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Differential scanning calorimetric analysis for monitoring the oxidation of heated oils

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Abstract

A simple and reliable differential scanning calorimetric (DSC) method was developed for monitoring the oxidation in heated oils. Three different types of edible oils, namely, corn oil (CO), refined, bleached and deodorised palm olein (RBDPO) and soybean oil (SO) were used in this study. The DSC method was based on the cooling thermogram of oil samples at a scanning rate of 1°C/min from −30 to −85°C. The cooling thermogram of oil showed a well-defined single crystallisation peak. Two DSC parameters of this single crystallisation peak, namely peak temperature and enthalpy were determined. In addition to the DSC method, the deterioration of heated oils was also quantified by means of seven chemical methods. A statistical comparative study was carried out on the DSC and chemical methods. The results show that there is good correlation between the DSC method and other standard chemical methods. In conclusion, the DSC method offers an alternative for the monitoring of the oxidation of heated oil due to its appreciable time-saving, use of small samples with minimal preparation, and absence of toxic chemicals. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Lipid oxidation is a major deteriorative reaction affecting edible oils and is a primary concern to manufacturers and consumers from a quality standpoint (Paul & Mittal, 1997). Many of the degradation products of edible oils are harmful to human health as they destroy vitamins, inhibit enzymes and potentially cause mutations or gastrointestinal irritations (Clark & Serbia, 1991). Inaccurate monitoring of oil quality can either risk the public health or cause financial losses to the food industry (Paul & Mittal, 1996). This shows the necessity for quality assessment of over-heated or frying oils, which is of a special importance to the food industry. Multidirectional changes in heated oils affect usefulness of various control methods (White, 1991). There are numerous analytical methods for estimating deterioration of edible oils, such as total polar compounds (TPC), free fatty acid (FFA) content, iodine value (IV), peroxide value (PV) and anisidine value (AnV) (Robards, Kerr & Patsalides, 1988; Fritsch, 1981). These methods have to give accurate results, independent of changes in composition of oxidation products or the analytical results have to be closely related to special oxidation products which are harmful or responsible for the off-flavour (Robards et al., 1988). However, these are time- and work-consuming methods and require the use of toxic chemicals that are hazardous to the analysts as well as to the environment.

Fast and reliable methods for testing both the immediate quality and the expected oxidation stage of heated oils are in great demand (Croon, Rogstad & Kiutamo, 1986). Therefore, a rapid and instrumental method is required to monitor and determine the extent of the oxidation process in heated oils. Nowadays, quick tests are available for rapid assessment of oil quality in the food industry. These include the Fritest®, based on colorimetric measurement of carbonyl compounds formed during thermal oxidation, the Spot test and the Shortening Monitor test, based on colorimetric measurement of free fatty acid content, as an indicator of hydrolytic rancidity, the Food Oil Sensor, based on changes in the dielectric constant of heated oils, and Oxifritest or RAU-test, based on the total amount of oxidised compounds (Melton, Jafar, Sykes & Triangano, 1994). However, the accuracy of the above tests is

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limited because the compounds involved may not be good indicators of the actual degree of deterioration that occurs in the complex process of heating or frying (Fritsch, 1981; Croon et al., 1986). Therefore, additional efforts are necessary to develop potential new techniques that may be used in the food industry.

Differential scanning calorimetry (DSC) has potential as a nonchemical method to determine oil quality parameters. DSC analysis offers a direct method to study the thermal properties of various materials (Biliaderis, 1983). It is the most widely used of all thermoanalytical techniques with applicability to polymers, pharmaceuticals, fats and oils and various inorganic materials (Dollimore, 1996). It provides unique energy profile information, which specifically measures the temperatures and heat flows associated with material transitions as a function of time and temperature. In the fats and oils industry, DSC cooling/melting thermograms give valuable information on the thermal properties of various products (Biliaderis, 1983). Edible oils, like other naturally occurring fats and oils, are composed of a complex mixture of 96–99% triglycerides. When subjected to the crystallisation conditions from the melted state, edible oils behave like high polymers, i.e. they pass through the stages of nucleation, activation, crystal growth, and finally reach the state of a crystal lattice (Kawamura, 1979). According to Jacobsberg and Ho (1976), factors influencing the crystallisation of palm oil are presence of impurities such as free fatty acids, partial glycerides and oxidation products. Since these impurities are known to increase during heating or frying processes, the crystallisation behaviour is particularly useful for predicting the degree of thermal degradation of heated oil. Therefore, the objective of this study was to lay the foundation for the development of a DSC technique to investigate the correlation between DSC thermogram parameters and other standard chemical methods in heated oils.

2. Materials and methods

2.1. Materials and treatments

Three different edible oils were used in this study. Commercial corn oil (CO), refined, bleached and deodorised palm olein (RBDPO) and soybean oil (SO) were purchased from a local retailer and were used for all experiments. Oil samples (4.5 kg) were placed in open deep fat fryers (Berto's electrical fryer ALT series, ELT 8B, Montegrotto T., Padova, Italy) and heated at 180°C. About 200 g samples were collected in screw-capped amber bottles at the start (180°C) (0 h) and at 2 h intervals for a period of 12 h. All samples were cooled down to room temperature, and stored under nitrogen at −10°C for further analyses. All chemicals and solvents used were of analytical grade unless otherwise specified.

2.2. Standard chemical analysis

The AOCS Official Methods were employed for determinations of TPC, IV, FFA, AnV and PV in the oil samples (AOCS, 1993). The Totox (total oxidation) value (TxV) measures oil deterioration and equals the AnV plus twice the PV (Baur, 1995). The fatty acid compositions of heated oils were analysed by gas chromatography after transesterification. Fatty acid methyl esters (FAME) were prepared by transesterification of oils with sodium methoxide and analysed on a Hewlett–Packard Model 5890 instrument (Palo Alto, CA, U.S.A.) equipped with a flame ionisation detector (FID) and a Hewlett–Packard Model 3392A integrator. A polar capilary column BPX70 (0.32 mm internal diameter, 30 m length and 0.25 µm film thickness; SGE International Pty. Ltd., Victoria, Australia) was used at a column head pressure at 10 psi. Helium (99.995%) at approximately 23 ml/min (measured at oven temperature 150°C) was used as the carrier gas, and nitrogen (99.999%) at 20 ml/min was used as the makeup gas. The FID and injector temperatures were both maintained at 220°C. The injection mode was splitless, and samples of about 1 µl were injected with a 10 µl loop. The initial column oven temperature was 115°C, temperature programmed to 180°C at 8°C/min; the oven was held at this temperature until the analysis was completed. The concentration of FAME was expressed in relative percentage. The ratios of C18:2/C16:0 were then calculated.

2.3. Instrumental analysis

A Perkin–Elmer differential scanning calorimeter, DSC-7 (Perkin–Elmer Corp., Norwalk, CT, USA) was used for thermal analysis of the oil samples. Purified nitrogen (99.999% purity) was the purge gas for the dry box and flowed at approximately 20 psi. The temperature and energy calibrations were performed using standard indium and *n*-dodecane thermograms, respectively. Samples of ca. 6–12 mg were weighed into aluminium pans and covers were hermetically sealed into place. An empty, hermetically sealed aluminium pan was used as reference. Prior to analysis of samples, the baseline was obtained with an empty, hermetically sealed aluminium pan. After the sample and reference pans were placed in the chamber at 30°C, the cell block of the DSC was heated rapidly to 80°C at 200°C/min and held for 5 min to destroy crystal nuclei, cooled rapidly at 200°C/min to −30°C and held for 5 min to allow for polymorphic changes and finally cooled at 1°C/min to −85°C to define the cooling profile. The cooling thermograms of samples showed a single exothermic/crystallisation peak. The temperature of peak and the enthalpy of fusion were obtained by analysing the thermogram with the 7 Series/UNIX DSC software library (Anon, 1995). The peak enthalpy value (assumed that peak enthalpy = | value from computer-generated data|) was expressed as Joules per gram of oil samples and calculated from the area below the crystallisation peak.

2.4. Statistical analysis

All experiments and/or measurements were duplicated. The relationships between each of the DSC thermogram parameters and standard chemical methods were determined by Pearson's correlation analysis with the SAS/STAT release 6.08 program (SAS Institute, Cary, NC, USA, 1989). Equations of regression lines between each of DSC thermogram parameters and standard chemical methods were established.

3. Results and discussion

Chemical characteristics and DSC thermogram parameters of the initial unheated oil samples used in this study are shown in Table 1. The changes in quality parameters of the oil samples used for heating up to 12 h are given in Table 2. Generally, experimental results of the TPC, FFA, AnV, PV and TxV, showed an increase with heating time. In contrast, the IV and C18:2/C16:0, DSC peak temperature and enthalpy of heated oils decreased with the ascending time of heating. In this study, heated oils exhibited a simple thermogram after cooling in the DSC with a well-defined single crystallisation peak as shown in Figs. 1–3 for CO, RBDPO and SO, respectively. From these figures, it is apparent that the DSC traces are affected in a systematic way by the increase in heating duration. In general, as the time of heating increased, the peak of crystallisation shifted to lower temperatures and enthalpy decreased dramatically. According to Hagemann and Tallent (1972), slow-scan cooling curves of unsaturated triglycerides generally showed an exotherm at approximately the melting point of the α-form. Berger and Akehurst (1966) also reported that the typical cooling thermogram of the edible oil showed a dominant exothermic peak at supercooling temperature range. Since the contents of unsaturated fatty acids were higher in CO and SO in comparison to RBDPO, the crystallisation peaks in CO and SO were more apparent than RBDPO. In heated oils, the oxidation products, such as polar compounds, dimers, polymers, hydroperoxides and aldehydes, increased during heating process. As their levels increase, such compounds would contribute to the changes in DSC crystallisation peak parameters. It is well known that the presence of free fatty acids, partial glycerides and oxidation products in oil tend to shift the melting range to a lower temperature (Che Man & Swe, 1995). The same phenomenon is expected for the changes in DSC crystallisation peak parameters. Further study on the crystallisation behaviour of polar and nonpolar fractions of heated oils gave supportive evidence of this phenomenon. Fig. 4, shows that the crystallisation peak was not observed in the polar fraction of heated oils. This may be attributed to the disappearance of unsaturated triglycerides and the formation of degradation products in the polar fraction.

The experimental results of the TPC are given in Table 2, which shows that TPC linearly increased with the decrease in peak temperature and enthalpy. The TPC for heated oils represented all oxidation and decomposition products formed during heating, and the size of the polar fraction indicated the degree of deterioration (Melton et al., 1994). It is seen that the RBDPO has lower values than CO and SO. Determination of polar compounds is now considered to be one of the best indicators for assessing oil deterioration

Table 1
Quality parameters of edible oils before heating process[a]

Parameter	CO	RBDPO	SO
Peak temperature (°C)	−53.86 ± 0.09	−38.34 ± 0.02	−54.96 ± 0.23
Peak enthalpy (J/g)[b]	37.65 ± 0.38	6.44 ± 0.07	33.73 ± 0.27
TPC (%)	8.58 ± 0.95	7.93 ± 0.16	7.53 ± 0.46
IV (g of I_2/100 g oil)	129.89 ± 0.18	57.00 ± 0.06	129.20 ± 0.36
FFA (%)	0.11 ± 0.01	0.14 ± 0.00	0.06 ± 0.00
AnV	2.79 ± 0.24	1.45 ± 0.20	1.54 ± 0.23
PV (meq/kg oil)	5.88 ± 0.17	1.33 ± 0.09	1.82 ± 0.06
TxV	14.56 ± 0.09	4.11 ± 0.01	5.33 ± 0.57
C18:2/C16:0	4.75 ± 0.07	0.26 ± 0.00	4.90 ± 0.12

[a] Mean value ± standard deviation of four determinations. Abbreviations: CO; corn oil; RBDPO, refined-bleached-deodorized palm olein; SO, soybean oil; TPC, total polar compounds; IV, iodine value; FFA, free fatty acids; AnV, anisidine value; PV, peroxide value; TxV, Totox value; C18:2/C16:0, ratio of linoleic acid/ palmitic acid.

[b] Peak enthalpy = |value from computer-generated data|.

Table 2
Changes in characteristics of edible oils during heating at 180°C[a]

Edible oil	Heating time (h)	Peak temperature (°C)	Peak enthalpy (J/g)[b]	Total polar compounds (%)	Iodine value (g of I_2/100 g oil)	Free fatty acids (%)	Anisidine value	Peroxide value (meq/kg oil)	Totox value	C18:2/C16:0
CO	0	−53.91 ± 0.14	34.04 ± 0.11	9.37 ± 0.43	130.6 ± 0.57	0.11 ± 0.02	3.95 ± 0.26	7.83 ± 0.18	19.6 ± 0.63	4.27 ± 0.06
	2	−55.13 ± 0.03	31.75 ± 0.16	12.5 ± 0.71	129 ± 0.07	0.12 ± 0.00	11.6 ± 0.02	8.92 ± 0.39	29.4 ± 0.76	4.00 ± 0.08
	4	−56.37 ± 0.04	29.92 ± 0.21	14.1 ± 0.21	128 ± 0.03	0.13 ± 0.00	16.7 ± 0.20	9.82 ± 0.11	36.3 ± 0.02	3.78 ± 0.02
	6	−57.76 ± 0.02	27.02 ± 1.05	16.5 ± 1.08	127 ± 0.10	0.14 ± 0.00	23.7 ± 0.50	10.2 ± 0.24	44.2 ± 0.03	3.61 ± 0.05
	8	−59.01 ± 0.07	25.64 ± 0.48	19.8 ± 0.21	126 ± 0.01	0.15 ± 0.01	28.6 ± 0.27	11.0 ± 0.15	50.5 ± 0.58	3.37 ± 0.04
	10	−61.05 ± 0.22	22.30 ± 0.51	22.4 ± 0.98	125 ± 0.31	0.18 ± 0.01	36.4 ± 1.36	11.8 ± 0.07	60.0 ± 0.37	3.25 ± 0.01
	12	−63.07 ± 0.01	18.86 ± 1.04	24.4 ± 0.76	124 ± 0.52	0.20 ± 0.01	45.9 ± 0.83	12.4 ± 0.55	70.6 ± 1.94	3.11 ± 0.09
RBDPO	0	−38.79 ± 0.06	5.15 ± 0.27	9.18 ± 0.23	55.4 ± 0.14	0.14 ± 0.00	2.42 ± 0.05	3.38 ± 0.26	9.17 ± 0.47	0.24 ± 0.01
	2	−39.72 ± 0.03	4.63 ± 0.07	12.0 ± 0.50	55.1 ± 0.03	0.17 ± 0.00	6.52 ± 0.05	5.60 ± 0.01	17.7 ± 0.07	0.23 ± 0.00
	4	−41.73 ± 0.07	4.19 ± 0.03	13.3 ± 0.36	54.6 ± 0.08	0.19 ± 0.00	9.17 ± 0.98	7.72 ± 0.25	24.6 ± 1.49	0.22 ± 0.00
	6	−43.56 ± 0.13	3.63 ± 0.03	15.1 ± 0.28	54.0 ± 0.05	0.22 ± 0.00	11.87 ± 0.12	8.23 ± 0.24	28.3 ± 0.35	0.22 ± 0.00
	8	−45.08 ± 0.28	3.20 ± 0.06	16.5 ± 0.10	53.5 ± 0.11	0.24 ± 0.00	12.84 ± 0.34	9.02 ± 0.15	30.9 ± 0.03	0.20 ± 0.00
	10	−47.76 ± 0.21	2.96 ± 0.04	18.7 ± 0.32	53.1 ± 0.08	0.26 ± 0.00	13.3 ± 0.05	9.91 ± 0.21	33.2 ± 0.37	0.19 ± 0.00
	12	−49.71 ± 0.03	2.19 ± 0.19	20.2 ± 0.34	52.6 ± 0.03	0.29 ± 0.00	14.12 ± 0.70	10.38 ± 0.55	34.9 ± 0.41	0.17 ± 0.01
SO	0	−56.42 ± 0.26	29.81 ± 0.38	9.69 ± 0.39	128 ± 0.32	0.06 ± 0.00	3.86 ± 0.12	2.67 ± 0.18	9.20 ± 0.24	4.48 ± 0.23
	2	−58.31 ± 0.24	27.07 ± 1.71	12.8 ± 0.71	124 ± 0.48	0.07 ± 0.00	12.0 ± 0.12	5.18 ± 0.21	22.3 ± 0.54	4.20 ± 0.02
	4	−59.58 ± 0.12	25.32 ± 0.15	14.6 ± 0.23	121 ± 0.30	0.08 ± 0.00	17.6 ± 0.30	6.75 ± 0.30	31.1 ± 0.60	4.01 ± 0.06
	6	−60.93 ± 0.13	24.24 ± 0.83	16.1 ± 0.46	118 ± 0.28	0.10 ± 0.00	21.4 ± 0.03	7.65 ± 0.13	36.7 ± 0.29	3.78 ± 0.03
	8	−62.50 ± 0.25	21.64 ± 0.57	18.4 ± 0.13	114 ± 0.04	0.10 ± 0.00	25.7 ± 0.19	8.34 ± 0.26	42.3 ± 0.33	3.62 ± 0.04
	10	−64.41 ± 0.01	20.51 ± 1.83	21.08 ± 0.52	111 ± 0.18	0.12 ± 0.00	30.7 ± 0.72	8.80 ± 0.13	48.3 ± 0.98	3.59 ± 0.00
	12	−66.58 ± 0.12	16.08 ± 1.20	25.4 ± 0.58	108 ± 0.01	0.14 ± 0.00	35.5 ± 1.09	9.61 ± 0.26	54.8 ± 0.57	3.39 ± 0.13

[a] Each value in the table represents the mean ± standard deviation of two measurements from two replicates. Abbreviations see Table 1.

[b] Peak enthalpy = |value from computer-generated data|.

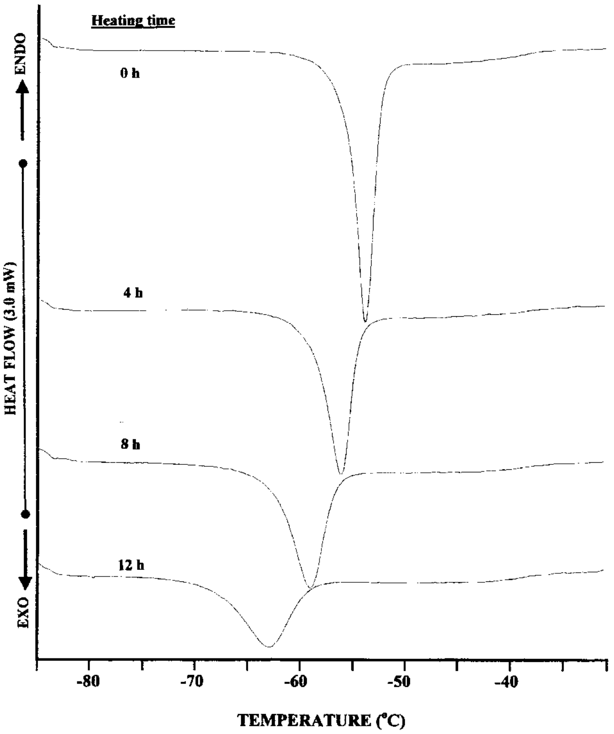

Fig. 1. Cooling thermograms of corn oil samples with different heating times (0, 4, 8 and 12 h).

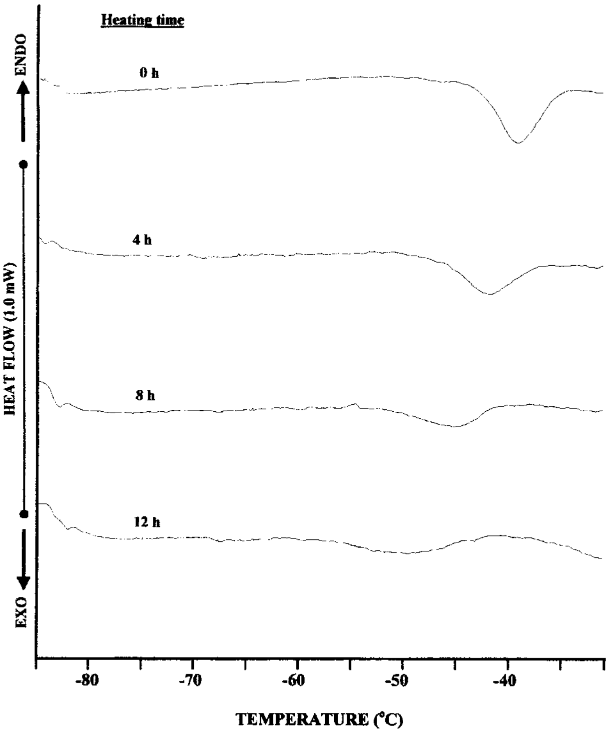

Fig. 2. Cooling thermograms of refined, bleached and deodorised palm olein samples with different heating times (0, 4, 8 and 12 h).

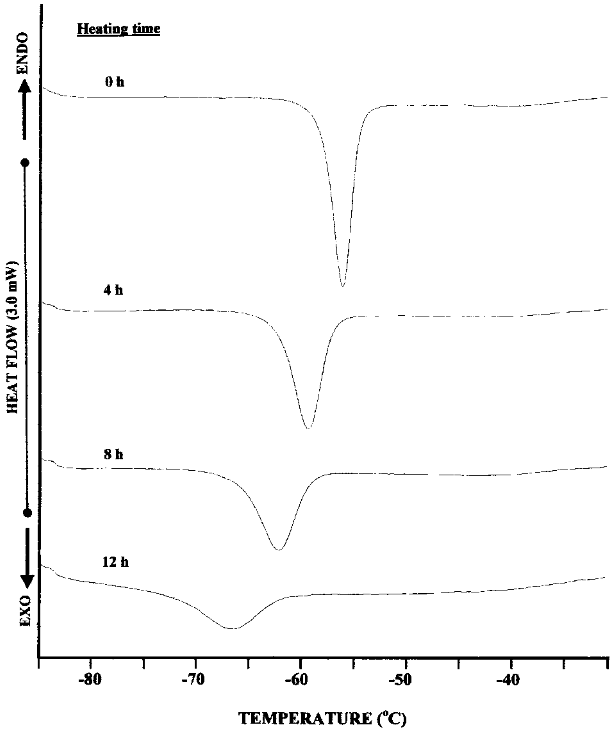

Fig. 3. Cooling thermograms of soybean oil samples with different heating time (0, 4, 8 and 12 h).

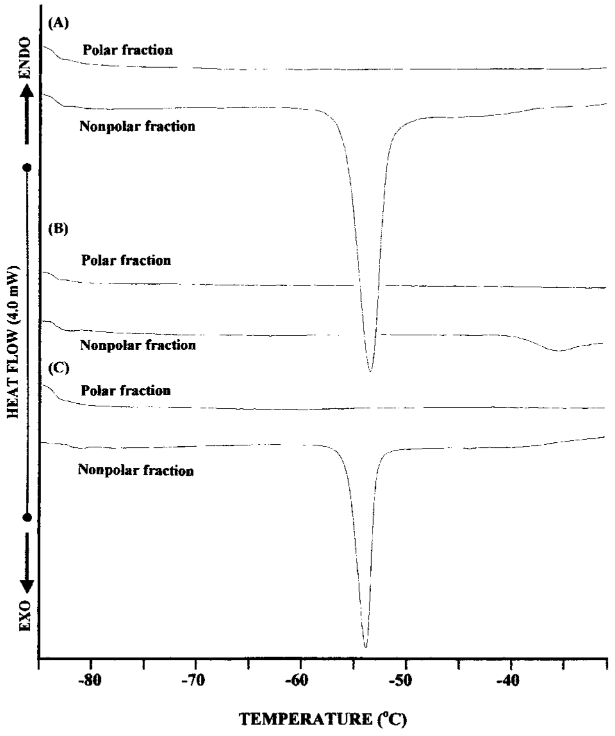

Fig. 4. Cooling thermograms of polar and nonpolar fraction of corn oil, refined, bleached and deodorised palm olein and soybean oil samples, respectively. (A) Corn oil sample (8 h at 180°C); (B) refined, bleached and deodorised palm olein sample (8 h at 180°C); and (C) Soybean oil sample (8 h at 180°C).

(Blumenthal, 1991). Many regulatory agencies in European countries have established the level of 25–27% total polar compounds as the rejection point for heated oils (Paul & Mittal, 1996; Firestone, Stier & Blumenthal, 1991). Although this method provides a good indication of oil deterioration, it is very time- and chemical-consuming (White, 1991).

The iodine value (IV) as shown in Table 2, showed a gradual decrease with the decrease in DSC thermogram parameters. The reductions in IV from 0 to 12 h were 6.00, 2.78 and 20.40 units for CO, RBDPO and CO, respectively. The reduction was highest for SO, followed by CO and RBDPO. The reduction in IV during heating is often taken as a measure of deterioration (Fritsch, 1981). The analysis is analogous to that for reduction of unsaturated fatty acids, but gives much more weight to the higher unsaturated.

The FFA values obtained in this study are shown in Table 2. The FFA values indicated a slight, gradual increase with the decline in DSC thermogram parameters. These values of the polyunsaturated oils were lowest with SO, followed by CO. The higher values obtained with RBDPO may be due to its initial high value and probably also, partly, due to its higher content of partial glycerides. The use of FFA content, the most common indicator of oil condition in the fats and oils industry, has come under criticism from various quarters on scientific grounds (Fritsch, 1981). Berger reported that the measurement of FFA could not determine suitability of heated oils for further use (Berger, 1984).

Table 2 also shows the increase in anisidine value (AnV) in heated oils. Generally, the AnVs increased markedly with decrease in DSC thermogram parameters. The AnVs of the RBDPO were always lower than that of CO and SO. The AnV is a more reliable and meaningful test because it measures the secondary products, which are more stable during the heating process. The possible drawback of AnV is that reactive aldehydic products can take part in polymerization (Al-Kahtani, 1991).

The changes in peroxide values (PVs) are shown in Table 2. The PVs showed an increase with the decrease in DSC thermogram parameters. These values were higher in CO, than RBDPO and SO. PV may be less reliable for monitoring thermal oxidation (Fritsch, 1981) because of the rapid decomposition of peroxides that are formed during primary oxidation to secondary oxidation products (Berger, 1991).

The total oxidation value (TxV), an extension of AnV and PV methods, is another useful indicator to measure the onset of progressive deterioration. The changes in TxVs are given in Table 2. These values indicated a marked increase with the reduction in DSC thermogram parameters. Similar to changes in PV and AnV, the RBDPO consistently had lower TxVs than CO and SO.

The changes in ratio of C18:2/C16:0 are presented in Table 2. Oxidation causes a decrease in the relative percentages of the unsaturated fatty acids and an increase in the relative percentages of the saturated fatty acids (Liu & White, 1992). Therefore, linoleic acid and palmitic acid are usually used as indicators of the extent of oil deterioration because linoleic acid is more susceptible to oxidation, whereas palmitic acid is more stable toward oxidation. Like changes in IV, these ratios declined with the decrease in DSC thermogram parameters. The decreases in C18:2/C16:0 across 12 h of heating were 1.16, 0.07 and 1.09 for CO, RBDPO and SO, respectively. Decreases for CO and SO were higher than for RBDPO because of their initial high levels of C18:2. Generally, oils with higher proportions of unsaturated fatty acids are more prone to oxidation than those containing lesser amounts.

The coefficients of correlation matrix between each of the DSC thermogram parameters and standard chemical methods are shown in Table 3. The DSC thermogram parameters showed excellent correlations with the standard analytical measurements, regardless the oil degradation treatment in this case, and independent of the edible oil source. The coefficients of correlation for each comparison were also highly significant ($P < 0.01$).

Table 3
Pearson correlation coefficient ($n = 6$) between wet chemical methods and DSC thermogram parameters[a]

	Peak temperature			Peak enthalpy[b]		
	CO	RBDPO	SO	CO	RBDPO	SO
TPC	−0.9876	−0.9842	−0.9938	−0.9834	−0.9871	−0.9890
IV	0.9940	0.9916	0.9939	0.9852	0.9875	0.9696
FFA	−0.9713	−0.9956	−0.9949	−0.9622	−0.9912	−0.9670
AnV	−0.9966	−0.9068	−0.9886	−0.9942	−0.9402	−0.9591
PV	−0.9741	−0.9272	−0.9386	−0.9792	−0.9401	−0.9131
TxV	−0.9955	−0.9224	−0.9784	−0.9945	−0.9449	−0.9500
C18:2/C16:0	0.9704	0.9711	0.9490	0.9717	0.9778	0.9278

[a] Significance at 0.01 level ($P < 0.01$). Abbreviations: see Table 1.

[b] Peak enthalpy = |value from computer-generated data|.

Table 4
Relationships between DSC thermogram parameters and other indicators of heated oil deterioration ($n=6$)[a]

Indicator (Y)	Edible oil	Regression equation	
		Peak temperature (X)	Peak enthalpy (X)[b]
TPC	CO	$Y=-79.480-1.662X$	$Y=44.264-1.007X$
	RBDPO	$Y=-25.960-0.938X$	$Y=28.734-3.706X$
	SO	$Y=-74.196-1.487X$	$Y=43.472-1.131X$
IV	CO	$Y=164.328+0.646X$	$Y=116.322+0.389X$
	RBDPO	$Y=65.228+0.255X$	$Y=50.329+1.004X$
	SO	$Y=243.379+2.052X$	$Y=81.726+1.530X$
FFA	CO	$Y=-0.429-0.010X$	$Y=0.307-0.006X$
	RBDPO	$Y=-0.333-0.013X$	$Y=0.399-0.049X$
	SO	$Y=-0.378-0.008X$	$Y=0.232-0.006X$
AnV	CO	$Y=-233.750-4.438X$	$Y=96.729-2.693X$
	RBDPO	$Y=-32.072-0.962X$	$Y=24.643-3.939X$
	SO	$Y=-165.929-3.051X$	$Y=74.216-2.263X$
PV	CO	$Y=-17.738-0.483X$	$Y=18.279-0.295X$
	RBDPO	$Y=-17.278-0.572X$	$Y=16.233-2.289X$
	SO	$Y=-32.036-0.637X$	$Y=18.151-0.474X$
TxV	CO	$Y=-269.225-5.403X$	$Y=133.286-3.283X$
	BDPO	$Y=-66.627-2.106X$	$Y=57.109-8.518X$
	SO	$Y=-230.000-4.326X$	$Y=110.517-3.211X$
C18:2/C16:0	CO	$Y=10.914+0.126X$	$Y=1.559+0.076X$
	RBDPO	$Y=0.489+0.006X$	$Y=0.117+0.025X$
	SO	$Y=10.323+0.105X$	$Y=2.014+0.079X$

[a] Significance at 0.01 level ($P<0.01$). Abbreviations: see Table 1.

[b] Peak enthalpy = |value from computer−generated data|.

As can be seen from Table 3, peak temperature was in strongly negative correlation to TPC, FFA, AnV, PV and TxV, and was in highly positive correlation to IV and C18:2/C16:0. In contrast, the peak enthalpy showed a significant positive correlation to TPC, FFA, AnV, PV and TxV, and a highly significant negative correlation to IV and C18:2/C16:0. In particular, the high correlation found between each of the DSC thermogram parameters, with changes in TPC, IV and FFA, suggests that DSC can be recommended as an appropriate objective method for assessing the extent of oxidation in edible oils. In view of the high correlation between each of the DSC thermogram parameters and standard chemical methods, linear regression equations between them were established (Table 4). However, in determination of the regression equation between methods, the different chemical compositions among different edible oils from different origins, makes it difficult to depend on a single regression equation for evaluating the degree of deterioration in heated oils.

In conclusion, the results of the present study suggest that the DSC method can be a reliable and efficient alternative to existing methods for monitoring the extent of lipid oxidation in various edible oils, with no need for chemical reagents and delicate skills. Our results represent a new technique useful for the assessment of oils of different quality.

Acknowledgements

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References

Anon. (1995). *7 Series/UNIX DSC7 Users Manual*. Software Version 4.0, Perkin–Elmer Corporation, Norwalk, CT, USA.

Al-Kahtani, H. (1991). Survey of quality of used frying oils from restaurants. *Journal of the American Oil Chemists Society, 68*, 857–862.

AOCS (1993). *Official methods and recommended practices of the American Oil Chemists Society* (4th ed.). Champaign, Illinois: American Oil Chemists's Society, ed. D. Firestone.

Baur, F. J. (1995). Analytical methods for oils and fats. In H. Lawson, *Food oils and fats* (pp. 291). New York: Chapman and Hall.

Berger, K. G. (1984). *The practice of frying*. PORIM Technology: Palm Oil Res. Inst. Malaysia, Kuala Lumpur, Malaysia, No. 9.

Berger, K. G., & Akehurst, E. E. (1966). Some application of differential thermal analysis to oils and fats. *Journal of Food Technology, 1*, 237–247.

Biliaderis, C. G. (1983). Differential scanning calorimetry in food research—a review. *Food Chemistry, 10*, 239–265.

Blumenthal, M. M. (1991). A new look at the chemistry and physics of deep-fat frying. *Food Technology 45*(2), 68–71,72.

Che Man, Y. B., & Swe, P. Z. (1995). Thermal analysis of failed-batch palm oil by differential scanning calorimetry. *Journal of the American Oil Chemists Society, 72*, 1529–1532.

Clark, W. L., & Serbia, G. W. (1991). Safety aspects of frying fats and oils. *Food Technology*, *45*(2), 84–86, 88, 89, 94.

Croon, L. B., Rogstad, A., & Kiutamo, T. (1986). A comparative study of analytical methods for quality evaluation of frying fat. *Fette, Seifen, Anstrichm., 88*, 87–91.

Dollimore, D. (1996). Thermal analysis. *Analytical Chemistry, 68*, 63R–71R.

Firestone, D., Stier, R. F., & Blumenthal, M. M. (1991). Regulation of frying fats and oils. *Food Technology, 45*(2), 90–94.

Fritsch, C. W. (1981). Measurements of frying fat deterioration: A brief review. *Journal of the American Oil Chemists Society, 58*, 272–274.

Hagemann, J. W., & Tallent, W. H. (1972). Differential scanning calorimetry of single acid triglycerides: effect of chain length and unsaturation. *Journal of the American Oil Chemists Society, 49*, 119–123.

Jacobsberg, B., & Ho, O. C. (1976). Studies in palm oil crystallisation. *Journal of the American Oil Chemists Society, 53*, 609–617.

Kawamura, K. (1979). The DSC thermal analysis of crystallisation behaviour in palm oil. *Journal of the American Oil Chemists Society, 56*, 753–758.

Liu, H. R., & White, P. J. (1992). Oxidative stability of soybean oils with altered fatty acid compositions. *Journal of the American Oil Chemists Society, 53*, 528–532.

Melton, S. L., Jafar, S., Sykes, D., & Trigiano, M. K. (1994). Review of stability measurements for frying oils and fried food flavour. *Journal of the American Oil Chemists Society, 71*, 1301–1308.

Paul, S., & Mittal, G. S. (1996). Dynamics of fat/oil degradation during frying based on physical properties. *Journal of Food Process and Engineering, 19*, 201–221.

Paul, S., & Mittal, G. S. (1997). Regulating the use of degraded oil/fat in deep-fat/oil food frying. *Critical Reviews in Food Science and Nutrition, 37*, 635–662.

Robards, K., Kerr, A. F., & Patsalides, E. (1988). Rancidity and its measurement in edible oils and snack foods. *Analyst, 113*, 213–222.

White, P. J. (1991). Methods for measuring changes in deep-fat frying oils. *Food Technology, 45*(2), 75–80.