Note

MICROCALORIMETRIC MEASUREMENT OF THE SPECIFIC HEAT OF *THYNNUS THUNNUS*

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ABSTRACT

The specific heat of *Thynnus Thunnus* from 295 to 413 K was measured using sealed samples of ca. 10 mg in a Calvet high temperature microcalorimeter. A drop method was used, the equipment being calibrated using the specific heat of copper, which gave values from 3.16 ± 0.03 J K^{-1} g^{-1} at 295 K to 3.75 ± 0.05 J K^{-1} g^{-1} at 413 K.

INTRODUCTION

The development of methods for measuring thermodynamic properties of natural biological materials is of interest, particularly when the methods can be applied to small samples. We report here a technique for deriving specific heats for samples of ca. 10 mg from measurements of the enthalpy increment relative to room temperature.

A Calvet high temperature microcalorimeter (Setaram Model, 0–1000 °C) was used for this method. The principle of the experiment was to drop a small sample at room temperature (T_1) into the calorimeter at temperature T_2, and hence measure $H_{T_2} - H_{T_1}$. As the sample had to pass through a furnace before reaching the calorimeter, precautions were needed to ensure that the sample was still at room temperature on entering the calorimeter. Samples were sealed into glass capillary tubes and although the temperature of the glass would increase on dropping it through the furnace, the thermal conductivity of the glass was low enough to ensure that the temperature of the sample remained unchanged during this process. The biological samples contained water, but by sealing into a glass capillary with a very small vapour space, errors due to the vaporization of water with increasing temperature were calculated to be negligible.

The calorimeter is a twin system. Marked pairs of glass capillaries were first dropped into twin cells to obtain a blank correction appropriate for that particular pair of capillaires. Then the same pairs of tubes were used,

TABLE 1

Calorimeter calibration at 141.2°C

Mass Cu (g)	Total Area (unit)	Blank (unit)	Total ΔH J	Sensitivity k (mJ (area unit)$^{-1}$)
0.080115	3614	307	3.733	1.129
0.077810	3459	260	3.642	1.133
0.066305	2894	593	3.088	1.342
0.081805	3623	250	3.811	1.130
0.073030	3136	297	3.401	1.198
				Mean $k = 1.131 \pm 0.002$

one filled either with copper wire for calibration, or with the sample to obtain $H_{T_2} - H_{T_1}$.

RESULTS

The calorimeter was calibrated at 51, 83, 112.2 and 141.2°C by drop experiments in which one of the glass tubes contained copper wire. The total ΔH was calculated from tabulated enthalpy values for copper in JANAF Thermochemical Tables [1], for a room temperature of 22°C. The detailed

TABLE 2

Variation of calorimeter sensitivity k with temperature

No. of expts.	T (°C)	k (mJ (area unit)$^{-1}$)
4	51.0	1.310 ± 0.030
4	83.0	1.175 ± 0.021
5	112.2	1.156 ± 0.017
5	141.2	1.131 ± 0.002

TABLE 3

Heat capacity of *thynnus thunnus*

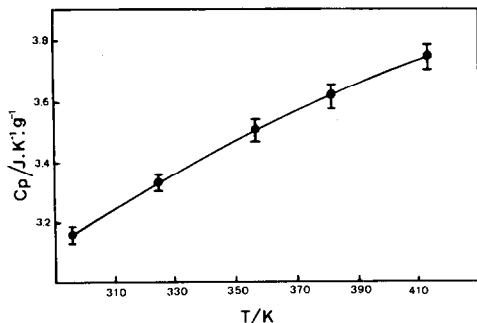| T (K)	No. of expts.	$H_T - H_{295}$ observed (J g^{-1})	$H_T - H_{295}$ calculated (J g^{-1})	C_p (J K^{-1} g^{-1})
295				3.16 ± 0.03
324	6	94.08 ± 1.82	93.1	3.33 ± 0.03
356	6	203.37 ± 2.50	203.4	3.50 ± 0.04
381	12	292.31 ± 1.81	292.3	3.61 ± 0.04
413	8	410.05 ± 2.40	410.1	3.74 ± 0.04

Fig. 1. Values of C_p plotted against T.

results at 141.2°C are given in Table 1. The sensitivity of the calorimeter varied with temperature as shown in Table 2.

For the experiments on *Thynnus Thunnus*, samples of ca. 10 mg at room temperature, 22°C (295 K), were dropped into the calorimeter at 51, 83, 108 and 140°C. After making the correction for the glass tubes, the heat quantity measured was $H_T - H_{295}$. The averages of 6–12 experiments at each temperature are given in Table 3.

The quantity $(H_T - H_{295})$ (J g^{-1}) was related to T by the cubic equation

$$(H_T - H_{295}) = -580.59 + 0.4893\,T + 5.987 \times 10^{-3}\,T^2 - 3.3 \times 10^{-6}\,T^3$$

Values calculated using this equation are given in Table 3. By differentiation of $(H_T - H_{295})$ with respect to T, C_p was derived and the values are listed in Table 3 and are plotted against T in Fig. 1. C_p shows a smooth increase from 295 to 413 K. A value of C_p for fresh fish at $T > 273$ K of 3.598 J K^{-1} g^{-1} was given by Harrel and Thelan [2], which is close to the values reported here.

ACKNOWLEDGEMENT

REFERENCES

1 JANAF Termochemical Tables. Nat. Bur. Stand., Washington, 1968.
2 Harrel, C.G. and Thelan, R.J., in Compilers Conversions Factors and Technical Data for the Food Industry, Burgess, Minneapolis, 1959, p. 468.