A Comparison of Oil Stability Based on the Metrohm Rancimat with Storage at 20°C

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The induction time for oxidative stability by the Rancimat method has been compared with peroxide development during storage at 20°C for six edible oils and rapeseed oil samples with added metal ions, antioxidants or phosphatidylethanolamine. The Rancimat method correlated highly ($r = 0.966$; $P = 0.000$) with oil stability measured by peroxide development for all samples except the oils containing added phosphatidylethanolamine or added butylated hydroxytoluene.

KEY WORDS: Induction time, oils, oxidation, peroxide values, shelf life.

The development of oxidative rancidity in edible oils and fats is one of the major factors affecting their use in foods. Rapid methods are required to predict the stability of edible oils and fats. The Metrohm Rancimat, developed as a rapid automated method (1), agrees well with the Active Oxygen Method (2,3). These methods allow the determination of the induction time, which is the time before rapid deterioration of the oil occurs. However, these methods differ from ambient storage conditions by the use of a flow of air and elevated temperatures to accelerate oxidative deterioration. The products formed in the accelerated tests include volatile dicarboxylic acids (4), which contribute to the change in electrical conductivity in the Rancimat test. These products differ from those formed under normal storage conditions, which mainly comprise hydroperoxides that are detected in the traditional peroxide value test. Therefore, a comparison of the oxidative stability of oils assessed by the Rancimat method with the stability found under ambient test conditions was performed to investigate the applications and limitations of the method.

MATERIALS AND METHODS

Refined, bleached and deodorized rapeseed oil was supplied by PURA Foods Ltd. (London, United Kingdom). All other oil samples were commercial samples purchased at a local store. Dipalmityl phosphatidylethanolamine and α-tocopherol were purchased from Sigma Chemical Co. (Poole, United Kingdom). Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) were purchased from Koch-Light Ltd. (Haverhill, United Kingdom). Ferric palmitate, prepared by the reaction of sodium palmitate and ferric choloride (5), was donated by X-C. Weng (Reading, United Kingdom). Copper stearate solution was prepared by mixing two volumes of hot (95°C) sodium stearate solution (0.25 M) with one volume of cupric chloride solution (0.25 M). The mixture was stirred at 70–80°C for 20 min and filtered under vacuum. The precipitate was washed four times with hot distilled water at 80°C and was then dried under vacuum for 2 h at 75°C. The metal salts were added to oils at 60°C when required. The Model 617 Rancimat (V.A. Howe & Co. Ltd., Banbury, United Kingdom), equipped with an electric heating block, was used without modification. Air flow rates were set at 15 L/h for all determinations. Glass reaction and air delivery tubes were scrupulously cleaned by boiling with sodium hydroxide solution (2% m/m) for one hour, followed by cooling and soaking in concentrated hydrochloric acid. The acid was washed off and the tubes were rinsed with distilled water. All determinations of induction periods were performed in duplicate. Oil samples (25 g) were stored in 100-mL beakers and loosely covered with a foil lid in the dark at 20 ± 5°C. Samples were removed periodically, and peroxide values were determined in duplicate by the colorimetric micromethod described by Asakawa *et al.* (6). Regression analysis of the data was performed with a Minitab program (7).

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RESULTS AND DISCUSSION

The peroxide value determination by the micromethod gave a reproducibility of ±0–6.5% from the mean for two determinations.

The times for various edible oil samples to reach peroxide values of 5, 10 and 20 meq/kg when stored at 20°C, and the mean Rancimat induction time at 100°C are given in Table 1. The data for the time to reach peroxide values of 5, 10 and 20 meq/kg have been plotted against Rancimat induction time (Fig. 1). The sample of rapeseed oil with added phosphatidylethanolamine lies well off the linear regression lines (Fig. 1), but a straight line correlation has been found for the other samples. The regression

TABLE 1

Times for Oil Samples to Reach Various Peroxide Values at 20°C Compared with Rancimat Induction Times (IT) at 100°C

Oil	Time (d) at 20°C to peroxide values (meq/kg)			Rancimat IT (h)
	5	10	20	
Refined olive	55	103	162	20.4
Rapeseed	30	55	82	14.4
Soybean	13	34	65	10.9
Corn	16	37	67	12.8
Safflower	10	25	44	6.8
Sunflower	13	25	54	7.9
Rapeseed oil + additives[a]				
0.14 ppm Fe	25	47	72	10.0
0.35 ppm Fe	24	41	60	8.7
0.05 ppm Cu	11	21	39	6.4
0.1 ppm Cu	8	16	34	5.0
0.25 ppm Cu	5	12	21	2.9
BHA (0.02%)	66	102	139	19.3
α-Tocopherol (0.02%)	12	36	69	11.1
BHT (0.02%)	>185	>185	>185	20.5
BHA (0.01%) + BHT (0.01%)	180	>185	>185	20.3
Phosphatidylethanolamine (0.1%)	14	32	60	22.8

[a]BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene.

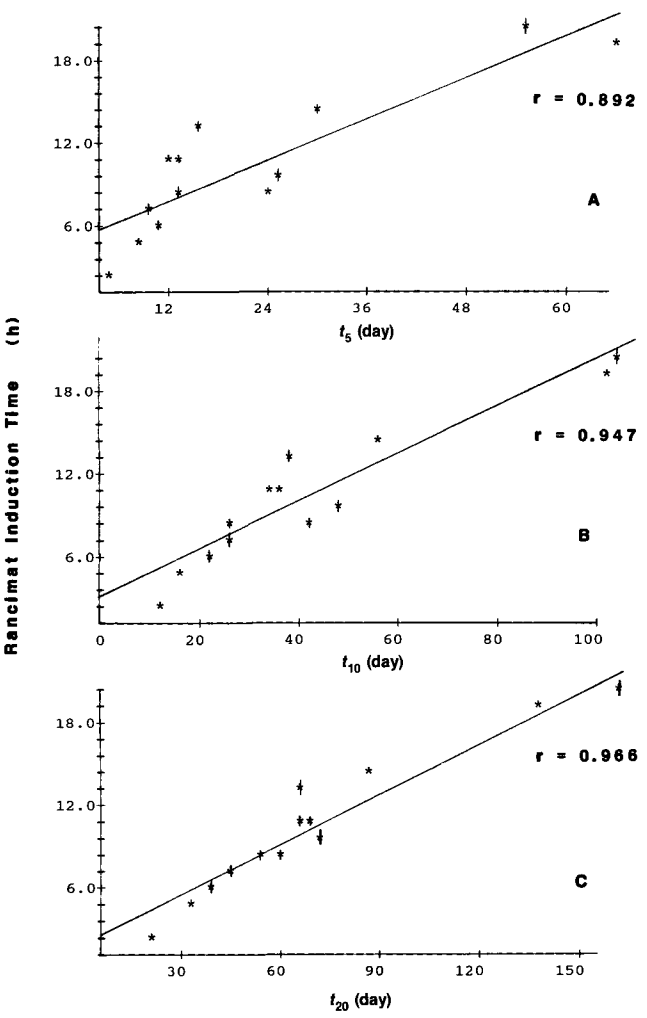

FIG. 1. Plot of Rancimat induction time at 100°C against storage time at 20°C for the peroxide value to reach (A) 5 meq/kg (t_5), (B) 10 meq/kg (t_{10}) and (C) 20 meq/kg (t_{20}). The vertical line through each point indicates the range of duplicate determinations.

equations (omitting the sample containing phosphatidylethanolamine) are:

$$IT = 0.126\ t_{20} + 1.70;\ \text{correlation coefficient, } r = 0.966\ (P = 0.000) \quad [1]$$

$$IT = 0.169\ t_{10} + 3.31;\ \text{correlation coefficient, } r = 0.947\ (P = 0.000) \quad [2]$$

$$IT = 0.250\ t_5 + 4.98;\ \text{correlation coefficient, } r = 0.892;\ (P = 0.000) \quad [3]$$

where IT is the Rancimat induction time at 100°C, and t_x is the time for the peroxide value to reach x meq/kg at 20°C. The correlation between the Rancimat induction time and the time to a peroxide value of 5 meq/kg is poorer than the correlations for the higher peroxide values, probably due to the fact that the peroxide value of the oils before storage was in the range of 0–2 meq/kg, which is significant when compared to 5 meq/kg. Fitting the Rancimat IT to an exponential correlation with t does not lead to a significant improvement in the correlation, except with t_5, where the following correlation can be fitted:

$$\log (IT) = 0.130\ t_5 + 1.46;\ \text{correlation coefficient, } r = 0.914\ (P = 0.000) \quad [4]$$

Because the rate of oil deterioration depends on the oil surface area exposed to the atmosphere and on the depth of oil used, the regression coefficients will be different in other studies. However, these studies showed that the Rancimat method correlated well with stability under ambient storage conditions for a wide range of edible vegetable oils.

The sample of rapeseed oil containing added phosphatidylethanolamine (0.1% m/m) deviated strongly from the correlation. The sample had a mean IT of 22.8 h (±0.4 h) in the Rancimat test at 100°C. Equations 1–3 predict 71, 115 and 167 d storage at 20°C to reach 5, 10 and 20 meq/kg, but the experimental values were 14, 32 and 60 d, respectively. Phosphatidylethanolamine is known to have a synergistic effect with a wide range of primary antioxidants (8–12). Dziedzic and Hudson (8) claimed that the synergistic effect of diphosphatidylethanolamine was at a maximum in the 100–140°C range and absent below 80°C. This lack of activity of phosphatidylethanolamine as an antioxidant at room temperature has been confirmed in this study, and the effect at 100°C in the Rancimat is presumably due to a synergistic effect with natural tocopherols present in the oil. Thus, the presence of significant levels of phosphatidylethanolamine may lead to misleading predictions of oil stability based on the Rancimat or other accelerated test methods involving elevated temperatures.

Samples containing BHT also deviated from the correlations. Rapeseed oil containing 0.02% BHA obeyed the correlations, but samples of rapeseed oil containing BHA (0.01%) and BHT (0.01%) had only reached a peroxide value of 5.2 meq/kg after 185 d storage, whereas the Rancimat IT of 20.3 h for this sample would predict that peroxide values of 5, 10 and 20 meq/kg would be reached after 61, 100.5 and 155 d at 20°C, respectively. The Rancimat IT of a sample containing 0.02% BHT was 20.5 h, and this would predict peroxide values of 5, 10 and 20 meq/kg after 62, 102 and 157 d at 20°C, respectively. However, the peroxide value had only reached 2.3 meq/kg after 185 d storage. The Rancimat method underestimated the stability of oil samples containing BHT, which agreed with the findings of Kochhar and Rossell (13) for samples containing BHT. The IT of BHT-containing samples in the Rancimat may be reduced by the volatility of the antioxidant.

Six vegetable oils and rapeseed oil containing additives were used in this study with composition ranges of 7.0–14.4% for saturated fatty acids; 13.7–75.8% for oleic acid; 9.6–75.9% for linoleic acid; and 0.3–10.2% for α-linolenic acid. Caution would be strongly advised in extrapolating correlations between Rancimat IT and storage at 20°C to oils and fats outside this range of composition, e.g., marine oils and animal fats.

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