

Analytical, Nutritional and Clinical Methods Section

## Comparative studies of oxidative stability of edible oils by differential scanning calorimetry and oxidative stability index methods

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### Abstract

A comparative study was conducted to determine the oxidative stability of twelve different edible oils with two different instruments: a differential scanning calorimeter and an oxidative stability index (OSI) instrument. The OSI instrument temperature was set at 110 °C. The differential scanning calorimetry (DSC) technique involved oxidation of oil samples in an oxygen-flow DSC cell. The DSC cell temperature was set at four different isothermal temperatures: 110, 120, 130 and 140 °C. A dramatic increase of evolved heat was observed with the appearance of a sharp exothermic curve during initiation of the oxidation reaction. The oxidative induction time ( $T_0$ ) was automatically determined by extrapolation of the downward portion of the DSC oxidation curve to the time axis. There was a good correlation ( $P < 0.0001$ ) between the DSC  $T_0$  and OSI values. The decrease in  $\log_{10}(T_0)$  with increasing DSC isothermal temperature was best fitted by a linear equation. DSC evidently provides a convenient way to determine the oxidative stability of various edible oils. © 2002 Elsevier Science Ltd. All rights reserved.

### 1. Introduction

Edible oil quality and stability are the main factors that influence its acceptability and market value (Smouse, 1995). Thus, maintenance of oil quality, acceptable to the consumer, is an important function of quality control in the oils and fats industry. Oxidative stability is one of the most important indicators for maintaining the quality of edible oils. It has been shown that oxidation of edible oils takes place through a chain reaction that essentially consists of an induction stage. The time before a dramatic increase in the rate of lipid oxidation is a measure of oxidative stability and is referred to as the induction time (Coppin & Pike, 2001). A number of methods have been developed for evaluating the oxidative stability of edible oil (Frankel, 1993).

Today, we often rely on various accelerated stability tests to quickly assess the stability of oils and fats. Since oxidation is the major cause of oil degradation (Paul & Mittal, 1997), most of the accelerated tests are designed to speed up the oxidation process by exposing oil samples to elevated temperatures in the presence of excess amounts of air or oxygen. Historically, the Schaal Oven Test and the Active Oxygen Method (AOM) have been the most widely used tests to evaluate oil stability (Wan, 1995). Currently, oxidative stability of oils and fats can be determined automatically by two commercially available instruments, the Rancimat from Brinkmann Instrument (Westbury, NY) and the Oxidative Stability Instrument (OSI) from Omnion, Inc. (Rockland, MA; Akoh, 1994).

Application of thermal analysis, for accelerated oil stability tests, has been studied by several researchers. Cross (1970) and Hassel (1976) used differential scanning calorimetry (DSC) at isothermal modes with an oxygen purge to measure the stability of oils. The end point of DSC was taken at the time where a rapid exothermic reaction of oil and oxygen occurred. Hassel's

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results showed that oil samples, which required 14 days via AOM, for example, were evaluated in less than 4 h by DSC (Hassel, 1976).

DSC techniques have the potential to be used as a non-chemical method to determine oil quality parameters. DSC provides unique energy profile information, which specifically measures the temperatures and heat flows associated with material transitions as a function of time and temperature. As mentioned earlier, determining the time when edible oils reach their critical levels of oxidative deterioration is a challenging task. Thus, a rapid method for judging the relative stability of oxidative degradation would be of great assistance in the development of edible oils. Therefore, the primary objective of the present study was to evaluate a simple and reliable DSC method for determination of the oxidative stability of edible oils and to correlate with the OSI instrument. A secondary objective was to study temperature effects on the DSC oxidative induction time ( $T_0$ ).

## 2. Materials and methods

### 2.1. Materials and treatments

Different vegetable oils ( $n=12$ ) from various plant origins were used in this study. These were coconut, palm kernel, refined-bleached-deodorised palm olein (RBDPO<sub>o</sub>), canola, corn, grapeseed, olive, peanut, safflower, sesame, soybean and sunflower oils. RBDPO<sub>o</sub> and palm kernel oil (PKO) were obtained from a local refinery. The other samples were purchased from several local retailers. All chemicals and solvents used were of AnalaR or HPLC grades (Merck, Darmstadt, Germany).

### 2.2. Chemical analyses

The AOCS Official Method was employed for determinations of free fatty acid content, iodine, peroxide and anisidine values in the oil samples (AOCS, 1993).

### 2.3. OSI analysis

The OSI was determined by OSI instrument (Omnion, Inc., Rockland, MA). The OSI analysis was determined as defined in AOCS Official Method Cd 12b-92 (AOCS, 1993). The instrument was run at 110 °C. Air-flow rate was set at 2.5 ml/s for all analyses.

### 2.4. DSC analysis

The oxidative stability of edible oil was determined by a Perkin-Elmer differential scanning calorimeter DSC-7 (Norwalk, CT). The equipment was calibrated with pure indium and the baseline was obtained with an

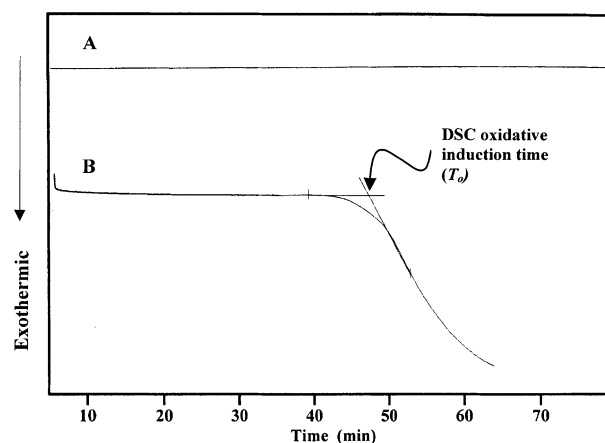


Fig. 1. Differential scanning calorimetry oxidation curve of corn oil. (A) Isothermal at 130 °C with nitrogen (99.999%) flowing at 50 ml/min; and (B) isothermal curve at 130 °C with oxygen (99.8%) flowing at 50 ml/min.

empty open aluminium pan (Anon, 1995). Oil samples of  $5.0 \pm 0.5$  mg were weighed into open aluminium pans and placed in the equipment's sample chamber. The isothermal temperature was programmed at four different temperatures (110, 120, 130, and 140 °C) and purified oxygen (99.8%) was passed through the sample enclosure at 50 ml/min. The  $T_0$  of the oxidative reaction corresponded closely to the intersection of the extrapolated baseline and the tangent line (leading edge) of the exotherm (Fig. 1, curve B).

### 2.5. Statistical analysis

All experiments were replicated four times. Data were analysed using SAS software (SAS Institute, Cary, NC, USA, 1989), and the Duncan multiple range test was used to compare differences among means. Significance was defined at  $P < 0.05$ . The SAS REG procedure was carried out on DSC  $T_0$  and OSI values. The relationship between DSC  $T_0$  and DSC isothermal temperature was also determined by the SAS REG procedure. This procedure was used to fit a simple linear equation to the results. The best-fit equations, including the slopes, the intercepts of regression lines and their coefficient of correlation and/or correlation of determination, were calculated.

## 3. Results and discussion

The initial characteristics of edible oils used in the present study are given in Table 1. The iodine values of these oils ranged from 9.37 to 145 g of I<sub>2</sub>/100 g oil. The oxidation process in edible oil is primarily an exothermic reaction. The exothermic oxidative reactions produce traces, such as in Fig. 1, curve B. No exothermic peak (no oxidation reaction) was detected when oil

Table 1  
Initial chemical characteristics of edible oils<sup>a</sup>

Oil	Iodine value (g of I <sub>2</sub> /100 g oil)	Free fatty acid (%)	Peroxide value (meq/kg oil)	Anisidine value
Canola	108±0.09	0.04±0.00	6.68±0.01	1.15±0.10
Coconut	9.37±0.19	3.93±0.14	1.72±0.04	1.31±0.07
Corn	129±0.47	0.12±0.01	3.93±0.01	3.79±0.01
Grapeseed	141±0.65	0.07±0.00	10.6±0.31	7.87±0.40
Olive	86.4±0.11	0.30±0.00	8.50±0.27	2.91±0.09
Peanut	95.2±0.53	0.05±0.00	6.82±0.06	5.22±0.14
PKO <sup>b</sup>	19.3±0.01	2.49±0.01	0.75±0.09	1.78±0.11
RBDPO <sub>O</sub> <sup>c</sup>	56.6±0.32	0.10±0.01	0.82±0.06	1.33±0.15
Safflower	145±0.46	0.09±0.00	5.07±0.15	6.41±0.16
Sesame	109±0.23	2.37±0.05	1.13±0.08	4.98±0.04
Soybean	136±0.19	0.05±0.00	2.39±0.09	2.05±0.11
Sunflower	140±0.71	0.06±0.00	9.10±0.14	10.7±0.10

<sup>a</sup> Each value in the table represents the mean value±standard deviation of triplicate analyses.

<sup>b</sup> PKO, palm kernel oil

<sup>c</sup> RBDPO<sub>O</sub>, refined-bleached-deodorized palm olein.

Table 2  
Differential scanning calorimetry (DSC) oxidative induction time ( $T_0$ ) and oxidative stability index (OSI) values of various edible oils<sup>a</sup>

Oil	DSC $T_0$ (min) <sup>b</sup>						OSI (min) <sup>c</sup>			
	110 °C	CV <sup>d</sup> (%)	120 °C	CV (%)	130 °C	CV (%)	140 °C	CV (%)	110 °C	CV (%)
Canola	259.96bB	0.21	126.41cE	0.12	61.67dE	0.11	37.41eD	2.62	366.00aE	0.95
Coconut	325.38bB	0.89	168.28 cD	0.43	86.60 dD	0.64	44.86 eC	1.42	675.00 aD	2.05
Corn	166.55 bC	0.18	83.57 cF	0.19	47.74 dF	0.41	21.45 eE	1.01	285.00 aF	1.22
Grapeseed	74.49 bD	0.43	36.29 cL	0.60	17.60 dJ	0.60	7.53 eI	4.34	124.50 aH	1.39
Olive	169.02 bC	0.82	51.00 cJ	2.50	21.99 dI	4.09	13.94 eG	4.01	291.00 aF	1.19
Peanut	127.21 bCD	0.56	67.36 cH	1.19	39.36 dG	0.36	12.33 eH	6.45	304.50 aF	1.71
PKO <sup>e</sup>	539.79 bA	1.04	273.36 cB	0.89	138.22 dC	0.92	70.13 eB	0.82	1608.00 aB	1.72
RBDPO <sub>O</sub> <sup>f</sup>	515.19 bA	0.29	287.42 cA	0.54	160.42 dA	0.37	82.36 eA	2.50	1531.50 aC	0.11
Safflower	88.61 bD	1.51	39.50 cK	0.77	18.19 dJ	1.41	8.17 eI	6.41	136.50 aH	1.27
Sesame	542.70 bA	0.01	251.70 cC	0.31	139.37 dB	0.25	69.55 eB	1.24	1992.00 aA	1.74
Soybean	124.13 bCD	1.12	65.55 cI	0.30	33.70 dH	0.54	20.00 eF	3.80	133.50 aH	3.89
Sunflower	131.88 bCD	0.76	70.50 cG	1.00	33.34 dH	1.91	19.98 eF	4.40	195.00 aG	0.00

<sup>a</sup> Means within each row with different letters (a–e) are significantly ( $P < 0.05$ ) different. Means within each column with different letters (A–L) are significantly ( $P < 0.05$ ) different.

<sup>b</sup> Each value in the table represents the mean of four measurements.

<sup>c</sup> Each value in the table represents the mean of two measurements.

<sup>d</sup> CV, coefficient of variation; DSC, differential scanning calorimetry; OSI, oxidative stability index.

<sup>e</sup> PKO, palm kernel oil

<sup>f</sup> RBDPO<sub>O</sub>, refined-bleached-deodorized palm olein

samples were scanned under nitrogen conditions (Fig. 1, curve A). The extrapolated  $T_0$  was taken as a measure of the relative stability of the oil toward oxidation. We are not considering the significance of peak area (enthalpy of oxidation) at present. Mean DSC  $T_0$  and OSI time and their coefficients of variation (CV) results are presented in Table 2. The OSI times ranged from 124.50 to 1992.00 min, while CV ranged from 0.00 to 3.89%. At the same temperature program (110 °C), DSC gave significantly ( $P < 0.05$ ) lower oxidative induction times than the OSI instrument. Depending on types of edible oils, the DSC  $T_0$  values were 7–260% lower than OSI times. This observation may be due to the fact that a smaller sample size was used in the DSC analysis (5 mg) as compared to OSI instrument (5 g).

Moreover, the ratio of surface to volume also plays an important role in this study. In terms of this ratio, oil samples in a DSC pan showed higher values than oil samples in a test tube (in OSI analysis). Generally, oxygen and edible oil could react more efficiently when a small oil sample size or oil sample with high ratio of surface to volume was used. Therefore, DSC produced a faster oxidative induction time than the OSI instrument.

Generally, edible oils with higher degree of unsaturation are more susceptible to lipid oxidation. Therefore, grapeseed, soybean, safflower or sunflower oil (IV > 130 g of I<sub>2</sub>/100 g of oil) showed significantly ( $P < 0.05$ ) lower induction times (both DSC  $T_0$  and OSI time) than coconut oil, RBDPO<sub>O</sub> or PKO. However, for sesame oil, a conflicting result was observed. This edible oil is

Table 3  
Pearson correlation coefficient matrix between differential scanning calorimetry (DSC) and oxidative stability index (OSI) methods<sup>a</sup>

	DSC110	DSC120	DSC130	DSC140
DSC110	–	–	–	–
DSC120	0.9840	–	–	–
DSC130	0.9809	0.9961	–	–
DSC140	0.9767	0.9936	0.9913	–
OSI110	0.9757	0.9508	0.9567	0.9345

<sup>a</sup> Significance at 0.01 level ( $P < 0.01$ ). DSC110, DSC at isothermal temperature 110 °C; DSC120, DSC at isothermal temperature 120 °C; DSC130, DSC at isothermal temperature 130 °C; DSC140, DSC at isothermal temperature 140 °C; OSI110, OSI at isothermal temperature 110 °C.

Table 4  
Relationships between oxidative stability index (OSI) values and differential scanning calorimetry (DSC) oxidative induction time ( $T_0$ ) at four different isothermal temperatures

Indicator (Y)	Indicator (X) <sup>a</sup>	Regression equation	P-value
OSI110	DSC110	$T_{0(\text{OSI110})} = 3.6371T_{0(\text{DSC110})} - 264.4083$	0.0001
	DSC120	$T_{0(\text{OSI110})} = 6.8863T_{0(\text{DSC120})} - 255.4094$	0.0001
	DSC130	$T_{0(\text{OSI110})} = 12.6859T_{0(\text{DSC130})} - 228.7697$	0.0001
	DSC140	$T_{0(\text{OSI110})} = 23.9094T_{0(\text{DSC140})} - 264.4083$	0.0001

<sup>a</sup> See Table 3.

Table 5  
Relationships between logarithm of DSC  $T_0$  value ( $\log_{10} T_0$ ) and DSC isothermal temperature ( $T$ ) of various edible oils<sup>a</sup>

Edible oil	Regression equation	Coefficient of determination ( $R^2$ )
Canola	$T = 56.0152 + 0.0284 \log_{10} T_0$	0.9934
Coconut	$T = 52.4619 + 0.0287 \log_{10} T_0$	1.0000
Corn	$T = 186.4782 - 0.0289 \log_{10} T_0$	0.9959
Grapeseed	$T = 168.1931 - 0.0323 \log_{10} T_0$	0.9994
Olive	$T = 82.3012 + 0.0362 \log_{10} T_0$	0.9618
Peanut	$T = 175.7655 - 0.0320 \log_{10} T_0$	0.9760
PKO <sup>b</sup>	$T = 47.5371 + 0.0295 \log_{10} T_0$	1.0000
RBDPO <sub>o</sub> <sup>c</sup>	$T = 212.8186 - 0.0264 \log_{10} T_0$	0.9989
Safflower	$T = 167.8706 - 0.0335 \log_{10} T_0$	0.9997
Sesame	$T = 47.4384 + 0.0293 \log_{10} T_0$	0.9977
Soybean	$T = 187.9975 - 0.0267 \log_{10} T_0$	0.9974
Sunflower	$T = 177.5643 - 0.0316 \log_{10} T_0$	0.9975

<sup>a</sup> Significance at 0.0001 level ( $P < 0.0001$ ).

<sup>b</sup> PKO, palm kernel oil

<sup>c</sup> RBDPO<sub>o</sub>, refined-bleached-deodorized palmolein

known for its high content of unsaturated fatty acids (IV of 109 g of I<sub>2</sub>/100 g of oil). Yet, its oxidative induction time was comparable or higher than edible oils containing lower amounts of unsaturated fatty acids. Sesame oil, from roasted sesame seeds, is known to be resistant to oxidative deterioration (Kikugawa, Arai, & Kurechi, 1983; Manley, Vallon, & Erickson, 1974). Its remarkable stability may be due to the presence of endogenous antioxidants (sesamol and sesaminol), together with tocopherols (Yoshida, 1994).

Significance testing showed that DSC isothermal temperature had a significant effect ( $P < 0.01$ ) on the DSC  $T_0$  (Table 2). For all edible oils, the  $T_0$  were sig-

nificantly ( $P < 0.05$ ) decreased as the isothermal temperature increased. Generally, with an increase in 10 °C (e.g. 110 to 120 °C), the  $T_0$  value was half of its previous reading (Table 2). This agrees with the Q<sub>10</sub> law for the relationship between temperature and rate of chemical reaction.

The coefficients of correlation matrix, between each DSC  $T_0$  value and OSI time, are shown in Table 3. The DSC  $T_0$  values showed excellent correlations with the OSI measurements, independent of the edible oil source. The coefficients of correlation ( $> 0.93$ ) for each comparison were also highly significant ( $P < 0.01$ ). In view of the high correlation between DSC  $T_0$  and OSI time,

linear regression equations were established (Table 4). However, in the determination of the regression equation between DSC  $T_0$  value versus OSI time, the different chemical compositions among different edible oils from various plant origins make it difficult to depend on a single regression equation for evaluating the relationship between these two methods.

Table 5 shows the regression equations of logarithm DSC  $T_0$  value versus DSC isothermal temperature. The result gave a linear relation ( $P < 0.0001$ ) for each type of edible oil. Generally, the results of the present study indicated that the coefficients of determination ( $R^2$ ) for linear regression were above 0.96. With this observation, one can easily predict the oxidative stability of a given edible oil when temperature is a known variable.

The high correlations found between DSC  $T_0$  values and OSI measurements imply that DSC can be recommended as an appropriate objective method for assessing the oxidative stability of various edible oils. The DSC method, because of its simplicity, absence of toxic chemicals and time-saving nature, could be used for routine analysis in the oils and fats industry. Our findings also indicate that DSC is a reliable technique for the assessment of oils of different chemical composition and at various keeping temperatures.

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