Olfactory Measurements Using an Ultra-High Speed Gas Chromatograph, The zNose®

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Abstract

Gas Chromatography is the preferred analytical method chosen for analysis of odors, fragrances, and other chemical vapors, yet this technology has been rejected by most electronic nose researchers and developers because it is slow. However, recent advances in GC technology may warrant a second look at this old technology. A handheld electronic nose, called the zNose®, incorporating an ultra-high speed chromatography column, a solid state sensor, a programmable gate array microprocessor, and an integrated vapor preconcentrator will be described in this paper.

Using the zNose® chemicals within any odor or fragrance can now be speciated and their concentration measured in less than 10 seconds with picogram sensitivity using a SAW sensor with electronically variable sensitivity. Odor concentration and intensity are measured directly with this new integrating GC detector. Unlike other electronic noses the zNose® produces high-resolution 2-dimensional olfactory images which are unique to many complex odors. Numerous examples involving food, beverages, petrochemicals, and biological odors will be presented. Digital processing (derivative) of the olfactory image produces conventional chromatograms of column flux vs retention time.

An important function of any electronic nose is to recognize odors and fragrances. A library of retention time indices for chemicals and their odors is an effective method of odor recognition, which will be described. The retention time indices (Kovats) of known chemicals relative to the retention time of homologic series such as the n-alkanes is a powerful analytical technique which allows the same library to apply equally to all other electronic noses using the same type of chromatographic column. A universal chemical library allows nose researchers to share and more easily validate their experimental findings.

Chemical sensor arrays have interested developers of neural networks and artificial intelligence algorithms for some time, yet physical sensors have limited performance because of overlapping chemical responses and physical instability. Using gas chromatography an array of virtual chemical sensors with non-overlapping response is possible. Long term stability and picogram sensitivity can now be achieved leading to renewed interest in application of artificial intelligence in olfactory measurements.

This paper will describe the ultra-high speed GC technology as well as present results for applications involving important vapors associated with a wide range of aromatic products and environments. Quantitative GC measurement techniques will allow electronic noses to obtain regulatory approval and recognition as true analytical instruments.

New Analytical Tool for Odor Measurements, the zNose®

A new type of ultra-fast gas chromatograph, the zNose®, is able to perform analytical measurements of volatile organic vapors and odors in near real time with picogram sensitivity. Because of its picogram sensitivity it is a useful tool for quantifying the organic chemistry of a diverse number of odors and fragrances. The zNose® separates and quantifies the organic chemistry of odors through ultra-high speed chromatography, typically in 10 seconds. Using an uncoated solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity has been achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. A portable zNose®, shown in Figure 1, is a useful tool for on-site odor and ambient air measurements as well

Figure 1- zNose® technology incorporated into 3 commercial instruments.

How the zNose® Quantifies the Chemistry of an Odor

A simplified diagram of the zNose® system shown in Figure 2 consists of two parts. One part or section uses helium gas, a capillary tube (GC column) and a solid-state detector. The other part consists of a heated inlet and a pump, which draws ambient air into the instrument at a fixed flow rate, typically 0.5 milliliter/second. 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 (odor) is first sampled and organic compounds within the air are 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 flow. The organic compounds are separated as they pass through a temperature programmed GC column. Each compound typically has a different velocity and exits the column at a characteristic retention time. Speciation or identification is based upon each compound's unique retention time. As each compound (analyte) exits the column it is detected and quantified by a solid-state mass detector consisting of a temperature controlled surface acoustic wave (SAW) crystal. Detector sensitivity (physical absorption onto the front quartz surface) is a function of crystal temperature and electronic temperature control is achieved by attaching the backside of the SAW crystal to a thermoelectric element.

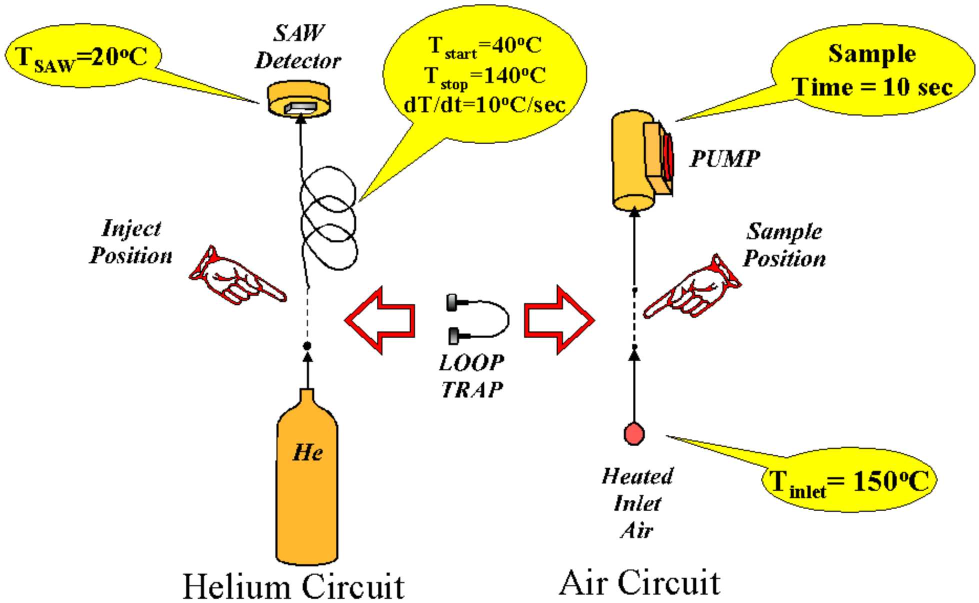

Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject positron.

A high-speed gate-array microprocessor controls the processing of odor samples and includes electronic flow control, timing, electronic injection, and temperature control for the column, inlet, detector, and other parts of the instrument. The user interface, which is responsible for sending macro instructions to the microprocessor and displaying measurement results, can be a laptop computer or a remote computer using a wireless modem (1 mile range). A software program allows users to select appropriate measurement methods and to identify specific organic compounds in odors or fragrances from a library of Kovats indices.

2 Dimensional Olfactory Images: Odor Intensity vs Volatility

The chemistry of odors and fragrances involve what are called organic compounds spanning an increasing molecular weight and decreasing volatility. As these organic compounds exit the column they impinge upon a constant temperature SAW mass sensor. Low molecular weight and more volatile organics condense and re-evaporate from the surface of the crystal quickly while high molecular weight compounds adhere to the crystal surface. In either case the frequency deviation of the crystal is proportional to the amount of each compound present in the effluent of the GC column. In effect the frequency deviation of the crystal can be used as a measure of the odor intensity vs volatility. A plot of frequency deviation vs time forms a high-resolution 2-dimensional olfactory image of odor intensity vs volatility as shown in Figure 3.

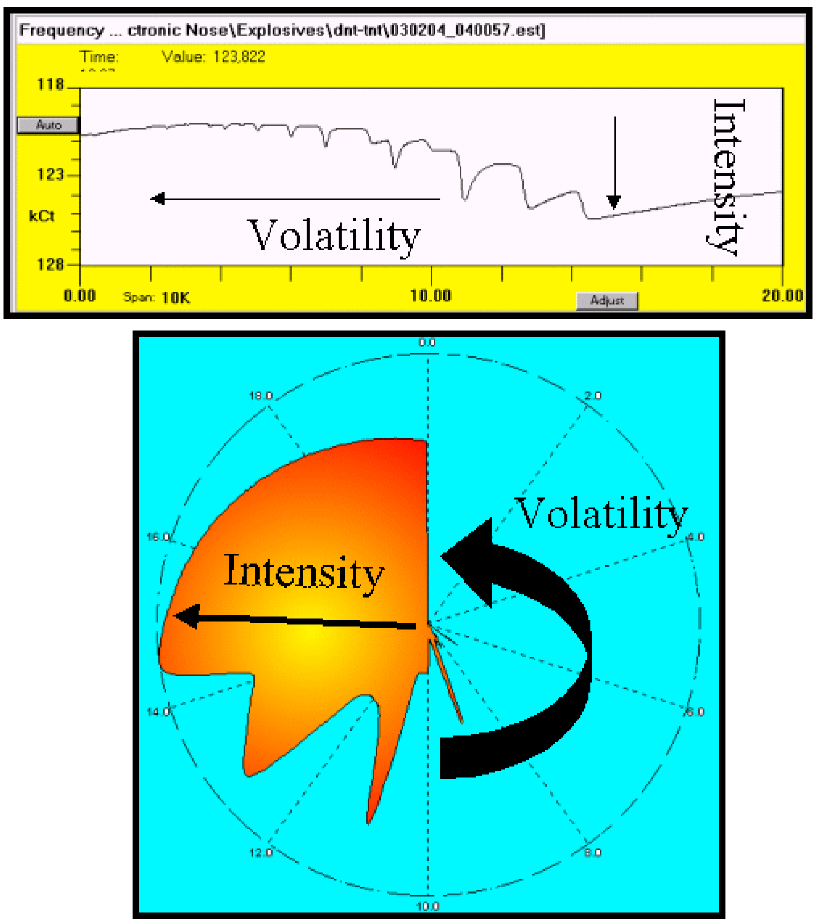

Figure 3- Olfactory images called Vaporprints™ are formed by plotting SAW sensor frequency deviation (radial) vs retention time. These images are high-resolution 2-dimensional images representing odor intensity vs volatility.

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Derivative of Intensity vs Volatility and Chromatography

The frequency deviation of the SAW sensor is proportional to the concentration of the compounds present in the odor as they are separated and exit the GC column. Chromatography is a measure of the rate at which compounds exit the GC column or commonly called column flux. A chromatogram of column flux is created by plotting the derivative of the sensor frequency deviation vs retention time in the column as shown in Figure 4.

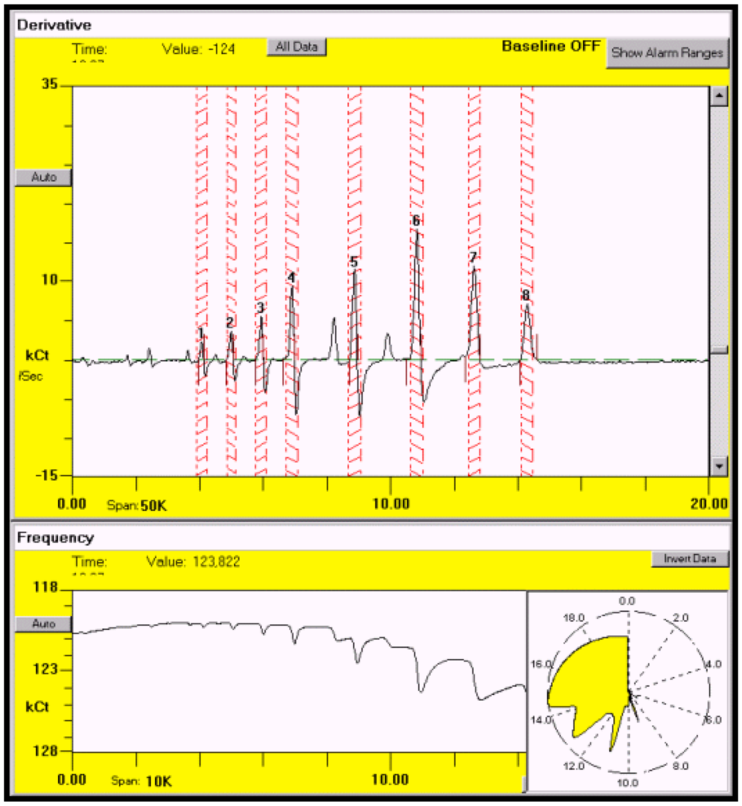


Figure 4- Derivative of odor intensity vs volatility yields chromatograph and unique retention times for compounds present in an odor.

Retention time is defined by maxima in the column flux (derivative). The retention time of each compound as it exits the column can be used to identify a compound within an odor provided it is separate from all other compounds within the odor. The zNose® is an ultra-fast GC, which separates and measures the concentration of the individual chemicals of an odor directly, typically in 10 seconds. Tabulating the retention times and detector counts (cts = frequency deviation) provides a quantitative measure of an odor's chemistry. The ability to measure the frequency deviation (concentration) associated with each 'derivative peak' enables the chemistry of the odor to be completely specified in terms of individual compounds with specific concentrations.

N-Alkane Odor Standard (Volatile and Semi-Volatile)

An odor standard of n-alkanes is used to calibrate not only sensitivity of the electronic zNose® but also it's specificity. Specificity is what allows the instrument to recognize known chemicals and/or chemical groups (odor signatures) and to deliver the appropriate response.

To create an n-alkane standard vapor for volatile alkanes C6-C14, 10 mL of methanol is placed is a 40 mL septa sealed vial and spiked with equal amounts of each alkane C6-C14 as shown in Figure 5. A concentration of 100 ppm for each alkane provides a convenient source of headspace vapors containing n-alkanes. To sample the vapor a side-ported needle attached to the inlet of the zNose® is inserted through the septa into the headspace vapors of the vial. A vent needle maintains atmospheric pressure within the vial by allowing ambient air to enter the vial while when the zNose® withdraws vapor samples, typically 0.5 mL/second. Alkane standard vapors created in this way deliver consistent and long lasting calibration vapors.

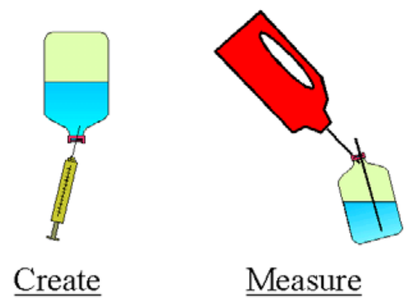


Figure 5- Creating and testing vapors containing alkanes with less than 14 carbon atoms.

Methanol containing 500 pg/µL n-alkanes (C16-C22) is used as an injectable vapor standard. Alkanes above C14 are considered semi-volatile and will not pass through unheated sample needles and need to be directly injected into the heated inlet of the zNose®.

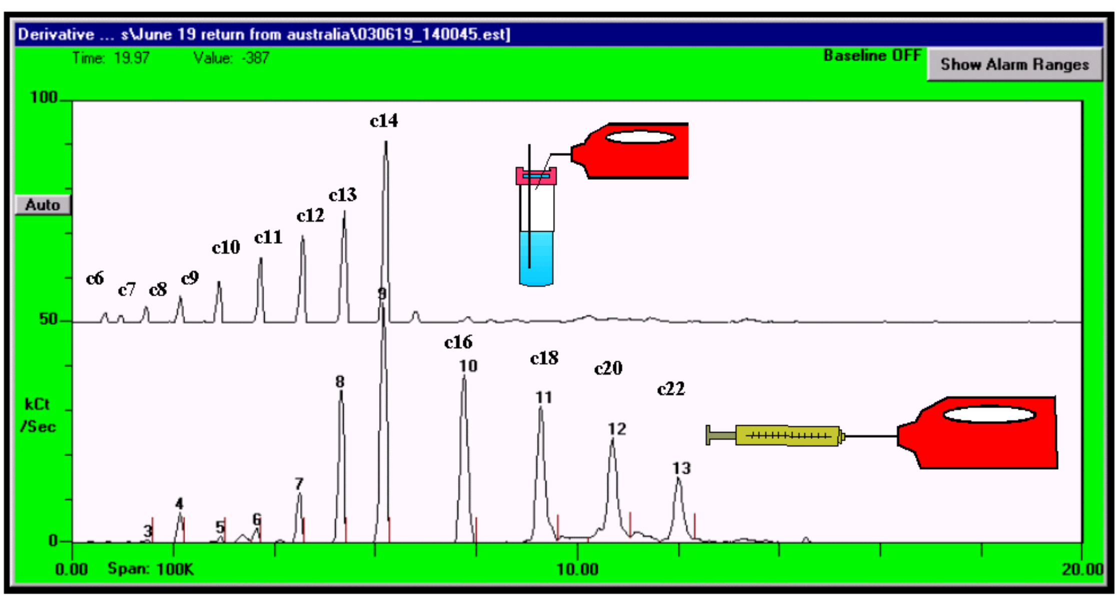


Figure 6- Retention time calibration using n-alkane response C6 to C22.

Creating a Reference Odor Standard: Kovats Indices

An important function of an electronic nose is to recognize odors and fragrances. The retention time indices (Kovats) of known chemicals relative to the retention time of a homologic series (e.g. n-alkanes) is an analytical technique which allows the same library to apply equally to all other electronic noses using the same type of chromatographic column..

From the chromatographic n-alkane responses of Figure 6, a reference file is created which contains the retention times of each alkane, an identification name, response factor, and other descriptors. Retention time is transformed into an index equal to the number of carbon atoms in each alkane multiplied by 100 e.g. C11=> 1100. Thus machine depend-

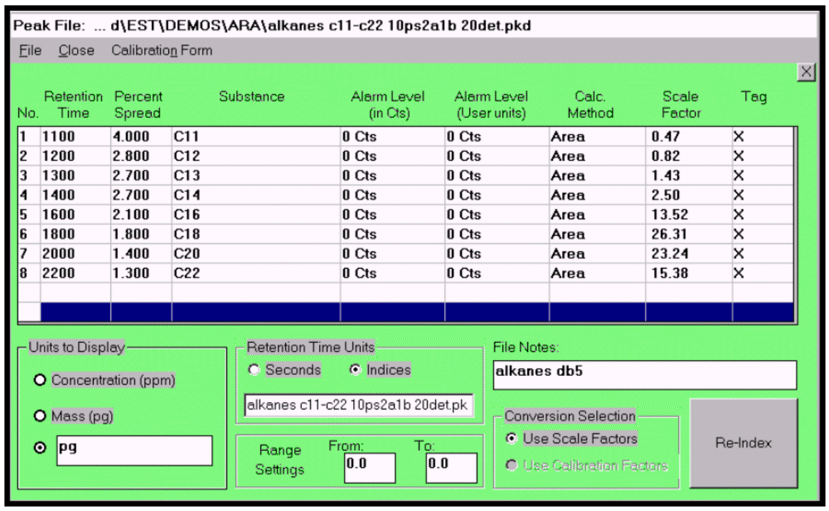


Figure 7- Parameter Definition and Calibration Table for Reference odor Standard.

ent retention time (in seconds) is transformed into a machine-independent index called Kovats indices. Using the n-alkane reference file, chromatographic data can be reduced to a list of odor chemicals (peaks) as shown in Figure 8.

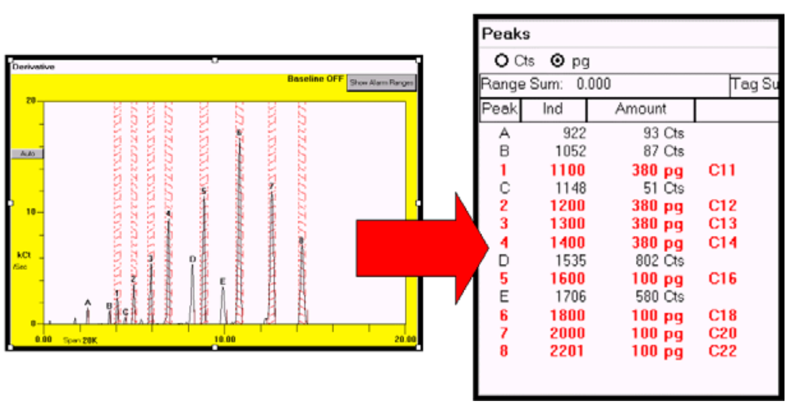


Figure 8- Chromatogram speciation expressed as a list of Kovats indices for each peak in the chromatogram.

A 'machine independent' Kovats index can be created for any volatile organic compounds by comparing its retention time against that of n-alkanes. The approach is illustrated in Figure 9 for ethyl caproate and ethyl caprylate, compounds commonly found in fermented beverages. A test vapor is created by injecting the compounds into an empty vial and measuring the chromatographic response and retention time. Using the n-alkane reference file, Kovats indices are automatically determined. Ethyl caproate has a Kovat index of 1020 and ethyl caprylate an index of 1220.

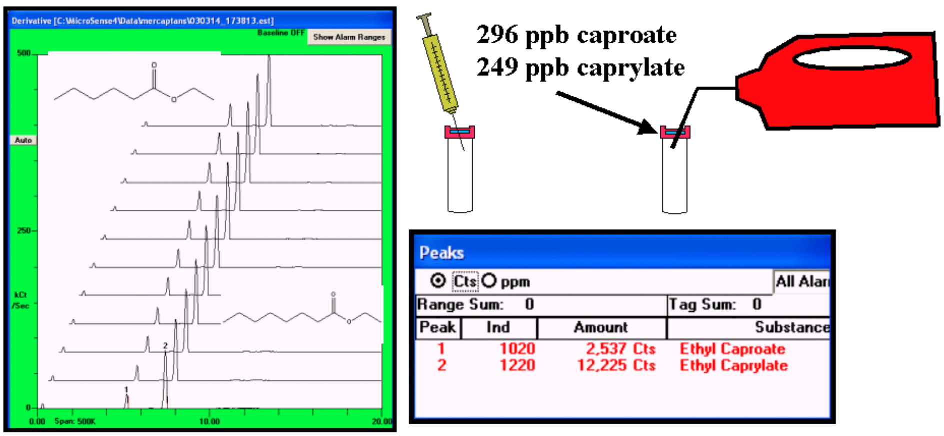


Figure 9- Calibration and Kovats determination using vapor standards

Library of Kovats Indices and Odors

The Kovats Indices for known chemicals are stored in a library together with their odor description or perception. When an unknown odor is analyzed the retention time of peaks are converted to Kovats indices and clicking on individual peaks with a mouse pointer brings up the nearest library entry. The lookup process is illustrated in Figure 10.

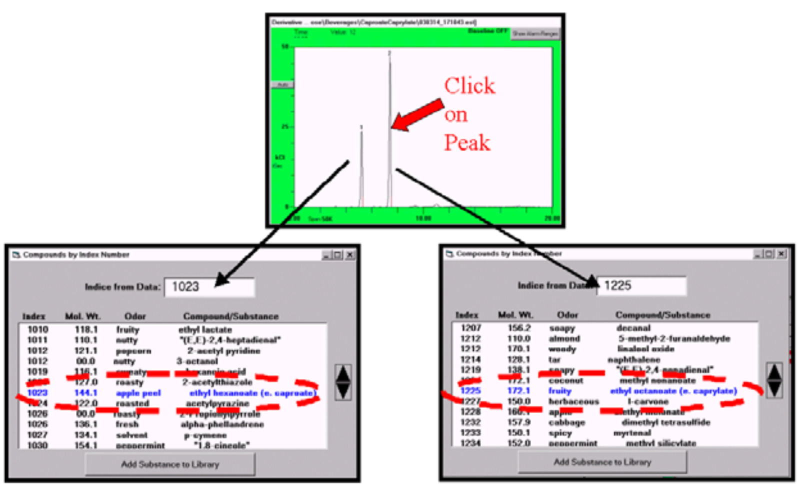


Figure 10- Software showing chromatogram response and library identification using Kovats Indices for individual peaks.

Virtual Chemical Sensors with Alarms

Kovats indices also provide the basis for creating virtual chemical sensors. Virtual sensors are defined by retention time windows and any peak response within the defining window is recognized and trigger a response if its intensity exceeds a preset alarm value.

Figure 11- Virtual chemical sensors created from a list of compound retention times.

Thus defined, chromatographic measurements are reduced to a simple user display of eight virtual sensors as shown in Figure 11. Virtual chemical sensors do not have overlapping responses and can provide orthogonal input data for subsequent analyses such as multi-variate statistics and principal component analysis (PCA).

Applications Examples

High resolution, 2-dimensional olfactory images can be useful tools for quickly assessing the quality of aromatic products. As an example the complex chromatogram of vegetable soup can be difficult to grasp yet the olfactory image of Figure 12 is easily recognized. Although, the olfactory image and chromatogram are simply related by a time

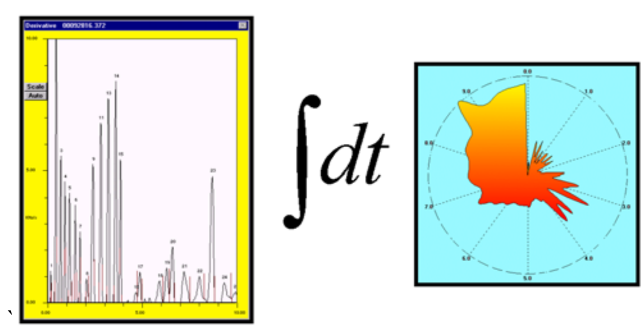


Figure 12- Olfactory image of aroma from vegetable soup.

integration, the olfactory images provides a more user friendly means of comparing different aromas.

An important application for electronic noses is in the field of security. The diverse nature of today's chemical and biological threats requires instruments, which can quickly adapt to new threats. Often threats can be identified by their odors and an example is the odor of explosives. Organic compounds commonly found in explosives can be identified by their unique Kovats indices. The retention times and Kovats indices of six of the most common were obtained by direct desorbtion with a methanol solution containing known concentrations and measuring the resulting Kovats index with a zNose® as shown in Figure 13.

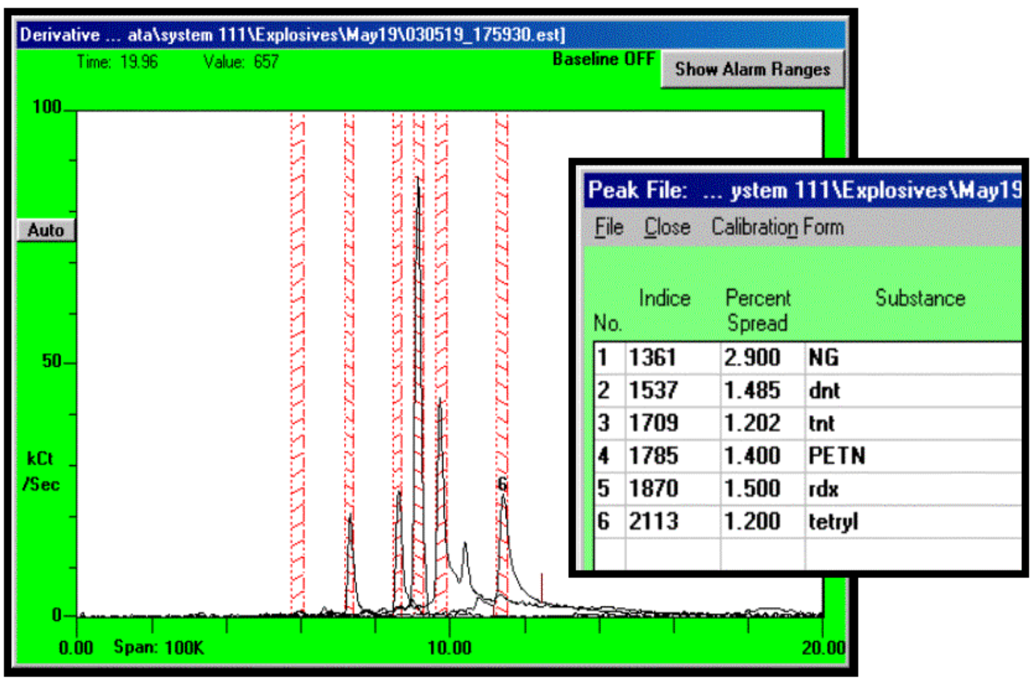
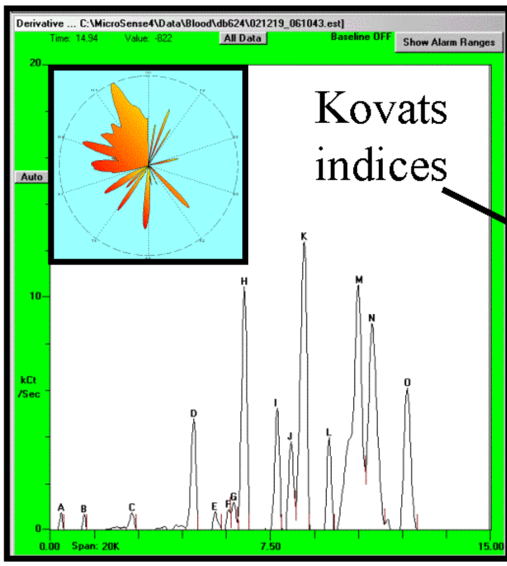
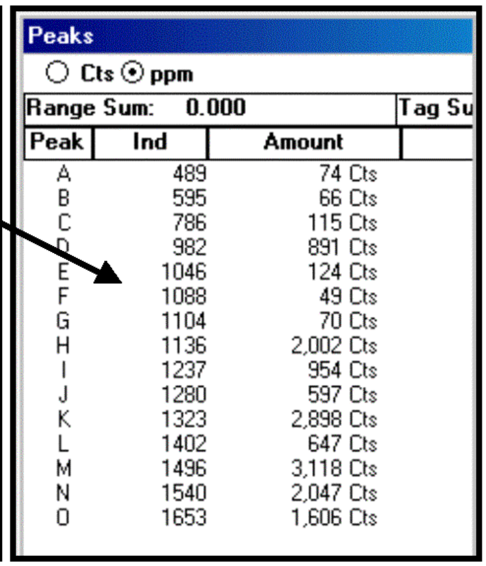


Figure 13- The retention time of a mixture containing common explosives like NG, DNT, TNT, PETN, RDX, and Tetryl were measured and compared to the retention time of N-alkane standard vapors. Peak identification windows are shown as red crosshatched regions.

Using a library of such indices virtually any zNose® can be made to recognize the presence of these compounds using only an n-alkane vapor standard to calibrate retention time. This gives security operators the ability to quickly adapt and recognize odors associated with threats based upon odor libraries.

Analysis of odors from biological samples is another important use for electronic noses. Odors may be the result of illness or metabolic diseases and quickly screening for them may provide advance diagnosis for medical researchers. As an example, shown in Figure 14 is the analysis of the odor chemistry from a single drop of human blood. Approximately 15 amino acid compound peaks are detected and their Kovats indices tabulated. The amino acids are the building blocks of life itself and directly mirror the chemistry of the blood.





Peaks

Cts ⦿ ppm

Range Sum: 0.000 | Tag Su

Peak	Ind	Amount
A	489	74 Cts
B	595	66 Cts
C	786	115 Cts
D	982	891 Cts
E	1046	124 Cts
F	1088	49 Cts
G	1104	70 Cts
H	1136	2,002 Cts
I	1237	954 Cts
J	1280	597 Cts
K	1323	2,898 Cts
L	1402	647 Cts
M	1496	3,118 Cts
N	1540	2,047 Cts
O	1653	1,606 Cts

Figure 14- The derivative of odor intensity is a chromatogram used to determine chemical retention times. Analysis of odor from amino acid standards showing Kovats indices and odor concentration in counts.

Summary of Results

A new type of electronic nose based upon ultra high-speed gas chromatography and a new solid state GC detector now allows the chemistry of odors to be qluantified in near real time with high precision, accuracy, and part per trillion sensitivity. Odors and aromas are characterized and compared using chromatograms to create virtual chemical sensors The sensitivity of the instrument allowed compound concentrations at part per trillion (picogram/milliliter) levels to be made. Identification of odors is greatly simplified by indexing retention time to a single N-alkane odor standard. A machine independent library of indices allows unknown odors to be quickly analyzed and compared to known odor signatures.

Because the electronic nose is based upon the science of gas chromatography, odor measurements can be easily confirmed and validated by independent laboratory measurements taken on quality control samples. The ability to rapidly perform analytical measurements on odors of all kinds in real time provides researchers with a cost effective new tool for monitoring volatile organic compounds.