Testing Natural Gas Using the zNose®

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Electronic Noses

Conventional electronic noses (eNoses) are designed to produce a recognizable response pattern using an array of dissimilar but not specific chemical sensors. The concept of an electronic nose has 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®, based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based entirely 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, precision, and accuracy. Satisfying the need for speed, 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. A portable zNose®, shown in Figure 1, is a useful tool for assessing the quality of aromatic products and monitoring a wide variety of chemical and biological processes.

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.

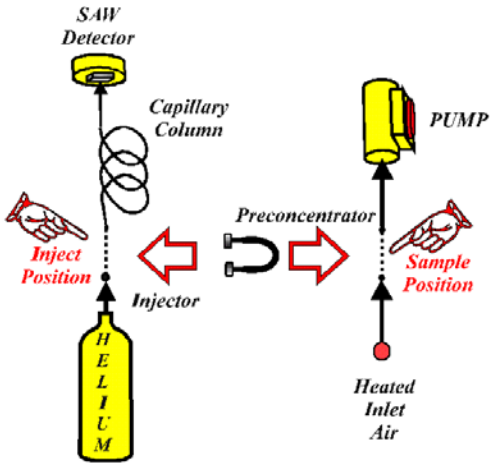

Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.

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.

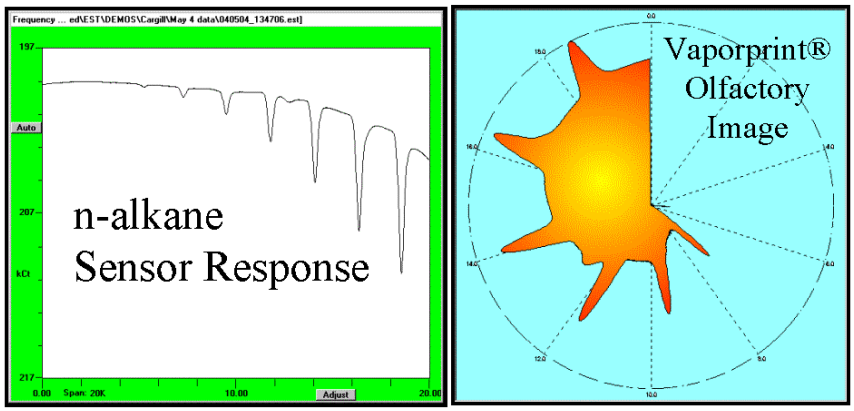

Figure 3- Sensor response to n-alkane vapor standard, here C6-C14, can be displayed as sensor output vs time or its polar equivalent olfactory image.

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 an retention time index of 1050.

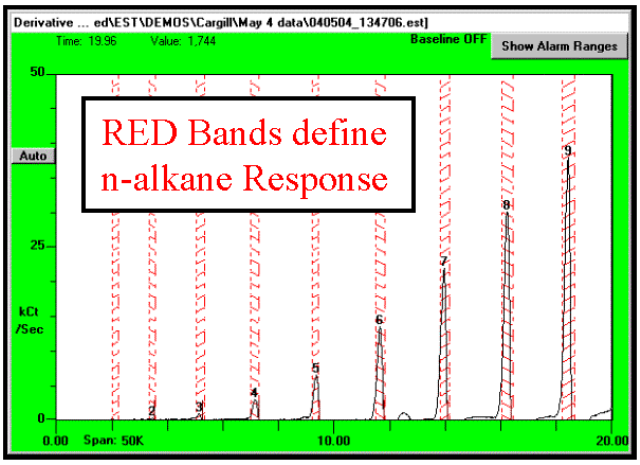

Figure 4= Chromatogram of n-alkane vapors C6 to C14).

Natural Gas

Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it often includes ethane, propane, butane, pentane and even higher molecular weight hydrocarbons. The composition of natural gas can vary widely. The natural gas used by consumers is by no means as pure methane. Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells. Natural gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate.

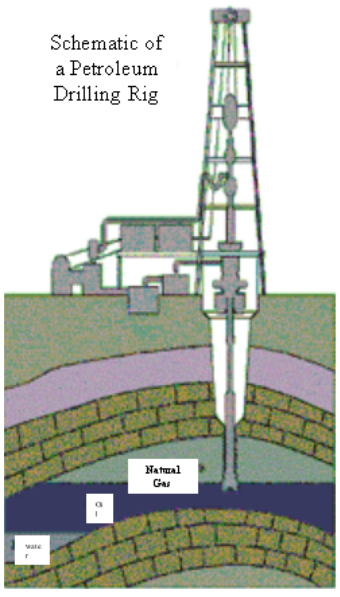

Figure 5- Petroleum drilling rig collects natural gas above oil deposit.

Figure 6- Gas refinery for producing natural gas product.

Tesing Natural Gas Samples

A sample of natural gas was collected from a local residence (Newbury Park, CA) using a one-liter tedlar bag. Approximately 5 milliliters was extracted and analyzed by zNose equipped with a one-meter db-624 column. The GC-method file (figure 3) details the instrument settings and temperatures used. A 10 second sample time is followed by a short 3 second wait after injection and before ramping the column from 40°C to 160°C at 5°C per second.

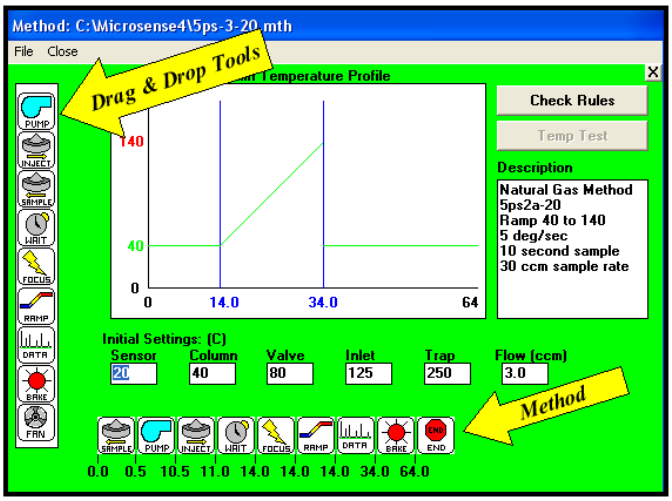

Figure 7- GC method file

A full screen view of a 20 second analysis (time-stamped file) of a natural gas sample is shown in Figure 8. The four major windows display operator notes, sensor output vs retention time, derivative of sensor output vs retention time (column flux), and tabulated peak retention time and un-calibrated peak area counts.

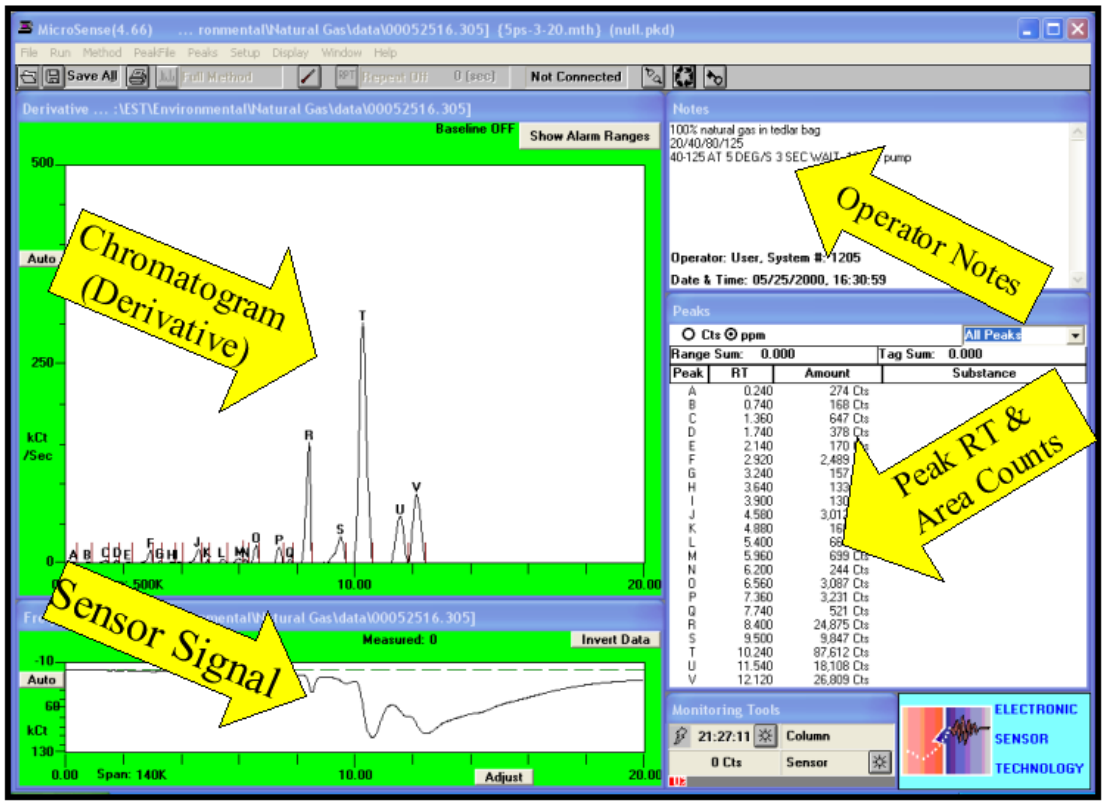

Figure 8- Full screen display of 20 second analysis.

Replicate Measurements (Speed & Precision)

Performing 5 replicate measurements on the natural gas sample at 1 minute intervals demonstrates the precision and retention time stability of the zNose®. The top trace is an analysis of the tedlar bag filled with clean nitrogen before filling with natural gas. Reduction of peak amplitude with time is due to absorption on walls of tedlar bag.

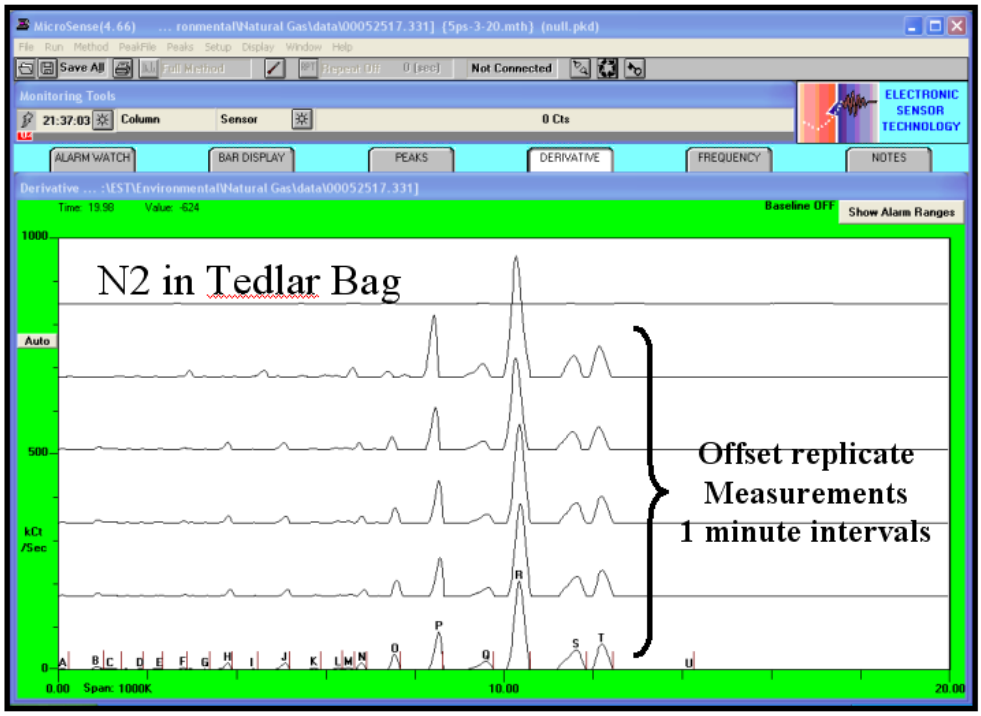

Figure 9- Replicate measurements showing repeatability and precision of measurement

Sensor Output vs Retention Time

The zNose uses a unique GC detector which is non-ionic and non-specific, hence, it detects everything and misses nothing. The sensor produces a frequency deviation proportional to the mass of analytes eluting from the GC column, hence it measures concentration (odor intensity) and not column flux as other GC detectors do. Because it is an integrator it has zero dead volume which is ideal for high speed chromatography. Odor intensity vs retention time also produces a distinctive olfactory image called a Vaporprint®.

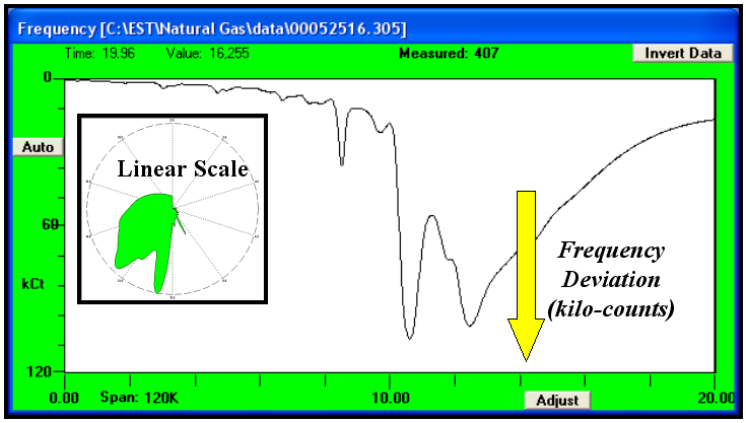

Figure 10- SAW sensor output shows odor concentration vs retention time. Polar plot displays olfactory image (Vaporprint®).

Derivative of Sensor output vs Retention Time

The derivative of sensor output frequency (odor intensity) yields column flux vs retention time or a conventional chromatogram. Vaporprint® images plotted on a logarithmic scale are used to enhance the view ability of trace compounds and give an overall view of the odor chemistry.

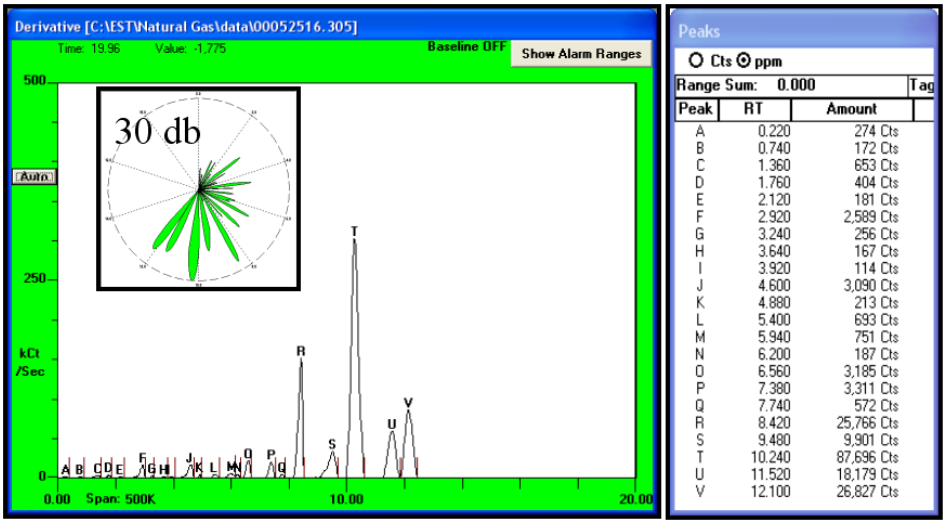

Figure 11- Derivative of odor intensity yields conventional chromatogram

Kovats Indexing to N-Alkane Standard Response

Comparing natural gas peak retention times to those of n-alkanes allows the zNose software to index retention times (Kovats indices). The advantage of this technique is that it makes retention time independent of the instrument and dependent upon n-alkane vapor standards. This in turn allows results from different instruments to be compared and validated by independent laboratory measurements.

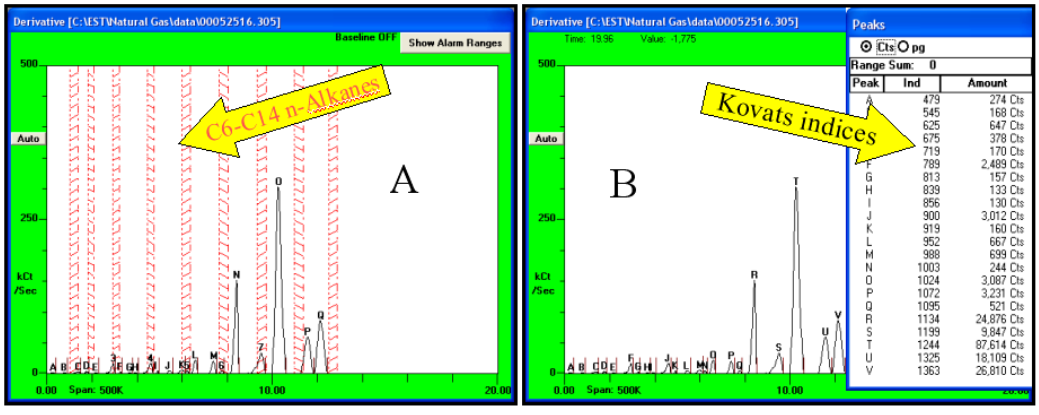

Figure 12- Referencing peak retention times to n-alkane response (C6-C14) shown as red bands (A) allows the software to express peak retention times as Kovats indices (B).

Peak Library – Compound Identification

Once the peaks have been indexed to n-alkanes it is possible to make a tentative identification based upon the Kovats indices. ZNose® software enables the creation of an unlimited number of such libraries specific to individual user applications. Existing libraries can be edited and new compounds added. As an example shown is the library entry for one of the natural gas peaks, NG-1244. Identification based upon Kovats indices is considered useful but only tentative until verification by independent analysis e.g. with a GC-MS.

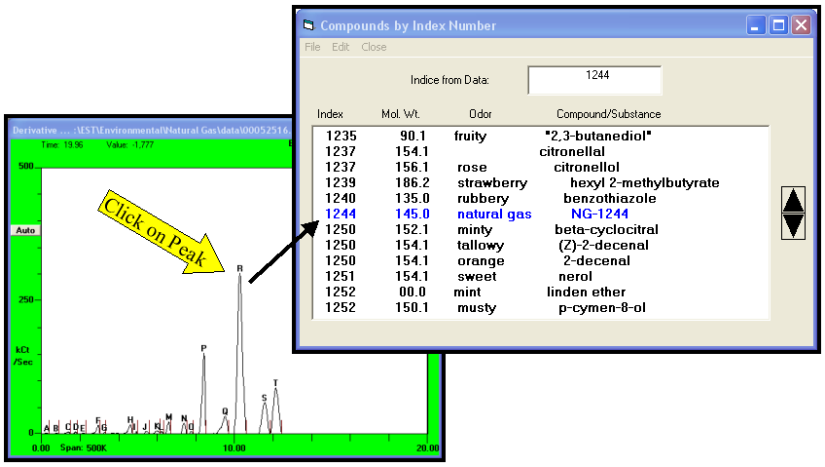

Figure 13- Click on any peak to identify odor using peak library based upon Kovats indices.

Low Molecular Weight Compounds

Delectability of low molecular weight compounds is dependent upon the temperature of the sensor crystal. In these measurements a detector temperature of 20°C was used however detector temperatures can be as low as 0°C. Response for the zNose is thus limited to compounds with boiling points above 0°C. The lowest weight compound detected (274 counts) in the natural gas sample can be seen to have an index of 479 or slightly below C5 (pentane). For reference background noise levels in the zNose are typically 1-10 counts.

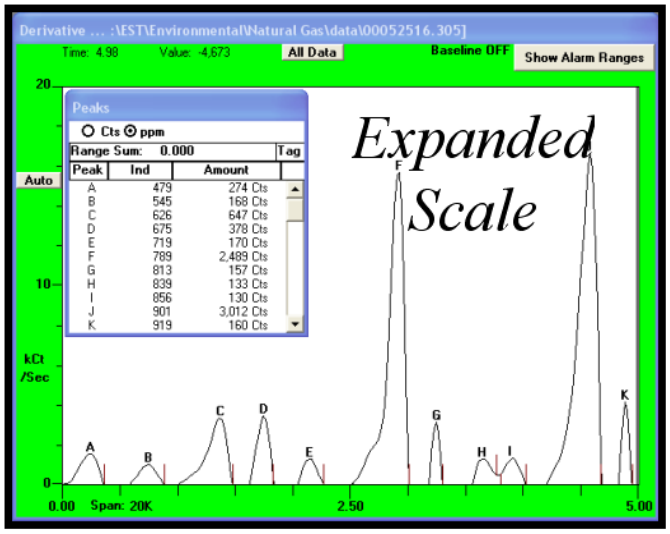

Figure 14- Expanding time and amplitude scale shows response from low molecular weight compounds (C4 to C10).

Peak Files, Calibration Factors and Alarm Levels

ZNose® software allows the user to easily create individual peak response factors and alarm levels. Using chemical standards the zNose can be calibrated in mass units (e.g. picograms), vapor pressure (e.g. ppm), or user units. Single point and multi-point calibration methods are possible. In this figure a virtual senor array for the eight major peaks detected in natural gas are created with a peak file. Scale factors (counts/ppm) shown are based upon an assumed concentration of 100 ppm for each compound. Arbitrary alarm levels are entered into the peak file as well. In effect the peak file defines a virtual sensor array for natural gas.

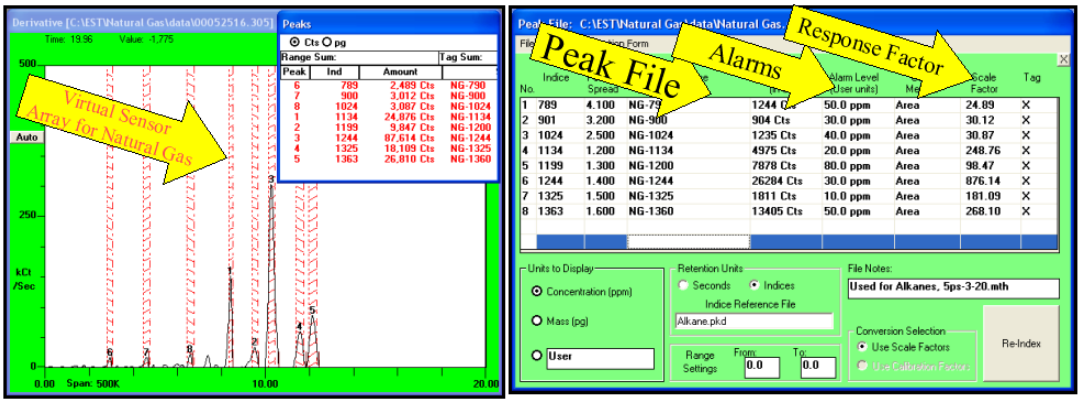

Figure 15- Creating a peak file allows scale factors and alarm values to be set for individual peaks which can be graphically set and displayed as red bands or virtual sensor regions.

Calibrated Readings

Once a peak file has been defined and scale factors determined, the software automatically displays peak readings in the desired units e.g. ppm. Referencing retention time to n-alkanes also provides a convenient peak naming convention in cases where the actual compound is unknown.

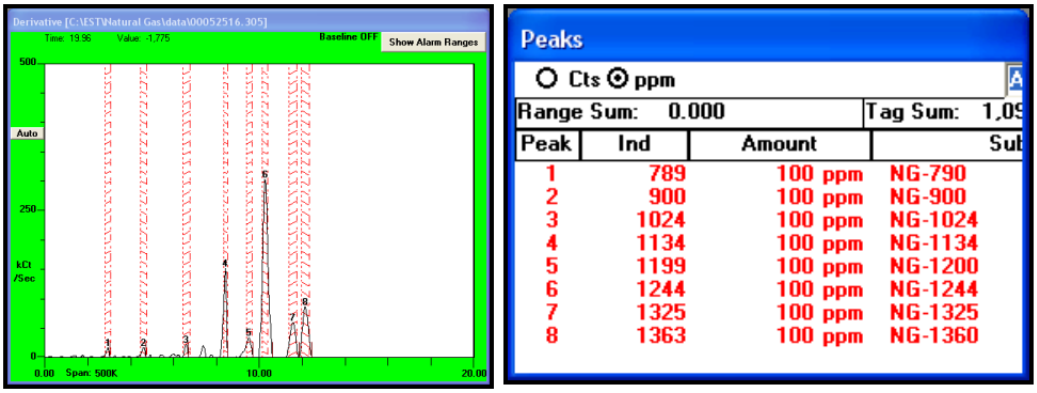

Figure 16- Using a peak file for natural gas peak concentrations are be displayed directly.

Virtual Chemical Sensors

It is often easier to display an array of chemical sensor readings rather than a chromatogram. Based upon alarm settings each sensor is capable of generating alarms whenever concentrations exceed the alarm value. Operating the zNose® in automatic measurement mode, the sensor array readings can be updated often e.g. once per minute. Using isothermal GC methods it is possible to update sensor readings as often as every 15 seconds. High-speed chromatography and virtual sensors are ideal for process control applications.

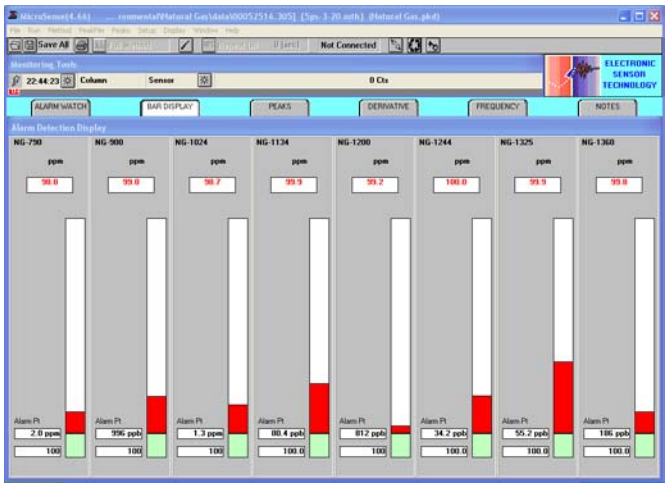

Figure 17- Display of virtual chemical sensor readings replaces the need to display chromatograms.

Summary

The zNose answers the need for speed, precision, and accuracy in the chemical analysis of all sorts of odors, fragrances, and vapors. Natural gas as it is received in the typical home is far from just pure methane and analysis of a random sample has shown organic compounds covering the entire hydrocarbon range up to nearly C15 are present at relatively high concentrations. The ability to create virtual chemical sensor arrays to monitor these compounds may provide a useful process- monitoring tool. Although the zNose contains only a single physical sensor, the ability to perform high-speed chromatography enables it to functionally perform as if it were an array of specific chemical sensors. Literally hundreds of virtual chemical sensors can be created.

The ability to perform hundreds of chromatographic analyses per day also provides a cost-effective solution to sample screening and process development in the laboratory. Whereas such projects can take months using a conventional long-column GC, with the zNose® it is often possible to complete development projects in less than a week. It is not difficult to see how the zNose® pays for itself in less than 30 days..