DETECTION OF EXPLOSIVES IN SOIL AND WATER WITH AN ELECTRONIC NOSE

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abstract

An Electronic Nose using fast gas chromatography (GC) and a Surface Acoustic Wave (SAW) resonator detector for the detection of explosives is described. The Model 7100 Vapor Analysis System provides a quantifiable response to multiple types of explosives simultaneously in a 10-30 second analysis. Extraction of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) from soil and/or water were easily obtained in minutes allowing the system to operate under field conditions. In this paper the sensitivity, accuracy, and precision of the SAW detector system will be presented.

The traditional electronic nose produces an olfaction response consistent with an array of sensors. However, the instability of the array sensors severely limits the usefulness of the array type system. The time-slice nature of digitized gas chromatography allows the SAW detector to simulate the response of a multi-sensor array with the number of sensors equal to the total number of time slices. Calibration is possible using a single standard solution for each compound or multiple compounds. With part per billion sensitivity to volatile organics and picogram sensitivity to semi-volatiles such as explosives, the Model 7100 qualified for field testing of explosives in soil and water under a U. S. EPA sponsored ETV program.

BACKGROUND

The detection of explosives in the soil and in water is a significant problem for the U.S. government and the populous at large. 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 any new technology which can speed up the characterization or remediation of these sites will have an enormous impact on the quality of these sites and the surrounding communities in the future. The U.S. EPA has undertaken the task of evaluating new technology for use in environmental areas of interest to both the federal, state and local governments through a program called the Environmental Technology Verification (ETV) Program. Electronic Sensor Technology (EST) has participated in two of these programs in the past several years. The first was the detection of polychlorinated biphenyls (PCBs) [1] in soils and the second was the wellhead monitoring of volatile organic compounds (VOCs) in ground water [2]. This versatile technology is briefly described below and the methods for detection of explosives in soil and water are presented.

The SAW Detector

Significant research has been performed with chemical coatings applied to Surface Acoustic Wave (SAW) crystals. A common approach is to expose an array of SAW crystals with different polymer coatings to the vapor to be characterized. In theory each polymer coating will adsorb the vapors differently and by comparing response patterns from the array of sensing crystals, identification can be accomplished. However, polymer coatings reduce the sensitivity of the SAW crystal and limit detection to nanogram levels. Further loss in sensitivity results because the collected vapor sample must be split between many sensing crystals. The lack of specificity of polymer coatings means that in general each coated crystal response overlaps the response of other crystals to some extent and in this case pattern recognition with over-lapping responses is very difficult. Coated crystals also suffer from long analysis times because of the need for the analyte to diffuse into and out of the coating.

A unique type of SAW vapor detector with picogram sensitivity and which does not use polymer coatings was developed [3] to solve the problems of slow response and low sensitivity. As a detector for use in a high speed gas chromatograph, the SAW detector is ideal. The detector has zero dead volume that maximizes its response to low levels of transient vapors. The detection area is approximately the same size as the inside diameter of a capillary column so that all the column effluent can be collected onto the sensor. The sensing crystal comprises a very high Q SAW resonator placed in contact with a small thermoelectric cooling element. A thermoelectric element provides the precise control of cooling needed for vapor adsorption and simultaneously the ability to clean the crystal using thermal desorption when needed.

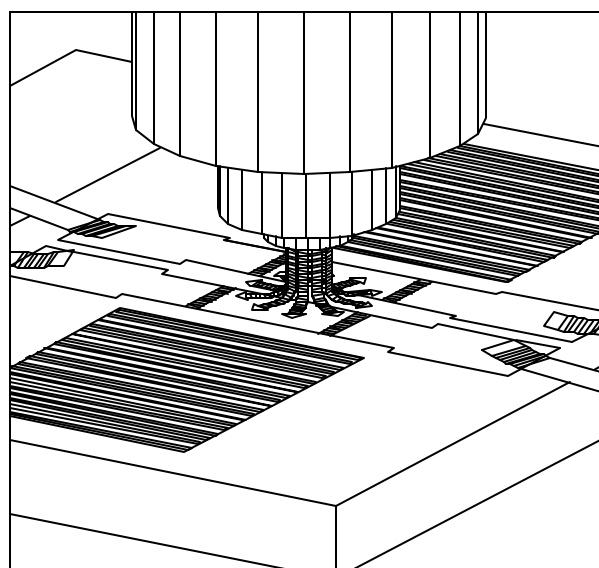The focused SAW resonator sensing element provides

Figure 1- GC/SAW nozzle interface showing interaction of column and acoustic cavity.

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part per billion sensitivity for volatile organics and part per trillion sensitivity for semi-volatile compounds. The crystal operates by maintaining highly focused and resonant surface acoustic waves at 500 MHz on the face of a single crystal quartz chip. By focusing the vapor through a micro-nozzle as shown in Figure 1, picogram sensitivity can be achieved. This result [4] is 1000 times lower than SAW crystals coated with polymers. Because the crystal is manufactured from single crystal quartz without polymer coatings, long term stability and precision is achieved over a wide temperature range.

GC/SAW Fast Chromatography System

By combining SAW detectors with high speed temperature programmed chromatographic columns, specificity over a wide range of vapors at the part per billion level in near real time (10 seconds) has been achieved [5]. The GC/SAW offers the advantages of a low cost solid state detector and the specificity of a temperature programmed GC column.

The major elements of a GC/SAW vapor detection system are shown in Figure 2. The analysis is performed in two steps corresponding to the two positions a GC valve. In the sample position vapor to be tested passes into a heated inlet where it is adsorbed onto sample preconcentrator loop trap. The trap contains absorbent specific to the desired analyte (e.g. Tenax) or for higher molecular weight compounds may be an open metal tube. Selection of sample time and flow rate determines the total amount of airborne vapors collected in the loop trap.

Figure 2-SAW/GC Detection System
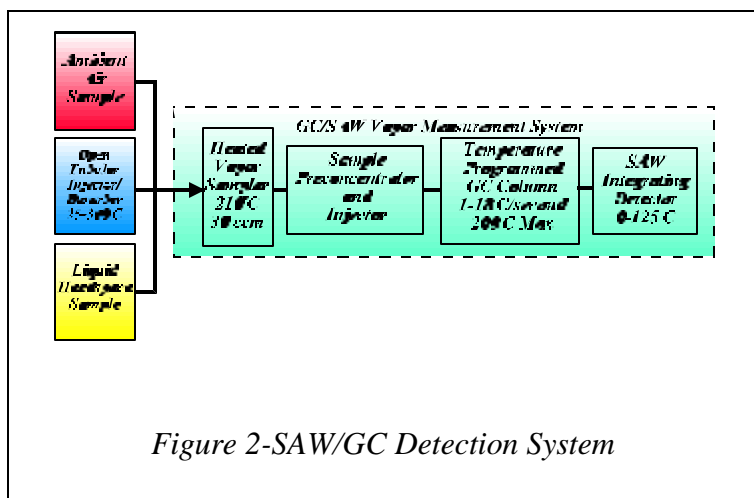
The GC valve is rotated to an inject position and the loop trap is rapidly heated by a capacitive discharge which causes trapped vapors to be transferred to the GC column via helium carrier gas. These vapors re-condense on the inlet of a chromatographic column held initially at low temperature. A microprocessor then applies a linear temperature ramped heating profile to the GC column. The column separates the injected compounds so they are eluted at different times where they then condense on the SAW crystal and are detected as frequency changes. The frequency is sampled at high speed and digitized as discrete time slices. The display of the derivative of these slices versus time gives a traditional chromatogram. However, each time slice is independent from those in proximity to it and can be viewed as a separate sensing element. These elements taken together make up a virtual array. When the system is used in this way, it is identical to an Electronic Nose with hundreds of sensors. It generates an output that is a visual representation of the sum of all the sensors called a Vaporprint™.

The Model 7100 GC/SAW system used in this study is shown in Figure 3. A laptop computer (not shown) provides a fully integrated user interface in a Windows 95 operating environment. The system was used to evaluate samples of soil and water as a prescreening assessment to participate in a U.S. EPA sponsored ETV program. The positive results presented here resulted in an invitation to participate in a field study taking place in Tennessee. Past field testing of similar systems has demonstrated the ability to detect a wide range of compounds including drugs, explosives, volatile organics, polychlorinated biphenyls, and dioxins [6,7]. Part per billion (picogram) sensitivity and field performance of the new technology has been validated by the Office of National Drug Control,

Figure 3 - The 7100 Vapor Analysis System

the Department of Energy, and the U.S. Environmental Protection Agency (EPA-ETV).

MATERIALS

Testing was performed on four explosives in soil and water. The explosives were shipped, stored on ice, direct from the ETV program sponsors. Six samples each in both matrices were evaluated. The samples consisted of a blank, a performance evaluation sample and four real world samples from two government owned facilities. The water samples were taken from the Volunteer Army Ammunition Plant in Chattanooga, Tennessee and the soil samples from the Louisiana Army Ammunition Plant in Shreveport. Louisiana. Calibration materials were obtained from AccuStandard (New Haven, Connecticut) as low concentration of individual compounds in acetone. All other solvents were reagent grade.

TESTING METHODS

Calibration

Calibration was performed on the instrument to determine the response factor for each of the anticipated explosive materials. Dilutions were made by injecting various volumes of the standards into 1 ml of acetone. The compounds were then injected as 1 μl aliquots directly into the instrument inlet during a 30 second sampling phase.

Figure 4 shows a typical chromatogram of a mixture of the four explosives injected directly into the inlet of the 7100. The injected levels were between 300 and 1200 pg. The column was ramped from 50 to 170°C at 18°C/sec and the detector was held at 30°C during the analysis. Sampling time was 30 seconds and the same conditions were maintained for the entire study. The data analysis for each run was completed in 10 seconds with the last peak of interest eluting in less than 5 seconds.

Data for the direct injection of the explosives RDX, TNT, 2,6 DNT and 2,4 DNT into the 7100 are shown in Table 1. The plotted results the calibration of the system are shown in Figure 5. TNT and 2,6 DNT show linear response over the range anticipated for the unknown samples. 2,4-DNT shows saturation of the trap at

higher concentrations. This is due to its higher volatility and the very small breakthrough volume of this compound in the trap used in the instrument. The decreasing response of RDX with lower concentration is probably due to loss of material on cold surfaces at the low concentrations.

Soil Analysis

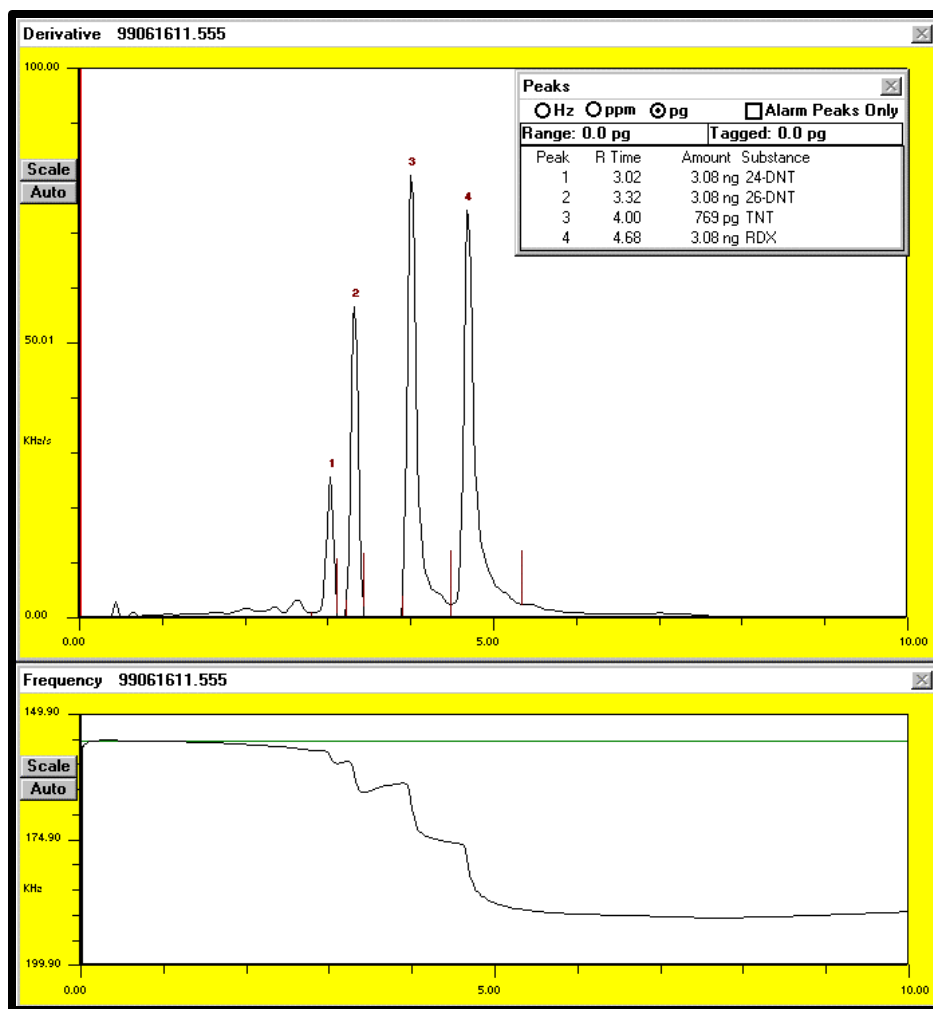| Peaks			
○Hz ○ppm ⊙pg			□Alarm Peaks Only
Range: 0.0 pg		Tagged: 0.0 pg	
Peak	R Time	Amount	Substance
1	3.02	3.08 ng	24-DNT
2	3.32	3.08 ng	26-DNT
3	4.00	769 pg	TNT
4	4.68	3.08 ng	RDX

*Figure 4 - Typical chromatogram of injection of explosives.. Upper race is
the derivative of the frequency data shown on the lower trace.*

Soil was analyzed by weighing 1 gm of soil into a 2 ml vial. One ml of acetone was added to the vial and the mixture was shaken vigorously for 3 minutes and then centrifuged. A known quantity of liquid was then extracted and measured into a new vial where it was diluted up to 1000:1 with acetone. One micro liter of diluted liquid was then injected into the inlet of the 7100. Inlet temperature was maintained at 200°C.

Reference	24-DNT	26-DNT	TNT	RDX	
'99061610.445	1321	1784	2561	1675	TNT/others
'99061610.481	1131	1512	1910	1372	TNT/others
'99061610.514	1304	1668	2123	936	TNT/others
'99061610.550	1309	1680	1983	1354	TNT/others
'99061610.585	1233	1476	1588	1452	TNT/others
average	**1259.6**	**1624**	**2033**	**1357.8**	
rsd	**6.3**	**7.9**	**17.4**	**19.7**	
'99061611.020	1871	2496	3882	3481	TNT/others
'99061611.053	2011	3010	4355	3039	TNT/others
'99061611.091	1820	2447	3743	3303	TNT/others
'99061611.324	1676	2595	4283	2894	TNT/others
'99061611.355	1765	2562	3296	2469	TNT/others
average	**1828.6**	**2622**	**3911.8**	**3037.2**	
rsd	**6.8**	**8.6**	**11.0**	**12.9**	
'99061611.422	2719	5949	9998	10310	TNT/others
'99061611.455	2543	6450	9496	10648	TNT/others
'99061611.485	2976	8882	11212	13547	TNT/others
'99061611.523	2761	5708	9178	8060	TNT/others
'99061611.555	2536	6092	11292	11636	TNT/others
average	**2707**	**6616.2**	**10235.2**	**10840.2**	
rsd	**6.7**	**19.6**	**9.5**	**18.5**	

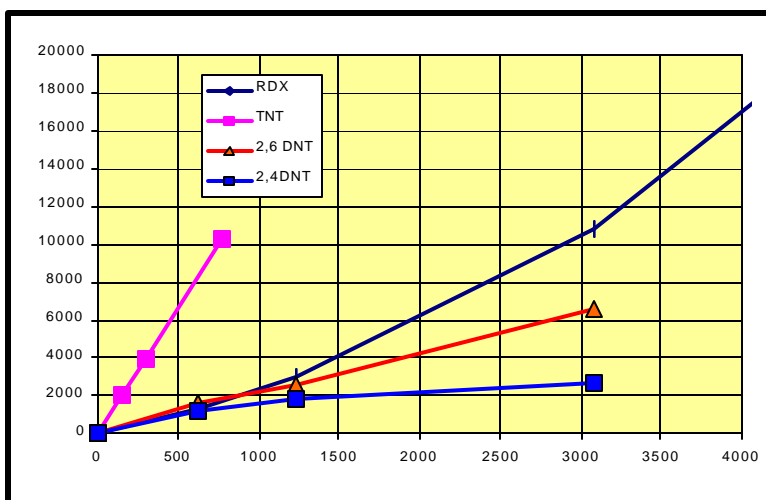*Table 1 – Summary of the calibration data for the direct injection of explosives.*

Figure 5 - Calibration Curves for four explosives. The x-axis is the number of pg injected, the y-axis is the signal from the instrument in Hz.

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Analyte recovery for the soil method was tested by spiking 1 gm of soil with 1 micro gram of TNT. The TNT was extracted as described above and then 1 micro liter (1 ng TNT) was injected. Average recovery over three samples was 109% with an RSD of 16% which was considered acceptable.

The method detection limits (MDLs) for the soil method were 488 µg/kg (ppbm) for 2,4-DNT, 463 µg/kg for 2,6-DNT, 15 µg/kg for TNT and 200 µg/kg for RDX. These values were well within the anticipated re-quirements of the ETV program. The MDLs of the two DNT isomers could be improved by using a different trap. The RDX MDL is limited by the loss of the compound at low levels of concentration.

Water Analysis

Water was analyzed using Supelco (Bellefonte, Pennsylvania) Sep-Pak RDX SPE cartridges. Each cartridge was conditioned by running 15 ml of acetonitrile followed by 30 ml reagent grade water through it at 10 ml/minute. 100 ml of the water sample was then drawn through the cartridge at the same rate using an adjust-able valve and a vacuum system to maintain flow. The cartridge was then flushed with 5 ml of acetonitrile re-sulting in a 20:1 concentration step. One micro liter of the extract was then injected into the 7100.

Analyte recovery for the water method was tested by spiking 100 ml of H_2O with 40 µg of TNT and then ex-tracting the explosive using the above method. Recovery exceeded 100% in two out of three attempts with the failure due to a mistake in the extraction process. These results were again deemed adequate to analyze the unknown samples.

The MDLs for the water method in µg/l (ppbv) were 24.4 for 2,4-DNT, 23 for 2,6 DNT 0.75 for TNT and 10 for RDX. Method detection limits for the water were limited by the 100 ml initial sample size. Using 500 ml samples as suggested in the Supelco literature would have given a larger concentration and enhanced the MDLs by a factor of 5.

RESULTS

The ETV program team submitted six samples of soil and six samples of water for analysis. 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. The anticipated result was known either due to spiking the sample with a known quantity of explosive (PE samples) or by previous measurement of the levels of explosives in these or similar soils. Each set of samples was sent to a reference laboratory for analysis using HPLC Method 8030.

Table II 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. In several cases the results obtained by the reference laboratory were not within the anticipated range, indicating that there is some problem with the reference lab or the comparison methodology. The results do show that for TNT and RDX in soil, the 7100 analysis was either within or very close to the anticipated result. The re-sults for water were also considered quite good for the TNT data. The RDX results were uniformly low and reported as below the detection limit. Some of the samples were well above the MDL of 10 µg/liter for RDX and yet were not detected. The extraction of RDX from Sep-Pak cartridges will be evaluated further during future testing.

TABLE II					
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 (mg/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 (mg/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					

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VAPORPRINTS

The 7100 is a quantitative instrument for the detection of vapors in a variety of matrices. However, the qualitative nature of an electronic nose is sometimes advantageous when a measurement of the difference between two samples is required but the exact nature of the difference is not fully understood. The VaporPrint is a visual way of presenting chromatographic information so that the human eye can more easily participate in the "pattern recognition" process. Figure 6 is a derivative VaporPrint of the explosive mix shown in Figure 4. The unique nature of this display is subject to the relative concentrations of the several components making up the mix. However, for some compounds, the relative distribution of the components is fixed and the resulting VaporPrint is unique. A frequency VaporPrint of gasoline is shown in shown in Figure 7 as a comparison. The dual nature of the 7100 as both a precision high speed gas chromatograph and multisensor electronic nose makes it a unique instrument for the analysis of vapors.
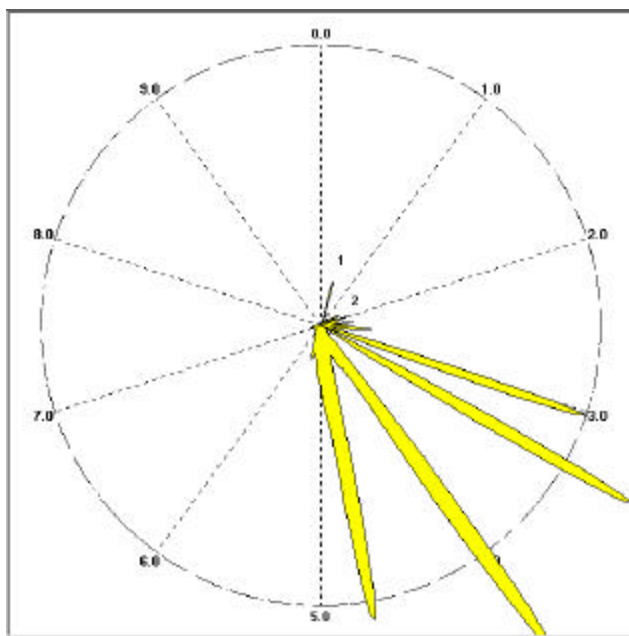

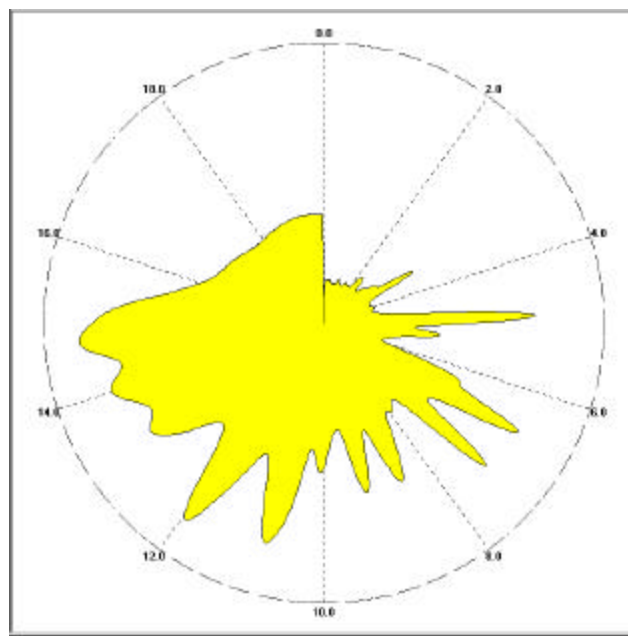*Figure 6 – Derivative VaporPrint of the explosive mix shown in Figure 4.*

Figure 7 – Frequency VaporPrint of a headspace sample of gasoline vapor.

SUMMARY AND CONCLUSIONS

The characteristics of a semi-portable instrument for the detection of vapors in air, water and soil has been described. The use of the instrument for the detection of explosive has shown that the 7100 can be used for rapid screening of soil and water for explosives at the µg/kg and water at the µg/l concentration level. Furthermore the instrument was used in a blind test sponsored by the U.S. EPA ETV program and was qualified as an acceptable technology to participate in a comprehensive field study of explosives in soil and water. The instrument can perform an analysis in just 10 seconds after injection of the sample. The fast response of the instrument also qualifies it as an Electronic Nose with the advantage that it has stable sensors that do not drift and do not require constant calibration.

REFERENCES

1 Dindal, Amy B., Bayne, Charles K. and Jenkins, Roger, A. - Oak Ridge National Laboratory and Billets, Steven and Coglin, Eric N. – U.S. EPA, "Environmental Technology Verification Report - Measurement of PCBs in Soils and Solvent Extracts," August 1998.

2 Einfeld, Wayne, Sandia National laboratory and Billets, Steven and Coglin, Eric N. – U.S. EPA, "Environmental Technology Verification Report - Measurement of Chlorinated Volatile Organic Compounds in Water," November 1998.

3 United States Patent No. 5,289,715, Vapor Detection Apparatus and Method Using an Acoustic Interferometer.

4 E. Staples, G. Watson, and W. Horton, "Spectral Density of Frequency Fluctuations in SAW Sensors," 186th Meeting of the ElectroChemical Society, Miami Beach, Florida, October 9-14, 1994.

5 Edward J. Staples and Gary W. Watson , "GC/SAW Non-Intrusive Inspection System", White House Conference, Office of National Drug Control Policy, New Hampshire, October 1995.

6 G.W. Watson and E.J. Staples, "SAW Resonators as Vapor Sensors," Proceedings of the 1990 Ultrasonics Symposium, pp.311-314, 90CH2938-9

7 G.W. Watson, W. Horton, and E.J. Staples, "GAS Chromatography Utilizing SAW Sensors," Proceedings of the 1991 Ultrasonics Symposium, pp.305-309.