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CRDEC-TR-88102

SURFACE ACOUSTIC WAVE DETECTION OF CHEMICAL WARFARE AGENTS

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October 1988

U.S. ARMY
ARMAMENT
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Aberdeen Proving Ground, Maryland 21010-5423

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SECURITY CLASSIFICATION OF THIS PAGE

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CALSSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-88102

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION CRDEC

6b. OFFICE SYMBOL *(if applicable)* SMCCR-RSL

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State, and ZIP Code)* Aberdeen Proving Ground, MD 21010-5423

7b. ADDRESS *(City, State, and ZIP Code)*

8a. NAME OF FUNDING/SPONSORING ORGANIZATION CRDEC

8b. OFFICE SYMBOL *(if applicable)* SMCCR-RSL

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)* Aberdeen Proving Ground, MD 21010-5423

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
	1C464724	D020	

11. TITLE *(Include Security Classification)* Surface Acoustic Wave Detection of Chemical Warfare Agents

12. PERSONAL AUTHOR(S) Davis, Dennis M., Ph.D.; Schiff, Leon J., Ph.D. (CRDEC); and Parsons, John A. (Geo-Centers, Incorporated)

13a. TYPE OF REPORT Technical

13b. TIME COVERED FROM 87 May TO 87 Oct

14. DATE OF REPORT *(Year, Month, Day)* 1988 October

15. PAGE COUNT 27

16. SUMPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
15	02	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

Surface Acoustic Wave, Detection,
~~SAW~~ Chemical Warfare Agents. (KR)
Microsensors,

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Surface Acoustic Wave (SAW) devices are potentially useful as small, sensitive chemical vapor sensors. The operating principles of these devices have been described in detail. The use of SAW devices for detecting dimethyl methylphosphonate (DMMP) vapor has been reported elsewhere. The basic operating principle of the SAW devices is the reversible adsorption of chemical vapors by adsorbent coatings that are sensitive and selective to the vapor that one is trying to detect. That is, SAW devices act as mass sensitive detectors. The SAW device used in this study consists of an array of four coated sensor elements with each coating giving a characteristic response to each of the vapors to be detected. The coatings used for the four sensors are fluoropolyol (FPOL), poly(ethylene maleate) (PEM), ethyl cellulose (ECEL), and polyvinyl pyrrolidone (PVP). The response of these four coatings to chemical agent simulant vapors has been reported (continued on reverse)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON

22b. TELEPHONE *(Include Area Code)* (301) 671-2914

22c. OFFICE SYMBOL SMCCR-SPS-T

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. ABSTRACT (continued)

previously. This report deals with isopropyl methylphosphonofluoridate (GB), pinacolyl methylphosphonofluoridate (GD), bis(2-chloroethyl)sulfide (HD), and O-ethyl S[2-(diisopropylamino)ethyl]methylphosphonothioate (VX). The response of the SAW to each vapor is determined as a function of the concentration of the vapors. Possible explanations of the anomalous behavior of the coatings to the chemical agents are presented.

PREFACE

The work described in this report was authorized under Project No. 1C464724D020, Chemical Detection and Warning Systems. This work was started in May 1987 and completed in October 1987.

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Acknowledgments

The authors would like to thank William Cutchin for providing the gas chromatographic analysis of the bubbler concentrations. Special thanks are also extended to Joe Hovanec for his help in preparing this report.

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SURFACE ACOUSTIC WAVE DETECTION OF CHEMICAL WARFARE AGENTS

1. INTRODUCTION

Surface Acoustic Wave (SAW) devices are potentially useful as small, sensitive chemical vapor sensors. The operating principles of these devices have been described in detail,[1] and the use of SAW devices for detecting dimethyl methylphosphonate (DMMP) vapor has been reported elsewhere.[2] The basic operating principle of the SAW devices is the reversible adsorption of chemical vapors by adsorbent coatings that are sensitive and selective to the vapor that one is trying to detect. That is, SAW devices act as mass sensitive detectors. The SAW device used in this study consists of an array of four coated sensor elements with each coating giving a characteristic response to each of the vapors to be detected. The coatings used for the four sensors are fluoropolyol (FPOL), poly(ethylene maleate) (PEM), ethyl cellulose (ECEL), and polyvinyl pyrrolidone (PVP). The response of these four coatings to chemical agent simulant vapors has been reported previously.[3] This report deals with GB, GD, HD, and VX. The response of the SAW to each vapor is determined as a function of the concentration of the vapors. Possible explanations of the anomalous behavior of the coatings to the chemical agents are presented.

2. *THEORY*

Each of the SAW sensors used in this study consists of a pair of interdigital electrode arrays that are lithographically patterned on a polished piezoelectric material (e.g., ST-quartz). When placed in an oscillation circuit, an acoustic Rayleigh wave may be generated by applying an RF voltage to one set of the interdigital arrays. The generated Rayleigh wave travels across the quartz surface until it reaches the opposite set of electrodes. Most of the energy is constrained to the surface of the piezoelectric material. The Rayleigh wave will

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[1] Snow, A., and Wohltjen, H., "Poly(ethylene maleate)-Cyclopentadiene: A Model Polymer-Vapor System for Evaluation of a SAW Microsensor," Anal. Chem. Vol. 56(8), p 1411 (1984).

[2] Miller, R.E., and Parsons, J.A., Detection of Dimethyl Methylphosphonate Using a Surface Acoustic Wave Vapor Detector, Paper #40, presented at the American Chemical Society 21st Mid-Atlantic Regional Meeting, Pomona, NJ, 20 May 1987.

[3] Davis, D.M., Miller, R.E., and Parsons, J.A., Surface Acoustic Wave Detection of Organophosphorus Compounds, CRDEC TR-88101, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, October 1988, UNCLASSIFIED Report.

interact with any material that is in contact with the surface (i.e, the coating). Any changes in the mass or mechanical modulus of the coating will produce a change in the velocity of the Rayleigh wave, resulting in a measurable shift in the sensors resonant frequency. This study used dual-delay line oscillators that resonate at a frequency determined by the wave velocity and the electrode spacing. The use of the delay line oscillators allows for the compensation of any temperature and vapor flow rate variations experienced by the sensor. This is accomplished by comparing the resonant frequency of a wave propagating across a coated surface with a wave that is propagating across an uncoated surface. A schematic of the 158 Megahertz (MHz)·dual-delay line oscillator used in this study is shown in Figure 1.

3. EXPERIMENTAL PROCEDURES

3.1 Equipment.

The equipment used in this study consisted of a SAW vapor sensor that was interfaced to an Apple IIe computer (Figure 2), and a Q5 vapor generator (Figure 3). The SAW sensor, obtained from Dr. Hank Wohltjen [Microsensor Systems, Incorporated (Fairfax, VA)], incorporates four separate 158 MHz dual-delay line oscillators that are coated with FPOL, PEM, ECEL, and PVP. The materials used for the sensor coatings were provided by Naval Research Laboratory and Microsensor Systems, Incorporated. The chemical structure of the coatings are shown in Table 1.

The coatings were applied to packaged, wire-bonded, bare oscillators using a standard air brush with compressed air as the propellant and solutions of the coatings dissolved in volatile solvents. Typical solutions for the air brush procedure are 0.1 wt % coating in chloroform. The wire-bonded, bare oscillator is composed of two sets of interdigital electrodes consisting of 50 gold-plated "fingers." The fingers are 7-µm wide, and the spacing between fingers measures 7 µm. The fingers were lithographically patterned onto ST-Quartz, a substrate material. The entire package was then placed into a Teflon cell for use. The total area of the dual-delay, line oscillator is approximately 1 cm^2. Because the area of the oscillator to be coated measured about 2 mm^2, a mask was placed over the oscillator to ensure proper deposition of the coatings. The film thickness was determined by measuring the frequency change of the oscillator's resonant frequency during the coating application. This frequency change was monitored by an oscilloscope. The coatings were applied to the wire-bonded, bare oscillators by the staff at Naval Research Laboratory (Washington, DC).

The low concentrations of the sample vapors were generated with a standard Q5 generator by passing dry zero air, at a known flow rate, through a porous alundum oxide thimble

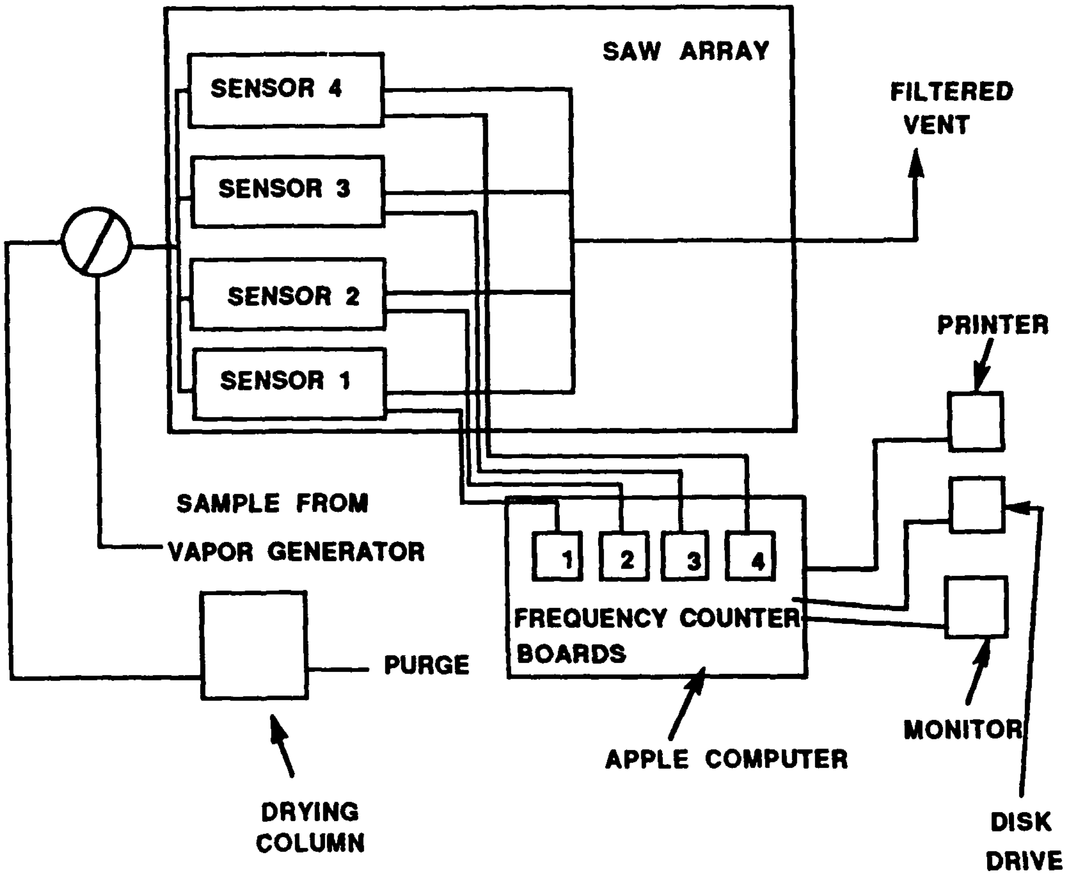


Figure 1. Block Diagram of the SAW Equipment.

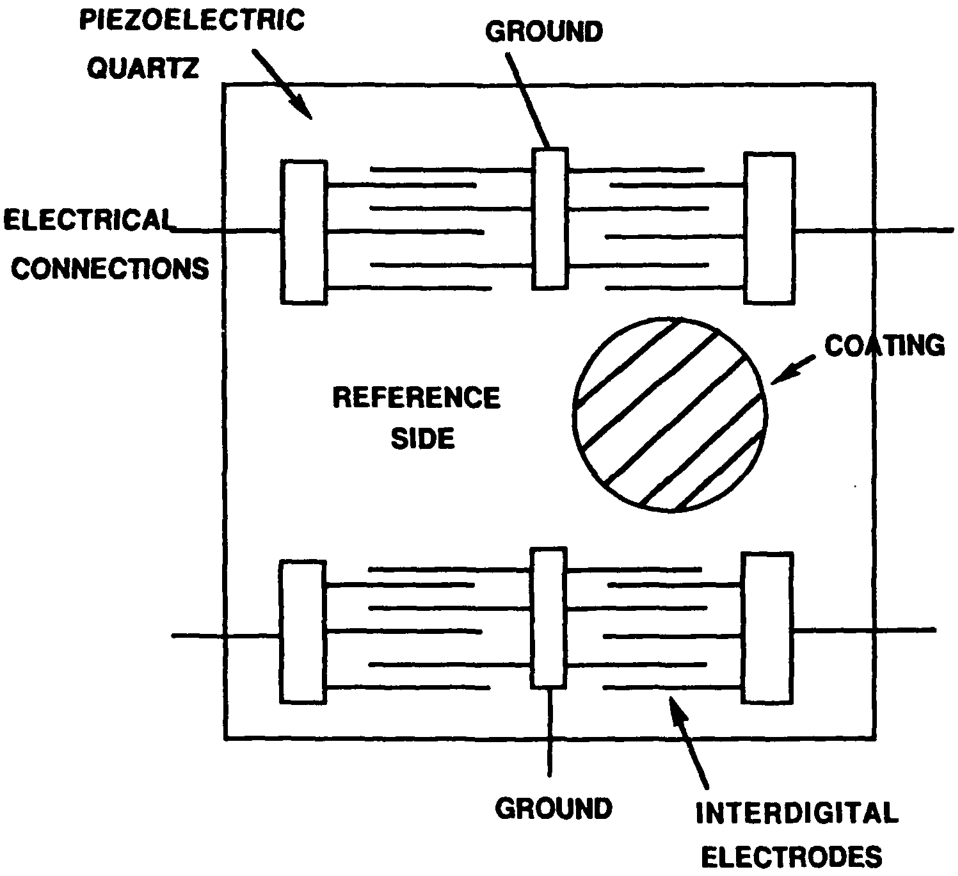


Figure 2. 158 MHz Dual Delay Line Oscillator.

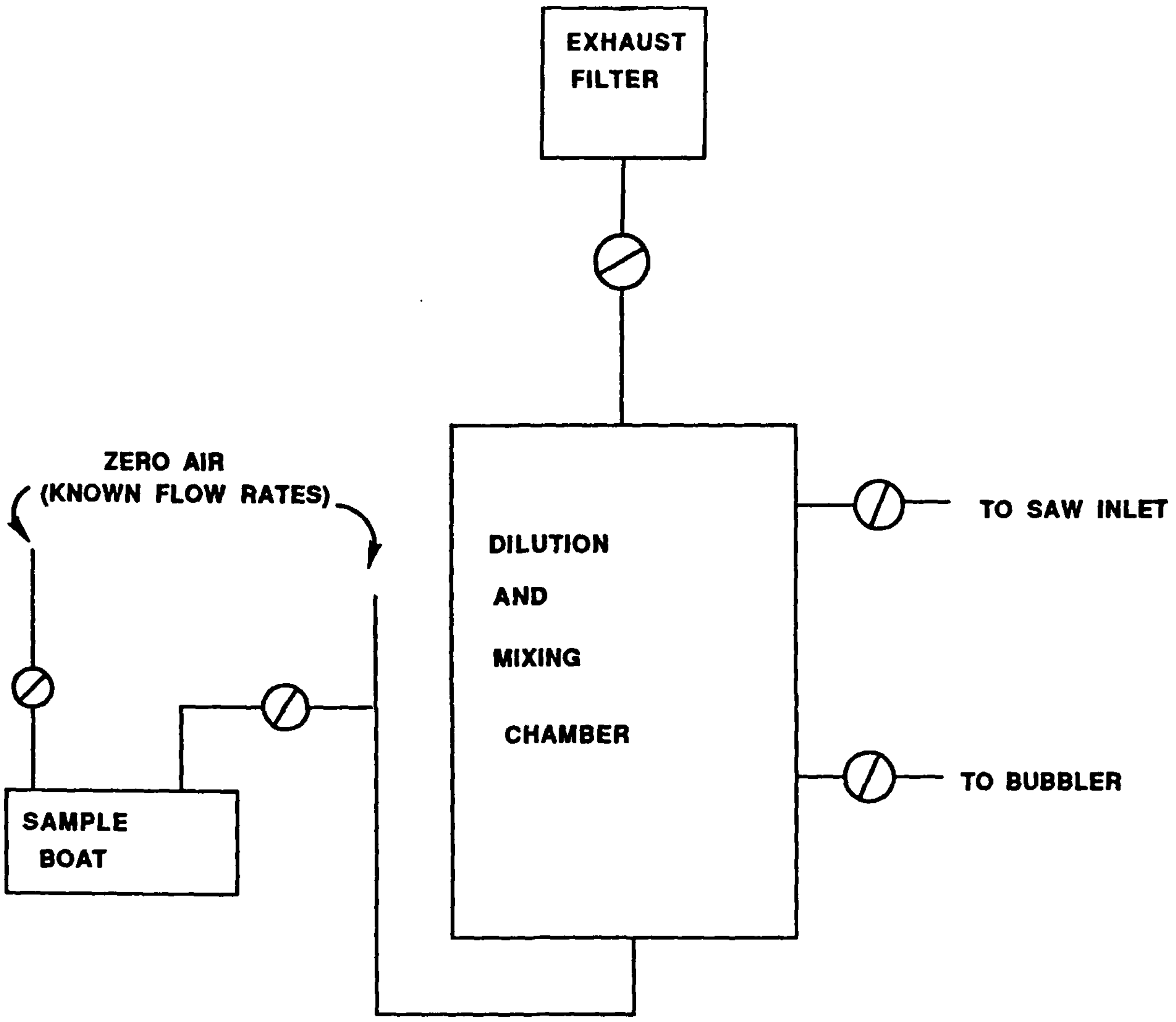
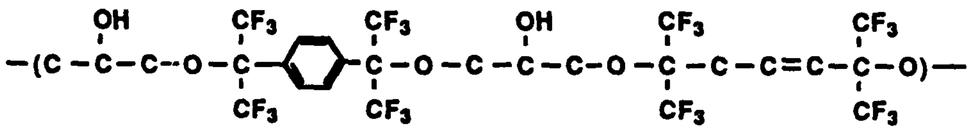
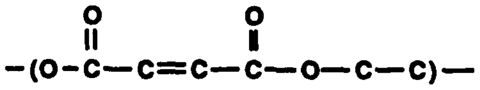


Figure 3. Diagram of a Q5 Vapor Generator.

Table 1. Chemical Structures of the Coatings.



Fluoropolyol

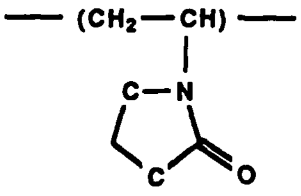


$-(O-\overset{\overset{O}{\|}}{C}-C=C-\overset{\overset{O}{\|}}{C}-O-C-C)-$

Poly(ethylene maleate)

$—(C_8H_{14}O_5)—$

Ethyl Cellulose



Polyvinyl Pyrrolidone

that is saturated with the liquid reagent. The porous thimble and the liquid reagent are both contained within a sample boat. This vapor is then mixed and diluted to the desired concentration with dry zero air in the generator's mixing chamber where the flow and concentration of the vapor are allowed to stabilize. Two sampling ports on the generator mixing chamber provide access to the sample vapor. One of the ports permits sampling of the vapor by the SAW device during its sampling cycle. The second port permits samples of the vapor to be removed for analysis. This second sample is removed by bubbling the vapor, at a known flow rate and sample collection time, through a set of two bubblers each filled with 10 mL of either 2-methoxyethanol or isopropyl alcohol. The bubblers are then analyzed using gas chromatography (GC). The first sampling port leads to a three-way, manually operated switching valve that allows the SAW device to sample the generated vapor or a purge of zero air. Typically, the SAW is exposed to the zero air purge for 2 min to establish an initial baseline. The switching valve is positioned to allow sampling of the vapor for approximately 2-5 min or until an equilibrium frequency shift is observed. Then, the switching valve is repositioned to allow sampling of the zero air purge, and the SAW establishes a final baseline.

The GC analyses were conducted on a Model 5880A Hewlett-Packard GC. The GC was equipped with a flame photometric detector (FPD) operated at 220 °C. The injection temperature of the GC was set to 250 °C. The column used for the analysis was a 6 ft by 0.2-mm column with 4.61% OV-101 and 3.39% OV-17 on a stationary phase of 100-120 Gaschrom Q. The sample size injected into the GC was 2 mL with a nitrogen flow rate of 30 mL/min. The temperature of the oven ranged from 60-250 °C. The concentrations of the vapors in the bubblers were based on peak area measurements and external standards. Peak tailing was generally observed for the samples. The concentration of the vapor in the Q5 generator was then calculated from the concentration of the bubbler using the time collection of the bubbler, flow rate of the sample through the bubbler, and the molecular weight of the sample.

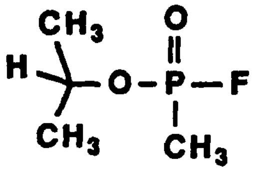
3.2 Chemicals.

The chemical agents used in this study were isopropyl methylphosphonofluoridate (GB), pinacolyl methylphosphonofluoridate (GD), and O-ethyl S[2-(diisopropylamino)ethyl]-methylphosphonothioate (VX), all organophosphorous compounds, and bis(2-chloroethyl)sulfide (HD), an organosulfur compound. The structures of these compounds are shown in Table 2.

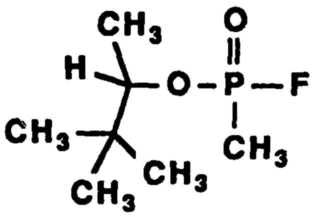
4. DISCUSSION AND RESULTS

Tables 3 through 6 contain the raw data for the responses of the coatings to the four vapor challenges. Figures 4 through 7 show typical response curves obtained for nominal

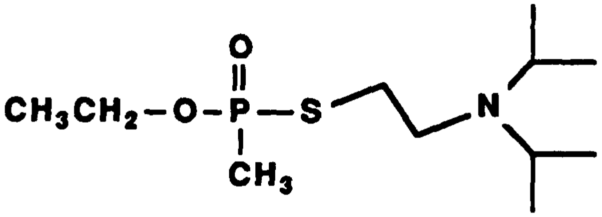
Table 2. Chemical Structures of the Agents.



GB
(Sarin)



GD
(Soman)



VX

$Cl—CH_2CH_2\text{-}S\text{-}CH_2CH_2—Cl$

HD
(Mustard)

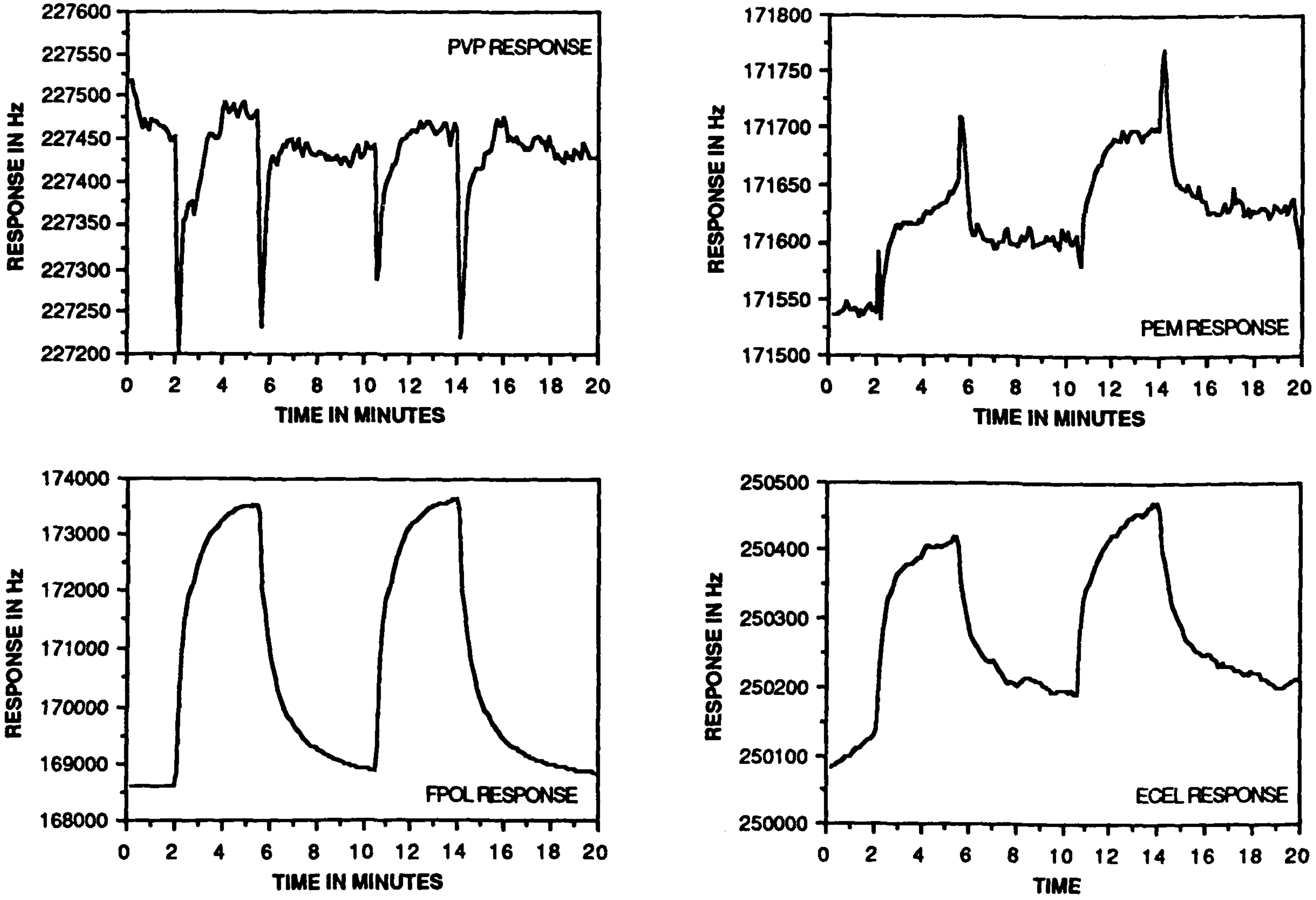


Figure 4. Typical SAW Responses to Nominal 10 ppm GB Vapor.

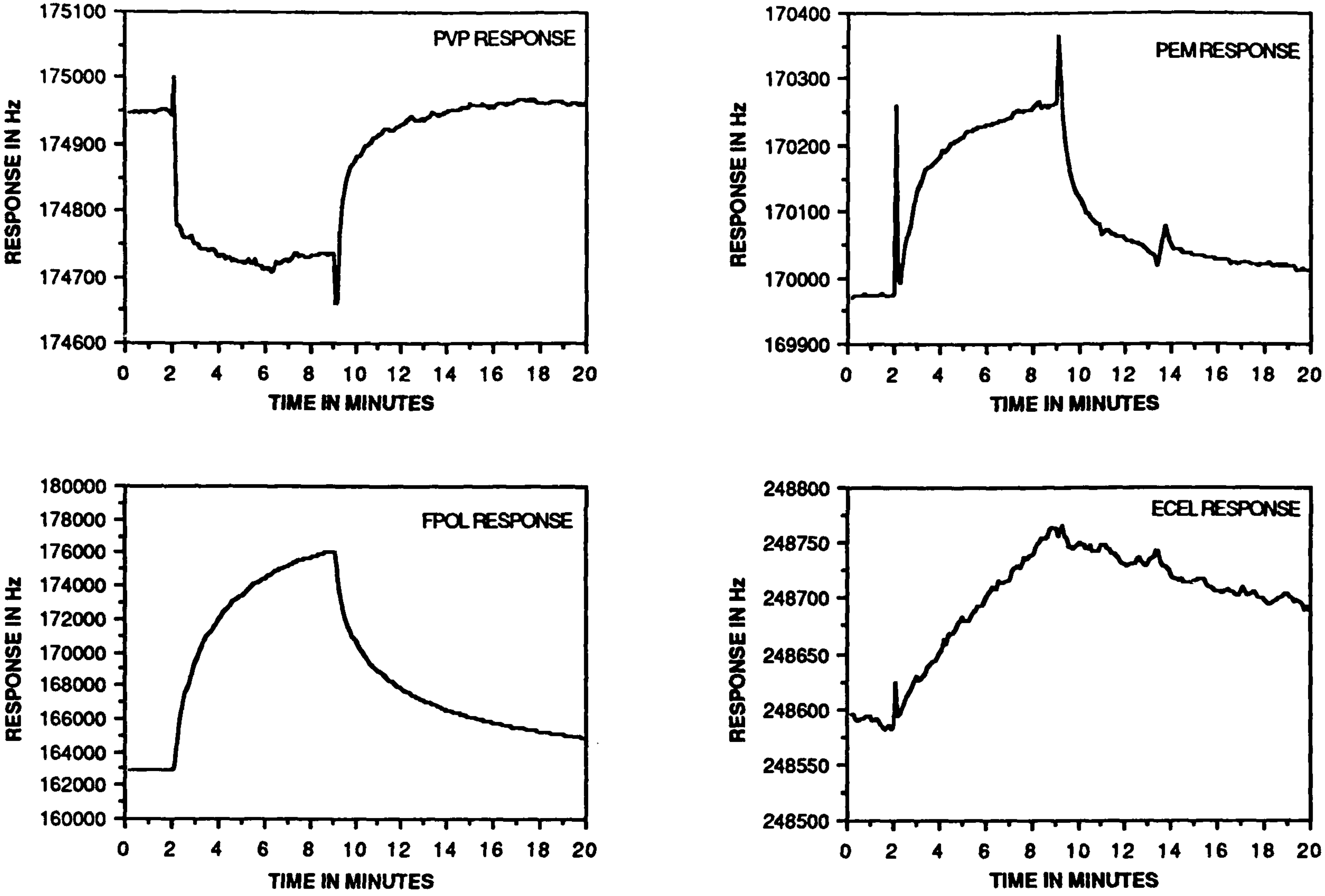


Figure 5. Typical SAW Responses to Nominal 10 ppm GD Vapor.

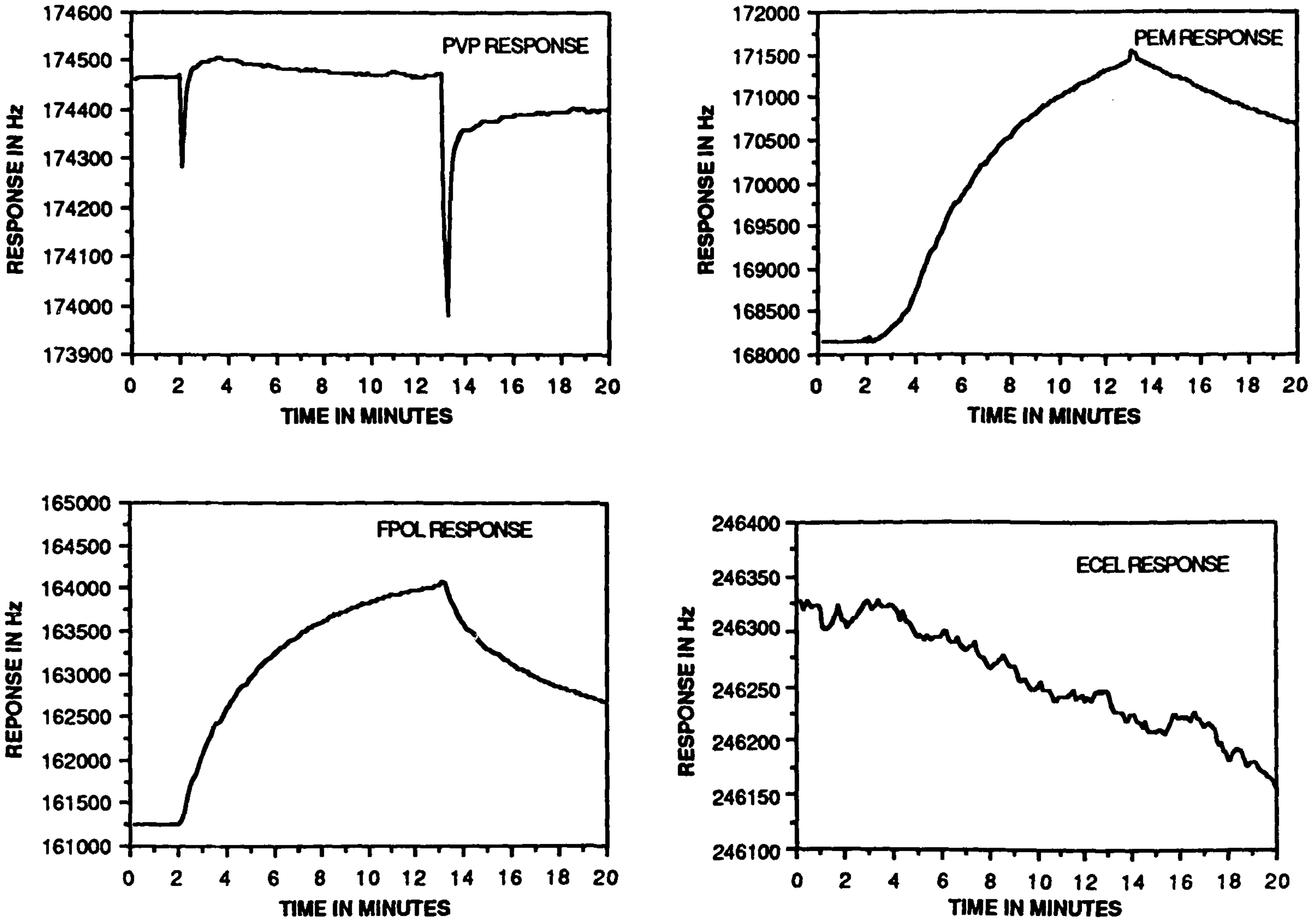


Figure 6. Typical SAW Responses to 328 ppb VX Vapor.

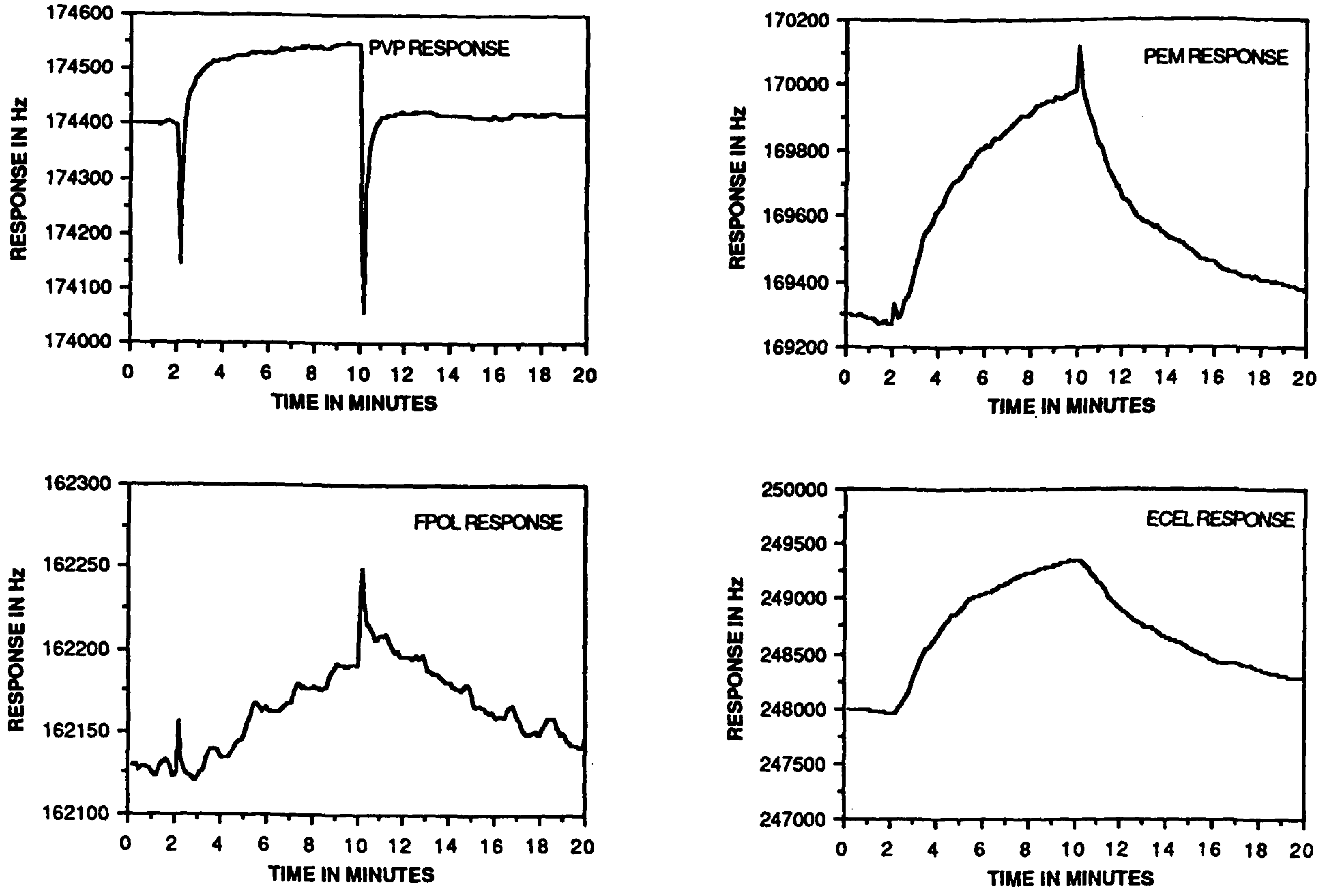


Figure 7. Typical SAW Responses to Nominal 10 ppm HD Vapor.

10-ppm concentrations of the test vapors for the four coatings. The responses reported in the tables are average values for the responses based on repeated exposures for each concentration run. Figures 8 through 11 are graphs of the frequency shift of the coatings versus concentration of the vapors in parts-per-million. In the coatings studies, the largest frequency shifts observed with the organophosphorus compound were for the FPOL coating with the next larger response being obtained for the PEM. Generally, for ECEL and PVP, the response was very small. For the HD, the largest shifts were for the ECEL coating; the next larger response was for the PEM coating.

4.1 Response to GB Vapor.

The frequency shifts observed for the coatings exposed to GB vapor are shown in Table 3. The frequency shifts recorded are the average frequency shifts obtained for the sensor response at any given concentration. Generally, the average response is the average of four different experimental runs with two exposures of the sensor to vapor per run. The data in Table 3 shows that the coating with the greatest response to GB vapor is generally the FPOL with the next greater response being obtained for either the ECEL or PVP, depending upon the concentration of GB being analyzed. The PEM coating exhibited no response to the GB vapor at concentrations less than 5 ppm.

Table 3. SAW Response to GB Vapor.

GB Concentration (ppm)	Frequency Shift (ΔHz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.105	-4 ± 11	-8 ± 16	14 ± 39	109 ± 39
0.272	-4 ± 6	-10 ± 9	3 ± 12	122 ± 20
0.544	-9 ± 4	-3 ± 9	11 ± 17	100 ± 22
2.74	1692 ± 144	-9 ± 12	84 ± 27	121 ± 55
5.49	3612 ± 28	47 ± 8	185 ± 21	84 ± 35
9.94	4638 ± 98	69 ± 15	234 ± 17	50 ± 25

It is not surprising that the FPOL has the largest response to the presence of the GB vapor because the coating was developed to respond to the presence of organophosphorus compounds. The surprising fact is that the level of the response is so small when compared to the levels obtained for chemical agent simulants.[3] The interaction between the GB vapor and the FPOL coating is much less than that observed for the simulants. This may be due to the presence of the P-F moiety in the GB molecule that is not present in the chemical agent simulants tested. Based on the results of the simulant work, one would expect the PEM coating to have a significant response

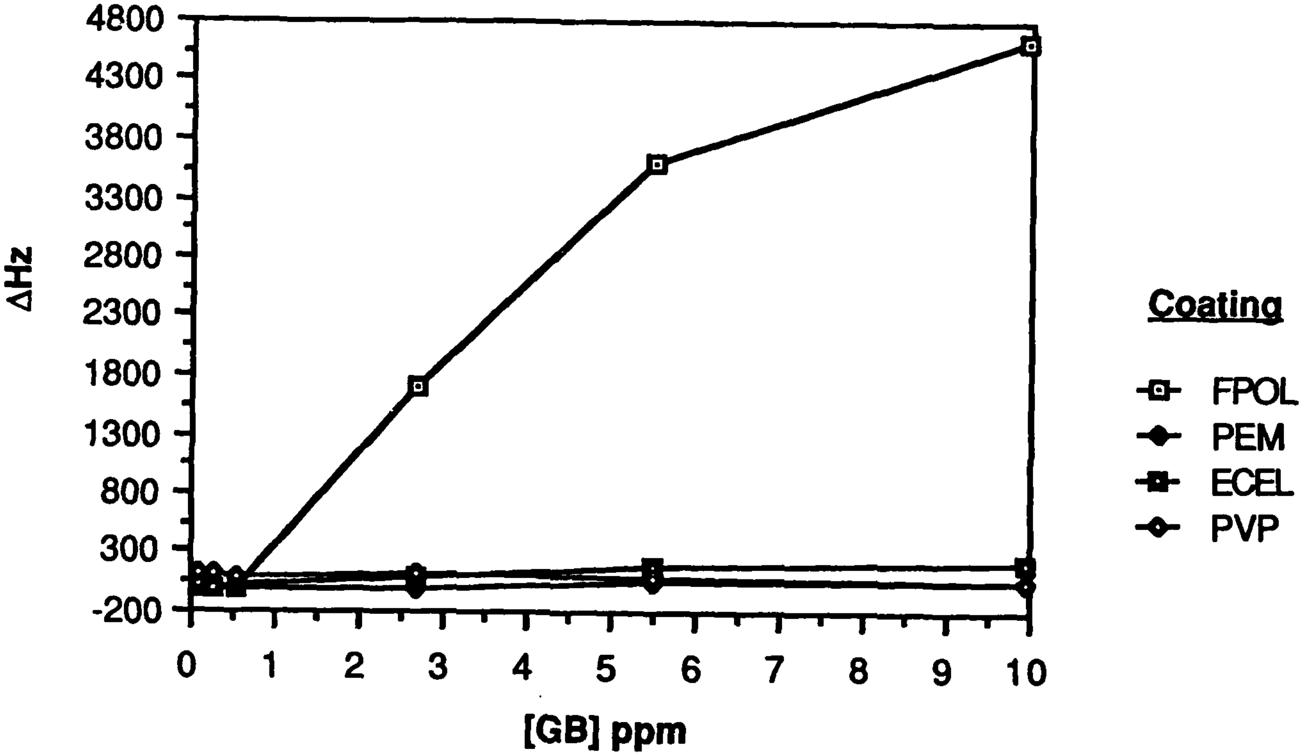


Figure 8. SAW Response to GB Vapor.

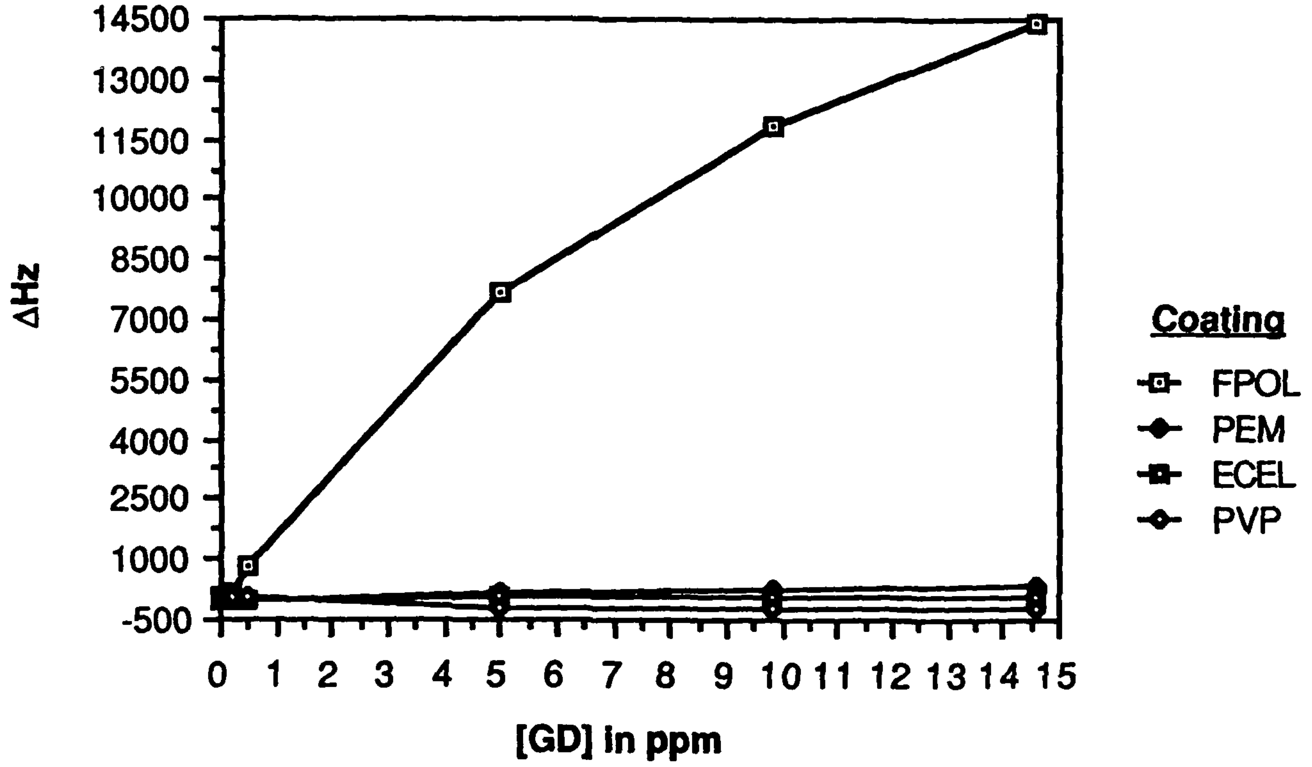


Figure 9. SAW Response to GD Vapor.

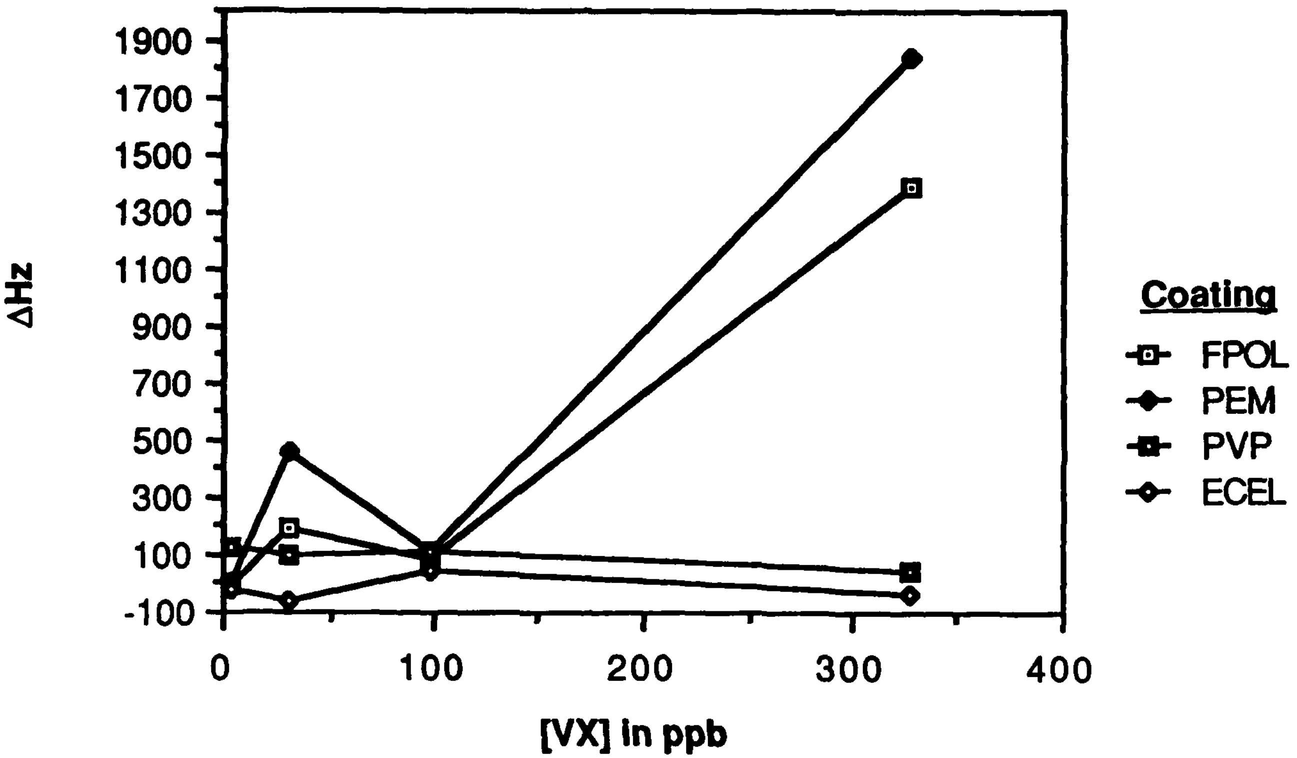


Figure 10. SAW Response to VX Vapor.

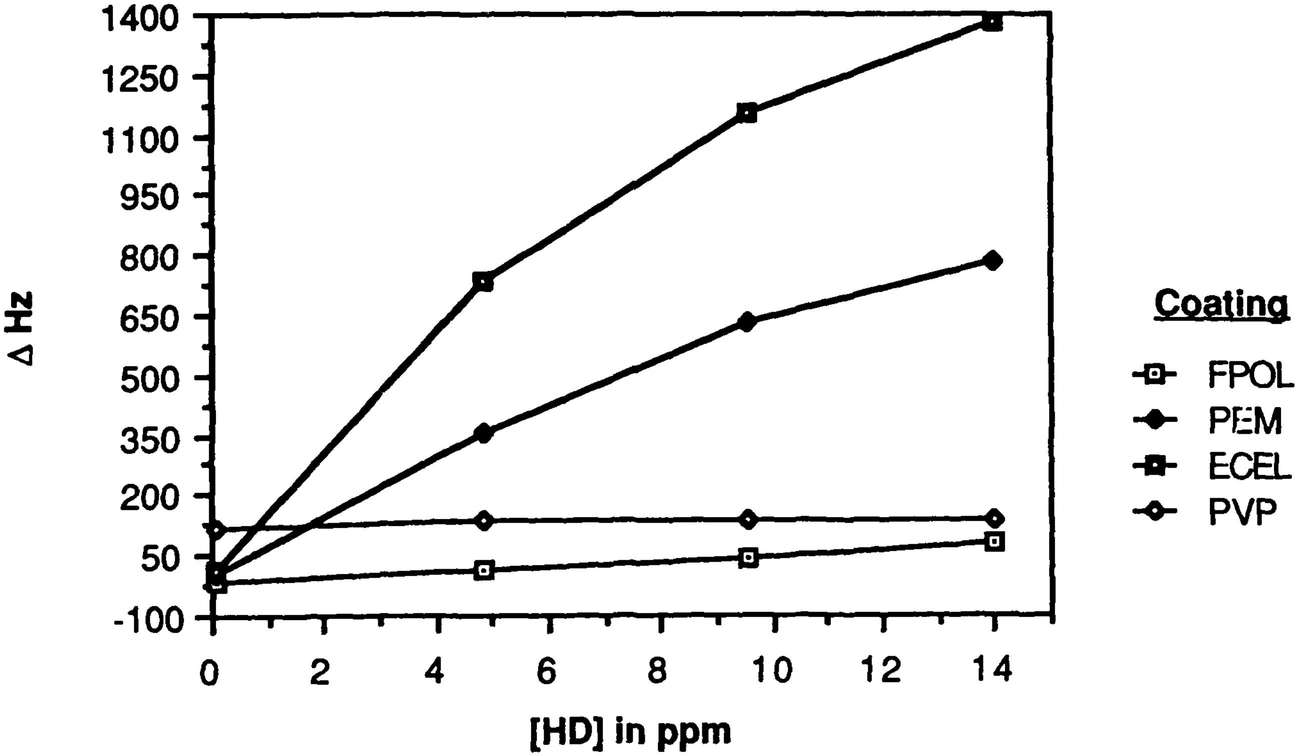


Figure 11. SAW Response to HD Vapor.

to GB, but that was not seen. Rather, a reaction of the PVP coating with the vapor was observed at low concentrations. A decreased response of PVP at higher concentrations of GB was noted, and this may be due to an irreversible adsorption of the vapor to the PVP coating. At low concentrations, the amount adsorbed was small, and the effects of irreversible adsorption did not appear to be great. The level of the response was fairly small but constant. At higher concentrations, the cumulative effect of the adsorbed vapor resulted in a decreased response.

The ECEL response was very small at lower concentrations, making it difficult to determine if any GB vapor was present. However, at higher concentrations, the response was large enough to be discerned from the baseline frequency readings. This response increase, with a corresponding increase in the concentration of the vapor, indicated that the adsorption of the vapor was reversible in nature. This was corroborated by the sensor frequency reading returning to its baseline value shortly after the vapor challenge was removed from the SAW device. Even though the response varied with a change in concentration and the interaction of the ECEL coating with the vapor was reversible, the response of the coating was small, making it a poor candidate for detecting chemical agents.

4.2 Response to GD Vapor.

The frequency shifts observed for the four sensor coatings exposed to GD vapor are shown in Table 4. Again, the largest response for GD vapor present was observed for the FPOL coating. The PEM response was the next larger, and the ECEL was the least responsive coating. There was a somewhat anomalous response observed for the PVP coating. At concentrations below 5 ppm, there was a positive frequency shift when GD was introduced to the SAW device. At concentrations above 5 ppm, a negative frequency shift was observed.

Table 4. SAW Response to GD Vapor.

GD Concentration (ppm)	Frequency Shift (ΔHz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.030	13 ± 5	-8 ± 5	4 ± 24	82 ± 9
0.100	55 ± 6	-11 ± 6	-2 ± 8	107 ± 8
0.200	146 ± 10	-10 ± 7	-2 ± 8	78 ± 8
0.499	842 ± 17	-15 ± 6	2 ± 11	90 ± 7
4.98	7681 ± 212	141 ± 8	77 ± 24	-232 ± 53
9.80	11889 ± 138	260 ± 28	111 ± 46	-217 ± 4
14.57	14378 ± 177	339 ± 21	110 ± 15	-231 ± 2

It is obvious from the data shown in Table 4 that none of the sensors exhibited the desired linear response with respect to the concentration of GD vapor. The FPOL response was large but was not directly proportional to the concentration of the vapor. Thus, if FPOL were used for detecting GD or similar compounds, a correction factor would have to be built into any algorithm that calculated the concentration.

The response of the PEM coating was anomalous in that a very small negative response to vapor concentrations below 0.5 ppm GD and a positive response of 100- and 350-Hz shift for vapor concentrations was observed between 5 and 15 ppm. The response was not linear with respect to concentration; but, there was a noticeable difference between the low concentrations and the high ones. The response level obtained was approximately four times as great as the response of this coating to GB vapor. Thus, the interaction of this coating with the GB and GD vapor was more dependent on the spatial configuration of the molecule than on the molecular weights. If the molecular weights of the two compounds were the only issue, the response to GD vapor would be 1.3 times greater than the GB vapor response.

An examination of the data for the PVP and ECEL coatings revealed that these two coatings permitted the differentiation between GD and GB vapors. Whereas the ECEL coating always exhibited a positive response to the GB vapor, a small negative response to low concentrations of GD and a small positive response to concentrations greater than 0.5 ppm was noted for GD. The response of the ECEL exposed to GD vapor was always less than its response to comparable concentrations of GB vapor. The opposite relationship was noted for the FPOL and PEM coatings. The PVP coating exhibited a small (generally less than 100 Hz) positive shift in the presence of GD vapor concentrations less than 0.5 ppm and a larger (approximately 200 Hz) negative shift at GD concentrations that were greater than 5 ppm. Thus, by combining the data from all four sensors, both the type (positive or negative) and the magnitude of the response made it possible to differentiate between GD and GB vapor using these coatings. An approximate concentration of the vapor present can also be determined using these sensors.

4.3 Response to VX Vapor.

The frequency shifts that were observed for the four sensor coatings are shown in Table 5. These data indicate that the responses of the FPOL and the PEM coatings are much larger than the responses obtained for the other organophosphorus agents. The order in which the concentrations (328 ppb, 30.75 ppb, 97.53 ppb, and 2.82 ppb) were run was very important for the VX. The order was important because the response of the coating never returned to its baseline value when the flow of VX-laden air to the sensor was interrupted.

Table 5. SAW Response To VX Vapor.

VX Concentration (ppb)	Frequency Shift (ΔHz) for Sensor FPOL	PEM	PVP	ECEL
2.82	-4 ± 8	4 ± 20	121 ± 10	-17 ± 20
30.75	189 ± 110	455 ± 414	101 ± 20	-64 ± 34
97.53	83 ± 102	114 ± 4	114 ± 4	-78 ± 29
328.0	1391 ± 841	1839 ± 62	43 ± 6	-27 ± 31

Even though the sensors responded very well to the presence of VX vapor, they were not practical for detecting VX because of the problem mentioned above. Because the response of the sensor did not return to its baseline value after the vapor challenge was removed, the magnitude of the response decreased with time. This was seen in the individual VX runs, and the trend is reflected in the average responses shown in Table 5. The cause of the problem may be attributed to the extremely low vapor pressure of the VX. Once the vapor was adsorbed on the coatings, a great deal of time was required to remove the relatively involatile VX from the surface. In our experiments, the baseline response could be achieved if clean, dry air was used to purge the SAW for approximately 2 weeks. The same result could also be accomplished by heating the SAW to increase VX's vapor pressure.

4.4 Response to HD Vapor.

The response of the four sensor coatings of the SAW device to the presence of HD, the only organosulfur compound that was tested, is shown in Table 6. Because no organosulfur simulants had previously been tested, there was really no sense of what to expect from the sensor elements. Thus, the positive responses of the ECEL and the PEM coatings and the negative responses of the FPOL and PEM coatings were interesting results. This indicated that there is a good possibility of differentiating between the blister and the nerve agents, the ultimate goal of any detection system.

Again, the data presented in Table 6 reveal that the responses of the sensor elements are not linear with respect to the concentration of the vapor challenge. However, there was a correlation between the concentration of the vapor and the response of the individual sensor elements. The magnitude of the responses obtained for the ECEL and PEM sensor coatings clearly indicated the concentration of the HD challenge. When this is taken in conjunction with the difference in the responses obtained for HD and organophosphorus vapors, it becomes evident that the SAW may be used to identify the type of agent present. A major problem that still remains is the lack of a large response to vapors in the sub parts-per-million range.

Table 6. SAW Response to HD Vapor.

HD Concentration (ppm)	Frequency Shift (ΔHz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.101	-12 ± 8	2 ± 19	18 ± 26	114 ± 4
4.87	13 ± 6	355 ± 11	731 ± 41	142 ± 5
9.52	44 ± 5	630 ± 11	1154 ± 12	138 ± 2
14.0	79 ± 20	785 ± 35	1385 ± 86	138 ± 14

5. CONCLUSIONS

The use of SAW devices for detecting chemical agent vapors has been demonstrated. There are still problems that must be addressed before they can be used as definitive sensors. These problems include:

- Reproducibility of the sensor elements and sensor coatings
- Improved stability of the sensor elements and sensor coatings
- Improved stability of the sensor elements, greater selectivity of the coatings
- Greater sensitivity of the SAW devices

These problems are important drawbacks to using the SAW devices as chemical agent detectors, but they are not insurmountable.