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# BEHAVIOR OF FOODS STUDIED BY THERMAL ANALYSIS
## Introduction

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## Abstract

In the investigation of foods by thermal analysis and calorimetric techniques, many physico-chemical effects can be observed in the temperature range between –50 and 300°C. These thermal phenomena may be either endothermic, such as melting, gelatinization, denaturation, evaporation or exothermic, such as crystallization, oxydation, fermentation. Glass transitions are observed as a shift in the base line; this information, associated with water content and water activity determinations, is of particular interest in relation to storage of food powders but also for gas retention in powders fore-seen to foam when dissolved.

The thermal behavior of foods strongly depends on their composition; we therefore present first the thermal characteristics of the major food constituents: carbohydrates, lipids, proteins, water and then of raw and reconstituted food.

**Keywords:** calorimetry, DSC, food, process safety, thermophysical properties

## Introduction

Chocolate bars should melt in the mouth and not in the hand, and the 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 of foods with thermal analysis and calorimetric instruments.

The physico-chemical behavior of foods strongly depends on their composition; we therefore first present the thermal characteristics of the major food constituents: carbohydrates, lipids, proteins, water and then the thermal behavior of raw and reconstituted food.

The thermal phenomena may be endothermic or exothermic. Some exothermic reactions present a hazard in industrial operations or during storage. They can lead either to self-ignition and to fires or even dust explosions in open systems such as spray-dryers, or to pressure increase and to bursting of closed vessels such as extraction cells.

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## Instruments and methods

For our studies of food material we have mainly used high pressure differential thermal analysis (Netzsch, Selb, Germany), heat flow or Calvet type calorimeters, a heat flow micro-DSC equipment (Setaram, Caluire, France) and a standard power compensation DSC (Pyris, Perkin Elmer, Norwalk, USA).

Scanning (heating and cooling) as well as isothermal modes were applied.

The measurements in relation with process safety were performed under pressure (25 bar of oxygen for example) or in sealed cells. Oxidation of lipids was studied isothermally under oxygen flow in order to have excess of oxygen.

The principles of the techniques of thermal analysis are described in a recent book [1].

## Thermal behavior of the main food constituents

### *Thermal behavior of carbohydrates*

For the carbohydrates, the main phenomena observed are release of crystallization water, melting, decomposition, gelatinization of starch in the presence of water, retrogradation of the gel as well as glass transition, relaxation and crystallization of amorphous samples [2–5]. Tables with melting and decomposition enthalpies are given in [2].

Glass transition and relaxation are often superimposed in the same temperature range; glass transition is however a reversible change in base line level and relaxation a non-reversible phenomenon. Thus, two scans (one directly after the other) of the same sample allow to distinguish between both phenomena.

For studying release of crystallization water in hydrates, thermogravimetry can be very useful by indicating to which endothermic phenomenon corresponds mass loss. The phenomena of gelatinization and retrogradation leading also to rheological modifications of the products, complementary information can be obtained by dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA), for instance [6]. Even retrogradation is a slow and low energetic phenomenon, it can be followed by isothermal microcalorimetry [7].

Only decomposition, which sometimes follows melting immediately, may present a hazard in industrial operations.

### *Thermal behavior of lipids (oils and fats)*

For the lipids, the main phenomena observed are crystallization, melting, polymorphism and oxidation [8–12]. Tables with oxidation induction times at temperatures around 100°C are given in [12].

The effect of emulsifier types on crystallization and melting characteristics can also be observed by this way. The examples of crystallization curves shown in Fig. 1, indicate that addition of emulsifiers A or B may lead to a higher or to a lower initial temperature of fat crystallization, in comparison with pure fat.

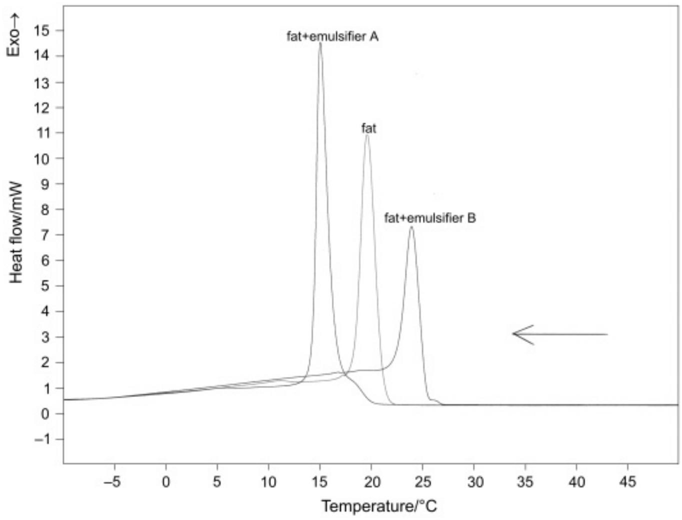


**Fig 1** Cooling curves of a fat in the absence of emulsifier, in the presence of emulsifier A or emulsifier B showing the effect on fat crystallization temperature (Micro-DSC III, Setaram, exothermic effect is upwards)

Only oxidation may present a hazard in industrial operations (risk of self-ignition leading to a fire), in particular if the contact surface between oxygen from air and the lipid is great.

*Thermal behavior of proteins*

For the proteins, the main phenomena observed are the denaturation [13–15] when the proteins are in solution, as well as glass transition and oxidation, when they are dried powders. The glass transition of proteins is a weak phenomenon; his detection is rather performed on the basis of rheological parameters obtained for example by dynamic mechanical thermal analysis [16].

Dry proteins may also present self-ignition when maintained in presence of enough oxygen.

*Thermal behavior of water*

Thermal analysis and calorimetry allow mainly to observe crystallization (super-cooling), melting (of ice) as well as vaporization. The enthalpies corresponding to these phenomena being quite high, even small samples of water or of dilute solutions can be analyzed by standard DSC.

## Thermal behavior of minor constituents

The minor constituents of food, such as caffeine or vitamins, may also be analyzed as such by these techniques.

Caffeine, for example, shows a solid-solid transition around 135°C and melting around 230°C.

## Thermal behavior of raw and reconstituted food

Most of these physico-chemical effects of the main food constituents are found again in the calorimetric curves of raw and reconstituted foods such as coffee beans, chicory roots, cereals or milk powders and infant formulas [17–20]. It must be remembered here that about all raw and reconstituted foods contain water and that therefore measurements of such products in sealed cells above 100°C must only be performed with great precaution because of pressure increase due to water vapor.

In addition to these mentioned phenomena, some interactions between food constituents, such as the Maillard reactions which are reactions between proteins and reducing sugars, may be observed as an exothermic phenomenon in calorimetric curves of milk powders or infant formulas for example. Here we can also mention lipid-amylose complexes, which happen in cereal based products around 100°C and are endothermic and reversible.

For minor constituents, the phenomena observed for the pure substances will however no more be observed once these constituents are dispersed in the food matrix. The high temperature stability mentioned before for caffeine explains that this substance is still available to the consumer after coffee roasting.

Melting of ice is often used to determine freezable water, which is considered as ‘free water’ by opposition to ‘bound water’ which is not freezable. In this context it must be known that the melting/crystallization enthalpy of water diminishes with decreasing temperature.

The enthalpy of vaporization of water at 100°C being so high, boiling is easily observed with open cells in food containing even small amounts of water. The problem is that the other exothermic effects such as carbohydrate crystallization or decomposition are thus no more observed clearly when open cells are used; therefore, the measurements under pressure of inert gas or the use of sealed cells.

Calorimetric techniques also allow to determine heats of solution of food powders, for example, in water or other solutions of interest.

In addition they allow determining specific heats of food products, a parameter which is often important for engineers. Tables with specific heats of coffee type products are given in reference [18], for values of other foods consider [21].

It must be mentioned that carbohydrate decomposition and lipid oxidation (especially if oil arises at the surface of the product) may also present a hazard in industrial operations related to raw and reconstituted foods.

## Microbiological studies

Calorimetric techniques used in isothermal mode also allow following the growth of microorganisms under aerobic or anaerobic conditions [22, 23].

## Process safety

The role of thermal analysis and calorimetry for determing safe conditions of industrial processes has already been explained elsewhere [24–28]. In the case of safety studies, thermal analysis and calorimetric techniques must sometimes be applied unconventionally as one has to carry out the measurements under conditions close to those of the process to be studied [29, 30].

## Conclusions

This short introduction demonstrates that thermal analysis and calorimetric techniques are very efficient to study a great number of physico-chemical effects in foods and thus allow to determine optimized processing of food.

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