Use of differential scanning calorimetry in the thermal characterization of meat. Part II

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INTRODUCTION

In a previous work (1) it was attemped to apply DSC to the thermal characterization of meat. To facilitate sampling on the proper scale of the microcalorimeter, i.e., a few miligrams, the meat consisting of a piece of calf veal of M. Semitendinosus was repeatedly extruded by a food chopper with 3 mm plate openings in order to homogenize it.

Then the meat was capsuled into hermetically sealed pans provided with an extra lid (1) - to avoid head space and to keep pan and sample in good thermal contact. In this manner, and under special conditions of manipulation, a series of about 20 samples was frozen at -40ºC in a freezing chamber previous to the thermal analyses.

Heat capacities and freezing enthalpic changes were determined by means of a Perkin Elmer DSC-2 provided with and Intracooler II cooling unit. A two-channel potentiometric plotter was used for the simultaneous dual-range recording of pure and aparent heat capacity effects in order to evaluate both thermal parameters, heat capacity and heat of transition, on the same thawing-DSCgram of each sample. In this way heat capacity values between -33 and +15ºC were reported with a mean standard error of about 3 % in replicated samples (n=15). These values were in very good agreement with those obtained by other authors using the more precise adiabatic calorimetry, so that DSC resulted in a good, simple and rapid technique for measuring heat capacities of meat.

Notwithstanding, while this aspect of the analysis was satisfactorily solved, difficulties arose when the evaluation of the freezing phenomena was the case. In fact, a very low heat of transition was recorded, 179.9 $\pm$ 1.6 kJ/kg (n=15), and although a normal initial melting temperature of about -24ºC was observed, it was considered that the extent of crystallization was not complete and the freezing - temperature was lowered down to -80ºC by using liquid nitrogen as a coolant. Six samples were then prepared and so analysed but no definite conclusions could be reached except that the samples behaved very irregularly, showing different kinds of thermograms, the important facts being: a) Some samples underwent undercooling and proved to be unfrozen when slowly (0.62ºC/min) cooled down to -60ºC; b) An abroup change in heat capacity appeared at different temperatures according to the thermal history of the sample and disappeared with annealing, which was assigned to a glass transition in the order of 0.72 kJ/kg; c)Sometimes the sample froze during heating (warm crystallization); d) The initial melting temperature was practically the same as before but heat of transition varied widely and, even, abnormally.

At that time, the study had to be interrupted due to technical reasons and this work is a continuation of it, the main objective being to see if inadequate thermal treatments, moisture losses of the meat during preparation for thermoanalysis, or any other cause, are responsible for the low values of the meeting enthalpy of ice on meat, which aparently leads to the high figure of near 20 % for the unfreezable water content.

EXPERIMENTAL

Materials

Meat, its preparation and analysis were the same as described elsewhere (1). Water content was 77.0%.

Thermal analysis

The grinded meat was inmediatly conditioned by filling completely a closed container to avoid losses by water evaporation, and kept in a refrigerator till sampling. The meat was then capsuled into - hermetically crimped volatile sample pans and subjected after weighing to thermoanalysis in a Perkin Elmer DSC-2 calorimeter fitted with a liquid nitrogen cooling unit (1). After this the sample was weighed again to check that no losses took place during the process. Then the capsule was carefully punctures in the cover (4 pin-holes) and transferred to a Perkin Elmer Thermogravimetric System TGS-2, where it was - subjected to a heating program of 10ºC/min till 125ºC and kept there up to content weight in order to determine the particular moisture constant of each capsuled sample (this was practically recorded within the first terty minutes of treatment).

RESULTS AND CONCLUSIONS

Moisture losses

Thermogravimetry showed that some losses ocurred during the preparation of meat. In the case of a careful handling of the sample the evaporation loss was around one per cent, i.e., typical moisture content of capsuled meat was 76.1% against 77.0% in bulk.

However, losses could account to levels much higher, 10% or more, if no special care is taken along the process of grinding, storage and capsulation and this fact, according to Maltini (2), could be the basis for the interpretation of the complicated behaviour exhibited by the above-mentioned six samples.

Thermal treatments

Different cooling treatments were tested in order to see if any variation in the crystallization extent could be detected.

Four samples were subjected to cooling rates of 160, 40, 10 and 2.5ºC/min either to -40 or -80ºC and their thawing thermograms were recorded.

When operating under normal conditions, i.e., with about 10 mg of sample, 10ºC/min of heating rate, 10 mcal/second-full scale of DSC sensitivity and 20 mv of span recorder, the melting peak of ice in meat covered about 60% of the recorder chart (230 mm) and the initial temperature, from which melting effects are observed, was around -25ºC, as described previously. But if sensitivity conditions are improved to detect more precisely the lowest temperature region some thermal effects were detected at temperature, as low as -43ºC when the sample was chilled down to -80ºC (160ºC/min of cooling rate). This thermal event had the appearance of a glass transition. The integration of the melting peaks, however, gave comparable results in all cases, as can be seen in the example of Figure 1.

Base line correction

From the above discussions it seems clear that the differences of 10-20% found previously (1) in the melting of ice in frozen minced meat remain injustified and we have to search for a cause - different from those studied before.

It has been already emphasized (1) that certain errors in peak integration may arise from uncertainties in the interpolation of the base line, which are of particular importance when a considerable increment in heat capacity is observed between pre- and post- transition regions. This could be our case - because heat capacities of frozen and thawed meat diferred by a factor of almost two (1).

Several methods of correcting DSC data for this and other effects have been proposed, that of Heuvel & Lind (3) being the most precise. It is a mathematical model incorporated into a computer - program, developed as a function of the heat capacity of the sample, the thermal resistance between - sample holder and sample, and the velocity of scanning.

Other simpler and graphical methods have been also published. We work out here the one proposed by Fernández-Martín (4) for the determination of the solid fat index of milk fat in globular state from dilatometric curves of creams. The method constructs the base line from the extrapolated pre- and post-transition traces and the vertical line drawn at the vertex of the peak. For a more precise application the vertical line must become slanting with a slope according to the thermal lag, thus the method coincides with that of Guttman & Flynn (5).

Figure 1.- Thawing DSCgram of sample no. 4 { Cooling Rate, 160ºC/min; Heating Rate, 10ºC/min; Weight, 10.32 mg; Water, 76.1 %

Cooling treatment		Area of melting
AT (ºC/min)	to(ºC)	(arbitrary units)
160	-80	281
	-40	281
40	-80	278
	-40	280
10	-80	282
	-40	278
25	-80	283
	-40	288

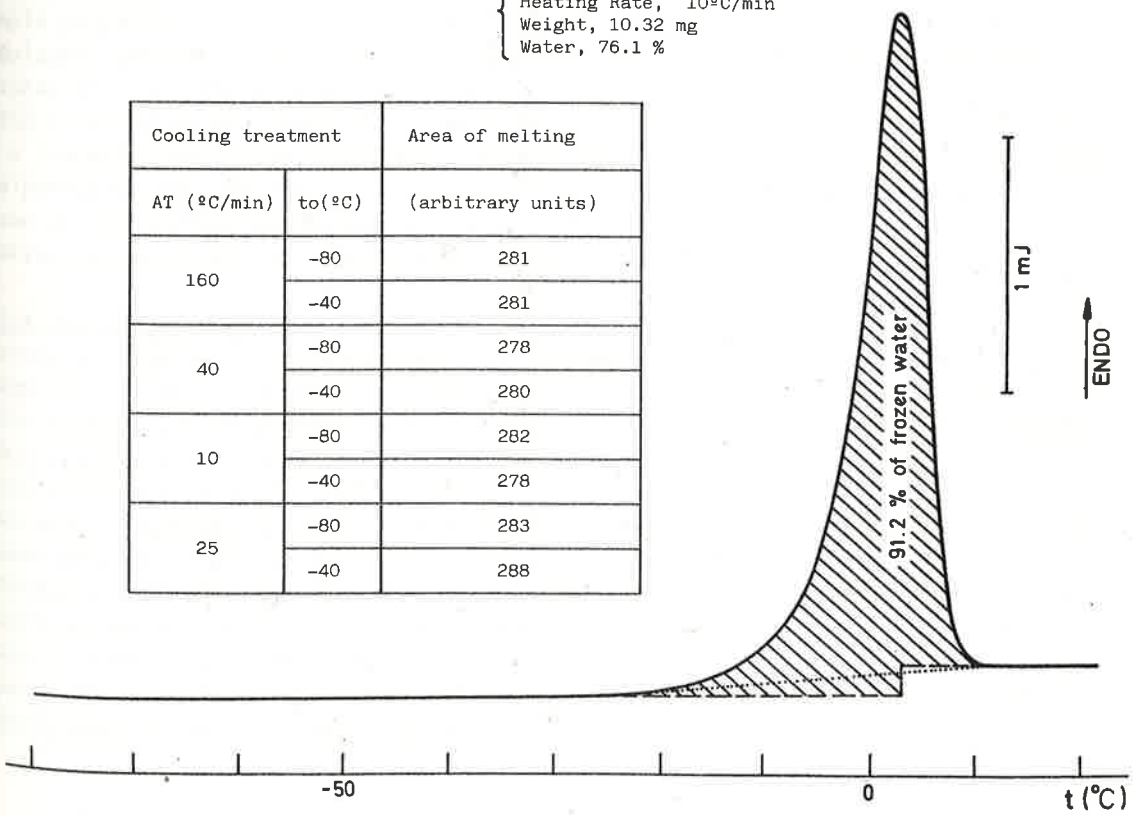

Figure 1 is the thawing thermogram of sample no. 2 after chilling down to -80ºC. It shows the several but significantly identical ice melting heats for the different thermal treatments.

The figure also presents both base line constructions and, while the simplest method gave a melting effect corresponding to a frozen water of 84.5% (using 333.5 kJ/kg as the ice melting heat), the correct method yielded the value of 91.2%, i.e., an unfreezable water content of 8.8%. This figure is a little bit lower than that reported of 10% by adiabatic calorimetry and the difference could lie in the grinding of the meat as a previous operation for DSC sampling. This might cause some initial unfreezable water of meat to be accesible to freezing after grinding.

In conclusion it can be said that DSC technique was a good tool for the determination of thermal parameters related to the freezing process of minced meat if precautions are taken for minimizing moisture losses during preparation and sampling. Cooling down to -40ºC was enough for the determination of unfrozen water content by integration from -25ºC provided that no linear interpolation of the base line is drawn-in.

REFERENCES

1) FERNANDEZ-MARTIN, F. and Sanz, P.D. (1979): Proceedings XV Int. Cong. Refrigeration, II, 309.

2) MALTINI, E. (1977): Bulletin I.I.R., Annexe 1977-1, 43.

3) HEUVEL, H.M. and Lind, K.C.J.B. (1970): Anal. Chem., 42, 1044.

4) FERNANDEZ-MARTIN, F. (1970): Revista Española de Lechería, 75, 3.

5) GUTTMAN, C.M. and Flynn, J.H. (1973): Anal. Chem., 45, 408.