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DIFFERENTIAL THERMAL ANALYSIS AND HEAT FLOW CALORIMETRY OF COFFEE AND CHICORY PRODUCTS

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ABSTRACT

The techniques of differential thermal analysis (DTA) and heat flow calorimetry were used to study the thermal behaviour of coffee and chicory products above 20°C. Intensive exothermic reactions were particularly evident when measurements were made under pressure, which prevents vaporization of the water contained in the products, in the temperature domain of interest.

INTRODUCTION

Differential thermal analysis (DTA) and heat flow calorimetry provide much information about the physical and chemical changes that occur in materials during heating. The principles of DTA [1] and heat flow calorimetry [2] are well known; such instruments have been used for many investigations.

Our interest in these techniques lies especially in the detection of exothermic reactions in foodstuffs. Such knowledge of food properties is important to the analyst (a thermogram can characterize a product) and also to the security engineer (the determination of reaction temperatures and enthalpies allows the establishment of safe industrial processing conditions).

The instruments used are a special high-pressure DTA apparatus [constructed by Netzsch following a Claudy and Bousquet (C.N.R.S.) patent] and a conventional heat flow calorimeter (Setaram C80). The measurements are performed under different atmospheres and most importantly under pressure to prevent water vaporization. Most thermograms of foodstuffs, performed at atmospheric pressure, show above 100°C an endothermic peak corresponding to water phase transition. The form and size of this peak depend on the moisture content of the food sample and on other factors such as the atmosphere above the sample or the heating rate. This endothermic peak often hides intensive exothermic phenomena due, for example, to pyrolysis reactions. In order to detect these other reactions, it is necessary to alter the atmosphere above the sample either by using gas flow or by reducing or increasing the pressure.

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INSTRUMENTS

A scheme of the Netzsch high-pressure DTA equipment is given in Fig. 1. The furnace and the cells can be put under pressures as high as 500 bar. As the outside of the autoclave is cooled, the pressure stays virtually constant even during heating of the furnace.

A scheme of the Setaram C80 heat flow (isotherm) calorimeter is given in Fig. 2. Different types of cells are provided. Closed cells allow measurements at constant volume (isochoric conditions): with them we avoid the loss of substances in the form of hot gases or vapours. With other cells, accessible directly from outside the calorimeter, it is possible to heat the sample under gas flow, vacuum or constant pressure. Compared to the DTA instrument the heat flow calorimeter needs slower heating rates, but it is much more sensitive.

Calorimeter thermograms and DTA diagrams present, respectively, heat flow (Q/t) and temperature difference (ΔT) between reference and sample cell as a function of time or temperature.

EXPERIMENTAL PROCEDURES

Both instruments allow the analysis of relatively large quantities of non-homogeneous material (whole coffee beans, 0.5 g for the DTA instrument and 2—4 g for the calorimeter).

The DTA apparatus gives better results when the sample is mixed with aluminium oxide. With the DTA instrument, the samples are analyzed under an atmosphere of inert gas (generally argon or nitrogen) at pressures indicated by the water vapour pressure tables.

The measurements with the heat flow calorimeter are performed under

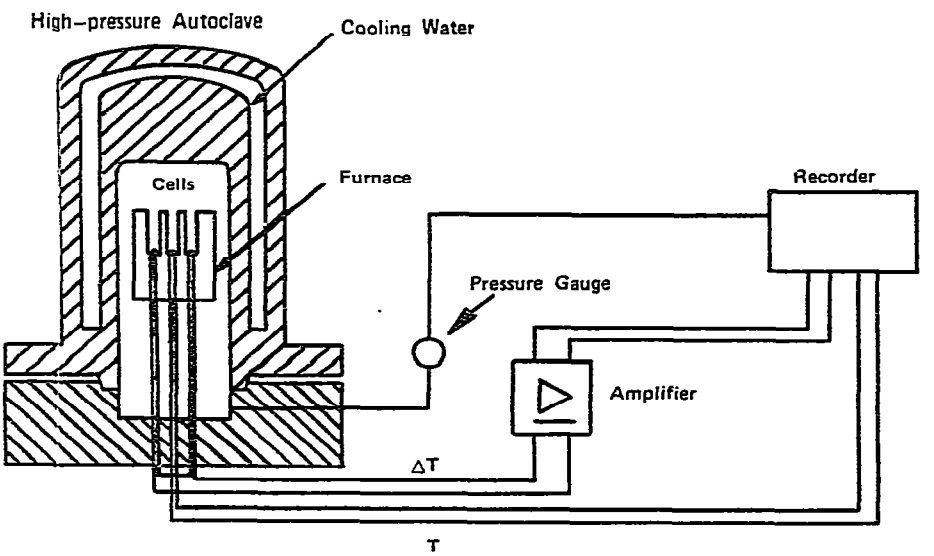

Fig. 1. Schematic representation of the Netzsch high-pressure equipment.

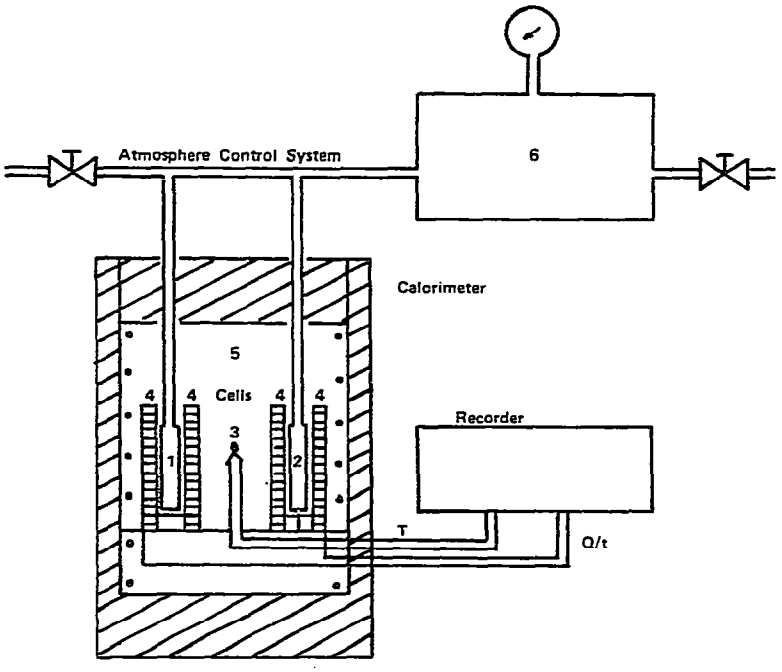

Fig. 2. Schematic representation of the Setaram C80 heat flow calorimeter. 1, Reference cell; 2, sample cell; 3, thermocouple; 4, thermopiles; 5, thermostatically controlled enclosure; 6, buffer reservoir.

different atmospheres. The reservoir in the atmosphere control system allows heating of the cells under constant pressure of inert gas. In closed cells the pressure rises during the measurement, due to heating, water vapour (at ther-

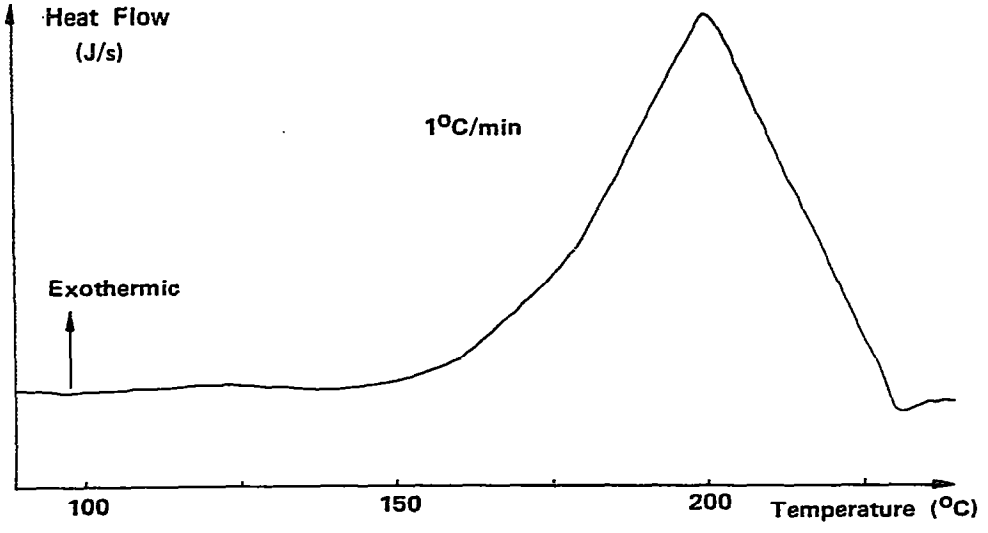

Fig. 3. Thermogram of green Arabica coffee beans. Atmosphere, 20 bar argon.

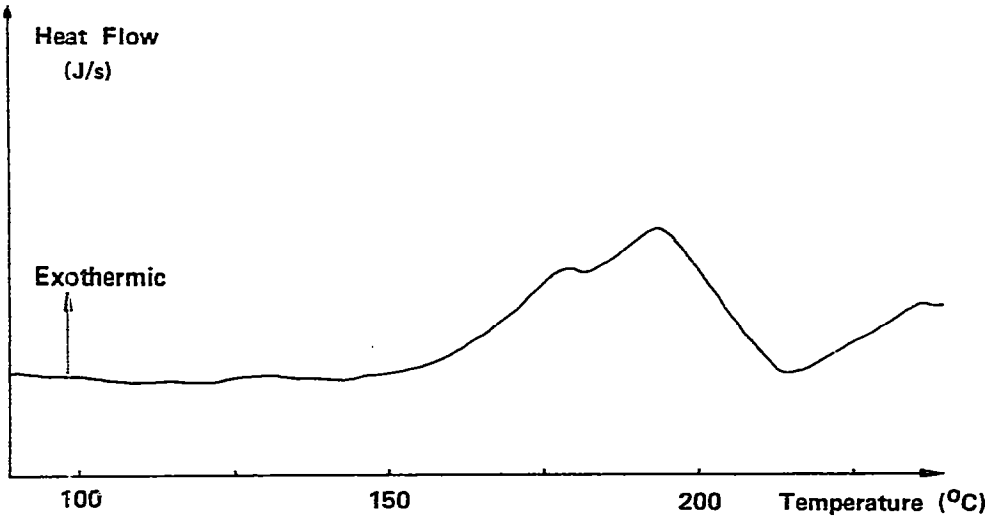

Fig. 4. Thermogram of green Arabica coffee beans. Atmosphere, 10 bar argon.

modynamic equilibrium) and degassing of the sample: the water phase transition peak does not occur.

ANALYSIS OF GREEN COFFEE BEANS

Samples of green Arabica coffee beans from Mexico were analyzed. With open cells, under atmospheric pressure the heat flow calorimeter thermograms showed an endothermic peak above 100°C (water phase transition) and at higher temperatures an exothermic tendency. These kinds of diagram correspond to those presented by Streuli [3], Quijano-Rico [4] and Baltes

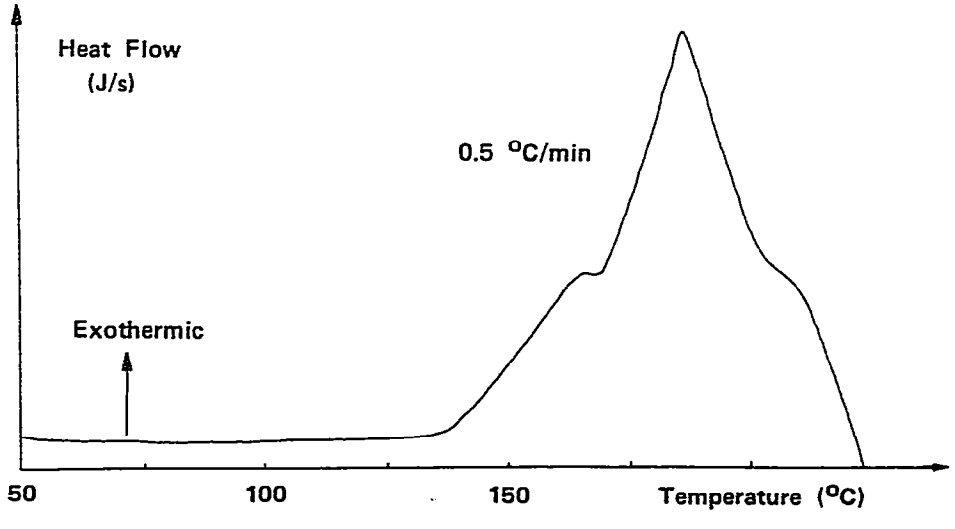

Fig. 5. Thermogram of green Arabica coffee beans. Atmosphere, 20 bar argon.

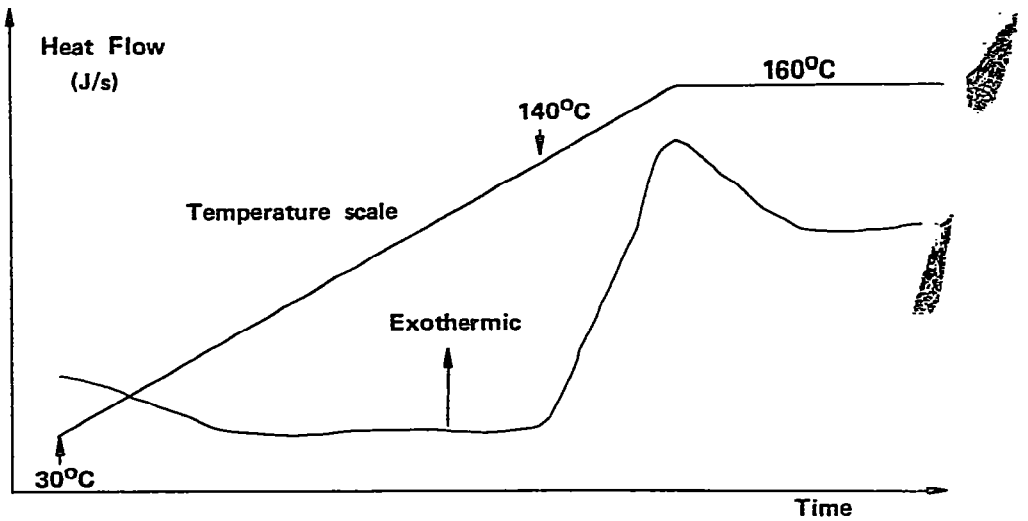

Fig. 6. Thermogram of green Arabica coffee beans. Atmosphere, 20 bar argon.

[5]. They do not give precise information about the beginning of the exothermic reactions and do not allow enthalpy determinations.

Measurements performed under 20—25 bar pressure (corresponding to the water vapour pressure at 212 and 224°C, respectively) of inert gas showed important exothermic phenomena above 140°C (Fig. 3). These are due to roasting and carbonization of coffee. At lower pressures (Fig. 4), the exothermic peak was partially masked (10 bar is the water vapour pressure at 180°C) by the water vaporization. Measurements performed with closed cells showed a similar thermogram to measurements under 20 bar pressure.

By heating more slowly (0.5°C min^{-1} instead of 1°C min^{-1}), we obtained

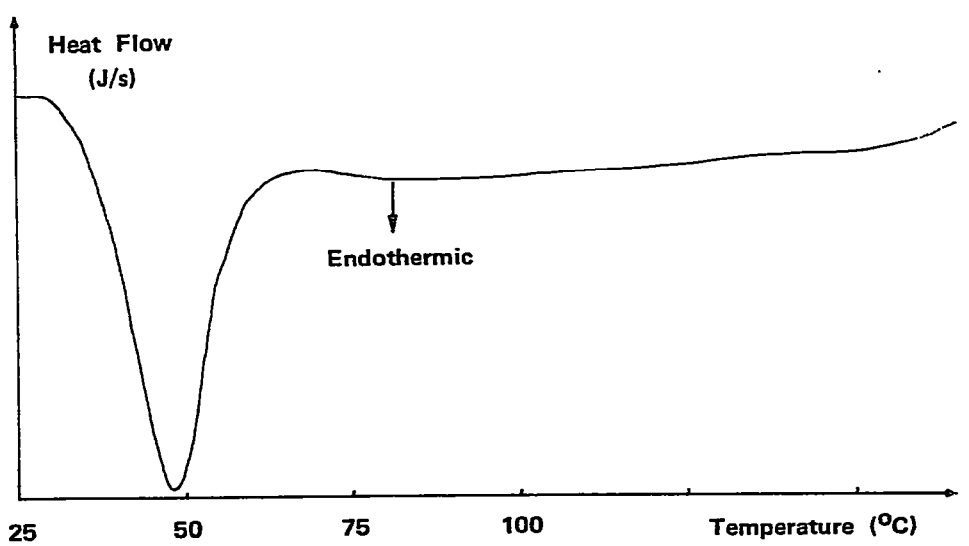

Fig. 7. Thermogram of raw fermented cocoa beans. Atmosphere, 20 bar argon.

(Fig. 5) a poorly resolved triplet; roasting and carbonization of coffee beans could not be clearly separated. The enthalpies corresponding to the peak between 140°C and 230°C (roasting and carbonization) had values around 250—375 J g^{-1} (60—90 cal g^{-1}).

Another thermogram (Fig. 6) showed that the exothermic reactions did not stop even when the temperature was maintained at 160°C. On the corresponding DTA diagrams of roasted coffee the peak appeared as a singlet.

In comparison, the thermogram of raw fermented cocoa beans (from Ghana) under identical (20 bar argon) conditions showed no significant exothermic reactions (Fig. 7). The endothermic peak just above ambient temperature corresponded to the fusion of cocoa butter.

ANALYSIS OF CHICORY

Chicory roots received from different countries were dried according to normal procedures. The DTA diagrams of dried chicory showed exothermic reactions (Fig. 8). These phenomena were even more intensive than for green coffee: enthalpies as high as 540—640 J g^{-1} (or 130—150 cal g^{-1}) were measured.

Dried chicory roots were roasted to different degrees. The exothermic reactions shown by these roasted chicories were more intensive at lower degrees of torrefaction (Fig. 9) and furthermore depended on the origin of the chicory. The temperature domain of the exothermic peak was lower than for coffee. We hope to relate these experimental findings to the chemical composition of the chicories [6] or to polysaccharide thermograms [5].

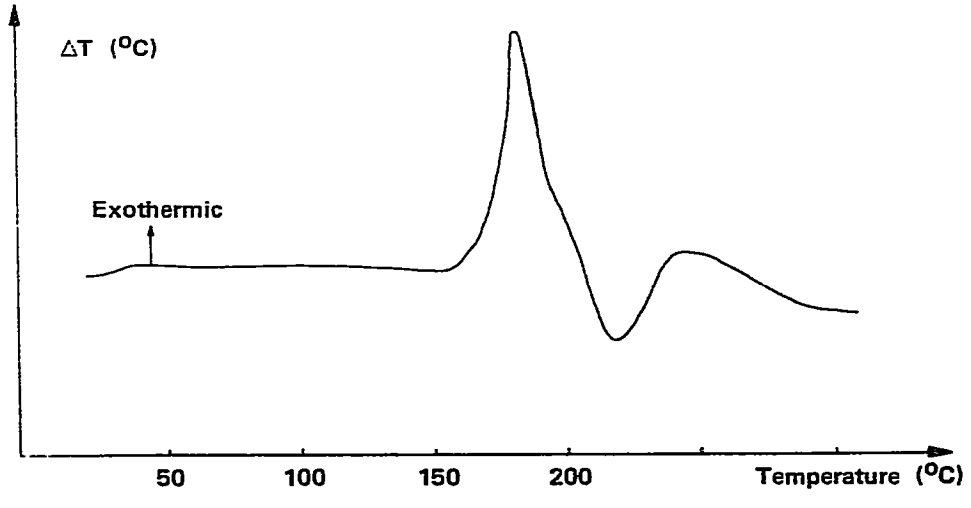

Fig. 8. DTA diagram of dried chicory from Linz (Austria). Atmosphere, 20 bar nitrogen.

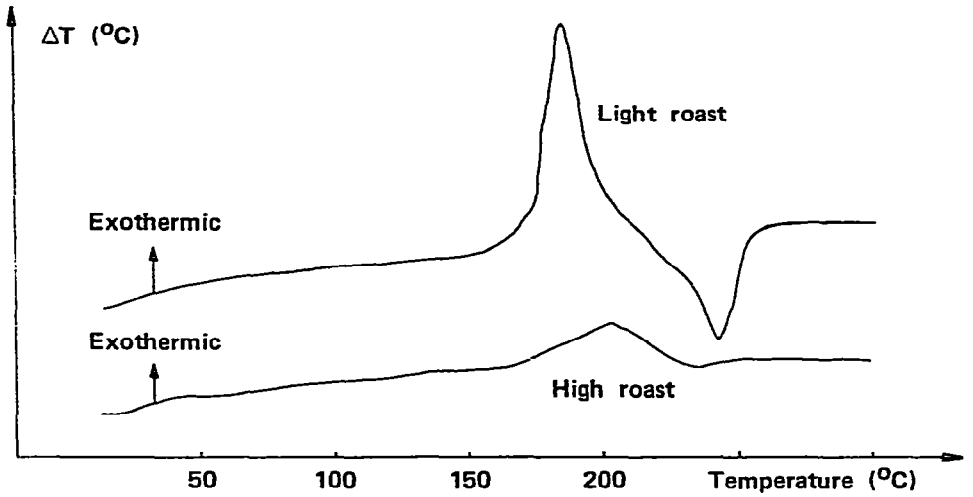

Fig. 9. DTA diagram of roasted chicories. Atmosphere, 20 bar nitrogen.

ANALYSIS OF COFFEE AND CHICORY SOLUBLE POWDERS

Soluble powders (from pilot plant batches) with different percentages of coffee and chicory were compared using the above techniques. Exothermic properties increase with proportion of chicory in the product (Fig. 10) but also with lower degrees of chicory torrefaction. When both components were present in the powder, the exothermic peak was a doublet; the first (or left) part is due especially to chicory, the second to coffee. It still seems difficult to determine precisely by this method the amount of coffee in a soluble powder.

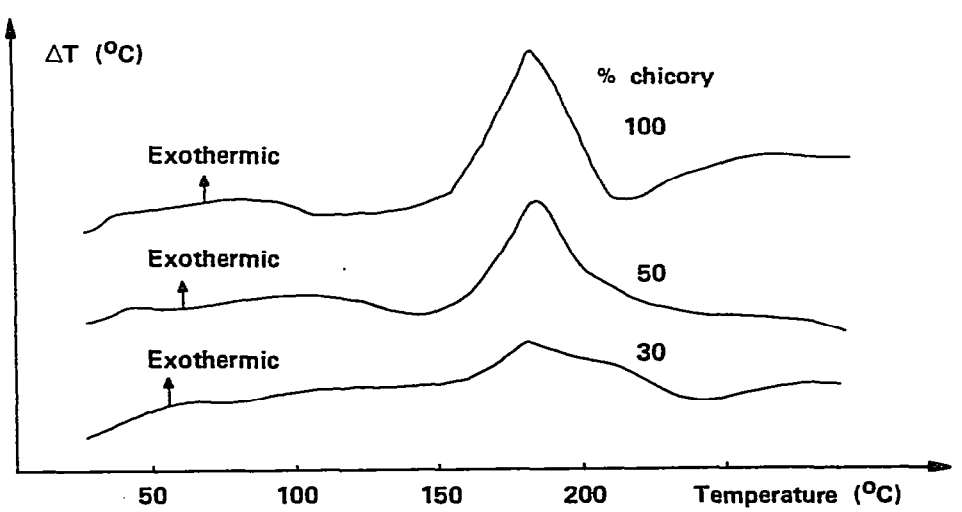

Fig. 10. DTA diagram of soluble coffee and chicory powders. Atmosphere, 20 bar nitrogen.

CONCLUSION

The analysis of coffee and chicory by DTA has given interesting qualitative information about the behaviour of these foodstuffs during heating. The greater sensitivity of the heat flow calorimeter gives the possibility of collecting better quantitative data.

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