

Real Time Environmental Screening of Air, Water and Soil Matrices Using a novel Field Portable GC / SAW System

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ABSTRACT

Analysis of volatile and semi-volatile organic compounds using field instruments is gaining popularity due to faster field screening, and sample preparation. A substantial reduction in the cost of sample analysis can be achieved if the field screening can be performed accurately. Although a number of field screening instruments such as gas chromatographs (GC) have emerged recently particularly for volatile organic chemicals measurement, there is still a lack of instruments versatile enough to analyse a wide range of organic compounds.

This paper details the development and application of a novel field portable GC system equipped with a Surface Acoustic Wave (SAW) detector. Unlike other types of GC detectors, the SAW detector is a temperature controlled integrating mass detector with zero retention volume and the ability to operate with chromatography peak widths measured in milliseconds. An internal sample pump and Tenax trap collect analyte vapours entrained within ambient inlet air. Speciation is accomplished using a short, temperature ramped GC column selected for its ability to separate analytes of interest. Detecting the total amount of each analyte as it exits the column performs quantification. By focusing the effluent from the column onto a specific area within a surface acoustic wave resonance-field on the surface of a temperature controlled piezoelectric crystal, picogram sensitivity is achieved.

Results from recent US EPA field validation studies using a GC/SAW are presented. Measurements of volatile compounds such as benzene, toluene and xylene (BTX) and semi-volatile Polychlorinated Biphenyl (PCB) in various matrices have been completed. The results of field tests have shown that it is possible to speciate and quantify a wide range of environmental pollutants in near real time (less than 10 seconds) with good precision. Utilising only 5 or 10 seconds to sample vapours containing these compounds, minimum detection levels are at parts per billion levels for volatiles and parts per trillion for semi-volatiles have been achieved.

Early separations of field samples that are below the regulatory level from those that are above and therefore require laboratory validation with a GC/MS is the main goal of field screening methods. Application of field screening methods using a GC/SAW system can reduce the cost associated with environmental site characterisation and monitoring.

SURFACE ACOUSTIC WAVE DETECTOR FOR GAS CHROMATOGRAPHY

A large amount of research has been performed with chemical coatings applied to SAW crystals. A common approach is to expose an array of SAW crystals with different polymer coatings to the vapour to be characterised. In theory each polymer coating will adsorb the vapours differently and by comparing response patterns from the array of sensing crystals, identification can be accomplished. However, polymer coatings reduce the sensitivity of the SAW crystal and limit detection to nanogram levels. Further loss in sensitivity results because the vapour sample must be split between many sensing crystals. Polymer coatings are not highly specific and in general each coated crystal response overlaps the response of other crystals to some extent and in this case pattern recognition with non-orthogonal (over-lapping) responses is very difficult.

A new type of SAW vapour detector with picogram sensitivity and which does not use polymer coatings has been developed [1]. The sensing crystal comprises a very high Q SAW resonator placed in contact with a small thermoelectric cooling element as depicted in Figure 1. The thermoelectric element provides the precise control of cooling needed for vapour adsorption and simultaneously the ability to clean the crystal using thermal desorption when needed.

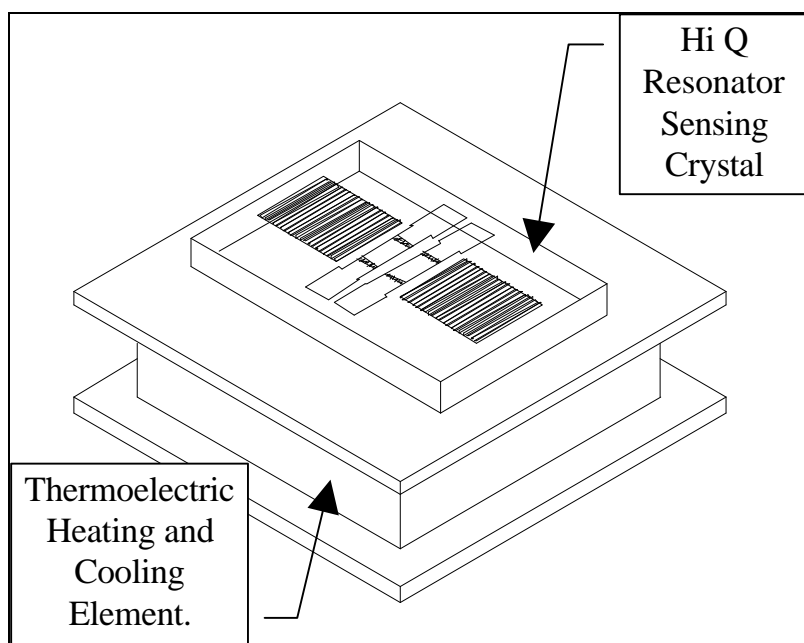


Figure 1- Thermoelectrically cooled SAW detector crystal.

The focused SAW resonator sensing element provides part per billion sensitivity for volatile organics and part per trillion sensitivity for semi-volatile compounds. The crystal operates by maintaining highly focused and resonant surface acoustic waves at 500 MHz on the face of a single crystal quartz chip. By focusing the vapour through a micro-nozzle as shown in Figure 2, femtogram sensitivity can be achieved. This result [2] is 1000 times lower than SAW crystals coated with polymers. Because the crystal is manufactured from single crystal quartz without polymer coatings, long term stability and precision is achieved over a wide temperature range.

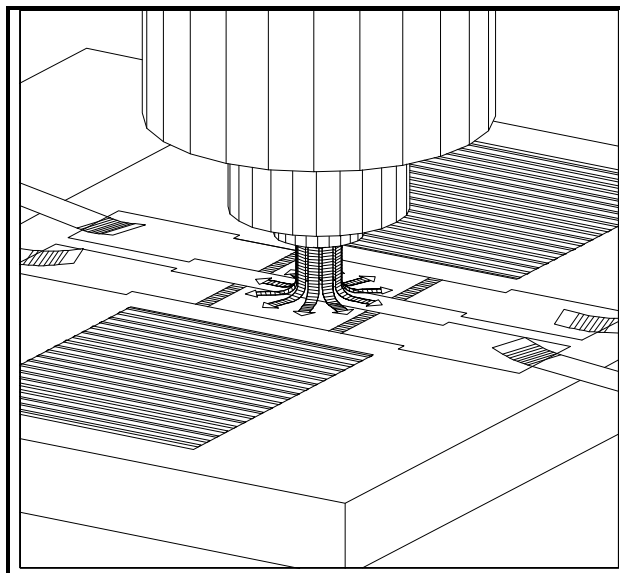


Figure 2- GC/SAW nozzle interface showing interaction of column and acoustic cavity.

The SAW sensor only requires a low voltage power source and because it is non-ionic, does not require a radioactive ionisation source. The ability to detect compounds based upon their ability to absorb onto a cooled surface provides detection capabilities which can be extended to an indefinite analyte list without regard to analyte polarity or electronegativity.

The uncoated SAW detector is only specific to vapour pressure. The specificity of the uncoated SAW detector is based upon the temperature of the crystal surface and the vapour pressure characteristics of the condensate itself. At a given crystal temperature only those analytes with dew points below the crystal temperature will condense and be detected. This provides a general method for separating volatile from non-volatile vapours based upon the selected operating temperature of the SAW crystal.

GC/SAW FAST CHROMATOGRAPHY SYSTEM

By combining SAW detectors with high speed temperature programmed chromatographic columns, specificity over a wide range of vapours at the part per billion level in near real time (10 seconds) has been achieved [3]. The GC/SAW offers the advantages of a low cost solid state detector and the specificity of a temperature programmed GC column.

The major elements of a GC/SAW vapour detection system are shown in Figure 3. The analysis is performed in two steps corresponding to the two positions of the GC rotary valve. In the sample

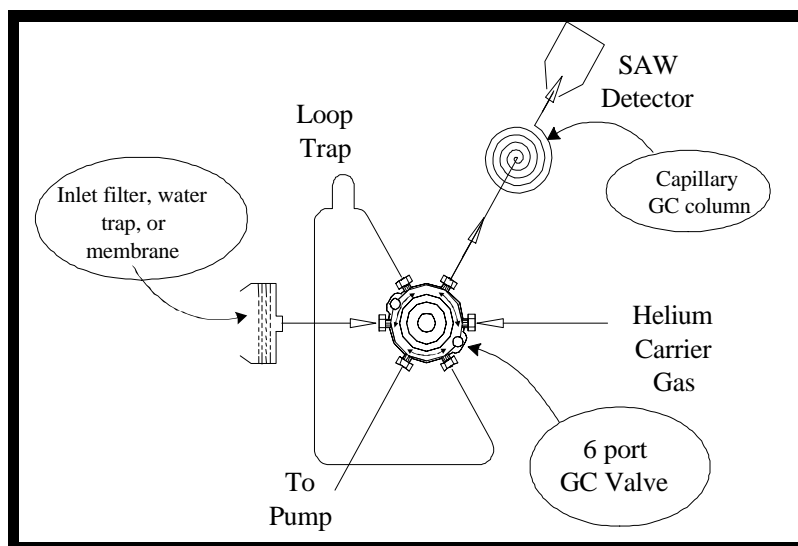


Figure 3-Schematic of GC/SAW System showing major elements of the system.

position (shown) air (stack emissions) to be tested pass through an optional inlet filter and through a loop trap. The trap contains absorbent specific to the desired analyte (e.g. Tenax). Selection of sample time and flow rate determines the total amount of airborne vapours collected in the loop trap.

The GC valve is rotated to its second position and the loop trap is rapidly heated by a capacitive discharge which causes trapped vapours to be transferred to the GC column. Transfer is aided by a helium carrier gas and these vapours re-condense on the inlet of a chromatographic column held initially at low temperature. A micro processor then applies a linear temperature ramped heating program to the GC column. The column separates the injected compounds in time and, as they are eluted from the column, they condense on the SAW crystal and are detected as frequency changes.

The speed of the analysis system is determined by the sample time and the analysis time. Typical sample times are 1 to 5 seconds and analysis times can be 10 seconds or less. Chromatographic peaks produced are measured in milliseconds. The ability to detect short duration peaks is made possible because the SAW detector is an integrating GC detector which by definition has zero dead volume. All other known GC detectors are differential and because of dead volume within the detector cannot operate with millisecond duration chromatographic peaks.

The GC/SAW system is able to simultaneously detect and quantify multiple chemical vapours within a single environmental sample. A field portable system was built to fit within a small suitcase. A laptop computer provides a fully integrated user interface in a Windows 95 operating environment. An internal microprocessor, gate array controller, and a small helium gas tank are housed within the base of the suitcase. Field testing of prototype systems, using Surface Acoustic Wave sensors and chromatographic columns, has demonstrated the ability to detect a wide range of compounds including drugs, explosives, volatile organics, polychlorinated biphenyl, and dioxins [4,5]. Part per billion (picogram) sensitivity and field performance of the new technology has been validated by the Office of National Drug Control, the Department of Energy, and the U.S. Environmental Protection Agency (EPA-ETV). Certification of the technology by the California Environmental Protection Agency is currently pending.

TEST RESULTS FOR VOLATILE ORGANICS IN WATER

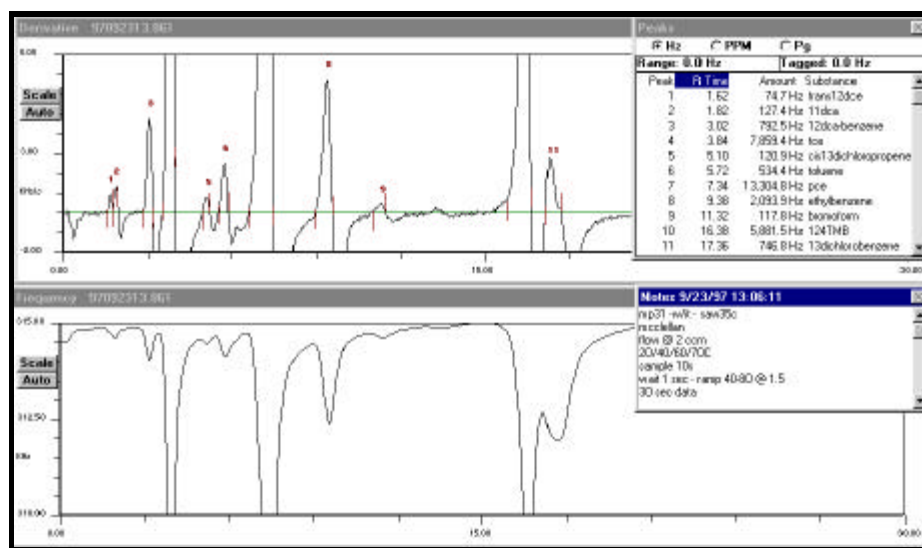


Figure 4- Chromatogram showing VOC screening of Water matrix.

Field testing of the GC/SAW was recently carried out using more than 30 different volatile organic analytes within water matrices. An chromatogram example of a water matrix containing VOC analytes with both high and low concentrations is shown in Figure 4. In this figure retention time and concentration measured in Hertz (Hz) for 11 different analytes is shown. Both BTEX and chlorinated solvents are represented in

the list of analytes. The water concentration of all analytes with the exception of four special analytes, benzene, 1,1 dichloroethane, trichloroethene, and tetrachlorethene, was 100 ppb. The concentration of the four special analytes was 500 ppb for benzene and 1,1 DCA, 1220 ppb for TCE and 1000 ppb for PCE. Performance of the instrument was related to measurement RSD and precision. Over the range tested (10-1000 ppb) RSD of four or more replicate samples was 10-20%. Precision over this range was analyte dependent and also typically 20% or better. In some cases the presence of high spikes and other interference could effect the measurement adversely. For screening operations, this was handled by requiring a laboratory site characterisation to determine analytes present before use of the screening GC/SAW.

TEST RESULTS FOR SEMI-VOLATILE PCBs AND DIOXINS IN SOIL

Preliminary testing of a GC/SAW with dioxin, furan, and PCB standards. Field testing of more than 200 PCB contaminated soil samples was performed as part of an EPA sponsored technology validation program (ETV). A more extensive testing program is planned as part of the proposed stack emissions study. The commercial GC/SAW currently manufactured by Amerasia was tested at the US Department of Energy's Oak Ridge National Laboratory in Oak Ridge, Tennessee. The GC/SAW was calibrated with a variety aroclor standards as an integral part of new GC/SAW EPA field method. A typical 10 second chromatogram obtained by exposing the system to a calibrated amount of PCB 1260 Aroclor® in Figure 5. Picogram sensitivity allowed the use of a quick liquid extraction in hexane to be tested without the need for concentration of the extract. Regulatory levels for PCBs were reached in the field in less than 5 minutes using the new GC/SAW method. Thus for this compound the scale factor was approximately 10 Hz/picogram. The GC/SAW had a noise floor of 10 Hz, hence the minimum

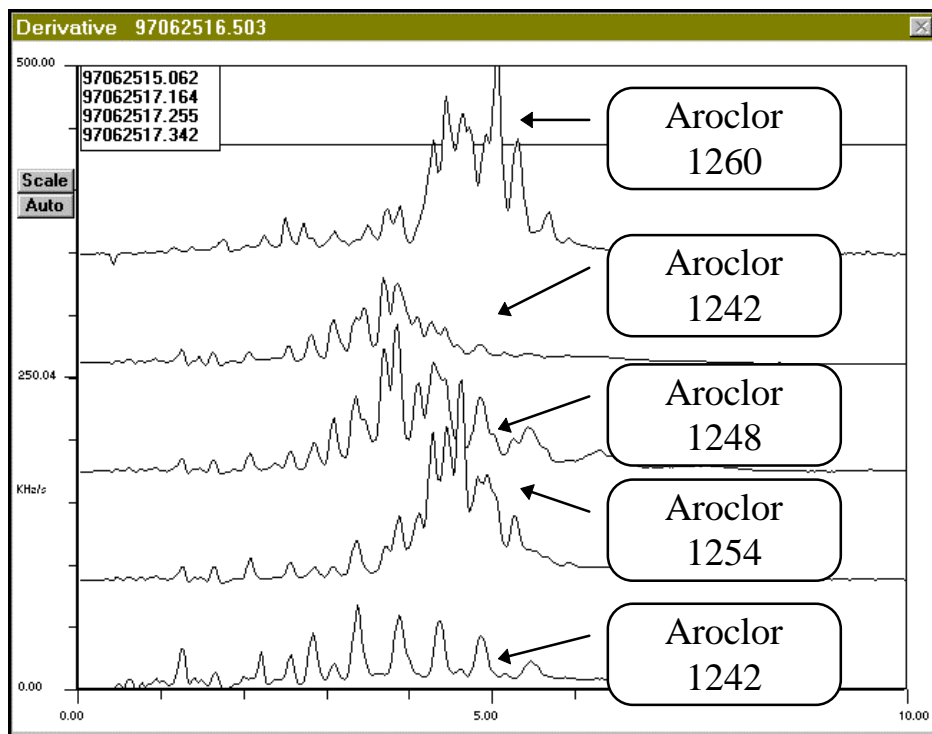


Figure 5- Analysis of semi-volatile PCB compounds in soil.

detection level was 3 picograms (signal to noise ratio = 3).

Similar results have been achieved with dioxins and furans. A 10 second duration chromatogram of 2,3,7,8-Tetrachlorodibenzodioxin is shown in Figure 7 and a 5 point calibration curve is shown in Figure 6. These results were obtained using direct thermal desorption of soil spiked with a dioxin standard solutions.

SUMMARY AND CONCLUSIONS

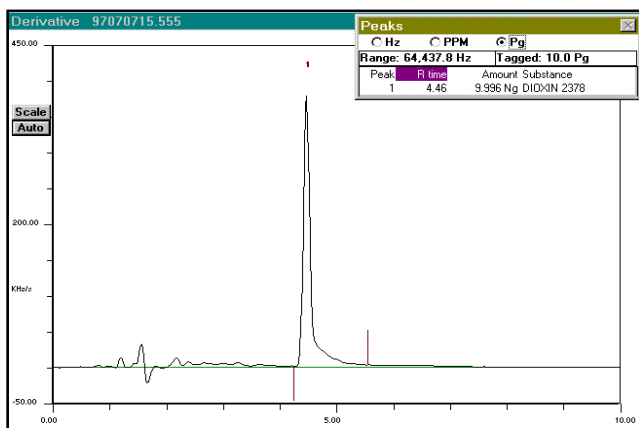


Figure 7- Chromatogram showing screening for 2378 dioxin in less than 10 seconds.

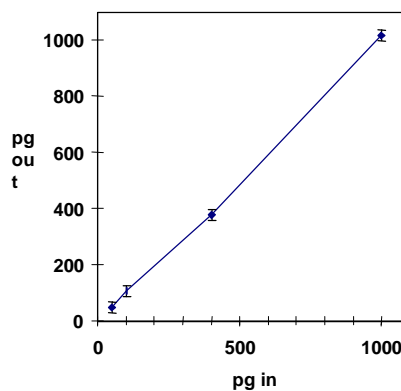


Figure 6- N point calibration for 2378 dioxin.

A number of conclusions were reached during field testing of GC/SAW systems with volatile and semi-volatile compounds in a variety of water and soil matrices. In general the sensitivity of the GC/SAW to volatile compounds was 1-10 part per billion (nanograms) while the sensitivity to semi-volatile compounds was 1-10 parts per trillion (picograms). As expected increasing sample time increased sensitivity, however, these results were achieved with a 10 second sample time. The instrument functioned well as a screening tool which allowed a site to be quickly evaluated and only meaningful samples collected for off-site laboratory validation. In effect this eliminated the testing of a large number of samples which did not contain any analytes above the regulatory limit.

REFERENCES

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