the freezable water content reaches a very low level. Table 2 demonstrates that the average unfreezable water content is higher at –5 and –10°C, and reaches a somewhat stable level between –15 and –40°C. The lower value at –20°C could be due to an experimental error. After –40°C, it dropped noticeably and levelled off at –50 and –65°C. Numerous researches have demonstrated this to be true, and have further shown that the water content which remains unfrozen (in this case after –65°C) may be deemed bound water [24–27].

At the end of this study, it was determined that the latent heat of melting generally increases as the temperature of freezing decreases (Table 1). The Table shows that, while the latent heat of thawing for fresh meat samples at –5, –10, –15 and –20°C is 135.4, 149.2, 185.0 and 197.5 kJ kg^{-1}, respectively; the latent heat of thawing at –30, –40, –50 and –65°C is 185.0, 175.8, 188.2 and 184.9 kJ kg^{-1}, respectively. The deviations in the latent heat of thawing for temperatures between –30 and –65°C may be attributable to the freezable water content of the samples almost completely reaching the frozen phase; in the temperature range from –30 to –65°C, it was thought that only 1–2% of the total freezable water content still remained in the liquid phase [24]. Similarly to these findings, Heldman [22] and Singh and Heldman [28] have shown that a direct relationship exists between the latent heat of thawing and the frozen water fraction for any given food product. The latent heat of thawing has the greatest effect on the total enthalpy; this effect is quantified as approximately 75% of the total enthalpy.

Table 2 gives the average unfreezable water contents of the meat samples at the different frozen DSC temperatures. The unfreezable water content decreases until –40°C, and then levels off at –50 and –65°C. The lower values at –20°C could be an experimental error (Table 2).

Table 2 Average determined unfreezable water contents of meat samples, with standard deviations (*Sd*)

DSC temperature/	Total water content/	Unfreezable water	
°C	%	%	*Sd*
–5	76.0	49.18	0.12
–10	"	43.98	0.56
–15	"	30.54	0.41
–20	"	25.81	0.23
–30	75.0	32.88	3.33
–40	"	33.92	0.84
–50	"	28.42	1.03
–65	"	29.69	0.37

Table 3 Determination of bound water content of different materials using different techniques, by different researchers

Food items	Total water/%	Unfreezable (bound) water content	Applied method	Researcher
Egg white	86.5	27.41–30.06	DTA	Parducci, Duckworth, 1972
		28.6	Calorimeter	Riedel, 1957
		3.0	Mathematical model	Pham, 1987
Orange juice	89.0	2.0	Calorimeter	Riedel, 1957
		1.9–3.7	Mathematical model	Schwartzberg, 1976
		2.1	Mathematical model	Chen, 1985
	50.0	1.7	Calorimeter	Riedel, 1957
		15–30	Mathematical model	Schwartzberg, 1976
		24.9	Mathematical model	Chen, 1985
Morina fish	82.0	8.0	Calorimeter	Riedel, 1957
		5.5	Mathematical model	Schwartzberg, 1976
		7.5	Mathematical model	Chen, 1985
	50.0	39.0	Calorimeter	Riedel, 1957
		25.0	Mathematical model	Schwartzberg, 1976
		41.9	Mathematical model	Chen, 1985
		25.7–27.0	DTA	Duckworth, 1971
		24.02–24.80	DTA	Parducci, Duckworth, 1972
Carrot	88.0	22.7–24.5	DTA	Duckworth, 1971
		9.4	DSC	Roos, 1986a
		3.8	DSC	Roos, 1986b
Lean meat	74.0	10.2	Mathematical model	Pham, 1987
		12.0	Calorimeter	Riedel, 1957
		8.8	Mathematical model	Schwartzberg, 1976
		10.8	Mathematical model	Chen, 1985
	50.0	40.9	Mathematical model	Pham, 1987
		36.0	Calorimeter	Riedel, 1957
		25.0	Mathematical model	Schwartzberg, 1976
		38.9	Mathematical model	Chen, 1985
White bread	37.3	36.2	Mathematical model	Pham, 1987
	36.7	7.9	DSC	Roos, 1986a

Numerous previous studies on different food materials indicated that the total freezable water content of any material is almost frozen at –40°C; after this temperature no freezable water remains as nonfrozen [8, 24, 26, 27]. Using an adiabatic calorimeter, Riedel [24] has shown that the freezable water content of beef is 78%, 86%, 90% and 92% at –5, –10, –20 and –40°C, respectively. Roos [6] conducted DSC studies on carrot, deer meat and bread, to determine the freezable and bound water contents of each sample. His studies were conducted by means of different techniques: the latent heat of thawing method and the enthalpy of thawing method. Calculations of the latent heat of thawing suggested that 79% of the total water content of deer meat was freezable water, while the enthalpy of thawing method yielded 91% of the total water content as freezable water, i.e. the difference in the freezable water contents of the deer meat samples at –65°C, according to the above two methods was 12%. On the basis of these findings, our results of 70% of the total water content as freezable water, as determined by the latent heat of thawing method, yields a freezable water content of 82% for the total enthalpy method. The difference between the freezable water content of meat at –65°C in the two methods (Roos [6] and our study with beef samples) is 9%. This may be due to the sensitivity of the DSC used in each study, and the conditions under which these studies were conducted. Wendlant [29] concluded that the following factors have the greatest impact on the results of these studies: the volume and geometry of the sample cell; the volume and width of the space where the thermocouples are connected; and the sensitivity and recording speed of the instruments used. The techniques used in the analysis of the results also play an important role in these differences.

Numerous studies have been conducted to determine the free and bound water contents of food products with different physicochemical properties, using different techniques (Table 3). These studies are still ongoing. The present study revealed that different techniques result in equally important deviations in the final calculations. Thus, it is imperative that further research works should be planned and implemented where the most sensitive, most reliable and fastest techniques are developed and employed.

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