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ORIGINAL RESEARCH

Sensing the Heat of Tomato Products Red: The New Approach to the Objective Assessment of their Color

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Abstract The concept of optothermal window (OW) detection was used for the first time to assess the color of several products (juice, purée, paste) derived from thermally processed tomatoes. Unlike traditional techniques that operate either in the reflectance or transmission mode, the method proposed here actually relies on indirect measurement of absorbance in optically opaque and scattering samples. Very good correlation between the magnitude of the OW signal and the color-related parameters [colorimetric index L^* and tomato paste index (TPI)] was observed.

Keywords Tomato-based products · Color · Light emitting diode · Optothermal window · Lycopene

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Introduction

Color is an important property of foods because it is often associated with the quality. To satisfy customer needs, food industry is perpetually trying to produce the products having natural, appealing colors. The availability of techniques capable of rapidly and accurately assessing/controlling the color of foods in a simple and inexpensive way is therefore a necessity.

The two classical methods used for assessment of food color are colorimetry and spectrophotometry in the visible. Most color measuring instruments require a sizable amount of material for analysis. The operation of established techniques relies on the measurement of radiation reflected by objects being investigated. It is customary to define a color in the CIELAB system by specifying three independent indices: L^*, a^*, and b^*. While L^* (varying from 0 to 100) is associated with the lightness, the values of index a^* change from positive (red) to negative (green). Similarly, colorimetric index b^* spans the range extending from positive (yellow) to negative (blue) values.

The experimentalist, when studying food color by methods operating in the reflectance mode [1] may encounter a number of potential difficulties. One among them is the fact that most colorimeters and spectrophotometers are actually designed for use with flat samples, which is seldom the case for foods. Temperature, humidity, translucence, as well as chemical and physical reactions taking place at the surface during the measurement are additional factors that could affect measurements.

This article is concerned with the development and application of the novel method for assessing food color. Unlike classical methods where reflected radiation is of relevance, the new approach relies on obtaining the meaningful information about the color by analyzing the radiation absorbed by test sample instead.

Initially, the concept of optothermal window (OW) detector was introduced and utilized for direct quantification of absorbance in optically opaque fluids and/or pastes. Practical examples include determination of total phenolic content in red wines [2] and rapid, direct (without a need for preparation/manipulation of the sample) measurement of lycopene (as specific analyte) concentration in a large diversity of tomato-based products [3, 4]. This is intrinsically substantially different from the situation encountered with conventional methods that require sample to be extracted (a time-consuming and costly procedure) prior to actual analysis. In addition, every step in a process of isolating the analyte from its original matrix brings along the possibility for uncontrollable loss of analyte material.

The aforementioned quantitative OW studies [3, 4] of lycopene in tomato-based products were performed with sophisticated argon ion laser emitting at 502 nm wavelength that corresponds to that at which lycopene exhibits strong absorption. Recently, argon laser as the radiation source has been replaced by the compact-size, inexpensive light-emitting diode (LED), and used as a simple, practical OW detector of lycopene in tomato-based foods [5]. Essential to this novel LED-OW concept is the fact that an optically opaque, tomato-based sample deposited on the surface of a thin, transparent sapphire disk characterized by a large radial expansion coefficient selectively absorbs periodically modulated LED radiation. An annular ring made of piezoelectric material is glued to the rear side of the crystal. As a consequence of absorption, thermal waves are generated within the sample. Because the incident LED radiation is periodically modulated at a certain frequency f, the absorbing sample itself also undergoes periodical heating and cooling. The generated thermal waves propagate in all directions, including that of sapphire disk, eventually causing its expansion; this latter is detected as an alternate voltage at the modulation frequency by the piezoelectric material. The amplitude of such complex electric OW signal depends on a number of sample- and detector-specific optical and thermal parameters; more details on this are disclosed elsewhere [3]. In general, after the calibration procedure using a strongly absorbing sample of known optical and thermal properties, the amplitude of the OW signal was demonstrated to contain information about the concentration of absorbing analyte.

Three important sample-related quantities that influence the amplitude of OW signal are the physical length L of the sample, the optical penetration depth $1/\beta_\lambda$ (β_λ is the absorption coefficient of the analyte per unit length at a given wavelength), and the so-called "thermal diffusion length" μ of the sample defined as $\mu = (\alpha/\pi f)^{1/2}$, where α the is specimen's thermal diffusivity. If the experimental conditions are such that condition $\mu < 1/\beta_\lambda < L$ is being met, the mathematical relationship for the amplitude of the OW signal simplify greatly. In practice, it is necessary to normalize the OW signal from the sample by rationing it to the OW signal obtained under identical experimental conditions from an ideal strong absorber such as black drawing ink. Such normalized signal S has no dimension and depends on μ and β_λ as shown by Eq. (1):

$$S = \frac{\beta_\lambda \mu}{\sqrt{(1+\beta_\lambda \mu)^2 + 1}} \tag{1}$$

From the experimentally obtained S, one computes the product $\beta_\lambda \mu$ using:

$$\beta_\lambda \mu = \frac{2}{\sqrt{\frac{2}{S^2} - 1} - 1} \tag{2}$$

The quantity β_λ is directly related to concentration c of the absorbing analyte because $\beta_\lambda = c\varepsilon_\lambda$ (with ε_λ being the molar extinction coefficient at a given analytical wavelength). The quantity $1/\beta_\lambda$ represents roughly the thickness of the heated layer in the sample characterized by its physical thickness L and thermal diffusivity α. On the other hand, thermal diffusion length μ indicates which portion of the heated sample layer can, at a given modulation frequency f, thermally communicate with the sapphire disk and thus also piezoelectric detector.

In this study, the LED-OW is proposed as a new method for assessment of red color of products derived from processed tomatoes. Tomato is an example of food-possessing intense natural color, and is also capable of imparting this color to a wide range of products. The characteristic red color of tomato is attributable to a combination of carotenoid pigments, among which lycopene is the most abundant. As for tomato-based products such as paste and purée, their color is, in addition to that of the original fruit, also related to the processing conditions. The assessment of the tomato paste color is therefore important not only because the latter influences appearance of the final product (soup, juice, etc.), but also because it serves as an indicator of the quality of original tomatoes, the efficiency of processing conditions, and the adequacy of quality control at the site of the paste manufacturer [6, 7].

The basic idea behind the undertaken LED-OW experiment was to find out whether or not the correlation can be established between colorimetric quantities (measured either directly or derived from traditional colorimetric measurements) and the magnitude of the OW signal.

Materials and methods

Overall, seven tomato-based products were investigated; the names of manufacturers are deliberately not disclosed. The selection of products included one tomato juice, two tomato purées, three tomato concentrates, and one tomato paste. In choosing the terminology, the following criterion was applied [8]. Tomato purée is a tomato concentrate with natural tomato solids [tomato-soluble solids (TSS)] greater than 10% but lower than 22%. Tomato concentrate implies a product with TSS ranging between 22 and 28%. Finally, tomato paste is the tomato concentrate containing at least 28% of the natural tomato solids. Five among seven commodities were selected for calibration purposes; the two remaining samples (one tomato purée and one tomato concentrate) served as the test specimens. All products were purchased in the local supermarket; the expiry date label was carefully noted.

Figure 1 is the exploded view of the setup used in LED experiment. Luxeon,star-/c,LXHL-LE5C Cyan LumiLED (Lumileds Lighting, San Jose, CA, USA) served as the radiation source (A). Relative spectral power intensity of the cyan LED extends from 460 to 570 nm. The peak is found at 500 nm—its half-width at half-maximum ($\Delta\lambda_{1/2}$) is about 30 nm. The total power emitted by LED was 70 mW. The beam passing through the LXHL-NX05 collimating lens (B) (from Luxeon, Irvine, CA, USA) mounted coaxial with LED, was then focused via a 25.4-mm-diameter and f = 19 mm planoconvex lens (C) from Melles-Griot (Melles-Griot, San Jose, CA, USA) into a 3-mm-diameter optical fiber (E). The 0.1 Hz–2 MHz function generator PM5131 (Koninklijke Philips Electronics NV, Eindhoven, Netherlands) provided the 5-V stabilized voltage for LED and the square-wave signal needed for the modulation of LED. The alignment of lenses (B) and (C) was accomplished via three precision micrometers [(F), (G), and (H)] with 5 μm resolution. The angle at which the radiation beam impinges on the optical fiber could be optimized by micrometer (I). The beam propagates through the optical fiber, the other end of which was gently pressed against the bottom of a Plexiglas cone (J) used to minimize reflections. The upper end of the cone touches the OW sensor that consists of the piezoelectric material (K) glued to the rear side of a thin sapphire disk (L).

Spatula was used to distribute the tomato-based sample (M) under investigation over the surface of the sapphire disk. It is important that the test sample uniformly covers the section of disk facing the incoming LED radiation. Likewise, the presence of

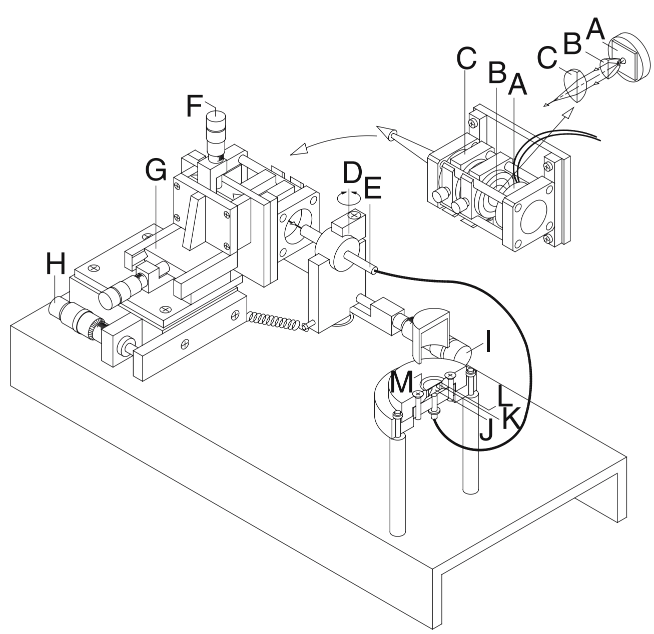

Fig. 1. Exploded view of the LED-OW setup used in this study.

air bubbles in the sample should be avoided. Unlike in traditional techniques, the actual quantity of sample taken for analysis is not relevant as long as condition $\mu < 1/\beta_\lambda < L$ is being satisfied. The OW signal from the LED-OW sensor was then detected by using SR830 DSP digital lock-in amplifier (Stanford Research Systems Inc., Sunnyvale, CA, USA) with a built-in preamplifier (10^8 Ω feedback resistance); the detection itself took place at the frequency of modulation. With sample loaded atop sapphire disk, a 30-s period was allowed for OW signal to stabilize before taking the measurements. Data acquisition and processing were automatically performed; approximately 1000 successive readings of the lock-in signal readout were made within 90 s prior to calculating the average and standard deviation. The sample was then rejected, sensor cleaned (water, ethanol, and cotton swabs), fresh quantity of sample deposited, and measurement repeated; overall, five such series have been performed with each specimen. All studies were performed at a modulation frequency of 8.3 Hz; the actual LED power reaching the tomato-based product was 1.75 mW. The measurements were normalized to OW signals obtained with the same setup and under identical experimental conditions from a black drawing ink used as a strongly absorbing reference sample.

Colorimetric measurements of indices *a**, *b**, and *L** were performed on Tricolor colorimeter LFM3 (Dr. Lange, Düsseldorf, Germany) using 45° measuring geometry. Tomato-based sample was spooned into a glass cup (provided with light protective black cover), placed on the instrument measuring port (well-defined aperture) and illuminated from below. Reproducible sample quantities were used at each load; the instrument was calibrated against dry enamel standard. Between two consecutive measurements, the cup and piston were washed with warm water and dried with tissue paper. Each tomato-based product was studied five times.

Tomato-soluble solids (TSS) were determined by using Abbe refractometer (Atago USA Inc., Bellevue, WA, USA); the dry matter content of samples investigated in this study were measured gravimetrically (oven maintained at 60°C for 24 h).

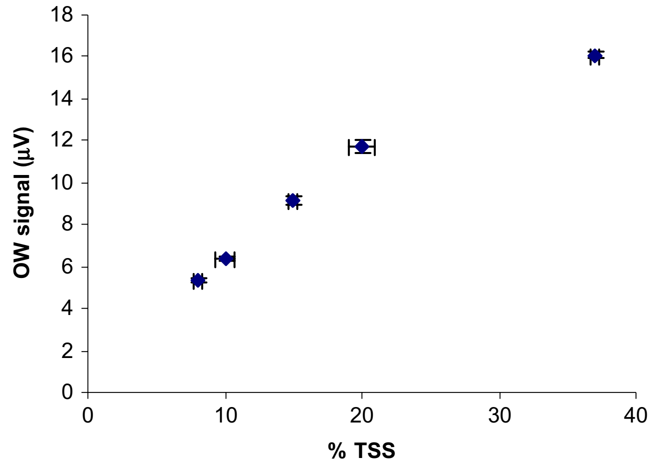

Fig. 2. Magnitude of the OW signal (at 8.3 Hz) as a function of TSS content. The samples with varying TSS content (8, 10, 15, and 20%) were obtained by diluting the triple concentrated tomato paste (TSS = 37%) with water.

Results

The main objective of the study was to explore the dependence between the magnitude of OW signal and the red color of the tomato-based products. The first test performed included a study of a triple concentrated paste (TSS, originally 37%) that was mixed with sufficient amount of distilled water to reduce dry matter content and thereby also TSS (lycopene is not soluble in water) to 20, 15, 10, and 8%. The outcome of OW experiment performed at 8.3 Hz using 1.75 mW LED power shows (Figure 2) a proportionality between the magnitude of the OW signal and the TSS: diluted samples produce lower OW signals than undiluted paste. At low TSS values linearity is clearly observed. The departure from the straight line observed in a case of undiluted sample is likely a result of the saturation ($\beta_\lambda\mu > 1$) of the signal at the highest TSS level. Under the given experimental conditions, the extent of reproducibility of OW studies was typically 2–3% of the measured value, as compared to 3% achieved in Brix measurements.

The conclusions stated above were confirmed by another LED-OW experiment performed at 8.3 Hz with 1.75 mW LED power on three different tomato-based products. Their TSS was reduced to 12% by dilution with distilled water. As expected, products characterized by similar TSS values were also found to produce OW signals of comparable strength.

Figure 3 shows the values of product 100*$\beta\mu$ calculated (Eq. (2)) from OW signals obtained in LED-OW experiments (8.3 Hz and 1.75 mW LED power) performed on five tomato-based samples and black ink, plotted versus index *L** acquired via colorimetric measurements on the same five products. The horizontal and vertical error bars in Figure 3 correspond to 1 standard deviation in LED-OW and colorimetric measurements. The "calibration" curve constructed from the outcome of LED-OW studies

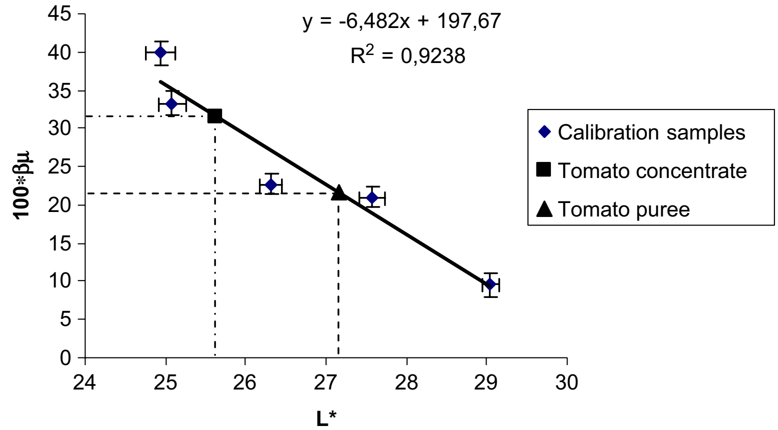

Fig. 3. Values (rhombs) of 100*$\beta\mu$ obtained in LED-OW study (at 8.3 Hz and 1.75 mW LED power) plotted as a function of index L^* (from the colorimetric measurements) for five tomato-based products. Standard deviations in the colorimetric and LED-OW measurements are being specified. This calibration curve was then used to determine L^* for the two test samples, i.e., tomato concentrate (square) and tomato puree (triangle) from the results of the LED-OW measurements.

performed on five calibrating samples (see rhombs in Figure 3) suggests a decrease of 100*$\beta\mu$ with increasing L^* values. Commodity with lower lycopene content (such as tomato juice) is characterized by a higher L^* value, whereas the products with higher lycopene content (e.g., tomato paste) exhibit lower L^* values. This observation is consistent with the expected result—at a given modulation frequency, the presence of more red pigment (lycopene) in the product implies a stronger absorption and hence higher 100*$\beta\mu$ value. On the other hand, for instruments such as colorimeter, more lycopene in the sample implies the presence of more absorbing material and therefore less transparency which, in turn, is associated with lower L^* value ($L = 0$ and $L = 100$ are associated with black and white, respectively).

The calibration curve shown in Figure 3 can be used to predict, based on the results of LED-OW measurements, L^* value for a test sample. For a tomato pureé (see triangle in Figure 3), the 100*$\beta\mu$ obtained in LED-OW experiment (8.3 Hz and 1.75 mW) is 21.675. Substituting this into the equation for the straight line shown in Figure 3 gives $L^* = 27.151$, which is close to a measured L^* value ($L^* = 26.656$). The percentile difference between calculated and measured values for L^* is 1.8%. For the tomato concentrate (square in Figure 3) that contains a larger amount of red pigment, one has 100*$\beta\mu$ = 31.594, from which $L^* = 25.621$ as compared to $L^* = 24.944$ determined by colorimetric experiment. In this case, the percentile difference between calculated and measured values is somewhat higher and amounts to $L^* = 2.8\%$.

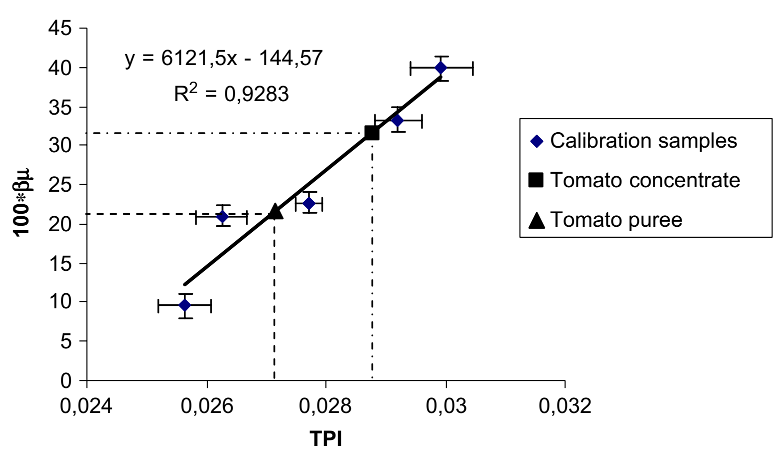

Fig. 4. Values (rhombs) of 100*$\beta\mu$ obtained in the LED-OW study (at 8.3 Hz and 1.75 mW LED power) plotted as a function of tomato paste index TPI calculated (Eq. (3)) from colorimetric measurements performed on five tomato-based products. Standard deviations for TPI and 100*$\beta\mu$ are also specified. This calibration curve was then used to determine TPI for the two test samples, i.e., tomato concentrate (square) and tomato puree (triangle) from the experimental data obtained in LED-OW measurements.

Another closely explored relationship in this study was that between $\beta\mu$ and the so-called tomato paste index (TPI) defined as [9]:

$$\mathrm{TPI} = \frac{a^*}{L^*\sqrt{a^{*2} + b^{*2}}} \quad (3)$$

Figure 4 displays the functional dependence between 100*$\beta\mu$ obtained in the LED-OW experiment (8.3 Hz and 1.75 mW LED power) and TPI computed on the basis of colorimetric data. The results were obtained from the same five tomato-based samples (rhombs in Figure 4) that were also used to construct the calibration curve in Figure 3. Error bars in Figures 3 and 4 indicate the extent of scatter observed in LED-OW and colorimetric measurements. As for colorimetry, five independent measurements for each sample were made and standard deviations for L^* and TPI were calculated. In relation to OW data, the error shown is the best-combined estimate of the five repeated series of measurements (multiple loads).

Again, one can use the calibration curve in Figure 4 to predict, based on the outcome of LED-OW measurements, the TPI of the test sample. For tomato pureé (triangle in Figure 4), the 100*$\beta\mu$ value obtained by LED-OW experiment is 21.675. For this $\beta\mu$, the equation 100*$\beta\mu$ = 6121.5TPI − 144.57 gives TPI = 0.02715. This TPI value is close to 0.0268 acquired for the same sample in colorimetric measurement of L^*, a^*, and b^*. The percentile difference between the calculated and measured TPI values is 1.3%. The same procedure was repeated for tomato concentrate (square in Figure 4). For experimentally obtained 100*$\beta\mu$ = 31.594, the corresponding TPI calculated from the equation representing the calibration line is 0.0288, as compared to 0.0290 determined experimentally. The percentile difference between calculated and measured TPI values is only 0.8%.

Conclusion

The concept of OW detector combined with a low-cost LED radiation source was applied for the first time to assess the red color of seven tomato-based products. The LED-OW approach determines the color of these commodities by sensing the heat generated in the same products as a result of absorption after exposing them to a periodically modulated radiation of appropriate wavelength. The LED-OW assessment of color is completely objective. The measurements were carried out at 8.3 Hz using 1.75 mW of LED radiation; experimental conditions were set up so as to satisfy the condition $\mu < 1/\beta_\lambda < L$. Bearing in mind the large range of samples studied here, the linear correlation (R^2 = 0.9238) found between 100*$\beta\mu$ obtained by LED-OW measurements and index L^* attained by colorimetric studies is reasonably high. The calibration line constructed with data collected in the LED-OW measurements performed on the five tomato-based samples allowed the accurate prediction of L^* index for the two test samples. Likewise, under similar experimental conditions, a linear relationship (R^2 = 0.9238) between 100*$\beta\mu$ obtained by LED-OW measurements and TPI (derived from colorimetric measurements of indices a^*, b^*, and L^*) was uniquely established. Again, as in the case of L^*, the calibration line allowed TPI for the two test samples to be predicted at a high level of precision (about 1%).

To the best of our knowledge, this study represents the first attempt of its kind. The results provide the evidence that red color (confined within the colorimetric parameters L^* and TPI) of tomato-based products can be readily assessed from LED-OW measurements assuming the calibration curves are known. Inversely, it should also be possible to estimate the concentration of the red pigment in tomato-based products from colorimetric measurements. However, before this can be accomplished, it is necessary to construct the new calibration curve showing 100*$\beta\mu$ obtained (at 8.3 Hz and 1.75 mW LED power) via LED-OW measurement as a function of total lycopene content [determined independently either by high-performance liquid chromatography (HPLC) or spectrophotometric studies]. Good thermal contact between the sample and sapphire disk is absolutely necessary. Because of the speedy response, intrinsic simplicity, low cost, and zero requirement for pretreatment of samples, determination of red pigment in such manner will be of a substantial value to the food industry. Attempts are now underway to explore other potentially useful relationships between the data obtained by LED-OW method and the combinations of colorimetric indices [10–12].

In the LED-OW experiment described here, the power of LED reaching the tomato-based sample under investigation was only 1.75 mW. The more efficient coupling of LED radiation into a fiber is likely to result in a substantially higher power density and hence also enhanced sensitivity of the LED-OW technique. Furthermore, emerging powerful LEDs with considerably improved spatial characteristics are expected to further boost the sensitivity.

In principle, the LED-OW concept is not limited to detection of the red color of tomato-based products. Instead, it is also applicable to the assessment of other colors provided, however, that requirement for the spectral coincidence between the emission of the source and the absorption of species under investigation is being met. A good example is the assessment of yellow margarine color; the experiment is currently in progress.

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