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Field Portable Detection of VOCs Using a SAW/GC System

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By
Francis Chang
Edward J. Staples

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For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Amerasia Technology, Inc.
2301 Townsgate Road
Westlake Village, California 91361

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1. Executive Summary

This report describes research on a fast GC vapor analysis system which uses a new type of Surface Acoustic Wave detector technology to characterize organic contamination in soil and groundwater. The project was sponsored by the Department of Energy, Morgantown Energy Technology Center, whose mission, in addition to other goals, is the development of tools and methods for characterization, remediation, and monitoring of underground environmental conditions..

The research tasks were to demonstrate delectability and specificity of a Surface Acoustic Wave Gas Chromatograph (SAW/GC) to a representative number of VOC materials followed by field demonstrations of the new technology at a DOE site. All tasks of the project were successfully carried out and a fast vapor analysis system based upon a new type of Surface Acoustic Wave detector technology was developed. The prototype analyzer has the ability to characterize organic contamination in soil and groundwater at the part per billion level in less than 10 seconds.

The detector is unique because it utilized an uncoated quartz crystal, contrary to current developments of using coated crystals. The uncoated SAW detector demonstrates very high sensitivity to very low detection levels, and integrated with chromatography provide speciation of compounds in less than 10 seconds. Compared through split-sampling analysis, the instrument maintains an error band of less than 20%.

Field tests were held at the DOE Savannah River, Idaho National Engineering Laboratory, Lawrence Berkeley, and Hanford sites. The performance of the SAW/GC analyzer was validated by comparing results taken with an on-site HP Chromatograph. Tests were performed with water, soil and gas samples. By these tests the SAW based analyzer demonstrated the ability to identify and quantify the presence of VOCs, PCBs, dioxins, and furans in less than 10 seconds.

Research findings demonstrated a high degree of specificity and with sensitivity at the picogram level. The SAW/GC satisfies the need for a field portable solid state analyzer with the ability to identify and quantify VOCs, PCBs, and dioxins over a concentration range of ppb to over 1000 ppm in near real time (e.g. < 10 seconds).

The advantages of the SAW/GC are portability, accuracy, and speed. The new surface acoustic wave sensor demonstrated sufficient specificity and sensitivity to be used as a fast trace analyzer or screening tool at DOE remediation sites. Using the SAW/GC analyzer as a field screening tool, cost savings over current techniques are estimated to be more than $50,000 per month.

Recommendations for further research are (1) to expand field demonstrations and data gathering to many other DOE sites, (2) to develop field test protocols compatible with EPA methods for screening DOE mixed waste with the SAW/GC, and (3) and to evaluate SAW/GC technology as a fieldable screening tool for dioxins and PCBs.

2. Introduction

Current piezoelectric or bulk acoustic wave (BAW) sensors, Lamb-wave sensors and shear mode plate sensors do not simultaneously have sufficient specificity and sensitivity for use as trace analyzers at DOE sites. The main problems for such sensors are low sensitivity and low or non-existent specificity at low concentrations. Typical field methods still employ tedlar bag sample collection followed by analysis with a gas chromatography system. Laboratory instruments do possess the required sensitivity and specificity, however in general they are not field portable and analysis time is slow, typically 20 minutes or more per sample. There is a need for a field portable solid state analyzer with the ability to identify and quantify VOCs over a concentration range of ppb to over 1000 ppm in near real time (e.g. < 10 seconds).

This report describes research on a fast GC vapor analysis system which uses a new type of Surface Acoustic Wave detector technology to characterize organic contamination in soil and groundwater in less than 10 seconds. The project was sponsored by the Department of Energy, Morgantown Energy Technology Center, whose mission, in addition to other goals, is the development of tools and methods for characterization, remediation, and monitoring of underground environmental conditions. The original SAW/GC technology development was carried out under a Small Business Innovative Research grant[1] to detect contraband materials such as drugs of abuse and explosives. Contraband materials are generally characterized as non-volatile because of their very low vapor pressures.

As part of the Research Opportunity Announcement (ROA), the fast SAW/GC was modified to detect VOC materials. These materials possess much higher vapor pressures and required modification of the existing contraband detection technology. First the inlet vapor collection must be equipped with a different type of absorber and second the GC column must be selected for optimal separation of the target VOC materials.

At this time all planned modifications have been completed. Quantitative identification of multiple organic materials at the ppb level was demonstrated in the laboratory. Also the system has been validation tested at the DOE Savannah River Site where known amounts of volatile organic compounds (VOCs) contaminate soil and groundwater exist. Oversight for the field testing and validation activities was performed by Joseph Rossabi, a senior engineer for the Environmental Sciences Section of Westinghouse.

The fast SAW/GC may satisfy the need for future on-line well monitoring equipment and portable testing as part of an ongoing remediation effort at SRS. Successful demonstration of the new technology may lead to the development of more advanced instruments which are small, portable, low cost, and satisfy regulatory screening requirements.

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[1]U.S. Coast Guard Research & Development Center, Contract No. DTRS-57-91-C-00003.

3. Purpose

The objective of the research was to evaluate the performance of a Surface Acoustic Wave (SAW) sensor coupled to a high-speed gas chromatograph (GC) for the detection of volatile organic compounds (VOCs) at DOE sites. Phase I of the research program was to establish operational methods for using the existing breadboard detection system. In this phase selected VOC compounds were identified and minimum detection limits for these materials determined. Under an optional Phase II effort, the completed detection system was to be taken to a DOE field site and used to monitor the contamination level of selected compounds.

A tasked objective was to test specific VOC materials with the SAW/GC analyzer. Sources for information used in the selection of suitable VOC materials included the DOE contracting officer, several DOE environmental site personnel, and the contractor principal investigator. The materials listed in Table I were used to quantify the performance of the SAW/GC sensor system.

Table I- VOC Materials Tested

Material Name	Formula
Trichloroethylene	C_2HCl_3
Tetrachloroethylene	C_2Cl_4
Carbon Tetrachloride	CCl_4
Chloroform	$CHCl_3$
Dichloromethane	CH_2Cl_2
1,2-Dichloroethane	$C_2H_4Cl_2$
1,1,1-Trichloroethane	CH_3CCl_3
1,1-Dichloroethylene	C_2H2Cl_2
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$
Trichlorofluoromethane	CCl_3F
Benzene	C_6H_6
Toluene	C_7H_8
Gasoline	-
Diesel Fuel	-

Minimum sensitivity goals in terms of a minimum detectable vapor concentration (at 20°C) for the selected materials was calculated based upon a 5 cc sample volume and are tabulated in Table II. These minimum detectable vapor concentrations were calculated using the materials vapor pressure at 20°C, its molecular weight, density, the universal gas constant, a SAW sensitivity of 50 kHz per μliter of VOC in liquid phase, and a vapor sampling volume of 5 cc. The sensitivity limit is dependent upon the predicted minimum

in mass sensitivity for a focused adsorption of VOC vapors using a SAW/GC nozzle[2]. It should be emphasized that the SAW/GC detector system[3] does not absorb VOC vapors, but rather it utilizes the physical principles of adsorption rather than chemical interactions associated with absorption of VOC vapors (e.g. polyisobutidene coated SAW crystals[4]).

Table II - Minimum Sensitivity Goals

Material Name	Minimum Detectable Vapor Concentration (ppm)
Trichloroethylene	5.36
Tetrachloroethylene	4.71
Carbon Tetrachloride	5.00
Chloroform	5.98
Dichloromethane	7.52
1,2-Dichloroethane	6.00
1,1,1-Trichloroethane	4.82
1,1-Dichloroethylene	6.05
1,1,2,2-Tetrachloroethane	4.60
Trichlorofluoromethane	5.23
Benzene	5.41
Toluene	4.53
Gasoline	5.0
Diesel Fuel	5.0

VOC materials offered a new challenge and required different GC methods to accommodate the different physical characteristics of VOCs. The proposed system goal was to develop an instrument capable of delivering useful chromatograms in less than 20 seconds. Existing chromatogram analysis typically span 30 minutes to hours. Inclusive of sampling time, typically 5 to 10 seconds, the total system measurement should not exceed 30 seconds to be considered a successful innovation.

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

[3]G.W. Watson, W. Horton, and E.J. Staples, "Gas Chromatography Utilizing SAW Sensors," Proceedings of the 1991 Ultrasonics Symposium, pp.305-309, IEEE No. 1051-0117/91/0000-0311.

[4]G.C. Frye, S.J. Martin, R.W. Cernosek, K.B. Pfeifer, and J.S. Anderson, "Portable Acoustic Wave Sensor Systems, Proceedings of the 1991 Ultrasonics Symposium, pp.311-316., IEEE No. 1051-0117/91/0000-0311.

4. Background

A diagram showing the major elements of a SAW/GC system are shown in Figure 1. Ambient air to be screened is passed through a inlet water trap attached to the inlet of the system. After removal of water vapor, VOC vapors are absorbed in a loop trap which contains a mixture of suitable absorbents. After a suitable sample time, these materials are thermally desorbed and transferred into helium carrier gas and focused on to the head of the chromatographic column. A microprocessor applies a linear temperature ramp heating program to the GC column. The column separates the injected compounds in time. They are eluted from the column and are detected by a SAW crystal detector.

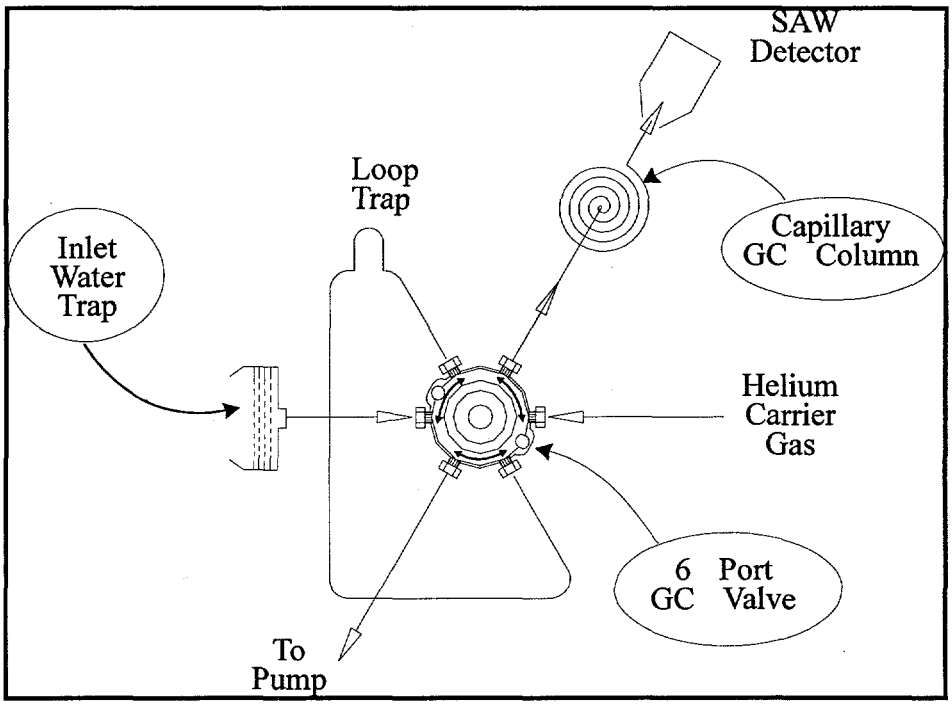

Figure 1- SAW/GC System Diagram showing major elements and their functional dependence.

A unique type of solid state GC detector, a SAW sensor, illustrated in Figure 2 has the ability to detect vapor quantities as small as one femtogram. The crystal itself maintains highly focused and resonant surface acoustic waves at a frequency of 500 Mhz on the face of a single crystal quartz chip. The stability of the resonance establishes a background noise floor for sensing vapors or aerosols which perturb the resonant frequency by changing the acoustic properties of the quartz surface. Which materials adsorb onto the surface of the crystal is determined by the temperature of the crystal. The temperature of the SAW sensing crystal is user controlled, 10°C to 100°C, and regulated by means of a thermoelectric cooler. Focused SAW resonator sensors have demonstrated dynamic ranges greater than 1 million and the ability to detect VOC vapors at the part per billion level without the need for polymeric films.

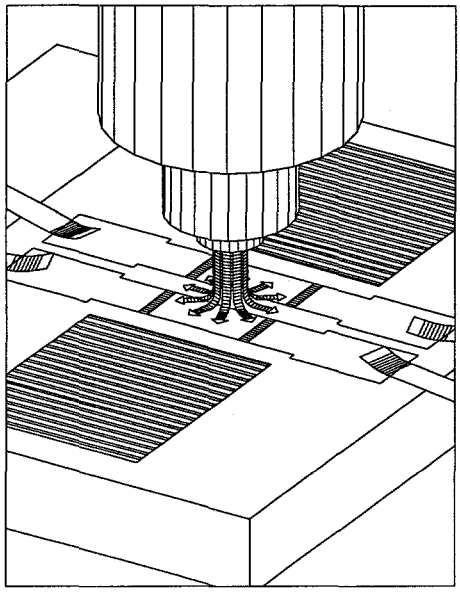

Figure 2- VOC vapors are focused by an exit nozzle onto a SAW resonator crystal detector.

A photograph of the current prototype SAW/GC system which was modified for VOC detection and tested is shown in Figure 3. The dimensions of the prototype are 20"x14"x24" and weight was approximately 50 pounds. The support cart contains the system electronics, N_2 and He gas bottles, and a laptop user interface for the system. The handheld SAW/GC module (not shown in the photograph) is attached to the module by means of a 6 foot umbilical cable. The system operates on standard 115 VAC power and power usage is rated at 200 watts maximum.

The prototype system was provided as a test platform and was only intended to validate the technology. Currently Amerasia Technology is now developing a portable system which will incorporate all of the findings and innovations derived from this project. The new system will be engineered into a portable unit half the size and weight of the prototype system shown.

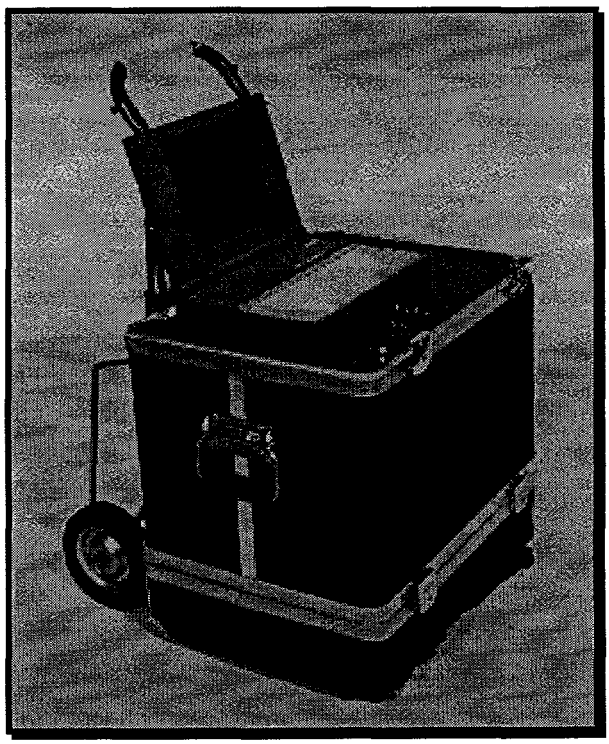

Figure 3- Prototype SAW/GC System provided for this project.

5. Results and Discussion - Phase I

The research began on June 21, 1994 with selection of suitable VOC test materials. After these materials were selected the prototype SAW/GC instrument was modified and optimized (Section 5.2) to detect them. These modifications required (1) selection and construction of a fast VOC column and (2) design and construction of a fast sampling preconcentrator.

5.1. Selection of VOC Test Materials

The first task of the project was to determine suitable VOC materials for testing the SAW/GC. Twelve single compounds were selected together with gasoline and diesel fuel, as representative of VOC materials found at environmental waste sites. Gasoline and diesel fuel represent complex mixtures of many different VOC materials and were intended to measure specificity and the ability of the system to differentiate and quantify multiple compounds within a soil matrix.

The materials selected represent a large range in density, molecular weight, boiling point, and vapor pressure at 20°C and this is evident in Table III.

Table III - VOC Material Characteristics

Material Name	Density (gm/cc^3)	Molecular Weight	Boiling Point (°C)	Vapor Pressure (ppm)
Trichloroethylene	1.464	131.39	86.9	75,000
Tetrachloroethylene	1.623	165.83	121	18,000
Carbon Tetrachloride	1.594	153.32	76.5	100,000
Chloroform	1.4832	119.38	61.7	182,000
Dichloromethane	1.327	84.93	40	452,000
1,2-Dichloroethane	1.235	98.96	83.47	206,000
1,1,1-Trichloroethane	1.337	133.41	74.1	126,000
1,1-Dichloroethylene	1.218	96.94	37.9	673,000
1,1,2,2-Tetrachloroethane	1.586	167.85	147	6,000
Trichlorofluoromethane	1.494	137.37	23.7	780,000
Benzene	0.879	78.12	80.1	107,000
Toluene	0.867	92.15	110.6	29,000
Gasoline[5]	-	95 avg.	-	340,000
Diesel Fuel	-	-	-	-

[5]Data for fresh gasoline obtained from **Soil Vapor Extraction Technology**, T.A. Pedersen and J.T. Curtis, Copyright 1991 by Noyes Data Corporation, Library of Congress Catalog Card Number: 91-12465, See pp.202-213..

5.2. Instrument Modification

During the period June 21, 1994 through September 30, 1994 research on suitable fast chromatography columns and preconcentrator was carried out. This phase of the project involved laboratory experimentation using a Varian Model 6000 gas chromatograph for SAW detector and capillary column validation. The VOC materials listed in table were obtained as either 500 ml neat samples or 1-5 gm neat samples depending upon their availability. These samples were used as a calibration samples to determine sensitivity, column retention times and column separation.

The laboratory Varian GC was set up to allow injections of the materials described above into the GC column and onto the SAW sensor crystal. This information gave preliminary scale factors for the detection of the various materials and allowed for the evaluation of SAW material detectability independent from other system parameters such as preconcentrator efficiency. Detector sensitivity was defined in terms of scale factor. Detector scale factor was defined as the ratio of the change in the SAW sensor frequency in Hz to the injected mass of an individual VOC material. Each material was introduced into the GC by bubbling nitrogen through the material in a glass impinging device. The vapor was carried into a 25 µl sample loop where it was injected onto the 10 meter DB-5 column. The total mass of the material injected was calculated by assuming saturated vapor in the sample loop.

Table IV shows a summary of SAW sensor results for the materials tested. The fourth column of the table is the expected signal in Hertz for a 1 ppm concentration in a 5 cc sample volume.

Table IV - SAW Sensor Results

Material	Retention Time[6], Sec	Injected mass[7], µg	Scale Factor[8] Hz/Ng	5cc sample[9] Hz/ppm	Vapor Pressure ppm
Freon-11	12.12	111.29	0.29	8.3	780,000
1,1 Dichloroethylene (DCE)	12.35	67.84	0.40	7.99	673,000
Dichloromethane (DCM)	13.26	39.9	0.48	11	452,000
1,2 Dichloroethane (DCA)	28.6	21.2	1.47	30.2	206,000
Chloroform (CF)	15.91	22.62	1.99	49.5	182,000
1,1,1 Trichloroethane (TCA)	16.48	17.45	2.35	65.14	126,000
Methyl Alcohol	12.79	3.85	1.51	10.0	116,000
Benzene	17.65	8.66	2.86	46.4	107,000
Carbon Tetrachloride (CT)	17.89	15.96	2.6	83.0	100,000
Trichloroethylene (TCE)	18.36	10.23	6.36	173.7	75,000
Toluene	24.52	2.8	15.5	297	29,000
Water	13.73	0.42	2.36	8.8	22,639
Tetrachloroethylene (PCE)	40.61	3.1	3.68	126.8	18,000
1,1,2,2 Tetrachloroethane	43.84	1.09	66.6	2,323	6,000

[6]Isothermal DB-5 Column, 100°C, 65°C nozzle

[7]Mass based upon saturated 25µliter volume.

[8]SF=GC peak area/injected mass

[9]Predicted peak area from 5cc volume with a 1 ppm vapor present.

The last column of Table IV shows the equilibrium vapor pressure of the various materials in descending order. The scale factor generally follows the inverse of this trend since the lower boiling materials are more likely to adsorb onto the SAW surface. Methanol and water fall outside the expected progression due to their lower molecular weight. As predicted, even the highest boiling material can be detected at the ppm level with a bare SAW crystal detector. **This result contradicts the previously held view that uncoated SAW devices cannot adsorb volatile compounds without polymer coatings**. In fact, experimental results suggest that SAW detectors have better signal to noise ratios without polymer coatings. This is because polymer coatings reduce the crystal Q which causes less frequency stability and hence greater detector background noise levels.

Laboratory experiments using gasoline and diesel fuels were also carried out. Figure 4 shows a gasoline vapors chromatogram obtained during the laboratory scale factor testing. This data was obtained by bubbling nitrogen through gasoline as described above. The upper trace is the derivative of the frequency, the lower trace is the frequency of the SAW as a function of time.

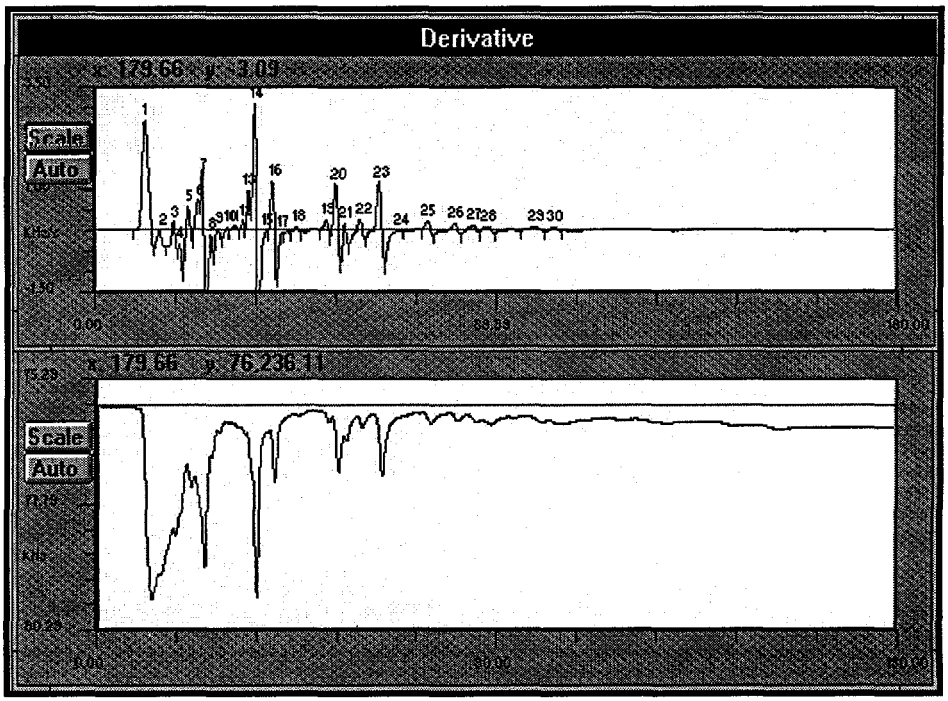

Figure 4 - Gasoline Vapor Chromatogram

Several different GC capillary columns were evaluated. For VOC work the excellent separation of DB-624 was confirmed and this column type was selected for incorporation into the final instrument. Retention time testing and characterization was carried out first on a 0.25 mm x 30 meter long DB-624 column. The VOC test vapors were injected using a 25 µl sample loop. Table IV shows experimental retention time data under isothermal column temperatures. The first column is the retention time in seconds

for all the compounds with the column at 100°C. The second and third columns show the retention time of several of the short and long elution time materials at 150°C and 200°C. The fourth column of the table is the signal in Hertz for the 25 microliter injected volume.

Tests of retention time for materials representing high to low boiling point materials provided data for development of a physical model to predict retention time for any column of arbitrary length. First the data was curve fit to the four compounds using the following relationship (Equation 1)for velocity as a function of temperature in the i-th compound.:

Equation 1: $$Vel(T,i) = g_i \bullet \exp\left(\frac{T-273}{\sigma_i}\right)$$

An accurate curve fit is obtained by subtracting the fixed delay of the column (approximately 88 seconds in this case) from the measured retention time. This is shown in Figure 5. The total retention time of the column for each material is obtained by

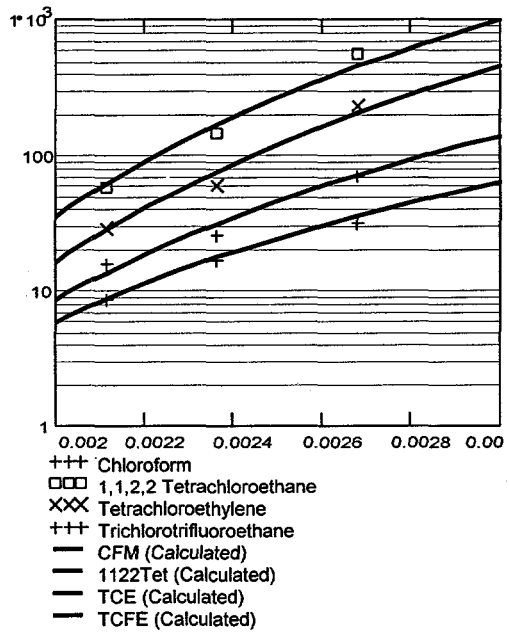

Figure 5- Retention time versus reciprocal temperature.

adding 88 seconds to the data of Figure 5.

The following relationship(Equation 2) was used to simulate a ramped column temperature as a function of time:

Equation 2: $$T(t) := To + \Delta t \cdot \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)$$

A simple ramp using a time constant τ=2 is shown in Figure 6. This speed is typical in performance to what the prototype SAW/ GC (Figure 3) system actually achieved.

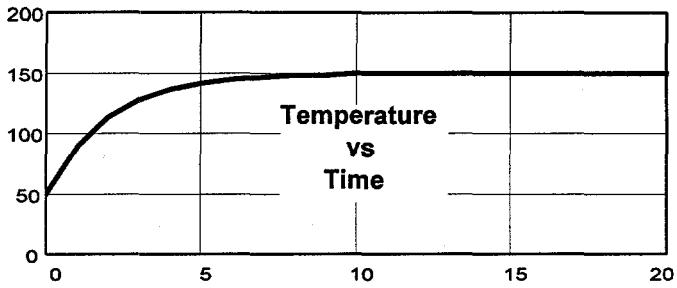

Figure 6-Column temperature versus time for τ=2.

Using the above relationship the velocity of each compound in the column as a function of time can be calculated and is shown in Figure 7. The actual velocity of each compound (Equation 3) is then given by:

Equation 3:

$$Vtota(t,i) := \frac{1}{\left(\frac{1}{VN \cdot \frac{100}{2.54}} + \frac{1}{ve(t,i)}\right)}$$

where VN is the fixed velocity in meters per second.

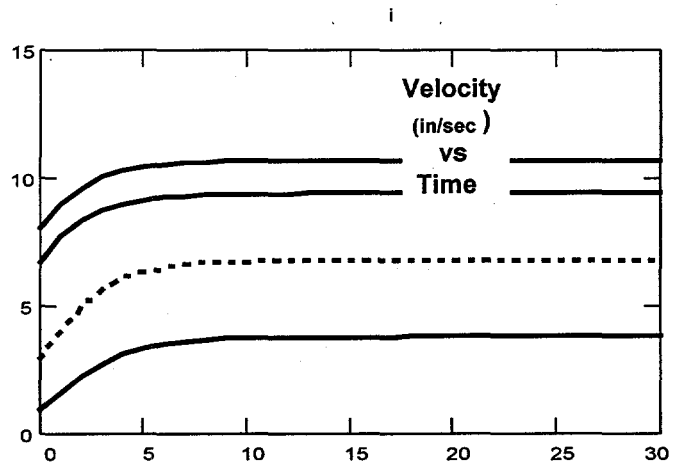

Figure 7-Velocity of each compound as a function of time.

Using velocity as a function of time, (Equation 4) the distance traveled through the column as a function of time found from the integral:

Equation 4:

$$x(t,i) := \int_0^t ve(t,i)\, d$$

This relationship enables prediction of the retention time for these compounds in a short column. For example, where the curves of Figure 8 intersect the top of the plot the retention time of a 25 inch column can be read off the bottom of the graph. 1,1,2,2 Tetrachloroethane will have a retention time of approximately 7.3 seconds. These relationships were used to predict column behavior for the selected compounds. For example the temperature ramp could be changed to a slower or faster time constant. Also, the maximum ramp temperature could be reduced to lengthen the retention time.

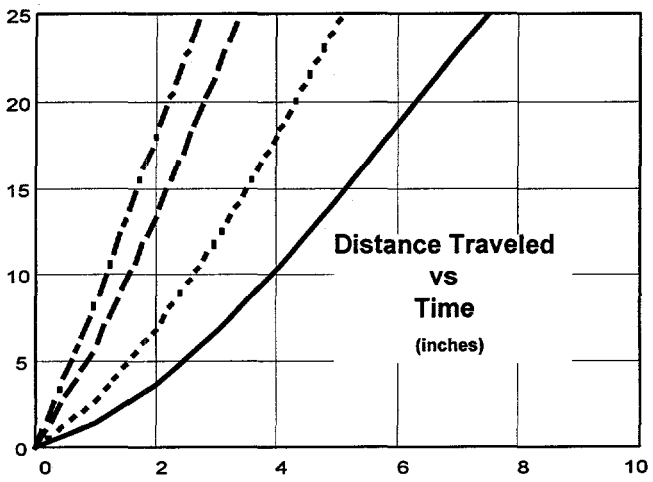

Figure 8- Distance traveled as a function of time for each compound. (based upon fitting retention time minus fixed delay)

Based upon these modeling results and confirmation by experimental data using the Varian GC system, a short DB-624 column was fabricated and installed in the prototype SAW/GC system. An initial column length of 32" was used and retention time of VOC vapors for two different carrier gas flow rates is shown in Table V .

Table V- DB 624 Column Results

Material	Retention Time (Flow rate 1.9 cc/min.)	Retention Time (Flow rate 5.6 cc/min.)
Toluene	9.88	3.68
Chloroform	3.80	1.36
1,1,2,2-Tetrachloroethane	39.68	15.56
Freon	2.16	0.76
Benzene	4.68	1.72
Carbon Tetrachloride	4.48	1.64
Dichloromethane	2.40	0.84
1,2-Dichloroethane	4.56	1.64
Tetrachloroethylene	12.76	4.84
1,1,1-Trichloroethane	4.16	1.52
1,1-Dichloroethylene	2.12	0.76
Trichloroethylene	3.80	2.20

5.3. Filtering and Preconcentration

An important element of the SAW/GC is the inlet trap. The prototype SAW/GC system required two types of inlet traps. The first trap is used to eliminate water vapor from the vapors being analyzed. The second trap is designed to preconcentrate the volatile organic vapors during sample time and to release inject them into the GC column. The original system did not contain a water trap and the preconcentration only trapped heavy, non-volatile materials such as drugs of abuse. During the laboratory phase of this project it was necessary to develop a water filter and a preconcentrator for VOCs.

Sensitivity to water for the SAW detector has been found to be quite low when compared to the other VOC materials (See Table IV). Nevertheless, in real operating environments relative humidity can be as high as 100% and this is equivalent to 20,000 ppm of water vapor. Using 8 Hz/ppm, an interfering signal as high 160 kHz could be present if water is not extracted from the inlet sample. Two types of inlet water trap (Nafion dryer type) were evaluated. One type consisted of a 0.063 inch O.D. tube of Nafion material which was encased in a plastic container of molecular sieve. The sample passing through the .063 inch tube gives up its water to the molecular sieve absorbent through the unique properties of the Nafion material. The other type was a coaxial arrangement with Nafion material down the center tube which carried the sample to be dried and an outer tube which confined a dry gas purge. The latter type lasts indefinitely but required a constant supply of dry purge gas, hence it was decided to use the dryer with molecular sieve absorbent. The resulting dew point of the sample gas was typically below -30°C after passing through either type of trap.

The prototype SAW/GC was equipped an inlet Nafion dryer filter. This filter uses a replaceable molecular sieve as the drying agent for the Nafion drying tube. Figure 9 shows the results of the detection of saturated water vapor at 20°C. Figure 10 shows the same sampling conditions after installing the inlet water filter. The peak due to water vapor is approximately 1400 Hz. Using the Nafion water filter, the water peak is no longer present. Further testing with all of the VOC materials indicated that the filter did not affect the sensitivity to VOC vapors.

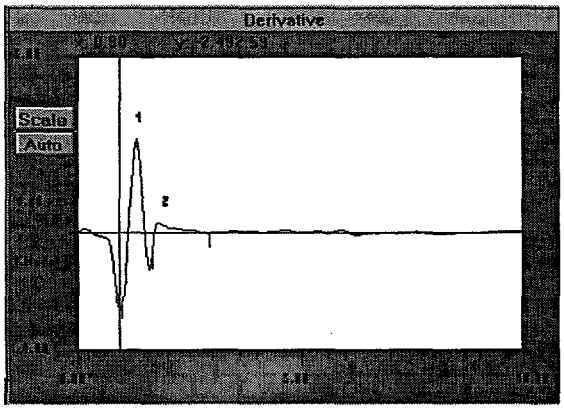

Figure 9-Response of system to saturated water vapor.

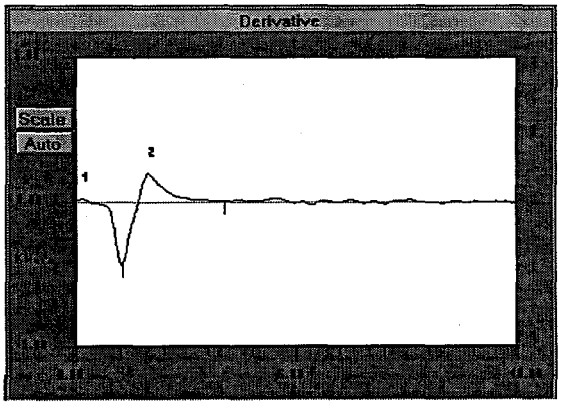

Figure 10- Water vapor response with Nafion dryer installed.

The set of selected VOCs were tested for their trapping ability in both Tenax-TA and Carbosieve S-III absorbent materials. Table VI and Table VII show a summary of the results. The first column gives the peak area of a retained volume of 37 µl. The second and third columns give the peak areas of trapped VOCs generated by heating the trap once and then heating it again. Next is the ratio of the peak area of the first trap heating to the peak area of the retained volume. This ratio gives an idea of how well material is trapped. The fifth column gives the ratio of first trap heating to the second trap heating. This determines the efficiency of the adsorbent. The last column gives a calculated scale factor which allows future predictions of expected signal.

Table VI - Carbosieve Trap Results

Material*	Retained Volume Area(Hz)	1st Focus Firing Area (Hz)	2nd Focus Firing Area (Hz)	Sig(1st)/ Sig(RV)	Focus (2)/(1)	Concentration (ppm)	Retained Vol Scale Factor (Hz/ppm/µl)
Toluene	7,272	3,253	2,168	.45	.67	935	.210
1,2-Dichloroethane	6,762	3,828	2,260	.57	.59	6,645	.028
Chloroform	18,313	1,308	1,094	.07	.84	5,871	.084
1,1,2,2-Tetrachloroethane	18,286	744	518	.04	.70	194	2.54
Trichloroethylene	13,993	5,679	2,015	.41	.36	2,419	.156
Dichloromethane	16,270	14,554	1,395	.90	.10	14,850	.03
Freon	12,172	769	426	.90	.55	25,161	.013
Tetrachloroethylene	10,055	908	595	.09	.66	580	.469
1,1,1-Trichloroethane	9,613	849	585	.09	.70	4,065	.064
Benzene	5,772	3,582	1,625	.62	.45	3,451	.045
1,1-Dichloroethylene	14,455	13,162	1,647	.91	.13	21,710	.018
Water	1,760	957	223	.54	.23	730	.065
Methanol	725	1,871	1,295	---	.69	3,742	.005

Table VII - Tenax Trap Results

Material	Retained Volume Area(Hz)	1st Focus Firing Area (Hz)	2nd Focus Firing Area (Hz)	Sig(1st)/ Sig(RV)	Focus (2)/(1)	Concentration (ppm)	Retained Vol Scale Factor (Hz/ppm/µl)
Toluene	3,259	3,442	67	1.06	0.02	935	0.09
1,2-Dichloroethane	4,031	2,396	---	0.59	---	6,645	0.02
Chloroform	9,496	1,806	---	0.19	---	5,871	0.04
1,1,2,2-Tetrachloroethane	6,387	58,313	56	9.13	---	194	0.89
Trichloroethylene	6,591	2,863	---	0.43	---	2,419	0.07
Dichloromethane	8,653	1,512	46	0.17	0.03	14,850	0.02
Freon	6,476	2,233	---	0.34	---	25,161	0.01
Tetrachloroethylene	3,367	5,065	59	1.50	0.01	580	0.16
1,1,1-Trichloroethane	3,879	2,638	---	0.68	---	4,065	0.03
Benzene	2,353	2,106	---	0.90	---	3,451	0.02
1,1-Dichloroethylene	11,249	3,248	97	0.29	0.03	21,710	0.01
Carbon Tetrachloride	5,471	2,056	---	0.38	---	3,226	0.05
Methanol	1,907	2,539	---	1.33	---	3,742	0.01

* Sampling volume is 30 cc

The prototype SAW/GC was calibrated after installing the modified column, inlet water filter, and VOC trap. A double-dilution calibration apparatus which could test mixtures of VOC compounds in a bubbler was constructed and used to test the system at low ppm levels for a mixture of Dichloromethane, chloroform, 1,2-Dichloroethane, Trichloroethylene, Toluene, and Tetrachloroethylene. The results are shown in the Table VIII below. The testing concentration used for each material in the mixture is shown in the second column and the amplitude in Hz for each compound detected in the third column. The test conditions were:

Inlet Sample flow: 45 cc/min
Sample time: 15 seconds
Dilution Ratio: 5/305
Source Temperature: -30°C
Trap Temperature: 70°C-220°C
SAW detector temp: 10°C

Table VIII - Calibration Results

VOC Material:	Test Concentration (ppm)	Detected Amplitude (Hz)	Detection Limit (ppm)	Scale Factor (Hz/ppm/cc)
Dichloromethane	133	678	5.88	0.45
Chloroform	37	63	17.62	0.15
1,2-Dichloroethane	45	144	9.38	0.28
Trichloroethylene	10	383	0.78	3.4
Toluene	2.4	272	0.26	10.1
Tetrachloroethylene	1.6	517	0.09	28.7

The detection limit for each compound (15 second sample) is shown in the fourth column and is based upon a signal to noise ratio of 3:1 equivalent to a peak amplitude of 30 Hz. The linear scale factor shown in the fifth column is calculated by normalizing the peak amplitude to concentration (ppm) and inlet flow volume (cc). In this case the inlet was flow was 45 cc/min and the sample time was 15 sec, therefore the flow volume was 11.25 cc. The linear scale factor for Toluene is then equal to 272 Hz/(11.25 •2.4)=10.1 Hz/ppm/cc. The first three tabulated materials have high vapor pressure and require a longer sample time to achieve a detection limit of 5 ppm. For example, sampling 1,2-Dichloroethane for 45 seconds will yield a detection limit of approximately 3.12 ppm.

The accuracy of the calibration system was checked using commercially available pre-mixed gas cylinders. As an example, 45 cc/min of nitrogen gas containing 10 ppm of trichloroethylene was sampled for 10 seconds and gave a signal amplitude of 625 Hz. This gives a 10 second detection limit of 0.48 ppm which compares favorably with the above result using the bubbler calibration system.

5.4. Field Testing

By the end of November the SAW/GC modifications were complete and laboratory scale testing continued throughout the months of December 1994 and January of 1995. During a program review held at Amerasia Technology on December 8, 1994, the prototype SAW/GC demonstrated simultaneous detection of six VOCs in water in less than 15 seconds.

The decision to start field testing was made and a site survey at Savannah River was conducted on January 20, 1995. The site survey was performed by E. Staples, T. Lim, and G. Watson from Amerasia Technology and E. Christy and C. Wyatt from METC. The site survey was hosted by Mr. Joe Rosabbi, a senior engineer working for Westinghouse Savannah River Company.

A preliminary test of gas samples taken from the Savannah river site was performed using the SAW/GC vapor analyzer. The bag was attached to the inlet of the Amerasia vapor detection system and a sample drawn from the bag using the system sampling pump. The sampling flow from the bag was approximately 45 ccm and the sample time nominally 10 seconds. A typical 10 second chromatogram is shown Figure 11. Peaks 1 and 2 correspond to TCE and PCE vapors and caused the system to alarm and quantify their presence in ppm. Minimum detectable signal levels for a 10 second sample are typically 100 ppb or less. Longer sample times produced ppt detection levels.

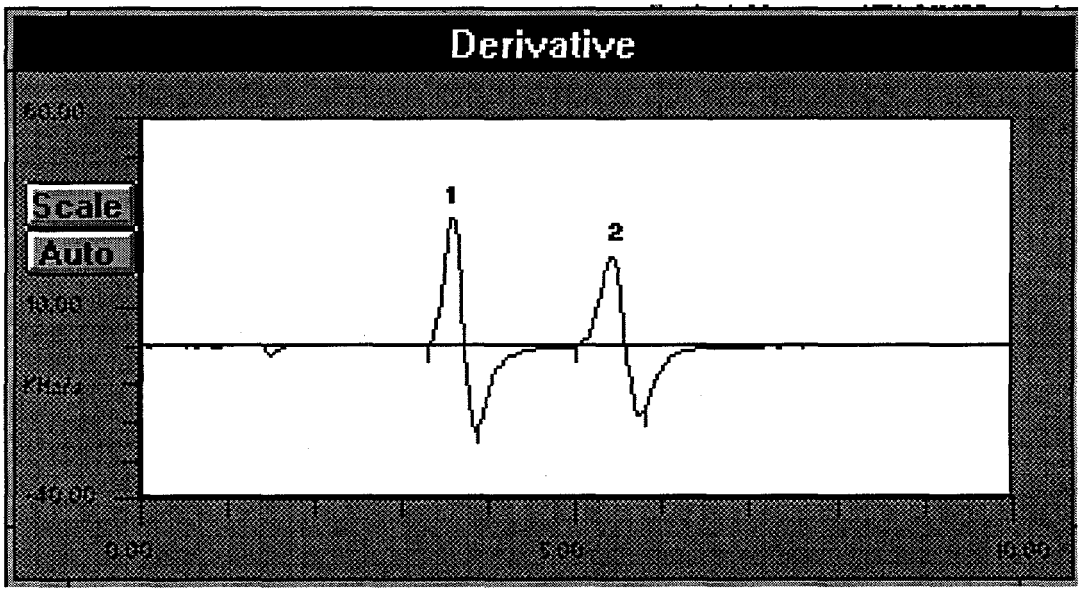

Figure 11- Chromatogram showing the presence of TCE and PCE vapors.

The design of the detection system software was modified to include engineering units in the display of the peak areas. A test protocol was written to include calibration using known concentrations of VOC vapors. During calibration the appropriate scale factor for the inlet preconcentrator and SAW detector combination was entered into the system software. The Windows® based software produced the analysis window shown Figure 12 where VOC Detection information is displayed. The operator can choose to display the peak area in Hertz, PPM, or picograms (PG) by simply picking a selection at

the top of the window. By providing the sample flow rate and scale factor in Hz/ppm/cc for each calibrated material, ppm is calculated from the instrument's sample time setting. These results were typical of the results obtained from the Savannah River Site gas bag sample. The 10 second sample limit of detection for TCE is 100 ppb and 10 ppb for PCE.

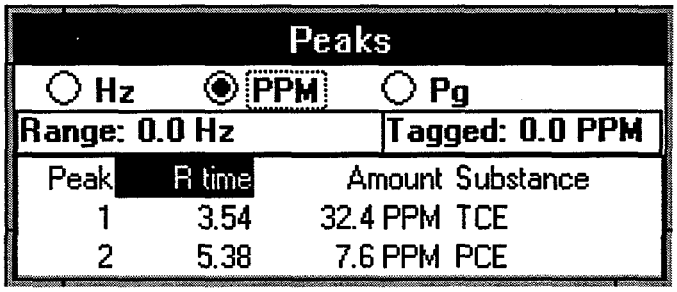

Figure 12- VOC concentration in ppm, picograms, or Hertz.

System repeatability typically shows ±250 ppb variability in amplitude when repeatedly sampling a 10 ppm concentration of TCE. The retention time variation is ±5 % of reading or 3.6 ± 0.180 seconds for TCE.

During January the SAW analyzer system was calibrated and alarms set for all VOC materials specified in task 1.1 of the work statement. The SAW/GC system as configured is shown in Figure 13 where the relative retention time, and alarm window spread (width of arrow) are superimposed against the SRS chromatogram.

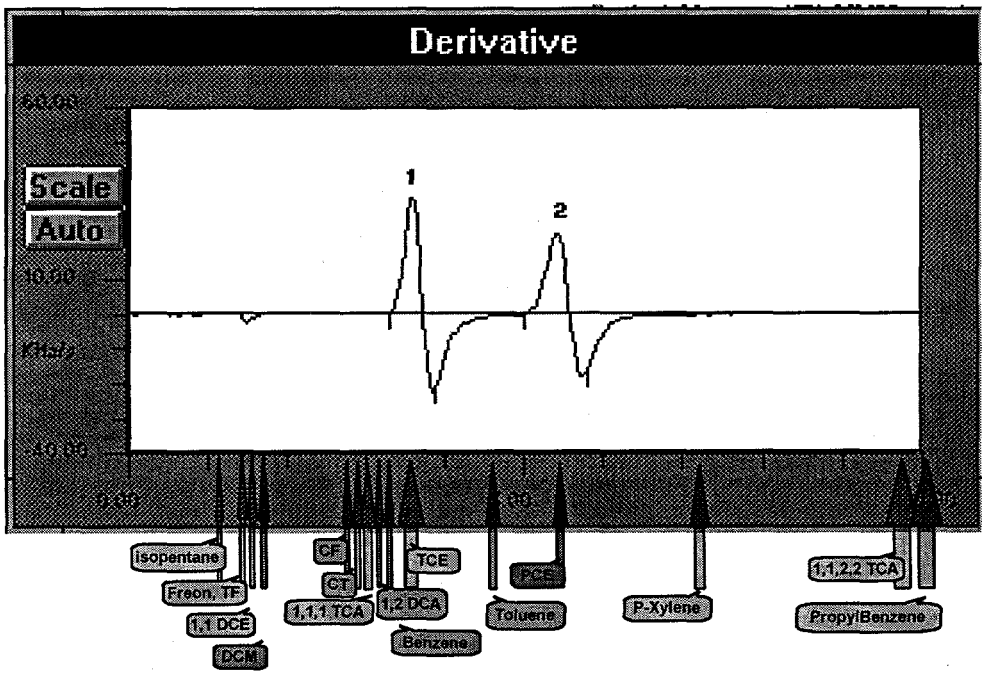

Figure 13- Individual alarms for many VOC materials can be set in amplitude and time span.

A test plan for field testing the SAW analyzer system was written which included a test protocol designed to establish scale factor and minimum detectable signal while in the field. On February 27th the SAW/GC arrived on site and field three days of field testing were completed. Field tests were carried out according to the Test Plan which included laboratory and well-head testing. A photograph of the system attached to a well head is shown in Figure 14.

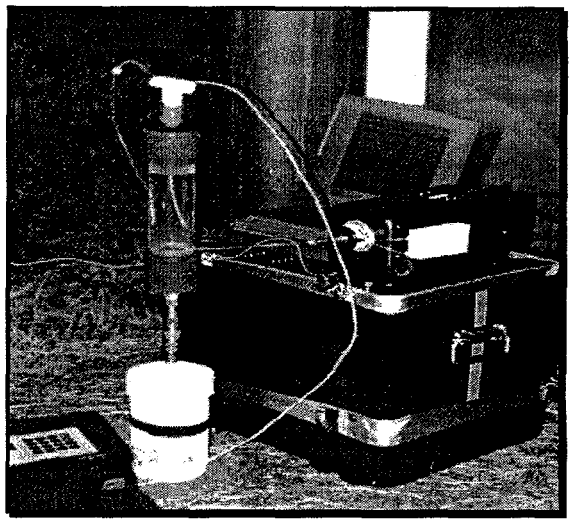

Figure 14- SAW/GC Vapor analyzer attached to well head.

The SAW/GC was tested over a wide range of VOC concentrations, primarily TCE and PCE (100 ppb to 1000 ppm). These tests were carried out by Gary Watson and David McGuire from Amerasia Technology and Joseph Rosabbi and Brian Rina from the Westinghouse Savannah River Company. Results indicate that the SAW/GC maintained its calibration throughout the tests and its accuracy tracked test results taken with an HP Chromatograph within a 20% error band.

Field tests were aided by the ability to transport the system to remote field sites in a vehicle which could supply power from a small inverter. This enabled the analyzer to operate for long periods of time (overnight) using the batteries of the car as shown in Figure 15

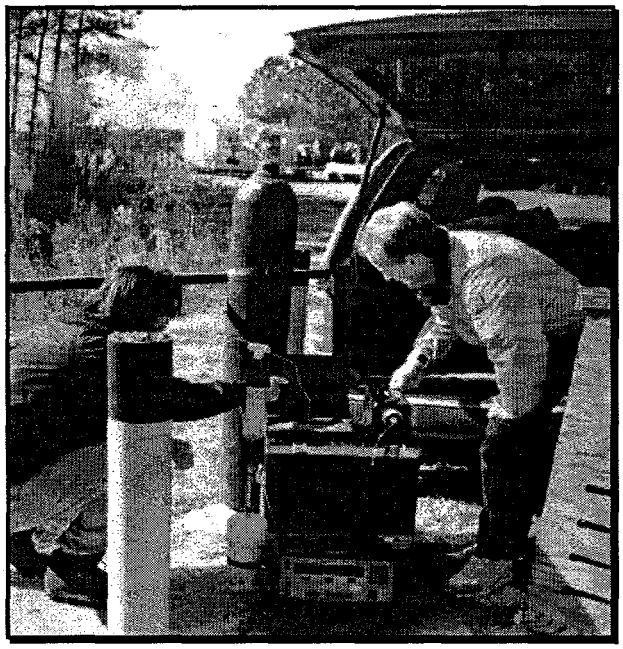

Figure 15-Testing using auto as a power source for the instrument.

The SAW/GC was tested against a laboratory GC manufactured by Hewlett Packard and used at the site as the primary standard against which all other instruments are checked. Over the concentration ranges tested for both PCE and TCE, the SAW/GC agreed with the HP instrument within a 20% error band. A 20% variation was within the anticipated experimental error due to variations in sampling conditions.

A second field testing of the SAW analyzer system at the Savannah River Site was carried out during latter part of March. The instrument's second field test was performed at the Savannah River Site in support of the Environmental Field Test Platform Workshop hosted by Dr. J. Rossabi.

The equipment was shipped to Augusta, Georgia and arrived on March 19. Field tests were carried out according to the Test Plan which included laboratory and well-head testing. The SAW/GC was tested over a wide range of VOC concentrations, primarily TCE and PCE (100 ppb to 1000 ppm). These tests were carried out by Ed Staples and Gary Watson from Amerasia Technology. The tests were witnessed by more than 100 participants of the workshop including Eddy Christy (METC program manager) and Chris Wyatt (Energetics), and Joseph Rossabi from the Westinghouse Savannah River Company. The system proved successful at field testing of gas, water, and soil samples. In addition the system was successfully evaluated using an ARA CONE penetrometer truck to deliver the samples for analysis by the SAW/GC system.

Accuracy was evaluated using Tedlar Bag samples supplied by the Savannah River Company. A typical on-screen display analysis for a tedlar bag sample containing PCE and TCE is shown in Figure 16.

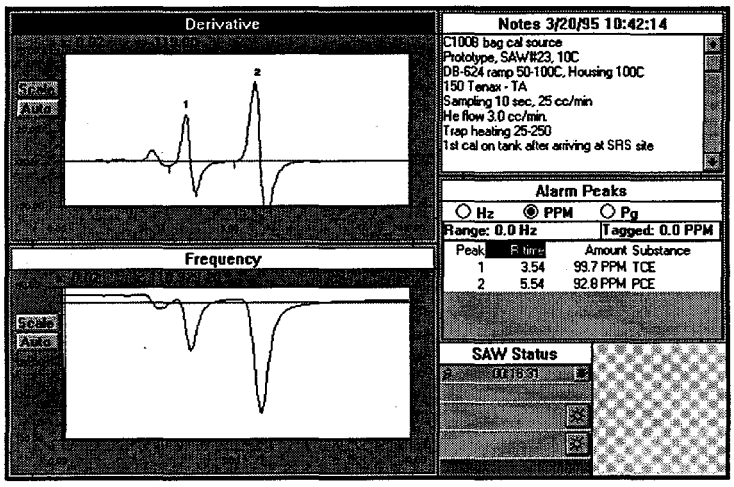

Figure 16- Screen information displayed for typical Tedlar calibration bag sample.

Tedlar bag calibration samples (10 ppm and 100 ppm) were tested multiple times and representative averages for these readings are shown in **bold** in Table IX.

Table IX-Tedlar Calibration bag results

	TCE	PCE
C-10-A Tedlar Bag	**10.1**	**10.4**
C-100-A	82.8	94.9
	79.6	95.4
	81.2	**95.15**
	TCE	**PCE**
C-100-B	80.4	95.1
	53.5	110.2
	86.2	114.6
	80.5	115.1
	86.7	124.2
	87.1	116
	79.067	**112.53**

Tedlar bag samples containing actual headspace vapors from wells were tested and these were typically contained amounts as high as several thousand ppm as shown in the tabulated results of Table XI. Water calibration standards were also tested using headspace vapors and Henry's law to determine solution concentrations. Typical results for water standards over the range 5-500 ppb are tabulated in Table X.

Table X-Water Calibration sample results

	TCE	PCE
5 ppb	~	1
10 ppb	~	1.2
50 ppb	0.324	2.3
	0.614	2.4
	0.469	**2.35**
100 ppb	1.7	4.4
	1.7	4.5
	1.7	**4.45**
300 ppb	6	11.6
	5.7	10.4
	5.5	10.2
	5.73	**10.73**
500 ppb	14.3	24.4
	12.9	22
	13.60	**23.20**

Table XI-Well samples showing high concentrations of PCE

	TCE	PCE
CPTRAM-4	478.2	4937
(change to 2 sec sampl	518	5947.7
without re-cal !!!)	489.3	4853.9
	499.7	5368
	496.3	**5276.7**
CPTRAM-15	58.5	201.9
	59.4	209.6
	56.5	204
	60.8	204.9
	58.5	205
	58.74	**205.08**
082-OUT Bed 1	~	1.4
	~	1.2
	~	1.1
	~	**1.23**

Additional testing of actual well water samples as well as headspace vapor measurements from soil samples are shown in Table XII and Table XIII.

Table XII-Additional well sample results

	TCE	PCE
MHT-17C (1st vial)	38.6	100.9
	39.6	114.9
	39.10	**107.90**
MHT-17C (2nd vial)	65	218.9
	58.8	195
	61.90	**206.95**
MHT-12C (1st vial)	5	15.2
	4.4	14.1
	4.70	**14.65**
MHT-12C (2nd vial)	5.3	16.2
	5.4	14.7
	5.35	**15.45**

Table XIII-Soil sample results

	TCE	PCE
15' Depth Soil Sample	~	**0.927**
20' Depth Soil Sample	~	**0.706**

All of these measurements were carried out in a very short period of time and demonstrate the cost savings which can be achieved. As an example consider that in one 2 hour period more than 75 well water and soil sample measurements were carried out in the field. Had these same samples required laboratory testing, more than 25 hours of laboratory test time would have been required. Assuming $100/hour laboratory

processing fee (probably low) this translates into a $2,300/day savings ($2,500-$200). The results are that in just 20 days of testing, the instrument would save approximately $50,000 in laboratory fees.

The accuracy of the prototype instrument as compared with the on-site HP GC is shown in Figure 17. In this figure the SAW/GC reading (ordinate) is within a 20% error band. The source of this error is believed due to a combination of sampling technique or interface, and variations within the instrument. The latter errors are currently being investigated with the goal of improving instrument accuracy and repeatability.

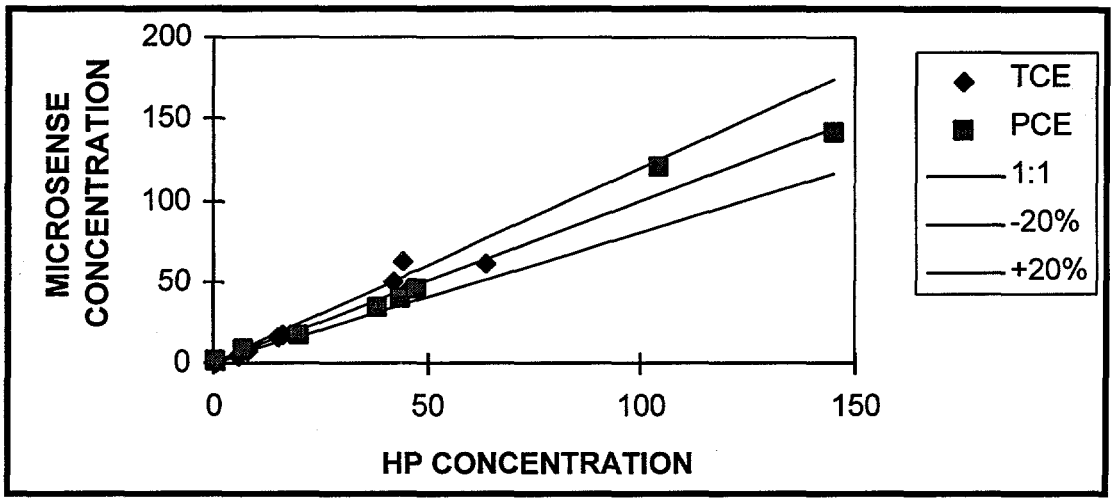

Figure 17- Comparative Accuracy HP Vs SAW/GC.

The instrument was also used to evaluate gas samples from a cone penetrometer (ARA) present at the workshop. During each 'push' of the penetrometer the SAW/GC was able to obtain 3-5 chromatograms. Each 'push' required the insertion of a 3' section into the penetrometer and thus chromatograms could be essentially in real time. For the ARA demonstration the site selected did not show any PCE or TCE, however, the SAW/GC did detect substantial Toluene present in the gas lines of the penetrometer, presumably from insufficient cleaning from a previous site.

6. Results and Discussion - Phase II

The major milestones for Phase I were completed in October of 1995 and a technical paper was presented at the METC Research Opportunities Conference held at Morgantown. The paper entitled "Field Portable Detection of VOCs Using a SAW/GC System" , summarized the project accomplishments during Phase I.

A new work statement for Phase II incorporated the following tasks: Compound Detection and Identification (6.0), Equipment Modification and Testing (7.1), Laboratory testing (7.2), DOE Field test planning (8.1) Field test execution (8.2) and EPA equivalency methods (9.0). The objectives of the Phase II research were construct a fieldable prototype screening instrument with new capabilities for detecting dioxins and pcbs in addition to VOC compounds. Additional field tests were to be carried out using this instrument at DOE sites.

6.1. Studies of Vapor Pressure- New Compounds

Studies of the physical properties of dioxins and furans was continued during the month of July. Compared to VOC materials such as toluene or TCE, dioxins and furans have very low vapor pressures. As presented in last month's report, their vapor pressure is typically 5-12 orders of magnitude lower. In effect, this means that these materials are very sticky and do not evaporate easily from a surface. To successfully detect these materials the SAW/GC instrument must be modified so that sticky materials can pass through the sample inlet into the column, and ultimately to the SAW detector where they are quantified. To achieve this the temperature of the system must be raised for non-volatile materials so that they do not stick on a cold spot. The use of the word 'cold' is clearly relevant to vapor pressure which is why the vapor pressure must be known to properly design the instrument.

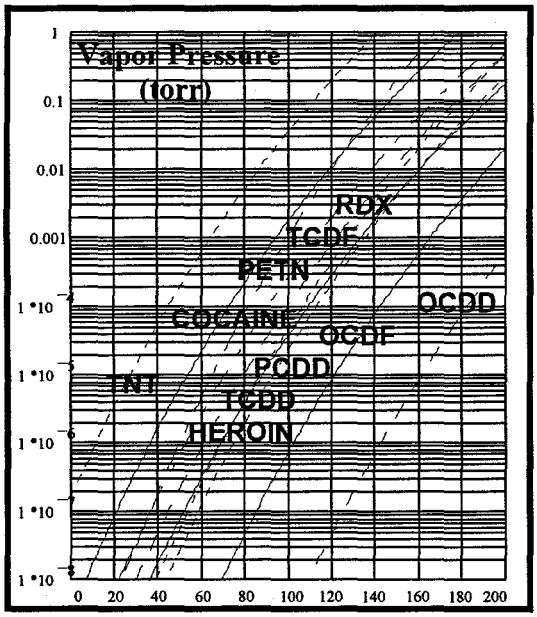

Figure 18-Vapor pressure comparison between dioxin/furans, drugs of abuse, and explosives.

Studies of vapor pressure for representative dioxins and furans are plotted in Figure 18. In this plot the vapor pressure of the dioxins and furans covers a range of 2x10-9 to 3x10-4 torr and their molecular weight covers the range 320-460. For comparison the vapor pressure of explosive materials, TNT, RDX, and PETN as well as the vapor pressure of cocaine are plotted. These materials appear to have very similar properties to the dioxins and furans. Their molecular weights are slightly less, 222-369, and their vapor pressure ranges 5x10-5 to 3x10-2.

From the vapor pressure and molecular weight of the materials the concentration of each in saturated vapor can be calculated using the universal gas law. The result for the above materials is shown in Figure 19 where concentration in picograms per cubic centimeter is shown Vs ambient temperature. These studies of dioxin and furan vapor pressures has shown that they are comparable, but slightly lower, than other materials which have been successfully detected using the SAW/GC method.

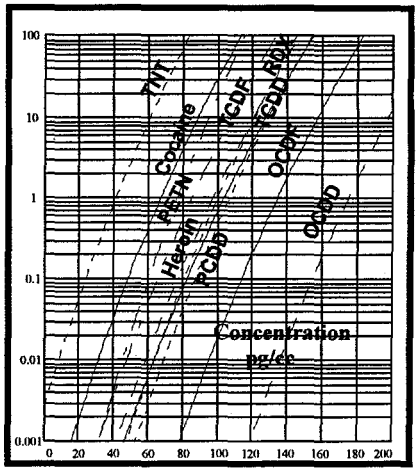

Figure 19- Comparison of concentrations for dioxin/furans, drugs of abuse, and explosives.

During the month of August, studies involving dioxins and furans concentrated upon an evaluation of current EPA methods for these materials in addition to those methods in use for VOCs. Of particular help was a visit to EPA-Chicago (Region 5) as well as participation in an American Chemical Society (ACS/EPA) short course on EPA methods for Water and Waste Analysis. Of interest to the work planned on dioxins and furans was the extreme toxicity of these materials as well as the use of safe laboratory procedures. Compared to VOC materials, dioxins and furans have very low vapor pressures and hence can be easily localized with proper procedures. Nevertheless, there is concern and two laboratories other than Amerasia's are being considered as test sites for these materials. The two laboratories are located in the Research Triangle of North Carolina. One laboratory is the EPA itself and the other is a private testing laboratory, Triangle Laboratories. Although these laboratories would make excellent technical evaluation sites, they are not located close to Amerasia and hence represent considerable expense in travel related costs. Currently we plan to locate similar testing laboratories within region 9 of the EPA or with CAL-EPA in Berkeley. Also, we are searching for a similar laboratory in the Los Angeles area.

A SAW/GC system modified for use with low vapor pressure compounds will now be tested on specific dioxin and furan compounds at the California EPA laboratories in Berkeley California. This work is being carried out in parallel with development of EPA equivalency methods (9.0) for VOC materials. Equipment Modification and Testing (7.1), is progressing on schedule and three prototype instruments will be used for laboratory (7.2) and Field testing (8.1).

During the month of October, studies involving dioxins and furans resulted in the development of a physical model describing the operating capabilities of SAW/GC vapor sensors. The world model is depicted in the plot of vapor pressure vs. temperature shown in Figure 32. Two rectangular regions are noted by a dark black border. The first region is occupied by volatile organic compounds. These materials rapidly enter the gaseous state and readily equilibrate any closed volume in a short time through the process of diffusion. The second region is termed the non-volatile region because here materials are characterized as having very low vapor pressures. These materials are very sticky and do not give off detectable vapor except at elevated temperatures.

With reference to the world as depicted in Figure 32, Amerasia is currently developing instruments for VOC and NVOC regions. The VOC instrument is equipped with special inlet water filter and a preconcentrating VOC trap. The GC method utilizes a relatively low inlet and column (ramped) temperature. The SAW detector itself is cooled by a thermoelectric cooler for maximum sensitivity. In contrast the NVOC instrument requires much higher inlet temperatures and a higher column temperature ramp. The NVOC instrument is equipped with a special trap to remove interference from volatile organic compounds. The SAW detector in this case is heated above ambient to further reduce interference from VOCs. Currently the Compound Detection and Identification task (6.0) has been completed. A SAW/GC system designed for use with low vapor pressure compounds (NVOCs) will be now tested first on specific dioxin and furan compounds at the California EPA laboratories in Berkeley California. The experimental results will be compared with the vapor pressure study projections.

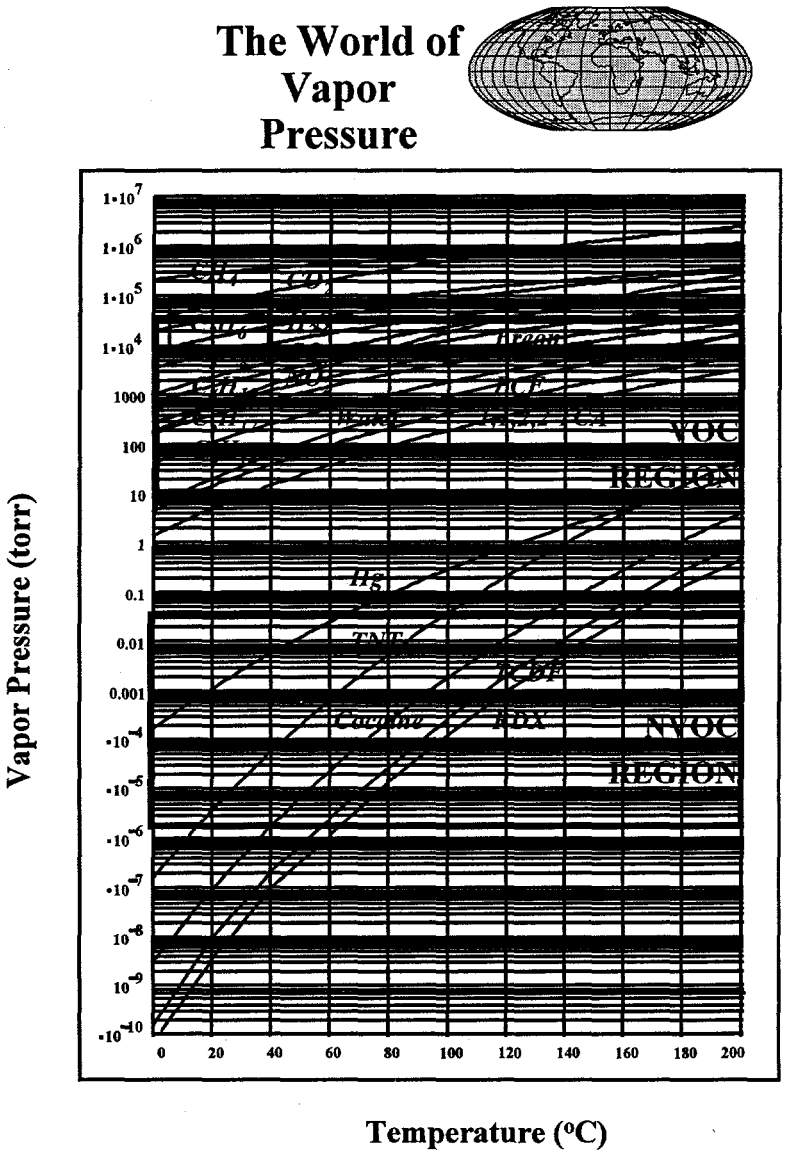

Figure 20- The World of Vapor Pressure spans more than 20 order of magnitude over a 200°C range.

During the month of November a test plan for evaluating the modified SAW/GC system with PCBs, dioxins and furans at the California EPA's Hazardous Materials Laboratory in Berkeley was developed. Based upon operating capabilities of SAW/GC vapor sensors and the compounds selected by the EPA, the system will be tested for specificity and sensitivity.

The most hazardous of these materials are 2,3,7,8-Tetrachlorodibenzo-p-dioxin, 2,3,7,8-Tetrachlorodibenzofuran, and 3,3',4,4'-Tetrachlorobiphenyl. These compounds together with their chemical formulations are shown in Figure 21. In addition each of these compounds is the basis of a congener family containing numerous isomers. As an example the PCB congener group is shown in Figure 22. Dioxins and furans comprise similar congener groupings and the multiplicity of isomers make these compounds a challenge for any type of instrumentation, including GC/MS.

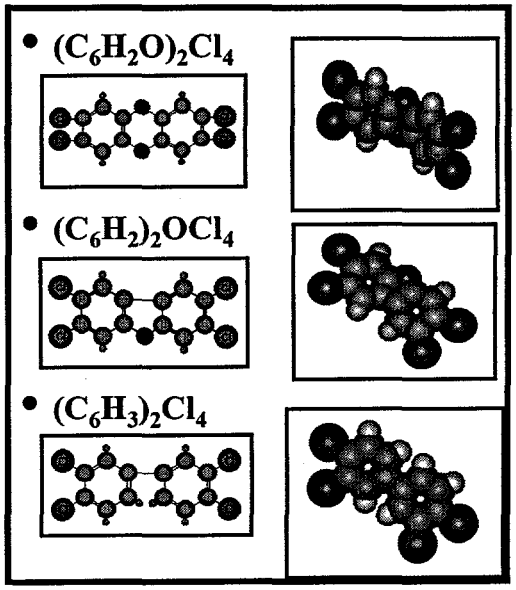

Figure 21- PCB, dioxin, and furan compounds.

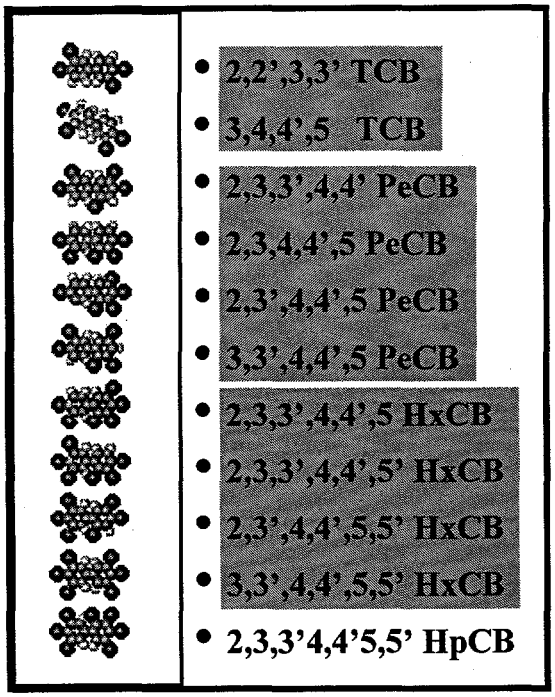

Figure 22- Polychlorinated biphenyl congener group.

The vapor pressure of these materials were studied as part of the compound identification task and based upon this study we believed that the SAW/GC method will be able to provide a fast and specific screening tool for thee materials. Currently laboratory testing for dioxins, PCBs, and furans is complex and costly. The cost for a typical laboratory analysis is 2000. If successful the SAW/GC would provide the DOE with a field screening tool for a fraction of this cost.

During the month of December a test plan for evaluating the modified SAW/GC system with PCBs, dioxins and furans at the California EPA's Hazardous Materials Laboratory in Berkeley was carried out. The test plan called for a SAW/GC system, modified to detect non-volatile compounds, to be placed in an approved and vented hood where it would be exposed to vapors and calibrated amounts of dioxins, furans, and PCBs. The objective of these tests were to determine the sensitivity and specificity of the instrument to this class of compounds. All compounds were selected Dr. Ruth Chang, an expert in this field and a staff member of the CAEPA's Hazardous Materials Laboratory.

The most hazardous of these materials are 2,3,7,8-Tetrachlorodibenzo-p-dioxin, 2,3,7,8-Tetrachlorodibenzofuran, and 3,3',4,4'-Tetrachlorobiphenyl. These compounds are made even more difficult due to the large number of isomers which are known to exist. Laboratory testing for dioxins, PCBs, and furans is costly. For a laboratory analysis the cost is ≈$2000. The SAW/GC screening tool would allow testing for these materials in real time without waiting for laboratory results. In view of the extreme toxicity of these materials this would greatly improve worker safety. The fieldable SAW/GC would be used as a screening tool and would not eliminate laboratory testing. Instead, it would indicate when or where laboratory testing is needed and where it is not needed. Hence a significant cost savings would be achieved by eliminating useless laboratory testing.

Testing was carried out using EPA prepared solvent solutions containing known amounts of dioxins, pcbs, and furans. For PCB materials the following solutions were used:

1. Aroclor 1260®
2. Aroclor 1254®
3. Aroclor 1248®
4. Aroclor 1221®
5. Dioxin/Furan in Toluene, (10 Ng/µl tcdd,3 Ng/µl ocdd/ocdf,1 Ng/µl tc-hep)

The Aroclor solutions are registered PCB mixtures in a solution of hexane. Concentration strengths varied between 0.1 ppm to 50 ppm. Aroclor 1260 contains two pentachlobiphenyl, three hexachlrobiphenyl, and one heptachlorobiphenyl compounds as indicated in Table I. Similar compositions are listed in tables II-IV for the other Aroclor mixtures.

Table XIV- Aroclor 1260 Mixture.

2,2',3,5,6 Pentachlorobiphenyl
2,2',4,5,5' Pentachlorobiphenyl
2,2',3,4',5',6 Hexachlorobiphenyl
2,2',4,4',5,5' Hexachlorobiphenyl
2,3,3',4',5,6 Hexachlorobiphenyl

2,2',3,4,4',5,5' Heptachlorobiphenyl

Table XV- Aroclor 1254 Mixture.

2,4,4',5 Tetrachlorobiphenyl
2,3',4',5 Tetrachlorobiphenyl
3,3',5,5' Tetrachlorobiphenyl
2,3,3',4',6 Pentachlorobiphenyl
2,3',4,4',5 Pentachlorobiphenyl
2,3,3',4,4' Pentachlorobiphenyl
2,2',3,4,4',5' Hexachlorobiphenyl

Table XVI- Aroclor 1248 Mixture.

2,2' dichlorobiphenyl
2,4' dichlorobiphenyl
2,2',5 trichlorobiphenyl
2,4',6 trichlorobiphenyl
2,4',5 trichlorobiphenyl
2,4,4' trichlorobiphenyl
2,2',3,5' Tetrachlorobiphenyl
2,3',4',5 Tetrachlorobiphenyl

Table XVII- Aroclor 1221 Mixture

2 isochlorobiphenyl
3 isochlorobiphenyl
4 isochlorobiphenyl
2,2' dichlorobiphenyl
2,4' dichlorobiphenyl
4,4' dichlorobiphenyl

All waste materials, used syringes, etc., were placed in a labeled waste bag within the hood provided. The SAW/GC was placed within the hood and operated with minimal sash opening to protect the operators. All personnel handling the materials (Dr. Ed Staples, G. Watson, and D. McGuire) were properly protected by disposable rubber gloves. The solutions were used to fill a micro-liter syringe and inject typically μl of the

solution into the inlet of the SAW/GC or into the packing of a flow and temperature controlled vapor generator.

A selected chromatogram for an Aroclor 1260 (0.2 ppm) mixture demonstrating the accuracy and sensitivity of the SAW/GC to PCB vapors is shown in *Figure 23*. These peaks are well above noise levels and their simultaneous presence would be indicative of PCBs from the Aroclor 1260 isomer group. During the testing a peak identification file was created using peak numbers and retention times for each group of materials. For example, in Aroclor 1260, peaks were annotated as AC1261, AC1262, etc.

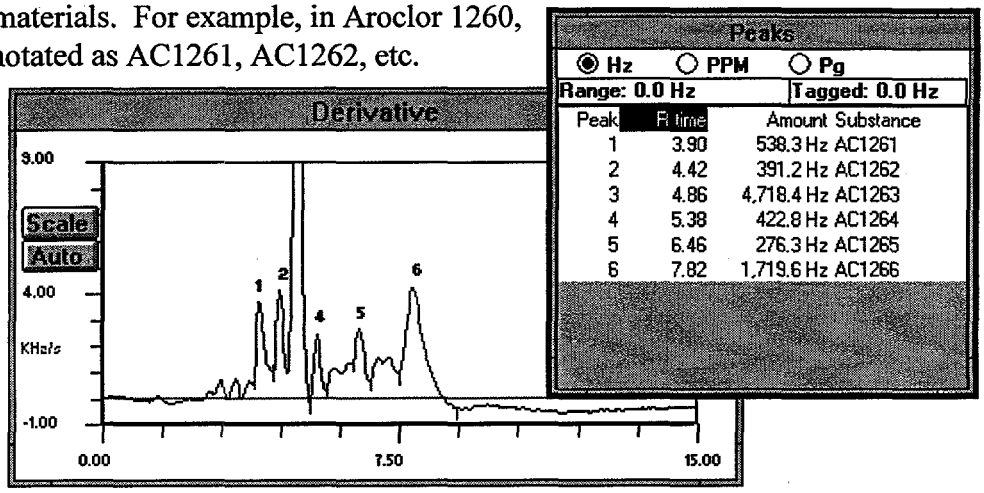

Figure 23- Response to Aroclor 1260 PCB mixture.

Each group of PCB isomers gave a characteristic pattern and using pattern recognition based upon the sum of identified (tagged)

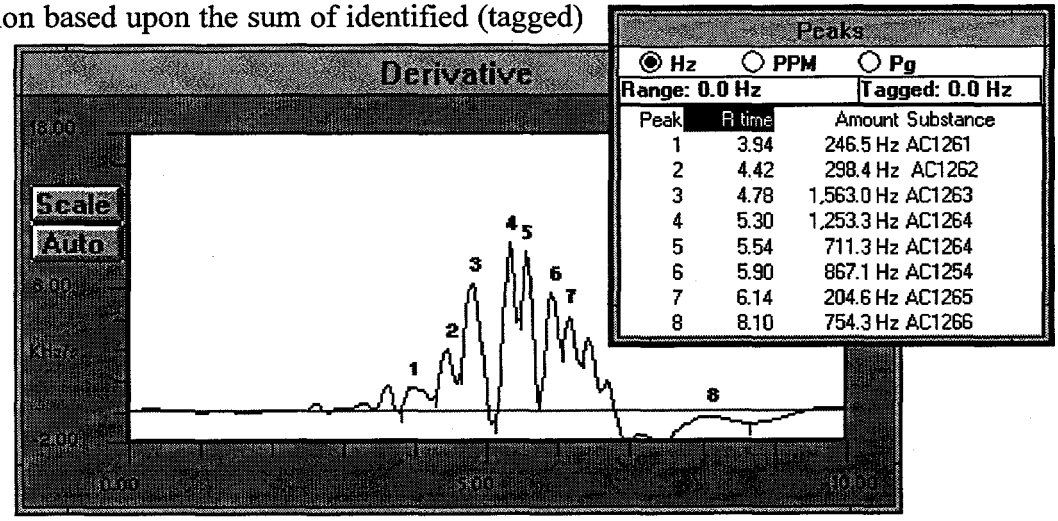

Figure 24- SAW/GC response from Aroclor 1254 PCB mixture

peaks, it could be properly identified. For example the chromatogram obtained with the Aroclor 1254 mixture is shown in Figure 24.

The dioxin/furan mixture gave quite different results and indicated a high sensitivity to dioxins for the SAW/GC as shown in the chromatogram below in Figure 25.

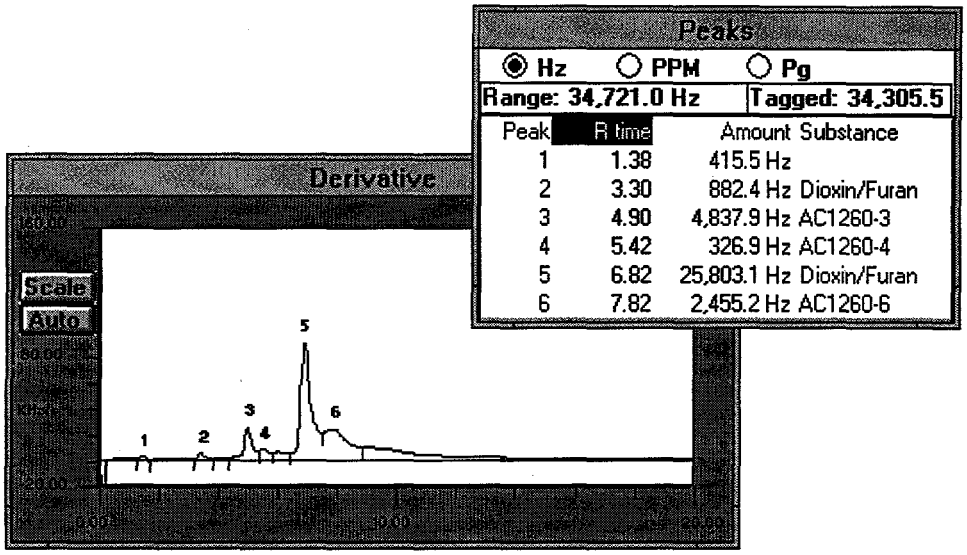

Figure 25= Response to dioxin/furan mixture.

Compared with the PCB results the dioxin/furan mixture gave much higher signals, typically 25,000 Hz, compared to 2,000 Hz for PCBs. Testing with the Aroclor 1248 and 1221 mixtures gave similar results but with reduced retention times due to the

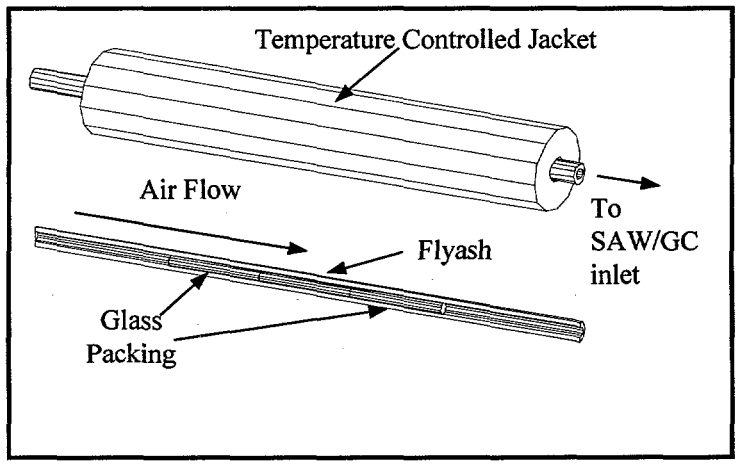

Figure 26- Temperature Controlled Vapor Source

fact that these mixtures contained more volatile PCBs. In summary these tests confirmed that the SAW/GC could be used as a screening tool at DOE sites where dioxins and PCBs are present or where incineration is suspected to be releasing these compounds into the atmosphere.

The results of the above testing determined that the SAW/GC system sensitivity or minimum detectable signal level for dioxins and furans was approximately 10 pg. Following this early work efforts were undertaken to evaluate fly-ash from actual incinerators. Flyash samples containing PCBs and dioxins were obtained from the CEPA and used to evaluate vapor extraction methods. The objectives were to use a SAW/GC to screen for dioxins and PCBs in Flyash. A fieldable vapor extraction technique, shown in Figure 26, analogous to some remediation efforts (but on a micro scale) was developed. An important advantage of the technique is that it is as simple as immunoassay but does not require the use of solvents with their containment and disposal problems. The extraction tube was placed within a temperature controlled jacket (25°C- 100°C, ±1°C) and 10 ccm of clean air was passed through the tube. The Flyash was held between two glass wool packing so only vapors could freely exit the tube. The extracted vapors of the compounds present in the Flyash were then sampled in real time by the SAW/GC.

A peak identification file was created using the chromatogram data obtained during testing of PCBs and dioxins at the CEPA hazardous materials laboratory. The extraction tube was heated until at 70°C vapors were detected as shown in the chromatogram of Figure 27 . At this temperature some small peaks identified as dioxins and PCBs are began to appear.

Raising the temperature to 80°C gave the chromatogram shown in Figure 28. The peaks are larger and the largest, at a retention time of 3.82 seconds, was identified as an

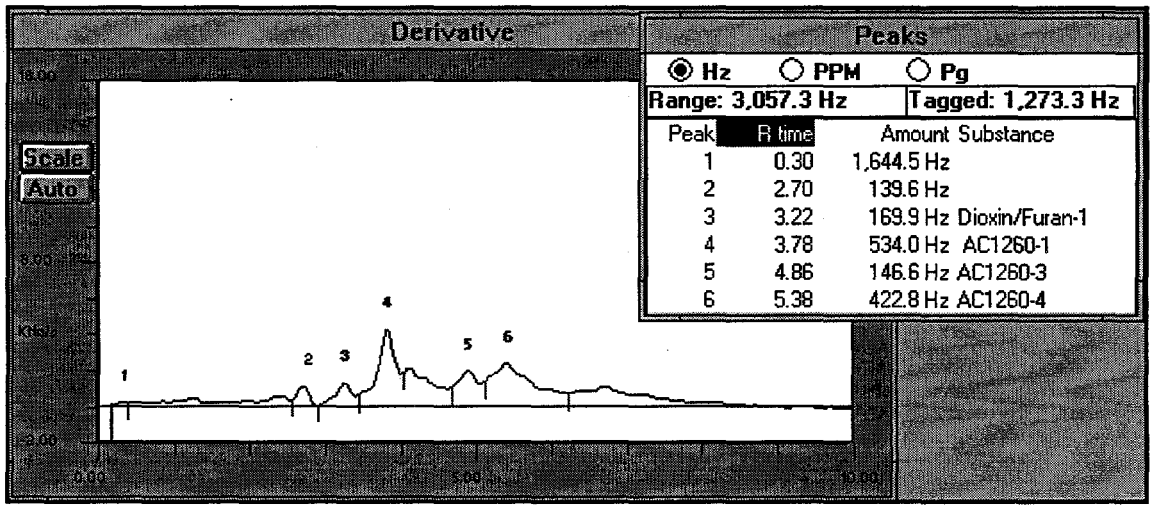

Figure 27- Flyash vapors obtained at 70°C.

aroclor-1 (PCB) peak. The peak detection and identification table in this figure is displaying peak areas in Hertz-(seconds) and the derivative plot spans 10 kHz/sec vertically. At these levels each sample is estimated to contain tens of picograms in each sample. Each sample was obtained by preconcentrating trapped vapors in a 60 ccm flow for 5 seconds. Thus the total volume of each vapor sample was 1 cubic centimeter.

Next the temperature was raised to 90°C and chromatograms. The results, shown in *Figure 29*, were very repeatable. The maximum vapor is now identified as AC1260-1a at a retention time of 3.7 seconds. AC1260-1 is barely visible and does not appear in the

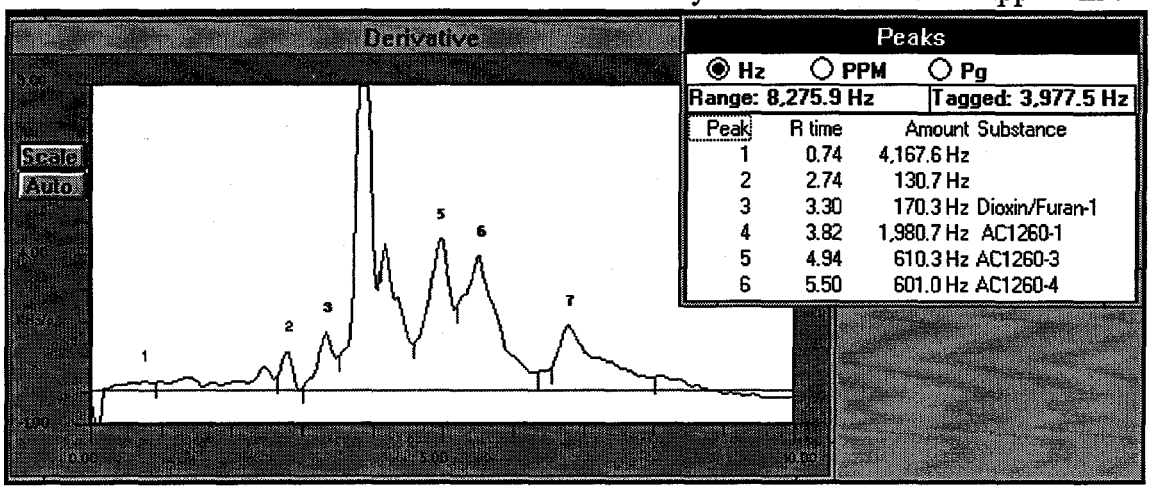

Figure 28- Flyash vapors obtained at 80°C

table because it's area is below the preset detection threshold of 100 Hz-sec. The remaining AC1260 peaks are consistent with the previous chromatograms at 80°C.

Next the temperature was raised to 95°C and repeatable chromatograms (shown in Figure 30 and Figure 31 were taken. In this chromatogram the peak identification table is

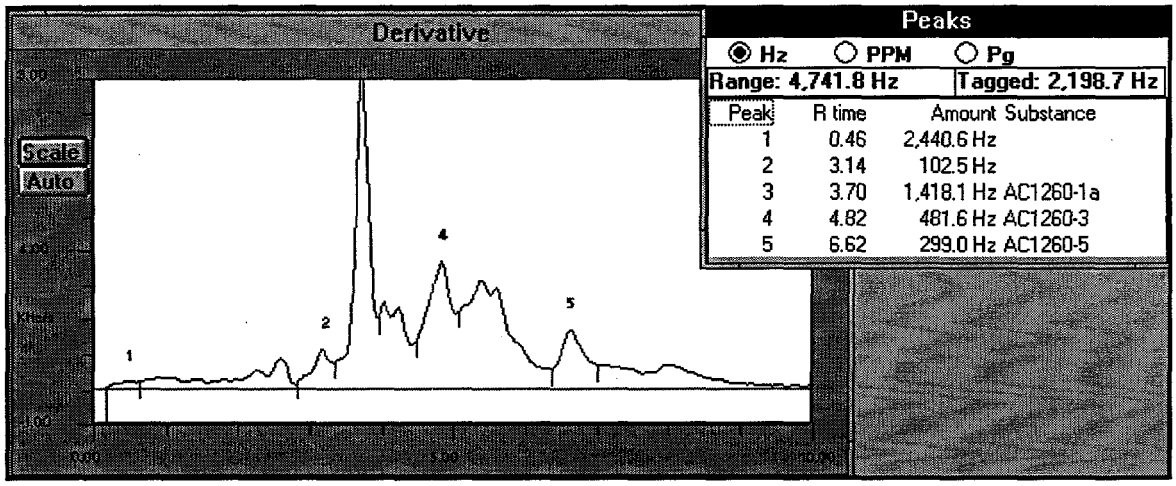

Figure 29-Flyash at 90°C.

indicating the detected compound mass in picograms because the "Pg" button shown in the top of the figure has been pressed. For these chromatograms the conversion from Hertz to picograms is based upon an estimated scale factor of 40 Hz/pg. This scale factor would be consistent with our past experience using materials of similar vapor pressure We plan to substitute individual scale factors based upon published vapor pressure coefficients into the peak files data as soon as it is available. The AC1260-1a peak has shifted its retention time to 3.5 seconds and indicates a vapor concentration of 68.2

picograms per cubic centimeter (5 second sample). AC1260-2 and Dioxin/Furan-2 are also large at more than 40 pg/cc.

In summary, the results of our experiments with dioxins and pcbs have shown that

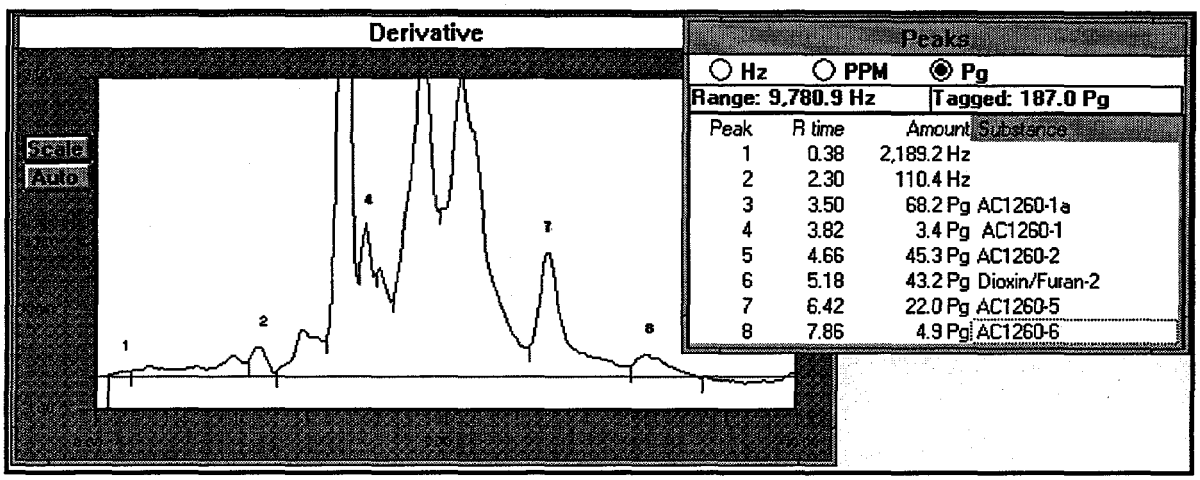

Figure 30-Flyash at 95°C.

the SAW/GC can be used to monitor these materials in real time. Vapor extraction appears to be a good method for screening flyash suspected of containing dioxins and pcbs. At moderate temperatures of 70-95°C we were able to obtain consistent and repeatable chromatograms with vapor concentrations of pcbs and dioxins up to 80 pg/cc. A chromatogram showing flyash vapors at 95°C is plotted in Figure 31. In this plot the vertical span has been increased to 20 kHz/sec and the horizontal span increased to 15 seconds.

For these first experiments we did not re-validate the peak identification table. In the future we will use known PCB mixtures to create fieldable calibration tubes for accurately setting retention time and validating the instrument in the field. Future experiments will attempt to perform a total PCB or dioxin analysis by totally extracting the material. We speculate that by measuring the time and the vapor concentration being extracted from a known weight of Flyash, we will be able to arrive at total Flyash content

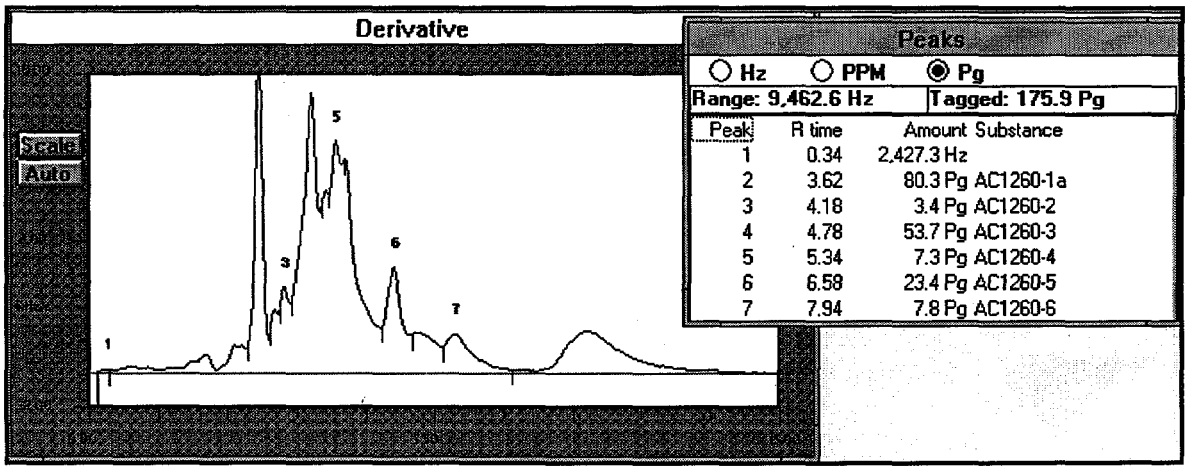

Figure 31-Flyash at 95°C using a 15 second time span and a 20 kHz vertical span.

by weight. Screening for dioxins using a vapor extraction technique is expected to be useful, particularly since the SAW/GC is able to perform this function in the field in essentially real time.

The most hazardous of these materials are 2,3,7,8-Tetrachlorodibenzo-p-dioxin, 2,3,7,8-Tetrachlorodibenzofuran, and 3,3',4,4'-Tetrachlorobiphenyl. These compounds are made even more difficult due to the large number of isomers which are known to exist. Laboratory testing for dioxins, PCBs, and furans is costly. For a laboratory analysis the cost is ≈$1500-2000. The SAW/GC screening tool would allow field testing for these materials in real time without waiting for laboratory results. In view of the extreme toxicity of these materials this would greatly improve worker safety. The fieldable SAW/GC would be used as a screening tool and would not eliminate laboratory testing.

6.2. Equipment Modification - Field Prototype

Laboratory prototype SAW/GC system was fabricated. The new SAW/GC system, depicted in Figure 32, differs from the research prototype tested during phase I at Savannah River. The size of the unit has been reduced by a factor of 2 and the complete system will now fit now a small suitcase.

To produce reliable systems, particularly for EPA certification/verification, it was

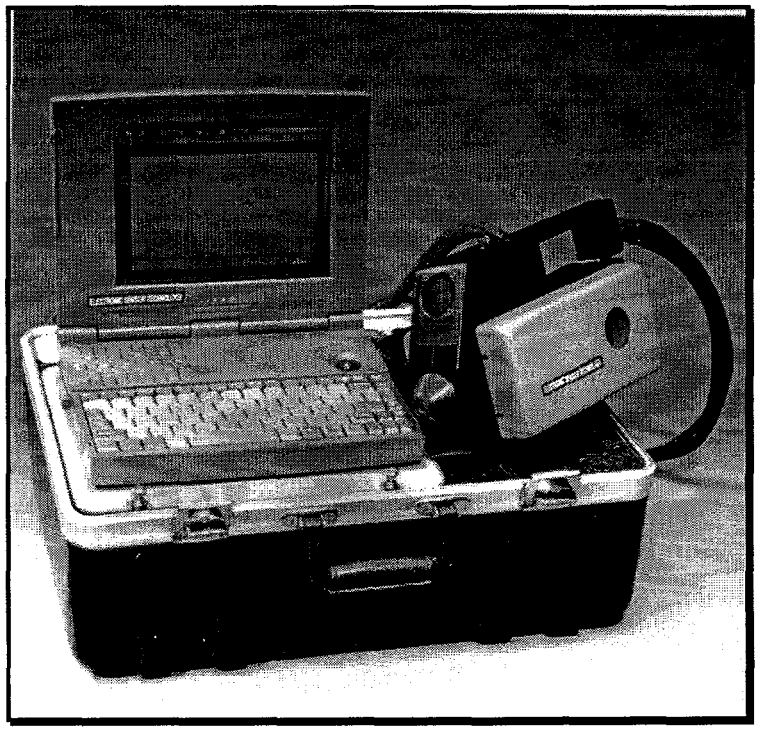

***Figure 32- Fieldable prototype SAW/GC vapor screening* instrument.**

necessary to implement a quality assurance plan. All parts were examined with reliability as a goal. It is anticipated that many DOE sites will want to field test these units so they must be built with this in mind. Also, as part of the new EPA validation program, it is

mandatory that a Quality Assurance Plan be part of any instrument used for regulatory purposes. The GC portions of the instrument are contained within a handheld sensing unit attached to a support base by means of an 8' umbilical which supplies electrical power and He carrier gas. Contained within the support base is an Intel microprocessor and programmable gate array capable of executing a wide variety of macro instructions and hardware configurations that give the instrument a wide selection of GC methods for optimal detection and quantification of inlet vapors. These prototype instruments are configured for detecting dioxins and furans.

6.3. EPA Methods Equivalency Studies

EPA Equivalency methods for the SAW/GC were developed for VOCs, dioxins, PCBs, and furans. EPA methods were evaluated and modified to take advantage of the instrument's speed. In particular the "600" series of waste water organic priority pollutants, the new "1600" series methods, "500 Series" drinking water methods, and the "8000 Series" methods for waste were examined. In addition to these, the new RCRA "SW-846" method was examined. As an example, shown in Figure 33, is a plot showing how the "600 Series" methods are related to the use of GC, HPLC, and GC/MS instruments with different classes of hazardous materials.

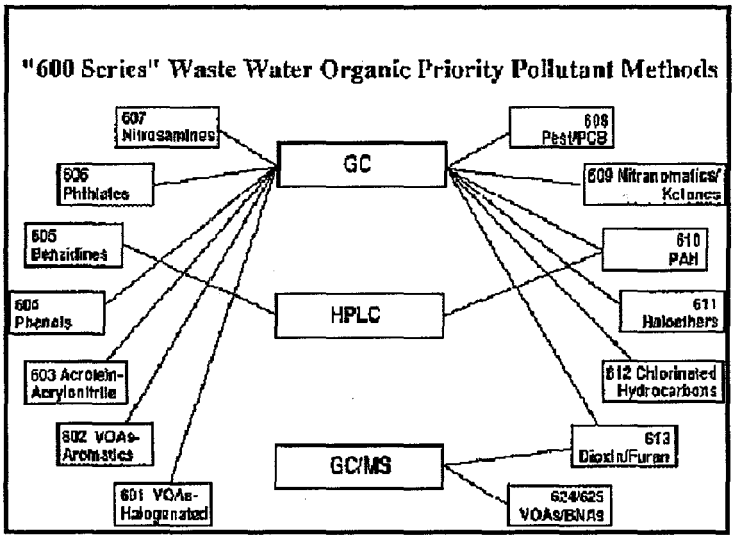

Figure 33– "600 Series" Waste Water Organic Priority Pollutant Methods.

A field screening method for the SAW/GC was developed. A portion of the method is diagrammed in Figure 34. The method is designed to utilize field validation using a calibration vapor standard prepared with a tedlar bag. For the Lawrence Berkeley site a tedlar bag was prepared with a 1 ppm vapor concentration of TCE and PCE. The method shown first requires a number of system checks and instrument confirmations such as carrier gas flow and column temperature settings. An important element of the SAW/GC method is the updating of notes throughout the process and the setting of the SAVALL flag. Each step of the method is then documented in the 'notes' window and

becomes a permanent part of the data record which is stored automatically as the data is taken. After the instruments completes a clean blank system test the notes are updated to reflect the next step which is calibration using the tedlar bag calibration sample. These chromatograms are used to update the system peak identification and measurement file with the appropriate retention time and scale factor.

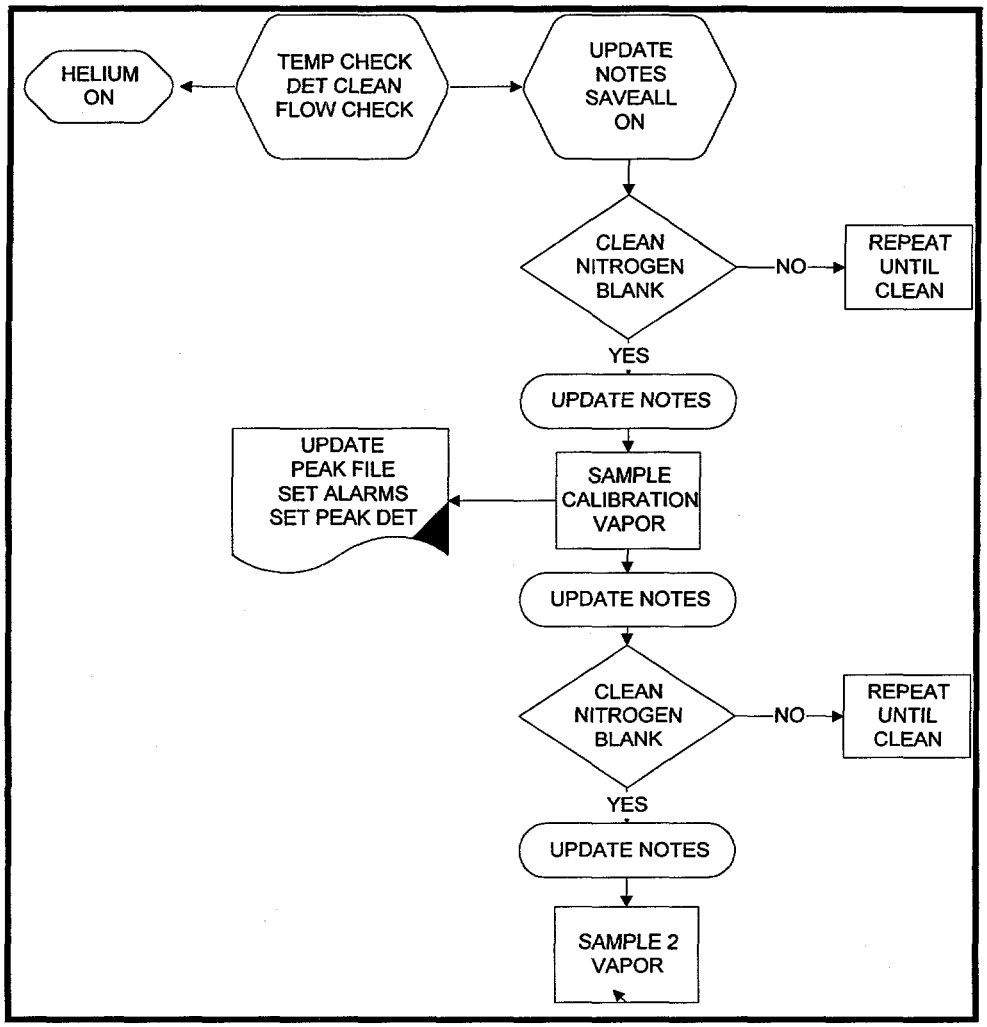

Figure 34- Procedures for field validation are vital for successful application of the new SAW/GC technology.

After calibration, the notes are changed to reflect the next step which is another blank test. After the instrument blank the notes are update for the next step which is the taking of data on the vapor sample to be analyzed. The final steps are to again clear the instrument by taking a blank chromatogram followed by a final calibration to insure that the instrument calibration has not changed.

Prototype systems were evaluated with two different GC columns, a DB-624 and a Carbowax Column. To obtain a different separation pattern a carbowax column was fabricated and installed in a SAW/GC. A comparison of retention time of a group of

VOCs for DB-624 and carbowax columns is shown in *Figure 35*. The separation of CT and TCE is much improved with the carbowax column, however this column would not

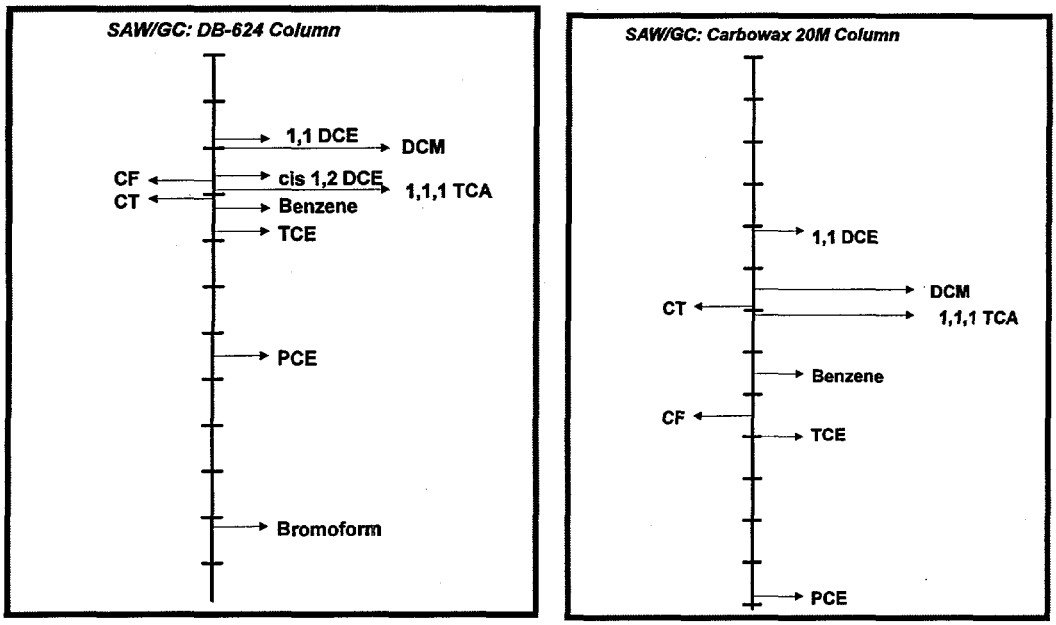

Figure 35- Comparison of different columns in SAW/GC.

be a good selection if 1,1,2,2 TCA were present.

Environmental testing of SAW/GC was carried out by placing systems in an environmental chamber and testing over a temperature range of 10°C to +35°C to simulate field conditions. The objective was to determine how retention time and hence peak identification was affected by ambient temperature changes. From field experience it had already been noted as a potential problem since calibration in the laboratory did not always give the same retention times as when in the field.

During the test the system was challenged by a tedlar bag mixture of TCE, PCE, and 1,1,2,2 TCA. The results of the test are shown in *Figure 36*. All three materials

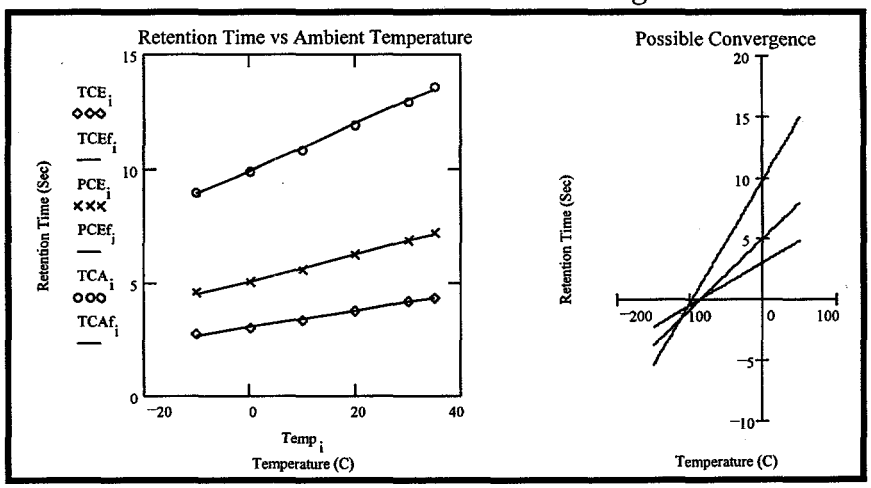

Figure 36- Environmental test results

showed a linear increase in retention time with temperature. Of considerable significance is that fact that all three curves extrapolate to a common point at approximately -100°C. Because of this a simple percentage change of retention time alarms within the system software will correct the problem. In effect if the retention time of a single peak changes by 10% of its retention time, then all peaks undergo a 10% of their respective retention times. In conclusion, retention time variations due to ambient temperature fluctuations are correctable in software and these changes are now being implemented..

Henry's Law experiments were also carried out using water solutions of TCE, PCE, and 1,1,2,2 TCA. The experiment was to test a matrix of aqueous solutions containing 100 ppb, 500 ppb, and 1000 ppb of TCE, PCE, and 1,1,2,2 TCA. Test vials (40 ml) with septum lids were prepared by diluting standard 10 ppm solutions of each. In

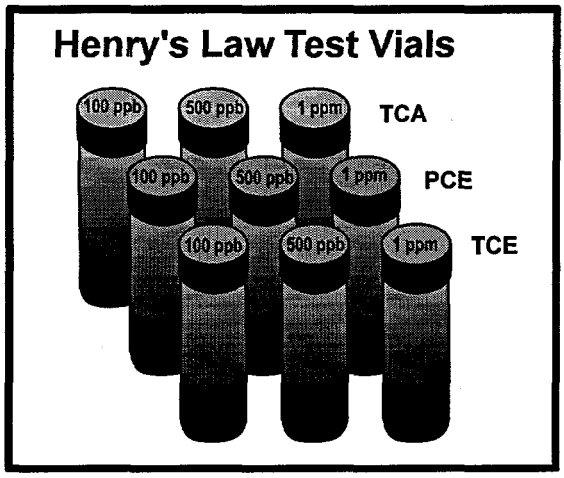

Figure 37- VOC water matrix.

effect a matrix of vials as shown in *Figure 37* was tested.

In the TCE test results there was considerable variability at the 100 ppb level and the 500 ppb solution appeared to be stronger than the 1 ppm solution. This was due to problems with solubility of TCE in water. Shaking the vial appeared to re-establish vapor equilibrium after extracting vapor from the vial and a 2nd sample always showed the effects of sampling 68 ccm X 10 seconds = 11 cc, or approximately 1/3 of the available headspace vapor was removed in each headspace sampling. The results with PCE show similar problems with solubility. There seemed to be a rather large and unpredictable variation between samples. 1,1,2,2 TCA test results did not show any solubility problems. All chromatograms were as expected and agreed with published Henry's Law coefficients.

Water solutions in VOA vials were compared with tedlar bag standards as shown in Figure 38. Tedlar bags were the clear choice based upon the variability of Henry's Law results. With solutions it was found that the solubility of the analytes played the

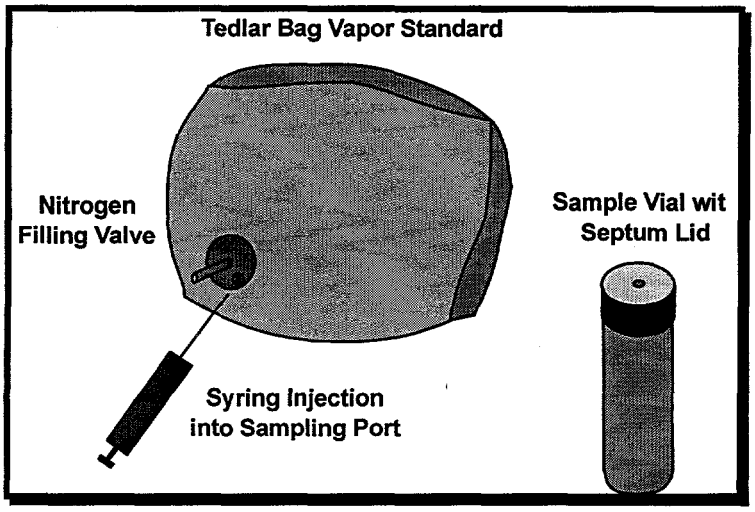

Figure 38- Field calibration using tedlar bags and VOA vials.

major role and there was not a reliable headspace within the vial. With tedlar bags the injection of a liquid analytes produced a very reliable vapor source with a low variation between multiple bags. The tedlar bag could also be prepared easily in the field using a hand pump as shown in Figure 39.

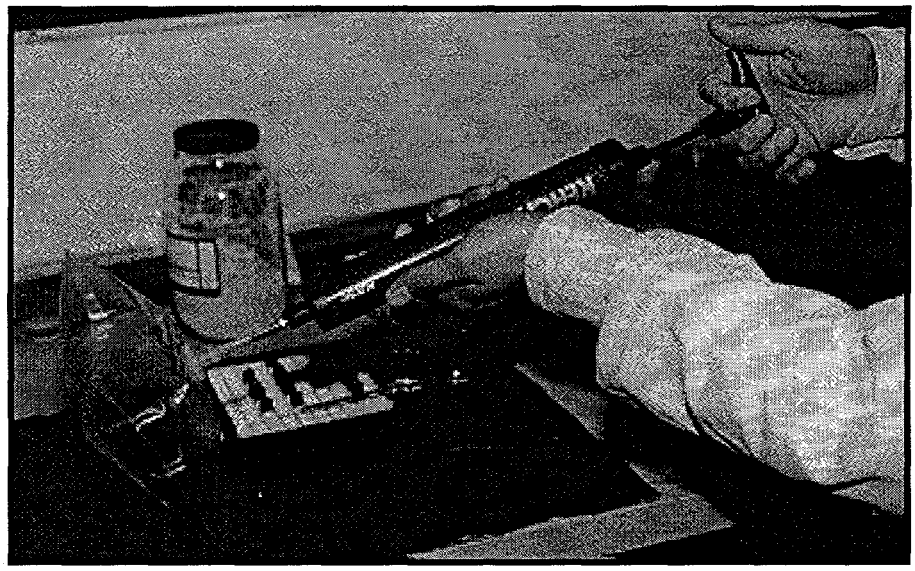

Figure 39- Filling a tedlar bag with a hand pump.

Preparation for field demonstrations required us to prepare a test plan which included test results for those compounds which would be encountered at the field site. The test plan provided a field method using tedlar bag standards prepared in the field.

The method included a recipe for producing standards over the range 0.1 ppm to 10,000 ppm. Each compound was tested and its scale factor and retention time entered into a peak table file as shown in Table VIII.

Table XVIII- Peak File Retention Times and Scale Factor

Substance	Scale Factor Hz/ppm*cc	Ret. Time @R.T.
trans DCE	2.5	2.3
cis DCE	10	2.9
Chloroform	12	3.1
Carbon Tet	2.25	3.3
TCE	65	4.2
DCP	32	4.4
PCE	200	6.9

6.4. Field Testing

In Phase II, Amerasia personnel visited a Chicago refinery managed by Rust International. There they were able to use the laboratory prototype SAW/GC instrument to characterize carbon scrubbers currently being used to trap VOCs. The result of these experiments is shown in Figure 40. Before entering the scrubber the system accurately detected Benzene at 38 ppm and Toluene at 100 ppm. After passing through the scrubber the SAW/GC confirmed the concentration of benzene to be 250 ppb and toluene to be 346 ppb. In addition to these elements the SAW/GC also indicated that other elements

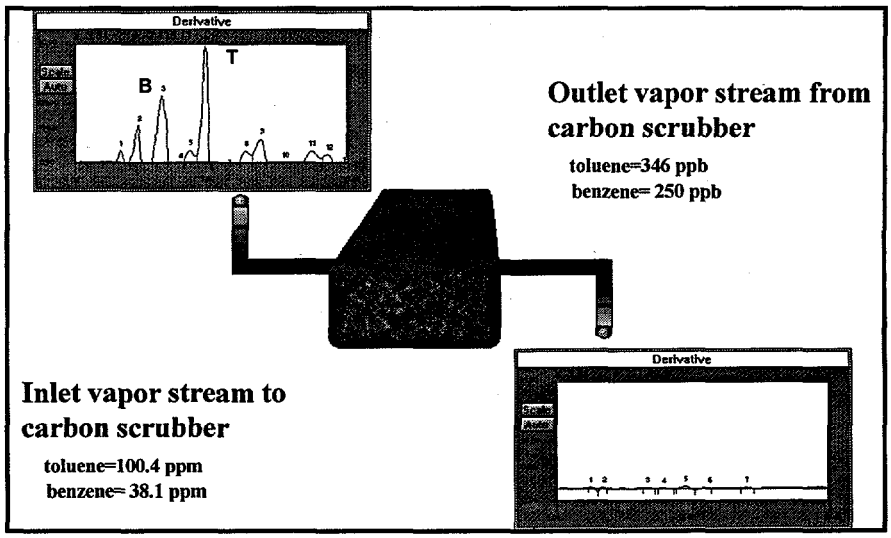

Figure 40- VOCs detected at the inlet and outlet of a carbon scrubber.

were present as well.

In late January of 1996 the system was used to evaluate the performance of a catalytic converter at a remediation site recommended by the EPA located in Port Hueneme, California. Photographs of the system at the site is shown in Figure 41 and Figure 42.

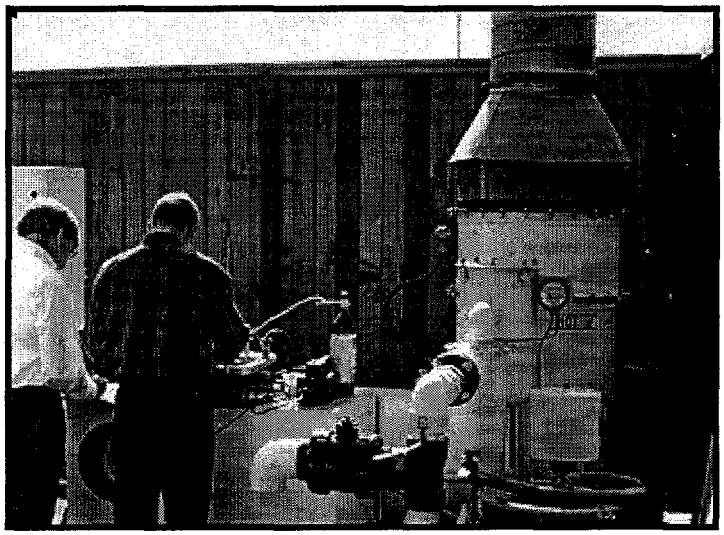

Figure 41- SAW/GC being used to measure inlet and outlet flow of a catalytic converter.

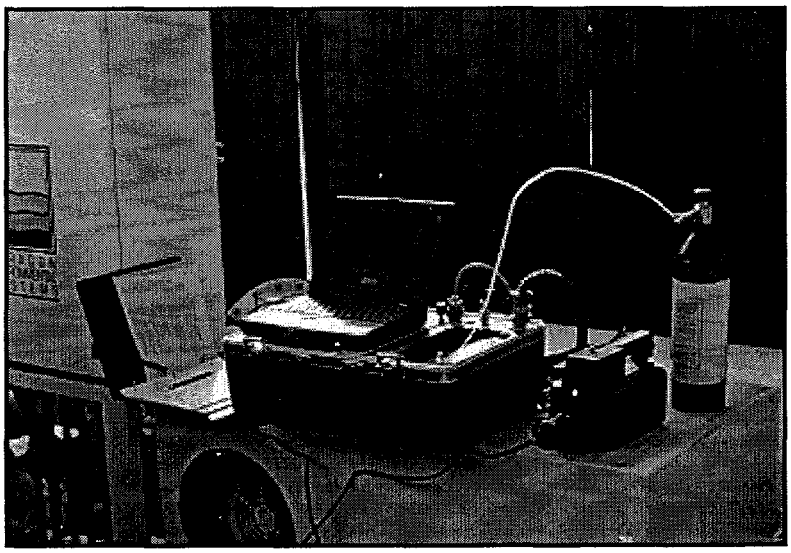

Figure 42- The field portable SAW/GC was validated with a calibration gas during the test.

The materials being remediated in the converter were primarily hydrocarbons such as Benzene, Toluene, Xylene, and Ethylbenzene, also known as BTEX. At this site an OVA flame ionization detector was being used to give total hydrocarbons. Two measurements were required, one with a carbon trap to remove methane and the other to give the total hydrocarbons including methane. The advantage offered by the SAW/GC was the ability to identify individual species and total hydrocarbon content without the need for carbon filtration to remove the methane.

A field test was carried out at Lawrence Berkeley Laboratory where soil contamination is being monitored. The technique currently being employed at this site utilizes pipes driven in to the ground at selected sample sites. Each pipe is fitted with a septum and periodic measurement of total VOC content with a photo-ionization detector (not specific) is required. Measurement confirmation is achieved by filling a summa canister with soil gas for laboratory analysis. The process is longer than desired and gives no real time information on individual species or migration of the plume. Two different field sites were used to demonstrate field screening with the instrument. Soil gas was tested by placing a sampling needle on the inlet of the instrument and then inserting the needle into the septum of the soil probe as shown in Figure 43.

Figure 43- Direct sampling of soil gas gives real time measurement of underground contamination.

At this site (near a building entrance) the concentration of soil contamination was found to be quite low and demonstrated the instrument's sensitivity. A typical chromatogram obtained at this site is shown in Figure 45. In this chromatogram 76 ppb TCE and 25 ppb PCE is detected in the soil gas. Identification and calibration was provided by a tedlar bag containing a 1 ppm standard of each species. The other species detected were not calibrated and hence not identified by name, however, based upon their relatively long retention times it is speculated that they are possibly heavy hydrocarbons, Xylene, or possibly TCA. Future laboratory testing will allow the preparation of

validation standards for the SAW/GC. It should noted that the chromatogram is only 15 seconds long.

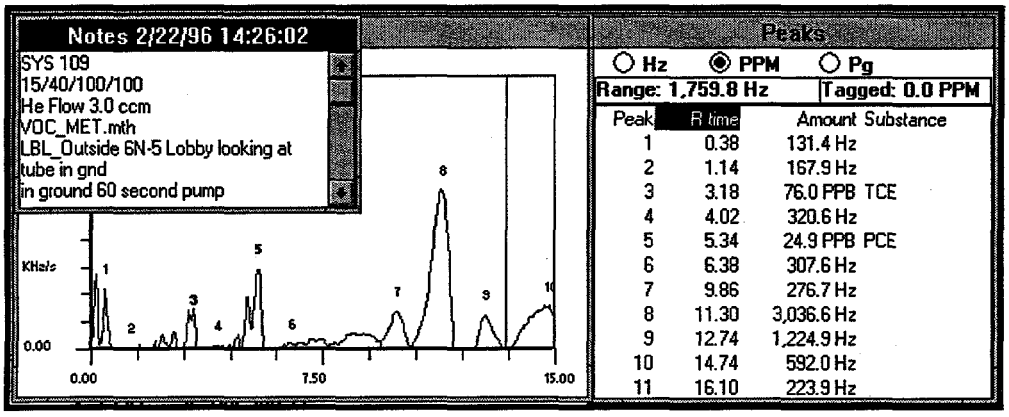

Figure 45-Chromatogram showing ppb sensitivity of the SAW/GC.

The second site selected, shown in Figure 44, was located on a hillside (everything is on a hill in the Bay area!). The hillside was the site of an active plume known to contain TCE and PCE. During the testing of the SAW/GC use of a field screening method requiring validation with a 1 ppm TCE/PCE tedlar bag standard was

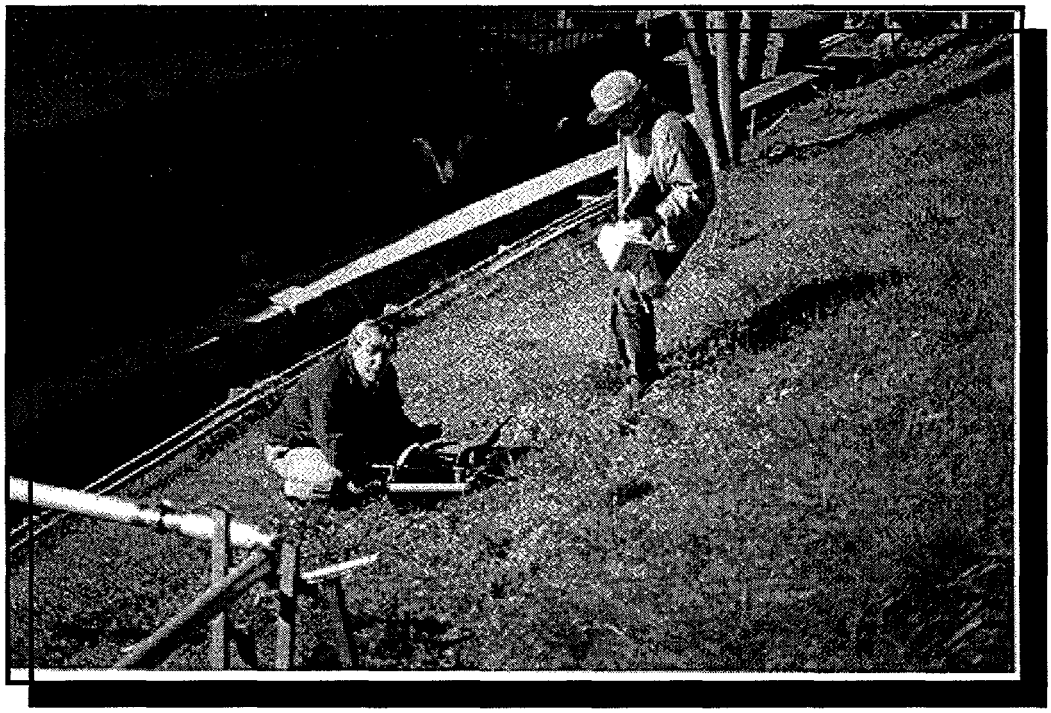

Figure 44-Operating the instrument in the field gives real time extends of underground plume.

demonstrated. Although we did have to search for some rocks to support the instrument case on the steep slope, it was not difficult or time consuming to take a measurement.

The SAW/GC was able to quantify individual compounds within the plume in real time. Shown in Figure 46 is a typical chromatogram taken at one point within the plume while the chromatogram of Figure 47 shows the results taken at a second location within the plume. At the first location the concentration of TCE and PCE was found to be approximately 1 ppm. At the second location, approximately 40 feet away from the first,

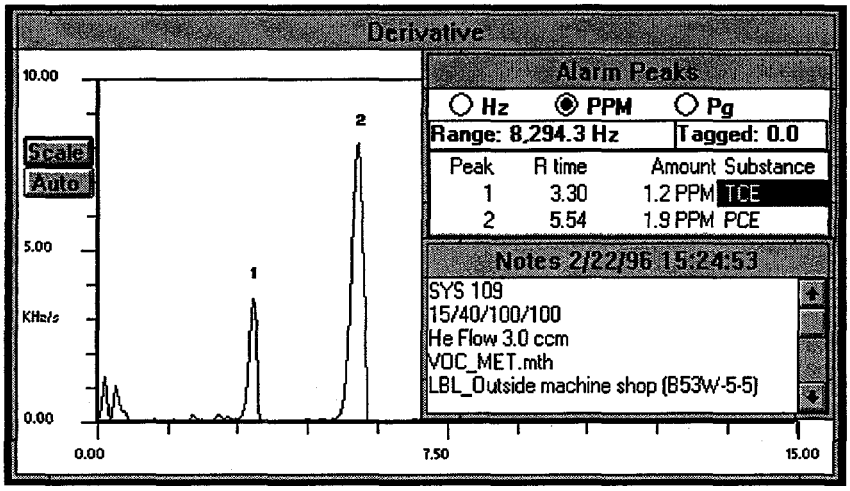

Figure 46- Plume contamination showing several ppm contamination of TCE and PCE.

the concentration of TCE dropped to approximately 300 ppb, while the PCE rose to almost 10 ppm. Also, a small trace amount of DCE was detected. The latter compound is much more volatile than TCE or PCE. In addition, an unidentified compound with a retention time of approximately 12 seconds was detected in the soil gas at this location. The importance of the above chromatograms is to demonstrate that the concentration of the individual species within the plume are spatially different. The SAW/GC was able to quantify that difference in real time without waiting for laboratory results.

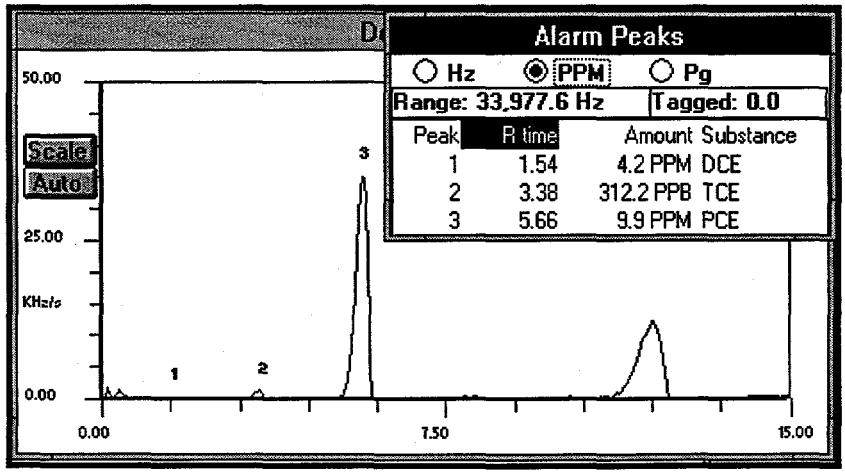

Figure 47- Second sample point within hillside plume.

A field test was performed at the Idaho National Engineering Laboratory. A field demonstration of high speed surface acoustic wave gas chromatography (SAW/GC) technology was conducted at INEL's Central and Test Area North sites on April 9-10, 1996. Here portable instruments are needed on-site for monitoring. The SAW/GC demonstrated real time and specific analysis of hazardous vapors with ppb sensitivity.

Two SAW/GCs were setup as a demonstration at the on-site Environmental Restoration Laboratory operated by Larry Lazarotto. The systems were tested using on-site calibration gases as well as tedlar bag standards prepared by sample injection. At INEL two prototype instruments were demonstrated in the laboratory and then transported to two different field sites for working demonstrations under actual field conditions. The first site was at the Central facility where the SAW/GC was evaluated as a well headspace monitor. Forty tedlar bags (mainly carbon tetrachloride, chloroform, and trichloroethylene) from all of their wells were evaluated in approximately 1 hour. Accuracy over the range 20-500 ppm was validated by more than 10 calibration runs taken during the demonstration. The second site was in Test Area North at the Ground Water Treatment Facility (GWTF). There the SAW/GC demonstrated detection of DCE, TCE, and PCE at the ppb level.

Unit 109: DB-624 Column

This system was tested with a INEL calibration bag containing 36 ppm chloroform, 80 ppm carbon tetrachloride, and 36.6 ppm trichloroethylene. A typical chromatogram obtained is shown in Figure 48. The scale factors used were 12, 2.25, and 65 Hz/ppm*cc respectively. The chloroform and TCE scale factors appear too high by factors of 2 or 3, however the CT scale factor is more than 10 times too high. This error appeared to be consistent and probably reflects the difference between the tedlar bag calibration method and the purchased tank mixture.

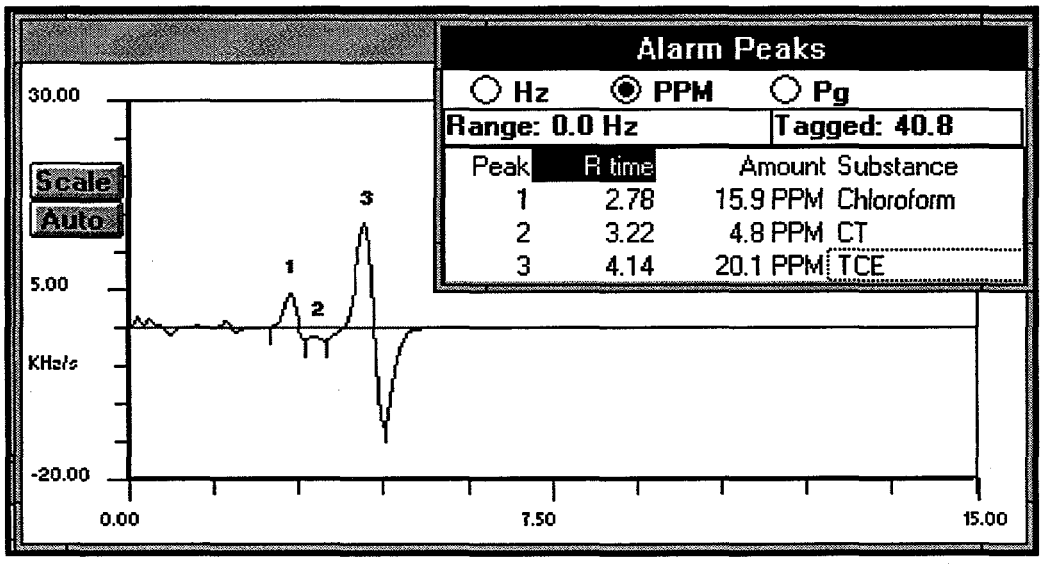

Figure 48- Chromatogram obtained on 36-80-36.6 chloroform, CT, and TCE.

Unit 111: Carbowax Column

The second system was also evaluated with the calibration bag (36-80-36.6) and the resulting chromatogram is shown in *Figure 49*. The use of carbowax column greatly improves the separation of carbon tetrachloride and TCE relative to the result achieved with a DB-624 column. The SAW/GC demonstrated its ability to utilize different columns and thus achieve an optimal selection for the compounds being analyzed.

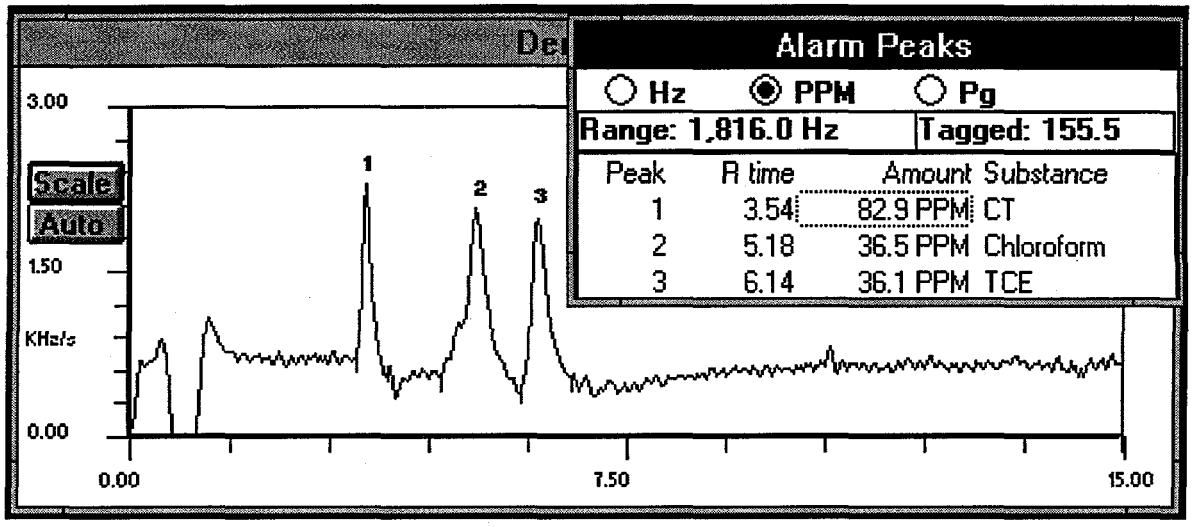

Figure 49- Carbowax column separation with 36-80-36.6 ppm chloroform, carbon tetrachloride, and TCE.

Central Facility

After the laboratory demonstration unit 111 was transported to the central facility where waste is currently being entombed. This site, shown in *Figure 50*, is surrounded by many test wells. Each well contains many sampling tubes and each collects vapors at different depths. From each well tedlar bags are filled from the sample tubes and

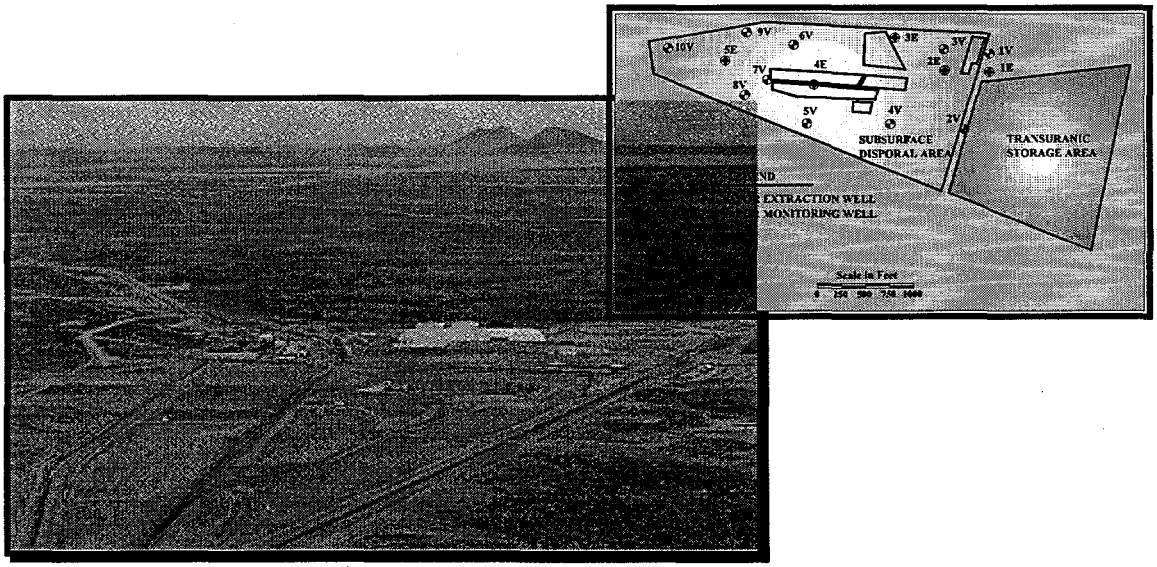

Figure 50- INEL Central facility.

transported to a mobile trailer laboratory. Monitoring requirements dictate that the well headspace vapors be periodically tested and reported.

At the central facility the SAW/GC was taken to a field trailer laboratory where tedlar bag samples from the test wells were also tested with two B&K instruments. The SAW/GC was set to take a 10 second sample at an inlet flow of 44 cc/min, or approximately 7 cc from each tedlar bag. The log of well gas chromatogram analyses of the tedlar bag samples taken at the mobile laboratory are shown in Table XIX.

Table XIX- Log of tedlar bag analysis from wells.

Time Stamp	Id.Name	CT ppm	CF ppm	TCE ppm
96040913.165	9301-4	247	57	45
96040913.203	6V-2	257	35	51.9
96040913.235	9302-1	103		163
96040913.255	8V-1	54		
96040913.304	8V-2	127		8.3
96040913.322	7V-1	236	7.4	43.9
96040913.334	5V-1			
96040913.350	9V-1	29.9		
96040913.362	DO2-8	219	65	29.7
96040913.373	10V-2	108		16
96040913.401	10V-1	58		3.7
96040913.421	2E-0	262	95	45
96040913.444	DO2-5	291	55	50
96040913.455	9301-1	72		15
96040913.471	3E-0	675	122	136
96040913.500	3E-0	644	131	154
96040913.511	8801-7	295	56.5	58.9
96040913.524	3V-1	324	53	64.5
96040913.551	9V	139	5.8	29.9
96040913.563	8801-1	199		125
96040913.575	8902-1	197	5.6	40.7
96040913.590	8901-0	545	157	99
96040914.002	8902-4	553	83	81
96040914.032	4E-0	300	50	62
96040914.045	4V-1	193	19.5	34
96040914.061	4V-2	129	10	21.4

For the above readings the scale factors for the SAW detector were as follows:

Table XX-Detector Scale Factors

Compound	Scale Factor
Carbon Tetrachloride	0.5 Hz/(ppm•cc)
Chloroform	2.0 Hz/(ppm•cc)
Trichloroethylene	2.0 Hz/(ppm•cc)

During the testing a tedlar bag (80 ppm CT, 40 ppm CF, 20 ppm TCE) was used to validate SAW/GC measurements. These chromatogram results are shown in Table XXI.

Table XXI- Chromatograms on Calibration standards

Time Stamp	Id.Name	CT ppm	CF ppm	TCE ppm
96040913.182	80/40/20	94.1	34.7	25.3
96040913.220	80/40/20	95.1	36	29.5
96040913.272	80/40/20	89.2	37.1	30.3
96040913.385	80/40/20	96	37.1	32.4
96040913.432	80/40/20	104.7	34.1	31.2
96040913.485	80/40/20	105.2	43.5	35.6
96040913.535	80/40/20	101.3	32.1	34.8
96040914.020	80/40/20	100.7	40.1	32.1
96040914.091	80/40/20	109	35.4	30.1
96040914.163	80/40/20	105.7	35.8	30.7
Averages		91.0	33.3	28.4
96040914.074	500	511.3		
96040914.115	500	478		
96040914.174	500	497		
Averages		495.4		

Testing at the Central site confirmed the speed of the SAW/GC. The time stamps show that approximately 40 chromatograms were taken during a time span of one hour (96040913.165-96040914.174=1.009 hours) or 1.5 minutes per chromatogram. Calibration gas analyses also show that the relative accuracy was within 10% of readings over the 0-500 ppm range.

While at the Central facility the SAW/GC was taken to a well head and demonstrated how samples might be directly collected in the field without the need and cost associated with tedlar bag extraction. Tedlar bag samples might still be used for confirmation by an off-site laboratory. Placed atop each well head was a matrix of valves and outlets which enable samples to be taken from different depths. The SAW/GC was taken to one such well head and simulated well sampling was demonstrated as shown in *Figure 51.*

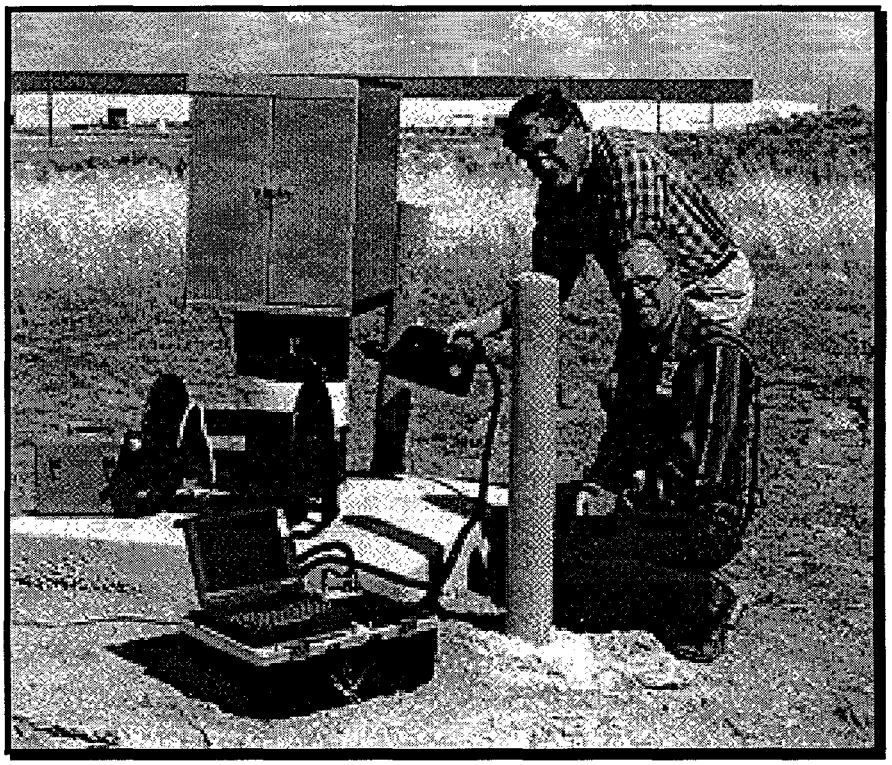

Figure 51- Larry and George demonstrate field sampling at well head using the SAW/GC.

Test Area North (TAN) Facility

At TAN we viewed the site where nuclear powered aircraft engines had been under development. At the site there is a contaminated water aquifer under remediation. The SAW/GC Unit 109 was transported to the Ground Water Treatment Facility (GWTF) shown in *Figure 52.* At the site out hosts were Dr. Barbara Keller and Marty Bartholomieu. Here contaminated water from the ground is treated and re-injected into the aquifer after it satisfies drinking water standards (<5 ppb).

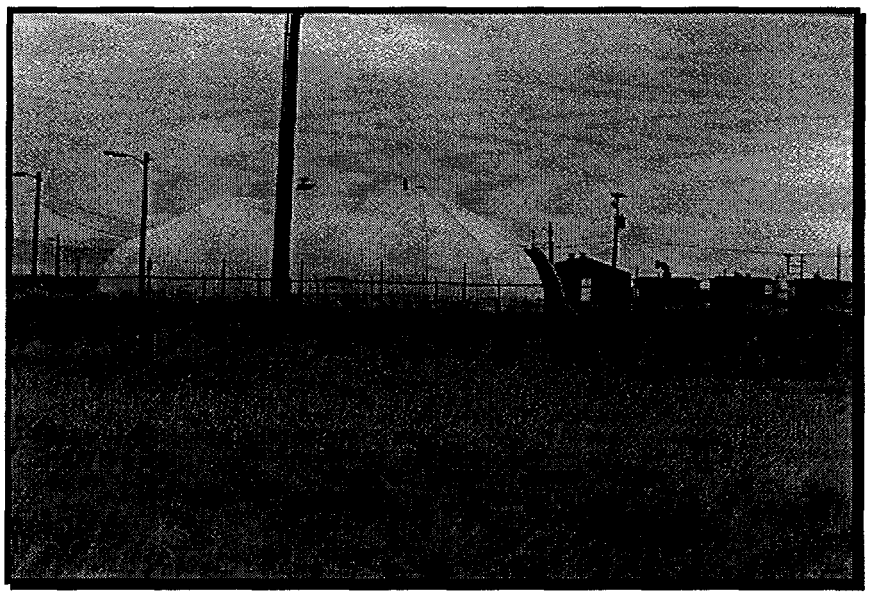

Figure 52- Ground Water Treatment Facility (GWTF) located at Test Area North (TAN).

At this site the water treatment facility was under going repairs and maintenance and was not operating. Accordingly, it was not possible to use the SAW/GC on actual headspace vapors from the process tanks tests of the instrument were done using calibration gases supplied from a certified tank source. The instrument was challenged with a mixture of *cis*-DCE, *trans*-DCE, vinyl chloride, DCP, TCE, and PCE. The concentration of all compounds within the mixture was 100 ppb. A typical chromatogram taken after a 20 second preconcentration is shown in *Figure 53*. In this chromatogram, peak 2 is a system peak and not from the calibration sample.

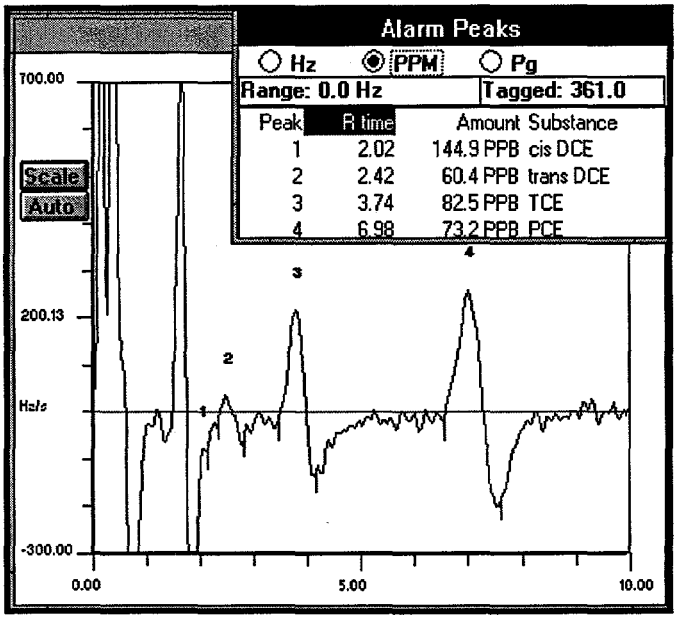

Figure 53- 30 second sample, 96041008.590.

Using the initial chromatogram (96041008.434) data, the SAW detector scale factor for TCE and PCE was set to the values shown in Table XXII. The values for both isomers of DCE were set according to previous chromatogram results taken at ppm concentration levels.

Table XXII-Detector Scale Factors

Compound	Scale Factor
cis-DCE	10 Hz/(ppm•cc)
trans-DCE	8 Hz/(ppm•cc)
Trichloroethylene	48 Hz/(ppm•cc)
Tetrachloroethene	95 Hz/(ppm•cc)

The results for a series of chromatograms taken with a 20 second preconcentration time are listed in Table XXIII. At the 100 ppb level the variation in readings or repeatability is typically 20% of reading.

Table XXIII- Results of testing at GWTF.

Time Stamp	TCE (ppb)	PCE(ppb)
96041008.434	99.0	97.7
96041008.445	123.5	84.8
96041008.460	109.3	99.2
96041008.471	81.7	70.0
96041008.482	101.8	81.3
96041008.493	116.7	80.1
96041008.504	113.1	69.9
96041008.515	99.0	69.4
96041008.530	92.8	94.4
96041008.541	96.6	84.0
96041008.560	81.5	72.6
Averages	101.36	82.13

The SAW detector was not able to detect vinyl chloride, *cis*-DCE, *trans*-DCE, or DCP at the part per billion level because of their comparatively low scale factors. However, *cis*- and *trans*-DCE were made detectable at the 100 ppb level by increasing the inlet preconcentration time to 30 seconds as shown in the chromatogram of *Figure 53*. With increased preconcentrator flow and/or lower detector temperature the scale factor for the volatile compounds can be increased for future designs of the instrument.

Hanford Technology Demonstration:

During the month of May a field demonstration of high speed surface acoustic wave gas chromatography (SAW/GC) technology was conducted at the DOE Hanford site, 200 Area West and 200 Area East. At these facilities there is a need for portable instruments to perform real time on-site monitoring. The systems must perform a fast and specific analysis on hazardous vapors with ppb sensitivity. At Hanford two prototype instruments with different columns were demonstrated in the laboratory and then transported to a field site for further demonstrations. The first site was at the Analytical Services Laboratory, Test Area West, where the SAW/GC was used to evaluate tedlar bag samples and summa canister samples from the field. The second site was at a tank farm near a 'canyon' processing building located in Test Area 200 East.

The Hanford site, Figure 54, is located in Washington State and covers an area of approximately 525 square miles. To the south of the site is Richland, a town which grew out from the original housing complex for the workers at the site. The Columbia River can be seen to flow through the site before turning south to pass by Richland. Historically this site was first used in 1944 to produce plutonium. The site was still active until the late 1950s. At the present time the major work being carried out at the site is monitoring and remediation of mixed waste.

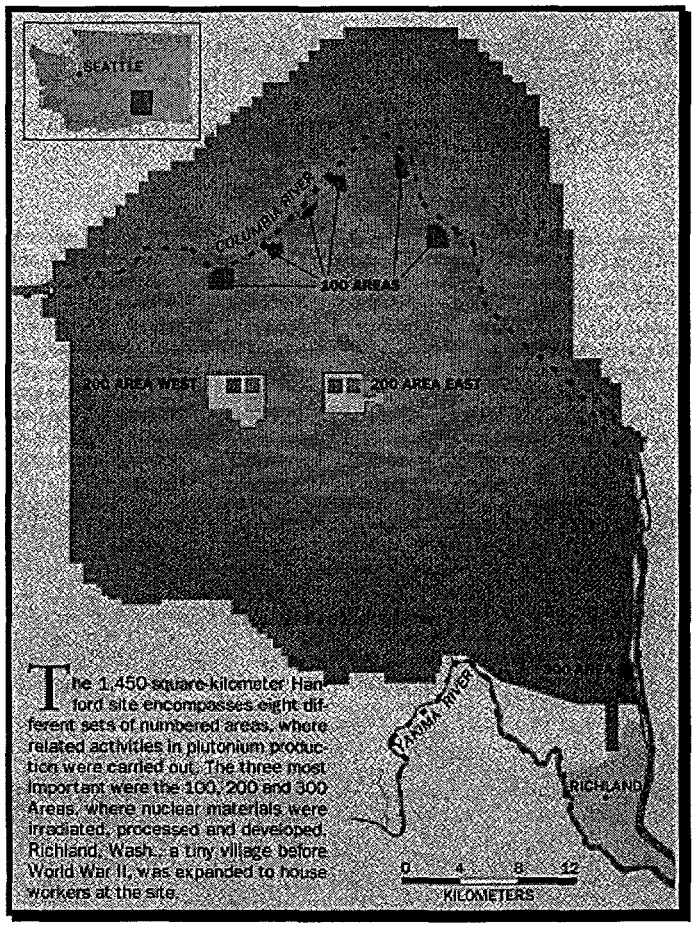

Figure 54- DOE Hanford site.

A large variety of different waste materials exists at the Hanford site. Considerable solvent spillage occurred in the past and this has produced ground water contamination expanding in the form of underground plumes. Mixed waste is also stored in buried tanks which require monitoring for air emissions. Because these emissions are not continuous and the tanks are subject to "burping", a real time monitor like the SAW/GC is needed to satisfy State emissions requirements.

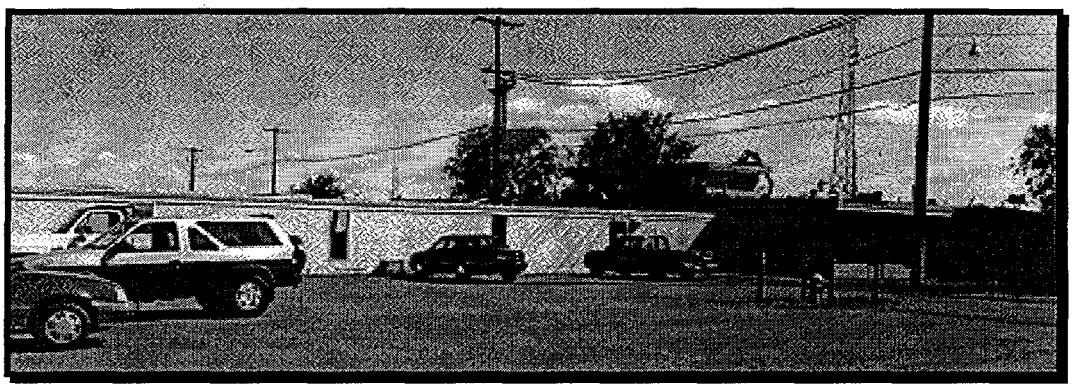

Figure 55- Weather station building, 200 area west.

Two prototype SAW/GC screening instruments were transported to Richland, Washington by Dr. Edward Staples and David McGuire. On the afternoon of their arrival they were briefed on the safety and security regulations of the site and given visitor badges and personal exposure monitors. On the next day the two instruments were transported to the Analytical Services Laboratory shown in *Figure 55*.

During the first half of the day the SAW/GCs were demonstrated in a laboratory environment. Tedlar bag standards were prepared and used to demonstrate the instruments real time speed and accuracy. An example is shown in *Figure 56* where a 15 second duration TCE/PCE chromatogram from the technology demonstration is shown.

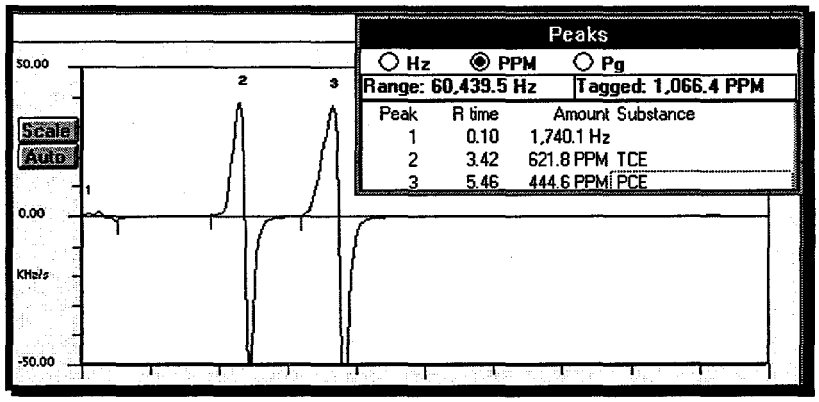

Figure 56- Tedlar bag calibration for TCE/PCE.

In the afternoon Dr. R.S. Viswannath and Dr. Markus Stauffer gave a facility tour and explained the details of their efforts to monitor emissions at the Hanford tank farms. Their particular problems centered around the tank farms which contain waste material from the production of plutonium. Their group is developing field methods for monitoring the headspace of the mixed waste. Some examples of their work are shown in *Figure 57* and *Figure 58*.

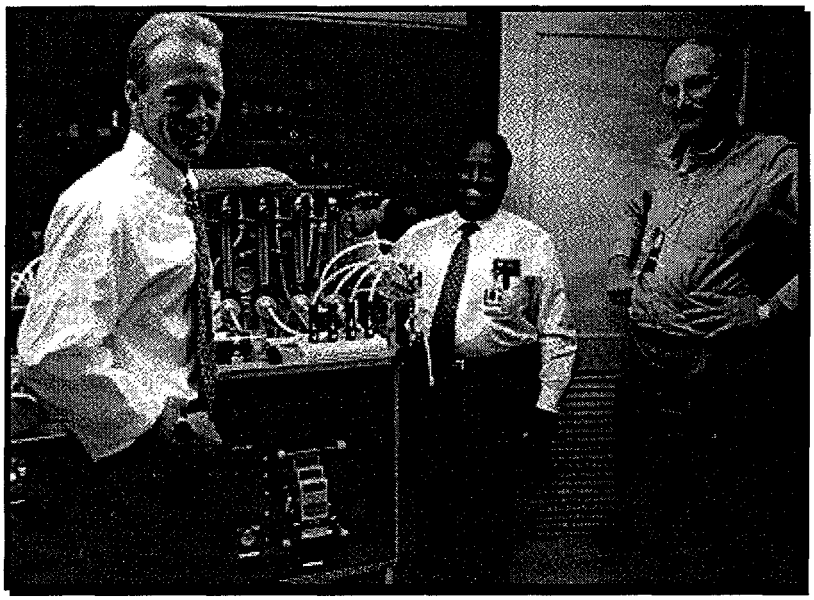

Figure 57- R.S. Viswannath and Markus Stauffer demonstrate automatic multi-port sampling apparatus to David McGuire.

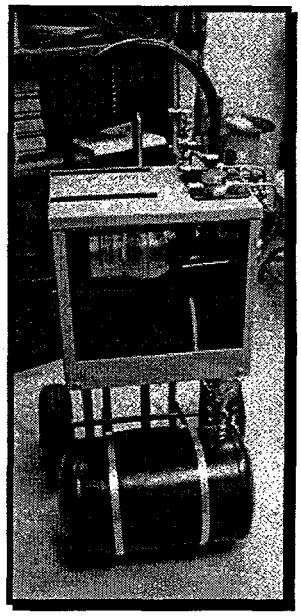

Figure 58- Portable summa canister filling apparatus.

The current approach is to acquire samples from the storage tanks using summa canisters. A mobile trailer, shown in *Figure 59*, contains the necessary filtering equipment to remove radio-nuclides and dust from air samples while the vapors from

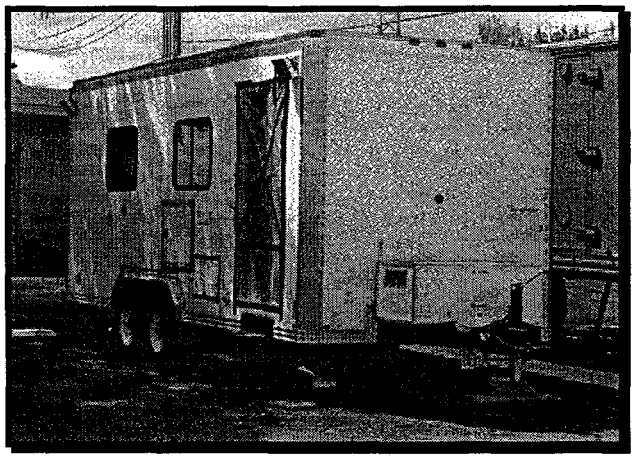

Figure 59- Mobile laboratory for on site analysis of canisters.

tanks are pumped into the canisters. These canisters are then transported to other mobile or fixed laboratories where they are tested by GC/MS instruments. The current analysis time is 50 minutes or more which is typical of GC/MS methods. The objective is to determine the total hydrocarbon emission from the tanks, according to an EPA method for TO-14 compounds. The development of a fast and accurate analysis system, such as the SAW/GC, will allow rapid field screening of emissions in less than 20 seconds. In cases where the screening test indicates laboratory confirmation is needed, a summa canister can be filled and sent to a laboratory for validation. Based upon estimated cost figures for this procedure, screening with the SAW/GC would save $50,000 per month by eliminating the need to test every headspace sample with the GC/MS.

To test TO-14 compounds using the SAW/GC, a certified 1 ppm mixture of VOCs supplied by the Analytical Services Laboratory was used. A typical chromatogram (negative peaks suppressed) obtained with the SAW/GC screening instrument is shown in *Figure 60*. The total length of the chromatogram is 20 seconds and most of the compounds elute in less than 10 seconds. In the upper right portion of the figure is a peak identification window labeled Alarm Peaks. In this window only software identified peaks are shown. Because the instrument was pre-calibrated for only a limited number of TO-14 compounds only 6 of approximately 17 peaks are shown. A software feature allows for summation of all peaks and all tagged peaks and could be used to give total hydrocarbon content over a specified range of retention times. Tagged peaks are individual material peaks which the operator intentionally marks as tagged. Total hydrocarbon content can be determined using the peak summation operators.

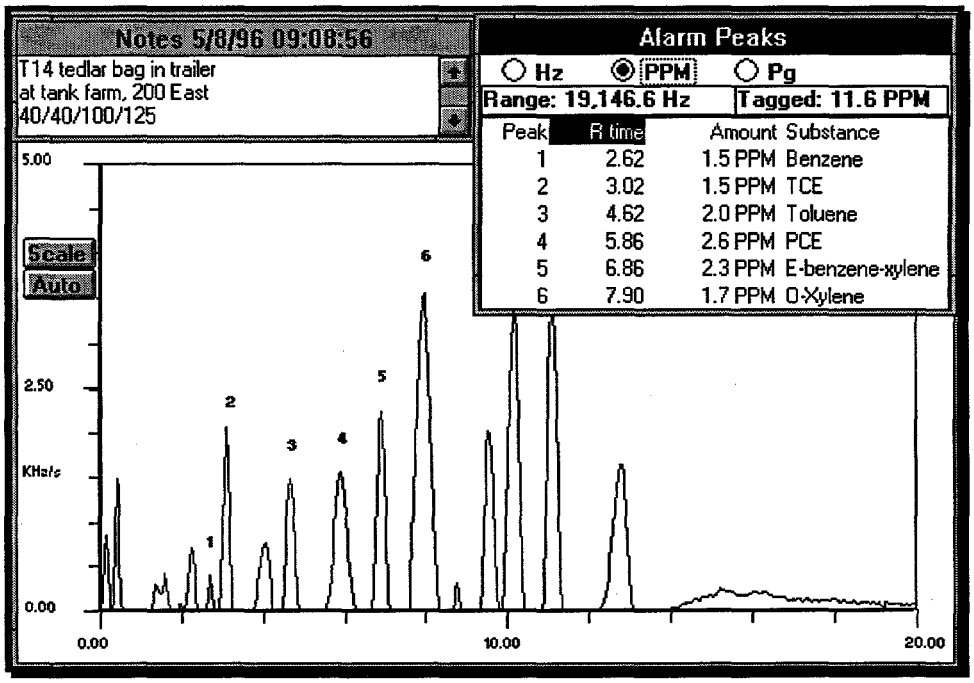

Figure 60- SAW/GC chromatogram obtained with 1 ppm concentration of TO-14 volatile organic compound mixture.

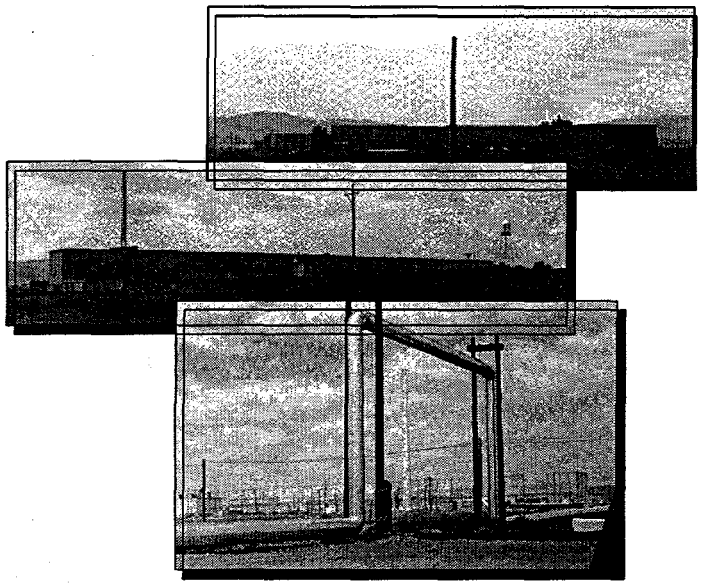

Figure 61- Canyon processing building.

On the second day of the technology demonstration the SAW/GC was taken to the tank farm where it was set up in a mobile laboratory. Here the instrument was demonstrated to personnel from other organizations with responsibility for monitoring the tanks. The tank farms exist near locations where plutonium was processed in buildings called 'canyons'. At Hanford there are approximately 5-7 such buildings and three of these buildings are shown in the photographs of *Figure 61*. An internal view of a typical canyon building is shown in *Figure 62*. These buildings, some longer than the Empire State building is tall, produced plutonium and a by-product of the process was mixed nuclear waste the consistency of peanut butter. The waste was placed in vented underground storage tanks, shown in *Figure 63* and

Figure 63- Tank farm.

VOC emissions from these 'tank farms' can produce toxic vapors. Hence, monitoring of VOC emissions is needed to comply with State regulations.

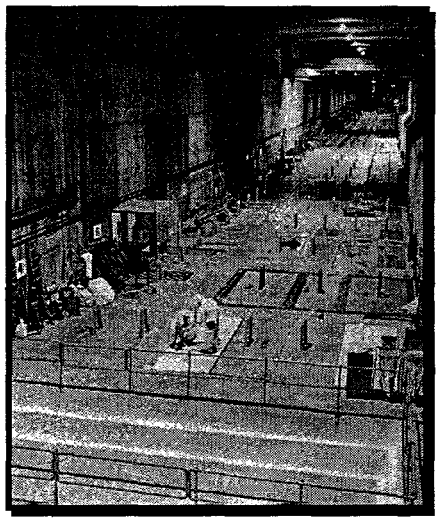

Figure 62- Inside of canyon building.

The TO-14 calibration mix contains 39 separate components which can be broken down into three subsets excluding 1,2 dibromoethane and bromomethane as shown in *Figure 64*. The groupings thus formed are called aromatics, chlorinated hydrocarbons, and halogens.

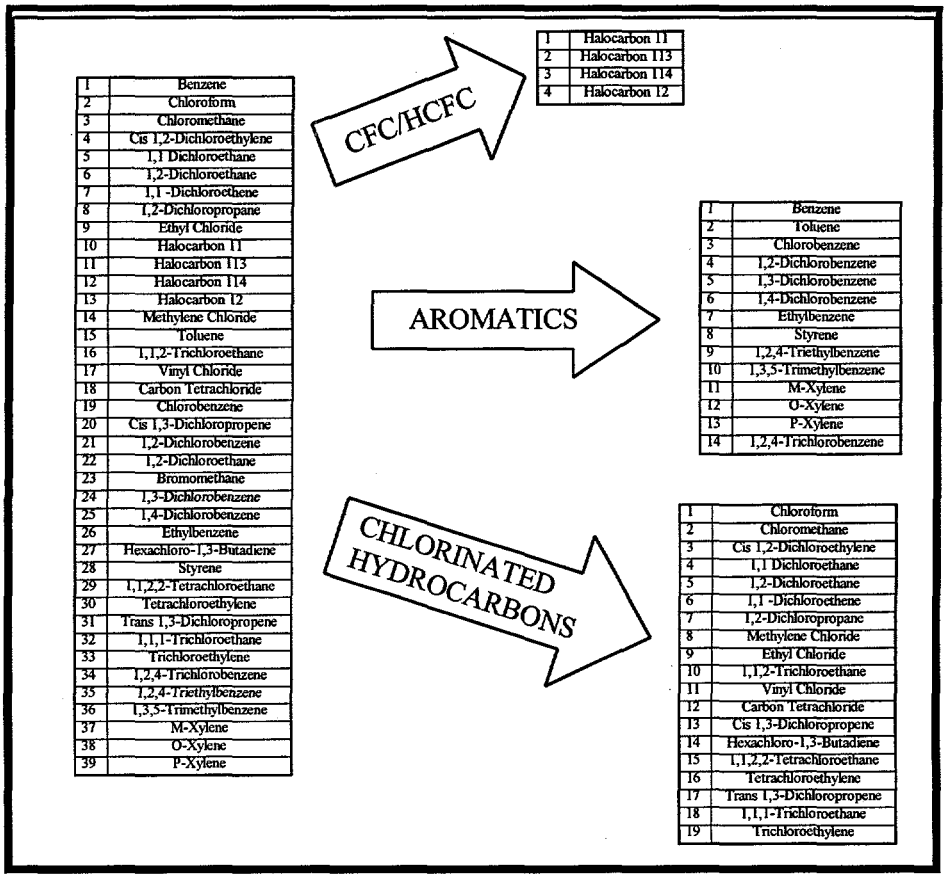

Figure 64- TO-14 Standards can be broken down into subsets.

The response of the SAW/GC when testing a tedlar bag filled with a 1 ppm concentration of TO-14 hydrocarbons is shown in *Figure 65*. In this figure both positive

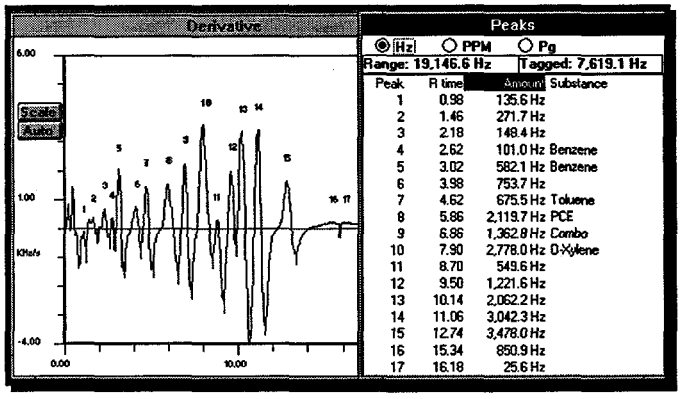

Figure 65- Detection of 17 distinct compounds or groups of compounds using DB-624 column.

and negative portions of the frequency derivative are shown. The 17 peaks detected represent those compounds in the TO-14 mixture detectable using a 5 second sample time, an inlet flow of 40 cc/min, and a SAW detection temperature of 40°C. Other, more volatile compounds, might be detected at lower detector temperatures, e.g. 20°C. Similarly the use of different sampling times allows the instrument to achieve greater sensitivity through preconcentration. For example, a 60 second sample time enables the instrument to quantify and screen vapors at the ppb level. Also, different GC methods involving temperature profiles, allow the instrument to separate compounds for better identification. A full parametric evaluation of all TO-14 compounds was beyond the scope of the Hanford demonstration, however separation was judged to be quite good for most.

Throughout the Hanford demonstration a tedlar bag was used as a calibration standard. Selected multiple chromatograms, shown in *Figure 66*, and covering a 2 hour period of time demonstrate the excellent stability of the SAW/GC instrument. The use of a calibrated tedlar bag standard as part of a measurement method has been discussed in previous reports and is the subject of the current CALEPA certification effort.

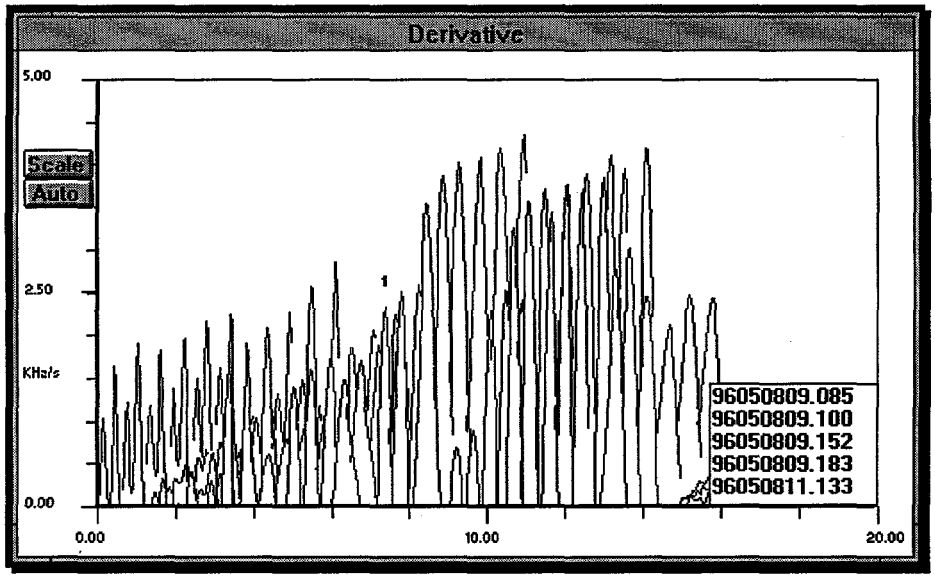

Figure 66- Multiple chromatograms using TO-14 standard mixture.

An important characteristic of a screening instrument is the ability to detect all target compounds with a low probability of false negatives. In the SAW/GC this is achieved because the detector responds to all condensable vapors universally. The SAW detector is not polar, nor is it chemical in nature. Rather, it achieves universal detection by being based upon physical absorption of vapors onto a temperature controlled pure quartz surface. With the proper detection temperature **all** compounds in the TO-14 mixture will condense and do not escape detection. Hence the probability of a false negative is very low.

7. Conclusions and Recommendations

The objective of the research was to develop a fast, low cost analyzer system for the detection of volatile organic compounds (VOCs) in soil and groundwater. The research tasks were to demonstrate the detection and speciation of a representative number of VOC materials followed by field demonstrations of the new technology at a DOE site. All tasks of the project were successfully carried out and a fast vapor analysis system based upon a new type of Surface Acoustic Wave detector technology with the ability to characterize organic contamination in soil and groundwater at the part per billion level in less than 10 seconds was developed. Additional tasks were to challenge the instrument with dioxins, pcb, and dibenzofurans and to obtain a California Environmental Agency Certification.

The detector is unique because it utilized an uncoated quartz crystal, contrary to current developments of using coated crystals. The uncoated SAW detector demonstrates very high sensitivity to very low detection levels, and integrated with chromatography provide speciation of compounds in less than 10 seconds. Compared through split-sampling analysis, the instrument maintains an error band of less than 20%.

The technology was demonstrated at several US DOE sites to include Savannah River, Idaho Falls, Hanford, Lawrence Berkeley Laboratory, and Livermore National Laboratory. It provided excellent chromatography at 10 seconds, impressing all viewers. Sites expressed a very high interest in obtaining the GC/SAW, however, needs leadership direction from Headquarter organizations to facilitate the deployment of the technology.

During two separate field tests held at the DOE Savannah River site, the performance of the SAW/GC analyzer was validated by comparing results taken with an on site HP Chromatograph. Tests were performed with water, soil and gas samples. By these tests the SAW based analyzer demonstrated the ability to identify and quantify the presence of TCE and PCE using a 5 second sample time followed by a 10 second analysis time. Minimum detectable signal levels for a 5 second sample were typically 100 ppb or less.

Notable conclusions were as follows:

1. Picogram sensitivity can be achieved using focused deposition of VOC vapors onto uncoated SAW sensors.

2. Selectivity and Sensitivity of the SAW sensor can be controlled using thermoelectric cooling and heating of the substrate crystal.

3. Good separation and specificity can be achieved in short, temperature ramped, capillary chromatography columns.

For the first time an acoustic wave sensor demonstrated sufficient specificity and sensitivity to be used as a fast trace analyzer or screening tool at DOE sites. With the development of the SAW/GC, problems of low sensitivity and specificity have been solved. The SAW/GC satisfies the need for a field portable, solid state analyzer with the ability to identify and quantify VOCs over a concentration range of ppb to over 1000 ppm in near real time (e.g. < 10 seconds).