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MICROSENSOR EVALUATION STUDIES

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Surface Acoustic Wave (SAW) devices are potentially useful as small and very sensitive chemical vapor sensors. The basic operating principle for the SAW devices is the reversible adsorption of chemical vapors by adsorbent coatings which are sensitive and selective to the vapors 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 providing a characteristic response to each of the vapors being detected. Results of experiments using fluoropolyol (FPOL), polyethylene maleate (PEM), polyvinyl pyrrolidone (PVP) and ethyl cellulose (ECEL) as the coatings, and dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), diethyl ethylphosphonate (DEEP), and dimethyl hydrogen phosphonate (DMHP), as the vapor challenges are reported. Included as an appendix is the work performed under subcontract

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by Microsensor Systems, Inc. of Fairfax, VA which examined the effects of temperature, vapor flow rate and aging on microsensor performance.

PREFACE

The work described in this report was authorized under Contract No. DAAA15-87-D-0007. This work was started in January 1987 and completed in July 1988.

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MICROSENSOR EVALUATION STUDIES

1. INTRODUCTION

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A major goal within the Chemical Research, Development and Engineering Center (CRDEC) for a number of years has been the development of an increased capability to detect chemical agents. The accomplishment of this goal includes improvement in detecting and identifying chemical agents in the presence of impurities and interferences and increased capability in determining smaller quantities of the agents. Surface acoustic wave (SAW) devices, which contain specific and specialized coatings, have become increasingly important as potential toxic and hazardous vapor detectors that are small, sensitive, reliable, rugged, and low cost. These devices, as chemical agent detectors, depend on the adsorption of chemical agent from the vapor stream being sampled. Critical to the success of the SAW device for this detection application is that it preferentially adsorbs only the agent of interest from the atmosphere, and that the adsorption of impurities and interferents be minimized. This report presents the results of examining the temporal responses of four SAW coatings to varying concentrations of four organophosphonates used as simulants. A report prepared by Microsensor Systems, Inc., Fairfax, VA, under subcontract to GEO-CENTERS, INC., examined the effect of temperature, vapor flow rate, and aging on microsensor performance. This report is included as an appendix. (A4)

Surface Acoustic Wave (SAW) devices are potentially useful as small, and very sensitive, chemical vapor sensors. The operating principles of these devices have been described in detail (1), and its utility in detecting dimethyl methylphosphonate (DMMP) vapor has previously been reported (2). The basic operating principle of the SAW device is the reversible adsorption of chemical vapors by adsorbent coatings which are sensitive and selective to the vapor being detected. 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 being detected. The coatings used for the four sensors are fluoropolyol (FPOL), poly(ethylene maleate) (PEM), ethyl cellulose (ECEL), and polyvinyl pyrrolidone (PVP). The chemical vapors which were detected are diethyl ethylphosphonate (DEEP), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), and dimethyl hydrogen phosphonate (DMHP). These vapors were selected because they are all organophosphonates and respond to the sensors as functions of molecular weight and vapor concentration. This assumes the solubilities of the organophosphorus compounds are similar for a specific coating.

2. THEORY

Each of the SAW sensors used in this study consists of a pair of interdigital electrode arrays which 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, with most of the energy being constrained to the surface of the piezoelectric material. The Rayleigh wave interacts with any material which is in contact with the surface, i.e. the coating. Any changes in the mass or mechanical modulus of the coating produce a change in the velocity of the Rayleigh wave, resulting in a measurable shift in the sensor's resonant frequency. This study uses dual delay line oscillators, which 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 which is propagating across an uncoated surface. A schematic of the 158 Megahertz (158 MHz) dual delay line oscillator used in this study is shown in Figure 1.

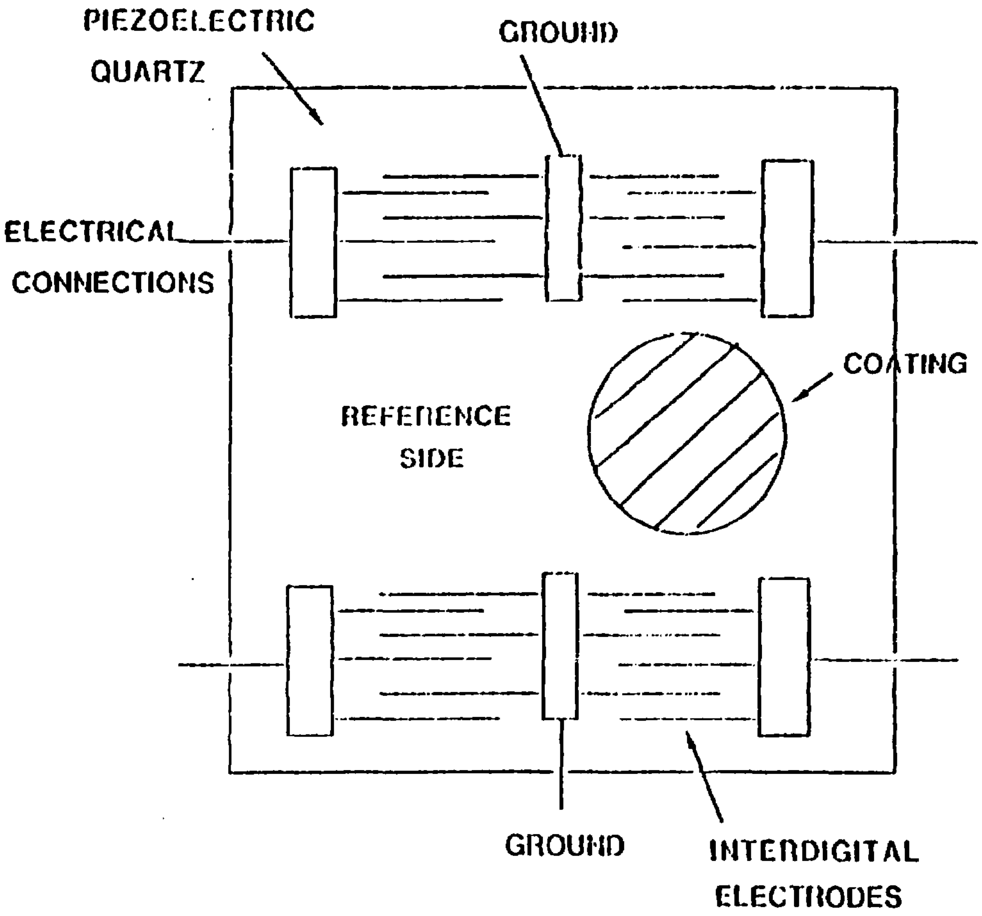


Figure 1. 158 MHz Dual Delay Line Oscillator

3. EXPERIMENTAL METHOD

3.1 Equipment

The equipment used in this study consists of a SAW vapor sensor which is interfaced to an Apple IIe computer (Figure 2), and a Q5 vapor generator (Figure 3). The SAW sensors, obtained from Microsensor Systems, Inc., Fairfax, Virginia, incorporate four separate 158 MHz dual delay line oscillators which are individually coated with one of the four coating materials (i.e. FPOL, PEM, ECEL, and PVP) to be tested. The chemical structures of the coatings are shown in Table I.

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% coating by weight in chloroform. The wire bonded bare oscillator is composed of two sets of interdigital electrodes consisting of fifty gold plated "fingers." The fingers are 7 micrometers in width, and spacing between fingers measures 7 micrometers. The fingers were lithographically patterned on to a substrate material, ST-Quartz. The entire package was then placed in a Teflon cell. The total area of the dual delay line oscillator is approximately 1 square centimeter (1 cm by 1 cm square). Since the area of the oscillator to be coated measured about two square millimeters, 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, with the frequency change being monitored by an oscilloscope.

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 which is

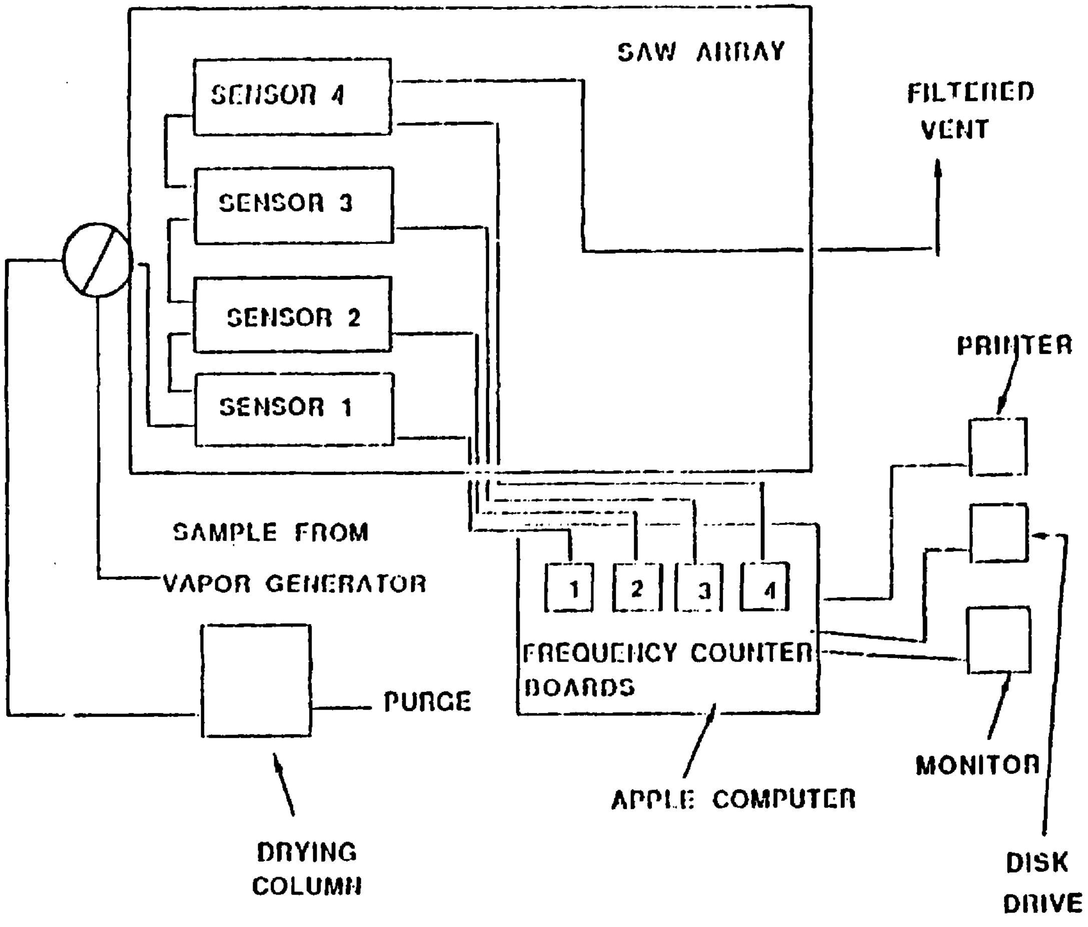


Figure 2. Block Diagram of the SAW Equipment

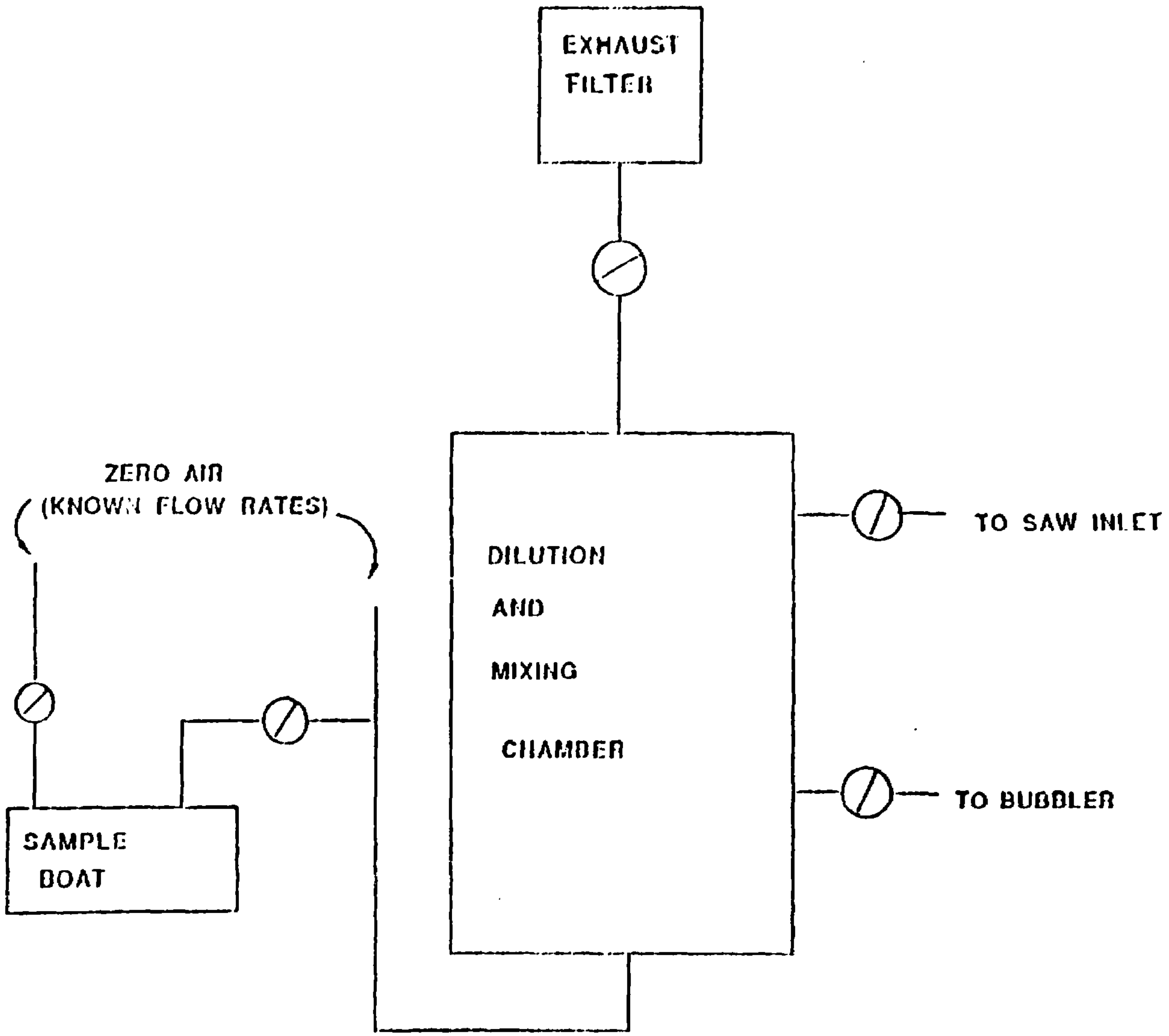
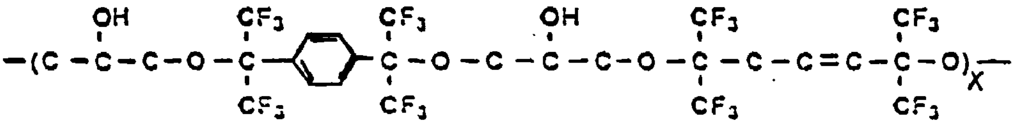


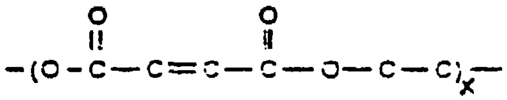
Figure 3. Diagram of a Q5 Vapor Generator.

TABLE I

CHEMICAL STRUCTURES OF THE COATINGS



Fluoropolyol

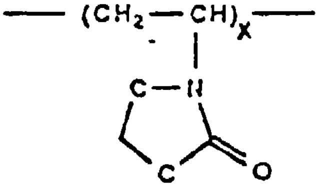


$$-(O-\overset{O}{\overset{\|}{C}}-C=C-\overset{O}{\overset{\|}{C}}-O-C-C)_x-$$

Poly(ethylene maleate)

$$-(C_8H_{14}O_5)_x-$$

Ethyl Cellulose



Polyvinyl Pyrrolidone

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, and 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 of which is filled with 10 milliliters of either 2-methoxyethanol or isopropyl alcohol. The bubblers are then analyzed using Gas Chromatography. The first sampling port leads to a three-way manually operating switching valve which allows the SAW device to sample the generated vapor, or a purge of zero air. Typically, the SAW samples the zero air purge for two minutes to establish an initial baseline. Then the switching valve is positioned to allow the sampling of the vapor for approximately two to five minutes, or until an equilibrium frequency shift is observed (Figures 4 to 7). Then the switching valve is repositioned to allow the sampling of the zero air purge and the SAW establishes a final baseline.

The gas chromatography analysis was conducted on a Model 5880A Hewlett-Packard GC. The GC was equipped with a flame photometric detector operated at 220°C. The injection temperature of the GC was set to 250°C. The column used for the analysis was a 6' by 0.2 mm I.D. column with 4.61% OV-101 and 3.39% OV-17 on a stationary phase of 100-200 Gaschrome Q. The sample size injected into the GC was 2 microliters, with a nitrogen flow rate of 30 milliliters per minute. Temperature programming of the oven in the temperature range 60°C to 260°C was used. The concentrations of the vapors in the bubblers were based on peak area measurements and external standards. It was noted that peak tailing was generally observed

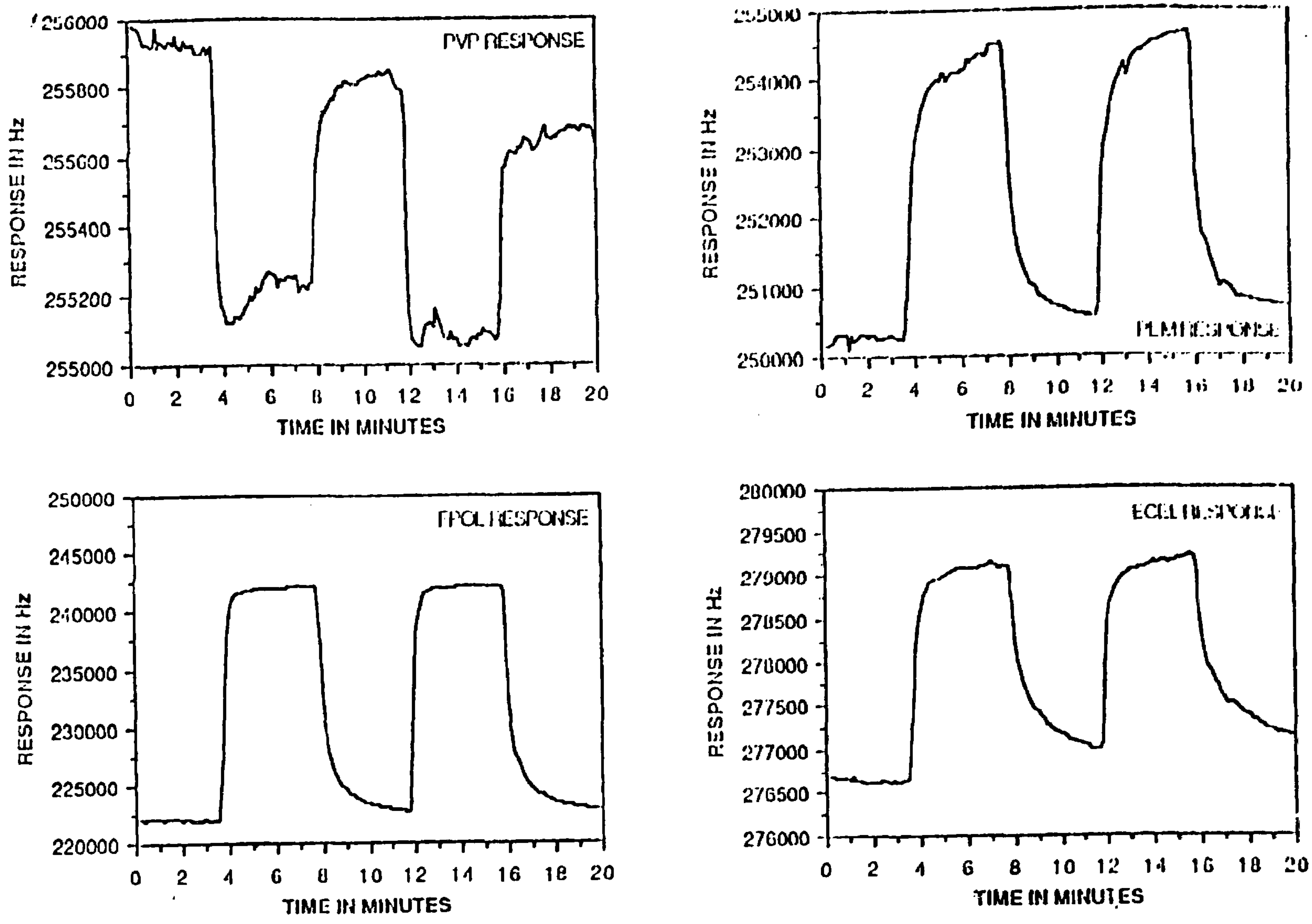


Figure 4. Typical SAW Responses to Nominal 10 ppm DMMP Vapor.

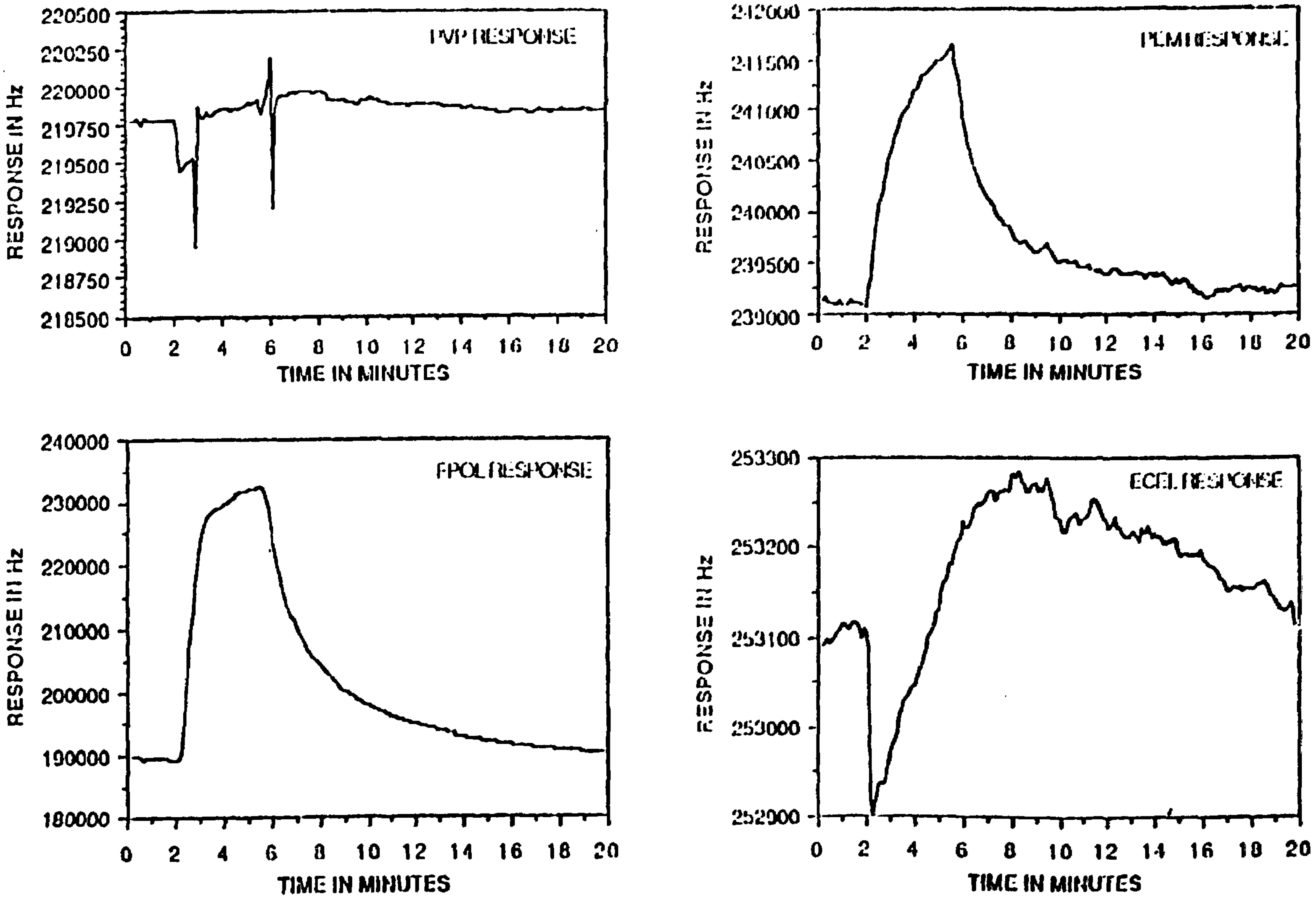


Figure 5. Typical SAW Responses to Nominal 10 ppm DIMP Vapor.

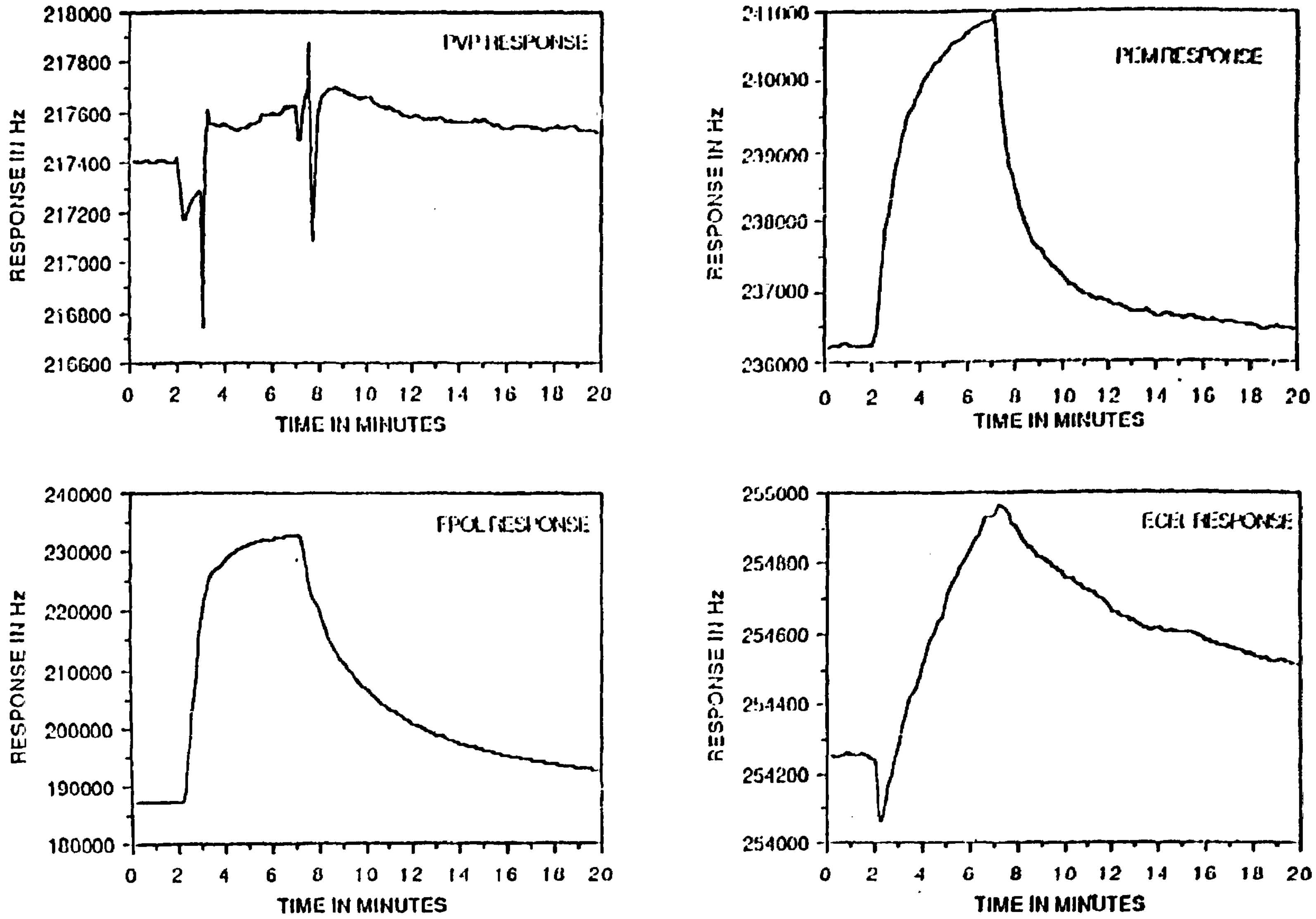


Figure 6. Typical SAW Responses to Nominal 10 ppm DEEP Vapor.

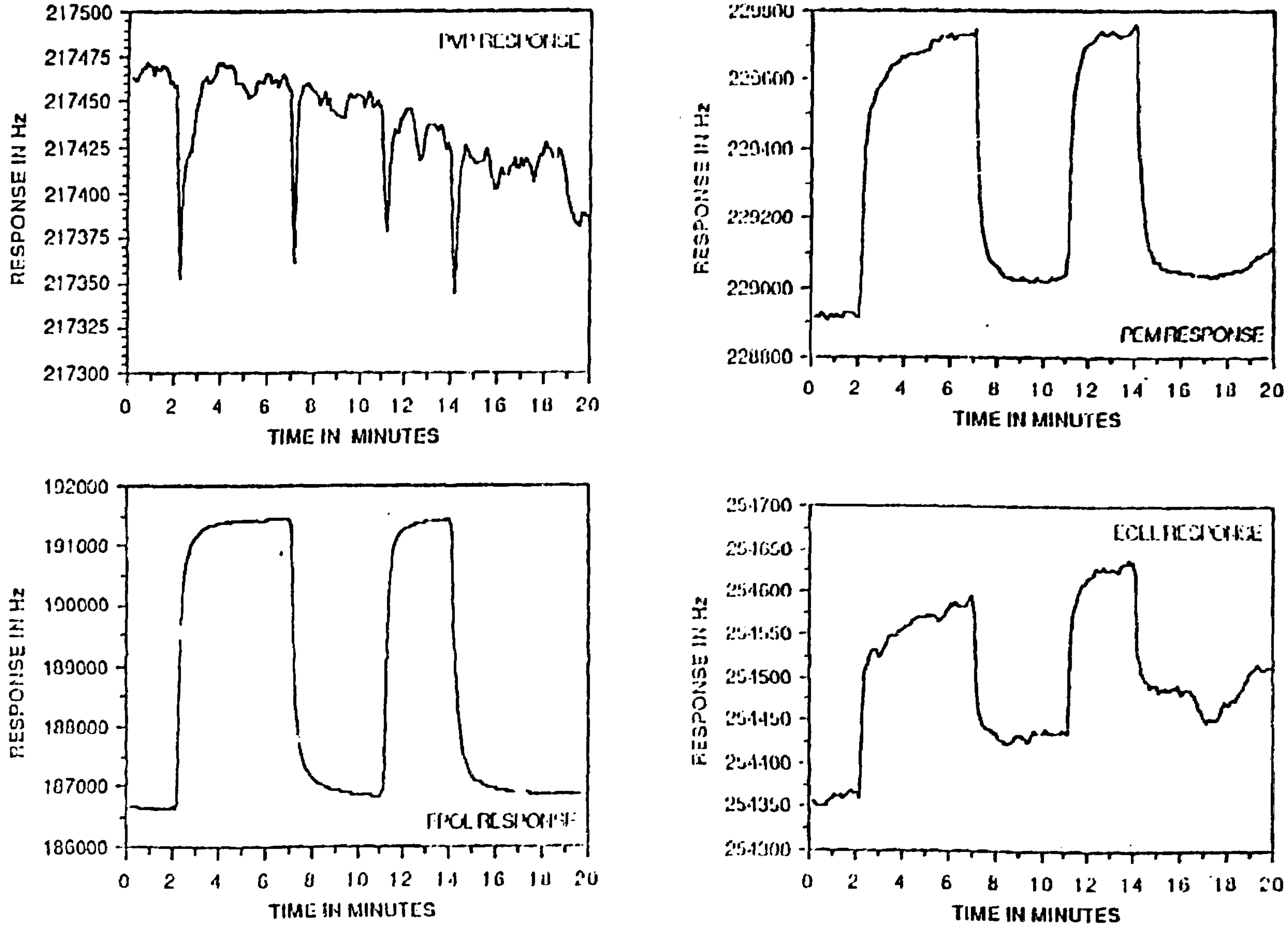


Figure 7. Typical SAW Responses to Nominal 10 ppm DMHP Vapor.

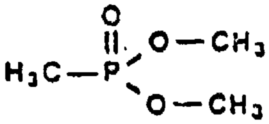
for the samples. The concentration of the vapor in the Q5 generator was then calculated from the concentration of the bubbler using the time of collection of the bubbler, flow rate of the sample through the bubbler, and the molecular weight of the sample.

3.2 Chemicals

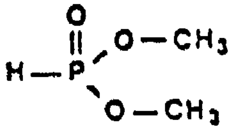
The organophosphorus compounds used in this study were dimethyl methylphosphonate (DMMP, 98% pure) which was obtained from the Stauffer Chemical Company, Westport, Connecticut, and dimethyl hydrogen phosphonate (DMHP, 83% pure), diisopropyl methylphosphonate (DIMP, 95% pure), and diethyl ethylphosphonate (DEEP, 97% pure), which were obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin. The purity of these compounds was determined using NMR analysis. The structures of these compounds are shown in Table II.

TABLE II

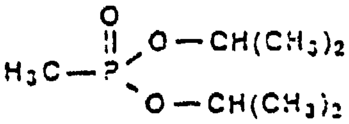
STRUCTURES OF THE ORGANOPHOSPHORUS COMPOUNDS



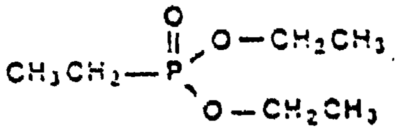
DMMP



DMHP



DIMP



DEEP

4. DISCUSSION AND RESULTS

Tables III through VI contain the response data of the four coatings to each of the four vapor challenges. Figures 4 through 7 show typical response curves obtained for a nominal ten parts-per-million challenge of each of the four test vapors to 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 corrected for coating thickness, in ΔHz/kHz coating, versus concentration of the vapors, in parts-per-million (ppm). Of the coatings studied, the largest frequency shifts observed are for the fluoropolyol coating, with the next larger response being obtained for the poly(ethylene maleate). For the other two coatings, the ethyl cellulose and polyvinyl pyrrolidone, there is generally a very small response. The frequency shifts for the sensors is the difference between the equilibrium frequency reading of the sensor with the sample present in the SAW, and the average of the baseline frequency reading of the sensor before the sample is introduced to the SAW and after the sample has been removed from the SAW.

4.1 Response to DMMP

The frequency shifts and concentration responses of the four sensor coatings to dimethyl methylphosphonate, DMMP, vapor are given in Table III and Figure 8, respectively. The frequency shift for Table III is the average frequency shift obtained for the sensor response. In general, the average is for four different runs with two exposures of the sensor to the vapor per run. Note from Table III, fluoropolyol exhibits the largest response, i.e. frequency shift, for DMMP vapor, with poly(ethylene maleate) exhibiting the next greater response. In general, the ethyl cellulose response is greater than the response obtained using the polyvinyl pyrrolidone. The polyvinyl pyrrolidone is the only

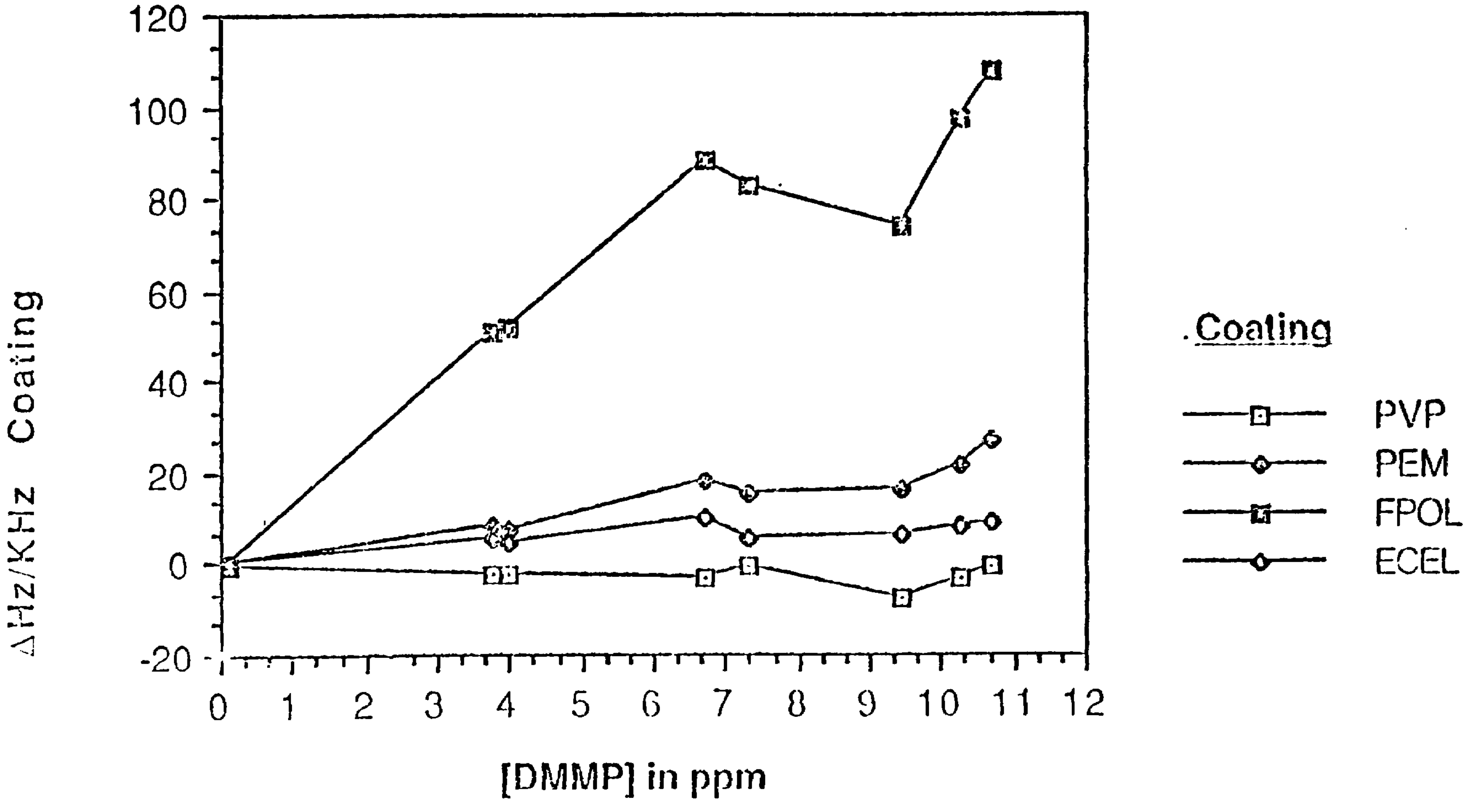


Figure 8. SAW Response to DMMP Vapor

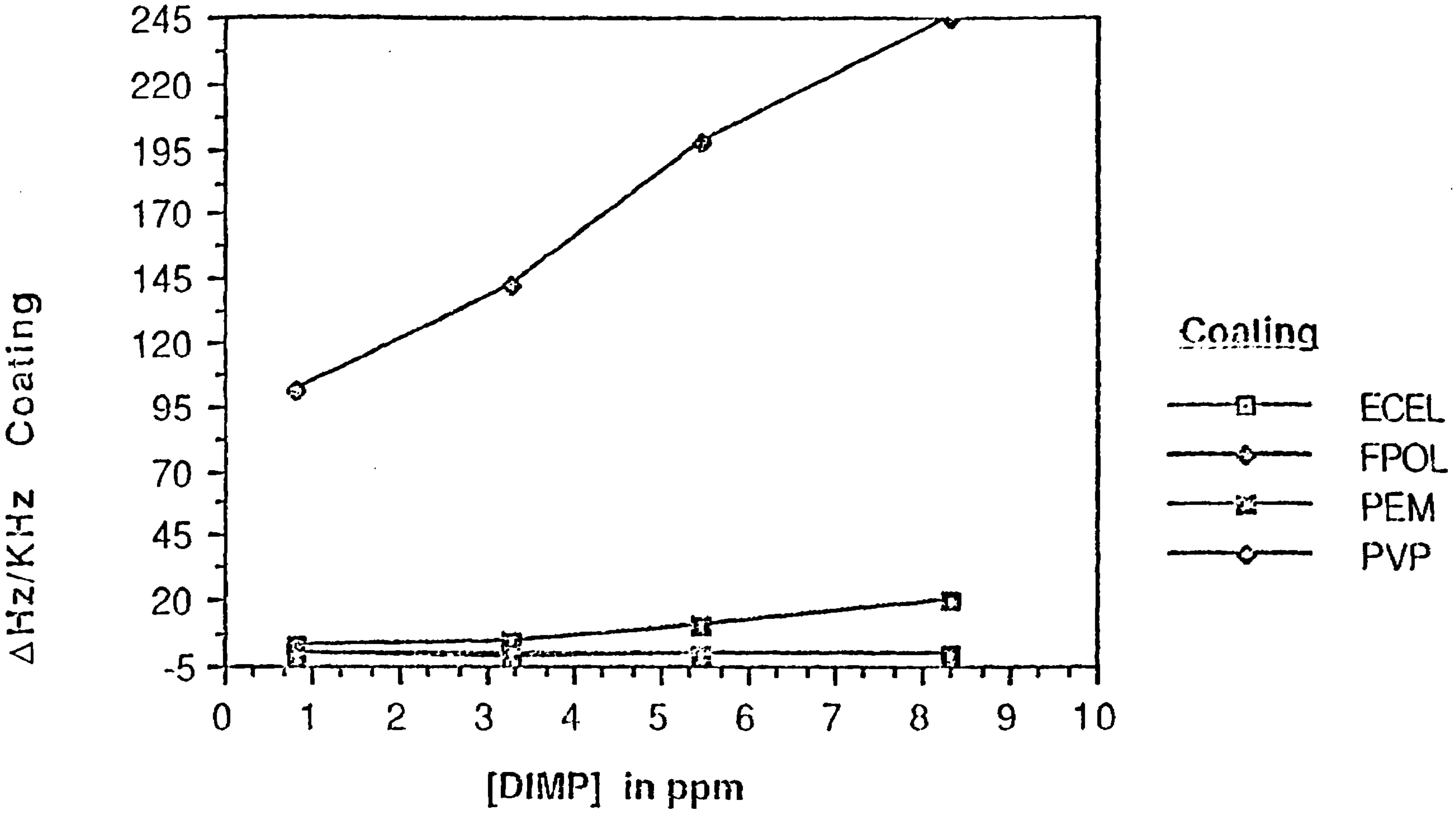


Figure 9. SAW Response to DIMP Vapor

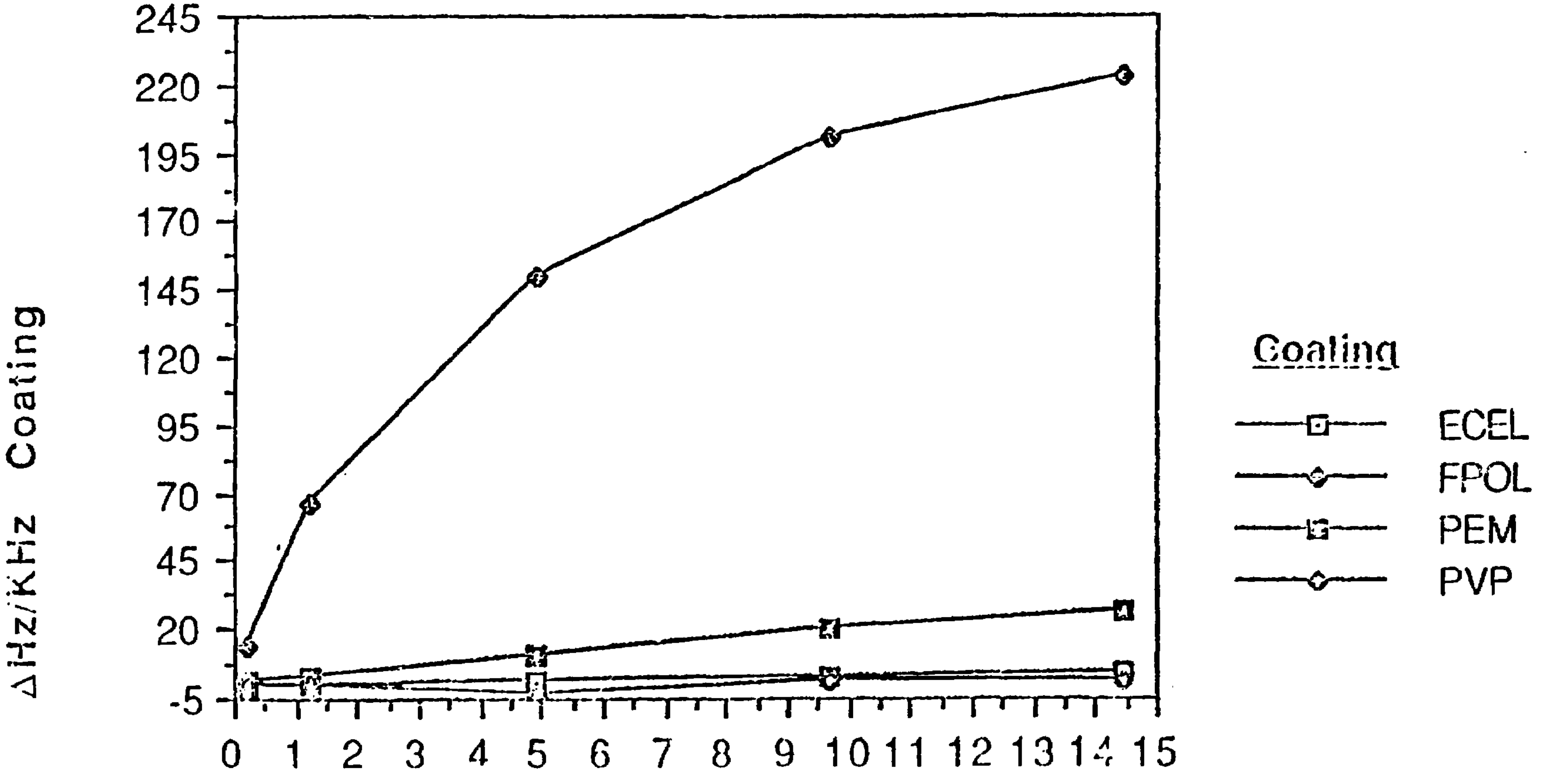


Figure 10. SAW Response to DEEP Vapor

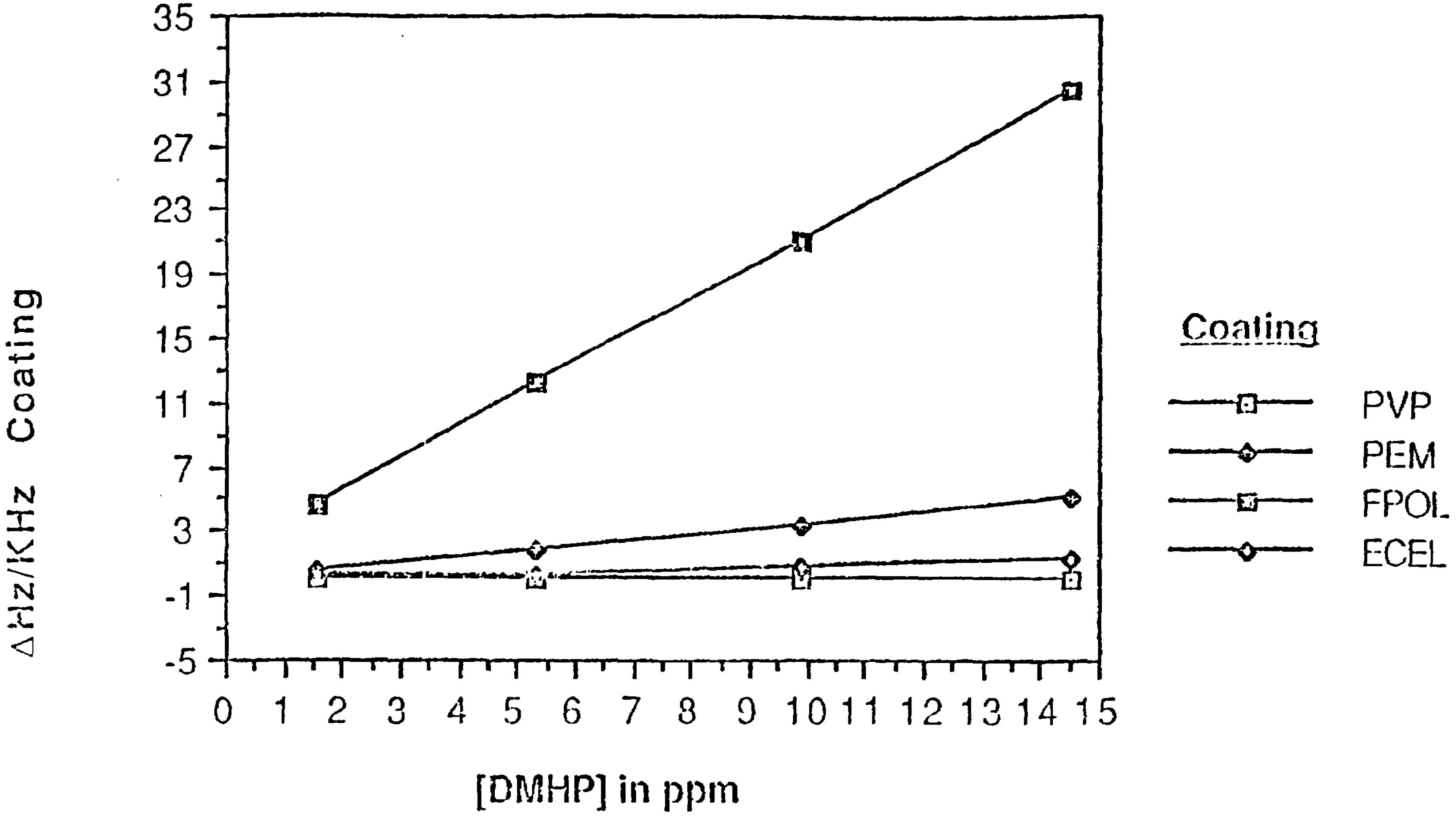


Figure 11. SAW Response to DMHP Vapor

sensor used in this study which exhibited a negative frequency shift when the DMMP vapor was introduced into the SAW.

TABLE III

SAW RESPONSE TO DMMP VAPOR

Concentration	Frequency Shift (ΔHz) for Sensor			
DMMP (in ppm)	FPOL	PEM	ECEL	PVP
0.033	36 + 12	15 + 7	45 + 58	18 + 15
0.044	46 + 10	4 + 9	-2 + 11	- 2 + 14
0.086	89 + 36	12 + 17	5 + 21	-23 + 29
0.105	19 + 7	11 + 5	9 + 17	17 + 18
3.77	11219 + 94	1781 + 26	1137 + 109	-420 + 139
4.00	11337 + 132	11532 + 33	1014 + 106	-403 + 145
6.72	19430 + 183	3934 + 54	2128 + 122	-674 + 30
7.33	18284 + 395	3437 + 150	1199 + 103	-154 + 139
9.44	16289 + 183	3514 + 51	1382 + 273	-1613 + 228
10.23	21418 + 845	4759 + 245	1703 + 322	-769 + 323
10.71	23718 + 344	5999 + 57	1948 + 281	-130 + 231

The interaction between the DMMP and the sensor coatings all seem to be reversible, but the solubility or strength of interaction of the coatings with the vapor vary greatly. The interaction of the polyvinyl pyrrolidone, PVP, with the DMMP is almost nonexistent, while the interaction of the fluoropolyol and poly(ethylene maleate) is much greater. This is evident from the relative intensities of the frequency shifts observed for the coatings. The interaction of the DMMP with the PVP is so small that it appears that the ST-Quartz interaction with the vapor is much greater. This would explain why a negative frequency shift is observed for the PVP coating, as any vapor adsorbed in the coating would result in a positive frequency shift. The only other explanation for the negative shift would be that the DMMP vapor is stripping the PVP coating off the oscillator. This does not appear to be the case because the sensor response returns to its baseline value when the DMMP vapor is removed from the SAW.

4.2 Response to DIMP

The frequency shifts and concentration responses observed for the four sensor coatings exposed to diisopropyl methylphosphonate, DIMP, vapor are shown in Table IV and Figure 9, respectively. Again it was noted that the fluoropolyol response is greater than the response obtained for poly(ethylene maleate), polyvinyl pyrrolidone or ethyl cellulose. Also, the magnitude of the fluoropolyol response obtained for the DIMP vapor is much greater than the response obtained for DMMP. The PEM response to the DIMP vapor is generally less than the response obtained for the DMMP vapor. If the response were truly a function of the molecular weight, the DIMP response would be approximately 1.45 times the response obtained for DMMP, the ratio of the molecular weights of the two compounds. The molecular weight of the DIMP is $\sim$180 grams/mole, and the molecular weight of the DMMP is $\sim$124 grams/mole. This ratio is not observed. In fact, the fluoropolyol response observed for the DIMP challenge is greater than 2 times that observed for the DMMP. The response of the PEM is the reciprocal of that ratio at 5 parts-per-million concentration. The ratio of the response of the PEM coating to DIMP and DMMP increases to approximately 1 at the higher concentrations. Thus, the FPOL coating appears to have a higher affinity for DIMP than DMMP. The reverse appears true for the PEM coating, at low concentrations but the affinity of the PEM coating for DIMP and DMMP approach the same value as the vapor challenge increases. This may occur because the amount of vapor adsorbed in the coating approaches a saturation point (e.g., maximum value).

TABLE IV

SAW RESPONSE TO DIMP VAPOR

Concentration	Frequency Shift (ΔHz) for Sensor			
DIMP (in ppm)	FPOL	PEM	ECEL	PVP
0.803	22194 + 252	683 + 32	-130 + 40	27 + 58
3.29	31418 + 202	1134 + 73	-215 + 39	-81 + 74
5.44	43398 + 708	2319 + 57	-89 + 37	74 + 39
8.33	53751 + 920	4409 + 286	50 + 111	-69 + 59

The best of all possible worlds would be to have the SAW sensor responses be linear with respect to concentration. This does not occur, even for the sensors which have small responses to the DIMP vapor. The PEM sensor is the closest there is to a linear response, while the worst is the PVP response. The FPOL response, while not linear, does increase with an increase in the concentration of the vapor.

4.3 Response to DEEP

The frequency shift and concentration responses of the SAW coatings to diethyl ethylphosphonate (DEEP) vapor, are shown in Table V and Figure 10, respectively. The molecular weight of the DEEP is ~166 grams/mole, so it might be expected that the SAW responses would lie between the response of the DIMP and the DMMP. In fact, the ratio of the responses of the sensors to DMMP, DIMP, and DEEP would be expected to be 1:1.45:1.33, respectively. This relationship holds for DIMP and DEEP at high concentrations, i.e. those concentrations above 5 ppm, for the FPOL coating. The ratio does not hold for the PEM coating at any concentration. The relationship does not fit the DMMP to DEEP ratio, for any sensor. The FPOL and PEM coatings appear to have a greater affinity for the DEEP vapor than they do for either the DIMP or DMMP vapors, as is evidenced by the slow return to baseline of the sensors after the vapor challenge has been removed. The affinity of the ECEL coating for the DMMP vapor is greater than its affinity for the DEEP vapor, and the affinity of the PVP coating for the DEEP vapor is greater than its affinity for the DIMP vapor. The response of the PVP coating is extremely erratic, and no trend has been noted for the vapors.

TABLE V

SAW RESPONSE TO DEEP VAPOR

Concentration DEEP (in ppm)	Frequency Shift (ΔHz) for Sensor FPOL	PEM	ECEL	PVP
0.201	3309 + 379	173 + 94	-41 + 59	-9 + 50
1.22	14476 + 43	687 + 60	53 + 30	8 + 43
4.90	32973 + 487	2476 + 44	248 + 28	-721 + 10
9.7	44085 + 1054	4535 + 46	598 + 45	168 + 17
14.45	49198 + 743	5735 + 110	759 + 69	134 + 68

4.4 Response to DMHP

The frequency shifts and concentration responses of the SAW sensor coatings to dimethyl hydrogen phosphonate (DMHP) vapor are shown in Table VI and Figure 11, respectively. The molecular weight of the DMHP is ∼110 grams/mole, thus it is the lightest of the organophosphorus compounds tested. If the responses of the coatings were strictly a function of the molecular weight, the ratio of the responses to DMMP, DIMP, DEEP, and DMHP would be 1:1.45:1.33:0.887, respectively. This relationship does not hold for any of the sensors tested, at any concentration. In general, the responses obtained for the DMHP vapor are an order of magnitude less than the responses obtained for any of the other vapors. This means the affinities of the coatings to DMHP vapor are much less than for the other three vapors. This may be due to the hydrogen that is attached directly to the phosphorous atom in this molecule. The other three vapors tested had either methyl or ethyl groups attached to the phosphorous. One result of the lower responses obtained for the DMHP vapor is that the responses of the FPOL and the PEM coatings are linear with respect to concentration. This linear response has not been obtained for any of the other vapors tested. The linear response may be attributed to the small amount of DMHP vapor adsorbed by the coatings. This low adsorption of the DMHP vapor gives a greater concentration range of the vapor available for testing before saturation of the coating occurs.

TABLE VI

SAW RESPONSE TO DMHP VAPOR

Concentration DMHP (in ppm)	Frequency Shift (ΔHz) for Sensor FPOL	PEM	ECEL	PVP
1.56	1029 + 54	98 + 41	38 + 34	-1 + 10
5.3	2691 + 34	410 + 22	89 + 21	4 + 18
9.89	4632 + 48	734 + 27	157 + 21	16 + 15
14.5	6699 + 97	1097 + 47	276 + 15	-7 + 11

5. CONCLUSIONS

From the data given in Section 4, it is observed that the response of the four coatings tested to the four vapors tested vary greatly. The polyvinyl pyrrolidone coating appears to be almost useless for the detection of organophosphorus compounds, as its response to the vapors is very small. When a response is noted for the polyvinyl pyrrolidone, the response appears erratic. There is no semblance of a relationship of the response to the concentration of the vapor challenge. Approximation of the response of the coating to the molecular weight of the compound also does not appear feasible because of the nature of the response.

The ethyl cellulose coating has a much higher response to the organophosphorus vapors than does the polyvinyl pyrrolidone coating, but its utility as a sensor for organophosphorus compounds appears limited. The response of the ECEL coating does not scale as a function of the molecular weight of the vapor, but it responds as a function of the concentration of each vapor, with the exception of the DIMP. Its utility as a sensor for the organophosphorus compounds is limited by the magnitude of the response. The sensor responses has a maximum response of 2128 Hz shift for ~10 ppm DMMP, but at sub ppm levels, the response is erratic and extremely small. Thus, it could be used as a coating to indicate there is a high concentration of the organophosphorus compounds, but low levels would go undetected, and the lower detection limits are needed for the chemical agents of which these compounds are simulants. Detection levels in the low parts-per-billion range or less are the ultimate goal of these devices.

The poly(ethylene maleate) coating also is of limited use as a sensor coating for organophosphorus compounds, because its response to low parts-per-million and parts-per-billion concentrations is very small. It is a better coating than either the ethyl cellulose or polyvinyl pyrrolidone coatings, but it is not as good as the fluoropolyol coating. Its response roughly scales as a function of the molecular weight of the vapor, but the response is more a function of the solubility of the vapor in the coating, which is what is expected.

The fluoropolyol coating appears to be the best coating tested for use in the detection of organophosphorus compounds. The response is an order of magnitude greater than the response obtained for poly(ethylene maleate), and the response roughly scales as a function of the molecular weight. A comparison of the FPOL response to the four vapors tested is shown in Figure 12. The response of the fluoropolyol coating to sub parts-per-million concentrations of DEEP vapor shows the utility of the coating. It is disappointing to note the low response of the FPOL coating to sub part-per-million concentrations of DMMP vapor. The GC analysis of the bubblers was of no use for sub ppm levels of the vapors, because the bubbler concentrations were below the limit of detection of the GC for the compounds. As the purpose of the SAW work is really to detect the chemical agents, the analysis of sub ppm levels needs to be performed in even greater detail.

The SAW device does indeed show promise for use in detecting organophosphorus compounds, but the choice of coatings is of paramount importance. The responses of the coatings tested range from no response for polyvinyl pyrrolidone to a very large response for the fluoropolyol. Even though the responses of the coatings are approximately a function of the molecular weight of the species, the solubility of the compound in the coating appears to play a much more important role in sensor response. All of the compounds tested have the same general form RP(O)OR', where R' and R groups vary in alkyl length. The compounds tested were selected as simulants for the chemical agents, but the response of the sensors to the agent vapors may not follow the trends noted for these simulants. The agents are organophosphorus compounds, but their geometries are vastly different than the simulants.

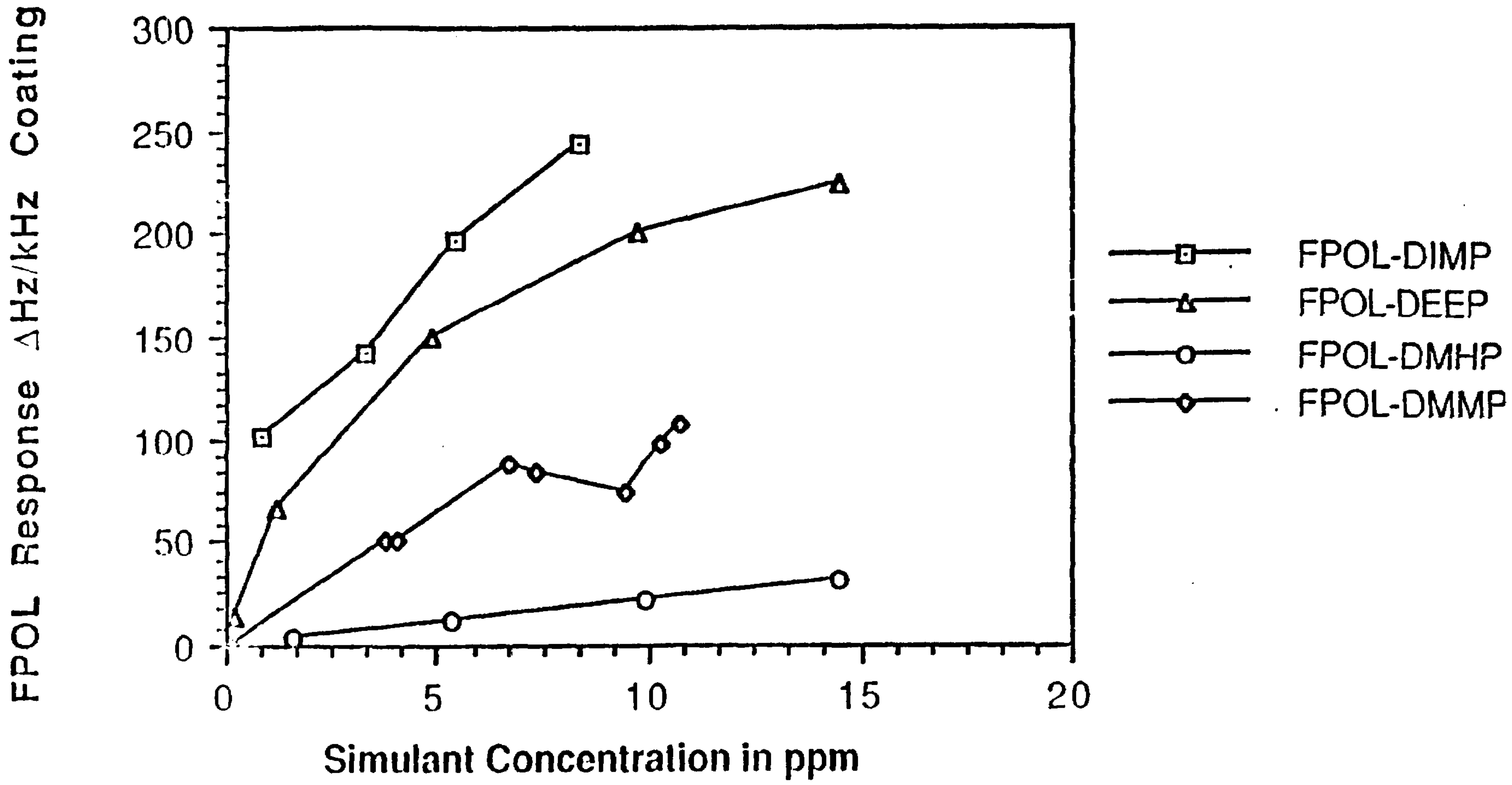


Figure 12. Comparison of the Response of FPOL to the Different Organophosphorus Compounds

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APPENDIX

SURFACE ACOUSTIC WAVE MICROSENSORS AS DETECTORS FOR TOXIC CHEMICAL VAPORS:

Effects of Temperature, Vapor Flow Rate and Aging on Microsensor Performance

Submitted to
GEO-CENTERS, INC.

by

MICROSENSOR SYSTEMS, INC.
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EXECUTIVE SUMMARY

Surface Acoustic Wave (SAW) microsensors have shown great promise as detectors for toxic and hazardous vapors, especially for their high sensitivity, reliability, small size and low cost. However, SAW microsensor systems designed and fabricated to date have also shown several potential limitations, primarily involving chemical selectivity of the coatings and their reduced sensitivity at temperatures approaching 50° C or above. In addition, there have been no studies in which SAW sensor systems were operated for extended periods in order to provide confidence in the long-term performance of the devices. Other sytstem parameters, such as vapor flow rate also have not been carefully evaluated. Several of these potential difficulties were addressed in this study.

The problem of selectivity of SAW coatings has been addressed in a number of previous studies. As the selectivity of a coating depends upon reversible interactions (e.g., solubility) with specific vapor molecules, it would be very unexpected to find a coating that would not interact to some limited extent at least with many potential interferring vapors. The prior studies demonstrated that multiple sensor arrays, in which each sensor responds somewhat differently to a chemical vapor challenge, can resolve many of the selectivity problems, when used with pattern recognition or artficial intelligence techniques to analyze the arrays of data.

As a result of this study it has been shown that:

1. The sensitivity of a SAW sensor does indeed decrease with increasing temperature;
2. The sensitivity of a SAW sensor is independent of vapor flow rate over the range of 25 to 115 ml/min;
3. The coating of a SAW sensor will respond more rapidly to a vapor challenge as the temperature increases; and
4. Over at least a 6 week period there was no effect of time or vapor cycling on the sensitvity of a SAW sensor.

Several recommendations resulting from this study were:

1. That the ageing study of the 12 Coated SAW sensors begun in this investigation be funded to continue for a 24 month period.

2. That in addition to a continuation of the ageing study, funding be included for temperature control of each sensor by use of thermoelectric devices.

3. That in the design and fabrication of future SAW microsensors that the reference delay line be isolated from the active delay line.

4. That in the design and fabrication of future SAW microsensors that higher frequency delay lines be considered to increase both sensitivity and rate of response.

SURFACE ACOUSTIC WAVE MICROSENSORS AS DETECTORS FOR TOXIC CHEMICAL VAPORS: EFFECT OF TEMPERATURE, VAPOR FLOW RATE AND AGEING ON MICROSENSOR PERFORMANCE

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ABSTRACT

Twelve 158 MHz dual SAW delay line oscillators with supporting electronics were used as chemical microsensors for this study. Three SAW sensors were coated with each of the following chemically selective coatings: a fluoropolyol (FPOL), ethyl cellulose (ECEL), poly(ethyleneimine) (PEI) and poly(isoprene) fluorinated alcohol (PIPFAI). The coatings were selected for their sensitivity to chemical warfare simulants, low molecular weight hydrocabons or water vapor. Each of the SAW sensors was exposed to vapors of DMMP, dimethyl adipate, toluene and water at concentrations covering some two orders of magnitude. Each SAW device was tested to determine the effect of temperature, vapor flow rate, ageing and repeated vapor exposure on their sensitvity and reproducibility. Experiments were carried out at temperatures from 23° to 42° C and gas flow rates of 25 to 115 cc/min. The sensitivities of the SAW devices decreased with increasing temperatures as one would predict from their increasing vapor pressure and their decreasing solubility in the polymers. No statistical differences were observed with changes in gas flow rate and the stability and performance of the devices were essentially unchanged over the duration of the study, i.e. there was no observed "ageing" of the sensors. It was further observed that controlling the device temperature to ±1° C noticeably improved the signal to noise ratio, by reducing temperature induced baseline drift, even though each SAW device is temperature compensated by a reference delay line oscillator. The results of the study further demonstrate that Surface Acoustic Wave devices, such as the 4-SAW Sensor Arrays, are indeed sensitive detectors of toxic organic vapors. The results also suggest several novel approaches for further improving SAW sensitivity and performance characteristics.

INTRODUCTION

Prior studies have demonstrated that Surface Acoustic Wave delay line oscillators can be very sensitive detectors of toxic vapors when coated with suitable organic films of controlled composition and thickness (1-9). Studies of SAW devices with resonant frequencies as high as 600 MHz have recently shown that many organic compounds can be detected at concentrations substantially below 100 parts per billion (by volume) at response times of a few seconds (10,11). For example, detection limits of approximately 10 and 100 ppb were reported for dimethylmethylphosphonate and dimethyl acetamide respectively, with response times of about 10 seconds, using a 290 MHz SAW device with a thin fluoropolyol coating. As SAW device sensitivity is known to increase with increasing frequency, we can anticipate still lower detection limits as higher frequency SAW sensor systems are further developed and evaluated. As more data become available on various SAW coatings, it appears that several show high selectivity for specific vapors or classes of vapors (10-12), especially for the organophosphonate compounds which have been most intensively studied. In addition to the selectivity inherent in the coatings themselves, it has been shown in a recent study that the use of arrays of coated SAW devices, in conjunction with appropriate pattern recognition software, can provide enhanced selectivity as well as sensitivity to a broad spectrum of organic vapors (13).

Even though it has been demonstrated that SAW devices have the sensitivity, selectivity, and response time necessary to be very effective sensors for a variety of toxic and hazardous vapors, there has been relatively little performance data reported beyond laboratory feasibility studies. Before SAW Sensor Arrays can confidently be used as routine field monitors for toxic and hazardous gases, a more extensive data base is needed on their long term performance characteristics. It must be demonstrated that their sensitivities, response times, and other performance parameters are not adversely affected by repeated exposure to a variety of adsorbed vapors, even at relatively high concentrations. The SAW devices, their supporting electronics, and especially their coatings must be stable for months of operation. The coatings must not degrade with time upon exposure to ambient air or undergo irreversible reactions with toxic vapors, or interfering gases. A successful vapor detection system for field use must also operate over a wide range of ambient temperatures with little variation in sensitivity. Although it was predicted and subsequently confirmed that SAW sensitivity decreases with increasing temperature, due in part to higher vapor pressures at elevated temperatures and to decreased solubility in the coatings (14), a careful experimental correlation of SAW coating sensitivity with temperature for a variety of vapors has not yet been made, nor has an optimal operating temperature been established. The effect of vapor flow rate on SAW performance also remained to be determined.

The present study was therefore undertaken in order to: (1) provide a more extensive data base on the performance of SAW microsensors as vapor detectors; (2) investigate two experimental parameters (temperature and vapor flow rate) identified as possible factors influencing or limiting the sensitivity and useful range of SAW sensors as vapor detectors; and (3) develop guidelines for improved SAW devices and sensor array systems that will achieve significantly lower detection limits and improved overall system performance.

THEORETICAL RESPONSE OF COATED SAW VAPOR SENSORS

The theoretically derived relationship describing the SAW delay line oscillator vapor sensor has been previously reported (5, 10). It was found that when organic, vapor sensing coatings are used on the piezoelectic substrates, the SAW oscillator frequency change, Δf, could be described by the reduced equation

$$\Delta f = (k_1 + k_2)\, f_0^2 h p' . \qquad (1)$$

In this equation f_0 is the unperturbed resonant frequency of the SAW oscillator, h is the coating thickness, p' is the coating density, $k_1 = -9.33 \times 10^{-8}$ m^2 s/kg and $k_2 = -4.16 \times 10^{-8}$ m^2 s/kg. Equ. (1) predicts that the signal obtained from a given mass loading (hp' product) will increase with the square of the operating frequency of the SAW oscillator. Furthermore, operating frequency determines the size of the device since it imposes size requirements on the interdigital electrodes used to generate the Rayleigh surface wave. As the operating frequency increases, the device area decreases. Higher operating frequencies also permit thinner coatings to be employed with corresponding improvements in response time, since vapor diffusion in the coatings will be more rapid. These considerations can be used to establish a set of scaling laws (9) that are useful in predicting the ultimate performance capabilities of SAW vapor sensor technology, assuming a constant temperature.

Even though SAW delay line oscillators are known to be very sensitive to changes in temperature, to a degree determined by the orientation and type of crystalline piezoelectric material used to fabricate the device, the specific dependence of a SAW vapor sensor on temperature would be difficult to predict from theory. Temperature not only affects the SAW velocity but also the physical dimensions (and hence delay time) of the device. In fact temperature sensors based on SAW delay line oscillators have been reported (15) with millidegree resolution, good linearity, and low hysteresis. For sensors that are not intended to measure temperature, the drift induced by temperature changes can be a serious problem, particularly at the lower limit of detectability. A common strategy to eliminate signal drift due to temperature changes involves the use of a dual delay line in which one of the delay lines is used as a reference, unperturbed by the vapors being measured, but experiencing the same temperature as the measuring delay line. This approach greatly improves but does not always eliminate the problem. For example (16), two individual 158 MHz oscillators may exhibit frequency shifts of about 2.9 KHz per degree C, while the temperature induced drift in frequency difference may be 30 times less (i.e. 0.10 KHz per degree C). Unsymmetrical stresses induced by the SAW packaging may be a major source of the residual uncompensated drift.

Changes in temperature will also have a pronounced effect on the coating/vapor interactions, and thus on device sensitivity. From thermodynamic considerations as the temperature increases, the vapor pressure, and thus the concentration of a gas in equilibrium with its adsorbed phase increases, effectively reducing the concentration of vapor in the SAW coating as well as the system sensitivity. There was also concern that the rate of flow of a gas over a SAW coating would affect the rate (or the extent) of transfer of a target compound from the gas to the adsorbed phase, and thus be a factor in determining system sensitivity. As the effects of both temperature and flow rate on SAW device performance cannot be adequately predicted theoretically, they are addressed experimentally in this study.

EXPERIMENTAL TECHNIQUES

SAW Device Configuration

The SAW dual delay line oscillators used as sensors in this study will ultimately be incorporated into 4 SAW Sensor Array Systems for additional test and evaluation. A typical 4 SAW array vapor sensor system is illustrated schematically in Figure 1. The SAW sensors selected for 4 SAW systems are 158 MHz dual delay line oscillators such as used in the present study. The 158 MHz devices were chosen as they have a small active area (8 mm^2) yet are large enough to be easily handled and coated. Also, sufficient research has been done with these devices to assure their sensitivity, reliability, and reproducible performance. The dual delay lines are each fabricated on a 50 mm x 50 mm ST-quartz die. Aluminum electrode metallizations are used. A thin SiO_2 overlayer (ca. 200 Angstrom) is used to protect the aluminum electrodes. The interdigital transducers (IDT) consist of 75 and 100 finger pairs having one-quarter wavelength finger widths and spacings. The acoustic aperature of the IDTs is 72 wavelengths. Each dual delay line oscillator is mounted in a standard 8 pin gold flat package with an internal volume less than 60 microliters with 1/16 inch inlet and outlet tubes for the test vapors. Electrical connections are wire-bonded from the device to the package connecting leads. The required RF amplifiers and support electronics for each SAW device are connected together with the SAW package on a small printed circuit board (7.5 cm x 5 cm) to form a complete vapor sensor subsystem. Electrical power, output signal, and vapor connections were made to each of the four boards comprising a 4-SAW Sensor Array. Sixteen separate 158 MHz SAW sensors boards were fabricated for coating and initial evaluation. Details of the operation of dual delay line dual delay line oscillators has been discussed in previous publications (9, 10).

In actual field use, a 4-SAW Array would be housed in an enclosure containing a regulated AC power supply, a 4 channel microcomputer controlled frequency counter, 1/8 inch Swagelock bulkhead fittings to provide vapor inlet and outlet to the sensor array, and a Teflon vapor distribution manifold. The four channel microcomputer-controlled frequency counter would measure and report the frequency of each SAW sensor every two seconds. The 24 bit counters have the ability to count frequencies as high as 10 MHz with a resolution of 1 Hz. The counter output is provided on a 9600 baud RS-232C serial communications line.

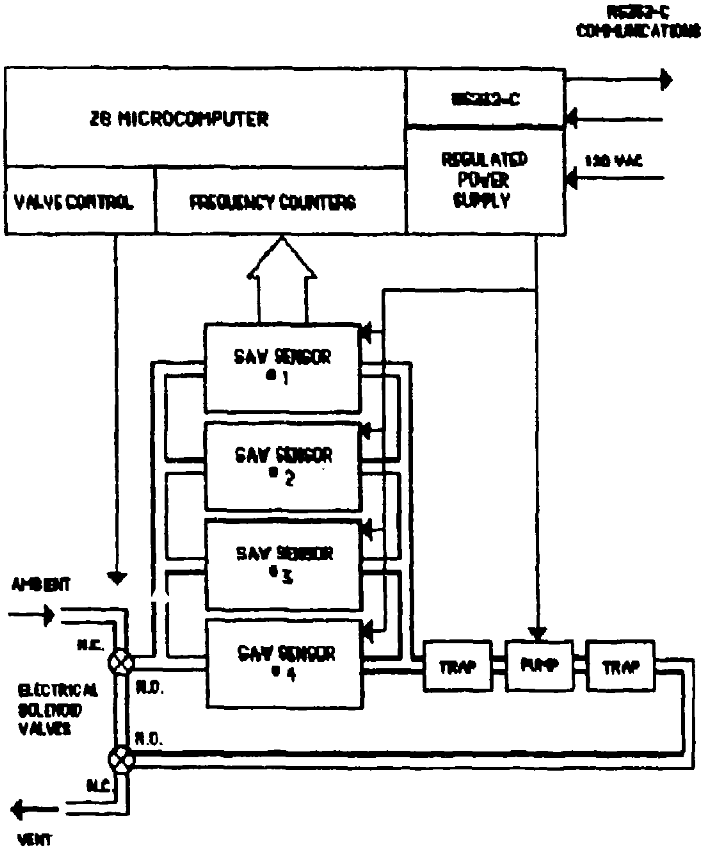

Figure 1. Schematic Diagram of Four SAW Sensor Array Vapor Detection System.

A 158 MHz SAW device is able to provide a resonant frequency shift of about 365 Hz when perturbed by a surface mass change of 1 nanogram, with a typical "noise" of less than 16 Hz RMS over a 1 second measurement interval (i.e. 1 part in 10^7). Thus the 1 nanogram mass change will provide a signal to noise ratio of almost 23 to 1. At around 25°C these devices have exhibited sensitivities to organophosphorus compounds of better than 0.1 mg/m^3.

Selective Coatings

The SAW coatings selected for this study were a fluoro-epoxy prepolymer (termed fluoropolyol) (FPOL), a poly(isoprene) fluorinated alcohol (PIPFAI), ethyl cellulose (ECEL), and poly(ethyleneimine) (PEI). These coatings were selected for their previously determined sensitivity to chemical warfare agent simulants, low molecular weight hydrocarbons and water vapor respectively. The technique selected to deposit these materials on the SAW devices was airbrushing. The coatings were applied by spraying a dilute solution of the coating polymer in a volatile solvent through a small mask positioned over the active area of the delay line to be coated. Compressed air was used as the propellant. The spray was delivered from a distance of about 6 inches while frequency changes were being monitored. Multiple short bursts of spray were delivered to the device surface until an approximately 250 KHz frequency shift was recorded. This corresponded to an average coating thickness or some 500 Angstroms for FPOL and PIPFAI and closer to 800 Angstroms for the hydrocarbon polymer films. The devices were allowed to sit in clean, dry air for about one day prior to testing. Four SAW devices were coated with each material, with the three showing the most similar response selected for the testing. The identification number of each SAW sensor selected for use, the coating applied to the surface and the coating thickness are given in Table 1.

Table 1. SAW Sensor Coatings

Sensor Number	Coating	Coating Thickness (Hertz)
8818-11	FPOL	264
8818-12	FPOL	265
8818-13	FPOL	279
8818-1	PIPFAI	302
8818-2	PIPFAI	275
8818-3	PIPFAI	283
8818-15	ECEL	265
8818-17	ECEL	260
8818-18	ECEL	278
B-022	PEI	258
8818-5	PEI	252
8818-7	PE I	252

Vapor Generation and Delivery System

Four test vapors were selected for use in this study. They were dimethylmethylphosphonate (DMMP), dimethyl adipate (DMA), toluene (TOL) and water (H2O). Each vapor was prepared and delivered at pre-selected concentrations using the commercially available Automated Vapor Generation System, VG-7000, from Microsensor Systems, Inc. The VG-7000 is a completely computer controlled vapor generation system that provides rapid set-up and precise control of vapor experiments for prolonged unattended operations. The system employs a novel dilution scheme based on pneumatic pulse width modulation to dilute source vapors with clean carrier gas (air) by factors from 1 (undiluted) to over 1,000,000. All surfaces exposed to chemicals in the VG-7000 are of Teflon to minimize adsorption and corrosion problems. A variety of vapor sources can be used. Bubblers are a very convenient source for the generation of vapors from chemicals that are liquid at room temperature. The bubblers are housed in a massive aluminum heat sink that can be held at a constant sub-ambient temperature by the circulatinon of thermostatted cooling water through the aluminum block. The bubblers were held at 15° C for this study. The range of vapor concentrations that are available depends, of course, on the saturated vapor pressure of the liquid. A source vapor can be diluted under computer control by as much as 1,000,000X, thereby allowing sub-ppm vapor concentrations to be generated directly from the neat liquid. The concentration of vapor actually delivered by the system is calibrated gravimetrically, by weighing the amount of vapor adsorbed on activated charcoal over an appropriate period of time.

During this study the vapor generator was programmed to deliver each vapor at a selected concentration for a period of five minutes, followed by five minutes of clean carrier gas. The cycle was repeated twice before going to the next concentration or to the next gas. All vapor concentratrions are reportred in mg/m^3. The vapor flow rate from the VG-7000 is controlled by electronic mass flow controllers and can be varied from 6.0 to 300.0 cc/min with an accuracy of ± 1% of full scale. The flow rate from the vapor generator for this study was 115 cc/min. Each of the SAW sensors was evaluated with the same vapors and at the same concentrations. The data reported for each experiment correspond to the frequency differences between the baseline (with clean carrier gas) and the maximum frequency observed at the end of the four minute vapor exposure cycle. An attempt was made to fit the observed frequency shift, Δf, vs. time curves to mathematical expressions in order to extrapolate the observed data to equilibrium adsorption concentrations for the vapor in the polymer films. However, in the time available no relationship was developed that proved satisfactory in all of the runs, thus the data reported are non-equilibrium adsorption values for most of the experiments.

Temperature and Flow Rate Studies

As indicated above, the purpose of these studies was to determine the effect of temperature and flow rate on the sensitivity of coated SAW sensors. As 50° C is near the maximum temperature a toxic vapor detector would likely encounter in the field or in a military specification, the temperature range of interest for this study was from approximately 20°C to 50° C. The three temperatures selected were: 23°,33° and 42° C, although for the DMMP studies the lower temperature was 24.1° rather than 23° C. Constant temperatures were maintained by placing the SAW

Sensors in a refrigerated chamber with an externally controlled thermostat. The actual temperature within the chamber for each experiment is reported with the results, and was constant to within ± 1° C. It should be noted that certain electrical components on the small circuit boards containing the SAW sensor packages do generate very small amounts of heat. Any conduction of heat to the sensor packages would raise the sensor temperature a small amount. It is estimated that this additional heat would be no more than a degree and would be essentially constant. The vapors entering the box were in each case generated in the VG-7000 at 15° C and were delivered at 115 cc/min serially to the SAW sensors. At each selected temperature, the SAW sensors were exposed to the test vapors at four concentrations. For example with DMMP, the concentrations were 96.2, 30.8, 6.2, and 1.54 mg/m^3. Due to insufficient time to carry out all planned experiments, some sets of the temperature response data are incomplete. Lower priority was given to those coating/vapor combinations exhibiting small frequency shifts with concentration, i.e., in which the sensitivity was low.

The vapor flow rates often used with the SAW sensors are near 120 cc/min, although other flow rates have also been reported and may be useful in certain sampling situations. It is therefore important to know whether or not the sensitivity of a SAW device will vary significantly with the flow rate, i.e., with a given vapor concentration will the rate (or amount) of vapor adsorption by the coating vary significantly with the rate at which the vapor stream flows past the SAW device. The flow rates of interest are generally between 20 and 120 cc/min. The flow rates selected for this study were 25, 75 and 115 cc/min., with a flow rate of 50 cc/min also used in the DMMP studies.

SAW Sensor Ageing Study

This study was designed to provide data on the performance of SAW sensors upon repeated exposure to various organic vapors over a period of months. Twelve SAW sensors, each with an identification number, were used in the study. Each was coated as described above with a vapor sensitive polymer. The SAW sensors, their coating type and coating thickness, are listed in Table 1. The amount of coating applied to a SAW device is important in that coating thickness primarily determines the magnitude of the frequency response for the device at a given vapor exposure concentration. The coating thickness also is important in determining the rate of response. This is discussed below in the Results section. In practice it is necessary to calibrate each sensor to account for differences in coating thickness.

In this study each of the SAW sensors was tested on a weekly basis. Two types of tests were performed. In a calibration test the SAW sensors were exposed to each test vapor at four different concentrations for a series of 4 minute on/off cycles. The other test was essentially a spot check of the calibration in which the sensors were checked at only one concentration for each vapor. The complete calibrations were planned to be carried out on a monthly basis, while the spot tests were to be repeated weekly. Between tests the vapor sensors were allowed to stand in the laboratory environment with no special precautions taken to protect the sensors from ambient vapors. The SAW sensors were tested at 23° ± 1°C. They were exposed to each vapor at four concentrations using a flow rate of 115 cc/min. The vapor concentrations were the same as used during the temperature and flow rate studies. The ageing studies began the last week of May 1988 and continued for 5 weeks, until the end of June, at which time they were discontinued due to the expiration of funds for the project. The SAW sensors will be retained at Microsensor Systems in the event that additional support becomes available to continue the study. It would be extremely useful if the ageing study could continue for at least two years to increase confidence that the SAW devices and coatings do indeed give reliable and reproducible performance for extended periods of time.

RESULTS

Temperature Studies

In general, as the temperature rises and the vapor pressure of a compound increases, one would expect the solubility of the vapor in a polymer to decrease, thereby reducing the response (and the sensitivity) of a polymer coated SAW sensor. Grate (17) explored this effect of temperature in a study based on the relationship,

$$\Delta H_t = \Delta H_m - \Delta H_v \qquad (2)$$

where H_t, H_m and H_v are the enthalpy of transfer of a vapor from the gas phase to solution, the enthalpy of mixing of the monomeric vapor with the solvent, and the enthalpy of vaporization of the vapor respectively. He reported that where the enthalpy of mixing is small and endothermic, and assuming an enthalpy of vaporization of 10 kcal mole^{-1}, the enthalpy of transfer would be about -10 kcal mole-1. He calculated that this would result in a decrease in the solubility of that test vapor in the polymeric coating of about 24% with a 5° C increase in temperature, from 25° to 30° C. The temperature data of this report were not analyzed in terms of equation (2) as the enthalpies of mixing are not know nor easily determined, and the frequency shift vs. time data were generally not equilibrium values.

A number of factors will affect the rate at which a given vapor will reach an equlibrium concentration with its dissolved phase in a polymeric SAW coating of a specific thickness. The rate of diffusion of the vapor molecules in the polymer will be a prime determining factor, and thereby the temperature of the polymer. For example, Figures 1 and 2 show the SAW frequency shift vs. time for 30.8 mg/m^3 DMMP in two different polymeric coatings at an equivalent temperature (23° C) and film thickness (approx. 500 Angstroms). The DMMP essentially reaches equilibrium concentration in the fluoropolyol coating (Fig. 1) within 3 minutes, whereas in PIPFAI it has not reached equilibrium after 15 minutes (Fig. 2), clearly showing the effect of polymer composition and structure on diffusion rate. The effect of increasing temperatures will be to decrease the concentration of dissolved vapor within the coating (as discussed above) but increase the rate of diffusion of the vapor molecules within the polymer. An example of this temperature effect is shown in Figure 3, which plots the frequency shift vs. time for 6 mg/m^3 DMMP on fluoropolyol coated SAW sensors at 23°, 33° and 42° C. At 42° C the DMMP has essentially reached equilibrium concentration after 3 minutes, whereas at 23° C the magnitude of the frequency shift is considerably larger (higher vapor concentration in the coating) but Δf is still increasing rapidly after 5 minutes, indicating a non-equilibrium situation. The decision was made to arbitrarily cycle all gas exposures at 4 minute on/off intervals, in order to obtain several repetitions of the experiments within a reasonable period of time, and then to develop an equation to describe the frequency vs. concentration curves and to use the equation to estimate the equilibrium values. Unfortunately time was not available on the project to complete development and application of the equation. However, the non-equilibrium data clearly show the trends with temperature and give valuable insight into new approaches that can be used in the development of SAW devices with improved performance.

Tables 2 through 5 give the SAW frequency response data recorded for each of the test vapors (DMMP, dimethyl adipate, toluene and water) on the coated sensors at 23° (24.1° for DMMP), 33° and 42° C. The most important and consistent data were for the those vapor/coating combinations that gave the greatest response, i.e., where the coatings showed the greatest sensitivity and/or selectivity. The fluorinated polymeric coatings showed the highest selectivity for DMMP, while ethyl cellulose gave a large response to toluene, and poly(ethyleneimine) was highly selective for water vapor. These vapor/concentration combinations are shown in Figures 4 through 8, where the frequency responses recorded during the 4 minute on/off vapor cycles are plotted against vapor concentration at each of the three temperatures. The data in all graphs show the expected decrease in frequency response with increasing temperature. The decrease of approximately 3,000 Hz for 30.8 mg/m^3 DMMP on FPOL, from 33° to 42° C, is in good agreement with data reported previously by Ballantine (18). Although the trends of the curves and their magnitudes are correct, it should be considered that most of the data was recorded before equilibrium was reached. Thus the magnitudes of the frequency shifts and any SAW sensitivities calculated from this data may be somewhat at variance with similar measurements made at equilibrium.

The sensitivity of a coated SAW sensor for a given vapor is normally determined from the slope of the frequency vs. concentration curve as it approaches very low concentrations. This procedure was not used in the present experiments as they were not designed to provide sufficient data at low vapor concentrations, and they did not assure that the test vapors had attained equilibrium partition between the vapor phase and dissolved phase in all coatings. The sensitivities of the various coatings were therefore calculated at each experimental temperature as Hertz/mg/m^3

for the test vapors at mid-range concentrations. The calculated sensitivity values are given in Table 6. The values in the table clearly show the decrease in SAW coating sensitivity with increasing temperatures and the selectivity of certain coatings for specific classes of compounds. For example, the fluorinated polymeric coatings are orders of magnitude more sensitive to DMMP than are ethyl cellulose or poly(ethyleneimine). These high sensitivities are in part due to the solubility of the organic phosphonates in the fluorinated polymers and in part to their high molecular weight and vapor pressure. Based on these sensitivities, DMMP should be readily detected down to concentrations of 0.05 mg/m^3 on FPOL and PIPFAI. Water vapor should be detectable at concentrations to 5 mg/m3 on poly(ethyleneimine) coated SAW sensors and toluene to concentrations of about 20 mg/m^3 on ethyl cellulose coatings.

The dependence of sensitivity on temperature is perhaps more clearly shown in Figures 9 thru 12 for those vapor/coating combinations showing some of the highest sensitivities. The plots for DMMP on FPOL as a function of concentration are of particular interest. It was shown above that DMMP vapor does reach equilibrium with its dissolved phase in FPOL at 42° C but not at the lower temperatures. Thus Figure 12 shows that the calculated sensitivites for DMMP at each concentration are very similar at 42° C, but diverge at lower temperatures. From prior studies we know that the DMMP sensitivity of FPOL is essentially constant with concentration in this concentration range.

Flow Rate Studies

The vapor concentration vs. frequency response data as a function of vapor flow rate are presented in Tables 6 to 10. The data for several vapor/coating combinations that exhibit high sensitivities are plotted in Figures 13 to 17. Even though there is some scatter in the data from different experiments, it is apparent that frequency responses for the coated SAW sensors (and thus their sensitivities in Hertz/mg/m^3) are not affected by differences in flow rate, at least for water, toluene, and DMMP within the range of flow rates studied. The data for dimethyl adipate appear to show a dependence on flow rate, however, it was later discovered that this was an experimental artifact due to hold-up and slow bleeding of the low volatility DMA in the Teflon vapor delivery lines at the temperature of the flow experiments, 23° C. The frequency vs. conc. curves from the flow rate studies at 23° C agree well with those from the temperature studies, demonstrating the general reproducibility of the SAW sensor experiments. The only large difference in response betwen the two sets of data was for water vapor. The lower frequency response for water vapor on poly(ethyleneimine) coated SAW sensors in the flow rate studies is believed to be due to a small drift in temperature to higher values during the experiment. This again demonstates the sensitivity of the coated SAW sensors to temperature and the benefits that could result from controlling the sensor temperature at or near 20° C.

Ageing Studies

The results of the SAW sensor/coating ageing studies are given in Tables 11 to 14 with selected data plotted in Figures 18 to 21. The most important observation to be made from the data is that even though there is some scatter in the data, there is no observed decrease in coating and sensor response over the duration of these tests. It is believed that the scatter in the data results from small variations in certain experimental variables from experiment to experiment, and are not due to changes in the sensors themselves. For example, between ageing runs the vapor generator VG-7000, the temperature control unit, the vapor delivery lines, etc. are used for other purposes. Thus when the test system is re-assembled, there could be small changes in temperature due to slightly different control settings, or differences in other parameters that are presently not being compensated for in the SAW Sensor systems as used in this study. The frequency responses of the SAW sensors were essentially the same as observed in the studies of temperature and flow rate in those instances where similar conditions were used. It should be noted that Sensor 8818-7 had a partially blocked vapor inlet tube that was not noticed until the experiments were underway. Once the inlet tube was repaired the sensor was again included in the study.

As with the temperature and flow rate studies, the most reproducible results were obtained for the coating/vapor combinations that demonstrated the highest sensitvities, such as DMMP on FPOL and PIPFAI. Another pertinent observation that can be made from the data in Figures

20 and 21 particularly, is that coatings of essentially the same "thickness" or amount can show somewhat different sensitivities. For example, the poly(ethyleneimine) (PEI) coatings on SAW Sensors 8818-5 and 8818-7 are essentially the same, both measuring 252 Hertz. However in Figures 21a and 21b it can be seen that Sensor 8818-7 consistently gives the greater frequency response. For toluene on ethyl cellulose (Figure 20), SAW Sensor 8818-18 had a somewhat thicker ethyl cellulose coating than Sensor 8818-17 and in this case did show a greater vapor sensitivity. It appears that for certain coatings, sensitivity may depend on more than the total amount of material on the surface. It may depend to a certain extent upon such coating properties as uniformity, density and structure.

Time Response of SAW Sensors to Vapor

As many of the frequency response values reported here had not reached the maximum or equilibrium level for the respective vapor concentration in the scheduled exposure time, a brief study was undertaken to better characterize the response times of the coatings to at least one test vapor. DMMP at 96.2 mg/m^3 was selected as the test vapor. The experiments were carried out at a vapor flow rate of 115 ml/min. at a temperature of 22.6° C. The sensors were exposed to the DMMP vapor until an equilibrium or maximum value had been reached for FPOL, ethyl cellulose, and poly(ethyleneimine), or until a pre-determined time had elapsed for the PIPFAI coated sensor, which continued to slowly adsorb vapor with time for as long as 30 minutes. The times were recorded for DMMP to reach its maximum frequency response on each coating. From this, the time to 95% of maximum response was calculated. The values for DMMP on PEI were so low that meaningful measurements could not be made. The experiment was carried out three times, at total elapsed exposure times of 900, 1000 and 1500 seconds. The time response data are given in Table 15.

The data show that DMMP at 96.2 mg/m^3 reaches maximum response on FPOL in 6 to 7 minutes at 22.6° C, and 95% of maximum in about a minute less. This is about twice the 3 minutes required for 30.8 mg/m^3 DMMP to reach maximum response on the same coating at 42° C. It required somewhat longer for the DMMP to reach maximum response on ethyl cellulose, 9 to 10 minutes, indicating a slower rate of diffusion of DMMP in that polymer. As expected, the PIPFAI data show a continual increase in frequency response with time for the duration of the vapor exposure. The plots of Figures 22a, 22b, and 22c show that with both FPOL and ethyl cellulose the DMMP quickly leaves the coating and the frequency response returns to baseline within a few minutes. The PIPFAI on the other hand appears to release the adsorbed DMMP at a much slower rate, similar to its rate of uptake. The FPOL and ethyl cellulose appear to be generally more useful coatings, especially if one is to make repetitive measurements, or wishes to develop an equation for predicting the performance of sensors.

CONCLUSIONS

It has been shown that SAW devices coated with thin films of chemically selective polymers decrease in vapor sensitivity with increasing temperature in the range from 23° C to 42° C. Considering the physical basis for this decreasing sensitivty, the effect should hold to higher and lower temperatures as well. The correlation of coating sensitivity with temperature is primarily a function of the decreasing solubility of vapors in the polymers as the temperature increases. Even though there is reduced vapor sensitivity at higher temperatures, the rate of coating response to a vapor will increase due to the more rapid rate of diffusion, thus at higher temperatures the time required to attain maximum response will be shorter. The SAW devices themselves, if they are properly temperature compensated, should have no loss of sensitivity going from room temperature to 50° C.

The data also show that the rate of adsorption and the equilibrium amount of a vapor adsorbed into a thin SAW coating are essentially independent of the rate of flow of the vapor stream through the SAW Sensor package. This was tested for flow rates from 25 to 115 ml/ min. Thus for SAW Sensors as manufactured and packaged by Microsensor Systems, Inc. there is a wide range of flow rates which can be utilized without concern for the effect on the sensor response.

The results of the ageing studies indicate that the sensitivities of the SAW Sensors and coatings were essentially unchanged over the duration of the experiments. The larger question of long-term stability, over a period of 12 to 24 months or longer, must still be addressed. The SAW sensors prepared and used in this study will be retained for possible continuation of the study in the next several months should funding be provided.

A number of observations were made regarding the rate of response of the different coatings to the vapors of interest. It was observed that the rate of response increases with increasing temperature, i.e., equilibrium adsorption is achieved more rapidly as would be predicted from the increase in rate of diffusion. For example with fluoropolyol at 22.6° C it required 6 to 7 minutes for DMMP to reach maximum adsorption (or eqilibrium). When the temperature was increased to 42° C the time to maximum adsorption was reduced to approximately 3 minutes. It was observed that it took longer for DMMP to reach maximum adsorption in ethyl cellulose, indicating a slower rate of diffusion. Water vapor on PEI appeared to reach equilibrium very quickly at all temperatures, as all frequency shift vs. concentration data were at equilibrium within the 4 min on/off vapor cycling period. It should be noted that times to maximum adsorption as observed in the experiments are somewhat longer than would be calculated strictly from diffusion times, due to the time required for the challenge vapor to sweep out the carrier gas or prior vapors from the vapor transfer lines and device package and to reach equilibrium concentrations in those spaces.

RECOMMENDATIONS

Based on the results of this study, a number of recommendations can be made for the development of improved SAW microsensors for the detection of toxic and hazardous vapors:

1. <u>Maintain SAW sensors at a constant, lower temperature.</u> If the SAW sensors are maintained at a constant, low (near 20° C) temperature, (for example by use of a very small thermo-electric cooler) they will have constant sensitivity throughout the temperature range of military interest and they will have lower noise.

2. <u>Ultimately go to higher SAW device frequencies</u>. Higher frequencies still offer several attractive and important advantages. First they require thinner coating films. The thinner films would respond more quickly to vapor exposure and would reach equlibrium more rapidly,

simplifying data analysis and improving accuracy. Second, the higher frequency devices will be inherently smaller and more sensitive.

3. Separate the active SAW delay line from the reference. As long as the active and reference SAW delay lines are side-by-side on a chip during the coating process, it will be possible to have small amounts of the coating inadvertently reach the reference. This could be a source of noise. In adition, at high vapor concentrations significant adsorption onto the reference sensor can occur which can produce anomolously low signals.

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Table 2. Effect of Temperature on the Response of Coated SAW Sensors to Dimethylmethylphosphonate (DMMP) Vapor.

1) DMMP on Poly(isoprene) Fluorinated Alcohol (PIPFAL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	24.1° C
96.2	37,355	43,196	38,523
	37,355	43,196	43,192
30.8	21,888	25,390	19,553
	22,180	--	24,223
6.16	5,107	5,107	3,940
	4,925	4,925	3,648
1.54	1,094	1,058	866

2) DMMP on Fluoropolyol (FPOL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	24.1° C
96.2	12,580	17,741	20,311
	12,257	18,063	22,579
30.8	6,129	9,677	10,644
	6,129	--	12,257
6.16	1,331	2,419	3,145
	1,210	2,339	3,105
1.54	322	605	857

3) DMMP on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	24.1° C
96.2	955	1,305	1,911
	919	1,360	1,911
30.8	349	551	716
	386	--	753
6.16	110	114	--
	--	105	128
1.54	--	27	23

4) DMMP on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	24.1° C
96.2	--	58	126
	--	--	136
30.8	--	--	78
	63	--	87
6.16	--	--	--
	--	--	39
1.54	--	--	29

Table 3. Effect of Temperature on the Response of Coated SAW Sensors to Dimethyl Adipate (DMA) Vapor.

1) DMA on Poly(isoprene) Fluorinated Alcohol (PIPFAI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
750	18,678	--	--
	--	--	--
375	--	3,648	5,253
	--	--	--
187.5	1,459	684	1,003
	--	684	1,076
60.0	383	237	365
	--	237	383
12.0	219	141	228
	155	--	--

2) DMA on Fluoropolyol (FPOL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
750	5,160	--	--
	--	--	--
375	--	2,661	3,629
	--	2,016	--
187.5	474	474	867
	--	433	887
60.0	151	151	292
	131	161	302
12.0	101	86	161
	50	--	--

3) DMA on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
750	276	--	--
	--	--	--
375	--	129	129
	--	--	--
187.5	--	69	27
	--	--	--
60.0	--	28	23
	--	--	28
12.0	--	--	--

4) DMA on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
750	339	--	--
	--	--	--
375	--	73	155
	--	73	--
187.5	48	34	58
	--	--	58
60.0	--	--	34
	--	29	--
12.0	--	--	--

Table 4. Effect of Temperature on the Response of Coated SAW Sensors to Toluene (TOL) Vapor.

1) TOL on Poly(isoprene) Fluorinated Alcohol (PIPFAI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
42,500	9,923	14,300	26,557
	--	--	22,763
10,625	2,116	2,261	--
	1,933	1,933	3,466
2,656	456	392	492
	410	337	547
680	137	104	182
	137	--	--

2) TOL on Fluoropolyol (FPOL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
42,500	7,580	8,709	15,805
	--	8,225	14,193
10,625	1,572	2,339	2,419
	1,532	2,258	--
2,656	368	605	605
	403	565	585
680	91	161	151

3) TOL on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
42,500	10,292	15,880	31,761
	9,999	15,880	31,761
10,625	2,941	4,779	--
	2,757	4,264	7,940
2,656	827	1,342	2,279
	790	1,287	2,132
680	221	368	643
	257	--	--

4) TOL on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
42,500	969	2,481	1,628
	--	2,403	--
10,625	387	581	--
	368	562	378
2,656	126	203	131
	136	203	136
680	--	92	58

Table 5. Effect of Temperature on Response of Coated SAW Sensors to Water (H2O) Vapor

1) Water on Poly(isoprene) Fluorinated Alcohol (PIPFAl)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
6,500	2,555	2,116	3,137
	--	--	--
1,625	566	429	602
	547	337	483
406	201	137	182
	160	--	128
104	68	104	--

2) Water on Fluoropolyol (FPOL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
6,500	1,895	2,218	--
	1,612	1,855	3,871
1,625	867	1,028	1,008
	847	907	988
406	202	746	232
	202	--	232
104	101	126	50
	--	--	50

3) Water on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
6,500	827	184	809
	772	--	698
1,625	152	92	257
	147	--	248
406	--	37	248
	--	--	252
104	--	--	156
			152

4) Water on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	42° C	33° C	23° C
6,500	13,643	23,256	58,295
	13,643	24,186	59,535
1,625	2,713	3,101	6,202
	2,713	3,101	6,202
406	698	329	717
	659	--	698
104	194	--	262
	--	--	242

Table 6. Effect of Temperature on the Sensitivity of Coated SAW Sensors to Test Vapors (Hertz/mg/m^3)

1) 375 mg/m^3 Dimethyl Adipate

Temp		Coatings		
°C	FPOL	PIPFAI	ECEL	PEI
42	2.53	7.78	--	0.27
33	2.53	3.65	0.37	0.18
23	4.62	5.35	0.37	0.31

2) 10.625 mg/m^3 Toluene

Temp		Coatings		
°C	FPOL	PIPFAI	ECEL	PEI
42	0.15	0.20	0.28	0.03
33	0.21	0.21	0.45	0.05
23	0.23	0.33	0.75	0.03

3) 1.625 mg/m^3 Water Vapor

Temp		Coatings		
°C	FPOL	PIPFAI	ECEL	PEI
42	0.53	0.34	0.09	1.67
33	0.56	0.26	0.06	2.51
23	0.62	0.37	0.16	3.81

4) 30.8 mg/m^3 DMMP

Temp		Coatings		
°C	FPOL	PIPFAI	ECEL	PEI
42	199	711	12.5	2.05
33	314	824	17.9	--
24.1	398	786	24.5	2.83

5) 6.16 mg/m^3 DMMP

Temp	Coatings
°C	FPOL
42	211
33	378
24.1	503

6) 1.54 mg/m^3 DMMP

Temp	Coatings
°C	FPOL
42	209
33	393
24.1	556

Table 7. Effect of Vapor Flow Rate on the Response of Coated SAW Sensors to Dimethylmethylphosphonate (DMMP)

1) DMMP on Poly(isoprene)Fluorinated Alcohol (PIPFAL)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz)			
	115 ml/min	75 ml/min	50 ml/min	25 ml/min
96.2	46,715	44,964	42,627	42,627
	46,131	44,379	--	--
30.8	25,693	25,109	28,028	23,357
	23,941	--	25,693	--
6.16	3,650	2,920	2,993	2,481
	3,650	--	--	--
1.54	1,004	666	657	529

2) DMMP on Fluoropolyol (FPOL)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz)			
	115 ml/min	75 ml/min	50 ml/min	25 ml/min
96.2	19,353	20,001	20,323	20,968
	19,353	20,001	--	--
30.8	9,193	10,000	10,807	11,291
	9,354	--	10,968	--
6.16	2,298	2,177	2,419	2,298
	2,257	--	2,419	--
1.54	655	1,004	605	564

3) DMMP on Ethyl Cellulose (ECEL)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz)			
	115 ml/min	75 ml/min	50 ml/min	25 ml/min
96.2	1,562	1,838	1,930	1,728
	1,471	1,765	--	--
30.8	607	781	882	781
	570	--	809	--
6.16	152	152	230	183
	138	--	184	--
1.54	45.9	41.4	73.5	45.9

4) DMMP on Poly(ethyleneimine) (PEI)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz)			
	115 ml/min	75 ml/min	50 ml/min	25 ml/min
96.2	116	168	145	136
	121	155	--	--
30.8	82.3	87.2	96.9	106.6
	92.0	--	72.7	--
6.16	48.4	--	58.1	48.4
	43.6	--	38.7	--
1.54	33.9	--	--	33.9

Table 8. Effect of Vapor Flow Rate on the Response of Coated SAW Sensors to Dimethyl Adipate (DMA)

1) DMA on Poly(isoprene) Fluorinated Alcohol (PIPFAL)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 115 ml/min	75 ml/min	25 ml/min
375	30,935	19,853	6,715
	--	--	--
187	18,970	9,927	3,212
	19,261	--	--
60	2,918	1,825	456
12	602	328	128
	547	--	--

2) DMA on Fluoropolyol (FPOL)

Vapor Conc MG/M^3	SAW Frequency Response, Δf (Hertz) 115 ml/min	75 ml/min	25 ml/min
375	11,935	7,904	3,468
	--	--	--
187	6,129	3,387	1,210
	6,452	--	--
60	1,311	1,210	323
	--	1,613	--
12	403	272	95.8

3) DMA on Ethyl Cellulose (ECEL)

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 115 ml/min	75 ml/min	25 ml/min
375	2,279	2,206	993
	--	--	--
187	1,581	1,471	625
	1,618	--	--
60	772	956	312
	--	956	--
12	331	230	91.9

4) DMA on Poly(ethyleneimine) (PEI)

Vapor Conc MG/M^3	SAW Frequency Response, Δf (Hertz) 115 ml/min	75 ml/min	25 ml/min
96.2	446	320	407
	--	--	--
30.8	252	160	223
	242	--	--
6.16	107	116	96.9
	--	107	--
1.54	46.5	33.9	--

Table 9. Effect of Vapor Flow Rate on the Response of Coated SAW Sensors to Toluene Vapor (TOL)

1) TOL on Poly(isoprene) Fluorinated Alcohol (PIPFAL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
42,500	--	30,949	25,693
	30,351	--	--
10,624	3,064	3,285	4,235
	1,824	--	--
2,656	228	474	620
	--	--	--
680	68.4	--	128

2) TOL on Fluoropolyol (FPOL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
42,500	--	16,775	15,162
	14,194	--	--
10,624	2,258	2,480	2,984
	1,774	--	--
2,656	252	403	474
	--	--	--
680	90.7	151	156

3) TOL on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
42,500	27,058	23,529	25,882
	26,470	--	--
10,624	7,499	7,794	8,235
	--	--	--
2,656	1,691	2,132	2,426
	--	--	--
680	460	607	809

4) TOL on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
42,500	--	678	872
	1,085	--	--
10,624	494	388	407
	465	--	--
2,656	136	126	348
	--	--	--
680	48.4	48.4	--

Table 10. Effect of Vapor Flow Rate on the Response of Coated SAW Sensors to Water Vapor (H_2O)

1) Water Vapor on Poly(isoprene) Fluorinated Alcohol (PIPFAL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
6,500	--	1,971	2,774
	2,299	--	--
1,625	429	365	328
	--	--	--
406	146	123	--
	150	--	--
104	--	--	--

2) Water Vapor on Fluoropolyol (FPOL)

Vapor Conc	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
6,500	--	1,492	2,339
	1,451	--	--
1,625	101	202	363
	70.6	--	--
406	75.6	45.4	131
	75.6	--	--
104	50.4	40.3	35.3

3) Water Vapor on Ethyl Cellulose (ECEL)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
6,500	--	551	551
	643	--	--
1,625	239	--	--
	--	--	--
406	174	91.9	101
	138	--	--
104	--	--	--

4) Water Vapor on Poly(ethyleneimine) (PEI)

Vapor Conc.	SAW Frequency Response, Δf (Hertz)		
MG/M^3	115 ml/min	75 ml/min	25 ml/min
6,500	35,349	35,969	36,589
	36,589	--	--
1,625	--	--	--
	--	--	--
406	795	853	1,027
	814	--	--
104	329	388	485

Table 11. Frequency Response of FPOL SAW Sensors to DMMP, Toluene, Water and Dimethyl Adipate as a Function of Time (Ageing).

1) DMMP on FPOL SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M³	5/31/88	6/06/88	6/17/88	6/23/88	6/27/88
a) Sensor 8818-12					
96.2	30,176	--	--	--	27,762
30.8	15,691	12,674	15,088	15,390	15,691
6.16	4,828	--	--	--	4,677
1.54	--	--	--	--	1,056
b) Sensor 8818-13					
96.2	21,217	--	--	--	27,762
30.8	10,035	8,745	8,602	8,745	10,035
6.16	2,796	--	--	--	2,580
1.54	--	--	--	--	591
c) Sensor 8818-11*					
96.2	--	--	--	--	--
30.8	--	--	--	--	--
6.16	--	--	--	--	--
1.54					

* Sensor 8818-11 only partially operative due to blocked vapor inlet tube.

2) Dimethyl Adipate on FPOL SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M³	6/01/88	6/09/88	6/17/88	6/23/88	6/28/88
a) Sensor 8818-12					
375	20,218	18,370	--	19,614	19,011
187	11,467	--	9,958	--	9,656
60	4,073	--	--	--	3,018
12	--	--	--	--	--
b) Sensor 8818-13					
375	7,741	6,881	--	7,168	6,881
187	3,584	--	1,792	--	3,011
60	1,075	--	--	--	770
12	--	--	--	--	--
c) Sensor 8818-11*					
375	--	--	--	--	--
187	--	--	--	--	--
60	--	--	--	--	--
12					

* Sensor 8818-11 only partially operative due to blocked vapor inlet tube.

3) Toluene on FPOL SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/02/88	6/09/88	6/17/88	6/23/88	6/29/88
a) Sensor 8818-12					
42,500	20,821	--	--	--	18,709
10,625	3,244	4,376	3,961	3,168	3,451
2,656	764	--	--	--	735
680	193	--	--	--	--
b) Sensor 8818-13					
42,500	16,056	--	--	--	16,630
10,625	2,867	3,011	2,222	3,942	2,724
2,656	537	--	--	--	538
680	157	--	--	--	--
c) Sensor 8818-11*					
42,500	--	--	--	--	12,425
10,625	--	--	--	--	2,656
2,656	--	3,030	2,727	3,939	701
680					

* Sensor 8818-11 only partially operative due to blocked vapor inlet tube.

4) Water Vapor on FPOL SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/03/88	6/10/88	6/18/88	6/24/88	6/30/88
a) Sensor 8818-12					
6,500	4,677	4,375	--	--	4,225
1,625	1,132	--	2,452	1,396	867
406	283	--	--	--	311
104	--	--	--	--	--
b) Sensor 8818-13					
6,500	1,792	1,792	--	--	1,792
1,625	340	--	734	394	340
406	89.6	--	--	--	55.5
104	--	--	--	--	--
c) Sensor 8818-11*					
6,500	1,584	1,508	--	--	1,660
1,625	245	--	453	217	226
406	82	--	--	--	57.5
104					

* Sensor 8818-11 only partially operative due to blocked vapor inlet tube.

Table 12. Frequency Response of PIPFAI SAW Sensors to DMMP, Toluene, Water and Dimethyl Adipate as a Function of Time (Ageing).

1) DMMP on PIPFAI SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 5/31/88	6/09/88	6/17/88	6/23/88	6/27/8
a) Sensor 8818-1					
96.2	57,231	--	--	--	52,992
30.8	25,436	21,197	20,145	19,607	25,436
6.16	2,782	--	--	--	2,650
1.54	--	--	--	--	464
b) Sensor 8818-2					
96.2	54,761	--	--	--	55,849
30.8	26,761	26,179	27,924	29,088	32,578
6.16	3,636	--	--	--	4,436
1.54	--	--	--	--	818
c) Sensor 8818-3					
96.2	45,210	--	--	--	45,210
30.8	19,779	16,388	18,931	19,779	20,344
6.16	2,119	--	--	--	2,366
1.54	--	--	--	--	530

2) Dimethyl Adipate on PIPFAI SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 6/01/88	6/09/88	6/17/88	6/23/88	6/28/88
a) Sensor 8818-1					
375	18,547	17,487	--	18,017	14,307
187	9,539	--	9,192	--	7,948
60	1,557	--	--	--	795
12	--	--	--	--	--
b) Sensor 8818-2					
375	17,453	19,198	--	16,761	17,453
187	10,181	--	9,599	--	9,453
60	2,473	--	--	--	1,673
12	--	--	--	--	--
c) Sensor 8818-3					
375	29,951	30,516	--	30,516	30,234
187	14,128	--	12,998	--	15,258
60	2,119	--	--	--	1,395
12	--	--	--	--	--

3) Toluene on PIPFAI SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 6/02/88	6/09/88	6/17/88	6/23/88	6/29/88
a) Sensor 8818-1					
42,500	24,906	--	--	--	19,077
10,625	2,219	4,968	2,119	7,286	2,119
2,656	166	--	--	--	124
680	--	--	--	--	--
b) Sensor 8818-2					
42,500	36,651	--	--	--	32,579
10,625	2,254	3,490	6,108	3,272	1,745
2,656	382	--	--	--	209
680	54.5	--	--	--	--
c) Sensor 8818-3					
42,500	25,430	--	--	--	22,040
10,625	1,501	2,649	2,049	7,286	1,166
2,656	291	--	--	--	221
680	110	--	--	--	--

4) Water Vapor on PIPFAI SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 6/03/88	6/10/88	6/18/88	6/24/88	6/30/88
a) Sensor 8818-1					
6,500	1,855	1,921	695	--	1,755
1,625	199	--	--	281	364
406	166	--	--	--	331
104	--	--	--	--	--
b) Sensor 8818-2					
6,500	5,236	5,527	3,781	--	4,072
1,625	382	--	--	709	436
406	182	--	--	--	182
104	--	--	--	--	--
c) Sensor 8818-3					
6,500	1,907	1,907	918	--	1,766
1,625	176	--	--	371	185
406	141	--	--	--	79.5
104	--	--	--	--	--

Table 13. Frequency Response of Ethyl Cellulose SAW Sensors to DMMP, Toluene, Water and Dimethyl Adipate as a Function of Time (Ageing).

1) DMMP on Ethyl Cellulose SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	5/31/88	6/09/88	6/17/88	6/23/88	6/27/88
a) Sensor 8818-15					
96.2	1,188	--	--	--	1,622
30.8	443	585	698	735	679
6.16	165	--	--	--	186
1.54	--	--	--	--	82.5
b) Sensor 8818-17					
96.2	2,231	--	--	--	1,308
30.8	866	--	885	--	673
6.16	337	--	--	--	336
1.54	--	--	--	--	144
c) Sensor 8818-18					
96.2	1,205	--	--	--	1,546
30.8	378	557	647	665	827
6.16	135	--	--	--	180
1.54	--	--	--	--	49.4

2) Dimethyl Adipate on Ethyl Cellulose SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/01/88	6/09/88	6/17/88	6/23/88	6/28/88
a) Sensor 8818-15					
375	905	1,433	--	2,075	1,490
187	830	--	--	--	905
60	405	--	--	--	368
12	--	--	--	--	--
b) Sensor 8818-17					
375	1,375	1,732	--	1,347	2,000
187	904	--	885	--	1,039
60	500	--	--	--	577
12	--	--	--	--	--
c) Sensor 8818-18					
375	2,373	3,380	--	3,308	3,164
187	1,618	--	2,158	--	2,050
60	845	--	--	--	737
12	--	--	--	--	--

3) Toluene on Ethyl Cellulose SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/02/88	6/09/88	6/17/88	6/23/88	6/29/88
a) Sensor 8818-15					
42,500	29,572	--	--	--	30,176
10,625	6,110	3,847	3,621	3,923	6,337
2,656	1,622	--	--	--	1,961
680	585	--	--	--	--
b) Sensor 8818-17					
42,500	22,780	--	--	--	20,317
10,625	6,772	3,694	3,848	2,155	6,619
2,656	1,501	--	--	--	2,309
680	500	--	--	--	--
c) Sensor 8818-18					
42,500	27,617	--	--	--	30,494
10,625	3,524	4,027	3,740	4,027	7,480
2,656	2,014	--	--	--	2,158
680	629	--	--	--	--

4) Water Vapor on Ethyl Cellulose SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/03/88	6/10/88	6/18/88	6/24/88	6/30/88
a) Sensor 8818-15					
6,500	1,132	981	--	--	1,282
1,625	94.3	--	207	160	137
406	189	--	--	--	104
104	--	--	--	--	--
b) Sensor 8818-17					
6,500	847	750	--	--	1,077
1,625	159	--	164	86.6	750
406	96.2	--	--	--	1,077
104	--	--	--	--	--
c) Sensor 8818-18					
6,500	1,079	1,582	--	--	1,654
1,625	89.9	--	494	468	521
406	180	--	--	--	98.9
104	--	--	--	--	--

Table 14. Frequency Response of Poly(ethyleneimine) SAW Sensors to DMMP, Toluene, Water and Dimethyl Adipate as a Function of Time (Ageing).

1) DMMP on Poly(ethyleneimine) SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	5/31/88	6/09/88	6/17/88	6/23/88	6/27/88
a) Sensor 8818-5					
96.2	129	--	--	--	124
30.8	99.2	74.4	84.3	124	139
6.16	49.6	--	--	--	81.8
1.54	--	--	--	--	66.9
b) Sensor 8818-7					
96.2	--	--	--	--	169
30.8	--	--	--	--	149
6.16	--	--	--	--	99.2
1.54	--	--	--	--	79.4
c) Sensor B-022					
96.2	194	--	--	--	213
30.8	116	150	165	165	155
6.16	72.7	--	--	--	84.8
1.54	--	--	--	--	53.3

2) Dimethyl Adipate on Poly(ethyleneimine) SAW Sensor

Vapor Conc.	SAW Frequency Response, Δf (Hertz)				
MG/M^3	6/01/88	6/09/88	6/17/88	6/23/88	6/28/88
a) Sensor 8818-5					
375	357	317	--	516	546
187	129	--	238	--	285
60	59.5	--	--	--	99.2
12	--	--	--	--	--
b) Sensor 8818-7					
375	238	253	--	417	2,143
187	159	--	238	--	317
60	149	--	--	--	397
12	--	--	--	--	--
c) Sensor B-022					
375	503	446	--	620	659
187	169	--	320	--	388
60	96.9	--	--	--	170
12	--	--	--	--	--

3) Toluene on Poly(ethyleneimine) SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 6/02/88	6/09/88	6/17/88	6/23/88	6/29/88
a) Sensor 8818-5					
42,500	536	--	--	--	635
10,625	218	129	154	198	124
2,656	179	--	--	--	114
680	76.4	--	--	--	--
b) Sensor 8818-7					
42,500	1,309	--	--	--	1,746
10,625	240	223	149	268	1,309
2,625	--	--	--	--	--
680	94.2	--	--	--	417
c) Sensor B-022					
42,500	1,357	--	--	--	1,783
10,625	543	426	126	388	601
2,656	133	--	--	--	145
680	55.2	--	--	--	--

4) Water Vapor on Poly(ethyleneimine) SAW Sensor

Vapor Conc. MG/M^3	SAW Frequency Response, Δf (Hertz) 6/03/88	6/10/88	6/18/88	6/24/88	6/30/88
a) Sensor 8818-5					
6,500	38,093	36,823	--	--	36,823
1,625	2,778	--	1,231	913	1,428
406	536	--	--	--	714
104	--	--	--	--	--
b) Sensor 8818-7					
6,500	45,711	43,172	--	--	40,632
1,625	4,603	--	2,381	1,666	2,460
406	526	--	--	--	536
104	--	--	--	--	--
c) Sensor B-022					
6,500	47,752	47,132	--	--	48,372
1,625	969	--	581	620	1,124
406	678	--	--	--	581
104	--	--	--	--	--

Table 15. Response Time of SAW Coatings to DMMP Vapor at 96.2 mg/m3, 115 min flow rate, and 22.6° C.

SAW 95% Sensor/Coating	Maximum Frequency (Hertz)	Time to Maximum (sec)	95& of Maximum Frequency (Hertz)	Time to 95% of Maximum (sec)
a) Total vapor exposure time of 900 sec.				
8818-12/FPOL	17,180	342	16,800	296
8818-3/PIPFAI	19,756	1,054	18,769	861
8818-18/ECEL	700	572	665	549
8818-5/PEI	--	--	--	--
b) Total vapor exposure time of 1000 sec.				
8818-12/FPOL	17,857	290	16,964	249
8818-3/PIPFAI	24,051	1,111	22,849	1,034
8818-18/ECEL	630	425	598	325
8818-5/PEI	--	--	--	--
c) Total vapor exposure time of 1500 sec.				
8818-12/FPOL	17,792	400	16,902	342
8818-3/PIPFAI	25,088	1,731	23,834	1,244
8818-18/ECEL	600	503	570	390
8818-5/PEI	--	--	--	--

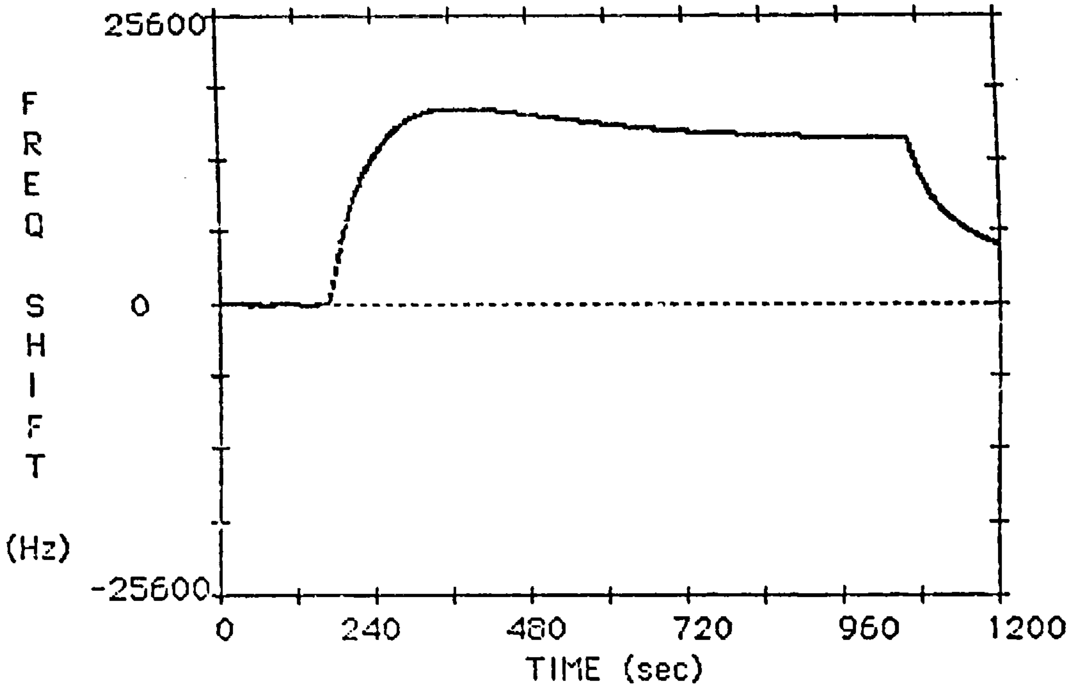


Figure 1. Frequency Response vs. Time For 30.8 MG/M3 DMMP on Fluoropolyol Coated SAW Sensor at 23°C.

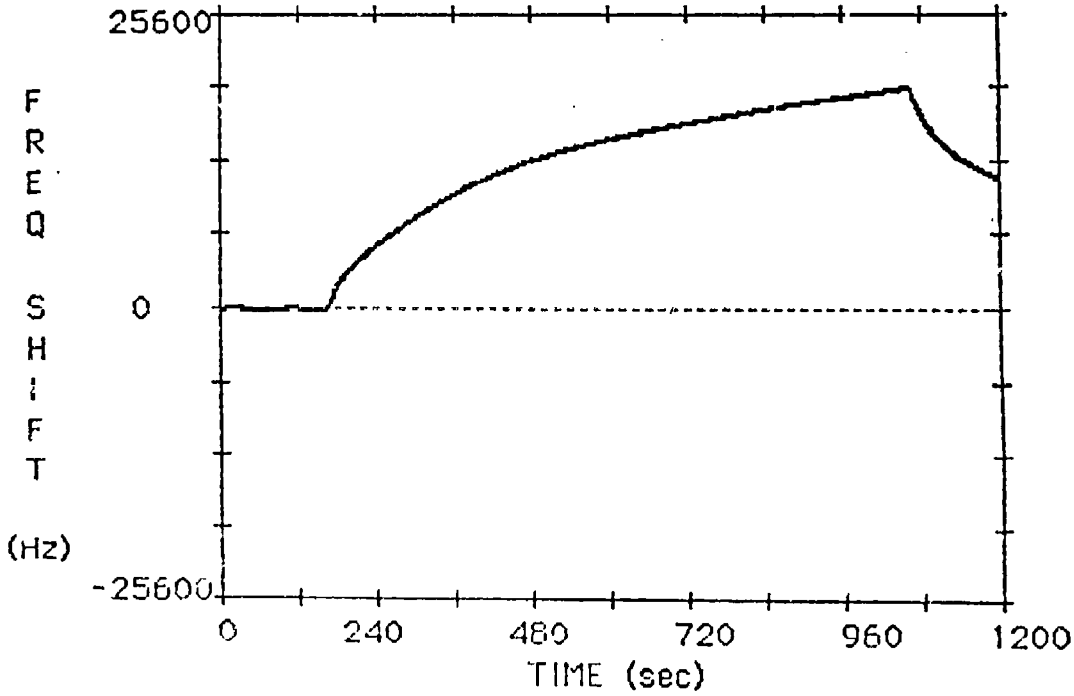


Figure 2. Frequency Response vs. Time For 30.8 MG/M3 DMMP on PIPFAI Coated SAW Sensor at 23° C.

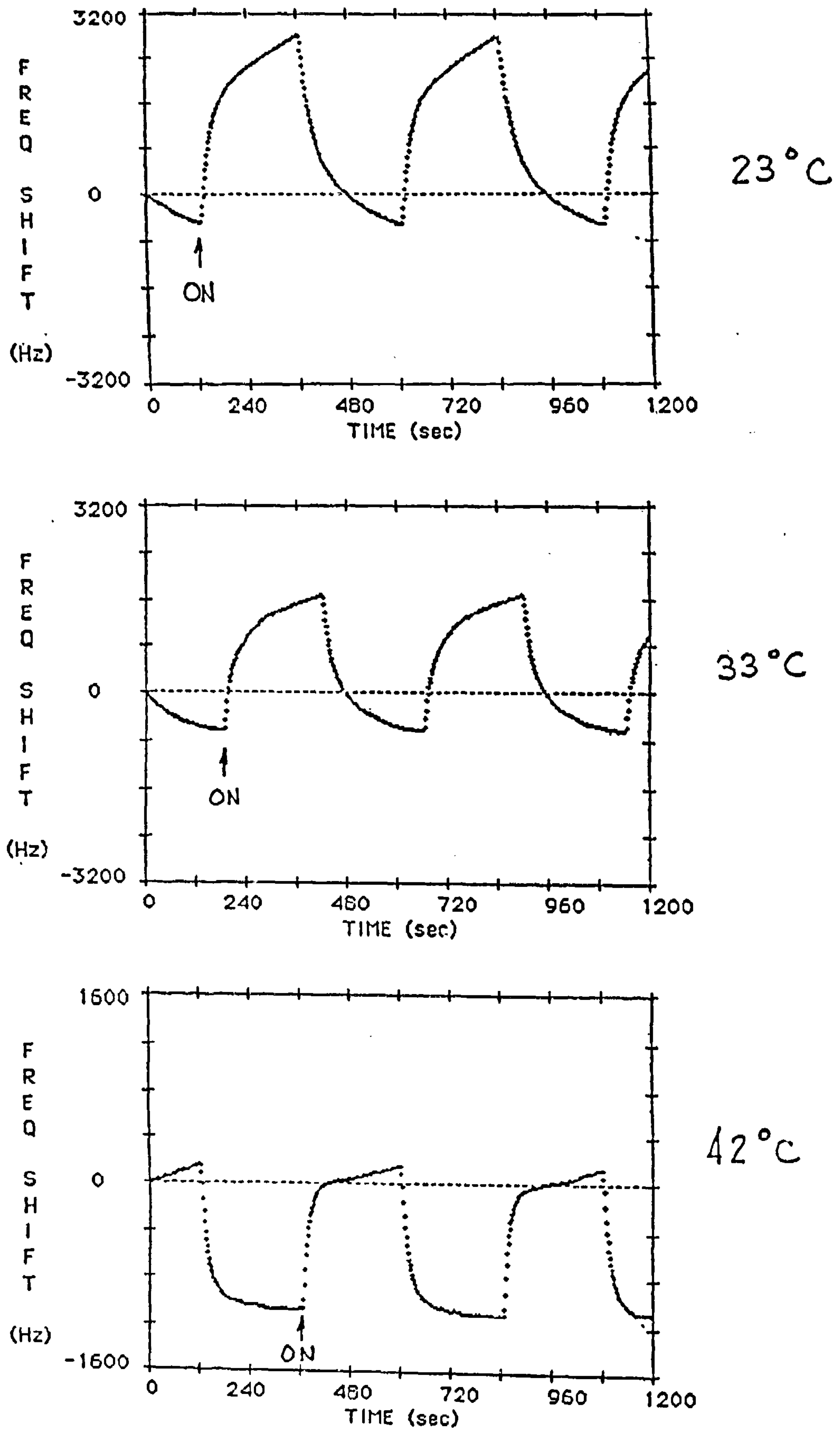


Figure 3. SAW Frequency Response vs. Time for 6 MG/M3 DMMP on Fluoropolyol Coated SAW Sensor as a Function of Temperature.

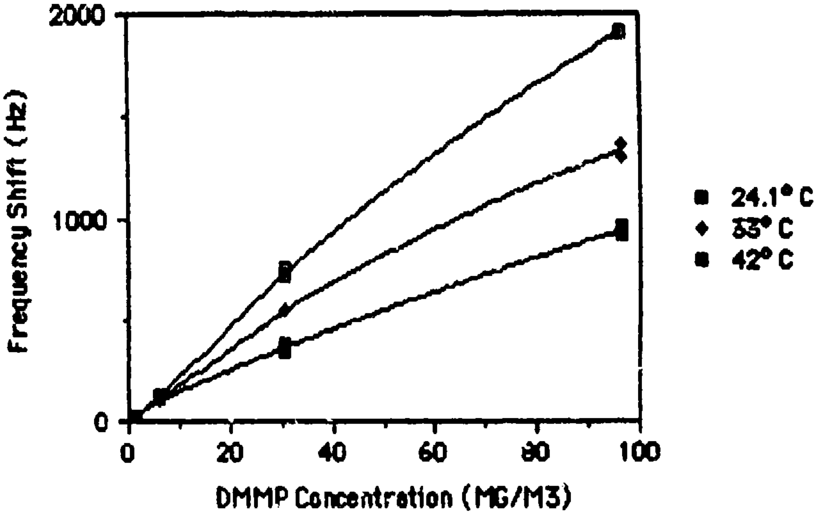


Figure 4. Frequency Response vs. DMMP Concentration as a Function of Temperature For Ethyl Cellulose SAW Sensor Coatings.

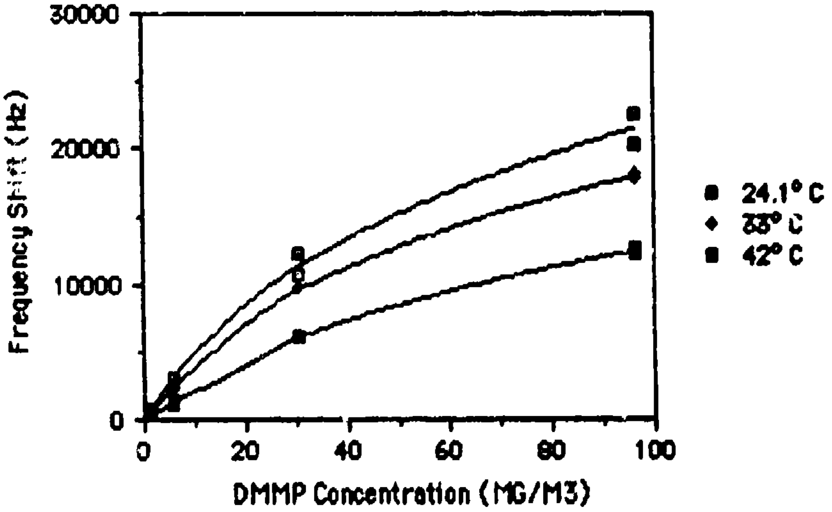


Figure 5. Frequency Response vs. DMMP Concentration as a Function of Temperature for Fluoropolyol SAW Sensor Coatings.

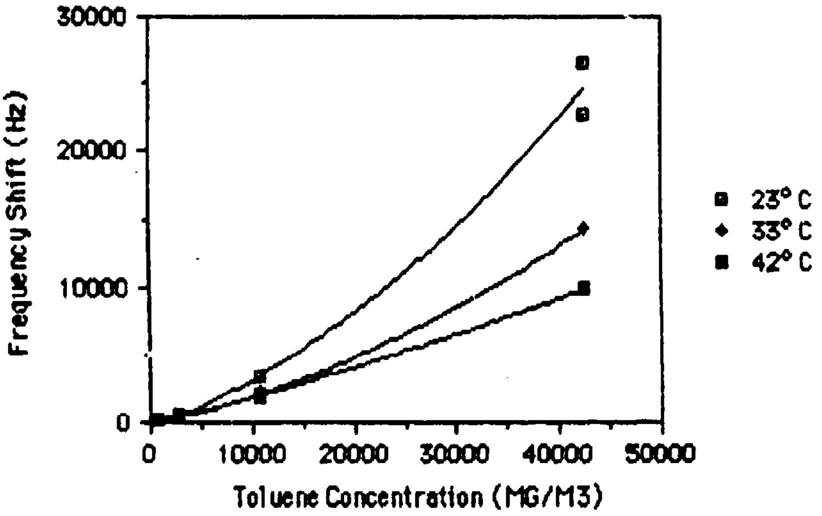


Figure 6. Frequency Response vs. Toluene Concentration as a Function of Temperature for PIPFAI SAW Sensor Coatings.

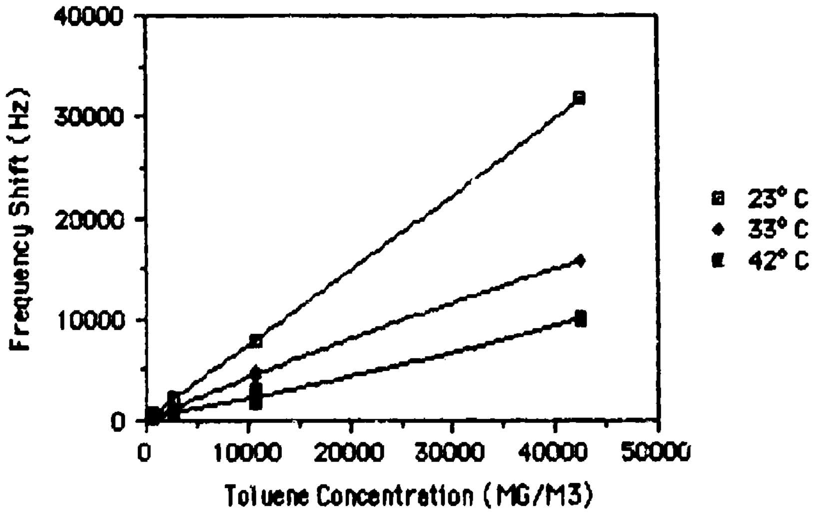


Figure 7. Frequency Response vs. Toluene Concentration as a Function of Temperature for Ethyl Cellulose SAW Sensor Coatings.

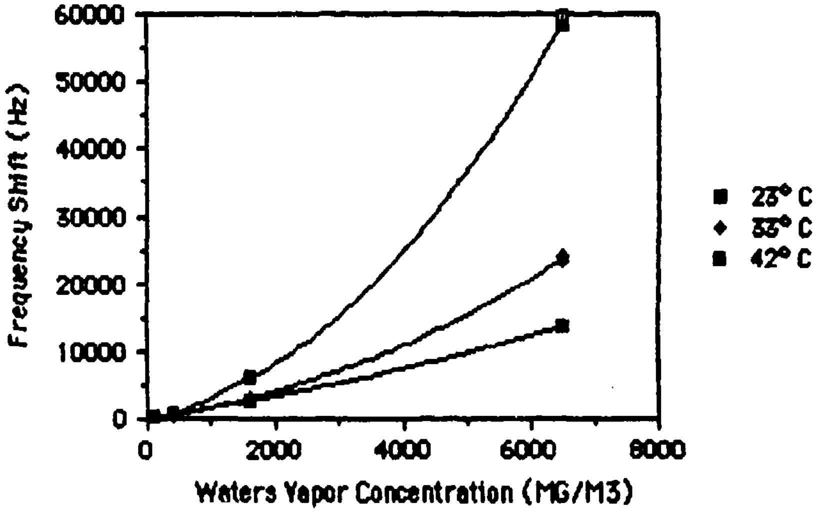


Figure 8. Frequency Response vs. Water Vapor Concentration as a Function of Temperature for Poly(ethyleneimine) SAW Sensor Coatings.

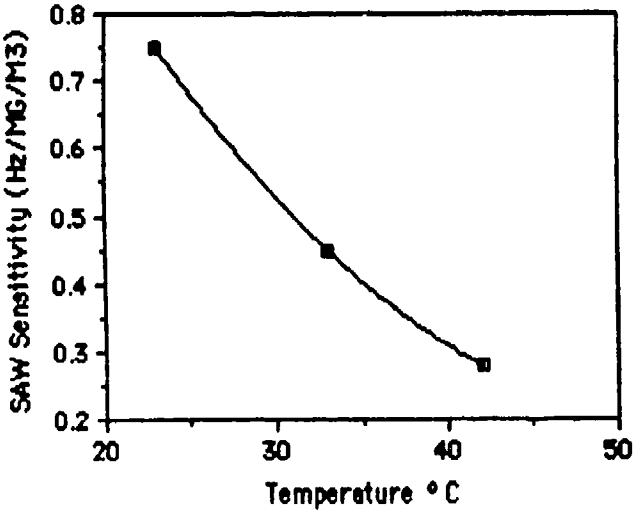


Figure 9. Effect of Temperature on the Sensitivity of Ethyl Cellulose Coated SAW Sensors to Toluene Vapor at 10,625 mg/m^3.

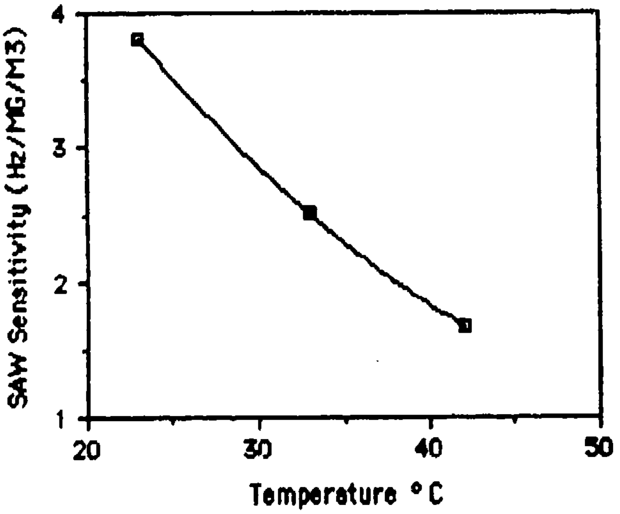


Figure 10. Effect of Temperature on the Sensitivity of Poly(ethyleneimine) Coated SAW Sensors to Water Vapor at 1,625 mg/m^3.

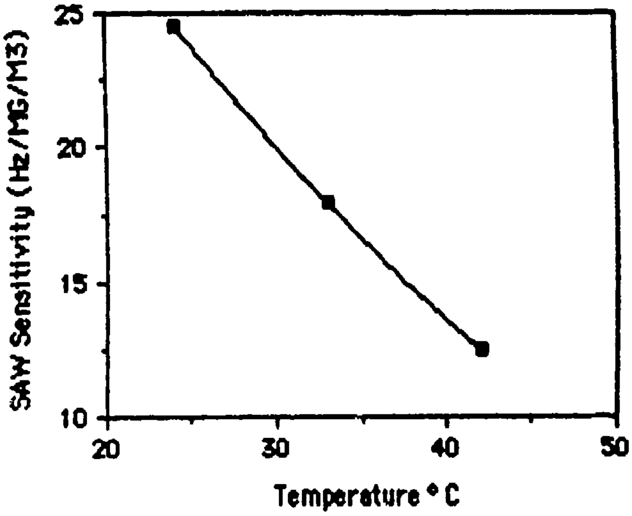


Figure 11. Effect of Temperature on the Sensitivity of Ethyl Cellulose Coated SAW Sensors to DMMP at 30.8 mg/m^3.

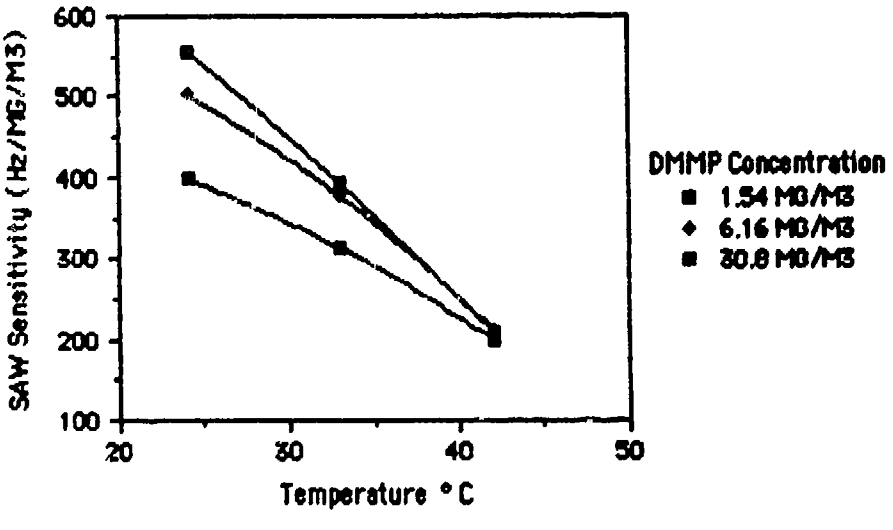


Figure 12. Effect of Temperature on the Sensitivity of FPOL Coated SAW Sensors to DMMP Vapor at Three Concentations.

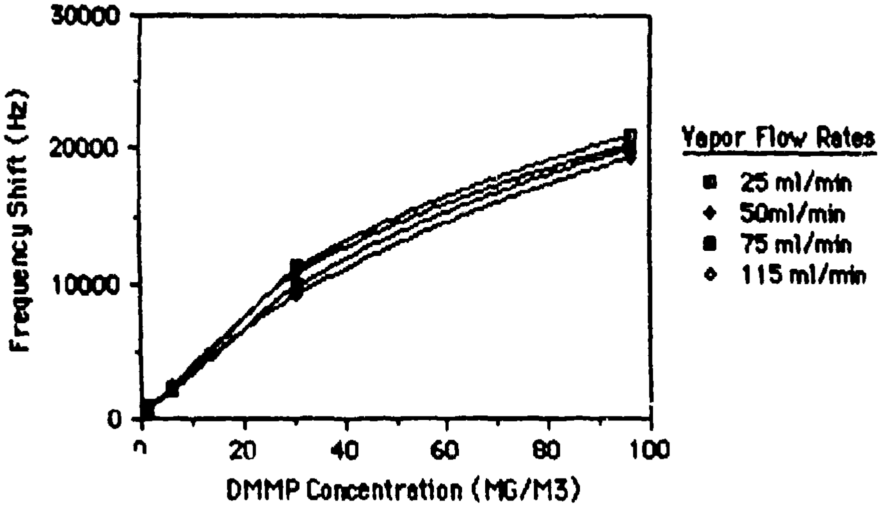


Figure 13. Frequency Response vs. DMMP Concentration as a Function of Vapor Flow Rate for Fluoropolyol SAW Sensor Coating.

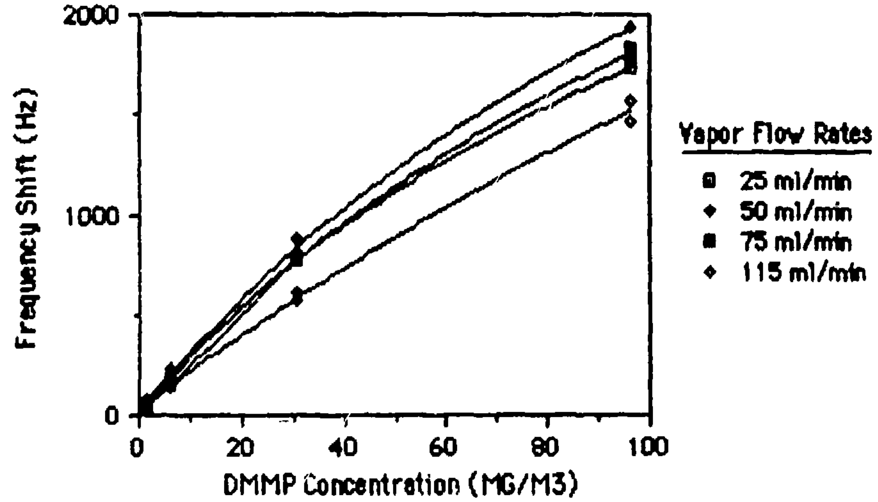


Figure 14. Frequency Response vs. DMMP Concentration as a Function of Vapor Flow Rate for Ethyl Cellulose SAW Sensor Coating

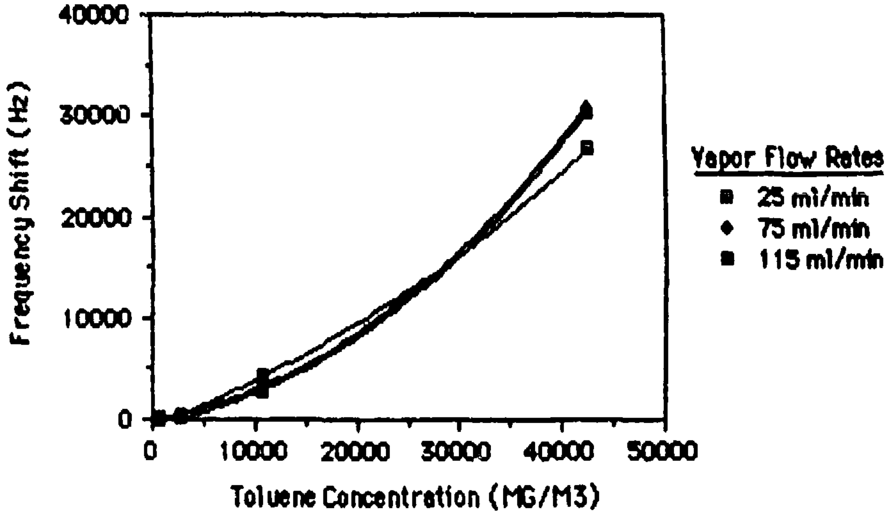


Figure 15. Frequency Response vs. Toluene Concentration as a Function of Vapor Flow Rate for PIPFAI SAW Sensor Coating.

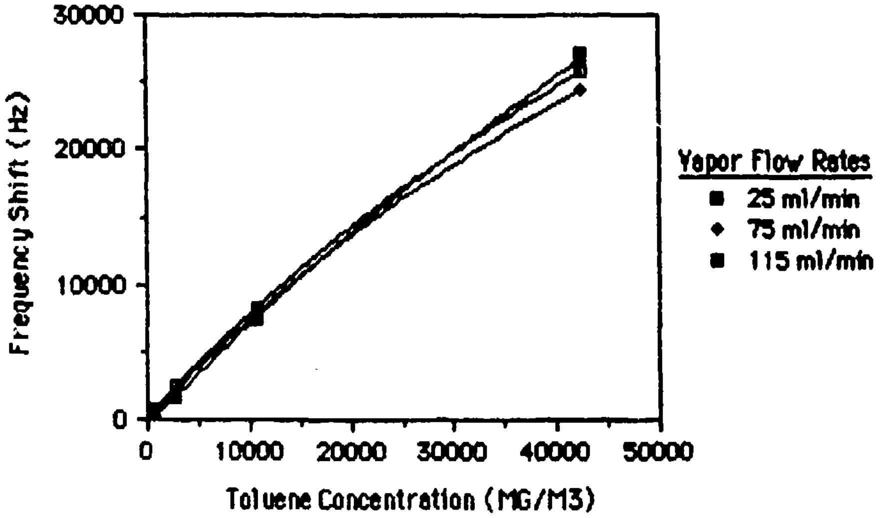


Figure 16. Frequency Response vs. Toluene Concentration as a Function of Vapor Flow Rate for Ethyl Cellulose SAW Sensor Coating.

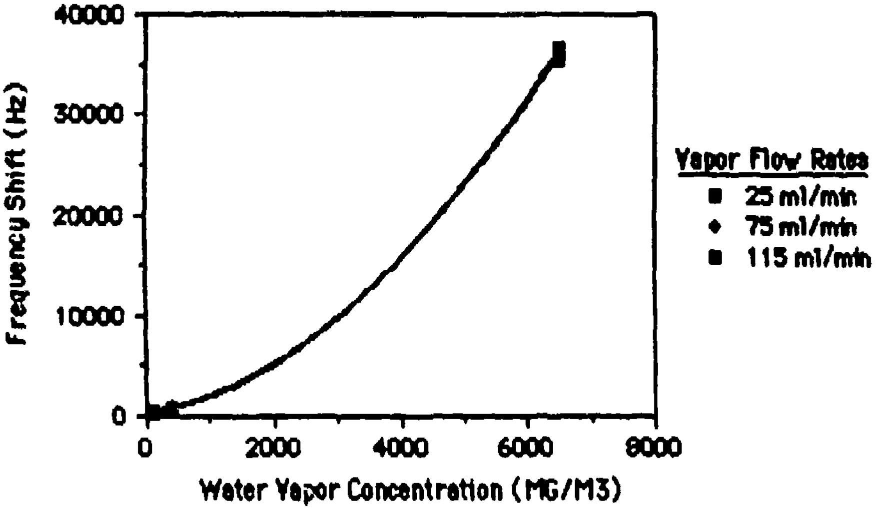


Figure 17. Frequency Response vs. Water Vapor Concentration as a Function of Vapor Flow Rate for Poly(ethyleneimine) SAW Sensor Coating.

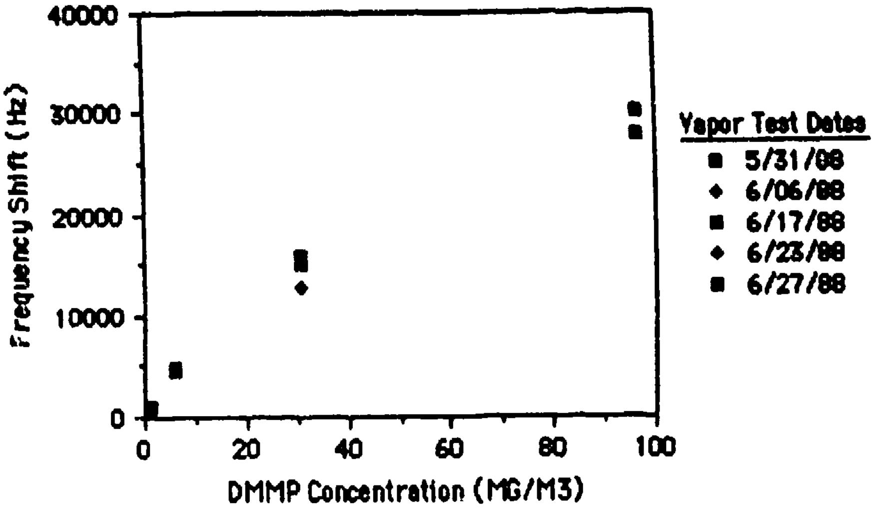


Figure 18a. Frequency Response vs Concentration for DMMP Vapor on FPOL Coated SAW Sensor 8818-12 as a Function of Time (Ageing).

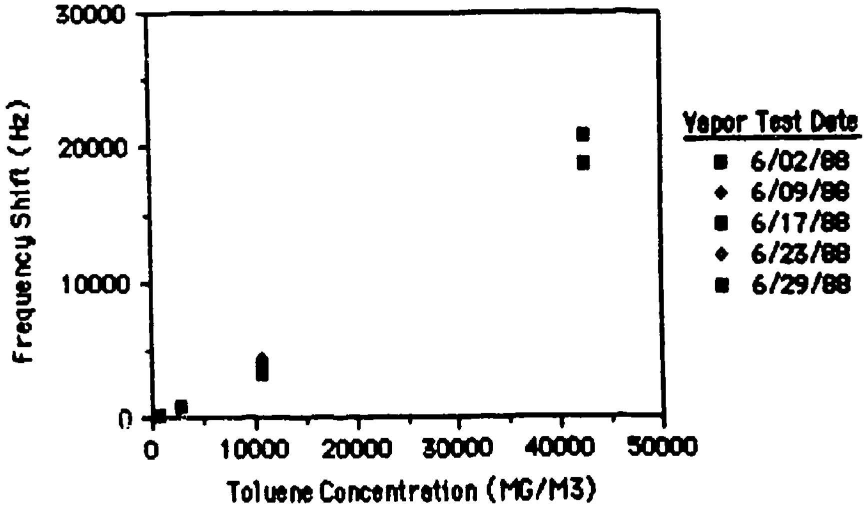


Figure 18b. Frequency Response vs Concentration for Toluene Vapor on FPOL Coated SAW Sensor 8818-13 as a Function of Time (Ageing).

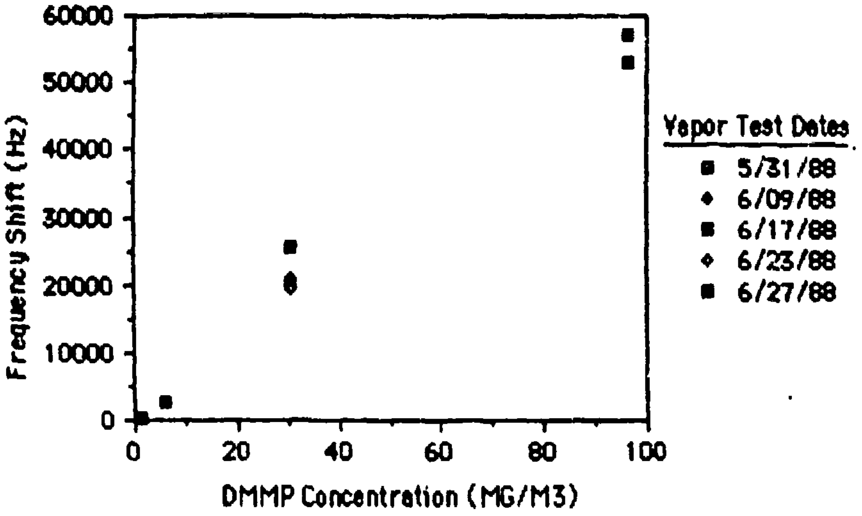


Figure 19a. Frequency Response vs. Concentration for DMMP Vapor on PIPFAI Coated SAW Sensor 8818-1 as a Function of Time (Ageing).

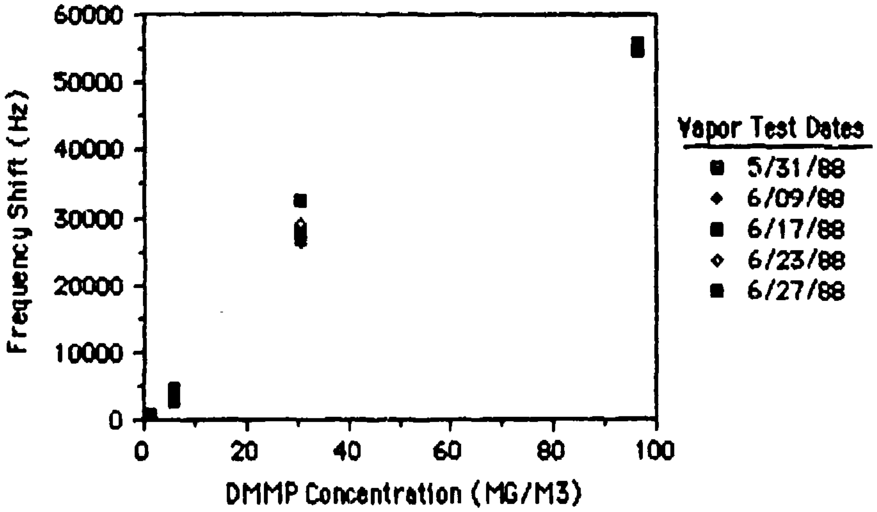


Figure 19b. Frequency Response vs. Concentration for DMMP Vapor on PIPFAI Coated SAW Sensor 8818-2 as a Function of Time (Ageing).

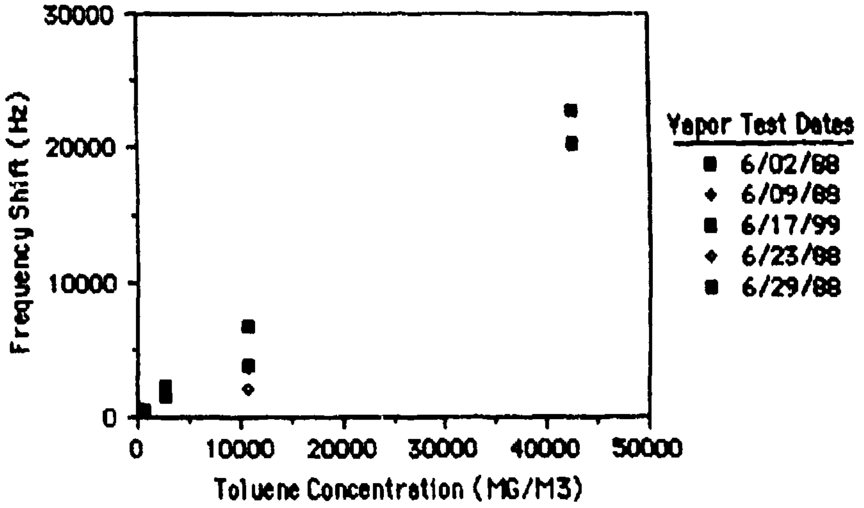


Figure 20a Frequency Response vs. Concentration for Toluene Vapor on Ethyl Cellulose Coated SAW Sensor 8818-17 as a Function of Time (Ageing).

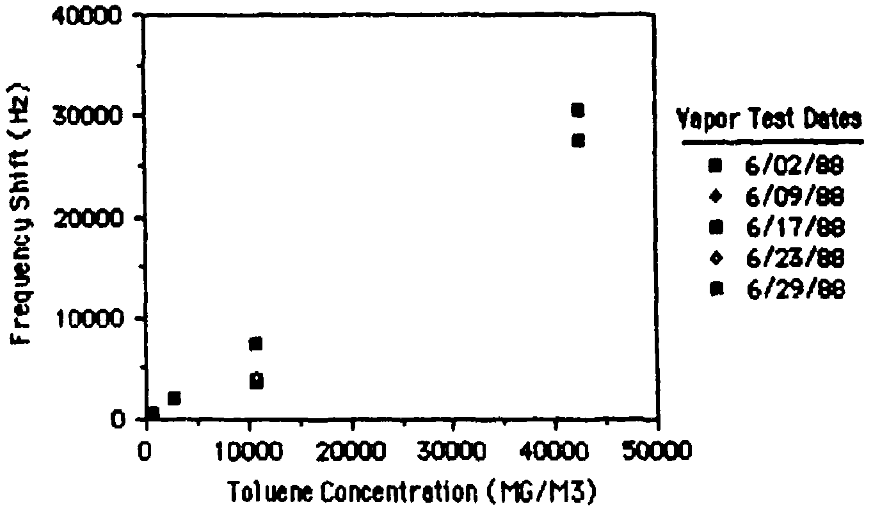


Figure 20b. Frequency Response vs. Concentration for Toluene Vapor on Ethyl Cellulose Coated SAW Sensor 8818-18 as a Function of Time (Ageing).

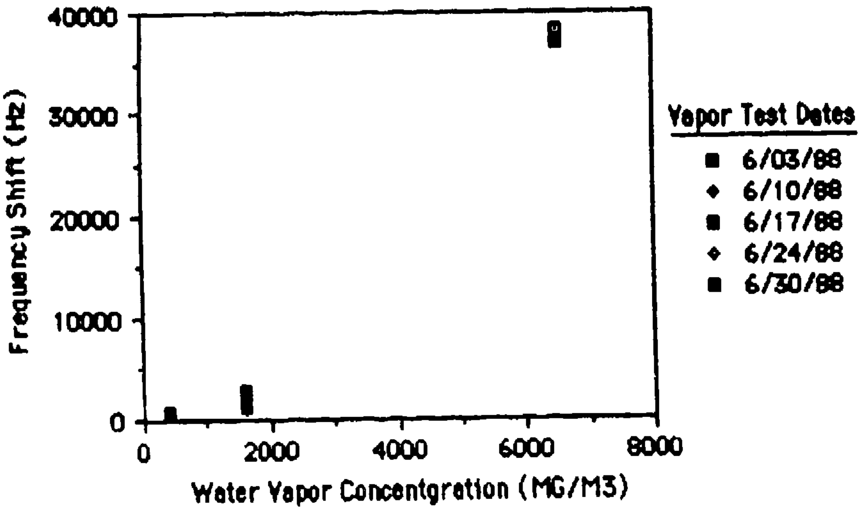


Figure 21a Frequency Response vs. Concentration for Water Vapor on Poly(ethyleneimine) Coated SAW Sensor 8818-5 as a Function of Time (Ageing).

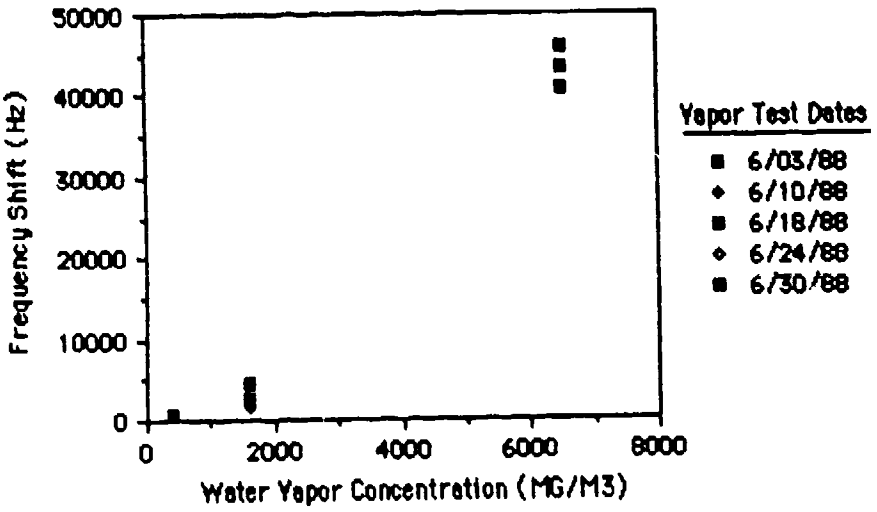
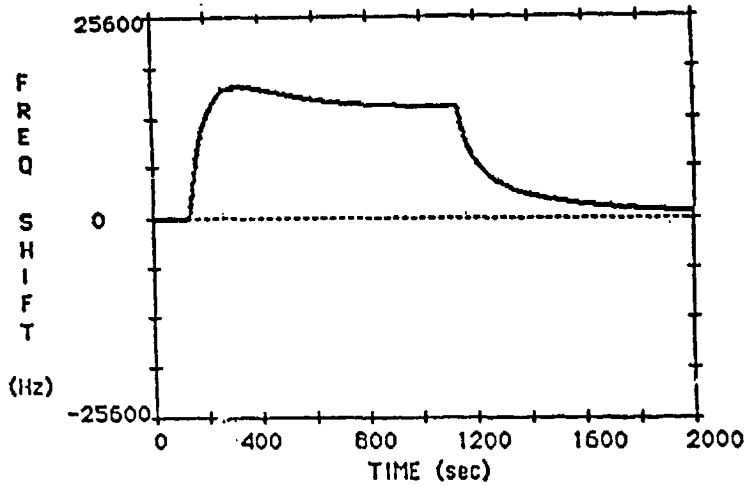


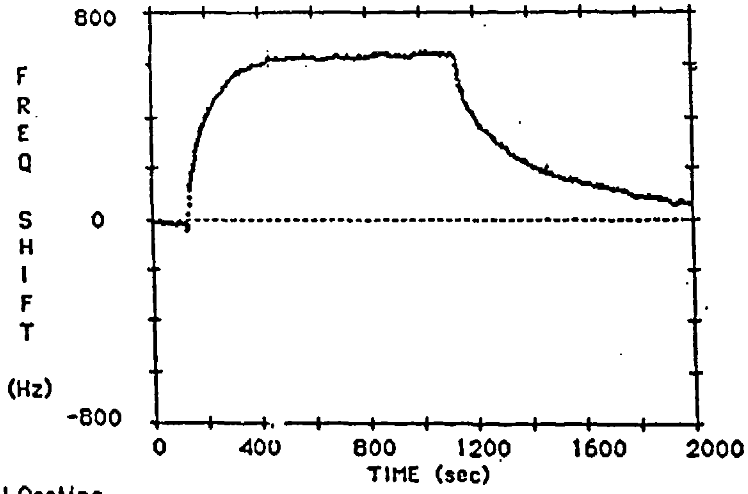
Figure 21b. Frequency Response vs. Concentration for Water Vapor on Poly(ethyleneimine) Coated SAW Sensor 8818-7 as a Function of Time (Ageing).

Figure 22. Frequency Response vs Time for DMMP on Coated SAW Sensors (96.2 mg/m^3, 115 ml/min flow rate, and 22.6° C)

a. Fluoropolyol Coating



b. Ethyl Cellulose Coating



c. PIPFAI Coating