Determination of the Oxidative Stability of Fats and Oils: Comparison between the Active Oxygen Method (AOCS Cd 12-57) and the Rancimat Method

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Oxidative stability is an important parameter in the characterization of fats and oils. The determination of this parameter with the Active Oxygen Method (AOM; AOCS Method Cd 12-57) is both very costly and labor intensive, owing to the repeated peroxide value determinations involved. The alternative rancimat method is based on the conductometric determination of volatile degradation products and features automatic plotting of the conductivity against time. The evaluation is performed graphically after completion of the experiment. The labor required for this method is considerably less as it is not necessary to perform titrations at regular intervals. In the determination of the peroxide values of six samples at three temperatures, ca 15 l mixed solvent and chemicals valued at SFr. 400 (ca $180 US) were consumed.

The induction times (t_I) determined with both methods using six different fats and oils show a good correlation (slope 1.005, correlation coefficient 0.987). The rancimat method thus yields results equivalent to the AOCS Method Cd 12-57, but offers a real alternative for the determination of oxidative stabilities owing to the appreciable saving in labor.

Oxidative stability is an important parameter for the quality assessment of animal and vegetable fats and oils. Autoxidation is effected by atmospheric oxygen; the oxidation process is initiated by radical reactions involving unsaturated fatty acids (1-3). The primary products formed are hydroperoxides, which then break down in a series of complex reactions, the exact nature of which is still under investigation; the secondary products include alcohols and carbonyl compounds (1-3). These can be oxidized further to carboxylic acids (4).

In order to determine oxidative stability, a fat is exposed to a stream of dry air at a temperature of 100-140 C. The progress of the oxidation curves can be followed by periodic determination of the peroxide value (PV) (Active Oxygen Method, AOM; AOCS Method Cd 12-57) or other parameters. The curves comprise an induction phase, in which practically no secondary products are formed, and an oxidation phase, during which a large increase in peroxide value and volatile products is detected.

The method developed by Hadorn and Zürcher (5) and which is used in the 617 Rancimat (METROHM AG, CH-9100 Herisau, Switzerland) (6) (Fig. 1) utilizes the fact that the greater part of the volatile products consists of formic acid (7). These volatile components are trapped in distilled water, measured conductometrically and the conductivity plotted automatically. The progress of the oxidation curves determined in this manner virtually parallels the development of the peroxide value (5). The t_I (point of greatest inflection) is determined graphically after completion of the experiment (tangential intersection point, see Fig. 2). The apparatus requires no supervision during the course of an experiment (e.g. overnight).

On the other hand, in the procedure involving the AOM, the peroxide value must be determined at regular invervals throughout the whole experiment. The end of the t_I is considered as the attainment of a PV of 100 μeq/kg and is evaluated by interpolation of two experimental points between PV = 75 μeq/kg and PV = 175 μeq/kg.

In what follows, it will be shown that the results obtained with the rancimat method correlate extremely well with those of the AOM test.

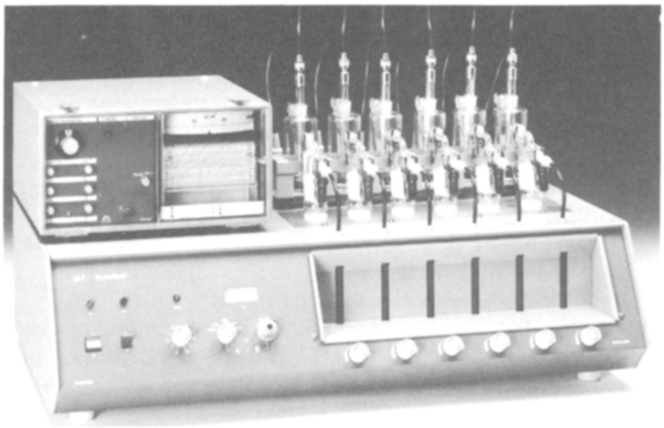

FIG. 1. 617 Rancimat.

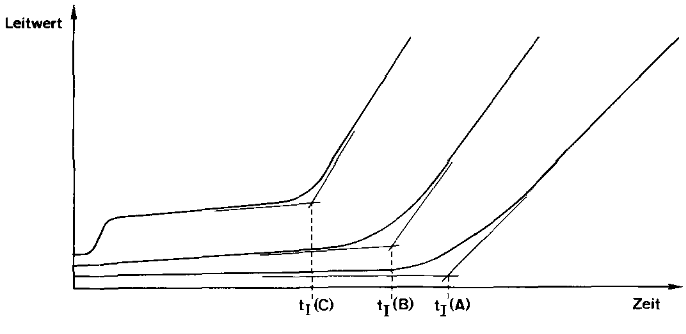

FIG. 2. Graphic determination of the induction time (t_I) by the tangent method. A and B, typical conductivity curves; C, curve with initial step.

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EXPERIMENTAL

Reagents. Chloroform (p.a.; No. 25690), glacial acetic acid (p.a.; No. 45730) and potassium iodide (p.a.; No. 60400) were obtained from Fluka (CH-9470 Buchs, Switzerland). As titrant, $Na_2S_2O_3$ 0.1 M (Titrisol®, E. Merck, Darmstadt, Federal Republic of Germany) was used. Deionized water was used as absorption solution for the conductivity measurements.

Method. All experiments were performed with a 617 Rancimat (METROHM AG, CH-9100 Herisau, Switzerland). Figure 3 shows a schematic view of the experimental arrangement.

The following fats and oils were investigated at temperatures of 100 C, 110 C and 120 C: peanut oil, sunflowerseed oil (60% essential fatty acids), olive oil, lard (pure), vegetable margarine and cooking butter (82% milk fat).

Rancimat experiments. Since the 617 Rancimat can accommodate six test samples, three determinations of two samples were carried out. The sample (2 g) was weighed out in the reaction vessel, which was then placed in the heating block for 10 min to preheat the sample. The air supply and the absorption vessels were connected and recording of the conductivity curves started.

AOM test (AOCS Method Cd 12-57). Samples (20 g) were weighed out in reaction vessels and the vessels preheated for 10 min. The first two vessels were connected to the air supply only. The third vessel was connected to the air supply and the absorption vessel; this experiment served to simplifiy identification of the induction time. In the region of the expected induction time (known approximately from the rancimat experiments), samples were taken from the reaction vessels and portions (5 g) used to determine the PV (8).

RESULTS AND DISCUSSION

*Induction times.*The induction times t_I of the fats and oils investigated are shown in Table 1 for the two methods employed. As expected, the AOM values are, almost without exception, slightly higher than the corresponding rancimat values. This is because the point of greatest inflection of the oxidation curve usually has already been passed at a PV of 100 μeq/kg. The values of the standard deviation (3 determinations) are comparable for both methods. It should be noted, however, that recording the progress of the conductivity value in the absorption vessel during the AOM measurements allowed the induction time to be estimated, hence greatly facilitating determination of the PV.

The results of the linear regression [t_I (rancimat) vs t_I (AOM)] are summarized in Table 2. The induction times

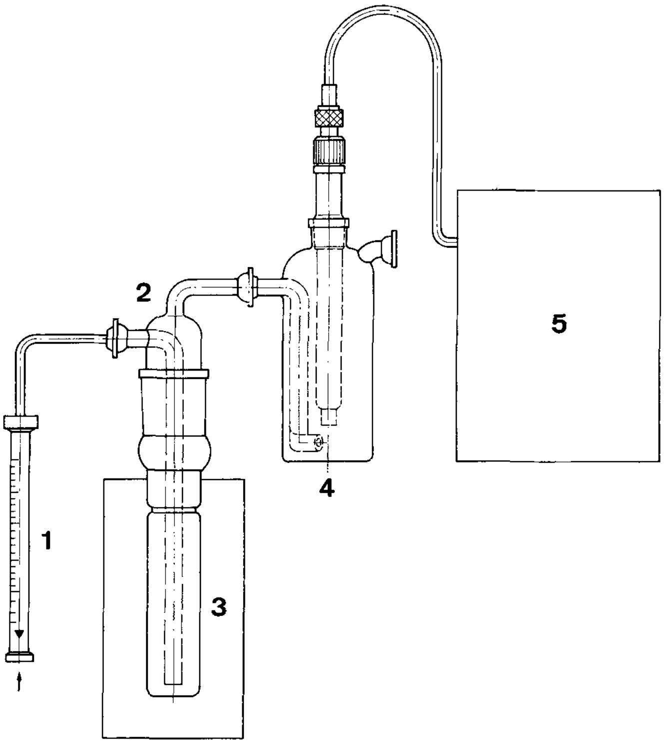

FIG. 3. Schematic view of a single test setup in the 617 Rancimat: 1, flowmeter, air flow 10 l/hr; 2, reaction vessel for oil or fat samples; 3, aluminum heating block, temperature control to ±0.1 C; 4, absorption vessel containing dist. water and double platinum foil electrode; 5, conductivity signal amplifier and 6-channel point recorder.

TABLE 1

Induction Times (t_I) determined by the AOM and the Rancimat Method at Various Temperatures

	Induction time at 100 C (hr)				Induction time at 110 C (hr)				Induction time 120 C (hr)			
	AOM[a]		Rancimat		AOM		Rancimat		AOM		Rancimat	
Sample	t_I[b]	S[c]	t_I	S	t_I	S	t_I	S	t_I	S	t_I	S
Peanut oil	14.18	0.05	13.80	0.08	7.65	0.07	7.25	0.10	3.92	0.15	3.25	0.12
Sunflower oil	8.32	0.53	9.27	0.20	4.40	0.02	4.55	0.05	2.37	0.00	2.27	0.08
Olive oil	30.90	0.23	29.37	0.72	14.20	0.05	12.95	0.45	7.70	0.00	6.42	0.13
Lard	4.42	0.10	1.02	0.03	2.70	0.02	0.57	0.02	0.55	0.02	0.33	0.05
Margarine	22.23	0.07	23.18	0.13	11.67	0.23	12.03	0.10	6.08	0.07	6.17	0.08
Cooking butter	22.22	0.20	20.88	0.08	11.12	0.13	9.33	0.00	8.78	0.10	5.03	0.12

[a] Active Oxygen Method, AOCS Method Cd 12-57.
[b] t_I: mean of 3 determinations.
[c] Standard deviation.

TABLE 2

Results of the Linear Regression[a]

Temperature (C)	A ± S_A (hr)	B ± S_B	r	n
100	−1.23 ± 1.61	1.02 ± 0.08	0.987	6
110	−1.02 ± 1.10	1.02 ± 0.11	0.976	6
120	−0.58 ± 0.91	0.68 ± 0.16	0.905	6
100 + 110 + 120	−0.92 ± 0.53	1.005 ± 0.04	0.987	18

[a] $Y = A(\pm S_A) + B(\pm S_B).X$ where X = induction time from AOM and Y = induction time using 617 Rancimat.

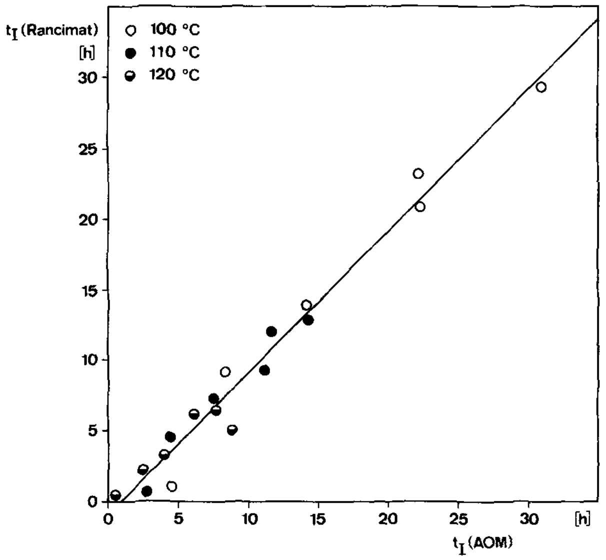

FIG. 4. Correlation between induction times (t_I) determined using the 617 Rancimat and by the AOM. Linear regression ($Y = A + BX$; n = 18): A = −0.92 ± 0.53 hr; B = 1.005 ± 0.041; r = 0.987).

TABLE 3

Experimental Temperature Coefficients (f_t)

	AOM[a]		Rancimat	
Sample	f_t	r[b]	f_t	r[b]
Peanut oil	1.9	>0.999	2.1	0.998
Sunflower oil	1.9	>0.999	2.0	>0.999
Olive oil	2.0	0.995	2.1	>0.999
lard	c		1.8	0.999
margarine	1.9	>0.999	1.9	>0.999
Cooking butter	c		2.0	0.997

[a] Active Oxygen Method, AOCS Method Cd 12-57.

[b] Correlation coefficient of the linear regression according to the equation: $\log t_t = A + BT$ where $B = -(\log f_t)/10$.

[c] These samples show a large deviation from linearity.

determined by both methods show a very good correlation at 100 and 110 C and also when all values are taken into consideration (Fig. 4).

With the values at 120 C, the correlation is clearly worse, but this is due primarily to the pair of values for cooking butter.

Temperature dependence of the induction times. In earlier works (5,9), the temperature coefficient f_t of the induction time for a temperature change of 10 C was reported as 2.0-2.9. The temperature coefficients f_t shown in Table 3 lie between 1.8 and 2.1 with regression coefficients (log t_t vs T) better than 0.99. Regression coefficients f_t (AOM) for lard and cooking butter could not be determined. In the case of lard, the induction times at 110 and 120 C compared to t_t at 100 C are considerably greater or less, respectively, than the values expected. Although the induction time for cooking butter is halved when the temperature is increased from 100 to 110 C, the measured induction time at 120 C is much longer than expected. The causes of these discrepancies are unknown.

The induction times determined using the rancimat method (conductometric indication) correlate extremely well with those of the Active Oxygen Method (AOCS Method Cd 12-57). The rancimat method, however, is considerably less costly and labor intensive than the AOM test. In the present work, ca. 15 l mixed solvent and chemicals valued at SFr. 400 (ca. $180 US) were used in the determination of the peroxide value. It also should be noted that the additional conductivity measurement in the AOM test considerably reduced the number of PV determinations normally carried out. An additional advantage of the rancimat method is that no supervision of the 617 Rancimat is required during measurement.

Selection of a suitable temperature also allows the induction time of fats and oils which are very stable towards oxidation to be brought into a reasonable range (5-20 hr). The induction time should not be too short, however, as the scatter in the values is then too great. When experiments are carried out at different temperatures, it is advisable to determine the temperature dependence (reduction in the induction time by a factor of ca. 2 with a temperature increase of 10 C). The results of any experimental determination of the induction times should include the temperature in each case [e.g. t_t (120 C)].

Thanks to the minimal labor requirement, the rancimat method is suitable not only for determination of the oxidative stability of fats and oils but also for investigations of antioxidants (10,11). Additional applications such as the investigation of pro-oxidants, influences of warehouse conditions (12), etc., are also possible.

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