Electronic Nose Simulation of Olfactory Response Containing 500 Orthogonal Sensors in 10 Seconds

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Abstract - An Electronic Nose using fast gas chromatography with an uncoated 500 MHz SAW resonator can produce an olfaction response consistent with an array of 500 or more orthogonal sensors in 10 seconds. This new eNose is providing law enforcement officers, environmental scientists, quality control specialists, and olfaction researchers with a new investigative tool. The GC/SAW is an optimal Electronic Nose which provides a recognizable high resolution visual image of specific vapor mixtures (fragrances) 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 such a wide diversity of applications.

Electronic Noses and Sensor Arrays

An array of sensors simulating the human olfactory response has become known as an Electronic Nose [1]. An Electronic Nose provides a recognizable image in N-dimensional space (where N equals the number of sensors) of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species. A useful model is a switch which serially polls the response of an array of sensors as shown in Figure 1. Electronic Noses with only a few sensors produce responses which are not correlated and multiple sensors respond to the same vapor e.g. overlap. Because of this, it is almost impossible to calibrate a sensor array with overlapping responses. However, if the sensors can be made orthogonal and arranged in a meaningful way, the chemical make up of the olfactory response can be quantified and calibrated using mixtures of chemical standards. The ideal array response is then an array of sensors which do not overlap and are orthogonal as shown in the lower trace of Figure 1.

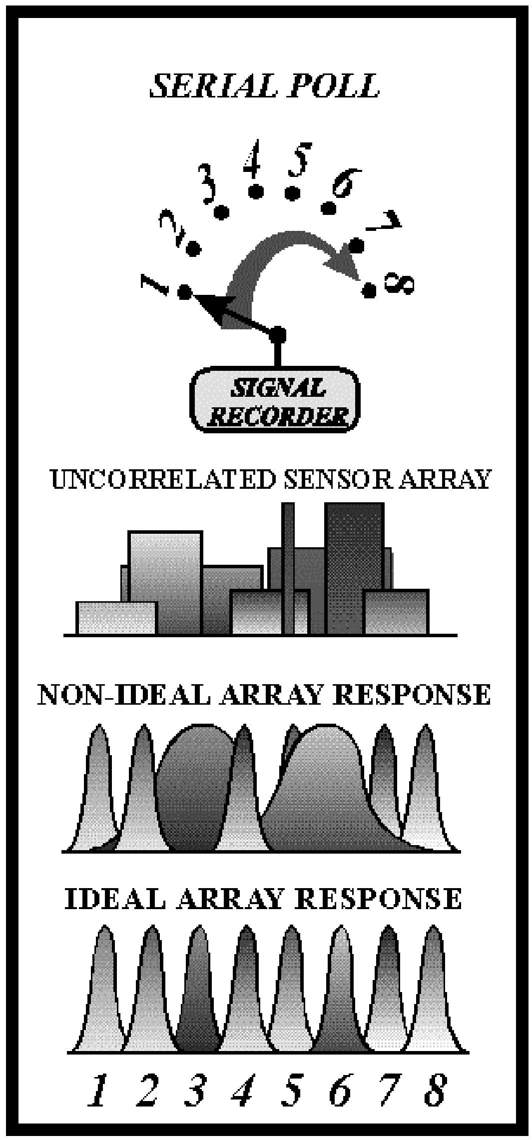

Figure 1- Serial polling of a sensor array reveals the degree of orthogonality in sensor responses.

GAS Chromatograph as a Sensor Array

A gas chromatograph produces the ideal time sequence or histogram of non-overlapping responses desired. The timing of each response correlates with the time it takes each chemical species to travel through a chemically coated capillary column. The chemical coating of the column causes an injected vapor sample to be dispersed into individual packets of different chemical species traveling at different velocities through the column.

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].

The GC/SAW electronic nose system diagram is depicted in Figure 2. 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 in-

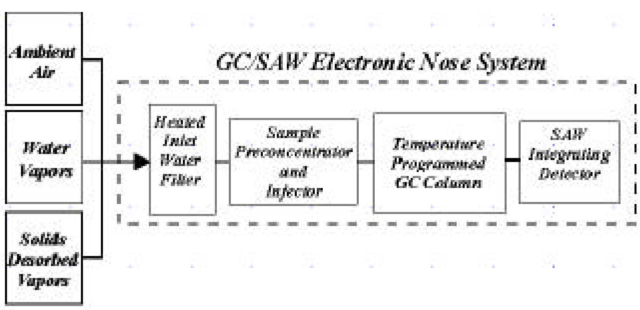

Figure 2- GC/SAW system diagram.

jected 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. The timeline sequence of events is depicted in Figure 3. The SAW resonator frequency is measured using a 20 millisecond gated reciprocal counter which produces 500 readings in 10 seconds. This translates into an array of 500 sensor readings with each chemical sensor being assigned to a unique retention time and frequency reading for that chemical.

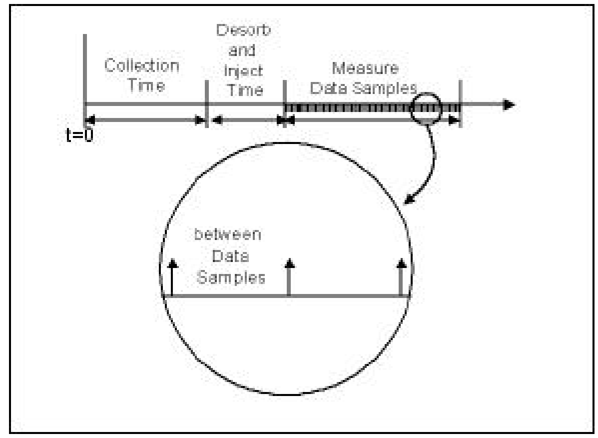

Figure 3- Time sequence showing histogram of 500 sensor readings spanning a 10 second period.

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 4, 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.

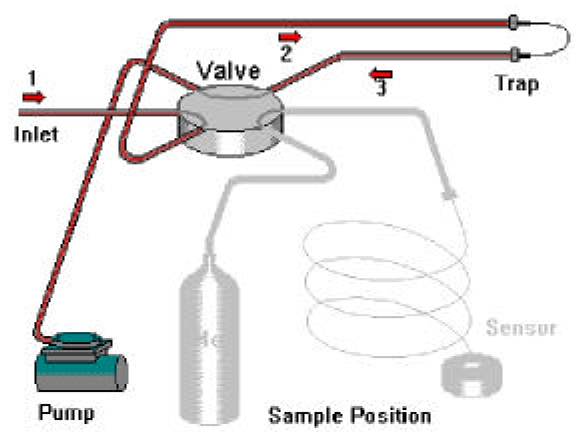

Figure 4- Sample collection step preconcentrates vapors in a trap while maintaining helium flow through the GC column to the SAW detector.

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.

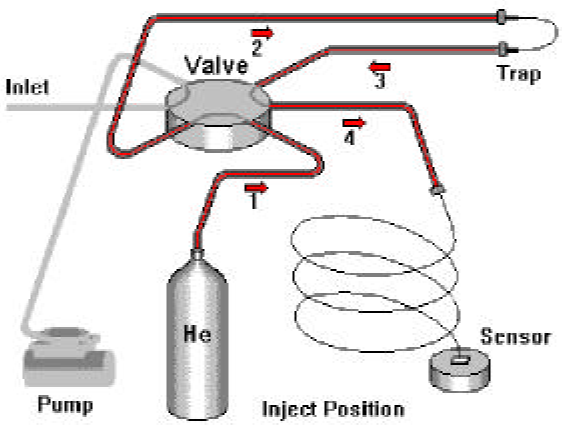

Figure 5- Vapor Analysis step injects trapped vapors into the helium carrier gas. Released vapors travel through the temperature programmed column and their retention time and frequency are measured by the SAW detector.

Immediately after the valve is switched into the analysis position 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 at a velocity determined by their relative vapor pressure and chemical affinity with the capillary coating.

The SAW detector, shown in Figure 6 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 desired 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 over a wide dynamic range.

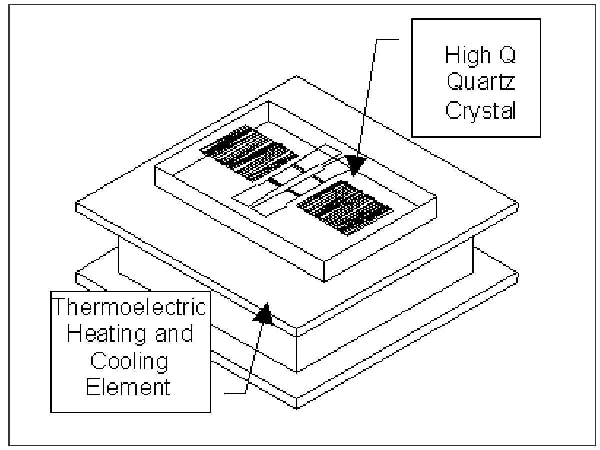

Figure 6- SAW detector uses a temperature controlled quartz substrate to absorb vapors as they exit the GC capillary column. Sensitivity is controlled by selecting the operating substrate temperature during chromatography.

The complete system is packaged in the benchtop instrument case shown in Figure 7. 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 processor. Macro instructions are provided by the user from a Windows® program operating on a Pentium laptop.

Figure 7- 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 in readings.

Because the SAW sensor uses no coatings it is stable and extremely sensitive. Minimum detection levels for 10 common volatile organic compounds in air and water are listed in Figure 8. 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 8- 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 9 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.

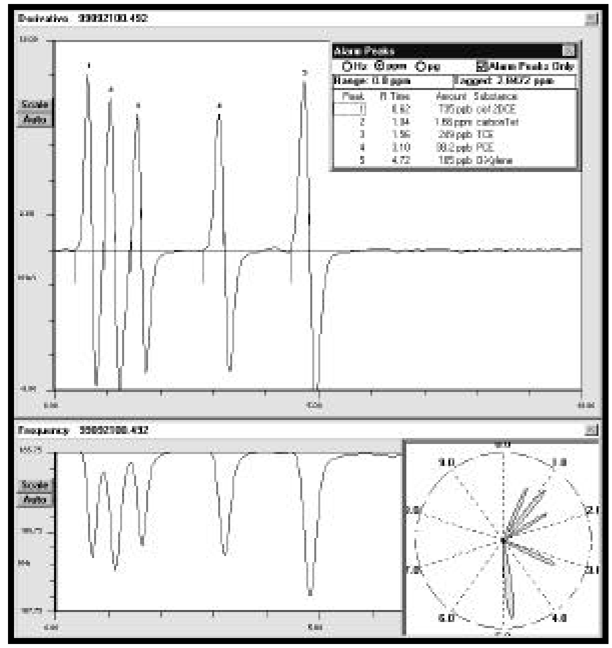

Figure 9- Two types of chromatogram are produced by the GC/SAW.

Each analyte retention time defines one chemical sensor of a five element array as shown in Figure 10. Using this display instead of chromatograms, subsequent testing is simplified through the use of individual alarms for each sensor.

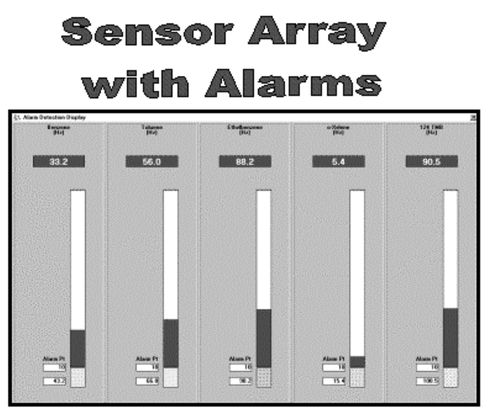

Figure 10- A five element sensor array defined by the five analyte retention times. Sensor readings are the frequency deviation recorded for of each analyte.

VaporPrint™ 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 has no need for artificial intelligence since the SAW detector can provide the operator with visually recognizable images while also quantifying the strength of each chemical within a fragrance. Like the plant leaves of Figure 11, only natural intelligence is required to associate the pattern with the plant.

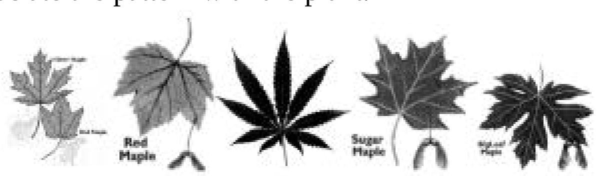

Figure 11- VaporPrint™ images, like leaf patterns, are easily recognized by humans.

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 12. The image is a closed polar plot of the odor amplitude (SAW detector frequency) with radial angles representing sensors (time, 0 and maximum time are vertical).

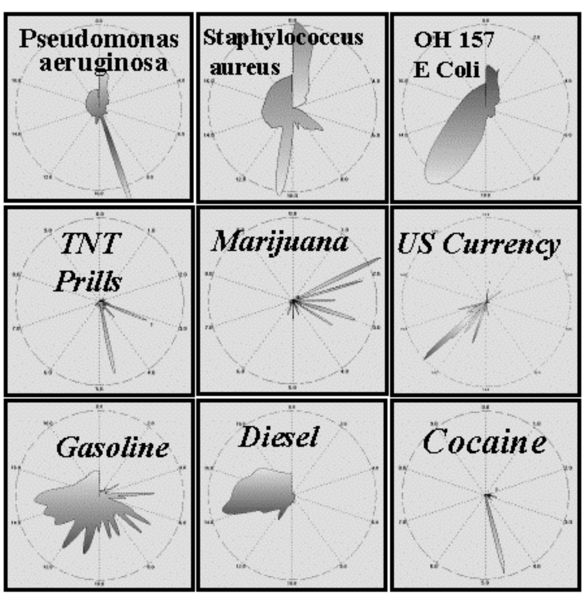

Figure 12- VaporPrint™ of some common odors.

Each odor or fragrance contains many different analytes with a distinct relationship to each other. A VaporPrint™ image allows a complex ambient environment to be viewed and recognized as part of a previously learned visual image set. Using the ability of the human operator to recognize visual patterns allows a quick and natural assessment of unknown smells or odors.

The VaporPrint™ images show the large diversity in odors. The top three images of Figure 12 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.

Applications of GC/SAW 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

Three application areas of interest in this paper are (1) plastic industry, (2) food and beverage industries, and (3) on-board sensors for automobiles.

The plastic packaging industry is ubiquitous and part of our every day existence. Plastic is a wonderful material but if not prepared correctly it can produce a foul odor which has been responsible for tainting of products placed within the plastic container.

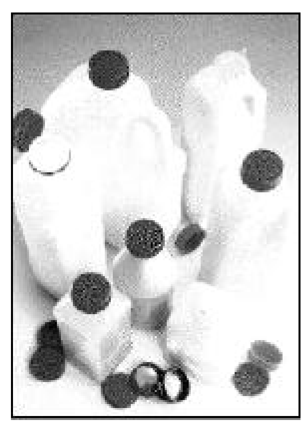

Figure 13- Plastic containers are sometimes responsible for producing unwanted odors.

An example of odors associated with good and bad plastic bottles is shown in Figure 14. In this case, bad plastic bottles were found to produce four distinct analyte peaks which had concentrations in the 1-2 ppm range. A 'substance-watch' sensor array is created for the bad compounds and the sensor array is incorporated into a quality control test. Human operators proved equally successful in quickly identifying bad bottles. Batch and lot testing proved successful in isolating those shipments with odors that might taint the customer's product.

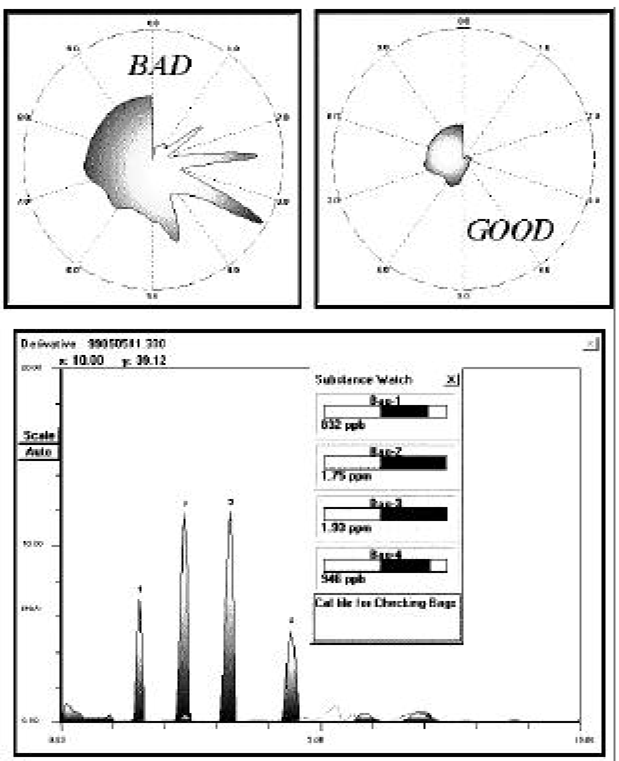

Figure 14- Good and bad plastic bottles can be distinguished and the strength of the offending analytes measured within 15 seconds.

Odors and fragrances are important for different reasons in the food and beverage industry. Here the freshness of ingredients becomes of primary concern. An example is the freshness of tomatoes which are the principal ingredient of spaghetti sauce and other well known recipes.

Shown in Figure 15 is a chromatogram of a vine ripened tomato. The strength of the volatile compounds correlate with the freshness of the tomato.

Shown in Figure 16 is a chromatogram of the Ragu Spaghetti sauce and the tomato analytes are clearly seen together with other added seasonings.

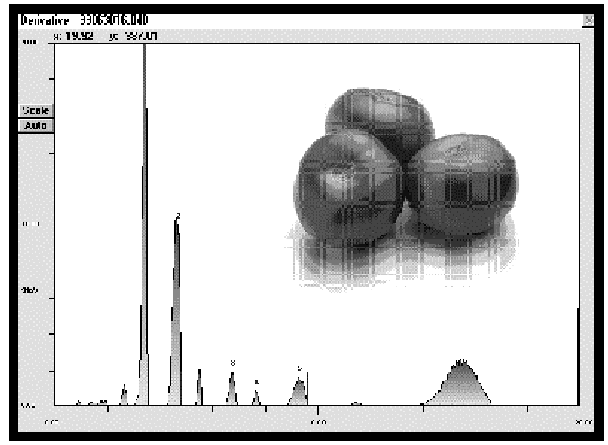

Figure 15- Ten second chromatogram of vine ripened tomatoes. High amplitude volatile compounds correlate with freshness.

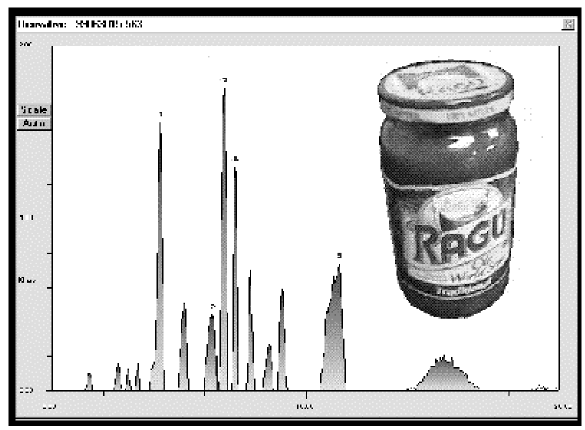

Figure 16-Ten second chromatogram of Ragu Spaghetti sauce. Note compounds from tomato as well as others introduced by seasoning.

VaporPrint™ images of tomatoes and ragu sauce, Figures 17 and 18, show how much easier it is for humans to read and interpret subtle differences in product quality.

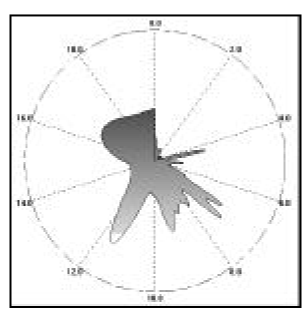

Figure 17- VaporPrint™ of Ragu Spaghetti sauce.

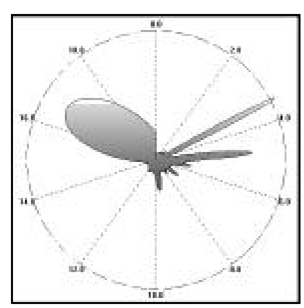

Figure 18- VaporPrint™ of a vine ripened tomato.

Automobiles are well known for their smog producing vapors and everyone is familiar with 'that new car smell'. Ever since automotive engineers began using microprocessors in automobiles there has been a demand for more and more on-board sensors to feed them. An on-board electronic nose has many uses such as monitoring the engine emissions and smog control system. Also, monitoring odors inside and outside the vehicle would provide warnings to the occupants when they were exposed to dangerous vapors such as benzene and toluene. An example of an auto exhaust chromatogram and the interior VaporPrint™ of a new Oldsmobile Alero is shown in Figure 19.

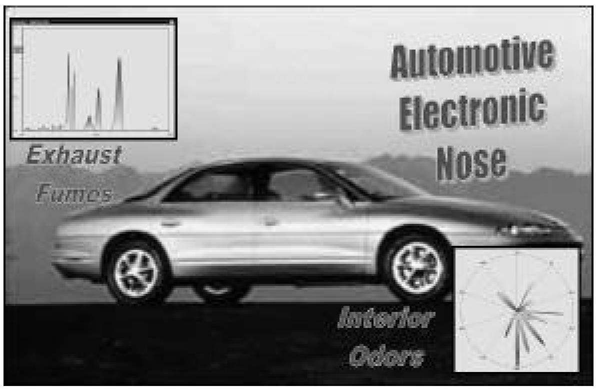

Figure 19- An automotive electronic nose will monitor engine emissions as well as interior odors.

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 serial model, the SAW/GC electronic nose can produce an olfaction response consistent with serially polling an array of 500 or more orthogonal sensors in just 10 seconds. This new eNose can give law enforcement officers, environmental scientists, quality control specialists, and olfaction researchers a new investigative tool.

The fast GC/SAW is an optimal Electronic Nose 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.

The SAW sensor output frequency forms a natural visual VaporPrint™ image of any fragrance and this is well suited to the pattern recognition skills of humans. These images together with the ability to detect an almost unlimited number of different chemicals and present it as a sensor array with alarms, forms the bases of a very friendly user interface.

The detection limits of the SAW detector are determined by the spectrum of SAW oscillator phase noise. The minimum detection level for volatile organic compound (VOC) vapors is 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.

Applications are wherever there are vapors, odors, smells, or fragrances to be measured. Environmental, law enforcement, food & beverage, medical, and automobiles are just a few good applications. Acceptance by the US EPA and other governing agencies is an indication that this technology has arrived.

References

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