GRASAS Y ACEITES, 58 (2),
ABRIL-JUNIO, 148-153, 2007,
ISSN: 0017-3495

Optimization of analytical methods for the assessment of the quality of fats and oils used in continuous deep fat frying

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RESUMEN

Optimización de métodos analíticos para la evaluación de la calidad de grasas y aceites utilizados en el proceso de fritura en continuo.

La aplicabilidad, repetibilidad y capacidad de diferentes métodos de análisis para discriminar muestras de aceites con diferentes grados de oxidación fueron evaluadas mediante aceites recogidos en procesos de fritura en continuo en varias empresas españolas. El objetivo de este trabajo fue encontrar métodos complementarios a la determinación del índice de acidez para el control de calidad rutinario de los aceites de fritura empleados en estas empresas.

La optimización de la determinación de la constante dieléctrica conllevó una clara mejora de la variabilidad. No obstante, excepto en el caso del índice del ATB, el resto de métodos ensayados mostraron una menor variabilidad. La determinación del índice del ATB fue descartada ya que su sensibilidad fue insuficiente para discriminar entre aceites con diferente grado de oxidación. Los diferentes parámetros de alteración determinados en los aceites de fritura mostraron correlaciones significativas entre el índice de acidez y varios parámetros de oxidación diferentes, como la constante dieléctrica, el índice de *p*-anisidina, la absorción al ultravioleta y el contenido en polímeros de los triacilgliceroles. El índice de acidez solo evalúa la alteración hidrolítica, por lo que estos parámetros aportan información complementaria al evaluar la alteración termooxidativa.

PALABRAS-CLAVE: Alteración – Control de calidad – Fritura en continuo – Grasas y aceites – Métodos de análisis.

SUMMARY

Optimization of analytical methods for the assessment of the quality of fats and oils used in continuous deep fat frying.

Frying oils with different alteration degrees were collected from continuous frying systems at various Spanish companies. These samples were used to evaluate the applicability, repeatability and capability of a number of methods to discriminate between samples of different degrees of oxidation. The objective of this work was to find complementary methods to the acid value determination for the routine quality control of the frying oils used in these companies.

The optimization of the dielectric constant determination was accompanied by a clear variability improvement. However, except for the TBA value, the methods assayed showed lower variability. In addition, TBA value determination was discarded because this parameter showed insufficient sensitivity to discriminate between oil samples with different degrees of oxidation. Relationships between the alteration parameters determined in the frying media showed significant correlations between the acid value and several different oxidation parameters, such as the *p*-anisidine value, dielectric constant, lipid UV absorption and polymerized triacylglycerol content. Thus, since the acid value exclusively evaluates the hydrolytic alteration, these parameters give complementary information because they evaluate the thermoxidative alteration.

KEY-WORDS: Alteration – Analytical methods – Continuous frying – Fats and oils – Quality control.

1. INTRODUCTION

Deep-fat frying is a process of cooking in which food is immersed into an edible oil or fat that serves as a heat-transfer medium and, in addition, such frying oil is an important ingredient of the fried food. During frying, oil is exposed to high temperature in the presence of air and moisture. Under these conditions, various chemical processes such as oxidation, hydrolysis and polymerization take place. These thermoxidative processes induce changes in the quality of the frying oils and, therefore, the follow up of the oils' deterioration is important for the production of high quality fried foods (Stevenson *et al.*, 1984; Pokorny, 1999).

Continuous frying leads to oils with a low level of degradation and results in a fairly constant quality of the fried product when the process is adequately controlled (Dobarganes *et al.*, 2002). In addition, if one begins with the premise that the ultimate achievable shelf life of the fried product depends on the quality of the frying oil throughout the process, frying oil would rarely need to be downgraded or discarded. Indeed, once the time and temperature requirements are set, frying becomes automatic (Banks, 1996a). Hence, continuous deep frying of snack foods appears to be a simple operation. However, the continuous production of high quality products with a crispy texture and appropriate flavor and shelf life is complex (Hammond, 2002).

Several analytical methods have been used to assess the quality of frying mediums and fried products (Stevenson *et al.*, 1984; White, 1991;

Melton *et al.*, 1994). Among these methods, the determination of the acidity is the most commonly used to check the quality of the frying oil and it is, in fact, very frequently the only method used in medium- and large-scale Spanish companies to monitor the frying process. However, this parameter exclusively evaluates the hydrolytic alteration, so it provides only partial knowledge on the whole deterioration of the medium. Therefore, the companies involved in the experiment were interested in simple and rapid methods useful for routine analysis and complementary to acidity determination. Therefore, in this study, several suitable methods to control the quality of the medium during continuous frying were optimized and their repeatability and sensitivity was evaluated. In addition, most of the assayed methods do not require expensive instruments.

2. MATERIALS AND METHODS

2.1. Reagents

All solvents used were of suitable grade for spectrophotometric or chromatographic analyses.

2.2. Samples

Twelve oil samples representing both fresh oils and oils from normal and extreme continuous frying conditions were taken. These samples were collected from three Spanish snack food factories which fried with various types of oils with different degrees of unsaturation: sunflower oil (SO), palm olein (PO) and a palm olein/sunflower oil blend (30:70, v/v). Samples were homogenized upon their arrival at the laboratory and divided into different volume aliquots and kept at −20 °C until the analysis.

Sunflower oils were collected from two different points of a direct-heated electric fryer (Alivio, Buenos Aires, Argentina) with 1200 L of oil capacity. SO 1 was collected from the finish frying area where the product was removed from the fryer by a takeout conveyor. SO 2 was collected from the sediment outlet. The frying temperature was 175-182 °C.

Palm olein samples were colleted from the sampling tap in a direct-heated electric fryer (FMC Foodtech, Chicago, IL, USA) with 500 L of oil capacity. The frying process began with fresh PO and after 1 h and two and a half days of continuous frying (daily frying period = 15 h 45 min), two samples were taken: initial PO (PO I) and PO at normal frying conditions (PO NFC), respectively. In addition, a sample of PO was collected at extreme frying conditions (PO EFC). According to the producer, PO EFC was discarded from frying and was much more altered than usual. The frying temperature was 190-206 °C.

PO/SO samples were collected from the sampling tap in an indirect-heated fryer (Florigo, Woerden, Netherlands) with 4250 L of oil capacity. The four samples (PO/SO 1, 2, 3 and 4) were collected on consecutive days at the end of the continuous frying operation (daily frying period = 16 h 15 min). The frying temperature was 175-180 °C.

Frying oil samples (approximately 250 mL) were collected in amber glass bottles, fitted with screw caps. Samples were filtered through a Whatman No. 1 filter paper (Maidstone, UK) and kept at -20 °C until the analysis. These samples were used to evaluate the repeatability, the applicability and the capability of the analytical methods assayed to discriminate between samples with different degrees of alteration.

2.3. Analytical methods

Viscosity determination

A Newtonian behavior was observed for all samples within shaving speeds of 120-250 (1/s). Thus, to determine the viscosity, a shaving speed of 180 (1/s) was chosen because it was situated in the middle of the assayed interval. The determination was made by means of a Mettler Rheomat RM 180 viscosimeter (Mettler-Toledo, Columbia, OH, USA) at 45 °C using a Clifton NE 4D Series thermostatic stirred bath (Nickel-Electro, North Somerset, UK) with the temperature electronically controlled with a high accuracy (± 0.01 °C).

Dielectric constant determination

The Food Oil Sensor (FOS) NI-21B (Northern Instruments, Lino Lakes, MN, USA) was used to measure the changes in the dielectric constant of the frying oils, using fresh oils as reference. The FOS readings (arbitrary units) range from 0.00 to 4.00.

In order to adapt the method to the oils used in continuous frying, the FOS measurement was optimized after studying the influence of the following factors:

Influence of the stabilization time

In order to get stable readings, the instrument was warmed for 45 min instead of the 30 min recommended in the operating manual.

In addition, the stability of the dielectric constant measurement was determined in eight aliquots of each type of oil (PO, SO, PO/SO blend). Each aliquot was placed in the sensor cup and readings were recorded every 2.5 min. Better precisions than at 0 min were obtained at 2.5, 5, 7.5 and 10 min (data not shown). Thus, the test light indicating the instrument's readiness to measure should remain on for 2.5 min prior to taking any measurements.

Influence of temperature

Temperature is a crucial factor for FOS readings, because the oil density decreases in indirect proportion with the temperature. Therefore, a

temperature increase means a smaller number of molecules per volume unit and, consequently, lower molecule interactions with the electric field and a dielectric constant decrease (Carey and Hayzen, 2001). Hence, the test light of the instrument is illuminated when the sample placed in the sensor cup reaches a stable temperature of 53.3 °C (reading temperature). The sample aliquots (2.5 mL) were preheated at 40, 55 and 60 °C and shaken in order to get a homogeneous sample and a stable reading temperature. Preheating temperatures above the reading temperature did not increase the repeatability (data not shown). Therefore, the samples were preheated for 5 min at 40 °C and gently shaken.

Influence of the electrical current

To avoid the influence of electrical oscillations in the readings, the instrument was connected to an uninterruptible power system using Mabis USS-400 (Mabis, Barcelona, Spain).

Drift of the instrument

Continuous use of the FOS instrument for several hours can cause small drifts in the FOS readings. This drift was recognized by Northern Instruments, who recommended that we check the reading with the zero standard oil (0.00) every one or two hours. In this study, the zero oil reading was measured every 30 min and shifts in the zero readings were recorded. This information was used to correct the drift of the instrument reading.

Influence of the air presence in the oil sample

Oil aliquots were ultrasonicated for 1 min to avoid the presence of air bubbles in the oil samples. Better precisions were obtained after sonication (data not shown).

Final method adopted

The FOS readings were measured using an uninterrupted line voltage. The instrument was switched on 45 min before the measurement. Samples were preheated for 5 min at 40 °C and gently shaken and ultrasonicated for 1 min in order to get a homogeneous oil, which was placed in the sensor cup. Readings were recorded after the test light had been on for 2.5 min. Moreover, the instrument was checked every 30 min with zero standard oil to evaluate the instrument drift. The differences between the readings of the zero oil were used to correct the instrument readings along the time in order to improve the accuracy of the results. Each sample was analyzed in triplicate.

Determination of the linoleic/palmitic ($C_{18:2\ n-6}/C_{16:0}$) ratio

In order to determine the $C_{18:2\ n-6}/C_{16:0}$ ratio, fatty acid methyl esters were prepared from oil samples according to Guardiola *et al.* (1994) with the addition of pentadecanoic acid methyl ester as internal standard.

Other internal standards such as heptanoic acid methyl ester ($C_{7:0}$), heptadecanoic acid methyl ester ($C_{17:0}$), nonadecanoic acid methyl ester ($C_{19:0}$) and tricosanoic acid methyl ester ($C_{23:0}$) were assessed. However, $C_{7:0}$ methyl ester was discarded due to its high volatibility and $C_{17:0}$, $C_{19:0}$ and $C_{23:0}$ methyl esters were discarded because they overlapped minor peaks of the frying oil samples, which may interfere in the accuracy of the quantification.

Fatty acid methyl esters were determined by gas chromatography on a fused silica capillary column (60 m × 0.25 mm i.d.) with a film thickness of 0.20 µm of 90% cyanopropyl + 10% cyanopropylphenylsilicone (SP 2380) from Supelco (Bellefonte, PA, USA).

Determination of the iodine and p*-anisidine values*

AOCS official methods Cd 1-25 and Cd 18-90 were used for the determination of the iodine value (IV) and *p*-anisidine value (AnV), respectively (AOCS, 1999).

Acid value determination

The EC method (Commission Regulation No. 2568/91) for olive and olive-residue oils was applied to frying oils. Diethyl ether/ethanol (1:1, v/v) is used as solvent, which makes it difficult to distinguish the visual end-point by means of phenolphthalein when the oils are moderately to highly colored. Eight sample aliquots of PO/SO blend (30:70, v/v) were analyzed (RSD = 2.9%; acidity mean = 0.22, expressed as % oleic). Afterwards, the AOCS method (Cd 3d-63) was assayed (AOCS, 1999). This method uses 2-propanol/toluene (1:1, v/v) as solvent, which easily dissolves the sample and facilitates the appreciation of a distinct and sharp end-point with phenolphthalein and, therefore, improves the precision of the determination (RSD = 1.7%; acidity mean = 0.19, expressed as % oleic).

Determination of the lipid UV absorption

The application of lipid UV absorption (232, 270 and 280 nm) to follow up lipid oxidation has been assessed through direct and derivative spectrophotometry (Corongiu and Banni, 1994; Baron *et al.*, 1997; Grau *et al.*, 2000a). Second-derivative spectrophotometry did not show any significant advantage over direct spectrophotometry (data not shown).

For these reasons, oil specific absorbances at 232 nm (K_{232}), 270 nm (K_{270}) and 280 nm (K_{280}) were measured according to the EC regulation (Commission Regulation No. 2568/91).

Determination of the thiobarbituric acid value (TBA)

The TBA value was determined according to Grau *et al.* (2000b) with some modifications:

sample weight (5 g of fresh or frying oil or fat) and homogenization step, which was carried out using a vortex instead of a high-speed homogenizer.

Determination of the polymerized triacylglycerols

Polymer content was determined following the IUPAC 2508 method with some modifications (IUPAC, 1992). High performance size-exclusion chromatography (HPSEC) was used to determine the percentage of polymerized triacylglycerols on an Agilent 1100 Series chromatograph equipped with a refractive index detector (Waldbronn, Germany), a 20 µL sample loop and two Ultrastyragel columns (Water Associates, Milford, MA, USA) of 500 and 100 Å connected in series. The columns (25 cm × 0.77 cm i.d.) were packed with a porous highly cross-linked styrenedivinilbenzene copolymer (7 µm) and were placed in an oven set at 35 °C. High-performance liquid chromatography grade tetrahydrofuran served as the mobile phase to elute compounds at a flow of 1 mL/min. The sample concentration was approximately 50 mg/mL in tetrahydrofuran.

Oxifrit test

The oxifrit test (Merck, Darmstadt, Germany), which is based on the reaction with the alteration compounds (Meyer, 1979), was applied to the samples. This test kit has a color scale consisting of four categories, namely "Good", "Still Good", "Replace" and "Bad".

2.4. Precision

The precisions of the optimized analytical determinations (viscosity, dielectric constant, linoleic acid/palmitic acid ratio, iodine value, acid value, specific absorbance at 232, 270 and 280 nm, *p*-anisidine value, polymerized triacylglycerol percentage) were assessed using PO/SO (30:70, v/v), SO and/or PO samples. Eight aliquots of each type of oil were weighed and analyzed. Then, the relative standard deviation (RSD) was calculated for all optimized methods.

2.5. Statistics

Spearman correlation coefficients were used to examine possible correlations between variables (viscosity, dielectric constant, $C_{18:2\ n\text{-}6}/C_{16:0}$ ratio, iodine value, acid value, K_{232}, K_{270}, K_{280}, *p*-anisidine value, TBA value and polymerized triacylglycerol content).

3. RESULTS AND DISCUSION

3.1. Precision of the analytical methods

Precision was used to correctly set-up and optimize some analytical methods. However, only the precisions of the finally applied methods are shown in Table 1. The precisions of these methods (RSD %) ranged from 0.9 to 4.1%, except for the determination of the TBA value (7.7%), which was discarded for this kind of samples, and for the determination of the dielectric constant. Despite the fact that the determination of the dielectric constant was carefully optimized, the variability of this method still remained high and ranged from 2.6 to 14.9% (Table 1).

3.2. Analysis of frying oil samples with a different alteration degree

Applicability of the optimized analytical methods

The TBA values were very low for oils coming from continuous frying. Some TBA values expressed as µg of malondialdehyde (MDA)/kg of sample were below the detection limit (5.2 µg/kg) and others were below the quantification limit (17.4 µg/kg). This is due to the low concentrations of the frying oils in fatty acids with more than two double bonds (Table 2), which are the main precursors of the MDA (Esterbauer *et al.*, 1991; Frankel, 1998). In fact, the oils used in this study showed a linolenic acid concentration under 1%, which is common for frying oils, and several authors and institutions recommend a maximum linolenic acid concentration of 2-3% (Firestone, 1996; Fox, 2001; Gupta, 2004). Thus, this method, in contrast with

Table 1
Precision of the analytical methods (n = 8) in various frying oils.

Methods	VIS[1]	DC			$C_{18:2\ n\text{-}6}/C_{16:0}$	IV			AV	K_{232}		K_{270}		K_{280}		AnV			TBA	PTG	
Frying oils	PO/SO blend[2]	PO/SO blend	PO	SO	PO/SO blend	PO/SO blend	PO	SO	PO/SO blend	PO/SO blend	PO	PO/SO blend	PO	PO/SO blend	PO	PO/SO blend	PO	SO	PO/SO blend	PO	SO
Precision	0.038[3] (1.9)	0.28 (14.9)	0.35 (7.7)	1.30 (2.6)	1.29 (1.0)	95.3 (4.6)	54.1 (1.1)	105.0 (1.1)	0.19 (1.7)	4.88 (2.8)	3.02[4] (2.9)	1.54 (1.4)	0.64[4] (1.3)	1.14 (1.8)	0.55[4] (1.2)	15.1 (0.7)	4.7[4] (3.1)	20.8[4] (2.6)	78.0 (12.6)	1.61 (4.1)	3.74 (1.4)

[1] VIS (viscosity, Pa·s); DC (dielectric constant, FOS arbitrary units); $C_{18:2\ n\text{-}6}/C_{16:0}$ (linoleic/palmitic acid ratio); IV (iodine value, % iodine absorbed); AV (acid value, % oleic acid); K_{232}, K_{270}, K_{280} (specific absorbances at 232, 270 and 280 nm); AnV (*p*-anisidine value, 100 times the specific absorbance at 350 nm); TBA (thiobarbituric acid value, µg of malondialdehyde/kg of sample); PTG (% polymerized triacylglycerols).
[2] PO/SO blend, palm olein/sunflower oil blend (30:70, v/v); PO, palm olein; SO, sunflower oil.
[3] Mean (percent relative standard deviation).
[4] These precisions were determined using frying oils from later samplings, not described in this paper.

Table 2
Fatty acid composition (area normalization) of the oils before frying

Fatty Acid	SO[1]	PO/SO	PO
12:0	tr[2]	tr	0.32
14:0	0.08	0.36	1.09
16:0	6.95	15.88	39.85
16:1	0.12	0.12	0.19
18:0	5.07	4.48	4.30
18:1 n-9	24.51	30.20	42.74
18:1 n-7	0.64	0.59	0.66
18:2 n-6	62.16	47.90	10.31
18:3 n-3	0.13	0.15	0.14
20:0	0.33	0.33	0.40

[1] SO, sunflower oil; PO/SO, palm olein/sunflower oil blend (30:70, v/v); PO, palm olein.
[2] tr, traces.

other methods used for assessing the content in secondary oxidation products (*p*-anisidine value, K_{270} and K_{280}), does not have enough sensitivity to discriminate between oil samples with a different oxidation degree (Table 3). Therefore, this method was discarded. Sebedio *et al.* (1991) have also reported very low TBA values for palm oil when it was subjected to continuous frying. However, the TBA values determined using the same method as that applied in our study were successfully used to follow up the oxidation of heated oils (corn and canola oils) at 170 °C for 20 hours (Dana *et al.*, 2003).

Using the Oxifrit test, all the assayed samples were scored as "good" (color 1) in the 4-color scale. Hence, this quick test was also discarded to follow up the alteration of these oil samples because its discrimination capacity was not enough. In fact, it is well known that continuous frying generally entails much lower alteration than discontinuous frying (Dobarganes and Márquez-Ruiz, 1998; Márquez-Ruiz *et al.*, 2004). This is due to a number of differences between continuous and discontinuous frying, but mainly to the much lower turnover ratio and less idle periods, which cause a lower alteration of the frying medium and the fried product during the continuous frying process (Morton and Chidley, 1988; Banks, 1996 a, b; Gupta *et al.*, 2004).

Oxidation of polyunsaturated fatty acids (PUFA) involves the formation of several derivatives with conjugated double bonds. This oxidation is accompanied by increases in the lipid UV absorption at certain wavelengths. The magnitude of these changes is not readily related to the degree of oxidation, because it also depends on the composition in unsaturated fatty acids. However, here and in other studies, the determination of the lipid UV absorption is used as a relative measurement of oxidation to compare oils having the same fatty acid composition.

K_{232} is a primary oxidation index which has been closely related to hydroperoxide content (Dobarganes *et al.*, 2002). In addition, the measurement of UV absorbance at 270 and 280 nm has been used in edible oils. Absorption at these wavelengths is mainly due to secondary oxidation products such as ethylenic diketones, conjugated ketodienes and dienals (White, 1995).

Lipid UV absorption at 232, 270 and 280 nm (Table 3) are good measurements to follow up the oxidation in frying oils. In agreement with our results, Masson *et al.* (1997) have observed significant

Table 3
Results of several different analytical methods for the oil samples

	VIS[1]	DC	$C_{18:2\ n-6}/C_{16:0}$	IV	AV	K_{232}	K_{270}	K_{280}	AnV	TBA	PTG
SO fresh[2]	0.048	REF[3]	9.25	119.1	0.03	5.81	0.86	0.67	5.5	ND[4]	nd[5]
SO 1	NA[6]	1.19	9.20	111.6	0.85	12.51	3.04	2.35	36.3	23.0	3.96
SO 2	0.050	1.33	9.10	106.9	0.87	16.79	2.69	2.01	36.7	19.0	4.10
PO/SO fresh	0.045	REF	3.10	95.3	0.03	4.90	1.19	0.93	5.0	ND	nd
PO/SO 1	0.050	0.46	1.64	81.5	0.25	5.74	1.47	1.15	12.4	18.5	1.95
PO/SO 2	NA	0.46	1.66	80.2	0.25	5.68	1.40	1.11	12.4	18.3	1.52
PO/SO 3	NA	0.40	1.96	91.2	0.20	4.44	1.43	1.12	13.1	tr[7]	1.57
PO/SO 4	NA	0.42	1.95	89.4	0.20	4.45	1.43	1.12	12.9	tr	1.70
PO fresh	0.042	REF	0.25	57.1	0.04	2.39	0.60	0.51	2.9	ND	nd
PO I	NA	0.49	0.23	55.9	0.07	4.45	1.53	1.16	20.7	78.4	0.77
PO NFC	NA	0.32	0.24	54.1	0.15	4.22	0.93	0.72	16.1	25.5	1.80
PO EFC	0.062	2.65	0.17	51.6	0.49	10.64	1.77	1.33	64.2	182.5	8.30

[1] VIS (viscosity, Pa·s); DC (dielectric constant, FOS arbitrary units); $C_{18:2\ n-6}/C_{16:0}$ (linoleic/palmitic acid ratio); IV (iodine value, % iodine absorbed); AV (acid value, % oleic acid); K_{232}, K_{270}, K_{280} (specific absorbances at 232, 270 and 280 nm); AnV (*p*-anisidine value, 100 times the specific absorbance at 350 nm); TBA (thiobarbituric acid value, µg of malondialdehyde/kg of sample); PTG (% polymerized triacylglycerols).
[2] SO fresh, sunflower oil not subjected to frying; SO 1, sunflower oil collected from the finish frying area; SO 2, sunflower oil collected from the sediment exit; PO/SO fresh, palm olein/sunflower oil blend (30:70, v/v) not subjected to frying; PO/SO 1, PO/SO 2, PO/SO 3, PO/SO 4, palm olein/sunflower oil blends (30:70, v/v) collected from the sampling tap during continuous frying; PO fresh, palm olein not subjected to frying; PO I, palm olein collected at the beginning of frying process; PO NFC, palm olein collected during normal frying conditions; PO EFC, palm olein collected during extreme frying conditions.
[3] REF, used as reference.
[4] ND, not detected, value under the detection limit.
[5] nd, not determined in fresh oils.
[6] NA, not analyzed because there was not enough sample.
[7] tr, traces, values between the detection limit and the quantification limit.

correlations between the conjugated dienes and other oxidation parameters determined during discontinuous frying with polyunsaturated oils.

p-Anisidine value measures the presence of certain secondary oxidation products (principally 2-alkenals and 2,4-alkadienals) and shows a good capability to discriminate between samples with different degrees of oxidation (Table 3). In fact, this method has previously been used to follow up the oxidation of frying oils (Grompone, 1991; Thompkins and Perkins, 1999; Houhoula *et al*., 2002).

Polymer content ranged from 0.77 to 8.30% (Table 3). Except for the 8.30% value, these percentages are similar to the ones previously reported for continuous frying oils (Sebedio *et. al*, 1991; Sebedio *et al*., 1996). According to Dobarganes and Márquez-Ruiz (1996), polymeric compounds constitute the major fraction among the different groups of alteration compounds, normally accounting for more than 50%. Furthermore, polymeric compounds have been found to correlate well with total polar compounds (Sebedio *et al*., 1991; Dobarganes and Márquez-Ruiz, 1995; Takeoka *et al*., 1997; Plessis and Meredith, 1999). In fact, the rejection limit established in Spain (BOE, 1989) for the total polar compound content (25%) in frying oils is equivalent to about 15% of polymeric compounds (Dobarganes and Márquez-Ruiz, 1996). Hence, none of the oils analyzed should show total polar compounds higher than 25%.

The viscosity of fresh and used frying oils is quite similar, which seems to indicate that this parameter shows insufficient sensitivity to discriminate between oil samples with a different degree of oxidation (Table 3). In fact this parameter is closely related to the polymerized triacylglycerol content (Masson *et al*., 1997; Gertz, 2000), which shows small increases during continuous frying (Sebedio *et al*., 1996).

The acid value clearly differentiates the fresh and used frying oils (Table 3) and in fact this hydrolytic parameter is the only one used to control the frying oils in most medium- and large-scale Spanish frying companies.

The dielectric constant also clearly increases between fresh and used frying oils (Table 3), which indicates that it is a good parameter to follow up the alteration of the frying medium during continuous frying. In fact, this parameter is closely related to the content of oxidation products (Fritsch *et al*., 1979), which show significant increases during continuous frying (Plessis and Meredith, 1999; Inoue *et al*., 2002).

Iodine value (IV) is a measure of the overall unsaturation and is widely used to characterize oils and fats. The changes in IV for the 3 oil types are shown in Table 3. The values for fresh SO, PO/SO and PO were 119.1, 95.3 and 57.1, respectively. After frying, the values of IV decrease from 2.1 to 15.8%. However, for the PO/SO blends the changes in IV seem to be affected by oxidation and by the variability of the blending operation. In fact, fresh PO/SO blend was handmade and the frying PO/SO blends were automatically made.

Similar results were observed for the $C_{18:2\ n-6}/C_{16:0}$ ratios. Changes in $C_{18:2\ n-6}/C_{16:0}$ ratios of the oils were mainly due to a decrease in the percentage of linoleic acid which is more susceptible to oxidation, whereas palmitic acid is more stable towards oxidation. The values for fresh SO, PO/SO and PO were 9.25, 3.10 and 0.25 respectively. After frying, the $C_{18:2\ n-6}/C_{16:0}$ ratio decreased from 0.5 to 47.1%. However, for the PO/SO blends these changes were also affected by the variability of the blending operation.

The two latter methods have been used to follow up the oxidation of oils during heating or frying (Augustin *et al*., 1987; Takeoka *et al*., 1997).

Correlations between the quality parameters

Table 4 lists the correlation coefficients obtained for the different oil quality parameters studied. As the value of the correlation coefficient between K_{270} and K_{280} was 1, only K_{270} correlation coefficients appear in Table 4. These results revealed a very good correlation between the acid value and other oil quality variables (dielectric constant, ultraviolet absorption, *p*-anisidine value and polymerized triacylglycerol percentage). These relationships have previously been reported by Pérez-Camino *et al.* (1988), who described good correlations between different selected methods (polar compounds, nonpolar dimers, polar methyl esters and smoke point) and the acid value that measures hydrolytic alteration. This alteration is predominant and the most important reaction during deep fat frying (Pokorny, 1998).

In addition, the dielectric constant reading values presented high correlations ($p<0.001$) with the *p*-anisidine value, K_{270}, K_{280} and with the acid value, whereas with K_{232} it was lower ($p=0.032$). This is in agreement with the results reported by several authors who show significant correlation coefficients between the dielectric constant and these alteration parameters (Fritsch *et al*., 1979; Chu, 1991; Al-Kathani, 1991; Plessis and Meredith, 1999). However, some authors (Al-Kahtani, 1991; Croon *et al*., 1986) have reported non-significant correlation coefficients between the acid value and the dielectric constant. The dielectric constant showed a similar behavior and evolution to lipid UV absorption (Al-Kathani, 1991; Fritsch *et al*., 1979), probably because both measurements are related to the content in oxidation compounds. The strong correlation between the dielectric constant and the *p*-anisidine value confirms the results reported by Al-Kahtani (1991) in frying oils. This last-named author found a highly significant correlation between the dielectric constant and the *p*-anisidine value ($p < 0.01$).

Moreover, the *p*-anisidine value shows high correlations with K_{270} and K_{280}, which could be due to aldehydic molecules that are reactive with *p*-anisidine and also absorb at 270 and 280 nm (Galanos *et al*., 1968; Grau *et al*., 2000a). Our results are in agreement with those previously

Table 4
Spearman correlation coefficient between various alteration variables of the oil samples

VIS[1]	DC	$C_{18:2\ n-6}/C_{16:0}$	IV	AV	K_{232}	K_{270}	AnV	TBA	PTG	
r^2=1 n=6	r=0.924** p (0.008) n=6	r=-0.203 p (0.700) n=6	r=-0.203 p (0.700) n=6	r=0.725 p (0.103) n=6	r=0.812* p (0.050) n=6	r=0.841* p (0.036) n=6	r=0.986** p (<0.001) n=3	r=0.866 p (0.333) n=3	r=0.866 p (0.333) n=3	**VIS**
	r=1 n=12	r=-0.211 p (0.510) n=12	r=−0.183 p (0.569) n=12	r=0.866** p (<0.001) n=12	r=0.620* p (0.032) n=12	r=0.901** p (<0.001) n=12	r=0.852** p (<0.001) n=12	r=0.393 p (0.383) n=7	r=0.533 p (0.139) n=9	**DC**
		r=1 n=12	r=0.986** p (<0.001) n=12	r=0.021 p (0.948) n=12	r=0.455 p (0.138) n=12	r=0.028 p (0.931) n=12	r=−0.196 p (0.542) n=12	r=−0.679 p (0.094) n=7	r=0.117 p (0.765) n=9	**$C_{18:2\ n-6}/C_{16:0}$**
			r=1 n=12	r=0.007 p (0.983) n=12	r=0.476 p (0.118) n=12	r=0.091 p (0.779) n=12	r=−0.182 p (0.572) n=12	r=−0.607 p (0.148) n=7	r=0.117 p (0.765) n=9	**IV**
				r=1 n=12	r=0.636* p (0.026) n=12	r=0.783** p (0.003) n=12	r=0.713** p (0.009) n=12	r=-0.214 p (0.645) n=7	r=0.733* p (0.025) n=9	**AV**
					r=1 n=12	r=0.643* p (0.024) n=12	r=0.462 p (0.131) n=12	r=-0.143 p (0.760) n=7	r=0.700* p (0.036) n=9	**K_{232}**
						r=1 n=12	r=0.832** p (0.001) n=12	r=0.214 p (0.645) n=7	r=0.567 p (0.112) n=9	**K_{270}**
							r=1 n=12	r=0.679 p (0.094) n=7	r=0.633 p (0.067) n=9	**AnV**
								r=1 n=9	r=0.214 p (0.645) n=7	**TBA**
									r=1 n=9	**PTG**

[1] VIS (viscosity, Pa·s); DC (dielectric constant, FOS arbitrary units); $C_{18:2\ n-6}/C_{16:0}$ (linoleic/palmitic acid ratio); IV (iodine value, % iodine absorbed); AV (acid value, % oleic acid); K_{232}, K_{270} (specific absorbance at 232 and 270); AnV (*p*-anisidine value, 100 times the specific absorbance at 350 nm); TBA (thiobarbituric acid value, µg of malondialdehyde/kg of sample); PTG (% polymerized triacylglycerols).
[2] r, Spearman correlation coefficient; p value is stated in parentheses.
* $p \leq 0.05$; ** $p \leq 0.01$.

reported by other authors (Al-Kahtani, 1991; Houhoula *et al*., 2002) in frying oils.

Moreover, the correlations between the lipid UV absorption (K_{232}, K_{270} and K_{280}) were highly significant. Thus, the changes of lipid UV absorption were paralleled, a fact that has been previously described in frying oils (Al-Kahtani, 1991; Che-Man and Tan, 1999; Önal and Ergin, 2002). Furthermore, several authors (Al-Kahtani, 1991; Masson *et al*., 1997; Che-Man and Tan, 1999; Houhoula *et al*., 2003) have indicated good correlations between lipid UV absorption at 232 nm and polymerized triacylglycerol content, and this could be attributed to the fact that conjugated dienes can form polymers during frying (Dobarganes and Márquez-Ruiz, 1996; Gertz *et al*., 2000).

Finally, the variables dependent on the PUFA content (iodine value and $C_{18:2\ n-6}/C_{16:0}$ ratios) showed poor correlations with other determinations, which means that continuous frying allows low degradation of unsaturated fatty acids.

4. CONCLUSION

In conclusion, the *p*-anisidine value, the dielectric constant, lipid UV absorption and polymerized triacylglycerol content could be complementary to acid value to control oil quality during continuous industrial frying. These parameters give complementary information to the acid value because they evaluate the thermooxidative alteration of the frying medium. In addition, the combination of the acid value and some of these parameters gives additional information about the oil that can be further related to the stability of the fried products, which should allow a more accurate and efficient control of the frying process.

ACKNOWLEDGEMENTS

This work was funded in part by research grants from the *Instituto Nacional y Tecnología Agraria y*

Alimentaria (INIA) and the *Ministerio de Educación, Cultura y Deporte*. The authors thank the companies that provided the frying oil samples: Fritravich, Risi and El Castillo.

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Recibido: 24/10/06
Aceptado: 1/2/07