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Characterisation of vegetable oils by surface acoustic wave sensing electronic nose

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Abstract

Flavour analysis is typically performed by human organoleptic analysis, which is often expensive and subjective. A novel approach using a surface acoustic wave sensing electronic nose (zNose™) for flavour analysis was explored to characterise 16 types of vegetable oils. Fatty acid composition, iodine value, peroxide value, *p*-anisidine value and free fatty acid analyses were conducted to determine the quality and characteristics of vegetable oils. The zNose™ was employed successfully for qualitative distinction of flavour in different vegetable oils. This is achieved using a visual fragrance pattern, called a VaporPrint™, derived from the frequency of the SAW detector. VaporPrint™ was shown to be particularly useful for assessing vegetable oil aroma profile in its entirety. This image 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 Chemometric method, particularly principal component analysis (PCA), was conducted for electronic nose data processing and identification. Analysis of the score plot of the PCA for the zNose™ measurement showed that 97% of the total variance in the data was described by PC 1 and PC 2. The loading plot revealed that five compounds (m, k, n, s, and p) were important for differentiate the vegetable oils.

Keywords: Characterisation; Electronic nose; Fingerprint; PCA; Vegetable oil

1. Introduction

Flavour is generally accepted as the most important sensory characteristic associated with foods. Flavour is usually divided into the subsets of taste and aroma, which are perceived in the mouth and the nose, respectively. In general, the aroma of a food consists of many volatile compounds, only a few of which are sensorially relevant (Blank, 1997). These compounds define the nature of a food and its product identity, as well as contribute to consumer preferences between brands of products. Human panellists are still the primary method used for characterisation of olfactory quality. However, this is a costly process, because a trained panel of experts can only work for relatively short periods of time.

The evolution of capillary column gas chromatography (GC) and the interfacing of GC with mass spectrometry (MS) have resulted in the separation and identification of numerous volatile compounds in different foods. However, these conventional analytical methods are not only time-consuming but the results are often inadequate (Gardner & Bartlett, 1994). Instead, the relationship between their sensory impacts is still unclear. Consequently, there is enormous demand for an electronic instrument that can mimic the human sense of smell and provide low-cost and rapid sensory information.

The term 'electronic nose' appeared around the late 1980s, when it was specifically used at a conference in 1987 (Gardner, 1987). Gardner and Bartlett (1994) defined an 'electronic nose' as 'an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition

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system, capable of recognizing simple or complex odour'. An array of sensors simulating the human olfactory response has become known as an eNose. An eNose provides a vectorial image in N-dimensional space (where N equals the number of sensors), of specific vapour mixtures containing possibly 100s of different chemical species. An eNose with only a few sensors produces responses which are not correlated and multiple sensors respond to the same vapour, e.g., overlap; therefore their sensitivity is very poor. Besides, drift counteraction is very difficult since different sensors or different layers of the sensor drift in their own way. In the chemical sense, this type of eNose may never be a quantitative measurement instrument.

Recently, a new approach, based upon fast chromatography and a single high quartz acoustic sensor has become commercially available: zNose™. The zNose™ solves these problems by simulating a virtual sensor array containing 100s of orthogonal sensors. Although only one physical sensor is used, sensor space is defined mathematically by assigning unique retention time slots to each sensor. Analysis of any odour is accomplished by serially polling a virtual sensor array or spectrum of retention times. The use of a single sensor has the great advantage of drastically reducing the drift errors. Moreover, sensitivity is quite high with part per billion levels being typical for volatile organics in air or water.

Different types of sensors, such as metal oxide semiconductors, conducting polymers and surface acoustic wave (SAW) sensors, have been used (Bartlett, Elliott, & Gardner, 1997; Hodgins, 1997). The requirement for the sensors in a electronic nose is that they have a partial sensitivity, i.e., that they can respond broadly to a range or class of gases rather that to a specific one, opposite to the ideal gas sensor, which should respond to only one gas (Gardner & Bartlett, 1994).

The electronic nose has a wide range of potential applications in the cosmetic, automotive and food industries, as well as in environmental pollutant monitoring (Mielle, 1996). Using an electronic nose would allow the odour quality to be followed continuously from raw material stage right through to the final product. Continuous monitoring would ensure the early detection of malodours and ultimately prove cost-effective (Bartlett et al., 1997).

Many publications report the application of different prototypes of electronic nose for the odour differentiation of olive oil. Most of the interest originates in the aromatic volatiles emitted by olive oils as a key characteristic in the quality control of this product (Guadarrama, Mendz, Sanz, Saja, & Ros, 2001). A metal oxide gas, sensor-based, electronic nose has successfully distinguished between sunflower oil and olive oil (Martin, Pavon, Cardero, & Pinto, 1999). Guadarrama et al. (2001) have purposely designed a polymeric sensor array for detection of olive oil aroma. The array of sensors, combined with a principal component analysis (PCA), allow the discrimination of olive oils of different qualities (extra virgin, virgin, ordinary and lampante) (Guadarrama, Mendz, Saja, Ros, & Olas, 2000), different varieties and different geographic origins (Guadarrama et al., 2001).

Olive oil analyses seem to be a promising application of the electronic nose. In this study, 16 different types of vegetable oils were characterised using a SAW sensor-based electronic nose. The objective of this study was to obtain an aroma fingerprint of each vegetable oil. This is a preliminary study to explore an alternative to quality control testing in the edible oil industry, to replace or reduce the traditional analytical methods which are costly, time consuming, involve the use of environmentally unfriendly chemicals, and are largely dependent on the skills of the analyst.

2. Materials and methods

2.1. Oil samples

Sixteen types of common vegetable oils were purchased from local groceries (canola oil, corn oil, coconut oil, extra virgin olive oil, grape seed oil, hazelnut oil, olive oil, palm olein, peanut oil, rapeseed oil, rice bran oil, sunflower oil, soybean oil, sesame oil, safflower oil, walnut oil). All samples were stored at −20 °C in screw-cap amber bottles and thawed prior to use. None of them were subjected to any treatment that might alter their composition.

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 by means of AOCS official methods (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 (FAC) of fats and oils were assayed by gas chromatography (GC) (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 μl of sample was injected into the instrument, with the 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 of 1.3 ml/min was used as carrier gas. The oven temperature was programmed at a rate of 10 °C/min from 160 °C (equilibrium for 1 min) to 200 °C (equi-

librium for 2 min), then increased to 240 °C at a rate of 20 °C/min and held for 1 min. The FID detector was used at a temperature of 275 °C.

2.3. The electronic nose apparatus

The electronic nose (4100 vapour analysis system, Electronic Sensor Technology, New Bury Park, USA) is a hand-held portable analyzer. The commercial expression of this technology, the zNose™, is based on fast chromatography; chemical analysis of any odour is accomplished in 10 s by a very fast separation of chemicals in sampled vapours.

The complete system was housed within a small carrying case. It consisted of a sensor head, a support chassis, and a system controller. The sensor head contained the hardware necessary to separate and detect materials. The support chassis included a small helium gas tank, power supply and electronics to run the system. The system controller was based on a laptop computer. The computer analysed the data and provided a user interface.

The advantages of this zNose™ are (1) portability (2) low voltage power source (3) high sensitivity and tenable specificity (determined by GC column) (4) low cost of manufacture (solid state sensor and electronics) (5) non-ionic detection (does not require radioactive ionization source) and (6) a simple easy-to-use graphical interface for unskilled inspection personnel.

Almost all the developers of artificial noses have tried to duplicate the sense of smell by combining biochemical coatings with silicon chips to produce arrays of sensors to detect the various components that make up an aroma. But the success of these so-called eNoses has been limited by their sheer complexity. To work well, they require enormous numbers of individual sensors to discern the thousands of aromatic hydrocarbons that waft through our noses very day (Staples, 2000). Unlike other electronic noses available in the marketplace, the detector of this zNose™ is manufactured from single quartz crystal without any polymer coatings; hence long term stability is achieved over a wide temperature range.

The SAW detector is only specific to vapour pressure. The specificity of the SAW detector is based upon 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 (Staples, 1998).

The speed of the analysis system was determined by the sample and analysis times. Typical sampling times were 1–5 s and analysis times can be 10 s or less. Chromatographic peaks produced are measured in milliseconds. The ability to detect short duration peaks was made possible because the SAW detector is an integrating GC detector with essentially zero dead volume. Part per billion (ppb) sensitivity has been achieved with volatile compounds and part per trillion (ppt) sensitivity for semi-volatile compounds.

2.4. Electronic nose analysis

Ten grams of each oil sample were weighed into a septa-sealed screw-cap bottle. After a headspace generation time of 3 min at 60 °C (in water-bath), the sample's vapour was introduced into the electronic nose. The flow rate (purified helium) was fixed at 30.0 cm^3, sampling time 5 s, and the temperature was programmed from 40 to 160 °C, at a rate of 5 °C/s.

Each cycle of operation included three phases, the sampling phase, the injection phase and the analysis. The system analyzed compounds by drawing an air sample via a pump into the inlet. The sample passed through the valve where the compounds were absorbed onto the trap tube. The valve was then rotated to put the trap in line with the column for injection sequence.

During the injection sequence, the trap was heated quickly by a short burst of current that vapourized the adsorbed material. The helium carrier gas then transported the material down to the capillary column. The column was heated under computer control and separated the compounds. Separation was achieved by means of an internal coating of a bound liquid phase. The solubility of a compound in this liquid phase determined the time required for an analyte to travel down the column.

During the analysis sequence, the materials sequentially exit the column where they land and stick on the SAW detector. 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 IF (intermediate frequency) was counted by the system microprocessor board. The system controller interpreted the detector response and attempted to identify and quantify each material. This frequency shift, caused by an analyte, was characteristic of the amount of material deposited on the detector and thus allowed quantification.

2.5. 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 analysis of variance using the SAS Statistical Computer Package Version 6.12 (SAS Institute, Inc., 1989). Duncan's multiple range test was used to compare differences among means. Significance was defined at $P < 0.05$.

2.6. Principal component analysis

There are many ways to analyze data collected by using an electronic nose. One popular way is using chemometric methods. Chemometric methods include procedures for multivariate data analysis. These are increasingly used in problems in which groups need to be differentiated, especially when large data sets are involved (Larrigaudiere, Lentherie, Puy, & Pinto, 2004). Chemometric techniques are used to present the data in an understandable graphical format. They provide quick answers and allow evaluation of the relationship between variables and between observations at a glance (Nicolas, Romain, & Maternova, 2001).

Principal component analysis is a very powerful multivariate statistics method used to analyze the inherent structure of the data. This unsupervised technique displays an interpretable overview of the main information in a multidimensional data table. The principal of PCA is to find the directions in space along which the distance between data points is the largest. This can be translated as finding the linear combinations of the initial variables that contribute most to making the samples different from each other. The information carried by the original variables is projected onto a smaller number of underlying (latent) variables called principal components. The first principal component covers as much of the variation in the data as possible. The second principal component is orthogonal to the first and covers as much of the remaining variation as possible, and so on. By plotting the principal components, one can view interrelationships between different variables, and detect and interpret sample patterns, groupings, similarities or differences.

In this paper, PCA was carried out on the electronic nose data to categorize the vegetable oils into different groups. Unscrambler v.7.6 (CAMO AS, Trondheim, Norway) software was used for these analyses.

3. Results and discussion

3.1. Chemical analysis

For the purpose of identifying natural fats and ascertaining their quality, a number of analytical tests are routinely employed. The test results of a sample of fat under assessment should fall within the range of established constants to confirm its identity. Iodine value (IV) is a measure of overall unsaturation and is widely used to characterize oils and fats. It is defined as the number of grams of iodine absorbed by 100 g of fat. Table 1 shows the IV of the 16 vegetables oils used in this study. Grape seed oil had the highest IV of 130; followed by sunflower oil (127) and soybean oil (126). These oils are a rich source of polyunsaturated fatty acids that possess health benefits, such as regulating blood cholesterol levels and lowering elevated blood pressure. In contrast, coconut oil had the lowest IV of 10.5. The saturated character of the oil imparts a strong resistance to oxidative rancidity.

The peroxide value (PV), anisidine value (AV) and free fatty acid (FFA) are good guides to the quality of oil. Good quality oil should have a PV less than 10 units before off-flavours are encountered (Rossell, 1994). From Table 1, all the oils had acceptable levels of PV which were less than 10 units. Exceptions to this were extra virgin olive oil and hazelnut oil which had PVs of

Table 1
Chemical characteristics of vegetable oils

Sample	*p*-Anisidine value	Iodine value (g of I_2/100 g oil)	Free fatty acid (%)	Peroxide value (meq/kg oil)
CaO	2.06 ± 0.37^{h}	110.93 ± 1.39^{c}	$0.10 \pm 0.00^{d,e,f}$	$5.00 \pm 1.40^{e,f}$
CnO	6.17 ± 0.21^{c}	120.36 ± 1.71^{b}	$0.11 \pm 0.01^{d,e,f}$	$5.97 \pm 0.01^{e,f}$
CtO	1.00 ± 0.07^{i}	10.46 ± 3.22^{j}	0.41 ± 0.04^{a}	$4.97 \pm 1.38^{e,f}$
EV	7.39 ± 0.22^{b}	82.01 ± 0.21^{h}	0.28 ± 0.00^{b}	14.92 ± 1.37^{b}
GsO	8.52 ± 0.43^{a}	129.45 ± 0.88^{a}	$0.11 \pm 0.00^{d,e,f}$	1.99 ± 0.01^{g}
HtO	7.65 ± 0.38^{b}	88.83 ± 1.17^{g}	$0.12 \pm 0.01^{d,e,f}$	22.89 ± 1.34^{a}
OeO	$5.43 \pm 0.30^{c,d}$	80.62 ± 2.34^{h}	0.22 ± 0.00^{c}	$6.00 \pm 0.00^{e,f}$
PO	2.96 ± 0.37^{g}	54.44 ± 0.04^{i}	$0.15 \pm 0.02^{d,e}$	7.99 ± 0.01^{d}
PtO	4.22 ± 0.34^{f}	100.98 ± 0.27^{e}	0.32 ± 0.00^{b}	$6.99 \pm 1.43^{d,e}$
RaO	$1.82 \pm 0.01^{h,i}$	111.84 ± 1.61^{c}	$0.04 \pm 0.00^{g,h}$	3.97 ± 0.03^{f}
RiO	$5.53 \pm 0.08^{c,d}$	95.85 ± 0.04^{f}	$0.08 \pm 0.01^{f,g,h}$	8.00 ± 0.01^{d}
SaO	1.18 ± 0.39^{i}	88.02 ± 0.98^{g}	0.03 ± 0.00^{h}	$4.96 \pm 1.44^{e,f}$
SeO	8.08 ± 0.48^{a}	105.82 ± 0.80^{d}	0.45 ± 0.08^{a}	$5.98 \pm 0.04^{e,f}$
SoO	2.09 ± 0.11^{h}	125.93 ± 1.87^{a}	$0.11 \pm 0.01^{d,e,f}$	3.98 ± 0.01^{f}
SuO	$4.52 \pm 0.95^{e,f}$	126.59 ± 0.53^{a}	$0.09 \pm 0.00^{e,f,g}$	3.99 ± 0.00^{f}
WtO	$5.15 \pm 0.16^{d,e}$	118.41 ± 4.65^{b}	0.15 ± 0.00^{d}	9.97 ± 0.01^{c}

Each value in Table represents the mean ± standard deviation of two analyses. Means within each column with different superscripts are significants ($P < 0.05$) different.

Abbreviations: CaO canola oil; CnO corn oil; Cto coconut oil; EV extra virgin olive oil; GsO grapeseed oil; HtO hazelnut oil; OeO olive oil; PO palm oil; PtO peanut oil; RaO rapeseed oil; RiO rice bran oil; SaO high oleic safflower oil; SeO sesame oil; SoO soybean oil; SuO sunflower oil; WtO walnut oil.

14.9 and 22.9, respectively, showing initial development of oxidative rancidity. These oils may have been on the shelf for some period of time because the label indicated that they were approaching the expiry date.

The AV estimates the level of aldehydes, principally 2-alkenals, a secondary break down component of oxidative deterioration present in the oil. The AV test is particularly useful for abused oils with low PVs such as frying oils. All the oils use in this study had an acceptable level of AV (<10 units) (Rossell, 1994), grape seed oil having the highest value of 8.5; sesame oil ranked second with 0.44 units less and coconut oil showed the lowest value of 1.0.

Free fatty acid is a measurement of hydrolytic rancidity, caused by a combination of enzymes and moisture. This is a problem mainly encountered in products based on lauric oils, such as coconut and palm kernel oil. The free fatty acids are liberated from the parent oils, which comprise large amounts of capric, lauric and myristic acids. These acids have a distinct soapy flavour and have lower flavour threshold values than the longer chain fatty acids found in other oils and fats (Rossell, 1994). As shown in Table 1, coconut oil had a quite high FFA value 0.41, that was between sesame oil (0.45) and peanut oil (0.32). Other oils were mainly within a FFA range of 0.1–0.2.

Table 2 shows the FAC of vegetable oils used in this study. They were all within the range indicated in the literature (White, 1992). Corn, peanut, olive, sunflower, sesame, safflower and rice bran oils were of the oleic/linoleic group, which contained mainly unsaturated fatty acids. The saturated fatty acid content was generally less than 20%, with the highly unsaturated fatty acids and trisaturated triglycerides being almost entirely absent from this group. Peanut oil differed from other vegetable oils as it contained 6% of long-chain saturated fatty acids that included arachidic (20:0), behenic (22:0), and lignosceric (24:0) acids. Selective breeds of low erucic acid rapeseed varieties were characterised by high levels of oleic acid but this oil was unusual in having substantial amounts of eicosenoic acid (C20:1) (Orthoefer, 1996).

Table 2
Fatty acid composition of vegetable oils. Each value is the mean of two analyses of one sample

Fatty acid	CaO	CnO	CtO	EV	GsO	HtO	OeO	PO	PtO	RaO	RiO	SaO	SeO	SoO	SuO	WtO
(Area %)																
C6:0	–	–	0.93 ± 0.1	–	–	–	–	–	–	–	–	–	–	–	–	–
C8:0	–	–	9.92 ± 0.2	–	–	–	–	–	–	–	–	–	–	–	–	–
C10:0	–	–	6.24 ± 0.2	–	–	–	–	–	–	–	–	–	–	–	–	–
C12:0	–	–	46.0 ± 1.4	–	–	–	–	0.26 ± 0.0	–	–	–	–	–	–	–	–
C14:0	–	–	18.21 ± 0.3	–	–	–	–	0.93 ± 0.2	–	–	0.53 ± 0.1	–	–	–	–	–
C16:0	6.08 ± 0.3	10.89 ± 0.1	7.70 ± 0.4	10.3 ± 0.4	7.16 ± 0.1	5.22 ± 0.0	12.3 ± 0.3	37.9 ± 2.9	9.03 ± 0.2	3.91 ± 0.1	20.6 ± 2.2	5.39 ± 0.2	9.24 ± 0.0	9.82 ± 0.7	7.19 ± 0.2	8.23 ± 0.6
C16:1	–	–	–	0.73 ± 0.0	–	–	1.50 ± 0.1	–	–	–	–	–	–	–	–	–
C18:0	2.01 ± 0.1	2.21 ± 0.1	2.54 ± 0.3	3.18 ± 0.1	3.84 ± 0.0	2.27 ± 0.1	1.60 ± 0.1	4.23 ± 0.3	2.58 ± 0.1	2.14 ± 0.0	2.05 ± 0.2	2.83 ± 0.0	5.54 ± 0.0	4.45 ± 0.1	4.20 ± 0.0	2.40 ± 0.0
C18:1	58.7 ± 0.2	31.4 ± 0.7	6.82 ± 0.8	77.21 ± 0.3	22.4 ± 0.2	76.6 ± 0.2	69.7 ± 0.4	44.82 ± 2.0	43.1 ± 0.1	63.4 ± 0	40.9 ± 1.1	74.7 ± 1.3	40.4 ± 0.3	26.0 ± 0.6	24.9 ± 0.16	18.18 ± 0.1
C18:2	22.5 ± 0.0	55.1 ± 0.8	1.65 ± 0.2	7.26 ± 0.0	66.6 ± 0.3	15.9 ± 0.3	12.3 ± 0.5	11.90 ± 0.8	38.8 ± 0.2	20.4 ± 0.2	33.6 ± 0.7	17.0 ± 1.1	44.8 ± 0.2	52.9 ± 1.0	63.7 ± 0.4	59.5 ± 0.1
C18:3	1.11 ± 0.0	0.41 ± 0.0	–	0.41 ± 0.0	–	–	0.50 ± 0.0	–	–	9.52 ± 0.2	0.60 ± 0.1	–	–	6.82 ± 0.2	–	11.7 ± 0.6
C20:0	1.06 ± 0.0	–	–	0.95 ± 0.0	–	–	1.07 ± 0.1	–	1.22 ± 0.0	0.4 ± 0.1	1.67 ± 0.1	–	–	–	–	–
C20:1	8.56 ± 0.2	–	–	–	–	–	–	–	2.06 ± 0.0	0.18 ± 0.0	–	–	–	–	–	–
C22:0	–	–	–	–	–	–	–	–	3.19 ± 0.2	–	–	–	–	–	–	–

Abbreviations: C6:0, caproic; C8:0, caprylic; C10:0, capric; C12:0, lauric; C14:0, myristic; C16:0, palmitic acid; C16:1, palmitoleic; C18:0, stearic acid, C18:1, oleic; C18:2, linoleic; C18:3, linolenic; C20:0, arachidic; C20:1, C22:0, behenic. See Table 1 for other abbreviations.

3.2. Electronic nose analysis

The flavour of fats and oils is one of the most critical factors influencing quality. By using a single, uncoated, high quartz surface acoustic wave resonator electronic nose, aroma profiles of 16 different vegetable oils were obtained. This electronic nose was based on the principal of gas chromatography. By measuring the time required for each chemical to reach the sensor and the amount it affects the SAW crystal's vibration, both the identity (retention time) and the quantity (amount) of the substance can be calculated by software incorporated in the

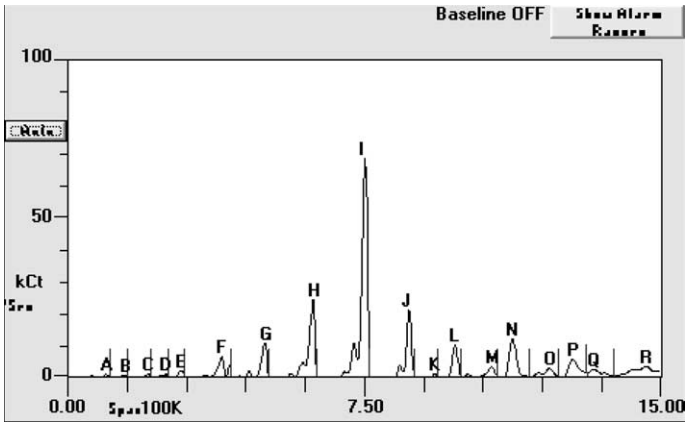

Fig. 1. Typical electronic nose chromatogram of vegetable oil sample.

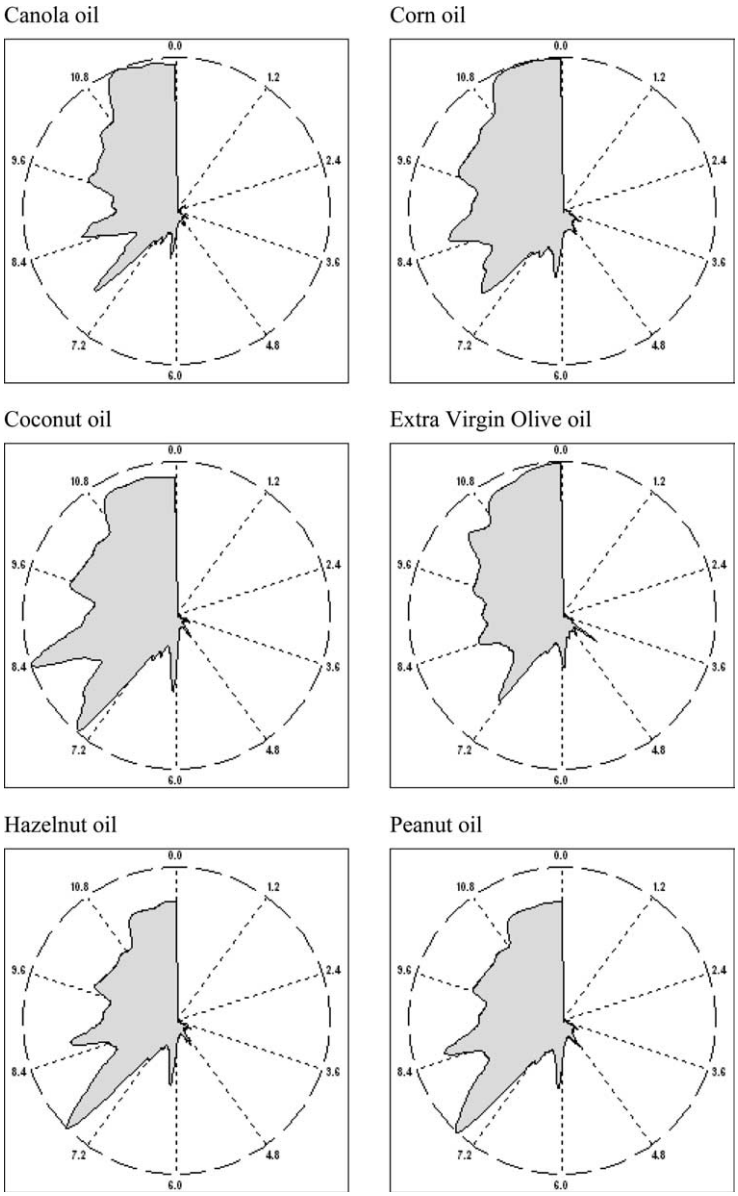

Fig. 2. VaporPrints^{TM} of different vegetable oils.

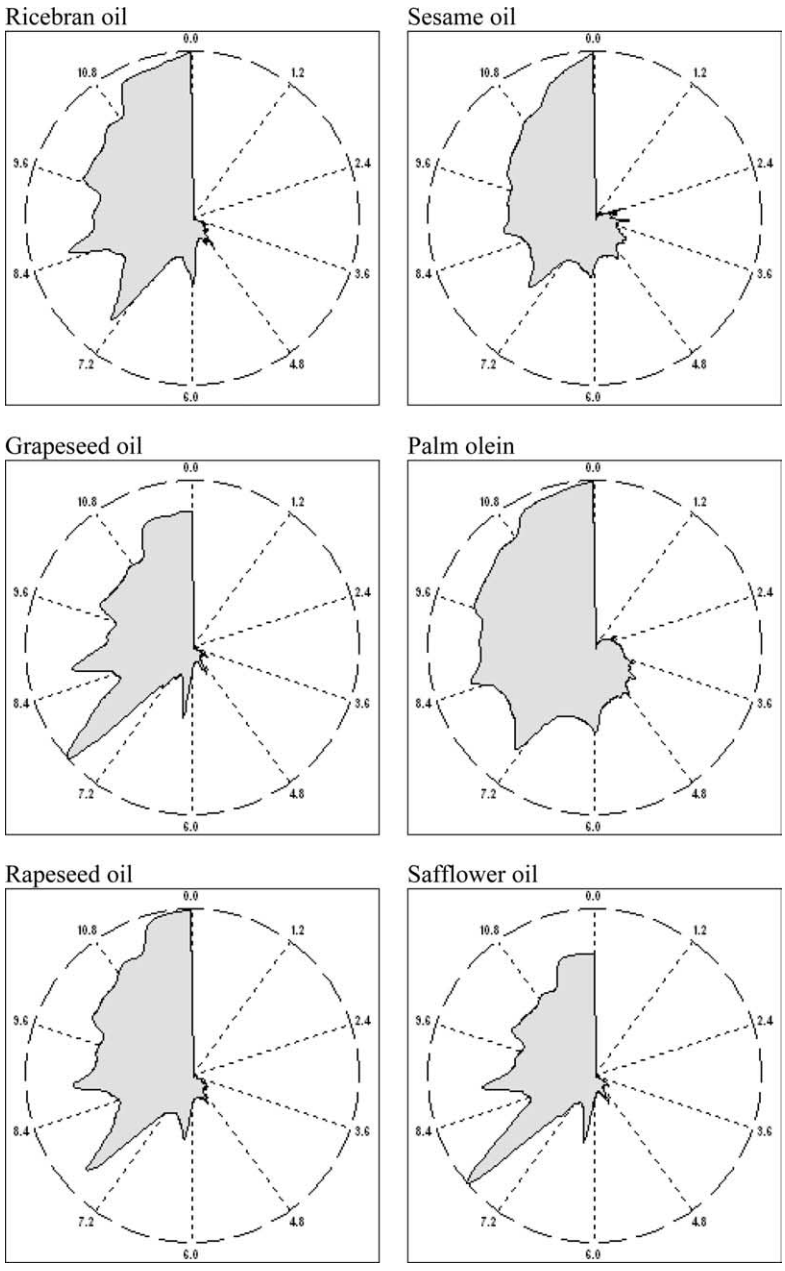

Fig. 2 (*continued*).

instrument. Fig. 1 shows a typical chromatogram for a vegetable oil sample.

An interesting attribute of this electronic nose was that it was very user-friendly, since it provided the operator with visually recognizable fragrance patterns. This image, called VaporPrint^{TM}, is a chemical signature of an odour. The VaporPrints^{TM} of 16 different types of vegetable oils are shown in Fig. 2. The image is a closed polar plot of the odour amplitude (SAW detector frequency) with radial angles representing sensor time (0 and maximum times are vertical). This image transfers the olfactory response to a visual response that will dramatically increase olfactory perception.

As observed from Fig. 2, each vegetable oil contained the same major compounds and taste testing showed that few panellists were able to discriminate between them. The unique nature of this display is subject to the relative concentrations of the several compounds making up the mix. However, for each sample, the relative distributions of the compounds were fixed (Staples, 1999), and so the resulting VaporPrint^{TM} was unique for each type of vegetable oil.

Specific data of each vegetable oil are shown in Table 3. There were 20 compounds (a–t, indicating different retention time) recorded within the analysis time of 0–12 s. Among them, 11 were common compounds for all the

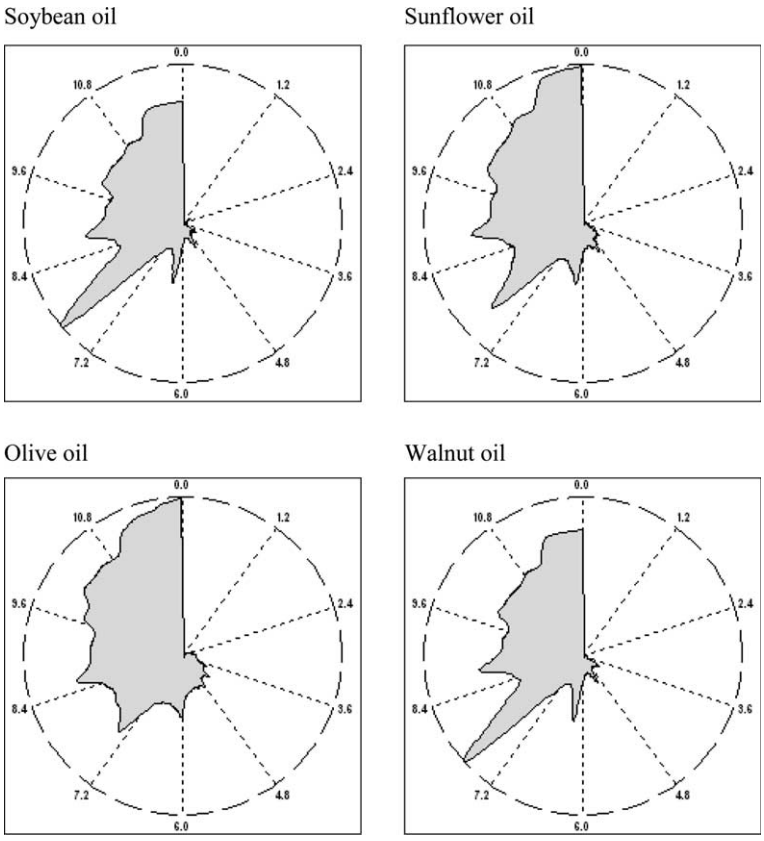

Fig. 2 (*continued*).

vegetable oil samples. However, different oils showed variations in the amounts of every compound. To get an overall view of the complex data, principal component analysis was carried out.

3.3. Principal component analysis

Principal component analysis was used to structure the data matrix. The first aim was to reduce the number of variables down to important factors only (Schweizer-Berberich, Vaihinger, & Gopel, 1994). Fig. 3(a) is a graph of the PCA loadings. Five variables (m, k, n, s, and p), which had a Euclidean distance from the origin that was greater than two standard deviations of the distance of the set were identified. The remaining variables were considered as unimportant for classification (low loading values along PC 1 and close to origin). By eliminating unimportant parameters, the cost and/or time of collecting the data can be reduced. Reduction of the number of variables can lead to improved performance. Including features that contain irrelevant information about the measurements can cause problems. Thus, it becomes important to use only high information descriptors (Eklov, Martensson, & Lundstrom, 1999).

The score plot of PC 1 versus PC 2 from the electronic nose analysis is presented in Fig. 3(b). The PC 1 and PC 2 factors resulted in a model that described 97% of the total variance in the data. This percentage was very high, and this value seemed sufficient to define a good model, especially for qualitative purposes. It was observed that PCA allowed easy distinction between the different vegetable oils.

The different vegetable oils were separated along the first PC. The first PC described 90% of the peak variation (Fig. 3(b)) and showed three well defined groups: coconut, corn, and canola oils with high positive scores; and peanut, grape seed, soybean, hazelnut, walnut and safflower oils with low positive scores; the rest had high negative scores (sesame, palm olein, olive, ricebran, rapeseed, sunflower and extra virgin olive oil) along PC 1. The high positive correlation between m and PC 1 indicated that the volatile profile of coconut oil had a higher proportion of m. Corn, canola, peanut, and grape seed oils contained less amount of m than did coconut oil, but they contained more of m than did soybean, hazelnut, walnut and safflower oils. Other vegetable oils with high negative scores corresponded to the lowest amount of m. Percentage of alteration was organised from right to left in relation to increasing amount of m. This indicates that the m variable had a major influence upon the differentiation of the vegetable oils.

Table 3
Electronic Nose data of various vegetable oils[a]

Sample	A	B	C	D	E	F	
CaO	30.5 ± 2.12^{defg}	–	139.3 ± 17.6^{b}	488.2 ± 90.3^{b}	–	2160.2 ± 132.4^{bc}	
CnO	45.8 ± 5.4^{d}	154.0 ± 46.6^{def}	203.8 ± 36.6^{a}	705.3 ± 60.0^{a}	–	3771.3 ± 480.0^{a}	
CtO	136.7 ± 22.2^{b}	811.8 ± 170.4^{a}	189.8 ± 43.7^{a}	695.7 ± 212.6^{a}	–	3855.0 ± 893.5^{a}	
EV	24.2 ± 6.0^{defg}	82.0 ± 24.0^{efg}	151.0 ± 0.0^{b}	128.2 ± 12.5^{de}	–	408.3 ± 93.7^{f}	
GsO	20.5 ± 3.4^{defg}	137.8 ± 25.7^{def}	149.8 ± 42.8^{b}	478.8 ± 114.1^{b}	–	2424.8 ± 610.6^{b}	
HtO	22.0 ± 3.6^{defg}	188.5 ± 44.0^{d}	168.2 ± 16.4^{ab}	437.8 ± 95.9^{b}	–	1885.8 ± 355.9^{cd}	
OeO	28.2 ± 6.6^{defg}	168.9 ± 36.9^{de}	68.3 ± 18.6^{c}	118.7 ± 32.7^{de}	–	420.8 ± 106.6^{f}	
PO	28.7 ± 8.1^{defg}	297.3 ± 75.7^{c}	83.0 ± 19.2^{dc}	76.3 ± 23.5^{e}	–	452.7 ± 94.0^{f}	
PtO	41.0 ± 10.3^{defg}	140.8 ± 40.5^{def}	168.8 ± 44.6^{ab}	512.0 ± 98.1^{b}	–	2301.3 ± 273.7^{b}	
RaO	12.2 ± 3.4^{fg}	30.5 ± 6.7^{g}	30.3 ± 4.5^{d}	56.2 ± 12.2^{e}	–	244.2 ± 42.6^{f}	
RiO	36.7 ± 7.4^{defg}	47.0 ± 14.3^{g}	64.2 ± 16.6^{cd}	109.3 ± 33.9^{de}	–	436.2 ± 107.1^{f}	
SaO	8.83 ± 2.5^{g}	72.2 ± 16.0^{fg}	82.2 ± 20.4^{c}	260.3 ± 49.1^{c}	–	1033.3 ± 244.3^{e}	
SeO	214.3 ± 61.3^{a}	380.5 ± 83.9^{b}	61.0 ± 14.1^{cd}	59.3 ± 13.5^{e}	381.8 ± 60.6	300.8 ± 71.8^{f}	
SoO	15.5 ± 2.4^{efg}	–	73.3 ± 14.9^{c}	286.2 ± 56.6^{c}	–	1581.7 ± 150.7^{d}	
SuO	12.7 ± 2.7^{fg}	–	–	34.2 ± 6.5^{e}	–	229.0 ± 26.5^{f}	
WtO	69.7 ± 3.9^{c}	74.3 ± 12.7^{fg}	83.5 ± 13.3^{c}	195.0 ± 47.0^{cd}	–	1176.7 ± 277.4^{e}	

Sample	G	H	I	J	K	L	M
CaO	–	$500.7 \pm 148.5b^{c}$	1944.8 ± 310.4^{d}	–	8739.8 ± 1817.7^{cd}	2555.7 ± 336.7^{a}	20320.5 ± 1599.4^{b}
CnO	–	762.8 ± 163.5^{a}	3583.2 ± 421.7^{b}	–	15059.5 ± 2023^{b}	5241.7 ± 808.8^{b}	21030.5 ± 2554.9^{b}
CtO	–	563.5 ± 129.0^{b}	4677.0 ± 1144.6^{a}	–	18099.0 ± 4619.9^{a}	–	30958.2 ± 8143.5^{a}
EV	2386.7 ± 94.6^{a}	517.3 ± 45.6^{bc}	460.2 ± 122.3^{g}	447.7 ± 69.3	2431.3 ± 353.8^{g}	–	1791.3 ± 279.8^{e}
GsO	–	326.8 ± 74.8^{de}	2667.8 ± 749.1^{c}	–	9070.4 ± 2388.8^{c}	–	20772.0 ± 6014.8^{b}
HtO	–	416.3 ± 98.6^{cd}	2081.7 ± 243.1^{d}	–	6697.7 ± 698.5^{de}	–	14797.5 ± 1689.7^{cd}
OeO	311.3 ± 61.3^{b}	–	395.2 ± 103.6^{g}	–	1304.5 ± 317.7^{g}	–	2715.0 ± 690.4^{e}
PO	316.0 ± 57.7^{b}	–	374.8 ± 61.4^{g}	–	1180.7 ± 327.3^{g}	–	2334.2 ± 600.9^{e}
PtO	–	357.8 ± 57.2^{de}	2741.8 ± 331.6^{c}	–	8893.0 ± 757.7^{c}	–	20672.3 ± 1878.3^{b}
RaO	160.8 ± 49.0^{c}	–	320.2 ± 78.7^{g}	–	1015.0 ± 249.4^{g}	–	2344.8 ± 656.4^{e}
RiO	159.8 ± 33.8^{c}	–	426.7 ± 66.5^{g}	–	1259.2 ± 147.9^{g}	–	2422.3 ± 175.04^{e}
SaO	–	181.2 ± 34.0^{f}	1467.5 ± 170.2^{g}	–	4405.0 ± 551.6^{f}	–	12171.2 ± 1413.4^{d}
SeO	–	–	299.5 ± 42.7^{ef}	–	502.2 ± 45.0^{g}	–	1158.5 ± 127.9^{e}
SoO	–	239.5 ± 40.4^{ef}	1880.8 ± 235.1^{g}	–	5880.7 ± 882.8^{ef}	–	17668.5 ± 2651.3^{bc}
SuO	158.8 ± 20.3^{c}	–	310.0 ± 26.4^{de}	–	983.5 ± 132.2^{g}	–	2202.3 ± 315.9^{e}
WtO	–	–	1351.5 ± 142.5^{f}	–	4212.2 ± 664.7^{f}	–	11759.5 ± 2078.6^{d}

Sample	N	O	P	Q	R	S	T
CaO	16251.7 ± 2842.5^{a}	1610.8 ± 336.8^{a}	6779.8 ± 1801.1^{b}	–	$4836.0 \pm 1042.9a$	15288.3 ± 3297.3^{a}	712.5 ± 195.3^{c}
CnO	13955.7 ± 3076.8^{b}	–	7700.3 ± 1486.7^{a}	–	$1958.7 \pm 526.5b$	10707.5 ± 1752.9^{b}	210.3 ± 60.7^{e}
CtO	16382.8 ± 3080.0^{a}	–	8072.2 ± 1490.3^{a}	–	$963.0 \pm 203.7c$	11052.5 ± 2378.3^{b}	503.2 ± 59.9^{cde}
EV	6253.7 ± 752.8^{de}	206.2 ± 48.2^{b}	2577.0 ± 350.8^{de}	–	$2266.5 \pm 600.0b$	$1977.0 \pm 202.8gh^{i}$	706.5 ± 132.3^{c}
GsO	8162.0 ± 2255.4^{c}	–	3754.0 ± 947.8^{c}	–	$860.8 \pm 200.9c$	5997.6 ± 1504.1^{c}	462.6 ± 116.1^{cde}
HtO	6003.2 ± 434.3^{cde}	41.5 ± 12.0^{c}	2980.3 ± 209.4^{cde}	–	678.2 ± 167.1^{cde}	4489.5 ± 393.5^{de}	4144.5 ± 849.3^{a}
OeO	1524.5 ± 331.1^{ghi}	30.0 ± 9.4^{c}	773.3 ± 201.1^{ghi}	611.6 ± 113.4^{a}	150.5 ± 22.5^{f}	1555.5 ± 317.3^{ghi}	392.3 ± 79.1^{de}
PO	1369.7 ± 367.9^{hi}	44.7 ± 7.8^{c}	639.8 ± 149.7^{hi}	15.6 ± 3.0^{b}	273.5 ± 49.0^{ef}	1043.8 ± 290.1^{hi}	309.8 ± 57.6^{de}
PtO	7904.8 ± 553.5^{cd}	–	3436.7 ± 246.9^{cd}	–	648.5 ± 70.1^{cde}	5417.7 ± 506.2^{cd}	320.2 ± 82.7^{de}
RaO	967.5 ± 224.7^{i}	46.2 ± 6.0^{c}	469.0 ± 91.7^{i}	–	294.0 ± 53.5^{ef}	762.3 ± 151.9^{i}	327.8 ± 62.0^{de}
RiO	1377.2 ± 142.9^{i}	29.3 ± 6.8^{c}	577.0 ± 127.3^{i}	–	334.5 ± 31.6^{def}	922.2 ± 132.9^{i}	311.2 ± 56.6^{de}

Table 3 (*continued*)

Sample	N	O	P	Q	R	S	T
SaO	3727.5 ± 442.7^{fg}	61.2 ± 16.1^{bc}	1643.0 ± 210.9^{fg}	–	567.0 ± 53.5^{cdef}	2633.7 ± 308.6^{fg}	621.2 ± 58.2^{cde}
SeO	504.3 ± 82.0^{i}	72.8 ± 21.4^{bc}	313.3 ± 47.3^{i}	–	220.8 ± 28.6^{ef}	408.5 ± 82.0^{i}	219.8 ± 48.9^{e}
SoO	4169.3 ± 399.7^{ef}	71.3 ± 16.5^{bc}	2127.7 ± 242.4^{ef}	–	777.8 ± 73.8^{cd}	3645.3 ± 504.5^{ef}	1034.5 ± 172.0^{b}
SuO	907.2 ± 118.5^{i}	48.8 ± 12.9^{c}	374.0 ± 49.0^{i}	–	291.3 ± 48.8^{ef}	744.5 ± 101.9^{i}	$318.3 \pm 31.9d^{e}$
WrO	3246.0 ± 423.5^{fgh}	70.2 ± 14.8^{bc}	1526.3 ± 206.4^{fgh}	–	601.8 ± 28.3^{cdef}	2483.2 ± 329.4^{fgh}	743.7 ± 95.3^{c}

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

A further separation among the vegetable oils was dominated by PC 2 (Fig. 3(b)) which described 7% of the peak variation. The corresponding loading plot revealed this separation to be related mainly to variables *n* and *s*. Percentage of alteration was organised from origin to high negative loading along PC 2 in relation to increasing amount of *n* and *s*. The high negative score of canola oil (Fig. 3(b)) was determined by the highest amount of *s* and second highest amount of *n* among all vegetable oils. Extra virgin olive oil contained significantly higher amounts of *n* than did sesame, palm olein, olive, ricebran, rapeseed, and sunflower oils that separated it out from of the cluster (Fig. 3(b)).

For those oils that overlap and form clusters on the PCA (walnut and safflower oils; sesame, palm olein, olive, ricebran, rapeseed and sunflower oils) there was no significant difference in the amount of the five influencing variables (m, k, n, s, p).

4. Conclusion

In this paper, we have presented the results of an evaluation of the application of the zNose™ for characterisation of vegetable oils. The ability of the zNose™ to qualitatively distinguish among 16 common vegetable oils was demonstrated. This indicated that the instrument had adequate selectivity and sensitivity to perform flavour identification in vegetable oils. The fats and oil industry are now able to see and measure the chemistry of odour of vegetable oils with the electronic nose. This electronic nose may potentially fulfil a real need in the fats and oils industry for objective, rapid quality-monitoring sampling systems that can characterize odour with a midrange precision. Thus it is important to determine whether the production system is running to specification without requiring human sensory panellists, or lengthy analytical methods and interpretation of the data.

Using an electronic nose would allow the odour quality of vegetable oils to be followed continuously from the raw material stage right through to the final product. It would be useful to incorporate electronic noses in the food industry to determine whether the deodorization process has been successfully completed. Besides that, with the standard vapour image of the fresh oil produced by the zNose™ it is possible to compare and monitor the chemical composition and quality of the entire production process to allow detection of rancidity or off-flavour at early stages, to improve cost-effectiveness. Authenticity is an issue of major concern in the food industry. With the characteristic aroma fingerprint of each vegetable oil, it is possible to detect any adulteration and allow adulterated oil to be viewed and recognized as part of a previously learned image set.

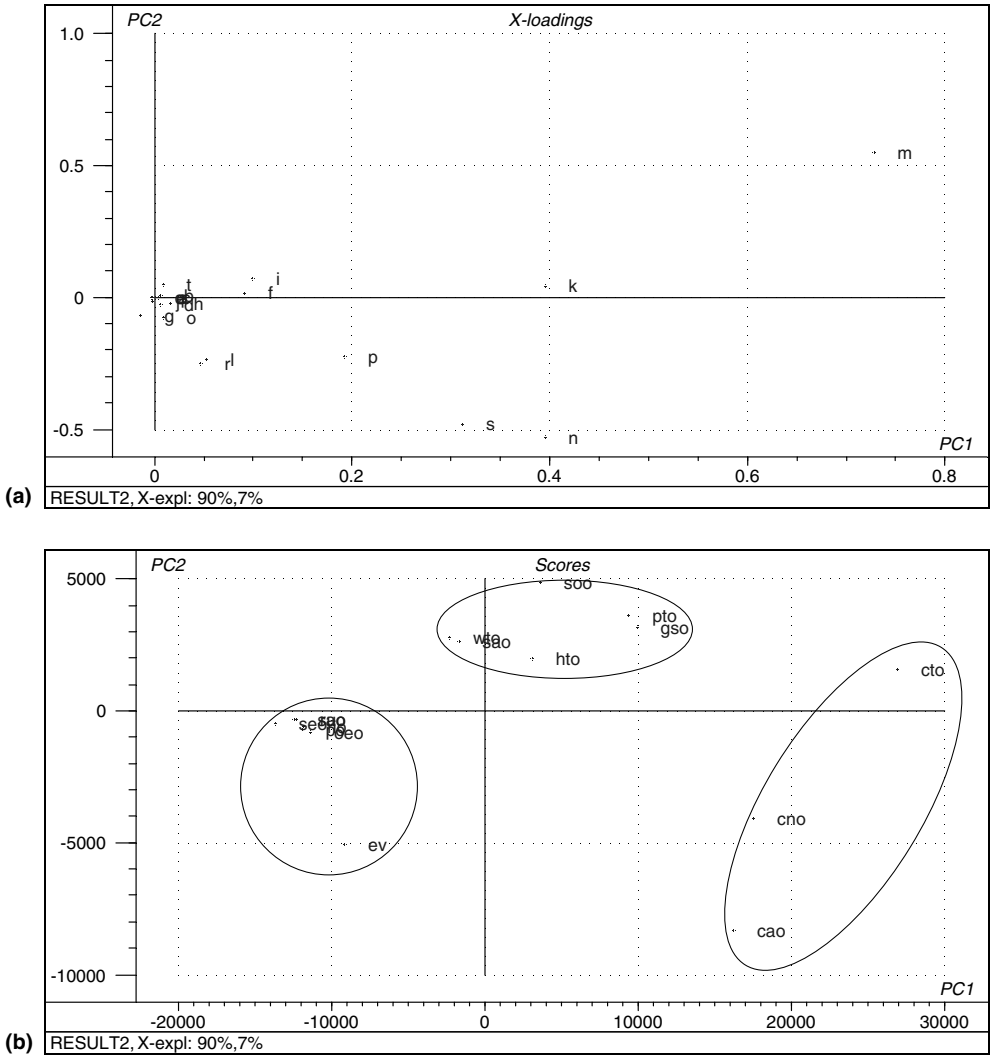

Fig. 3. Principal component analysis of the electronic nose data: (a) 20 electronic nose variables (loading plot); (b) 16 different vegetable oils (score plot).

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