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HEAT CAPACITY OF CHEESE
Determination or calculation?

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The heat capacity of several samples of hard cheese, semi-hard cheese and soft cheese was determined by conventional differential scanning calorimetry (DSC) and by temperature modulated DSC. Additionally, the gross composition of the cheeses was analysed, and equations from the literature were used to calculate the heat capacity therefrom. Both analytical methods were suitable to determine the heat capacity of the cheese samples whereas only one out of three equations proposed for the calculation of the heat capacity of foods from composition data led to results which were comparable with analytical data. As the equation coefficients for particular constituents are responsible for the deviations in the calculated heat capacities the differences between calculated and measured values increase with a decreasing moisture content of the cheeses.

Keywords: *cheese, DSC, heat capacity, MDSC*

Introduction

The proper design of processing units for the food industry requires the exact knowledge of the heat capacity (c_P), especially when the uptake, the release or the transfer of heat energy is involved. It is especially the dimensioning of aggregates used in refrigeration or freezing which largely depends on the calorimetric properties of a particular food [1, 2].

The analytical solution to measure c_P is the classical Dewar calorimeter or, nowadays, to use differential scanning calorimetry (DSC). As the above mentioned methods are either tedious to perform or require a sophisticated equipment, respectively, a number of attempts have been undertaken to calculate the heat capacity by means of empirical equations and/or equations based on compositional data. Empirical equations for c_P calculation are available in literature for, e.g., different apple varieties [3], potatoes [4], pistachios [5], or pasta [6]. The first equation to calculate c_P from food composition was published in 1892 by Siebel [7], and other models solely based on the moisture content of the food were introduced later [8, 9]. In more advanced models for c_P calculation the mass fractions of fat solids (X_F) and non-fat solids (X_{NF}) [10, 11], or the mass fractions of fat, protein (X_P), carbohydrates (X_C) and ash (X_A) [12] were additionally introduced. The well-known models of Charm [10] and Heldman and Singh [12] are given in Eqs (1) and (2), respectively:

$$c_P = 2.093X_F + 1.256X_{NF} + 4.187X_W \tag{1}$$

$$c_P = 1.675X_F + 1.549X_P + 1.424X_C + \\ + 0.837X_A + 4.187X_W \tag{2}$$

Choi and Okos [13] included a term for fibre content and also introduced constituent-specific polynoms for the calculation of the temperature-dependent heat capacity coefficients X_i of the pure components c_{Pi}:

$$c_P = \sum_{i=1}^{n} X_i c_{Pi} \tag{3}$$

Unfortunately, the application of these models does not lead to comparable c_P values when a food with a particular composition is considered. This is obvious because the coefficients in the respective equations differ largely between, e.g., in the case of fat, 1.675 [11], 2.012 kJ kg^{-1} K^{-1} [13, here at 20°C] and 2.093 kJ kg^{-1} K^{-1} [10]. Assuming that a dairy product such as quarg contains 80% moisture, 50% fat in dry matter, 9% protein and 1% ash, the heat capacity calculated by Eqs (1) and (2) gives 3.68 and 3.67 kJ kg^{-1} K^{-1}, respectively, and the Choi and Okos model [13] results in c_P=3.73 kJ kg^{-1} K^{-1}. However, when considering a cheese variety with a considerably lower moisture content of 30% and a similar ratio of fat to dry matter, which is typical for e.g., Parmigiano Reggiano, the calculated heat capacity is 2.43 [10] and 2.36 [12] but 2.63 kJ kg^{-1} K^{-1}, thus more than 10% higher, when using the Choi and Okos's [13] Eq. (3). This difference may be considered as being large enough to account for significant errors when designing cooling rooms.

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The objective of the current research was, therefore, to measure the heat capacity of several cheese varieties by means of conventional DSC, which requires the measurement of an empty pan, a reference with known c_P, and the sample, and modulated DSC which allows the direct determination of the heat capacity in one single measurement [14–17]. Cheese composition was analysed by standard methods and then used for the calculation of c_P as described above.

Experimental

Materials

17 cheese samples (hard, semi-hard and soft varieties) were purchased in local supermarkets. After grating the cheese and mixing an appropriate portion, the moisture content was determined by the oven method at 103°C [18]. After charring the sample, ash was determined by means of a combustion oven [19]. Protein content was determined by the Kjeldahl method using a nitrogen-to-protein conversion factor of 6.38 [20], and fat content was determined using butyrometers [21]. Additional to the cheese samples, several types of vegetable oil were analysed (only DSC measurements).

Differential scanning calorimetry

The measurements were performed with a DSC Q100™ equipped with an RSC refrigerated cooling system (TA Instruments, Alzenau, Germany). Dry N_2 gas was purged through the DSC cell with a flow rate of 50 mL min^{-1}. Approx. 10 mg of the oil or cheese samples were weighed into aluminium pans, which were then hermetically sealed. Each determination was performed in triplicate (oil samples) or in duplicate (cheese samples).

In conventional DSC measurements either an empty pan, a sapphire in a pan or the sample loaded to the pan was equilibrated at 0°C for 5 min and then subjected to a temperature ramp ($\dot{q}$) of 10 K min^{-1} up to 90°C. A maximum difference in pan mass of 50 µg was tolerated. The mass (m_S), the heat capacity of the sapphire ($c_{P,S}$) and the temperature-dependent heat flow in sapphire ($\dot{Q}_S$) and empty pan measurements ($\dot{Q}_E$) were used to calculate the temperature-dependent, dimensionless calibration constant $E(T)$ [14] by

$$E(T)=\frac{c_{P,S}\,\dot{q}m_S}{60[\dot{Q}_S(T)-\dot{Q}_E(T)]} \tag{4}$$

$E(T)$ was then used to calculate the heat capacity of the cheese sample by using the appropriate heat flow and mass ($\dot{Q}_C$, m_C)

$$c_P=\frac{60E(T)[\dot{Q}_C(T)-\dot{Q}_E(T)]}{\dot{q}m_C} \tag{5}$$

In the modulated DSC experiments an equilibration period of 5 min at 0°C was followed by $\dot{q}$=5 K min^{-1} to 90°C. Superpositioned to this ramp was a temperature modulation with an amplitude of 2 K and a period of 10 s. The calibration constants necessary for c_P calculation were taken from tabulated $c_P(T)$ values for the sapphire and corresponding $c_P(T)$ measurements.

Results and discussion

Table 1 shows the heat capacities of some oil samples determined by conventional DSC and by temperature modulated DSC. For both methods and for each particular sample the ratio of standard deviation to arithmetic mean, i.e., the coefficient of variation, exceeded 0.06 only twice, and the average difference between conventional DSC results and modulated DSC results as estimated by a dependent-samples t-test [18] is statistically insignificant (P>0.05). Additionally, the c_P values are fairly in accordance with literature data for the heat capacities of edible oils between 50 and 80°C, which range between 1.89 and 2.23 kJ kg^{-1} K^{-1} for lard and peanut oil, respectively [19–21]. For sunflower oil, Fig. 1 shows the heat flow measured in conventional DSC and the heat capacity measured in modulated DSC experiments as a function of temperature. In the modulated DSC experiments the averaged heat capacity increased from 1.859 kJ kg^{-1} K^{-1} at 30°C to 1.901 kJ kg^{-1} K^{-1} at 60°C. Despite the fact that fat coefficients calculated according to Choi and Okos [13] are certainly higher (2.024 kJ kg^{-1} K^{-1} at 30°C and 2.055 kJ kg^{-1} K^{-1} at 60°C), the measured rise in c_P due to the increase in temperature is fairly in accordance with literature [14].

The composition of the different cheeses included in this study is summarised in Table 2. Moisture content ranged between approx. 21% (rind of

Table 1 Heat capacity (50°C) of oil samples

Oil sample	c_P^*/kJ kg^{-1} K^{-1}	
	DSC	TMDSC
Olive oil	1.99±0.02	1.92±0.04
Sunflower oil	2.04±0.07	1.88±0.10
Rapeseed oil	2.03±0.06	1.93±0.05
Soy oil	2.06±0.11	1.96±0.10
Butter oil	1.79±0.05	1.89±0.15
Lard	1.88±0.12	1.93±0.06

*Mean values and standard deviations are based on triplicate measurements

Table 2 Composition of the cheese samples

No.	Sample	X_W	X_P	X_F	X_A	X_T
1	Cheddar	0.340	0.243	0.379	0.039	1.001
2	Emmental #1 (body)	0.362	0.301	0.306	0.038	1.007
3	Emmental #1 (rind)	0.296	0.336	0.324	0.042	0.998
4	Emmental #2	0.364	0.286	0.319	0.032	1.001
5	Irish Farmer cheese	0.371	0.294	0.288	0.043	0.994
6	Parmigiano Reggiano (body)	0.306	0.335	0.301	0.047	0.989
7	Parmigiano Reggiano (rind)	0.206	0.416	0.343	0.044	1.009
8	Vorarlberger Bergkäse (body)	0.340	0.271	0.357	0.038	1.006
9	Vorarlberger Bergkäse (rind)	0.286	0.298	0.389	0.038	1.011
10	Edam cheese #1	0.458	0.238	0.274	0.039	1.009
11	Edam cheese #2	0.467	0.305	0.183	0.043	0.997
12	Grünländer light	0.477	0.328	0.148	0.038	0.990
13	Leerdammer	0.426	0.265	0.278	0.039	1.008
14	Butterkäse	0.464	0.226	0.281	0.034	1.005
15	Gouda	0.467	0.229	0.281	0.034	1.012
16	Leerdammer lightlife	0.485	0.299	0.169	0.043	0.995
17	Feta	0.589	0.151	0.221	0.039	1.000
18	Feta light	0.606	0.198	0.133	0.048	0.985
19	Camembert #1 (body)	0.505	0.174	0.287	0.027	0.993
20	Camembert #1 (rind)	0.486	0.180	0.274	0.044	0.984
21	Camembert #2 (body)	0.594	0.240	0.128	0.029	0.991
22	Camembert #2 (rind)	0.600	0.223	0.101	0.053	0.977

X_W, fraction of moisture; X_P, protein fraction; X_F, fat fraction; X_A, ash fraction; $X_T=X_W+X_P+X_F+X_A$

Parmigiano Reggiano cheese, sample #7) and 61% (Feta cheese light, sample #18). Minimum and maximum values for the absolute fat content were approx. 10% (rind of Camembert, sample #22) and 39% (rind of Bergkäse, sample #9), respectively. The crude protein content ranged between 15% (sample #17) and approx. 34% (sample #3), and the ash content ranged between 2.7% (sample #19) and 4.7% (sample #6). The actual sum of the measured components varied between 98.4 and 101.2%, which is within the experimental error. Usually, the carbohydrate content (including organic acids) in different cheese varieties is much less than 1% [21].

The particular fractions, which were then rescaled to a sum of 100%, served as a basis for the calculation of the heat capacity according to Eq. (1) (non-fat solids were calculated as the sum of protein and ash) and Eq. (2). For the Choi and Okos model [13; Eq. (3)], 50°C were used as reference temperature. The selection of this temperature was necessary because the DSC curves obtained from both conventional and modulated DSC showed some irregularities for a temperature <30°C presumably because of the occurrence of melting processes, which can be attributed to the heterogeneous composition of the milk fat (Fig. 2).

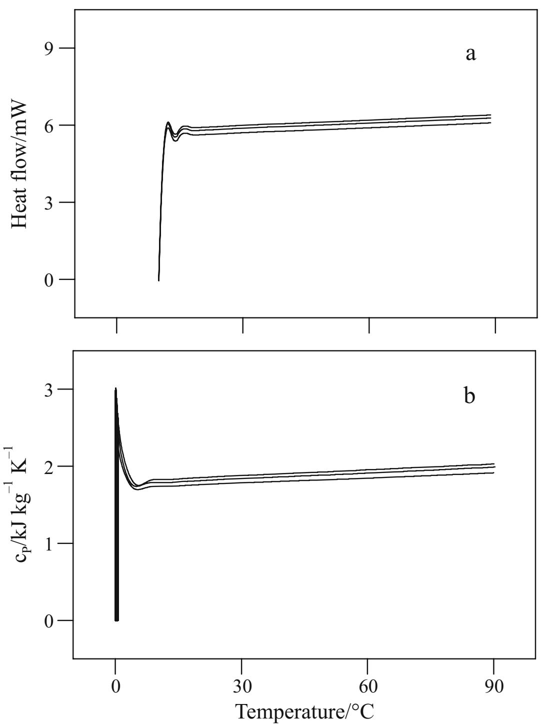

Fig. 1 Temperature functions of sunflower oil (n=3): a – heat flow in conventional DSC and b – heat capacity in modulated DSC

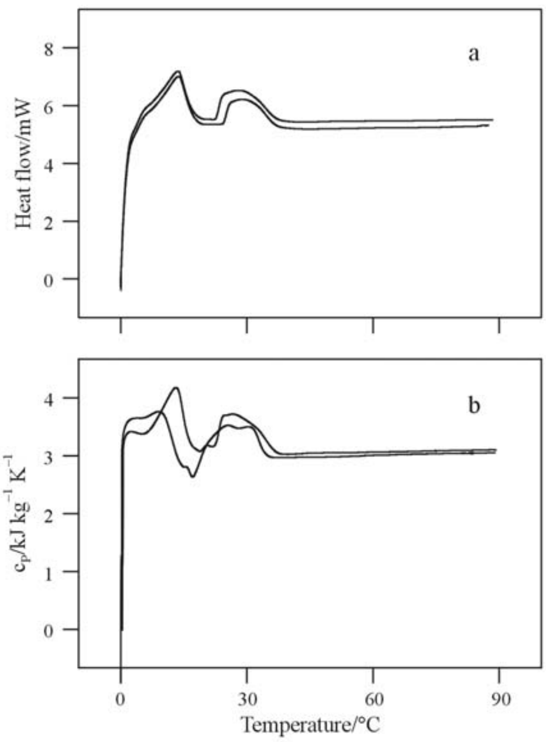

Fig. 2 Temperature functions of Gouda cheese (n=2): a – heat flow in conventional DSC and b – heat capacity in modulated DSC

In Fig. 3 the heat capacities calculated by Eqs (1)–(3) are plotted for each sample together with the c_P values measured by conventional DSC and modulated DSC. One-way analysis of variance revealed that the differences between the results achieved with the different methods are highly significant ($P<0.001$). Despite the broad range of the heat capacity of the samples under study a multiple mean comparison showed that the mean c_P values calculated with the Charm method (2.69±0.293 kJ kg^{-1} K^{-1}) or with the Heldman and Singh method (2.74±0.280 kJ kg^{-1} K^{-1}) did not differ from each other but were significantly lower than the results of the Choi and Okos [13] calculation (2.94±0.245 kJ kg^{-1} K^{-1}) which, in turn, were found to be on a comparable level with conventional DSC results (2.94±0.244 kJ kg^{-1} K^{-1}) and modulated DSC results (2.97±0.210 kJ kg^{-1} K^{-1}). The statistical relevance of the differences between the methods was further confirmed by dependent-sample difference tests with conventional DSC results serving as a reference (Table 3). The mean differences were almost zero for modulated DSC or c_P values calculated according to Choi and Okos [12] but highly significant as regards the calculation by Eqs (1) and (2).

The heat capacities of the six hard cheeses (only measurements of cheese body) investigated in this study by means of conventional DSC ranged between 2.63 and 2.83 kJ kg^{-1} K^{-1} with an arithmetic mean of 2.76±0.091 kJ kg^{-1} K^{-1}. This range is much more narrow than values published in the literature [23–27], indicating that experimental details might show an additional impact on the results. A c_P of 2.99±0.039 kJ kg^{-1} K^{-1} (n=7) for semi-hard cheese is in good agreement with data from Hakl and Barton [23] (2.98 kJ kg^{-1} K^{-1}) but much lower than 3.45 kJ kg^{-1} K^{-1} which was reported for Cuartirolo Argentino cheese [28]. The four samples of soft

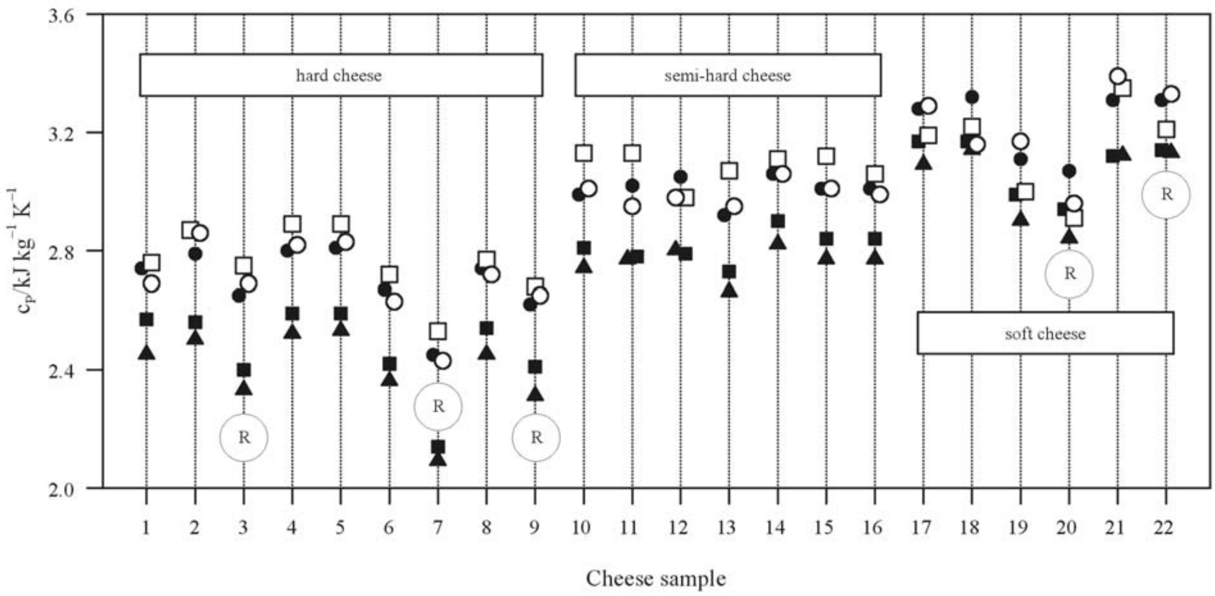

Fig. 3 Heat capacity of different cheese varieties measured by ❍ – conventional DSC and ☐ – TMDSC as compared to heat capacity calculated from composition data according to ● – Choi and Okos for 50°C [13], ■ – Charm [10] and s – Heldman and Singh [12]. Sample numbers are explained in Table 2. R, cheese rind specimens

Table 3 Mean differences between conventional DSC results and other methods

Method	Difference/ kJ kg^{-1} K^{-1}	Standard deviation/ kJ kg^{-1} K^{-1}	t–value	Significance
TMDSC	–0.02	0.117	–0.75	n.s.
Choi and Okos [13]	0.01	0.102	0.64	n.s.
Charm [10]	0.20	0.098	10.22	<0.001
Heldman and Singh [12]	0.26	0.113	11.10	<0.001

n.s., not significant (P<0.05)

cheese showed an average c_P of 3.25±0.109 kJ kg^{-1} K^{-1}. As the moisture content in these cheeses was considerably higher, it is not surprising that the differences between measured data and heat capacities calculated by Eqs (1) and (2) were diminishing.

Conclusions

The results show that deviations between measured heat capacity and heat capacity calculated on the basis of compositional data largely depend on the mathematical expression used for c_P estimation. Conventional or modulated DSC appear as a reliable tools to determine c_P accurately and quick, thus minimizing potential errors which arise from the application of calculation equations and from compositional analyses, representing the basis of c_P calculation.

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