Thermochimica Acta, 93 (1985) 133-136
Elsevier Science Publishers B.V., Amsterdam

LOW TEMPERATURE DSC FOR BIOLOGICAL SYSTEMS

*Teruyuki Fujita, The Institute of Applied Microbiology, University of Tokyo, Tokyo, Japan
Ryozo Kato, Sinku-Riko Inc., Yokohama, Japan

ABSTRACT

Design and testing of a low temperature DSC of conduction type with high sensitivity using larger vessels of about 1.5 ml were described. The main technical characteristics of DSC are as follows: operational temperature range is -150~120°C; rate of cooling and heating is 0.01~1°C/min; volume of calorimetric vessels are 1 ml; sensitivity is 3.68µJ/sec/µV; accuracy of temperature recording is 0.1°C. Test experiments on starches, proteins and alcoholic drinks indicate that the DSC is available for studies on dilute solutions and solids of biological materials and also on the biological-water systems.

INTRODUCTION

There exist a number of different types of calorimeters that might be generally classified as DSC. Several commercial instruments of moderate sensitivity have been available for some systems. These instruments are excellent for many studies involving neat samples or samples at very high concentration since they can resolve changes in heat capacity of the order of 1 part in 100. Because of their small sample size and the lack of strict adiabativity, however, the sensitivity is not adequate for many type of biological studies. Until recently no DSC with high sensitivity using larger vessels has been commercially available for studies on dilute solutions or solids of biological materials. Design and testing of a DSC of conduction type to meet these conditions are described in this paper. Provisions for cooling made it possible to be used for calorimetric studies on freezing behaviors of water in biological materials, which are of interest but rarely carried out so far. Although suitable for other purpose as well, it has been specifically designed to satisfy the needs of the biologist, food chemist, pharmacologist interested in thermal analyse of biological materials. The test experiments were carried out on characterization of starches, protein denaturation and quality assesments of alcoholic drinks.

Proceedings of ICTA 85, Bratislava

EXPERIMENTAL

The cross section of the DSC is shown in Fig. 1. In a copper heat sink, there are two holes containing two identical vessels, one for sample and the other for reference uses. The thermopile plates situated between the vessels and heat sink are used for measuring the heat flow difference between the heat flowing to the sample and the heat flowing to the reference vessel. The thermopile plate used is a semiconductor thermoelectric module with a temperature sensitivity of 12.4 mV/°C. A platinum plate heater placed between the heat sink and a thermal conduction bar were used for temperature indication and heating of the heat sink. Temperature of a adiabatic shield is controlled by a heater and a thermopile fitted to the shield. The measuring temperature range is from -150°C to +120°C and the program rate of heating and cooling can be selected in the range of 0.01°C/min to 1°C/min (-100°C～+120°C). The vessels made of copper with a volume of 1.5 ml are corrosion-resistant by coating and are tightly sealed by using heat-resistant rubber packings fitted to screw caps. The calibration experiments with benzophenon indicated that the maximum sensitivity of the calorimeter is

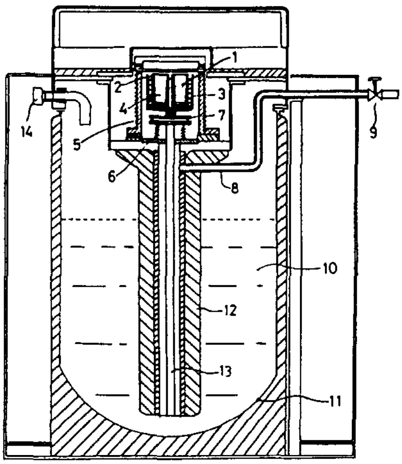


Fig. 1. Cross-sectional view of the DSC. (1), sample vessel; (2), thermopile plate; (3), heat sink; (4), reference vessel; (5), adiabatic shield; (6), thermal insulator; (7), platinum; (8), liquid N_2 gas control tube; (9), liquid N_2 gas control valve; (10), liquid N_2 ; (11), Dewar's vessel; (12), styrofoam insulator; (13), thermal conduction bar; (14), liquid N_2 inlet tube.

3.68 μJ/sec/μV and the accuracy of the temperature indication is 0.1°C. The calorimeter ensures a constant cooling rate by using a precision electrical controller and adjusting the volume of liquid nitrogen which fills the thermal conduction bar fitted to the heat sink.

RESULTS AND DISCUSSION

The DSC curves of the potato and wheat starches are shown in Fig. 2. The difference in curves were characterized by a endothermic peak observed in a temperature range of 62°C to 71°C. Whatever the true mechanism of the thermal processes may be, the curves are manifestations of the molecular composition of the starches (1). The results suggest that the DSC is available for the characterization of starches.

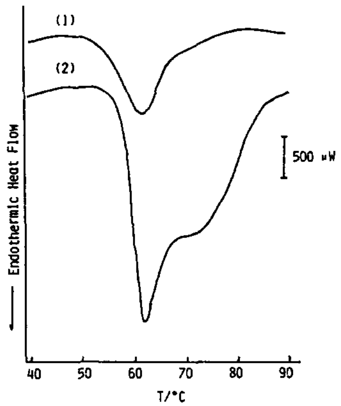
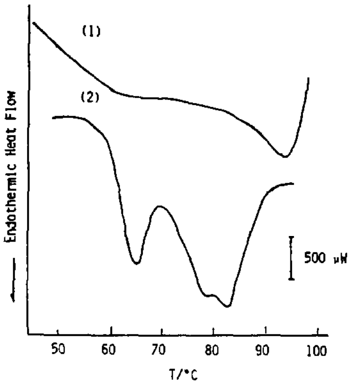


Fig. 2. DSC curves of wheat(1) and potato(2) starches. water content, 48%; sample volume, 0.75 ml; heating rate, 0.8°C/min

Fig. 3 shows typical DSC curves of egg white. The curve for a raw sample shows two main peaks at 60~66°C and at 75~85°C which may be due to the denaturation of protein components of egg white, a complex mixture of proteins (2), whereas a broad peak at about 95°C is observed for a dry solid of the sample. The difference between the patterns of curves may be interpreted by the change of the protein structure caused by dehydration.

In Fig. 4, a freezing curve of ethanol-water mixture is compared with that of commercial whisky of the same ethanol concent-



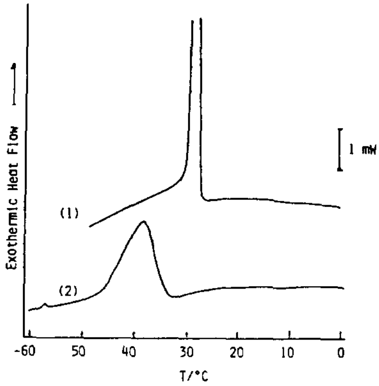


Fig. 3 (left). DSC curves of the dehydrated (1) and raw (2) egg whites. sample weight, 33 mg(1); 1150 mg(2); heating rate, 0.8°C/min.

Fig. 4 (right). Freezing DSC curves of ethanol-water mixture(1) and a commercial whisky(2) with the same ethanol concentration. ethanol concentration, 4.3%; sample volume, 0.5 ml; cooling rate, 1°C/min.

ration. The curves of ethanol-water mixture shows a sharp peak, while that of the whisky shows a broad peak with a additional small one at lower temperature. The heat of the peak of the whisky observed at -37.5°C was smaller than that of the ethanol-water mixture at -27°C. The results suggest that the interaction between water and ethanol in the whisky is more complex and stronger than that in the ethanol-water mixture (3).

The low temperature DSC described in this paper have proved to be useful for studies on thermal behaviors of many biological materials of various states in the wide temperature range.

REFERENCES

1 K. Morita, Anal. Chem. 28 (1956) 64
2 J.W. Donovan, C.J. Mapes, J.G. Davis and J.A. Garibaldi, J. Sci. Food Agric. 26 (1975) 73
3 K. Koga and H. Yoshizumi, J. Food Sci. 42 (1977) 213