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Effect of protein content on the thermal effusivity of foods

G. Szafner[1*], O. Dóka[2] and N. Gombkötő[3]

[1] Hungarian Dairy Research Institute Ltd., Lucsony street 24, H-9200, Mosonmagyaróvár, Hungary

[2] Department of Physics and Chemistry, Faculty of Engineering, Informatics and Electrical Engineering, Széchenyi István University. Egyetem sq. 1, H-9026, Győr, Hungary

[3] Department of Economics, Faculty of Agricultural and Food Sciences, Széchenyi István University, Vár 2, H-9200, Mosonmagyaróvár, Hungary

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ABSTRACT

The availability of thermophysical properties of both foods and their constituents is of considerable importance to the industry. The thermal effusivity is one of the less explored thermophysical parameters. It governs the penetration of heat into materials and is defined as the square root of the product of thermal conductivity of the material, volume-specific heat capacity, and density. This paper describes the application of a relatively new inverse photopyroelectric method (IPPE) to determine thermal effusivity of dehydrated whey protein isolate and egg white powder versus protein content. In both cases the effusivity values decreased linearly with increasing protein content. One percent increase in protein content of whey protein isolate and egg white lead to 6.5 and 7.2 $Ws^{1/2}\,m^{-2}\,K^{-1}$ decrease in effusivity values, respectively.

KEYWORDS

whey protein, egg protein, thermal effusivity, photopyroelectric method

* Corresponding author. Tel.: +3630/4932065; fax:+3696/215789. E-mail: gszafner@mtki.hu

1. INTRODUCION

There is a general requirement in modern food processing that during the manufacturing process most physical properties should be controlled. Therefore, knowledge of thermal properties (conductivity, specific heat capacity, thermal diffusivity, and effusivity) is important in simulation and control of various food processing operations (Datta, 2007).

The photopyroelectric method (PPE) is one of the applied techniques by which thermal properties (effusivity, diffusivity) of various foods can be detected. The PPE method offers several advantages: the method is non-destructive, relatively fast, no sample preparation is required prior to analysis, and additionally only a small quantity of sample is needed (Chirtoc et al., 1992). Practically, two configurations can be distinguished: the standard (SPPE) and the inverse (IPPE) configurations. In both configurations the sample is heated by a modulated laser beam. The difference between the two configurations is the laser-pyroelectric foil-sample position. While in the SPPE configuration, the modulated laser beam is adsorbed directly by the sample. In the IPPE configuration, the modulated laser beam is absorbed by the pyroelectric foil itself instead of the sample (Dadarlat and Neamtu, 2009).

Nowadays, whey and egg proteins are among the most applied ingredients of animal origin in the food industry. Whey proteins are very often used to improve food products because of their high nutritional quality. The most often utilised whey protein-based ingredients are whey protein concentrate (WPC) and whey protein isolate (WPI). Whey protein isolates have higher protein concentration and contain less contaminants than WPC (Morr and Foegeding, 1990). Whey protein isolate contains at least 90% protein, and the two major whey proteins are β-lactoglobulin and α-lactalbumin (Voswinkel and Kulozik, 2011).

The advantages of egg powders over liquid eggs are their easier transportation and longer shelf life. Three types of egg powders are available commercially, namely egg white, egg yolk, and whole egg powders. Egg white powder commonly contains more than 80% protein and less than 0.5% fat. The main constituents of protein in egg white are ovalbumin, conalbumin, and lysozyme (Wu et al., 2010).

Whey and egg white proteins are thermally unstable; therefore, knowledge on their thermophysical properties is essential for the determination of technological parameters in food processing.

Protein content is one of the quality parameters of foods and thermal properties are influenced by the composition of foods (Sablani and Rahman, 2003), therefore, the effect of the protein content on the thermal properties is obvious. Many sensitive analytical methods for determination of protein have been developed: examples are the widely applied Kjeldahl method (AOAC, 1990), Dumas method (Jung et al., 2003), infrared spectroscopy (Wu et al., 2008), gel electrophoresis (Hedrick and Smith, 1968; Gygi et al., 2000), and the bicinchoninic acid assay (also known as Smith assay) (Smith et al., 1985).

The objective of the investigation described in this paper is to determine the thermal effusivity values of whey and egg white proteins and to find out whether there is any difference between the effects of different proteins on the thermal effusivity of rehydrated proteins. The measurements were carried out by inverse photopyroelectric method, and the obtained data were analysed by statistical method (analysis of variance).

2. THEORETICAL BACKGROUND

Thermal effusivity e depends on the thermal conductivity κ, density ρ, and the volume specific heat capacity c at constant pressure of the sample (Balderas-Lopez and Mandelis, 2003). It is defined as $e = \sqrt{\kappa\rho c}$, and can be determined directly by one single IPPE measurement.

In the IPPE method, the sensor is a pyroelectric foil made from polyvinylidene fluoride (PVDF) coated on both sides with metal. When the pyroelectric foil is heated, a polarised charge is generated on both sides of the foil.

Such heating can be accomplished by a modulated laser beam. In the IPPE configuration, the modulated laser beam is absorbed at the blackened rear side of the pyroelectric foil, which leads to periodic heating. This periodic heating is given by the following relationship (Marinelli et al., 1992):

$$T = T_0 + T_{\mathrm{dc}} + T_{\mathrm{ac}} \tag{1}$$

where T_0 is the ambient temperature, T_{dc} is the *dc* component of the temperature (depends on the modulation frequency and the geometry of the sensor), T_{ac} is the ac (oscillating) component of the temperature field.

Due to the temperature change, the polarised charge quantity differs on the two surfaces of the foil, which leads to a polarised current described by Mandelis and Zver (1985):

$$I_f = \frac{\Delta Q_f}{\Delta t} \tag{2}$$

where ΔQ_f is the polarised charges quantity and Δt is the time interval. The polarised charge density is given by:

$$\Delta Q_f = \frac{\Delta\sigma_f \cdot A}{\Delta t} \tag{3}$$

where $\Delta\sigma_f$ is the polarised charge density and A is the surface area of the pyroelectric sensor. This generated polarised charge was detected with a phase sensitive lock-in amplifier, which amplified the signal with the same periodicity as that of the modulation frequency. The obtained voltage $V(\omega)$ depends on the impedance of the sensor and electronic equipment. Therefore, an ideal current source, the signal $V(\omega)$ is given by Azmi et al. (2004):

$$V(\omega) = \frac{ARPi\omega}{1 + i\omega\tau_e} T(\omega) = \frac{ARPi\omega}{1 + i\omega\tau_e} \left(\frac{1}{2\pi} \int_0^{\infty} e^{-i\omega t_t(t)dt} \right) \tag{4}$$

where P is the pyroelectric coefficient, ω is the angular modulation frequency, while τ_e and R are the time constant and the resultant resistance of the electrical circuit, i is the imaginary unit, T is the average temperature of the pyroelectric sensor, and t is the time.

If the sample is thermally thick ($L_s >> \mu_s(\omega)$, where L_s is the thickness of the sample, μ_s is the thermal diffusion length of the sample at the modulation frequency) and optically opaque ($L_s >> \delta s(\omega)$), where δs is the optical absorption length of the sample), the amplitude of the output signal is given in Equation (5) (Marinelli et al., 1992):

$$V(\omega) = \frac{I_0 \eta_s AR}{L[1 + (\omega\tau_e)^2]^{1/2}} \cdot \frac{P}{\rho_f c_f} \cdot \frac{e^{\sqrt{\omega/2D_s} \cdot L_s}}{e_s\left(e_g/e_s + 1\right)\left(e_f/e_s + 1\right)} \tag{5}$$

where I_0 is the intensity of the illuminating laser light at the sample's surface, L is the thickness of the pyroelectric sensor, c_f is the heat capacity of the sensor, η_s is the nonradiative quantum efficiency, ρ_f is the density of the sensor, e is the base number of the natural logarithm, while e_s, e_f and e_g refer to the thermal effusivity of sample, foil, and the contacting gas, respectively. Furthermore, L_s and D_s are the sample's thickness and thermal diffusivity, respectively.

For a given experimental arrangement this implies that the ratio of the signal V_{sample} obtained from the sample being studied and the signal $V_{\text{reference}}$ acquired from a reference sample (thermo-physical parameters of which are well known) is solely a function of their effusivities, i.e. (Dadarlat et al., 1996):

$$e_{\text{sample}} = \frac{e_{\text{reference}} \cdot V_{\text{reference}}}{V_{\text{sample}}} \tag{6}$$

Clearly, measuring the photopyroelectric signal on the sample (V_{sample}) and on the reference ($V_{\text{reference}}$) specimen (usually water) and knowing the effusivity value of the reference material, one can determine the thermal effusivity of the unknown sample using Equation (6).

3. MATERIALS AND METHODS

The WPI powder was produced by the Hungarian Dairy Research Institute Ltd. (Hungary, Mosonmagyaróvár) and the egg white powder was kindly donated by Capriovus Ltd. (Hungary, Budapest). Table 1 shows the chemical and physical properties of WPI and egg white powders.

Before the measurements, the WPI and egg white powders were rehydrated with different amounts of deionised water at 50 °C. The solutions were kept at room temperature with continuous stirring at two relative centrifugal forces (rcf) for 4 h. From both powders, six different samples were prepared. Table 2 shows the amount of added water to the powders as well as the total solid and protein contents in g/100 g samples. The lowest protein contents in WPI and egg white powder solutions were 4.74 and 9.75, while the highest 36.91 and 34.10 g/100 g respectively.

Table 1. Chemical-physical properties of whey protein isolate (WPI90) and egg white powders

Samples	Total solids (TS) g/100 g	Protein (TN × 6.38) g/100 g	Protein/TS g/100 g	Fat g/100 g	Ash g/100 g	pH	Insolubility index ml/50 ml
WPI powder*	95.85	91.70	95.67▲	0.34	2.22	6.57	<0.1
Egg white powder*	94.99	82.44	86.79▲	0.30	5.71	7.56	0.7

*Measured with following methods: protein: ISO/IDF (2004a); fat: ISO/IDF (2004b); ash: ISO/IDF (2008); pH: ISO/IDF (2010); insolubility index: ADPI (1992); ▲ Calculated value.

Table 2. Added water content of the whey protein isolate (W) and egg white (E) solutions

Sample	Amount of powder (g)	Added water (g)	Total solids of the sample (g/100 g)	Protein content of the sample (g/100 g)
W_1	5.17	94.94	4.95	4.74
W_2	10.05	90.09	9.62	9.20
W_3	20.03	80.39	19.12	18.29
W_4	30.09	70.04	28.80	27.56
W_5	20.23	30.03	38.56	36.91
W_6	14.94	30.16	31.75	30.38
E_1	2.07	15.97	11.00	9.45
E_2	2.35	9.94	18.33	15.76
E_3	3.42	10.26	23.96	20.61
E_4	4.50	10.78	28.23	24.27
E_5	5.78	9.72	35.74	30.74
E_6	7.77	11.01	39.66	34.10

Thermal effusivity values were measured with a home-made IPPE setup (Fig. 1). A He-Ne laser (Melles-Griott, Model 05-LHP-141) operating at 632 nm was used as light source. The power of the unmodulated laser beam was 3.6 mW. The laser beam was modulated by an acousto-optical modulator (Isomet Co., Model 1205-603D) driven by a TTL signal provided by the lock in amplifier. The modulated beam was directed by means of a plane mirror to the blackened side of the PVDF foil. The generated IPPE signal was amplified by the lock-in amplifier (Stanford Research Systems, Model SR830) and forwarded to the computer for data processing. Sequences of 128 successive readouts of the IPPE signal from the lock-in amplifier were measured for a single sample load, and the calculated average value was taken as a representative signal. The loadings were repeated three (egg proteins) and nine (WPI) times, finally, the average of measured values considered as representative for the thermal effusivity.

The effusivity values obtained were compared by ANOVA (analysis of variance) to determine whether the effusivity of the two factors (egg protein and WPI) examined differed at the 95% significance level. However, the application of ANOVA assumes three requirements: (1) standard deviations of the sample series have to be equal; (2) both of the series have normal

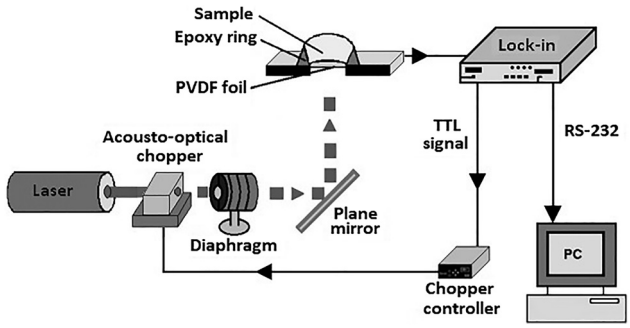

Fig. 1. The schematic diagram of the home-made IPPE measurement system

distribution; (3) values of the mutual observation for both series (values of protein content for egg and WPI) must be the same as well. Fulfilment of the above-mentioned requirements was examined and the method was applied for the comparison of the effusivity values.

4. RESULTS AND DISCUSSION

According to the reference method, first the amplitude of the IPPE signal in distilled water (reference sample) was measured as a function of the modulation frequency. The measured signal was linear between 0.2 and 1.3 Hz. 0.5 Hz was chosen as measuring frequency because of the favourable signal to noise ratio at this frequency. The obtained signal of the distilled water was 145 μV at 0.5 Hz. The effusivity value of distilled water at room temperature is well known in the literature (Bicanic et al., 1992; Marín, 2007) as 1,589 $Ws^{1/2}\,m^{-2}\,K^{-1}$.

As a next step, the IPPE signals of the prepared samples (W_1–W_6 and E_1–E_6) were measured and on the basis of Equation (6) the effusivity values were calculated. Fig. 2 shows the effusivity values of rehydrated WPI90 powder samples versus the protein content. As can be seen in Fig. 2, the effusivity values of rehydrated WPI powder samples decreased linearly ($y = -6.56x + 1563.8$, $R^2 = 0.971$) versus the increasing protein content.

In Fig. 3 the effusivity values of rehydrated egg white powder are plotted versus the protein content. Similarly to the rehydrated WPI powder samples, the effusivity values of the rehydrated egg white powder samples decreased as the protein content increased. The correlation is linear with a rather high determination coefficient ($y = -7.25x + 1567.6$, $R^2 = 0.986$). In both Figures 0 g/100 g means the effusivity value of distilled water (1,589 $Ws^{1/2}\,m^{-2}\,K^{-1}$).

As to the lines of best fits, the slope was higher for rehydrated egg white powder. Increasing the egg white protein content in rehydrated powder by 1% leads to effusivity decrease of 7.25 $Ws^{½}\,m^{-2}\,K^{-1}$. In the case of rehydrated WPI powder, the same step led to a decrement in effusivity of 6.56 $Ws^{½}\,m^{-2}\,K^{-1}$. These data suggest that effusivity of rehydrated egg white

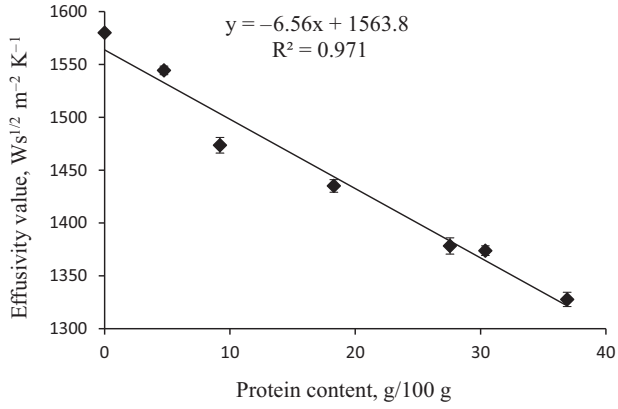

Fig. 2. The effusivity value of rehydrated whey protein isolate (WPI90) samples versus the protein content ($n = 9$)

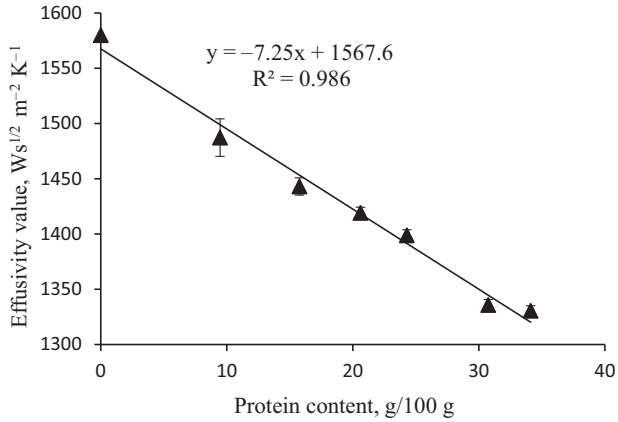

Fig. 3. The effusivity value of egg white samples versus the protein content

powder is a little bit more sensitive (~10%) to the presence of water than the rehydrated WPI powder.

As the obtained effusivity values of the rehydrated WPI and egg white powder samples are very close to each other, the above described statistical analysis was performed to determine the statistical significance ($P < 0.05$).

For our results, the mentioned first two statistical conditions are met, namely, the standard deviations do not differ at the 95% significance level and the distributions are also normal. However, the third condition is not met because of the different protein values, and therefore, the ANOVA method may not be applied directly. In such case there are two possibilities to equalise the values of mutual observation and to apply ANOVA.

The first solution is that we construct once again two functions similar to Fig 2 and 3, but this time ignoring the effusivity of water. Thus, we again fit straight lines to the remaining twice six data pairs. Based on the obtained fitted equations, the effusivity values can be determined at the very same protein content. Therefore, we calculated the effusivity values between 5 and 30 g/100 g protein contents in 5 g/100 g steps. Thereafter, ANOVA can already be applied to the values thus generated (two times seven values) as the effusivity values belong to the same protein content. Comparing the results of the analysis, the empirical F value was much lower than the critical F value, in other words, the empirical value was included in the critical interval. So, the thermal effusivity values of the two proteins (egg white and WPI) were not significantly different at 95% level.

The second procedure is to divide the values of effusivity by the associated protein values thereby generating two times six ratios. These ratios constitute the mutual observation values in pairs, and these might be already applied in the analysis. From here, we can follow the same procedure as above. The relation of the obtained two F values were similar to the first case. So, the thermal effusivities of the two proteins were again not significantly different.

When the effects of fat content (Szafner et al., 2011) and protein content on the thermal effusivity is compared, it can be observed that the thermal effusivity value is much more sensitive to the fat content of the food samples than to protein content.

5. CONCLUSIONS

The demonstrated IPPE method was shown to be capable of detecting changes in thermal effusivity in samples of WPI and egg white powder solutions with varying protein contents. The correlation was linear with rather high coefficient of determination (R^2) in both cases. One percent increase in the protein contents of rehydrated WPI and egg white resulted in 6.5 and 7.2 $Ws^{1/2}\,m$ decrease in the values of thermal effusivity, respectively.

The observed decrease in thermal effusivity can be explained by two factors: i) an increase in protein content modifies the structure (and so thermal properties) of the samples leading to a decrease in effusivity values; ii) if the effusivity value of protein is calculated from the thermal conductivity, specific heat, and density values of proteins, a value of approximately 750 $Ws^{1/2}\,m^{-2}\,K^{-1}$ is obtained. This value is about half of the water's effusivity, and as the amount of protein increases, the water content decreases in the prepared protein-water systems.

The outcome of the statistical analysis confirmed that the thermal effusivity values of the rehydrated WPI and egg white proteins are not significantly different at $P = 0.05$ level.

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