Quantitative Evaluation of Perfume Fleuressence Samples using the zNose®

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Electronic Noses

Conventional electronic noses (eNoses) produce a recognizable response pattern using an array of dissimilar but not specific chemical sensors. Electronic noses have interested developers of neural networks and artificial intelligence algorithms for some time, yet physical sensors have limited performance because of overlapping responses and physical instability. eNoses cannot separate or quantify the chemistry of aromas.

A new type of electronic nose, called the zNose®, is based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part-per-trillion sensitivity. Separation and quantification of the individual chemicals within an odor is performed in seconds. Using a patented solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity is achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. In this paper a portable zNose®, shown in Figure 1, is shown to be a useful quality control tool for quantifying the concentration of chemicals used in 25 basic fleuressence aromas as well as a perfumery mixture or designer perfume. A 'good' perfume aroma as determined by a trained perfumery technician can be easily quantified in near real time. The 'good' chemical signature once defined allows for objective and quantitative quality control testing with zNose® analyzers integrated into the perfume production process.

Figure 1- Portable zNose® technology incorporated into a handheld instrument.

How the zNose™ Quantifies the Chemistry of Aromas

A simplified diagram of the zNose™ system shown in Figure 2 consists of two parts. One section uses helium gas, a capillary tube (GC column) and a solid-state detector. The other section consists of a heated inlet and pump, which samples ambient air. Linking the two sections is a "loop" trap, which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two step process. Ambient air (aroma) is first sampled and organic vapors collected (preconcentrated) on the trap. After sampling the trap is switched into the helium section where the collected organic compounds are injected into the helium gas. The organic compounds pass through a capillary column with different velocities and thus individual chemicals exit the column at characteristic times. As they exit the column they are detected and quantified by a solid state detector.

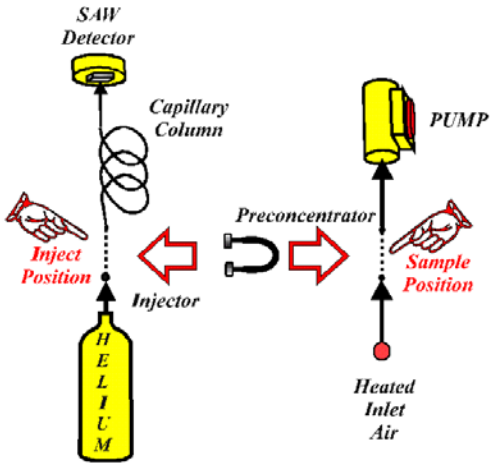


Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.

An internal high-speed gate array microprocessor controls the taking of sensor data which is transferred to a user interface or computer using an RS-232 or USB connection. Aroma chemistry, shown in Figure 3, can be displayed as a sensor spectrum or a polar olfactory image of odor intensity vs retention time. Calibration is accomplished using a single n-alkane vapor standard. A library of retention times of known chemicals indexed to the n-alkane response (Kovats indices) allows for machine independent measurement and compound identification.

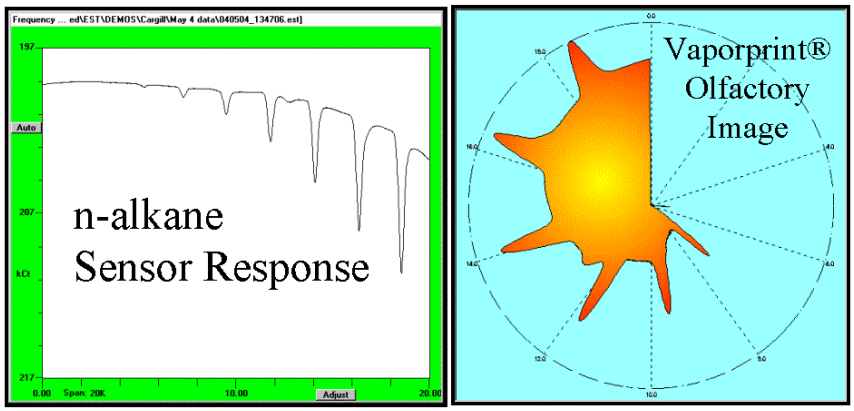


Figure 3- Sensor response to n-alkane vapor standard, here C6-C14, can be displayed as sensor output vs time or its polar equivalent olfactory image.

Chemical Analysis (Chromatography)

The time derivative of the sensor spectrum (Figure 3) yields the spectrum of column flux, commonly referred to as a chromatogram. The chromatogram response (Figure 4) of n-alkane vapors (C6 to C14) provides an accurate measure of retention times. Graphically defined regions shown as red bands calibrate the system and provides a reference time base against which subsequent chemical responses are compared or indexed. As an example, a response midway between C10 and C11 would have a retention time index of 1050.

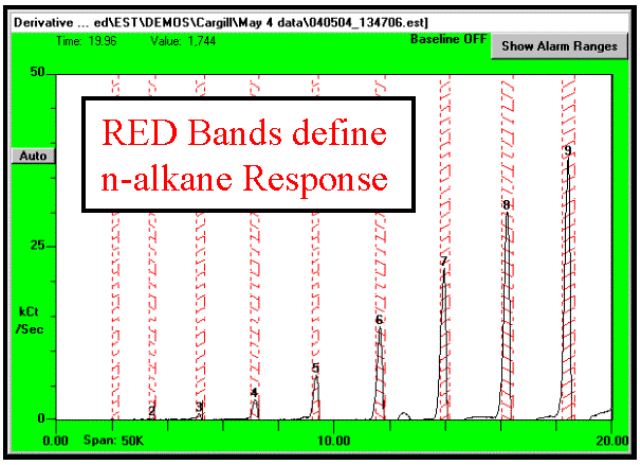


Figure 4 - Chromatogram of n-alkane vapors C6 to C14).

Flueressence Samples

A set of primary odor perfume compound bases containing one or more aroma chemicals can act as a set of basic fleuressence groups useful for perfume compounding. Fleuressence bases are prime olfactory notes from which complex perfume aromas can be created. A perfumery training kit with 25 fleuressence bases representing a set of prime notes was obtained from Perfumers World http://www.perfumersworld.com). The bases and their aroma note descriptor or names are listed in Table I.

Table I- Fleuressence Bases

A	Aldehyde	N	Narcotic
B	Iceberg	O	Orchid
C	Citrus	P	Phenolic
D	Dairy	Q	Balsamic
E	Edible	R	Rose
F	Fruits	S	Spice
G	Green	T	Tar/Smoke
H	Herb	U	Animalic
I	Iris	V	Vanilla
J	Jasmine	W	Wood
K	Konifer	X	Musk
L	Linalool	Y	Yeast/Mossy
M	Muguet	Z	Zolvent

Figure 5- Perfumery training kit

Aroma Testing Methods

Injecting a small amount of fleuressence base into a septa-sealed vial produces a known concentration of vapor, which can then be sampled by the zNose® vapor analyzer. Internal temperatures of the analyzer are set to 160°C and 200°C for the vapor inlet. A short one-second sample time (0.5 mL) is best when using undiluted base materials.

Figure 6- Testing materials are 40 mL septa sealed vials, a 1-10 µL syringe, fleuressence samples, and a zNose® vapor analyzer.

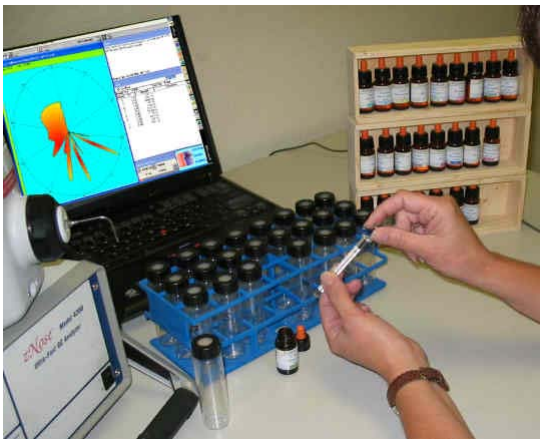


Figure 7- Step one is draw 2 µL from Fleuressence vial into a clean syringe.

Figure 8- Step two is to inject 2 µL of fleuressence through septa and into 40 mL to create vapor sample.

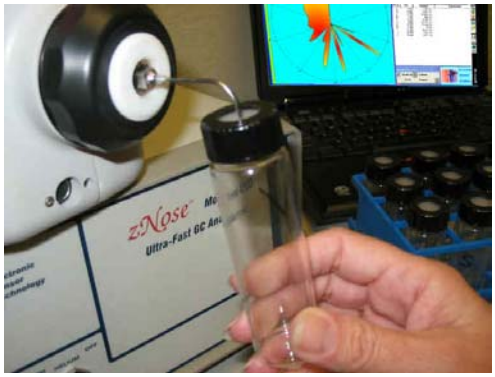


Figure 9- Step 3 is to attach vial to inlet of zNose®. A sample needle works well for volatile compounds. Above C12 compounds begin to condense onto the walls of the relatively cool sample needle.

Figure 10- Removing septa cap and pressing vial against Teflon face of zNose® inlet enables direct sampling of high molecular weight compounds by the 200°C inlet of the zNose.

Experimental Results

For all vapor samples tested the column (a db624) was temperature programmed to rise from 40°C to 160°C at 10°C/second and data acquisition (chromatogram) time was 20 seconds. A detector temperature of 60°C was used unless stated otherwise.

A. Aldehyde

The vapors from the aldehyde fleuressence base produced two primary compounds with indices of 1104 and 1332 and concentration counts of 4,519 and 11,114 respectively. Significant other compounds at much lower concentrations had indices of 1016, 1234, 1438, 1516, and 1584. The Vaporprint® image shows aroma concentration (radial) vs retention time (angle) with 0 and 20 seconds at the top of the figure 11.

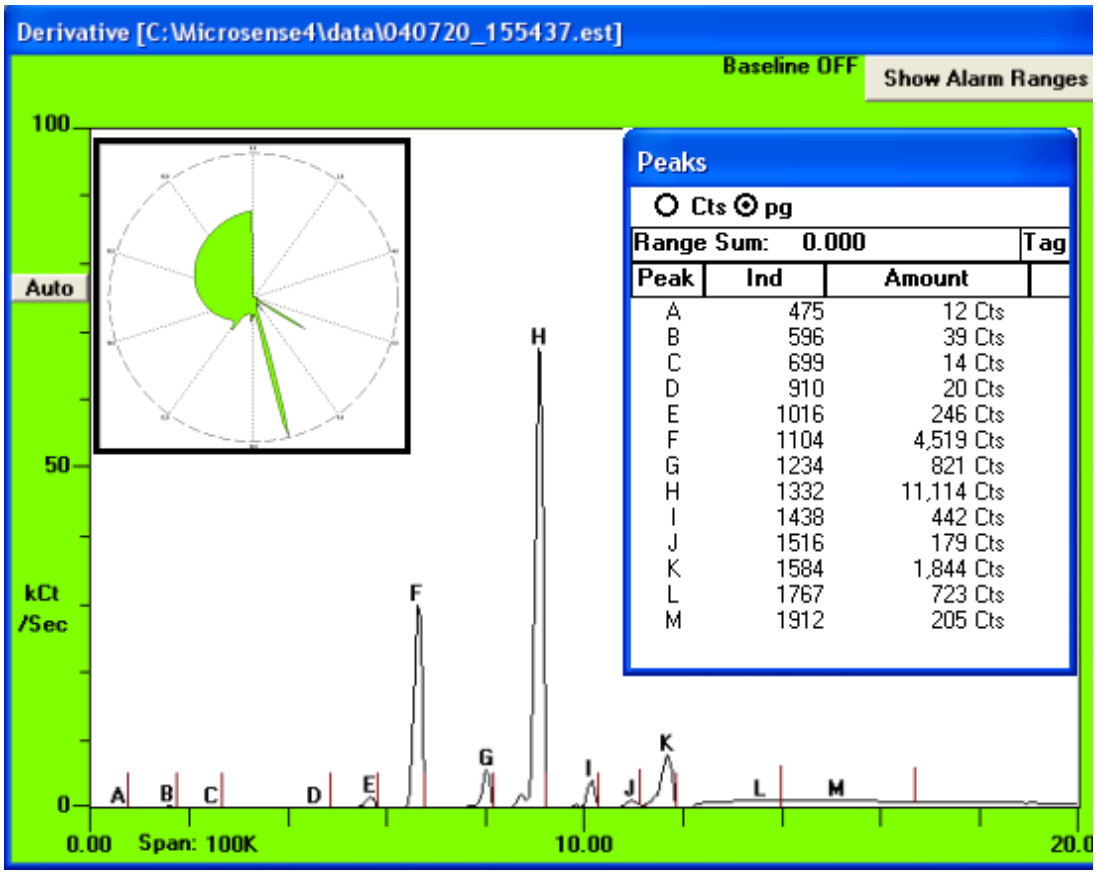


Figure 11- Chromatogram of Aldehyde fleuressence

B. Iceberg

The iceberg fleuressence contained a single major compound with an index of 1225 and a concentration of 20,007 counts. A minor secondary compound with an index of 1062 and a concentration of 1,800 counts was also detected.

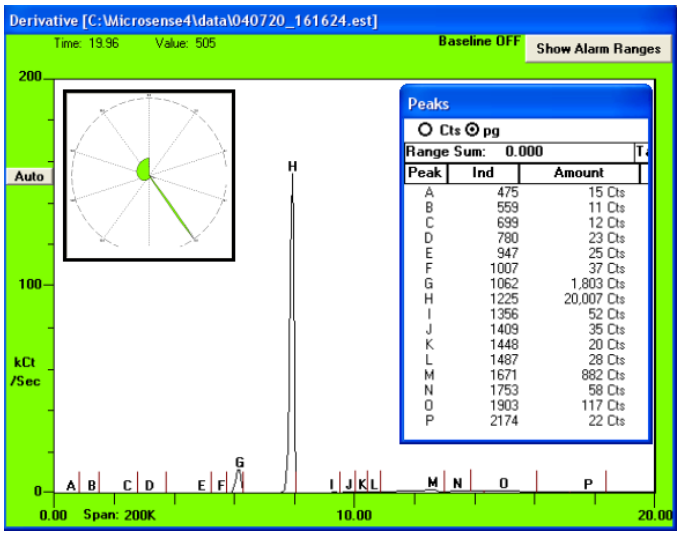


Figure 12- Chromatogram of Iceberg fleuressence

C. Citrus

The citrus fleuressence contained a single major compound (limonene) with an index of 1057 and a concentration of 17,929 counts. Minor secondary compounds with indices of 947, 1002, 1275, and 1405 were also detected.

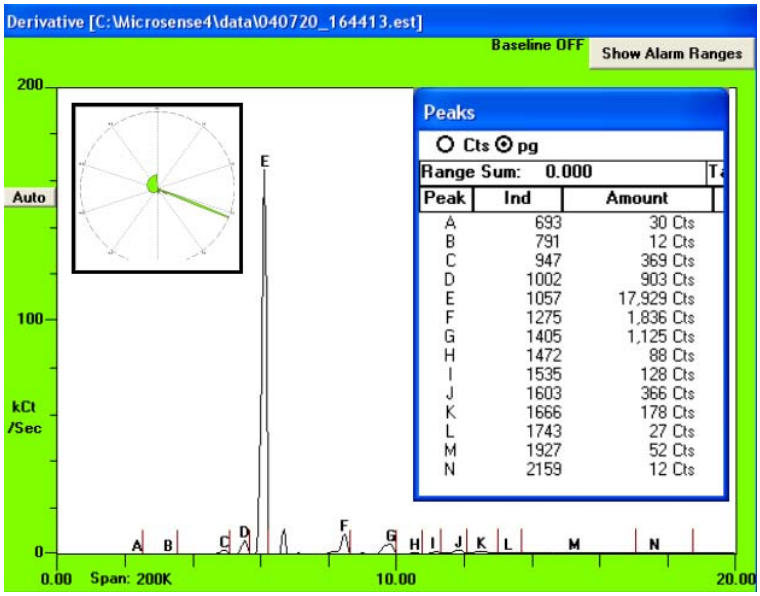


Figure 13- Chromatogram of Citrus fleuressence.

D. Dairy

The dairy fleuressence contained two major compound peaks with indices of 1452 and 1583 and concentrations of 3,823 and 2,965 counts respectively. Significant minor compounds with indices of 603, 1058, 1279, 1393 and 1651 were also detected. The rounded portion of the Vaporprint® image is associated with the presence of high molecular weight compounds.

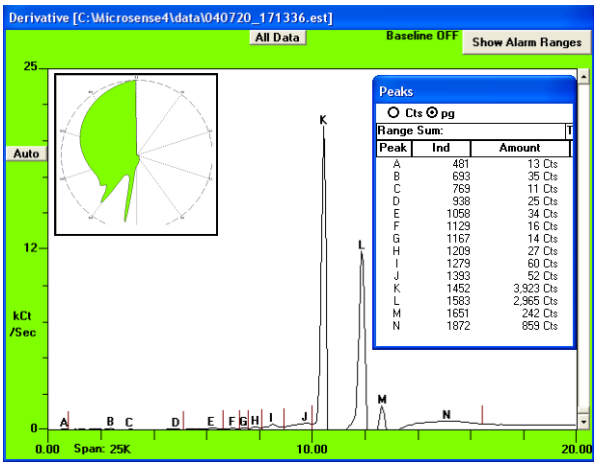


Figure 14- Chromatogram of Dairy fleuressence.

E. Edible

The edible fleuressence contained two major closely spaced compound peaks with indices of 1097 and 1120 and concentrations of 2,752 and 3,832 counts respectively. Significant minor compounds with indices of 805, 965, 1274 and 1398 were also detected.

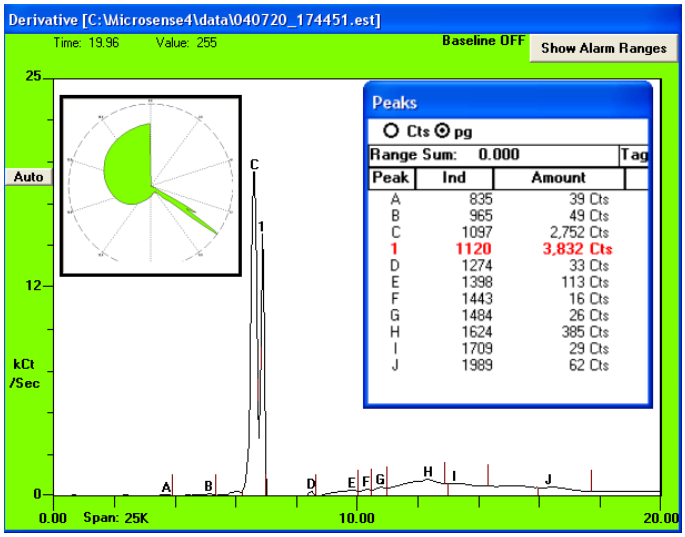


Figure 15- Chromatogram of edible fleuressence.

F. Fruit

The fruit fleuressence contained three major compound peaks with indices of 1111, 1329, and 1461 and concentrations of 34,982, 22,317 and 19,439 counts respectively. Significant minor compounds with indices of 830, 1054, 1219, 1274, 1542, 1651, 1804, and 1994 were also detected.

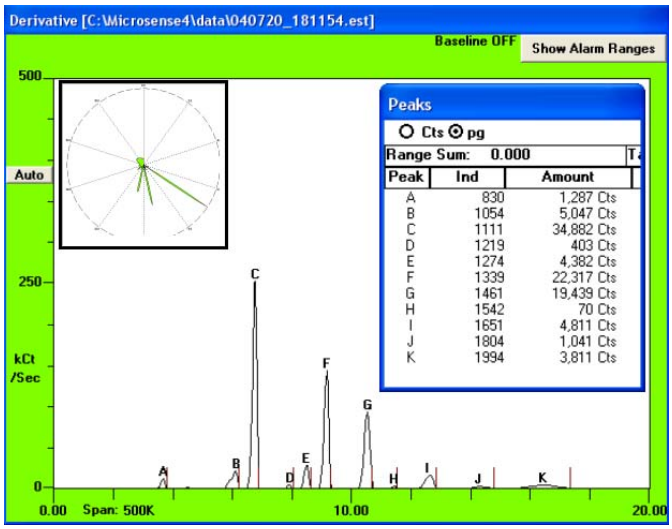


Figure 16- Chromatogram of Fruit fleuressence.

G. Green

The green fleuressence contained a major compound peak with an index of 910 and a concentration of 6565 counts. Significant minor compounds with indices of 1093, 1120, 1224, 1269, 1339, 1402, 1443, 1511, 1565, 1637, 1723, and 1858 were also detected.

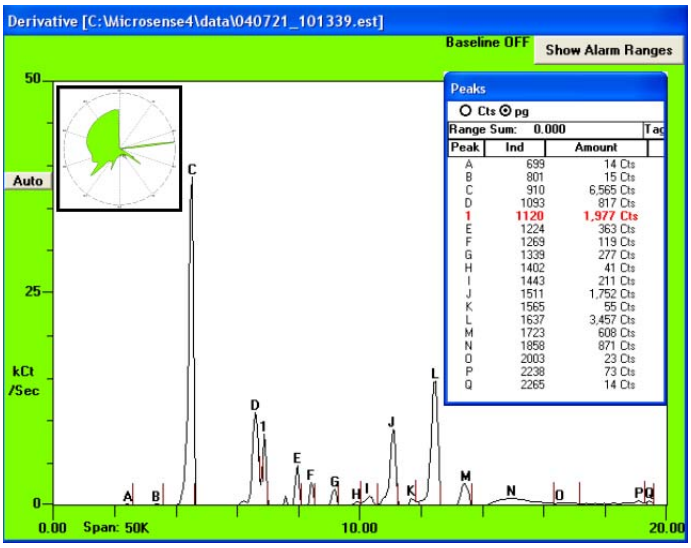


Figure 17- Chromatogram of Green fleuressence.

H. Herb

The herb fleuressence contained a major compound peak with an index of 1139 and a concentration of 47,348 counts. Significant minor compounds with indices of 693, 910, 952, 1010, 1062, 1209, 1283, 1407, 1556, and 1587 were also detected

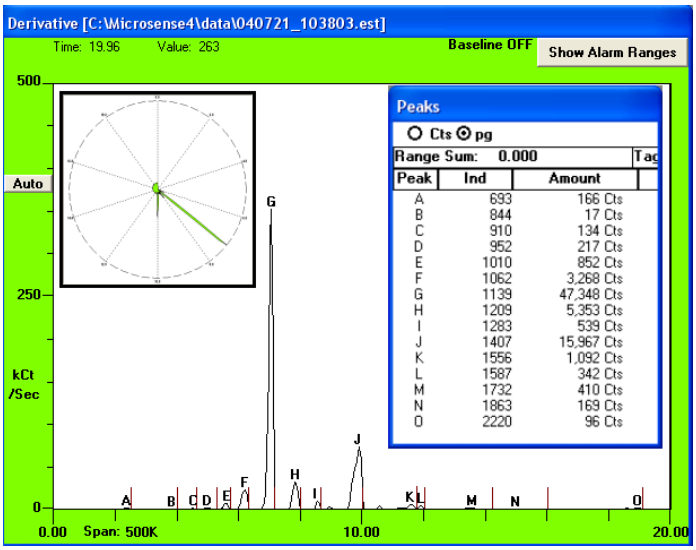


Figure 18- Chromatogram of Herb fleuressence.

I. Iris

The iris fleuressence contained major compound peaks with indices of 1484 and 1533 and concentrations of 15,717 and 72,716 counts respectively. Significant minor compounds with indices of 830 and 1366 were also detected.

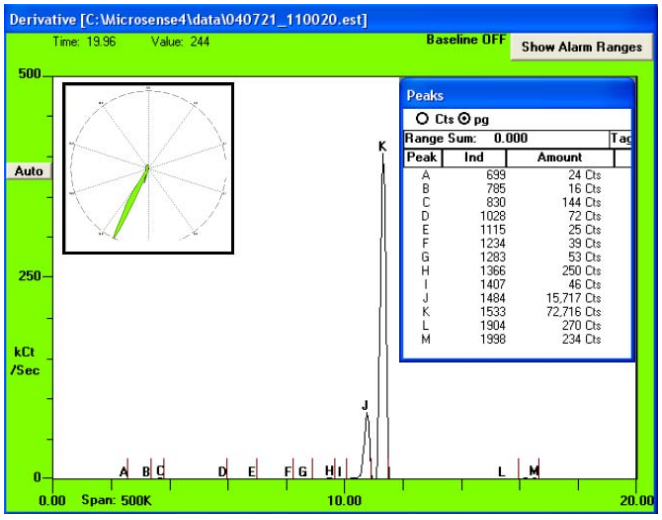


Figure 19- Chromatogram of Iris fleuressence.

J. Jasmine

The jasmine fleuressence contained a major compound peak with an index of 1224 and a concentration of 34,912. Significant minor compounds with indices of 910, 1028, 1115, 1316, 1366, 1434, and 1470 were also detected.

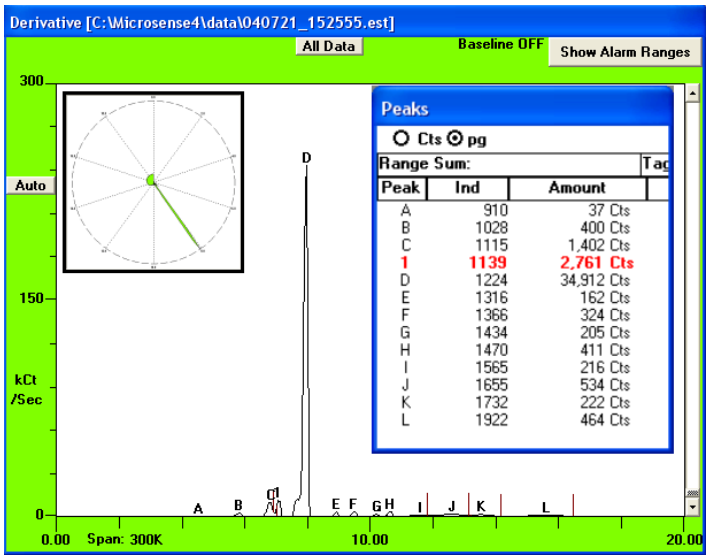
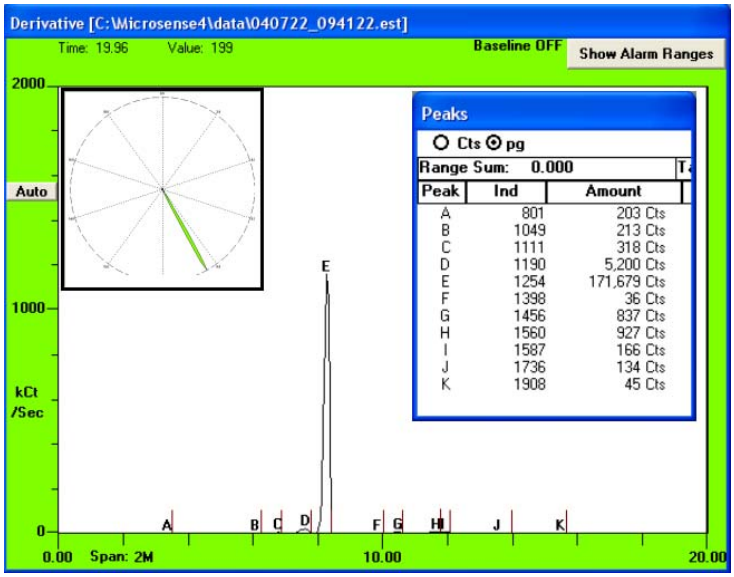


Figure 20- Chromatogram of jasmine fleuressence.

K. Konifer

The konifer fleuressence contained a major compound peak with an index of 1254 and a concentration of 171,679 counts. Significant minor compounds with indices of 1049, 1111, 1190, 1456, and 1560 were also detected



L. Linalool

The linalool fleuressence contained a major compound peak with an index of 1140 and a concentration of 73,221 counts. No significant minor compounds were detected.

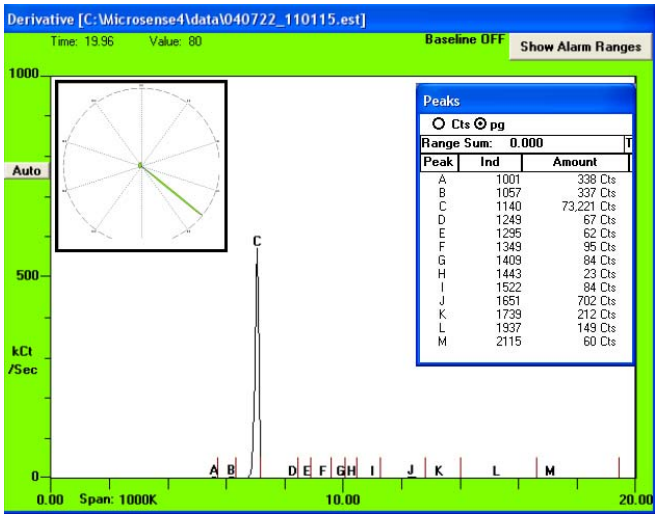


Figure 22- Chromatogram of linalool fleuressence.

M. Muguet

The muguet fleuressence contained major compound peaks with indices of 1136, 185, 1268, and 1359 and with peak concentrations of 5,673, 8,228, 1,778, and 8,757 counts respectively. Significant minor compounds with indices of 1100, 1527, 1591, 1749, and 1942 were also detected.

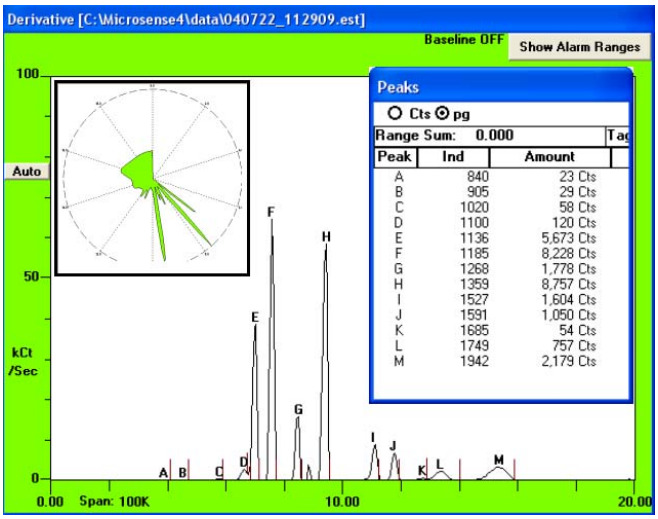


Figure 23- Chromatogram of Muguet fleuressence.

N. Narcotic

The narcotic fleuressence contained major compound peaks with indices of 1136, 1185, 1213, and 1428 with peak concentrations of 7667, 2377, 3845, and 14,581 counts respectively. Significant minor compounds with indices of 1057, 1100, 1359, 1606, 1754, and 2085 were also detected

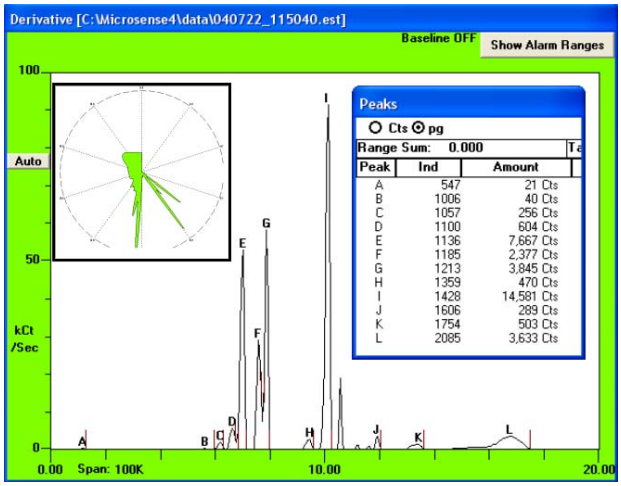


Figure 24- Chromatogram of narcotic fleuressence.

O. Orchid

The orchid fleuressence contained major compound peaks with indices of 1213, 1479, and 1601 and with peak concentrations of 2436, 17386, and 38,257 counts respectively. Significant minor compounds with indices of 775, 905,1057, 1113, 1140, 1419, 1532, and 1764 were also detected.

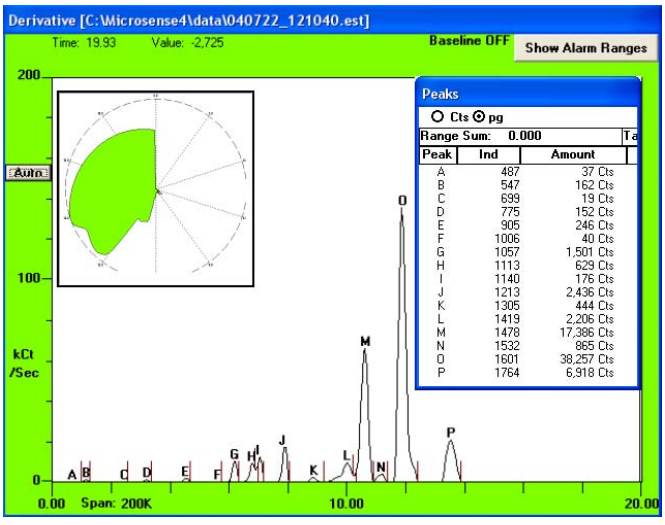


Figure 25- Chromatogram of orchid fleuressence.

P. Phenolic

The phenolic fleuressence contained major compound peaks with indices of 1185, and 1222 and with peak concentrations of 4,962 and 3,577 counts respectively. Significant minor compounds with indices of 1596 and 2050 were also detected.

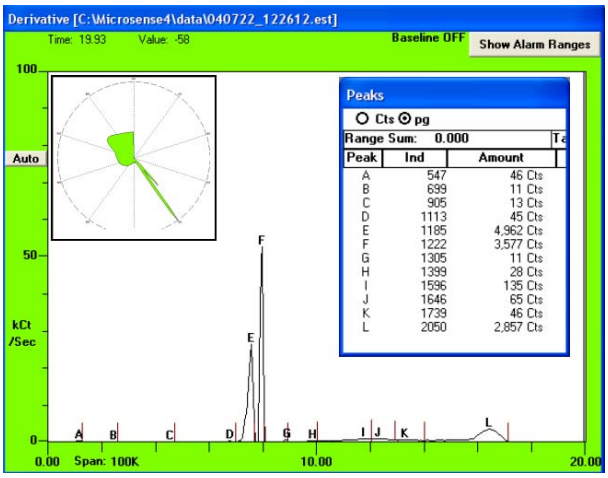


Figure 26- Chromatogram of phenolic fleuressence.

Q. Balsamic

The balsamic fleuressence contained major compound peaks with indices of 1053, 1109, 1213, and 1414 and with peak concentrations of 775, 2639, 2166, and 1497 counts respectively. Significant minor compounds with indices of 1001, 1577 and 2070 were also detected.

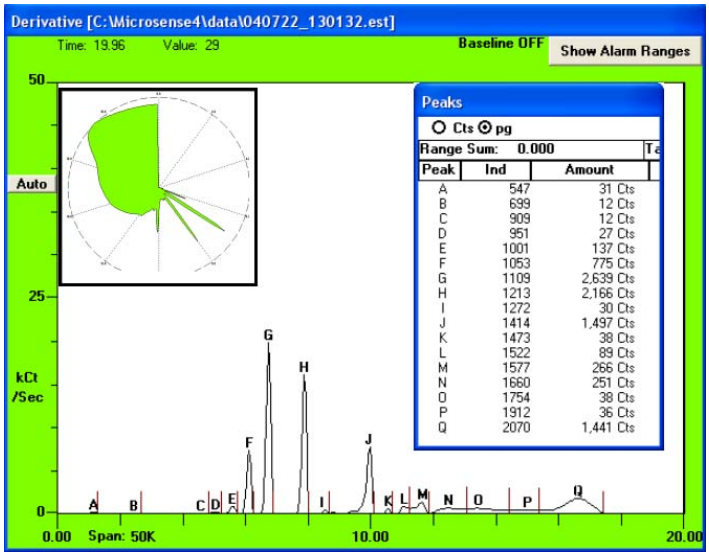


Figure 27- Chromatogram of balsamic fleuressence.

R. Rose

The rose fleuressence contained a single major compound with an index of 1190 and a peak concentration of 21,176 counts. Significant minor compounds with indices of 1140, 1268, and 1547 were also detected

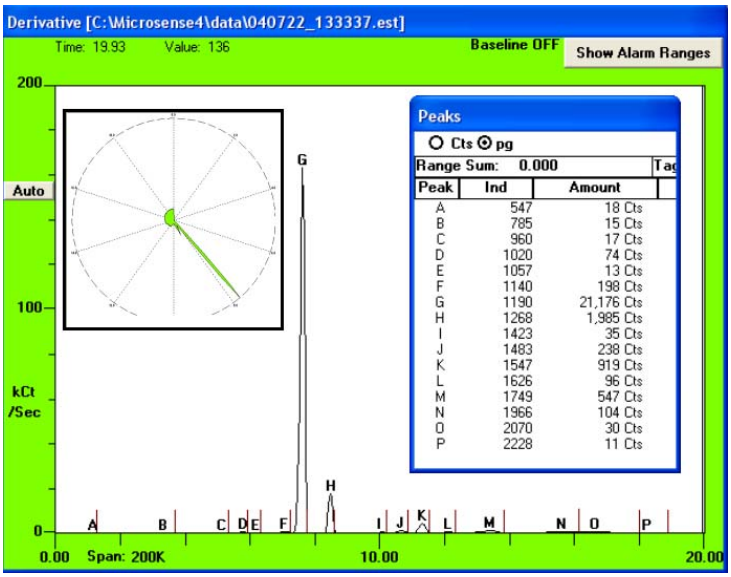


Figure 28- Chromatogram of rose fleuressence.

S. Spice

The spice fleuressence contained a single major compound peak with an index of 1423 and a peak concentration of 53,246 counts. Significant minor compounds with indices of 1140, 1355, 1518, 1672 and 1772 were also detected.

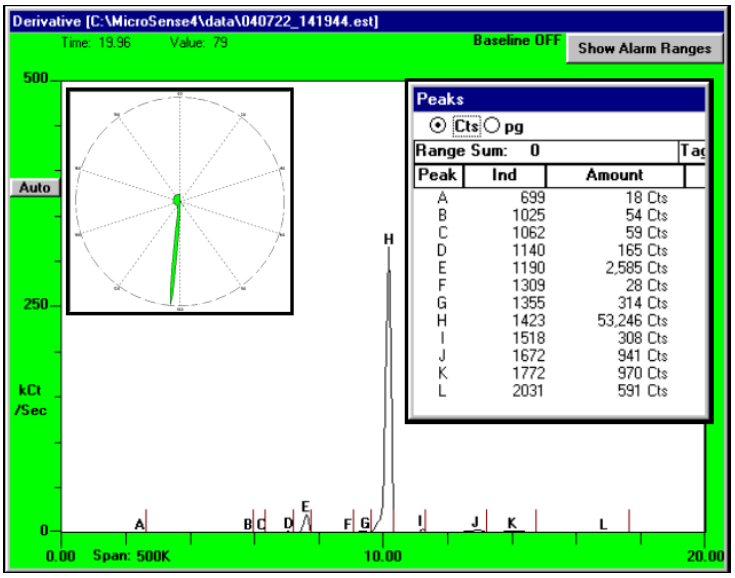


Figure 29- Chromatogram of spice fleuressence.

T. Tar and Smoke

The tar and smoke fleuressence contained major compound peaks with indices of 1095, 1163, 1268 and 2139 and with peak concentrations of 2701, 5174, 5167 and 45,465 counts respectively. Significant minor compounds with indices of 709, 790, 905, 974, 1029, 1057, 1364, 1449, 1493, 1532, 1562 and 1596 were also detected.

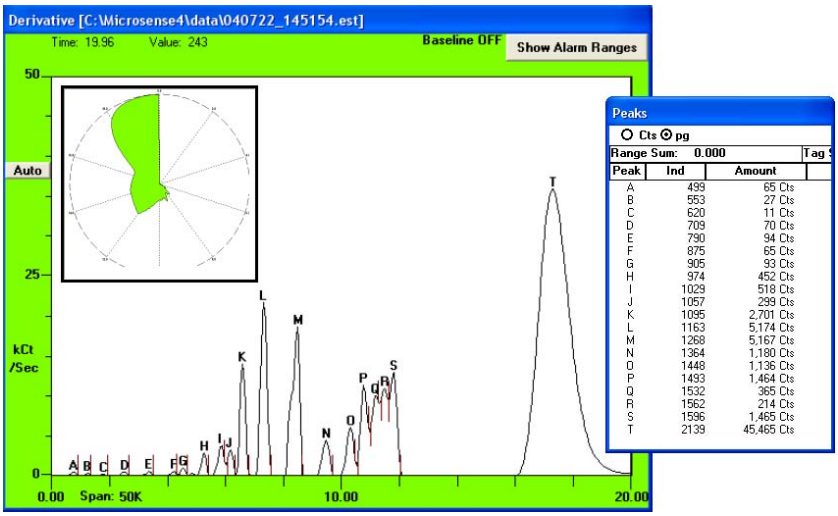


Figure 30- Chromatogram of tar and smoke flueressence.

U. Animalic

The animalic fleuressence contained major compound peaks with indices of 1140, 1433, 1483, 1517, 1557, 1774, and 2085 and with peak concentrations of 16,484, 12,631, 12,300, 2,027, 3,871, 9,207 and 8,944 counts respectively. Significant minor compounds with indices of 919, 1006 and 1057 were also detected.

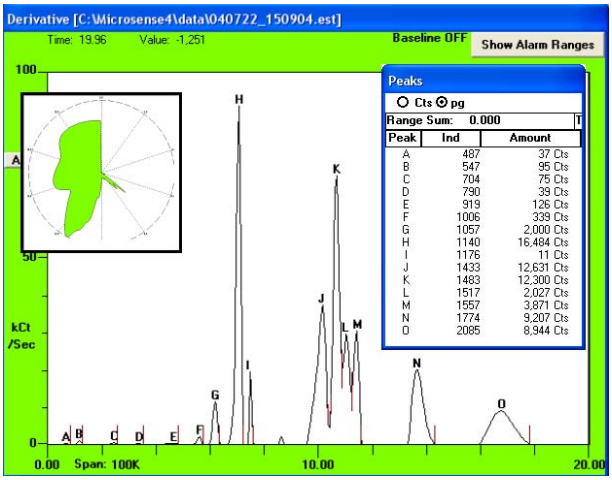


Figure 31- Chromatogram of animalic fleuressence.

V. Vanillin

The vanillin fleuressence contained major compound peaks with indices of 1433 and 1577 and with peak concentrations of 9,548 and 3,891 counts respectively. Significant minor compounds with indices of 1527 and 2085 were also detected.

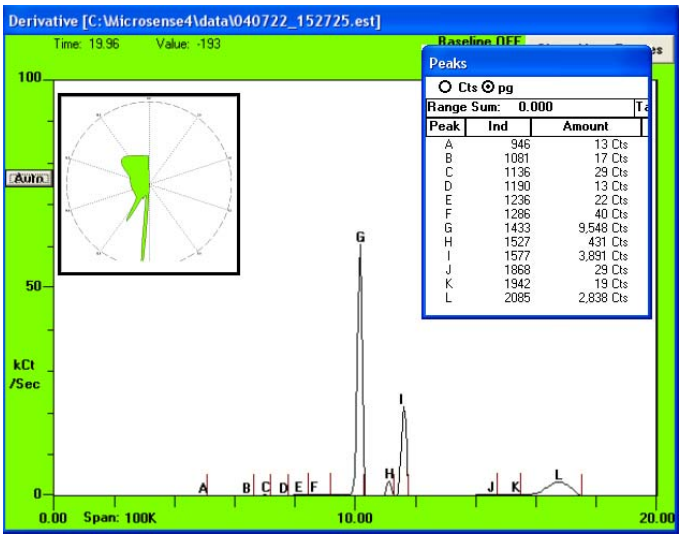
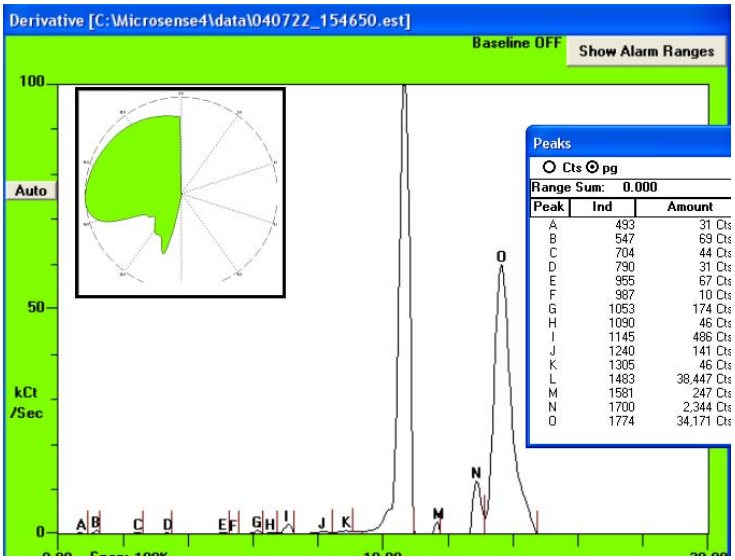


Figure 32- Chromatogram of vanillin fleuressence

W. Wood

The wood fleuressence contained major compound peaks with indices of 1483 and 1774 and with peak concentrations of 38,447 and 34,171 counts respectively. Significant minor compounds with indices of 1053, 1145, 1581, and 1700 were also detected.



X. Musk

The musk fleuressence contained major compound peaks with indices of 1591 and 1685 and with peak concentrations of 5,572 and 6,570 counts respectively. Significant minor compounds with indices of 983, 1086, 1140, 1226, and 1305 were also detected.

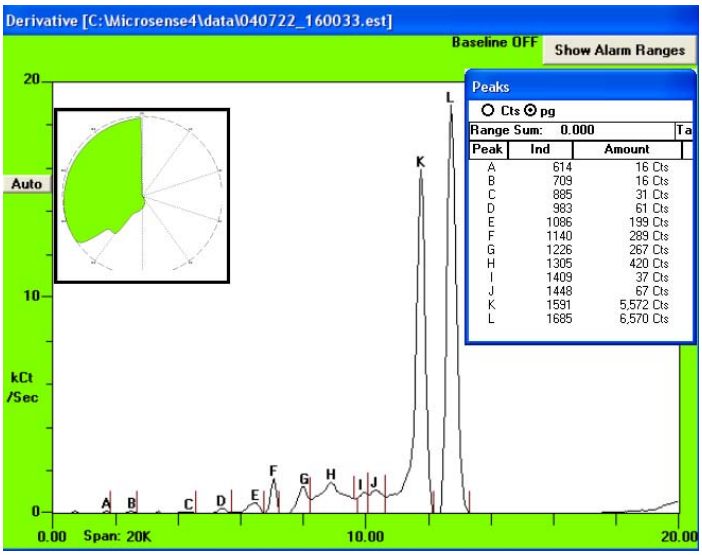


Figure 34- Chromatogram of Musk fleuressence.

Y. Yeast-Mossy

The yeast-mossy fleuressence contained major compound peaks with indices of 1209, 1234, and 2084 and with peak concentrations of 19,575, 1,190 and 60,211 counts respectively. Significant minor compounds with indices of 924, 1036, 1081, 1097, 1429, 1678, and 1750 were also detected

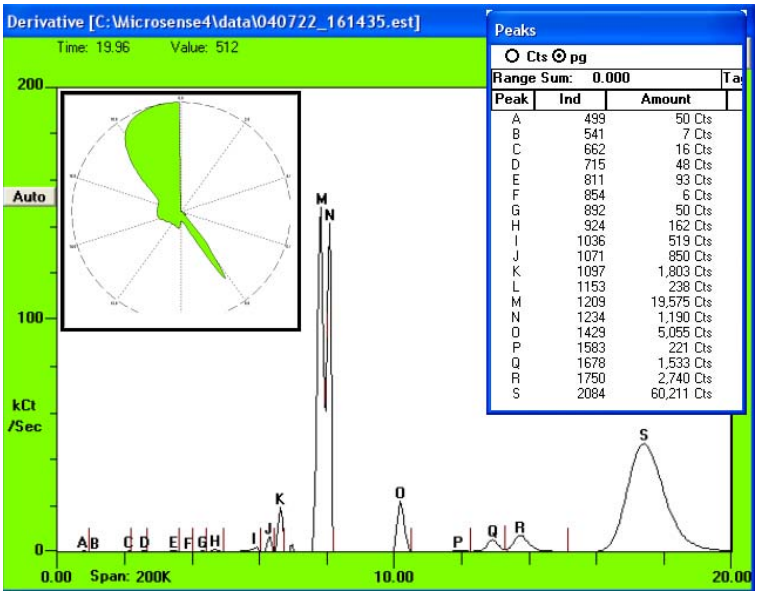


Figure 35- Chromatogram of yeast-mossy fleuressence.

Z. Zolvent

This solvent base mix produces a much lower concentration aroma than the fleuressence bases so the analysis was done with a 20°C detector and a 10-second sample of headspace vapors from 3 mL of zolvent in a 40 mL vial.

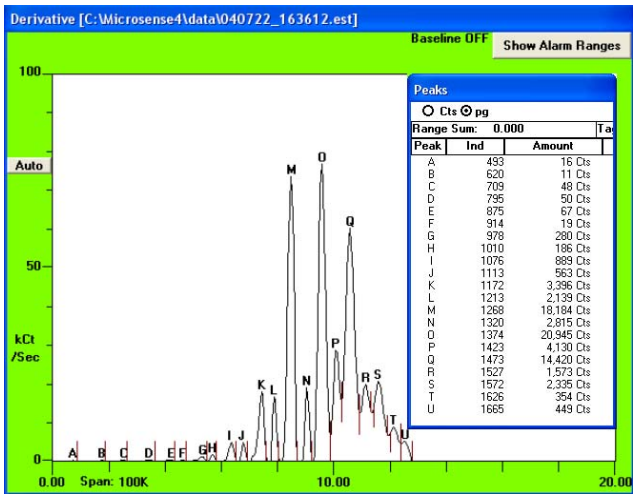


Figure 36- Chromatogram of Zolvent mixing solution.

Summary of Vaporprint® Olfactory Images

Olfactory images from all twenty-five fleuressence bases are shown in figure37 for visual comparison.

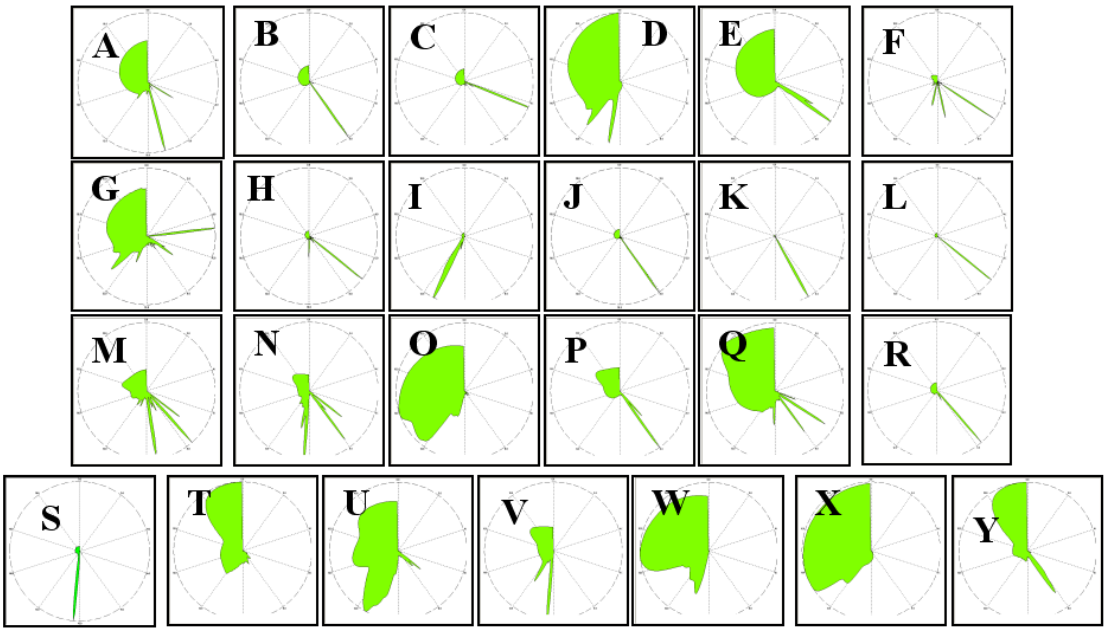


Figure 37- Summary of fleuressence olfactory images.

Channel Number 5 Perfume

This popular perfume was testing using the same method used on the fleuressence bases e.g. 2 µl in 40 mL vial, 1-second sample, 60 °C detector and 10°C/second column ramp rate. The perfume contained a major compound peak with an index of 1,135 and a concentration of 4,578 counts. Many significant minor compounds were also clearly evident and some did not easily separate using this fast method.

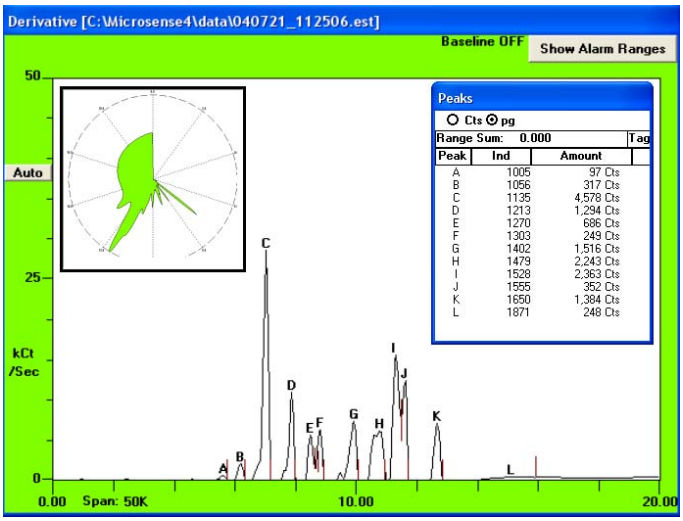


Figure 38- Chromatogram of Channel No. 5.

Slowing the analysis method using a 3°C/second column ramp allowed the perfume compounds to be better defined and separated while reducing the detector temperature to 20 °C improved the sensitivity to volatile compounds. This analysis reveals approximately 18 minor compound peaks in addition to the primary aroma compound (index 1130).

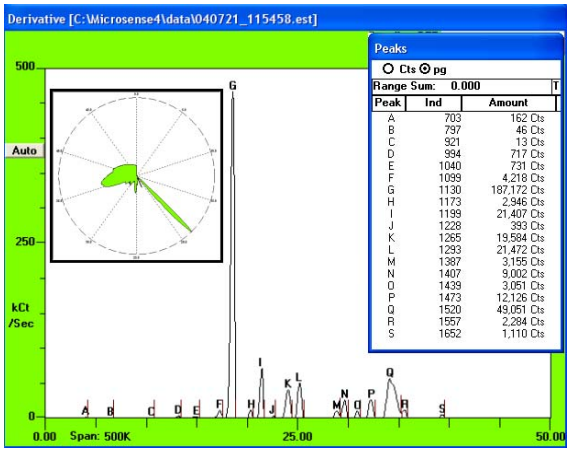


Figure 39- Chromatogram of Channel No. 5 aroma using slower method.

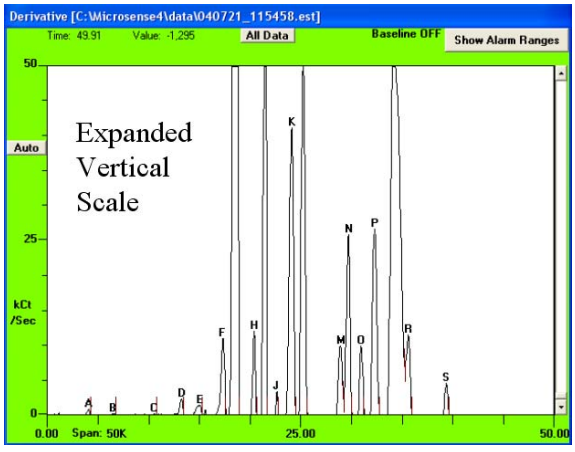


Figure 40- Expanded scale showing trace elements of Channel No. 5 perfume.

Summary

Chemical profiling of aroma fleuressence samples judged to represent 25 basic olfactory notes has been shown to be fast and quantitative using an ultra high speed gas chromatograph called the zNose®. It is possible to quantitively measure quality in a fast and efficient manner and compare the chemical signature of perfumes created by trained perfumery technicans. Indexing of retention times for target compounds using an n-alkane perfume standard provides a convenient method of identification, eleminates the need for multiple chemical standards, and allows for instrument independent chemical libraries.

Dynamic headspace analysis using ultra-high speed gas chromatography can be coupled with sensory data to affect an objective method of classifying perfumes by fleuressence notes or olfactory images. The chemical image and sensory data can be subjected to pattern recognition using multivariate analysis, principal component analysis (PCA) and partial least squares (PLS) methods to determine perfume classications or model human perception. Proper choice of samples and use of optimized variables as well as preprocessing of chemical data, including scaling, transformation, and normaliation, may also prove useful in assessing quality.

. The zNose® is a tool which provides perfumery experts the speed, portability, precision, and accuracy needed for cost-effective quality control measurements. Such measurements, because they are based upon well known chromatographic methods, can easily be validated by independent laboratory testing. A ‘good’ perfume aroma as determined by a trained perfumery technician can now be quantified in near real time. The ‘good’ chemical signature once defined, allows for objective and quantitative quality control testing with other zNose® analyzers integrated into perfume production process often located in remote geographical locations.

Figure 41- A happy perfumery technician.