STUDY ON THE EFFECT OF RE-HEATING FRYING OILS BY USING LASER INDUCED FLUORESCENCE TECHNIQUE

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Abstract: The aim of this research work is to study the effect of re-heating of some food oils commonly used for cooking and frying in Sudan. Corn and cottonseed oils have been chosen for this purpose. The Laser Induced Fluorescence (LIF) technique is adopted in this study. According to the LIF spectra patterns the oils can be classified into two types, where corn LIF spectrum showed one single peak while the cottonseed LIF spectrum exhibited two peaks. The spectra were repeatedly recorded before and after boiling the oils in a period of five days. The results revealed that re-heating the oils several times changes their chemical structures as well as their physical properties.

Keywords: LIF, frying oils, corn, cottonseed, re-heating, fatty acids, Cholesterol.

1. Introduction

There is a general confusion about the process of reusing cooking and frying oils many times. Is it true that re-heating oils can change their properties and thus lead to health problems? In order to answer this and to eliminate any ambiguity regarding whether or not a negative health impact occurs, two of the commonly used frying oils in Sudan were investigated using the LIF technique.

It is worth to mention that the LIF technique is a powerful tool commonly used in studying chlorophyll related subjects; these include chlorophyll concentration, crop yield assessment, relation to photosynthesis, nitrogen status detection, and estimation of green area index [1-5]. The technique is also utilized in pigment analysis [6]. Furthermore, it is also employed as a tool in determining the fatty acids in fish oil [7]. In this research work the method is adopted to examine the effect of re-heating cocking and frying oils.

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2. Samples under study

Oils are classified as liquid fats. Seeds are the source of the most of the commercial oils; they are very rich source of energy, enabling the body to absorb certain vitamins (A, D, E, and K). High temperatures affect the omega3 fatty acids and damaged oils. Hydrogenated fats increase the *bad* LDL cholesterol and decrease the *good* HDL cholesterol [8].The elements contained in the fatty acids are: Carbon (C), Hydrogen (H) and Oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end [9]. Accordingly, our discussion will be limited to these elements.

The corn oil extracted from corn seed is rich in double unsaturated fatty acid, which is an essential fatty acid. Corn oil is odorless, has very little taste, and has high smoke point, which makes it good for frying [10].

Cottonseed oil, extracted from cotton seeds, is used in some margarine and is generally considered as the most insecticidal of the vegetable oils. Many commercial products available contain cottonseed oil.

3. Experimental Work

The LIF spectrometer employed in this work is available in the Laser physics lab, department of physics, faculty of science, university of Khartoum.

The laser used in this study is blue diode laser model NLHV500A fabricated by Nichia Corporation, Japan, with the following characteristics: Wavelength = 396 nm, Threshold (th) = 29.3 mA, Operating current (I0p) = 32.7 mA, Operating power (P0) = 5 mW. The spectrometer is connected to a PC, the data were transferred through the ocean optics software into spectra on the PC screen.

4. Fluorescence Setup

The diode laser device emits laser with a compatible wavelength to excite the molecules (atoms) of the sample. The Laser is focused by a lens to the beam splitter which splits the beam into two branches one goes to the monochrometer as a reference and the other to the sample via the fiber where a coupling lens system couples the laser spot (beam) into the fiber. The fluorescence signal returns back from the sample through the fiber to the beam splitter and a filter. The filter cuts the undesirable wavelength and allows the fluorescence beam. Another fiber optics takes the fluorescence signal to the monochrometer then to the analyzer.

5. Results and Discussion

The LIF spectrometer is calibrated using Helium - Neon (HeNe) laser source (632 nm). The fiber optics positioned in front of the laser path. The recorded spectrum showed a sharp

intense peak of the He Ne laser source at the value of 631.7 nm, in a good agreement with the theoretical value.

5.1. LIF Spectra of the Oils Samples:

The LIF spectra of the two oils samples were recorded at room temperature. These are illustrated in Figs. (1, 2).

The LIF spectrum of the corn oil recorded before heating the oil is shown in Fig.(1). One peak was observed centered at 478.50 nm wave length with peak intensity 1848.00 arbitrary units, (a.u.). Also, note that the laser source signal is appeared as a small peak at 406.77 nm wavelength with intensity 141.50 (a.u.). This peak has been considered as a reference for further calculations of peak intensities ratio. To assign an element to the observed wavelength an atomic spectra database was approached.





Fig.(1): Shows the LIF spectrum of the corn oil measured at room temperature before heating

Fig.(2): Shows the LIF spectrum of the cottonseed oil measured at room temperature before heating

This is provided by the National Institute of Standards and Technology (NIST), [11]. The suggested element that responsible for the central peak excited by the laser was found to be oxygen, in accordance with fatty acids compound.

The LIF spectrum of the cottonseed, Fig.(2) contained two well resolved signals in addition to the laser source signal. The first peak (with short wavelength) is more broaden and centered at 502.02 nm with intensity of 1125.00 a.u. The second sharp and more intense peak is positioned at 673.40 nm, the intensity was found to be 3232.00 a.u. the suggested elements for these two wavelengths are oxygen and carbon, respectively.

In order to examine the effect of re-heating oils, the measurements were continued for further five days. The procedure followed in this research work was as follows: First, the LIF

spectrum of the oil sample was recorded at room temperature before heating. Second, another LIF spectrum was recorded after the oil is heated to its boiling temperature and cooled back to room temperature again.

The next group of spectra, Figs.(3, 4), illustrates the LIF spectra of oil samples before and after the process of re-heating. For the seek of comparison we placed the original spectrum of each oil sample in the same figure.



Fig.(3): Shows the LIF spectra of the Corn oil at the first day before heating (dotted line) and at the fifth day after heating (solid line)

The LIF spectra suggested that the examined oils can be, according to the number of peaks involved, categorized into two types. Corn oil showed single broad peak at 505.32 nm, with peak intensity 890.00 a.u., Fig.(3). While cottonseed oil, Fig.(4), exhibited one single peak at 503.25 nm with intensity 1871.00 a.u. Note that while the process of re-heating was repeated, remarkable irreversible changes in the LIF spectra appeared. The long wavelength's peak (673.40 nm), is dramatically disappeared upon re-heating the oil, and while the short wavelength peak remained with intensity being increased compared to the original.

It is clear that from the LIF spectra of the corn oil the peak intensity is decreased with time, i.e. with the number of times the oil is re-heated. This suggests that a change in the chemical compound of the oil has been occurred. Recalling the database adopted from the NIST, this implies that the concentration of the element (oxygen) which is responsible for this wavelength is decreased. Regarding the cottonseed oil, Fig.(4), the long wave peak is completely disappeared after five days, i.e. when the oil is re-heated five times to its boiling temperature.



Fig.(4): Shows the LIF spectra of the Cottonseed oil at the first day before heating (dotted line) and at the fifth day after heating (solid line)

These changes in the LIF spectra of the oils samples studied in this research work suggest corresponding changes in the elements concentration.

5.2. Variation of the area under the curve:

Furthermore, an additional work was performed on the peak intensities of the LIF spectra. The variations in the peak intensities were calculated within the period of the experiment. These are shown in Fig.(5). The LIF measurements were taken at room temperature. The graph shows the data of the samples as grouped for the period of measurements. The vertical axis represents the peak intensities ratio. The ratio is calculated relative to the reference laser peak intensity. According to the graph, the intensities of the sample oils were clearly decreased during the thermal treatment. These results reflect changes in the oils compound.

The first peak has been considered as the main peak of the LIF spectrum for the measurements of the area under the curve, (auc). The parameters obtained by fitting the LIF spectra by using standard procedures [12, 13], were calculated and the parameters obtained are given in Table (1).



Fig.(5): Shows the peak intensity ratios for the corn and the cottonseed oils followed in five days. The ratio is calculated relative to the laser peak intensity

It was also noticed, as mentioned before, the central LIF peak of the corn oil is much decreased by the repeated process of re-heating, in contrast to the cottonseed LIF peak which is permanently disappeared. This suggests that re-heating oils more than one time produces great change in the basic structure of the oils. Previously, we studied the physical properties of frying oils when re-heated to their boiling temperatures, [14]. The results obtained showed that there was a changed in the refractive index, the viscosity, the density and the specific heat of the oils when subjected to a repeated process of re-heating. The results confirmed that cooking at high temperatures will alter the thermal and the optical properties of the oils. Some researchers deduced that re-heating oils produces oxidation and causes bond break of the fatty acids.

The oils that exposed to heat and light for long times are susceptible to oxidation reduction and perhaps change in their tastes. Therefore, cooking at high temperatures can change oils compositions; the heat damages the fatty acids.

Oil	A [Arb.]	x _c [nm]	FWHM	yo	σ	\mathbf{R}^2
			[nm]		[nm]	
Corn 01*	108681	479.63	71.51	125.33	30.36	0.92
	±935	±0.27	±0.65	±2.77	±0.28	
Corn	92283	524.23	114.22	107.76	48.49	0.95
15**	±635	±0.31	±0.79	±1.49	±0.33	
Cotton-	61241	673.50	20.28	307.62	08.61	0.65
seed 01	±1225	±0.19	±0.46	±7.03	±0.19	
Cotton-	199546	523.61	111.02	118.59	47.13±	0.95
seed 15	±1351	±0.30	±0.76	±3.22	0.32	

Table (1): Curve fitting results of the LIF spectra of the sample oils.

A: Gaussian area, x_c : Peak centre, FWHM: Full Width at Half Maximum, y_o : Base line offset, σ : Standard Deviation.

* 01 = Fitting parameters for the oil sample in the first day before heating.

**15 = Fitting parameters for the oil sample in the fifth day after heating

6. Conclusion

In this research work we examined the effect of re-heating the corn and cottonseed oils that commonly used in cooking and frying. We used the Laser Induced Fluorescence (LIF) technique. The results deduced from this research confirmed that cooking at high temperatures will alter the properties of the oils, if not damaged them. The LIF spectra of the thermally treated oils changed dramatically when compared with the raw oils. This reflects a change in the chemical structures of the oils. Also one concluded that the concentration of some of the basic elements that constitute the oil such as oxygen and carbon has been noticeably changed.

The recommendation drawn from this study is that; frying oils must not be used more than one time, since their properties will be changed. Repetition of re-heating oils to their boiling temperatures will damage them. The chemical structures will be distorted implying a possibility of changing the oils into harmful substances.

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