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Direct Measurement of Thermal Effusivity of Avian Eggs and Their Constituents: A Photopyroelectric Study

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Summary

The front configuration photopyroelectric method has been used to determine, in a nondestructive fashion, thermal effusivity of the yolk and the white of eggs of several bird species as well as of the blends of a single egg yolk and egg white (also called liquid eggs) of different avian eggs. Statistically significant differences in thermal effusivity of egg whites were observed in ten out of twenty-one comparisons made. However, in the case of egg yolks, the differences were observed in twenty among twenty-one comparisons carried out. These observations are related to a varying fat content of egg yolk and a large amount of water found in egg white. The effusivity of the blends prepared from yolks and eggs varies because the contents of the yolk and white in avian eggs differ.

Key words: thermal properties of avian eggs, thermal effusivity, heat penetration coefficient, photopyroelectric method

Introduction

Dynamic (thermal diffusivity, thermal conductivity) and static (volume-specific heat) thermophysical properties of foods are both of relevance as they affect the optimal planning for the application of thermal energy in industrial processing (*1*). Different methods to determine thermophysical properties are presently available: differential scanning calorimetry (DSC) (*2*), the Fitch method (*3*), the line-heat-source method (*4,5*), the transient hot-wire method (*6*), *etc*. The last two methods are capable of measuring thermal diffusivity and thermal conductivity (*7*). The photopyroelectric (PPE) technique (*8*), however, is a relatively new method that allows for the assessment of thermal effusivity *e*. Basically, this last parameter, which governs the penetration of heat into materials, is defined as the square root of the product of thermal conductivity κ of a sample, volume-specific heat capacity c_v and density ρ:

$$e=(\kappa\cdot\rho\cdot c_v)^{1/2} \qquad /1/$$

The PPE method, essentially a photothermal approach, offers several advantages: no preparation of the sample is required prior to the analysis, the method is nondestructive and fast, and in addition, only small quantity of sample is needed (*9*). Two variants of PPE method are distinguished: the back (BPPE) and the front (FPPE) configuration (*10*). In both configurations the sample is heated by the periodically modulated beam of (laser)

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radiation. The difference between the two configurations is in the orientation of the incident radiation relative to the test sample. While in the BPPE configuration the sample is directly irradiated from above, in the FPPE geometry the radiation impinges on the backside of the pyroelectric sensor carrying the test sample. In the BPPE configuration, the thickness of the sample is important when the sample is thermally thick (*i.e.* its physical thickness is larger than the thermal diffusion length at a given modulation frequency), as the heat generated due to absorption cannot warm up the pyroelectric foil. In the FPPE configuration, however, the radiation impinges initially on the absorbing pyroelectric foil and therefore the thickness of the sample plays no role of significance in the generation of the PPE signal (*11*).

Eggs and the products derived from eggs are the raw materials often processed by the baking and dried pasta industries. In addition, fresh eggs and products such as mayonnaise and salad dressings that are rich in egg content are in the current trade flow. The eggs are consumed mainly because of their high biological value, as well as their vitamin (almost all types of vitamins are present) and protein content (*12*).

Specific heat and thermal conductivity of yolk and white (two major constituents of eggs) and of their blends have been determined previously (*13*). The composition of eggs, especially the water and fat content, affects their thermophysical properties (*14*). For example, hen's egg yolk contains (in %): protein 16.5, fat 31.2, water 49.7, minerals 1.7 and other constituents 1.9. On the other hand, hen's egg white contains typically (in %): water 87.6, protein 10.6, minerals 0.7, fat 0.01 and residual compounds 1.1. The dry matter content of hen's egg yolk is 48–50 %, some 80 % of this is water-soluble, while the remaining 20 % is the fat-soluble plasma (*15*). The composition of various avian eggs differs greatly (*16*): *e.g.* the yolk of a duck's egg contains (in %): water 43.51, protein 16.0, fat 37.25 and ash 1.59 (*17*), which is very much different from the composition of hen's egg.

The objective of the study described in this paper is to determine thermal effusivity of egg yolk and white from different avian eggs by means of the FPPE method. In addition, thermal effusivity of the blends containing one egg yolk and one egg white has also been studied.

Theoretical Background

Standard manner to obtain thermal effusivity is to calculate this quantity from the independent measurements of κ, c_v and ρ. Unlike this, FPPE is the method capable of measuring the effusivity directly, *i.e.* by a single measurement. In the FPPE measurement the detector is a thin pyroelectric polyvinylidene fluoride (PVDF) foil with metallized coating on both sides. The absorption of the modulated laser radiation at the rear side of the foil (painted black) generates periodic heating. The subsequent temperature rise of the pyroelectric foil is accompanied by a larger change of polarized charge density ΔQ_p and the current between the two sides of the foil (*18*). If the electrodes are attached to both sides of the pyroelectric foil, the polarisation current I_p is given by:

$$I_p = \frac{\Delta Q_p}{\Delta t} \qquad /2/$$

where Δt is the time interval.

The temperature of the irradiated pyroelectric foil varies with the same periodicity as that of the modulation frequency f itself. Consequently, a change of charge density ΔQ_p induced at the angular modulation frequency $\omega=2\pi f$ by such temperature variations leads to an oscillating voltage $V(\omega)$, commonly termed as the FPPE signal. This latter is detected at the modulation frequency f by means of the two-phase lock-in amplifier (*19*) and its magnitude $V(\omega)$ can be expressed as (*20*):

$$V(\omega) = \frac{p \cdot L_p \cdot \Theta_p}{\varepsilon \cdot \varepsilon_0} \qquad /3/$$

where p is the pyroelectric coefficient, Θ_p and L_p are the temperature and the thickness of the PVDF foil respectively, while ε and ε_0 are the dielectric constant of the PVDF foil and the permittivity constant of vacuum, respectively. Thermal effusivity e_s of the unknown sample is then deduced from FPPE signals V_s and V_r obtained under identical experimental conditions from the sample of interest and the reference substance (such as water for example) of known thermal effusivity e_r, *i.e*:

$$e_s = \frac{e_r \cdot V_r}{V_s} \qquad /4/$$

Eq. 4 is valid only under some special experimental conditions, namely if the sensor is opaque and thermally thin and the sample is thermally thick. The biaxially stretched piezo PVDF foil used in this study was 25 μm thick, which is much shorter than the thermal diffusion length in the foil (147 μm) at modulation frequency of 0.5 Hz (*21*). The physical thickness of the sample can be readily deduced from its cylindrically shaped volume (400 μL). In our experiment the thickness of the sample as well as of the reference substance (water) was approx. 2 mm, while at 0.5 Hz the thermal diffusion length of water was about 298 μm. Although the exact value of thermal diffusion length in egg samples is not known, based on a high water content in egg white, it can be concluded that the samples are also thermally thick.

Materials and Methods

Seven avian eggs (of hens, Chinese hens, geese, ducks, guineafowls, quails and pheasants) were studied; three eggs of each bird species were selected for investigation. After breaking the egg (with hands), the white and the yolk were carefully separated; these two constituents were used at a later stage to produce the blends. The series of blends (one blend for each sort) was prepared by mixing the white (W) and the yolk (Y) of the egg from each bird species as shown in Fig. 1.

The homogeneity of blends was accomplished by manual mixing (using a small spatula) and the degree of homogenization was eventually estimated by a visual inspection. The actual duration of mixing depends on the ratio of egg yolk and white. Obviously, if the content of egg white in a blend is high, it takes longer to obtain

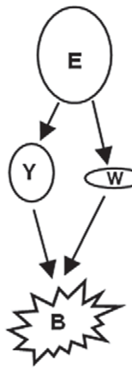

Fig. 1. The scheme showing the sequence of steps followed when preparing the samples for analysis by FPPE method. The egg yolk (Y) and egg white (W) from an egg (E) were separated manually. The blend (B) was prepared from the yolk and the white of the single egg. The FPPE studies were performed with Y, W and B of all avian eggs

homogeneous samples. In order to eliminate air bubbles, which can potentially influence the thermal contact between the sample and the pyroelectric foil, the blends were manually agitated for 3 min at 297 K. Three independent measurements were performed of each of the twenty-one samples (seven samples of egg white, seven of egg yolk and seven blends); the quantity of the sample used for the analysis was the same (400 μL) in all experiments.

The FPPE measurements were conducted using a home-made experimental set-up shown in Fig. 2. The radiation source was a continuous-wave He-Ne laser emitting 3.6 mW at 632 nm. The laser beam was modulated using an electro-optical chopper driven by the TTL signal provided by the lock-in amplifier. The modulated laser beam was directed at the blackened rear side of the PVDF foil by means of a plane mirror, and an FPPE signal fed to the lock-in amplifier interfaced with the computer for data processing. Blackening of the rear surface of the foil in this FPPE configuration is essential because it ensures that the radiation of the incident laser beam will be completely absorbed regardless of the excitation wavelength. The sequence of 256 successive readouts of the FPPE signal from the lock-in amplifier were measured for a single sample load, and the calculated average value was taken as a representative signal.

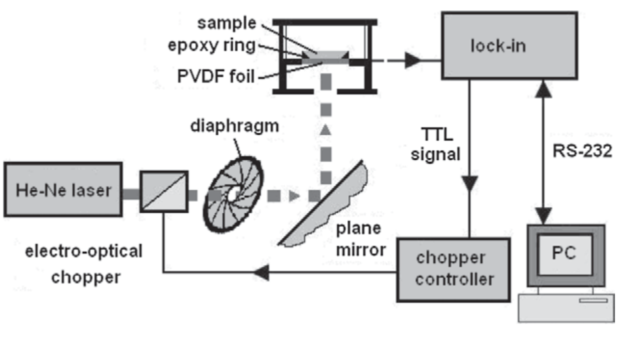

Fig. 2. The schematic diagram of the home-made set-up for FPPE measurements

Results and Discussion

The magnitude of FPPE signal depends on the modulation frequency *f*. For practical reasons it is preferable to operate the FPPE set-up at frequencies that are within the linearity range of the FPPE signal *vs.* $f^{1/2}$ plot. Outside the linearity range the FPPE signal shows a tendency towards saturation. In the FPPE measurements performed on distilled water for 0.1 Hz<f<4 Hz, the amplitude of the FPPE signal was shown to be linear with $f^{1/2}$ in a range extending from 0.1 to 2 Hz. Fig. 3 displays the amplitude of the FPPE signals for distilled water and the yolk of the hen's egg; both are linear within the frequency range of interest. Because of the favourable signal to noise ratio, the modulation frequency of 0.5 Hz was eventually selected for the remaining measurements.

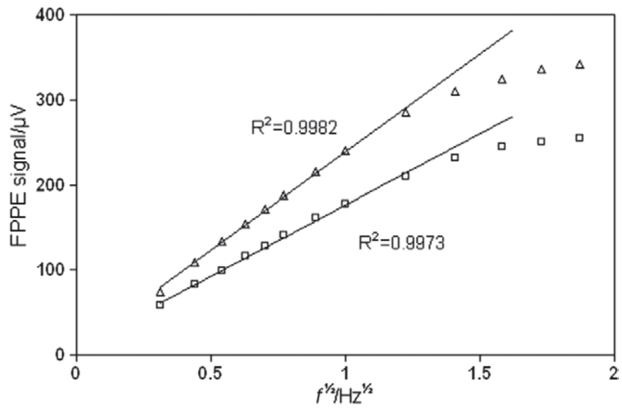

Fig. 3. The FPPE amplitude obtained from distilled water (△) and egg yolk (□) plotted *vs.* the square root of the modulation frequency *f*

To calibrate the response of the given experimental set-up, the FPPE signal from distilled water needs to be measured (at 0.5 Hz). The value of thermal effusivity of distilled water at room temperature was taken from the literature (*21,22*). Then FPPE signals from yolks and whites from different avian eggs were measured. Once FPPE signals from the unknown sample and the reference sample (water) are available, thermal effusivity *e* of the sample can be calculated from Eq. 4. Data shown in Table 1 represent the average values of three inde-

Table 1. Thermal effusivity of egg yolk, egg white and the blends of a single egg yolk and egg white for various avian eggs

Species	Yolk	White	Blend of a single egg yolk and white
	$(W\cdot s^{½})/(m^2\cdot K)$		
duck	1038±2	1517±5	1172±3
guineafowl	1049±5	1475±16	1267±23
pheasant	1055±6	1471±13	1261±16
goose	1065±2	1530±8	1278±6
Chinese hen	1086±4	1538±8	1265±5
hen	1122±31	1511±21	1305±3
quail	1144±5	1519±4	1354±8

The results are expressed as mean values±standard deviation

Table 2. Results of the statistical analysis (F- and *t*-tests)

Species	guineafowl	pheasant	goose	Chinese hen	hen	quail
duck	* +	* # +	# +	# +	# +	# +
guineafowl		#	* #	* #	* # +	* # +
pheasant			* #	* #	* # +	* # +
goose				#	# +	# +
Chinese hen					# +	# +
hen						# +

*refers to a significant difference between the pairs of different egg whites, while # is related to a significant difference between the two different egg yolks. Finally, symbol + is reserved for blends prepared from the yolk and white of an egg (p=0.95)

pendent measurements. Clearly, *e* values of an egg yolk are significantly lower than those of egg white; this trend was true for all eggs independently of the bird species. Thermal effusivity of egg yolk varies between 1030 and 1150 $(W\cdot s^{1/2})/(m^2\cdot K)$, while for egg white effusivity spans the range of values extending from 1470 to 1545 $(W\cdot s^{1/2})/(m^2\cdot K)$. As for the blends, thermal effusivities found are between *e* values of a pure egg yolk and a pure egg white.

Higher effusivity of an egg white is due to its larger water content and lower amount of fat (duck, goose, Chinese hen, hen, quail). Likewise, lower effusivity of egg yolk is ascribed to the lower water content and reduced amount of fat (duck, guineafowl, pheasant, goose, Chinese hen). Consequently, in the case of a blend, the effusivity is expected to be influenced not only by effusivities of egg yolk and egg white, but also by their mass ratio. This is clearly seen when comparing the hen's and quail's eggs; it can be noticed that effusivities of egg yolks are the highest, while the same trend is not observed for the egg whites. On the other hand, thermal effusivities of blends (liquid eggs) are largest in these two cases, which is due to the relatively high egg white to egg yolk mass ratio.

The experimental data were statistically analyzed by applying the F and *t*-tests at p=0.95 level; the outcome is shown in Table 2. Seven different avian eggs were investigated, which implies (7×6)/2=21 possible comparisons for each parameter of interest. With the total number of parameters of three, the overall number of meaningful comparisons amounts to 63.

Table 2 indicates that in a majority of cases F- and *t*-tests at p=0.95 level show significant differences. However, in five cases (guineafowl/hen, guineafowl/quail, pheasant/hen, pheasant/quail and pheasant/duck), significant differences in thermal effusivity of egg yolk, egg white and the yolk/white blends were observed. This is evident in Table 2 from three symbols (*, # and +) appearing in five row/column intersections. In nine cases the effusivity of egg yolk (but not of the egg white) and of blend (symbols # and +) shows significant differences. Finally, the white and the yolk (but not the blend) of the egg displayed significant differences in four cases. There was only one case (duck/guineafowl) in which thermal effusivity of the egg white and the blend differs significantly. For pheasant/guineafowl and Chinese hen/goose comparisons significant difference was observed only in egg yolks. Remarkable is the fact that thermal effusivity of yolk differs significantly for all eggs with the exception of duck/guineafowl comparison. At the same time, egg whites are significantly different in only ten out of 21 comparisons, presumably due to the high water content in the egg white. For a blend of a single egg, effusivity is influenced (see Table 1) by the effusivities of the egg yolk and white as well as by the yolk/white ratio for different classes of eggs.

Conclusion

The home-made experimental set-up was demonstrated to be capable of measuring thermal effusivity of different egg constituents in a simple and rapid manner. Thermal effusivities of egg yolk and white are characteristic for the specific avian egg, as confirmed by statistical analysis. The observed differences among thermal effusivities of egg yolk are greater than those found for egg white; this is ascribed to various contents of water and fat. Furthermore, effusivities of the blends prepared from a single egg differ from the effusivity of egg yolk or egg white of the very same egg.

Direct measurement of effusivity can be important in the confectionary industry where eggs characterized by a high content of egg white are preferred. Other potential applications include the preparation of foam and the production of pastas.

It has already been stated that thermal effusivity of a material sample can be computed provided that its density, specific heat and thermal conductivity are known. An attempt was made here to compare thermal effusivity of hen's eggs obtained directly by this FPPE experiment, and the effusivity calculated from the literature data for κ, ρ and c_v (*13*); no significant difference between the two values was found. In the absence of the literature data for thermal effusivity, the measurements of κ, ρ and c_v, although independent and time consuming, are indispensable. This problem is, however, conveniently circumvented by the FPPE method, which permits a rapid, direct and accurate measurement of thermal effusivity providing substantial savings in terms of both, investment cost and time.

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