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# Edible Oil Deterioration Analysis via. Optochemical Spectrum Analyzer

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## Abstract

*The kinetic reaction of reused cooking oil was studied for the present work. The kinetic reaction of reused sunflower oil (auto-oxidation) is obtained in terms of variation of absorption coefficient of unexposed sunflower oil as 0.05 similarly for exposed sunflower oil as 0.075. At room temperature, the optimum intensity obtained from optical absorption spectroscopy study is 0.267 for unexposed sunflower oil and 0.194 for exposed sunflower oil. However, the result indicated that FTIR spectroscopy is accurate and precise enough for such determination. Free fatty acid (FFA) % = 26, acid % ~ 53 and safonication % ~ 192 get reduced in exposed oil was investigated.*

**Keywords:** Friction; oxidation; Sunflower oil; Vegetable oil.

## Introduction

Fried oil produces undesirable constituents that may cause health hazards [1-8]. Lipid oxidation is one of the important processes in deterioration reaction. It is initiated by various factors such as light, elevated temperature, oxygen and moisture. During process, the oils are subjected to thermal oxidation, polymerization and hydrolysis, which affect on flavour, colour and chemical structure of the processed oil. This is more admissible at seashore region [9-10].

Deteriorated fried oil generally affects the free fatty acid level percentage (FFA %), colour and the polarity of the oil. This can be used to discard the fried oil. Traditional chemical methods of oil analysis are commonly time consuming and/or needs the substantial amounts of solvents. Hence the simple, efficient and rapid test is needed in order to capably monitor oil quality. Optical transmission analysis system along with optical absorption spectroscopic method and its chemical structural analysis by Fourier transform infrared (FTIR) is an important tool used for quality control and monitoring process in the food industry. It is less expensive, better in performance and easy to use as compare to other methods. In this study, optical absorption/transmission measurement and the absorption coefficient of unexposed/exposed (virgin/oxidised) sunflower oil are determined. However, its the possibility of using the whole spectra from Fourier transform infrared (FTIR) spectroscopy to classify and differentiate among various intensities of oil rancidity and to discriminate between good, marginal, and unacceptable frying oils was investigated.

## Experimental Work

For present study, the two types of sunflower oils were used: extra virgin sunflower oil and exposed sunflower oil purchased from local supermarkets. The possible antioxidant effect of oregano in oil was tested.

This method measures the oxidative deterioration with the specifically designed absorption/transmission spectrum analyser. Absorption coefficient their special attentions to oxidative deterioration are studied separately. In order to know if deterioration of edible oil can be determined by measurement of absorption/transmission intensity and capacitance, this study used a liquid dielectric constant measurement device adopting the principle of cross capacitance measurement as shown in figure

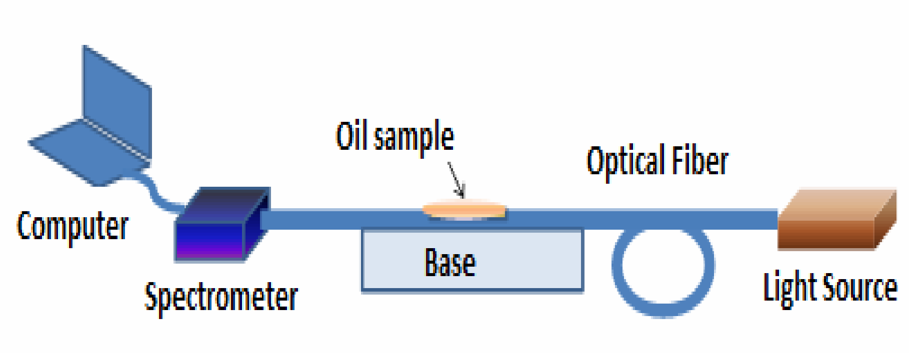


Figure 1. Absorption / transmission spectrum analyser

FTIR spectra were recorded for all the exposed and unexposed samples with a resolution of 4 $cm^{-1}$ and with full scan from 4000 - 400 $cm^{-1}$. The spectrophotometer data also recorded for the entire sample performed at room temperature. The free fatty acid percentage (FFA %), value are obtained by chemical titration method.

## Results and Discussions

### Oxidative effect and analysis

From Figure 2, it observed that the absorption coefficient of unexposed sunflower is ~ 0.27, which is more than the exposed sunflower oil i.e. ~ 0.20. It reveals that the oxidation effect is more at exposed sunflower oil than the virgin oil. There is a major shift in wavelength around 6.78 nm in exposed and unexposed sunflower oil. The maximum intensity for unexposed sunflower oil is at ~ 370.33 nm while for exposed sunflower oil it is at ~ 363.55 nm. It indicates that the exposed sunflower oil is more oxidised and deteriorate than the unexposed sunflower oil. Figure 3 shows the variation in absorption coefficient for exposed and unexposed sunflower oil.

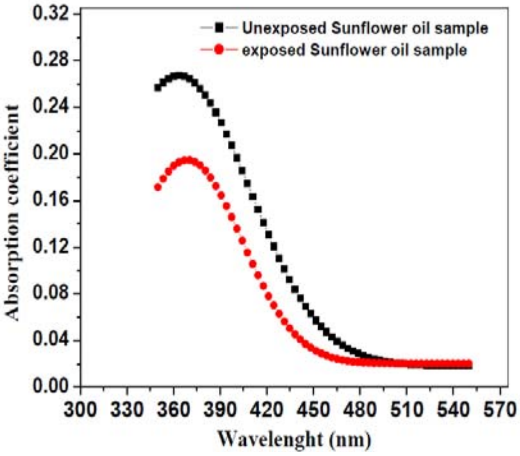
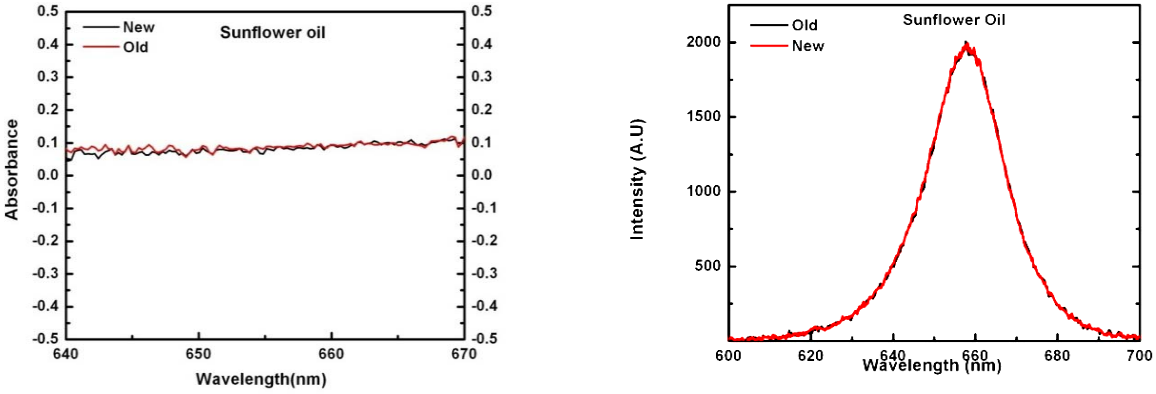


Figure 2. Variation of absorption coefficient with wavelength



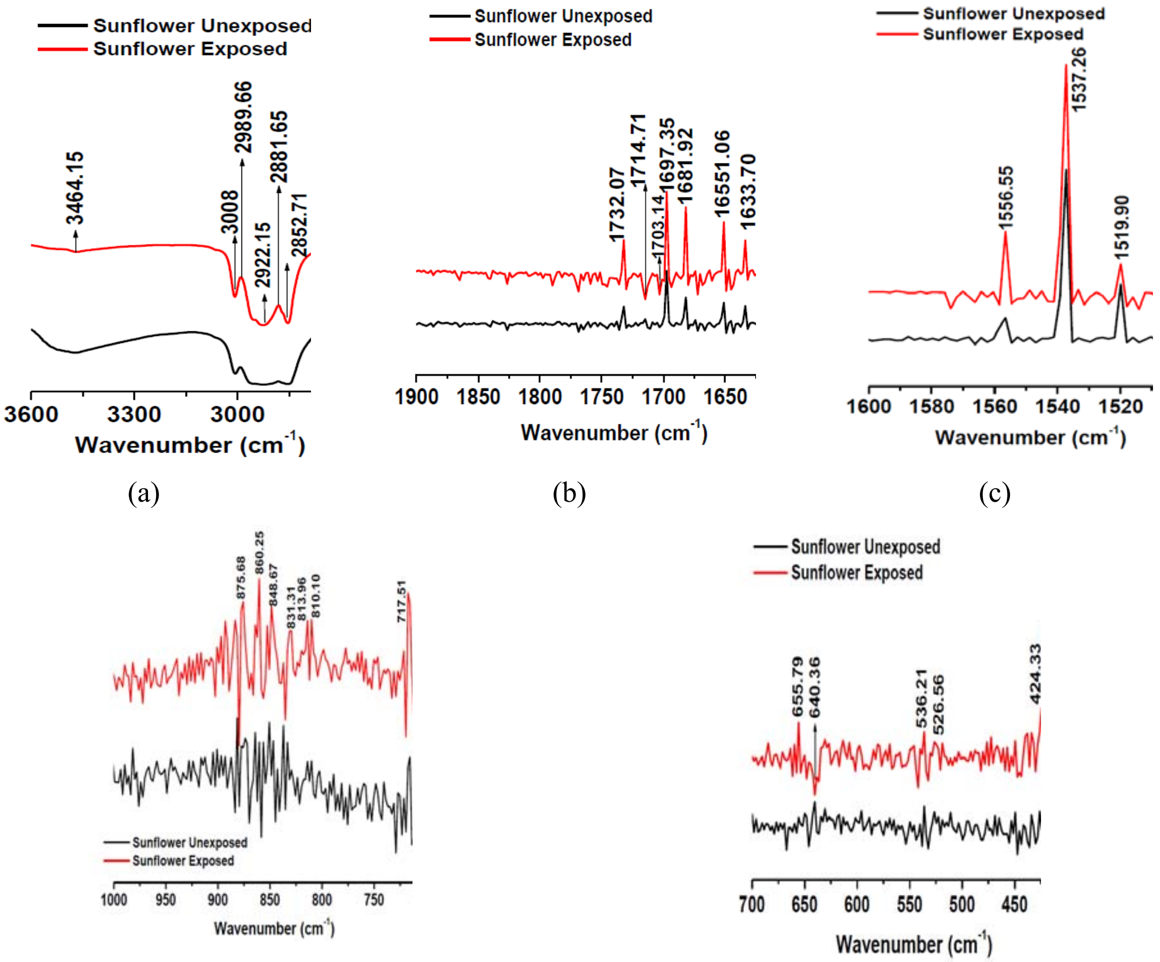
(a) (b)

Figure 3. Variation of (a) absorption coefficient (b) transmitted intensity with wavelength for sunflower oil

It can be seen that absorption coefficient is minimum for unexposed sunflower oil (~ 0.05) and for exposed sunflower is observed to be (~ 0.075). Similarly, from Figure 3(b) it is seen that the variation in intensity (a.u.) for sunflower oil. It can be seen that the intensity is nearly same for both exposed and unexposed sunflower oil.

## FTIR analysis study

The FT-IR spectra of lipids contain predominantly bands arising from vibrations of the hydrocarbon chains, with some contributions from those of polar groups. Figure 4 (a) to (e) show the FT-IR spectra of exposed and unexposed sunflower oils in different range of wavenumber.



(a) (b) (c)

(e) (f)

Figure 4. FTIR spectra of exposed and unexposed sunflower oils in region (a) 2700 -3600 cm$^{-1}$ (b) 1600 - 1900 cm$^{-1}$ (c) 1500 - 1600 cm$^{-1}$ (d) 700 - 1000 cm$^{-1}$ and (e) 400 - 700 cm$^{-1}$

From FT-IR data, following observations are summarised in points [Table 1].

i) The bands observed at about 1537.26 cm$^{-1}$ , 1556.55 cm$^{-1}$, 1519.90 cm$^{-1}$ and 1504.47 cm$^{-1}$ are due to symmetric rock in cis. double bond, in-phase methylene twist, scissoring mode of methylene, and wagging mode of methylene respectively [9-13].

ii) The bands observed at 3008 cm$^{-1}$ and 2989.66 cm$^{-1}$ are due to asymmetric stretching vibration mode of C-H bond, the peaks at 2881.65 cm$^{-1}$and 2852.71 cm$^{-1}$ are due to symmetric stretching vibration mode of C-H bond in methylene group.

iii) The major differences among the exposed and unexposed sunflower oil samples spectra are located at the bands 2854.64, 2881.65, 2989.66 and 3008 cm$^{-1}$ [Figure 4(a)], which correspond to vibrations in cis double bonds. The intensities of these bands reflect the un-saturation and correlate with the iodine values of the oils. They differ in the percentage of saturated, mono- and polyunsaturated fatty acids, the iodine values ranging between 80 for virgin olive and 166 for sunflower oils [13-19].

iv) Figure 4 shows the regions of the most prominent changes in the FT-IR spectrum of sunflower oil during the oxidation process. Generally, the bands, which were not involved in C-C losses or isomerisation did not change during the oxidation process.

v) In exposed sunflower oil, a change of the C=O carboxylic acid band was observed, which indicates that hydrolysis is taking place. Hydrolysis occurs at higher temperatures but near sea shower region may get capture easily and in presence of moisture. It was therefore decided to use the intensity of this band to normalize the intensities of the bands shown in figures. This was done in order to better visualize the general tendency of the bands to increase, decrease or to be shifted. The normalization corrected for small intensity variations across the whole spectrum that occurred due to changes of the density and viscosity of the oil.

vi) Carotenoids have antioxidant properties as radical scavengers and singlet oxygen quenchers in lipid oxidation. The antioxidative behaviour of carotenoids is closely related to its own oxidation and the loss of carotenoids could be clearly observed at the beginning of the heating period in the band at 2922.15 and 2881.65 $cm^{-1}$.

vii) Regions of the most prominent changes in the FT-IR spectrum of sunflower oil during oxidation are: (i) 400 - 700 $cm^{-1}$, (ii) 700 – 1000 $cm^{-1}$ and (iii) 2700 - 3600 $cm^{-1}$. Trans-9, 10- and cis - 9, 10 - epoxystearic acids are oxidation products of the oleic acid with the oxirane group at the double bond site. Apart from the C=C–H stretching region both oils exhibit bands of medium intensity at 3008 $cm^{-1}$. They coincide with the major bands of the other oil like sunflower oil and other bands present in the spectra are very weak. Consequently, the identification of this kind of compounds in the oxidized oils was not possible.

viii) The FT-IR intensity is due to the conjugation with C=C bond, the bands at 1633.70, 1651.06, 1681.92 and 1697.35 $cm^{-1}$ are due to the symmetric stretching mode of vibration.

ix) For the studied oils, bands appear at 1714.71 $cm^{-1}$ and 1732.07 $cm^{-1}$ are due to the C=O stretching mode of vibrations, as can be seen in Figure 4 (b) for sunflower oil. With the help of spectra of the reference compounds, these bands can be assigned the C=O stretching mode of vibration of unsaturated carboxylic acid.

## General loss in cis double bonds

The most characteristic changes in the lipid structure during oxidation are the loss of unsaturation due to attack of oxygen and the following radical reactions. The general loss in cis. double bonds during the oxidation process can be observed in the bands 3008 and 1537.26 $cm^{-1}$ in both oils spectra. These bands remain unaltered.

Figure 4 (a) shows changes in the C=C and C=O stretching region during the oxidation process of sunflower oil. Spectra have been normalized to the intensity at 2922.15 $cm^{-1}$ and the spectra of the non-oxidized oils have been subtracted.

Apart from the above-mentioned bands, a decrease in the band at 640.36 $cm^{-1}$ is observed [Figure 4 (e)]. This band was assigned to trans double bonds in a spectroscopic study of fatty acid methyl esters in the autoxidation of alkyd resin coatings. Nevertheless, trans double bonds are formed during the oxidation process, and therefore, it should increase. So we conclude that the band at 640.36 $cm^{-1}$ corresponds more probably to the out of phase H-C= C-H wagging vibration of cis. double bonds, which must also be expected at this frequency.

Figure 4(c) and (d) show the changes in all these bands for sunflower oil, concerning the cis. double bond stretching ν(C=C), band at 1697.35, 1681.92, 1651.06, 1633.70 and 1614.41 $cm^{-1}$. These changes and the apparent increase in the degree of un-saturation are due to different ν(C=C) bands, arising from trans double bonds generated during the oxidation process, that overlap with the band due to cis. double bonds. FT-IR spectra show the regions of the most prominent changes in sunflower oil during oxidation: (i) 700 - 1000 $cm^{-1}$ [Figure 4 (d)] and (d) 2700 - 3600 $cm^{-1}$[Figure 4 (a)].

A broad band appears in the region between 3008, 2922.15 and 2852.71 $cm^{-1}$ as oxidation proceeds, as can be seen in Figure 4 (a) for sunflower oil. In this way, one broader band is observed at around 3464.15 $cm^{-1}$. This broadness of peak in the exposed oil is observed due to the diol formation in oxidation reaction. The characteristic broad peak observed at 3464.15 $cm^{-1}$ is due to the O-H symmetric stretching vibration, whereas this peak is not observed in the unexposed sunflower oil.

Table 1. FT-IR data for the exposed and unexposed sunflower oils

| Frequencies ($cm^{-1}$) | Materials | |
|---|---|---|
| | Sunflower oil unexposed | Sunflower oil exposed |
| O-H stretch | - | 3464.15 broad |
| Ar. C-H stretch | 3008 | 3008 |
| Aliphatic. C-H stretch Un symmetry. | 2989.66, 2922.15 | 2989.66, 2922.15 |
| Aliphatic. C-H stretch symmetry | 2881.65, 2852.71 | 2881.65, 2852.71 |
| C=O stretch | 1732, 1714, 1697.35, 1681.82 | 1732, 1714, 1697.35, 1681.82 |
| C=C stretch | 1655.06, 1633.70 | 1655.06, 1633.70 |
| C-H bend | 1556.55, 1537.26, 1519.90, 1504.47 | 1556.55, 1537.26, 1519.90, 1504.47 |
| C=C bend (Trans) | - | 640.36 |

From the FT-IR analysis it is concluded that, the exposed oils having two new characteristic bands, which indicate the formation of oxidized product in the form of diol and trans lenoleic acid.

## Conclusions

Specifically designed absorption and transmission spectrum data analyser, FT-IR spectral regions, chemical titration method confirmed to be very useful for the determination of adulteration as well as for the study of the oxidation process. The maximum intensity for pure sunflower oil is observed at ~ 370.33 nm similarly for exposed sunflower oil at ~363.55 nm. It indicates that the exposed sunflower oil is more oxidised and deteriorated. From FT-IR analysis it is concluded that, the exposed oils having two new characteristic bands, which indicates the formation of oxidized product in the form of diol and trans lenoleic acid, which reduces FFA% (~ 26), acid value in percentage (~ 53) as compare to un-exposed sunflower FFA % (~ 82) and acid value % (~ 165). The developed method is rapid, no excessive sample preparation is required, and it is not involving the hazardous solvents and reagents. This method could be useful to evaluate the oxidative state of cooking oils in a simple and swift way for household application and food industry.

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## References

[1] S. L. Melton, S. Jafar, D. Sykes, and M. K. Trigiano, “Review of stability measurements for fryingoils and fried food flavour,” J. American Oil Chemists Soc., vol. 71, no. 12, pp. 1301 – 1308, 1994.

[2] F. T. Orthoefer, “Care of food service fryingoils,” J. American Oil Chemists Soc., vol. 65, no. 9, pp. 1417 - 1419, 1988.

[3] A. J. Paradis, and W. W. Nawar, “Evaluation of new methods for the assessment of used frying oils,” J. Food Sci., vol. 46, pp. 449 - 451, 1981.

[4] Y. A. Tan, S. H. Ong, K. G. Berger, H. H. Oon, and B. L. Poh, “A study of the cause of rapid color development heated refined palm oil,” J. American Oil Chemists Soc., vol. 62, issue 6, pp. 999 - 1006, 1985.

[5] V. K. Tyagi, and A. K. Vasishtha, “Changes in the characteristics and composition of oils during deep-fat frying,” J. American Oil Chemists Soc., vol. 73, issue 4, 499 - 506, 1996.

[6] F. R. De Voort, A. A. Ismail, J. Sedman, J. Dubois, and T. Nicodemo, “The determination of peroxide value by Fourier transform infrared spectroscopy,” J. American Oil Chemists Soc., vol. 71, issue 9, 921 – 926, 1994.

[7] F. R. Van de Voort, J. Sedman, and A. A. Ismail, “A rapid FTIR quality control method for

determining fat and moisture in high-fat products," Food Chemistry, vol. 48, pp. 213 - 221, 1993.

[8] P. J. White, "Methods for measuring changes in deep-fat frying oils," Food Tech., vol. 45, issue 2, pp. 75 - 80, 1991.

[9] H. Yang, and J. Irudayaraj, Characterization of semisolid fats and edible oils by Fourier transform infrared photo acoustic spectroscopy," J. American Oil Chemists Soc., vol. 77, issue 3, pp. 291 - 295, 2000.

[10] W. T. Kim, M. Y. Choi, H. W. Park, and J. H. Park, "Measurement and analysis of deterioration in the automotive engine Oil," Spring proceeding of KSNT (Korean Soc. of Non-Destructive Testing), 220 -224, 2003.

[11] R. D. Lee, H. J. Kim, Y. P. Semenov, "Capacitive sensor for in-situ measurement of deterioration of car engine oil," The Korean Sensors Soc., vol. 10, issue 4, pp. 266 - 272, 2001.

[12] W. -S. Choo, J. Birch, and J. -P. Dufour, "Physicochemical and quality characteristics of cold-pressed of flaxseed oils," J. Food Composition & Analysis, vol. 20, pp. 202 - 211, 2007.

[13] E. Choe and D. B. Min, "Mechanisms and factors for edible oil oxidation," Comprehensive reviews in food science and food safety, vol. 5, pp. 169 - 186, 2006.

[14] O. Loreau, A. Maret, D. Poullain, J. M. Chardigny, J. L. Sébédio, B. Beaufrère, and J. P. Noël, "Large-scale preparation of (9Z,12E)-1-(13)C-octadeca-9,12-dienoic acid, (9Z,12Z,15E)-1-(13)C-octadeca-9,12,15-trienoic acid and their 1-(13)C all-cis isomers,". Chem. & Phys. of Lipids, vol. 106, issue 1, pp. 65 - 78, 2000.

[15] A. Rollett, "Zur kenntnis der linolensäure und des leinöls," Z. Physiol. Chem., vol. 62, issue, 5 - 6, pp. 422, 1909.

[16] T. G. Green, and T. P. Hilditch, "The identification of linoleic and linolenic acids," Biochem. J., vol. 29, issue 7, pp. 1552 - 63, 1935.

[17] J. Sandri, and J. Viala, "Direct preparation of (Z, Z)-1,4-dienic units with a new C6 homologating agent: synthesis of alpha-linolenic acid," Synthesis, vol. 3, issue 3, 271 – 275, 1995.

[18] D. J. Chapman, J. De-Felice, and J. Barber, "Growth temperature effects on thylakoid membrane lipid and protein content of pea chloroplasts 1," Plant Physiol. vol. 72, issue 1, pp. 225 - 228, 1983.

[19] S. M. Innis, "Fatty acids and early human development," Early Human Development, vol. 83, issue 12, pp. 761 -766, 2007.