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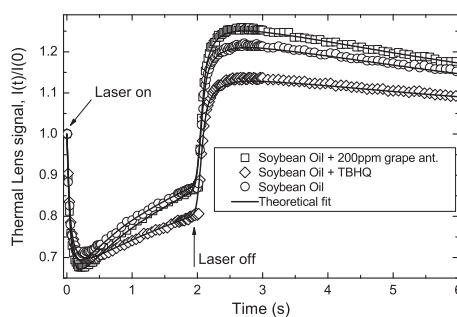
Investigation into photostability of soybean oils by thermal lens spectroscopy

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HIGHLIGHTS

- We propose a time-resolved thermal lens method to analyze photostability of edible oils.
- Photoreaction, heat and mass diffusions are considered during local laser excitation.
- Photoreaction cross-section is measured.
- Synthetic antioxidant appears to be much more efficient than the natural antioxidant.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessment of photochemical stability is essential for evaluating quality and the shelf life of vegetable oils, which are very important aspects of marketing and human health. Most of conventional methods used to investigate oxidative stability requires long time experimental procedures with high consumption of chemical inputs for the preparation or extraction of sample compounds. In this work we propose a time-resolved thermal lens method to analyze photostability of edible oils by quantitative measurement of photoreaction cross-section. An all-numerical routine is employed to solve a complex theoretical problem involving photochemical reaction, thermal lens effect, and mass diffusion during local laser excitation. The photostability of pure oil and oils with natural and synthetic antioxidants is investigated. The thermal lens results are compared with those obtained by conventional methods, and a complete set of physical properties of the samples is presented.

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Introduction

Food industry has been continuously focusing on the improvement and development of crops. Several strategies have been applied to improve nutritional values of plants and to determine ideal conditions for storage and commercialization. For instance, the physico-chemical stability is an important parameter to ratify

the functionality, quality and shelf life of a commercialized product [1,2].

Edible oils are known to be chemically unstable and may go through degradation processes when undergoing extraction processes, contacting with oxygen, experiencing temperature variations and exposure to ultraviolet and visible radiation. Furthermore, the occurrence of photo-oxidation generates toxic compounds, such as peroxides [3–5], leading to the production of off-flavors and odors, as well as discoloration, which may affect product quality. As a result, synthetic antioxidants, such as

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tert-butylhydroquinone (TBHQ), are used to postpone the initiation or decrease the rate of oxidation. However, toxic and carcinogenic effects of synthetic antioxidants in animals and humans have been observed [6]. Therefore, the photostability is a parameter which has been adopted to verify the quality and the shelf life of vegetable oils, especially those intended for human and animal consumption.

The analysis of oil photostability has been performed by several experimental techniques [7–11], although it is mostly accessed by accelerated storage testing light bulb method [12,13]. However, most of these methods requires a long time procedure for the experimental investigation, which may take weeks or even months. Moreover, these techniques use high consumption of chemical inputs for the preparation or extraction of sample compounds. Therefore, the application of faster methods without chemical inputs may bring advances in this area.

Photothermal methods are known to be very sensitive and fast tools for material characterization. With the interests in the investigation into photostability, time-resolved thermal lens (TL) spectroscopy has been very successful in determining photophysical parameters and kinetics of photochemical reactions in a variety of solutions [14–20]. TL signal results from changes in the refractive index in the sample, which is generated by a heating produced by optical absorption of an excitation laser. The signal is proportional to the optical absorption coefficient of the sample and, therefore, sensitive to changes in the concentration $C(r, t)$ of the absorbing species. The method was applied to examining photoinduced chemical reactions in aqueous solutions [21–25] and hydrocarbon fuels [26]. The theoretical description of the TL effect employed in those studies relied on the time- and spatial-dependence of the optical absorption coefficient with the changes by optical bleaching and mass diffusion within the excited volume of the sample. Although quantitative agreement was observed between theory and experiments, the analytical expression used was obtained under approximations for the spatial distribution of the concentration. The solution for the concentration of species was determined by assuming a spatial average of each term of the concentration equation as $C(t) = \langle C(r, t) \rangle_r$, resulting in a simple form for the effective rate equation, $dC(t)/dt = -K_T C(t)$. The total reaction rate K_T represents the averaged rates of photobleaching and molecular diffusion. The absorption coefficient is written in terms of the equilibrium ratio between the molar absorptivities of the products and reactants, ϵ , in the illuminated volume by $\beta(t) = \beta[(1 - \epsilon)C_R(r, t) + \epsilon]$ [27]. β is the absorption coefficient at $t = 0$.

For complex systems such as the oils investigated in this research, these approximations may no longer be valid, and require general solutions for both concentration and heat conduction equations, which may end up with numerical solutions. In this work, we solve these equations numerically considering real boundary conditions and apply this theory to quantify photophysical parameters of edible oils. Photostability of vegetable oils are analyzed under exposure to UV light using the TL method. The theoretical model and experimental results are in excellent agreement, and physico-chemical properties are quantitatively determined. Natural antioxidant (essential grape seed oil) is compared with synthetic antioxidant (TBHQ) in soybean oils in terms of the antioxidation efficiency. The photoreaction cross-section is obtained from regression analysis, and the results reveal that synthetic antioxidant are more efficient compared with natural antioxidants.

Theory

The well-known mode-mismatched TL method [28] is used in this work. In this configuration, the sample is excited and probed

by TEM₀₀ Gaussian laser beams of different radii in the sample. A temperature gradient is produced in the sample by optical absorption of the excitation laser, resulting in a refractive index gradient and then in a lens-like optical element. The focusing or defocusing effect of the lens-like optical element on the probe beam is detected by measuring the time-dependent intensity variation at the probe beam center in a far-field region.

When the excitation laser induces a chemical reaction in a photoreacting solution, the spatial concentration distribution of the absorbing species is modified in the excited volume, generating a mass (species concentration) gradient. As a result, a time- and spatially-dependent absorption coefficient distribution is formed, which alters the TL signal accordingly. The photoreaction process can be assumed to be first-order or of pseudo first-order, and the time and spatial dependence of the species concentration is given by the solution of the following partial differential equation

$$\frac{\partial}{\partial t} C(r, t) - D_m \nabla^2 C(r, t) = -\theta_R e^{-2r^2/w_e^2} C(r, t) [1 - H(t - \xi)], \quad (1)$$

where $\theta_R = 2P\sigma/(\pi w_e^2 E_e)$, $E_e = hc/\lambda_e$ is the excitation energy, σ is the photoreaction cross-section, h is Planck's constant, D_m is the mass diffusion coefficient and w_e and P are the radius and the optical power of the excitation laser, respectively. $H(x)$ is the HeavisideTheta function and accounts for turning the source term in the differential equation on (laser-on; $\xi > t$) and off (laser-off; $\xi < t$). The diffusion term in Eq. (1) accounts for the movement of photochemically modified species from outside to inside the excited volume by mass diffusion. It is assumed that the drift of particles by the thermal gradient (Soret effect) and convection effects do not contribute to the concentration changes. The term on the right side of Eq. (1) accounts for the distorted Gaussian shape of the initial energy density of the excited state because of photodegradation [20].

The time- and spatial-dependent optical absorption coefficient affects directly the temperature distribution in the sample and consequently the TL signal. Assuming an isotropic and weakly absorbing material, the distribution of the temperature rise is described by the differential equation for heat conduction

$$\frac{\partial}{\partial t} T(r, t) - D_{th} \nabla^2 T(r, t) = \theta_{th} [(1 - \epsilon)C(r, t) + \epsilon] e^{-2r^2/w_e^2} [1 - H(t - \xi)], \quad (2)$$

where $D_{th} = k/(\rho C_p)$ is the thermal diffusivity; k is the thermal conductivity; ρ is the mass density, and C_p is the specific heat of the sample. $\theta_{th} = 2P\beta/(\rho C_p \pi w_e^2)$, where β is the optical absorption coefficient of the reactants.

The distribution of the temperature represented by Eq. (2) changes the refractive index accordingly. The wavefront of the probe beam is slightly distorted when it propagates through the illuminated volume of the liquid sample. This distortion can be expressed with an additional phase shift to the probe beam by $\Phi(r, t) = (2\pi/\lambda_p)L [n(r, t) - n(0, t)]$ [22,23], where $n(r, t) = n_0 + (dn/dT)T(r, t) + (dn/dC)C(r, t)$, n_0 is the refractive index, L is the sample thickness, dn/dT and dn/dC are the refractive index temperature and concentration coefficients, respectively, at the probe beam wavelength λ_p . The phase shift can be written in terms of $\Phi(r, t) = \theta_T [T(r, t) - T(0, t)] + \theta_C [C(r, t) - C(0, t)]$, with $\theta_T = (2\pi/\lambda_p)L(dn/dT)$ and $\theta_C = (2\pi/\lambda_p)L(dn/dC)$.

After emerging from the sample, the probe beam propagates to the plane of the detector and the intensity of the probe beam center is calculated using Fresnel diffraction theory [28] by

$$I(t) = \left| \int_0^\infty \frac{2r}{w_p^2} \exp \left[-(1 + iV) \frac{r^2}{w_p^2} - i\Phi(r, t) \right] dr \right|^2, \quad (3)$$

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