【論文】

イワシ筋肉の比熱に及ぼす成分組成と温度の影響

Effects of composition and temperature on the specific heat of Japanese anchovy (*Engraulis japonicus*) muscle

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食品の加熱過程で起こる変化を理解するためには，正確な食品の熱物性値が必要不可欠である．本研究では，粗脂肪含量の異なるカタクチイワシ筋肉の比熱（比熱容量）を示差走査熱量計（DSC）によって測定し，粗脂肪含量や水分含量および温度の影響を調べた．カタクチイワシ筋肉の粗脂肪と水分を定量した結果，購入時期や筋肉の位置によって粗脂肪含量が大きく異なったとしても，粗脂肪含量と水分含量の合計はほぼ一定であることが示された．DSC 測定より求めた 100°C における比熱の値は水分含量の増加とともに直線的に増加することが明らかになった．また，62～115°C の温度範囲において，比熱の値が温度の上昇とともにわずかながら直線的に増加することが示された．以上の結果をもとに比熱推算のための実験式を得て推算精度を検討したところ，実験結果を良好に近似することが示された．

Precise knowledge of thermophysical properties is essential to understand the dynamics of thermal processing of foods. In this study, specific heat values of Japanese anchovy muscles with different fat contents were measured by using differential scanning calorimetry (DSC). As the results of quantification of crude fat and moisture contained in the muscles, the sum of the crude fat content and the moisture content was almost constant even though the fat content varied by the purchase month and by the body position. The specific heat of anchovy muscle evaluated at 100°C increased linearly with the moisture content. The specific heat also increased slightly but linearly with elevating temperature from 62 to 115°C. An empirical equation was deduced based on the above results and found to give fairly good approximations to the measured values of specific heat.

[**Keywords**: specific heat, Japanese anchovy, thermal process, DSC]

1. INTRODUCTION

Final quality of processed food products is closely related to their thermal treatment history. Thus the knowledge of thermophysical properties of food materials is crucial for the design, modeling, simulation, and evaluation of thermal processing. Full understanding and good prediction of the thermophysical properties of foods in relation to their compositions and structures are essential.

Anchovies are the world's most captured fish [1]. However, their traditional utilization as a raw material for ready-to-eat products has been very poor except in a few countries. In Japan, Japanese anchovy (*Engraulis japonicus*) has been utilized for several types of products, including dried products (mezashi, niboshi) and retort heated ready-to-eat products. Recently, utilization of eviscerated anchovy to retort heated products has begun extending also in other countries such as Peru and Spain.

Anchovies are typical fatty fish species which show a large variation of crude fat content depending on such factors as age, sex, season, and location [2]. Their thermophysical properties would exhibit variation due to such change in the chemical composition. In terms of appropriate modeling of thermal processing of anchovy, thermophysical properties are to be understood not as constants but as variables depending on its chemical composition. It is known for many fatty fish species that the sum of crude fat content and moisture content of

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muscle tissue is almost constant in spite of seasonal fat content variation [2-4]. Moreover, the contents of carbohydrates and ash are known to be low and show no significant seasonal change [5-7]. The content of the rest, mostly consisted of proteins, is thus considered to be constant. Such information on the chemical composition inspires us the possibility of understanding the thermophysical properties of anchovy as a function of its crude fat content or moisture content.

This study is focused on the specific heat (specific heat capacity) of the muscles of Japanese anchovy with different fat contents. We determine the specific heat in a temperature range between 62°C and 115°C by using differential scanning calorimetry (DSC). DSC needs only a small amount of sample for the measurement. This is an excellence of the method because the chemical composition of anchovy muscle may show a variation through its body. We also measure the crude fat content and the moisture content of anchovy muscles to study the relationship between them. In general, the moisture content greatly influences the specific heat of foods since water has a much higher specific heat than the other major constituents [8]. We finally present an empirical equation for predicting the specific heat in terms of the moisture content and temperature.

2. MATERIALS AND METHODS

2.1 Samples

Japanese anchovy, caught off the coast of Chiba prefecture, Japan, was purchased at Tsukiji fish market (Tokyo, Japan) monthly from September 2009 to June 2010. The total length and weight of the fish bodies were 13.29±0.61 cm and 19.84±2.49 g, respectively. After transported on ice, the fish bodies were headed, gutted, and tailed within the day of catch (referred to as HGT body hereafter). HGT bodies still in the state of *rigor mortis* was deep frozen (KQF-5AL, Air Operation Technologies, Inc., Japan) in its individual quick frozen mode and stored at -80°C (VT-208, Nihon Freezer Co., Ltd., Japan). Just before use, frozen HGT bodies were laid on ice to be thawed. Before completely thawed, they were skinned and boned. Skinned and boned HGT bodies thus prepared were cut transversally to the body axis into six sections having the same length (sections I to VI) as shown in Fig. 1, to check any difference in specific heat by body position.

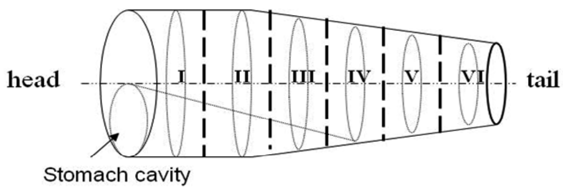

Fig. 1 Sections I to VI of a skinned and boned HGT body prepared in this study.

2.2 Crude Fat and Moisture Contents

Skinned and boned HGT bodies and the sections I to VI were subjected to quantification of crude fat and moisture contents. Pieces of each sample were grounded with mortar and pestle. Crude fat content was determined by Soxhlet method [9] using a 5-g portion of the grounded sample. Moisture content was determined on wet basis by drying a 2-g portion of the grounded sample at 105°C to a constant weight [9].

2.3 Determination of Specific Heat

All the specific heat measurements were performed on a Perkin-Elmer DSC 7 (Perkin-Elmer, Waltham, MA, USA). Thin slice of muscle sample (57±0.1 mg) cut off from the center part of each HGT section was put in a large volume stainless steel pan (7.2 mm in diameter and 2.4 mm in height; Perkin-Elmer). After sealed with a stainless steel cover and a rubber O-ring, the pan was kept in ice bath at 0°C until the measurement. Use of such pans with high-pressure proof encapsulation permits suppressing the endothermic signal resulting from the volatilization of water. Heating was conducted at a constant rate of 10°C/min from 50°C to 120°C as illustrated in Fig. 2, with an empty pan as the reference. Nitrogen gas was used as a purge gas through the measurement at a flow rate of 20 cm^3/min.

According to Höhne *et al.* [10], a baseline run and a calibration run were conducted prior to a run with a muscle sample under the identical experimental conditions. Through these 3 runs, the same empty reference pan was used and never removed from the DSC furnace. The baseline run took an empty pan as the sample, to determine the DSC signal level without any additional heat flow to the sample and its drift with temperature. The calibration run took a sapphire calibration standard (6 mm in diameter, 8.94 mg in weight; Perkin-Elmer) as the sample. With the known value of specific heat of the calibration standard, $C_{p,cal}$, the specific heat of the muscle sample, C_p, was calculated as follows:

$$C_p = \frac{m_{cal}}{m} \times \frac{\phi - \phi_0}{\phi_{cal} - \phi_0} \times C_{p,cal} \quad (1)$$

where m and m_{cal} represent the masses of muscle sample and calibration standard, respectively; ϕ, ϕ_{cal}, and ϕ_0 represent the DSC signal levels obtained for muscle sample, calibration standard, and baseline, respectively. When the isothermal signal levels before and after heating differed in a run, the offset of isothermal levels was corrected by linear interpolation.

For validation purpose, the specific heat of water was measured at a heating rate of 10°C/min. The specific heat value obtained at 75°C was 4.182±0.005 kJ/(kg·K) (n=3), showing only 0.25% difference from the literature value of 4.1927 kJ/(kg·K) [11]. It was observed that the heating rate affected the measurement; variation of ±5°C/min in the heating rate brought about ±1.5% variation in the specific heat value. Based on these results, a heating rate of 10°C/min was employed in this study.

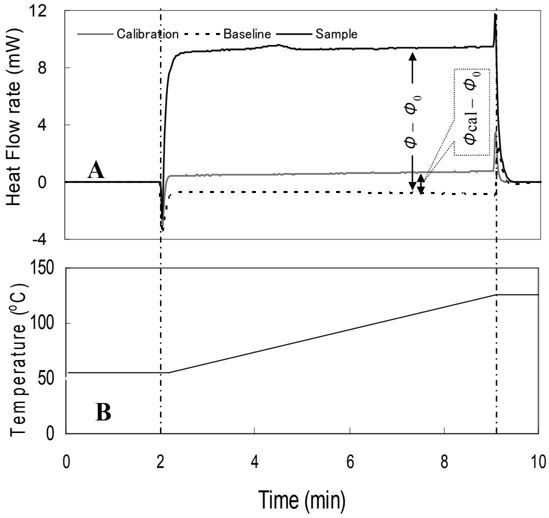

Fig. 2 Typical DSC thermograms obtained for three serial runs (A) with the same schedule of heating (B).

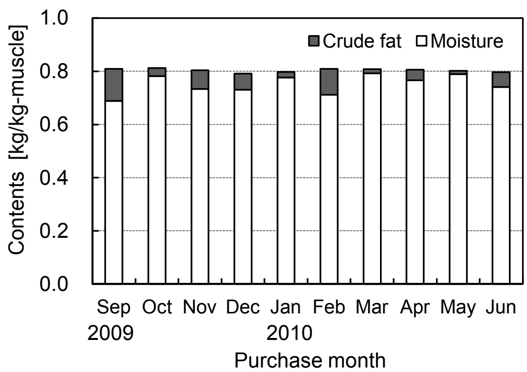

Fig. 3 Changes in the moisture and crude fat contents of HGT bodies purchased through the period from September 2009 to June 2010.

3. RESULTS AND DISCUSSION

3.1 Crude Fat and Moisture Contents

Figure 3 shows the average values of crude fat content and moisture content of skinned and boned HGT bodies of monthly purchases. A remarkable variation in the crude fat content was found during the period; the crude fat content ranged from 0.0132±0.0003 (May 2010) to 0.1214±0.0005 (September 2009). It was also found that the sum of crude fat and moisture contents was almost constant irrespective of purchase month and amounted to 0.8038±0.0067. Thus the change in crude fat content was compensated by the change in moisture content. Similar relationship between the crude fat content and moisture content were reported for other fatty fish species [2-4]. A negative linear correlation between the crude fat and moisture contents was confirmed also for the muscle of Japanese anchovy.

Table 1 shows the crude fat and moisture contents of the six sections. The sections were prepared from skinned and boned HGT bodies of two different purchase months, accordingly with different crude fat contents. High fat (HF) bodies were of September 2009 purchase, and low fat (LF) bodies were of May 2010 purchase. LF sections

Table 1 Crude fat and moisture contents of the six sections from low fat and high fat bodies.

Section	Low fat body			High fat body		
	$100X_F$	$100X_W$	$100(X_F+X_W)$	$100X_F$	$100X_W$	$100(X_F+X_W)$
I	1.21±0.33	79.06±0.62	80.27	5.40±0.33	75.11±0.21	80.51
II	1.26±0.18	78.98±0.18	80.24	7.93±0.25	72.31±0.18	81.23
III	1.28±0.29	78.96±0.38	80.24	10.56±0.33	70.66±0.35	81.32
IV	1.31±0.35	78.59±0.24	79.90	11.36±0.19	69.02±0.26	80.38
V	1.33±0.51	78.86±0.41	80.19	11.79±0.22	69.21±0.14	81.00
VI	1.32±0.03	78.90±0.31	80.28	12.06±0.21	68.86±0.11	80.92

X_F: crude fat content [kg/kg-muscle], X_W: moisture content [kg/kg-muscle].
For X_F (n=3) and X_W (n=5), the experimental results are shown as mean ± standard deviation.
X_F+X_W represents the sum of the means of X_F and X_W.

presented no significant differences (one-way analysis of variance, $p>0.05$) in the crude fat content and in the moisture content. However HF sections showed an increase in the crude fat content from section I to VI; the section closer to the tail showed higher crude fat content and lower moisture content, though the variation was small in the tail half (sections IV to VI). The results also showed that the sum of the both contents was approximately constant through the fish body.

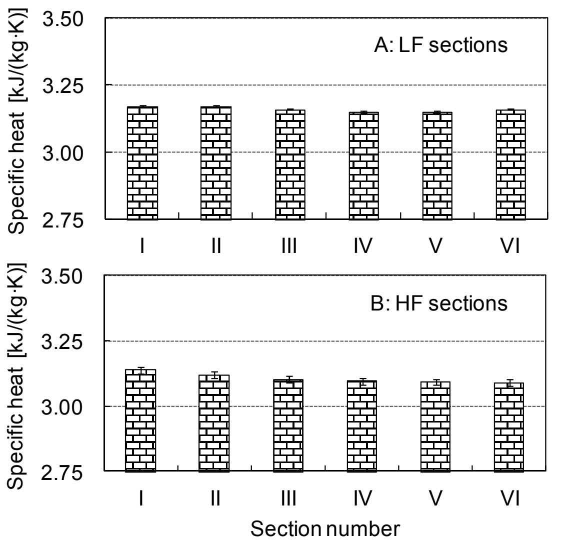

Fig. 4 Specific heat of law fat (LF) and high fat (HF) sections evaluated at 100°C. A: LF sections, B: HF sections.

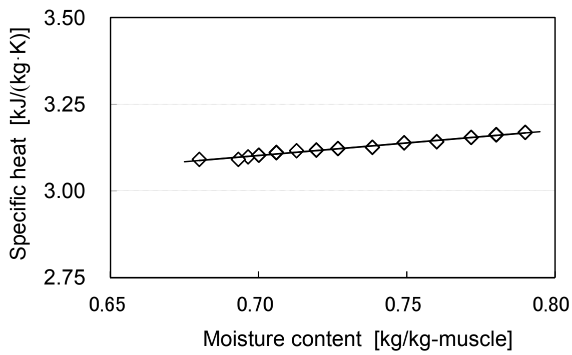

Fig. 5 Specific heat of sections evaluated at 100°C as a function of the moisture content.

3.2 Specific Heat

Figure 4 shows specific heat values of LF and HF sections evaluated at 100°C. Difference in specific heat was too small for LF sections, the mean and standard deviation for the six sections being 3.16±0.01 kJ/(kg·K). The variation in specific heat was larger for HF sections, the specific heat ranging from 3.09 to 3.14 kJ/(kg·K). The results may be explained by the difference in the moisture (or crude fat) content among the sections; LF sections showed no significant differences in the moisture content, whereas HF bodies showed lower moisture content in sections closer to the tail. Thus the lower the moisture content, the lower the specific heat. This is reasonable because the specific heat of water is larger than those of fats and oils.

Figure 5 shows dependence of the specific heat evaluated at 100°C on the moisture content. Various sections with different crude fat contents and of different purchase months were subjected to the measurement. The dependence was well described by a line expressed by the following equation, the coefficient of determination (R^2) being 0.985.

$$C_p = 0.72X_W + 2.597 \quad (2)$$

where X_W is the moisture content ($0.68 \le X_W \le 0.79$). Though the effect of composition on specific heat was not so large, the specific heat value of anchovy muscle at 100°C was shown to have a linear correlation with its moisture content.

Figure 6 shows temperature dependence of specific heat of selected sections with different moisture contents. In the temperature range from 70 to 85°C, a small but broad endothermic peak was observed for each sample. This peak indicated the thermal denaturation of a muscle protein, actin [12]. The endothermic enthalpy of the actin denaturation depends on the thermal history during the processing and should be considered separately from the intrinsic specific heat. Thus we will discuss elsewhere about the endothermic enthalpy of the actin denaturation. Except the temperature range, the specific heat increased slightly but linearly with temperature. The temperature dependence of the specific heat was thus weak for anchovy muscle similarly to those of other foods [13]. The slope of the increase was slightly higher for the low moisture sample. As a result, a higher moisture content sample showed a higher specific heat through the temperature range of the measurement. Combination with the moisture content dependence expressed by Eq. (2) resulted in the following equation for the specific heat of Japanese anchovy muscle.

$$C_p = K(X_W)(\theta - 100) + 0.72X_W + 2.597 \quad (3)$$

$$\begin{cases} K(X_W) = 0.0006 & (0.68 \le X_W \le 0.75) \\ K(X_W) = -0.01X_W + 0.0081 & (0.75 \le X_W \le 0.79) \end{cases}$$

where θ represents temperature (°C). Accuracy of the estimation by Eq. (3) is illustrated in Fig. 7. The correlation coefficient between the predicted value and the measured one was 0.992.

In the specific heat measurements, each sample pan was almost full with 57 mg of a muscle sample. A large amount of the sample was favorable to obtain a high level of DSC signal, though we confirmed the variation due to sample size (30−57 mg) was within ±0.5%. Although the shape of the sample inside the pan might affect the measurement due to difference in heat transfer resistance, the samples almost fully packed in the pan probably contributed to make similar shapes from the viewpoint of heat transfer.

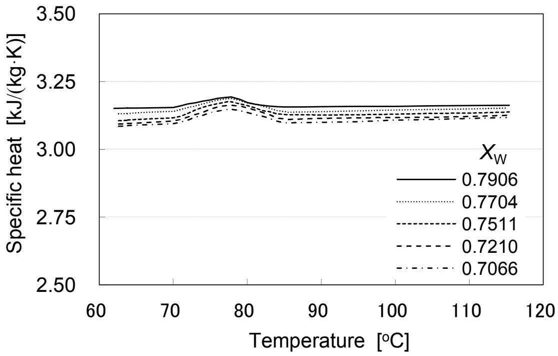

Fig. 6 Temperature dependence of specific heat of sections with different moisture contents.

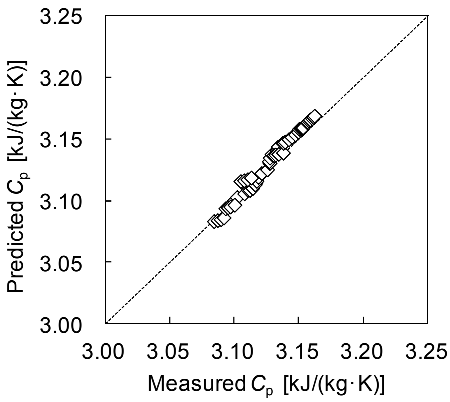

Fig. 7 Correlation of the specific heat values predicted by Eq. (3) with the values measured for various HGT sections in the temperature range of 62−115°C excluding 70−85°C.

Zhang *et al.* [14] reported the specific heat of loin meat of skipjack tuna (*Katsuwonus pelamis*) with a moisture content of 0.708 to be 3.584±0.092, 3.626±0.119, 3.699±0.141 kJ/(kg·K) at 50, 85, and 105°C, respectively. Perez-Martin *et al.* [15] reported the specific heat of loin meat of albacore tuna (*Thunnus alalunga*) with a moisture content of 0.673 to be 3.19, 3.33, and 3.39 kJ/(kg·K) at 51, 83, and 108°C, respectively. Compared with those values, the specific heat of Japanese anchovy was lower and the temperature dependence was weaker. Since the moisture content of the Japanese anchovy was higher than those reported cases, the low specific heat cannot be explained by the difference in moisture content. Heat capacity of fats and proteins contained in the muscle may differ among the species and affect the overall specific heat.

4. CONCLUSIONS

The specific heat of Japanese anchovy muscles with different crude fat contents was determined by DSC. We obtained the following conclusions.

1. The sums of the crude fat content and the moisture content were approximately the same even though the crude fat content varied due to the season and due to the body position.
2. The specific heat of anchovy muscles evaluated at 100°C increased linearly with the moisture content. The specific heat also increased slightly but linearly with temperature.
3. Equation (3), deduced on the basis of the above results, was found to give fairly good approximations for the measured values of specific heat.

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NOMENCLATURE

C_{p} : specific heat, kJ/(kg·K)
m : mass of the sample, kg
X_F : crude fat content, kg/kg-muscle
X_W : moisture content, kg/kg-muscle
ϕ : DSC signal level, mW
θ : temperature, °C

Subscript
cal : calibration standard
0 : baseline

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