Field Analysis Using A Novel Electronic Nose As An Environmental Tool

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 - Faster qualitative and quantitative analyses of chemical compounds are becoming a necessity in today's complex competitive environment. Of all the devices developed for on-site analysis, the electronic nose is the most versatile in terms of its ease of use and number of potential applications. An Electronic Nose is a vapor analyzer, which provides a recognizable image of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species. The electronic nose described in this paper is a universal detector with very fast response (10 seconds), a large dynamic operating range of vapor concentrations, and ppb sensitivity. Called a zNose™, to distinguish it from sensor arrays called eNoses, it is a combination of fast chromatography, an integrating surface acoustic wave sensor, and a programmable gate array (PGA) microprocessor. Because it is able to speciate and accurately measure the concentration of individual analytes present in odors, smells, and fragrances, it is the only electronic nose to receive validation from both the US EPA and the Office of National Drug Control Policy (ONDCP).

Introduction

Instruments which electronically simulate the human olfactory response using arrays of dissimilar sensors have become known as eNoses [1]. The general idea is patterned upon a human which has 10 million smell receptors in their noses. After more than 5 years development eNose technology can only barely mount an array of 32 sensors with weak specificity, overlapping chemical responses, and low sensitivity. Non-specific chemical sensing arrays cannot meet basic quality control criteria using chemical standards. Because individual sensors respond to many chemical compounds, just different ones (sometimes), a non-specific sensor array cannot be calibrated using mixtures of analytes of known concentration.

To create an electronic nose with certifiable performance a virtual chemical sensory array 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 analyte peak half-widths are measured in milliseconds and column effluent is collected on a temperature-controlled quartz chip.

Because it is a visual fragrance pattern, a VaporPrint™ image can be recognized and studied much more easily by the human brain than an actual olfactory stimuli. Each odor, fragrance, or smell produces a unique VaporPrint™ image which allows a complex ambient environment to be viewed and recognized if part of a previously learned image set.

This paper presents data from several on-site investigations using a GC/SAW electronic nose. These studies involved capturing the olfactory images of problem environmental odors such as swine, sludge, and waste water. Other on-site investigations required coupling the zNose™ to a GPS receiver to test for water contamination surrounding an off-shore oil platform. Also of interest is testing for tainting in drinking wines. These studies demonstrate that speed and EPA validated accuracy and precision can now be achieved on-site with a GC/SAW electronic nose.

GC/SAW Electronic Nose

Early electronic noses rejected chromatography techniques because they were slow. However, the development of integrating GC detectors [2] together with direct column heating [3] has recently produced a GC/SAW electronic nose technology with precision, accuracy, and 10 second speed [4,5,6].

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.

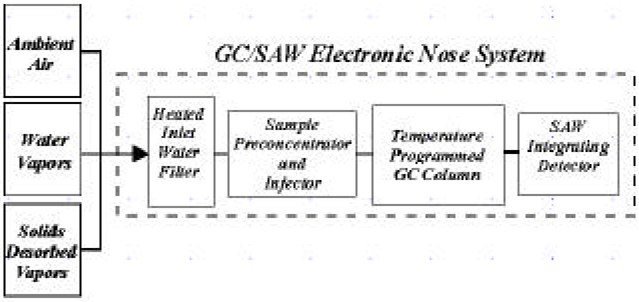


Figure 1- GC/SAW system diagram.

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.

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^{o}C.

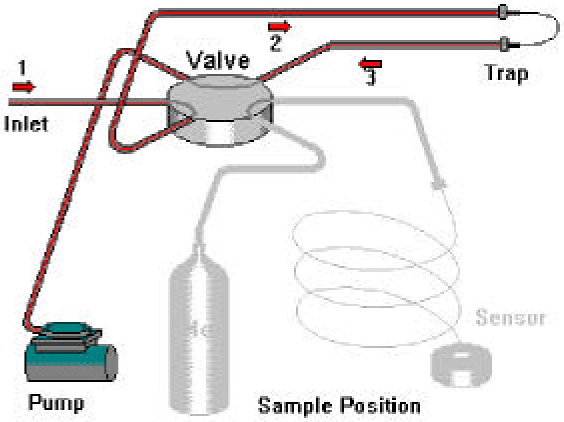


Figure 2- Step 1: Sample collection step preconcentrates vapors in a trap while maintaining helium flow through the GC column to the SAW detector.

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.

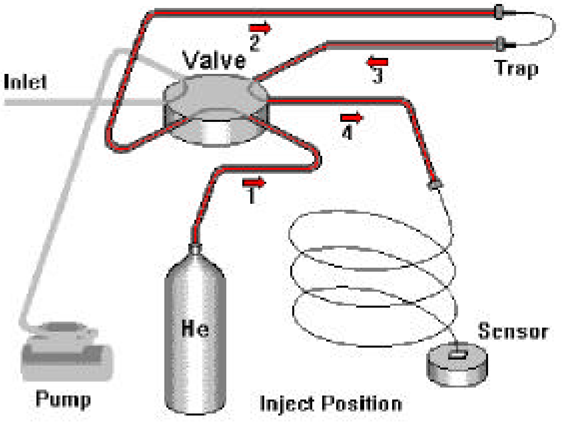


Figure 3- Step 2: Vapor Analysis injects trapped vapors into the helium carrier gas. Released vapors travel through the column and their retention time and frequency are measured by the SAW detector.

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

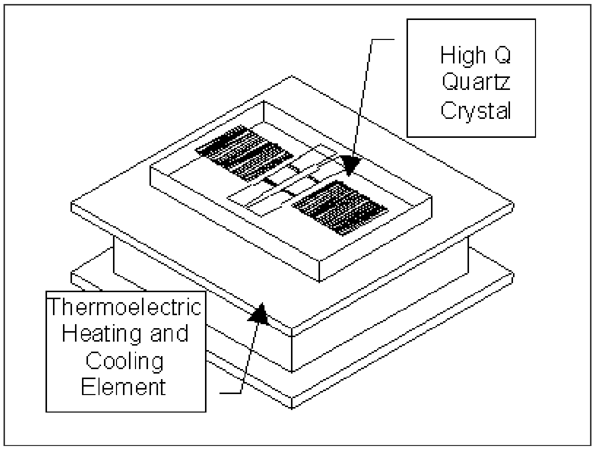


Figure 4- SAW detector uses a temperature controlled quartz substrate to absorb vapors as they exit the GC capillary column. Sensitivity is controlled by selecting the operating substrate temperature during chromatography.

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.

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.

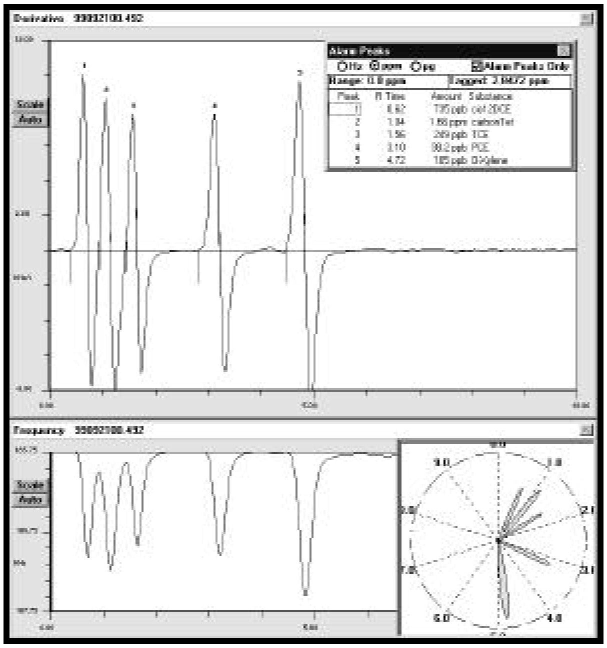
Figure 5- GC/SAW benchtop system contains an internal supply of helium carrier gas with capacity for more than 300 chromatograms. Sample pump, preconcentrator, and temperature programmed GC column are all controlled by an internal gate array processor which responds to the user's laptop computer connected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

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 eNose is sensitive enough to determine drinking water levels by simply smelling the headspace vapors above a water sample.

	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.

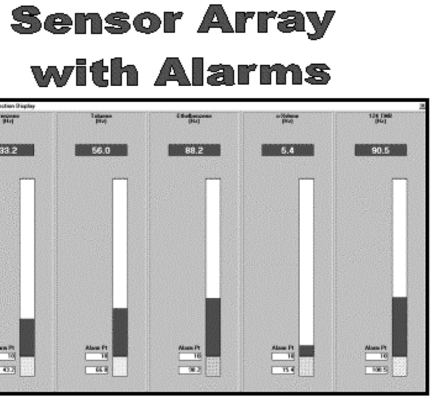
Because the GC/SAW can speciate with orthogonal sensors it can be calibrated using a single mixture of standard analyte concentrations. An analysis of a vapor mixture of five analytes is shown in Figure 7 as an example. The lower trace shows the frequency of the SAW detector while the upper trace displays the derivative of frequency. As each analyte leaves the column it is absorbed and then evaporates from the quartz surface. This causes the frequency of the detector to decrease in proportion to the amount of vapor absorbed followed by a return to its unperturbed value. The derivative of frequency is used to determine the time of maximum effluent flux also called the retention time of each analyte.



Peak	R Time	Amount	Substance
1	0.62	795 ppb	cis12DCE
2	1.04	1.58 ppm	carbonTet
3	1.56	249 ppb	TCE
4	3.10	88.2 ppb	PCE
5	4.72	185 ppb	OXylene

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

Each analyte retention time defines one chemical sensor of a virtual five element array as shown in Figure 8. Using this display instead of chromatograms, subsequent testing is simplified through the use of individual alarms for each sensor.



Benzene (Hz)	Toluene (Hz)	Ethylbenzene (Hz)	o-Xylene (Hz)	124 TMB (Hz)
33.2	56.0	88.2	5.4	90.5

Figure 8- A five element sensor array defined by the five analyte retention times. Sensor readings are the frequency deviation recorded for of each analyte.

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..

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 9. 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).

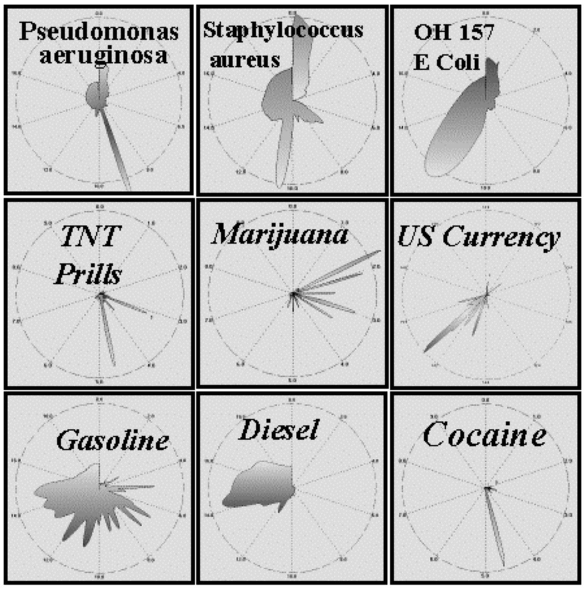


Figure 9- VaporPrint™ of some common odors.

The VaporPrint™ images show the large diversity in odors. The top three images of Figure 9 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.

On-Site Applications of Electronic Nose Technology

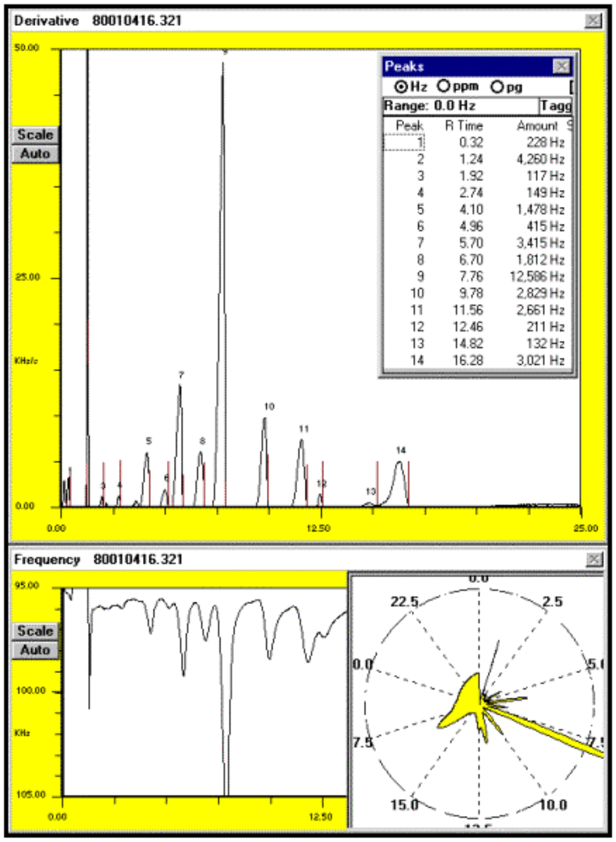
The number of successful applications is expanding rapidly and with considerable diversity. Because chromatography is an accepted analytical technique, GC/SAW technology is able to satisfy and follow accepted testing methodology. The ability to perform these methods with precision, speed, and accuracy is unique to the GC/SAW eNose. Olfactory imaging is proving more useful than at first expected because of the human ability to recognize subtle visual changes in VaporPrint™ images

Five application areas of recent interest are (1)animal factory waste, (2) water aquifer contamination, (3) sludge cleanup monitoring, (4) pollution from off-shore oil platforms, and (5) testing of wine for process contamination.

The term 'animal' factory has become associated with the production of meat from cows, chickens, and swine. These factories produce prodigious amounts of waste and in many cases there has been considerable damage to the environment either through run-off into streams and rivers or through odors which can permeate large areas of the country. Currently odors associated with animal waste are characterized by odor panels consisting of humans operating as sensors. Their responses are only semi-quantitative and very subjective. Even so, there are established measurement standards on which are based legal statutes and even penalties for those factories which do not control their odors.

An electronic nose which can speciate and quantify the chemicals present in these odors is useful because it removes the ambiguity of human odor panel measurements.

An example of odors associated with swine production is shown in Figure 10. In this analysis 14 primary compounds are speciated and their concentration measured in 20 seconds. The high concentration of volatile methane is shown in the very sharp peak at the beginning of the chromatogram. The VaporPrint™ image shown in the lower right inset gives human operators an overall assessment of the odor and can be recognized as 'pig' odor.



Peaks

⦿Hz ○ppm ○pg

Range: 0.0 Hz

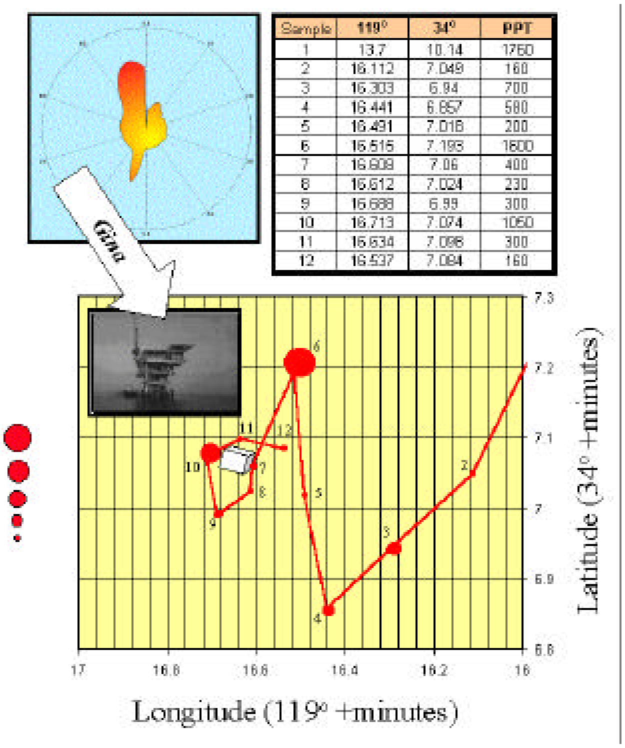
Peak	R Time	Amount
1	0.32	228 Hz
2	1.24	4,260 Hz
3	1.92	117 Hz
4	2.74	149 Hz
5	4.10	1,478 Hz
6	4.96	415 Hz
7	5.70	3,415 Hz
8	6.70	1,812 Hz
9	7.76	12,586 Hz
10	9.78	2,829 Hz
11	11.56	2,661 Hz
12	12.46	211 Hz
13	14.82	132 Hz
14	16.28	3,021 Hz

Figure 10- Odors associated with swine production can be a health and environmental problem which can be quantified by electronic noses.

Waste from many sources, such as animal factories and fertilizers many times is responsible for polluting rivers, streams, and underground water aquifers. The electronic nose provides a method for on-site characterization and measuring the concentration of polluting chemicals. Shown in Figure 11 the zNose™ is being used to measure the concentration of trichloroethylene in well water. Limits of detection are typically 500 ppt and this is within most drinking water standard limits.

Figure 11- On investigations with the electronic nose include well water and contamination in water aquifers.

Water pollution is not just limited to rivers and streams but can also extend to oceans as well. One example is pollution which can occur surrounding oil well platforms and drilling operations. To measure ocean contamination on-site the zNose™ was taken aboard a sailboat and the concentration of polyaromatic hydrocarbons (PAH) in the sea water surrounding the oil well measured. Typical results are shown in Figure 12 where concentration is indicated by a red ball. The largest balls correspond to the highest concentration of PAH. The VaporPrint™ image was characteristic of pollution due to diesel fuel. To make the measurement meaningful the location of the test sample was simultaneously measured by connecting a GPS receiver to the zNose™. The software of the zNose™ is designed to interface with GPS receivers so that every on-site analysis also includes the correct time, latitude, longitude, and altitude of the measurement. Actual concentrations and their latitude and longitude are shown in the accompanying table. An electronic nose and a GPS receiver are very effective in creating a spatial plot of chemical concentrations as part of an on-site survey of pollution.



Sample	119°	34°	PPT
1	13.7	10.14	1760
2	16.112	7.049	160
3	16.303	6.94	700
4	16.441	6.857	580
5	16.491	7.018	200
6	16.515	7.193	1600
7	16.608	7.06	400
8	16.612	7.024	230
9	16.688	6.99	300
10	16.713	7.074	1060
11	16.634	7.098	300
12	16.537	7.084	160

Figure 12-On-site investigations can be carried from a vessel at sea. In this example pollution surrounding was measured on-site from a sailboat using a GPS receiver.

In another example the zNose™ was used to characterize and monitor the level of waste removal from a sludge tank as a result of filtering and bio-remediation. Vapor samples were collected from the sludge in tedlar bags. The vapor in each bag was analyzed on-site and the results are shown in a series of six chromatograms arranged in a waterfall display in Figure 13. The top three traces were taken sequentially on untreated sludge and the presence of a large number of volatile organics is noted and the concentration of each can be quantified.

The lower three traces of figure 13 are sequential measurements of the filtered and bio-degraded sludge. The degree of cleanup is now a simple matter of subtracting the before and after concentrations. Each measurement was repeated at a 1 minute interval, and allowing for several QC assurance runs on standard concentrations, the total on-site test takes no more than ten minutes.

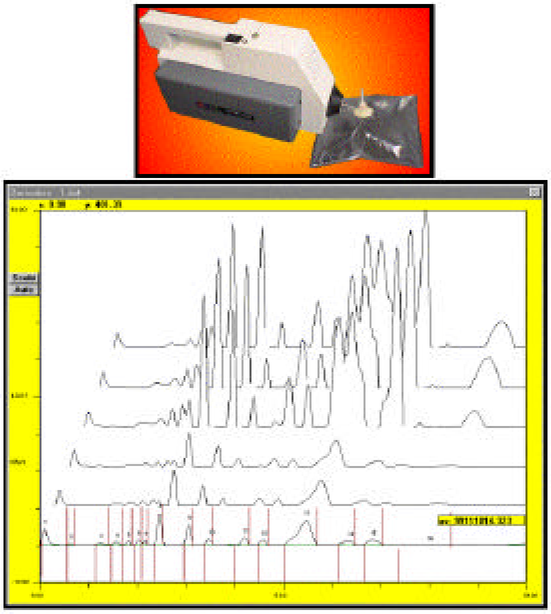


Figure 13-Before and after chromatograms of filtered and biodegraded sludge

Electronic noses are ideal for monitoring quality control in chemical processes. For example, quality control in the processing of food and beverages for human consumption is important to everyone. One of the more exacting processes is the creation of a great wine where even minute traces of contamination can destroy the product.

The zNose™ is a useful tool for monitoring the quality of wine process on-site from beginning to end. Testing can be either by piercing the cork to test the bottle or barrel headspace or simply by analyzing the headspace in a glass of wine as shown in Figure 14. In this case the glass is covered with a piece of paper and the side-ported sample needle passes through a small hole in the paper. Run to run repeatability is excellent and the concentration of the headspace vapors remain constant for a considerable time.

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. An example is illustrated in the two VaporPrint™ images shown at the bottom of Figure 14. The image on the right is that of normal wine, in this case a Zinfandel wine. The image on the left is that of the same wine contaminated with pipe sealant. This problem occurred in a winery when there was a plumbing leak and subsequent repairs were not properly done. The resulting contamination transferred to the wine and destroyed the wine within a large number of bottles before it was discovered.

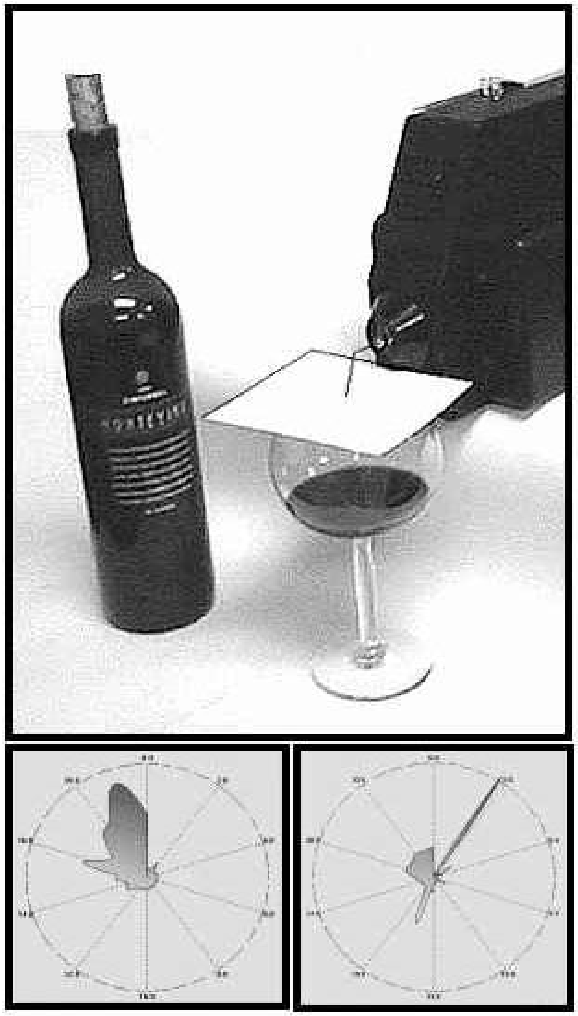


Figure 14- Vaporprints of contaminated and normal wine

Unlike sensor arrays, the zNose™ is able to quantify virtually all of the products of distillation even in the presence of large amounts of alcohol because chromatography is used to speciate. Even whisky, which contains approximately 43% alcohol, can be analyzed, its quality tested, and the aging process verified with an electronic nose.

Summary and Conclusions

A fast gas chromatography system with an integrating detector can transform the human olfactory response into a visual response. Viewed as a virtual sensor array, the SAW/GC electronic nose can produce an olfaction response consistent with serially polling an array of 500 or more chemcial sensors in just 10 seconds. This new zNose™ can give law enforcement officers, environmental scientists, quality control specialists, and olfaction researchers a new on-site investigative tool.

The fast GC/SAW is a useful on-site measurement instrument which provides a recognizable high resolution visual image of specific vapor mixtures containing many different chemical species. The GC/SAW simultaneously is able to quantify the concentration of the individual chemical compounds present in odors universally. It is this universality which leads to a wide diversity of applications.

Minimum detection level for volatile organic compound (VOC) vapors are nominally 1 part per billion while sensitivity to semi-volatile compounds is 1 picogram or 1 part per trillion. High sensitivity, universal selectivity, integrated output, and high stability make the SAW detector one of the most sensitive GC detectors known.

On-Site applications are wherever there are vapors, odors, smells, or fragrances to be measured. Environmental, law enforcement, and chemical processes are just a few good applications. Validation by the US EPA and other governing agencies is an assurance that quality control of the measurement can be verified.

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