Zagazig J. Agric. Res., Vol. 46 No. (5) 2019 1489-1502

Food, Dairy and Home Economic Research

http:/www.journals.zu.edu.eg/journalDisplay.aspx?Journalld=1&queryType=Master

THE EVALUATION OF DEEP FRYING OIL QUALITY WITH THE SPECTROPHOTOMETRIC METHOD FOR THE RAPID ASSESSMENT OF TOTAL POLAR COMPOUNDS

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Received: 30/05/2019; Accepted: 14/07/2019

ABSTRACT: This study focuses on the evaluation of official methods for determining frying oil quality with the new spectrophotometric method. The performance of these methods was examined by usage intermittent deep fat frying of potato chips in sunflower oil for 40 hr. at five consecutive days (8 hr., daily). Chemical analysis is the most reliable way to measure decomposition compounds in frying oil. With the prolonged frying time the amount of total polar compounds (TPCs) rises steadily. It has been suggested that the determination of TPCs is the most reliable method for the measurement of oil deterioration during deep frying processes. Beside, other oil quality indices during 40 hr. of intermittent deep fat frying were analyzed by the official methods and/or by rapidly spectrophotometric absorbance methods. Principal component analysis and linear regression analysis were used in order to assess the obtained results. The results were used to calibrate this spectrophotometric absorbance method. There was a strong correlation (r = 0.999) between quick spectrophotometric absorbance values and TPCs content in the same set of oil samples. The equation for conversion of the spectrophotometric absorbance values to TPCs content is: $Y = -57.0083 + 2.64X + 0.049 X^2$. Consequently, spectrophotometric absorbance method was developed to assess deep fat frying oil quality. This study was conducted to examine the relationship of TPCs contents determined by spectrophotometric method with physical, chemical indices and sensory evaluation. TPCs content was found to be correlated with refractive index (r = 0.950), viscosity (r = 0.989), colour (r = 0.993), acid value (r – 0.899), iodine number (r = 0.947), P-anisidine value (r = 0.987), TBA test (r = 0.875), oxidized fatty acids (OFAs) (r = 0.975). Also, TPCs content was correlated with flavour (r - -0.752), greasiness (r - -0.917), crispy texture (r = -0.559) and overall acceptability (r = -0.649).These results showed that the new spectrophotometric absorbance method of frying oil is a good, rapid, simple, convenient and reliable indicator during deep fat frying of sunflower oil tested.

Key words: Analytical chemistry, deep frying, frying oil, quality index, quick test, spectrophotometry.

INTRODUCTION

Deep fat frying at 180°C is one of the most commonly used procedures for the preparation of foods. Desirable texture and flavour can be generated during frying; however, when the oil is used repeatedly at high temperatures in the presence of air, thermal oxidation occurs and the oil deteriorates (**Zhang *et al.,* 2012**). During the frying process the oil undergoes several physical and chemical changes caused by heat, water and air, such as changes in refractive index, viscosity, acid value, peroxide value, p-anisidine, and TBA test **(Vijayan *et al.,* 1996)**. With prolonged frying time the accumulation of deterioration products leads to organoleptic failures and a decrease of the nutritive value (**Hein *et al.,* 1998**). Intermittent deep fat frying showed that when oil heated for only 62 hr., for several intervals, it contains as much polar materials as oil heated continuously for 166 hr., **(Hassan and Abou-Arab, 2004; Mlcek *et al.*, 2015).**

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Measurement of heat abuse of oils should be based on the change described. Many methods of analysis measure the formation of volatile or nonvolatile decomposition or some portions or indicators of change in fraction (**Nayak *et al.,* 2015; Weisshaar, 2014**). Total polar components (TPC) are a representative measurement of the total alteration of the frying oil. In most European countries, the limits for rejection and replacement of a frying oil range between 25 – 27% for TPC. Frying oils and fats are absorbed by cooked food and so become part of our diet (**Andrikopoulos *et al.,* 2003; Kalogianni *et al.,* 2016)**. Therefore, oil quality control during deep fat frying is essential for the food industry. A variety of methods are available for assessing degradation of frying oil. Chemical analyses measure decomposition compounds reliably in the frying oil (**Qing, 2000**), but are very time-consuming, costly, tedious usually require reasonable analytical expertise. During frying, unsaturated compounds formed in the oil are believed to absorb electromagnetic energy over the visible spectrum (**Osawa *et al.,* 2007; Soares and Rocha, 2018).**

Darkening of oil during frying may be related to the leaching of pigments from the food into the oil, Maillard reaction, and increased absorption of blue light by conjugated double bonds (diene) or trible bonds (triene) formed by isomerization and migration of diene or triene (**Mlcek *et al.,* 2015**). Substances contain suitable unsaturated groups are amenable to direct spectrophotometric examination and the method is extremely sensitive even with a small quality of sample **(Soares and Rocha, 2018)**.

Many attempts were under taken to replace the chemical consuming method. To substitute for chemical methods used for the quality control of frying oils, the measurement of dielectric properties with a food oil sensor, nuclear magnetic resonance spectroscopy and near infrared spectroscopy proved to be suitable **(Hein *et al.,* 1998**). Iodine value is an important quality parameters for evaluation of the oxidative stability of oils, but the official methods are time-consuming and demand large amounts of reagents and solvents. Spectrophotometric determination of iodine value based on the discolouration of a triiodide aqueous solution due to halogenation of the unsaturated compounds in the samples. The objective of this work was to produce a practical method for monitoring the quality of sunflower oil during fat frying process with a spectrophotometric absorbance quick test that has a good correlation to the official methods and prediction models for measuring physicochemical and sensory evaluation induces during deep fat frying process.

MATERIALS AND METHODS

Materials

Sunflower oil was purchased from oils and Detergents Company, Sohag, Egypt. The selection of sunflower oil was based on their different physical, chemical and sensory properties, which were expected to change differently during the intermittent deep fat frying.

Potato (*Solanum tuberosum*) tubers were purchased from the local market of Assiut.

Reagents: All chemicals were obtained from Sigma Chemical Company (Germany) and purchased from El-Gamhouria Trading Chemicals and Drugs Co, Egypt.

Methods

Frying experiments

In frying experiments, about 2.5 L of refined sunflower oil was heated in stainless steel vessels with a surface area (A) of approximately 11 × 22/7, and 70 mm height (H) with volume 2659 cm^3 at 180°C ± 10. Each repeated frying experimented series consisted of 85 frying batches of 10 min frying each and was conducted five consecutive days. At two hr. intervals during frying process, about fifty milliliters of heated oil was withdrawn and kept in brown bottles in freezer at -10°C until used. Potato tubers prepared before they were fried, potatoes were washed, sorted, peeled and sliced to a thickness of 1.2 – 1.3 mm. Potato slices were placed in a stainless steel basket, and a ratio of oil to potato slices of 8: 1 (*W/W*), *viz*, a batch of about 300 gm. Potato chips was deep fat fried into the heated oil for 10 min. (**Hassan and Abou-Arab 2004).**Fried slices were sampled at starting of frying process at the first day and daily after 8 hr., for sensory evaluation.

Analytical methods

Colour was determined using a spectrophotometer (6405 UV/Vis. Spectrophotometer) at 420 nm of 5% (wt/vol.) solution of oils in chloroform as described by **Hassan (1980)**. Oil viscosity was determined according to the method of **Tsaknis *et al.* (1998)** using a Brookfield viscometer with spindle No. 2 at temperature of 24°C. Refractive index was measured according to the method described by **AOCS (1993)**. Total polar compounds, p-anisidine and peroxide values were determined by AOCS method (**AOCS, 2001**). Acidity was expressed as oleic acid, and iodine number (measuring the amounts of halogen absorbed by the unsaturated fatty acids) was determined by AOAC methods (**AOAC, 2005**). Conjugated diene and conjugated triene were measured using ultra violet absorption at 232 and 268 nm, respectively (6405 UV/Vis spectrophotometer) as described by **Danopouls and Ninni (1972)**. Thiobarbituric acid (TBA) test was determined as mg malonaldehyde/kg oil as described by **Keeney (1971)**. Oxidized fatty acids (OFAs) was conducted as described by **Abd-El-Ghany (2006)**.

Sensory evaluation of potato chips

Potato chips samples were evaluated for flavour, crisp, greasiness and overall acceptability by a 5-point hedonic scale, according to the procedure of **Mohamed (1991)**.

Determination of oil induces using the spectrophotometric method

This quick method for evaluating the frying oil quality which used in deep frying applications in food science. Detailed information of this method related to chemical and physical analyses, and research results were declared in **Qing (2000), Kalogianni *et al.* (2016), Li *et al.* (2016) and Soares and Rocha (2018)**.

Spectrophotometric absorbances measurement oil samples was placed in a standard disposable cuvette (1 cm optical path), and warmed in a 60°C oven for 15 min. before measuring the spectrophotometric absorbance using (6405 *UV/V* is spectrophotometer), the spectrophotometer was zeroed against air without using any cuvette (**Qing, 2000**). The oil samples absorbance were measured at 490 nm. Wave length 490 nm had the highest correlation value for sunflower oil, consequently this wave length was chosen. To investigate the relationship of physical, chemical induces and sensory evaluation in sunflower oil during intermittent deep fat frying process with the spectrophotometric absorbance method; principal component analysis and linear regression analysis were used in order to assess the obtained results.

Statistical analysis and mathematical models

Data from physical and chemical analysis and sensory evaluation were analyzed statistically using analysis of F-test, t-test, correlation and regression as described by **Snedecor and Cochran (1980)**. A correlation and/or regression tests were applied to study the relationship between different oil qualities induces and TPCs. Simple and multiple regression analyses were carried out using Excel program "Windows, 2010".

RESULTS AND DISCUSSION

Correlation Models between Total Polar Compounds Determined by the Official Method and/or Spectrophotometric Absorbance Method

Chemical evaluation is still the most reliable method for the quality survey of used frying oils. If chemical analysis can be carried out, judgment is commonly made on the basis of acid value, iodine number, peroxide value, p-anisidine value, TBA value, TPC content, oxidized fatty acids and conjugated double or triple bonds. None of these methods proved to be completely satisfying, but some can be used to characterize the quality of frying oils roughly. Observing the regulations used for frying oils in different countries (**Hein *et al.,* 1998**), it is obvious that in almost allover the world the determination of total polar compounds (TPC) by preparative column chromatography is used for the quality control of oils. It has been suggested, that the determination of TPC is the most reliable method for the measurement of oil deterioration during frying (**Mlcek *et al.,* 2015; Nayak *et al.,* 2015).**

As the preparative column chromatography method is very time and chemical consuming. A number of attempts have been undertaken to find simpler and more rapid techniques for the determination of TPC. The survey of several frying processes proved that a determination of the TPC by the use of a spectrophotometric absorbance method is possible. In comparison to the customary preparative column chromatography with the method presented is easier to carry out, more reproducible, need less time and avoid the use and the disposal of chemicals.

Results for the correlation between TPCs were determined by **AOCS (2001)** and TPCs were determined by spectrophotometric absorbance method during intermittent deep fat frying of potato chips for 40 hr. at five consecutive days (8 hr., daily) are presented in Table 1. There were significant ($P \geq 0.05$) differences in all the results analyzed for all treatments. TPCs content of sunflower oil measured by the AOCS method were 11.18, 20.20, 24.15, 28.58 and 35.54% during intermittent frying for 40 hr. at five consecutive days (8 hr., daily) respectively. But in this respect, it is worthy to mention that TPCs content measured by spectrophotometric method were 0.51, 0.99, 1.40, 1.99 and 2.75 during the same set of sunflower oil samples. With prolonged frying time the amount of TPCs rises steadily. It has been suggested that the determination of TPC is the most reliable method for the measurement of oil deterioration during frying (**Hein *et al.*, 1998**). The principle of this method is based mainly on the measurement of the spectrophotometric absorbance of total polar compounds in frying oil such as (free fatty acid, oxidized, polymerized emulsified and pyrolyzed) in the used frying oils (Maximal absorbance is around 490 nm) (**Qing *et al.*, 1999; Weisshaar, 2014**). This indicates that the spectrophotometric absorbance of frying oil measuring at 490 nm is a good parameter to use oil quality characterizes. The results were used to calibrate this spectrophotometric method. There was a strong correlation ($r = 0.999$) between the spectrophotometric absorbance and TPC content in the same set of sunflower oil samples. The linear regression equations for prediction the TPCs content of the sunflower oil are shown in bottom Table 1. During deep fat frying, oil breaks down, acids, peroxides and other radicals were formed in the frying oil. These cause some molecules in the oil to become somewhat polar (**Qing *et al.*, 1999**). As the number of TPC increases, the spectrophotometric absorbance increases. The equation for conversion of the spectrophotometric absorbance to TPCs content is:

$$Y = 14.339 + 6.937554 X$$

Where:

$Y = TPC_s$ determined by AOCS method

$X = TPC_s$ determined by spectrophotometry

It can be estimated from Table 1, that if a 27% TPC limit is not to be exceeded in the frying oil, the absorbance at 490 nm should be ≤ 1.81. This value is similar to the value calculated from the calibration equation. However, results showed that the spectrophotometric absorbance method readings were much closer to the corresponding TPCs obtained by AOCS method. As soon as spectrophotometric absorbance had reached 1.81, the intermittent deep frying process stopped. Thereupon, the spectrophotometric method estimates carefully TPCs during frying as well as it evaluates deep fat frying oil quality. The spectrophotometric method is reliable, simple, rapid and low cost. Spectrophotometric absorbance method was quick, consequently it used in evaluate of frying oil. These findings could be supported by **Vijayan *et al.* (1996), Qing (2000), Mlcek *et al.* (2015), Kalogianni *et al.* (2016) and Soares and Rocha (2018)**.

Physical Properties of Sunflower Oil as Affected by Deep Frying of Potato Chips

Chemical reactions like oxidation, polymerization, hydrolysis, *etc*., take place in the food system, which ultimately alters the physical and chemical properties of oil (**Zhang *et al.*, 2012**). Consequently, so many by-products such as free fatty acids, aldehydes, cyclic compounds, dimer and polymer are produced. Results in Table 2 reveal that, sunflower oil became dark after each patch of deep fat frying. The colour of the oil deteriorated continuously with the elongation of frying times. Also, oil viscosity and refractive index increases significantly with extension the frying times. Previous studies of deep fat frying have shown that refractive index, viscosity and colour increase during deep fat frying (**Qing *et al.*, 1999**).

Regression Models and Correlation between Physical Properties and Total Polar Compounds Determined by Spectrophotometry

Significant changes in oil colour were observed with sunflower oil degradation and frying time. The oil sample continued to darken as the deep fat frying period increased. During

Table 1. Correlation models between total polar compounds (TPC_s) determined by the official method and total polar compounds determined by spectrophotometry of sunflower oil during intermittent frying of potato chips for 40 hr., at five consecutive days (8 hr., daily)

Frying period daily/hr.	Frying days									
	1		2		3		4		5	
	Y	X	Y	X	Y	X	Y	X	Y	X
0	6.35	0.05	9.92	0.45	17.90	0.80	22.25	1.10	26.45	1.70
2	6.64	0.10	12.45	0.58	18.45	0.89	24.48	1.50	28.72	2.01
4	6.86	0.19	15.55	0.70	20.56	0.99	26.46	1.75	30.27	2.30
6	10.44	0.30	18.47	0.85	22.89	1.15	27.39	1.90	34.43	2.55
8	11.18	0.51	20.2	0.99	24.15	1.40	28.58	1.99	35.54	2.75
LSD 5%	0.55	0.09	0.87	0.12	1.16	0.10	1.10	0.09	1.35	0.20
Model (Y = TPCs by AOCS method)	Y = 5.88085 + 11.081 X		Y=1.30464 + 19.6266 X		Y = 9.137545 + 11.140014 X		Y = 14.399 + 6.937554 X		Y=10.75507 + 8.9863 X	
X = TPCs by spectrophotometry,										
Correlation coefficient	r = 0.996		r = 0.993		r = 0.969		r = 0.993		r = 0.982	

Table 2. Physical properties of sunflower oil as affected by deep frying of potato chips for consecutive five days (8 hr. daily)

Frying period		Refractive index	Viscosity	Colour
Day	hr.			
First	0	1.4775	50.30	0.020
	3	1.4881	51.60	0.022
	6	1.5170	52.70	0.023
	8	1.5860	53.55	0.024
Second	0	1.6574	54.50	0.025
	3	1.6847	55.75	0.027
	6	1.6980	56.85	0.030
	8	1.7095	56.95	0.033
Third	0	1.7981	58.60	0.035
	3	1.8050	59.35	0.036
	6	1.8445	61.50	0.037
	8	1.8615	61.68	0.038
Fourth	0	1.8785	62.40	0.040
	3	1.8841	63.00	0.041
	6	1.8990	63.20	0.042
	8	1.8950	63.72	0.048
Fifth	0	1.9015	64.70	0.050
	3	1.9213	66.25	0.052
	6	1.9640	69.95	0.058
	8	1.9882	70.55	0.060

deep fat frying, unsaturated compounds formed (fat soluble colour compounds) in the oil are believed to absorb electromagnetic energy over the visible spectrum (**Zhang *et al.,* 2012; Weisshaar, 2014)**. Darkening of oil during deep fat frying may be related to the leaching of pigments from the foods into the oil, Maillard reaction, and increased absorption of blue light by conjugated double bonds formed by isomerization and migration of double bonds (**Zhang *et al.,* 2012**). Substance containing suitable unsaturated groups are amenable to direct spectrophotometric examination and the method is extremely sensitive even with a small quantity of oil sample.

Table 3 shows the correlation between physical parameters and TPCs determined by spectrophotometric absorbance method of oil.

Intermittent deep fat frying of sunflower oil showed an increase in refractive index (RI), viscosity (V) and colour. This increment may be related to polymer formation and thermal degradation of the oil (**Nayak *et al.,* 2015**).

It can be seen that the correlations between RI, V and colour with TPCs determined by spectrophotometric absorbance method are very high (r = 0.950, r = 0.989 and r = 0.993) respectively. This indicates that TPCs determined by spectrophotometric method can be used to indicate the changes in RI, V and colour, consequently its degradation during intermittent deep fat frying. The optimum correlation equations obtained were:

For RI:

$Y = 1.4344 + 0.0194\ X$

$Y = 0.0872\ X + 0.00059\ X^2$

Correlation coefficient was 0.950

Where:

Y = RI

X = TPCs determined by spectrophotometric method.

For viscosity

$Y = 46.812 + 0.75327\ X$

$Y = 2.966\ X + 0.0193\ X^2$

Correlation coefficient = 0.989

Where:

Y = viscosity

X = TPCs determined by spectrophotometric method.

For colour:

$Y = 0.0101 + 0.00156\ X$

$Y = 0.175 + 0.0789\ X - 0.00099\ X^2$

Correlation coefficient was 0.993

Where:

Y = colour

X = TPCs determined by spectrophotometric method.

Thus, consequently spectrophotometric absorbance is a good indicator for monitoring oil quality during intermittent deep fat frying.

Chemical Indices of Sunflower Oil as Affected By Deep Frying of Potato Chips

Findings in Table 4 show visible changes of chemical indices in sunflower oil occur rapidly during deep fat frying of potato chips for consecutive five days (8 hr., daily), include an increase in acid value, p-anisidine value, TBA value, oxidized fatty acids (OFA_S). Fluctuations increase in peroxide value and ultra violet absorptions whether on 232 nm or 268 nm. And decrease in iodine number. These results could be supported by **Hassan and Abou-Arab (2004) and Nayak *et al.* (2015).**

Regression Models and Correlation between Chemical Properties and Total Polar Compounds Determined by Spectrophotometric Method

Deep fat frying, used repeatedly at high temperature, is subject to a series of degradation reaction and formation of a variety of decomposition compounds. These decomposition products have negative effects on the quality of the frying oil and the sensory evaluation of the fried food **(Freitas and Ferreira, 2013).**

Chemical analysis measure decomposition products reliably in the frying oil **(Qing, 2000**), but are time-consuming, costly, and usually require reasonable analytical expertise. A significant feature of a rapid method is its ability

Table 3. Regression models and correlation between physical properties and total polar compounds of sunflower oil during intermittent frying of potato chips for 40 hr., at five consecutive days (8 hr., daily).

Physical parameters	Model (Y = physical parameters and X = Total polar compounds by spectrophotometry	Computed F	Tabulated F	LSD 5%	Correlation coefficient
Refractive index (RI)	$Y = 1.4344 + 0.0094 X$ $Y = 0.0872 X + 0.00059 X^2$	3.67	3.33	0.002	r= 0.950
Viscosity (CP)	$Y = 46.812 + 0.75327 X$ $Y = 2.966 X + 0.0193 X^2$	112.73	3.33	0.602	r= 0.989
Colour	$Y = 0.0101 + 0.00156 X$ $Y = 0.175 + 0.0789 X – 0.00099 X^2$	16.79	3.33	0.004	r= 0.993

Table 4. Chemical indices of sunflower oil as affected by deep frying of potato chips for consecutive five days (8 hr., daily)

Frying period		Acid value	Iodine value	Peroxide value	P-anisidine value	TBA test	K232 value	K268 value	Oxidized Fatty acids
Day	hr.								
First	0	0.50	132.70	8.5	5.3	3.50	1.95	0.93	2.40
	3	0.60	132.65	9.0	6.5	3.80	2.10	1.20	2.50
	6	0.70	130.50	9.5	7.10	3.90	3.30	1.40	2.60
	8	0.80	128.62	20.5	9.20	4.00	4.5	1.50	2.70
Second	0	0.90	125.34	18.70	10.50	4.10	5.95	1.55	3.85
	3	1.00	124.50	25.40	12.50	4.15	6.25	1.65	4.60
	6	1.20	122.32	27.30	14.50	4.40	6.50	1.70	5.70
	8	1.25	121.81	18.40	15.20	5.10	6.00	1.75	5.80
Third	0	0.93	120.70	15.50	16.40	5.30	5.20	1.65	5.90
	3	1.30	121.80	17.50	19.50	5.35	5.40	1.55	6.70
	6	1.35	117.45	21.00	20.70	5.50	5.50	1.50	6.80
	8	1.30	120.53	15.90	21.80	6.00	5.95	1.65	6.94
Fourth	0	1.00	118.21	11.50	22.50	6.30	5.30	1.70	7.52
	3	1.50	119.97	21.50	24.50	6.38	6.70	1.90	7.59
	6	1.70	118.20	22.30	25.80	6.45	6.95	1.95	7.68
	8	1.40	117.30	17.90	28.20	6.60	7.75	1.97	7.83
Fifth	0	1.30	115.95	14.70	29.70	7.00	7.90	1.99	8.10
	3	1.50	117.15	15.50	33.70	7.50	7.95	1.98	8.74
	6	1.60	113.50	18.70	34.50	8.00	8.65	1.99	8.95
	8	1.78	110.25	22.50	35.60	8.90	8.97	2.04	11.23

to correlate with analytical methods. If chemical analysis can be carried out, judgment is commonly made on the basis of acidity, iodine number *etc*. This is why all samples were analyzed using the analytical methods. Prior to the correlation of the results of rapid methods with analytical ones it was considered useful to assess the performance of analytical methods using spectrophotometric absorbance method in order to detect patterns of similar performance of the methods on sunflower oil samples. Free fatty acids (acid value) are formed during oxidation, hydrolysis and pyrolysis as a result of cleave of triglyceride (**Zhang *et al.,* 2012)**. Table 5 illustrate the correlation between some chemical characteristics method. Frying oil showed an increase in TPCs content. Results for the chemical characteristics are presented in Table 3. There were significant ($P \geq 0.05$) differences in all the results analyzed for chemical properties. The steady rise in acid value can be related partly to both the hydrolysis of triglyceride of oil and to the carboxylic groups present in the formed polar polymeric products during deep fat frying (**Li, *et al.,* 2016**). Previous studies of frying oils have shown that free fatty acids content increases during deep frying (**Qing, 1999**).Similar results were obtained in this study with a rapid increase in acid value levels occurring after 32 hr. of deep frying. Although the changes of acid value were correlated with the changes in TPCs content during frying in this study, it is not recommended to use acid value as indicator for evaluating the frying oil. The optimum correlation equations obtained were:

$Y = 0.44441 + 0.0426 X$

$Y = 0.175 + 0.0789 X – 0.00099 X^2$. Correlation coefficient was 0.899

Where:

Y = Acid value

X = TPCs determined by spectrophotometric method.

Iodine value is proportional to the degree of unsaturation of the oil and indicates its oxidative stability (**Soares and Rocha, 2018)**.

It is worthy to mention that the declining in iodine number can be attributed partly to unsaturated fatty acid oxidation (**Kalogianni *et al.,* 2016**). The linear regression equations for predication the iodine number of frying oil were:

$Y = 134.581 – 0.7595 X$

$Y = -4529.64 + 625.91 X – 17.28 X^2$. Correlation coefficient was 0.947

Where:

Y = Iodine number

X = TPCs determined by spectrophotometric method.

Peroxide value is one of the most frequently determined quality parameters during frying. Peroxide value indicates the degree of oxidation in the substance and measures the amount of total peroxides as a primary product of oil oxidation, which can be used to monitor the initial stage of oxidation (**Li *et al.,* 2016**).

In this respect, fluctuation values in peroxide value can be related to the rate of peroxides formation were more than their degradation, and *vice versa* when decreased. These findings could be supported by **Wu and Nawar (1986), Andrikopoulos *et al.* (2003) and Soares and Rocha (2018)**. Peroxide value fluctuated and increased slowly during the frying process for 20 – 40 hr., which was related to the formation of secondary oxidation products. The formation of secondary oxidation products namely ketones, hydrocarbons, aldehydes and alcohols, which are from unstable primary oxidation products, can be used to explain this fluctuation **(Li *et al.,* 2016**).

With regard to UV absorption of sunflower oil during intermittent deep frying of potato chips either UV absorption at 232 or UV absorption at 268 nm was fluctuated. This may be attributed to the volatilization of aldehyde and ketonic compounds which have been formed during the early stage of deep fat frying of potato chips in sunflower oil. But in this respect, it is worthy to mention that peroxide value, UV absorption at 232 nm and at 268 nm were weakly significantly correlated to TPCs determined by spectrophotometric method ($r = 0.280$, $r = 0.875$ and $r =0.319$), respectively.

Table 5. Regression models and correlation between chemical properties and total polar compounds (TPC_s) of sunflower oil during intermittent frying of potato chips for 40 hr., at five consecutive days (8 hr., daily)

Chemical parameters	Model (Y = Chemical parameters and X = Total polar compounds by spectrophotometry	Computed F	Tabulated F	LSD 5%	Correlation coefficient
TPCs	Y = - 0.07896 + 1.0007947 X Y = -57.0083 + 2.64 X + 0.049 X^2	10.56	3.33	1.39	r = 0.999
Acid value	Y = 0.44441 + 0.0426 X y = 0.175 + 0.0789 X – 0.00099 X^2	9.60	3.33	0.065	r = 0.899
Iodine number	Y = 134.581 – 0.7595 X Y = - 4529.64 + 625.91 X – 17.28 X^2	4.01	3.33	8.98	r = 0.947
Peroxide value	Y = 14.5 + 0.1834 X Y= 9.496 + 0.856 X – 0.02 X^2	16.10	3.33	3.58	r = 0.280
P-anisidine value	Y = - 0.191 + 1.17424 X Y = 3.062 + 0.671 X + 0.015 X^2	497.08	3.33	1.49	r = 0.987
TBA value	Y = 2.098 + 0.205 X Y = 616.32 – 83.0364 X + 2.31 X^2	25.66	3.33	0.090	r = 0.989
K_{232}	Y = 1.925113 + 0.2298 X Y = 1.326 + 0.3102 X – 0.00222 X^2	3.75	3.33	0.222	r = 0.875
K_{268}	Y = 20.49511 – 0.80994 X Y = 332.79 – 29.4433 X + 0.792 X^2	13.43	3.33	0.65	r = 0.319
Oxidized fatty acids	Y = 0.77582 + 0.3142 X Y = - 0.3363 + 0.4636 X – 0.00412 X^2	27.02	3.33	0.083	r = 0.975

P-anisidine value is used to measure the secondary oxidation products content in oil. The primary oxidation products are unstable and those compounds decompose to the secondary oxidation products during frying process, which contributes to the increase both of p-anisidine value and TBA value (**Zhang *et al.*, 2012).**

It is worth mentioning that during frying, a considerable increase in both of p-anisidine, TBA values and oxidized fatty acids. The linear correlation equations for prediction p-anisidine value were:

Y = - 0.191 + 1.17424 X

Y = 3.062 + 0.671 X + 0.015 X^2. Correlation coefficient was 0.987

Where:

Y = p-anisidine value

X = TPCs determined by spectrophotometric method.

Results declared that p-anisidine value increased and reached a maximum value at 40 hr., of the frying process.

The thiobarbituric acid (TBA) test is a condensation reaction between TBA and malonaldeyde, which is the most predominant secondary oxidation products of food lipids (**Abd-El-Ghany, 2006**). Therefore, the TBA value is considered a good chemical quality to identify the oxidative state of frying oil and measure the secondary oxidation products. The linear correlation equations for prediction of TBA values were:

Y = 2.098 + 0.205 X

Y = 616.32 – 83.0364 X + 2.31 X^2. Correlation coefficient was 0.989

Where:

Y = TBA values

X = TPCs determined by spectrophotometric method.

These results are in agreement with those, reported by **Hassan and Abou-Arab (2004) and El-Naggar (2007)**.

In this respect, the oxidized fatty acids content is considered one of the components of TPCs, which comprise both of fatty acids methyl ester polymers (FAP), fatty acid methyl ester dimer (FAD) and oxidized fatty acid methyl ester monomers (OFAs). It is also considered as a good measurement for the oxidative deterioration of oils during deep fat frying. It is worth mentioning that during intermittent deep fat frying of potato chips in sunflower oil, a considerable increase in OFAs. The linear correlation equations for prediction of OFAs content were:

$Y = 0.77582 + 0.3142\ X$

$Y = -\ 0.3363 + 0.4636\ X - 0.00412\ X^2$. Correlation coefficient was 0.975

Where:

Y = Oxidized fatty acids (OFAs) content.

X = TPCs determined by spectrophotometric method.

These results could be supported by **Tompkins and Perkins (1999), Hassan and Abou-Arab (2004) and Kalogianni *et al.* (2016).** This suggests that oxidation, polymerization and polar compounds formation are strongly and positively related with one another whereas hydrolysis and therefore free fatty acids (acid value) formation is independently related to repeated oil use (**Li *et al*., 2016; Soares and Rocha, 2018**). Several European countries use this spectrophotometric method for evaluating frying oil quality and the critical value for an oil regarded as deteriorated is 0.7-1%, which is equivalent to threshold range of polar components (**Kalogianni *et al*., 2016**). The results were used to calibrate this spectrophotometric method. There was a strong correlation (r = 0.975) between the spectrophotometric absorbance values and OFAs content in the same set of oil samples. If 1% OFAs is used as the maximal level allowed in the frying oil (**Kalogianni *et al*., 2016**), the spectrophotometric absorbance of frying oil at 490 nm should be $\leq$ 1.10. Thereupon, Spectrophotometric method estimate carefully TPCs content during deep fat frying as well as it estimates both of TBA test, P-anisidine value and oxidized fatty acids content.

Sensory Evaluation of Fried Potato Chips In Sunflower Oil as Affected by Deep Frying Process

Results in Table 6 illustrate the sensory evaluation of potato chips during intermittent deep fat frying of sunflower oil for consecutive five days. Deep frying of potato chips at high temperature enhances the sensorial properties which include the unique fried flavour, golden brown colour and crispy texture then reduces the sensorial properties with elongation of frying times. Therefore, it is necessary to understand the physical, chemical and sensorial changes during intermittent deep fat frying and their correlation with the total polar compounds aiming at establishing prediction models for estimating physical, chemical and sensorial indices to monitor the quality of fried foods. These results are in agreement with those, reported by **Qing *et al.* (1999), Zhang *et al.* (2012) and Nayak *et al.* (2015).**

Regression Models and Correlation between Sensory Evaluation and Total Polar Compounds Determined by Spectrophotometry

Sensory evaluation is often the better method of evaluating food samples. However the outlay, availabilities and disquiet of preceding a sensory panel often make it unworkable and alternative instrumental methods must be used instead. Therefore, it is important to know the relationship between instrumental methods, such as between TPCs content, and sensory evaluation.

The results indicated that TPCs content of the oil samples tended to increase with frying time, whereas the sensory intensity tend to decrease. The regression models and correlation between sensory scores and TPCs content are shown in Table 7. There were significant ($P \geq 0.05$) differences in all the results analyzed for the sensory evaluation during intermittent deep fat frying of potato chips for 40 hr. at five consecutive days. There was a negative correlation of – 0.752 between TPC contents and average flavour intensity score. The linear regression equations for prediction the flavour scores during frying of potato chips for 40 hr., were:

Table 6. Sensory evaluation of fried potato chips in sunflower oil as affected by deep frying for consecutive five days (8 hr. daily)

Frying period		Flavour	Crispy texture	Greasiness	Overall acceptability
Day	hr.				
First	**0**	3.80	3.60	4.00	3.60
	3	3.90	3.90	4.10	3.80
	6	4.00	4.20	4.20	4.00
	8	4.30	4.20	4.30	4.40
Second	**0**	4.60	4.80	4.40	4.60
	3	4.50	4.70	4.30	4.504.40
	6	4.40	4.50	4.20	4.30
	8	4.30	4.50	4.20	
Third	**0**	4.20	4.40	4.20	4.20
	3	4.10	4.30	4.10	4.10
	6	4.15	4.20	4.00	4.10
	8	4.15	4.20	3.90	4.00
Fourth	**0**	4.00	4.20	3.80	4.00
	3	4.00	4.10	3.80	4.00
	6	3.80	4.10	3.70	3.90
	8	3.70	4.00	3.60	3.80
Fifth	**0**	3.50	3.90	3.60	3.70
	3	3.60	3.80	3.50	3.60
	6	3.50	3.70	3.40	3.60
	8	3.20	3.60	3.20	3.40

Table 7. Regression models and correlation between sensory evaluation and total polar compounds of sunflower oil during intermittent frying of potato chips for 40 hr., at five consecutive days (8 hr., daily).

Sensory attributes	Model (Y = Sensory attributes and X = Total polar compounds by spectrophotometry	Computed F	Tabulated F	LSD 5%	Correlation coefficient
Flavour	$Y= 4.602 – 0.03609 X$ $Y = 181.851 – 23.851 X + 0.6566 X^2$	3.72	3.33	0.253	r = - 0.752
Crispy texture	$Y = 4.575 – 0.0246723 X$ $Y = 3.585 + 0.1083 X – 0.003666 X^2$	6.29	3.33	0.474	r = - 0.559
Greasiness	$Y = 4.636 – 0.04147 X$ $Y = 17.12 – 1.72 X + 0.0463 X^2$	3.52	3.33	0.314	r = - 0.917
Overall acceptability	$Y = 4.481 – 0.0282456 X$ $Y = 3.593 + 0.0911 X – 0.0033 X^2$	4.29	3.33	0.410	r = - 0.649

$Y = 4.602 – 0.03609 X$

$Y = 181.851 – 23.851 X + 0.6566 X^2$

Where:

Y = flavour score

X = TPCs content determined by spectrophotometry.

Concerning fried food crisp intensity scores showed a slight tendency to increase with frying time, and the correlation between fried food crisp intensity and TPC_S content was -0.559. Whereas, fried food greasiness intensity showed a strong tendency to increase with frying time, the scores for greasiness of the potato chips were highly correlated with the TPC_S content of sunflower oil (r=-0.917).The linear regression equations for prediction the greasiness scores during frying of potato chips for 40 hr. were:

$Y=4.636-0.04147X$

$Y=17.12-1.72X+0.0463X^2$

Where:

Y = Greasiness score.

X = TPCs content determined by spectrophotometry.

Additionally, the following regression model shows that overall acceptability scores and TPCs content had a moderately significant correlation of – 0.649.

$Y = 4.481 – 0.0282456 X$

$Y = 3.593 + 0.0911 X – 0.0033 X^2$

Where:

Y = overall acceptability score.

X = TPCs content determined by spectrophotometry.

Similar results were found with other types of fried foods (**Tompkins and Perkins, 1999; Qing, 2000; Hassan and Abou-Arab, 2004; Kalogianni *et al.,* 2016).**

Conclusions

Spectrophotometric absorbance method is feasible for evaluate of sunflower oil during intermittent deep fat frying of potato chips for 40 hr. at five consecutive days, and requires only inexpensive and widely available equipment. Moreover, it minimized the consumption of samples and chemicals. Principal component analysis and linear regression analysis were used in order to assess the obtained results. TPCs content generally has strong correlation to physicochemical analysis and sensory evaluation intensity scores (for crispy texture, flavour, greasiness and overall acceptability). The results obtained agreed with the reference methods used for vegetable oil analysis, and can be used as a routine test for assessing frying oil quality.

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تقييم جودة زيت القلي العميق بالطريقة الإسبكتروفوتوميترية للتقدير السريع للمركبات القطبية الكلية

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تركز هذه الدراسة على تقييم بعض الطرق الرسمية لتقدير جودة زيت القلي مع الطريقة الإسبكتروفوتوميترية الجديدة، وتقييم أداء هذه الطرق من خلال القلي العميق والمتقطع لشرائح البطاطس المقلية في زيت دوار الشمس لمدة ٤٠ ساعة خلال خمسة أيام متوالية بواقع ثماني ساعات يومياً، وتعتبر التحليلات الكيميائية من أهم الطرق لقياس المركبات المتحللة بزيت القلي، وبتقدم مدة القلي ترتفع قيمة المركبات القطبية الكلية؛ مما يقترح أن تقدير المركبات القطبية الكلية هو أكثر طرق التقدير ثقة لقياس تدهور الزيت أثناء عمليات القلي العميق، بجانب تحليل عناصر جودة الزيت الأخرى خلال ٤٠ ساعة من القلي العميق والمتقطع سواء بواسطة الطرق الرسمية أوطريقة الامتصاص الإسبكتروفوتوميترية السريعة، وتم دراسة الارتباط بينهما لتقييم النتائج المتحصل عليها، واستخدمت نتائج الدراسة لمعايرة النتائج مع طريقة الامتصاص الإسبكتروفوتوميترية؛ حيث لوحظ ارتباط قوى (٠,٩٩٩) بين قيم الامتصاص الإسبكتروفوتوميترية ومحتوى المواد القطبية الكلية فى الزيت المعامل بنفس الطريقة، وأن معادلة تحويل قيم الامتصاص الإسبكتروفوتوميترية إلى محتوى المواد القطبية الكلية هى : $Y = - 57.0083 + 2.64X + 0.049X^2$، وتم استخدام طريقة الامتصاص الإسبكتروفوتوميترية لتقييم جودة زيت القلي، كما هدفت هذه الدراسة الي ربط محتوى المواد القطبية الكلية المقدرة بالطريقة الإسبكتروفوتوميترية بمقاييس الخصائص الطبيعية، والكيميائية، والحسية؛ حيث وجد أن الارتباط بين المواد القطبية الكلية ومعامل الانكسار (٠,٩٥٠)، واللزوجة (٠,٩٨٩)، واللون (٠,٩٩٣)، ورقم الحموضة (٠,٨٩٩)، والعدد اليودي (٠,٩٤٧)، ورقم البار أنيسيدين (٠,٩٨٧)، ورقم حمض الثيوباربتيوريك (٠,٨٧٥) ومحتوى الأحماض الدهنية المؤكسد (٠,٩٧٥) كما لوحظ وجود ارتباط بين المواد القطبية الكلية والنكهة (-٠,٧٥٢) وصفة التشحم (-٠,٩١٧)، وصفة القرمشة (٠,٥٥٩)، وتوضح النتائج أن طريقة الامتصاص الإسبكتروفوتوميترية لزيت القلي طريقة جيدة ، وسريعة ، وبسيطة ، ومريحة ، ومؤشر يمكن الاعتماد عليه لتقدير خصائص الجودة لزيت دوار الشمس المختبر أثناء عمليات القلي العميق.

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