Thermochimica Acta, 72 (1984) 201—204
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ON-LINE AQUISITION, STORAGE AND INTERACTIVE TREATMENT OF DIFFERENTIAL SCANNING CALORIMETRY THERMOGRAMS IN A COMPUTER

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ABSTRACT

A procedure is described for aquisition of thermograms from differential scanning calorimetry in a computer. An example of the interactive treatment of the data (baseline subtraction, calculations of area etc.) at a graphic terminal is demonstrated together with examples of plotting several thermograms in one diagram. The thermograms presented are resulting from current food science projects.

INTRODUCTION

Differential scanning calorimetry (DSC) has become a well-established method for monitoring heat-induced changes in the properties of materials[1]. In food science[2], DSC is used for studying the thermodynamic properties of pure proteins (order → disorder transition = denaturation), fats, water, complex food systems (e.g. meat)[3] and gelling polysaccharides (e.g. starch)[4]. In many of these applications there is a need for high sensitivity (0.1-0.5 mcal/ sec.) to detect weak signals, resulting in reduced signal/noise-ratio and irreproducible and curved baselines. To meet these problems and also to make the routine data-treatment less time-consuming there is a need for computerization. Existing software for baseline subtraction and area calculation[5,6] were found unsatisfactory for the present high-sensitivity data.

METHODS

Instrumentation

At the Norwegian Food Research Institute, two DSC-instruments (Perkin-Elmer DSC-2) are connected to a mini-computer (NORD 10/S, Norsk Data, Oslo, Norway) with a CAMAC process interface. A DC-voltage corresponding to the differential heat input is amplified and transmitted to the computer through a multiplexer and a 12 bit analogue-to-digital converter. The interface includes digital input signals to indicate start and stop of the temperature scanning. The sample temperature is computed based on parameters given by the operator. Parameters describing the sample, enthalpy and temperature calibration constants and conditions for the DSC-run are defined before each run. The computer

0040-6031/84/$03.00

has a hard-disk for data storage and a graphic terminal with a hardcopy unit (Tektronix 4014) for thermogram plotting.

Software

Software (Fortran-77) has been developed including programs for the following operations: Operator communication, parameter definition, data aquisition, calibration, storage, plotting, non-linear baseline estimation and subtraction, calculation of onset and max. temperatures of the thermogram peaks, calculation of area (apparent enthalpy), and plotting of several thermograms in one diagram for comparison.

The baseline estimation is based on the model:

$$Y = A+BT+Ce^{D\cdot T}.$$

Y is the DSC-signal, T is the temperature (K) and A, B, C and D are baseline constants. These constants are estimated iteratively, using progressively better D-values in least squares regression of Y on T and $e^{D\cdot T}$ over selected segments of the thermogram.

Onset temperature of a peak is determined as the intersection between the estimated baseline and the tangent to a linear segment of the peak (fitted by the method of least squares).

Two different methods for computation of apparent enthalpy are incorporated in the software, one is based on a summing up of the stored digitalized datapoints between temperature limits specified by the operator, the other one multiplies the peak's height with its width at 1/2 peak height.

The plotting, computations etc. of the thermograms are performed by interactive treatment of the data at the graphic terminal.

APPLICATIONS IN FOOD SCIENCE

In Fig. 1 an example of the interactive treatment of a meat sample thermogram is shown. The "raw" thermogram is first plotted on the terminal screen (Fig. 1a), and new "start"- and "stop"-temperatures for the plot are defined. In Fig. 1b, two segments of the baseline are chosen and the baseline beneath the peak(s) is estimated and plotted. The estimated baseline is then subtracted, the corrected thermogram plotted and temperature limits for the area calculations determined (Fig. 1c). Fig. 1d shows the segment of the peak chosen as basis for determination of a tangent and the peak onset temperature. The calculated areas, peak onset and peak max temperatures and the final plot of the termogram are shown in Fig. 1e.

Fig. 1f shows another thermogram of a meat sample with a slightly different

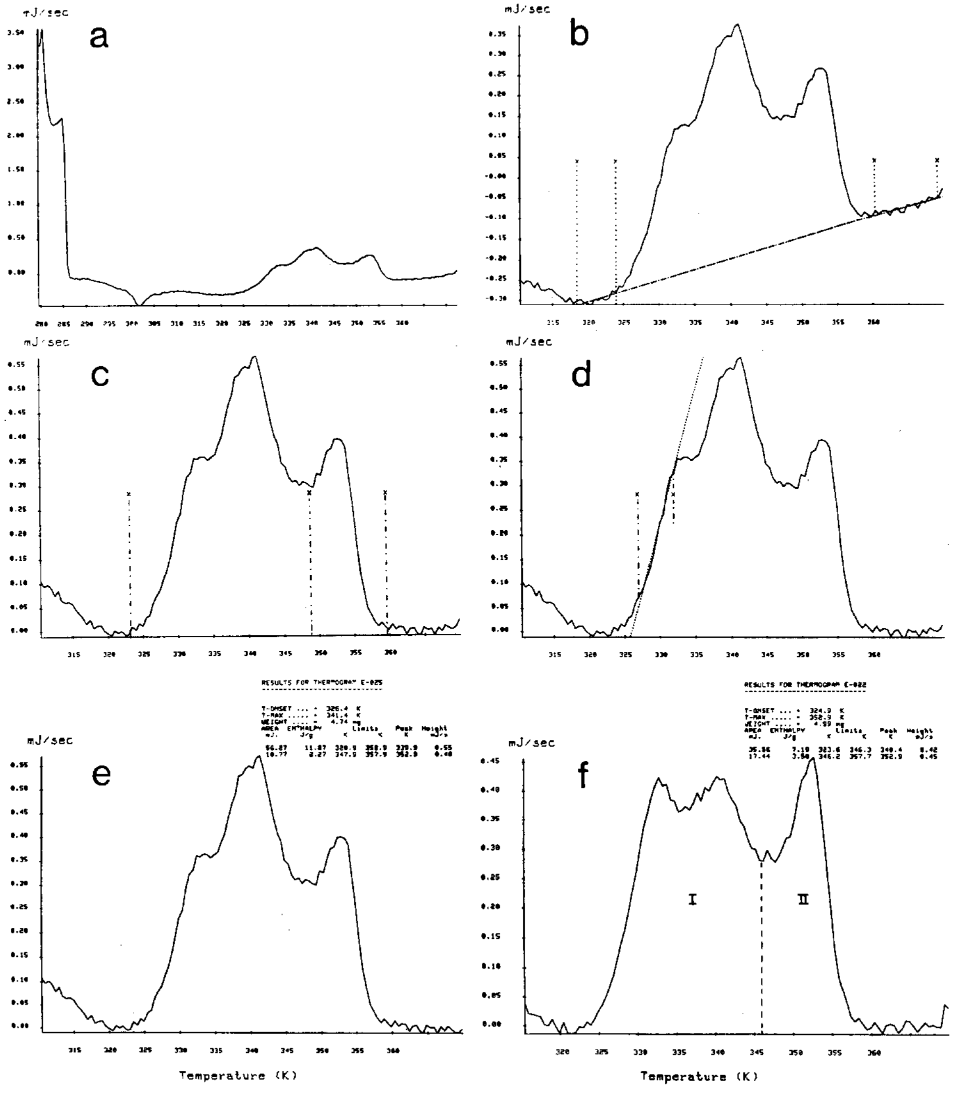

Figure 1. An example of the interactive treatment of a meat sample thermogram.

composition. The peaks represent the denaturation of myosin (I) and actin (II).

In Fig. 2, three different examples are shown, using the possibility of plotting several thermograms in one diagram. In Fig. 2a, the thermograms of frozen meat ground at different temperatures are compared. The analysis showed only minor differences in the thermograms[7].

Gelatinization of potato starch in the presence of ethanol is shown in Fig. 2b. The gelatinization temperature is slightly decreased for concentrations of

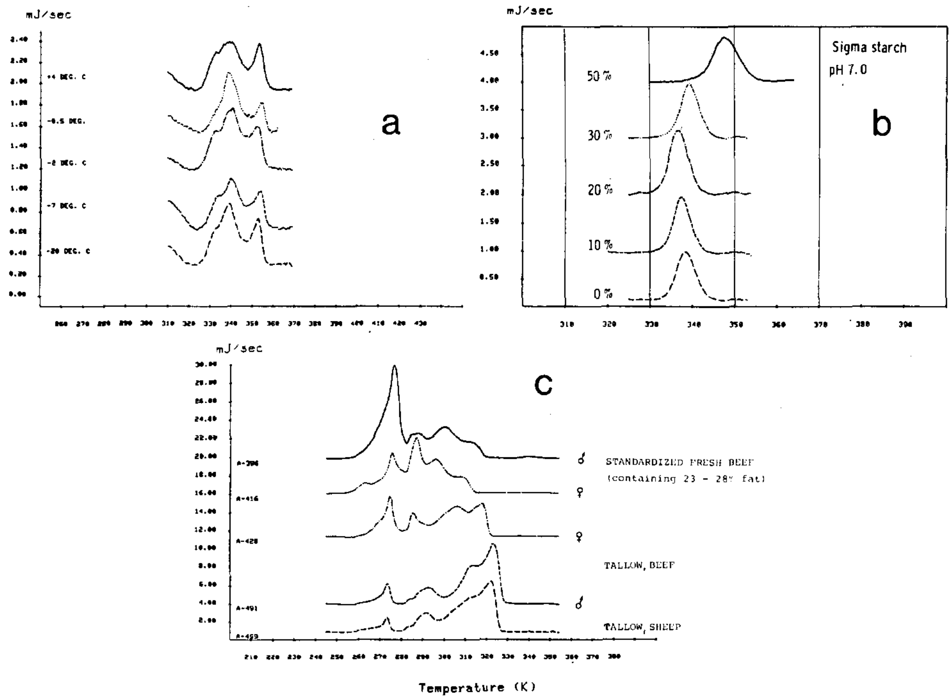

Figure 2. Three examples of plotting several thermograms in one diagram. (a) Comparision of remaining undenatured protein in frozen meat grinded on a frozen meat grinder at different temperatures.[7] (b) Gelatinization of potato starch as a function of increasing hydrophobicity (ethanol-concentration).[4] (c) Comparision of thermograms of fats from different sources.[8]

ethanol up to ~20% and increases rapidly thereafter[4].

Fig. 2c presents a comparison of fats from different sources. Using this plotting routine, different thermograms can easily be compared, and differences can be revealed[8].

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