CHAPTER 4

RESULTS

4.1 PALM-OLEIN OIL

4.1.1 Composition of oils

The fatty acid composition of the two palm-olein oils that were used to prepare the blend of palm-olein oil used for the shelf-life test is given in Table 7. The fatty acid composition of typical palm-olein oil (Codex Alimentarius Commission, 1997) has been included.

Table 7: Fatty acid composition (g/100 g fatty acids) of the two palm-olein oils used and that of typical palm-olein oil (Codex Alimentarius Commission, 1997).

Fatty acids	Palm-olein oil fresh	Palm-olein oil from storage	Typical palm-olein oil
C12 : 0	0.26	0.23	0.1-0.5
C14 : 0	0.90	0.97	0.9-1.4
C15 : 0	0.05	0.04	ND*
C16 : 0	36.95	37.15	38.2-42.9
C16 : 1	0.17	0.21	0.1-0.3
C18 : 0	4.29	4.45	3.7-4.8
C18 : 1	45.15	41.38	39.8-43.9
C18 : 2	10.75	13.86	10.4-13.4
C18 : 3	0.17	0.17	0.17-0.6
C20 : 0	0.42	0.37	0.2-0.6
C20 : 1	0.18	0.17	ND*
C22 : 0	0.09	0.14	ND*
C24 : 0	0.11	0.10	ND*

- ND – Non detectable, defined as ≤ 0.05 g/100 g fatty acids

The detection limit (< 0.1 mg/kg) of the iron and copper content, which were determined to assess the initial quality content of the oils, was too high to be of practical value. The moisture and TBHQ contents of the oil are given in Table 8.

Table 8: Moisture and TBHQ content of composite palm-olein oil.

	Moisture g/100 g	TBHQ (mg/kg)
Palm-olein oil	0.13	Not detected*

* Non detectable defined as ≤ 2.0 mg/kg TBHQ

4.1.2 Shelf-life tests

The four sample treatments will in future be identified as Control (no addition of copper), 0.035 mg/kg, 0.17 mg/kg and 0.69 mg/kg copper-containing samples.

The data showed that the sample treatment with the sample containing 0.17 mg/kg copper, at Week 29, was suspect. The data was subjected to Dixon's test for outliers on the residuals of the regressions lines of the variables (Snedecor and Cochran, 1980). The data for Week 29 qualified as an outlier, at 99 % confidence level and was then omitted. All the curves of that sample were interpolated between Weeks 26 and 34.

Values shown in the figures are means of at least duplicates (see section 3.3.1). Error bars and standard deviation in figures and tables are not shown in order for legible interpretation of results. Statistical analysis of data to compare treatments of each parameter is given in section 4.3.

4.1.2.1 Free fatty acids

The effect of storage at 50°C on the four sample treatments over a period of 52 weeks is given in Figure 3.

The FFA content of the samples increased over the storage period. The FFA increased gradually up to Week 40, after which a sharp increase occurred in all the samples. The FFA of the Control increased the most, followed by a slightly lower rate of increases in FFA in the copper-containing samples. The sample with the highest concentration of copper (0.69 mg/kg) had the lowest FFA content after the storage period.

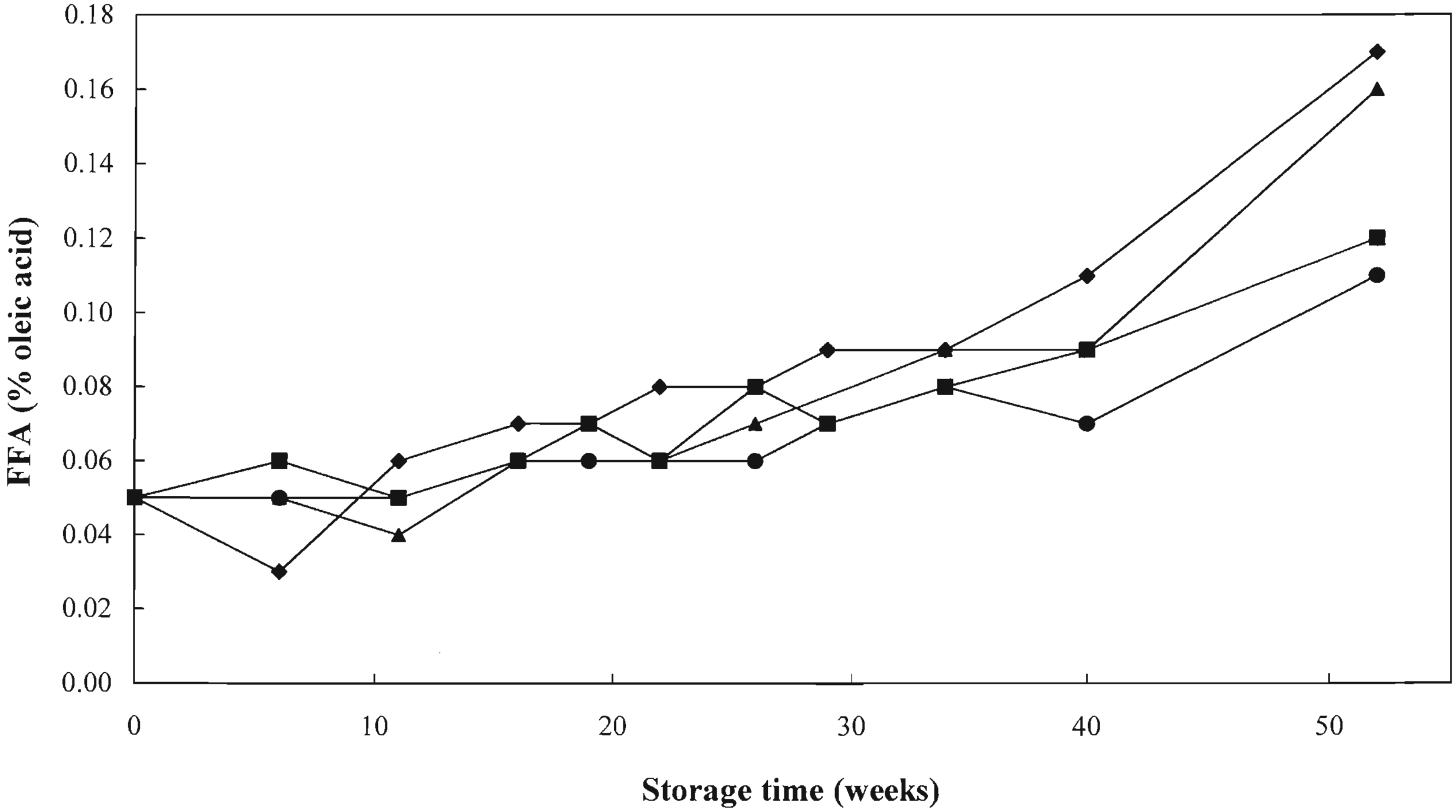

Figure 3: The effect of storage on the FFA content (% oleic acid) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.2 Peroxide value

The effect of storage at 50°C on the PV of the four sample treatments is given in Figure 4.

The PV of the Control increased steadily and reached a plateau at Weeks 34-40, after which it appeared to decrease. The highest PV obtained for the Control was 28.8 meq/kg at Week 40. The samples containing copper had low peroxide values (< 5.0 meq/kg) up to Week 26, after which the values for the samples containing 0.035 mg/kg and 0.17 mg/kg copper gradually increased, whereas the values for the sample containing 0.69 mg/kg copper remained stable. The PV of the sample containing 0.17 mg/kg copper increased sharply after Week 40 to 14.0 meq/kg, whereas the sample containing 0.035 mg/kg copper increased steadily after week 26 to reach a value of 10.7 at Week 52. The sample with the highest concentration of copper (0.69 mg/kg) had the lowest PV after the 52 week storage period of 1.6 meq/kg.

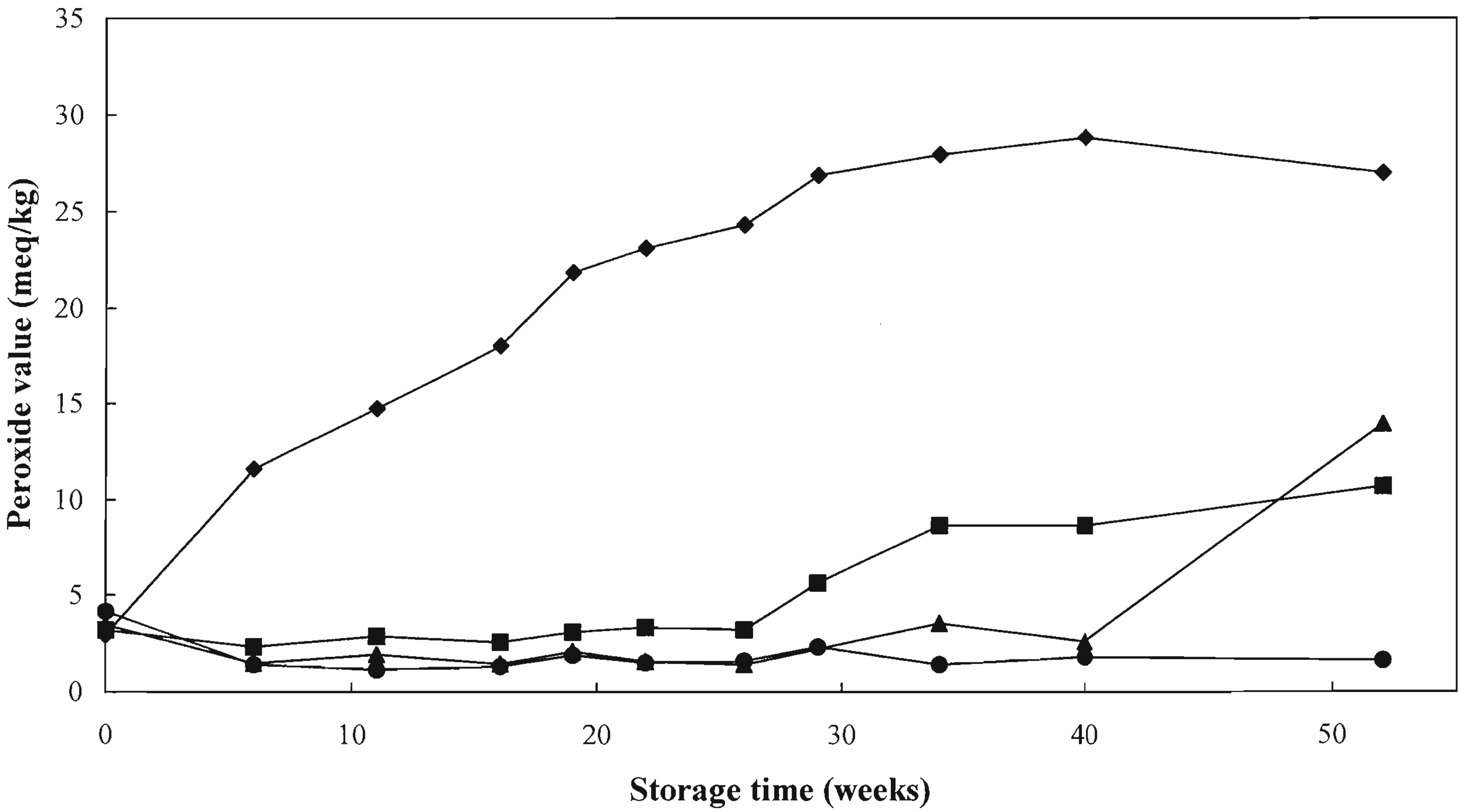

Figure 4: The effect of storage on the peroxide value (meq/kg) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.3 Anisidine value

The effect of storage at 50°C on the AV of the four sample treatments is given in Figure 5.

In general, the AV of all the samples increased. The AV of the Control increased steadily up to Week 40, after which there was a sharper increase to a value of 15.2. 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 copper, whereas the sample with 0.69 mg/kg copper increased steadily. At Week 52 the AV of the samples containing copper was approximately double than that of the Control.

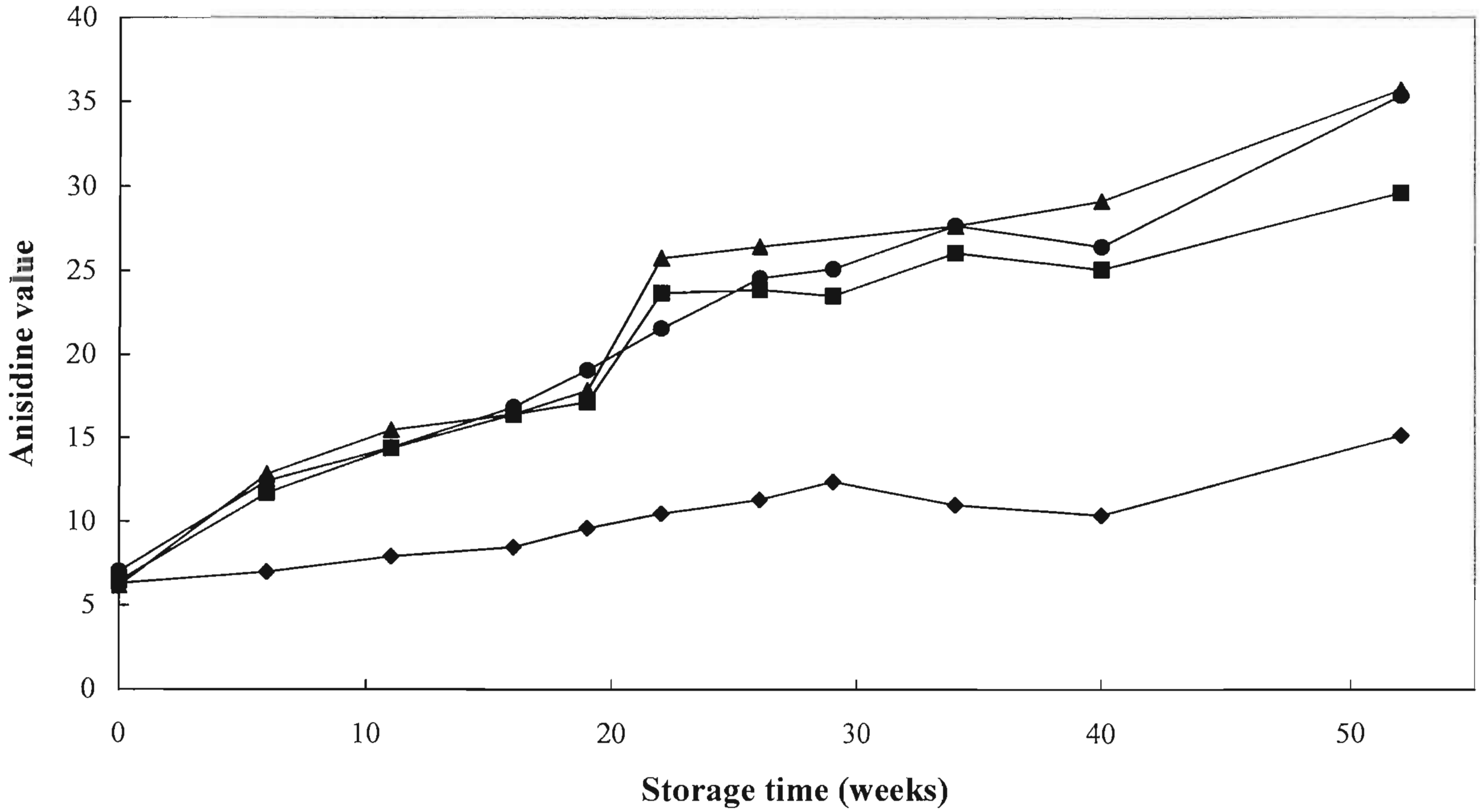

Figure 5: The effect of storage on the anisidine value of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.4 Totox value

The effect of storage at 50°C on the Totox value of the four sample treatments is given in Figure 6.

The calculated Totox values (2PV +AV) of all the samples increased gradually during the 52 week storage period. The Totox value of the Control increased at a much faster rate than the copper-containing samples and had consistently higher values than the copper-containing samples. The different concentrations of copper did not appear to affect the rates of increase in the samples up to Week 26, after which the highest concentration of copper (0.69 mg/kg) had the lowest Totox values and the lowest concentration of copper (0.035 mg/kg) the highest values of the copper-containing samples. However, at Week 52 the 0.17 mg/kg sample had the highest Totox value.

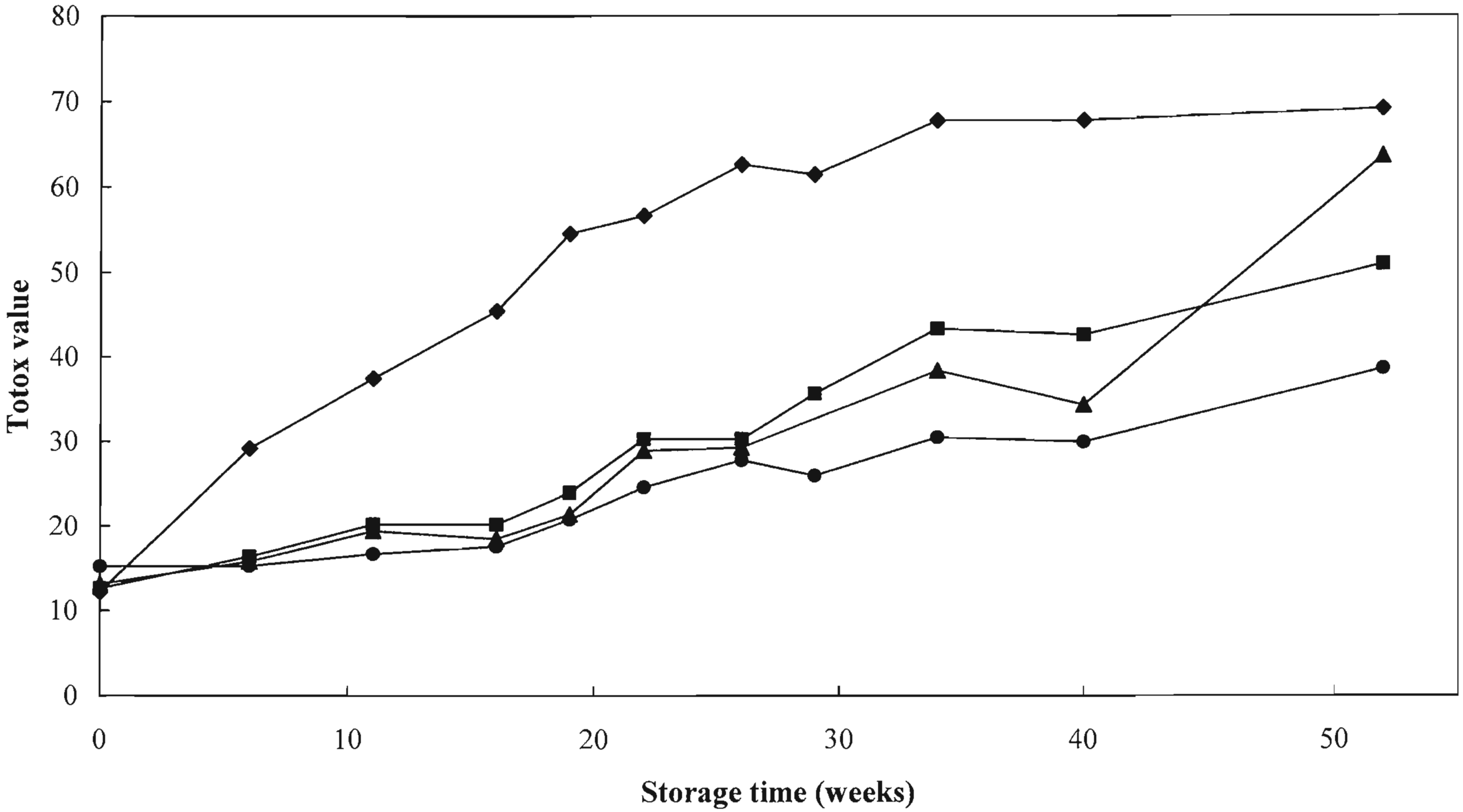

Figure 6: The effect of storage on the Totox value of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.5 Oxidative Stability Index

The effect of storage at 50°C on the oxidative stability conducted at 120°C of the four sample treatments is given in Figure 7.

The copper-samples showed marked differences from the Control at Day 0 where progressively higher concentration of copper have concurrent lower OSI values. There was a steady decline in OSI (in hours) of the Control and the sample with 0.035 mg/kg copper, that was very similar apart from the initial values. The values for the Control decreased by half the number of hours (11 hours) from Day 0 to Week 52, whereas the values for the sample with 0.035 mg/kg copper decreased by 2.5 hours from 0 to Week 52. The oxidative stability of the sample with 0.17 mg/kg copper remained fairly stable up to Week 40, after which it decreased significantly to half the number of hours. The oxidative stability of the sample with 0.69 mg/kg copper remained stable from the start of the shelf-life test up until Week 52 with an oxidative stability index of only 3–4 hours.

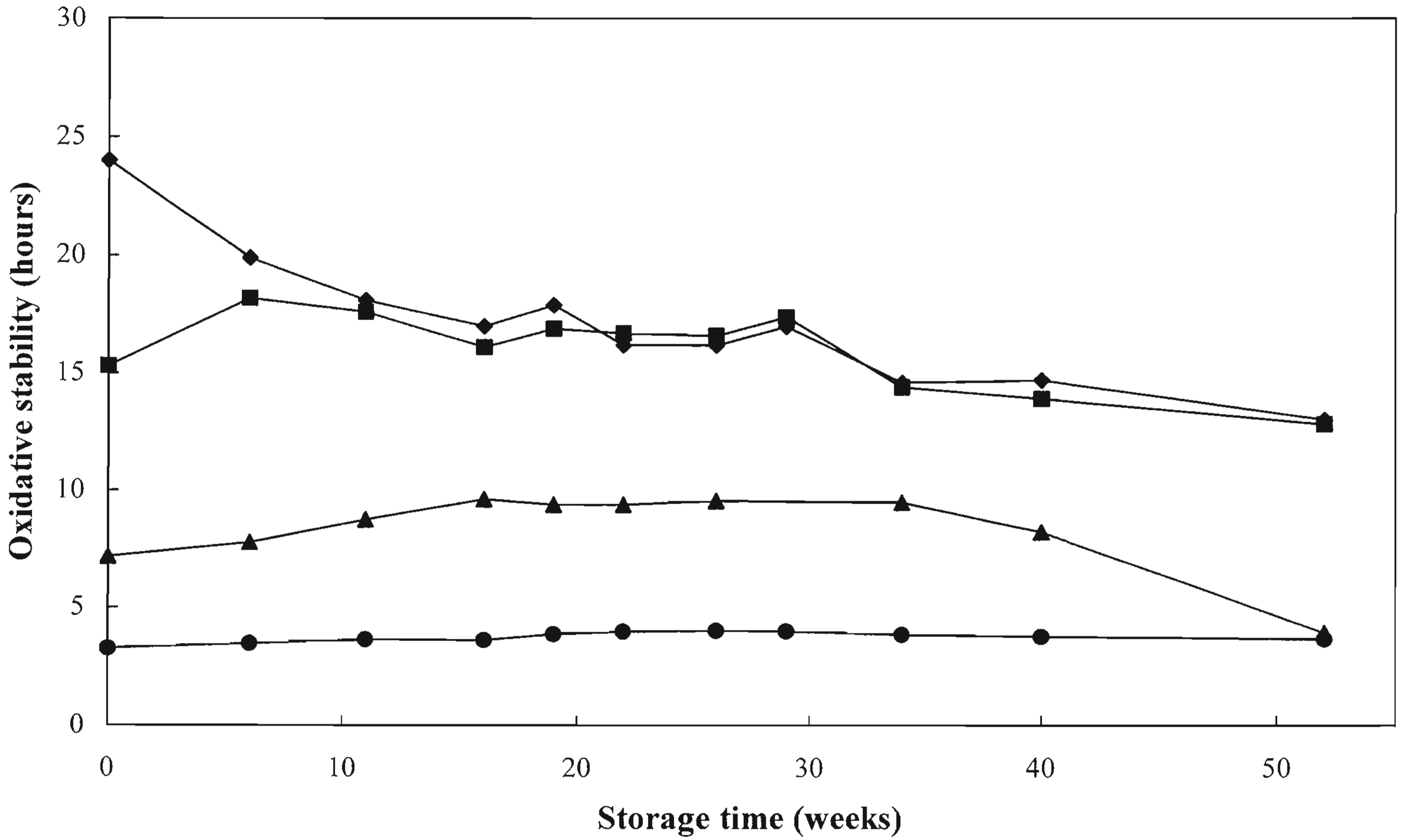

Figure 7: The effect of storage at 50°C for 52 weeks on the oxidative stability (hours) conducted at 120° of palm-olein with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.6 Tocopherols

The detection limit for tocopherols is 0.1 mg/100 g and therefore tocopherols such as β- and γ-tocopherol that might have been present at levels less than the detection limit were not reported.

Total tocopherols

The effect of storage at 50°C on the total tocopherol content of the four sample treatments is given in Figure 8. The total tocopherols of the Control remained the highest of all the samples over storage, but declined from 53.7 mg/100 g to 32.2 mg/100 g by Week 52. The total tocopherol contents of the 0.17 and 0.69 mg/kg copper samples showed a slight decrease at Day 0 when the copper was added. All the copper-containing samples showed a sharp decline within the first 6 weeks as measured at Week 6. After Week 6 the treatments containing 0.17 and 0.69 mg/kg copper maintained a gradual decrease and the sample with the lowest concentration of copper (0.035 mg/kg) remained constant up to Week 52. The decrease in total tocopherols was concomitant with concentration of copper added. The change in total tocopherols and the individual tocopherols content (mg/100 g) from the initial values to the values at Week 52 is given in Table 9.

Table 9: Total and individual tocopherols (mg/100 g) content of palm-olein at Day 0 and after 52 week storage period at 50°C.

	Tocopherol content (mg/100 g)				
		Week 52			
Tocopherols	**Day 0**	Control	0.035 mg/kg copper	0.17 mg/kg copper	0.69 mg/kg copper
Total tocopherols	53.7	33.2	15.7	2.5	3.4
Alpha-tocopherol	14.8	7.3	2.6	0	0
Alpha-tocotrienol	14.2	6.3	2.2	0	0
Gamma-tocotrienol	19.2	14.2	6.9	0	0
Delta-tocotrienol	5.5	5.4	4.1	2.5	3.4

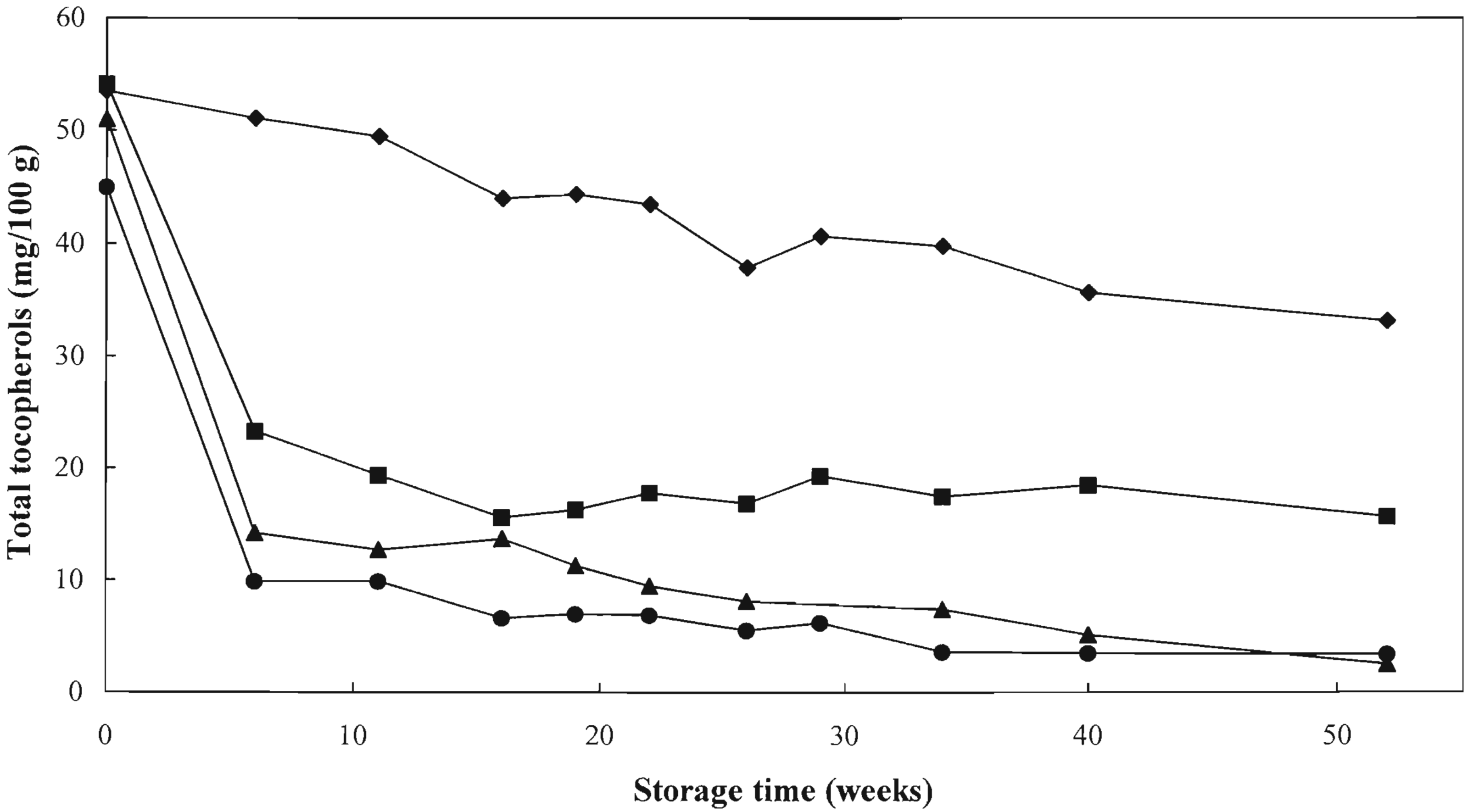

Figure 8: The effect of storage on the total tocopherol content (mg/100 g) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

Alpha-tocopherol

The effect of storage at 50°C on the alpha-tocopherol content of the four sample treatments is given in Figure 9.

The Control sample decreased gradually from Day 0 to Week 52. The alpha-tocopherol contents of the 0.17 and 0.69 mg/kg copper samples revealed slight decreases at Day 0 with further sharp decreases until Week 6 and no alpha-tocopherol remained in the 0.17 and 0.69 mg/kg copper samples after Week 22. The alpha-tocopherol of the sample with the lowest concentration of copper (0.035 mg/kg) remained reasonably constant after Week 6 with the values fluctuating between 0.8-2.9 mg/100 g.

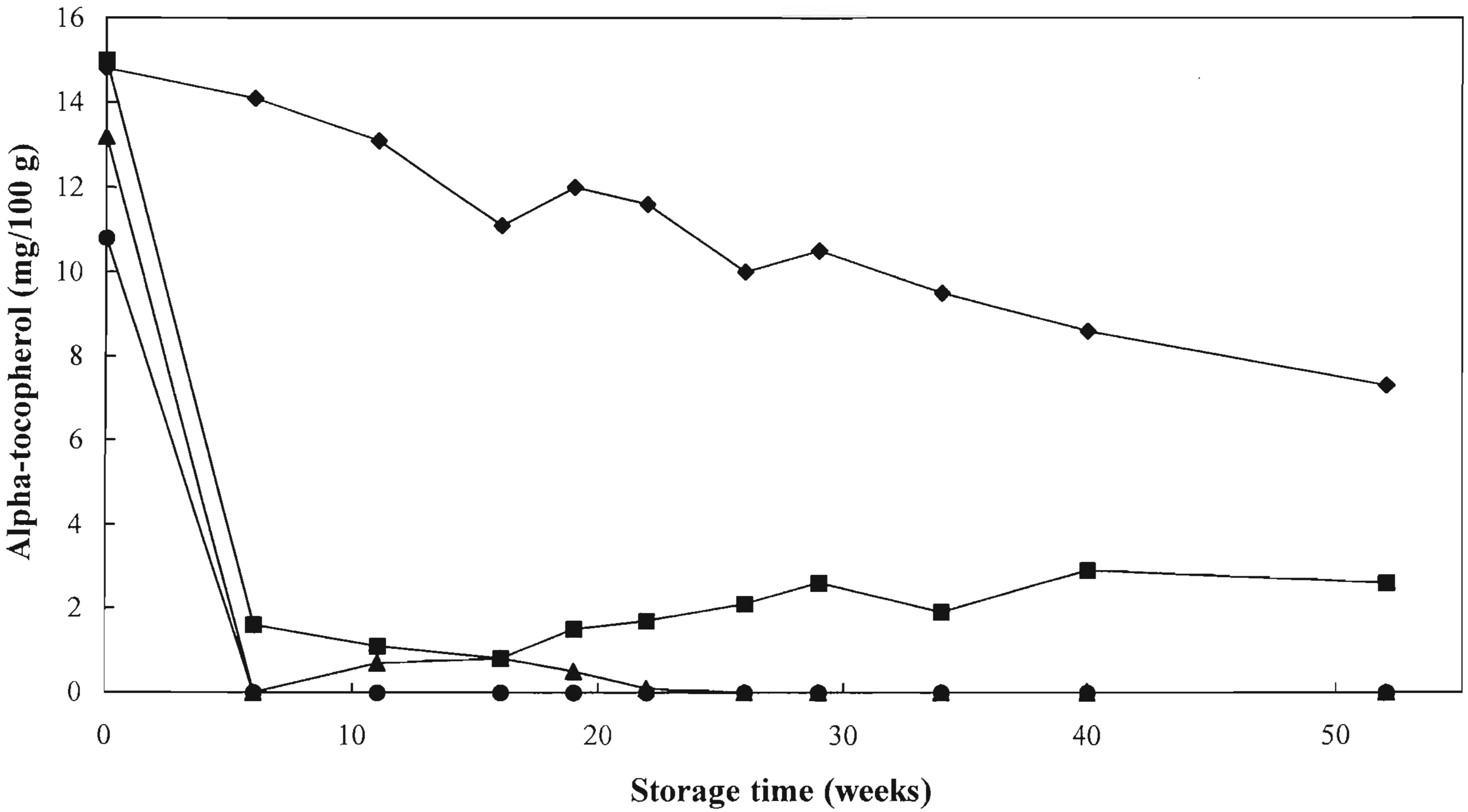

Figure 9: The effect of storage on the alpha-tocopherol content (mg/100 g) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

Alpha-tocotrienol

The effect of storage at 50°C on the alpha-tocotrienol content of the four sample treatments is given in Figure 10.

The alpha-tocotrienol decreased in a similar manner to the alpha-tocopherol, as can be seen from Figure 10. The Control sample decreased gradually from Day 0 to Week 52. The alpha-tocotrienol content of the 0.69 mg/kg copper sample had decreased somewhat at Day 0 after addition of copper. However, the alpha-tocotrienol content of the 0.17 mg/kg copper sample did not show a slight decrease at Day 0 as it had with the alpha-tocopherol. The alpha-tocotrienol in the samples containing copper decreased drastically within the first 6 weeks and no alpha-tocotrienol remained in the 0.17 and 0.69 mg/kg copper samples after Week 22. The alpha-tocotrienol of the sample with the lowest concentration of copper (0.035 mg/kg) remained reasonably constant after Week 6 with the values fluctuating between 0.7-2.4 mg/100 g in similar fashion to alpha-tocopherol.

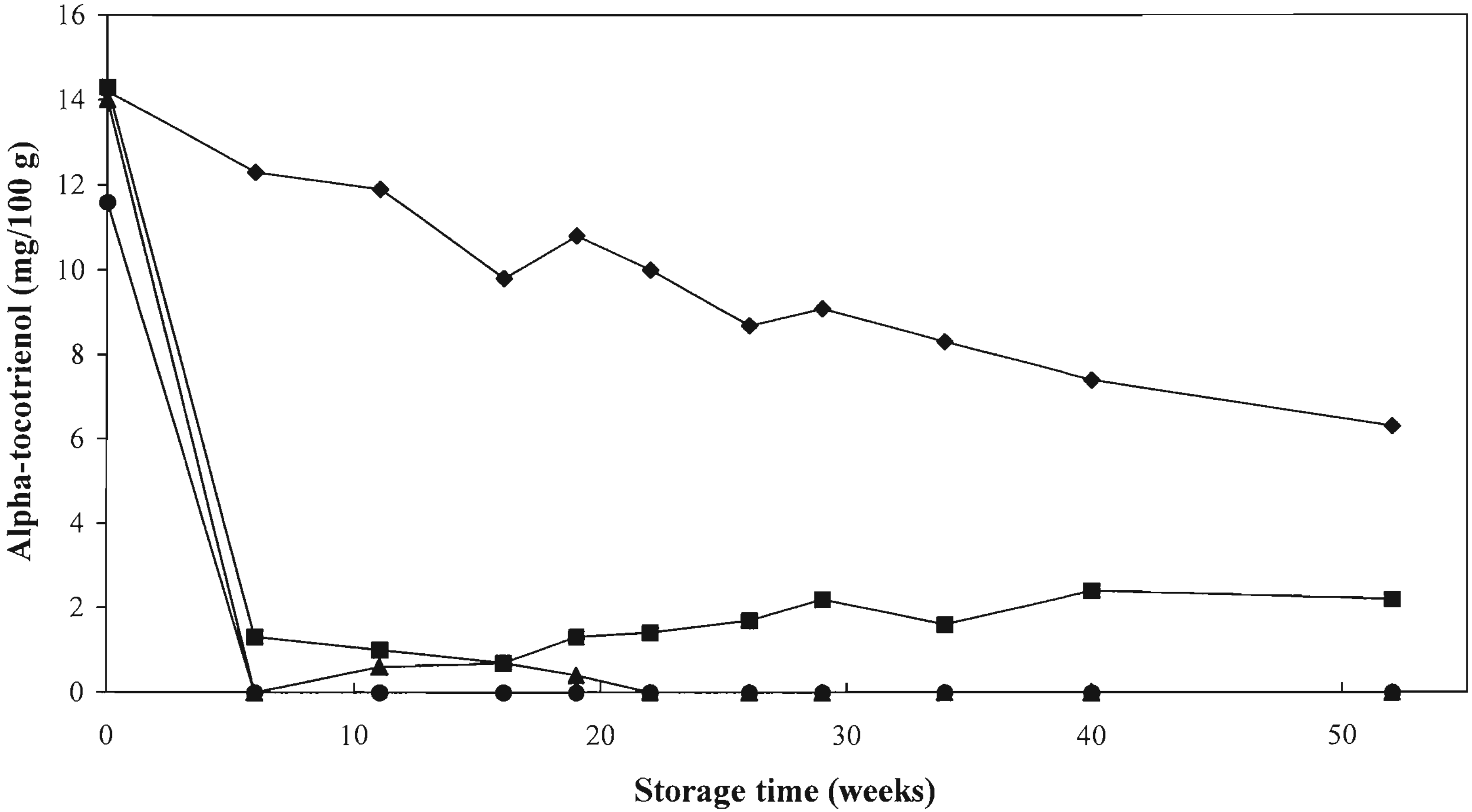

Figure 10: The effect of storage on the alpha-tocotrienol content (mg/100 g) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

Gamma-tocotrienol

The effect of storage at 50°C on the gamma-tocotrienol content of the four sample treatments is given in Figure 11.

The gamma-tocotrienol decreased in a different manner when compared to alpha-tocopherol and alpha-tocotrienol. The decrease was gradual from Day 0 to Week 52 for all the samples, although the gamma-tocotrienol of the Control sample decreased at a slower rate than the samples containing copper. The decrease in gamma-tocotrienol was concomitant with concentration of copper added. At Week 52 the two samples with the highest concentrations of copper (0.17 and 0.69 mg/kg) did not have any gamma-tocotrienol remaining, whereas the samples with 0.035 mg/kg copper and the Control still had 7.0 and 14.0 mg/kg gamma-tocotrienol remaining, respectively.

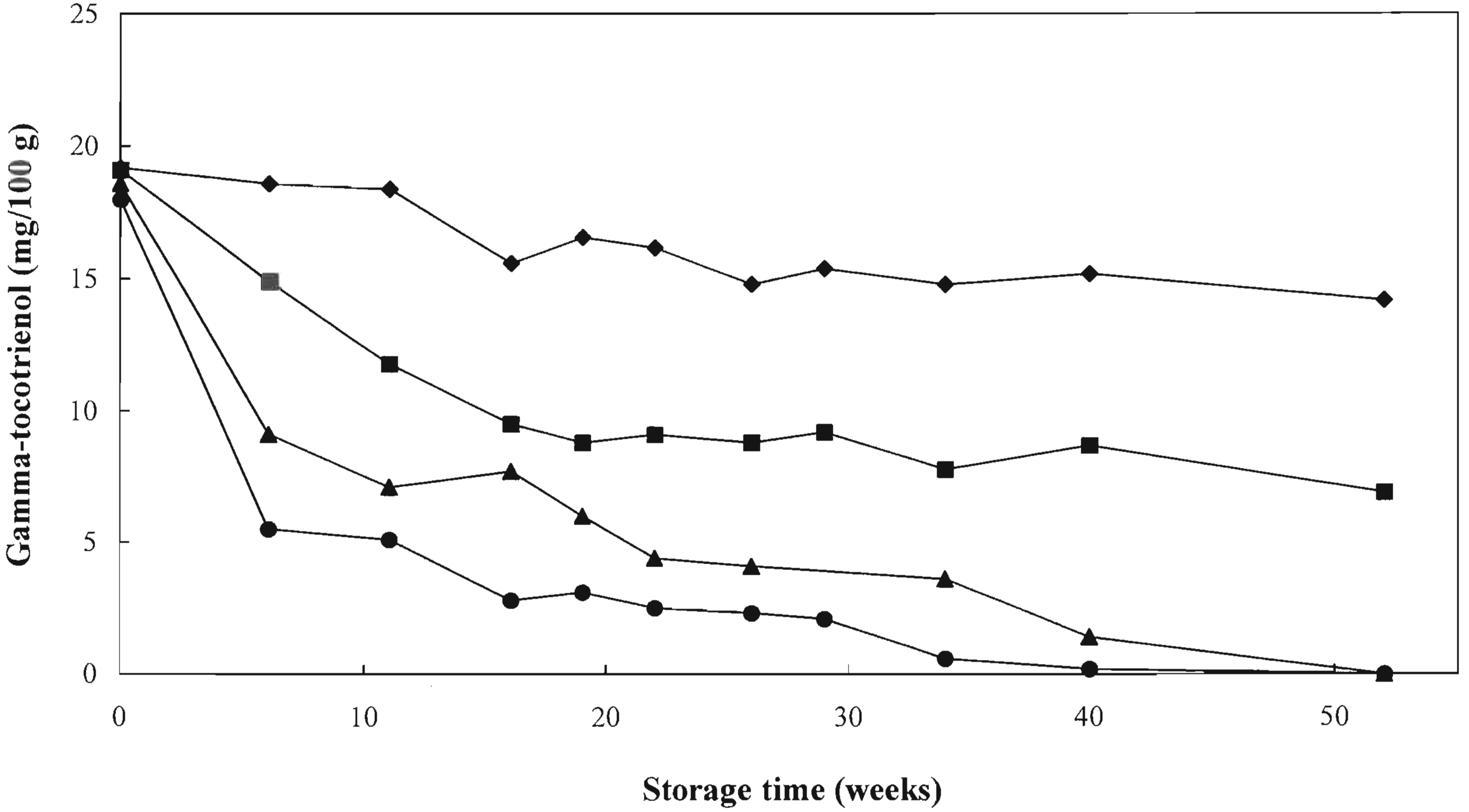

Figure 11: The effect of storage on the gamma-tocotrienol content (mg/100 g) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

Delta-tocotrienol

The effect of storage at 50°C on the delta-tocotrienol content of the four sample treatments is given in Figure 12.

The delta-tocotrienol showed the least decrease during the storage period of all the tocopherols. The delta-tocotrienol decreased very slowly over the storage period in the Control as well as the copper-containing samples. The delta-tocotrienol of the Control sample did not decrease substantially during the storage period, whereas in the samples containing copper the delta-tocopherol did decrease somewhat. The delta-tocotrienol content of the 0.035 mg/kg copper sample decreased by approximately a quarter and the 0.17 mg/kg by half and the 0.69 mg/kg by less than half (Table 9).

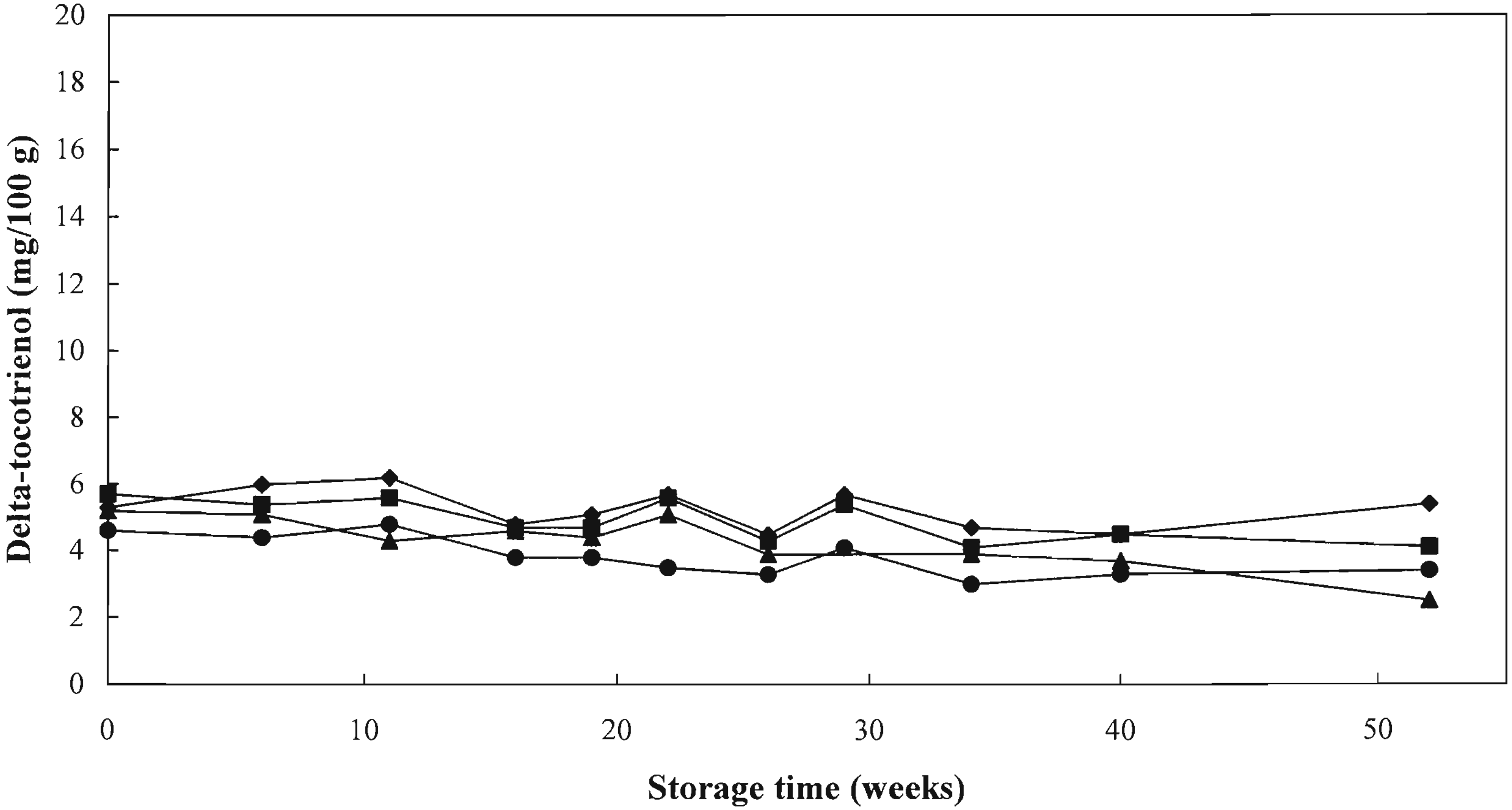

Figure 12: The effect of storage on the delta-tocotrienol content (mg/100 g) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.7 Conjugated diene and triene values

Conjugated diene (UV 232 nm)

The effect of storage at 50°C on the conjugated diene value of the four sample treatments is given in Figure 13.

There was a slight increase in the conjugated diene value during the storage period for all the samples. The Control generally had slightly higher values than the samples containing copper, although two copper-containing samples had slightly higher values at Day 0 than the Control. The values of all copper-containing samples decreased to levels below that of the Control at Week 6 and remained below the Control for the rest of the storage period, apart from the 0.17 mg/kg copper sample that reached the same value at Week 52 than the Control.

Conjugated triene (UV 268 nm)

The effect of storage at 50°C on the conjugated triene value of the four sample treatments is given in Figure 14.

The conjugated triene value of the Control increased only slightly over the storage period from 0.74 at Day 0 to 1.33 at Week 52 However, the values of the copper-containing samples increased up to 2.65, 2.73 and 2.84 for the 0.035, 0.17 and 0.69 mg/kg copper samples, respectively from initial values of 0.81, 0.87 and 0.96. The differences between the three concentrations of copper were minimal.

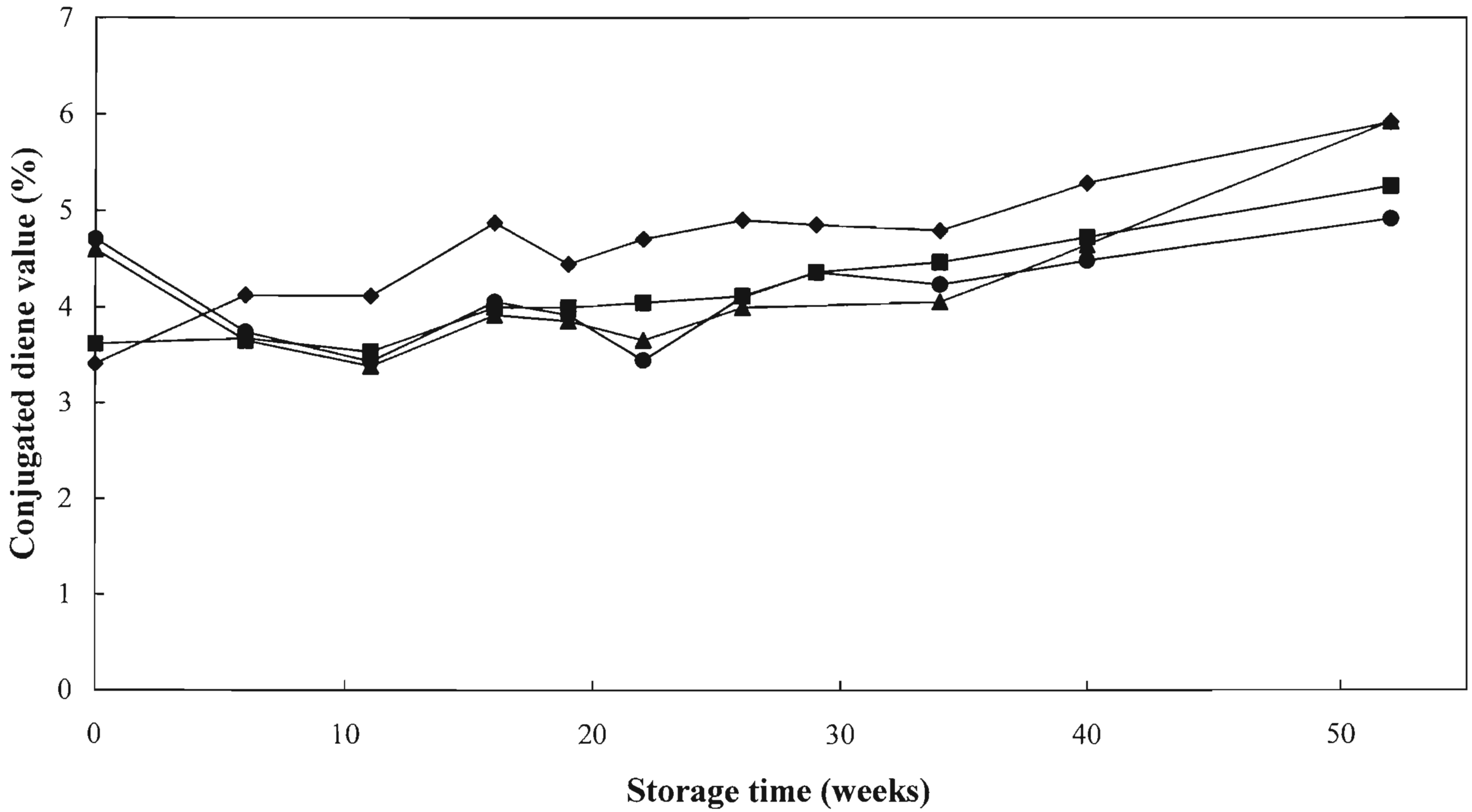

Figure 13: The effect of storage on the conjugated diene value (%) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

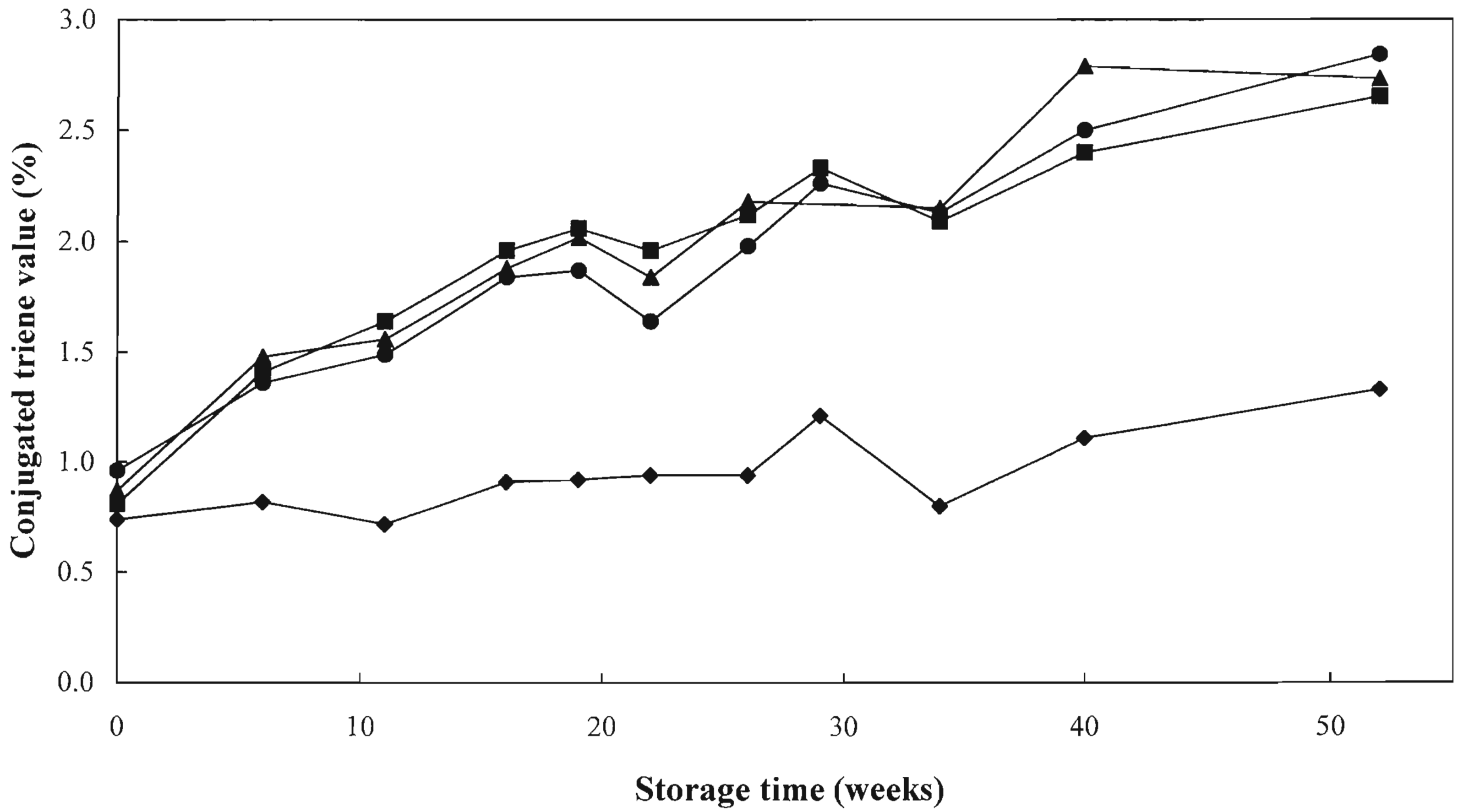

Figure 14: The effect of storage on the conjugated triene value (%) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.8 Iodine value

The effect of storage at 50°C on the IV of the four sample treatments is given in Figure 15.

Very little change occurred in the iodine value during storage at 50°C. The initial IV was 58.8 and at Week 52 the values obtained were 58.4, 58,2, 57.3 and 58.1 for the Control, 0.035, 0.17 and 0.69 mg/kg copper samples, respectively. The IVs of the copper-containing samples did not appear to differ markedly from the IV of the Control.

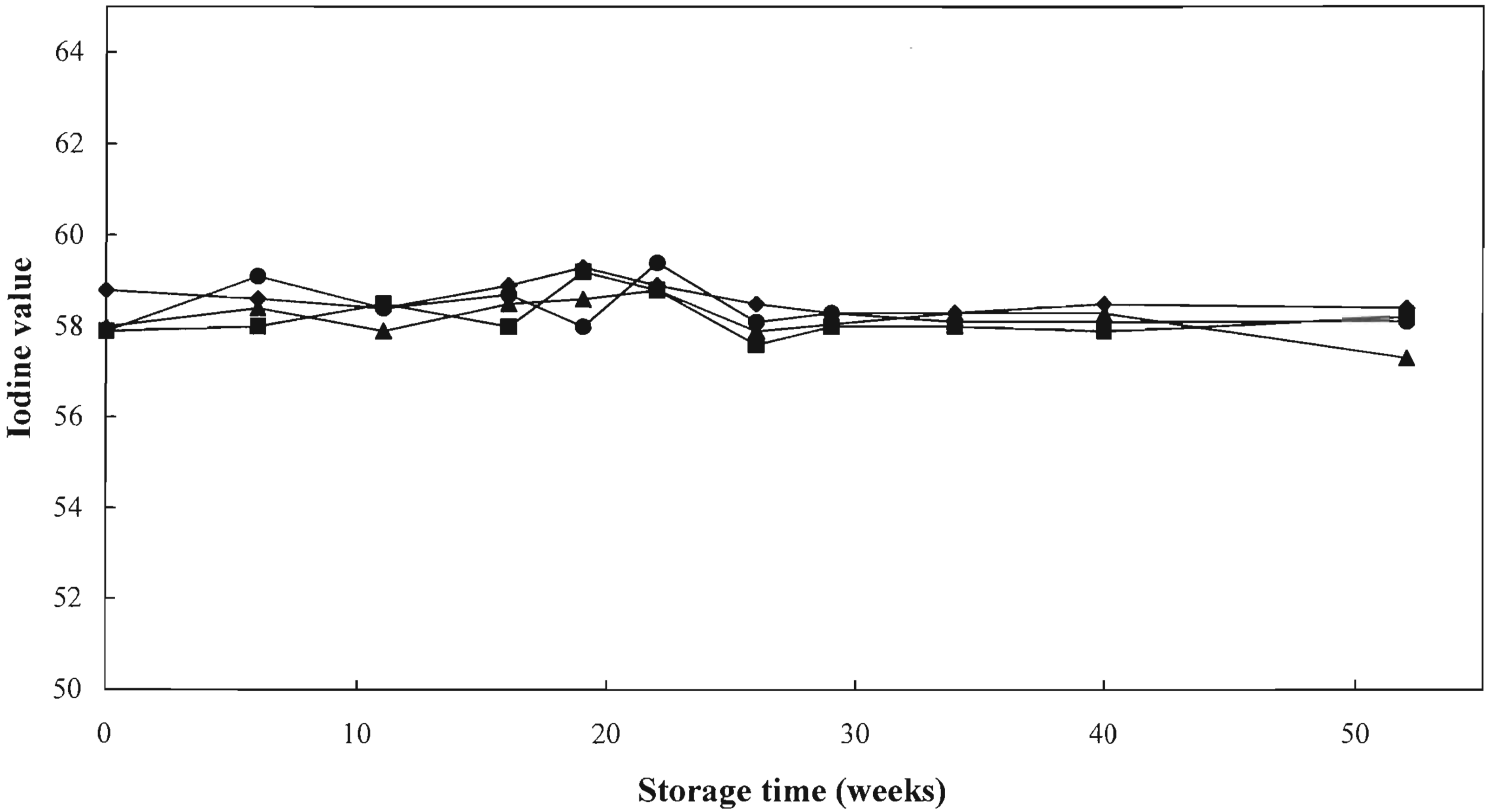

Figure 15: The effect of storage on the iodine value of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.9 Headspace volatile components

Total volatile peak area

The effect of storage at 50°C on the total volatile peak area of the samples is shown in Figure 16. The total volatile peak area for all the samples increased gradually during the storage period. The sample with the most copper generally had the highest total volatile peak area. The order of the rest of the samples' peak areas is not clear as the values fluctuated between the samples, although it does appear as if the 0.035 mg/kg copper sample generally had the lowest peak area.

trans-2-hexenal

The effect of storage at 50°C on the t-2-hexenal content of the four sample treatments is given in Figure 17. Low values of trans-2-hexenal were obtained for all the samples stored at 50°C. The values showed no pattern within the narrow fluctuation range of 0-2.3 mg/kg.

Hexanal

The effect of storage at 50°C on the hexanal content of the four sample treatments is given in Figure 18. Hexanal content increased over time for all the samples. The hexanal content of the Control sample increased most, whereas the hexanal 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 copper sample.

trans,trans-2,4-decadienal

The effect of storage at 50°C on the t,t-2,4-decadienal content of the four sample treatments is given in Figure 19. The Control sample did not form t,t-2,4-decadienal over the storage period. The samples containing copper all showed an increase in t,t-2,4-decadienal over time. 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. After Week 16 the 0.17 mg/kg copper sample generally had the lowest values of the three copper-containing samples.

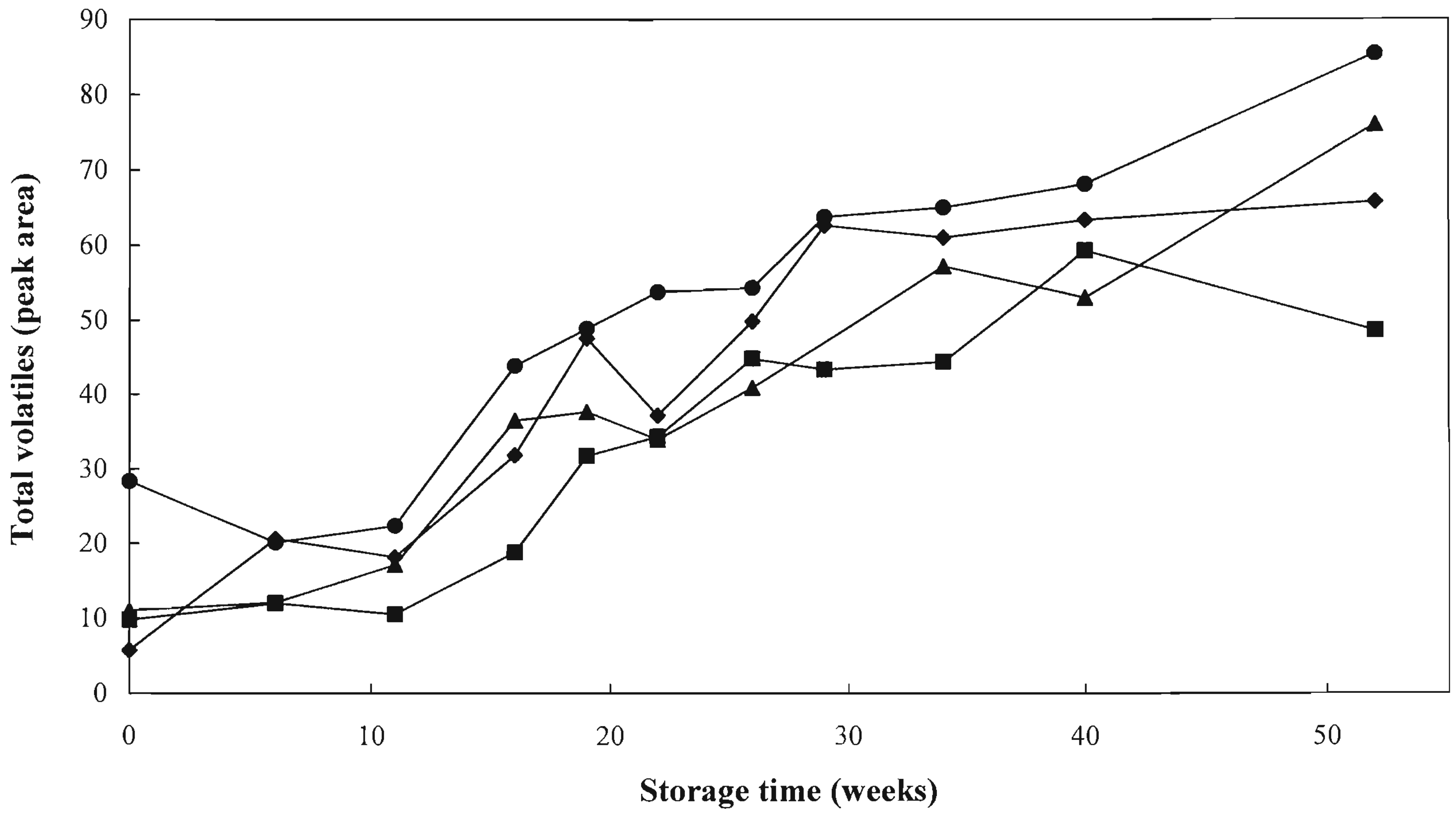

Figure 16: The effect of storage on the total volatile peak area of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

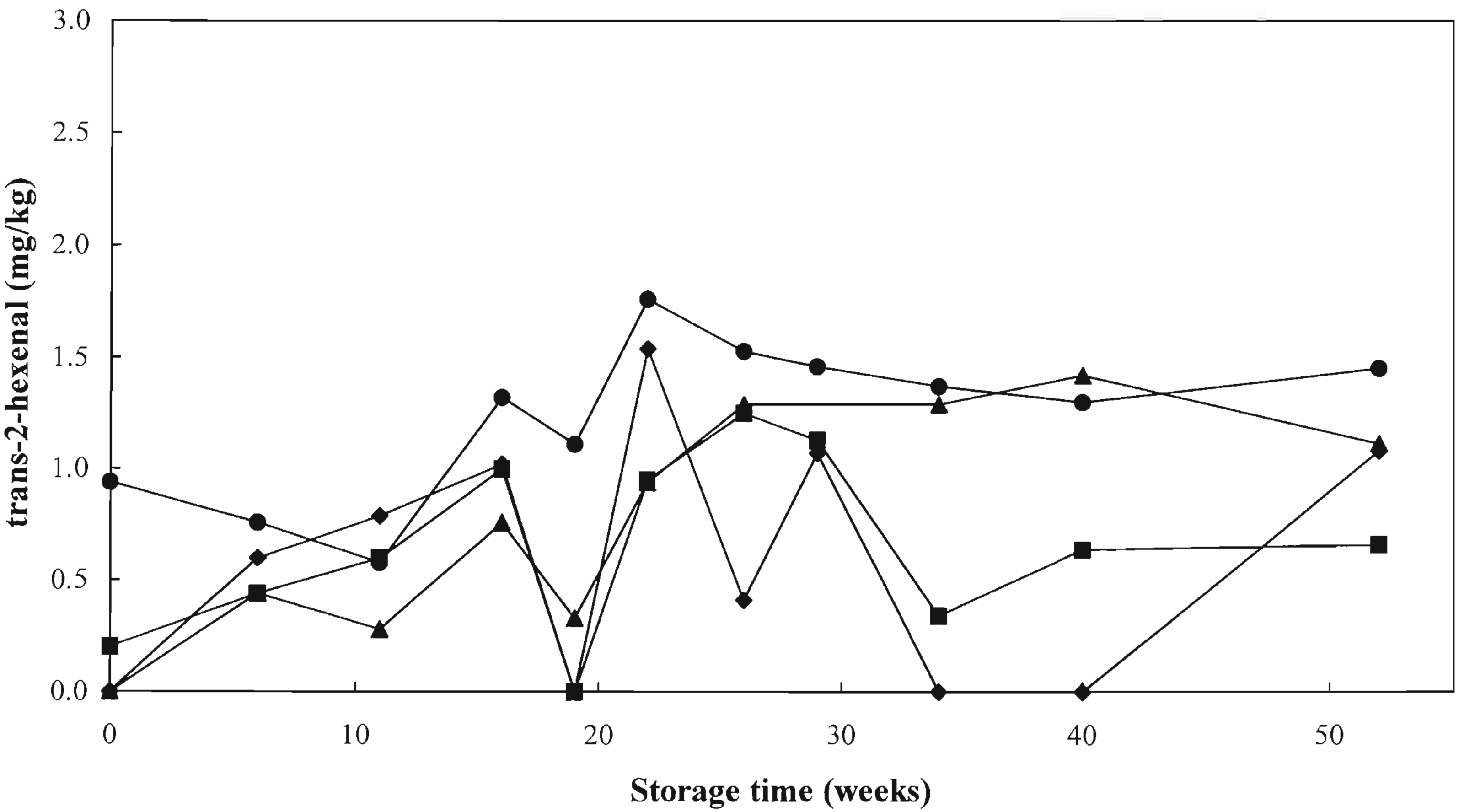

Figure 17: The effect of storage on the trans-2-hexenal content (mg/kg) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

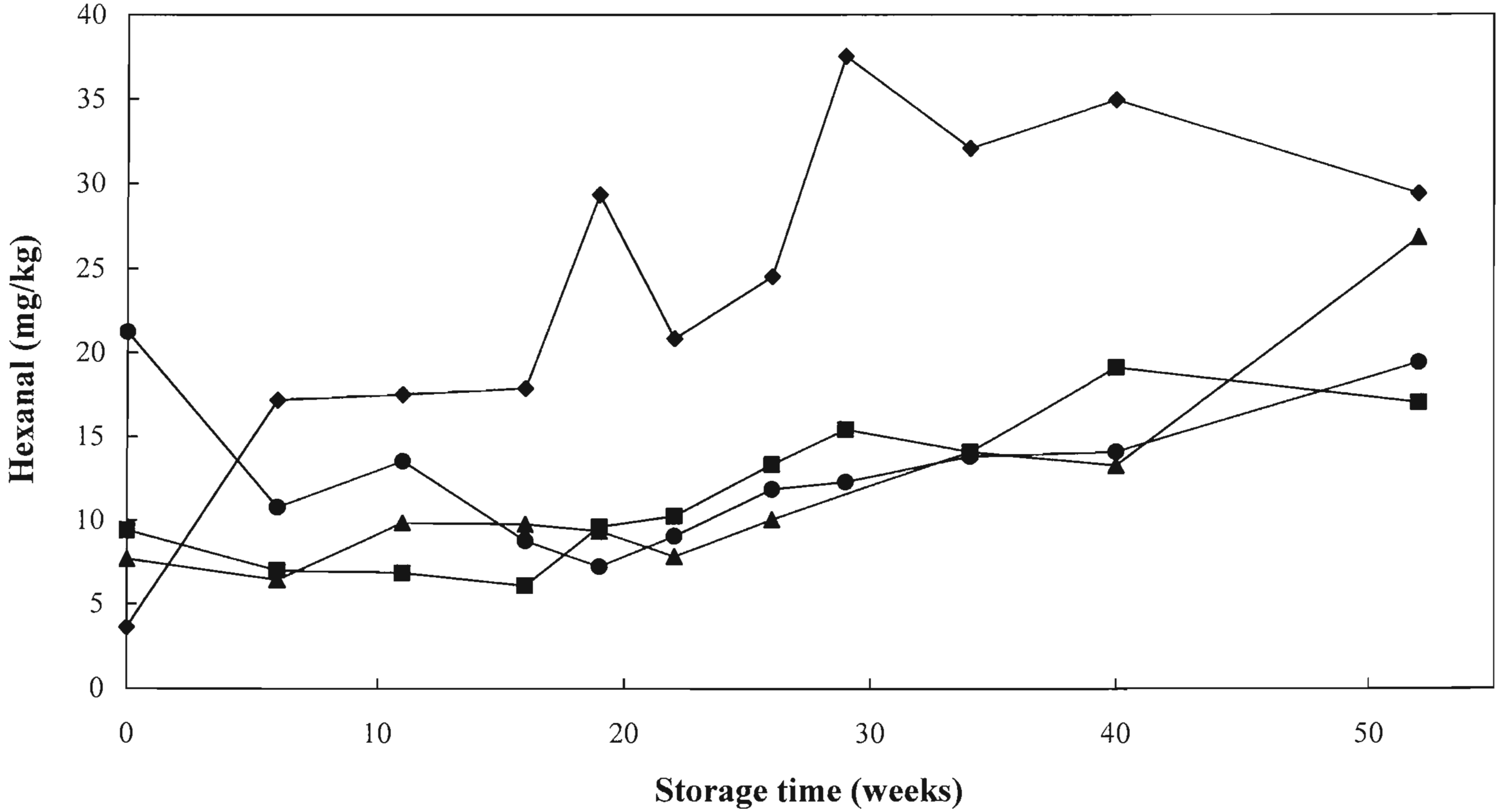

Figure 18: The effect of storage on the hexanal content (mg/kg) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

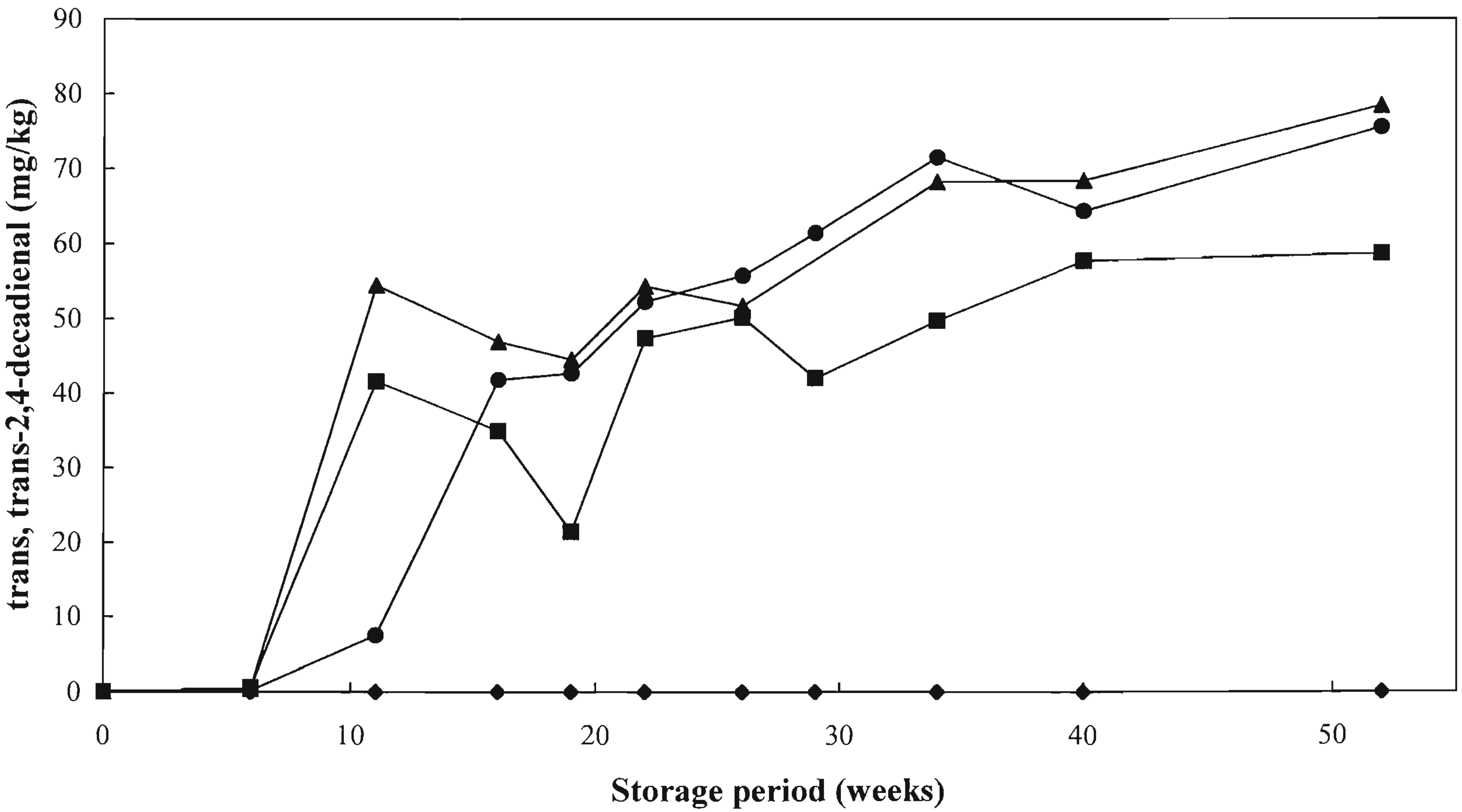

Figure 19: The effect of storage on the trans, trans-2,4-decadienal content (mg/kg) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

Pentanal peak area

The effect of storage at 50°C on the pentanal content of the four sample treatments is given in Figure 20. The Control had the lowest values and the values increased very gradually from Day 0 to Week 52. The 0.69 mg/kg copper-containing sample appeared to have the highest values that increased at a faster rate than the values of the Control from Day 0 to Week 52. The 0.035 mg/kg copper-containing sample had values higher than the Control and increased steadily from Day 0 to Week 40 after which the values decreased at Week 52. The 0.17 mg/kg copper-containing sample had values that increased between those of the 0.69 mg/kg and 0.035 mg/kg copper-containing samples from Day 0 up to Week 34, after which the values decreased.

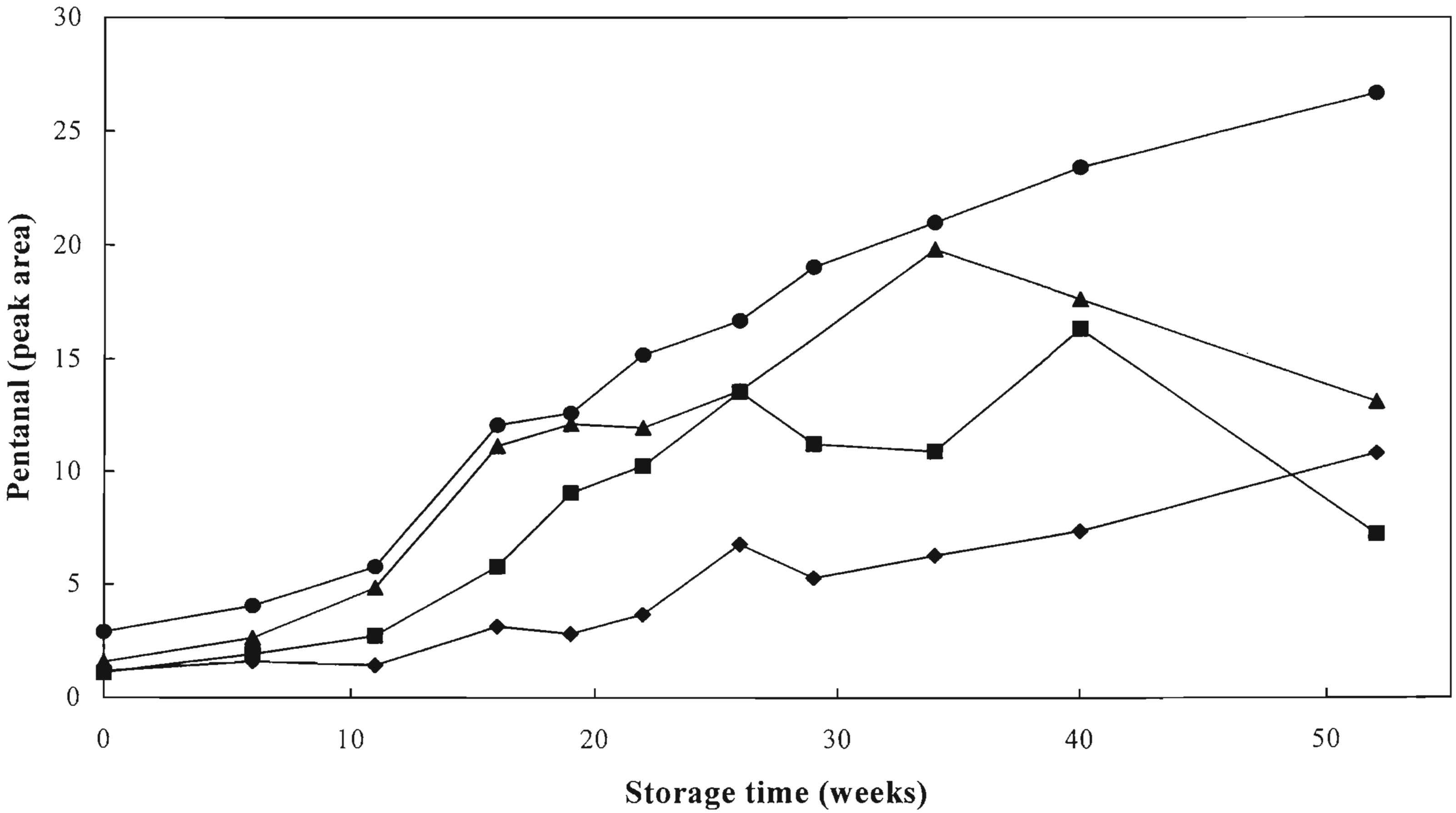

Figure 20: The effect of storage on the pentanal (peak area) of palm-olein stored at 50°C for a period of 52 weeks with different concentrations of copper added to the oil. Control sample (◆), 0.035 mg/kg copper (■), 0.17 mg/kg copper (▲) and with 0.69 mg/kg copper (●).

4.1.2.10 Sensory evaluation

The four categories used to evaluate the oils were:

1) Odour bland, weak characteristic odours
2) Weak off-odours or loss of characteristic odours
3) Moderate off-odours, slightly rancid
4) Strong off-odours, rancid, painty

Graphs were drawn with two combinations (options) of the categories: Oil identified as **Fresh** was grouped by either category **1)** only (Option 1) or the combination of categories **1)** and **2)** (Option 2). Oil identified as **Rancid** as a combination of categories **2)**, **3)** and **4)** or **3)** and **4)**.

The reasoning behind this was that for Option 1, anything that was not bland or characteristic of the oil, would be deemed off-odoured or rancid. The reasoning for Option 2 was that some panelists would seldom or never categorise an oil as fresh and would thus select category **2)** even though the oil was deemed fresh.

Thus:	**Option 1:**	Fresh	1)
		Rancid	2), 3) and 4)
	Option 2:	Fresh	1) and 2)
		Rancid	3) and 4)

According to O'Mahoney (1986) the statistical guideline would be that if 8 or 9 out of 12 panelists regard the oil to be rancid it would be significant at the 20 % and 10 % level of significance, respectively. This applies for a one-tailed paired-comparison difference test of rancid and fresh oil. For the 5 % level of significance 10 out of 12 panelists must deem the oil to be rancid.

The results of the sensory evaluation conducted by 12 panelists are given in Figures 21 and 22 where Figure 21 shows results of Option 1 and Figure 22 the results of Option 2.

Control

At the storage time where the number of panelists that judged the oil to be rancid surpassed the number of panelists that judged the oil to be fresh, thus where the Fresh and Rancid lines cross and part permanently, the oil can be deemed rancid. Thus, according to Option 1, the majority of the panelists (8) judged the Control rancid by Week 40, although the oil was deemed rancid more convincingly at Week 52 by a majority of panelists (11). According to Option 2, the Control oil was rancid by Week 52 according to a majority of panelists (9). The lines of the Control and the 0.17 mg/kg copper sample (Fresh and Rancid) of Option 2 overlapped from Week 34, which resulted in the Control lines to be hidden underneath the 0.17 mg/kg copper sample lines.

Sample with 0.035 mg/kg copper

According to Option 1, the majority of the panelists (10) judged the oil to be rancid by Week 40. However, according to Option 2 the oil had not reached rancidity at Week 52.

Sample containing 0.17 mg/kg copper

According to Option 1, the oil was rancid by Week 26 with a majority of panelists (10). However, according to Option 2 the majority of panelists (9) judged the oil to be rancid at Week 52. The data point at Week 29 has been excluded from all the previous data as it was clearly shown to be an outlier, but for the sensory evaluation it has been included to demonstrate that most of the panelists could pick up that the oil at Week 29 was rancid.

Sample containing 0.69 mg/kg copper

According to Option 1, the oil was clearly rancid by Week 26 according to a majority of panelists (10). However, according to Option 2 the oil only appeared to be convincingly rancid by Week 52 with a majority of panelists (9).

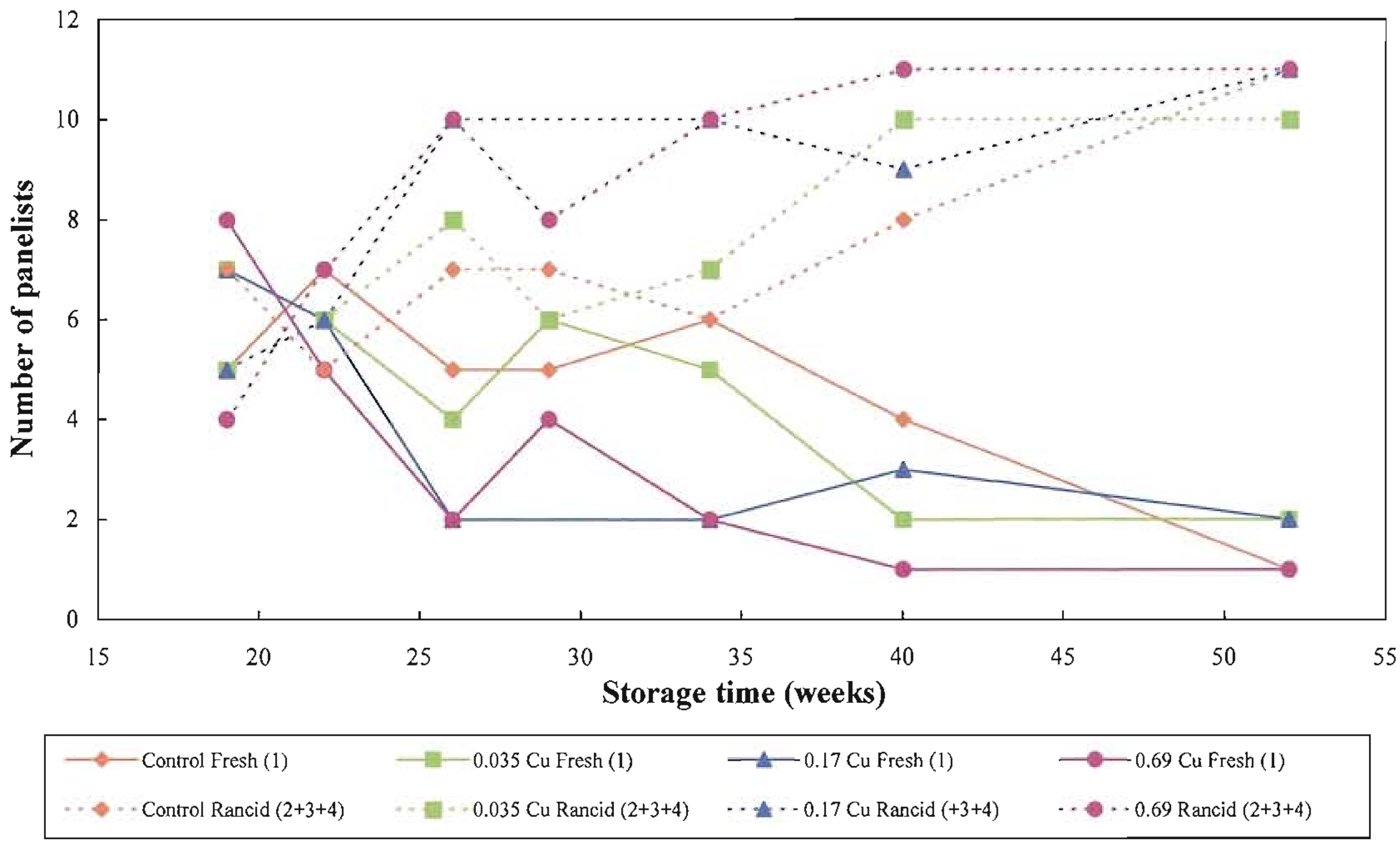

Figure 21: The effect of storage on the sensory quality of palm-olein oil stored at 50°C for a period of 52 weeks. (Option 1).

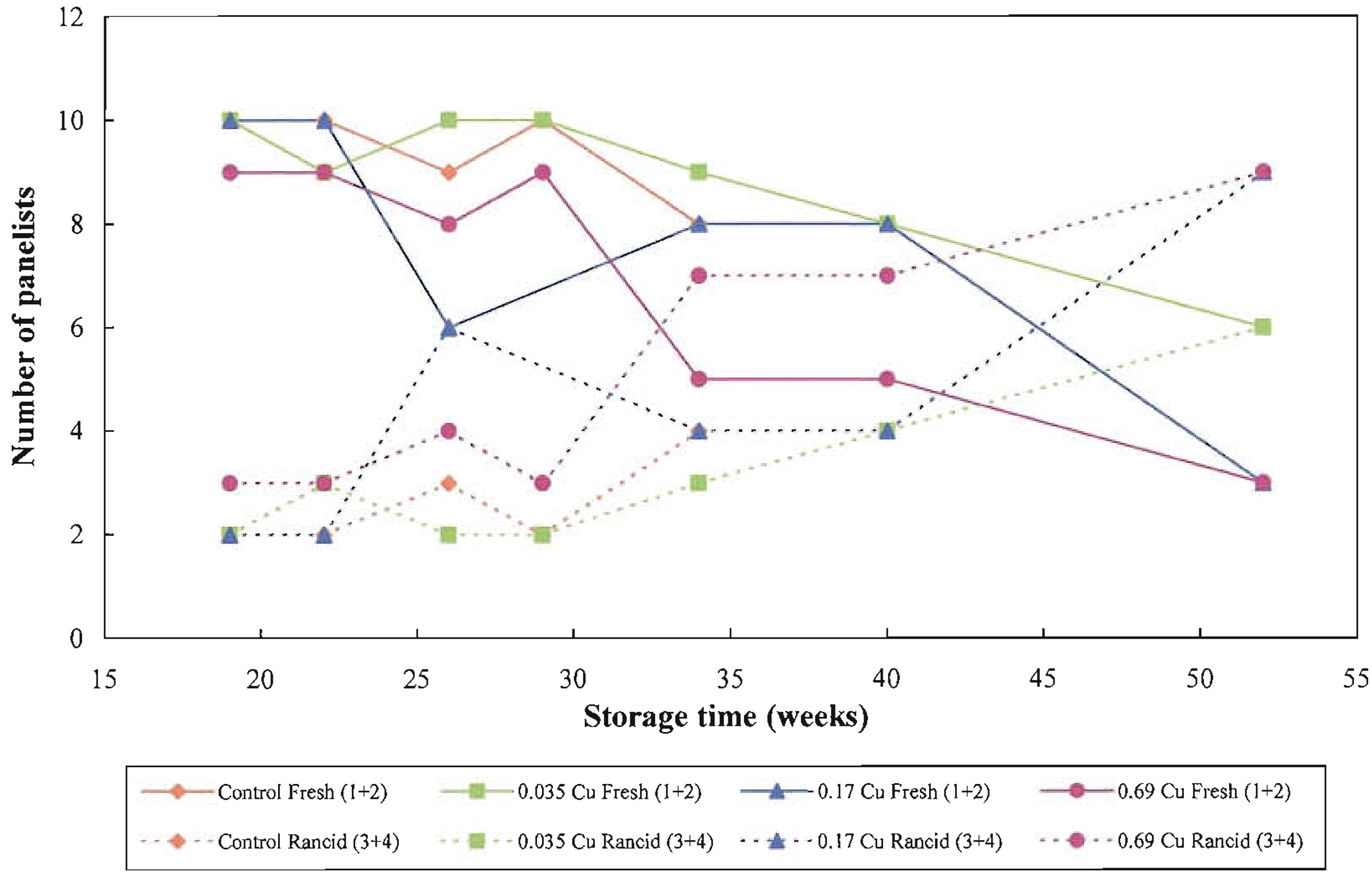

Figure 22: The effect of storage on the sensory evaluation of palm-olein oil stored at 50°C for a period of 52 weeks. (Option 2).

A summary of the results is presented in Table 10.

Table 10: Estimation of rancidity onset time by means of sensory evaluation and chemical parameters.

Samples	Storage time (weeks) at which oil is deemed to be rancid		
	Sensory evaluation*		Chemical parameters♦
	Option 1 Fresh (1), Rancid (2+3+4)	Option 2 Fresh (1+2), Rancid (3+4)	
Control	52	52	22
0.035 mg/kg copper	40	>52	6
0.17 mg/kg copper	26	52	6
0.69 mg/kg copper	26	52	6

* A majority of 9 out of 12 sensory panelists deemed the oil rancid

♦ Chemical parameters defined in Section 3.4 Modelling

4.1.3 Modelling

4.1.3.1 Models

The models are based on the following equation:

Shelf-life (weeks) = B (Intercept) + B_1Variable$_1$ + B_2Variable$_2$ + ·········B_iVariable$_j$

where B_i regression coefficients

Variable$_j$ independent variables such as FFA, PV etc., selected for model by multiple regression.

Model 1

All the data were used to create Model 1. The results of the variables selected by multiple regression to be used in the model are shown in Table 11. The variables were FFA, PV, AV, UV 232 nm, UV 268, OSI, total volatile components, hexanal, t-2-hexenal, t,t-2,4-decadienal, pentanal, total tocopherols, α-tocopherol, α-tocotrienol, γ-tocotrienol, δ-tocotrienol, IV, polyunsaturated fatty acids and copper content.

Table 11: Regression summary for dependant variable: shelf-life of Model 1.

N = 12 cases	**B** regression coefficients	Standard error of B coefficients	p-level
Intercept	23.0	5.85	0.004
AV	-1.31	0.483	0.026
OSI	0.507	0.170	0.017
FFA	-217.4	89.3	0.041

Where R^2 = 0.8115

F (3, 8) = 18.1

Standard error of estimate = 3.54

Explanation of the symbols used (Flury and Riedwyl, 1988; Miller and Miller, 1988; Farrant, 1997):

R^2: square of the correlation coefficient measures the degree of association between the dependant and the independent variables

F: a test of the significance of the relationship between the dependant variable and the set of independent variables. In this case the numerator was calculated to have 3 (4 regression coefficients – 1) degrees of freedom and the denominator had 8 (12 cases – 4 regression coefficients) degrees of freedom.

p-level: resulting probability value from t- and F-test indicates the significance of the values obtained

Std error of estimate: measurement of the dispersion of the observed values about the regression line

The graph of the predicted versus the observed values is shown in Figure 23.

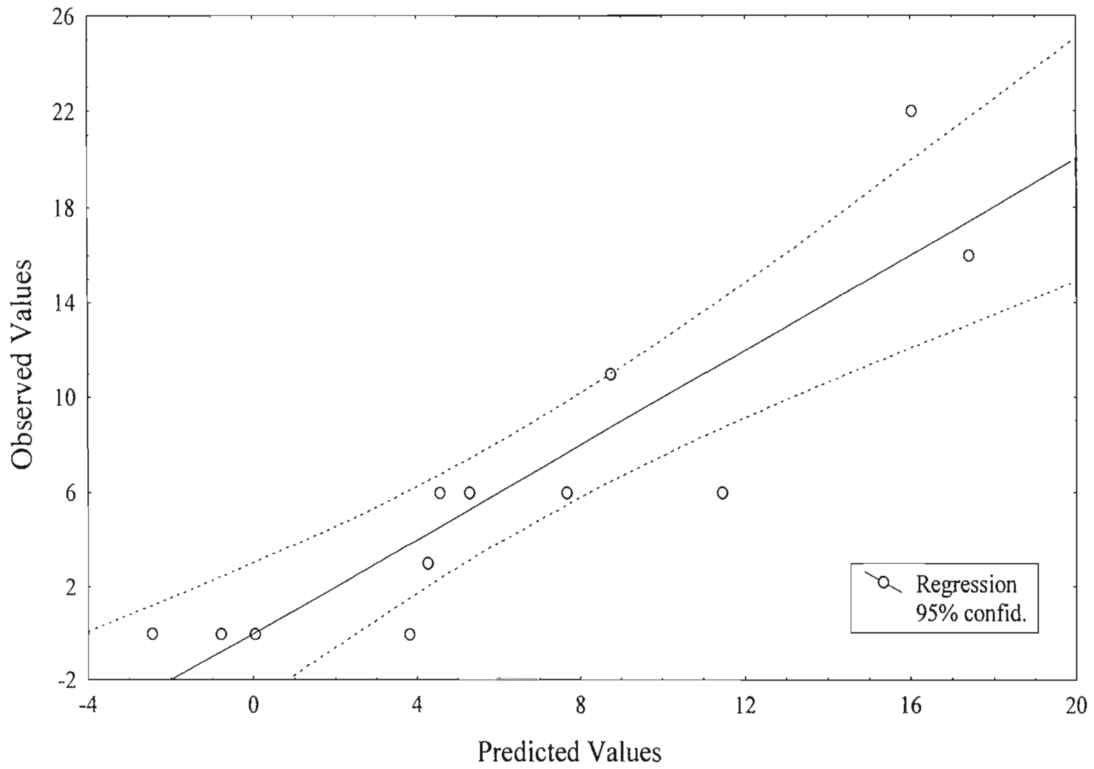

Figure 23: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 1. The dependant variable is the shelf-life.

Model 2

The squares of the values obtained were used to create Model 2. The multiple regression results are shown in Table 12.

Table 12: Regression summary for dependant variable: shelf-life of Model 2.

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	28.7	10.9	0.034
Alpha-tocopherol^2	-0.05	0.038	0.243
FFA^2	-2975	630	0.002
OSI^2	0.02	0.005	0.003
Conjugated triene^2	-11.5	5.00	0.055

Where R^2 = 0.9146

$F(4, 7)$ = 18.7

Standard error of estimate = 2.549

The graph of the predicted versus the observed values is shown in Figure 24.

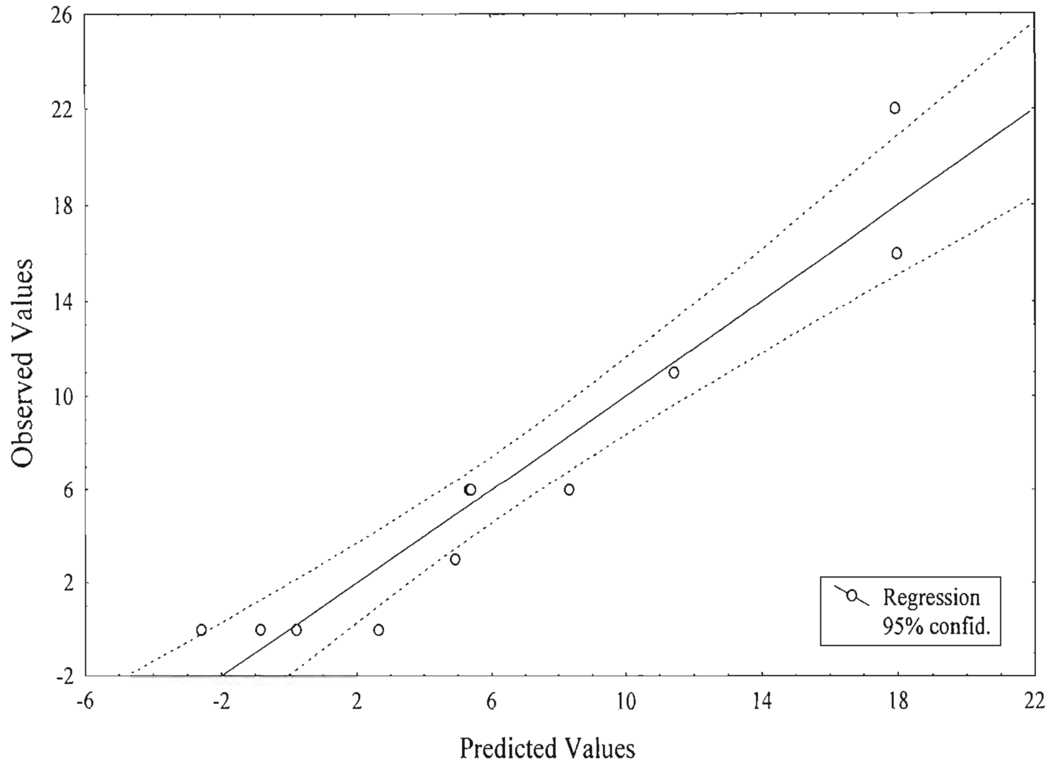

Figure 24: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 2. The dependant variable is the shelf-life.

Model 3

The weighted values (see Materials and Methods, section 3.4) obtained for each variable was used to create Model 3. The multiple regression results are shown in Table 13.

Table 13: Regression summary for dependant variable: shelf-life of Model 3.

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	23.0	5.84	0.004
Weighted AV	-2.29	0.844	0.026
Weighted OSI	0.197	0.066	0.017
Weighted FFA	-3.33	1.37	0.041

Where R^2 = 0.8115

$F(3, 8)$ = 11.5

Standard error of estimate = 3.54

The graph of the predicted versus the observed values is shown in Figure 25.

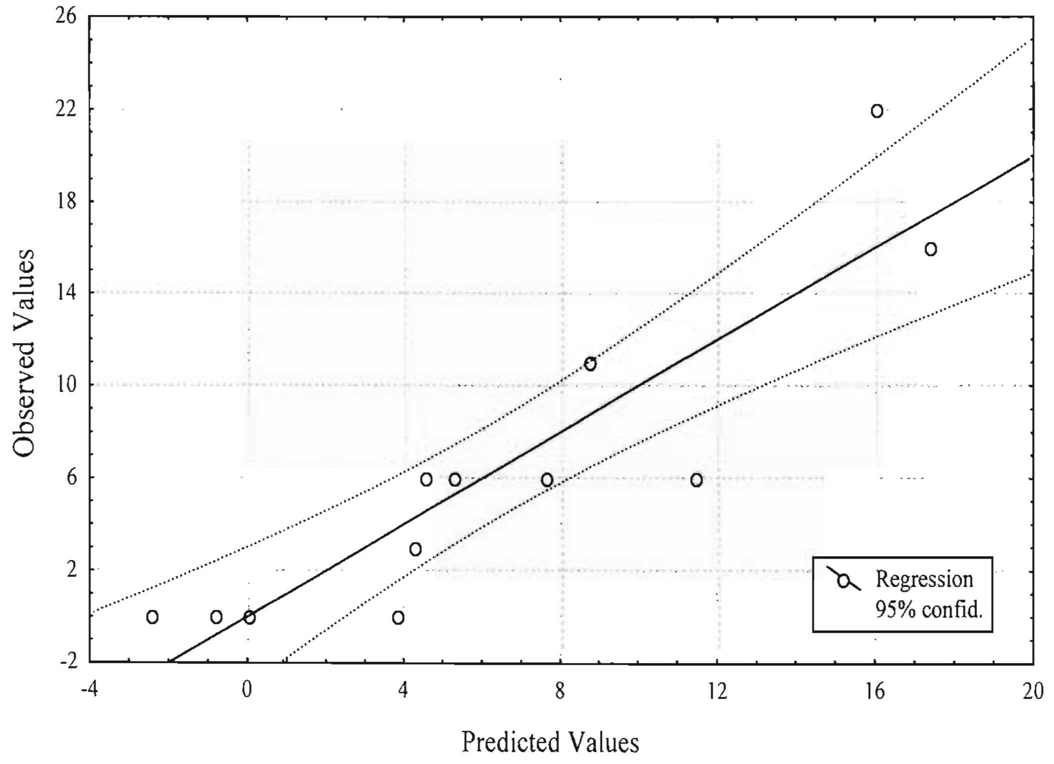

Figure 25: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 3. The dependant variable is the shelf-life.

Model 4

The weighted values obtained for the square value of each variable was used to create Model 4. The multiple regression results are shown in Table 14.

Table 14: Regression summary for dependant variable: shelf-life of Model 4

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	28.7	10.9	0.034
Weighted alpha-tocopherol^2	-0.005	0.004	0.243
Weighted FFA^2	-45.5	9.64	0.002
Weighted OSI^2	0.009	0.002	0.003
Weighted conjugated triene^2	-0.682	0.296	0.055

Where R^2 = 0.9146

$F(4, 7)$ = 18.7

Standard error of estimate = 2.55

The graph of the predicted versus the observed values is shown in Figure 26.

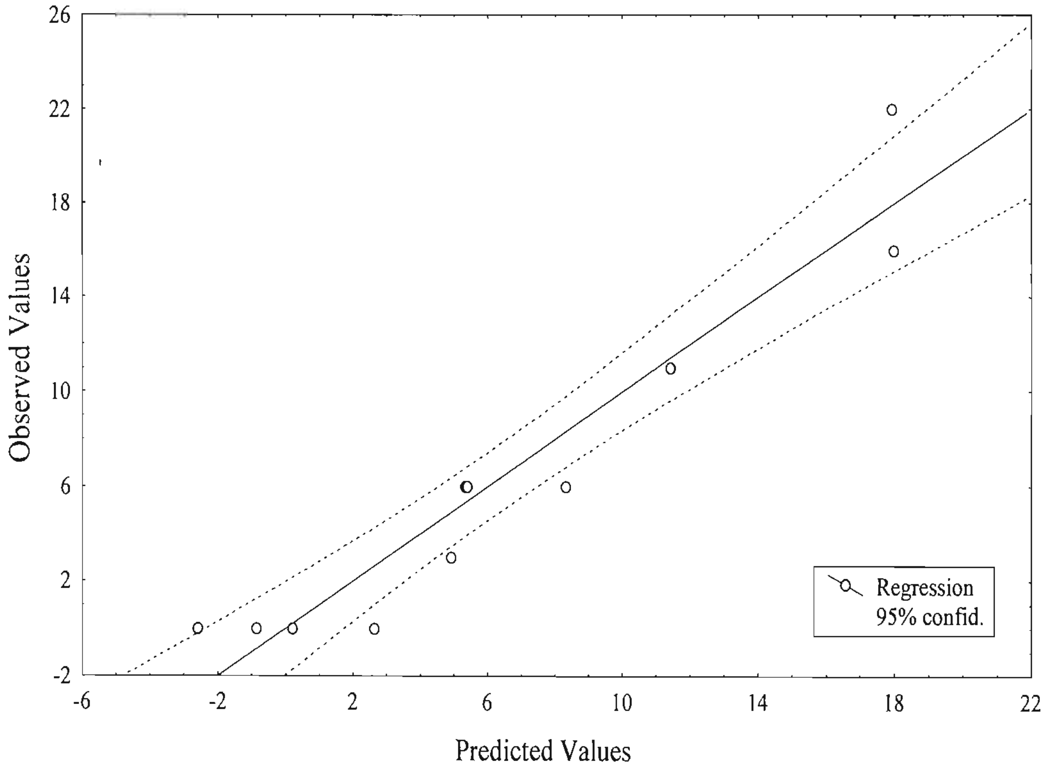

Figure 26: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 4. The dependant variable is the shelf-life.

Model 5

A complex model (Ideal model) where the measured values and the square of those values of all of the variables were used to create Model 5. The results of the variables selected by the multiple regression program are shown in Table 15.

Table 15 Regression summary for dependant variable: shelf-life of Model 5

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.0	3.86	0.000
AV	-1.23	0.312	0.006
OSI^2	0.072	0.020	0.010
OSI	-1.31	0.530	0.042
FFA	-136	61.9	0.063

Where R^2 = 0.9316

$F(4, 7)$ = 23.8

Standard error of estimate = 2.28

The graph of the predicted versus the observed values is shown in Figure 27.

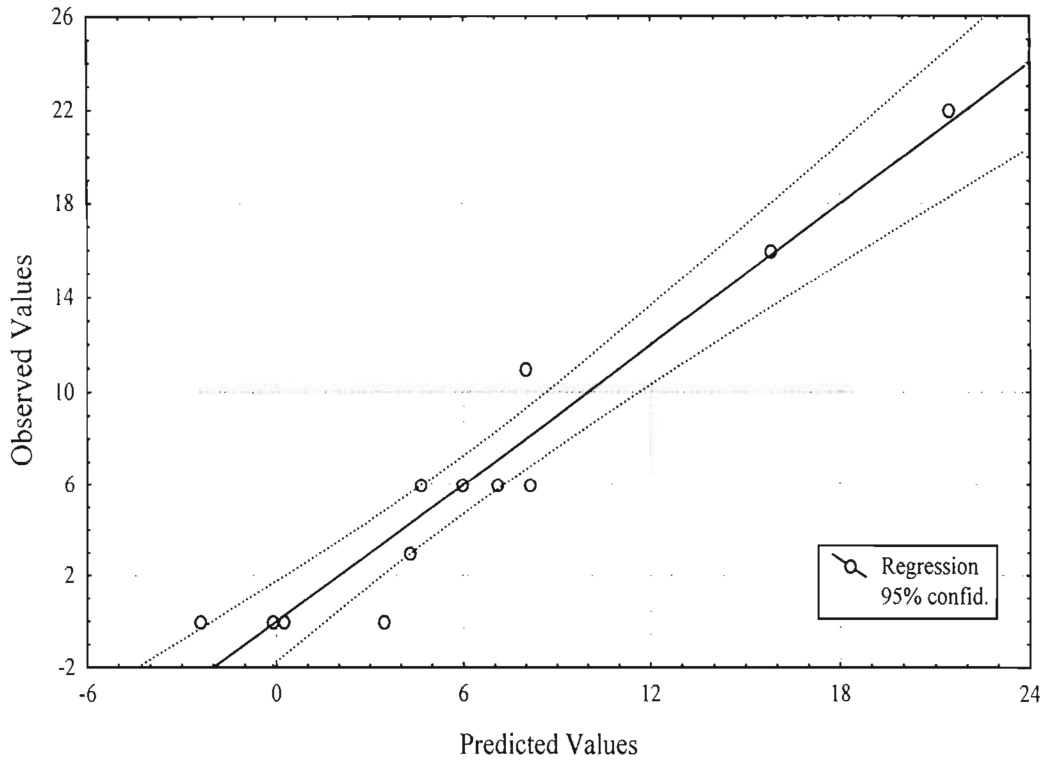

Figure 27: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 5. The dependant variable is the shelf-life.

Model 6

A simple model (Practical model) with variables that are simple methods of analyses was used to create Model 6. The measured values and the square of those values were used to create the model. The measured values for FFA, PV, OSI and conjugated diene/triene value, as well as the square of these values were utilised to create Model 6. The multiple regression results are shown in Table 16.

Table 16: Regression summary for dependant variable: shelf-life of Model 6.

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.7	3.54	0.000
Conjugated triene value	-12.6	2.41	0.001
FFA^2	-1840	430	0.004
OSI^2	0.070	0.017	0.005
OSI	-1.30	0.440	0.021

Where R^2 = 0.9546
F (4, 7) = 36.8
Standard error of estimate = 1.86

The graph of the predicted versus the observed values is shown in Figure 28.

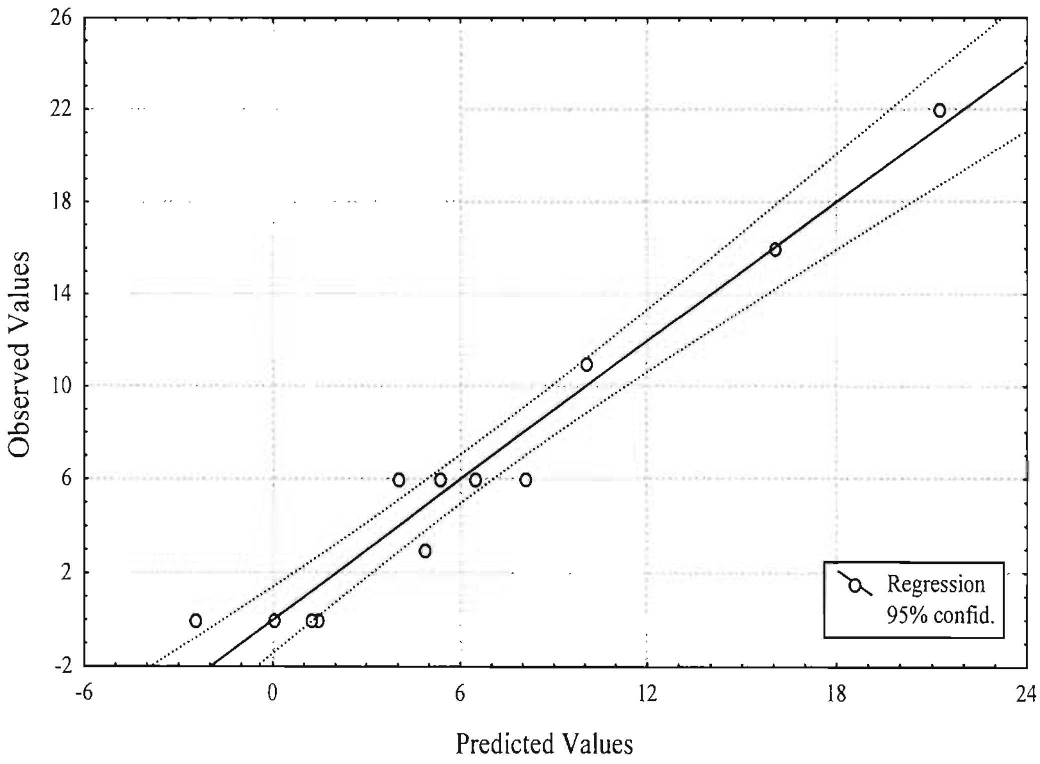

Figure 28: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 6. The dependant variable is the shelf-life.

Model 7

The OSI value and its square were used to create Model 7. The multiple regression results are shown in Table 17.

Table 17: Regression summary for dependant variable: shelf-life of Model 7.

N = 12 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	10.6	5.18	0.071
OSI^2	0.11	0.037	0.016
OSI	-2.18	0.951	0.048

Where R^2 = 0.6985

$F(2, 9)$ = 8.30

Standard error of estimate = 4.56

The graph of the predicted versus the observed values is shown in Figure 29.

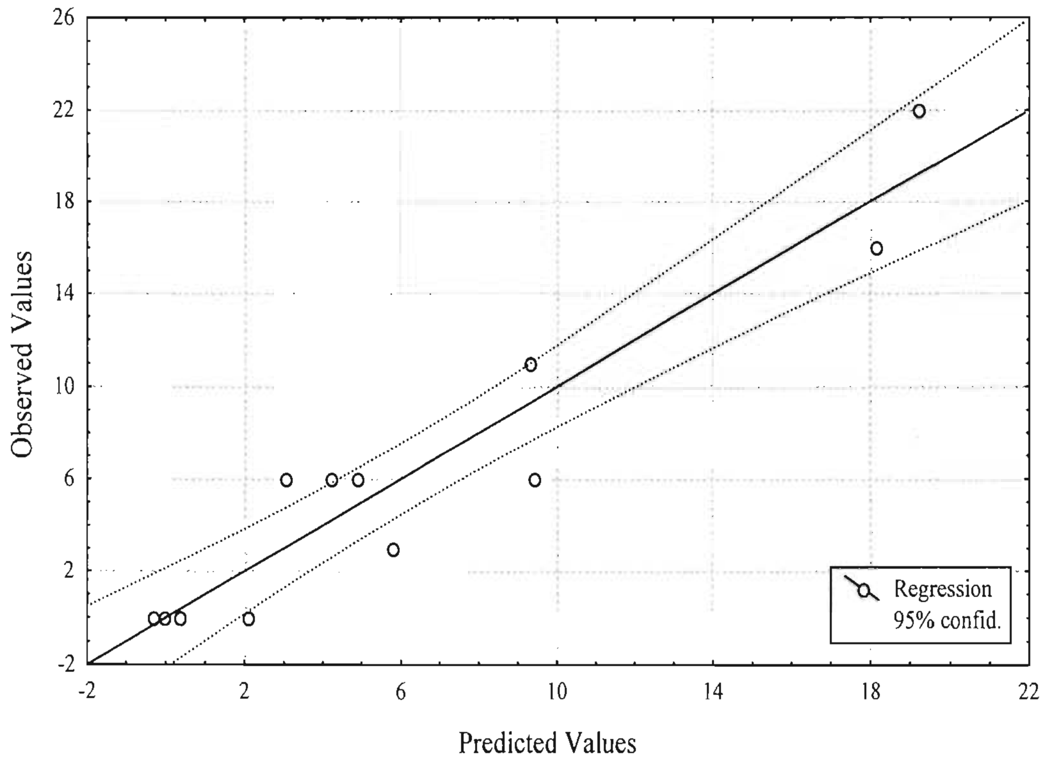

Figure 29: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 7. The dependant variable is the shelf-life.

Model 8

A complex model (Ideal model) as in Model 5, but based on the sensory evaluation, was used to create Model 8. The multiple regression results are shown in Table 18.

Table 18: Regression summary for dependant variable: shelf-life of Model 8.

N = 35 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	20.5	2.33	0.000
Pentanal peak area	-0.446	0.188	0.025
FFA	-95.4	21.8	0.000
AV	-0.728	0.131	0.000
Alpha-tocopherol^2	0.030	0.006	0.000
Copper^2	24.7	3.19	0.000
Total volatile peak area^2	-0.002	0.001	0.001
OSI	1.51	0.093	0.000

Where R^2 = 0.9891

F (7, 27) = 350.4

Standard error of estimate = 1.62

The graph of the predicted versus the observed values is shown in Figure 30.

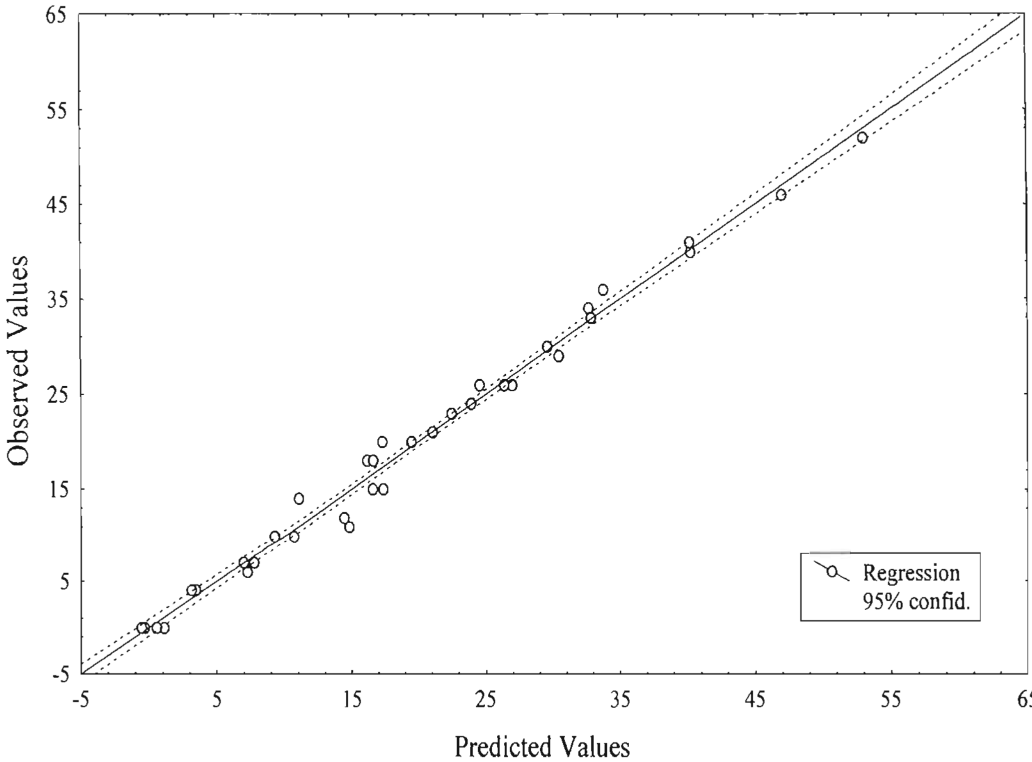

Figure 30: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 8. The dependant variable is the shelf-life.

Model 9

A simple model (Practical model) as in Model 6, but based on the sensory evaluation, was used to create Model 9. The multiple regression results are shown in Table 19.

Table 19: Regression summary for dependant variable: shelf-life of Model 9.

N = 35 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	46.2	2.93	0.000
Conjugated triene value	-14.4	1.34	0.000
OSI^2	0.053	0.005	0.000
FFA	-220	27.7	0.000

Where R^2 = 0.9306

$F(3, 31)$ = 138.6

Standard error of estimate = 3.83

The graph of the predicted versus the observed values is shown in Figure 31.

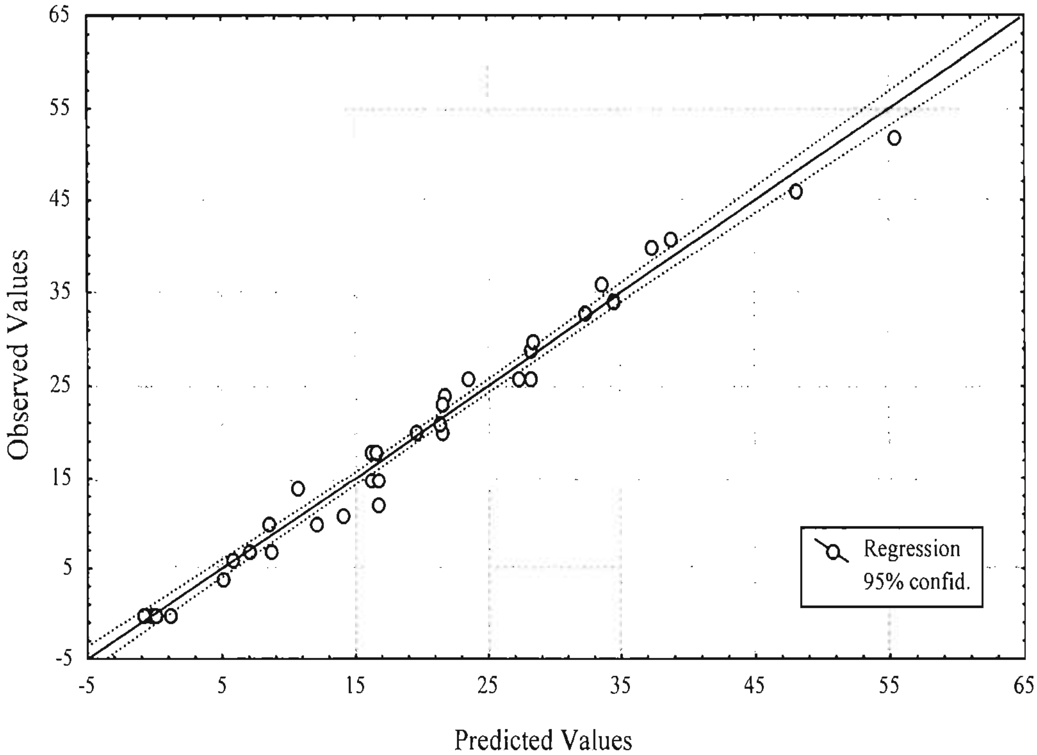

Figure 31: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 9. The dependant variable is the shelf-life.

Model 10

A model using only OSI and OSI^2 as in Model 7, but based on the sensory evaluation, was used to create Model 10. The multiple regression results are shown in Table 20.

Table 20: Regression summary for dependant variable: shelf-life of Model 10.

N = 35 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	23.1	6.80	0.002
OSI	-3.45	1.30	0.012
OSI^2	0.209	0.054	0.001

Where R^2 = 0.5495

$F(2, 32)$ = 19.5

Standard error of estimate = 9.60

The graph of the predicted versus the observed values is shown in Figure 32.

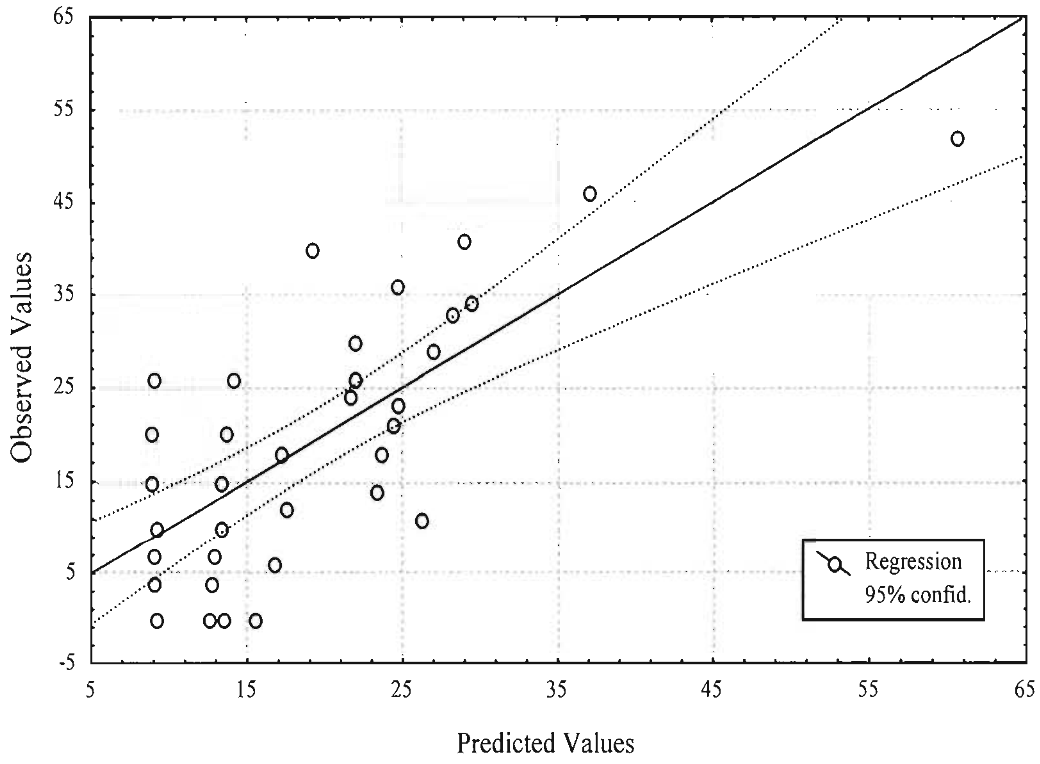

Figure 32: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 10. The dependant variable is the shelf-life.

4.1.3.2 Jackknifing

The practical applicability and reliability of the models was tested applying the jackknifing procedure (Hair et al, 1998).

PV and AV based models

The results of the jackknifing are shown in Table 21. Where the "Ideal model" is as described for Model 5, "Practical model" as described for model 6 and the OSI model as described for Model 7.

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Table 21: Jackknifing results of three selected predictive models for palm-olein oil that was stored for a period of 52 weeks at 50 °C where the shelf-life of the samples was based on the PV and AV values.

		Ideal model		**Practical model**		**OSI model**	
Excluded case	**Observed value**	Predicted value	Observed minus predicted	Predicted value	Observed minus predicted	Predicted value	Observed minus predicted
1	22	19.3	2.7	18.1	3.9	20.0	2.0
2	6	9.2	-3.2	9.2	-3.2	2.3	3.7
3	6	5.8	0.2	5.0	1.0	-0.69	6.6
4	6	8.4	-2.4	6.9	-0.9	3.8	2.2
5	16	15.3	0.7	16.1	-0.1	9.8	6.2
6	0	4.9	-4.9	2.9	-2.9	8.4	-8.4
7	0	-4.5	4.5	-4.6	4.6	0.4	-0.4
8	0	0.4	-0.4	2.3	-2.3	7.2	-7.2
9	11	7.5	3.5	9.8	1.2	6.6	4.4
10	6	4.1	1.9	3.4	2.6	5.2	0.8
11	3	4.5	-1.5	5.3	-2.3	7.4	-4.4
12	0	-0.3	0.3	0.1	-0.1	4.9	-4.9
Mean			0.1167		0.1250		0.0533
Std error of estimate			2.8006		2.6189		5.1430
95% confidence interval			± 6.2		± 5.8		± 11.3

All of the predicted values of the jackknifing results of the Ideal, Practical and OSI models were within the 95 % confidence level of 6.2, 5.8 and 11.3 weeks, respectively. The observed minus predicted values (errors) of the models is represented graphically in Figure 33. The errors were grouped into 3 categories namely: 0 to ± 2 weeks, ± 2 to ± 4 weeks and more than + 4 weeks and less than – 4 weeks on the x-axis. The percentage cases with an error falling in each category were calculated from the total number of cases, which were 12 in this instance. The total percentage of cases with an error between 0 to ± 2 weeks was 50, 41.7 and 25 % for the Ideal, Practical and OSI models, respectively. The percentage cases with an error between ± 2 to ± 4 were 33.4, 50 and 16.7 % for the three models in the same order, respectively. The percentage cases with an error of more than + 4 weeks or less than – 4 weeks were 16.6, 8.3 and 58.3 % for the three models respectively.

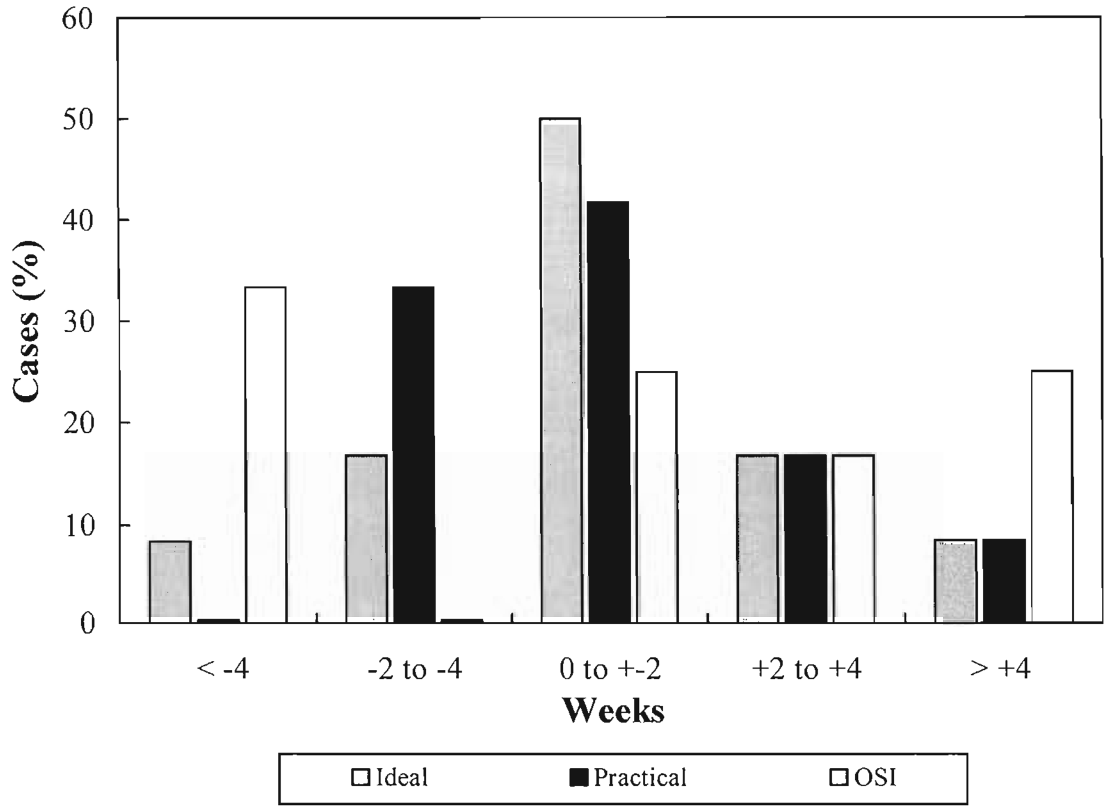

Figure 33: The percentage cases that fall within < - 4, - 2 to - 4, 0 to ± 2, 2 to + 4 and > + 4 weeks when the jackknifing procedure had been applied to the Ideal, Practical and OSI models where the shelf-life was based on PV and AV values.

Sensory based models

The results of the jackknifing on the selected models that were based on sensory evaluation are shown in Table 22.

The 95 % confidence level of prediction for the Ideal model is 7.3 weeks with one case outside the level of confidence and for the Practical model the 95 % level of confidence is 8.3 weeks with one case outside the level of confidence and in the OSI model two cases are on or outside the 95 % confidence level of 21.4 weeks.

Table 22: Jackknifing results of three selected models that were based on the sensory evaluation.

Excluded case	Observed value (weeks)	Ideal model		Practical model		OSI model	
		Predicted value	Observed minus predicted	Predicted value	Observed minus predicted	Predicted value	Observed minus predicted
1	52	58.1	-6.1	56.6	-4.6	73.4	-21.4
2	40	40.5	-0.5	35.6	4.4	18.1	21.9
3	26	29.2	-3.2	25.3	0.7	8.0	18.0
4	26	32.9	-6.9	21.2	4.8	11.9	14.1
5	46	51.9	-5.9	49.6	-3.6	35.9	10.1
6	34	37.7	-3.7	30.1	3.9	29.1	4.9
7	20	15.6	4.4	16.9	3.1	8.1	11.9
8	20	19.0	1.0	15.9	4.1	12.6	7.4
9	41	39.9	1.1	40.0	1.0	28.2	12.8
10	29	31.3	-2.3	28.1	0.9	26.9	2.1
11	15	20.2	-5.2	19.5	-4.5	8.4	6.6
12	15	18.6	-3.6	14.4	0.6	13	2.0
13	36	33.6	2.4	32.9	3.1	24.2	11.8
14	24	30.9	-6.9	18.2	5.8	21.5	2.5
15	10	10.8	-0.8	11.0	-1.0	9.1	0.9
16	10	9.1	0.9	7.0	3.0	13.8	-3.8
17	33	32.8	0.2	34.8	-1.8	27.9	5.1
18	21	20.6	0.4	16.0	5.0	24.5	-3.5
19	7	8.3	-1.3	6.5	0.5	9.2	-2.2
20	7	11.2	-4.2	6.9	0.1	13.6	-6.6
21	30	29.5	0.5	29.0	1.0	21.5	8.5
22	18	15.9	2.1	19.8	-1.8	23.9	-5.9
23	4	5.2	-1.2	11.7	-7.7	9.4	-5.4
24	4	2.9	1.1	10.8	-6.8	13.7	-9.7
25	26	24.4	1.6	29.3	-3.3	21.7	4.3
26	14	10.1	3.9	12.7	1.3	23.7	-9.7
27	0	-0.4	0.4	2.3	-2.3	9.8	-9.8
28	0	-0.7	0.7	3.5	-3.5	14.1	-14.1
29	23	23.6	-0.6	24.5	-1.5	24.8	-1.8
30	11	17.1	-6.1	13.9	-2.9	27.0	-16
31	18	11	7	6.8	11.2	17.1	0.9
32	6	8.4	-2.4	9.0	-3.0	17.2	-11.2
33	12	18	-6	18.5	-6.5	17.7	-5.7
34	0	1.4	-1.4	2.5	-2.5	16.3	-16.3
35	0	8.2	-8.2	-3.4	3.4	14.3	-14.3
Mean			-1.3943		0.0171		-0.3314
Std error of estimate			3.5984		4.0867		10.527
95% confidence interval			± 7.3		± 8.3		± 21.4

The observed minus predicted values (errors) of the models are represented graphically in Figure 34. The percentage cases with an error falling in each category were calculated from the total of 35 cases. The total percentage of cases with an error between 0 to ± 2 weeks was 45.7, 37.1 and 11.4 % for the Ideal, Practical and OSI models, respectively. The percentage cases with an error between ± 2 to ± 4 was 22.9, 34.3 and 31.4 % for the three models in the same order, respectively. The percentage cases with an error of more than + 4 weeks or less than – 4 weeks was 31.4, 14.3 and 74.2 % for the three models respectively.

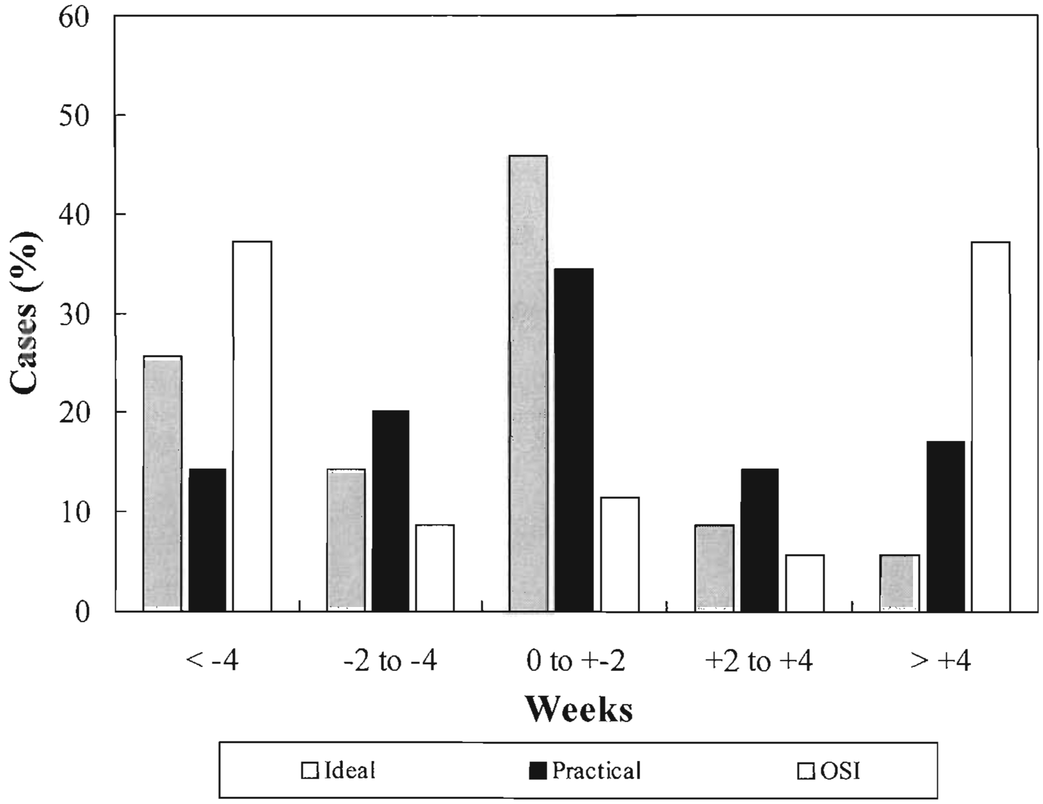

Figure 34: The percentage cases that fall within < - 4, - 2 to - 4, 0 to ± 2, 2 to + 4 and > + 4 weeks when the jackknifing procedure had been applied to the Ideal, Practical and OSI models where the shelf-life was based on the sensory evaluation.

4.2 SUNFLOWER SEED OIL

4.2.1 Composition of oil

The fatty acid composition of the sunflower seed oil that was used for the shelf-life test is given in Table 23. The fatty acid composition of typical sunflower seed oil has been included (Codex Alimentarius Commission, 1997).

Table 23: Fatty acid composition (g/100 g fatty acids) of the sunflower seed oil used and that of a typical sunflower seed oil (Codex Alimentarius Commission, 1997).

Fatty acids	Sunflower seed oil	Typical sunflower seed oil
C14 : 0	0.07	ND*-0.2
C16 : 0	6.23	5.6-7.6
C16 : 1	0.07	ND*-0.3
C18 : 0	5.62	2.7-6.5
C18 : 1	20.18	14.0-39.4
C18 : 2	65.08	48.3-74.0
C18 : 3	0.08	ND*-0.2
C20 : 0	0.36	0.2-0.4
C20 : 1	0.12	ND*-0.2
C22 : 0	0.94	0.5-1.3
C24 : 0	0.25	0.2-0.3

* ND – Non detectable, defined as ≤ 0.05 g/100g fatty acids

The copper, iron, moisture and TBHQ contents are given in Table 24.

Table 24: Copper, iron, moisture and TBHQ content of the sunflower seed oil.

	Copper mg/100g	Iron mg/100g	Moisture g/100g	TBHQ (mg/kg)
Sunflower seed oil	< 0.48	0.17	0.17	Not detected*

* Not detectable defined as ≤ 2.0 mg/kg TBHQ

4.2.2 Shelf-life tests

The four sample treatments were the sunflower seed Control oil, sunflower seed oil with 54 mg/kg TBHQ added, sunflower seed oil with 217 mg/kg TBHQ added and sunflower seed oil with 435 mg/kg TBHQ added.

4.2.2.1 Free fatty acids

The effect of storage at 30°C on the FFA (% oleic acid equivalents) content of the four sunflower seed oil sample treatments is given in Figure 35.

The FFA content of all the samples increased gradually over the 52 weeks. The FFA content of the Control increased from 0.10 % oleic acid at Day 0 to 0.36 % oleic acid at Week 52, which was slightly higher than the samples with TBHQ. The sample with the highest concentration of TBHQ (435 mg/kg) had the lowest FFA value of 0.31 % oleic acid at Week 52.

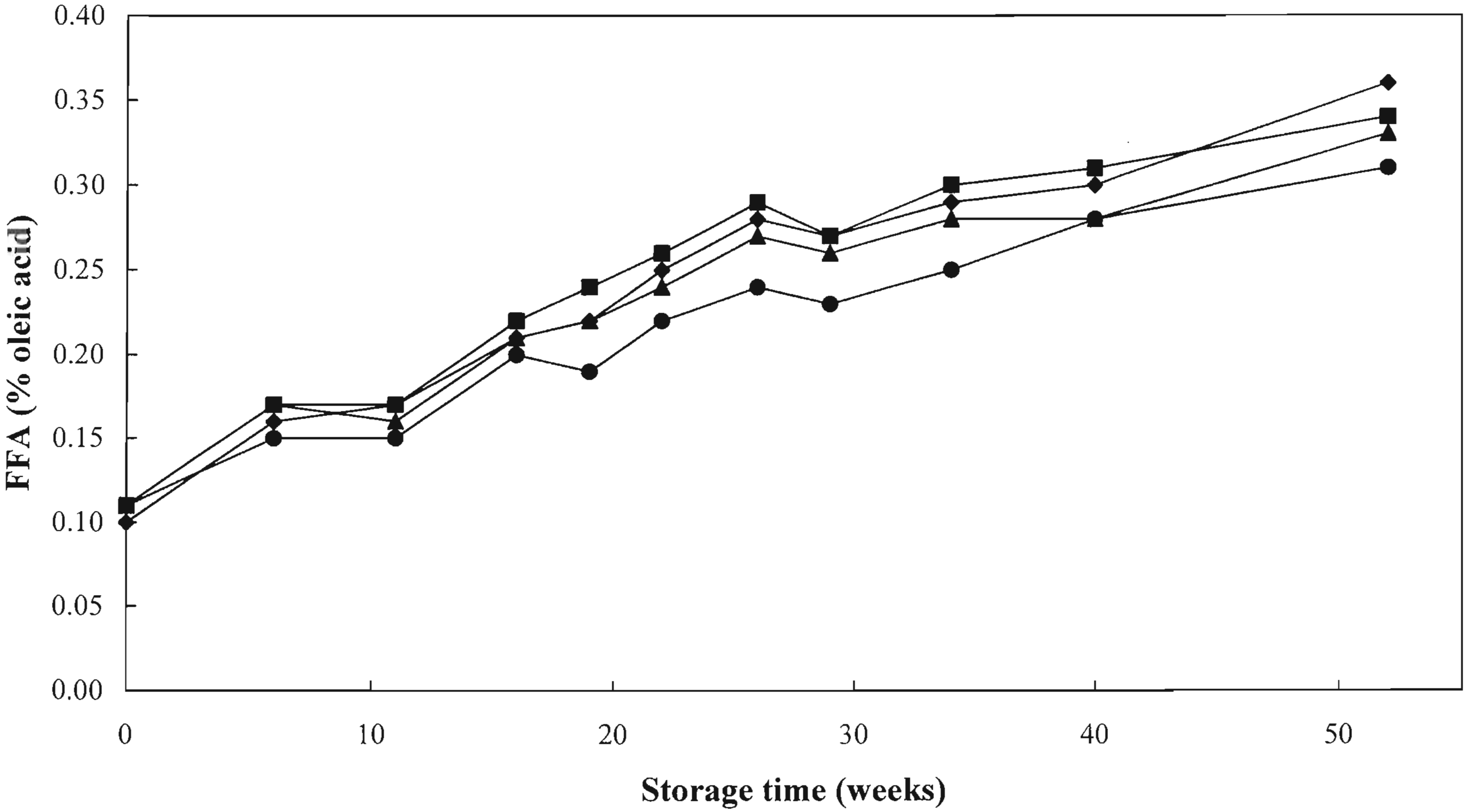

Figure 35: The effect of storage at 30°C for 52 weeks on the free fatty acid (% oleic acid) content of the sunflower seed oil samples: Control (♦); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.2 Peroxide value

The effect of storage at 30°C on the PV of the four sample treatments is given in Figure 36.

The PV of all the samples increased steadily up to Week 34, after which the samples containing TBHQ reached a plateau and the Control appeared to decrease. The rate of increase for the Control sample was highest followed by the sample with 54 mg/kg TBHQ, then 217 mg/kg TBHQ and the slowest rate was the sample with 435 mg/kg TBHQ. The Control sample reached the highest PV at Week 34.

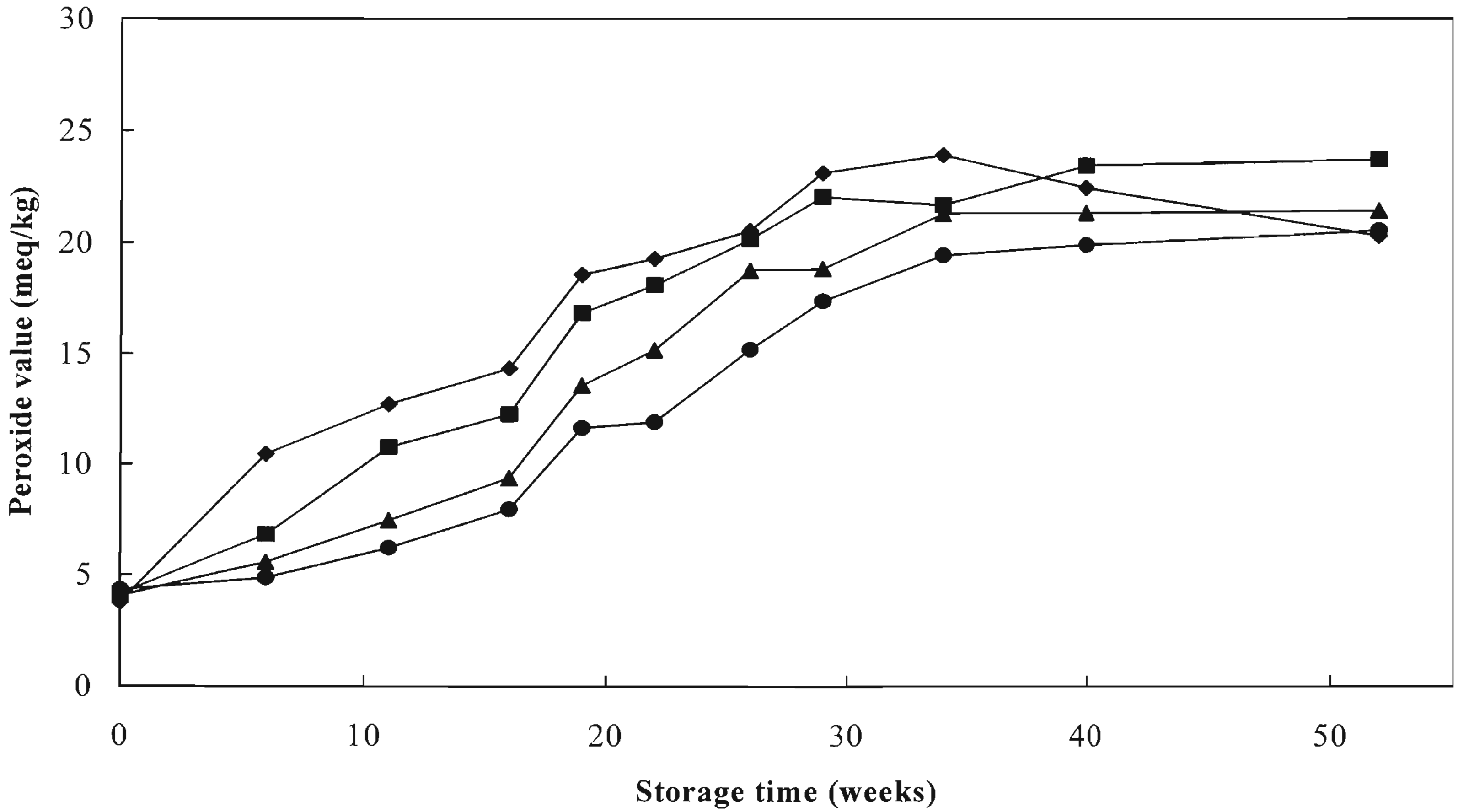

Figure 36: The effect of storage at 30°C for 52 weeks on the peroxide value (meq/kg) of the sunflower seed oil samples: Control (♦); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.3 Anisidine value

The effect of storage at 30°C on the AVs of the four samples is given in Figure 37.

There was an increase in AV for all the samples. The AV for the Control was the highest. The AV for the Control appeared to remain constant from Week 40 onwards. The increase in AV for the sample with 54 mg/kg TBHQ was slightly higher than for the samples with 217 and 435 mg/kg. The AV of the samples containing 217 and 435 mg/kg TBHQ increased at very similar rate with little difference in their values. It appears that the samples containing TBHQ reached a plateau after Weeks 22–26.

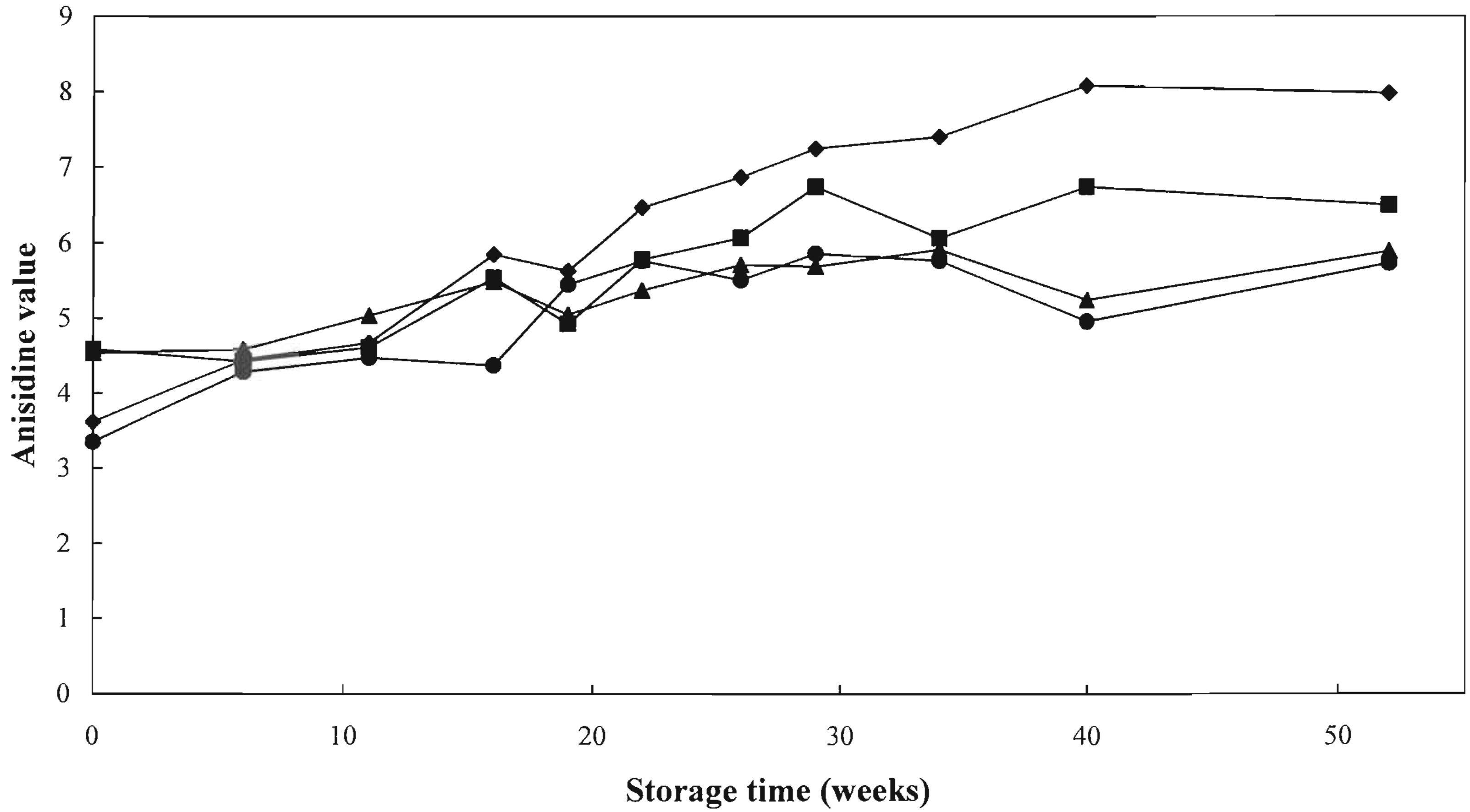

Figure 37: The effect of storage at 30°C for 52 weeks on the anisidine value of the sunflower seed oil samples: Control (♦); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.4 Totox value

The effect of storage at 30°C on the Totox value of the four samples is given in Figure 38.

The Totox value (2PV + AV) of all the samples increased during the storage period. The increase in Totox value of the Control was the highest followed in order by lower levels in the 54, 217 and 435 mg/kg TBHQ containing samples respectively. The values of the Control sample appeared to decrease after Week 34, whereas the values for the TBHQ containing samples seemed to reach a plateau after Week 34.

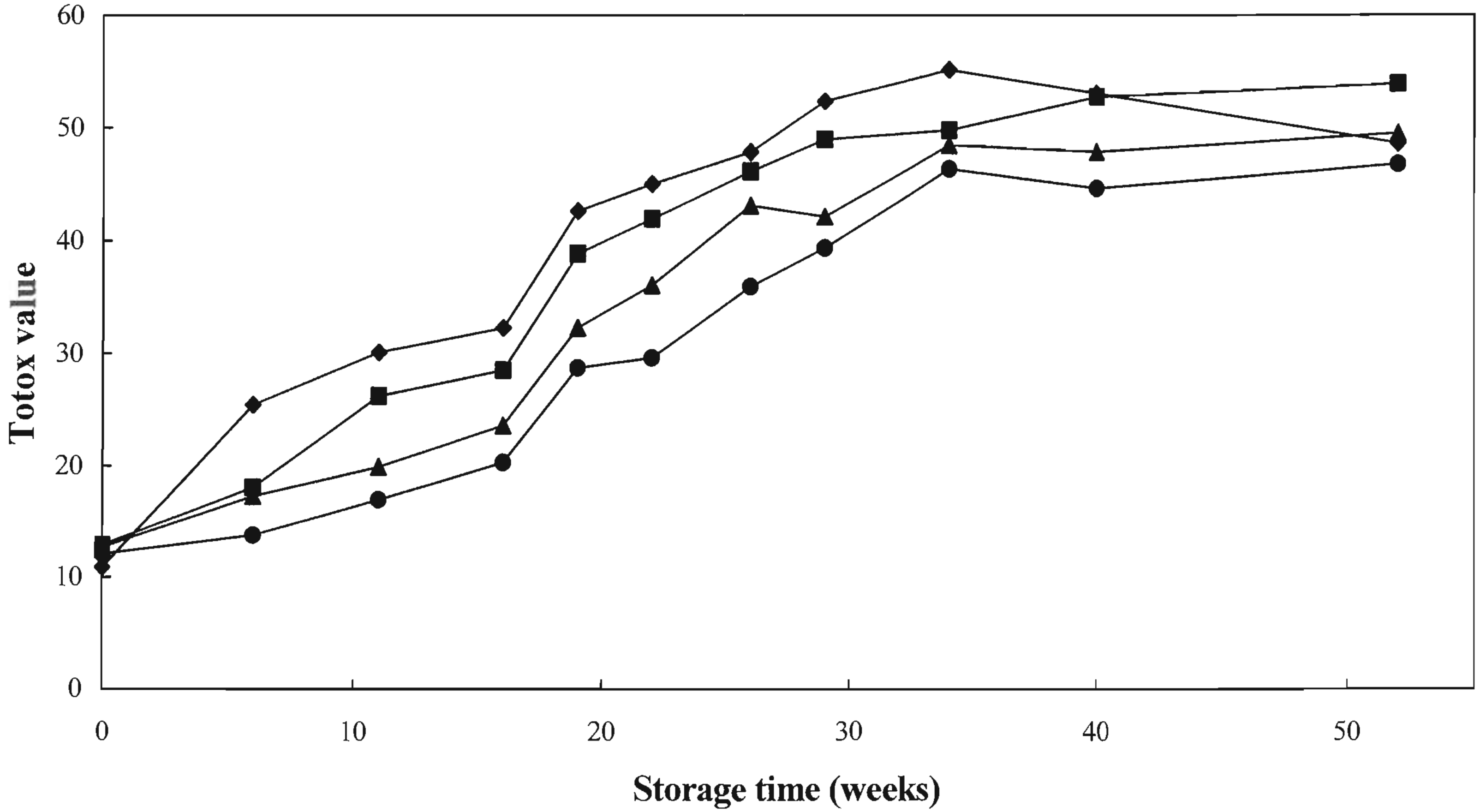

Figure 38: The effect of storage at 30°C for 52 weeks on the Totox value of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.5 Oxidative stability Index

The effect of storage at 30°C on the OSI conducted at 100°C of the four treatments is given in Figure 39.

There were pronounced differences in the curves and oxidative stability values of the four sample treatments. The Control had the lowest values. The oxidative stability of the Control was at 9.1 h at time 0 storage and decreased slowly to 6.7 h at Week 52. The higher the concentration of TBHQ in the samples, the longer the oxidative stability was. The oxidative stability of the sample with 54 mg/kg TBHQ was slightly better than the Control sample. The oxidative stability started at 16.6 h and decreased to 7.9 h at Week 52. The sample with 217 mg/kg TBHQ had double the stability of the 54 mg/kg TBHQ. At time 0 it was 32.1 h and decreased to 15.5 h at Week 52. The sample with 435 mg/kg had values of about 10 h longer than the sample with 217 mg/kg TBHQ. It started at 43.5 h and decreased to 27.6 h at Week 52. The initial decrease in time 0 to Week 11 was more rapid for the samples with 217 and 435 mg/kg TBHQ and was followed by a more gradual decrease in oxidative stability values.

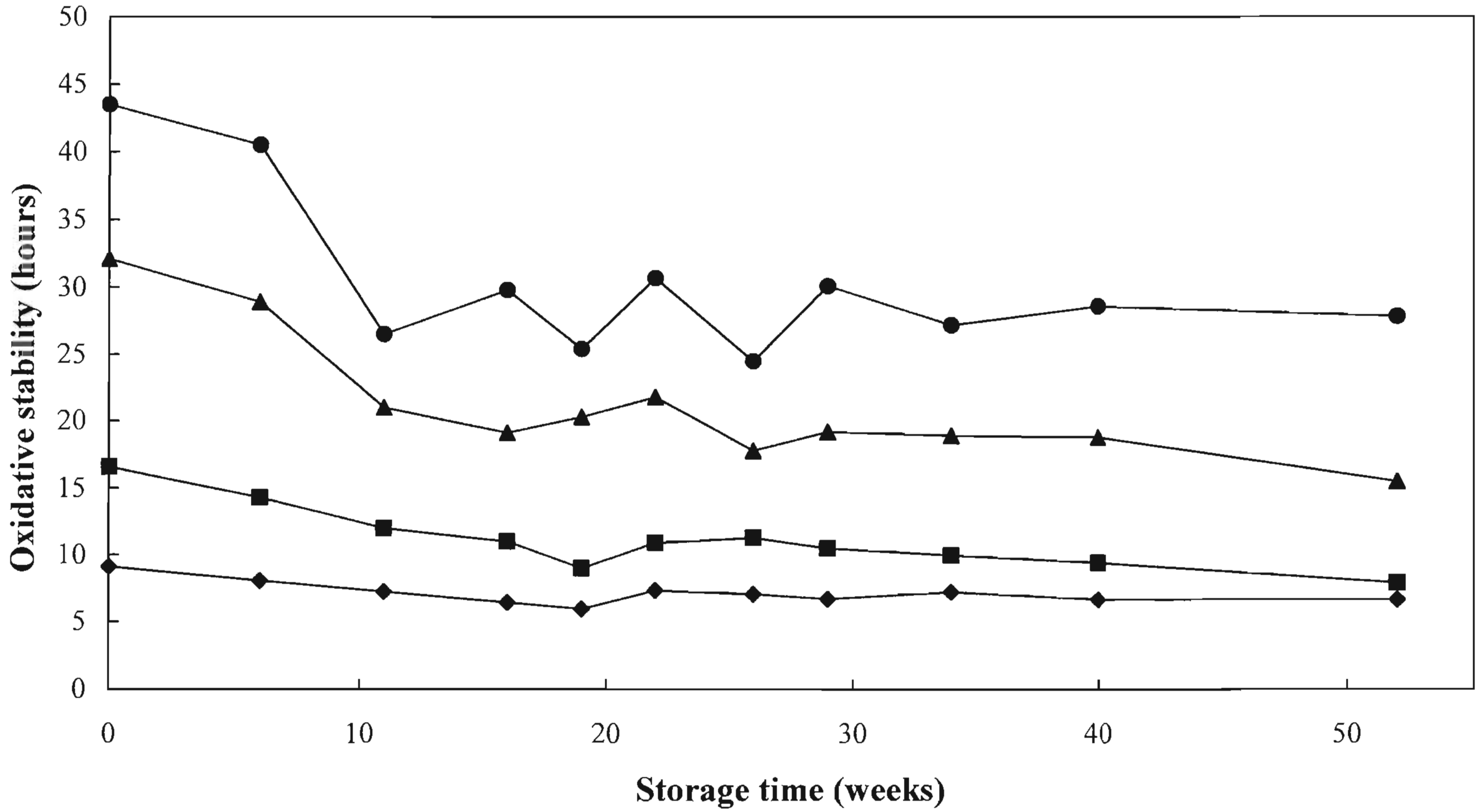

Figure 39: The effect of storage at 30°C for 52 weeks on the oxidative stability (hrs) conducted at 100° C of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.6 Tocopherols

Total tocopherols

The effect of storage at 30°C for a period of 52 weeks on the total tocopherol content of the four treatments is given in Figure 40.

The total tocopherol content in all the samples decreased only slightly over the 52-week storage period. The sample with the highest concentration of TBHQ (435 mg/kg), had slightly higher values after 52 weeks than the other samples, 41.6 mg/100 g compared to 38.4, 38.9 and 38.8 mg/100 g for the Control, 54 mg/kg and 217 mg/kg TBHQ containing samples, respectively.

The change in total and individual tocopherol content (mg/100 g) from the values obtained at Day 0 and after 52 weeks of storage is given in Table 25.

Table 25: Total and individual tocopherols (mg/100 g) of sunflower seed oil after 52-week storage period at 30°C.

Tocopherols	**Tocopherol content (g/100 g)**				
	Day 0	**Week 52**			
		Control	54 mg/kg TBHQ	217 mg/kg TBHQ	435 mg/kg TBHQ
Total tocopherols	47.2	38.4	38.9	38.8	41.6
Alpha-tocopherol	46.2	36.6	37.1	37.0	39.8
Beta-tocopherol	0.5	1.34	0	0	0
Gamma-tocopherol	0.9	1.8	1.7	1.8	1.8

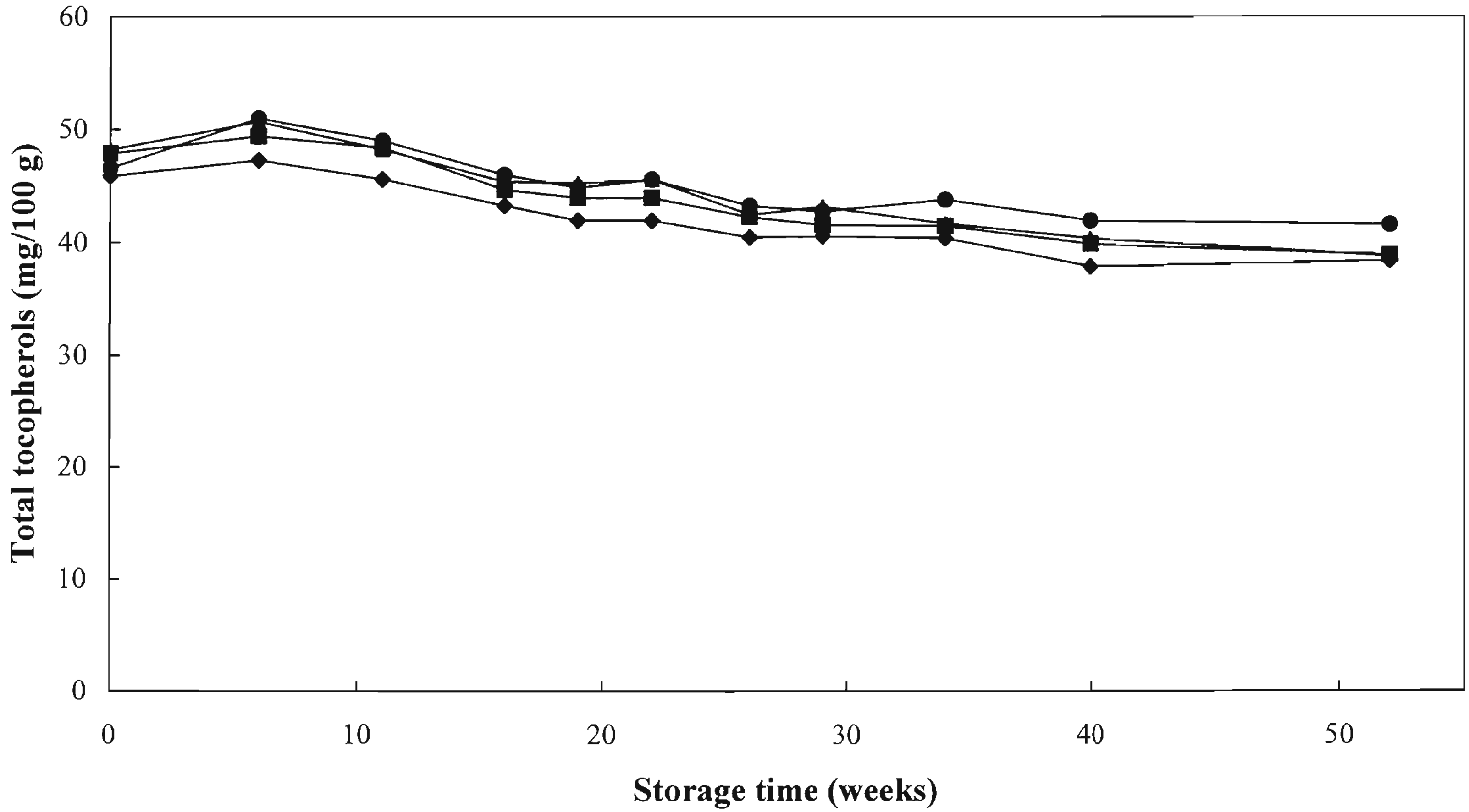

Figure 40: The effect of storage at 30°C for 52 weeks on the total tocopherol content (mg/100 g) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

Alpha-tocopherol

The effect of storage at 30°C for a period of 52 weeks on the alpha-tocopherol content of the four treatments is given in Figure 41.

The decrease in alpha-tocopherol in all the samples during the storage period appeared very similar to the decrease of the total tocopherols. The sample containing 435 mg/kg TBHQ once again had slightly higher values of alpha-tocopherol 39.8 mg/100 g at Week 52 compared to the 36.6, 37.1 and 37.0 mg/100 g alpha-tocopherol values of the Control and the 54 and 217 mg/kg TBHQ containing samples, respectively.

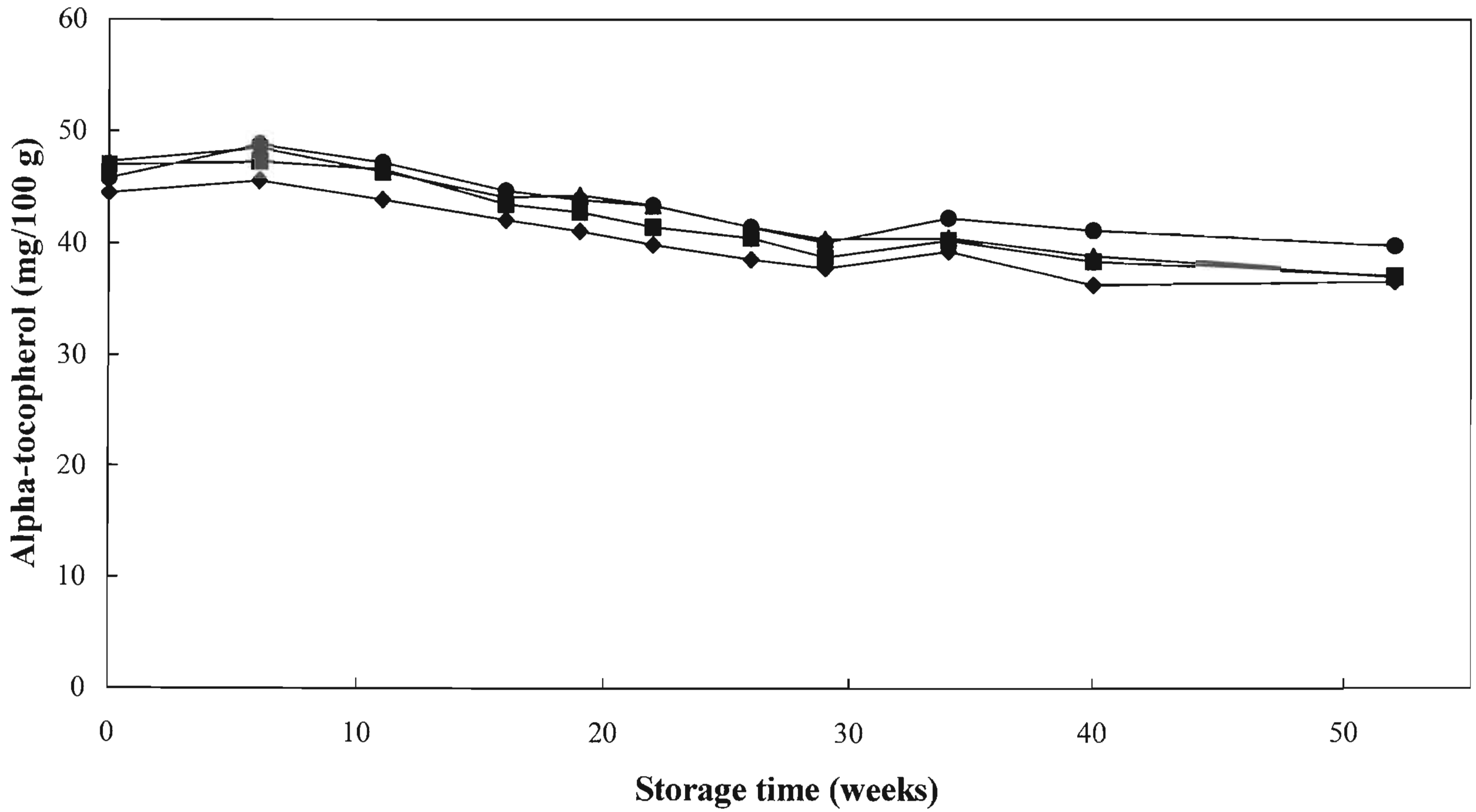

Figure 41: The effect of storage at 30°C for 52 weeks on the alpha-tocopherol content (mg/100 g) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

Beta-tocopherol

The effect of storage at 30°C for a period of 52 weeks on the beta-tocopherol content of the four treatments is given in Figure 42.

Low values of beta-tocopherol were obtained for all the samples during the storage period. The values showed no pattern and fluctuated in a narrow range of 0-1.35 mg/100g.

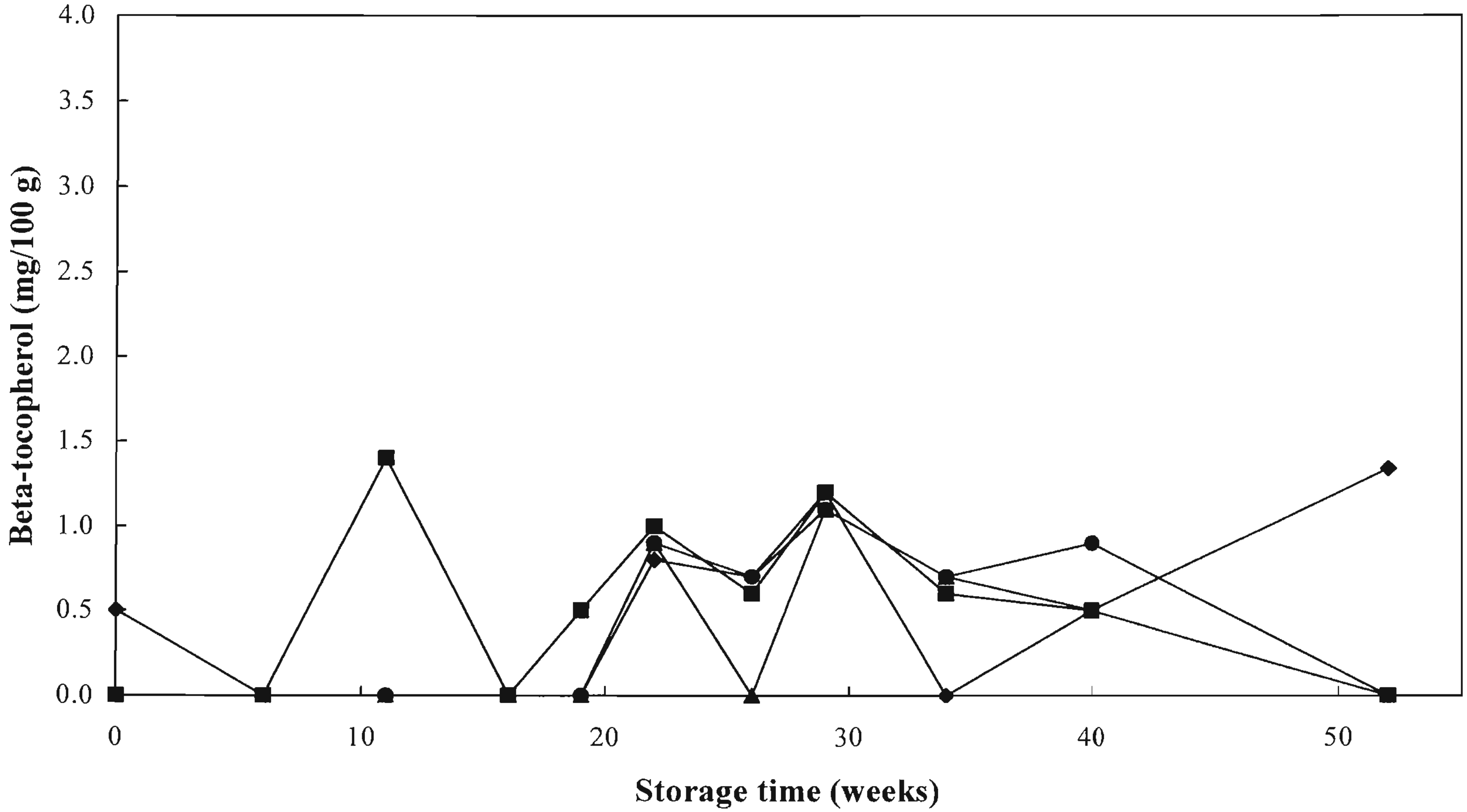

Figure 42: The effect of storage at 30°C for 52 weeks on the beta-tocopherol content (mg/100 g) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

Gamma-tocopherol

The effect of storage at 30°C for a period of 52 weeks on the gamma-tocopherol content of the four treatments is given in Figure 43.

The gamma-tocopherol content was also low and fluctuated between 0.9-2.2 for all of the sample values during the storage period. The variations are due to sampling and analytical error and no conclusion about increases or decreases would be possible.

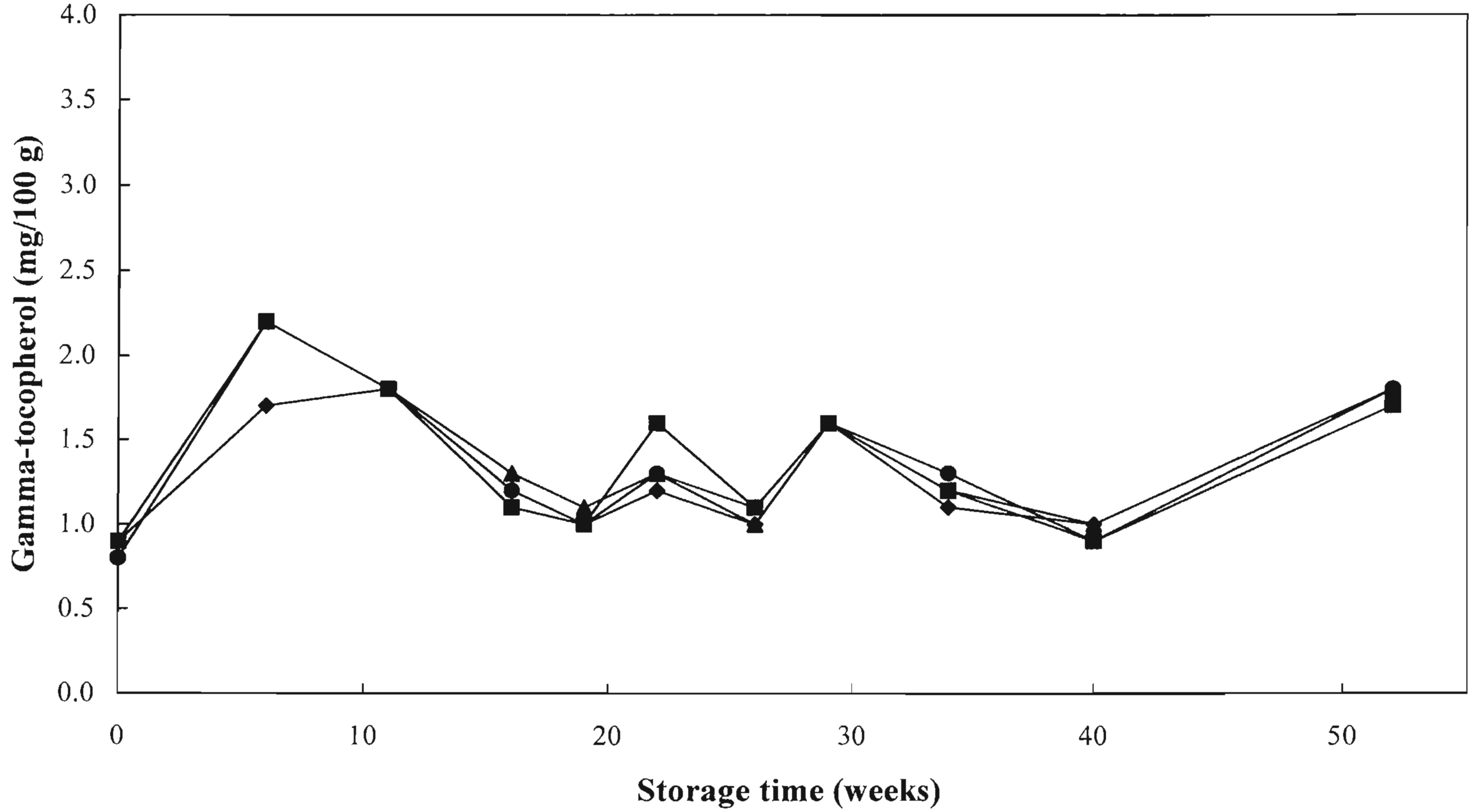

Figure 43: The effect of storage at 30°C for 52 weeks on the gamma-tocopherol content (mg/100 g) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.7 Conjugated dienes and triene values

The effect of storage at 30°C for a period of 52 weeks on the conjugated diene and triene values of the four treatments are given in Figures 44 and 45, respectively.

Conjugated dienes (UV 232 nm)

For all samples there was only a very slight increase in CV during storage. The values of the Control appeared to be higher than the values of the samples containing TBHQ. The values for the 54 mg/kg TBHQ sample were lower than the Control and slightly higher than the 217 and 435 mg/kg TBHQ samples. The 435 mg/kg sample appeared to have the lowest values.

Conjugated trienes (UV 268 nm)

The conjugated triene value did not appear to have increased markedly in any of the samples during the storage period.

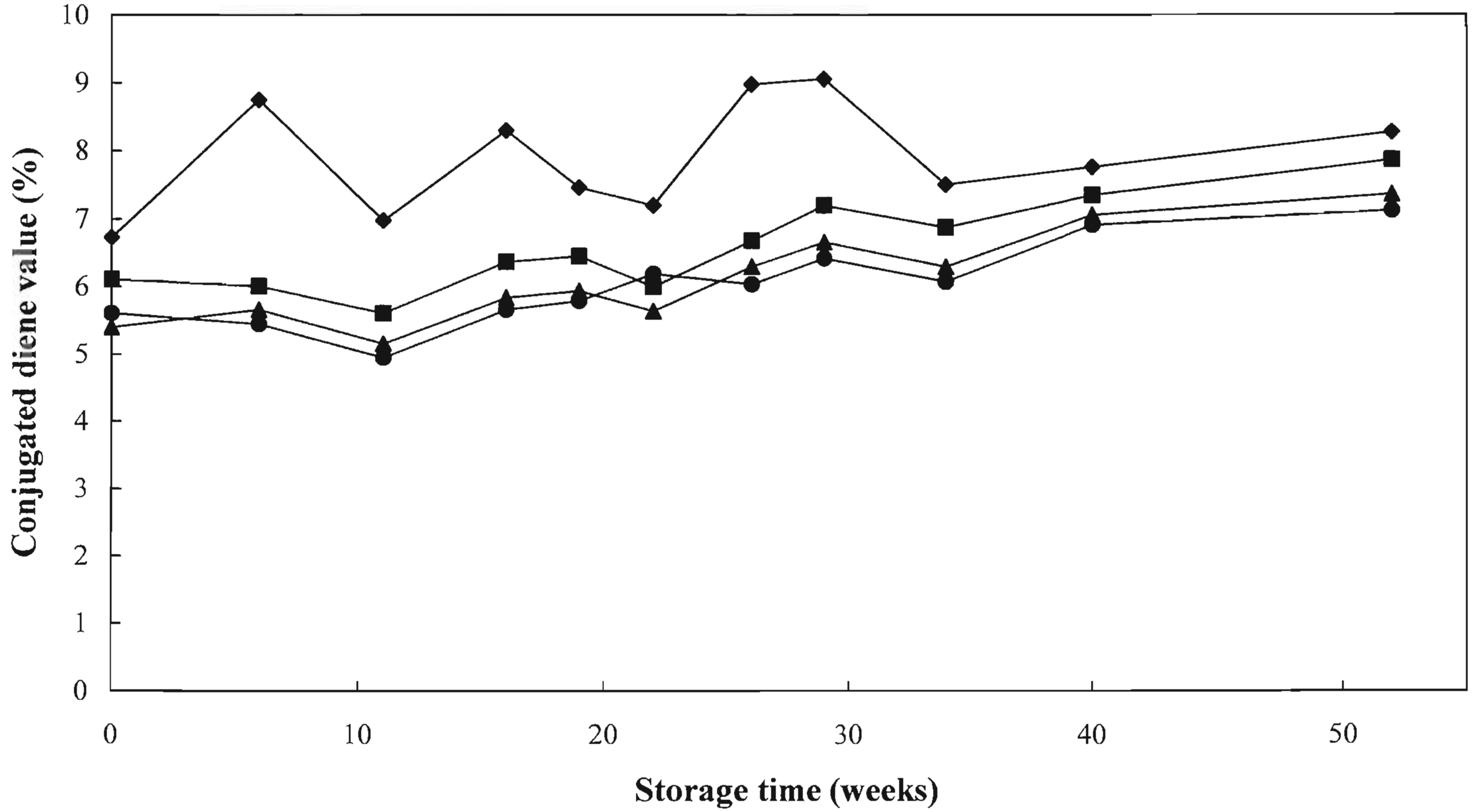

Figure 44: The effect of storage at 30°C for 52 weeks on the conjugated diene value (%) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

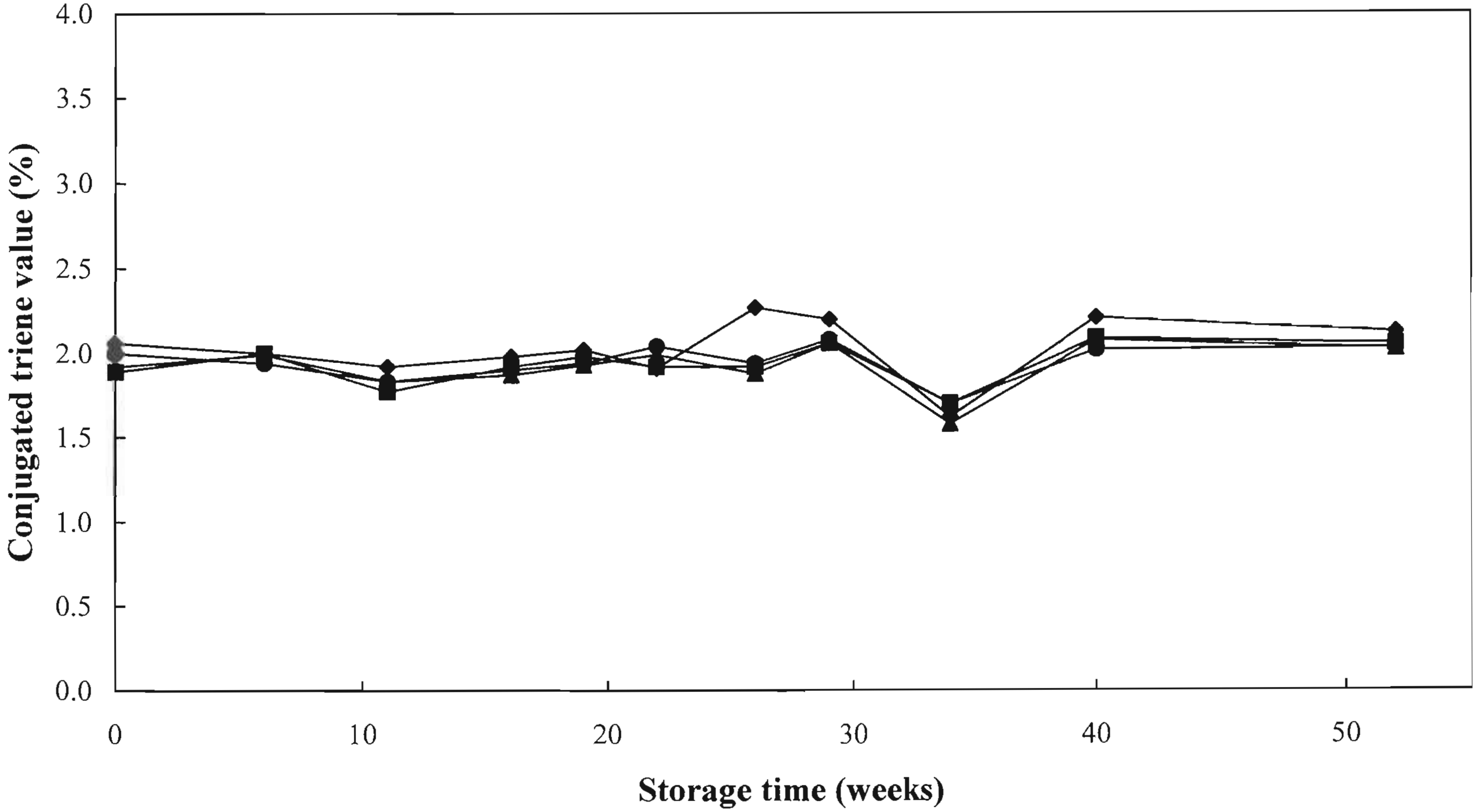

Figure 45: The effect of storage at 30°C for 52 weeks on the conjugated triene value (%) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.8 Iodine value

The effect of storage at 30°C on the IV on the four treatments is given in Figure 46. The IV hardly changed during the storage period with a range of 131.1 (lowest value obtained) and 132.2 (highest value obtained) between the samples. No clear trend or difference between samples took place seen.

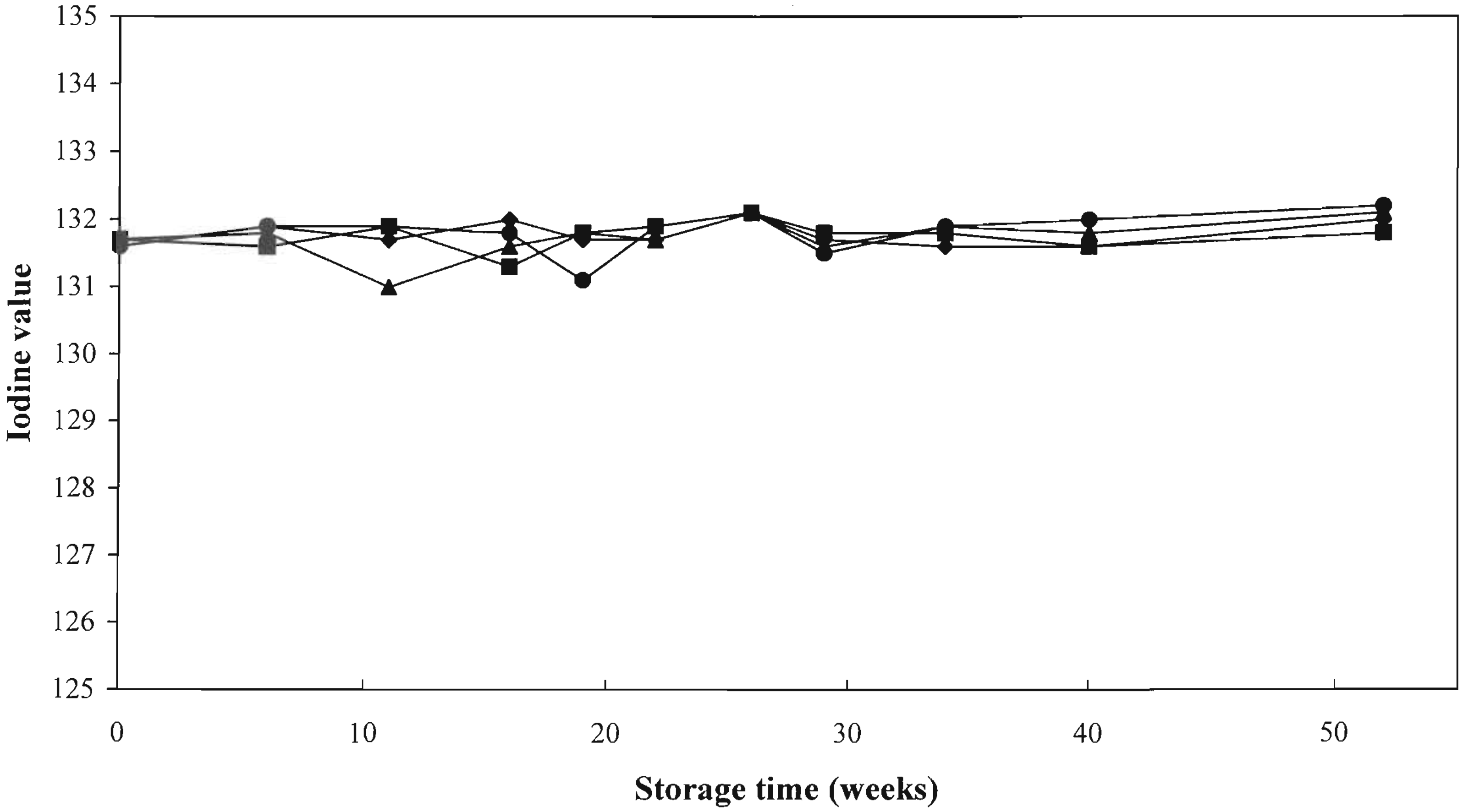

Figure 46: The effect of storage at 30°C for 52 weeks on the iodine value of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.9 Headspace volatile components

Total volatile peak area

The effect of storage at 30°C on the total volatile peak area of the samples is shown in Figure 47. The total volatile peak area increased gradually for all the samples during the storage period. The Control appeared to have the highest peak area throughout the storage trial, although on one occasion at Week 34 it had the same peak area as the 54 mg/kg TBHQ sample followed by a sharp increase to Week 40 and a sharp drop thereafter. The peak areas of the TBHQ containing samples were very similar up to Week 26, after which the 54 mg/kg had slightly higher peak areas than the 217 and 435 mg/kg TBHQ samples. At Weeks 34 and 40 the 217 mg/kg TBHQ sample had higher peak areas than the 435 mg/kg TBHQ sample but at Week 52 the 217 mg/kg TBHQ sample had lower peak areas than that of the 435 mg/kg TBHQ sample.

Hexanal

The effect of storage at 30°C on the hexanal content of the four sample treatments is given in Figure 48. The Control showed the highest values during the storage period and the 435 mg/kg TBHQ sample had the lowest values. After Week 30 the hexanal values reflected the TBHQ levels. The 217 mg/kg TBHQ samples followed with slightly higher values than the 435 mg/kg samples and the 54 mg/kg had slightly higher values than the 217 mg/kg samples. The values appeared to have reached a maximum at Week 40. After Week 40 the values for the Control decreased slightly, the 217 mg/kg sample remained stable and the 54 and 435 mg/kg samples increased slightly.

trans-2-hexenal

The effect of storage at 30°C on the t-2-hexenal content of the four sample treatments is given in Figure 49. Low values of trans-2-hexenal were obtained for all the samples during the storage period. The values showed very little variation between the samples with a fluctuation range of 0-1.9 mg/kg.

trans, trans-2,4-decadienal

The effect of storage at 30°C on the t,t-2,4-decadienal content of the four sample treatments is given in Figure 50. Trans, trans-2,4-decadienal was only detected in the samples from Week 34 and onwards in the storage trial. A considerate amount of variation was found in the values for all the samples and no pattern could be discerned for or between any of the samples.

Pentanal

The effect of storage at 30°C on the pentanal content of the four sample treatments is given in Figure 51. The pentanal peak area increased during the storage period for all the samples. It appeared that the peak area for the Control sample was higher than for the samples containing TBHQ, although at times the peak area decreased to less or similar values than that of the TBHQ containing samples. The Control and the 54 mg/kg TBHQ values decreased after Week 40. The TBHQ containing samples had similar values up to Week 26, after which the 435 mg/kg sample had the lowest values followed by the 217 mg/kg TBHQ sample and then the 54 mg/kg TBHQ sample. The value of the 54 mg/kg sample decreased at Week 52 to less than the values of the 217 and 435 mg/kg TBHQ samples.

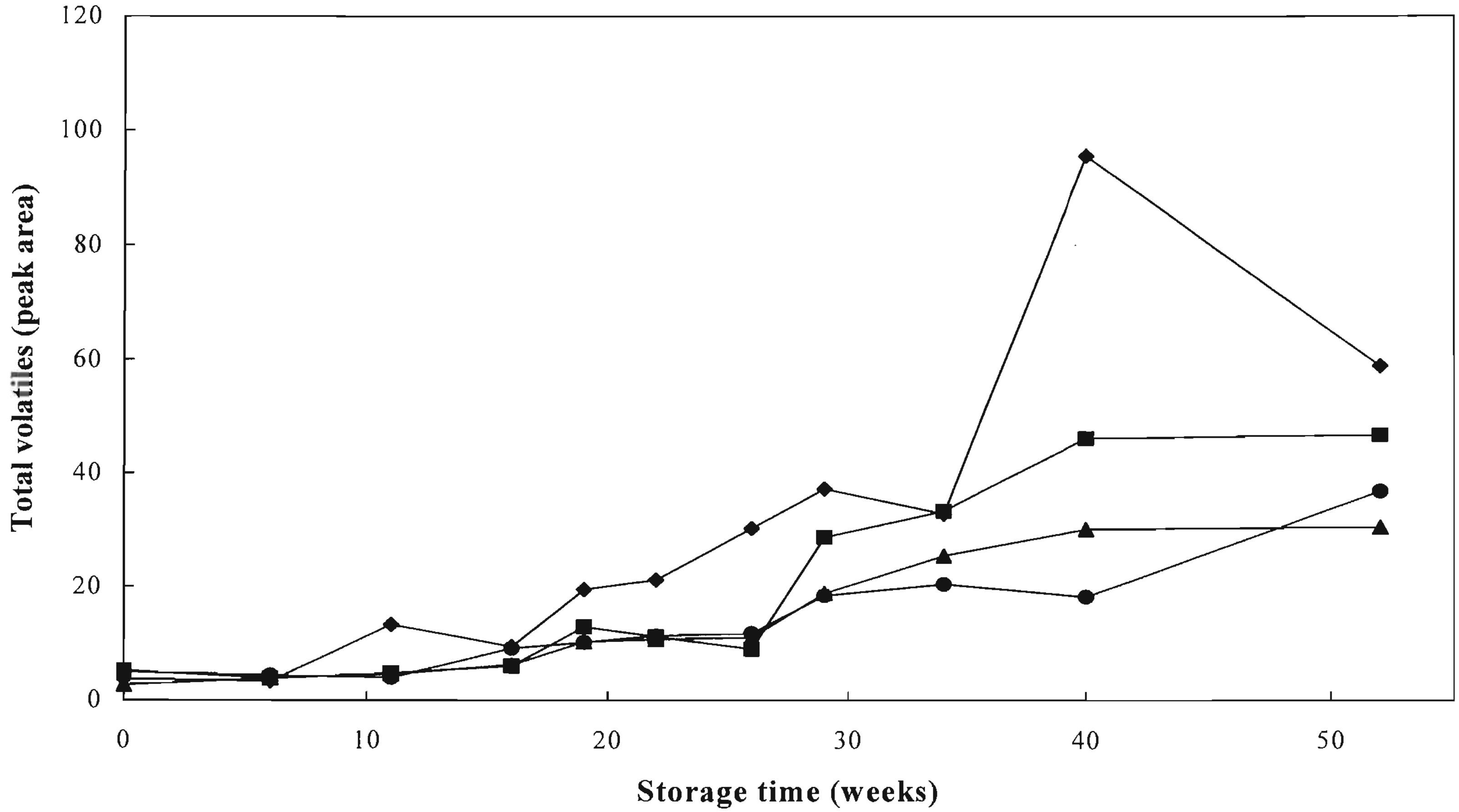

Figure 47: The effect of storage at 30°C for 52 weeks on the total volatile peak area of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

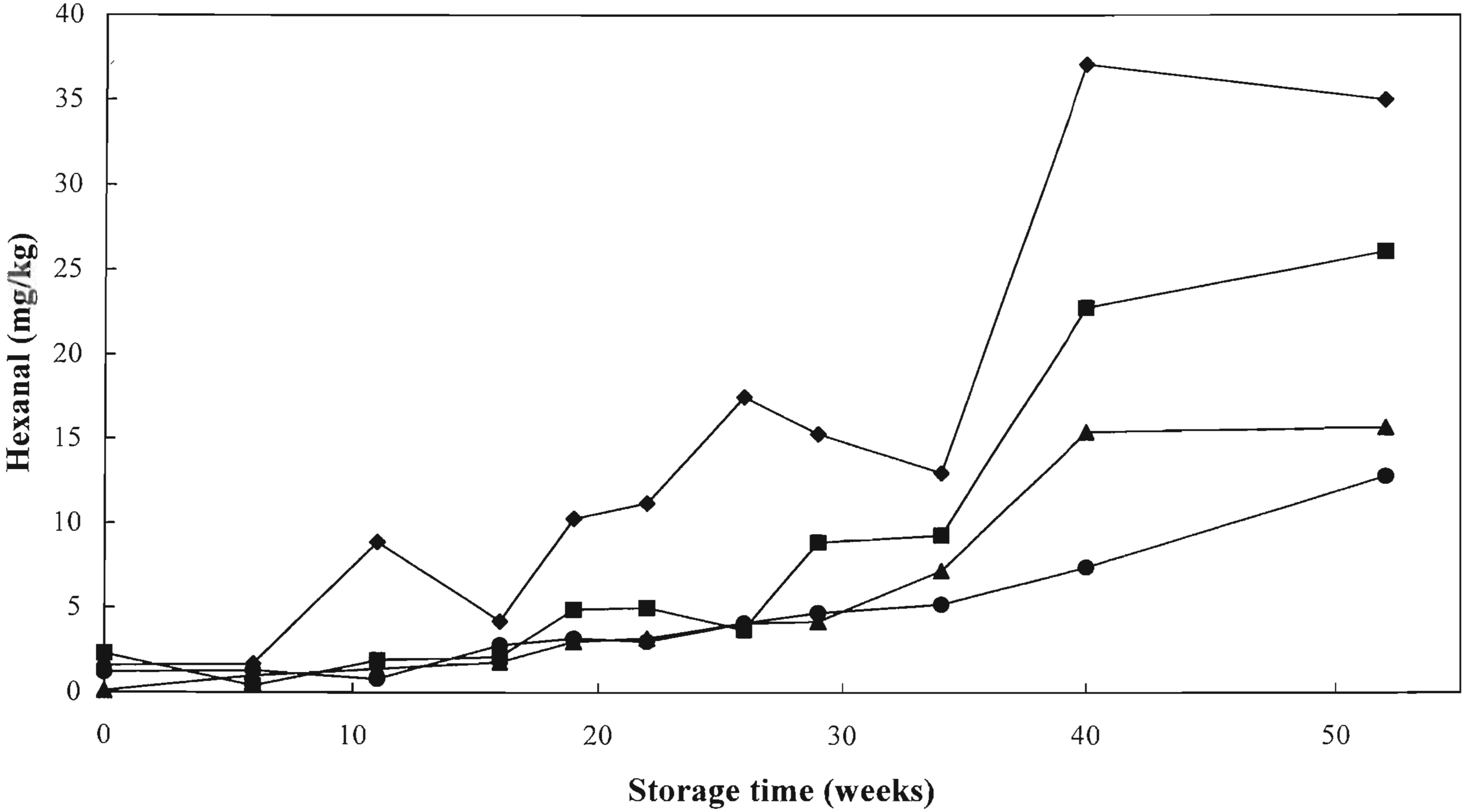

Figure 48: The effect of storage at 30°C for 52 weeks on the hexanal content (mg/kg) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

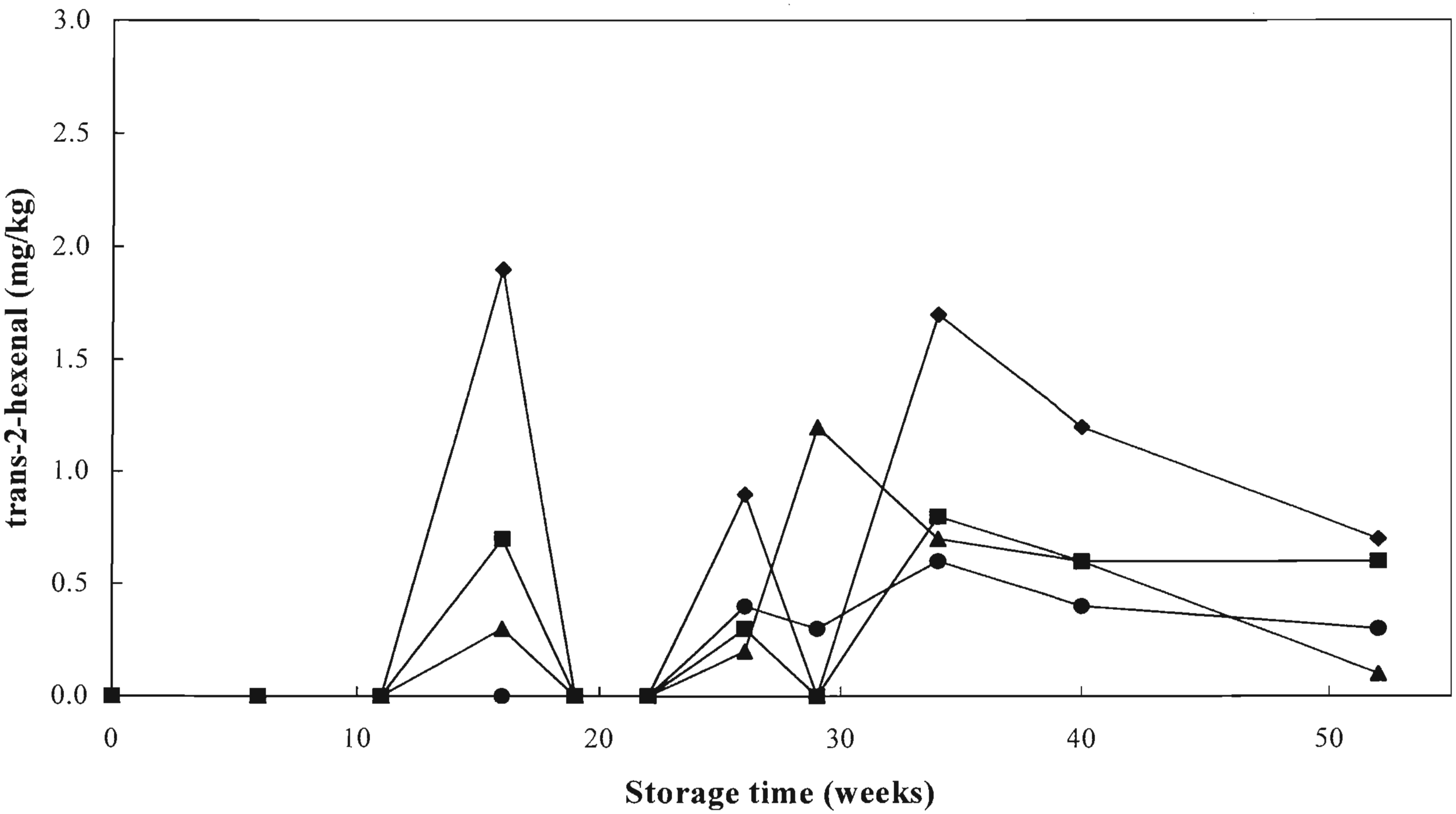

Figure 49: The effect of storage at 30°C for 52 weeks on the trans-2-hexenal content (mg/kg) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

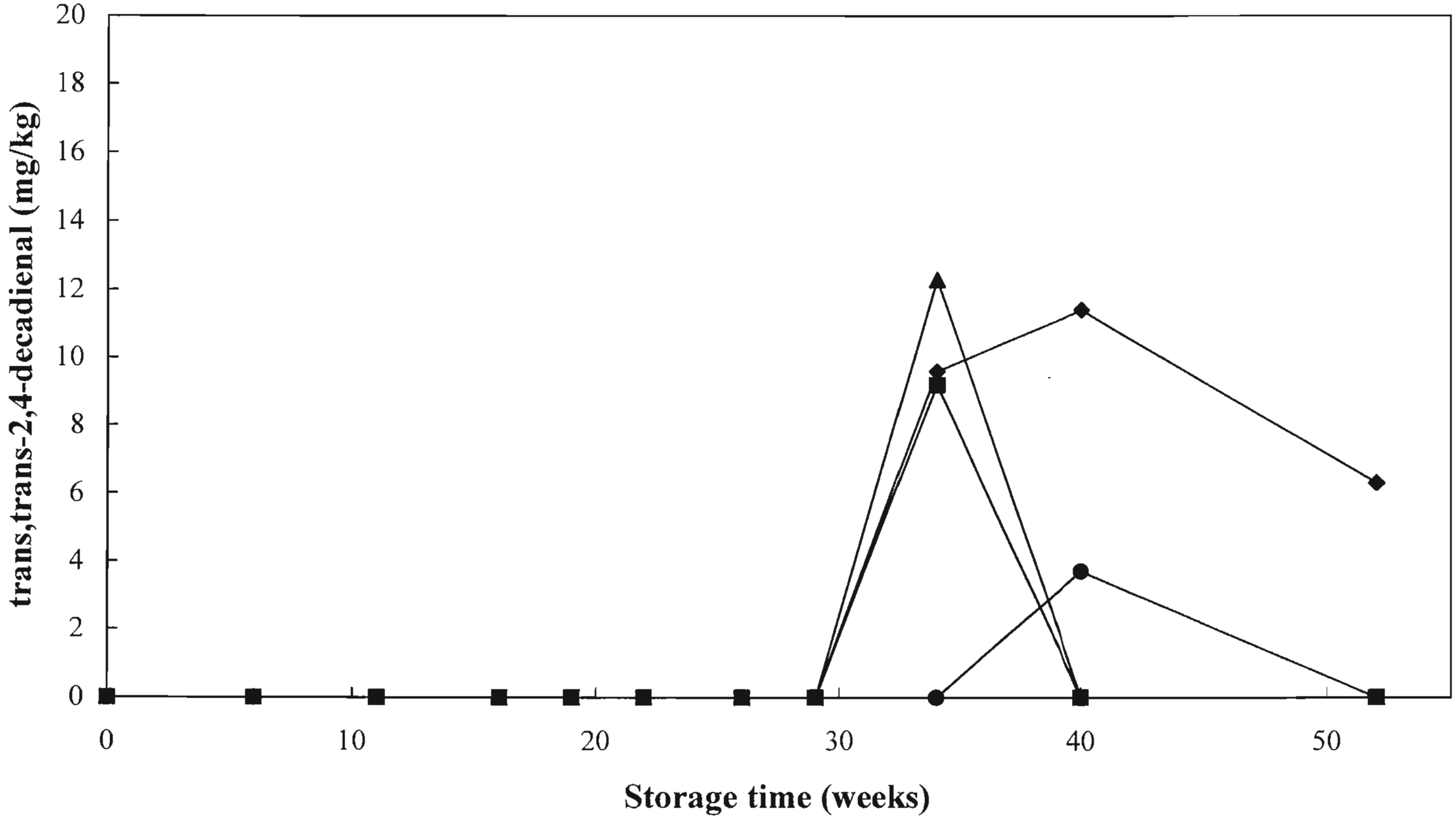

Figure 50: The effect of storage at 30°C for 52 weeks on the trans, trans-2,4-decadienal content (mg/kg) of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

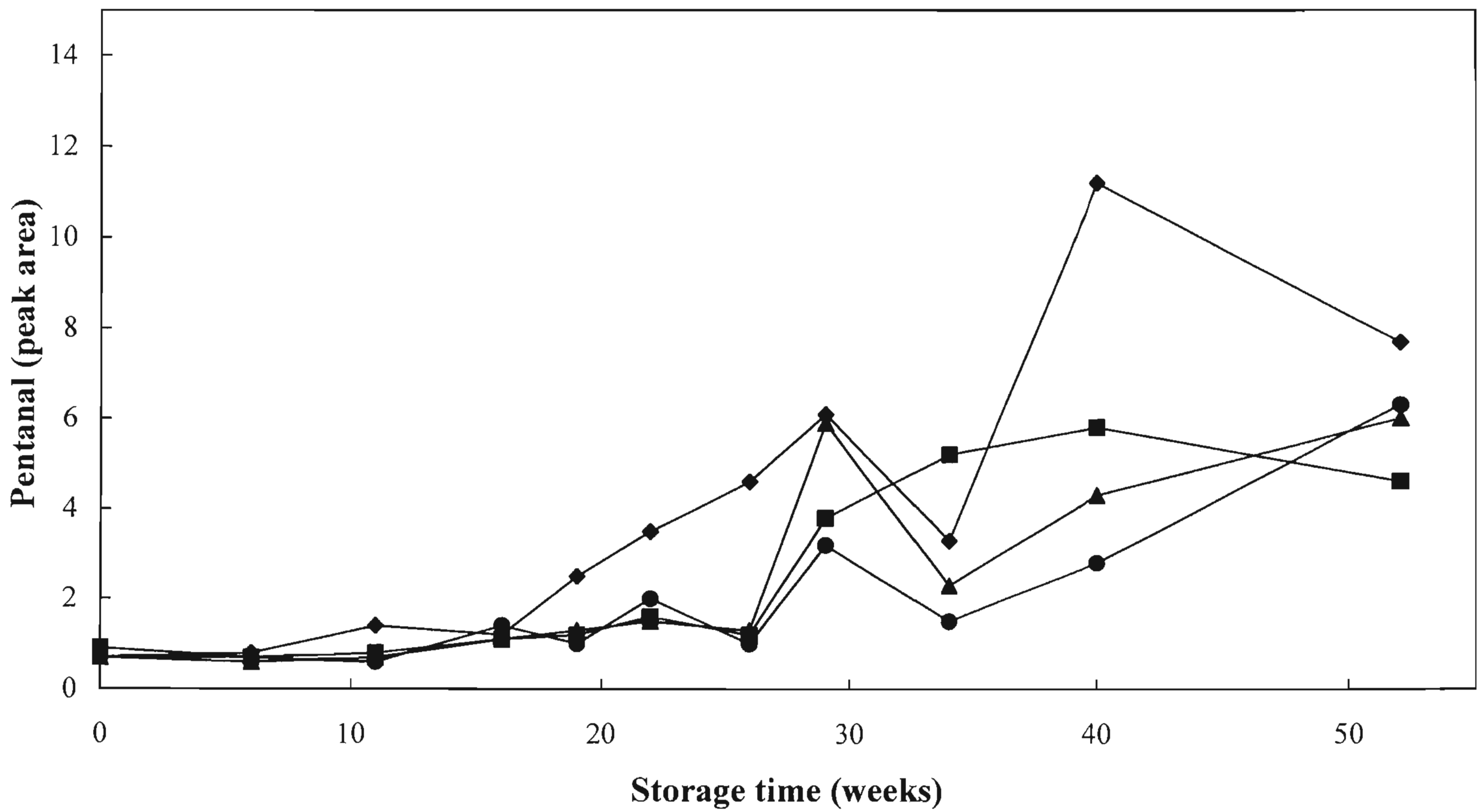

Figure 51: The effect of storage at 30°C for 52 weeks on the pentanal peak area of the sunflower seed oil samples: Control (◆); with 54 mg/kg TBHQ (■); with 217 mg/kg TBHQ (▲) and with 435 mg/kg TBHQ (●).

4.2.2.10 Sensory evaluation

The results of the sensory evaluation conducted by 10 panelists can be seen in Figures 52 and 53 where Figure 52 shows results of Option 1 and Figure 53 the results of Option 2. The four categories as well as the Options 1 and 2 used to evaluate the oils were the same as for the palm-olein oil, see section 4.1.2.10.

According to O'Mahoney (1986) the statistical guideline, would be that if 7 or 8 out of 10 panelists regard the oil to be rancid it would be significant at the 20 % and 10 % level of significance, respectively. This applies for a one-tailed paired-comparison difference test of rancid and fresh oil. For the 5 % level of significance, 9 out of 10 panelists must deem the oil to be rancid.

Control

According to Option 1, all of the panelists judged the oil to be rancid by Week 29. However, according to Option 2 the majority of panelists (8) judged the oil to be rancid by Week 40.

Sample containing 54 mg/kg TBHQ

According to Option 1, all of the panelists judged the oil to be rancid by Week 29. However, according to Option 2 a majority of panelists (6) judged the oil to be rancid by Week 52 although it was not a conclusive judgement.

Sample containing 217 mg/kg TBHQ

According to Option 1, the majority of the panelists (8) judged the oil to be rancid by Week 26 and all the panelists judged the oil to be rancid by Week 52. However, according to Option 2 a majority of panelists (8) judged the oil to be rancid by Week 52.

Sample containing 435 mg/kg TBHQ

According to Option 1, the majority of the panelists (8) judged the oil to be rancid by Week 29 and all the panelists judged the oil to be rancid by Week 52. However, according to Option 2 an unconvincing majority of panelists (7) judged the oil to be rancid by Week 52.

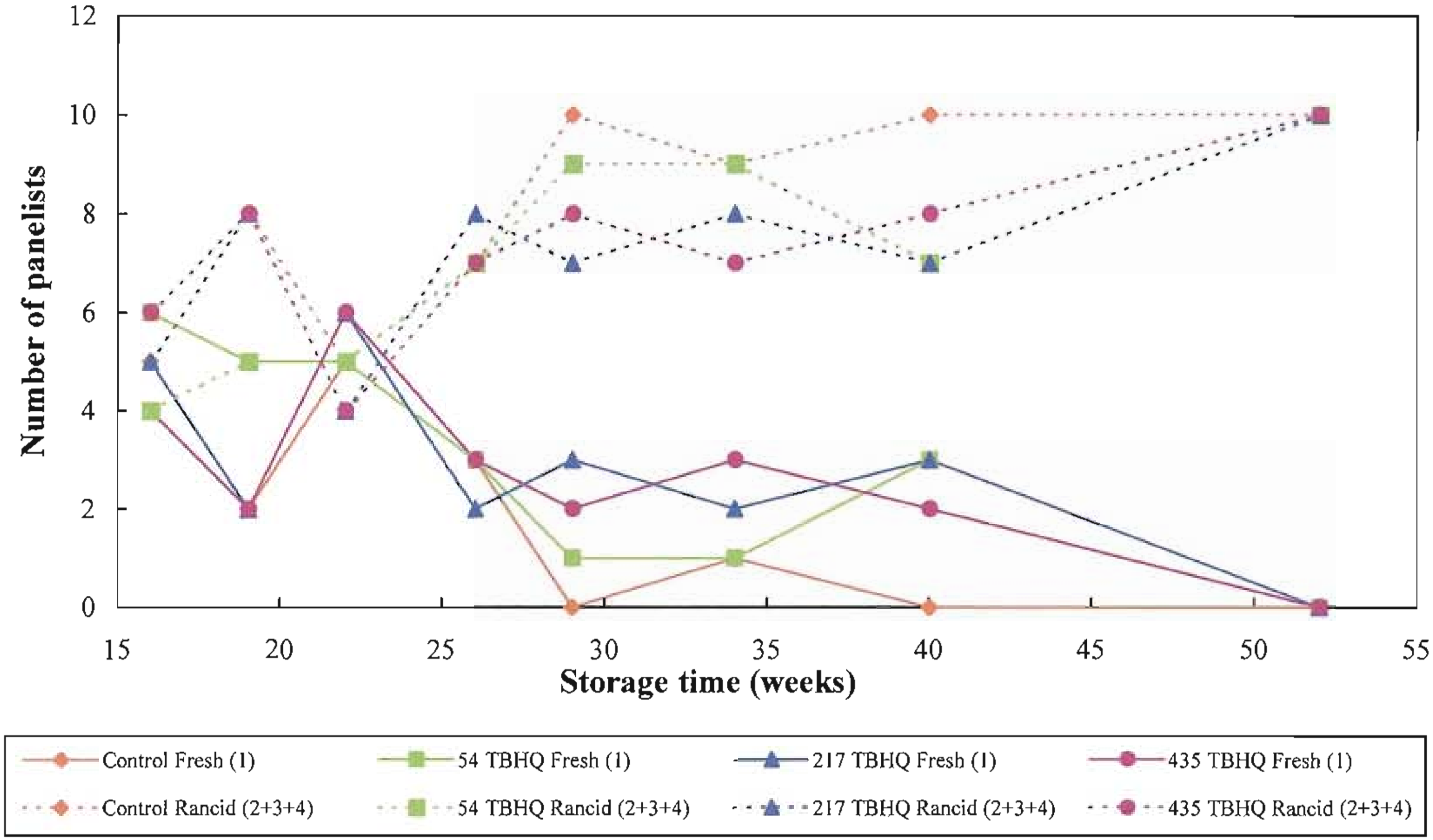

Figure 52: The effect of storage on the sensory quality of sunflower seed oil stored at 30°C for a period of 52 weeks (Option 1).

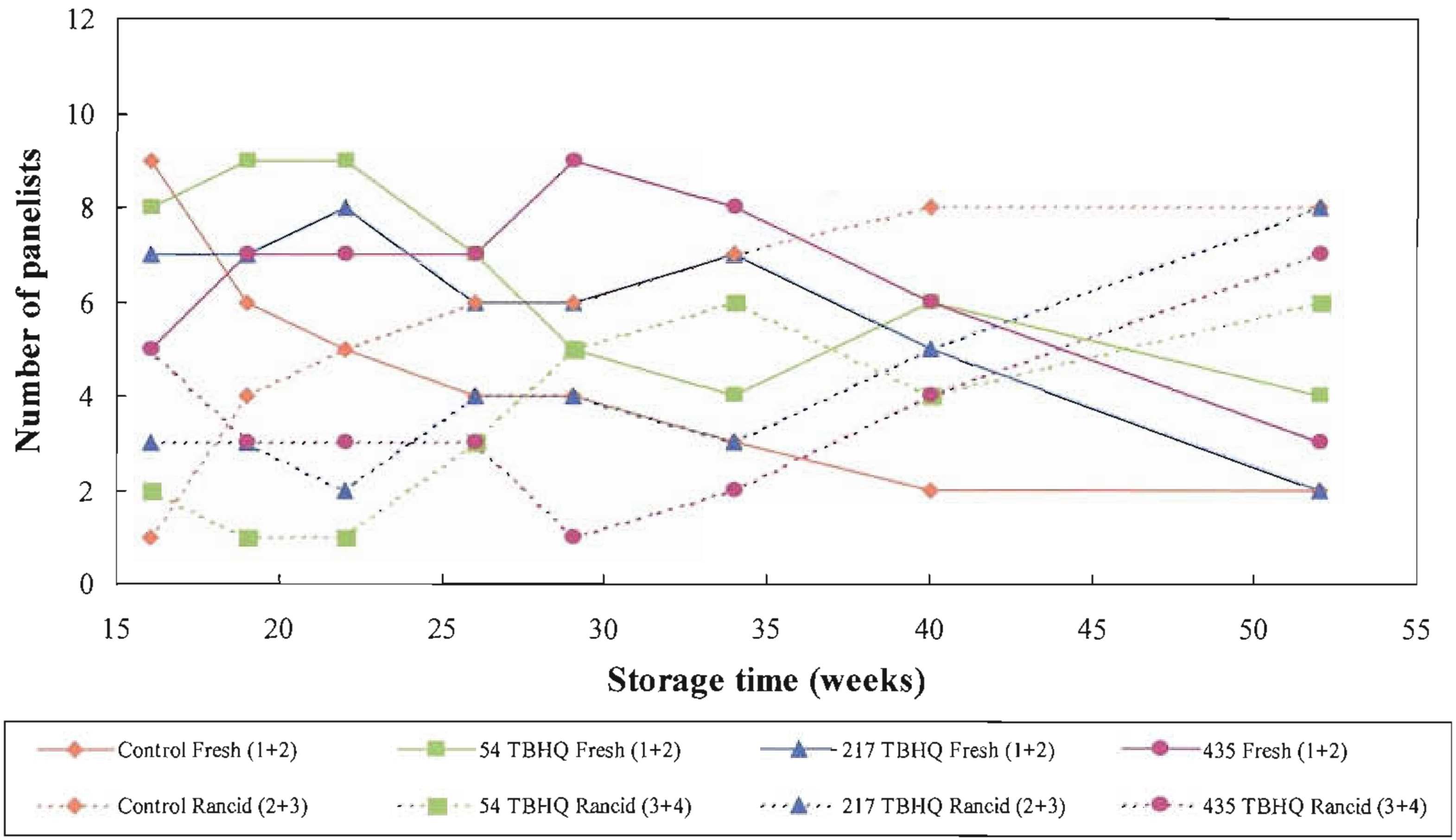

Figure 53: The effect of storage on the sensory quality of sunflower seed oil stored at 30°C for a period of 52 weeks. (Option 2).

A summary of the results is presented in Table 26.

Table 26: Estimation of onset of rancidity time by sensory evaluation and chemical parameters.

Samples	**Storage time (weeks) at which oil was deemed to be rancid**		
	Sensory evaluation*		**Chemical parameters♦**
	Option 1 Fresh (1), Rancid (2+3+4)	Option 2 Fresh (1+2), Rancid (3+4)	
Control	29	40	26
54 mg/kg TBHQ	29	>52	26
217 mg/kg TBHQ	26	52	34
435 mg/kg TBHQ	29	>52	52

* A majority of 8 out of 10 sensory panelists deemed the oil rancid

♦ Chemical parameters defined in Section 3.4 Modelling

4.2.3 Modelling

4.2.3.1 Models

Model 1

All the data were used to create Model 1. The results of the variables selected by multiple regression to be used in the model are shown in Table 27. The variables were the following FFA, PV, AV, UV 232 nm, UV 268 nm, OSI, total tocopherols, α-tocopherol, γ-tocopherol, β-tocopherol, total volatile components, hexanal, t-2-hexenal, t,t-2,4-decadienal, pentanal, IV, polyunsaturated fatty acids and TBHQ content.

Table 27: Regression summary for dependant variable: shelf-life of Model 1.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	10.8	10.3	0.303
TBHQ	0.05	0.003	0.000
FFA	-161	12.2	0.000
Pentanal	-2.12	0.526	0.000
Conjugated triene value	18.0	4.96	0.001

Where R^2 = 0.9597

$F (4, 29)$ = 172

Standard error of estimate = 2.93

The graph of the predicted versus the observed values is shown in Figure 54.

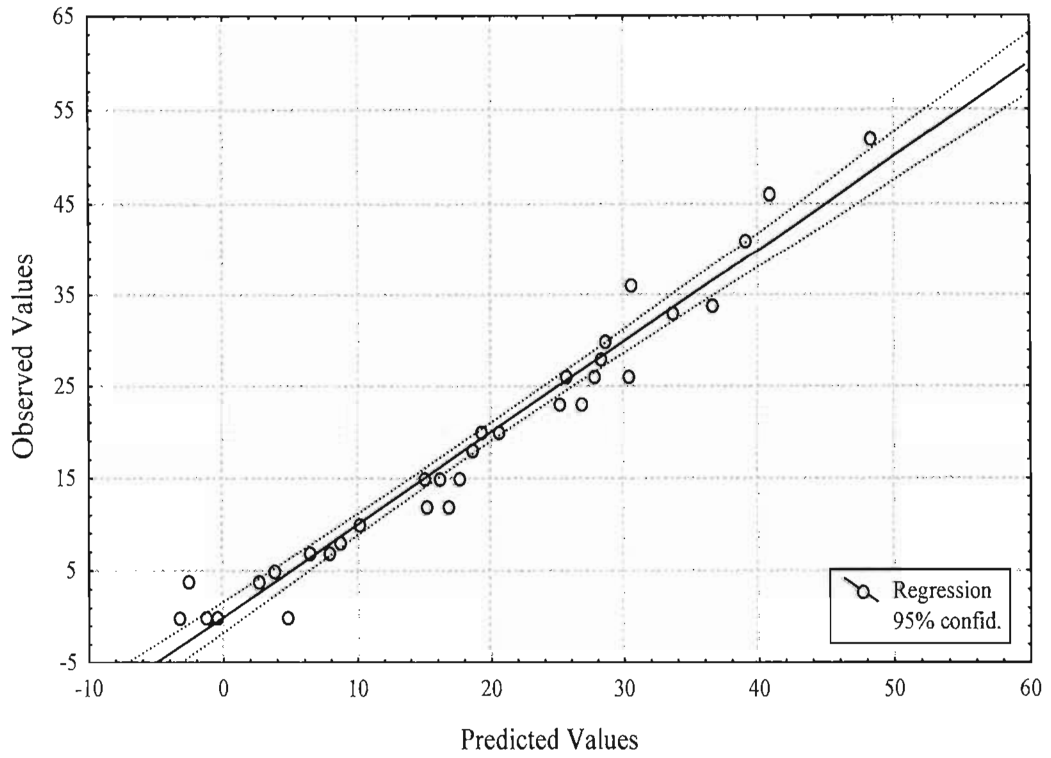

Figure 54: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 1. The dependant variable is the shelf-life.

Model 2

The squares of the values obtained were used to create Model 2. The results of the variables selected by multiple regression to be used in the model are shown in Table 28.

Table 28: Regression summary for dependant variable: shelf-life of Model 2.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.7	1.08	0.000
PV^2	-0.014	0.006	0.043
$TBHQ^2$	0.0001	0.000	0.000
FFA^2	-281	40.6	0.000
OSI^2	0.008	0.001	0.000
Total volatile area^2	-0.014	0.010	0.000
Hexanal	0.042	0.010	0.000

Where R^2 = 0.9853

$F (6, 27)$ = 301

Standard error of estimate = 1.84

The graph of the predicted versus the observed values is shown in Figure 55.

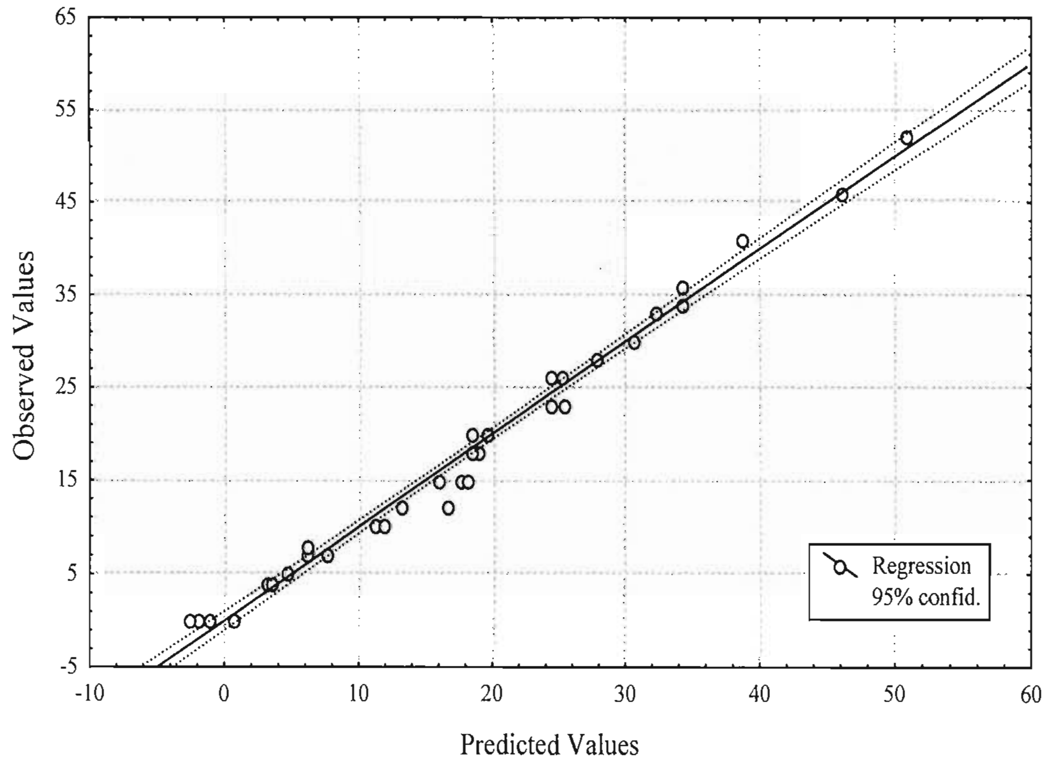

Figure 55: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 2. The dependant variable is the shelf-life.

Model 3

The weighted values were calculated and used to create Model 3. The TBHQ value was not weighted as the values used were the amounts added and thus no standard deviation could be calculated for them. The results of the variables selected by multiple regression to be used in the model are shown in Table 29.

Table 29: Regression summary for dependant variable: shelf-life of Model 3.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	10.8	10.3	0.303
TBHQ	0.052	0.003	0.000
Weighted FFA	-1.30	0.098	0.000
Weighted pentanal	-3.48	0.863	0.000
Weighted conjugated triene value	2.24	0.619	0.001

Where R^2 = 0.9597

$F (4, 29)$ = 172

Standard error of estimate = 2.93

The graph of the predicted versus the observed values is shown in Figure 56.

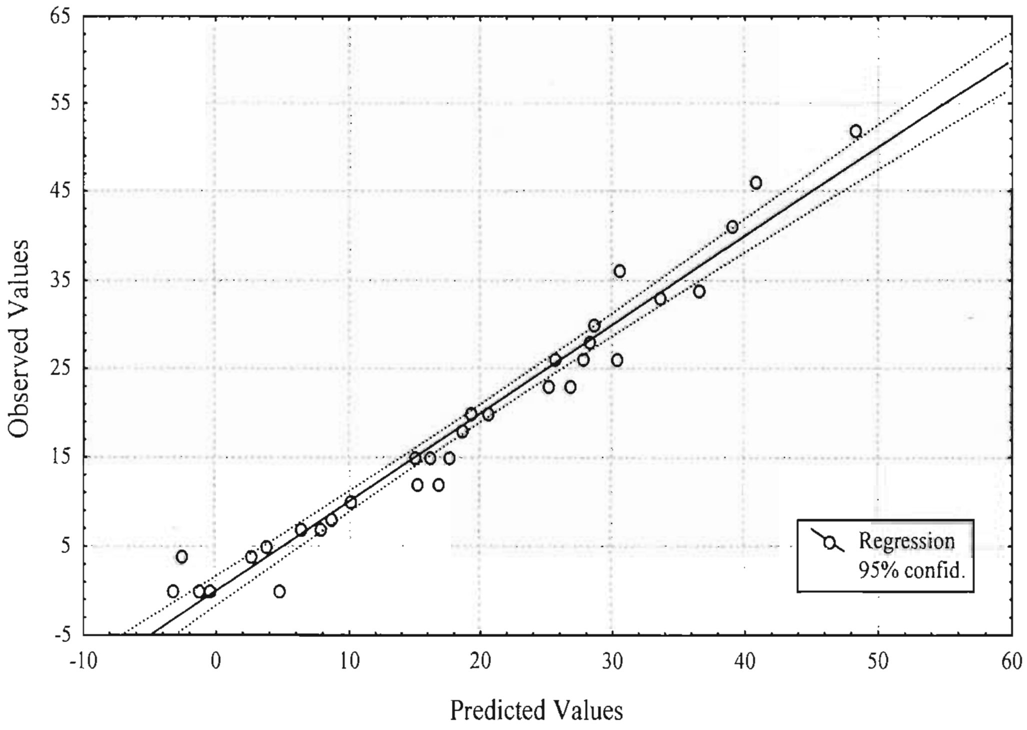

Figure 56: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 3. The dependant variable is the shelf-life.

Model 4

The calculated weighted values of the squares of the data were used to create Model 4. The TBHQ value was not weighted as the values used were the amounts added and thus no standard deviation could be calculated for them. The results of the variables selected by multiple regression to be used in the model are shown in Table 30.

Table 30: Regression summary for dependant variable: shelf-life of Model 4.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.7	1.08	0.000
Weighted PV^2	-0.004	0.002	0.043
$TBHQ^2$	0.00009	0.000	0.000
Weighted FFA^2	-2.26	0.327	0.000
Weighted OSI^2	0.006	0.001	0.000
Weighted total volatiles $area^2$	-0.189	0.033	0.000
Weighted $hexanal^2$	0.170	0.040	0.000

Where R^2 = 0.9853

$F(6, 27)$ = 301

Standard error of estimate = 1.84

The graph of the predicted versus the observed values is shown in Figure 57.

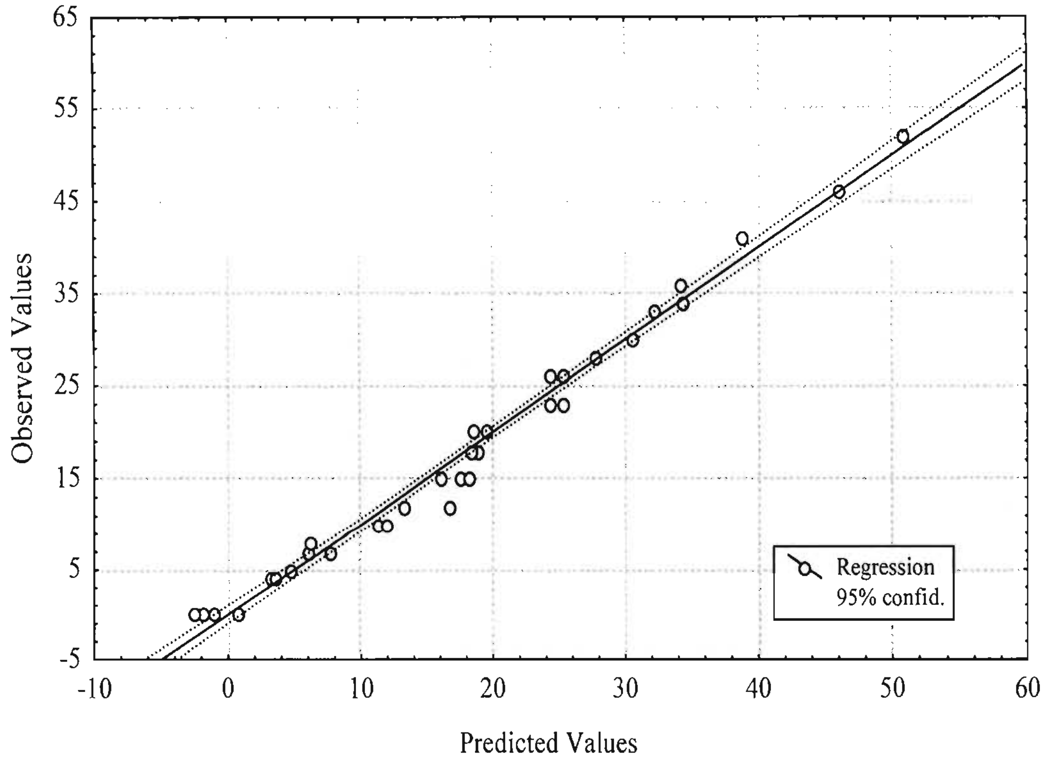

Figure 57: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 4. The dependant variable is the shelf-life.

Model 5

The values obtained and their squares were used to create Model 5. The results of the variables selected by multiple regression to be used in the model are shown in Table 31.

Table 31: Regression summary for dependant variable: shelf-life of Model 5.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	29.1	1.12	0.000
PV	-0.489	0.154	0.004
$TBHQ^2$	0.0001	0.000	0.000
FFA^2	-249	38.6	0.000
OSI^2	0.007	0.001	0.000
Total volatiles $area^2$	-0.015	0.002	0.000
$Hexanal^2$	0.044	0.009	0.000

Where	R^2	=	0.9875
	F (6, 27)	=	355
	Standard error of estimate	=	1.69

The graph of the predicted versus the observed values is shown in Figure 58.

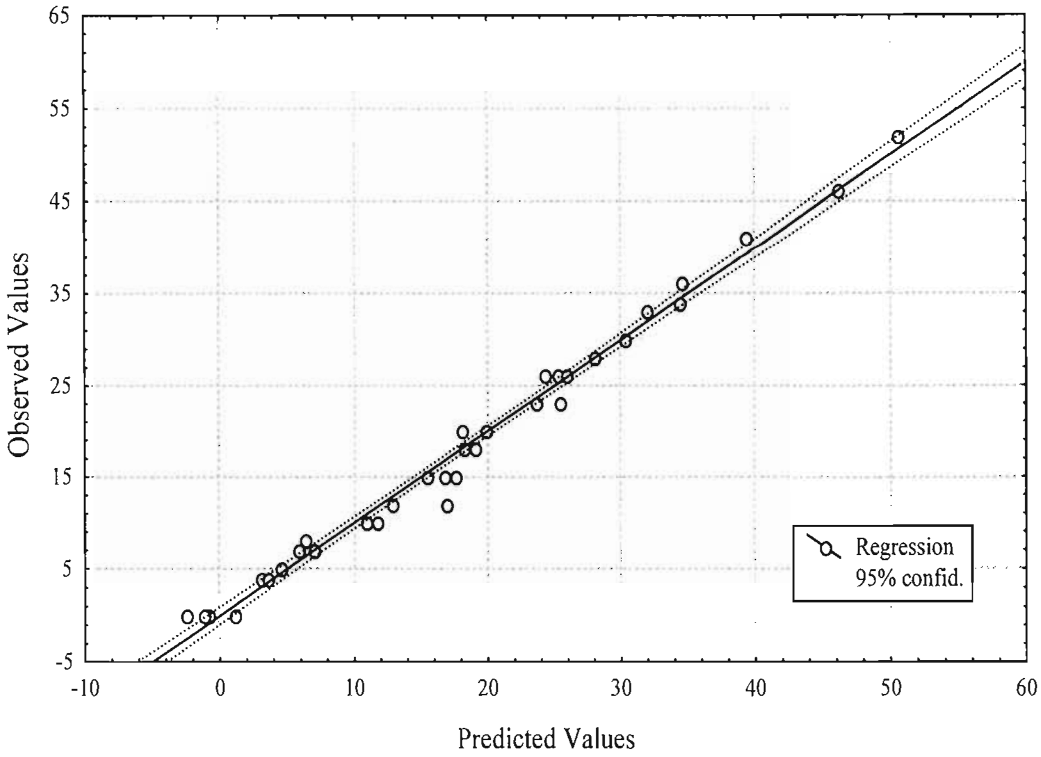

Figure 58: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 5. The dependant variable is the shelf-life.

Model 6

The values obtained and their squares, excluding the TBHQ value, were used to create Model 6. The results of the variables selected by multiple regression to be used in the model are shown in Table 32.

Table 32: Regression summary for dependant variable: shelf-life of Model 6.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.6	1.93	0.000
OSI^2	0.007	0.001	0.000
FFA^2	-249	38.6	0.000
Pentanal	-1.23	0.653	0.070

Where R^2 = 0.9233

$F_{(3, 30)}$ = 120

Standard error of estimate = 3.98

The graph of the predicted versus the observed values is shown in Figure 59.

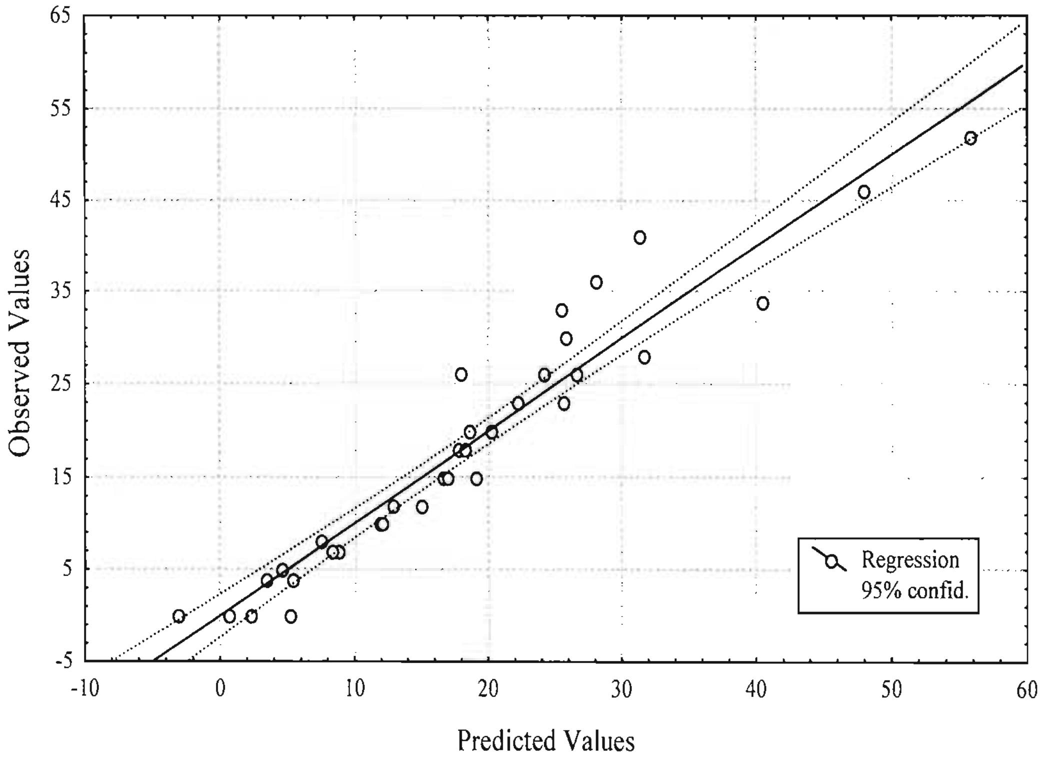

Figure 59: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 6. The dependant variable is the shelf-life.

Model 7

Model 7 is the simple model that was created with the values of simple methods of analyses and their squares. The simple methods of analyses are FFA, PV, OSI and conjugated diene/triene. The results of the variables selected by multiple regression to be used in the model are shown in Table 33.

Table 33: Regression summary for dependant variable: shelf-life of Model 7.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	11.5	8.65	0.194
OSI^2	0.018	0.002	0.000
FFA^2	-757	211	0.001
FFA	-160	86.4	0.074

Where R^2 = 0.9231
F (4, 26) = 120
Standard error of estimate = 3.98

The graph of the predicted versus the observed values is shown in Figure 60.

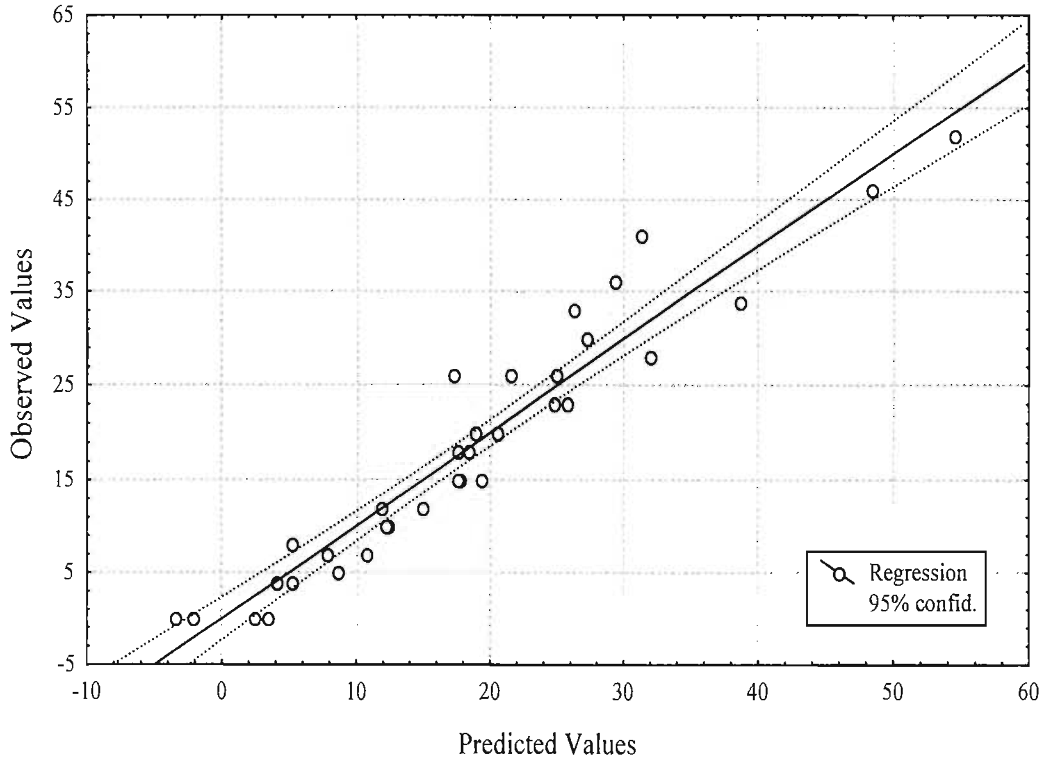

Figure 60: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 7. The dependant variable is the shelf-life.

Model 8

The OSI value and its square were the only variables used to create Model 8. The multiple regression results are shown in Table 34.

Table 34: Regression summary for dependant variable: shelf-life of Model 8.

N = 34 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	11.2	6.56	0.099
OSI	-0.401	0.669	0.553
OSI^2	0.031	0.015	0.047

Where R^2 = 0.5483

$F(2, 31)$ = 18.8

Standard error of estimate = 9.50

The graph of the predicted versus the observed values is shown in Figure 61.

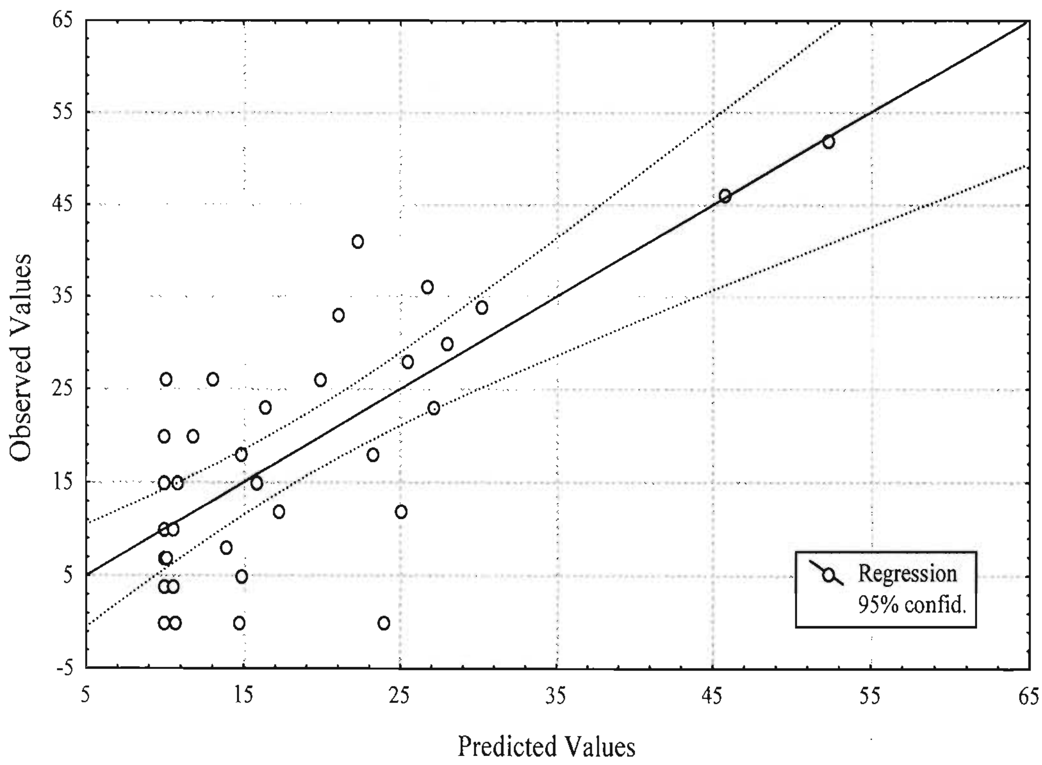

Figure 61: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 8. The dependant variable is the shelf-life.

Model 9

Model 9 is based on the sensory evaluation (Option 1) and the values obtained and their squares were used to create model. Results of the variables selected by multiple regression are shown in Table 35.

Table 35: Regression summary for dependant variable: shelf-life of Model 9.

N = 31 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	26.3	5.08	0.000
FFA	-125	30.5	0.001
TBHQ	-0.076	-12.8	0.000
PV	-0.558	0.131	0.000
OSI^2	0.005	0.009	0.000
$TBHQ^2$	0.0001	0.000	0.000
Pentanal	-0.686	0.253	0.013
Alpha-tocopherol^2	0.017	0.006	0.007
FFA^2	184	76.5	0.025
Total tocopherols^2	-0.008	0.004	0.059

Where R^2 = 0.9930

$F\ (9,\ 21)$ = 338

Standard error of estimate = 0.921

The graph of the predicted versus the observed values is shown in Figure 62.

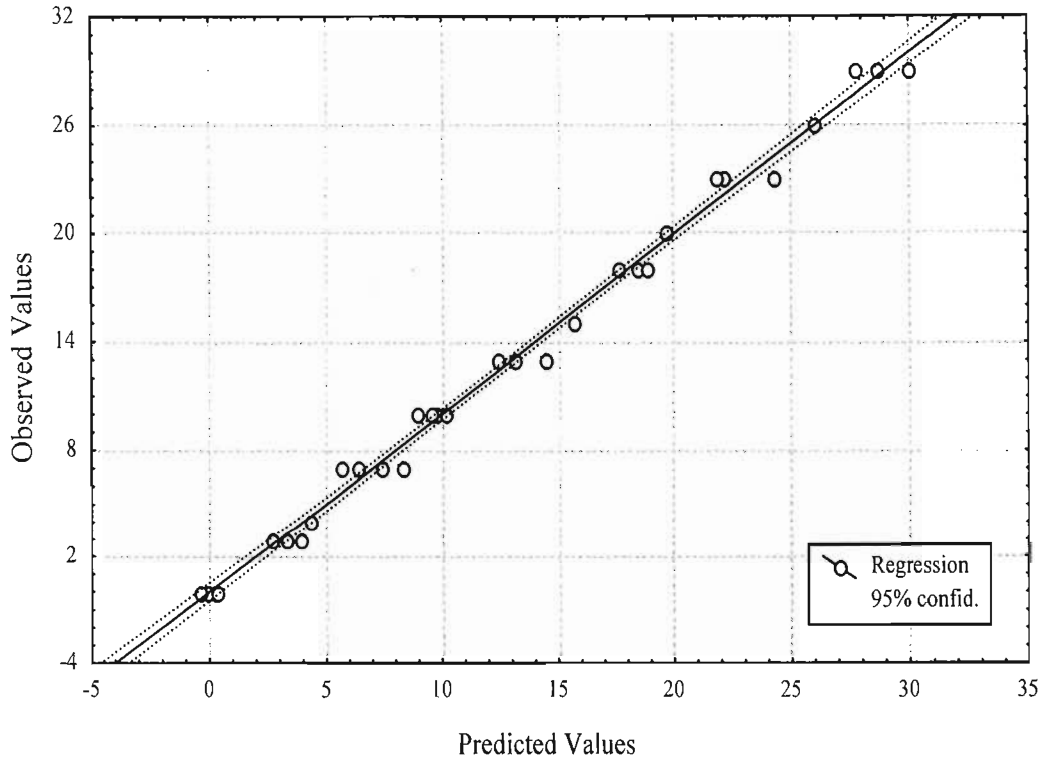

Figure 62: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 9. The dependant variable is the shelf-life.

Model 10

Model 10 is based on the sensory evaluation and the values obtained and their squares, excluding TBHQ content, were used to create model. Results of the variables selected by multiple regression are shown in Table 36.

Table 36: Regression summary for dependant variable: shelf-life of Model 10.

N = 31 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	35.7	5.92	0.000
FFA	-187	37.4	0.001
OSI	-1.13	0.118	0.000
OSI^2	0.020	0.003	0.000
PV	-0.723	0.185	0.001
Alpha-tocopherol^2	0.011	0.003	0.000
FFA^2	330	93.1	0.002

Where	R^2	=	0.9839
	F (6, 24)	=	244
	Standard error of estimate	=	1.32

The graph of the predicted versus the observed values is shown in Figure 63.

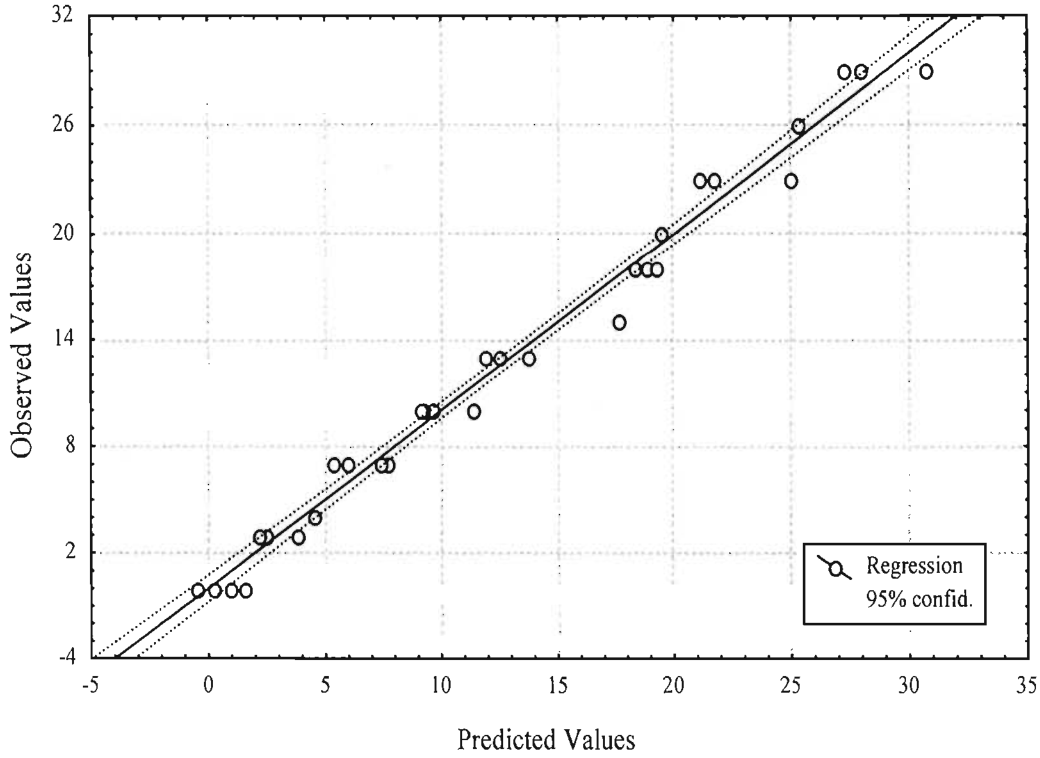

Figure 63: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 10. The dependant variable is the shelf-life.

Model 11

Model 11 is the simple model based on the sensory evaluation that was created with the values of simple methods of analyses and their squares. The results of the variables selected by multiple regression to be used in the model are shown in Table 37.

Table 37: Regression summary for dependant variable: shelf-life of Model 11.

N = 31 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	50.8	1.88	0.000
FFA	-59.3	19.2	0.005
OSI	-1.14	0.156	0.000
OSI^2	0.020	0.003	0.000
PV	-1.15	0.190	0.000

Where R^2 = 0.9691

F (4, 26) = 204

Standard error of estimate = 1.76

The graph of the predicted versus the observed values is shown in Figure 64.

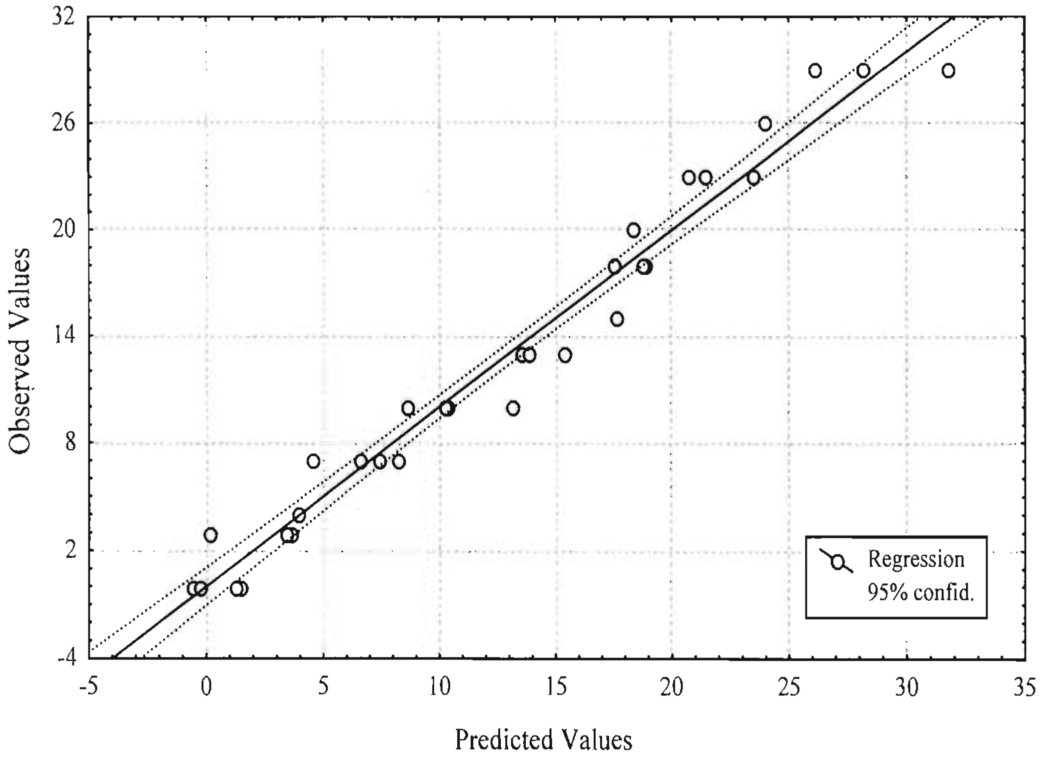

Figure 64: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 11. The dependant variable is the shelf-life.

Model 12

The OSI value and its square were the only variables used to create Model 12, which was based on the sensory evaluation. The multiple regression results are shown in Table 38.

Table 38: Regression summary for dependant variable: shelf-life of Model 12.

N = 31 cases	**B** regression coefficients	Standard error of **B** coefficients	p-level
Intercept	16.4	6.04	0.011
OSI	-0.75	0.650	0.256
OSI^2	0.023	0.014	0.130

Where R^2 = 0.1437

F (2, 31) = 2.35

Standard error of estimate = 8.91

The graph of the predicted versus the observed values is shown in Figure 65.

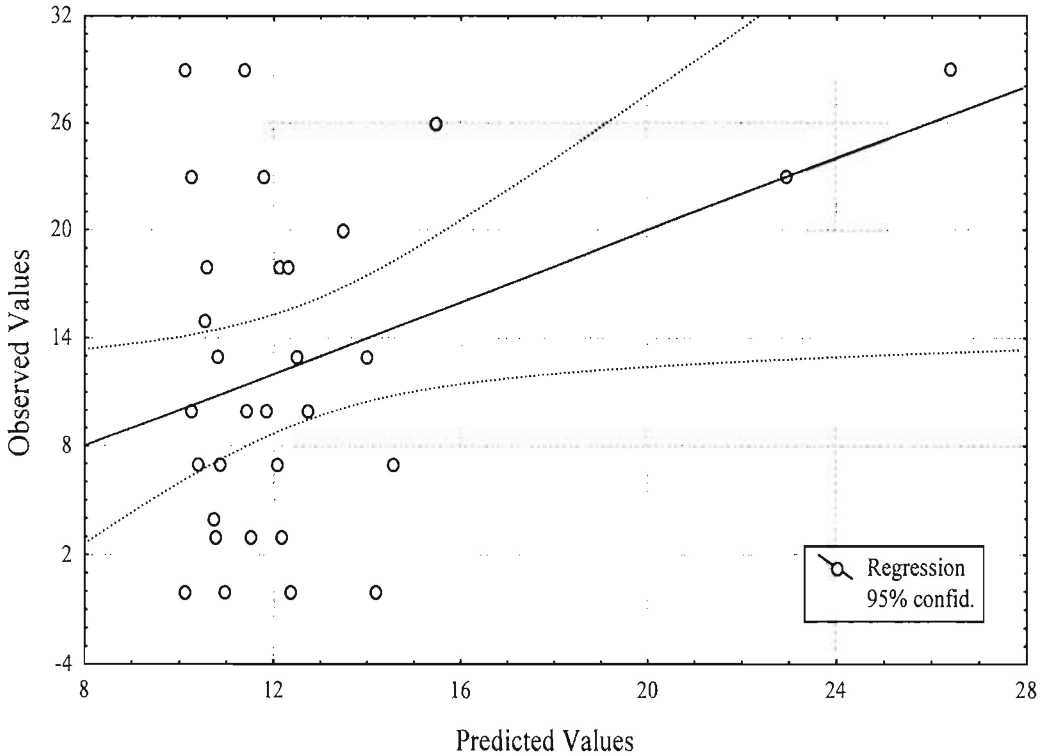

Figure 65: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 12. The dependant variable is the shelf-life.

4.2.3.2 Jackknifing

The practical applicability and reliability of the selected models was tested by applying a jackknifing procedure.

Models based on PV and AV

The results of the jackknifing are shown in Table 39 where the Ideal models are as described for Model 5 including TBHQ content and Model 6 excluding TBHQ content, Practical model as described for model 7 and the OSI model as described for Model 8. The number of weeks that would comply with a 95 % confidence level has been calculated for the models. The number of weeks needed for the Ideal model with TBHQ included to comply was 5.5 weeks and 1 case of the jackknifing results was found to be outside the limit. For the Ideal model excluding TBHQ it was 8.5 weeks with 2 cases found to be outside the limit. The Practical model had to comply with 8.7 weeks and 2 cases of the jackknifing results were outside, whereas the OSI model had to comply with 19.9 weeks with 2 cases found to be outside the limit.

The observed minus predicted values (errors) of the models is represented graphically in Figure 66. The errors were grouped into 3 categories, namely: 0 to ± 2 weeks, ± 2 to ± 4 weeks and more than + 4 weeks and less than – 4 weeks on the x-axis. The percentage cases with an error falling in each category were calculated from the total number of cases, which were 34 in this instance, and a frequency diagram was drawn. The total percentage cases with an error between 0 to ± 2 weeks were 70.6, 47.0, 29.4 and 14.7 % for the Ideal + TBHQ, Ideal – TBHQ, Practical and OSI models, respectively. The percentage cases with an error between ± 2 to ± 4 were 23.5, 26.5, 44.1 and 14.7 % for the four models in the same order, respectively. The percentage cases with an error of more than + 4 weeks or less than – 4 weeks was 5.9, 26.5, 26.4 and 70.6 % for the four models, respectively.

Table 39: Jackknifing results of four selected models that were based on the PV and AV values.

Excluded case	Observed shelf-life	Ideal model incl. TBHQ		Ideal model excl. TBHQ		Practical model		OSI model	
		Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted
1	26	25.0	1.0	23.6	2.4	18.7	7.3	8.9	17.1
2	26	25.9	0.1	26.7	-0.7	24.6	1.4	12.4	13.6
3	34	34.5	-0.5	41.2	-7.2	39.8	-5.8	29.8	4.2
4	52	49.2	2.8	58.0	-6.0	55.9	-3.9	52.5	-0.5
5	20	17.7	2.3	18.5	1.5	18.7	1.3	9.0	11.0
6	20	19.9	0.1	20.2	-0.2	20.5	-0.5	11.4	8.6
7	28	28.1	-0.1	31.9	-3.9	32.3	-4.3	25.2	2.8
8	46	46.1	-0.1	48.6	-2.6	49.0	-3.0	45.5	0.5
9	15	17.2	-2.2	16.8	-1.8	18.0	-3.0	9.3	5.7
10	15	17.9	-2.9	19.3	-4.3	19.9	-4.9	10.6	4.4
11	23	25.5	-2.5	25.6	-2.6	25.9	-2.9	16.0	7.0
12	41	38.9	2.1	30.6	10.4	30.6	10.4	21.1	19.9
13	10	10.9	-0.9	12.0	-2.0	12.6	-2.6	9.8	0.2
14	10	11.9	-1.9	12.1	-2.1	12.4	-2.4	10.5	-0.5
15	18	19.3	-1.3	17.7	0.3	18.3	-0.3	14.6	3.4
16	36	34.2	1.8	27.6	8.4	28.7	7.3	26.0	10.0
17	7	7.0	0.0	8.9	-1.9	10.9	-3.9	10.3	-3.3
18	7	5.7	1.3	8.3	-1.3	7.7	-0.7	10.3	-3.3
19	15	15.5	-0.5	17.1	-2.1	17.7	-2.7	15.8	-0.8
20	33	31.7	1.3	25.1	7.9	25.8	7.2	20.2	12.8
21	4	2.9	1.1	3.3	0.7	5.2	-1.2	10.5	-6.5
22	4	3.6	0.4	5.4	-1.4	4.0	0.0	10.8	-6.8
23	12	12.8	-0.8	15.1	-3.1	15.0	-3.0	17.4	-5.4
24	30	30.3	-0.3	25.4	4.6	26.9	3.1	27.8	2.2
25	0	-3.6	3.6	-3.7	3.7	-2.5	2.5	11.0	-11.0
26	0	-1.6	1.6	0.9	-0.9	-4.2	4.2	11.1	-11.1
27	8	6.2	1.8	7.4	0.6	5.0	3.0	14.1	-6.1
28	26	26.3	-0.3	17.1	8.9	16.7	9.3	19.5	6.5
29	5	4.4	0.6	4.2	0.8	8.8	-3.8	15.4	-10.4
30	23	23.8	-0.8	22.0	1.0	24.9	-1.9	27.4	-4.4
31	0	-3.4	3.4	5.8	-5.8	3.8	-3.8	15.4	-15.4
32	18	18.2	-0.2	18.2	-0.2	17.6	0.4	23.5	-5.5
33	12	18.1	-11.8	13.0	-1.0	11.8	0.2	25.8	-13.8
34	0	4.4	-4.4	3.4	-3.4	3.6	-3.6	25.4	-25.4
Mean			-0.182		-0.097		-0.018		-0.009
Std error of estimate			2.7099		4.1961		4.2956		9.8010
95 % confidence interval			± 5.5		± 8.5		± 8.7		19.9

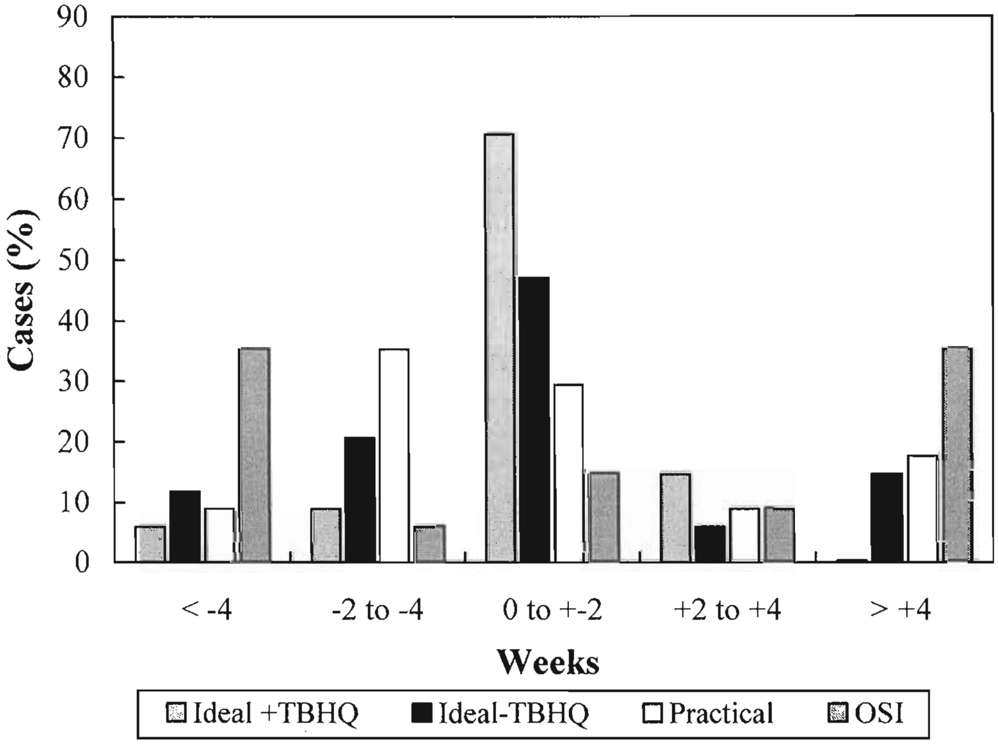

Figure 66: Percentage cases within each week category of the jackknifing results of the four models based on PV and AV values that was grouped into 3 categories namely: 0 to ± 2 weeks, ±2 to ±4 weeks and more than + 4 weeks and less than - 4 weeks.

Models based on sensory evaluation.

The results of the jackknifing are shown in Table 40 where the Ideal models is as described for Model 9 including TBHQ content and Model 10 excluding TBHQ content, Practical model as described for Model 11 and the OSI model as described for Model 12.

The same 95 % confidence level was applied to these models with the following results: the Ideal model including TBHQ had 6.1 weeks limits with one case not complying, the Ideal model excluding TBHQ had to comply within 3.5 weeks and 2 cases did not comply, the Practical model had to fall within 4.0 weeks and no cases were found to be outside the limits and the OSI model had to fall within 19.0 weeks with one case found to be outside the 95 % limit.

Table 40: Jackknifing results of four selected models that were based on the sensory evaluation.

Excluded case	**Observed shelf-life**	**Ideal model incl. TBHQ**		**Ideal model excl. TBHQ**		**Practical model**		**OSI model**	
		Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted	Predicted shelf-life	Observed minus predicted
1	29	31.6	-2.6	32.8	-3.8	32.7	-3.7	10.2	18.8
2	29	32.7	-3.7	26.4	2.6	25.4	3.6	8.9	20.1
3	26	40.8	-14.8	24.9	1.1	23.4	2.6	14.4	11.6
4	29	25.6	3.4	26.3	2.7	27.1	1.9	23.2	5.8
5	23	21.8	1.2	21.4	1.6	21.1	1.9	10.8	12.2
6	23	21.4	1.6	20.6	2.4	20.2	2.8	9.6	13.4
7	20	19.6	0.4	19.3	0.7	18.0	2.0	12.9	7.1
8	23	25.6	-2.6	26.7	-3.7	23.7	-0.7	22.9	0.1
9	18	18.5	-0.5	18.4	-0.4	19.0	-1.0	11.5	6.5
10	18	19.1	-1.1	19.1	-1.1	17.5	0.5	10.2	7.8
11	15	15.9	-0.9	17.9	-2.9	17.9	-2.9	10.2	4.8
12	18	17.3	0.7	19.4	-1.4	18.8	-0.8	11.8	6.2
13	13	14.9	-1.9	13.8	-0.8	15.7	-2.7	12.4	0.6
14	13	13.1	-0.1	12.4	0.6	13.7	-0.7	10.7	2.3
15	10	9.5	0.5	11.8	-1.8	13.7	-3.7	10.2	-0.2
16	13	12.1	0.9	11.5	1.5	13.9	-0.9	14.1	-1.1
17	10	10.2	-0.2	9.6	0.4	10.4	-0.4	13.1	-3.1
18	10	8.7	1.3	9.2	0.8	8.5	1.5	11.5	-1.5
19	7	7.5	-0.5	7.7	-0.7	7.4	-0.4	10.6	-3.6
20	10	9.3	0.7	9.0	1.0	10.3	-0.3	12.0	-2.0
21	7	6.9	0.1	5.8	1.2	6.5	0.5	12.5	-5.5
22	7	5.2	1.8	5.1	1.9	4.3	2.7	11.0	-4.0
23	4	4.4	-0.4	4.6	-0.6	3.9	0.1	11.2	-7.2
24	7	8.5	-1.5	7.4	-0.4	8.4	-1.4	15.2	-8.2
25	3	3.5	-0.5	4.0	-1.0	3.6	-0.6	13.1	-10.1
26	3	4.9	-1.9	2.2	0.8	-0.3	3.3	11.1	-8.1
27	0	0.3	-0.3	1.1	-1.1	-0.7	0.7	10.8	-10.8
28	3	2.5	0.5	2.0	1.0	3.4	-0.4	12.2	-9.2
29	0	-0.1	0.1	1.9	-1.9	1.8	-1.8	13.7	-13.7
30	0	-0.6	0.6	0.2	-0.2	-0.4	0.4	11.5	-11.5
31	0	0.59	-0.6	-0.9	0.9	1.9	-1.9	15.4	-15.4
Mean			-0.7		0.0		0.0		0.1
Std error of estimate			2.9952		1.6989		1.9716		9.3022
95 % confidence interval			± 6.1		± 3.5		± 4.0		19.0

The observed minus predicted values (errors) of the models is represented graphically in Figure 67. The percentage cases with an error falling in each category were calculated from the total of 31 cases. The total percentage cases with an error between 0 to ± 2 weeks were 83.8, 80.6, 70.9 and 19.4 % for the Ideal + TBHQ, Ideal – TBHQ, Practical and OSI models, respectively. The percentage cases with an error between ± 2 to ± 4 were 12.9, 19.4, 29.0 and 12.9 % for the four models in the same order, respectively. The percentage cases with an error of more than + 4 weeks or less than – 4 weeks was 3.2, 0, 0 and 67.8 % for the four models respectively.

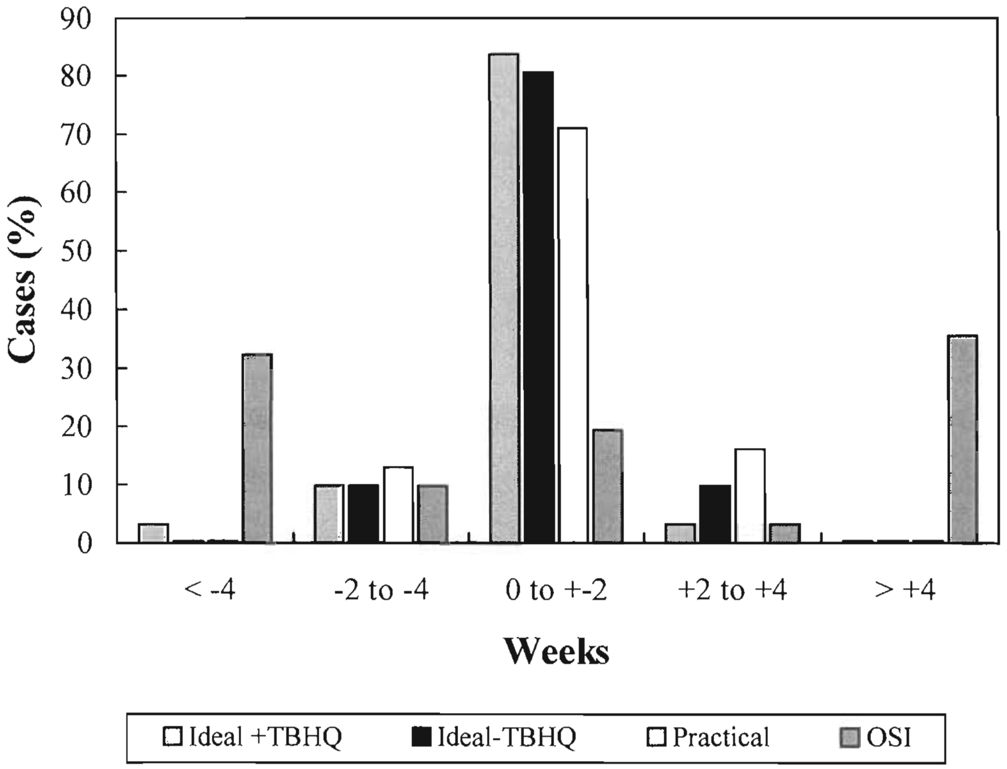

Figure 67: Percentage cases within each week category of the jackknifing results of the four models based on sensory evaluation that was grouped into 3 categories namely: 0 to ± 2 weeks, ±2 to ±4 weeks and more than + 4 weeks and less than - 4 weeks.

4.3 STATISTICAL ANALYSIS

The treatments were compared statistically for each parameter to determine if the trends differed significantly from each other.

4.3.1 Palm-olein oil

Best fitting equations (response for variable versus storage time), either linear regression lines ($y = a + bx$) or quadratic curves ($y = a + bx + cx^2$) were fitted to the curves of each treatment and the intercepts (a) and slopes (b) of the linear regression lines and the intercepts (a), b and c coefficients of the quadratic curves were pair-wise subjected to the t-test at the 99 % confidence level. In the cases where no result is shown a line or curve could not be fitted to the sample curve as no values were obtained. The results for the intercepts of the linear and quadratic equations fitted to the data are shown in Table 41. The results for the slopes (b) of variables that had linear regression lines fitted are shown in Tables 42, whereas the results for the b and c coefficients of quadratic curves fitted to the data are in Table 43.

Statistical analysis of trans-2-hexenal was not included as the values of all the samples showed very little change with a fluctuation of t-2-hexenal content between 0-2.3 mg/kg in total.

The symbols used in the tables have the following meanings:

S	=	significantly different at 99 % confidence level
NS	=	not significantly different at 99 % confidence level
-	=	no values obtained for a sample treatment and it was therefore not possible to fit a regression line or quadratic curve
↑	=	indicates significantly higher absolute values for the coefficient of the first named treatment than the second named treatment
↓	=	indicates significantly lower absolute values for the coefficient of the first named treatment than the second named treatment

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Table 41: t-test results at 99 % confidence level of intercepts (a) for each comparison of the different treatments of palm-olein oil.

Variable	Comparisons of treatments					
	Control versus 0.035 mg/kg copper	Control versus 0.17 mg/kg copper	Control versus 0.69 mg/kg copper	0.035 mg/kg versus 0.17 mg/kg copper	0.035 mg/kg versus 0.69 mg/kg copper	0.17 mg/kg versus 0.69 mg/kg copper
FFA	NS	NS	NS	NS	NS	NS
PV	S ↑	S ↑	S ↑	NS	S ↑	NS
AV	S ↓	S ↓	S ↓	S ↓	NS	S ↑
Totox	S ↑	S ↑	S ↑	NS	NS	NS
OSI	NS	S ↑	S ↑	S ↑	S ↑	S ↑
Total tocopherols	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Alpha tocopherol	S ↑	S ↑	S ↑	S ↑	S ↑	-
Alpha tocotrienol	S ↑	S ↑	S ↑	S ↑	S ↑	NS
Gamma tocotrienol	S ↑	S ↑	S ↑	S ↑	S ↑	NS
Delta tocotrienol	NS	S ↑	S ↑	S ↑	S ↑	NS
CV 232 nm	S ↑	NS	S ↑	NS	NS	NS
CV 268 nm	S ↓	S ↓	S ↓	NS	NS	NS
IV	NS	NS	NS	NS	NS	NS
Total volatiles	NS	NS	NS	NS	S ↓	S ↓
Hexanal	S ↑	S ↑	S ↑	NS	NS	NS
t,t-2,4-decadienal	-	-	-	NS	NS	NS
Pentanal	S ↓	S ↓	S ↓	NS	S ↓	S ↓

The results showed that the majority of the intercepts differed statistically from each other, the exceptions being the curves of the FFA and IV variables, where the intercepts of all the sample treatment comparisons did not differ significantly from each other.

Table 42: t-test results at 99 % confidence level of the slopes (b) for each comparison of the different treatments that has been subjected to linear regression curves of palm-olein oil.

Variable	Comparisons of treatments					
	Control versus 0.035 mg/kg copper	Control versus 0.17 mg/kg copper	Control versus 0.69 mg/kg copper	0.035 mg/kg versus 0.17 mg/kg copper	0.035 mg/kg versus 0.69 mg/kg copper	0.17 mg/kg versus 0.69 mg/kg copper
FFA	S ↑	S ↑	S ↑	NS	S ↑	S ↑
PV	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
AV	S ↓	S ↓	S ↓	S ↓	S ↓	S ↑
OSI	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Total tocopherols	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Alpha tocopherol	S ↑	S ↑	S ↑	S ↑	-	-
Alpha tocotrienol	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Gamma tocotrienol	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Delta tocotrienol	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
CV 232 nm	S ↑	S ↑	S ↑	S ↓	NS	S ↑
CV 268 nm	S ↓	S ↓	S ↓	S ↓	S ↑	S ↑
IV	S ↑	S ↑	S ↑	NS	S ↓	S ↓
Total volatiles	S ↑	S ↑	S ↓	S ↓	S ↓	S ↓
Hexanal	S ↑	S ↑	S ↑	NS	S ↓	S ↓

The t-test results of the b and c coefficients of variables that had quadratic curves fitted to them are shown in Table 43.

Table 43: t-test results of comparisons of b and c quadratic coefficients of the treatments of palm-olein oil.

Variable	Coefficient	Comparisons of treatments					
		Control versus 0.035 mg/kg copper	Control versus 0.17 mg/kg copper	Control versus 0.69 mg/kg copper	0.035 mg/kg versus 0.17 mg/kg copper	0.035 mg/kg versus 0.69 mg/kg copper	0.17 mg/kg versus 0.69 mg/kg copper
Totox	b	S↑	S↑	S↑	S↓	S↑	S↑
	c	S↑	S↑	S↑	S↓	S↑	S↑
t,t-2,4-decadienal	b	-	-	-	S↓	S↑	S↑
	c	-	-	-	S↓	S↑	S↑
Pentanal	b	S↓	S↓	S↓	S↓	S↓	S↓
	c	S↓	S↓	S↓	S↓	S↓	S↓

Most of the slopes of the sample treatment comparisons of the variables differed significantly from each other. The slopes of 5 sample treatment comparisons of the FFA, CV 232, IV and hexanal variables were significantly different from each other and only one treatment comparison of each variable mentioned was not significantly different (0.035 versus 0.17 mg/kg copper for FFA, 0.035 versus 0.69 mg/kg copper for CV 232 nm, 0.035 versus 0.17 mg/kg copper for IV and 0.035 versus 0.17 mg/kg copper for hexanal). The dissimilarity between the different slopes of the treatments can be gauged from the graph of each variable.

4.3.2 Sunflower seed oil

Best fitting equations, either linear regression lines (y = a + bx) or quadratic curves ($y = a + bx + cx^2$) were fitted to the curves of each treatment and the intercepts (a) and slopes (b) of the linear regression lines and the intercepts (a), b and c coefficients of the quadratic curves were pair-wise subjected to the t-test at the 99 % confidence level. The results for the intercepts of the linear and quadratic equations fitted to the data are shown in Table 44. The results for the slopes (b) of variables that had linear regression lines fitted are shown in Tables 45 whereas the results for the b and c coefficients of quadratic curves fitted to the data are in Table 46.

Statistical analysis of beta-tocopherol, trans-2-hexanal and trans,trans-2,4-decadienal was not included as the values of all the samples showed very little change with broad fluctuations within the low values obtained.

The symbols used in the tables have the same meaning as in palm-olein oil.

Table 44: t-test results at 99 % confidence level of intercepts (a) for each comparison of the different treatments of sunflower seed oil.

Variable	Comparisons of treatments					
	Control versus 54 mg/kg TBHQ	Control versus 217 mg/kg TBHQ	Control versus 435 mg/kg TBHQ	54 mg/kg versus 217 mg/kg TBHQ	54 mg/kg versus 400mg/kg TBHQ	217 mg/kg versus 435 mg/kg TBHQ
FFA	NS	NS	NS	NS	S ↑	NS
PV	NS	NS	S ↑	NS	S ↑	NS
AV	NS	NS	NS	NS	NS	NS
Totox	NS	NS	S ↑	NS	NS	NS
OSI	S ↓	S ↓	S ↓	S ↓	S ↓	S ↓
Total tocopherols	NS	NS	S ↓	NS	NS	NS
Alpha tocopherol	NS	S ↓	S ↓	NS	NS	NS
Gamma tocopherolsl	NS	NS	NS	NS	NS	NS
CV 232 nm	S ↑	S ↑	S ↑	S ↑	S ↑	NS
CV 268 nm	NS	NS	NS	NS	NS	NS
IV	NS	NS	NS	NS	NS	NS
Total volatiles	NS	NS	NS	NS	NS	NS
Hexanal	NS	S ↑	S ↑	NS	NS	NS
Pentanal	NS	NS	NS	NS	NS	NS

The results showed that none of the intercepts of the sample treatment comparisons of the following variables AV, gamma-tocopherol, CV 268, IV, total volatiles and pentanal, differed statistically from each other. All the intercepts of the sample treatments of OSI differed significantly from each other and the CV 232 had 5 significant differences in the sample treatments intercepts with only 217 mg/kg TBHQ versus 435 mg/kg TBHQ being not significantly different. The remainder of the curves for the variables FFA, PV, Totox, total tocopherols and hexanal, had one or two of the intercepts of the sample treatment comparisons that differed significantly from each other.

Table 45: t-test results at 99 % confidence level of the slopes (b) for each comparison of the different treatments that has been subjected to linear regression curves of sunflower seed oil.

Variable	Comparisons of treatments					
	Control versus 54 mg/kg TBHQ	Control versus 217 mg/kg TBHQ	Control versus 435 mg/kg TBHQ	54 mg/kg versus 217 mg/kg TBHQ	54 mg/kg versus 435 mg/kg TBHQ	217 mg/kg versus 435 mg/kg TBHQ
FFA	S↓	S↑	S↑	S↑	S↑	S↑
AV	S↑	S↑	S↑	S↓	S↑	S↑
Total tocopherols	S↓	S↓	S↓	S↓	S↓	S↓
Alpha tocopherol	S↓	S↓	S↓	S↓	S↓	S↓
Gamma tocopherol	S↓	S↓	S↓	NS	NS	NS
CV 232 nm	S↑	S↑	S↑	S↑	S↑	S↑
CV 268 nm	S↑	S↑	S↑	S↑	NS	S↓
IV	S↑	S↑	S↓	NS	S↓	S↓
Total volatiles	S↑	S↑	S↑	S↑	S↑	S↑
Pentanal	S↑	S↑	S↑	S↑	S↑	S↑

Most of the slopes of the sample treatment comparisons of the variables differed significantly from each other. The slopes of 5 sample treatment comparisons of the CV 268 and IV variables were significantly different from each other and only one treatment comparison for each variable mentioned was not significantly different (54 versus 435 mg/kg TBHQ for CV 268 nm and 54 versus 217 mg/kg TBHQ for IV). In the gamma-tocopherol variable slopes of the Control versus the TBHQ samples differed significantly from each other, whereas the samples containing TBHQ did not differ significantly from each other. The dissimilarity between the different slopes of the treatments can be gauged from the graph of each variable.

Table 46: t-test results of comparisons of b and c quadratic coefficients of the treatments of sunflower seed oil.

Variable	Coefficient	Comparisons of treatments					
		Control versus 54 mg/kg TBHQ	Control versus 217 mg/kg TBHQ	Control versus 435 mg/kg TBHQ	54 mg/kg versus 217 mg/kg TBHQ	54 mg/kg versus 435 mg/kg TBHQ	217 mg/kg versus 435 mg/kg TBHQ
PV	b	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
	c	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
Totox	b	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
	c	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
OSI	b	S ↓	S ↓	S ↓	S ↓	S ↓	S ↓
	c	S ↓	S ↓	S ↓	S ↓	S ↓	S ↓
Hexanal	b	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑
	c	S ↑	S ↑	S ↑	S ↑	S ↑	S ↑

All of the coefficients for the slopes of the sample treatment comparisons of the variables differed significantly from each other.