

Ultraviolet Spectrophotometric Evaluation of Corn Oil Oxidative Stability during Microwave Heating and Oven Test

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The effect of microwave heating on the oxidative stability of corn oil was determined by absorptivity in the UV spectrum and by peroxide and acid values. Oil samples with antioxidants BHA/BHT (1:1; 200 mg kg⁻¹), with and without citric acid, were heated in a microwave oven (800 W, 2450 MHz) for 0–36 min. Absorptivity at 232 and 270 nm increased during microwave exposure. Control values of absorptivity at 232 nm increased from 3.568 to 12.874 after 36 min of heating. Peroxide value showed a significant difference in the initial stage of heating (0–6 min), but after this time, the peroxide value decreased due to the instability of hydroperoxides at high temperatures. Control 232 nm absorptivities after 6 days in the oven test were similar to those after 32–36 min of microwave heating. Effective antioxidants in the oven test did not show any protection during microwave heating. UV spectrophotometry is a suitable tool for microwave oxidation monitoring.

Keywords: Microwave heating; oven test; corn oil; stability; antioxidants

INTRODUCTION

Autoxidation is considered to be the main route of edible oil deterioration, which produces undesirable odors and flavors developed during storage and heating. The unpleasant flavor of oxidized oils has been attributed to primary and secondary products of unsaturated fatty acids (Rovellini et al., 1997). Oxidation of polyunsaturated fatty acids is accompanied by an increase in the ultraviolet (UV) absorption: lipids with dienes or polyenes show a shift in their double-bond positions due to isomerization and conjugation formation, and the resulting conjugated dienes exhibit an intense absorption at 232–234 nm. Determination of absorptivity (extinction coefficient) in the UV spectrum is simple, does not depend on chemical reaction or color development, and requires a small sample size (Rovellini et al., 1997; Shahidi, 1995).

Antioxidants are the main additives that protect food quality by retarding oxidative breakdown of lipids. Synthetic phenolic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), are commonly added to oils to retard oxidative changes during storage and heat because of their effectiveness (Wanasundara and Shahidi, 1994; Sherwin, 1978). Storage of oil samples at high temperatures (oven test) is employed for monitoring oxidative stability of oils and for antioxidant choice, but it requires some days for a conclusion (Shahidi, 1995; Hawrysh et al., 1992; McMullen et al., 1991; Hawrysh et al., 1988). The results of an oven test (62.8 °C) for antioxidant selection were well related to the ambient storage of Brazil nut crude oil. The antioxidant TBHQ performed better than BHA and BHT in the oven test and maintained a good quality of oil during ambient storage for up to 180 days (Regitano-d'Arce and Vieira, 1996). However, the oven test results should not be applied to predict oil performance under high heating conditions of food processing.

Heating by microwave is produced by interaction of an electromagnetic field with chemical constituents of foods. These interactions generate heat due to molecular friction and excitation. The application of microwave energy reduces speed and time when it is compared with other methods of heating (Datta and Hu, 1992; Schiffmann, 1992; Fellows, 1989; Decareau and Peterson, 1986; Mudget, 1982). Due to these characteristics, many studies have been conducted to investigate the nutritional properties of food treated in a microwave oven. Specifically in vegetable oils and fatty foods, there are works about fatty acid isomerization and vitamin loss. These works indicated occurrence of oxidation in the oils.

With interest in the potential physiological effects of trans fatty acids, Mai et al. (1980) heated peanut oil in a microwave oven (675 W) during 5, 7, 10, and 15 min and determined the fatty acid composition by gas chromatography. No trans fatty acid was detected after 15 min. The effect of microwave heating on tocopherol contents was investigated in linseed, soybean, corn, olive, and palm oil. After 10 min of exposure, the amount of tocopherols decreased substantially and the occurrence of oxidation was monitored by the increase in peroxide, *p*-anisidine, TBA, and carbonyl values (Yoshida et al., 1990). Tocopherol lost from microwave-heated virgin olive oil was compared to the frying-pan effect. Olive oil (200 mL) was heated during 8 min (to 250 °C), and peroxide value increased from 10.4 to 18.0 mequiv kg⁻¹. Acid value did not increase (Ruiz-Lopez et al., 1995). Some physical and chemical parameters in sunflower and virgin olive oil heated by microwave were evaluated by using 100 mL oil samples treated in a microwave oven (170 °C, 120 min) and in an electric conventional oven (170 °C, 120 min). Absorptions in the UV and visible spectra were determined. After treatment in the microwave oven, significant alterations in the parameters studied were observed (Albi et al., 1997a,b). Chemical reactions involving long-chain fatty acid esters, which usually require many hours of heating

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Table 1. Initial Quality of Corn Oil

parameter	oil
absorptivity at 232 nm	3.377
absorptivity at 270 nm	1.404
peroxide value (mequiv kg ⁻¹)	1.40
acid value (% FFA as oleic acid)	0.025
iodine value (Wijs) (mg of I 100 mg ⁻¹)	116.18

or stirring at room temperature, could be accelerated by the use of microwaves (Lie Ken Jie and Yan-Kit, 1988).

In this work the oxidative alterations of corn oil as a result of microwave heating were analyzed. The objective was to examine changes in physical and chemical parameters and to evaluate the efficacy of a combination of BHA and BHT, selected previously in an oven test, in retarding the oxidation of corn oil subjected to accelerated storage condition (microwave heating).

EXPERIMENTAL PROCEDURES

Samples. Commercial refined, bleached, and deodorized corn oil was obtained from an industrial plant. It contained no added antioxidants originally. The antioxidants butylated hydroxyanisole (BHA)/butylated hydroxytoluene (BHT), 200 mg kg⁻¹, BHA/BHT 200 mg kg⁻¹ plus citric acid (CA), 100 mg kg⁻¹, and CA 100 mg kg⁻¹ were applied directly to the oil samples before the accelerated tests, and samples with no added antioxidants were kept as a control.

(1) *Oven Test.* Three samples (20 g) of each oil treatment were placed in 50 mL beakers and held in an oven at 63 ± 1 °C for up to 0, 1, 2, 3, 4, 5, and 6 days. Immediately after each storage period, oil samples were analyzed.

(2) *Microwave Heating.* Three samples (20 g) of each treatment were placed in 50 mL beakers and covered with a PVC film. Twelve samples were placed at equal distances on a rotary plate of the microwave oven and heated for up to 0, 2, 4, 6, 8, 10, 12, 16, 20, 24, 28, 32, and 36 min. Oil temperature was determined after every microwave exposure period with a K thermocouple. Immediately after each heating period, oil samples were analyzed.

Reagents. All of the reagents and solvents used were of analytical reagent grade.

Equipment. The microwave oven was a Sanyo EM 804 T GR, with 800 W effective power and 2450 MHz frequency. A Shimadzu UV 1203 spectrophotometer, with the software Personal spectroscopy 1.1, was used to determine absorptivity at the UV spectrum. A K thermocouple Hanna instruments, model HI 93530A, was used for determining samples temperature.

Analytical Procedures. Lipid oxidation was determined by absorptivity at 232 and 270 nm and by UV scans (220–320 nm), following the analytical methods described by IUPAC (1979), method II.D.23. Oil samples were diluted in isoctane, and absorbance readings were multiplied by a concentration factor (g mL⁻¹) to give the absorptivity values at each wavelength. Acid value (Ca 5a-40), peroxide value (Cd 8-53), and iodine value (Cd 1-25) were determined according to AOCS (1983) methods.

Statistical Analysis. Each reported value is the mean of three replicates. Statistical analysis was conducted in a randomized complete factorial model, and Tukey test ($P < 0.05$) was applied to treatments and exposure time average values.

RESULTS AND DISCUSSION

The corn oil used in this study had a good initial quality (Table 1).

Oven Test. Data for peroxide values for corn oil samples subjected to 3 days of oven test (Figure 1) showed no difference due to treatment. However, as oven storage time increased, significantly faster devel-

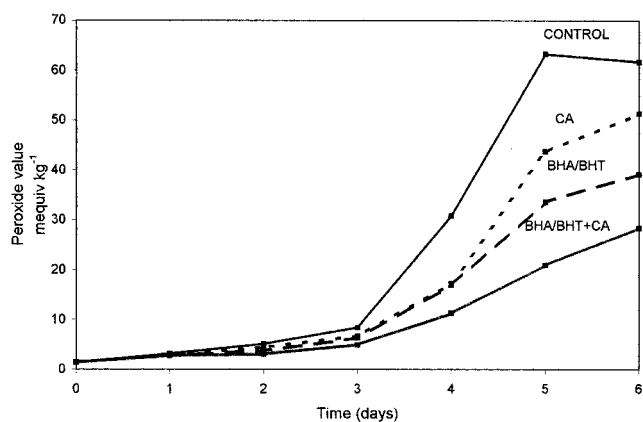


Figure 1. Peroxide value of corn oil during oven test (63 °C). CV = 20.958%.

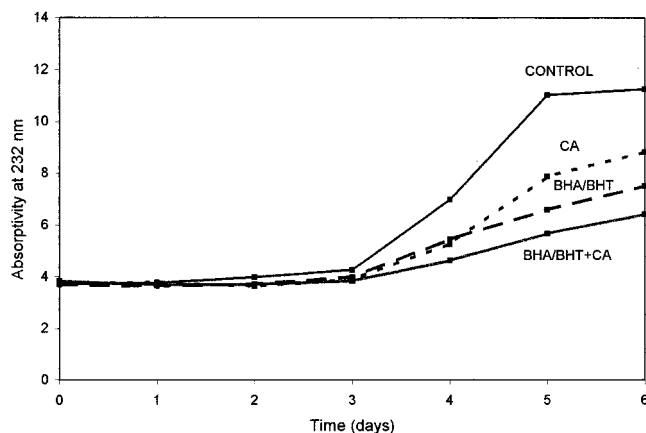


Figure 2. Absorptivity at 232 nm of corn oil during oven test (63 °C). CV = 7.299%.

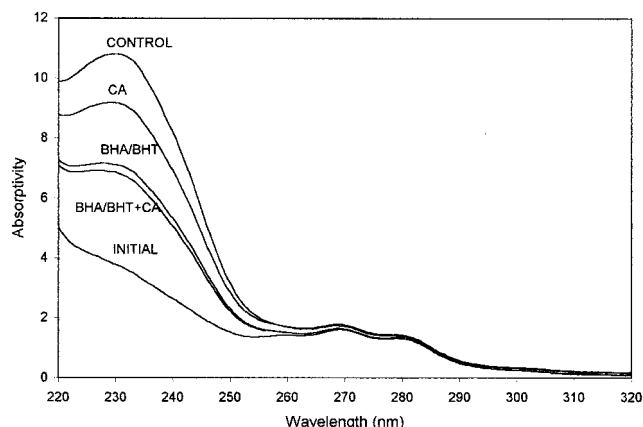


Figure 3. UV scans of corn oil after 6 days of oven test (63 °C).

opment of peroxides occurred in control samples. After 6 days of oven test, values for BHA/BHT and BHA/BHT + CA treated oils were significantly lower (39.14 and 28.37 mequiv kg⁻¹, respectively) than those for control samples (61.69 mequiv kg⁻¹). The coefficient of variation (CV%) of peroxide value data was the highest, perhaps due to the temporary nature of hydroperoxides. Formation of hydroperoxides is coincidental with conjugation of double bonds in polyunsaturated fatty acids, measured by absorptivity at the UV spectrum (Shahidi, 1995). Absorptivity at 232 nm, due to the formation of primary compounds of oxidation, showed a pattern similar to that of the peroxide value, ensuring its use

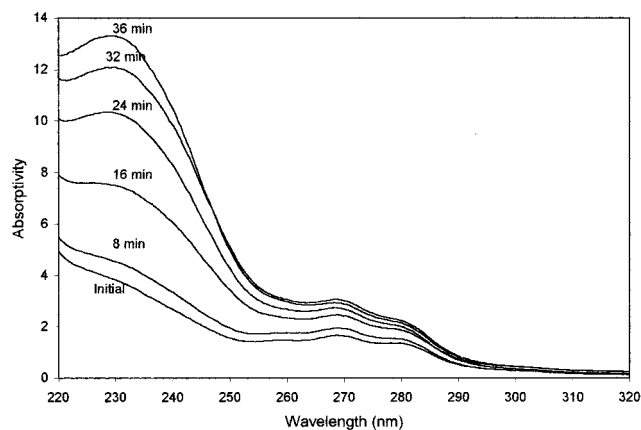


Figure 4. UV scans of control corn oil samples heated in microwave oven.

Table 2. Absorptivity at 232 nm of Corn Oil Heated by Microwave

time (min)	oil treatment ^a			control
	BHA/BHT + CA, 200 + 100 mg kg ⁻¹	BHA/BHT, 200 mg kg ⁻¹	CA, 100 mg kg ⁻¹	
0	3.674 ^e	3.681 ^f	3.652 ^g	3.568 ^d
2	3.680 ^e	3.579 ^f	3.723 ^g	3.648 ^d
4	3.921 ^{de}	3.897 ^f	3.860 ^g	3.963 ^d
6	4.365 ^{de}	4.238 ^f	4.284 ^g	4.326 ^d
8	4.535 ^{de}	4.542 ^f	4.546 ^g	4.422 ^d
10	5.341 ^{de}	5.071 ^{ef}	5.044 ^{ef}	4.990 ^d
12	5.397 ^d	5.203 ^{ef}	5.450 ^{ef}	5.267 ^d
16	7.353 ^c	6.775 ^{de}	7.098 ^{de}	7.022 ^c
20	8.373 ^c	7.634 ^d	8.146 ^d	8.099 ^c
24	10.392 ^b	10.262 ^c	10.220 ^c	10.283 ^b
28	10.555 ^b	11.319 ^{bc}	11.099 ^{bc}	10.038 ^b
32	12.968 ^a	12.311 ^{ab}	12.073 ^{ab}	11.429 ^{ab}
36	13.467 ^a	13.143 ^a	13.106 ^a	12.874 ^a

^a Means within the same column sharing a common letter are not significantly different at $p < 0.05$. CV = 8.797%.

as a substitute for the peroxide value (Figure 2). The BHA/BHT efficacy was improved by CA during the oven test, and UV scans showed this effect (Figure 3). At 270 nm no differences were detected among the treatments. Acid value did not detect differences either.

As the antioxidant combinations showed activity in different degrees during the oven test, the same treatments were applied to corn oils submitted to microwave heating.

Microwave Heating. Temperatures reached 219.6, 250, and 278.5 °C after 10, 20, and 36 min of heating, respectively. Heating in a microwave oven revealed great alterations in UV spectrophotometric data in oil due to lipid oxidation. Oven test showed that BHA/BHT delayed oil oxidation, but to a lesser extent than BHA/BHT + CA. However, there were no differences between antioxidant-added samples and the control exposed to microwave heating. Absorptivity at 232 nm increased gradually with the increase in microwave exposure time, due to the formation of conjugated dienes (Table 2). Control values of absorptivity at 232 nm shown by 6-day oven test samples were similar to absorptivity values for samples heated during 28–32 min in the microwave oven.

Peroxide value was not a good index for measurement of oxidation because hydroperoxides are unstable on heating at high temperatures. Although rancidity development is related to the rate of hydroperoxides, the

Table 3. Peroxide Value (Millequivalents per Kilogram) of Corn Oil Heated by Microwave

time (min)	oil treatment ^a			control
	BHA/BHT + CA, 200 + 100 mg kg ⁻¹	BHA/BHT, 200 mg kg ⁻¹	CA, 100 mg kg ⁻¹	
0	2.01 ^d	2.3 ^d	2.14 ^c	1.98 ^c
2	2.51 ^d	2.64 ^{cd}	2.51 ^c	2.84 ^{bc}
4	5.23 ^{ab}	5.51 ^{ab}	5.60 ^a	6.27 ^a
6	6.57 ^a	6.75 ^a	5.40 ^a	5.61 ^a
8	3.97 ^{bcd}	3.33 ^{cd}	3.33 ^{bc}	3.04 ^{bc}
10	3.67 ^{bcd}	4.28 ^{bc}	3.01 ^c	3.21 ^{bc}
12	2.42 ^d	3.42 ^{cd}	2.92 ^c	3.30 ^{bc}
16	4.67 ^{abc}	4.33 ^{bc}	5.10 ^{ab}	4.38 ^{ab}
20	3.26 ^{cd}	3.52 ^{cd}	3.09 ^c	2.84 ^{bc}
24	3.51 ^{bcd}	2.96 ^{cd}	3.08 ^c	3.19 ^{bc}
28	3.22 ^{cd}	3.74 ^{bcd}	3.02 ^c	2.69 ^{bc}
32	2.45 ^d	3.16 ^{cd}	3.01 ^c	2.54 ^{bc}
36	2.88 ^{cd}	2.84 ^d	2.68 ^c	3.32 ^{bc}

^a Means within the same column sharing a common letter are not significantly different at $p < 0.05$. CV = 19.984%.

Table 4. Absorptivity at 270 nm of Corn Oil Heated by Microwave

time (min)	oil treatment ^a			control
	BHA/BHT + CA, 200 + 100 mg kg ⁻¹	BHA/BHT, 200 mg kg ⁻¹	CA, 100 mg kg ⁻¹	
0	1.633 ^h	1.640 ^g	1.628 ^h	1.584 ^f
2	1.637 ^h	1.601 ^g	1.650 ^h	1.626 ^f
4	1.661 ^h	1.644 ^g	1.644 ^h	1.673 ^{ef}
6	1.857 ^{gh}	1.803 ^{fg}	1.819 ^{gh}	1.860 ^{de}
8	1.936 ^g	1.960 ^{ef}	1.958 ^{fg}	1.970 ^d
10	2.249 ^{ef}	2.158 ^e	2.126 ^{ef}	2.067 ^d
12	2.190 ^f	2.185 ^{de}	2.323 ^{de}	2.096 ^d
16	2.435 ^{de}	2.410 ^{cd}	2.324 ^{de}	2.340 ^c
20	2.530 ^{cd}	2.431 ^c	2.542 ^{cd}	2.527 ^{bc}
24	2.685 ^{bc}	2.794 ^b	2.576 ^c	2.665 ^{ab}
28	2.769 ^{ab}	2.886 ^{ab}	2.679 ^{bc}	2.699 ^{ab}
32	2.927 ^a	2.949 ^a	2.979 ^a	2.891 ^a
36	2.838 ^{ab}	2.697 ^{ab}	2.851 ^{ab}	2.833 ^a

^a Means within the same column sharing a common letter are not significantly different at $p < 0.05$. CV = 3.743%.

hydroperoxides are not directly responsible for rancid off-flavors. Peroxide value increased until 4–6 min of heating for all samples, but it decreased after 6 min (Table 3). This resulted in formation of aldehydes and ketones (rancid off-flavor compounds) followed by a significant increase in absorptivity at 270 nm from 6 min of heating (Table 4). This would be in agreement with the results of Albi et al. (1997a), who found greater values of absorptivity at 270 nm in olive and sunflower oils heated for 120 min (170 °C) in a microwave oven.

UV scanning detected alterations in the spectrum of microwaved samples, and Figure 4 shows the results for control samples. Acid value increased within 36 min of heating.

In conclusion, the potential antioxidant activity of BHA/BHT and CA observed in preventing corn oil oxidation in the oven test had no effect under high-temperature conditions of microwave heating. Heating by microwave energy accelerates lipid oxidation, and UV spectrophotometry was a good index to measure oxidative alterations. Although the antioxidants added to oils were not as effective in retarding the oxidation of the oil during microwave heating as they were in the oven test, microwave heating followed by UV spectrophotometry analysis can be a good and fast tool to compare relative oil stabilities.

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