

# **Total Petroleum Hydrocarbon Analysis (TPH-g) Using A SAW/GC: Real-Time Analytical Data for Environmental Clean-Up Operations**

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## **Introduction**

A major contributor to atmospheric and ground water pollution is caused by fuel hydrocarbons. These problems can often occur through accidental emission during storage or use. Out of the millions of underground fuel storage tanks that are in place throughout the country many are leaking and many more are destined to produce leaks at some future date. The problem is serious enough that under the law (40CFR 260 subtitle I of RCRA) legislation exists that deals only with of leaking underground fuel tanks (LUFT) concerns.

During clean up operations at LUFT sites which sometimes cost many millions of dollars site operations are driven by fugitive hydrocarbon levels. Hydrocarbon concentrations are usually derived by sub-soil sampling followed by time consuming laboratory analysis. Field portable instruments for the analysis of fuel hydrocarbons must be able to provide legally defensible data acquired by the application of strictly applied methods as defined by state and federal government. (i.e. CA LUFT Method 1000 or EPA SW846 methods).

This paper describes research on a fast GC vapor analysis system with a new type of Surface Acoustic Wave detector to characterize organic contamination in soil and groundwater. The project was sponsored by the Department of Energy, Morgantown Energy Technology

Center. Field screening using SAW/GC technologies can result in great cost saving particularly when the SAW/GC technology can emulate one of the EPA methodologies. TPH-g methodology has particular relevance to LUFT sites and can provide a total integration number based on a selected range of alkane or aromatic hydrocarbons.

## **Technology Description**

The structure of a SAW/GC is shown in Figure 1. The system utilizes a two position, 6 port GC valve to switch between sampling and injection modes. In the sample position air is passed through an inlet water trap and through a sample loop trap. The function of the loop trap is to concentrate VOC materials when in the sample position. During sampling helium carrier gas flows down a capillary column and impinges onto the surface of a temperature controlled SAW resonator crystal<sup>1</sup> as shown in Figure 2.

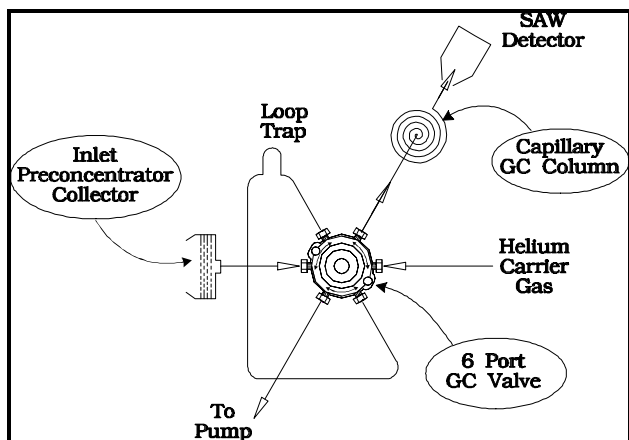
Switching the valve causes helium carrier gas to flow backwards through the loop trap and onto the column. In the inject position the loop trap is rapidly heated to 200°C causing the trapped VOC materials to be released into the GC column. The temperature of the GC column is linearly raised to approximately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

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<sup>1</sup> United States Patent No. 5,289,715, Vapor Detection Apparatus and Method Using an Acoustic Interferometer.

materials to travel down the column and exit at a time characteristic of the VOC material.

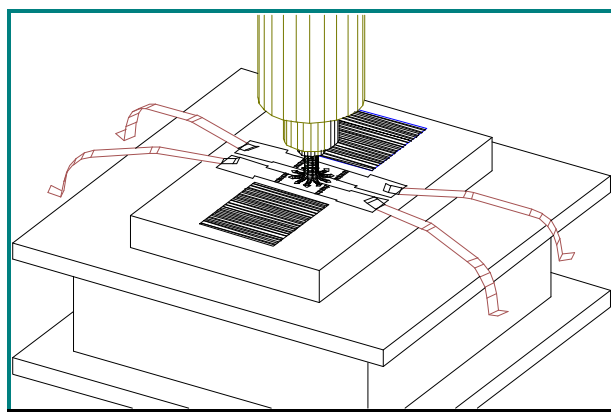
The focused SAW resonator is a universal type of GC detector. VOC materials



**Figure 1- SAW/GC System Description.**

as they exit the GC column are condensed on the surface of the resonator and 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, as shown in *Figure 3*, the crystal can be made specific to materials based upon each material's vapor pressure.

Since the crystal acts as a micro-balance it integrates the total amount of material present and to obtain a conventional chromatogram plot

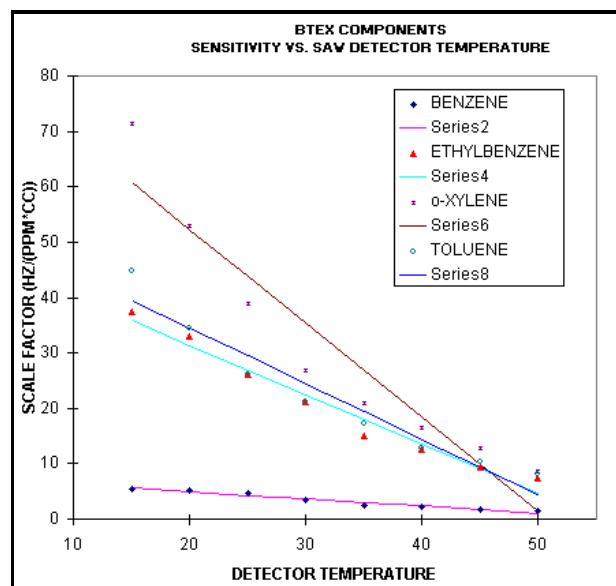


**Figure 2- Surface Acoustic Wave Detector.**

of retention time, the derivative of frequency Vs

time is calculated. This is in contrast to a conventional GC detector which detects the flux and peak integral calculations are required to obtain the amount of each material present.

Recent research has shown that C6 to C12 n-alkanes and BTEX 2 hydrocarbons can be resolved and quantified using a rapid field portable GC/SAW. Chromatograms are typically



**Figure 3- BETX Scale factor Vs Detector Temperature.**

obtained in under 15 seconds. Because of gasoline's highly complex nature in terms of possible number of analytes for prescreening using this method a selected number of marker compounds are produced in each chromatogram which act as calibration points. The retention time on the GC column defines a range for each compound in terms of its carbon number. Each TPH-g analysis produces a series of representative peaks in terms of carbon number which can be matched to actual site chromatograms. Integration of all the collected peaks related to the calibration peaks produces a number which is equivalent to the total amount

<sup>2</sup> BETX aromatic hydrocarbons are benzene, Ethylbenzene, toluene and the positional (*o,m,p*) isomers of xylene.

of hydrocarbon fuel present. This number is representative of a TPH-g number and indicates the degree of contamination in terms of available hydrocarbon emission. The TPH numbers obtained in this manner leads to

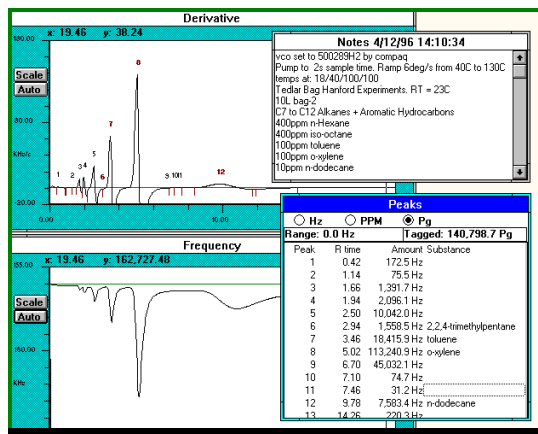


Figure 4- Calibration for C7-C12 and BTEX

early indications of the severity of pollution which is notorious for its ability to quickly degrade after sample collection. Using SAW/GC methods produces immediate access to analytical data in terms of chemical species and concentration. Figure 4 shows a chromatogram obtained with this instrument giving retention time data in terms of an n-alkane series and BTEX family of aromatic hydrocarbons. A sample chromatogram of gasoline vapors entrained in a soil matrix is

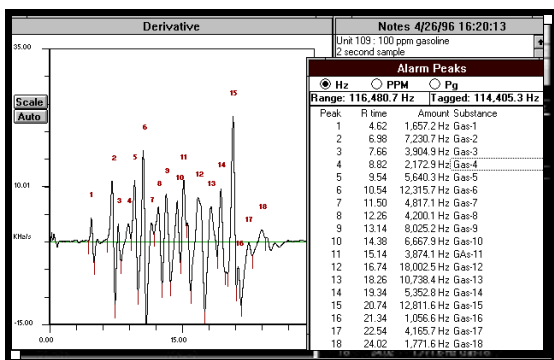


Figure 5- SAW/GC response to Gasoline vapors.

shown in Figure 5.

## Field Test Results

To field test the laboratory prototype the instrument was transported to the DOE's Savannah River Site, Idaho National Engineering Laboratories, Lawrence Berkeley Laboratories, and to the Hanford Site where it was used to obtain real time measurements of well head gases and tank emissions. Although the instrument was capable of battery operation for limited periods of time, uninterrupted power was

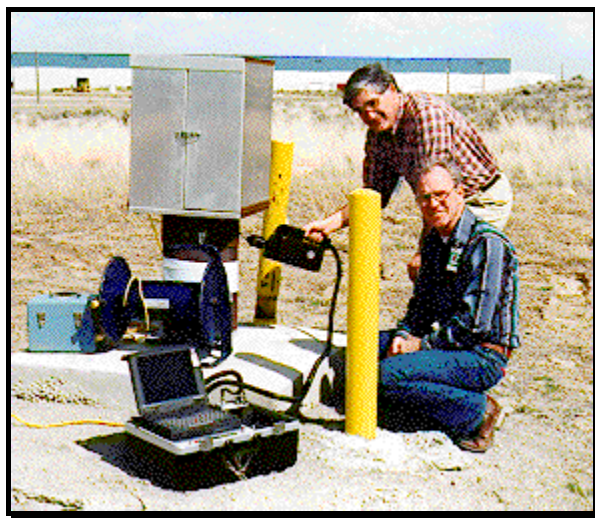


Figure 6- SAW/GC at a remote wellhead.

most reliably obtained from the automobile which was used to transport the system to each well head as shown in Figure 6.

To verify the accuracy of the instrument, calibrated tedlar bag samples were used to calibrate the SAW/GC. The user interface consisted of a Windows® program displaying two chromatograms, one is the derivative of SAW frequency and the other is SAW frequency Vs time. The duration of the chromatograms are typically 10 seconds and peak widths are measured in milliseconds. Because the SAW detector is an integrator, fast GC pulses are not missed and the chromatography can be very fast. The operator can display quantitative

information as ppm/ppb, in mass units of picograms or nanograms, or alternately in SAW units of frequency. In all DOE comparisons using laboratory analysis by GC/MS, the SAW/GC accuracy was within 20% of laboratory findings.

### **Application or Benefits**

There are many related applications for SAW/GC technology. While at DOE remediation sites the instrument was also used to measure catalytic converter performance, DNAPL probe experiments, VOC break through in carbon scrubbers and to characterize mixed waste tank emissions. The SAW/GC screening instrument, shown in *Figure 7*, was found to be a good tool for real time monitoring of stack



***Figure 7- SAW/GC Field Screening Instrument.***

emissions involving dioxins and PCBs. Sensitivity to non-volatiles was typically in the picogram range.

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 expensive laboratory testing, are high. It is anticipated that SAW/GC technology will have a positive impact on the cost of environmental remediation and restoration.

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