Nerve Gas Detection Using a SAW/GC

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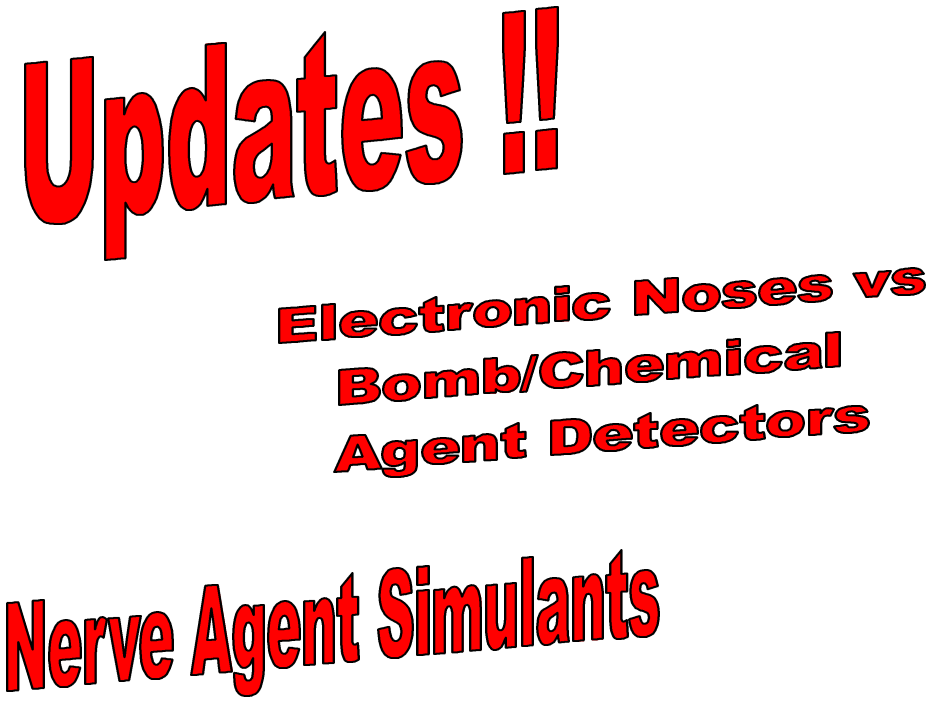
Abstract

This paper describes the design, implementation and performance of the SAW/GC with nerve gasses. A brief description of the basic operation of the Gas Chromatograph is given emphasizing the integration of the Surface Acoustic Wave (SAW) detector. A description of the available instruments and their use is provided. A plot of vapor pressure versus temperature and the range (over six orders of magnitude) covered by chemical warfare agents is discussed. The sensitivity of many of these nerve agents and simulants was measured at a certified surety laboratory. The sensitivity of these agents were consistently measured in the picogram (typically one part per trillion sensitivity) level as shown by actual chromatographs taken at the surety laboratory. A plot of an N-point calibration for the agent Sarin is given. This calibration curve validates the sensitivity levels that can be achieved for the agent Sarin. Chromatographs of stimulants taken in the presence of gasoline and JP-8 fuels are provided showing that the effect of these interferents can be overcome. Finally, a brief summary of results and conclusions is given.



Nerve Gas Detection Using a SAW/GC

Introduction

Chemical agent detection and quantification at the part per trillion level (picograms) can be performed using a Surface Acoustic Wave (SAW) vapor detector and fast gas chromatography (GC) system. Independent testing of the performance of a commercial SAW/GC system with actual nerve agents and simulants has demonstrated the sensitivity and specificity of this new technology. Size, weight, power, and operational requirements for the field portable GC/SAW may prove useful for trace detection of chemical agents in the field.

Surface Acoustic Wave Detectors and Gas Chromatography

A large amount of research has been performed with chemical coatings applied to SAW crystals. In theory each sensor will adsorb the vapors differently and by comparing response patterns from the array of sensing crystals, identification can be accomplished. Unlike previous sensor arrays, the GC/SAW recently developed by Electronic Sensor Technology provides a vapor signature equivalent to using a 100 sensor array in less than 10 seconds. Furthermore, each sensor response is independent of all other sensors in the array and can be calibrated quickly using nerve gas simulants.

The high performance of the vapor analyzer is derived from a new type of SAW vapor detector[1] with picogram sensitivity and which does not use any type of polymer coatings to limit the lifetime of the sensor. 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 temperature needed for accurate quantification of vapor concentration. The thermoelectric element is also used to desorb and clean the crystal when needed.

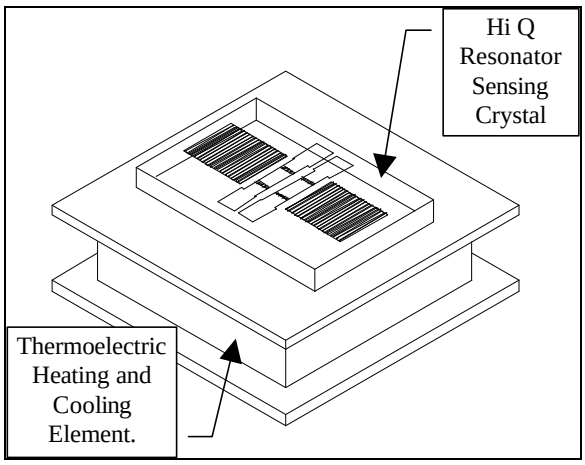


Figure 1- Thermoelectric cooling regulates the desorbtion of vapors onto the SAW sensing crystal.

The SAW resonator sensing element provides sensitivity a thousand times higher than previous SAW sensor designs. The crystal itself maintains highly focused and resonant, surface acoustic waves at 500 MHz on the face of

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

a single crystal quartz chip. By focusing of vapor through a micro-nozzle as shown in Figure 2, femtogram sensitivity can be achieved. To date[2] this result is 3 orders of magnitude lower than any previous solid state sensor. Because the crystal is manufactured from single crystal quartz without any polymer coatings, long term stability is achieved over a wide temperature range. Additionally the SAW sensor only requires a low voltage power source, is non-ionic and does not require a radioactive or high voltage ionization source. The ability to detect compounds universally provides detection capabilities which can be extended to an indefinite number of chemical agents without regard to analyte polarity or electronegativity.

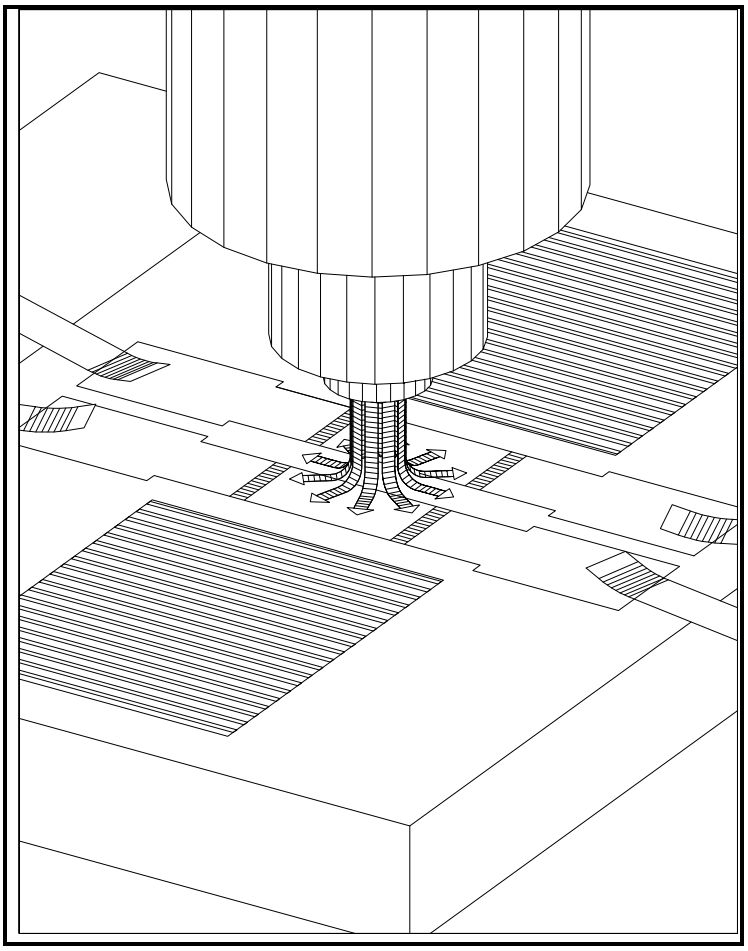


Figure 2- SAW/GC nozzle interface showing interaction of column effluent and acoustic cavity.

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

The SAW detector is only specific to vapor pressure. The specificity of the SAW detector is based upon the temperature of the crystal surface and the vapor 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 vapors based upon the operating temperature of the SAW crystal.

By combining SAW detectors with high speed chromatographic elements, specificity over a wide range of vapors at the part per trillion level in near real time (10 seconds) has been achieved[3]. The SAW/GC approach offers the following advantages:

1. Low cost of manufacture (solid state)
2. High specificity as determined by GC column
3. Non ionic detection (no radioactive ionization source)

The major elements of a SAW/GC vapor 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 position (shown) air to be tested passes through an optional inlet filter and then through a loop trap. The trap may contain absorbent to assist in concentrating the desired analytes (e.g. Tenax). Selection of sample time and flow rate determines the total amount of airborne aerosol or vapor collected in the loop trap.

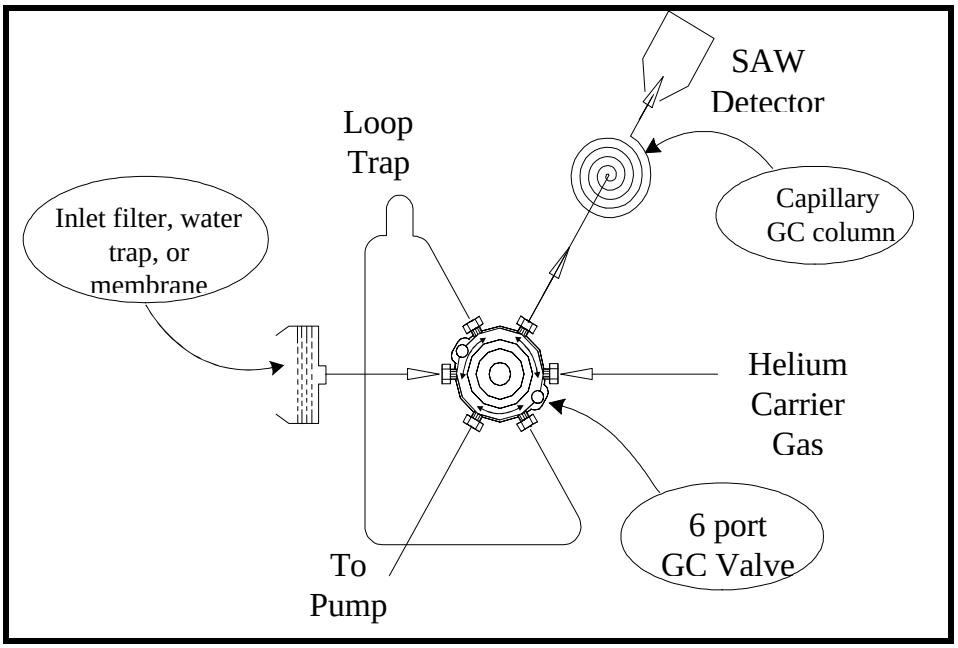


Figure 3-Schematic of SAW/GC System showing major elements of the system.

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

The GC valve is rotated to its inject position and the loop trap is rapidly heated by a capacitive discharge which causes trapped vapors to be transferred to the GC column. Transfer is aided by helium carrier gas and these vapors re-condense on the inlet of the chromatographic column 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 with essentially zero dead volume. All other known GC detectors are differential and because of dead volume within the detector cannot efficiently detect millisecond duration chromatographic peaks.

An advantage of the SAW/GC design is the ability to simultaneously detect and quantify multiple chemical vapors within a single environmental sample. Analysis systems, based upon Surface Acoustic Wave sensors and miniature chromatographic columns, have also demonstrated the ability to detect drugs, explosives, volatile organics, polychlorinated biphenyl, and dioxins[4,5].

Commercial Production of SAW/GC Chemical Analysis Systems

Electronic Sensor Technology currently produces two models of its commercial SAW/GC. A handheld field analysis system, designated the model 4100, and a portable benchtop model, designated the model 7100, are shown in Figure 4. Part per trillion (picogram) sensitivity and overall performance of the product has been validated by the Office of National Drug Control, the Department of Energy, and the U.S. Environmental Protection Agency. Certification of the technology for VOCs, PCBs, and dioxins by the California Environmental Protection Agency is currently pending.

The model 4100 is designed to function as a handheld portable analyzer for screening of objects and packages. The complete system is housed within a small carrying case and the GC portion of the system is completely contained within a handheld module. A laptop computer provides a convenient user interface integrated into a Windows 95 operating environment. An internal microprocessor, gate array controller, and a small helium gas tank are housed within the carrying case. The model 7100 is housed within a portable laboratory instrument case and is designed for use at a portable laboratory site.

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

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

Figure 4- Model 4100 handheld SAW/GC Vapor Analyzer.

Figure 5- Model 7100 Portable SAW/GC Vapor Analyzer.

Test Results with Live Nerve Agents

The vapor pressure of chemical warfare agents spans approximately six orders of magnitude as shown in Figure 6. The more volatile agents are phosgene and hydrogen cyanide and these compounds have vapor pressures comparable to Freon. Mid range agents are GB, BD, BA, and GF. These compounds have vapor pressures that are comparable to gasoline and jet fuel. Mustard and VX are considered the least volatile agents with vapor pressures in the 1 to 10 ppm range. Their vapor pressure is comparable to that of dinitrotoulene (DNT), nitroglycerin, and TNT. Although these are the heaviest in this group, their vapor pressure is considered high compared to non-volatile compounds such as drugs of abuse (cocaine) or polychlorinated biphenyl (PCB).

The above plot is used to determine the operating parameters of the SAW/GC method required for a vapor detection. In general, retention time is inversely proportional to vapor pressure and the SAW/GC system operating temperatures were selected so that there were no cold spots to prevent passage of vapor samples through the inlet, valve, and column to the detector.

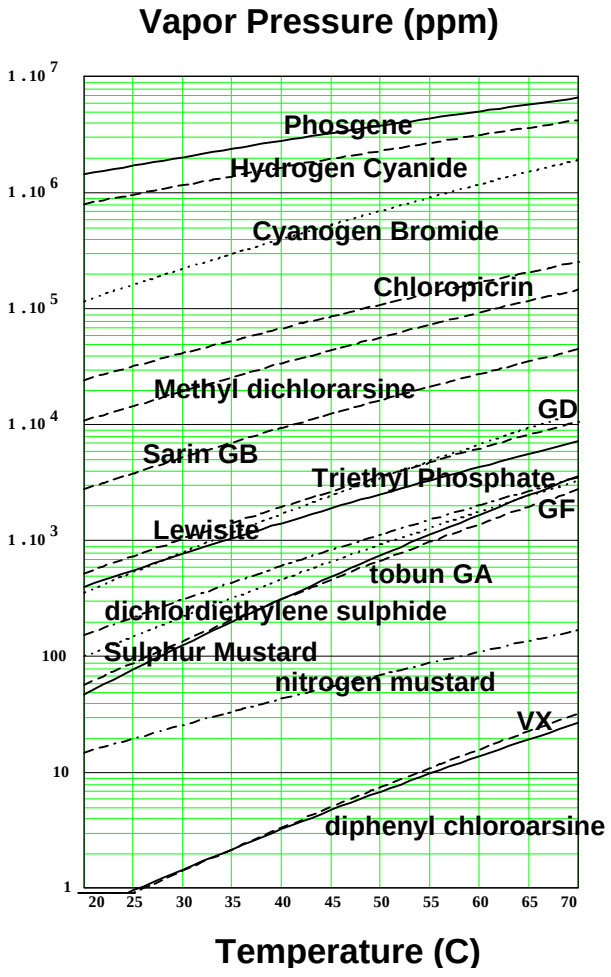


Figure 6- Vapor pressure of Chemical Warfare Agents.

Testing of a SAW/GC with actual chemical nerve agents was performed. A model 4100 handheld SAW/GC analyzer was tested at the MidWest Research Institute's surety laboratory in Kansas City. The SAW/GC was tested with a variety of agents and agent simulants which included GD, GB (Sarin), triethyl phosphate (TEP), and dimethyl methylphosphonate (DMMP). A typical 10 second chromatogram obtained by exposing the system to a calibrated amount of GB together with a surrogate DMMP is shown in Figure 8. Picogram sensitivity for Sarin was confirmed by a 1960 Hz response from injection of 1.9 nanograms of Sarin. Thus for this compound the scale factor was approximately 10 Hz/picogram. The SAW/GC had a noise floor of 10 Hz, hence the minimum detection level was 3 picograms (signal to noise ratio = 3).

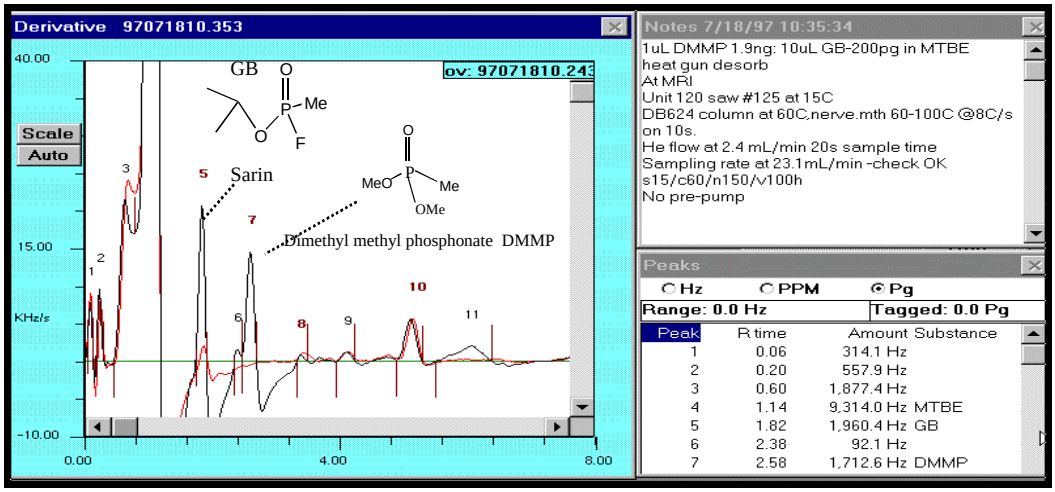


Figure 8- Preliminary test results on three common nerve gas simulants

Other nerve gas simulants such as triethyl phosphate, dimethyl methylphosphonate, and 2-chloroethyl ethyl sulfide (mustard gas) are shown together in the chromatogram of Figure 7. Response to chemical stimulants is important since these are used to calibrate and test the response of the system in the.field

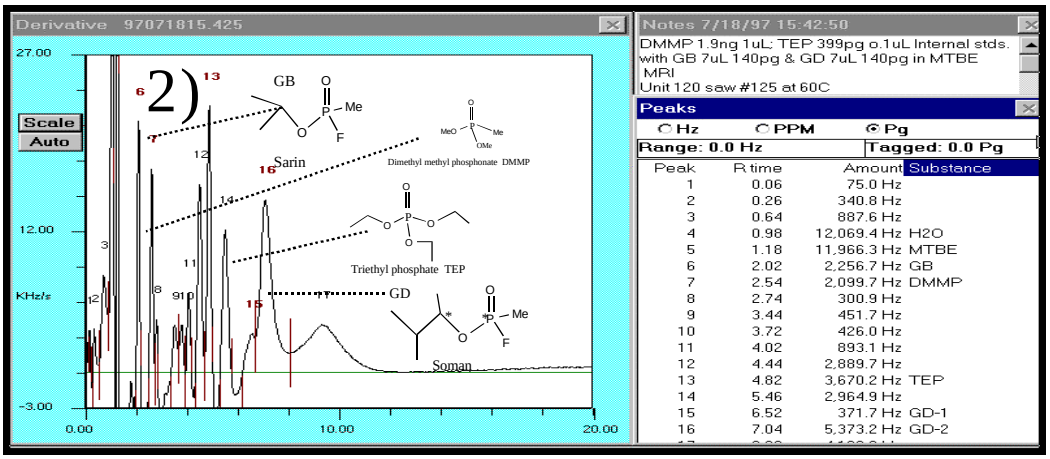


Figure 7- GD, Soman, GB, TEP, and DMMP

A complete 6 point calibration curve for Sarin is shown in Figure 9. This curve was obtained by repeated exposure to 20 picogram quantities of nerve agent within a methyl tetra-butyl ether. The picogram sensitivity and linearity of the SAW/GC is readily apparent.

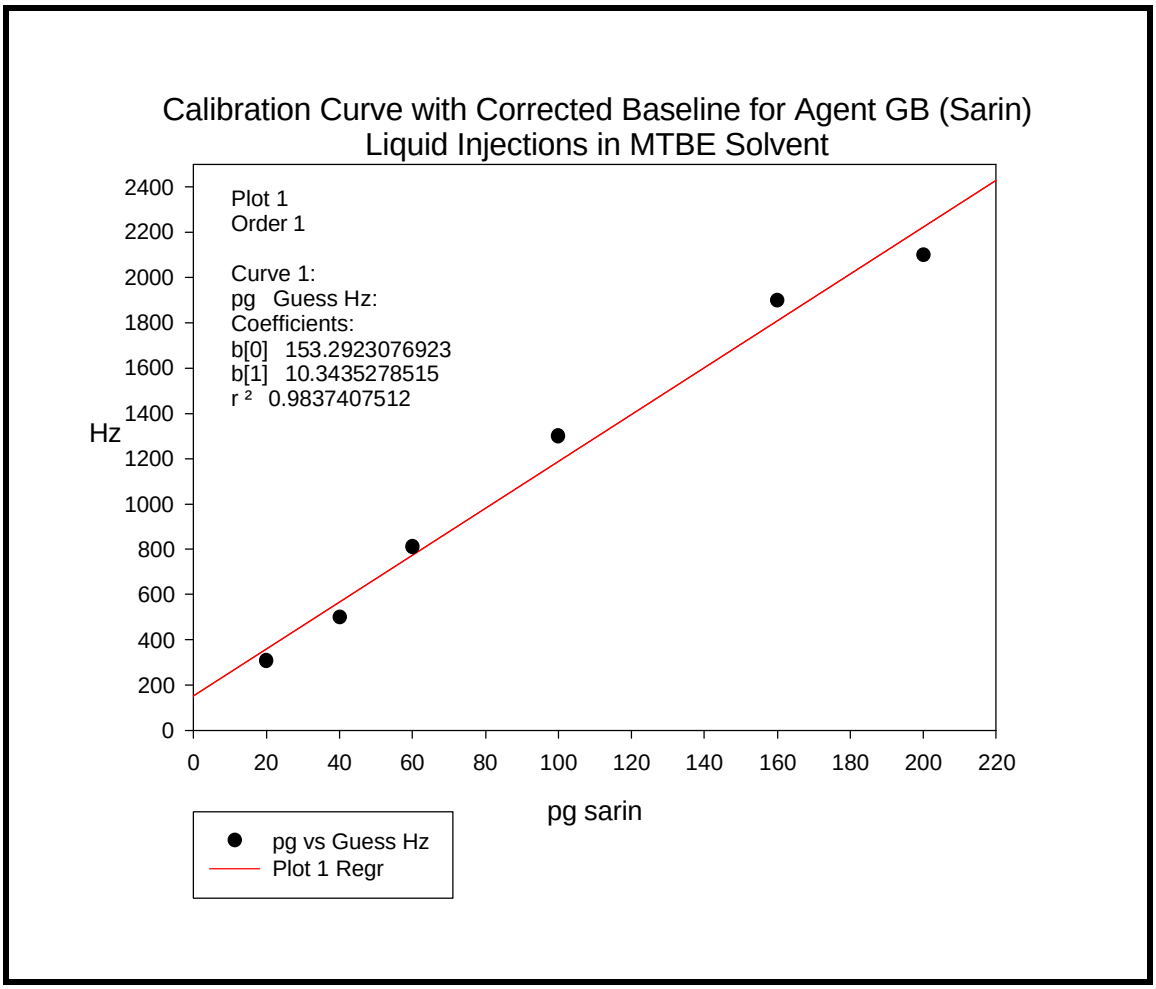


Figure 9- N point calibration for Sarin (GB)

Interference, particularly from gasoline, diesel, and JP-8 fuels were evaluated with the SAW/GC and can be potential problems in detecting nerve agents where these compounds are present. Testing the SAW/GC confirmed that these fuel vapors have similar vapor pressure to that of the mid-level agents such as GB, GD, and GA. It is possible that they can interfere with the detection of these nerve agents and cause false alarms. The degree of interference is determined by the particular column phase being used in the system, and the relative strength of the vapors. An example is the chromatogram of Figure 10 where saturated gasoline vapors give a 27.6 ppb false alarm for the simulant chloro-ethylsulfide (cees). Diesel fuel vapors did not interfere, however, JP-8 vapors (Figure 11) causes a 72 ppb false alarm level for DMMP.

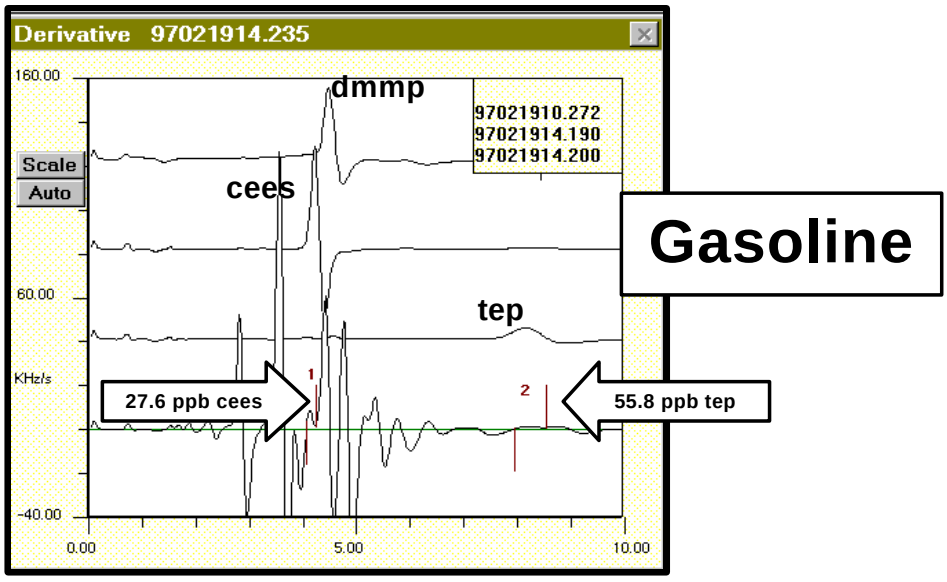


Figure 10- Interference of gasoline vapors with dmmp, cees, and tep.

Interference from gasoline, diesel, and JP-8 fuels can be mitigated or eliminated by two techniques: (1) the use of two or more GC columns with different phases and (2) pattern recognition algorithms to recognize and warn the operator of possible interference. The later would alert the operator while the former would eliminate the problem by greatly increasing specificity of the detection process. As an example, in the above figures it would be quite easy to recognize the presence of gasoline or JP-8 fuels from their vapor signature. Similarly, compound peaks at retention times corresponding to known nerve agents would not be consistent with fuel vapor signatures and could be used to activate an alarm.

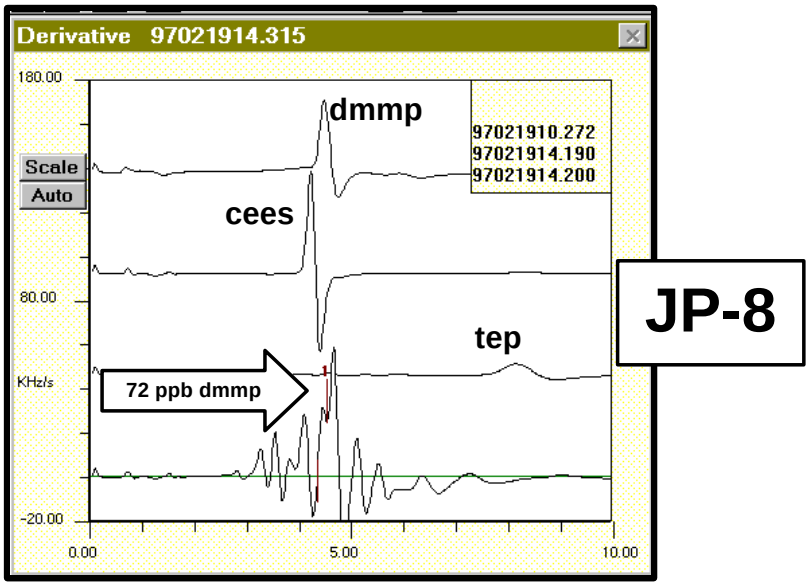


Figure 11- Interference by JP-8 fuel vapors.

Summary and Conclusions

The conclusions reached during testing of SAW/GC systems with actual and simulant nerve agents were as follows:

1. Sensitivity of the SAW/GC to nerve agents is 1 part per trillion (picograms) using short (5 second) sample times.
2. Sensitivity of the SAW/GC to nerve agents is in parts per trillion range if sample integration times greater than 10 seconds are used.
3. Co-ilution from gasoline, JP-8, and diesel fuels can interfere with some mid-level nerve agents and is column dependent.
4. Pattern recognition can identify gasoline, JP-8 and other hydrocarbon fuels.
5. Interference can be removed or eliminated using two dissimilar GC columns.

The sensitivity of SAW/GC is more than adequate to detect nerve agents present in concentrations harmful to humans. For example, fast response (10 seconds) levels for VX, GA, GB, GD, and GF are 1000 picograms or 1 nanogram. Levels for other more volatile agents are even higher. At these concentrations the SAW/GC will exhibit signal to noise ratios as high as 100 to 1. Detection of low concentration exposure levels (e.g. 1 picogram) for extended periods of time are equally achievable since the SAW/GC can accumulate several milliliters of vapor sample in 10 seconds which will produce 10 or more picograms and this can be detected with a 10 to 1 signal to noise ratio.