

Innovative Field Portable, Rapid Site Characterization and Monitoring Systems

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INTRODUCTION

This paper describes research on a fast GC vapor analysis system that uses a new type of Surface Acoustic Wave detector technology for characterizing organic contamination in soil and groundwater. Under a successful United States Federal Aviation Agency (FAA) technology program¹ and a U.S. Coast Guard Small Business Innovative Research (SBIR) contract², a laboratory breadboard system was developed to detect explosives and contraband drugs of abuse. A proof of concept prototype was built and demonstrated for this project. Follow-on awards resulted in a portable fast gas chromatograph that detects contraband drugs of abuse. The system was again modified to detect compounds of pollution related to environmental site characterization and monitoring. The effort in developing this capability was sponsored by the United States Department of Energy (DOE).

DESCRIPTION OF THE TECHNOLOGY

The SAW/GC instrument is comprised of a head assembly that contains the capillary column, the SAW detector and the support chassis. The support chassis contains the helium carrier gas, laptop computer and the related micro-processors. There are two modes of operation: Sample and Inject. The system utilizes a two position, 6 port GC valve to switch between sampling and injection modes. In the sample position, environmental air containing the suspect compounds, is passed through an inlet preconcentrator or water trap and then through a sample loop trap. The function of the loop trap is to concentrate VOC materials when in the sample position. During the sample mode, helium carrier gas flows down a capillary column and impinges onto the surface of a temperature controlled SAW resonator. Trapped on the surface of the resonator as VOC materials exit the GC column, they cause a change in the characteristic frequency of the crystal. The adsorption efficiency of each VOC material is a function of the crystal temperature and by operating the crystal at different temperatures the crystal can be made specific to materials based upon that materials vapor pressure. Also, since the crystal acts as a micro-balance it integrates the total amount of material present. To obtain a conventional chromatogram plot of retention time, the derivative of frequency versus time is calculated. This is in contrast to a conventional GC detector which detects the flux and where peak integral calculations are required to obtain the amount of each material present.

Switching the valve to the inject position causes helium carrier gas to flow backward through the loop trap and onto the column. After the valve is switched into the inject position the loop trap is rapidly heated to 200°C causing the trapped VOC materials to be released into the GC column. The temperature of the GC column is linearly raised to approximately 125°C over a 5-10 second time and this causes the VOC materials to travel down the column and exit at a time characteristic of the VOC material.

Surface Acoustic Wave (SAW) sensors are quartz crystals which have patterned electrodes to allow a high frequency (60-1000 Mhz.) surface acoustic wave to be maintained on their surface. The frequency of the crystal is dependent on the spacing of the electrode pattern, the temperature of the crystal, and the condition of the surface. The innovative feature of the SAW resonator is that the temperature of the SAW sensor can be programmed using a thermoelectric cooling/heating module bonded under the SAW crystal. The thermoelectric module is controlled by computer and thus allows the SAW crystal to be maintained at temperatures between 0 ° C and 115 ° C (lower temperatures can be obtained by cascading thermoelectric coolers). The SAW resonator can be cooled during the analysis time when the materials are eluting from the column, thus insuring that materials will adsorb onto the SAW surface.³ More significantly, at the end of the analysis period, the SAW can be heated to > 100 ° C to boil off materials from the previous injection and thus rejuvenating it for the subsequent analysis. This feature makes it unique among existing piezoelectric sensors. Table 1⁴ shows a comparison of SAW with other typical GC sensors. Because the electrode pattern of a SAW crystal is fixed, the frequency of the SAW sensor is dependent on the mass of material when the molecules of that material are adsorbed onto the quartz surface.⁵ The SAW detector, incorporated with the theory of gas chromatography, allows for the analysis of suspect compounds to new ranges of specificity and concentration.⁶

PROJECT OBJECTIVES

The DOE research objectives were to demonstrate detectability and specificity of a Surface Acoustic Wave Gas Chromatograph (SAW/GC) for a representative number of Volatile Organic Compounds (VOC) materials. Once the VOC compounds were identified, data gathering and field demonstrations of the new

analyzer were executed at a DOE site. Field testing of the SAW/GC was performed at the DOE Savannah River Facility, Augusta, Georgia. Matrix testing was performed with water, soil and gas samples. The performance of the SAW/GC analyzer was validated by comparing results taken with an on-site HP chromatograph. Through these tests, the system, based upon surface acoustic wave/ gas chromatography, demonstrated the ability to identify and quantify the presence of VOCs.

RESULTS AND ACCOMPLISHMENTS

To demonstrate the technology, a portable laboratory scale instrument was constructed and tested with the representative VOC materials listed in Table 2. Each material was tested with a calibrated vapor source either purchased as calibrated bottled gas or created by injection into a known volume (tedlar bag). Calibration results based upon a 10 second sample are listed in Table 3. In general, the sensitivity of the instrument for all materials was 1 ppm or better. For materials with lower vapor pressure, such as Toluene and tetrachloroethylene, sensitivity extends well into the ppb range. To achieve ppt sensitivity it is only necessary to extend sample time. However, the advantage of a short sample times is near real time operation.

FIELD TEST RESULTS

The prototype instrument was shipped to the DOE Savannah River Facility, Aiken, SC, where it was used to obtain real time measurements of well head gases. Place in a small van, the system was transported to numerous well heads for sample analysis. The instrument was designed for battery power, however, it was discovered that it could operate for long periods of time by drawing power from the transport vehicle. Power was supplied utilizing a 110 volt DC-AC inverter connected to the automobile battery.

Samples were taken under 3 modes: (1) the instrument was stationary and engineers brought tedlar bags to a central point for well-head analysis; (2) the system was mounted in the van and driven to various well head locations for sample analyte analysis using tedlar bags; (3) the system was driven next to a well head and with the detectable head unit, connected to a sampling port for direct injection of sample analytes.

To verify the accuracy of the instrument, calibrated tedlar bag samples were used to calibrate the SAW/GC. A typical output screen for one such bag containing approximately 100 ppm TCE and PCE is shown in Figure 2.. The user interface shows two chromatograms, one is the derivative of SAW frequency and the other is SAW frequency vs. time. The duration of the chromatogram is 10 seconds and retention times for TCE and PCE is 3.54 and 5.54 respectively. The operator can display quantitative information as ppm/ppb, in mass units of picograms or nanograms, or alternately in SAW units of frequency.

Many different measurements were taken and compared with an on-site HP GC as shown in Figure 3. The results of this relative comparison indicate that the SAW/GC and the HP GC agree within approximately 20%. Much of the variation is attributed to variations in sampling and preconcentration within each instrument.

APPLICATION , BENEFITS AND ISSUES

Those involved in environmental characterization and monitoring are demanding innovative technologies that are significantly lower in cost while providing rapid methodologies for the collection and analysis of soil, water, and air samples in the field. The SAW/GC instrument, if properly integrated into the sampling/analytical plan, represents a significant savings in cost and time. The instrument can be effective if the 2 major criteria are met affirmatively: (1) Is there a need for measurement or monitoring decision making data "in situ"? and (2) Is there a critical need to make decisions in the field in real time, e.g. 8 hours or less.

On-site Monitoring (OM) is useful for the following situations:

- Define emergency response actions
- Assess impacts to potable water
- Monitor purge water
- Define the extent of soil contamination
- Determine migration pathways
- Estimate the amount of contaminated soils

- Screen ground water during exploratory drilling
- Obtain ground water samples without monitoring wells
- Screen monitor wells
- Determine sources of contamination

Rapid on-site screening and analysis has been identified as a potential solution to four major issues. Applied On-Site efforts identify capabilities to the following issues:

- **Operator Safety-** Is the exposure level too high for site personnel? A significant problem exists regarding the safety of personnel involved in characterization and remediation. Several solutions exist using amino-assay kits, however, specificity and real time analysis is limited. The SAW/GC analyzer represents a solution for identifying suspect compound specificity and concentration in near real time (10 seconds).
- **Real-Time Analysis-** How can we identify contaminated areas by reducing the total number of samples taken for analysis? Past site characterization techniques follow a pattern of sending samples at regular intervals to a reference laboratory for validation of suspected areas of contamination in both specificity and concentration.. Fixed laboratory costs range from \$600 to 700 per sample and average 6 days from sample submittal to reporting of analyte results. Mobile field laboratories range from \$250 to \$300 per sample and can process between 30 to 40 samples a day. A portable SAW/GC instrument can be utilized effectively by defining the three to four (instead of 40) compounds in the suspect analyte you are searching for at the site. This planning will allow for site screening for mixed waste by identifying commonly related compounds.
- **Screening-** Where will we most likely find contamination? Reducing the turn-around time associated with analyzing compounds will save money. Field personnel can make decisions in hours instead of waiting days for the return and analysis of data. The use of a portable SAW/GC allows an operator to rapidly screen for suspect compounds and in turn make cost effective decisions. . Compounds found in rapid screening are confirmed by a reference lab for compliance risk assessment. This reduces the cost of site assessment and remediaton.
- **Primary Remediation Site -** Can we characterize the primary location to remediate by identifying the “hot spots” of contamination? Historically, field portable instruments were limited because they lacked specificity and sensitivity. The advantages of the SAW/GC are portability, accuracy, and speed. The new SAW 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, which require expensive laboratory testing, are estimated to be more than \$50,000 per month. The cost of the SAW/GC screening instrument will be recovered within less than two months of operation.

SAW/GC technology provides both advantages and disadvantages to current analytical methods. A brief comparison is as follows:

Advantages

- Easy to learn the Instrument
- Easy to Use
- Inexpensive, and portable

Disadvantages

- On Site Personnel must be mechanically competent
- Field personnel must have the authority to make decisions
- Cost effective if a large number of samples

- Capable of correlation with laboratory analysis
- Verifiable and reproducible
- Capable of calibration to contamination matrix
- Contaminant must be known prior to site activities
- Heterogeneous conditions may lead to inconsistent data sets
- Field screening methods may not be applicable to all site conditions

FUTURE PLANS

There are many related applications for SAW/GC technology. While at Savannah River the instrument was also used to measure catalytic converter performance, DNAPL probe experiments, and to characterize VOC break through in carbon scrubbers. Future plans are to use the instrument in field conditions to measure performance against existing methods.

Based upon the current results the goals are to begin development of SAW/GC screening instruments for use at DOE remediation sites. The commercialization effort is being carried out by Electronic Sensor Technology, Inc., a limited partnership company managed by Amerasia Technology and tasked with the development of SAW/GC instruments.

The commercialization effort is being aided by a partnership between Amerasia Technology, Inc., and the U. S. Department Of Energy Morgantown Energy Technology Center. This new program will involve continued Field testing at DOE sites, EPA certification and verification, and the development of new SAW/GC instruments to detect and quantify Dioxins, Furans, and PCBs at DOE sites. The new units are smaller in size and contain improvements noted from the Savannah River Field work. These units will be available for field demonstrations and data gathering in the First Quarter of 1996. Designated the Model 4100, it has been designed for environmental needs. A photograph of the Model 4100 is shown in Figure 4.

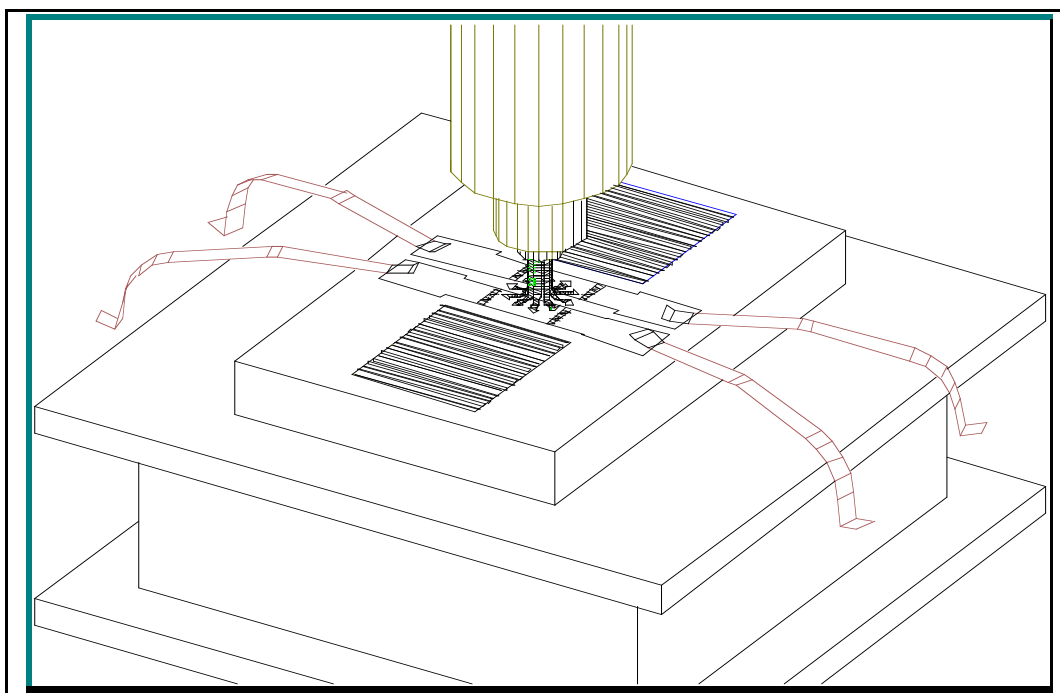


Figure 1- Surface Acoustic Wave Detector

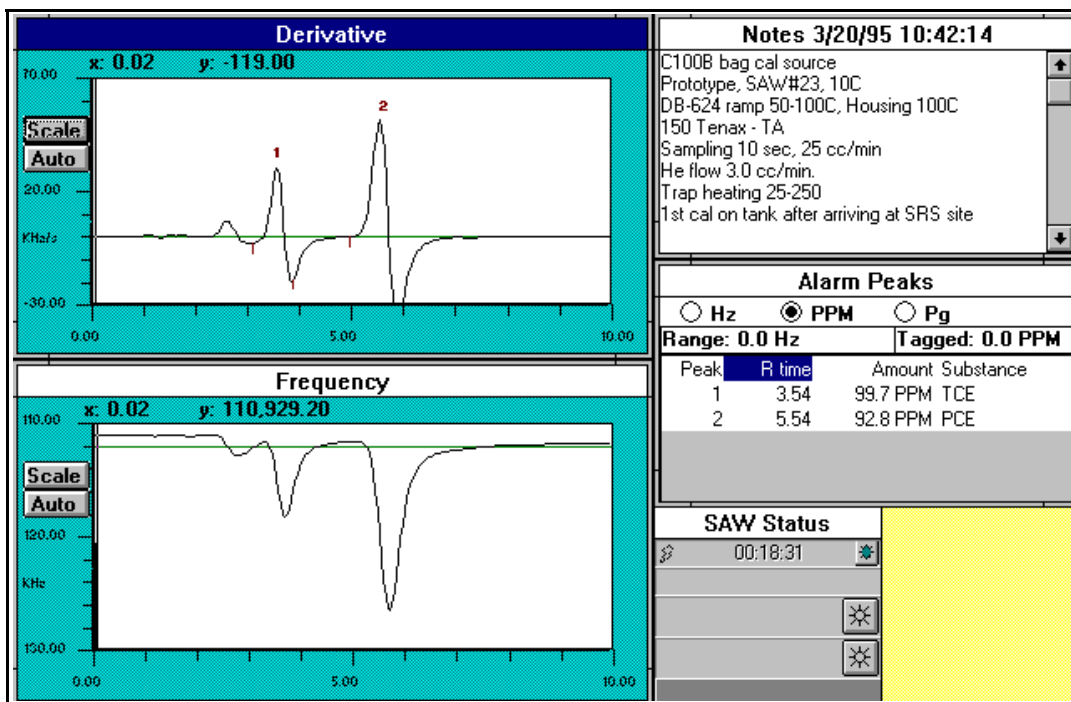


Figure 2-Typical screen display showing PCE (92.8 ppm) and TCE (99.7 ppm) tedlar bag calibration results.

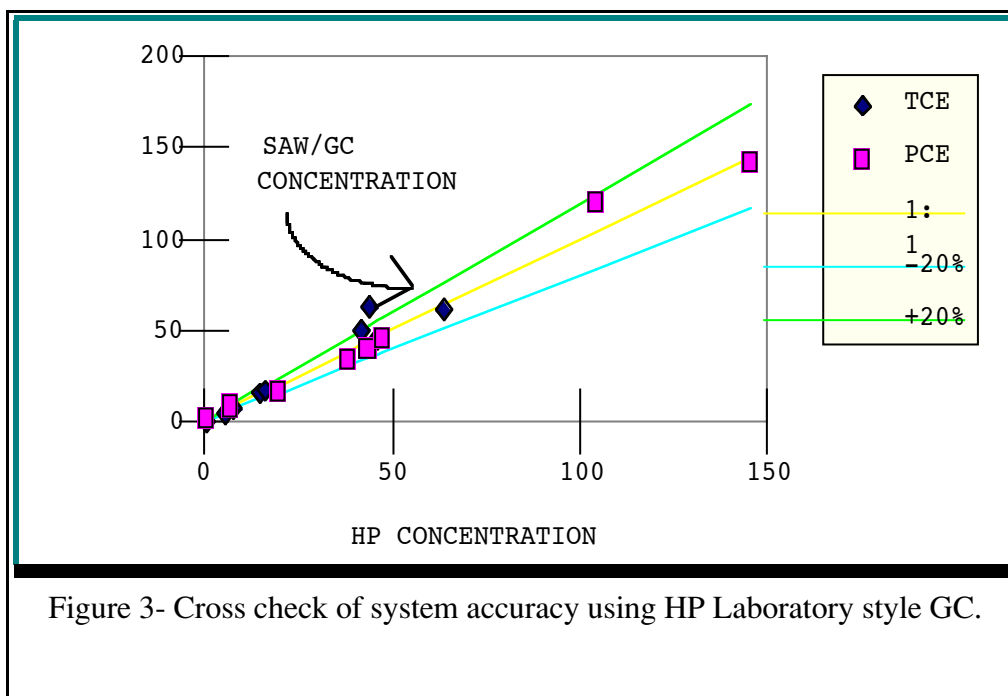


Figure 3- Cross check of system accuracy using HP Laboratory style GC.

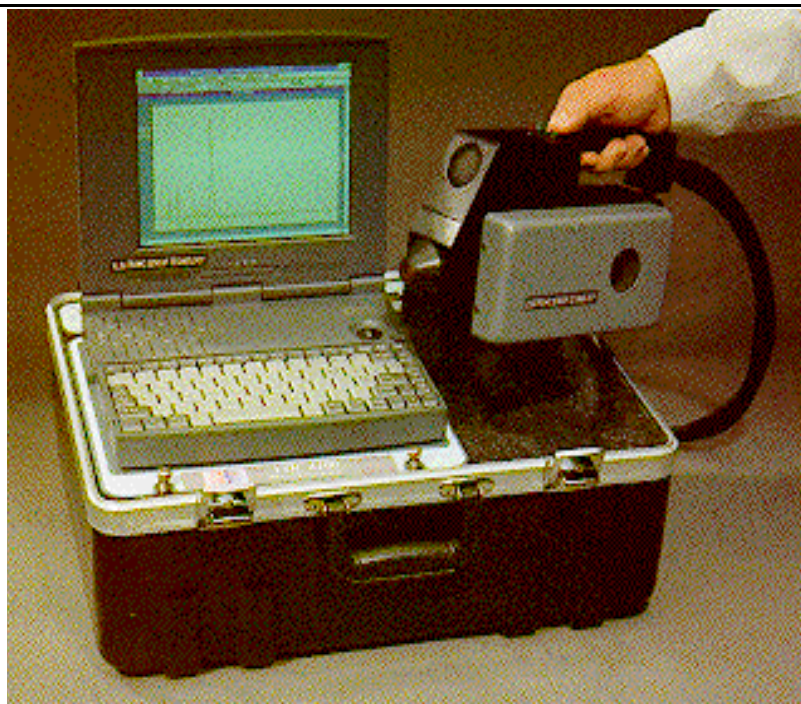


Figure 4 Photograph of the Model 4100 SAW/GC Field Unit

Table 1 Comparison of SAW Detector with other Detectors

| Detector | Detection Limit (Femtograms/sec) | Dynamic Range |
|--------------|-------------------------------------|------------------|
| TCD | 6,666 | 10 ⁵ |
| ECD | 100 | 10 ⁴ |
| FID, C | 5,000 | 10 ⁷ |
| NPD, N | 400 | 10 ⁴ |
| FRPD, P | 900 | 10 ⁴ |
| SAW, mass | 1 | 10 ⁶ |

Table 2 - VOC Materials Tested

| Material Name | Formula |
|--------------------------------|--------------|
| Trichloroethylene | C 2 H Cl 3 |
| Tetrachloroethylene | C 2 Cl 4 |
| Carbon Tetrachloride | C Cl 4 |
| Chloroform | C H Cl 3 |
| Dichloromethane | CH 2 Cl 2 |
| 1, 2 - Dichloroethane | C 2 H 4 Cl 2 |
| 1, 1, 1 - Trichloroethane | CH3 CCl 3 |
| 1, 1 Dichloroethylene | C2 H2 Cl 2 |
| 1, 1, 2, 2 - Tetrachloroethane | C2 H2 Cl 4 |
| Trichlorofluoromethane | C Cl 3 F |
| Benzene | C 6 H 6 |
| Toluene | C 7 H 8 |
| Gasoline | -- |
| Diesel Fuel | -- |

Table 3 - Calibration Results of Selected Materials

| VOC Material | Test Concentration (ppm) | Detected Amplitude (Hz) | Detection Limits (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 |
| Tetrachloroethylene | 10 | 383 | 0.78 | 3.4 |
| Toluene | 2.4 | 272 | 0.26 | 10.1 |
| Tetrachloroethylene | 1.6 | 517 | 0.09 | 28.7 |

¹ SAW New Detection Concepts, FAA contract number DDTFA03-87-C-00002

² E.J. Staples, "Cocaine/Heroin Detection Technologies - Phase II Contract No. DTRS-57-89-C-00126, Dept. of Transportation, Transportation Systems Center, Kendall Square, Cambridge, MA, Mar. 1991.

³ E.J. Staples, G.W. Watson, and W.J. Horton, "Temperature Programmed Desorption Characteristics of SAW Resonators", Proceedings of the 1991 Ultrasonics Symposium, pp. 317-320.

⁴ Hewlett-Packard 5890 Series II Specification Guide , Feb. 1990.

⁵ G.W. Watson and E.J. Staples, "SAW Resonators As Vapor Sensors", Proceedings, 1990 Ultrasonics Symposium, pp. 305-309.

⁶ United States Patent No. 5,289,715, Vapor Detection Apparatus And Method using an Acoustic Interferometer