Sunflower Oil Used for Frying: Combination of Column, Gas and High-Performance Size-Exclusion Chromatography for Its Evaluation

F.J. Sánchez-Muniz[a,*], C. Cuesta[b] and C. Garrido-Polonio[a]

[a]Departamento de Nutrición y Bromatología, I (Nutrición), Facultad de Farmacia, Universidad Complutense and [b]Instituto de Nutrición y Bromatología (CSIC), Facultad de Farmacia, Universidad Complutense, E-28040 Madrid, Spain

The alterations of a sunflower oil were evaluated by column, gas and high-performance size-exclusion chromatography after being used for deep-fat frying fifteen repeated and discontinuous times. Polar compounds increased significantly (6.2 ± 0.3% to 18.7 ± 0.8% in oil). Linoleic acid decreased (53.8 ± 0.2 to 48.1 ± 0.8 mg/100 mg oil) while oleic acid remained unaltered after 15 fryings. Saturated fatty acids such as palmitic and stearic, also remained unaltered. Triglyceride polymers (0.1 ± 0.0 to 2.4 ± 0.2 mg/100 mg oil), triglyceride dimers (1.0 ± 0.2 to 6.7 ± 0.3 mg/100 mg oil) and oxidized triglycerides (3.4 ± 0.2 to 7.6 ± 0.3 mg/100 mg oil) increased significantly in the oil used 15 times to fry potatoes. These thermoxidative compounds correlated well with the number of fryings (r = 0.9864, r = 0.9535 and r = 0.9758, respectively). Diglyceride compounds remained unaltered, while free fatty acids increased from 0.4 ± 0.0 to 0.6 ± 0.0 mg/100 mg oil. Both of these, which are characteristic of hydrolytic alteration, did not correlate significantly (r = 0.5985 and r = 0.4261, respectively) with the number of fryings. These data suggest that a thermoxidative process, rather than a hydrolytic one, took place in this study.

KEY WORDS: Column chromatography, deep-fat frying, gas chromatography, HPSEC, polar compounds, sunflower oil, thermoxidation.

Analysis of decomposition products from the thermal and oxidative treatment of fats and oils has been widely studied (1–4). However, systematic studies concerning deep-fat frying are far from complete. The chemical reactions occurring during deep-fat frying differ from those that happen when the fat is only continuously heated (5,6). Frying is a complex process because many factors are at work (1,3). This complexity prompted the investigation of fryer designs and operating conditions. Details of frying methods have been described previously (4). Model systems have been employed to simplify and control the various parameters affecting the frying process (1,3,6). The combination of these parameters determines the rate at which the individual reactions take place.

Deep-fat frying, with or without fast turnover of fresh oil, should also be considered (4,7). In addition, it has also been observed that repeated and intermittent heating, as in household frying, increases the degradation of lipids, probably owing to peroxide formation and decomposition during reheating, cooking and cooling cycles. Finally, the advantages and limitations of the analytical procedures employed also have to be taken into account.

The aim of this study is to establish the deterioration of a sunflower oil used in 15 repeated and intermittent deep-fat fryings of potatoes without turnover of fresh oil, while controlling the frying process variables described above. The alteration of this sunflower oil was evaluated by measuring both the percentage of the unaltered part of the oil, *i.e.*, nonpolar triglycerides, and the percentage of the altered part of the oil, *i.e.*, polar triglycerides, by the column-chromatographic method of Waltking and Wessells (8). Further, variations in the oil's fatty acid composition were measured. In addition, the polar fraction was examined by high-performance size-exclusion chromatography (HPSEC) to investigate the thermoxidative and hydrolytic modifications. Although many analytical methods have been employed for this purpose, the HPSEC technique may be considered one of the most promising. This is because it increases the possibility of quantitating all the groups of altered compounds: polymers and dimers of triglycerides, oxidized triglycerides, diglycerides and free fatty acids (9).

EXPERIMENTAL PROCEDURES

Performance of frying. Sunflower oil (Córdoba, Spain) and potatoes were purchased at a local store. The oil was stored below 15°C in the dark and used as purchased. Analysis of the raw potatoes showed the following components: moisture 77.3 ± 0.9%, protein (wt% fresh matter) 2.5 ± 0.2 and fat (wt% fresh matter) 0.2 ± 0.05.

Domestic deep-fat fryers with 3-L aluminum vessels were used for frying. The pooled potatoes were chopped into slices *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 contents to make up the volume of the other fryers to 3 L. This was done to avoid using fresh oil to replenish the fat removed along with the fried potatoes. More extensive details of the frying method have been described previously (4). A total of 15 dryings were carried out. Time required to reach and keep 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 to begin with a new frying cycle. The total time for the heating was 10 min. Two fryings were carried out successively, then the oil was cooled to room temperature. After 5 h two more sets of successive fryings were carried out, again letting the oil cool to room temperature until the next day. Each day the same frying operations were repeated. The 15 fryings took place over four consecutive days. Only three fryings were performed on the last day. The total time the oil was heated throughout the whole experiment was about 5 h, 50 min. Figure 1 shows the temperature evolution during the frying process.

Aliquots of 50 mL from the unused oil and from the 4th, 8th, 12th and 15th fryings were taken for analysis.

Determination of the percentage of polar fractions. The polar fraction was evaluated by the column chromatography method of Waltking and Wessels (8), with a modified proportion of petroleum ether/dietyl ether used to fill the column and to elute the nonpolar fraction.

*To whom correspondence should be addressed.

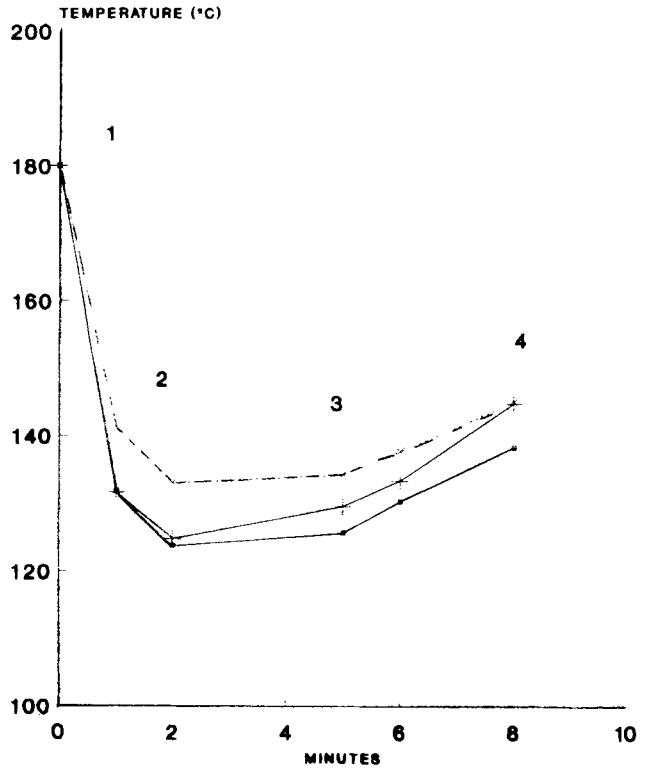

FIG. 1. Temperature evolution during potato frying. 1, Introduction of potatoes; 2, temperature decrease because of water evaporation; 3, temperature increase because of absorption of oil by food and less water evaporation; 4, end of the frying operation.-⊟-, First frying; +, eighth frying; -X-, fifteenth frying.

An accurately weighed sample of 1 ± 0.01 g of sunflower oil was dissolved in 20 mL petroleum ether/diethyl ether (87:13, vol/vol) when unused oil was analyzed, and 90:10 (vol/vol) when used oil was analyzed. The sample was then transferred to a silica-gel chromatography column by following the methods of Dobarganes *et al.* (10). A final elution of the column with chloroform/methanol (1:1, vol/vol) was performed to improve the recovery of the sample. Three samples each of unused oil and used oil from the 4th and 8th fryings, and two samples each of the oil from the 12th and 15th fryings were taken for analysis.

The separation of the nonpolar and polar fractions was checked by thin-layer chromatography (TLC) on 0.5-mm thick 60 F 250 silica gel plates (20 × 20 cm glass). Polar and nonpolar fractions were diluted 50 times (wt/vol) in hexane/diethyl ether (80:20, vol/vol). Samples were applied as 10-μL spots with a 705 Hamilton microsyringe. Plates were developed with hexane/diethyl ether/acetic acid (80:20:1, vol/vol/vol) in a lined tank for *ca.* 25 min (*ca.* 17 cm) and then removed, letting the solvent evaporate. The spots were visualized by coating with iodine vapors.

Gas chromatographic analysis of fatty acid esters. Samples of the oil were saponified and then methylated according to Metcalfe *et al.* (11) to achieve complete conversion to methyl esters. Saponification was done for 15 min with 40 mL/g 0.5 N NaOH in methanol. The esters were extracted in hexane, freed of moisture over sodium sulfate and dried under nitrogen gas. The measurements of the methyl esters were performed according to Metcalfe *et al.* (11).

A Hewlett-Packard 5710 chromatograph (Palo Alto, CA) equipped with flame detection and oven temperature programming was used. The oven temperature was held for 8 min at 170°C and then ramped from 170 to 240°C at 2°C/min. The upper-limit oven temperature was held 4 min prior to recycling. The injector and the detector blocks were set at 250 and 300°C, respectively. Carrier gas (nitrogen) flow rate was set at 30 mL/min. The oven was fitted with stainless-steel columns packed with 10% Supelcoport 2330 (Supelco, Inc., Bellefonte, PA) on 100–120 Chromosorb WAW (6/feet, 1/8 inch). Sample size was 0.5 μL. The methyl esters were identified by comparing their relative and absolute retention times with those of commercial standards. Peak areas were measured with a Perkin Elmer Minigrator M-2 7123A integrator (Norwalk, CT). Peaks were quantitated in mg/100 mg oil as previously described (12,13).

HPSEC. The polar fraction previously obtained by column chromatography, as described before, was analyzed by HPSEC, following the method of Dobarganes *et al.* (14), to obtain further information about hydrolytic and/or thermoxidative alterations occurring in the sunflower oil during frying. Isolated polar fractions were analyzed in a Konic 500 A chromatograph (Barcelona, Spain) with a 10-μL sample loop. A Hewlett-Packard 1037 A refractive index detector and two 300 mm × 7.5 mm i.d. (5 μm particle size) 10 μm and 50 μm pL gel (polystyrene-divinylbenzene) columns (Hewlett-Packard) connected in series were operated at 45°C. High-performance liquid chromatography (HPLC)-grade tetrahydrofuran served as the mobile phase with a flow of 1 mL/min. Sample concentration was 10–15 mg/mL in tetrahydrofuran. All eluents, as well as samples, were precleaned by passing them through a filter (2 μm) as described in previous work (15).

To evaluate the hydrolytic and thermoxidative products, pure fatty acids, diglycerides, triglycerides and total polar fractions at different concentrations were studied. Correlations obtained between the detector response and the weight of different compound groups injected were linear ($r \sim 0.99$). The response factors for fatty acids, diglycerides, triglycerides and total polar components were similar. Because standards for triglyceride dimers and triglyceride polymers are not available, regression lines relating retention times and molecules weight (MW) of compounds such as free fatty acids, monoglycerides, diglycerides and triglycerides were drawn. Then, the retention times of the sample chromatogram peaks were extrapolated on an extension of these regression lines. An MW of ∼ 1800 and an MW of ∼ 3000 corresponded to MW of triglyceride dimers and triglyceride trimers, respectively (16).

Statistical analysis. Paired Student's *t*-test and the Pearson product-moment linear correlation test were used for statistical evaluation (17).

RESULTS AND DISCUSSION

As shown in Figure 1, the temperature of the medium during potato frying remains below 140°C during almost the whole process. According to Blumenthal (18), wetting of the heater surfaces ultimately led to complete carbonization of an oil layer and the formation of an insulating blanket around the heater elements. Insulation leads to higher temperature on the heater surfaces as the con-

trollers call for more heat from the sources. The water loss produced throughout the successive fryings of potatoes (19) would produce wetting of the heater surfaces, and would also explain the higher temperature observed at the fifteenth frying than at the first and eighth fryings in the present study.

In general, the decomposition products formed during frying can be divided into two broad classes—volatile and nonvolatile decomposition products. The formation of nonvolatile decomposition products is due largely to thermal oxidation and polymerization of the unsaturated fatty acids present in the frying medium. The rate of oxidation is reported to be roughly proportional to the degree of unsaturation of the fatty acids present (3,10).

Sunflower oil, which contains more than 50% linoleic acid (Table 1), would be susceptible to oxidation. This is of great interest to the deep-fat frying industry, because of the necessity of maintaining a good-quality frying medium as long as possible when foodstuffs, such as potato chips are being fried. Potato chips absorb fat at levels of 27–40% of their weight (18–20).

Measurements of fatty acid esters are given in Table 1. Linoleic acid decreased significantly, from 53.8 ± 0.2 mg/100 mg oil to 48.1 ± 0.8 mg/100 mg oil, which indicates a decrease of linoleic acid in the fryer of about 10.6%. However, no significant variations were found for oleic, palmitic or stearic acid concentrations.

The high level of alteration with respect to fatty acids observed after 15 fryings in the sunflower oil is in agreement with Dobarganes *et al.* (10), who indicated that alterations of used frying fats are related to the unsaturated fatty acid content of the fat as well as to the heat treatment itself and the number of fryings.

Several authors (1,3,19) have pointed out that heat treatment of fats induces modifications of fatty acids with two and three double bonds, as was found in this study. Measurements of nonpolar and polar triglyceride fractions are given in Table 2. The polar fraction of the oil showed a significant increase, from 5.7 ± 0.4% for unused oil to 18.4 ± 0.1% after 15 fryings, while the nonpolar fraction decreased significantly, from a basal value of 93.7 ± 0.3% to 81.3 ± 0.8%, after fifteen fryings.

Total alteration, defined as the sum of the polar fraction plus the unrecoverable fraction, increased from 6.2 ± 0.3% for unused oil to 18.7 ± 0.8% for oil in the 15th frying. Cuesta *et al.* (13) also reported an increase of the polar fraction with the number of fryings when samples from used olive oil in 15 deep-fat fryings of potatoes were analyzed. According to Fedelli (21), the rate of degradation is proportional to the temperature and frying time.

HPSEC was used to further examine the polar and polymeric materials in the oil. The HPSEC chromatograms of the polar fractions from unused and used sunflower oil are presented in Figure 2. Data obtained in this study (Table 3) indicate a clear tendency of the oil to increase in triglyceride polymers (2.4 ± 0.2 mg oil *vs.* 0.1 ± 0.0 mg oil), triglyceride dimers (6.7 ± 0.3 mg oil *vs.* 1.0 ± 0.2 mg oil) and oxidized triglycerides (7.6 ± 0.3 mg oil *vs.* 3.4 ± 0.2 mg oil), which represent thermoxidative alteration.

As described by Pérez-Camino *et al.* (12), quantitation of diglycerides allows determination of the contribution of hydrolytic alteration. After 15 fryings, diglycerides of the oil remained unaltered (1.4 ± 0.0 mg oil *vs.* 1.4 ± 0.1 mg oil). However, free fatty acids increased from 0.4 ± 0.0 mg oil to 0.6 ± 0.0 mg oil. These results indicate that

TABLE 1

Fatty Acid Composition of Unused Sunflower Oil and After Successive Fryings of Potatoes[a]

Times fried	C16:0 mg/100 mg oil	C18:0 mg/100 mg oil	C18:1 mg/100 mg oil	C18:2 mg/100 mg oil
0	6.9 ± 0.3	3.9 ± 0.1	30.1 ± 0.3	53.8 ± 0.2
4	7.2 ± 0.2	3.7 ± 0.1	29.8 ± 0.3	51.3 ± 0.4
8	6.8 ± 0.1	3.5 ± 0.2	28.6 ± 0.6	48.3 ± 0.6[b]
12	7.2 ± 0.1	3.7 ± 0.1	29.9 ± 0.6	48.4 ± 0.7[b]
15	7.4 ± 0.5	3.6 ± 0.1	30.3 ± 1.3	48.1 ± 0.8[b]

[a]Values (mean of three samples ± SD) for the same fatty acid bearing a letter are significantly different ($P < 0.05$, paired Students' *t*-test) with respect to the basal value.

TABLE 2

Relative Percentages of Polar and Nonpolar Fractions of Triglycerides by Column Chromatography[a]

Times fried	Number of samples	Nonpolar fraction	Polar fraction	Unrecoverable fraction	Total alteration[b]
0	3	93.7 ± 0.3	5.7 ± 0.4	0.5 ± 0.7	6.2 ± 0.3
4	3	89.3 ± 0.7[a]	9.8 ± 1.0[a]	0.9 ± 0.8	10.7 ± 0.6[a]
8	3	85.5 ± 0.8[a]	14.5 ± 0.8[a]	−0.1 ± 0.1	14.4 ± 0.8[a]
12	2	83.6 ± 0.8[a]	15.5 ± 0.7[a]	0.9 ± 1.4	16.4 ± 0.8[a]
15	2	81.3 ± 0.8[a]	18.4 ± 0.1[a]	0.3 ± 0.3	18.7 ± 0.8[a]

[a]Values (mean of the indicated samples ± SD) for the same fraction bearing a letter are significantly different ($P < 0.05$ paired Student's *t*-test) with respect to the basal value.

[b]Defined as the sum of the polar fraction plus the unrecoverable fraction.

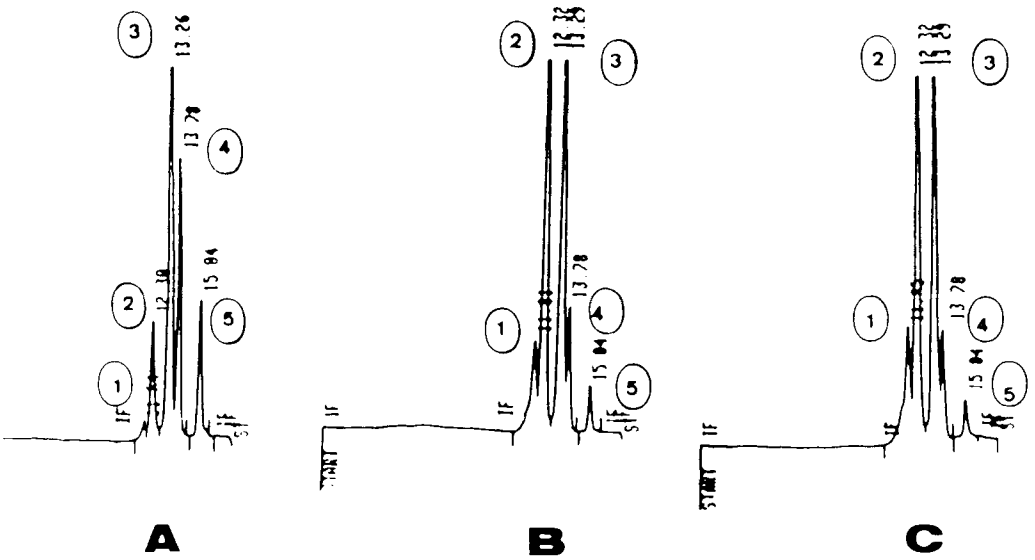

FIG. 2. High-performance size-exclusion chromatograms of unused (A) and used oil samples: eighth (B) and fifteenth (C) fryings. 1, Triglyceride polymers; 2, triglyceride dimers; 3, oxidized triglycerides; 4, diglycerides; 5, free fatty acids. Conditions: Column-series connected 10 μm and 50 μm PL gel (polystyrene-divinylbenzene), 300 mm × 7.5 mm i.d., 5 μm particle size; eluant tetrahydrofuran at 1 mL/min in tetrahydrofuran, 10 μL injection volume, refractive index detection.

TABLE 3

Distribution of Polar Components in Different Groups of Alteration Compounds in Unused Sunflower Oil and After Being Used 8 and 15 Times to Fry Potatoes[a]

	Times fried		
	0 (n = 3)	8 (n = 3)	15 (n = 2)
Thermoxidative alteration:			
Triglyceride polymers (mg/100 mg oil)	0.1 ± 0.0	1.4 ± 0.1[a]	2.4 ± 0.2[a]
Triglyceride dimers (mg/100 mg oil)	1.0 ± 0.2	5.6 ± 0.4[a]	6.7 ± 0.3[a]
Oxidized triglycerides (mg/100 mg oil)	3.4 ± 0.2	5.2 ± 0.3[a]	7.6 ± 0.3[a]
Hydrolytic alteration:			
Diglycerides: (mg/100 mg oil)	1.4 ± 0.1	1.5 ± 0.1	1.4 ± 0.0
Free fatty acids (mg/100 mg oil)	0.4 ± 0.0	0.8 ± 0.1[a]	0.6 ± 0.0[a]

[a]Values (mean of the indicated samples ± SD) for the same compound bearing a letter are significantly different ($P < 0.05$, paired Student's *t*-test) with respect to the basal value. n, number of analysis.

in deep-fat frying of potatoes in sunflower oil thermoxidative reactions were more prevalent than hydrolytic reactions. This is also shown in Table 4, where the ratio of thermoxidized (polymers plus dimers and oxidized triglycerides) to hydrolytic (diglycerides plus free fatty acids) compounds rose 3.4 times ($P < 0.05$).

Kupranycz *et al.* (22) found that sunflower oil after both 8 and 16 h of thermal oxidation contained substantially higher amounts of both dimeric and higher-oligomeric triglycerides than the unused oil. These authors indicated that the rates of dimeric triglycerides formation, during the first 8 h of heating, exceeded the rates of trimeric and higher-oligomeric triglyceride formation. The rate of dimer formation decreased during the 8–16 h of heating, and the amounts of higher-oligomeric triglycerides continued to increase at a steady rate throughout the 16 h heating period.

Perrin *et al.* (23) analyzed samples from sunflower oil oxidized by deep-fat frying until stable foam formation. They reported the presence of dimers at levels between 12.1 and 12.9% of the oxidized mixtures. Gere (24) also reported the presence of dimeric triglycerides in sunflower oil used in deep-fat frying.

Linear correlations between total polar contents or the different polar compounds and the number of fryings are shown in Table 5. Total polar compounds, triglyceride polymers and triglyceride dimers showed a high ($r > 0.95$) and significant correlation ($P < 0.01$) with the number of fryings. In addition, diglyceride levels ($r = 0.5985$) and free fatty acids ($r = 0.4261$) were not significantly correlated with the number of fryings. Correlations between total polar compounds and the different groups of alteration compounds are also presented in Table 5. A high correlation between total polar compounds and triglyceride polymers, triglyceride dimers, oxidized triglycerides or total thermoxidized compounds was found ($r > 0.965$; $P < 0.01$). Diglycerides, free fatty acids or total hydrolytic products showed insignificant correlations with the total polar fractions.

In short, discontinuous and successive fryings of potatoes in sunflower oil, without addition of fresh oil during frying, increased the level of total polar compounds in the oil. Thermoxidative alterations took place instead of the hydrolytic process, as evidenced by the correlation found for thermoxidative alteration (triglyceride polymers, triglyceride dimers or oxidized triglycerides) with the number of fryings.

TABLE 4

Ratios of Nonpolar Compounds to Different Groups of Alteration Compounds and Ratios of Thermoxidative Alteration Compounds to Hydrolytic Alteration Compounds in Unused Sunflower Oil and After Being Used 8 and 15 Times to Fry Potatoes[a]

	Times fried		
	0 (n = 3)	8 (n = 3)	15 (n = 2)
Nonpolar compounds/polar compounds	15.3 ± 0.4	5.9 ± 0.4[a]	4.4 ± 0.2[a]
Nonpolar compounds/thermoxidative alteration compounds	20.8 ± 1.1	7.0 ± 0.5[a]	4.9 ± 0.3[a]
Nonpolar compounds/hydrolytic alteration compounds	52.1 ± 2.7	37.2 ± 3.0[a]	40.7 ± 0.1[a]
Thermoxidative alteration compounds/hydrolytic alteration compounds	2.5 ± 0.1	5.3 ± 0.7[a]	8.4 ± 0.3[a]

[a]Values (means of the indicated samples ±SD) for the same parameter bearing a letter are significantly different ($P < 0.05$, paired Student's t-test) with respect to the basal value. n, number of analysis.

TABLE 5

Pearson Product-Moment Correlations Between Different Groups of Alteration Compounds in the Oil and Number of Fryings, and Between Total Alteration Compounds and the Different Groups of Alteration Compounds in the Oil

Polar compounds/no. of frying	0.9842 ($P < 0.01$)	Polar commpounds/triglyceride polymers	0.9956 ($P < 0.01$)
Triglyceride polymers/no. of frying	0.9864 ($P < 0.01$)	Polar compounds/triglyceride dimers	0.9863 ($P < 0.01$)
Triglyceride dimers/no. of frying	0.9535 ($P < 0.01$)	Polar compounds/oxidized triglycerides	0.9659 ($P < 0.01$)
Oxidized triglycerides/no. of frying	0.9758 ($P < 0.01$)	Polar compounds/thermoxidative alteration compounds	0.9996 ($P < 0.01$)
Thermoxidative alteration/no. of frying	0.9866 ($P < 0.01$)	Polar compounds/diglycerides	0.7790 NS
Diglyceride/no. of frying	0.5985 NS[a]	Polar compounds/free fatty acids	0.5489 NS
Free fatty acids/no. of frying	0.4261 NS	Polar compounds/hydrolytic alteration compounds	0.6464 NS
Hydrolytic alteration/no. of frying	0.5329 NS		

[a]NS, nonsignificant correlation.

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