Monitoring the storage stability of RBD palm olein using the electronic nose

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Abstract

Storage stability of RBD palm olein was monitored using a surface acoustic wave (SAW) sensor-based electronic nose. Fatty acid composition, iodine value (IV), peroxide value (PV), and free fatty acid content (FFA) analyses were used to determine the quality of the oils and to compliment the electronic nose data. A descriptive test was carried out by sensory analysis with ten trained panellists. The results from the electronic nose showed significant difference between fresh oil and rancid oil. High resolution olfactory imaging, called VaporPrint[TM], was shown to be particularly useful for assessing oil quality in its entirety. A high correlation was observed between electronic nose responses and chemical test data, as well as sensory evaluation score, by using Pearson's correlation. It can be concluded that the SAW sensor based electronic nose may be utilized as an analytical tool to follow the progress of oxidation and breakdown of vegetable oil.
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1. Introduction

Vegetable oil quality and stability are the main factors that influence its acceptability and market value. Oxidative stability is one of the most important indicators of the keeping quality of vegetable oils (Tan & Che Man, 2002). In general, the term rancidity has been used to describe the mechanisms by which lipids alter in the presence of oxygen or air (Hamilton, 1989). Today, rancidity in processed food is becoming increasingly important as manufacturers require longer shelf-lives and because of public awareness of nutritional issues.

Oxidative deterioration of fat results in the development of a pungent and offensive off-flavour and the destruction of vitamins (A, D, E, K and C), essential fatty acids, chlorophylls, carotenes, amino acids, proteins, or enzymes by the production of toxic or physio-logically active compounds (Gardner, 1979) and is believed to lead to deteriorative processes in man, including aging (Pearson, Gray, Wolzak, & Horenstein, 1983).

In general, the time before a dramatic increase in the rate of lipid oxidation is a measure of oxidative stability and is referred to as the induction time (Coppin & Pike, 2001). Historically, the Schaal Oven Test (SOT) and the Active Oxygen Method (AOM) have been the most widely used tests for evaluating oil stability (Wan, 1995). Many objective instrumental and chemical methods have been proposed over the years to evaluate the quality and stability of vegetable oils.

However, faster qualitative and quantitative analyses of chemical compounds are becoming a necessity in today's complex competitive environment. Of all the devices developed, the concept of an electronic nose is becoming popular. Electronic noses made their appearance in the market almost a decade ago. The electronic nose is preferred to routine laboratory analysis

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because it is rapid, simple and easy-to-handle (Biswas, Heindselmen, Wohltjen, & Staff, 2004).

An electronic nose is a vapour analyzer and, the working principle is claimed to mimic the human nose. The sensory array represents the sensors in the human nose. The circuitry represents the conversion of the chemical reaction on the human sensors to electrical signals into the brain. Finally, the software analysis represents the brain itself. The electronic nose is therefore analogous to the human olfactory system.

An electronic nose must have the ability to recognize as well as quantify many different complex fragrances. This is achieved using a visual fragrance pattern, called a VaporPrint™ derived from the frequency of the surface acoustic wave (SAW) detector. A VaporPrint™ is created by transforming the time variable to a radial angle with the beginning and end of the analysis occurring at 0° or vertical. A complete chromatogram always spans 360°. A VaporPrint™ image allows a complex ambient environment to be viewed entirely. Using the unsurpassed ability of humans to recognize patterns, skilled operators are able to assess the nature of vapours and to look for analytes of interest rapidly (Staples, 1999). The objective of this study was to develop a rapid method to identify and quantify the storage stability of RBD palm olein using a SAW sensor-based electronic nose.

2. Materials and methods

2.1. Oil samples

RBD palm olein was purchased from local refineries. The oil was stored at 2 different storage temperatures: room temperature, 28 ± 1 °C and accelerated temperature using an oven at 60 °C. Data was collected every 2 days for a duration of 52 days.

2.2. Chemical analysis

The chemical analyses, namely free fatty acid content (FFA), peroxide value (PV), *p*-anisidine value (AV), and iodine value (IV), were carried out using AOCS official methods Ca 5a-40, Cd 8-53, Cd 18-90, and Cd 1b-87, respectively (AOCS, 1996). All chemicals and solvents used were of analytical grade unless otherwise specified.

The individual fatty acid composition of fats and oils were analysed using gas chromatography (Hewlett-Packard model 5890 instrument, Palo Alto, CA). 0.95 ml of petroleum spirit was added to 50 mg of sample, followed by 0.05 ml of sodium methoxide (PORIM, 1995). Samples were transesterified to convert the fatty acids into relatively volatile methyl ester derivatives (FAME). 0.8 ml of sample was injected into the instrument, with an inlet temperature at 240 °C. A capillary column BPX70 was used with the column head pressure maintained at 145 kPa. Helium (99.95%), with a flow rate 1.3 ml/min, was the carrier gas. The temperature was programmed from 160 °C, equilibrium for 1 min, and then increased to 200 °C at a rate of 10 °C/min, and equilibrium for 2 min. Finally, the temperature was increased to 240 °C at a rate of 20 °C/min and held for 1 min. An FID detector was used with the temperature set at 275 °C.

2.3. Sensory evaluation

A descriptive test was carried out for sensory analysis conducted at the Malaysian Palm Oil Board (MPOB) with 10 trained panellists. Two separate sessions were conducted for oil samples stored at room temperature and oven temperature 60 °C. Six samples, coded with 3 random digits, were evaluated during each session (2, 12, 22, 32, 42 and 52 day). 10 g of oil were weighed into a 30 ml screw cap amber glass bottle. Before evaluation, the bottles were kept for 30 min in a 50 °C regulated oven to help the odour develop in the headspace. This preparation facilitated odour perception by the panellists. Panellists were then instructed to remove the lid of the bottle and take three short sniffs. They were asked to rate the overall intensity of the samples according to a predetermined attribute scale, ranging from 1 (extreme) to 10 (bland) according to Method Cg 2-83 (AOCS, 1996).

2.4. Electronic nose equipment specifications

The electronic nose (4100 vapour analysis system, Electronic Sensor Technology, New Bury Park, USA) is a hand held portable analyzer. The complete system includes a sensor head, a support chassis, and a system controller, is housed within a small carrying case. The sensor head contains the hardware necessary to separate and detect materials. The support chassis include a small helium gas tank, power supply and electronics to run the system. The system controller is based on a laptop computer.

This electronic nose uses a single, uncoated, high quartz SAW sensor. The SAW crystal consists of an uncoated 500 MHz acoustic interferometer or resonator bonded to a Peltier thermoelectric heat pump with the ability to heat or cool the quartz crystal. This detector possesses advantages, such as high sensitivity, easy-to-handle signal, low power and long term stability. Coatings are not used because they reduce the resonator Q, introduce instability, and require excessive time for equilibrium. Sensitivity is excellent because there is no dilution of sample vapour. Minimum detection levels for semi-volatile compounds typically extend well into the part-per-trillion (ppt) range. The temperature of the quartz substrate is held constant during chromatogra-

phy and provides a method for adjusting the sensitivity of the detector.

2.5. Electronic nose analysis

10 g of each oil sample were weighed into septa-sealed vials. After a headspace generation time of 3 min at 60 °C (in water-bath), the sample's vapour was pumped (5 s) into the electronic nose with a side-ported sampling needle through the septa. The electronic nose used a two step process to analyse vapours. The first step samples vapours (inlet 200 °C) and concentrates them in a Tenax trap. Sample preconcentration is carefully controlled to produce a repeatable and accurate collection of ambient vapours for analysis in the second step.

In the second step, the trap is rapidly heated and released vapours are re-focussed on the head of the relatively low temperature (40 °C) capillary column. This system is based on the principal of gas chromatography. The column temperature is programmed (from 40 to 160 °C, at a rate of 5 °C/s) to follow a linear rise to its maximum temperature, causing the different chemical component in the sample to be released, travel through the column, and land on the surface of the SAW crystal (temperature controlled at 30 °C). The flow rate (purified helium) was fixed at 3.0 ml/min.

The SAW detector is only specific to vapour pressure. The specificity of the SAW detector is based on the temperature of the crystal surface and the vapour pressure characteristics of the condensate itself. At a given crystal temperature only, those analytes with dew points below the crystal temperature will condense and be detected. This provides a general method for separating volatile from non-volatile vapours, based upon the operating temperature of the SAW crystal.

The added mass of the material lowered the oscillating frequency of the SAW crystal. This frequency was mixed with a reference frequency and the resulting intermediate frequency (IF) was counted by the system microprocessor board. By measuring the time required for each chemical to reach the sensor and the amount it effects the crystal's vibration, both the identity of the substance and the quantity in which it is present can be calculated by software incorporated in the instrument. Sensor space is defined mathematically according to retention time slots. Separation of different compounds is greatly improved. The entire testing process takes approximately 1 min per sample.

2.6. Data analysis

All measurements were duplicated. The results were expressed as the mean values and standard deviations of two replications. All data were subjected to two-way analysis of variance using SAS Statistical Computer Package Version 6.12 (SAS, 1989). Duncan's multiple range tests were used to compare differences among means. Significance was defined at $P < 0.05$. Electronic nose data were further analysed to obtain the trendline equation as well as the R^2 value using the Microsoft excel software. Pearson correlation coefficient between electronic nose method, sensory analysis and other chemical tests were calculated with the chemical component with the highest R^2 value using the Microsoft excel software.

3. Results and discussion

3.1. Chemical analyses

3.1.1. Characteristics of fresh RBD palm olein

The initial characteristics of RBD palm olein used in this study are given in Table 1. The RBD palm oil was of good quality, as indicated by its initial low PV of 0.6 meq/kg and FFA content of 0.1%. The fatty acid composition of RBD palm olein was within the range for Malaysian palm olein (Tan & Oh, 1981).

3.1.2. Quality changes in RBD palm olein over storage

It is a well-known fact, that when vegetable oils are exposed to oxidizing environments, they undergo oxidative degradation. Oxidation is the single most important reaction of oils, leading to rancidity and toxicity. The changes in quality parameters of RBD palm olein in storage are given in Table 2. Table 3 gives the fatty acid composition of the used RBD palm olein over time. The oil system with a temperature at 60 °C experienced a greater degree of deterioration than the oil system at room temperature. The extent of oil deterioration was best reflected in the changes in PV and FFA content. The IV and AV also provided supporting evidence for the extent of oil deterioration. However, the

Table 1
Characteristics of fresh RBD palm olein used in storage sexperiments[a]

Characteristics of the oil	Value[b]
PV (meq hydroperoxide/kg oil)	0.6 ± 0.0
IV (g of I_2/100 g oil)	56.3 ± 0.7
FFA content (%)	0.1 ± 0.0
AV	1.41 ± 0.04
Fatty acid composition (%)	
$C_{12:0}$	0.36 ± 0.04
$C_{14:0}$	1.38 ± 0.08
$C_{16:0}$	45.6 ± 1.01
$C_{18:0}$	3.13 ± 0.09
$C_{18:1}$	40.9 ± 0.71
$C_{18:2}$	8.64 ± 0.33
$C_{18:2}/C_{16:0}$ ratio	0.19 ± 0.01

[a] RBD, refined, bleached and deodorized; FFA, free fatty acid.
[b] Each value is the mean of four analyses from two replication.

Table 2
Changes of quality parameters of RBD palm olein during storage[a]

Characteristics	Day	System 28 ± 1 °C	System 60 °C
PV (meq hydroperoxide/kg oil)	2	0.60 ± 0.00^a_A	0.60 ± 0.00^b_F
	12	0.60 ± 0.00^b_A	14.9 ± 0.62^a_E
	22	0.60 ± 0.14^b_A	38.5 ± 0.18^a_D
	32	0.55 ± 0.07^b_A	50.2 ± 0.25^a_C
	42	0.50 ± 0.14^b_A	56.3 ± 1.88^a_B
	52	0.55 ± 0.07^b_A	70.1 ± 2.42^a_A
FFA Content (%)	2	$0.12 \pm 0.00^a_{BC}$	0.11 ± 0.01^b_C
	12	0.11 ± 0.00^a_C	$0.12 \pm 0.01^a_{BC}$
	22	0.11 ± 0.01^b_C	$0.12 \pm 0.01^a_{BC}$
	32	0.11 ± 0.01^b_C	0.14 ± 0.01^a_B
	42	0.13 ± 0.01^a_B	0.14 ± 0.03^a_B
	52	0.15 ± 0.01^b_A	0.22 ± 0.02^a_A
IV (g of I_2/100 g oil)	2	56.8 ± 0.44^a_A	57.2 ± 0.13^a_A
	12	56.8 ± 0.34^a_A	$56.8 \pm 0.99^a_{AB}$
	22	57.1 ± 0.22^a_A	$56.8 \pm 0.23^a_{AB}$
	32	55.6 ± 0.12^a_B	55.9 ± 0.14^a_B
	42	57.3 ± 1.01^a_A	54.5 ± 0.73^b_C
	52	$56.5 \pm 0.67^a_{AB}$	53.6 ± 0.38^b_C
AVs	2	1.76 ± 0.00^a_B	1.56 ± 0.13^a_F
	12	1.67 ± 0.22^b_B	2.45 ± 0.29^a_E
	22	1.87 ± 0.15^b_B	3.45 ± 0.25^a_D
	32	1.94 ± 0.26^b_B	4.69 ± 0.37^a_C
	42	$2.40 \pm 0.32^b_{AB}$	5.60 ± 0.25^a_B
	52	2.89 ± 0.56^b_A	8.16 ± 0.38^a_A

[a] Each value in the table represents the mean $\pm$ standard deviation of six analyses from two replications. Means within each row with different superscripts are significantly ($P < 0.05$) different. Means within each column with different subscripts are significantly ($P < 0.05$) different. See Table 1 for abbreviations.

Table 3
Fatty acid composition and ratio of $C_{18:2}/C_{16:0}$ of RBD palm olein during storage[a]

System	Day	Fatty acid (%)						
		$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:2}/C_{16:0}$
28 ± 1 °C	2	0.71	1.25	44.8	3.05	41.0	9.16	0.21
	12	1.60	1.86	45.2	2.87	39.9	8.51	0.19
	22	1.23	1.62	47.5	2.60	38.9	8.21	0.17
	32	0.44	1.47	45.4	3.15	40.7	8.89	0.20
	42	0.43	1.45	44.9	3.21	41.0	9.00	0.20
	52	0.57	1.70	46.7	3.02	39.1	8.87	0.19
60 °C	2	0.97	1.39	44.0	3.07	41.6	9.01	0.20
	12	0.49	1.57	46.5	3.09	39.6	8.83	0.19
	22	0.45	0.65	45.7	2.94	40.8	8.50	0.19
	32	0.43	1.47	45.9	3.14	40.7	8.35	0.18
	42	0.54	1.66	47.3	3.01	39.8	7.71	0.16
	52	0.57	1.65	46.9	3.04	40.3	7.56	0.16

[a] Mean of four analyses from two replications. See Table 1 for abbreviation.

changes in these values were not as apparent as those in the PV and FFA content.

3.1.3. Changes in PV and FFA content

The changes in PV and FFA content over storage are presented in Table 2. The PV rose and fell over storage, which is the same pattern as observed for peroxides in most storage studies (Rady & Msdkour, 1995). Peroxides are unstable and can break down to carbonyl and aldehydic compounds under conditions of high heat, air, and light (Perkins, 1967). The results of this study showed that, at 60 °C, the formation of peroxides increased rapidly from day 0 to day 52. At room temperature (28 ± 1 °C), which acted as a control, the PVs

were significantly ($P < 0.05$) lower than the system at 60 °C throughout the duration of the study.

FFA content is a measure of the acidic components in the oil. Generally, the determination of FFA by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis (Sherwin, 1968). Although the FFA content is an index of hydrolytic rancidity, it was nevertheless measured, as free acids contribute to the development of off-flavours and off-odours in the product. At the end of the storage period, FFA content was 0.22% at 60 °C as compared to 0.15% at room temperature system.

Table 4
Sensory scores for rancid odour of RBD palm olein under storage test[a]

Day	System 28 ± 1 °C	System 60 °C
2	$8.11 \pm 1.96_A^a$	$8.00 \pm 1.41_A^a$
12	$8.10 \pm 1.66_A^a$	$7.00 \pm 2.11_{AB}^a$
22	$7.50 \pm 2.07_A^a$	$6.10 \pm 1.79_{BC}^a$
32	$7.50 \pm 1.96_A^a$	$4.90 \pm 1.66_{CD}^b$
42	$7.60 \pm 1.65_A^a$	$3.60 \pm 1.78_{DE}^b$
52	$6.30 \pm 2.45_A^a$	$3.00 \pm 1.25_E^b$

[a] Means of 10 observations. Means within each row with different superscripts are significantly ($P < 0.05$) different. Means within each column with different subscripts are significantly ($P < 0.05$) different. Odour intensity score: 10(bland) to 1(extreme). See Table 1 for abbreviation.
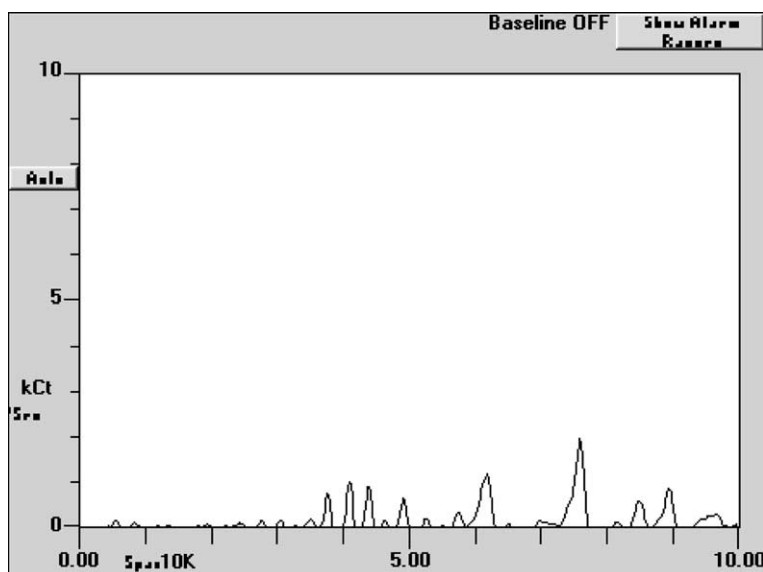

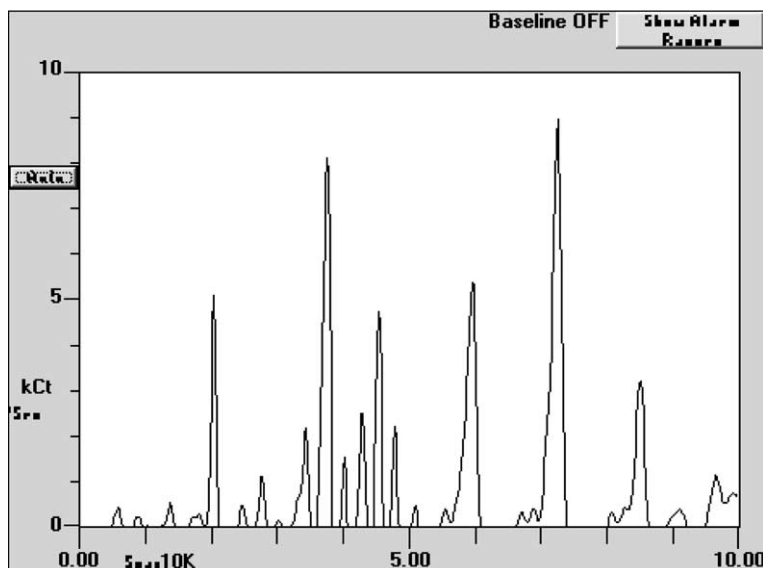Fig. 1. Electronic nose chromatogram for fresh palm olein.

Fig. 2. Electronic nose chromatogram for oxidized palm olein (60 °C day 52).

3.1.4. Changes in IV and AV

Changes in IV and AV during 60 consecutive days of storage in both systems are given in Table 2. IV is a measure of overall unsaturation and is widely used to characterize oils and fats. A decrease in IV is consistent with the decreasing number of double bonds in oil as it
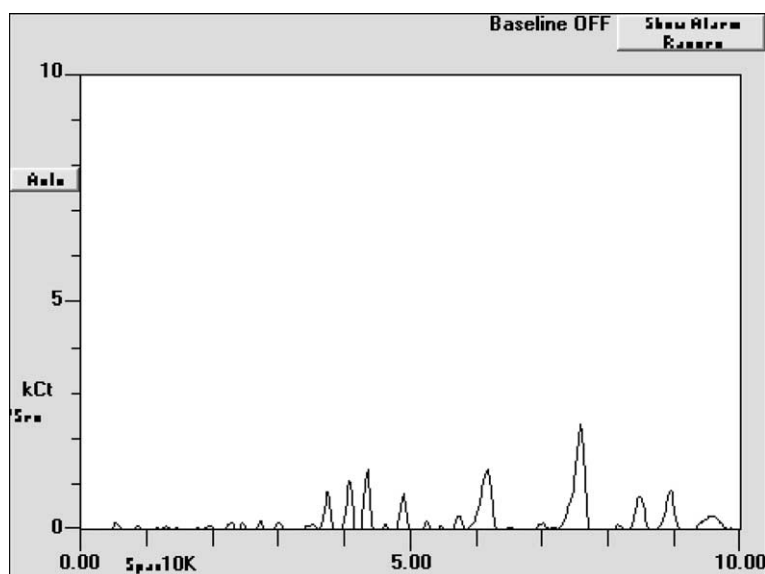

Fig. 3. Electronic nose chromatogram for palm olein (28 ± 1 °C day 52).

Table 5
Electronic nose results of RBD palm olein under storage test[a]

System	Day	Compound						
		A	B	C	D	E	F	G
28 ± 1 °C	2	9.9 ± 3.4^a	4.8 ± 0.7^b	9.5 ± 1.9^c	9.4 ± 2.8^b	11.0 ± 3.0^a	53.7 ± 9.6^b	65.0 ± 4.8^b
	12	7.9 ± 1.7^a	2.0 ± 0.3^d	6.0 ± 0.8^d	8.0 ± 2.0^{cb}	12.0 ± 2.8^a	43.4 ± 8.7^b	65.9 ± 12.3^b
	22	9.8 ± 1.5^a	2.0 ± 0.2^d	5.5 ± 1.0^d	7.1 ± 0.2^{cb}	5.1 ± 0.5^b	56.7 ± 7.7^b	73.0 ± 4.5^b
	32	8.5 ± 1.4^a	3.1 ± 0.4^c	3.9 ± 0.8^d	4.0 ± 0.7^c	11.6 ± 1.1^a	57.8 ± 14.6^b	70.5 ± 17.3^b
	42	8.9 ± 0.9^a	3.4 ± 0.7^c	22.3 ± 2.1^a	4.5 ± 0.7^c	5.3 ± 0.6^b	53.0 ± 15.0^b	80.8 ± 7.0^b
	52	8.6 ± 2.1^a	6.1 ± 1.0^a	12.0 ± 2.4^b	15.2 ± 4.0^a	13.4 ± 2.8^a	83.0 ± 4.1^a	107.2 ± 9.3^a
60 °C	2	17.8 ± 2.6^c	6.5 ± 1.3^d	11.5 ± 2.1^c	15.3 ± 4.3^d	27.6 ± 8.7^c	131 ± 22.1^c	124 ± 32.8^d
	12	18.2 ± 3.1^c	10.0 ± 1.0^{cd}	14.0 ± 1.8^c	17.2 ± 2.0^{cd}	30.5 ± 4.2^c	144 ± 13.8^c	153 ± 14.1^{cd}
	22	19.7 ± 2.2^c	11.0 ± 1.0^{cd}	19.4 ± 2.1^c	20.0 ± 2.6^c	32.0 ± 5.5^c	140 ± 16.5^c	162 ± 26.0^c
	32	19.7 ± 2.6^c	12.6 ± 1.9^c	22.0 ± 3.2^c	25.5 ± 1.3^c	30.5 ± 5.3^c	143 ± 24.0^c	177 ± 11.7^c
	42	34.0 ± 3.2^b	30.2 ± 2.8^b	193 ± 14.8^b	29.0 ± 1.0^{ab}	62.3 ± 5.0^b	359 ± 70.2^b	225 ± 42.0^b
	52	42.0 ± 4.5^a	46.2 ± 606^a	344 ± 26.5^a	32.0 ± 1.0^a	93.2 ± 9.8^a	958 ± 152.6^a	301 ± 1.3^a
		H	I	J	K	L	M	
28 ± 1 °C	2	17.3 ± 4.8^d	127 ± 8.0^c	18.8 ± 1.7^b	125 ± 6.1^c	69.8 ± 16.5^b	65.3 ± 4.2^b	
	12	22.8 ± 2.5^{cd}	139 ± 23.9^{cb}	19.4 ± 2.1^b	132 ± 23.6^c	70.0 ± 7.5^b	67.7 ± 17.4^{ab}	
	22	39.7 ± 4.6^b	166 ± 34.4^{cb}	19.0 ± 0.3^b	209 ± 37.5^b	41.8 ± 10.8^c	64.0 ± 10.5^b	
	32	40.8 ± 11.1^b	170 ± 32.8^b	19.3 ± 4.6^b	230 ± 25.0^b	50.0 ± 4.3^c	72.0 ± 8.4^{ab}	
	42	31.2 ± 7.4^{cb}	164 ± 34.2^{cb}	23.5 ± 5.5^b	187 ± 47.8^b	43.7 ± 9.6^c	66.2 ± 7.4^{ab}	
	52	76.3 ± 17.7^a	257 ± 27.9^a	36.4 ± 1.3^a	281 ± 17.1^a	94.0 ± 15.3^a	79.9 ± 4.7^a	
60 °C	2	113 ± 33.3^c	380 ± 107^d	26.2 ± 4.2^c	851 ± 115.4^c	304 ± 80.5^c	187 ± 45.4^c	
	12	154 ± 12.2^b	527 ± 34.2^c	26.2 ± 1.5^c	1017 ± 87.4^c	314 ± 6.4^c	250 ± 20.1^b	
	22	162 ± 18.7^b	506 ± 54.7^b	28.8 ± 4.2^c	995 ± 114.5^c	348 ± 29.2^c	246 ± 21.5^b	
	32	188 ± 9.0^b	446 ± 51.8^{cd}	32.7 ± 3.7^c	$1298 \pm 48..4^b$	336 ± 57.6^c	292 ± 10.6^{ab}	
	42	239 ± 58.7^a	898 ± 171^b	49.2 ± 11.0^b	1495 ± 357^b	466 ± 78.7^b	325 ± 70.9^a	
	52	260 ± 2.0^a	1053 ± 75.3^a	56.5 ± 0.8^a	1763 ± 173^a	607 ± 87.3^a	325 ± 28.1^a	

[a] Each value in the table represents the mean $\pm$ standard deviation of six analyses from two replications. Means within each column with different superscripts are significantly ($P < 0.05$) different.

becomes oxidized. The changes in IV over 52 days were 3.67 and 0.34 g of I_2/100 g oil stored at 60 °C and room temperature, respectively. The significantly ($P < 0.05$) bigger change in IV at 60 °C showed that more oxidation of unsaturated fatty acids was occurring in this system at a greater rate.

The peroxides in oxidized oil are transitory intermediates, which decompose into various carbonyl and other compounds. AV was measured to quantify the level of aldehydes, principally 2-alkenals, present in the stored oil. The analysis is based on the colour reaction of anisidine and unsaturated aldehydes (Eskin et al., 1996). The AV increased significantly ($P < 0.05$) over 52

days of storage at 60 °C. At the end of the storage period, the change in AV was 6.60. However, there was only a minor change in AV (1.13 at room temperature during storage).

3.1.5. Changes in fatty acid composition and $C_{18:2}/C_{16:0}$

The changes in the fatty acid composition of oil systems over 52 days of storage are given in Table 3. There was a decrease in linoleic acid ($C_{18:2}$) whereas palmitic acid ($C_{16:0}$) increased with storage time. The result showed that the decreases in $C_{18:2}$ were higher when stored at 60 °C than at room temperature. The decrease in $C_{18:2}$ were mainly due to oxidation products, which
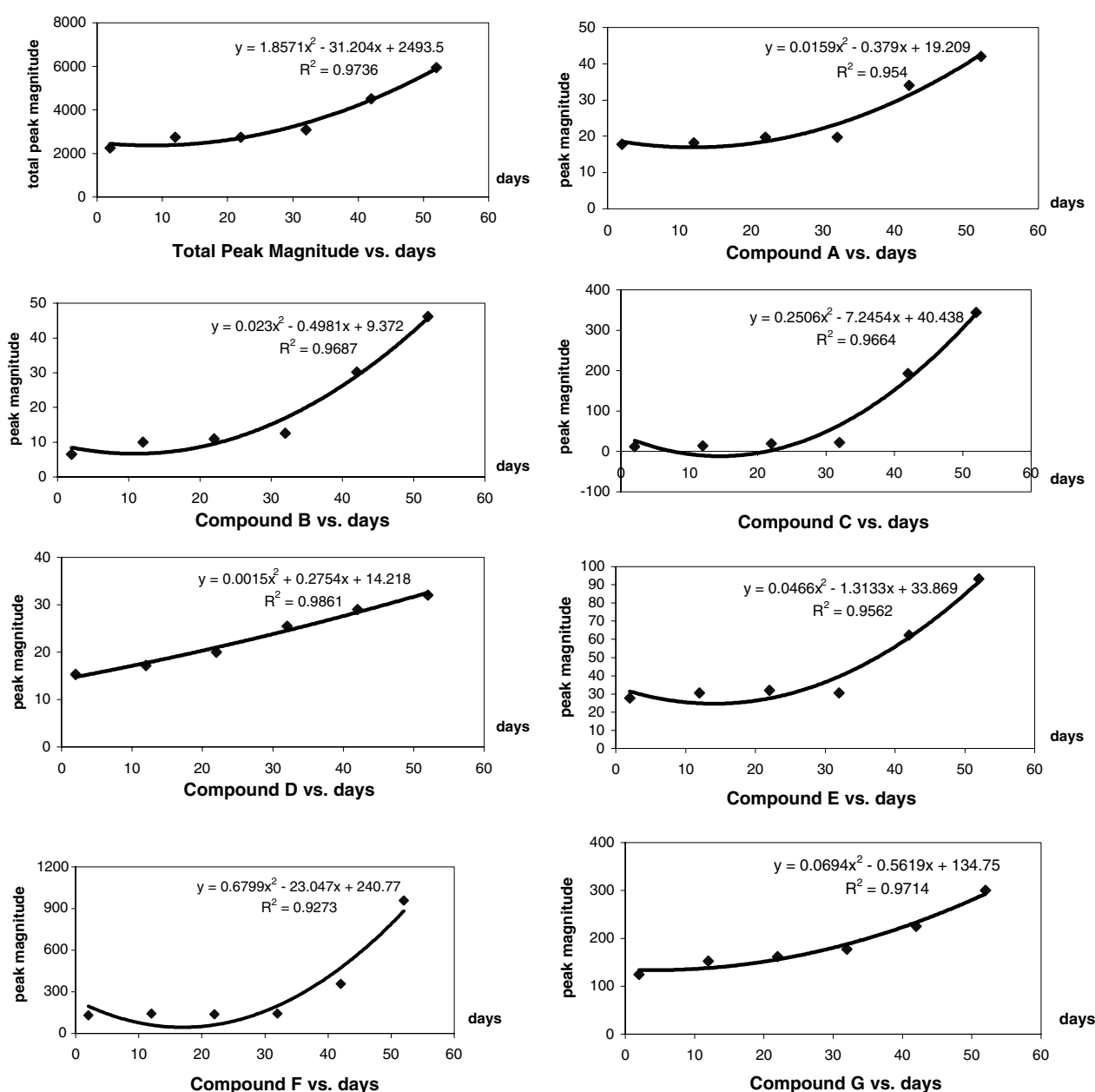

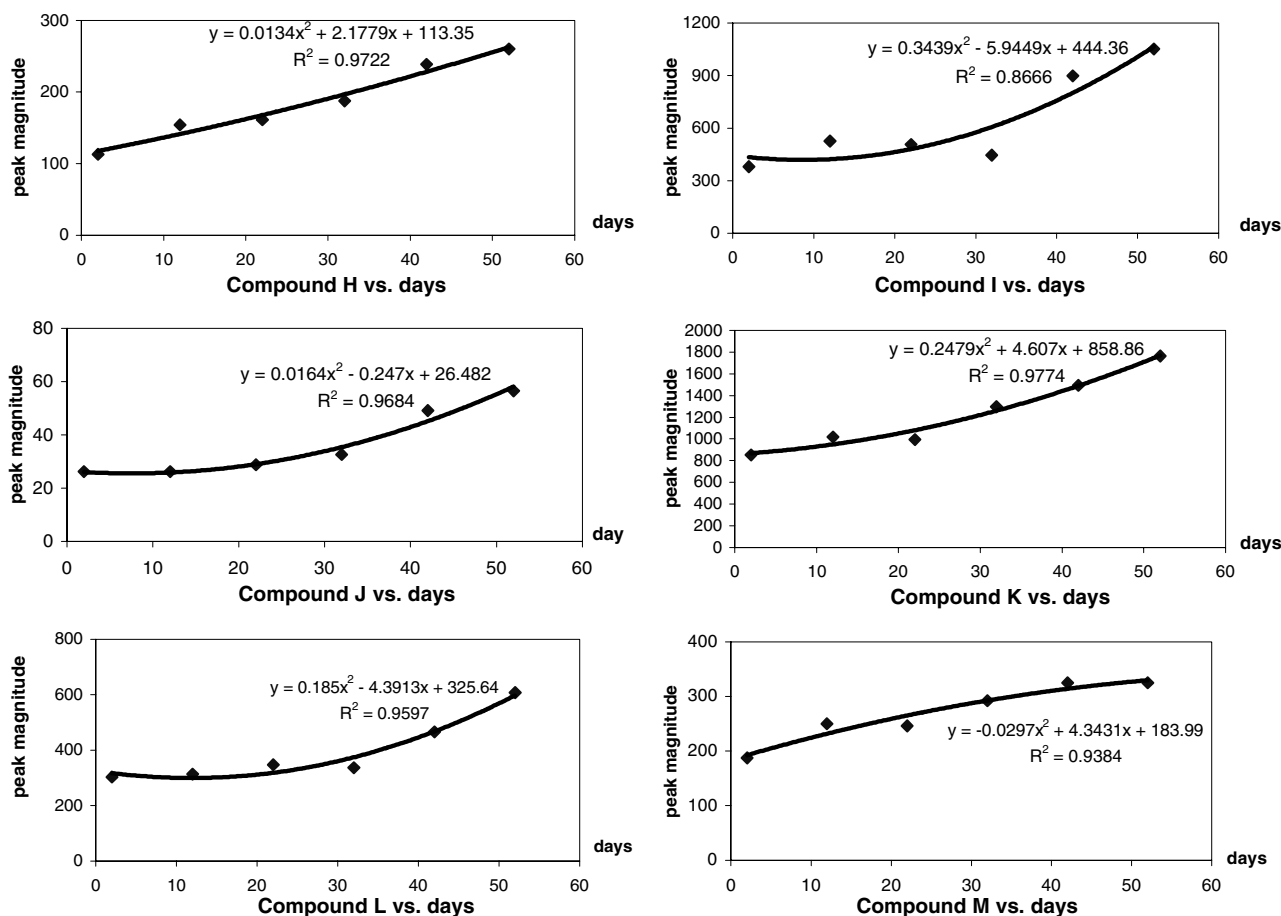Fig. 4. Total peak magnitude and thirteen different SAW readings (A–M) versus oxidation time.

Fig. 4. *(continued)*

decreased the percentage of unsaturated fatty acid composition.

Linoleic acid and palmitic acid are usually used as indicators to measure the extent of fat deterioration because linoleic acid is more susceptible to oxidation, whereas palmitic acid is more stable to oxidation. Therefore, the ratio $C_{18:2}/C_{16:0}$ was also used to indicate the degree of oxidative deterioration of oil. The ratios of $C_{18:2}/C_{16:0}$ are presented in Table 3. In the oil system stored at 60 °C, the ratio declined rapidly across the days of storage. These results showed that the system at 60 °C experiences a greater rate of oxidation than the room temperature system.

3.2. Sensory evaluation

The results of sensory evaluation of the palm olein storage test carried out are given in Table 4. Sensory evaluation remains the ultimate measure of rancidity, as no combination of chemical or physical tests is currently capable of assessing the composite sensory profile of a food (Robards, Kerr, & Patsalides, 1988). As oxidation increases, the intensity score (10 = bland, 1 = extreme)

gradually decreases from the initial value of 8.00 (faint: typical of most freshly deodorized oils) to 3.00 (strong) for the system 60 °C. Generally, changes of sensory scores for rancid odour over time agreed with changes in PV with a negative correlation. There were significant ($P < 0.05$) differences between both sets of sample over the storage period. These results showed that, the panellists were able to recognise and quantify the rancid off-flavour of the samples.

3.3. Electronic nose analysis

The chromatogram from the electronic nose is a graphical display of the derivative of the frequency change versus time. Fig. 1 displays a typical derivative chromatogram for fresh RBD palm olein. Measurements of stored RBD palm olein are given in Figs. 2 and 3, for storage at 60 and 28 ± 1 °C, respectively. There are more chemical compounds found in RBD palm olein stored at system 60 °C than at 28 ± 1 °C in terms of numbers of peak and the peak size. Since chromatography is an accepted analytical technique, GC/SAW technology was able to satisfy and follow the accepted

testing methodology. The ability to perform these methods with precision, speed, and accuracy is unique to the GC/SAW electronic nose.

In fast chromatography, the chromatogram duration is 10 s and peak widths are in milliseconds. The SAW resonator frequency was measured using a 20 ms gated reciprocal counter which produced 500 readings in 10 s. This translated into an array of 500 sensor readings with each chemical sensor being assigned to a unique retention time and frequency reading for that chemical. The sensor responses are nearly orthogonal with minimum overlap. A virtual sensor array with as many chemical sensors needed for any odour, fragrance, or smell can be created and saved for later retrieval. Hence, for this electronic nose, the chemical sensor space was defined mathematically by assigning unique retention time slots to each sensor.

Table 5 shows the detail of each peak (individual chemical component) from the electronic nose analysis. The results show significant difference ($P < 0.05$) for all chemical compounds present in the oil sample stored at room temperature and 60 °C. Fourteen different SAW readings were plotted versus oxidation time. The 14 parameters were total peak magnitude and the presence of 13 different chemical compounds (A–M). The plots are shown in Fig. 4. The data were fitted to a curve, using the linear regression technique and the coefficient of variation (R^2) was calculated. The results show that the relationships between the oxidation time and the parameters are not linear but curvilinear. The same trend has been observed in another study in which sunflower oil was used (Biswas et al., 2004). A second order polynomial fit appears to present a good relationship ($R^2 > 0.90$) for most of the parameters. The only exception was for chemical compound I, with $R^2 = 0.87$ (Table 6).

For RBD palm olein, it appears that the best consistent relationship (highest R^2) occurs between oxidation time and chemical compound D ($R^2 = 0.99$), followed by chemical compound K ($R^2 = 0.98$). Pearson correlation coefficients were calculated using these two parameters. This was carried out to see if any correlation existed between the electronic nose methods and sensory evaluation, as well as other chemical tests. An ideal correlation was observed in the case of the electronic nose response of chemical compound D and sensory panel score ($R^2 = -0.99$). The other values are given in Table 7.

A unique approach of this electronic nose was to use two-dimensional olfactory images, called VaporPrint[TM]. Chromatographic results show the trees of the forest, but the VaporPrint[TM] displays the forest of trees in its entirety. This approach provides a high resolution image which changes the olfactory response to a visual response. It is produced by a polar plot of chromatogram, using retention time as the angular variable and the SAW detector response as the radial variable. A gallery of VaporPrint[TM] for RBD palm olein stored at two different temperatures is shown in Figs. 5 and 6.

The data showed that the changes in the strength of the volatile compounds correlate with the freshness of the RBD palm olein. In this case, the rancid/oxidized RBD palm olein stored at 60 °C was found to produce distinct peaks in the range 3–5 s. These peaks

Table 7
Pearson correlation coefficients

	Chemical compound D (60 °C)	Chemical compound K (60 °C)
Sensory score	−0.994	−0.968
PV	0.964	0.916
FFA content	0.834	0.901
IV	−0.969	−0.991
AV	0.974	0.981
Ratio $C_{18:2}/C_{16:0}$	−0.966	−0.964

Cell contents: Pearson correlation P-value.

Table 6
Analysis of electronic nose individual chemical component from RBD palm olein under storage test (to summarize Fig. 4)

| Parameter	Trendline equation	R^2
Total peak magnitude	$y = 1.8571x^2 - 31.204x + 2493.5$	0.9736
Chemical component A	$y = 0.0159x^2 - 0.379x + 19.209$	0.9540
Chemical component B	$y = 0.023x^2 - 0.4981x + 9.372$	0.9687
Chemical component C	$y = 0.2506x^2 - 7.2454x + 40.438$	0.9664
Chemical component D	$y = 0.0015x^2 + 0.2754x + 14.218$	0.9861
Chemical component E	$y = 0.0466x^2 - 1.3133x + 33.869$	0.9562
Chemical component F	$y = 0.6799x^2 - 23.047x + 240.77$	0.9273
Chemical component G	$y = 0.0694x^2 - 0.5619x + 134.75$	0.9714
Chemical component H	$y = 0.0134x^2 + 2.1779x + 113.35$	0.9722
Chemical component I	$y = 0.3439x^2 - 5.9449x + 444.36$	0.8666
Chemical component J	$y = 0.0164x^2 - 0.247x + 26.482$	0.9684
Chemical component K	$y = 0.2479x^2 + 4.607x + 858.86$	0.9774
Chemical component L	$y = 0.185x^2 - 4.3913x + 325.64$	0.9597
Chemical component M	$y = -0.0297x^2 + 4.3431x + 183.99$	0.9384
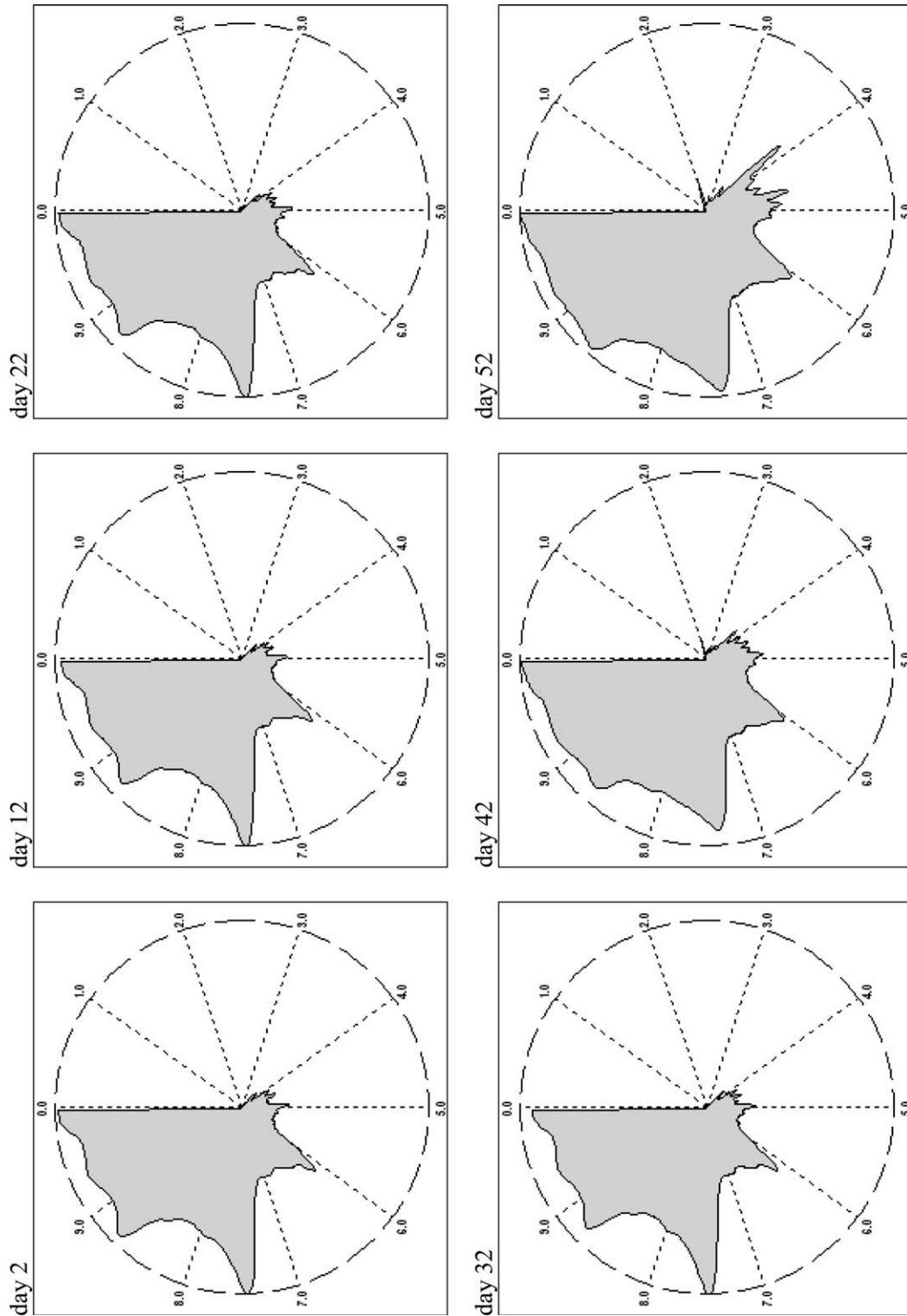
Fig. 5. VaporPrint[TM] of RBD palm olein stored at oven temperature (60 °C).

dramatically increased on day 52, which is obviously an exception to the normal pattern. In contrast, oils stored at room temperature had the basic pattern present in the fresh sample (day 2). The primary usage of Vapor-Print[TM] was to provide the odour concentration and characteristic shape at a glance. This image provides the human operator with a useful tool for comparing subtle differences in odour and aroma. A skilled operator can frequently judge product quality by observing this image.
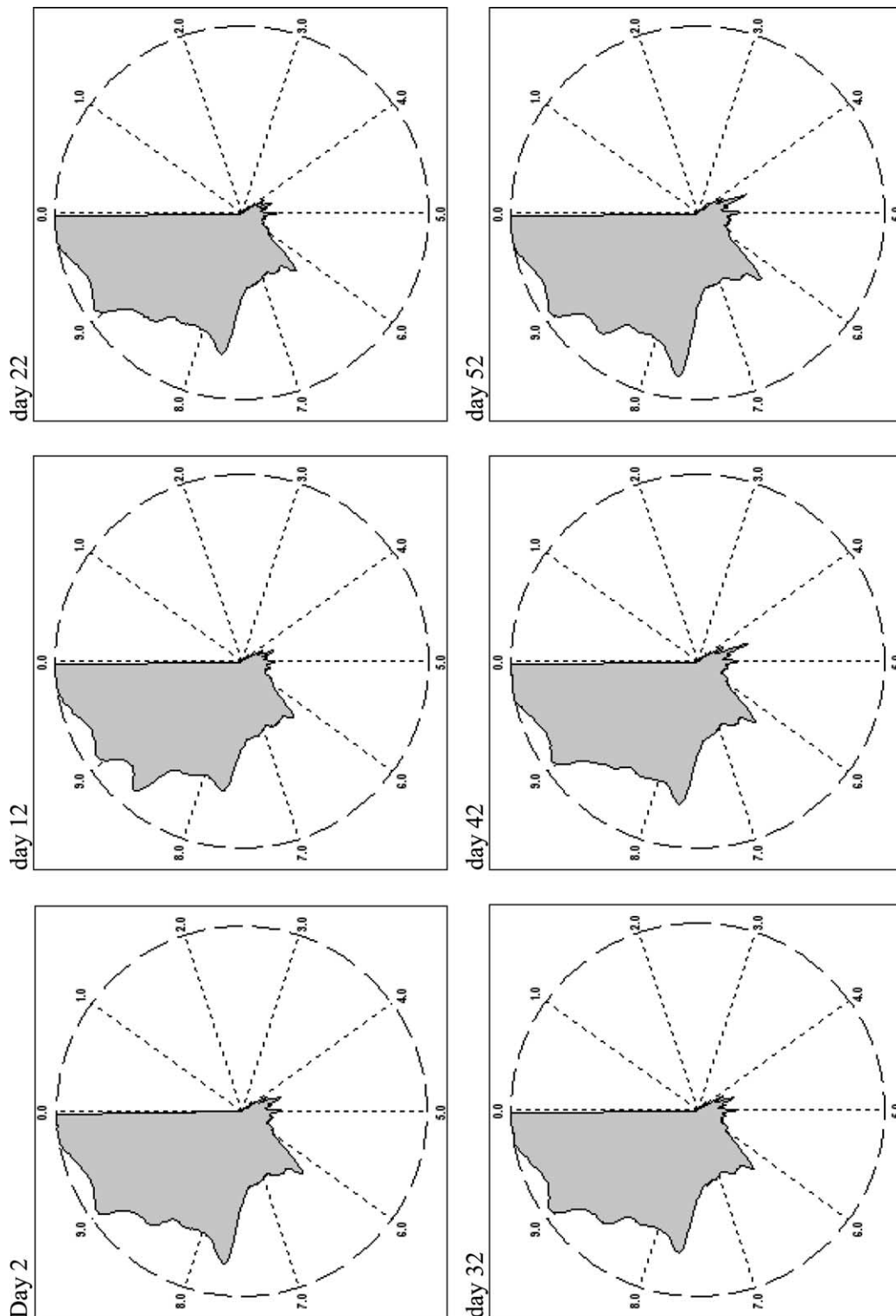
Fig. 6. VaporPrint^{TM} of RBD palm olein stored at room temperature (28 ± 1 °C).

4. Conclusion

It can be concluded that the electronic nose can be utilized as an analytical tool for following the progress of oxidation in RBD palm olein. The electronic nose measurement, performed on a daily basis, will help to identify the changes in headspace and relate these to rancidity. Professional panellists may judge odours and aromas faster, but the electronic nose can be much more analytically consistent. The ability to quantify and

understand the human perception of smell or taste may provide valuable insights into how to define and quantify food quality in chemical terms. Once the optimum chemistry is defined, the electronic nose will be able to compare and monitor the chemical composition and quality of the oil. Quality control personnel will be able to analyze hundreds of samples per day, as compared to weeks. Savings in time and labour can readily be calculated. The practical application of the electronic nose will possibly ensure higher quality standards for vegetable oil refining and food processing industries as well as detection of adulteration, with less burden and faster results than current quality control analytical methods.

Acknowledgements

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