The First Quantitatively Validated Electronic Nose for Environmental Testing of Air, Water, and Soil

Edward J. Staples
Electronic Sensor Technology, 1077 Business Center Circle, Newbury Park, California,
Ph. 805-480-1994, FAX 805-480-1984, Email: staples@estcal.com

Abstract - The first EPA-ETV validated electronic nose with the ability to speciate, quantify, and create a visual olfactory image of environmental pollutants and odors with speed, accuracy, and precision is presented in this paper. Fast and portable chemical analyses has become a necessity in today's complex environment. Of all the chemical devices under development, an electronic nose to mimic (improve) the human olfactory response while also providing quantitative chemical analysis has been the most sought because of its versatility and widespread usage. A new type of electronic nose, called a zNose™, is based upon a very fast (10 second) gas chromatography (GC) coupled with a single, non-specific surface acoustic wave (SAW) mass detector.

Introduction

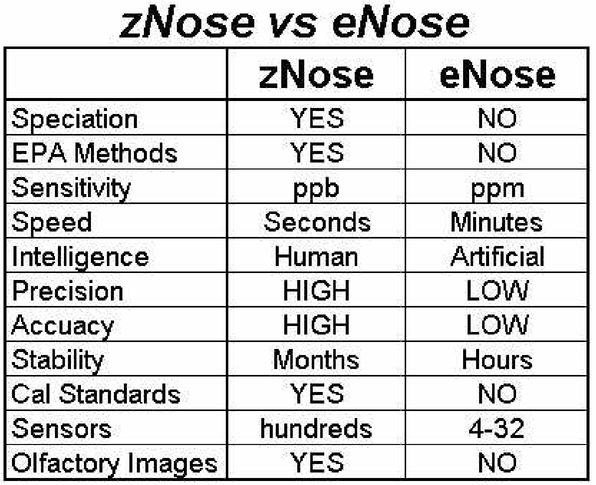
An array of sensors simulating the human olfactory response has become known as an electronic nose [1]. Electronic noses, called eNoses, utilize non- or weakly specific arrays of physical sensors to produce an N-dimensional response (where N equals the number of sensors) of specific vapor mixtures (fragrances) and this response can be analyzed by principal component analysis. Unfortunately, eNoses using uncorrelated sensor arrays only produce chaotic patterns that cannot be recognized except with sophisticated computer software. Unable to speciate, this type of electronic nose can not be calibrated with chemical standards and therefore is not accepted for use in quantitative scientific methods of measurement.

The development of a solid state integrating GC detector [2] with direct column heating [3] has produced a different type of electronic nose, called a zNose™, which can be used to perform quantitative scientific testing in the field as shown in Figure 1.

Figure 1- The zNose™ being used to measure the concentration of volatile organics in water aquifer.

The zNose is able to speciate chemical vapors with precision, accuracy, and 10 second speed [4,5,6] and the performance of this new zNose™ technology has been verified by the US EPA Environmental Technology Verification (ETV) program [7]. These results demonstrate for the first time that an electronic nose can be used in the field to quantitatively characterize and measure environmental pollutants according to accepted scientific principles.

Features which distinguish the two types of electronic noses are tabulated in Figure 2. Because chromatographic speciation is achieved, calibration standards can be used according to EPA methods. Since only one physical sensor is used sensitivity is quite high with part per billion levels being typical for volatile organics in air or water. As expected with good chromatography, precision and accuracy are high. Unlike chemically coated sensors, which are known for their instability, the solid state GC detector is able to maintain calibration for months. Finally, the zNose is able to produce high resolution visual olfactory images which can be easily recognized by human operators.



zNose vs eNose

	zNose	eNose
Speciation	YES	NO
EPA Methods	YES	NO
Sensitivity	ppb	ppm
Speed	Seconds	Minutes
Intelligence	Human	Artificial
Precision	HIGH	LOW
Accuacy	HIGH	LOW
Stability	Months	Hours
Cal Standards	YES	NO
Sensors	hundreds	4-32
Olfactory Images	YES	NO

Figure 2- Comparison of zNose Vs eNose technology characteristics.

GC/SAW Electronic Nose

The new GC/SAW zNose™ quantifies the olfactory response by simulating hundreds of speciated chemical sensors spanning a continuous range (chromatogram) of retention time. The GC/SAW electronic nose system diagram is depicted in Figure 3. 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 concentrated 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.

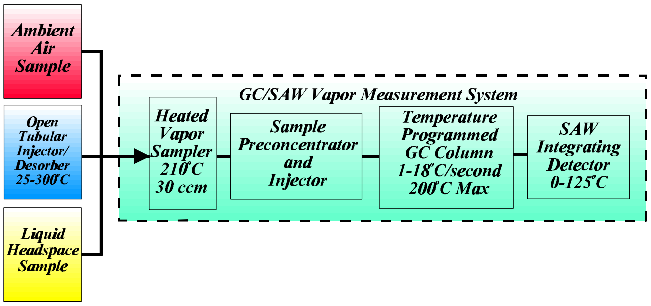


Figure 3- GC/SAW system diagram.

The GC/SAW electronic nose uses a two step process to analyze vapors. The first step samples ambient inlet vapors and concentrates them in a Tenax trap. Sample preconcentration is carefully controlled to produce a repeatable and accurate collection of ambient vapors for analysis in the second step.

In step 2 the trap is rapidly heated and release vapors are re-focused on the head of the relatively low temperature (40^{o}C) capillary column. Then the column temperature is programmed to follow a linear rise to its maximum temperature causing the different chemical species in the sample to be released, travel through the column, and collect on the surface of a temperature controled surface acoustic wave (SAW) crystal.

The SAW crystal, shown in the upper right of 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 crystal. 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.

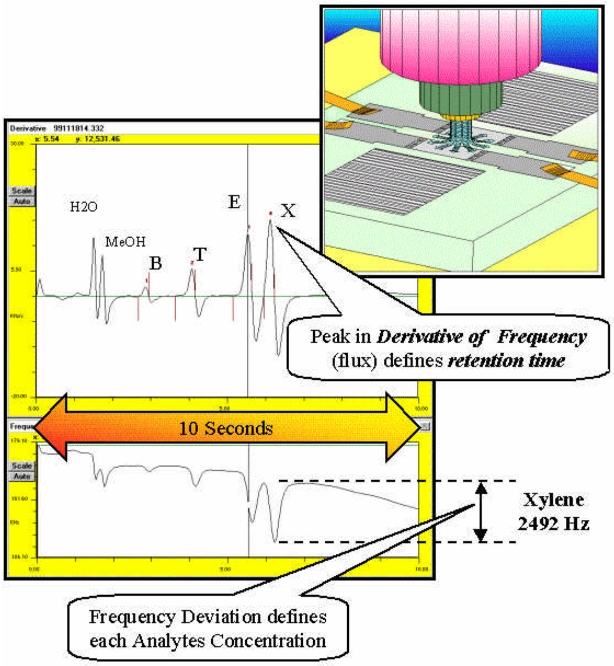


Figure 4- Absorption and desorption of analytes onto SAW crystal creates a frequency chromatogram (lower trace). The derivative of frequency chromatogram produces a flux chromatogram for determining retention time.

The complete GC system is contained in the handheld enclosure which is attached to a support module through an 8 foot umbilical cable. Only helium gas and electrical power is required to operate the system. An internal helium tank enables more than 300 chromatograms to be taken before refilling. 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

In a scientific measurement method, quality assurance is dependent upon reliable and accurate calibration standards. An accurate calibration standard can be created by filling tedlar bags from a certified high pressure tank of known vapor concentration. In Figure 5, a tedlar bag is filled with a known concentration of benzene-toluene-ethylbenzene-Xylene (BTEX) vapor which provides a reliable BTEX calibration standard.

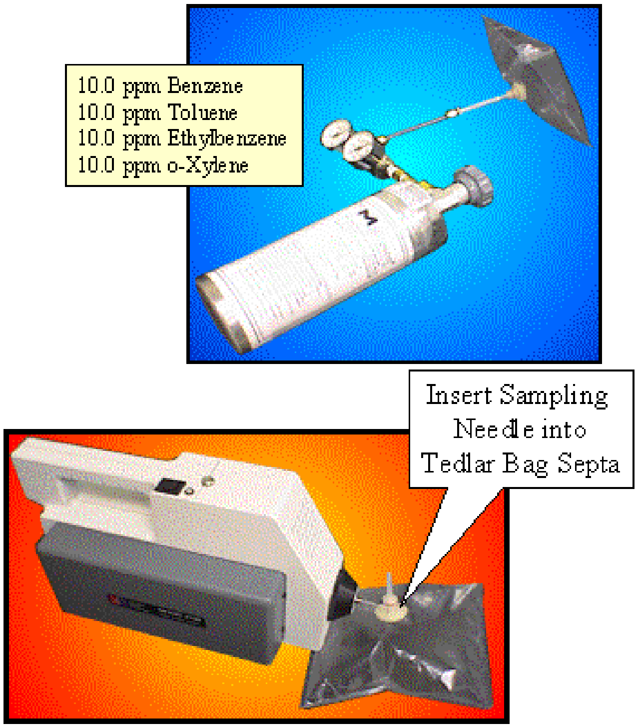


Figure 5-Using a certified tank of vapors to fill tedlar bags with standard concentrations of calibration vapors.

Because the GC/SAW can separate and speciate the individual analytes, calibration can be performed using a single measurement of a mixture of standard analyte concentrations. A typical zNose™ measurement of a mixture of BTEX, water, and methanol is shown in Figure 6. 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 [8].

It is clear that a virtual sensor array with as many chemical sensors as can be speciated can be created. Thus, for a chromatography system, chemical sensor space is defined mathematically by assigning unique retention time slots to each sensor. Once sensors have been defined the accuracy and precision of each sensor can be evaluated.

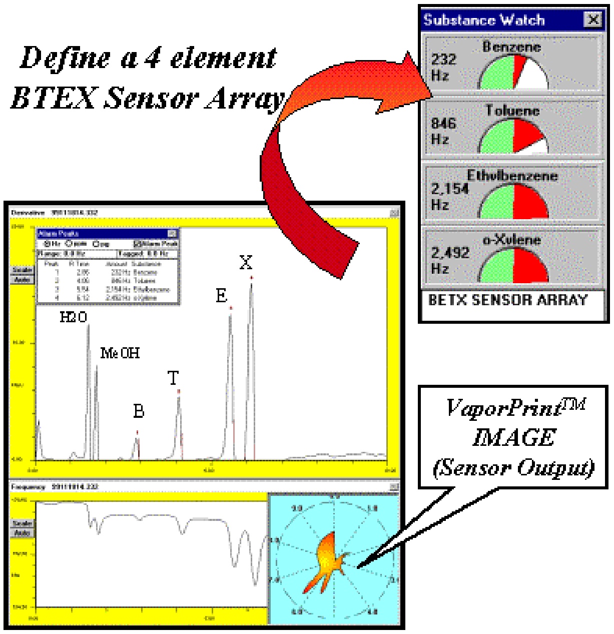


Figure 6- Creating a virtual sensor array for testing precision and accuracy.

Precision is the ability to repeat a measurement and accuracy is the ability to obtain the correct answer. In just one evaluation of accuracy and precision a series of seven identical measurements were performed on a tedlar bag containing a concentration of BTEX vapors spanning 182-364 ppb. The results of the 7 replicate measurements are shown in the lower table and include a calculation of standard deviation and minimum detection level (MDL) according to analytical testing methodology. In all cases the standard deviation of the measurements was less than 1-2%. For toluene, ethylbenzene, and xylene the MDLs were less then 10 ppb. For benzene, the MDL was approximately 20 ppb.

RAW DATA (7 Replicate Measurements)

	SAW Sensor Reading (Hz)						
Run Number	***1***	***2***	***3***	***4***	***5***	***6***	***7***
Benzene	232	234	238	239	236	232	243
Toluene	846	860	858	867	865	875	882
Ethylbenzene	2154	2162	2127	2154	2141	2152	2183
o-Xylene	2492	2521	2550	2527	2514	2536	2503

COMPUTED DATA

	Vapor Pressure (ppb)	***Average (Hz)***	***Std. Deviation (Hz)***	***Std. Deviation (%)***	***Min Det Level - ppb (3.143 x Std.Dev. x R.F.)***
Benzene	364	236.3	4.0297	1.7054%	19.5
Toluene	182	864.7	11.7433	1.3581%	7.8
Ethylbenzene	185	2153.3	17.3370	0.8051%	4.7
o-Xylene	185	2520.4	19.6372	0.7791%	4.5

Figure 7-Replicate measurements determine standard deviation which defines minimum detection level.

Because the SAW GC detector uses no coatings it is stable and very sensitive. Minimum detection levels for 10 common volatile organic compounds as determined by replicate measurements in air and water are listed in Figure 8.

	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.

VaporPrint™ Imaging

An important attribute of an electronic nose is the ability to produce visual olfactory images. Un-speciated sensor arrays must utilize principal component analysis techniques to recognize relatively coarse sensor patterns. This approach has had limited success and provides little or no information regarding the chemistry of the fragrance.

In contrast, a gas chromatograph is able to produce a coherent 10 second spectrum of the vapor pressure of the chemicals present in any odor or fragrance. A GC equipped with an integrating SAW detector can produce high resolution visual images of odor intensity as well.

The GC/SAW electronic nose mimics olfaction by producing visual sensory images called VaporPrints™. As an example images associated with fuel and gasoline are shown in Figure 9. High resolution (500+ pixel) visual images can be recognized by humans as well as computers. Such images allow a complex environment to be viewed and recognized as part of a previously learned image set.

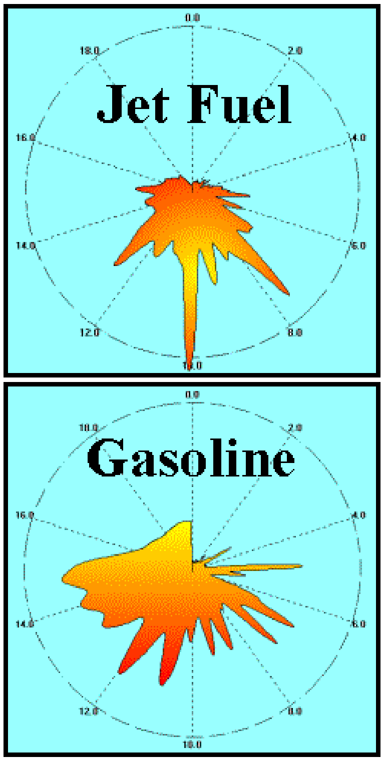


Figure 9- An olfactory image, called a VaporPrint™ , of jet fuel and gasoline. Radial amplitude is proportional to odor intensity.

Bacteria is known to produce characteristic odors and these too can be recognized from visual patterns. Shown in Figure 10 are images associated with e. Coli and Pseudomonas Aeruginosa bacteria in water. E. Coli frequently contaminates underground water aquifers from leaking septic tanks and Pseudomonas is often found in public swimming pools and spas.

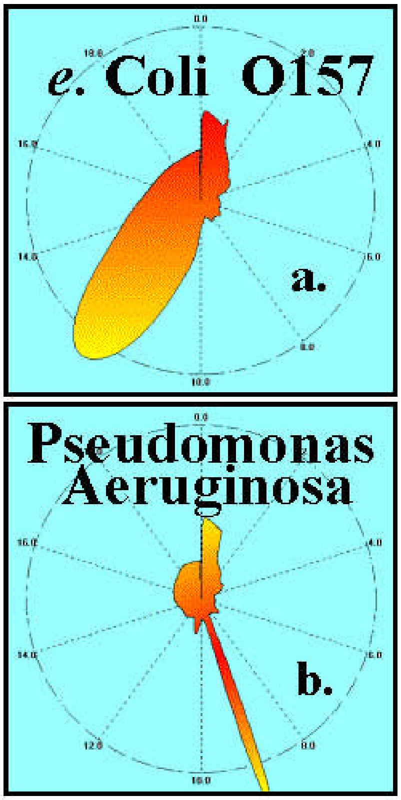


Figure 10- VaporPrint™ images of bacteria in water which can cause infectious disease .

A dramatic increase in olfactory perception is achieved in humans using a visual fragrance pattern response. The VaporPrint™ images show a large diversity between different odors. Their advantage is in their ability to provide an overall view of the odor or fragrance showing the vapor concentration and characteristic shape at a glance.

Environmental Applications

The number of environmental applications of the GC/SAW zNose™ are diverse and numerous. Because chromatography is an accepted analytical technique, GC/SAW technology is able to satisfy and follow accepted EPA testing methodology in the field. The ability to evaluate environmental pollution with precision and accuracy in the field in seconds, allows the zNose™ to analyze hundreds of samples per day on-site [9].

Water pollution is not limited to just rivers and streams but can extends to the oceans as well. One example is pollution which can occur surrounding off-shore oil well platforms and drilling operations.

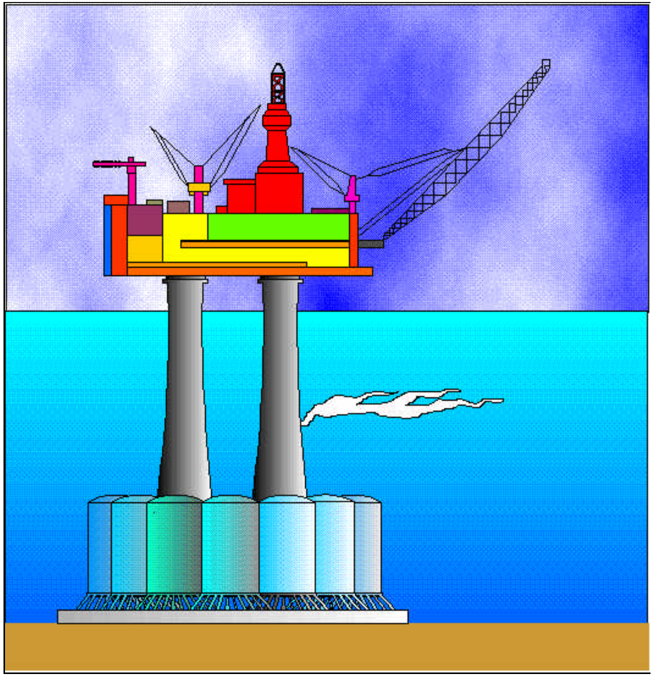
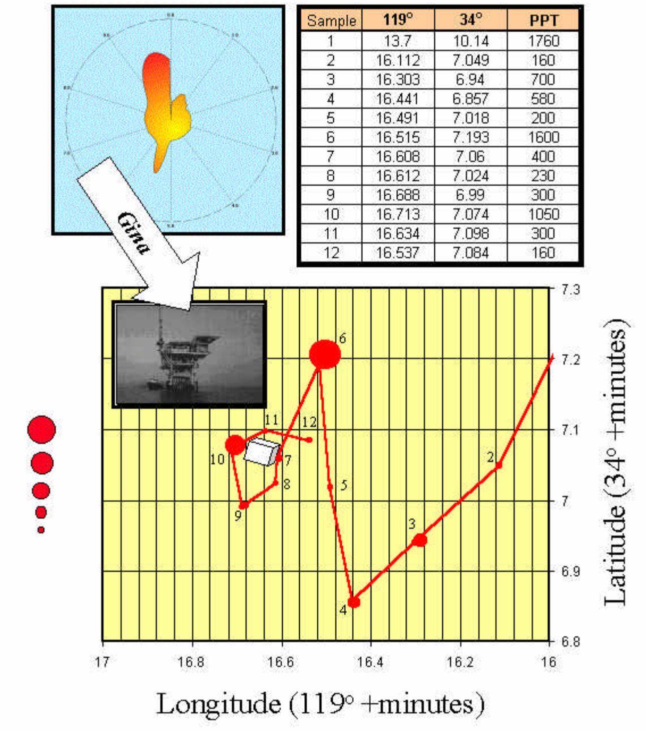


Figure 11-On-site investigations can be carried from a vessel at sea. In this example pollution surrounding was measured on-site from a sailboat using a GPS receiver.

To measure ocean contamination surrounding these sites 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 is very effective in creating a spatial plot of chemical concentrations as part of an on-site survey of pollution



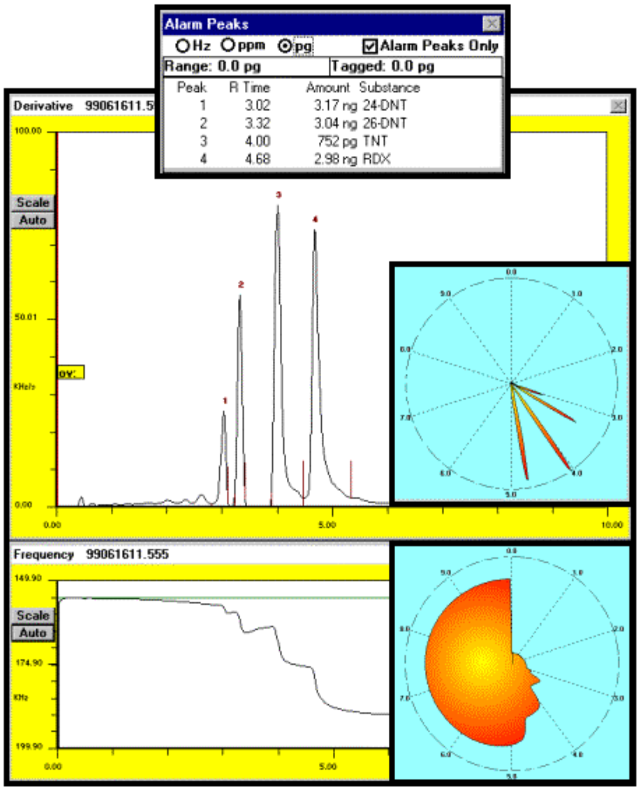
Sample	**119°**	**34°**	**PPT**
1	13.7	10.14	1760
2	16.112	7.049	160
3	16.303	6.94	700
4	16.441	6.857	580
5	16.491	7.018	200
6	16.515	7.193	1600
7	16.608	7.06	400
8	16.612	7.024	230
9	16.688	6.99	300
10	16.713	7.074	1050
11	16.634	7.098	300
12	16.537	7.084	160

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.

The detection of explosives and unexploded ordinance in the soil and water is another significant environmental problem for the world. Enormous quantities of explosives have been dumped onto military bases for the past 100 years both as expended ammunition and as waste from the manufacture of military ordinance. The cleanup job is enormous and electronic nose technology can speed up the remediation of these sites.

The GC/SAW can speciate and quantify vapor concentrations of multiple types of explosive compounds with a 10 second analysis period. For accurate soils measurements a solvent extraction of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitrotoluene (2,4-DNT) is used with direct injection.

Figure 13 shows a calibration response using a 1 microliter acetone injection of 2,4 DNT, 2,6 DNT, TNT, and RDX. A DB-5 microbore column was used with a programmed temperature ramp of 50^o to 170^{o}C at 18^{o}C/sec. The SAW detector was held at 30^o C. Sampling time was 30 seconds and all compounds eluted in less than 5 seconds.



Range: 0.0 pg

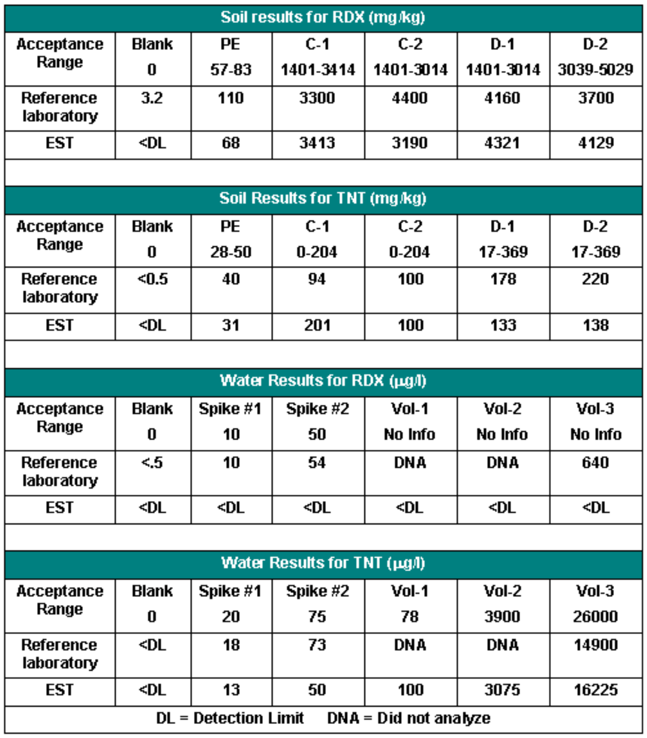
Tagged: 0.0 pg

Peak	R Time	Amount	Substance
1	3.02	3.17 ng	24-DNT
2	3.32	3.04 ng	26-DNT
3	4.00	752 pg	TNT
4	4.68	2.98 ng	RDX

Figure 13- Analysis of calibration standard containing 2,4 DNT, 2,6 DNT, TNT, and RD\X.

Six samples of soil and six samples of water were obtained from the EPA-ETV for analysis [10]. Each sample was measured twice and the results were returned to the EPA for scoring. The returned scores were compared with an anticipated result and a reference laboratory result. Each set of samples was also sent to a reference laboratory for analysis using HPLC Method 8030.

Figure 14 shows the data returned from the ETV Program team after compiling the submitted results. The table is divided into four areas, TNT and RDX in both soil and water. No DNT isomers were found in EST's data or the reference lab results. The acceptance range is bracketed to show a range of acceptable results and in all cases the GC/SAW analysis was either within or very close to the reference laboratory results.



Soil results for RDX (mg/kg)						
Acceptance Range	Blank 0	PE 57-83	C-1 1401-3414	C-2 1401-3014	D-1 1401-3014	D-2 3039-5029
Reference laboratory	3.2	110	3300	4400	4160	3700
EST	<DL	68	3413	3190	4321	4129

Soil Results for TNT (mg/kg)						
Acceptance Range	Blank 0	PE 28-50	C-1 0-204	C-2 0-204	D-1 17-369	D-2 17-369
Reference laboratory	<0.5	40	94	100	178	220
EST	<DL	31	201	100	133	138

Water Results for RDX (µg/l)						
Acceptance Range	Blank 0	Spike #1 10	Spike #2 50	Vol-1 No Info	Vol-2 No Info	Vol-3 No Info
Reference laboratory	<.5	10	54	DNA	DNA	640
EST	<DL	<DL	<DL	<DL	<DL	<DL

Water Results for TNT (µg/l)						
Acceptance Range	Blank 0	Spike #1 20	Spike #2 75	Vol-1 78	Vol-2 3900	Vol-3 26000
Reference laboratory	<DL	18	73	DNA	DNA	14900
EST	<DL	13	50	100	3075	16225

DL = Detection Limit DNA = Did not analyze

Figure 14- Comparison of GC/SAW and reference laboratory results using samples supplied by the US EPA-ETV Program Office.

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 GC/SAW electronic nose is fast (10 seconds), operates over a wide range of vapor concentrations, has picogram sensitivity, and is simple to use and calibrate.

Using visual olfactory images and 10 second chromatograms to quickly vapors and odors while simultaneously speciating and quantifying analytes is useful in many environmental monitoring applications involving air, water, and soil.

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. Quality control of virtually any environmental measurement can be 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.

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