# Real Time Characterization of Food & Beverages using an Electronic Nose with 500 Orthogonal Sensors and VaporPrint™ Imaging

**Edward J. Staples**
**Electronic Sensor Technology, 1077 Business Center Circle, Newbury Park, California,**
**Ph. 805-480-1994, FAX 805-480-1984, Website: WWW.ESTCAL.COM**

***Abstract*** - A new Electronic Nose simulating the response from up to 500 sensors is providing food and beverage manufacturers, quality control specialists, and olfaction experts with a new investigative tool. The zNose™ can also provide a recognizable visual image of vapor mixtures (fragrances) containing hundreds of different chemical species in 10 seconds or near real time. This electronic nose is designed to quantify and characterize all types of smells universally and is the only electronic nose currently validated by the US EPA.

This paper describes how the instrument works, its accuracy and precision, and the results from studies of vapors associated with food and beverages. The objective was to evaluate sensitivity, specificity, and the overall usefulness of this new quality control technology. The work focused upon foods and beverages as well as the quality of plastics used in their packaging.

## Introduction

An array of sensors simulating the human olfactory response has become known as an Electronic Nose [Ref. 1]. Electronic noses provide recognizable visual images in N-dimensional space (where N equals the number of sensors) of specific vapor mixtures (fragrances).

An electronic nose, based upon fast chromatography, is able to simulate a sensor array containing hundreds of orthogonal (non-overlapping) sensors. Chemical analysis of any odor is accomplished in 10 seconds by a very fast separation of chemicals in sampled vapors. For a chromatography system, chemical sensor space is defined mathematically by assigning unique retention time slots to each sensor. Part per billion (ppb) sensitivity has been achieved with volatile compounds and part per trillion (ppt) sensitivity for semi-volatile compounds.

To create an electronic nose with certifiable performance a virtual chemical sensory array [2] has been created using Fast Gas Chromatography (FGC) to speciate odors, fragrances, and smells into individual chemical spectrum responses. In FGC, direct column heating creates a speciated spectrum of chemical vapor pressure in seconds rather than minutes. The desired olfactory image is a spectrum of compound concentration. This is accomplished using a new GC detector, which measures the concentration directly in proportion to the frequency of a surface acoustic wave (SAW). In this GC/SAW electronic nose, individual peaks half-widths are measured in milliseconds and column effluent is collected on a temperature-controlled quartz chip.

## GC/SAW Electronic Nose

Early electronic noses rejected chromatography techniques because they were slow. However, the development of integrating GC detectors [3] together with direct column heating [4] has recently produced a GC/SAW electronic nose technology with precision, accuracy, and 10 second speed [5,6,7].

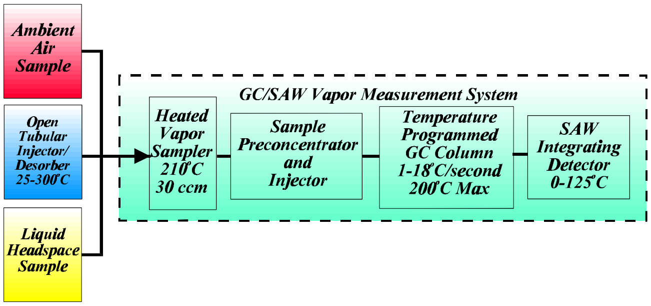


***Figure 1- GC/SAW system diagram.***

The GC/SAW electronic nose system diagram is depicted in Figure 1. Input vapors, odors, smells, or fragrances from either air, water, or solids enter the system through a temperature-controlled inlet and are preconcentrated for a carefully measured period of time. The preconcentrated vapors are injected as a short pulse into a temperature programmed capillary column. The dispersed column effluent then passes to a SAW integrating detector, which records the time and amount of each chemical response.

## How the Systems Works

The GC/SAW electronic nose uses a two step process. Each step in the process corresponds to the position of a six port two-position rotary valve. In the first step (sample collection), depicted in Figure 2, inlet air containing vapors is pumped through a small section of capillary, which traps and preconcentrates the vapors. During sample collection pure helium carrier gas flows through the GC capillary to the SAW detector. The sample pumping time is carefully controlled to produce a repeatable and accurate collection of ambient vapors for analysis.

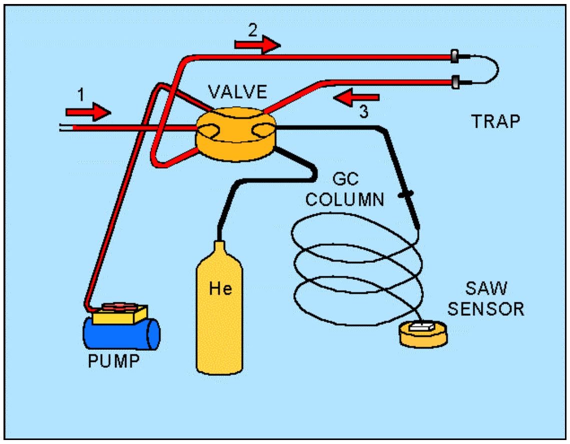


*Figure 2- Step 1: Sample collection step preconcentrates vapors in a trap while maintaining helium flow through the GC column to the SAW detector.*

In step 2 (Analysis) the rotary valve is switched to the second position which causes helium carrier gas to flow backwards through the trap before passing through the capillary column to the SAW detector. The initial temperature of the GC column is held low at nominally 40°C.

Immediately after the valve is switched into the analysis position, Figure 3, a 10-millisecond pulse of high current is passed through the trap causing it to rapidly heat and release trapped vapors. The vapors are then swept by helium carrier gas into the GC capillary column where they again are trapped and focused by the relatively low temperature of the column. At this point the column temperature is programmed to follow a linear rise to its maximum temperature. This causes the different chemical species to be released and travel through the column.

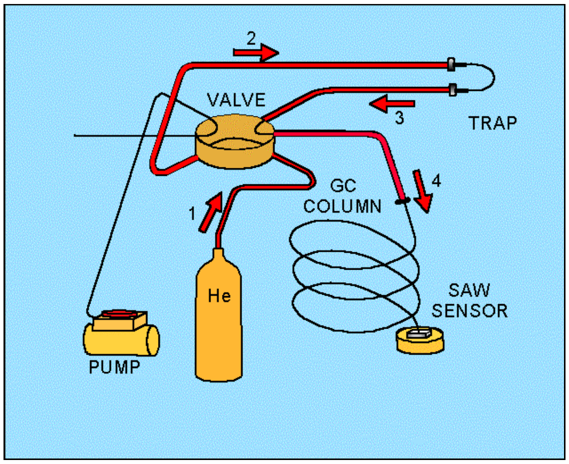


*Figure 3- Step 2: Vapor Analysis injects trapped vapors into the helium carrier gas. Released vapors travel through the column and their retention time and frequency are measured by the SAW detector.*

The SAW detector, shown in Figure 4 consists of an uncoated 500 MHz acoustic interferometer or resonator bonded to a Peltier thermoelectric heat

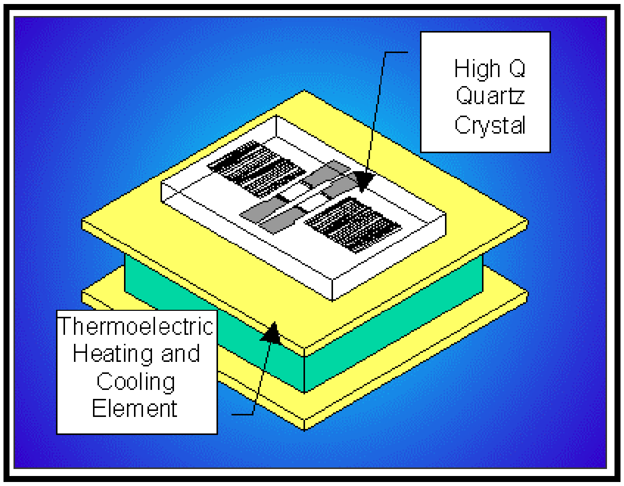


*Figure 4- SAW detector uses a temperature controlled quartz substrate to absorb vapors as they exit the GC capillary column. Sensitivity is controlled by selecting the operating substrate temperature during chromatography.*

pump with the ability to heat or cool the quartz substrate. Coatings are not used because they reduce the resonator Q, introduce instability, and require excessive time for equilibrium. The temperature of the quartz substrate is held constant during chromatography and provides a method for adjusting the sensitivity of the detector.

The complete system is packaged in the benchtop instrument case shown in Figure 5. Within the system is enough helium gas to perform more than 300 chromatograms in the field. Chromatography and all system parameters are controlled by an internal programmable gate array (PGA) microprocessor. Macro instructions are provided by the user from a Windows® program operating on a Pentium laptop.

***Figure 5- GC/SAW benchtop system contains an internal supply of helium carrier gas with capacity for more than 300 chromatograms. Sample pump, preconcentrator, and temperature programmed GC column are all controlled by an internal gate array processor which responds to the user's laptop computer connected by an RS-232 link.***

## Accuracy and Precision

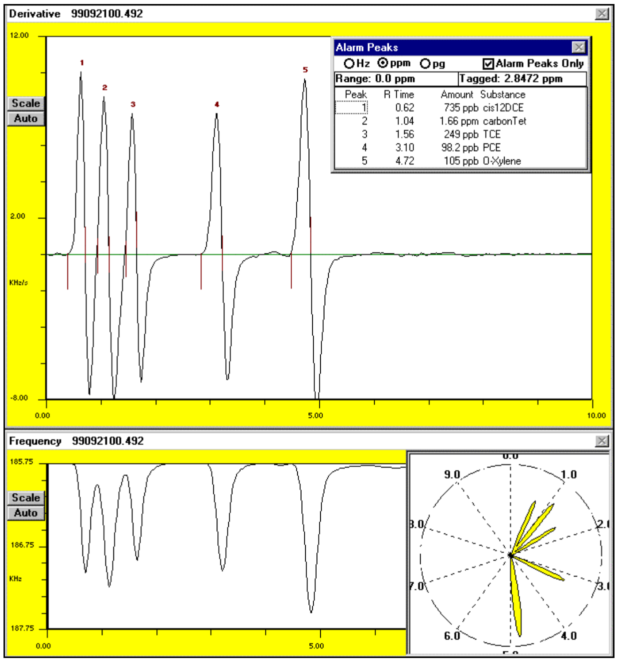
The GC/SAW is the only electronic nose technology to have been validated by both the US Environmental Protection Agency (EPA) as well as the White House Office of National Drug Control (ONDCP). Precision is the ability to repeat a measurement and accuracy is the ability to obtain the correct answer. When presented with constant vapor standards, the GC/SAW electronic nose typically achieves 1-2% variation (RSD) in readings.

Because the SAW sensor uses no coatings it is stable and very sensitive. Minimum detection levels for 10 common volatile organic compounds in air and water are listed in Figure 6. The GC/SAW zNose™ is sensitive enough to determine drinking water levels by simply smelling the headspace vapors above a water sample.

Because the GC/SAW can speciate with orthogonal sensors it can be calibrated using a single mixture of standard analyte concentrations. An analysis of a vapor mixture of five analytes is shown in Figure 7 as an example. The lower trace shows the frequency of the SAW detector while the upper trace displays the derivative of frequency. As each analyte leaves the column it is absorbed and then evaporates from the quartz surface. The frequency of the detector decreases in proportion to the amount of vapor absorbed followed by a return to its unperturbed value. Each analyte retention time defines one chemical sensor of a virtual five element array

|  | MINIMUM DETECTION LEVEL |  |
|---|---|---|
| *Analyte* | AIR (ppb) | WATER (ppb) |
| Chloroform | **45** | **0.65** |
| *Cis* 1,2 Dichloroethene | **47** | **1.7** |
| Benzene | **42** | **0.96** |
| Carbon Tetrachloride | **130** | **16.49** |
| Trichloroethylene | **6.3** | **0.40** |
| Toluene | **11** | **0.15** |
| Tetrachloroethylene | **5.7** | **0.57** |
| Ethylbenzene | **2.7** | **0.07** |
| *O*- Xylene | **2.5** | **0.11** |
| 1,1,2,2 Tetrachloroethane | **3.6** | **0.56** |

***Figure 6- Minimum detection levels for air and water were measured with a 30 second vapor sample.***



Alarm Peaks

○ Hz ● ppm ○ pg ☑ Alarm Peaks Only

Range: 0.0 ppm | Tagged: 2.8472 ppm

| Peak | R Time | Amount | Substance |
|---|---|---|---|
| 1 | 0.62 | 735 ppb | cis12DCE |
| 2 | 1.04 | 1.66 ppm | carbonTet |
| 3 | 1.56 | 249 ppb | TCE |
| 4 | 3.10 | 98.2 ppb | PCE |
| 5 | 4.72 | 105 ppb | O-Xylene |

*Figure 7- Two types of chromatogram are produced by the GC/SAW.*

## VaporPrint$^{TM}$ Imaging

A useful attribute of an electronic nose is the ability to recognize fragrance patterns. Uncorrelated sensor arrays must utilize artificial intelligence and neural networks to recognize sensor patterns. This approach has had limited success and is not user-friendly. The GC/SAW Electronic Nose does not require artificial intelligence since the SAW detector can provide the operator with visually recognizable image while also quantifying the strength of each chemical within a fragrance.

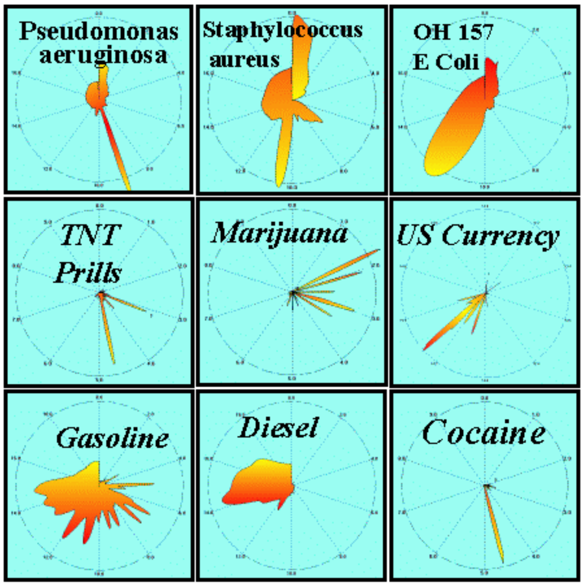


*Figure 8- VaporPrint™ of some common odors.*

A dramatic increase in olfactory perception is achieved in humans by transferring the olfactory response to a visual fragrance pattern response, called a VaporPrint™ image. Images recorded for many common odors are shown in Figure 8. The images are closed polar plots of the odor amplitude (SAW detector frequency) with radial angles representing sensors time (0 and maximum time are vertical).

The VaporPrint™ images show the large diversity in odors. The top three images of Figure 8 are from infectious bacteria. Pseudomonas can be a problem at public swimming pools, hospital Staph infections are well known, and E. Coli OH157 has caused death in humans. The middle set of images (as well as the lower right image) might be of interest to law enforcement officers since they are odors associated with illegal contraband. The remaining images are commonly seen near leaking fuel tanks.

## Food and Beverage Applications

The number of successful food and beverage applications of the GC/SAW zNose™ is expanding rapidly and with considerable diversity. Because chromatography is an accepted analytical technique, GC/SAW technology is able to satisfy and follow accepted FDA testing methodology. The ability to perform these methods with precision, speed, and accuracy is unique to the zNose™. Five application areas of recent interest are (1)Beer, (2) Bottled Water, (3) Sesame Oil, (4) Whisky, and (5) Wine.

Ten second chromatographic analysis of four common American beers are shown in Figure 9. It is clear that each beer contains the same major compounds and in fact taste testing has shown that few are able to discriminate between them. However, the ability to identify and quantify each compound as well as any compounds, which are not desired, is proving to be of great value in controlling quality control throughout the beer manufacturing process. An electronic nose, which can speciate and quantify the chemicals present in beverages is useful because it removes the ambiguity of human odor panel measurements.

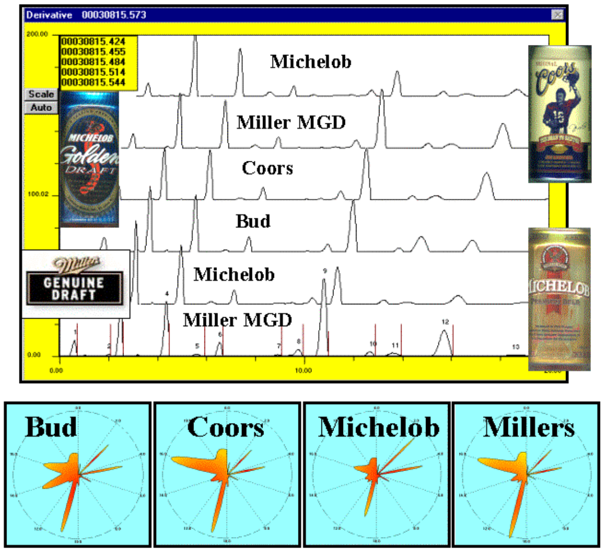
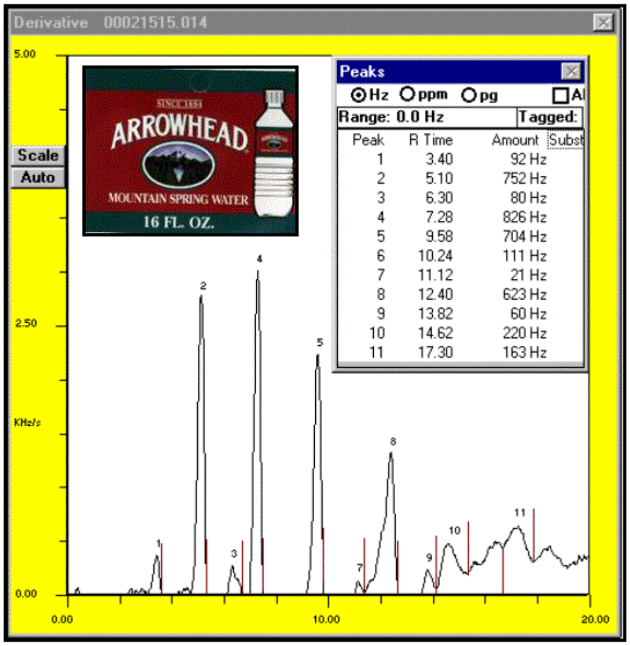


*Figure 9- Comparison of the headspace vapors from four popular American beers.*

An example of quality control for perhaps the most common beverage, bottled water, is shown in Figure 10. Off-odors associated with contamination are actually quite common in bottled water and are due to either latent bacteria or absorption of aromatics from the plastic container. The compounds shown in Figure 10 are from the plastic bottle and can give the water a very bad taste.



Peaks

⦿ Hz ○ ppm ○ pg ☐ Al

Range: 0.0 Hz Tagged:

| Peak | R Time | Amount | Subst |
|---|---|---|---|
| 1 | 3.40 | 92 Hz | |
| 2 | 5.10 | 752 Hz | |
| 3 | 6.30 | 80 Hz | |
| 4 | 7.28 | 826 Hz | |
| 5 | 9.58 | 704 Hz | |
| 6 | 10.24 | 111 Hz | |
| 7 | 11.12 | 21 Hz | |
| 8 | 12.40 | 623 Hz | |
| 9 | 13.82 | 60 Hz | |
| 10 | 14.62 | 220 Hz | |
| 11 | 17.30 | 163 Hz | |

*Figure 10- Odors associated bottled water indicating contamination from improperly cured plastic bottles .*

An important ingredient used throughout the food industry is vegetable oil used for cooking and as a flavor additive. An example is sesame oil, which can be obtained in several grades. Shown in Figure 11 are VaporPrint™ images obtained by testing the headspace vapors from seven different grades of sesame oil. Olfactory imaging is proving more useful than at first expected because of the human ability to recognize subtle visual changes in VaporPrint™ images

Although in Figure 11 there is considerable difference in the olfactory images of sesame oil, it is clear that not all grades can be discriminated simply by VaporPrint™ images. To perform a more detailed discrimination the zNose™ can create a virtual sensor array to quantify the concentration of the eleven most common compounds present in the oil. The process of creating orthogonal virtual sensor arrays, Figure 12, begins with an examination of the vapor chromatogram obtained from the oil. Because chromatography separates the 11 most common compounds the concentration can be measured without interference, hence orthogonality.

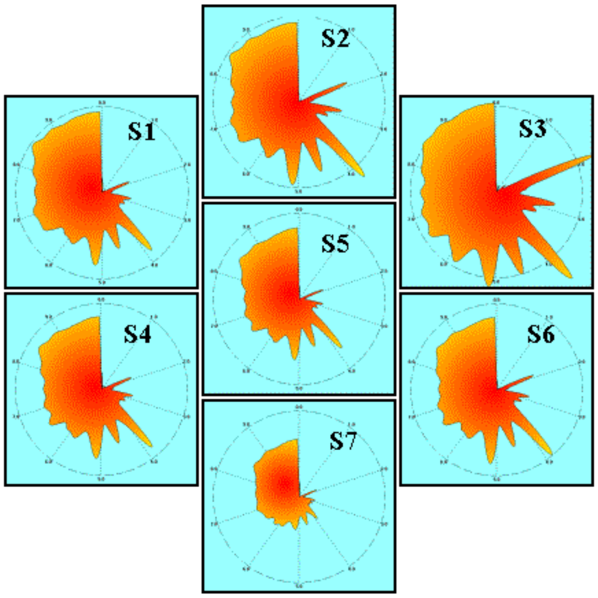


*Figure 11-Olfactory images, VaporPrint™ , used to characterize seven grades of sesame oil.*

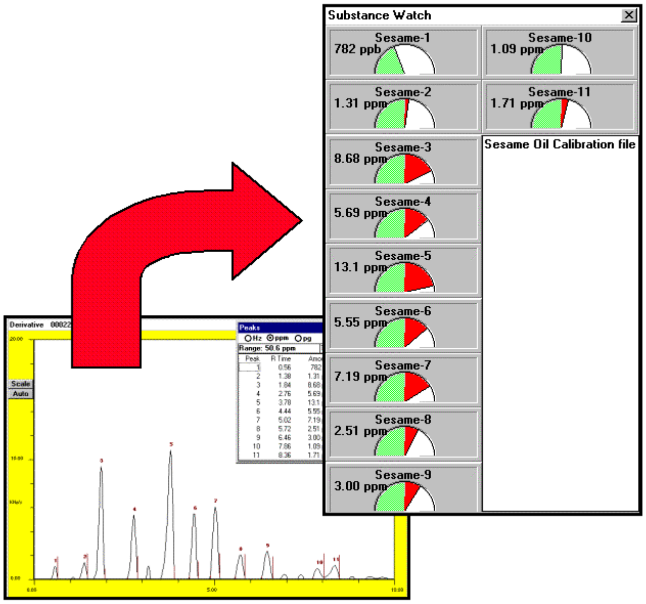


***Figure 12-Virtual sensor arrays are created by separating the chemicals and assigning a sensor to each to measure the concentration of that compound.***

By measuring each grade of oil and recording the concentration of each compound a procedure based upon the concentration of each analyte can be determined. Such a procedure follows a logic diagram based upon this characterization. Using such a process all seven grades of oil can be separated as shown in Figure 13.

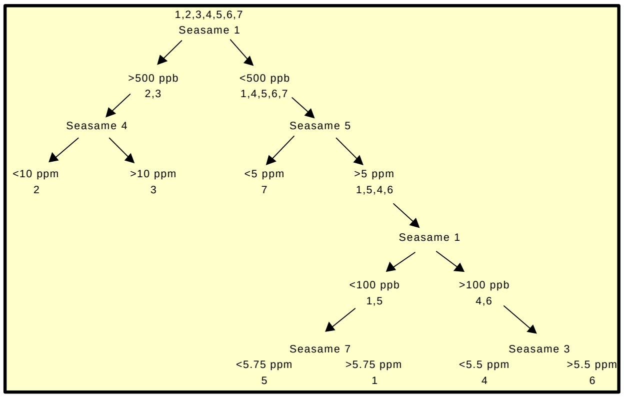


Figure 13-Using a series of logic gates, each grade of sesame oil can be identified.

There are many beverages, which can be characterized by the zNose™, and one, which demonstrates the versatility of the technique, is whisky. Whisky can be very difficult because of the high (43%) concentration of alcohol. Because high speed chromatography is used, the alcohol can be separated from the other aromatic elements and the concentration to the overall aroma of each compound measured. As an example, shown in Figure 14 are three different types of whisky: American Bourbon, French Cognac, and Nikka Whisky from Japan. Each were evaluated using both concentration chromatograms as well as VaporPrint™ images.

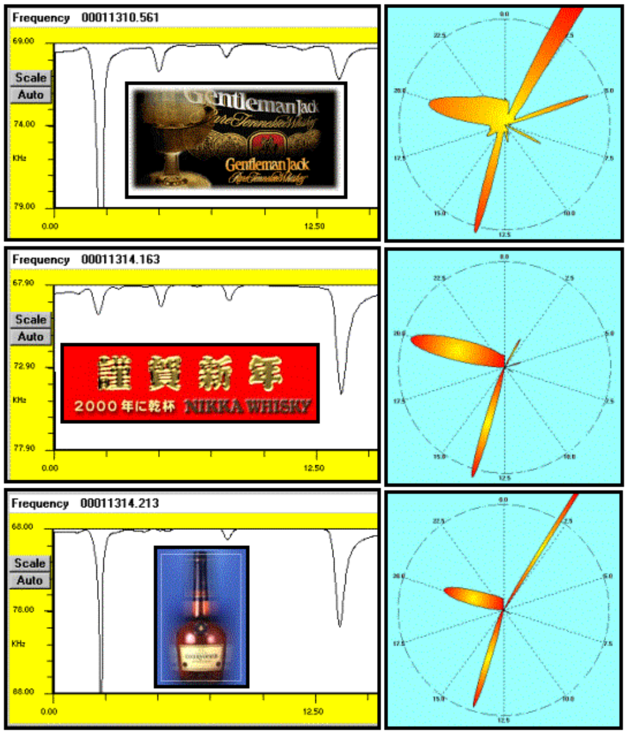


***Figure 14-Olfactory chromatograms and VaporPrint™ images for American bourbon, French cognac, and Nikka Whisky.***

A final application of electronic noses is the characterization of wine. Such characterization must be accurate and requires part per billion and even part per trillion sensitivity since a great wine can be destroyed by even these small traces of contamination. Test results for three different wines with the zNose™ is illustrated in Figure 15. Here chromatograms for Shiraz, Gewurtztraminer, and Cabernet Sauvignon are compared. It is clear that many of the products of distillation are the same however there are different compounds introduced by the process (cooperage) as well.

The zNose™ is a useful tool for monitoring the quality of the wine processing from beginning to end. Testing can be either by piercing the cork to test the bottle or barrel. Simply analyzing the headspace in a glass of wine as shown in Figure 15 can also evaluate wine quality. In this case the glass is covered with a piece of paper and a sample needle passes through a small hole in the paper. Run to run repeatability is excellent and the concentration of the headspace vapors remains constant for a considerable time.

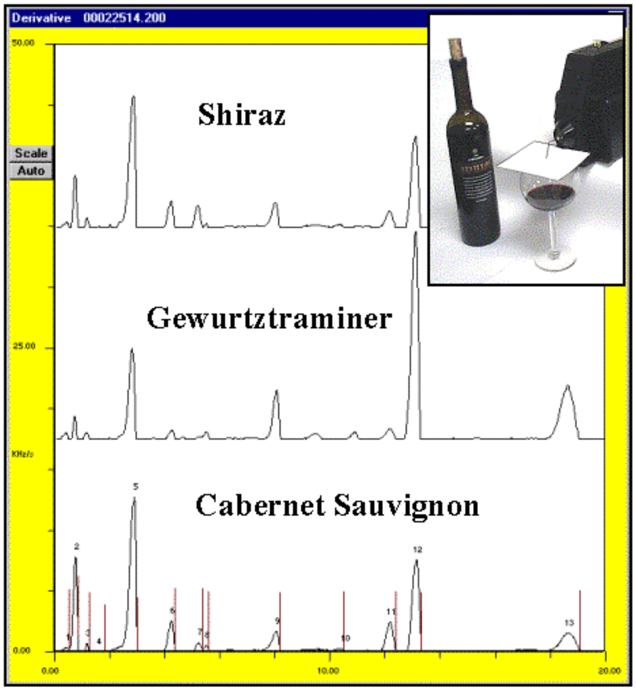


*Figure 15- Fast chromatogram analysis of Shraz, Gewürztraminer, and Cabernet Sauvignon wines.*

Wine contamination can come from many parts of the process. For example most are familiar with trichloroanisole (TCA) which is formed when bacteria within the cork comes into contact with bleach which is used to whiten the corks. Far more serious problems can occur when the process equipment becomes contaminated. Using an electronic nose such sources of contamination can be quickly detected and corrected before the wine is bottled.

## Summary and Conclusions

A new type of Electronic Nose using fast chromatography can now provide a recognizable visual image of specific vapor mixtures (fragrances) containing hundreds of different chemical species. The electronic nose is fast (10 seconds), operates over a wide range of vapor concentrations, has picogram sensitivity, and is simple to use and calibrate.

Unlike an array of physical sensors, a fast gas chromatography system with an integrating detector can transform the human olfactory response into a true visual response. Viewed as a virtual sensor array, the GC/SAW electronic nose can produce an olfaction response consistent with serially polling an array of hundreds of orthogonal chemical sensors. The GC/SAW simultaneously is able to quantify the concentration of the individual chemical compounds.

Quality control of virtually any food or beverage can be now be achieved with speed, precision, and accuracy. Validation by the US EPA and other governing agencies is an assurance that quality control of the measurement itself can be verified.

## References

[1] H.T. Nagle, S. Schiffman and R. Guitierrez-Osuna, “The How and Why of Electronic Noses”, IEEE Spectrum, pg. 22-33, September 1998.

[2] P. Mielle, “Flavour Sensors Become Smart…”, Proceedings of 2nd International Symposium Olfaction & Electronic Noses, 2-3 October 1995, Toulouse, France

[3] G.W. Watson and E.J. Staples, “SAW Resonators as Vapor Sensors,” Proceedings of the 1990 Ultrasonics Symposium, pp.311-314, 90CH2938-9

[4] G.W. Watson, W. Horton, and E.J. Staples, “GAS Chromatography Utilizing SAW Sensors,” Proceedings of the 1991 Ultrasonics Symposium, pp.305-309.

[5] E. J. Staples and G.W. Watson, “A GAS Chromatograph Incorporating an Innovative New Surface Acoustic Wave (SAW) Detector,” Pittcon Conference, 1-5 March 1998, New Orleans, Louisiana, Paper 1583CP

[6] E.J. Staples, T. Matsuda, and S Viswanathan, “Real Time Environmental Screening of Air, Water and Soil Matrices Using a novel Field Portable GC/SAW System,” Environmental Strategies for the 21st Century, Asia Pacific Conference, 8-10 April 1998, Singapore

[7] E.J. Staples, “Electronic Nose Simulation of Olfactory Response Containing 500 Orthogonal Sensors in 10 Seconds,” Proceedings of the 1999 IEEE Ultrasonics Frequency Control and Ferroelectrics Symposium, Lake Tahoe, CA, Oct 18-21,1999