Development Of A Novel Electronic Nose As An Environmental Tool

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ABSTRACT

Faster qualitative and quantitative analyses of chemical compounds are becoming a necessity in today's complex competitive environment. Of all the devices developed, the concept of an electronic nose is becoming popular, in terms of its ease of use and versatility. 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 is a universal detector with very fast response (in the order of 5 seconds) and a large dynamic operating range of concentrations. The first U.S. EPA electronic nose concept has not come from a sensor array but rather from a very fast gas chromatograph (GC) and a new zero dead volume integrating GC detector. In this GC/SAW system, individual analyte peak half-width is measured in milliseconds and every picogram of material is collected on a temperature-controlled quartz crystal. The surface of the quartz crystal also is host to a high Q surface acoustic wave (SAW) interferometer, sometimes called a SAW resonator, and this produces a frequency proportional to the amount of column effluent deposited on the quartz surface. An electronic nose must have the ability to recognize as well as quantify many different complex fragrances. This is achieved using pattern recognition and a visual fragrance pattern, called a VaporPrint™ derived from the frequency of the SAW detector. Each chemical, odor or fragrance contains many analytes with a distinct relationship to each other. A VaporPrint™ image is created by a radial plot of SAW resonator frequency with time being the angle variable. A complete chromatogram always spans 360 degrees. A VaporPrint™ image allows a complex ambient environment to be viewed and recognized if part of a previously learned image set. Using the unsurpassed ability of the human to recognize patterns allows skilled operators to quickly assess the nature of environmental vapors and to look for analytes of interest such as volatile organics. This paper presents the development and application of a novel electronic nose for the measurement of volatiles, and semi-volatiles, in a complex environmental surrounding. A number of case studies including validation under the U.S. EPA ETV program will be discussed. The use of the electronic nose concept in the detection and monitoring of an environmental complex involving air, water and soil matrices will be explored.

INTRODUCTION - Electronic Noses and Sensor Arrays

A type of vapor analyzer using an array of dissimilar sensors simulating the human olfactory response has become known as an Electronic Nose [Ref. 1]. An Electronic Nose provides a recognizable visual image of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species. An electronic nose is designed to quantify and characterize all types of smells universally. Sensors are selected for their chemical affinities and chemisorbing polymer films are commonly used for this purpose. Many sensors can be used and a serial polling of each sensor reading produces a histogram of sensor outputs as indicated in Figure 1. The responses are uncorrelated and sometimes multiple sensors respond to the same vapor e.g. overlap. Because of this, it is almost impossible to calibrate this type of Electronic Nose with test vapors containing more than one compound. A further issue is sensitivity because the vapor sample being tested by the array must be shared among each sensor in the array.

In this paper a new type of electronic nose based upon fast chromatography is introduced. Sensor space is defined mathematically according to retention time slots. Separation of different compounds is greatly improved. In the optimal or ideal response there is no overlap of sensor outputs and each sensor output corresponds to only one analyte or chemical compound. Different chemical species have different retention times and hence these vectors can be given names like carbon tetrachloride' or 'trichloroethylene'. With an Electronic Nose based upon gas chromatography, orthogonality of retention time vectors is a function of the column chemical phase and temperature profile.

Fast Gas Chromatography as an Electronic Nose

A new fast gas chromatography system using a Surface Acoustic Wave (SAW) detector [Ref. 2] is depicted in Figure 2. The system includes a heated inlet, vapor preconcentrator, temperature ramped and direct heated GC column, and a SAW detector. Sensitivity is excellent because the SAW detector has picogram sensitivity and there is no dilution of vapor sample. The system inlet can sample odors in ambient air, desorbed vapor from soil samples, or headspace vapors from water samples.

The SAW detector produces a variable frequency in response to analytes condensing and evaporating on the surface of a quartz crystal. The lower trace in Figure 3 displays the frequency histogram while the upper trace displays the derivative of frequency (column flux) and produces the familiar peaks of chromatography. Because the SAW detector measures the integral of the chromatogram peaks it is called an integrating detector.

In fast chromatography the chromatogram duration is 10 seconds, peak widths are in milliseconds, and retention time is resolved to within 20 milliseconds. Thus, potentially 500 sensors in 10 seconds can be polled serially. The 'sensor' responses are nearly orthogonal with minimum overlap. This feature allows for easy minimum detection level determination using a standard chemical mixture.

In Figure 3 are also shown VaporPrints™ images [Ref. 3] of both the detector frequency and derivative of frequency. These images are formed by transforming the time variable to a radial angle with the beginning and end of the analysis occurring at 0^o or vertical.

VaporPrint™ Images and Pattern Recognition

A polar plot of chromatogram time with the radial direction being the sensor signal or the derivative of sensor signal provides an important graphical feature well suited Electronic Nose pattern recognition algorithms [Reg. 4,5]. The SAW sensor detects the amount of analyte condensing (and evaporating) on a quartz surface and the SAW frequency corresponds to the total (integral) amount of analyte condensed. The SAW crystal is the only integrating GC detector, all others detect the flux of column flow. The derivative of the detector output is only used to determine retention time. The amount of analyte detected is determined by sensor frequency.

The process of vapor identification and recognition for the GC/SAW Electronic Nose is depicted in Figure 4 using mushroom vapors as an example. After 5 seconds of sampling the vapor is analyzed to form VaporPrint™ images, chemical chromatograms, and post the status of selected sensor alarms within 10 seconds.

The ability to form a sensor array with alarms enables the system to monitor only those analytes of interest, e.g. odors from automobiles. For the automobile exhaust example there are benzene, toluene, ethylbenzene, xylene, and trimethylbenzene. We simply select the retention times of these compounds as the five sensor vectors to be monitored. A simple array of sensor meters then is displayed and this represents an automobile nose. It only takes a software click to load another set of sensors and we have can have a nose for tobacco.

Several electronic nose pattern recognition algorithms based upon sliding sets of correlation's using known compound patterns associated with complex fragrances were evaluated The objective was to find the best "pattern recognition algorithm". Thus far nothing approaching the performance of a human operator has been found. The situation is demonstrated in the pictures of plant leafs shown in Figure 5. For a human, identification of the marijuana leaf is simple and immediate, while for computation algorithms the task can be daunting, long, and tedious.

Humans are practically optimal at recognizing VaporPrint™ patterns, however they are properly trained. VaporPrint™ images became richer with more complex and volatile compounds as found in food and perfumes. Some example images from infectious bacteria, pollutants, drugs of abuse, and flammable fuels are shown in Figure 6. Experience has shown that human operators are able to recognize certain images or food smells because they looked like common shapes.

Environmental Applications

There are many important environmentally related applications for an Electronic Nose. Air pollution and many different types of odors are common pollutants which require monitoring and quantification. The exhaust from automobiles and trucks is a very good example of environmental air pollution.

Water pollution occurs where there are leaking fuel tanks or where spills have occurred and organics have entered the aquifers. Water pollution associated with rivers, lakes, and water aquifers represents approximately 60% of the world environmental problems. Because pollutants in water are volatile, water pollution can be measured simply by testing the headspace vapors above the water. This makes it possible to evaluate water pollution simply by smelling the water.

Environmental pollution in soil (solid matrices) is also an important application for electronic noses, particularly, when the nose is configured to detect semi-volatile compounds like pesticides, PCBs, and dioxins. Using direct desorbtion or liquid extraction techniques with soil based upon EPA methods provides techniques for evaluating this type of soil contamination.

Performance Validation of Electronic Nose Performance

To validate the performance of new technology the US Environmental Protection Agency (EPA) recently established an Environmental Technology Validation (ETV) program. Commercial electronic noses are available in handheld or benchtop configurations as shown in Figure 7. The US EPA ETV program evaluated these commercial noses. Studies included field demonstrations for volatile organic compounds (VOC) as well as semi-volatile PCBs. The commercial units included a GC/SAW electronic nose that performed flash chromatography, VaporPrint™ imaging, and configuration of custom sensor arrays with user defined alarm levels. With single-handed ease, this instrument delivered 10 second chromatograms using a patented Surface Acoustic Wave (SAW) sensor. The electronic noses were designed to operate in the field as well as in the laboratory. The system included a Pentium computer with pre-installed Office97® and PCAnywhere® software for remote operation. Options also include a low-cost GPS receiver for accurately recording the location of each measurement.

The minimum detection levels for 10 common VOCs in air and water were evaluated and the results are shown in Table I. The GC/SAW electronic nose is the first to receive validation from the US EPA for environmental monitoring of VOCs in water and PCBs in soil. Also, the White House Office of National Drug Control Policy (ONDCP) has validated the performance of this electronic nose for detecting drugs of abuse and the nose can now be purchased from the Government Services Administration (GSA).

Summary and Conclusions

A commercially available Electronic Nose can provide environmental engineers with a new tool for characterizing pollution in air, water, and soil. The Electronic Nose provides a recognizable visual image of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species. The new electronic nose is fast (10 seconds), operates over a wide range of vapor concentrations, has picogram sensitivity, and is simple to use and calibrate. The Electronic Nose has the ability to recognize as well as quantify many different and sometimes complex fragrances. This is achieved using pattern recognition and a visual fragrance pattern, called a VaporPrint™ derived from an integrating solid-state detector. A VaporPrint™ image allows a complex ambient environment to be viewed and recognized as part of a previously learned image set.

The speed and sensitivity of the Electronic Nose and has been validated for environmental monitoring by the USEPA and for drugs of abuse by the ONDCP. In addition, the new Electronic Nose is GSA listed and is approved for use under the ONDCP/GSA "1122" program. Because the Electronic Nose can adapt and learn to recognize new vapors, it is a useful new tool for environmental protection agencies and many other Federal and State agencies concerned with protecting and improving the environment.

References

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Table I – Electronic Nose Minimum Detection levels in Air and Water

	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

Figures

Figure 1- Histogram produced by serially polling sensor arrays.

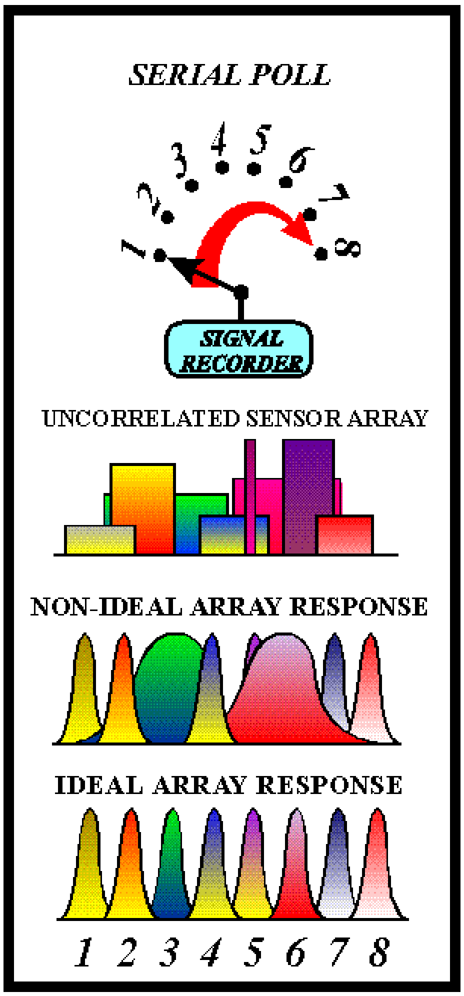

Figure 2- GC/SAW System Description

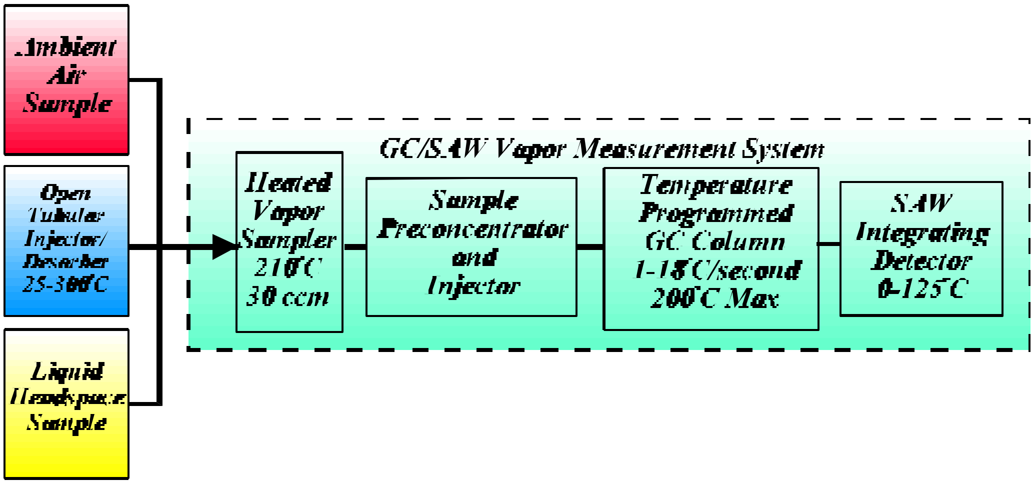

Figure 3- Gas Chromatograms used to create VaporPrint™ images.

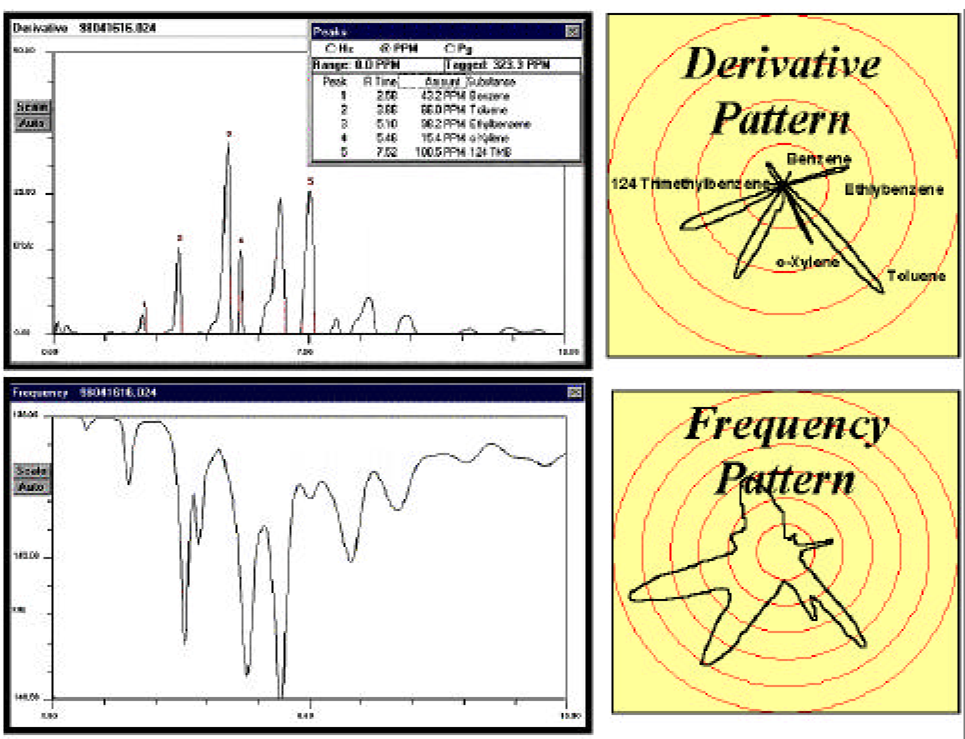

Figure 4- Pattern Recognition Process including the setting of alarms on individual sensor elements.

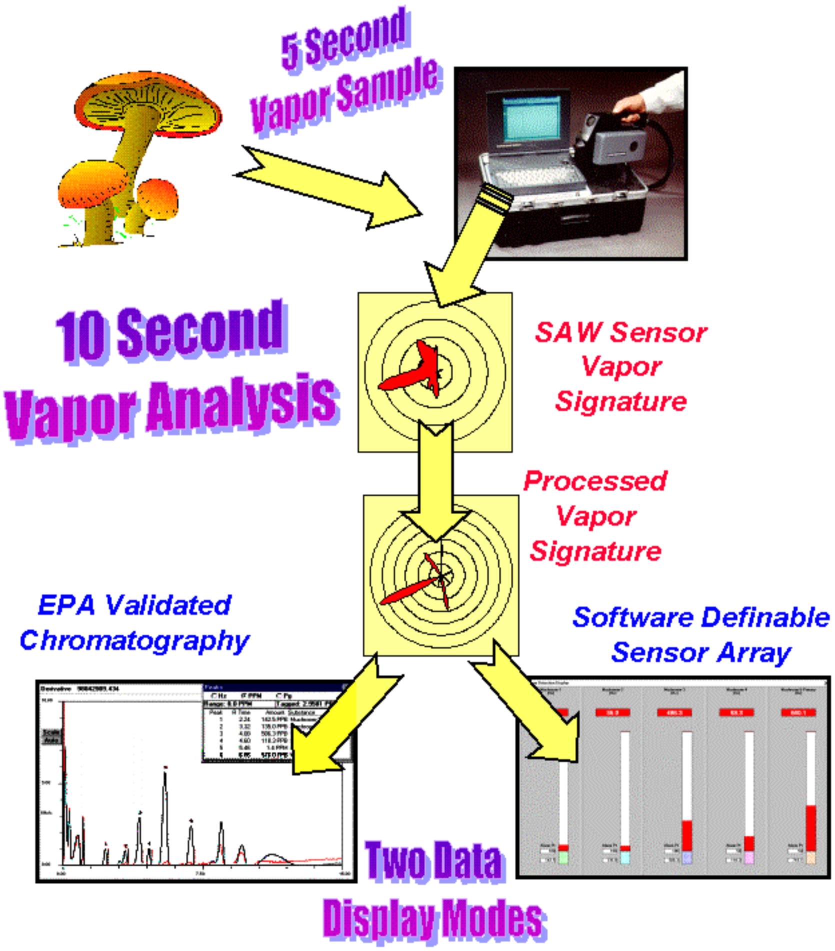

Figure 5- The human is an optimal pattern recognizer

Figure 6- VaporPrints™ for common infectious diseases, explosives, pollution, drugs, and Flammable Fuels

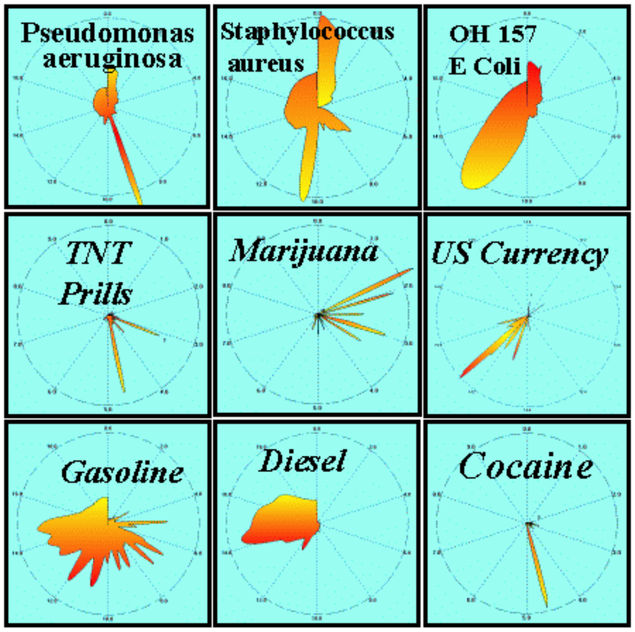

Figure 7 – Commercial Electronic Noses available as handheld or benchtop instruments.