

**TOMATO PASTES AND THEIR MOISTURE CONTENT AS DETERMINED
VIA THE MEASUREMENTS OF THERMAL EFFUSIVITY BY MEANS OF
INFRARED PHOTOTHERMAL RADIOMETRY AND INVERSE
PHOTOPYROELECTRIC TECHNIQUE**

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Abstract

Infrared photothermal radiometry and inverse photopyroelectric method were used to determine thermal effusivity for tomato pastes characterised by a varying dry matter content. Unlike commonly adapted techniques, the two methods used here are reasonably fast and do not require the application of substantial external heat input; positive correlation between the effusivity and moisture content is high.

Key words: tomato, infrared, photothermal, radiometry

Introduction

Water, the most commonly substance found in foods is important to the food quality in respect of the storage lifetime and taste. Consequently, methods capable of reliably and rapidly determining the moisture content (MC) in foods are often needed in industrial production processes.

The most commonly used methods for assessing MC are all based on the application of external heat.¹ Thermogravimetry (TGY), the most widely adopted approach implies placing of a test sample for prolonged time intervals in a drying oven (maintained at the pre-selected temperature) with a hot circulating air. The sample under investigation is weighted (M_1) at the beginning and then re-weighted again (M_2) at the

end of the drying process. The MC (expressed in percents) is calculated from the resulting weight loss ($M_1 - M_2$) and the original weight M_1 according to $MC(\%) = 100 (M_2 - M_1) / M_1$. The analysis time of TGY is quite long (typically a day); in addition TGY cannot discriminate between the loss of water from the volatile components or from the decomposition of sample at a too high temperature. Shorter drying analysis times are achievable with the moisture balance (MB) the operational principle of which relies on the heating of the sample with IR (or microwave) radiation or a halogen lamp; decreasing sample weight is then on-line detected by means of a sensitive balance. In the freeze-drying (FD) method, the initially frozen test sample is later exposed to a high vacuum while at the same time maintaining the temperature high enough for moisture to evaporate.²

The major objective of the research study described in this paper was to explore whether infrared photothermal radiometry (PTR) and inverse photopyroelectric technique (IPPE) could prove useful for rapid assessment of MC in tomato pastes. Unlike traditional approaches discussed above that all require elevated temperatures, the PTR and IPPE, both being the variants of photothermal (PT) techniques, are fast and operate at a room temperature.

One among physical quantities that can be directly measured by the PTR and IPPE is the thermal effusivity (often termed heat penetration coefficient) e defined as $e = (\lambda \rho c_p)^{0.5}$ with λ , ρ and c_p being thermal conductivity, density and specific heat at the constant pressure, respectively. Since by virtue of definition e depends on the composition of food, it is also expected to be sensitive to MC. Using data obtained in PTR and IPPE experiments performed on a number of tomato pastes characterised by a known MC, one could try to construct the “calibration curve” that, at a later stage can be used to indirectly determine MC of the unknown tomato paste.

Although thermal effusivity is of considerable interest to food engineering designers, there still is a general lack of data for this quantity. Most likely this is due to the fact that in order to determine e , one must perform three independent measurements (λ , ρ and c_p) each of which is time consuming. Unlike this, PTR and IPPE allow for a direct determination of e by a single measurement.

Experimental

Five tomato pastes (assigned codes A to E) used in this study were purchased in different supermarkets and kept sealed in the refrigerator until the actual tests. The experiments were carried out approximately one year prior to the expiry date of the products. The samples included concentrated pastes, double concentrated pastes and triple concentrated pastes. The dry matter content (DMC) of all test samples was determined in our own laboratory using TGY and IR heating.

The principle of the PTR method and basic constructional details of the experimental set-up (Figure 1) used for the non-destructive and non-contact determination measurement of ϵ are described elsewhere.³ Mechanically modulated 10P(20) radiation emitted by CO₂ laser was used for the excitation. At the power level used here (400 mW) neither damage to the sample nor the effects of convection have been observed. A flat-bottomed glass dish (diameter 20 mm, height about 7 mm) served to accommodate the paste; following vigorous (manual) mixing tomato paste was scooped, evenly distributed in a dish and its surface flattened. The quantity of paste in the dish was approximately the same for all samples. The dish with the paste was mounted onto the x-y-z translation stage oriented as shown in Figure 1.

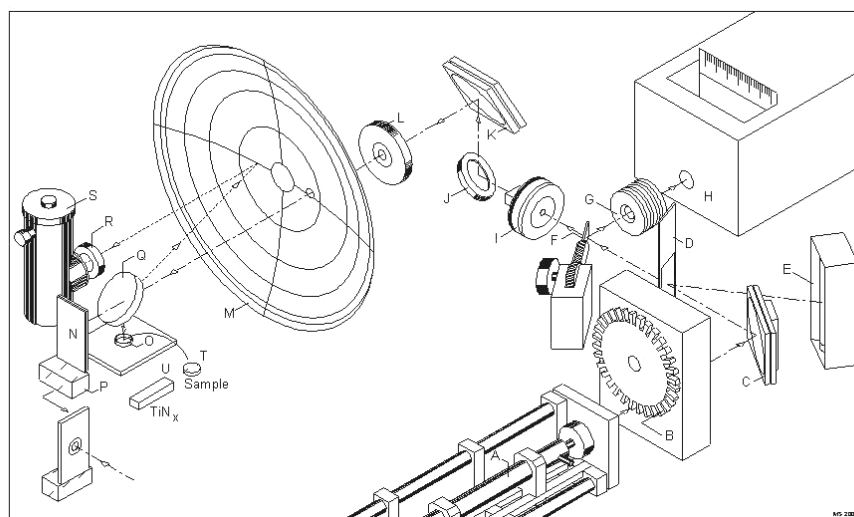


Figure 1. The experimental set-up for infrared photothermal radiometry. The components include laser (A), chopper (B), mirror (C), imaging plate (D), UV lamp (E), beam diverter (F), power detector (G), spectrum analyzer (H), attenuator (I), mirrors (J and K), lens (L), parabolic reflector (M), sample holder for vertical geometry (N), sample holder for horizontal geometry (O), reflector (Q), supporting block (P), LiF filter (R), cryogenic detector (S), sample (T) and TiN_x plate (U).

To calibrate the amplitude and the phase response of the PTR set-up the 1% aqueous solution of agar and the TiN_x plate (kindly provided by Siemens GmbH) have been used. The absorption coefficient of agar (surface absorber) at 10P(20) laser line was assumed equal to that of water (850 cm⁻¹). The effusivity of TiN_x (another surface absorber) is 2600 W s^{1/2}/m² K. The PTR measurements were conducted using frequencies between 12.8 to 98 Hz range; at these modulation frequencies corresponding thermal diffusion lengths in water samples are about 60 μm and 20 μm respectively. Each tomato paste was studied at least three times under comparable experimental conditions. The amplitude and the phase of the lock-in signal were on-line monitored (sampling rate of 500 readings during 18 seconds). After approximately 90 seconds the amplitude reached a constant level; it was this very value that was read off consistently and taken as the input parameter in the calculation for effusivity.³ The phase reached the steady state level sooner than the amplitude.

The IPPE method was demonstrated repeatedly as a suitable and accurate technique for quick and direct assessment of e .⁴ Basic operational principles and construction of the cell can be found elsewhere.⁵ In this study the 25 μm thick metalized PVDF foil was used as the pyroelectric sensor. The critical frequency (defined as a modulation frequency at which the thermal diffusion length in the PVDF film equals the physical thickness (i.e. 25 μm) of the foil) is 27 Hz. Ten milliwatts of 632.7 nm He-Ne laser radiation was used to heat the rear face of the PVDF foil. The thickness of the sample deposited atop the foil (good thermal contact between the sample and the foil is a necessity) was typically 5 mm. For tomato paste of that thickness critical frequency is about 1.7 MHz. From the allowed range of modulation frequencies (1.7 MHz to 27 Hz), 0.1 Hz (provided by the acousto-optical modulator) was chosen for the actual IPPE measurements. At 0.1 Hz the PVDF foil that is thermally thin while the paste is both, thermally thick and optically opaque. In this particular IPPE case, a relatively simple mathematical expression applies⁵ for effusivity does apply: the unknown effusivity of tomato paste can be readily determined by measuring (for a given experimental geometry), the amplitudes of the IPPE signals obtained from a tomato paste and water for which $e=1590$ W s^{1/2}/m² K.

Results

About 3 g of each tomato paste were transferred in a metal dish and weighed (Mettler Toledo PG803) to the nearest 0.001 g. For each tomato paste three samples have been prepared, placed (simultaneously) in Memmert oven (maintained at 105°C) with the circulating air, dried (for 24 hours) and re-weighed. The average values of MC and the extent of the reproducibility (standard deviation) based on the three independent measurements are displayed in Table 1.

Table 1. Moisture content of test samples determined by thermal gravimetry.

sample	moisture content (%)
brand A	(62.37±0.06); n=3
brand B	(62.68±0.09); n=3
brand C	(69.72±0.12); n=3
brand D	(77.20±0.08); n=6
brand E	(81.71±0.14); n=3

Likewise, three samples of each paste were prepared for the PTR study. It is well known that in a typical PTR experiment the magnitude of the lock-in signals obtained at various modulation frequencies correspond to different depths in the sample.⁶ Therefore, to obtain a value for e that is representative for a tomato paste, the amplitude and a phase of the lock-in signals were recorded at 12.8, 25, 40, 78 and 98 Hz. In order to get a representative value for effusivity, data for e calculated from PTR signals obtained from the samples at different modulation frequencies were arithmetically averaged. Figure 2 shows the dependence of e on MC; as expected, highest e correlates with the largest amount of water and vice versa.

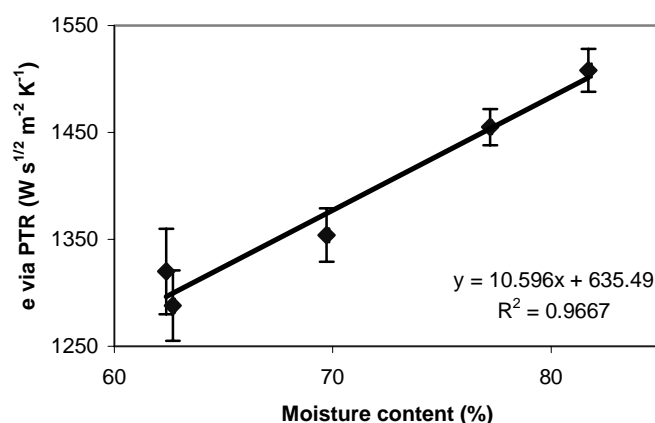


Figure 2. Thermal effusivity obtained by infrared PTR plotted versus the moisture content of five tomato pastes. Data points represent the averages of three independent measurements.

The reproducibility (typically $\pm 3\%$ as derived from the five consecutive measurements, i.e. each sample was loaded five times) in PTR measurements of e might, next to the factors such as sample's intrinsic non-homogeneity and the sampling procedure, also be influenced by the effect of drying occurring during the actual experiment. On the other hand, the repeatability (i.e. standard deviation based on 2500 consecutive readings of the lock-in signal taken at a given frequency during a 90 seconds period) associated with the single load measurement was very good and typically did not exceed 0.2%.

Next all test samples were examined using the IPPE method; the results of the measurements carried out at 0.1 Hz are shown in Figure 3. Again, e correlates positively with MC; each data for e is the average of three consecutive measurements. The response of the IPPE set-up was calibrated (with water) between two consecutive measurements. Despite the outstanding repeatability (better than 0.2%) for the amplitude of the lock-in signals on a single IPPE measurement, the precision in determining e is estimated to 6%.

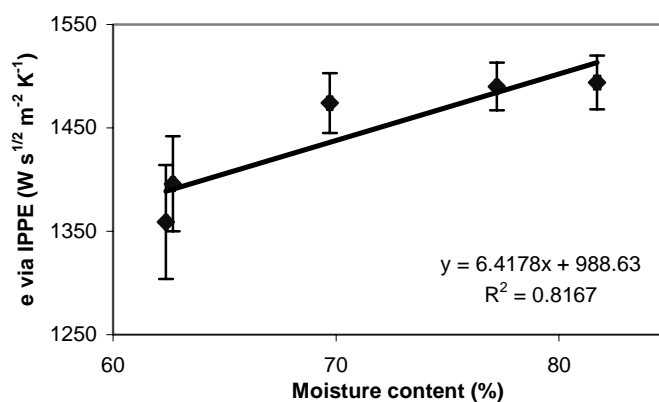


Figure 3. Thermal effusivity obtained by IPPE method plotted versus the moisture content of five tomato pastes. Data points represent the averages of three independent measurements.

That a correlation between e and MC indeed exists was demonstrated during the IPPE study conducted with samples of a triple concentrated paste that was deliberately diluted by water. By adding well known quantities of water to such tomato paste one could produce "synthetic" samples (all prepared from one and the same paste, minimising the effect of the sample matrix) with the actual MC varying between 95% and 65% respectively.

Conclusion

It was demonstrated that thermal effusivity (at 293 K) determined by PTR and IPPE in a non-destructive manner is indicative for MC in various tomato pastes. Considering the likely extent of structural variability in tomato pastes the obtained correlation coefficients can be considered as high. Neither of the two proposed photothermal techniques requires the substantial heat inputs and only a short time is needed to complete the measurements. This makes PTR and IPPE useful when a short measuring time is a priority.

For meaningful interpretation both methods must be calibrated. Pure water was used in IPPE studies while the 1% aqueous solution of agar and a TiN_x plate were used to calibrate the amplitude and the phase response of the experimental set-ups used in PTR studies. The absolute values for e obtained by PTR and IPPE are comparable. In general sampling and the distribution (homogeneity) are likely to influence the results. It appears that the reproducibility of IPPE measurements is below than that achieved in the PTR studies. In particular, occasional difficulties in IPPE experiments were experienced for a paste with lower moisture content; the consistency of this product may be responsible for accidental poor thermal contact. The repeatability in PTR and of IPPE on a single measurement was outstanding (better than 0.2%). To what it concerns the accuracy of PTR and IPPE, no definite conclusions about the correctness of the results can be made at present since the "tomato paste standard" with a well known effusivity was not available.

Present study was restricted to tomato paste having relatively low MC. The same approach can be extended to other tomato products (examples are passata, ketchup, tomato juice etc.) with a higher MC. In addition, the potential of SPPE, another photothermal technique, as a candidate method for assessment of moisture it worth investigating. Unlike the geometry encountered in the IPPE experiment, in the SPPE (standard photopyroelectric) configuration it is a sample, rather than the PVDF foil that is directly irradiated.^{7,8} Provided the thickness of the sample is accurately known SPPE method enables one to determine sample's thermal diffusivity α . This latter defined as $\alpha = \lambda / \rho c_p$ is, just as e , dependent on the sample's composition and can, under specific experimental conditions, be determined from the slope of the measured phase-frequency plot. The SPPE method also allows one to observe phase transitions; the critical

temperature T_{cr} at which the phase transition takes place could serve as a precise criterion for MC of the test sample. A comparison study in which a number of methods (NMR, SPPE, IPPE, PTR, TGY, IR heating and FD) are applied to assess MC in a wide range of products derived from processed tomatoes is currently underway.

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Povzetek

Za določitev parametrov toplotne prevodnosti paradižnikovih mezg z različnimi vsebnostmi suhe snovi smo uporabili infrardečo fototermično radiometrijo in inverzno fotopiroelektrično metodo. Za razliko od tehnik v običajni uporabi sta primerno hitri in uporaba močnih zunanjih virov toplote ni potrebna, pozitivna korelacija med parametri in vsebnostjo vode pa je velika.