



Nonradiative analysis of adulteration in coconut oil by thermal lens technique

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Received: 17 October 2018 / Accepted: 25 May 2019 / Published online: 1 June 2019
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Abstract

Adulteration of food is a serious issue that impacts personal and social health. Using highly sensitive and nondestructive single-beam thermal lens technique, the present work analyses the adulteration of edible coconut oil with hazardous paraffin oil. The present study overcomes the limitations with conventional spectroscopic technique, as it employs the photothermal technique for the trace detection of adulterants and nonradiative energy release. Samples prepared with trace amount of paraffin oil in coconut oil were subjected to ultraviolet (UV)–visible spectroscopic characterization. The study reveals that the optical absorption and thermal diffusivity decrease with the increase of the adulterant.

1 Introduction

Food safety is the concern of every society, for food borne illnesses have become very common. The consumption of contaminated food is the main cause of food borne diseases. Adulteration, a form of contamination, refers to the addition of harmful or unwanted substances to food with the intention of profit. This adversely affects the quality and nature of healthy and hygienic food and harms human health leading to various food borne diseases. Hence, food safety and its testing methods have been the focus of the scientific world [1]. Like all food products, edible oils face serious threat of adulteration because of its high cost and demand. With its rich-saturated fatty acids and antioxidants, coconut oil is known for its antifungal, antibacterial, and antiviral properties. The thermal properties of coconut oil, in pure or blended form, make it a suitable candidate as lubricant, transformer oil, and bio-fuel applications [2, 3]. Though coconut oil is commonly adulterated with palm oil and paraffin oil, the latter can induce serious health issues, as it is a mineral oil derived from petroleum [4].

We normally evaluate the quality of food with our sense organs. With the advent of various types of sensors, the

identification and estimation of adulteration have become possible. Various techniques such as Fourier transform infrared (FTIR) [5], Near Infrared (NIR) [6], Raman, and UV–Visible spectroscopic techniques [7–9] are widely used in food science for quality analysis. The changes in composition of the sample due to adulteration have significant effects in the spectral signatures of peaks in the FTIR, NIR, UV–visible, and Raman spectrum. Multivariate data analyzing techniques such as discriminant analysis (DA) and principal component analysis (PCA) are used along with these spectroscopic techniques to quantify and classify the adulterants in edible oils [7, 10]. These conventional spectroscopic techniques have the inherent disadvantage of scattering and reflection of incident radiations that can cause errors in the measurement [11–13]. Therefore, sensitive and cost-effective techniques are to be developed to overcome the limitations of conventional spectroscopic techniques [14, 15]. Photothermal phenomena offer several nondestructive techniques for the thermal and optical characterization of a material [12, 16–18].

Photothermal methods have emerged as a sensitive and nondestructive tool for material characterizations with the advent of lasers and detection systems. Since only the absorbed photons contribute to the photothermal signal, these techniques offer high sensitivity [19]. Photo-pyroelectric, thermal lens, photoacoustic, and photothermal beam deflection techniques are some among them [20–23]. The ultra-sensitivity (capable of detecting 10^{-6} – 10^{-4} °C) and lesser sample requirement make thermal lens technique suitable for adulteration studies [24–29]. The

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thermal lens technique finds application in reaction kinetics, trace analysis, and absolute quantum yield measurement [17]. The present work explores the nonradiative de-excitation upon photo-excitation in thermal lens technique to analyze the adulteration in coconut oil.

2 Materials and methods

To investigate the adulteration in coconut oil a single-beam thermal lens setup [30] is used, as shown in Fig. 1. The intensity modulated laser beam (TEM₀₀) from an 80 mW He–Cd Laser (Kimmon Koha IK5651R-G)-emitting radiations at 442 nm is used as the source. The laser beam is focused by a convex lens of 20 cm focal length. An electro-mechanical chopper (Stanford Research Systems SR530 4–3700 Hz) operating at a low frequency of 4 Hz is used to modulate the laser beam. The sample taken in a quartz cuvette (1 × 1 × 4.5 cm³) is placed at the focal plane [30]. The molecules of the medium absorb the incident optical power and get excited. The nonradiative de-excitation of these molecules results in the liberation of energy in the form of heat which induces local variation in the refractive index. This region acts like a concave lens that diverges the laser beam and reduces the intensity at the beam center. The reduction in the beam center intensity with time is given by [31, 32]

$$I(t) = I(0) \left[1 - \theta \left(1 + \frac{t_c}{2t} \right)^{-1} + \frac{1}{2} \theta^2 \left(1 + \frac{t_c}{2t} \right)^{-2} \right]^{-1}, \quad (1)$$

where $I(t)$ and $I(0)$ represent the intensity at time t and $t=0$, respectively, t_c represents the characteristic time constant, and θ represents a function of $I(0)$ and $I(\infty)$ (intensity at steady state). The characteristic time constant gives the time taken for the formation of the thermal concave lens. This time constant is related to the thermal property—thermal

diffusivity (D)—of the sample, which is a measure of the transient heat flow, and the radius of the laser beam at the beam waist (ω) through the relation [31]:

$$D = \frac{\omega^2}{4t_c}. \quad (2)$$

The beam radius measured from the beam profile yielded the value 0.11 mm which is used for calculating the D value.

The parameter θ is related to the optical energy (P_{th}) at the wavelength λ_L , the change in refractive index ‘ n ’ with temperature ‘ T ’ and the thermal conductivity ‘ k ’ through the relation [33]:

$$\theta = \frac{P_{th} \frac{dn}{dT}}{\lambda_L k}. \quad (3)$$

The parameter θ can also be calculated by the equation $\theta = 1 - (1 + 2I)^{\frac{1}{2}}$, where $I = \frac{I(0) - I(\infty)}{I(\infty)}$ [12, 34].

The self-focusing/defocusing phenomenon occurring in the liquid layer due to the laser beam interaction induces a change in the focal length of the focusing lens. For a liquid medium with refractive index ‘ n ’ and thickness ‘ l ’, the change in focal length ‘ Δf ’ of a focusing lens with focal length ‘ f ’ in the air is given by

$$\Delta f = l \left(1 - \frac{f}{\sqrt{n^2 f^2 + (n^2 - 1) r^2}} \right), \quad (4)$$

where ‘ r ’ is the radius of the laser beam incident on the focusing lens.

Since $r \ll f$ for the thermal lens experiment, the above equation can be simplified as

$$\Delta f = l \left(1 - \frac{1}{n} \right). \quad (5)$$

This is the correction to the focal length of the lens [35].

In the present work, the adulterated samples are prepared by adding paraffin oil (1, 2, 3, 4, 5, and 10 ml) to 100 ml pure coconut oil. To understand the nature of optical energy absorption, the UV–visible spectrum of the samples is recorded in PerkinElmer lambda 950 UV/Vis/NIR spectrometer. To determine the thermal diffusivity of the sample, the time-dependent intensity change at the beam center is fed to a sensitive photodiode using a multimode optical fiber. The detector output is analyzed using a 500 MHz digital storage oscilloscope (DSO) (Teledyne Lecroy–Wavesurfer 3054). The thermal lens signal thus recorded is curve fitted using Eq. (1) to obtain the parameters t_c and θ from which the thermal diffusivity of the sample is calculated using Eq. (2) [36]. The thermal diffusivity values are calculated from each of

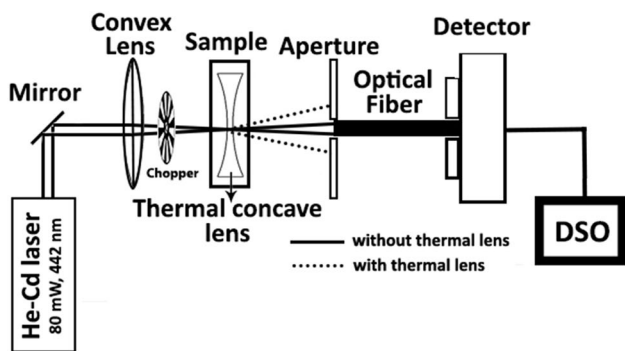


Fig. 1 Schematic representation of single-beam thermal lens setup

the six consecutive thermal lens signal obtained in the DSO and the whole process is repeated twice with the two separately prepared identical samples. Then, the average value is taken as the thermal diffusivity of the sample. The standard error in the thermal diffusivity value is $\pm 0.01 \times 10^{-7} \text{ m}^2/\text{s}$. Hence, all the thermal diffusivity values are within the error limit.

3 Results and discussion

To understand the adulteration in coconut oil by liquid paraffin oil, the highly sensitive thermal lens technique has been employed in the present work. Even trace amount of adulterant can alter the physical property of the substance. Here, coconut oil is adulterated with paraffin oil in trace amount and the variation in the thermal property of coconut oil is analyzed. Adulterants affect thermal diffusivity, which is a measure of the thermal inertia of a sample. The

thermal diffusivity values of coconut oil with less than 10% of paraffin oil measured by the single-beam thermal lens technique are shown in Fig. 2. From Fig. 2, it can be seen that the thermal diffusivity decreases with greater quantity of paraffin oil. In other words, the propagation of heat energy through the medium decreases with the increase of paraffin oil. It is well known that liquid paraffin is an excellent material for thermal energy storage [37]. The study reveals that coconut oil, which contains more than 99.06% of fatty acids [38], loses its heat conducting property upon adulteration with paraffin oil, which is a mixture of alkanes [39, 40]. Thus, the amount of alkane in the mixture can be taken as an indicator of the level of adulteration.

Since the thermal lens technique depends on the optical energy absorbed, a study of photon absorption with wavelength is essential. Figure 3a shows the UV visible absorption spectrum of pure coconut oil and paraffin oil. From Fig. 3a, it can be seen that the difference in absorbance is only up to 450 nm. Since the two oils exhibit almost the same optical behavior in the visible region, it is difficult to make a quick analysis. At the wavelength of the laser used in the thermal lens setup, the samples show a difference in absorbance. From Fig. 3b, the variation of absorbance at 442 nm with the quantity of paraffin oil shows that the increase in the adulteration level results in hypochromic shift.

From Eq. (3), it can be seen that the value of θ varies with the optical power absorbed and the temperature-dependent refractive index. The plot of magnitude of θ vs. quantity of paraffin oil, shown in Fig. 4, also exhibits a decrease with the increase in quantity of paraffin oil. Since only the absorbed photons contribute to the thermal lens signal through nonradiative de-excitation, this technique can offer higher sensitivity in tracing the adulterant.

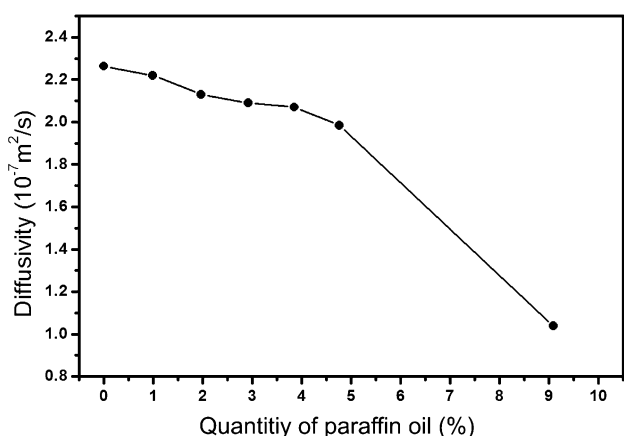


Fig. 2 Variation in diffusivity with the quantity of paraffin oil

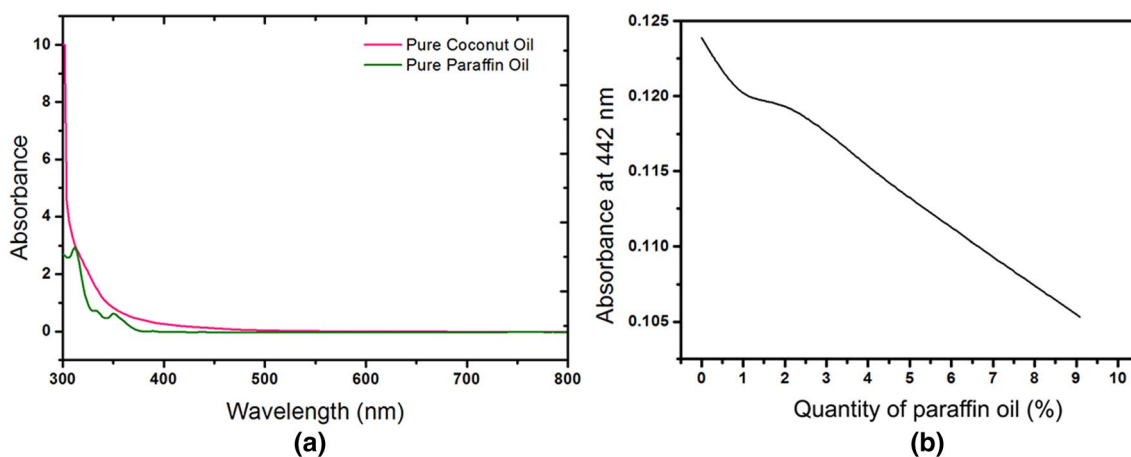


Fig. 3 a Absorption spectra of pure coconut oil and paraffin oil. b Variation of absorbance at 442 nm with quantity of paraffin oil

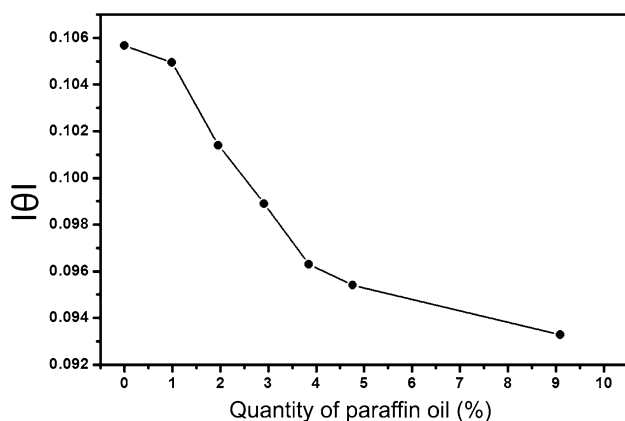


Fig. 4 Variation of magnitude of parameter θ with quantity of paraffin oil

4 Conclusion

Food adulteration and food borne diseases have emerged as a serious social problem to be addressed by the scientific community. The present work is an attempt to analyze adulterated coconut oil through thermal lens technique. The heat generated as a result of nonradiative de-excitation has been indirectly employed in identifying the level of adulteration. The coconut oil samples are prepared with trace amount of paraffin oil that is commonly available in the market. The samples are subjected to UV–visible spectroscopic characterization which shows a hypochromic shift with an increase in the quantity of paraffin oil. The thermal lens study shows that the thermal diffusivity decreases with the level of adulteration.

Acknowledgements Vimal Raj is grateful to the Council of Scientific and Industrial Research (India) for research fellowship.

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