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Thermal behaviour of foods

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INTRODUCTION

Chocolate bars should melt in the mouth and not in the hand, and heating of oil should not lead to a kitchen fire. Based on such common examples, we may understand the interest in studying the thermal behavior and properties of foods.

In the investigation of foods by thermal analysis and calorimetric techniques, many effects can be observed in the temperature range between −50 and 300 °C. These thermal phenomena may be either endothermic (such as melting, denaturation, gelatinization and evaporation) or exothermic processes (such as crystallization and oxidation). Through precise knowledge of such effects, optimal conditions for safe storage or processing of foods can be defined. The main operations concerned are the following:

around 0 °C	freezing and freeze-drying
around 70 °C	pasteurization, solid–liquid extraction
around 100 °C	drying
around 140 °C	ultra high temperature sterilization (of milk products)
above 140 °C	roasting (of coffee and coffee surrogates)

Thus, the thermal and also, more generally, the physico-chemical properties of foods are of particular interest to the food technologist.

To introduce the subject, we first present some general aspects of food constitution and of the most useful calorimetric techniques in this context. As the thermal behavior of foods strongly depends on their composition, we concentrate at first on the thermal characteristics of food constituents: water, lipids, glucides, proteins and minor constituents, and then consider composite and reconstituted foods. Process safety aspects are also considered.

WHAT ARE FOODS?

Foods are materials, in a raw, processed or reconstituted form, which are consumed by humans or animals for their growth, health and satisfaction.

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Chemically, foods are mainly composed of water, lipids, glucides and proteins. In addition, they contain comparatively small proportions of some minerals and various organic substances. Minerals are often analyzed globally as ash. The organic substances can be vitamins, emulsifiers, acids, antioxidants, pigments, polyphenols or flavors.

In some cases, foods contain physiologically active substances, such as caffeine or theobromine, and even toxic substances (natural toxins in mushrooms, or produced by microorganisms).

Enteral and parenteral solutions are also foods, in the same context as fruits, fruit juices, milk, milk powders, meat and animal (pet) food.

The main constituents referred to above are responsible for the physical properties (structure, texture and color) as well as flavor of foods. Sometimes specific natural or synthetic ingredients (such as salt or antioxidants) are added to improve the food properties [1–3].

THERMAL ANALYSIS AND CALORIMETRIC TECHNIQUES OF INTEREST

Differential scanning calorimetry (DSC) is the main approach used today for studying thermal properties of foods (phase transitions, reactions and specific heats). Older systems, such as containers fitted with sensors which follow the rising temperature of a heating bench, autoclaves with additional pressure sensors, or differential thermal analysis (DTA) instruments, are still useful [4–9].

However, the trend is towards using microcalorimeters with high sensitivities, especially for a more sensitive observation of the weak thermal phenomena occurring between 0 and 100 ° C [10–13]. Parameters such as the heat of solution may also be of interest, so the use of solution calorimeters or of heat flux calorimeters with stirring devices is also recommended for studying certain food systems [14].

DSC instruments such as power-compensation DSC, heat flux DSC or intermediate systems have proved their worth for studying foods or food constituents. The most important criteria for selecting the appropriate instrument for a specific problem are: temperature range, sample size, sensitivity and resolution. When studying food constituents, analysis of small samples gives a better resolution of thermal effects; this can be important for studying the polymorphism of fats, and is an absolute necessity for purity determinations. In contrast, large samples represent better the bulk material for composite foods; heat flux calorimeters with large crucibles are therefore often preferred [14]. This criterion is particularly important in the field of process safety, especially for adiabatic calorimeters [15]. Moreover, experiments with large samples must be performed at low heating rates.

Additional complementary data on food and food constituents are obtained by other thermal analysis techniques, such as thermomanometry, thermogravimetry (TG), thermomicroscopy or hot stage microscopy (HSM), differential mechanical (thermal) analysis (DMA or DMTA), titration calorimetry and microwave dielectric measurements during temperature scan.

Adiabatic bomb calorimeters are used to determine the heat of combustion of foodstuffs. Although the values may be important in the context of process safety, they are mainly used to calculate caloric values of food for human nutrition or when foods (usually oils) are used as energy sources for engines.

THERMAL BEHAVIOR OF FOOD CONSTITUENTS

Water

Water is present in most natural foods, at levels up to 90–95% w/w in some fruits (oranges) and vegetables (tomatoes). Most beverages contain high proportions of water. Water exists in foods in various forms: free water, water droplets, water adsorbed on a surface, chemically bound water, crystal water and composition water. Often, water is removed from processed foods as it affects keeping quality, or to reduce weight and volume of products. In most cases, however, part of this water is extremely difficult to remove so that even dehydrated foods may contain 2–3% residual water. The physics of water, as a pure substance and as part of biological systems, has been studied by many workers [16–18]; the basic phenomena have been described in books edited by Franks [19].

As shown in Fig. 1, water has three phase transitions in the temperature range of interest: crystallization on cooling (or ice melting on heating), vaporization (or vapor liquefaction) and sublimation.

Relatively high enthalpy values accompany melting and vaporization (334 J g^{-1} at 0 °C and 2250 J g^{-1} at 100 °C under atmospheric pressure respectively). Thus, these two endothermic phenomena are easily observed when studying foods by calorimetric techniques. Sublimation (freeze-drying) takes place only under high vacuum, so that this phenomenon is more difficult to detect [18].

A large number of studies have dealt with the behavior of water below 0 °C (e.g. supercooling of water-in-oil emulsions); and determinations of free and bound water around 0 °C [20–25]. The crystallization enthalpy of water depends on temperature (see ref. 19), which may be important in emulsions with supercooling effects. Moreover, the difference in the specific heats of ice (2.05 J g^{-1} K^{-1}) and water (4.18 J g^{-1} K^{-1}) may introduce some error.

Around 100 °C, thermal analysis measurements with open crucibles distinguish between adsorbed, absorbed or crystal water. Thus, DSC curves, TG curves or microwave dielectric measurements give information on water

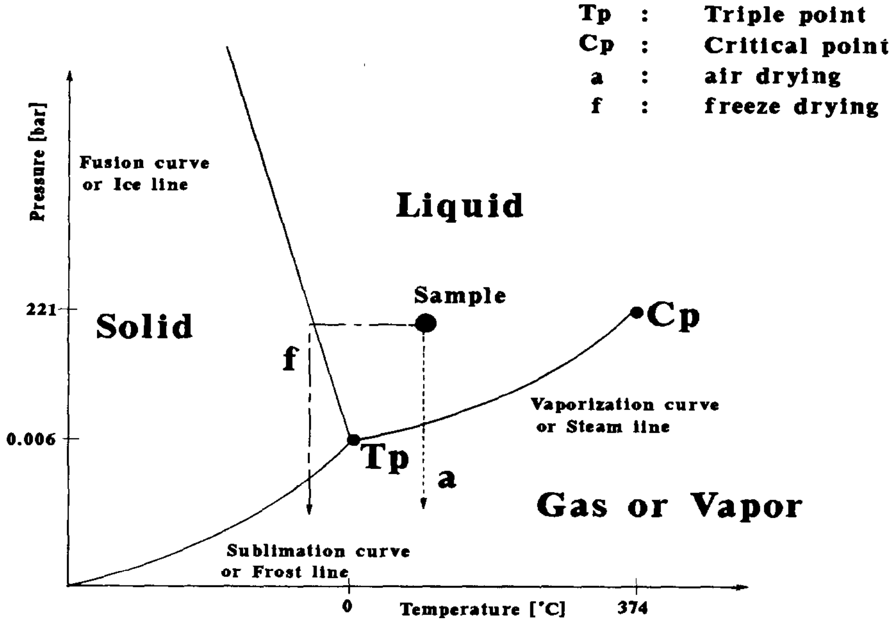

Fig. 1. Phase diagram of water with indication of the course of two different drying processes.

content or on the state of drying of foods [26–29]. The peak due to water vaporization in calorimetric curves often masks other phenomena of interest, such as crystallization or decomposition of carbohydrates. To observe such effects, analyses have to be performed in sealed crucibles (or under pressure). In such cases, however, it is important, for reasons of safety, to remember that the water vapor pressure increases rapidly with temperature, especially above 150 °C. At 300 °C, the water vapor pressure already amounts to 85 bars!

Lipids

The physical properties of edible fats and oils are closely related to those of triglycerides, which constitute the major part of lipids (molar ratio higher than 90%). The occurrence of more than one crystalline form (polymorphism) is a general characteristic of lipids or triglycerides in the solid state. A fat's ability to undergo polymorphic changes is important, mainly because of its effect on food texture and appearance [30]. It has been proved that DSC is one of the most efficient techniques to study the phase changes of lipids including solid–liquid (melting), liquid–solid (crystallization) and solid–solid transitions [31–36]. The temperature range between −50 and 80 °C is of special interest; melting enthalpies are between 100 and 200 J g^{-1}. In the context of quality control, such calorimetric curves can be used as fingerprints for the considered fats. As examples, Figs. 2 and 3 present

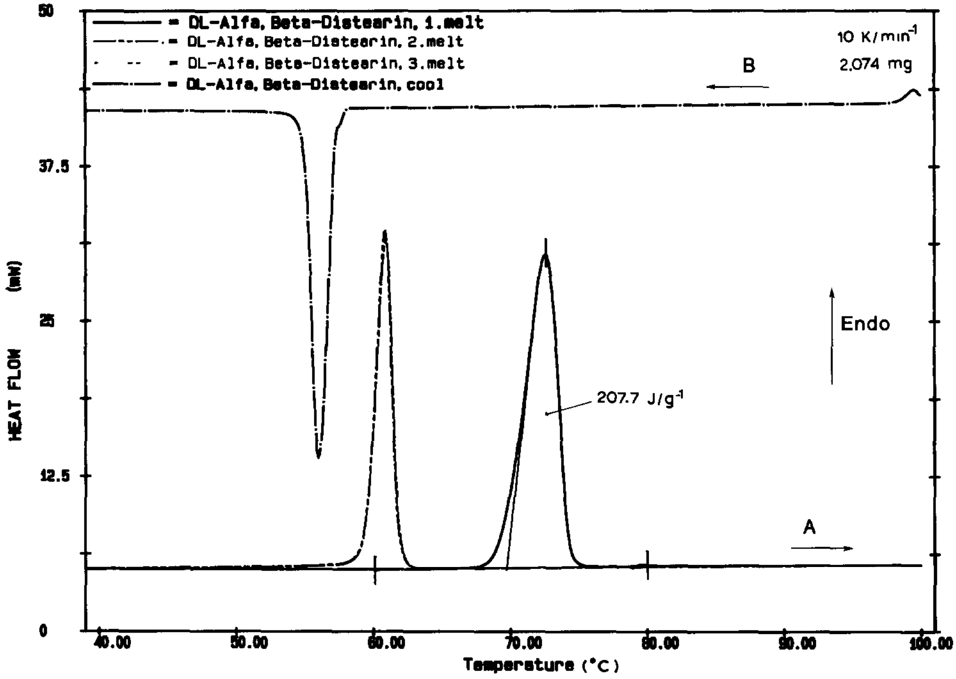

Fig. 2. (A) Heating curves of α-, β-distearin, showing the melting of the stable polymorphic form (at 70 °C) during the first run and the melting (at 60 °C) of a less stable polymorphic form during the second and third runs (superimposed). (B) Cooling curve of α-, β-distearin, showing crystallization at 55 °C. Courtesy of Perkin Elmer (CH). Instrument DSC 7.

the thermal polymorphism of two glycerides, distearin and tristearin, as displayed by a power compensation DSC instrument.

The influence of composition, processing parameters, thermal history and aging can be clearly described by means of DSC investigations on lipid polymorphism. Contamination of fats can also be detected in calorimetric curves recorded during crystallization [37] or melting [38] of lipid mixtures. In the same way, the Solid Fat Index (SFI) representing the ratio of solid to liquid in a partially crystallized lipid at a given temperature can be obtained from the calorimetric melting curve by sequential peak integration [31,39,40]. SFI values are currently used in the fat industry for quality control or for monitoring processes such as fractionation, hydrogenation and tempering. They are determined from the equation

$$\mathrm{SFI(T)} = \frac{\int_{T_0}^{T} H(T)\,\mathrm{d}T}{\int_{T_0}^{T_1} H(T)\,\mathrm{d}T}$$

where T_0 is the onset temperature of melting and T_1 is the end temperature of melting.

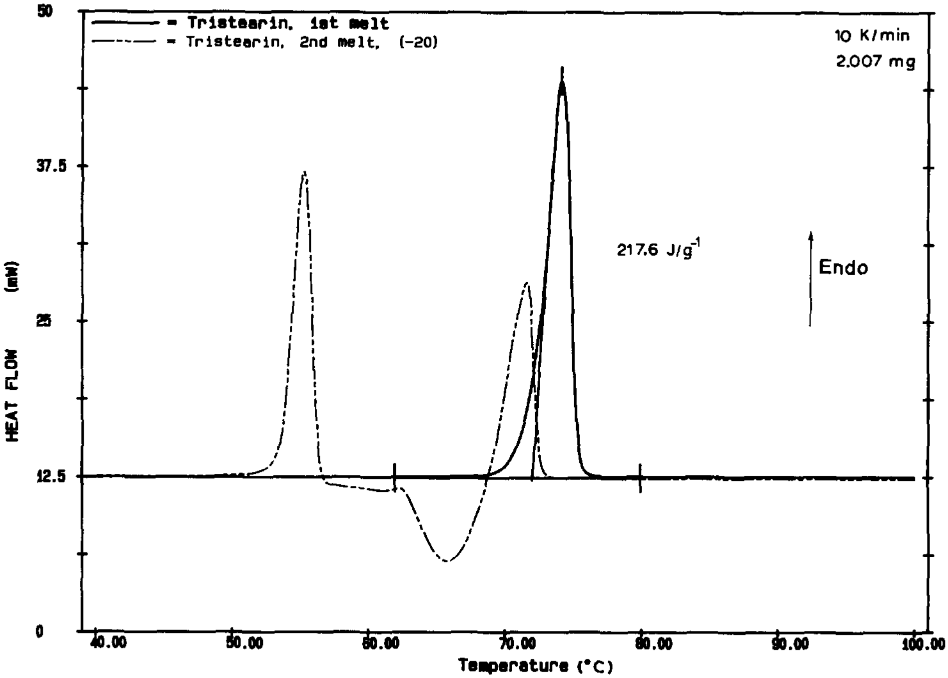

Fig. 3. Calorimetric curves of tristearin showing, during the first heating, the melting around 75 °C of the stable polymorphic form and, during the second heating, the melting of two less stable forms around 55 °C and 70 °C, with partial crystallization around 65 °C. Courtesy of Perkin Elmer (CH). Instrument DSC 7.

Lipid oxidation is an exothermic phenomenon which can be followed, at least at elevated temperatures, by DSC or (preferably) by isothermal calorimetry [41–44]. Measurements can be performed under a static air

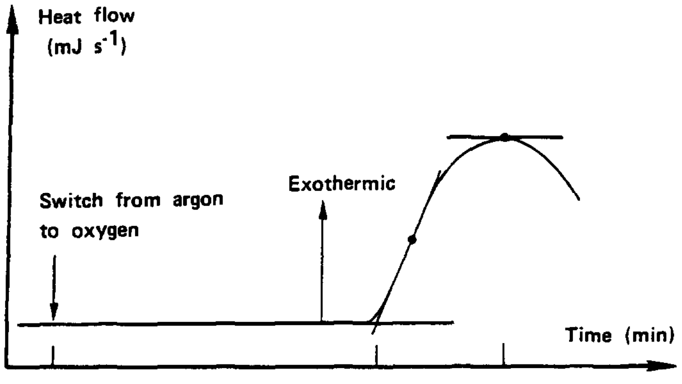

Fig. 4. Determination of induction times A and B. A: Time lag between start of oxidation and start (extrapolated onset) of exothermic heat flow. B: Time lag between start of oxidation and maximum of exothermic heat flow. Adapted from ref. 41, and reprinted with the permission of Elsevier Science Publishers.

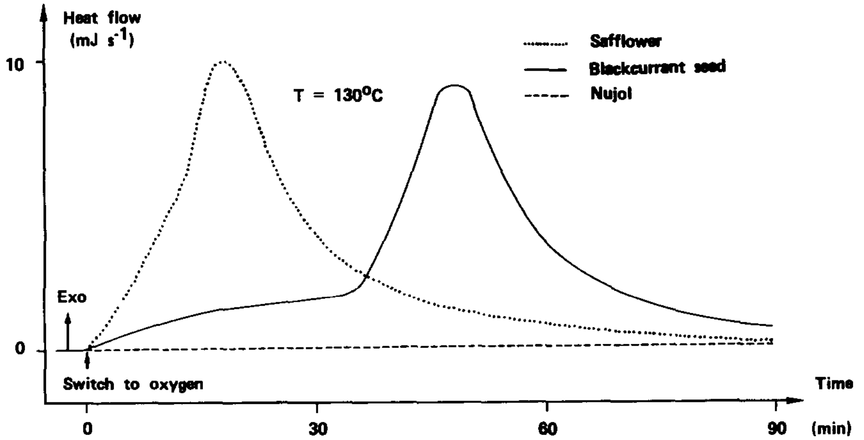

Fig. 5. Calorimetric curves of three oils with different stabilities, oxidized at 130 ° C under oxygen flow. Reprinted from ref. 41 with the permission of Elsevier Science Publishers. Instrument: Setaram DSC 111, isothermal mode.

atmosphere, or better under oxygen flow or oxygen pressure. In the isothermal mode, induction times can be defined according to published procedures using other techniques (see Fig. 4). Figure 5 compares the oxidative stability at 130 ° C of three very different oils (safflower, blackcurrant seed and Nujol). Induction time values can be used to determine the oxidative stability of lipids [41,42] or the efficiency of food antioxidants [41,43].

Thermal data on most triglycerides and lipids are compiled in handbooks [45]. In addition, DSC and microcalorimetry are very often used to study transitions in biological membranes, as lipids are major constituents of living cells.

Carbohydrates

During heating of carbohydrates one generally observes first fusion and then exothermic decomposition (pyrolysis), which often follows melting immediately [46–48]. Other effects may also be detected: vaporization of water in hydrated carbohydrates, glass transitions and crystallization of amorphous sugars. Figure 6 presents the calorimetric curves of amorphous sucrose and amorphous cellobiose (both heated in sealed crucibles) between 70 and 270 ° C. The onset temperatures of the exothermic decomposition observed on heating these carbohydrates in sealed vessels varied between 100 and 230 ° C [46]; the corresponding enthalpies ranged from 300 to 800 J g^{-1}. Onset temperatures of fusion were found between 60 and 220 ° C with enthalpies from about 40 to 330 J g^{-1}. All values given above should be considered as approximate. With open containers the temperature range of thermal effects is much higher, probably because various hot gases are released together with the decomposition [47,48]. It has long been known

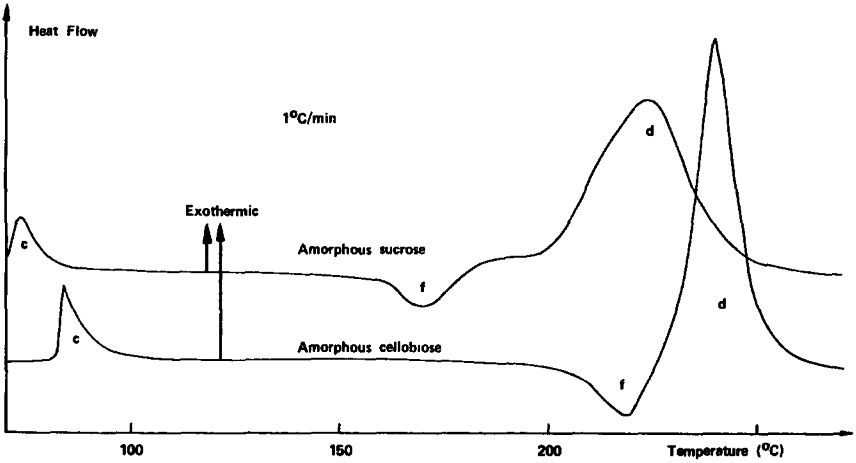

Fig. 6. Calorimetric curves of amorphous sucrose and cellobiose (both heated in sealed crucibles): c, crystallization; f, fusion; d, decomposition. Reprinted from ref. 46 with the permission of John Wiley and Sons. Instrument: Setaram C80.

that amorphous carbohydrates have a glass transition around 50 °C [49]. However, in relation to storage stability, glass transitions and crystallization studies are today very current [50–54], and even sub-zero glass transitions have been detected for aqueous solutions [55].

For extrusion or similar cooking processes, many workers study in particular the endothermic gelatinization of starches and other carbohydrates (e.g. carrageenans) in the presence of water, as well as the retrogradation of the gelatinized products [56–67]. Starch gelatinization is defined as the collapse (disruption) of molecular order within the starch granule, as shown

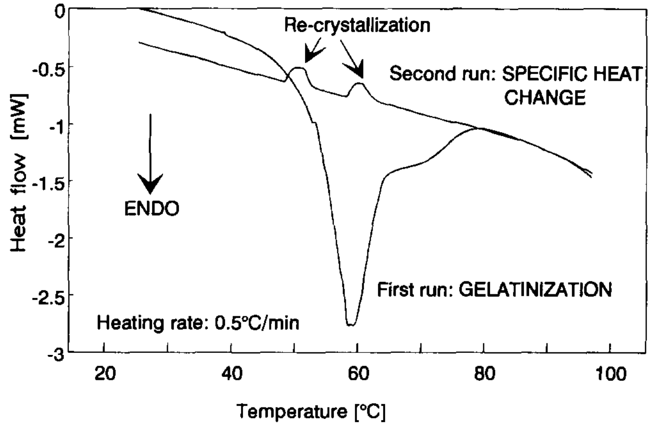

Fig. 7. Gelatinization and specific heat change of native wheat starch (water solution of 40% DM). Adapted from ref. 69 and reprinted with the permission of AFCAT. Instrument: Setaram Micro-DSC.

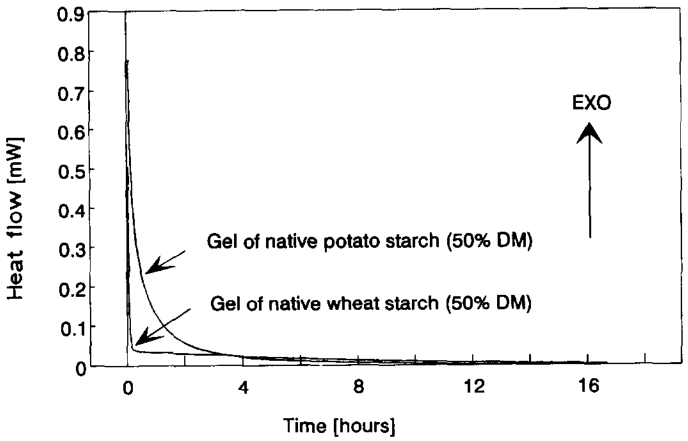

Fig. 8. Retrogradation at 4 °C of gels obtained from native wheat and potato starches (water solutions of 50% DM). Adapted from ref. 69 and reprinted with the permission of AFCAT. Instrument: Setaram Micro-DSC, isothermal mode.

by irreversible changes in properties such as granular swelling, native crystalline melting, loss of birefringence and starch solubilization [68]. In a calorimetric curve (see Fig. 7), gelatinization is observed as a peak around 60 °C (depending in particular on the salt content), together with specific heat change. Enthalpies of about 10–20 J g^{-1} dry matter (DM) are measured when the moisture content is about 50%.

Starch retrogradation is defined as a process which occurs when gelatinized starch molecules begin to reassociate in an ordered structure; under favorable conditions, a crystalline order appears [68]. The heat slowly released by the recrystallization of the gel can be detected by means of a microcalorimeter [69] (see Fig. 8). However, most workers follow the retrogradation indirectly by observing the melting of the microcrystals formed after a given storage period. The corresponding broad melting peak is found in the calorimetric curves between 40 and 80 °C; the measured enthalpies are generally lower than 10 J g^{-1} DM and are often called retrogradation enthalpies.

Proteins

The functional properties (solubility, antigenicity, viscosity, capacity to form a gel or to emulsify lipids) of foods such as dairy products are essentially determined by their proteins. Heat treatments of proteins in water induce damage (denaturation) to the molecular structure [70,71]. Calorimetric techniques allow the measurement of the energy changes that accompany conformational transitions in proteins. The methods of investigation as well as many results were first presented by Privalov [72,73]. The denaturation of proteins in aqueous solution is seen as one or two endother-

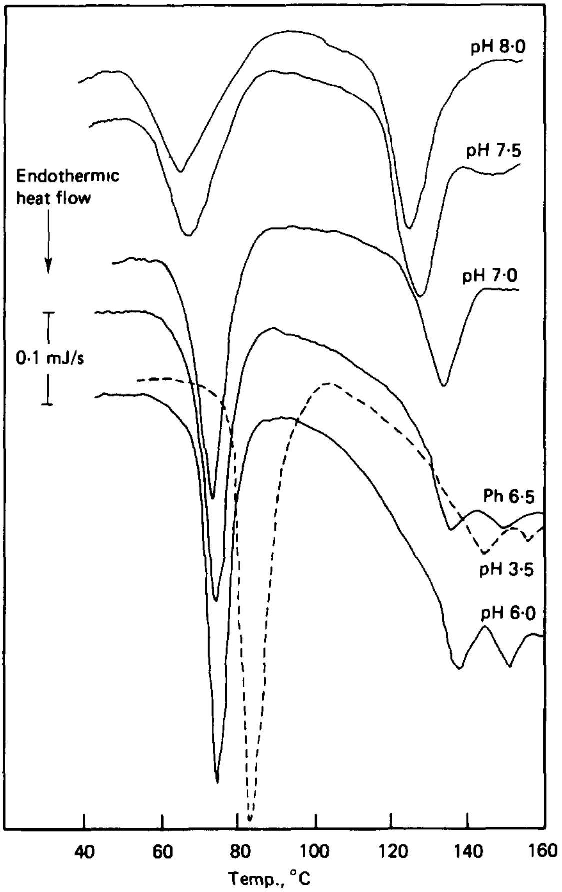

Fig. 9. Calorimetric curves showing the heat denaturation of β-lactoglobulin in solution as a function of temperature at pH 3.5 and in the pH range 6.0 < pH < 8.0. Reprinted from ref. 75 with the permission of Cambridge University Press. Instrument: Du Pont thermal analyzer 990.

mic phenomena encountered in the temperature range between 40 and 160 °C. The corresponding enthalpies are very weak: values between 1 and 20 J g^{-1} DM are generally observed.

Calorimetric techniques have been used extensively to determine the conditions (pH, buffer, temperature, ionic strength, salt or carbohydrate content of the solution) which best maintain the physicochemical properties of proteins [74–77], and to study whey proteins, especially β-lactoglobulin (see Fig. 9) and α-lactalbumin, as well as soy proteins [78]. Similarly, the thermal denaturation of legume proteins such as legumin and vicilin [79], of egg white [80,81], and of meat [82], fish [83] and cereal proteins [84] has been studied with the help of DSC. DSC curves demonstrate the stabilizing effect of iron binding (or other metal ions) on protein (Fig. 10) [85]. The thermal denaturation of enzymes also gives information on their inactivation [86].

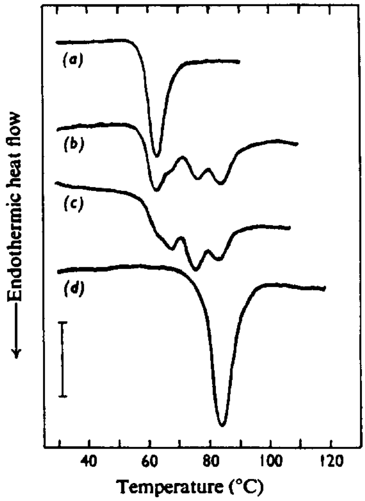

Fig. 10. Calorimetric curves showing the heat denaturation of ovotransferrin (conalbumin) in solution. (a) Apo-ovotransferrin; (b) and (c) ovotransferrin 39% saturated with iron; (d) ovotransferrin fully saturated with iron. The bar represents a heat flow of 500 μJ s^{-1}. Reprinted from ref. 85 with the permission of The Biochemical Society and Portland Press. Instrument: Du Pont thermal analyzer 990.

The loss of gel structure can be observed for meat gelatine by DSC around 30 °C [87].

Although calorimetry of proteins is rarely performed on dry samples, this kind of analysis allows at least investigation of protein oxidation.

Minor constituents

Physiologically active substances which are present in minor quantities in foodstuffs can be studied in their pure forms, or in aqueous solutions. Crystalline caffeine has been studied extensively in the anhydrous or mono-

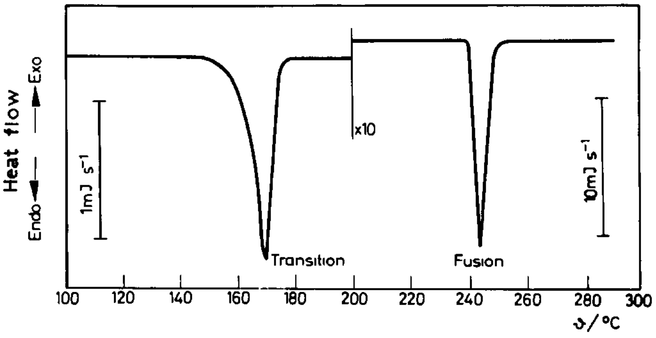

Fig. 11. Calorimetric curve of pure β-caffeine. Reprinted from ref. 88 with the permission of John Wiley and Sons. Instrument: Du Pont thermal analyzer 990.

hydrate form or in solution, particularly by calorimetric techniques [88–90]. Caffeine shows a solid–solid transformation around 140 °C and melts at around 235 °C, as shown in the calorimetric curve of Fig. 11.

THERMAL BEHAVIOR OF RAW AND RECONSTITUTED FOODS

Phenomena related to food composition

Depending on the food composition, most of the main phenomena mentioned for the major constituents (carbohydrate melting excepted) are observed again with raw and reconstituted foods; however, the corresponding peaks in the calorimetric curves are broader. The effects due to minor constituents can be detected only in special cases.

Around 0 °C, the melting curves of water in high-moisture foods such as ice creams introduce the differentiation between "bound" and "free" water. The amount of free water relative to the total amount of water is given by

$$R = \frac{\Delta H_{\mathrm{m}}}{(1-S)\,\Delta H_{\mathrm{w}}}$$

where S is the percentage of solute (or of dry matter), $1-S$ is the percentage of water, ΔH_{m} is the measured fusion enthalpy (J g^{-1}) and ΔH_{w} is the fusion enthalpy of pure water (J g^{-1}).

Figure 12 presents calorimetric curves with ice melting peaks for various foods [91].

A detailed description of the low-temperature behavior of many foods has been given by Riedel [92,93]. The enthalpy differences, normed at −40 °C,

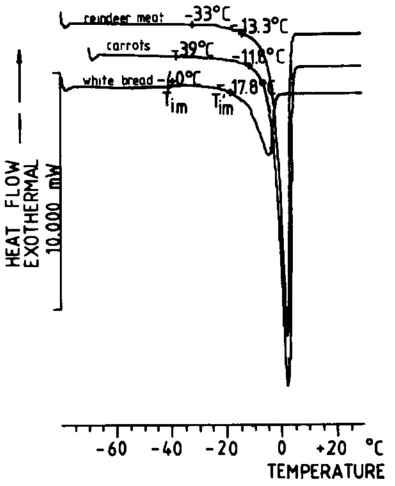

Fig. 12. Low-temperature calorimetric curves of carrots, reindeer meat and white bread, showing ice melting. Reprinted from ref. 91 with the permission of the Institute of Food Technologists. Instrument: Mettler DSC 30.

have been compiled in tables or nomographs which are very useful for chemical engineering calculations. Calorimetric cooling curves generally show freezing and supercooling very clearly; the temperature range of freezing is of particular interest in relation to freezing or cold storage.

Around ambient temperature, fat melting can be observed in reconstituted foods and even in some raw foods, e.g. cocoa beans. In the context of lipid research, modern instrumentation (DSC, microcalorimetry) allows the study of phase transitions, even in complex biological membranes [94–96].

Around 70 ° C, gelatinization of finely divided flours (starches) mixed with water can be observed. Retrogradation, for instance bread staling, can also be studied [97]. Crystallization of amorphous sugars, for example, crystallization of amorphous lactose in milk powders [98] can be detected in reconstituted foods. However, protein denaturation is no longer detected clearly when studying liquid whole-milk products containing lipids, lactose, calcium, etc.

Around and above 100 ° C, boiling of water is generally prevented by using sealed containers; this allows the detection of other phenomena such as carbohydrate decomposition. This is observed in the calorimetric curves of reconstituted foods such as milk powders, and in the curves of raw foods such as coffee beans, chicory roots and cereal grains [98–101].

Lipid oxidation can be observed if the lipids are on the food surface and thus in contact with oxygen; this condition can be fulfilled for some processed and some reconstituted foods.

The oxidation of minor constituents such as polyphenols is a possible cause of self-heating in hay, above the temperatures normally reached during fermentation; to measure the heat released by these phenomena specific calorimetric experiments have to be performed.

Interaction between food constituents

In addition to the caloric phenomena due to each constituent alone, there are also interactions between food constituents. The corresponding thermal effects can be detected in model binary mixtures, and sometimes, with more difficulty, in raw or reconstituted foods.

Maillard reactions, the browning reactions between protein and reducing sugars, are observed in the calorimetric curves of lactose–casein mixtures or in those of milk powders [98]. Maillard reactions are exothermic, take place above ambient temperature, and depend on the moisture content of the product. The corresponding enthalpies are not so important (less than 100 J g^{-1} DM).

Phase transitions of starch–lipid complexes are also seen in calorimetric curves. These weak endothermic phenomena happen around 100 ° C and have enthalpies less than 10 J g^{-1} DM [57]. Sometimes, interactions between water and the foods or food constituents (dissolution, absorption or desorption) in addition to interactions of cations and sugars in water are studied [102–104].

Biological processes

Many foods are obtained by fermentation. In this context, measuring the heat released during the fermentation process gives information relevant for dimensioning fermenters, or for safety [105,106]. On the other hand, microorganisms can lead to spoilage of wet foods during storage. Calorimetric techniques are therefore also used to obtain a basic knowledge of the metabolic activities of bacteria, yeasts and fungi [107]. A calorimetric method has been proposed to determine bacterial thermal death times [108].

SELF-HEATING, SELF-IGNITION AND SAFETY ASPECTS

Self-heating, self-ignition and rise in pressure

Fires and dust explosions are known hazards in many industries, including the food industry. Self-heating and self-ignition studies are thus often of interest to develop better defined safety conditions for high-temperature processing operations when sufficient oxygen is available.

Studies of spontaneous combustion of powders very often consider sample deposition on a heating plate or in a furnace heated to a known temperature. The data obtained by these tests are generally compiled as minimum ignition temperatures for dust layers [109]. Similar measurements of self-ignition temperatures can be performed by using differential thermal analysis (DTA) techniques with air or oxygen atmosphere. The sample can be heated under oxygen flow or pressure. The well-defined measuring conditions are an advantage, in particular the precise heating rates possible with DTA instruments [110,111]. Figure 13 presents the DTA curves of cellulose heated and burnt under 25 bars of oxygen.

Self-heating can lead to self-ignition of the food, if sufficient oxygen is available. The main phenomena involved in thermal runaway of food products are fermentation, carbohydrate decomposition, lipid oxidation and probably polyphenol and protein oxidation. However, other weaker exothermic effects such as Maillard reactions could participate in the initial temperature increase.

If oxygen is in low concentrations, it is often the elevated pressure, as a result of the rise in temperature in a closed medium, which presents a risk (of bursting the autoclave, for example). Further dangers can come from degassing, associated with fermentation or decomposition reactions; the gas emitted could lead to a rise in pressure (or be inflammable).

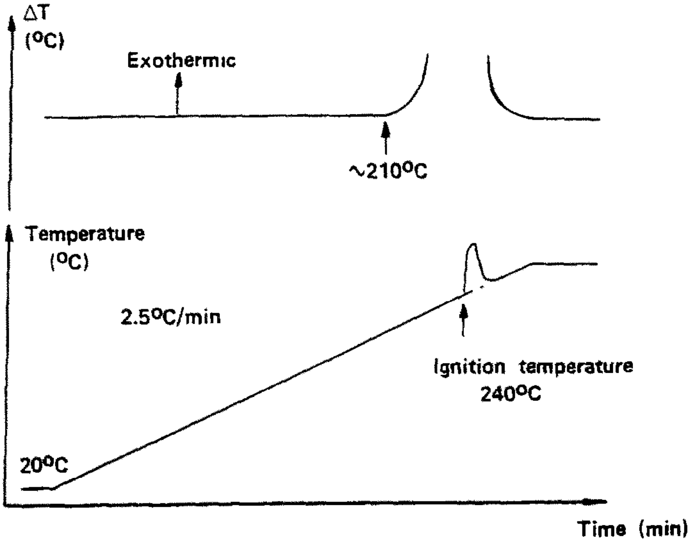

Fig. 13. DTA curves of cellulose heated and burnt under 25 bars of oxygen. Reprinted from ref. 112 with the permission of Elsevier Science Publishers. High-pressure DTA 404 H instrument from Netzsch.

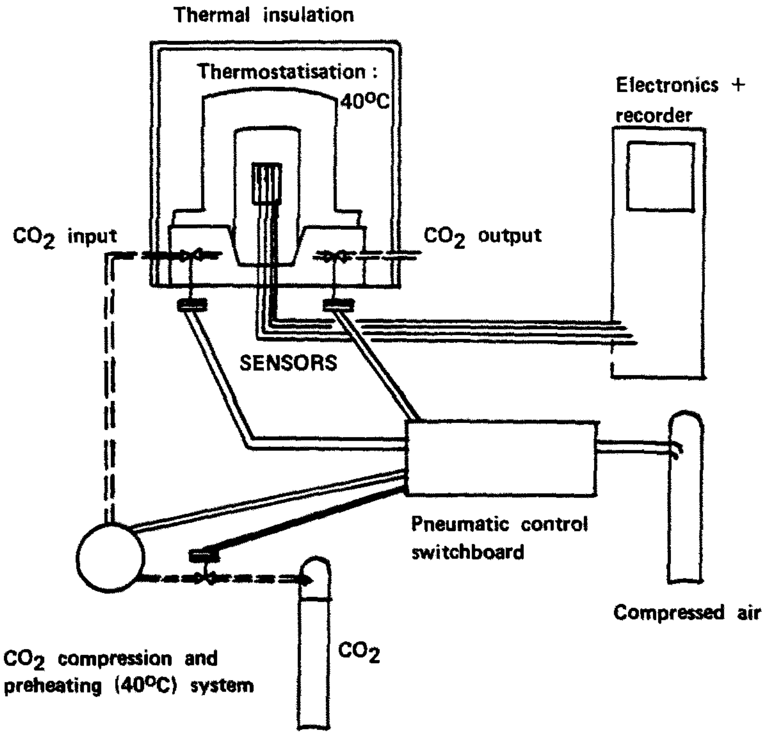

Fig. 14. Scheme of a DTA experiment under supercritical CO_2. Reprinted from ref. 112 with the permission of Elsevier Science Publishers. High-pressure DTA 404 H instrument from Netzsch.

Simulation of process conditions

Sometimes, thermal analysis techniques must be applied unconventionally if we are to be able to carry out the measurements under conditions close to those of the studied process. Thus, for example, the calorimetric study of a sample in a sealed cell simulates what happens in a homogeneously heated autoclave. DTA or DSC measurements can also be carried out under a constant pressure of an inert gas, or even under supercritical CO_2 [112]. Figure 14 presents a scheme for a DTA experiment under supercritical CO_2.

OTHER THERMODYNAMIC PARAMETERS

Specific heat

It is evident that calorimetric techniques are often used to determine specific heats of foods; the methods, and a synthesis of results, have been presented in the literature [113].

The use of a standard such as synthetic sapphire simplifies the determination of specific heats; by measuring the standard, an empty cell, and the substance, the specific heat value C_2 of the sample can be obtained directly by comparison. For a given temperature,

$$C_2 = C_1 \frac{m_1}{m_2} \frac{(Q_2 - Q_0)}{(Q_1 - Q_0)}$$

where m_1 is the mass of the standard substance, m_2 is the sample mass, C_1 is the specific heat of the standard substance, and Q_0, Q_1 and Q_2 are the required heat quantities for the empty cell, the standard substance and the sample respectively.

The values obtained vary between 0.9 J g^{-1} K^{-1} for very dry food products to 4.18 J g^{-1} K^{-1} for water; it is therefore evident that the moisture content of a food has a strong influence on its specific heat value.

Heats of combustion

During burning of a food product, a large amount of energy is liberated. Values determined with calorimetric bombs correspond to about 39 kJ g^{-1} for fat, 23 kJ g^{-1} for protein and 17 kJ g^{-1} for carbohydrate.

Heat conductivity and thermal diffusivity

Other parameters such as heat conductivity or thermal diffusivity can be of interest to the food technologist and can, in some cases, be determined by calorimetry, using special experiments.

Heats of solution

The dissolution of ingredients, minerals, food constituents or even foods in water or in other solvents can be observed by calorimetry. The data are determined in the isothermal mode.

RELATED TECHNIQUES

Some related thermal analysis techniques give mechanical and rheological rather than thermal information; these techniques include thermodilatometry (which is no longer of great interest for food studies), dynamical mechanical analysis (DMA) and dynamical mechanical thermal analysis (DMTA) [114].

Other techniques, such as X-ray diffraction, near-IR reflectance (NIR), low- and high-resolution nuclear magnetic resonance (NMR), microscopy and light scattering, give information which characterizes a food before or after a thermal treatment. Low-resolution NMR, for instance, is well known for giving SFI values of fats rapidly, which correspond to those obtained by DSC [40]. X-Ray diffraction can also be adapted, by temperature control of the sample, to follow the lipid phase transitions by recording the diffraction patterns vs. temperature [115,116]. If the (lipid) sample is placed in a temperature-controlled cell, even microscopic techniques can be used to follow crystal growth or melting [117].

It is also worth noting that, for caffeine solutions, a thermodynamic parameter such as the enthalpy of dimerization of caffeine in water can be determined comparatively by dissolution calorimetry and by high-resolution NMR [118,119].

Thermal analysis techniques can also be coupled with other instruments such as mass spectrometers or gas chromatographs. Using such techniques, the gases evolved during decomposition can be analyzed.

Finally, mathematical models help in applying thermodynamic data to engineering problems.

CONCLUSION

Other reviews of this type exist, and there are some books on the thermophysical properties of foods [120–126].

It should become clear from this review that calorimetry, DTA and DSC give relevant, reproducible data which are of great importance in many fields of food technology, because this information characterizes the food globally. From the basics of food technology it is easy to understand that calorimetric techniques help in quality control, improvement of food characteristics, development of new operations, and process safety [127–134].

Many thermal effects, which have been neglected until now, mainly because of experimental difficulties, remain to be studied.

Finally, food is sometimes used as a symbol, like the cheese in a fable of La Fontaine, to express things which are true in other fields. It is also true that many other fields, such as pharmaceuticals analysis, polymer physics or chemistry, material and safety sciences, and semi-conductor physics, have helped us to understand the thermal and more generally the physico-chemical behavior of foods [135–140].

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REFERENCES

1 N.N. Potter, Food Science, AVI, Westport, CT, 1986.
2 H.D. Belitz and W. Grosch, Lehrbuch der Lebensmittelchemie, Springer-Verlag, Berlin, 1982.
3 H. Chiba, Food Science and Technology, Elsevier, Amsterdam, 1979.
4 E. Calvet and H. Prat, Microcalorimétrie, Masson, Paris, 1956.
5 W. Hemminger and G. Höhne, Calorimetry: Fundamentals and Practice, Verlag Chemie, Weinheim, 1984.
6 G. Widmann and R. Riesen, Thermal Analysis: Terms, Methods, Applications, A. Hüthig. Verlag, Heidelberg, 1987.
7 J. Sestak, Thermophysical Properties of Solids, Elsevier, Amsterdam, 1984.
8 W. Hemminger and H.K. Cammenga, Methoden der thermischen Analyse, Springer-Verlag, Berlin, 1989.
9 B. Miller, Thermal Analysis, Wiley, New York, 1982.
10 P.L. Privalov, V.V. Plotnikov and V.V. Filimonov, Precision scanning microcalorimeter for the study of liquids, J. Chem. Thermodyn., 7 (1975) 41–47.
11 I. Wadsö, Isothermal biocalorimetry. A status report. Thermochim. Acta, 88 (1985) 35–48.
12 L. Benoist, Recent developments in bio-calorimetry with micro DSC, Thermochim. Acta, 163 (1990) 111–116.
13 K.S. Krishnan and J.F. Brands, in C.H. Hirs and S.N. Timasheff (Eds.), Enzyme Structure, Academic Press, New York, 1978.
14 P. Le Parlouër and J. Mercier, Introduction d'une nouvelle méthode de mesure de chaleur spécifique, Journ. AFCAT, Orsay, 8 (1977) 41–48.
15 D.I. Townsend and J.C. Tou, Thermal hazard evaluation by an accelerating rate calorimeter, Thermochim. Acta, 37 (1980) 1–30.
16 F. Franks and S.F. Mathias, Biophysics of Water, Wiley, Chichester, 1982.
17 D. Simatos and J.L. Multon, Properties of Water in Foods, Nato ASI Series, Martinus Nijhoff, Dordrecht, 1985.
18 R.B. Duckworth (Ed.), Water Relations in Foods, Academic Press, London, 1975.
19 F. Franks (Ed.), Water: a Comprehensive Treatise, Plenum, New York, 1982.
20 E. Buzagh-Gere, J. Simon and S. Gal, Characterization of differently bound water by means of the constants of thermal decomposition kinetics, Z. Anal. Chem., 264 (1973) 392–396.
21 G.N. Ling and Z.L. Zhang, Studies on the physical state of water in living cells and model systems, Physiol. Chem. Phys. Med. NMR, 15 (1983) 391–406.
22 D. Clausse, L. Babin, F. Broto, M. Aguerd and M. Clausse, Kinetics of ice nucleation in aqueous emulsions, J. Phys. Chem., 87 (1983) 4030–4034.

23 F. Broto and D. Clausse, A study of the freezing of supercooled water dispersed within emulsions by differential scanning calorimetry, J. Phys., C, 9 (1976) 4251–4257.

24 D.S. Reid, Fundamental physicochemical aspects of freezing, Food Technol., 37 (1983) 110–115.

25 A.S. Bakshi and R.M. Johnson, Calorimetric studies on whey freeze concentration, J. Food Sci., 48 (1983) 1279–1283.

26 M. Tomassetti, L. Campanella and M. Delfini, Determination of water in plant samples: a comparative thermogravimetric and NMR study on different species of seeds, Thermochim. Acta, 105 (1986) 179–190.

27 S. Quinquenet, M. Ollivon, C. Gabrielle-Madelmont and M. Serpelloni, Polymorphism of hydrated sorbitol, Thermochim. Acta, 125 (1988) 125–140.

28 M. Ollivon, S. Quinquenet, M. Seras, M. Delmotte and C. More, Microwave dielectric measurements during thermal analysis, Thermochim. Acta, 125 (1988) 141–153.

29 S.D. Holdsworth, Dehydration of food products. A review, J. Food Technol., 6 (1971) 331–370.

30 C.E. Clarkson and T. Malkin, Alternation in long-chain compounds. II. An X-ray and thermal investigation of the triglycerides, J. Chem. Soc. (1934) 666–671.

31 E. Kaisersberger, DSC investigations of the thermal characterization of edible fats and oils, Thermochim. Acta, 151 (1989) 83–90.

32 J. Schlicher Aronhime, Application of thermal analysis (DSC) in the study of polymorphic transformations, Thermochim. Acta, 134 (1988) 1–14.

33 D.M. Manning and P.S. Dimick, Crystal morphology of cocoa butter, Food Microstruct., 4 (1985) 249–265.

34 G. Ziegleder, DSC—Thermoanalyse und Kinetik der Kristallisation von Kakaobutter, Fat Sci. Technol., 92 (1990) 481–485.

35 R.E. Timms, Phase behaviour of fats and their mixtures, Prog. Lipid Res., 23 (1984) 1–38.

36 V. Gibon, F. Durant and C. Deroanne, Polymorphism and intersolubility of some palmitic, stearic and oleic triglycerides: PPP, PSP and POP, J. Am. Oil Chem. Soc., 63 (1986) 1047–1055.

37 B. Kowalski, Sub-ambient differential scanning calorimetry of lard and lard contaminated by tallow, Int. J. Food Sci. Technol., 24 (1989) 415–420.

38 P. Lambelet, O.P. Singhal and N.C. Ganguli, Detection of goat body fat in ghee by differential thermal analysis, J. Am. Oil Chem. Soc., 57 (1980) 364–366.

39 C. Deroanne, L'analyse calorimétrique différentielle, son intérêt pratique, pour le fractionnement de l'huile de palme et la détermination de la teneur en phase solide, Lebensm. -Wiss Technol., 10 (1977) 251–255.

40 P. Lambelet, C. Desarzens and A. Raemy, Comparison of NMR and DSC methods for determining the solid content of fats, Lebensm. -Wiss. Technol., 19 (1986) 77–81.

41 A. Raemy, I. Froelicher and J. Löliger, Oxidation of lipids studied by isothermal heat flux calorimetry, Thermochim. Acta, 114 (1987) 159–164.

42 R.L. Hassel, Thermal analysis: an alternative method of measuring oil stability, J. Am. Oil. Chem. Soc., 53 (1976) 179–181.

43 T.A. Pereira and N.P. Das, The effects of flavonoids on the thermal autoxidation of palm oil and other vegetable oils determined by differential scanning calorimetry, Thermochim. Acta, 165 (1990) 129–137.

44 B. Kowalski, Determination of oxidatative stability of edible vegetable oils by pressure differential scanning calorimetry, Thermochim. Acta, 156 (1989) 347–358.

45 T.H. Applewhite, Bailey's Industrial Oil and Fat Products, Wiley, New York, 1985.

46 A. Raemy and T.F. Schweizer, Thermal behaviour of carbohydrates studied by heat flow calorimetry, J. Therm. Anal., 28 (1983) 95–108.

47 M.C. Ramos-Sanchez, F.J. Rey, M.L. Rodriguez-Mendez, F.J. Martin-Gil and J. Martin-Gil, DTG and DTA studies on typical sugars, Thermochim. Acta, 134 (1988) 55–60.

48 A.E. Pavlath and K.S. Gregorski, in D. Dollimore (Ed.), Proc. 2nd Eur. Symp. Thermal Analysis, Aberdeen 1981, Heyden, London, 1981, pp. 251–254.

49 G.S. Parks, H.M. Huffman and F.R. Cattoir, Glass. II. The transition between the glassy and liquid states in the case of glucose, J. Phys. Chem., 32 (1928) 1366–1379.

50 T.M. Herrington and A.C. Branfield, Physico-chemical studies on sugar glasses. I. Rates of crystallization, J. Food Technol., 19 (1984) 409–425.

51 T.M. Herrington and A.C. Branfield, Physico-chemical studies on sugar glasses. II. Glass transition temperature, J. Food Technol., 19 (1984) 427–435.

52 E.C. To and J.M. Flink, 'Collapse', a structural transition in freeze dried carbohydrates. III. Prerequisite of recrystallization, J. Food Technol., 13 (1978) 583–594.

53 K.J. Zeleznak and R.C. Hoseney, The glass transition in starch, Cereal Chem., 64 (1987) 121–124.

54 Y. Roos and M. Karel, DSC study of phase transitions affecting the quality of dehydrated materials, Biotechnol. Prog., 6 (1990) 159–163.

55 H. Levine and L. Slade, A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPS), Carbohydr. Polym. 6 (1986) 213–244.

56 K. Eberstein, R. Höpcke, G. Konieczny-Janda and R. Stute, DSC-Untersuchungen an Stärken, Starch, 32 (1980) 397–404.

57 C.G. Biliaderis, C.M. Page, L. Slade and R.R. Sirett, Thermal behavior of amylose–lipid complexes, Carbohydr. Polym. 5 (1985) 367–389.

58 T. Shiotsubo and K. Takahashi, Differential thermal analysis of potato starch gelatinization, Agric. Biol. Chem., 48 (1984) 9–17.

59 C.I. Pravisani, A.N. Califano and A. Calvelo, Kinetics of starch gelatinization in potato, J. Food Sci., 50 (1985) 657–660.

60 L. Slade and H. Levine, Non-equilibrium melting of native granular starch, Carbohydr. Polym., 8 (1988) 183–208.

61 J. Longton and G.A. Le Grys, Differential scanning calorimetry studies on the crystallinity of ageing wheat starch gels, Starch, 33 (1981) 410–414.

62 K.J. Zeleznak and R.C. Hoseney, The role of water in the retrogradation of wheat starch gels and bread crumb, Cereal Chem., 63 (1986) 407–411.

63 A.C. Eliasson, in R.D. Hill and L. Munch (Eds.), New Approaches to Research on Cereal Carbohydrates, Elsevier, Amsterdam, 1985.

64 A. Matsunaga and K. Kainuma, Studies on the retrogradation of starch in starchy foods, Starch, 38 (1986) 1–6.

65 Ph. Roulet, W.M. MacInnes, P. Würsch, R.M. Sanchez and A. Raemy, A comparative study of the retrogradation kinetics of gelatinized wheat starch in gel and powder form using X-rays, differential scanning calorimetry and dynamic mechanical analysis, Food Hydrocolloids, 2 (1988) 381–396.

66 K. Münzig, Demonstration of changes in structure in cereal starches by heat flux DSC, Thermochim. Acta, 151 (1989) 57–62.

67 C. Rochas and M. Rinaudo, Calorimetric determination of the conformational transition of kappa carrageenan, Carbohydr. Res., 105 (1982) 227–236.

68 W.A. Atwell, L.F. Hood, D.R. Lineback, E. Varriano-Marston and H.F. Zobel, The terminology and methology associated with basic starch phenomena, Cereal Foods World, 33 (1988) 306–311.

69 A. Raemy, C. Kaabi and W.M. MacInnes, Mise en évidence de la rétrogradation de l'amidon par microcalorimétrie isotherme, Journ. AFCAT, Clermont-Ferrand, 20–21 (1990) 73–78.

70 A.I. Hohlberg, Kinetics of bean protein thermal denaturation, J. Food Processing Preservation, 11 (1987) 31–42.

71 D.J. Wright, in B.J. Hudson (Ed.), Development in Food Proteins—1, Applied Science Publishers, London, 1982, pp. 61–89.

72 P.L Privalov, in C.B. Anfinsen, J.T. Edsall and F.M. Richards (Eds.), Advances in Protein Chemistry, Vol. 33, Academic Press, New York, 1979, pp. 167–241.

73 P.L. Privalov, in C.B. Anfinsen, J.T. Edsall and F.M. Richards (Eds.), Advances in Protein Chemistry Vol. 35, Academic Press, New York, 1982, pp. 1–104.

74 K.H. Park and D.B. Lund, Calorimetric study of thermal denaturation of β-lactoglobulin, J. Dairy Sci., 67 (1984) 1699–1706.

75 J.N. De Wit and G. Klarenbeek, A differential scanning calorimetric study of the thermal behaviour of bovine β-lactoglobulin at temperatures up to 160 ° C, J. Dairy Res., 48 (1981) 293–302.

76 J.W. Donovan and K.D. Ross, Increase in the stability of avidin produced by binding of biotin. A differential scanning calorimetric study of denaturation by heat, Biochemistry, 12 (1973) 512–517.

77 M. Rüegg, U. Moor and B. Blanc, Hydration and thermal denaturation of β-lactoglobulin. A calorimetric study, Biochim. Biophys. Acta, 400 (1975) 334–342.

78 S. Damodaran, Refolding of thermally unfolded soy proteins during the cooling regime of the gelation process: effect on gelation, J. Agric. Food Chem., 36 (1988) 262–269.

79 D.J. Wright and D. Boulter, Differential scanning calorimetric study of meals and constituents of some food grain legumes, J. Sci. Food Agric., 31 (1980) 1231–1241.

80 K. Watanabe, S. Hayakawa, T. Matsuda and R. Nakamura, Combined effect of pH and sodium chloride on the heat-induced aggregation of whole egg proteins, J. Food Sci., 51 (1986) 1112–1114, 1161.

81 P.-O. Hegg, H. Martens and B. Löfqvist, The protective effect of sodium dodecylsulfate on the thermal precipitation of conalbumin. A study on thermal aggregation and denaturation, J. Sci. Food Agric., 29 (1978) 245–260.

82 D.J. Wright and P. Wilding, Differential scanning calorimetric study of muscle and its proteins: myosin and its subfragments, J. Sci. Food Agric., 35 (1984) 357–372.

83 R.J. Hastings, G.W. Rodger, R. Park, A.D. Matthews and E.M. Andersen, Differential Scanning Calorimetry of fish muscle: the effect of processing and species variation, J. Food Sci., 50 (1985) 503–510.

84 V.R. Harwalkar and C.-Y. Ma, Study of thermal properties of oat globulin by differential scanning calorimetry, J. Food Sci., 52 (1987) 394–398.

85 J.W. Donovan, R.A. Beardslee and K.D. Ross, Formation of monoferric ovotransferrins in the presence of chelates, Biochem. J., 153 (1976) 631–639.

86 B.S. Chang, K.H. Park and D.B. Lund, Thermal inactivation kinetics of horseradish peroxidase, J. Food Sci., 53 (1988) 920–923.

87 S.E.B. Petrie and R. Becker, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 2, Plenum, London, 1970, pp. 225–238.

88 H. Bothe and H.K. Cammenga, Phase transitions and thermodynamic properties of anhydrous caffeine, J. Thermal Anal., 16 (1979) 267–275.

89 H. Bothe and H.K. Cammenga, Calorimetric investigation of aqueous caffeine solutions and molecular association of caffeine, Thermochim. Acta, 69 (1983) 235–252.

90 A. Cesaro and G. Starec, Thermodynamic properties of caffeine crystal forms, J. Phys. Chem., 84 (1980) 1345–1346.

91 Y.H. Roos, Phase transitions and unfreezable water content of carrots reindeer meat and white bread studied using DSC, J. Food Sci., 51 (1986) 684–686.

92 L. Riedel, Kalorimetrische Untersuchungen an dem System Kaffe-Extrakt/Wasser, Chem. Mikrobiol. Technol. Lebensm., 4 (1974) 108–112.

93 L. Riedel, Enthalpiemessungen an Lebensmitteln, Chem. Mikrobiol. Technol. Lebensm., 5 (1977) 118–127.

94 J. Suurkuusk, B.R. Lentz, Y. Barenholz, R.L. Biltonen and T.E. Thompson, A calorimetric and fluorescent probe study of the gel–liquid crystalline phase transition in small, single-lamellar dipalmitoylphosphatidylcholine vesicles, Biochemistry, 15 (1976) 1393–1401.

95 R.N. McElhaney, The use of differential scanning calorimetry and differential thermal analysis in studies of model and biological membranes, Chem. Phys. Lipids, 30 (1982) 229–259.

96 U.H. Egli, R.A. Streuli and E. Dubler, Influence of oxygenated sterol compounds on phase transition in model membranes. A study by differential scanning calorimetry, Biochemistry, 23 (1984) 148–152.

97 P.L. Russell, A kinetic study of bread staling by DSC and compressibility measurements, J. Cereal Sci., 1 (1983) 285–296, 297–303.

98 A. Raemy, R.F. Hurrell and J. Löliger, Thermal behaviour of milk powders studied by differential thermal analysis and heat flow calorimetry, Thermochim. Acta, 65 (1983) 81–92.

99 A. Raemy, Differential thermal analysis and heat flow calorimetry of coffee and chicory products, Thermochim. Acta, 43 (1981) 229–236.

100 A. Raemy and P. Lambelet, A calorimetric study of self-heating in coffee and chicory, J. Food Technol., 17 (1982) 451–460.

101 A. Raemy and J. Löliger, Thermal behavior of cereals studied by heat flow calorimetry, Cereal Chem., 59 (1982) 189–191.

102 L. Riedel, Calorimetric measurements of heats of hydration of foods, Chem. Mikrobiol. Technol. Lebensm., 5 (1977) 97–101.

103 Y.-N. Lian, A.-T. Chen, J. Suurkuusk and I. Wadsö, Polyol–water interactions as reflected by aqueous heat capacity values, Acta Chem. Scand., A36 (1982) 735–739.

104 N. Morel-Desrosiers and J.-P. Morel, Interactions between cations and sugars, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 3461–3469.

105 I. Marison and U. Von Stockar, A calorimetric investigation of the aerobic cultivation of *Kluyveromyces fragilis* on various substrates, Enzyme Microb. Technol., 9 (1987) 33–43.

106 P. Weppen and D. Schuller, Microcalorimetric studies of the mode of action of environmental chemicals on continuous microbial cultures, Thermochim. Acta, 72 (1984) 95–102.

107 I. Lamprecht, Growth and metabolism in yeasts, in A.E. Beezer (Ed.), Biological Microcalorimetry, Academic Press, London, 1980, pp. 43–112.

108 L. E. Grieme and D.M. Barbano, Method for use of a differential scanning calorimeter for determination of bacterial thermal death times, J. Food Protection, 46 (1983) 797–801.

109 P. Field, Dust Explosions, Elsevier, Amsterdam, 1982.

110 D. Davies, A.R. Horrocks and M. Greenhalgh, in D. Dollimore (Ed.), Proc. 2nd Eur. Symp. Therm. Anal., Aberdeen, 1981, Heyden, London, 1981, p. 588.

111 A. Raemy and J. Löliger, Self-ignition of powders studied by high pressure differential thermal analysis, Thermochim. Acta, 85 (1985) 343–346.

112 A. Raemy, P. Lambelet and J. Löliger, Thermal analysis and safety in relation to food processing, Thermochim. Acta, 95 (1985) 441–446; A. Raemy and M. Gardiol, Paramètres thermodynamiques et sécurité des opérations industrielles, ASIC, 12th Colloque, Montreux, 1987, pp. 320–330.

113 N.N. Mohsenin, Thermal Properties of Foods and Agricultural Materials, Gordon and Breach, New York, 1980.

114 W.M. MacInnes and Ph. Roulet, Dynamic-mechanical properties of starch gels, Rheol. Acta, 26 (1988) 431–434.

115 I.T. Norton, C.D. Lee-Tuffnell, S. Ablett and S.M. Bociek, A calorimetric, NMR and X-ray diffraction study of the melting behavior of tripalmitin and tristearin and their mixing behavior with triolein, J. Am. Oil Chem. Soc., 62 (1985) 1237–1244.

116 L. Hernqvist, B. Herslöf, K. Larsson and O. Podlaha, Polymorphism of rapeseed oil with a low content of erucic acid and possibilities to stabilize the β'-crystal form in fats, J. Sci. Food Agric., 32 (1981) 1197–1202.

117 K. Kawamura, The DSC thermal analysis of crystallization behavior in palm oil, J. Am. Oil Chem. Soc., 56 (1979) 753–758.
118 A. Cesaro, E. Russo and V. Crescenzi, Thermodynamics of caffeine aqueous solutions, J. Phys. Chem., 80 (1976) 335–339.
119 I. Horman and B. Dreux, Estimation of dimerisation constants from complexation induced-displacements of ^{1}H-NMR chemical shifts: dimerisation of caffeine, Helv. Chim. Acta, 67 (1984) 754–764; 68 (1985) 72–75.
120 C.G. Biliaderis, Differential scanning calorimetry in food research—A review, Food Chem., 10 (1983) 239–265.
121 A. Schiraldi, Calorimetry, thermal analysis and chemical thermodynamics in food science, Thermochim. Acta, 162 (1990) 253–264.
122 M. Peleg and E.B. Bagley, Physical Properties of Foods, AVI, Westport, CT, 1983.
123 R. Jowitt, F. Escher, M. Kent, B. McKenna and M. Rogues, Physical Properties of Foods, Elsevier Applied Science, London, 1987.
124 H.J. Hinz, Thermodynamic Data for Biochemistry and Biotechnology, Springer-Verlag, Berlin, 1986.
125 P.C. Bowes, Self-heating: Evaluation and Controlling the Hazards, Elsevier, Amsterdam, 1984.
126 V.R. Harwalkar and C.Y. Ma (Eds.), Thermal Analysis of Foods, Elsevier Applied Food Science Series, London, 1991.
127 M.J. Lewis, Physical Properties of Foods and Food Processing Systems, VCH Verlag, Weinheim, 1987.
128 P. Zeuthen and J.C. Cheftel (Eds.), Thermal Processing and Quality of Foods, Elsevier Applied Science, London, 1984.
129 S. Friberg, Food Emulsions, Marcel Dekker, New York, 1976.
130 L. Rey (Ed.), Freeze-drying/Lyophilisation, Hermann, Paris, 1966.
131 E.H. Battley, Energetics of Microbial Growth, Wiley, New York, 1987.
132 N.L. Kent, Technology of Cereals, Pergamon, New York, 1983.
133 B.M. McKenna, Engineering and Food, Elsevier Applied Science, London, 1984.
134 T.M. Hardman, Water and Food Quality, Elsevier Applied Science, London, 1989.
135 D. Giron, Thermal analysis in pharmaceutical routine analysis, Acta Pharm. Jugosl., 40 (1990) 95–157.
136 S.R. Elliott, Physics of Amorphous Materials, Longman Scientific Technical, London, 1990.
137 L.C. Chen and F. Spaepen, Calorimetric evidence for the microquasicrystalline structure of ‘amorphous’ Al/transition metal alloys, Nature, 336 (1988) 366–368.
138 G.P. Johari, S. Ram, G. Astl and E. Mayer, Characterizing amorphous and microcrystalline solids by calorimetry, J. Non-Cryst. Solids, 116 (1990) 282–285.
139 E. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981.
140 B. Wunderlich, Macromolecular Physics, Academic Press, New York, 1980.