

Changes in chemical quality indices during long-term storage of palm-olein oil under heated storage and transport-type conditions

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Abstract: Six quality indices, namely free fatty acids (FFA), peroxide value (PV), anisidine value (AV), oxidative stability index (OSI), total tocopherols and headspace volatiles (hexanal, *t*-2-hexenal and *t,t*-2,4-decadienal), were evaluated in a long-term storage trial of 52 weeks at 50 °C of palm-olein, a monounsaturated oil. Three concentrations of copper (0.035, 0.17 and 0.69 mg kg⁻¹) were added. FFA values for all the sample treatments increased slightly over the storage period but remained within acceptable limits. PV of the copper-containing samples declined initially and then remained stable up to week 40, after which it increased slightly for the 0.035 and 0.17 mg kg⁻¹ samples. However, PV of the control (no added copper) increased steadily to above the acceptable limit. AV of the copper-containing samples increased much more than that of the control. OSI and total tocopherol values of the copper-containing samples were markedly lower than those of the control. *t*-2-Hexenal did not increase during the storage period, whereas hexanal increased in the copper-containing samples but at a slower rate than in the control. Conversely, the copper-containing samples had high levels of *t,t*-2,4-decadienal but the control had none. AV, OSI and total tocopherols are the most valuable quality indices for assessing monounsaturated oil quality, whereas FFA, PV and headspace volatiles can be misleading.

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INTRODUCTION

An oil that is becoming increasingly important worldwide is palm oil. Palm oil and its fractionated products are produced in and exported from countries such as Malaysia and Indonesia. Palm oil is a monounsaturated oil with good inherent stability, although long periods of bulk transport at elevated temperatures can affect its quality. Different fractions of the oil are used for various applications, but the most commonly used is palm-olein oil.¹ High-melting, stable oils without *trans* fatty acids are in demand. Palm-olein oil seldom needs hydrogenation; this is advantageous, as hydrogenation leads to the formation of *trans* fatty acids.² In addition, warm climates along with long transport distances at elevated temperatures to ensure that the oil remains in liquid form, as well as extended periods of unfavourable storage conditions in underdeveloped countries, necessitate the use of stable oils.³ However, potential contamination of the oil with pro-oxidants such as iron or copper in the hulls of transport tankers, pipelines and truck holders cannot be ignored.^{3,4} It is thus crucial to be able to estimate the quality and stability of such oils which are to be used in food applications.

Various oxidative quality indices such as peroxide value (PV), anisidine value (AV), headspace volatiles, thiobarbituric acid (TBA) test, conjugated dienes and oxidative stability index (OSI) have been evaluated extensively.^{5–7} These indices and combinations of them have been used to study lipid oxidation. For example, PV, AV, free fatty acids (FFA), polar compounds and weight gain were used to study the oxidative deterioration of crude sunflower oils obtained by either pressing or solvent extraction and stored at different temperatures with varying oxygen concentrations.⁸ Good correlation between percentage polar compounds and peroxide value was found. Andersson and Lingnert⁹ investigated lipid oxidation in rapeseed oil during storage at 40 °C without and with added copper and with different oxygen headspace concentrations. Copper was stated to be the most pro-oxidative metal. Volatile oxidation products (hexanal and 2-hexenal) and oxygen consumption were monitored. Samples containing copper promoted 2-hexenal formation. In another study, four analytical methods, namely PV, AV, oxygen consumption and volatile aldehydes, were evaluated to characterise rapeseed oil triacylglycerols

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(TAG), butter TAG and their 1:1 mixture.¹⁰ They were stored in the dark at 40 °C for a period of 28 days. It was found that each of the analytical methods could be replaced by one another as long as one oil type was studied. PV measurements were most sensitive and repeatable. Although various short-term studies have been conducted,^{8–11} the effect of long-term storage on such indices remains to be investigated.

The purpose of this study was to evaluate the merits of six different indices often used in the assessment of oil quality, namely PV, FFA, AV, headspace volatiles, Rancimat (OSI) and tocopherol content, when applied to palm-olein oil stored at 50 °C for up to 1 year. Additionally, three different levels of copper were added to the oil. Possible interaction with one or more of the indices was investigated.

EXPERIMENTAL

Materials

Two different fully refined, bleached and deodorised (RBD) palm-olein oils were combined for the storage trial. Both oils were imported from Malaysia. One oil had been in frozen storage at –20 °C for a period of 1 year and the other was received from the supplier just before the start of the trial. Both oils were free of the antioxidant butylated hydroxyquinone (TBHQ). This was confirmed by testing for TBHQ according to the method of Anderson and Van Niekerk,¹² with modifications to the mobile phase. A 1 g sample (weighed accurately to four decimal places) of oil was dissolved in the mobile phase consisting of 6% isopropanol in hexane. The oil was analysed for FFA, PV and fatty acid composition prior to the start of the storage trial. The results obtained for FFA (0.5 g kg⁻¹ expressed as oleic acid), PV (2.96 meq kg⁻¹) and fatty acid composition were found to be within acceptable limits for good-quality palm-olein oil.

Storage procedure

Palm-olein oil was prepared without copper and with three different concentrations of copper. Copper acetate, which was chosen as it is soluble in methanol and is in organic form similar to fatty acids, was dissolved in methanol to introduce copper into the oil with heating and mixing. All samples had methanol added to them to eliminate any possible effect of methanol. The calculated final concentrations of copper (Cu) in the oil were 0.035, 0.17 and 0.69 mg kg⁻¹. Aliquots (100 ml) of each concentration, as well the control with no added copper, were placed in 100 ml non-transparent (opaque) plastic containers with screw tops for storage. A set of four samples, namely 0.035, 0.17 and 0.69 mg kg⁻¹ copper and the control, was analysed on day 0. The samples were stored in an incubator equipped with a fan that was set at 50 °C, as monitored by a thermometer. A set of samples was taken out at 11 time intervals for analyses (including day 0) during the storage period of 1 year.

Samples remaining after analyses, or awaiting analyses at a later stage, were stored at –20 °C.

Chemical analyses

All analyses were performed at least in duplicate except where there was insufficient equipment capacity, in which case appropriate repeat analyses were performed. AOCS¹³ methods were used to determine FFA (Cd 3a-63) with a standard error of 0.0153, PV (Cd 8–53) with a standard error of 0.6060, fatty acid composition (Ce 2–66) and AV (Cd 18–90) with a standard error of 1.7471. The induction period in hours (with a standard error of 0.3879) as measured by OSI was determined using a Metrohm 679 Rancimat (Metrohm, Herisau, Switzerland) at 120 °C and an airflow of 201 h⁻¹. Tocopherols were measured by normal phase HPLC using a fluorescence detector with excitation at 295 nm and emission at 330 nm as described by Van Niekerk,¹⁴ with modification to the mobile phase where 1% isopropanol in hexane was used. Separation was obtained by using a 25 cm Lichrosorb Diol 5 µm column (Merck, Darmstadt, Germany) and applying a flow rate of 0.8 ml min⁻¹. The standard error of the method was 0.3466. Volatile analyses were performed by static headspace gas chromatography (GC)/flame ionisation detection (FID). A Varian Genesis (Palo Alto, USA) equilibrium headspace sampler and a Varian (Palo Alto, USA) 3800 GC with a Restek Rtx-5, 30 m, 0.25 µm film thickness, 0.32 mm id (poly-5% diphenyl/95% dimethylsiloxane) column (Chromspec, Brockville, Canada) were used. A 2 g sample (weighed accurately to four decimal places) was placed in a 20 ml headspace vial and sealed with a crimp cap. The samples were equilibrated at 80 °C for 240 min, after which 120 µl of the headspace was injected in splitless mode onto the column. The line temperature was 150 °C and the loop temperature 120 °C. The temperature of the oven was held at 40 °C for 1 min and then increased to 240 °C at a rate of 10 °C min⁻¹. The detector was set at 240 °C. Three volatiles; namely hexanal (standard error 0.5552), *trans*-2-hexenal (standard error 0.5372) and *trans,trans*-2,4-decadienal (standard error 6.354), were determined. The analysis was performed in triplicate.

Statistical analyses

The tabulated data showed that the sample treatment with the sample containing 0.17 mg kg⁻¹ copper at week 29 was suspect. The data were subjected to Dixon's test for outliers on the residuals of the regressions lines of the variables.¹⁵ The data for week 29 qualified as an outlier at 99% confidence level and were thus omitted.

The different treatments for each variable were compared with each other to determine if they differed significantly by fitting the most appropriate curve. Table 1 shows the correlation coefficients for all the curves. Poor correlation coefficients could generally be attributed to data lines that had very small slopes. The coefficients of the curves were subjected to a one-sided Student distribution test (*t*-test).¹⁶

Table 1. Correlation coefficients for the fitted curves of each index

Index ^a	Correlation coefficient (R ²)			
	Control	0.035 mg kg ⁻¹ copper	0.17 mg kg ⁻¹ copper	0.69 mg kg ⁻¹ copper
FFA	0.8190	0.5945	0.7682	0.7219
PV	0.7640	0.8143	0.5098	0.0255
AV	0.6842	0.9053	0.9146	0.9513
OSI	0.8285	0.4928	0.1449	0.2514
Total tocopherols	0.9038	0.3505	0.9402	0.8434
Hexanal	0.6045	0.7373	0.7401	0.0818
<i>t,t</i> -2,4-Decadienal	—	0.6315	0.7088	0.9210

^a FFA, free fatty acids; PV, peroxide value; AV, anisidine value; OSI, oxidative stability index.

RESULTS AND DISCUSSION

Free fatty acids

The effect of storage at 50 °C on the FFA of the four sample treatments over a period of 52 weeks is shown in Fig 1. The FFA content of the samples increased gradually up to week 40, after which a sharp increase occurred in all the samples. The FFA of the control sample increased the most, followed by a slightly lower rate of increase in FFA in the copper-containing samples. The sample with the highest concentration of copper (0.69 mg kg⁻¹) had the lowest FFA content at the end of the storage period. Linear regression lines ($y = a + bx$) were fitted to each treatment and the intercepts (a) and slopes (b) were subjected to the *t*-test. The intercepts did not differ significantly from each other at the 99% test level, apart from the control sample versus the 0.69 mg kg⁻¹ copper sample. The slopes all differed significantly at the 99% test level. Although the treatments were statistically significantly different, in practical terms this would not be of importance, as the FFA values for all the treatments are still within the limit of 3.0 g kg⁻¹ oleic acid prescribed by the Codex Alimentarius Commission.¹⁷ The gradual increase in FFA indicates that very slight hydrolysis of the triglycerides occurred during storage.

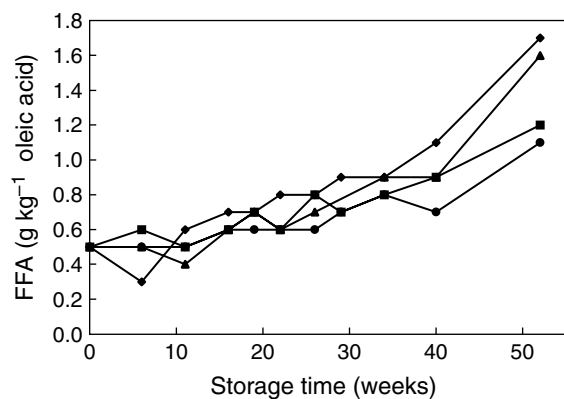


Figure 1. Changes in free fatty acid value (g kg⁻¹ oleic acid) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50 °C: diamonds, control; squares, 0.035 mg kg⁻¹ Cu; triangles, 0.17 mg kg⁻¹ Cu; circles, 0.69 mg kg⁻¹ Cu.

Peroxide value

The effect of storage at 50 °C on the PV of the four sample treatments is shown in Fig 2. PV measures primary oxidation products.¹⁸ The PV of the control sample increased steadily and reached a plateau at weeks 34–40, after which it appeared to decrease. The samples containing copper had surprisingly low peroxide values (<5.0 meq kg⁻¹) up to week 26, after which the values for the samples with 0.035 and 0.17 mg kg⁻¹ copper gradually increased. The PV of the sample containing 0.17 mg kg⁻¹ copper increased sharply after week 40 to 14.0 meq kg⁻¹, whereas the PV of the sample containing 0.035 mg kg⁻¹ copper increased steadily after week 26 to reach a value of 10.7 meq kg⁻¹ at week 52. The sample containing the highest amount of copper (0.69 mg kg⁻¹) remained stable from day 0 and had the lowest PV of 1.6 meq kg⁻¹ after the 52 week storage period. Linear regression lines were fitted to the graphs and it was found that the intercepts differed significantly from each other for most of the samples; only the samples with 0.035 versus 0.17 mg kg⁻¹ copper and 0.17 versus 0.69 mg kg⁻¹ copper did not differ significantly in that respect. The slopes of all the samples differed significantly from each other at the 99% test level.

Abdel-Aal and Abdel-Rahman¹¹ reported an increase in PV level with the addition of copper

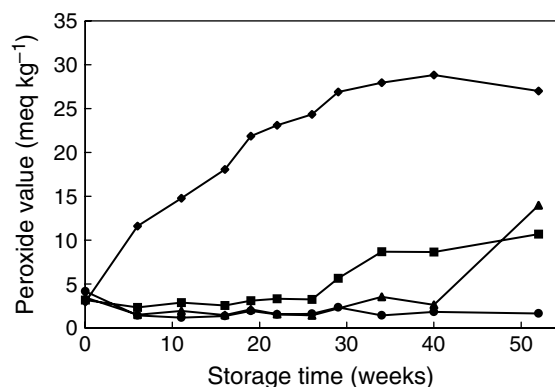


Figure 2. Changes in peroxide value (meq kg⁻¹) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50 °C: diamonds, control; squares, 0.035 mg kg⁻¹ Cu; triangles, 0.17 mg kg⁻¹ Cu; circles, 0.69 mg kg⁻¹ Cu.

in polyunsaturated oils (cottonseed, sunflower and soybean) stored at 26–28 °C with periodic sampling up to 119 days. Benjelloun *et al*¹⁹ as well as Gordon and Mursi²⁰ found that metal traces in rapeseed oil increased PV as measured in hours and 20 days respectively. Chong and Gapor²¹ added iron to palm-olein oil, stored the oil for a period of 26 days at 60 °C and found that with the addition of iron the PV increased. The low levels of peroxides in this storage trial of the samples containing copper can be explained by the fact that this is a long-term oxidation study on monounsaturated oil where the peroxide intermediates were probably converted to secondary, more stable oxidation products within a short time span. High levels of peroxides were thus not detected, probably because they were produced within hours, or in the first few days, after the addition of copper. This is supported by the fact that the peroxides in the control increased, as expected, and then started to decrease. The control sample reached the suggested PV maximum guideline¹⁷ for a refined oil of 10 meq kg⁻¹ by week 6.

Anisidine value

The effect of storage on the AV of the four sample treatments is shown in Fig 3. AV is an assay for secondary oxidation products that occur after primary oxidation products (hydrogen peroxides) have been degraded to secondary oxidation products such as 2-alkenals.²² The AV of the control sample increased steadily up to week 40, after which there was a more pronounced increase to the value of 15.2 mmol kg⁻¹. The AV of the samples containing copper increased at a much faster rate. The AV increased sharply after week 19 for the samples with 0.035 and 0.17 mg kg⁻¹ copper, whereas the AV for the sample with 0.69 mg kg⁻¹ copper increased steadily up to week 52. The AV of the samples containing copper was approximately double the value of the control sample at week 52. Linear regression lines were fitted to the graphs and it was found that the intercepts differed significantly from each other for most of

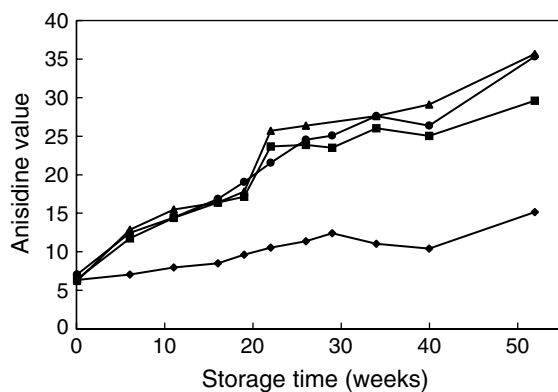


Figure 3. Changes in anisidine value (mmol kg⁻¹) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50 °C: diamonds, control; squares, 0.035 mg kg⁻¹ Cu; triangles, 0.17 mg kg⁻¹ Cu; circles, 0.69 mg kg⁻¹ Cu.

the samples; only the samples with 0.035 versus 0.69 mg kg⁻¹ copper and 0.17 versus 0.69 mg kg⁻¹ copper did not differ significantly in that respect. The slopes of all the samples differed significantly at the 99% test level. Practically, the difference between the samples containing copper would not be meaningful.

According to White,²² an acceptable AV for well-refined oils is between 1 and 10 mmol kg⁻¹, whereas oils with high levels of polyunsaturated fatty acids might have higher levels even when fresh. Monounsaturated oil would thus be expected to have lower levels of AV than polyunsaturated oil. The AV of the control sample fluctuated between 9.6 and 11.3 mmol kg⁻¹ from week 16 up to week 40 and reached a value of 15.2 mmol kg⁻¹ at week 52. All the samples containing copper had exceeded the suggested level by week 6. It thus appears that the presence of copper led to the rapid formation of excess secondary oxidation products at an early stage of the storage trial.

Oxidative stability index

The effect of storage on the oxidative stability of the four sample treatments is shown in Fig 4. The initial values of the different treatments are different. The control had the highest initial OSI value, followed by the oil with the lowest concentration of copper, and the lowest initial OSI value was found for the oil with the highest concentration of copper. The steady decline in OSI (in hours) of the control sample and the sample with 0.035 mg kg⁻¹ copper was very similar apart from the initial values. The value of the control sample decreased by 11 h, which is half of the initial value, from day 0 to week 52, whereas the value for the sample with 0.035 mg kg⁻¹ copper decreased by 2.5 h from day 0 to week 52. The OSI of the sample with 0.17 mg kg⁻¹ copper remained fairly stable up to week 40, after which it decreased significantly by half the number of hours. The OSI of the sample with 0.69 mg kg⁻¹ copper remained stable with the lowest values of 3–4 h from the start of the shelf life trial up until week 52. Linear regression lines were fitted to

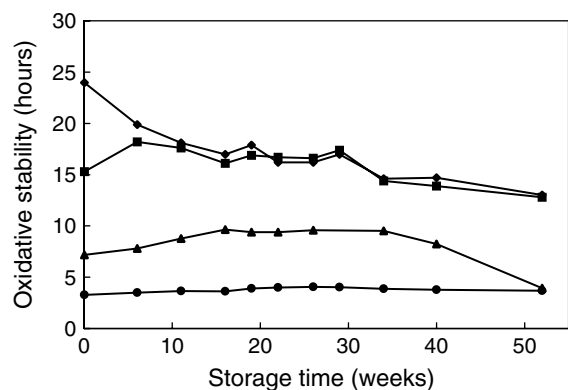


Figure 4. Changes in oxidative stability index (h) at 120 °C of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50 °C: diamonds, control; squares, 0.035 mg kg⁻¹ Cu; triangles, 0.17 mg kg⁻¹ Cu; circles, 0.69 mg kg⁻¹ Cu.

the graphs and it was found that the intercepts as well as the slopes differed significantly from each other for all the samples at the 99% test level.

It is evident that copper is a strong pro-oxidant from the low OSI values obtained in the samples containing copper. The resistance to oxidation was compromised from the time of addition. Increased concentrations of copper decrease the OSI concomitantly. Gordon and Mursi²⁰ obtained similar results with rapeseed oil.

Total tocopherols

The effect of storage on the total tocopherol content of the four sample treatments is shown in Fig 5. The initial values were slightly different from each other. The control and 0.035 mg kg⁻¹ copper samples started at day 0 with similar initial values, whereas the 0.17 mg kg⁻¹ copper sample had a slightly lower initial value, followed by the 0.69 mg kg⁻¹ copper sample. A possible explanation for the difference in initial total tocopherol values is that the copper-containing samples generated more radicals than the control sample. These radicals were quenched by the tocopherols, therefore leading to a decrease in the measurable total tocopherol content in the samples containing copper, especially in those containing increased levels of copper. The total tocopherols of the control sample remained the highest of all the samples, with a steady decline from 525 to 322 mg kg⁻¹ at week 52. The total decline in the tocopherol content of the control sample was thus 203 mg kg⁻¹. The samples containing copper showed a marked decrease in tocopherols from day 0 when the copper was added, with another sharp decline within the first 6 weeks as measured at week 6. The tocopherols decreased sharply up to week 16, after which the two treatments with 0.17 and 0.69 mg kg⁻¹ copper maintained a gradual decrease and the treatment with the lowest concentration of copper remained constant up to week 52. The tocopherol content decreased concomitantly with higher concentrations of copper added. This is evident from the linear regression lines that were fitted

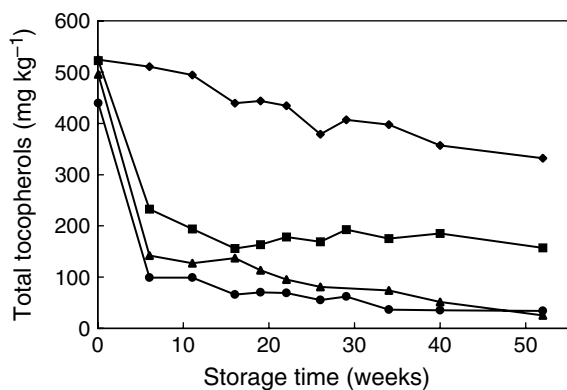


Figure 5. Changes in total tocopherols (mg kg⁻¹) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50 °C: diamonds, control; squares, 0.035 mg kg⁻¹ Cu; triangles, 0.17 mg kg⁻¹ Cu; circles, 0.69 mg kg⁻¹ Cu.

to the graphs, and it was found that the intercepts as well as the slopes differed significantly from each other for all the samples at the 99% test level.

The hydroperoxides formed during the propagation step of oxidation are split in the presence of copper and iron to form peroxy (ROO[•]) or alkoxy (RO[•]) radicals, at which stage the chain-breaking antioxidants such as tocopherols donate their phenolic hydrogen atom to quench further reactions.²³ Owing to their antioxidant activity, the tocopherols are themselves altered to yield a number of products such as quinones, dimers, trimers and epoxides.^{23,24} This explains the rapid decrease in total tocopherol content in the samples containing copper.

Headspace volatiles

Trans-2-hexenal showed very little change in all the samples over the 52 week storage period, its content fluctuating between 0 and 2.3 mg kg⁻¹ (data not shown). The hexanal content (Fig 6) increased over time in all the samples. The hexanal content of the control sample increased the most, whereas the hexanal content of the samples containing copper increased at a slower rate over the storage period. There was no difference in the rate of increase between the copper-containing samples, however, there were higher initial concentrations of hexanal in the copper-containing samples and a higher final concentration of hexanal in the 0.17 mg kg⁻¹ copper sample. The *t,t*-2,4-decadienal content over the storage period is shown in Fig 7. The control sample did not form *t,t*-2,4-decadienal over the storage period. The control probably oxidised preferentially via the formation of 13-OOH hydroperoxides to hexanal, which would not have led to the formation of *t,t*-2,4-decadienal. However, the samples containing copper all showed an increase in *t,t*-2,4-decadienal over time that could be explained by the decomposition of 9-OOH hydroperoxides. There was hardly any *t,t*-2,4-decadienal formed up to week 6, but this was followed by a rapid increase in *t,t*-2,4-decadienal up to week 11, after which it increased gradually up to week 52. Linear regression lines were fitted to the hexanal graphs and it was found that the intercept of the control sample differed significantly from those of the copper-containing samples, although the latter did not differ significantly between themselves at the 99% test level. The slopes of all the samples differed significantly from each other at the 99% test level, apart from the 0.035 versus 0.17 mg kg⁻¹ copper samples. An exponential curve ($y = a + bx + cx^2$) was fitted to the *t,t*-2,4-decadienal graphs. The graphs resembled approximate S-curves, but, for the purposes of the statistical analyses, an exponential curve was fitted from week 6. The control sample was not included, as no *t,t*-2,4-decadienal had been detected during the storage period. The intercepts (a) of the samples containing copper did not differ significantly from each other at the 99% test level, whereas the b and c values differed significantly from each other at the 99% test level.

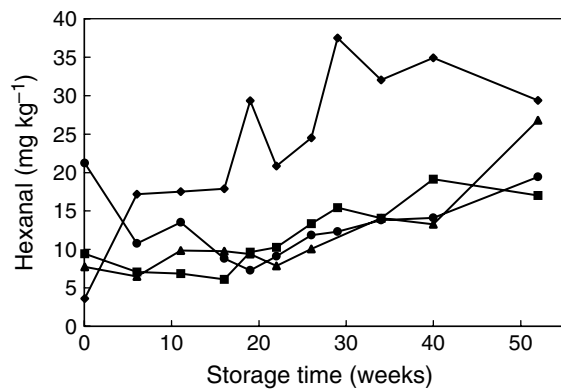


Figure 6. Changes in hexanal content (mg kg^{-1}) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50°C : diamonds, control; squares, $0.035 \text{ mg kg}^{-1} \text{ Cu}$; triangles, $0.17 \text{ mg kg}^{-1} \text{ Cu}$; circles, $0.69 \text{ mg kg}^{-1} \text{ Cu}$.

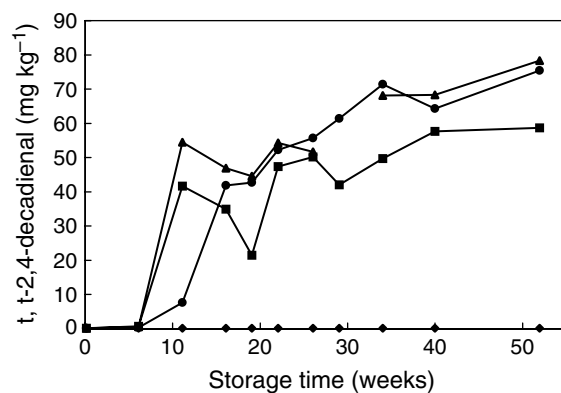


Figure 7. Changes in *trans,trans*-2,4-decadienal content (mg kg^{-1}) of palm-olein oil with different concentrations of copper and a control without copper during storage for 52 weeks at 50°C : diamonds, control; squares, $0.035 \text{ mg kg}^{-1} \text{ Cu}$; triangles, $0.17 \text{ mg kg}^{-1} \text{ Cu}$; circles, $0.69 \text{ mg kg}^{-1} \text{ Cu}$.

Typical palm-olein contains 40–44% 18:1 (oleic acid), 10.4–13.4% 18:2 (linoleic acid) and a small amount (0.17–0.6%) of 18:3 (linolenic acid).¹⁷ 2-Hexenal or 3-hexenal is formed mainly from linolenic acid,^{25,26} and this explains why little change in *trans*-2-hexenal concentration was observed over the storage period. According to Kochhar,²⁵ the formation of hexanal is due to the decomposition of linoleate 13-OOH hydroperoxide, whilst the formation of *t,t*-2,4-decadienal is due to the decomposition of 9-OOH hydroperoxide. Secondary decomposition of *t,t*-2,4-decadienal leads to hexanal formation.²⁶ The high initial hexanal values for the sample containing 0.69 mg kg^{-1} copper could be explained by immediate decomposition of *t,t*-2,4-decadienal to hexanal, followed in time by further decomposition of hexanal to hexanoic acid and peroxides.²⁶ The increase in *t,t*-2,4-decadienal in the samples containing copper indicates that mainly 9-OOH hydroperoxides were formed in the presence of copper. Some of the *t,t*-2,4-decadienal decomposed further to hexanal. The control sample oxidised preferentially via the formation of 13-OOH hydroperoxides to hexanal.

Andersson and Lingnert⁹ found that the hexanal as well as the 2-hexenal content increased during storage of rapeseed oil at 40°C for a period of 35 days on addition of copper. This is as expected in an oil that contains linoleic and linolenic acids. It is clear that monounsaturated oils behave differently.

Interrelationships between indices

The release of FFA is due to hydrolytic activity and thus no significant relationship could be expected with the other variables that determine oxidative rancidity. PV and hexanal followed similar trends, with low values for the samples containing copper and much higher values for the control sample. It is of interest to note that the PV/hexanal relationship is confirmed by the 0.17 mg kg^{-1} copper sample, which displayed increased values at week 52 for both variables and a decreased OSI value. The increase in PV and hexanal towards the end of the storage trial in the copper-containing samples (apart from PV of the 0.69 mg kg^{-1} sample) can be explained by oxidation of oleic acid and further degradation to hexanal via its oxidation products. Linoleic acid is more susceptible to oxidation than oleic acid and would thus be oxidised preferentially before oleic acid.²⁵ AV and *t,t*-2,4-decadienal had inverse trends compared with those for PV and hexanal. The AV/*t,t*-2,4-decadienal relationship is expected, as the AV procedure measures aldehydes and primarily 2-alkenals such as *t,t*-2,4-decadienal.²² The relationship between the OSI value and total tocopherols is evident in that the OSI value decreased with a decrease in total tocopherols.

CONCLUSIONS

The pro-oxidant effect of copper on a monounsaturated oil can easily be overlooked if only certain oil quality indices are applied. FFA is known to indicate hydrolytic activity and is not useful as an indicator of oxidative rancidity, whereas PV is generally regarded as a reliable, easy to determine indicator of primary oxidation. However, in this study, PV failed to indicate oil quality, so the determination of PV can lead to false conclusions. AV is a very reliable indicator of oxidative rancidity and is determined by a reasonably straightforward spectrophotometric method. OSI is a useful indicator of oil stability, and its determination using automated equipment is easy to perform. OSI is especially helpful when used in comparison of oxidative stabilities of the same oil type. Headspace volatiles have been found to correlate well with flavour quality in some oil types^{27,28} and could therefore be a practical alternative for sensory evaluation, but the analysis requires sophisticated instrumentation. Interpretation of the volatile profile is difficult and it would be misleading to rely on only one or two volatiles for the evaluation of a monounsaturated oil. The total tocopherol content is an important indicator of damage to an oil. However, the analysis also involves sophisticated instrumentation and is best utilised in

combination with other indices. The results presented lead us to conclude that monounsaturated oil quality is best reflected by AV, OSI and total tocopherols. AV and OSI are the cost-effective methods suggested to be utilised by less sophisticated laboratories.

REFERENCES

- Mohd Suria Affandi Y, Refining and downstream processing of palm and palm kernel oils, in *Selected Readings on Palm Oil and Its Uses*, Ed by Technical Committee of 1994 Palm Oil Familiarization Programme. Palm Oil Research Institute of Malaysia, Kuala Lumpur, pp 35–59 (1994).
- O'Brien RD, *Fats and Oils: Formulating and Processing for Applications*. Technomic Publishing, PA, pp 47–180 (1998).
- Willems MGA, Palm oil: quality requirements from a customer's point of view. *J Am Oil Chem Soc* **62**:454–459 (1985).
- Pike M, Growth in importance of palm oil in the 1970s, in *Fats and Oils: Chemistry and Technology*, Ed by Hamilton RJ and Bhati A. Applied Science Publishers, London, pp 215–247 (1980).
- Tian K and Dasgupta PK, Determination of oxidative stability of oils and fats. *Anal Chem* **71**:1692–1698 (1999).
- Frankel EN, In search of better methods to evaluate natural antioxidants and oxidative stability in food lipids. *Trends Food Sci Technol* **4**:220–225 (1993).
- Rossell B, Measuring resistance to oxidative rancidity. *Lipid Technol* **4**:39–44 (1992).
- Crapiste GH, Brevedan MIV and Carelli AA, Oxidation of sunflower oil during storage. *J Am Oil Chem Soc* **76**:1437–1443 (1999).
- Andersson K and Lingnert H, Influence of oxygen and copper concentration on lipid oxidation in rapeseed oil. *J Am Oil Chem Soc* **75**:1041–1046 (1998).
- Lampi A-M, Piironen V, Hopia A and Koivistoinen P, Characterization of the oxidation of rapeseed and butter oil triacylglycerols by four analytical methods. *Lebensm Wiss Technol* **30**:807–813 (1997).
- Abdel-Aal MH and Abdel-Rahman AY, Effect of some trace elements and type of containers on the stability of cottonseeds, sunflower and soybean oils during storage. *Riv Sost Grasse* **63**:357–360 (1986).
- Anderson J and Van Niekerk PJ, High-performance liquid chromatographic determination of antioxidants in fats and oils. *J Chromatogr* **394**:400–402 (1987).
- AOCS, *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 5th edn, Ed by Mehlenbacher VV, Hopper TH, Sallee EM, Link WE, Walker RO, Walker RC and Firestone D. AOCS Press, Champaign, IL (1997).
- Van Niekerk PJ, The direct determination of free tocopherols in plant oils by liquid–solid phase chromatography. *Anal Biochem* **55**:533–537 (1973).
- Snedecor GW and Cochran WG, *Statistical Methods*, 7th edn. Iowa State University Press, Ames IA, pp 280, 490 (1980).
- Miller JC and Miller JN, *Statistics for Analytical Chemistry*, 2nd edn. Ellis Horwood, Chichester, pp 53–77 (1988).
- Codex Alimentarius Commission on Fats and Oils, *Joint FAO/WHO Food Standards Programme*. FAO, Rome (1999).
- Hudson BJF and Gordon MH, Evaluation of oxidative rancidity, in *Rancidity in Foods*, 3rd edn, Ed by Allen JC and Hamilton RJ. Chapman and Hall, London pp 54–67 (1994).
- Benjelloun B, Talou T, Delmas M and Gaset A, Oxidation of rapeseed oil: effect of metal traces. *J Am Oil Chem Soc* **68**:210–211 (1991).
- Gordon MH and Mursi E, A comparison of oil stability based on the Metrohm Rancimat with storage at 20 °C. *J Am Oil Chem Soc* **71**:649–651 (1994).
- Chong CL and Gapor AMT, Effects of moisture and trace metals on oil quality, in *Proceedings of Workshop on Quality in the Palm Industry*. Edited by Conference Committee, Palm Oil Research Institute of Malaysia, Kuala Lumpur, pp 46–66 (1985).
- White PJ, Conjugated diene, anisidine value and carbonyl value analyses, in *Methods to Assess Quality and Stability of Oils and Fat-containing Foods*, Ed by Warner K and Eskin NAM. AOCS Press, Champaign, IL, pp 159–178 (1995).
- Bramley PM, Elmadfa I, Kafatos A, Kelly FJ, Manios Y, Roxborough HE, Schuch W, Sheehy PJA and Wagner K-H, Vitamin E. *J Sci Food Agric* **80**:913–938 (2000).
- Frankel EN, Antioxidants in lipid foods and their impact on food quality. *Food Chem* **57**:51–55 (1996).
- Kochhar SP, Oxidative pathways to the formation of off-flavours, in *Food Taints and Off-flavours*, Ed by Saxby MJ. Chapman and Hall, Glasgow, pp 168–225 (1996).
- Przybylski R and Eskin NAM, Methods to measure volatile compounds and the flavor significance of volatile compounds, in *Methods to Assess Quality and Stability of Oils and Fat-containing Foods*, Ed by Warner K and Eskin NAM. AOCS Press, Champaign, IL, pp 107–133 (1995).
- Warner K and Frankel EN, Flavor stability of soybean oil based on induction periods for the formation of volatile compounds by gas chromatography. *J Am Oil Chem Soc* **62**:100–103 (1985).
- Morales MT, Rios JJ and Aparicio R, Changes in the volatile composition of virgin olive oil during oxidation: flavors and off-flavors. *J Agric Food Chem* **45**:2666–2673 (1997).