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Evaluation of a sunflower oil used for frying by different analytical indexes and column and gas chromatography

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Prüfung im Sonnenblumenöl, das zum Fritieren benutzt wurde, mittels verschiedener analytischer Kennzahlen und Gaschromatographie

Summary: The alteration of a sunflower oil used repeatedly and discontinuously for frying potatoes on 15 successive occasions was studied. For this purpose, standard analytical indexes, such as fatty acids, gas chromatography, refraction and color indexes, and acid value were compared with a chromatographic method that quantifies the polar compounds originated during fryings. Total polar content increased significantly ($p < 0.05$) from 6.2 ± 0.3 mg/100 mg oil to 18.7 ± 0.8 mg/100 mg oil in the last frying. Linoleic acid decreased significantly ($p < 0.05$) from 53.8 ± 0.2 mg/100 mg oil to 48.1 ± 0.8 mg/100 mg oil at the 15th frying, while oleic acid concentration remained unaltered throughout the frying operations. The color index, and acid value, showed a significant increase ($p < 0.05$) after 15 fryings. Color index, acid value, and total polar content highly and significantly correlated with the number of fryings ($0.981 > r > 0.933$; $p < 0.01$). Linoleic acid concentrations also significantly correlated ($r = -0.692$; $p < 0.05$) with the number of fryings performed. Acid value, color index, and linoleic acid concentration also showed high and significant correlation with the percentage of total polar component of the oil ($r = 0.9272$, $r = 0.9065$ and $r = -0.764$ respectively; all $p < 0.01$). These data suggest that standard methods such as acid value and color index can be applied and are as useful as silica-gel chromatographic evaluation in the monitoring of frying operations, provided that initial values of both the color index and acid value are available.

Zusammenfassung: Es wurden die quantitativen Veränderungen eines Sonnenblumenöls, das 15 mal aufeinanderfolgend für die Fritierung von Kartoffeln benutzt wurde, untersucht. Dazu wurden analytische Routinemethoden, wie die Gaschromatographie der Fettsäuren, die Bestimmung des Refraktions- und Farbindexes sowie der Säurezahl mit einer absorptionschromatographischen Methode zur Bestimmung der polaren Verbindungen, die während des Fritierens entstehen, verglichen. Der Gehalt polarer Verbindungen stieg signifikant ($p < 0{,}05$) von $6{,}2 \pm 0{,}3$ mg/100 mg Öl auf $18{,}7 \pm 0{,}8$ mg/100 mg Öl bei der letzten Fritierung. Die Konzentration an Linolensäure verminderte sich dagegen signifikant ($p < 0{,}05$) von $53{,}8 \pm 0{,}2$ mg/100 mg Öl auf $48{,}1 \pm 0{,}8$ mg/100 mg Öl beim 15. Durchgang. Der Gehalt an Ölsäure veränderte sich dagegen nicht. Der Farbindex und die Säurezahl stiegen signifikant ($p < 0{,}05$) nach 15 Fritierungen. Die Veränderung des Farbindexes, der Säurezahl und des Gesamtgehalts polarer Verbindungen wiesen eine hohe und signifikante Korrelation zur Anzahl der Fritierungen auf ($0{,}98 > r > 0{,}933$; $p < 0{,}01$). Der Gehalt an Linolensäure zeigte ebenfalls eine signifikante Korrelation zur Anzahl der Fritierungen ($r = -0{,}692$; $p < 0{,}05$). Die Säurezahl und der Farbindex sowie der Gehalt an Linolensäure zeigten ebenfalls eine hohe und signifikante Korrelation zum Anteil der polaren Verbindungen ($r = -0{,}9272$ bzw. $r = 0{,}9065$ bzw. $r = -0{,}764$; alle $p < 0{,}01$). Unsere Ergebnisse zeigen, daß Routinemethoden, wie Säurezahl oder Farbindex, die wir für die Bestimmungen im Sonnenblumenöl benutzt haben, genauso nützlich sein können wie andere mehr spezifische Methoden, wenn man die Ausgangswerte dieser Indizes für das zu behandelnde Öl hat.

Key words: Deep-fat frying – sunflower oil – column chromatography – color index – acid value – fatty acid esters

Schlüsselwörter: Sonnenblumenöl – Fritieren – Säulenchromatographie – Refraktionsindex – Fettsäurengehalt

Introduction

In deep fat frying the fat is exposed to the action of several agents: moisture from the foodstuff that involves it in hydrolytic alteration, atmospheric oxygen entering the oil that gives rise to an oxidative alteration, and the temperature at which the operation takes place that accelerates chemical changes. In addition, the unsaturation of the fatty acids of the oils and nature of the food are also involved in the formation of a complex mixture of products (11, 14).

In consequence, there is a need to define the point at which the fats or oils ought to be discarded. This is linked to the content of polar compounds formed during fryings. Polar compounds formation also correlates to the way frying is performed (6, 15). Today, it is considered that either a fat or an oil for frying purposes must be discarded when its polar content is higher that 25 % (3, 8, 19).

Waltking and Wessels (25) described a method, later recommended by IUPAC, for the evaluation of compounds specifically related to frying degradation. The above-mentioned method is based on the separation by column chromatography on silica-gel of two fractions, one containing the unaltered part of the fat or nonpolar components, which are unaltered triglycerides, and a second one concentrating the altered products or polar components of frying fats.

However, for several decades the measurements of frying fat alteration have been carried out almost exclusively by means of physical and chemical indexes, which still constitutes a common and useful practice (7, 14, 18). Among the physical test, the colorimetric indexes (related to altered compounds such as unsaturated carbonyl compounds) are now widely accepted. In addition, among the chemical tests, acid value is a standardized method for free fatty acids evaluation. On the other hand, the analytical indexes based on physical and chemical changes are widely used in the fried-foodstuff-related industries, because they are easy to analyze and of the present modestly priced analysis devices, together with the reproducible results. Nevertheless, it is necessary to have a reference value for the unheated fat, as described previously (7).

Recently in Spain, a marked increase in the consumption and use for frying purposes of sunflower oil and a decrease in the use of olive oil have been described (17).

Economical reasons are involved in the use for frying of sunflower oil instead of olive oil. The latter oil, however, is shown more adequate for frying purposes because of its thermal stability.

The aim of this report is to evaluate the alteration of a sunflower oil used in 15 fryings of potatoes, measuring the polar triglyceride content, and employing standard analytical methods such as refraction and color indices, acid value, and fatty acid methyl esters-gas chromatography. In addition, correlations between these standard analytical methods and percentage of total polar content were established. Some further correlations were also established between data obtained using all the indexes studied and the number of fryings carried out.

Material and methods

Experimental procedures

Performance of fryings: Refined sunflower oil and potatoes were purchased at a local store. The oil was stored below 15 °C in darkness and used as purchased. As to the raw potatoes analysis, the amounts of their components included: moisture 77.3 ± 0.9 %, protein (g % fresh matter) 2.5 ± 0.2, fat (g % fresh matter) 0.2 ± 0.05.

Performance of fryings was carried out in domestic deep-fat fryers with a 3 l aluminium vessel. The peeled potatoes were chopped into slices of ca. 2-mm thick. The proportion of food to frying oil in the repeated fryings was kept at 500 g/3 l by eliminating one fryer after each four fryings and emptying its content to make up the volume of the other fryers to 3 l because so much oil is removed along with the fried potatoes.

Time required to reach and maintain the bath oil at 180 °C before introduction of potatoes was 20 min. Potato slices were then fried for 8 min. After the end of each frying, the oil was again heated to 180 °C before beginning a new frying (time required 10 min). A set of two fryings was successively carried out, then the oil was allowed to cool to room temperature until the next day. Every day the same frying procedure was repeated. The fryings took place over four consecutive days. On the last day only three fryings were performed. The overall time the oil was heated throughout the whole experiment can be estimated to be 5 h, 50 min.

Aliquots of 50 ml from the unused and from the fourth, eighth, 12th, and 15th fryings were taken for analysis.

Analytical indexes: After the fourth, eighth, 12th, and 15th fryings, the oil losses in each fryer were measured and potatoes were taken for fat content analysis.
- Fat content was evaluated after several extractions with cool diethyl-ether.
- Refraction index was evaluated following the procedure outlined in (22).
- Color index was determined according to the method of Wolff (26).
- Acid value was performed according to the method outlined in (23).

Column chromatography: Polar fractions were evaluated by the column chromatographic method of Waltking and Wessel (25), slightly modified, as previously described (6).

Two samples of unused oil and used oil from the fourth, eighth, 12th and 15th fryings were taken for analysis.

The purity of this fraction was then checked by thin-layer chromatography with Merck plates (60F 250, 0.5-mm thickness) using a mixture of hexane/dietyl ether/acetic acid (80 : 20 : 1) as solvent system (6).

Gas chromatographic analysis of fatty acid esters: Samples of the oils were saponified and then methylated according to the method outlined in (16). Details of the gas chromatographic analysis performed using stainless steel columns (6 feet, 1/8 inch) packed with 10 % Supelcoport 2330 on 100–120 Chromosorb W AW (Supelco, Inc. Bellefonte, PA) were given in a previous work (6).

Statistical analysis: Oil volume loss, and weight and fat content of fried potatoes after different fryings were compared using the unpaired Student's *t*-test. Values obtained by the different methods were compared with their respective basals by the paired Student's *t*-test (9). Pearson linear correlation was applied to assess the relationship between the different alteration compounds and between the products and the number of frying operations (9).

Results and discussion

Generally, the adverse effects on the nutritional quality of fried food are due to oxidation products which remain in the fat used for cooking. This is of great interest when a foodstuff such as potato chips is being fried; they absorb ca. 27–40 % of this deteriorated fat (13, 21). Hence, there is a necessity to use a good quality frying medium and to maintain it in that state as long as possible.

The uptake of the sunflower oil by the potatoes is shown in Table 1. Considering that the fat content of raw potatoes was low (0.2 g % fresh matter), the fat content of fried potatoes should be related only with the frying bath oil absorption by the potatoes. Results are given in Table 1. In this study, during the frying process there was an average volume loss of oil in the fryer of 63.6 ml per frying. Using an analogous study design for frying potatoes in olive oil our group found an average volume loss of oil of 56.3 ml per frying. The average weight of fried potatoes from each frying was 200 g. Taking into account that weight of raw potatoes was 500 g for each frying, an about 60 % percentage weight decrease of potatoes was found (unpublished data). According to Blumenthal (3) and Guillaumin (13), during deep-fat frying food loses water which is transformed into steam. The weight of fried potatoes increases significantly ($p < 0.05$) with the number of fryings (Table 1) which is in accord with those of Guillaumin (13), who described that when frying medium begins to be abused there is a rise in the viscosity of the fat and the uptake of this fat by the food increases.

Table 1. Oil volume loss per fryer, and weight and fat content of fried potatoes after successive fryings (x)

Number of fryings	Oil volume loss (ml/fryers)	Weight of fried potatoes (g)	Fat content of potatoes (y) (g/100 g dry matter)
0– 4	52.6 ± 6.5 (6)	179.4 ± 1.4a (24)	26.7 ± 1.9ab (3)
5– 8	70.3 ± 6.1b (5)	207.3 ± 4.7b (20)	26.8 ± 0.5a (3)
9–12	66.4 ± 5.9b (4)	201.2 ± 12.8b (16)	29.9 ± 1.1b (3)
13–15	71.1 ± 10.7b (3)	212.8 ± 3.5c (12)	29.5 ± 1.2b (3)

(x) Values (mean ± standard deviation for the (within parentheses) indicated number of samples analyzed) in the same column bearing different letters are significantly ($p < 0.05$, unpaired Student's *t*-test) different

(y) Fat contents of fried potatoes were measured at frying numbers 4, 8, 12, and 15

Determination of total polar material in a frying fat provides a reliable measurement of the extent of deterioration in most cases (12). Changes in other analytical indexes such as refraction and color indexes, acid value and changes in the concentration of fatty acids are the most standard methods judged reliable for monitoring frying operation (6, 12, 18).

In Table 2 are given the results of the analytical indexes based on general chemical and physical changes obtained from the unused sunflower oil and the corresponding oil after different fryings.

Table 2. Analytical indexes based on general chemical and physical changes, total polar content, and changes in linoleic and oleic fatty acids in the sunflower oil used in 15 successive fryings of potatoes (x)

Number of fryings	Indexes Refraction	Color	Acid value	Oleic acid (mg/100mg oil)	Linoleic acid (mg/100mg oil)	Total polar content (mg/100mg oil)
0	1.4732 ± 6.10x10^{-5}	1.8 ± 0.1	0.28 ± 0.02	30.1 ± 0.3	53.8 ± 0.2	6.2 ± 0.3
4	1.4726 ± 2.10x10^{-5}	3.1 ± 0.7	0.32 ± 0.01	29.8 ± 0.3	51.3 ± 0.4	10.7 ± 0.6a
8	1.4731 ± 6.10x10^{-5}	3.4 ± 0.8	0.38 ± 0.20	30.0 ± 0.6	50.7 ± 0.6a	14.4 ± 0.8a
12	1.4737 ± 6.10x10^{-5}	4.7 ± 0.9a	0.44 ± 0.05a	29.9 ± 0.6	48.4 ± 0.7a	16.4 ± 0.8a
15	1.4738 ± 5.10x10^{-5}	6.0 ± 0.5a	0.51 ± 0.08a	30.3 ± 1.3	48.1 ± 0.8a	18.7 ± 0.8a

(x) Values (mean of three samples ± standard deviation) for the same column bearing the letter a are significantly ($p < 0.05$, paired Student's *t*-test) different in respect to basal value

Refraction index remains unaffected in agreement with results reported previously (24). Thus, no significant correlation was found between this index and the number of fryings ($r = 0.46$) (Table 3). Nevertheless, in other studies using different fryings oils several authors (4, 5) found a slight increase in the refraction index. This index did not show any significant correlation with the total polar content (Table 3). However, in a previous work a significant correlation was found between refraction index and total polar content in an olive oil used to fry potatoes (7).

Table 3. Pearson product-moment correlations between the different indexes measured in the oil and the number of fryings of potatoes, and between total polar content and the different indexes measured in the oil (x)

Refraction index/no. of fryings	0.4601	Polar content/Refraction index	0.3922
Color index/no. of fryings	0.9330b	Polar content/Color index	0.9065b
Acid value/no. of fryings	0.9357b	Polar content/Acid value	0.9272b
Oleic acid content (mg/100 mg oil)/ no. of fryings	-0.6247	Polar content/Oleic acid (mg/100 mg oil)	-0.3986
Linoleic acid content (mg/100 mg oil)/no. of fryings	-0.6920a	Polar content/Linoleic acid (mg/100 mg oil)	-0.7640b
Total polar content (mg/100 mg oil)/no. of fryings	0.9809b		

(x) Values bearing the letters a or b are significant ($p < 0.05$ or $p < 0.01$, respectively)

After 15 fryings the color index of the oil showed a significant increase and a high and significant correlation between color index and the number of fryings (Table 3). El-Zeany (10) indicated a darkening in the frying oils used which was attributed to the presence of unsaturated carbonyl compounds or to nonpolar compounds of foodstuff solubilized in the fat.

The acid value increased significantly ($p < 0.05$) from an initial value of 0.28 to 0.51 in the last frying; the correlation between the acid value and the number of fryings was high and significant (Table 3). Increases in acid value are fundamentally due to both hydrolytic reactions and the increase of free fatty acids, as was described in (14). However, according to Fritsch (12) determination of free fatty acids does not differentiate between acids formed by oxidation and those formed by hydrolysis. Thus, the increase in free fatty acids would be a poor measure of frying fat deterioration.

Total polar content or total alteration, defined as the sum of the eluted polar fraction plus the unrecoverable fraction, increased from 6.2 mg/100 mg in the unused oil to 18.7 mg/100 mg oil in the last frying as is shown in Table 2. Some authors (7) also reported the increase of polar fraction with the number of fryings when samples from olive oil used in 15 deep-fat fryings of potatoes were analyzed. Cuesta et al. (6) have indicated that the speed of degradation is proportional to the temperature and the duration of frying. However, in a previous work (15) performed with olive oil used for frying potatoes under analogous experimental conditions, lower values of polar content of 2.0–9.0 mg/100 mg oil were found than those in this study.

After being used in successive fryings of potatoes linoleic acid decreased significantly ($p < 0.05$) from 54 mg/100 mg oil to 48 mg/100 mg (Table 2). Oleic acid concentration remained unaltered throughout frying operations. These results are in accord with those previously found (5, 6, 13), which had pointed out that heat treatment of fats induces modifications of fatty acid with two and three double bonds, which leads to polar compounds of high molecular weight.

According to Bender (1) changes due to the degradation of a fat affected its palatability more than its nutritive value. Most of the identified compounds from heated oils have often been quoted as the usual products of oxidation responsible for the „flavor" deterioration of oils (20).

Billek (2) found that the smell and taste of fats that contained more than 25 % polar material were still acceptable but when the content topped 30 % the fats were considered unacceptable and therefore deteriorated. In the present work a level of ≈ 19 % was found. These results suggest that the sunflower oil used for frying is still acceptable and could be employed for more potato fryings.

In conclusion, discontinued potato fryings in a sunflower oil, without turnover of unused oil, increase total polar components, color index, and acid value while the contents of linoleic decreased. Correlations suggest that standard analytical methods such as acid value and color index can be applied in the monitoring of frying operations and are as useful as the silica-gel column chromatographic method, provided that the values of the color index and acid value in the unused oil are known.

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