SURFACE ACOUSTIC WAVE (SAW) PERSONAL MONITOR FOR TOXIC GASES

N. L. Jarvis, H. Wohltjen, and J. R. Lint
Microsensor Systems, Inc.
6800 Versar Center
Springfield, VA 22151

ABSTRACT

A demonstration model 4-sensor Surface Acoustic Wave (SAW) Personal Monitor for Toxic Gases was designed and built, with emphasis on minimizing the overall system size, weight, power consumption, and complexity. The completed demonstration unit contained four 158 MHz SAW delay lines, supporting RF electronics, microcomputer (microcontroller), a miniature pump, valve, gas transfer lines, and a small scrubber to provide a clean, dry, air source to establish sensor baseline frequencies. The demonstration unit weighs approximately 2 pounds. The projected size of the follow-on unit is expected to be 6" x 3" x 1". Unlike previous SAW vapor sensor arrays, which utilized coatings that interact reversibly with specific classes of toxic organic vapors, this SAW Personal Monitor takes advantage of sensor coatings that react irreversibly with toxic chemicals. Thus it can more easily and effectively determine total exposure to a given toxic gas. The following toxic inorganic gases were selected for study with the demonstration system: HCl, NO_2, SO_2, NO_2, H_2S and NH_3. Coating materials were selected that react irreversibly with each gas. The coatings were applied to the SAW sensors and their performance evaluated for exposure to a single gas. The results show that suitable materials are available for use as dosimeter coatings for SAW sensors. Thus the potential exists for developing an effective SAW Personal Monitor for detecting and monitoring each of the above gases, except NO_2, at concentrations well below the OSHA "action levels".

INTRODUCTION

In all areas of environmental monitoring, as well as industrial hygiene, there is a need for smaller, more sensitive, and inexpensive personal monitors (e.g., dosimeters) for toxic gases and vapors. For example, personnel involved in field screening must be concerned with their personal health and safety when working at a field site, and may often require accumulated exposure data for various toxic gases. SAW sensor technology, however, is not limited to use in a Personal Monitor (e.g., a toxic gas monitor that can be worn on clothing). The same sensor technology could be extended to the development of small, hand-held or in-situ monitors for a variety of field screening applications.

There are a number of techniques currently being used to acquire toxic exposure data, however, each have their limitations. In the future large numbers of more effective monitors will be required for the rapid and reliable detection and/or monitoring of toxic gases and vapors at ever lower concentrations, in response to increasingly stringent state and federal health and environmental regulations. Chemical microsensors have demonstrated the sensitivities and physical properties needed to meet the size, cost, and performance requirements of a new generation of personal monitors, and should ultimately find a wide range of applications within the industrial, medical, and environmental communities (1 - 13).

Of the chemical microsensors that have been investigated to date, SAW devices, which measure changes in mass when a chemically specific surface coating adsorbs or reacts with an appropriate gas, are the best characterized and the most promising for rapid development. SAW devices have been shown to respond in just seconds to selected vapors at concentrations down to the parts per billion range for specific organic chemicals. Because of their solid state construction and compatibility with integrated electronics, they can be easily incorporated into very small, lightweight instruments, small enough to be worn on clothing. The primary challenge remaining in the development of SAW based microinstruments is the development of more selective and sensitive SAW coatings for specific gases and vapors. Other technical areas to be addressed are the miniaturization of supporting electronic components and the development of computer software to facilitate sensor operation, data analysis, and data reporting.

OBJECTIVE

The objective of the present study was to demonstrate the feasibility of developing a miniaturized Surface Acoustic Wave (SAW) Personal Monitor with the size, sensitivity, selectivity, reliability, and low power consumption appropriate for wearing on clothing. To achieve this objective it was necessary demonstrate that: (1) the SAW sensors and necessary support electronics can be sufficiently miniaturized; (2) chemically selective SAW coating materials are available or can be developed for the detection of a wide range of toxic gases; and (3) the SAW sensors and their coatings can be sufficiently sensitive to specific toxic gases to meet the requirements of field screening, personal safety, and related monitoring applications.

SAW SENSOR INSTRUMENTATION

1. SAW Sensor Operating Principles

SAW devices are mechanically resonant structures whose resonance frequency is perturbed by the mass or elastic properties of materials in contact with the device surface. Rayleigh surface waves can be generated on very small polished chips of piezoelectric materials (e.g. quartz) on which an interdigital electrode array is lithographically patterned. When the electrode is excited with a radio frequency voltage, a Rayleigh wave is generated that travels across the device surface until it is "received" by a second electrode. The Rayleigh wave has most of its energy constrained to the surface of the device and thus interacts very strongly with any material that is in contact with the surface. Changes in mass or mechanical modulus of a surface coating applied to the device produce corresponding changes in wave velocity. The most common configuration for a SAW vapor/gas sensor is that of a delay line oscillator in which the RF voltage output of one electrode is amplified and fed to the other. In this way the device resonates at a frequency determined by the Rayleigh wave velocity and the electrode spacing. If the mass of the coating is altered, the resulting change in wave velocity can be measured as a shift in resonant frequency. SAW vapor/gas sensors are similar to bulk wave piezoelectric crystal sensors, except they have the distinct advantages of substantially higher sensitivity, smaller size, greater ease of coating, uniform surface mass sensitivity, and improved ruggedness. Practical SAW sensors currently have active surface areas of a few square millimeters and resonance frequencies in the range of hundreds of MHz. However, SAW devices having total surface areas significantly less than a square millimeter and resonant frequencies in the gigahertz range are possible using modern microlithographic techniques. Such devices would ultimately increase device sensitivity as well as decrease size. Most of the SAW vapor sensors reported in the literature employ two delay line oscillators fabricated side by side on the same chip, with one delay line used to monitor the toxic chemical and the other to act as a reference to compensate for changes in ambient temperature and pressure.

2. SAW Sensitivity and Selectivity

A 158 MHz SAW device having an active area of 8 mm^2 will give a resonant frequency shift of about 365 Hz when perturbed by a surface mass change of 1 nanogram. This sensitivity is predicted theoretically and has been confirmed experimentally. The same device exhibits a typical frequency "noise" of less than 15 Hz RMS over a 1 second measurement interval (i.e. 1 part in 10^7). Thus, the 1 nanogram mass change gives a signal to noise ratio of about 24 to 1. For vapor or gas sensing applications, the objective is to have the chemical selectively adsorb onto the mass sensitive surface of the device. Chemically selective coatings are used for this critical operation.

3. Selective Coatings

The operational behavior of a Surface Acoustic Wave device can be very sensitive to changes in density, elastic modulus, and viscosity of the surrounding medium; however, SAW devices are not inherently sensitive to the chemical properties of the medium surrounding the device. When coated with a chemically selective thin film they can exhibit remarkable sensitivity to small quantities of a chemical vapor or gas. The development of such selective coatings for toxic chemicals can take two directions, (1) coatings that will selectively and reversibly adsorb a selected vapor or gas by matching "solubility" characteristics; and (2) coatings that react chemically and irreversibly with a selected vapor or gas. SAW selectivities in excess of 10,000 to 1 for certain toxic chemical agents have been demonstrated using the "solubility" approach. Much greater selectivities should be possible using chemically reactive coating/vapor (gas) combinations.

SAW INSTRUMENTATION DEVELOPMENT

1. Miniaturization of SAW Sensor Array and RF Electronics

Ultimate miniaturization would be achieved by going to hybrid circuitry, where the sensors and support RF electronics could be reduced in size to a few cm^2 or less. Hybridization, however, will require a major engineering effort and was beyond the scope of this study. The emphasis was therefore on the selection and arrangement of the discrete components and electronic packages to minimize the size of the demonstration unit. The basic design of the system is essentially the same as used in previous SAW Vapor Monitors. The four coated SAW dual delay line devices were mounted in small, gold IC packages. The lids of each package were modified with short, 1/16" ID, gold plated gas inlet and outlet tubes to provide the toxic gases access to the sensors. A fifth SAW dual delay line, sealed to prevent exposure to the ambient environment, was place in a separate package. In the demonstration unit, this fifth device was used as a reference for all other sensors to compensate for changes in temperature and pressure. The output of the 4 SAW Sensor Array was integrated with a 4 channel frequency interface card to generate the measured

frequency differences, Δf, and with an onboard microcomputer (microcontroller) for data analysis.

2. Instrument Configuration

The system was designed with three circuit cards: a sensor card, a four channel frequency interface card, and a microcomputer card. The entire instrument will fit in an enclosure 4-3/4" x 8" x 3", allowing room for the necessary pumps, valves and gas transfer lines. The system was designed for either battery operation or with a 120 VAC 50-60 Hz power supply. 1/8" Swagelok bulkhead fittings on the enclosure provided gas inlet and outlet to the system. Except for the stainless steel Swagelok fittings on the front of the enclosure, all surfaces in contact with the gas up to the SAW devices are either Teflon or gold.

The four channel microcomputer controlled frequency counter measures and reports the frequency of each SAW sensor every two seconds while controlling the solenoid valves by means of a solid state relay. For laboratory evaluation of the demonstration model SAW Personal Monitor for Toxic Gases, the counter output is provided on a 9600 baud RS-232C serial communications line. For better control and monitoring of the demonstration model, and it's subsystems, all communication with the unit was through the RS-232 line and a personal computer with a serial communication port. In a follow-on program, a different communication scheme will be devised so that the user will have the option of entering all instructions directly on the instrument. Also, all concentration data and/or signals will be presented on visual (LCD) displays or by audio alarms mounted on the instrument enclosure. There will still be the option of communicating with the SAW Personal Monitor via a personal computer to retrieve data stored in memory.

In the demonstration unit, the onboard Octagon SB S-150 microcomputer was programmed to control operation of the system, but not for analysis of the sensor array data. Development of a sensor array data analysis program is planned for the follow-on effort. With the demonstration unit, the performance of each SAW sensor, and it's coating, was evaluated individually against a specific toxic gas. There are a number of experimental variables that also require computer control and or analysis. For example, due to the possible adsorption/desorption of ambient gases (especially water vapor) on the coatings, the computer must continually determine the actual baseline for each sensor, by intermittently providing clean, dry (filtered) air to the sensors. The computer must also store calibration data for each sensor and provide total exposure values on demand and/or activate an alarm when certain values are exceeded. Figure 1 provides a pictorial layout of a SAW Array Personal Exposure Monitor.

SAW COATING SELECTION

1. Selection of Candidate Coatings

A series of candidate materials was selected for screening as coatings for the SAW devices. They were selected on the basis of their known reactivity with the toxic gases chosen for evaluation. The coatings selected for screening against the reactive gases are given in Table 1.

Table 1. Candidate Coating Materials for SAW Sensors

Candidate Coating	Reactive Gas
Diphenylbenzidine	NO_2
2,4, Dinitrophenylhydrazine	NO_2
o-Toluidine	NO_2
Triethylenediamine (TEDA)	SO_2
$Na[HgCl_2]$ (hydrate)	SO_2
$Pb(C_2H_3O_2)_2 \cdot 5H_2O$	H_2S
$CuSO_4 \cdot 5H_2O$	H_2S
$K[Ag(CN)_2]$	H_2S
Ninhydrin	NH_3
$CoCl_2 \cdot 6H_2O$	NH_3
Polyvinylpyridine (PVP)	HCl

2. Coating of SAW Devices

Each of the above coatings was applied to two 158 MHz Saw devices. Each SAW device to be coated was inserted into a suitable connector mounted on a circuit board that contained the necessary electronics to operate the device and provide frequency signals to an external data aquisition system. Prior to coating, each dual 158 MHz SAW device was ultrasonically cleaned in isopropanol or chloroform, dried in a stream of compressed dry, zero air, and positioned in the coating apparatus. In all but a few instances, the coatings were applied by a spray deposition technique developed by Microsensor Systems. The primary requirement is that the coating material must be soluble in a volatile solvent. Zero air was used to generate a fine mist of the specific coating solution. A mask was placed over the SAW device so that only the interdigitated delay lines were coated.

The quantity of coating material deposited on each delay line was closely monitored by the computer data system which reported the mass of material deposited as an increase in frequency, Δf. The amount of coating material applied was held closely to 250 KHz ± 50 KHz. The frequency shift, Δf, corresponds to coating thickness, assuming uniform surface coverage. Once the coatings were applied, the SAW devices were covered and stored in a low humidity ($\le$ 10% RH) environment until ready for testing. As the candidate coating materials given in Table 1 are generally hygroscopic, it can be assumed that a certain amount of water will be associated with each coating and must be considered in subsequent gas interactions.

SAW ARRAY
PERSONAL EXPOSURE MONITOR
PICTORIAL LAYOUT

(PHASE II)

REPLACEABLE
SAW SENSORS
(4 UNDERNEATH
SCREW-ON LID)

2X24 CHAR. LCD DISPLAY

6-1/4"

I/O

SENSOR BOARD

I/O

INTERFACE BOARD

RS232 SERIAL COMM.

2"
(ASSEMBLED HT.)

MICROCOMPUTER
BOARD

4-1/2"

DC
MOTOR

AMBIENT
VAPOR
INLET

N.O.

SOLENOID
VALVE

COM

VENT

DIAPHRAGM
PUMP

N.C.

DESSICANT

6 V @ 1.2 Ah
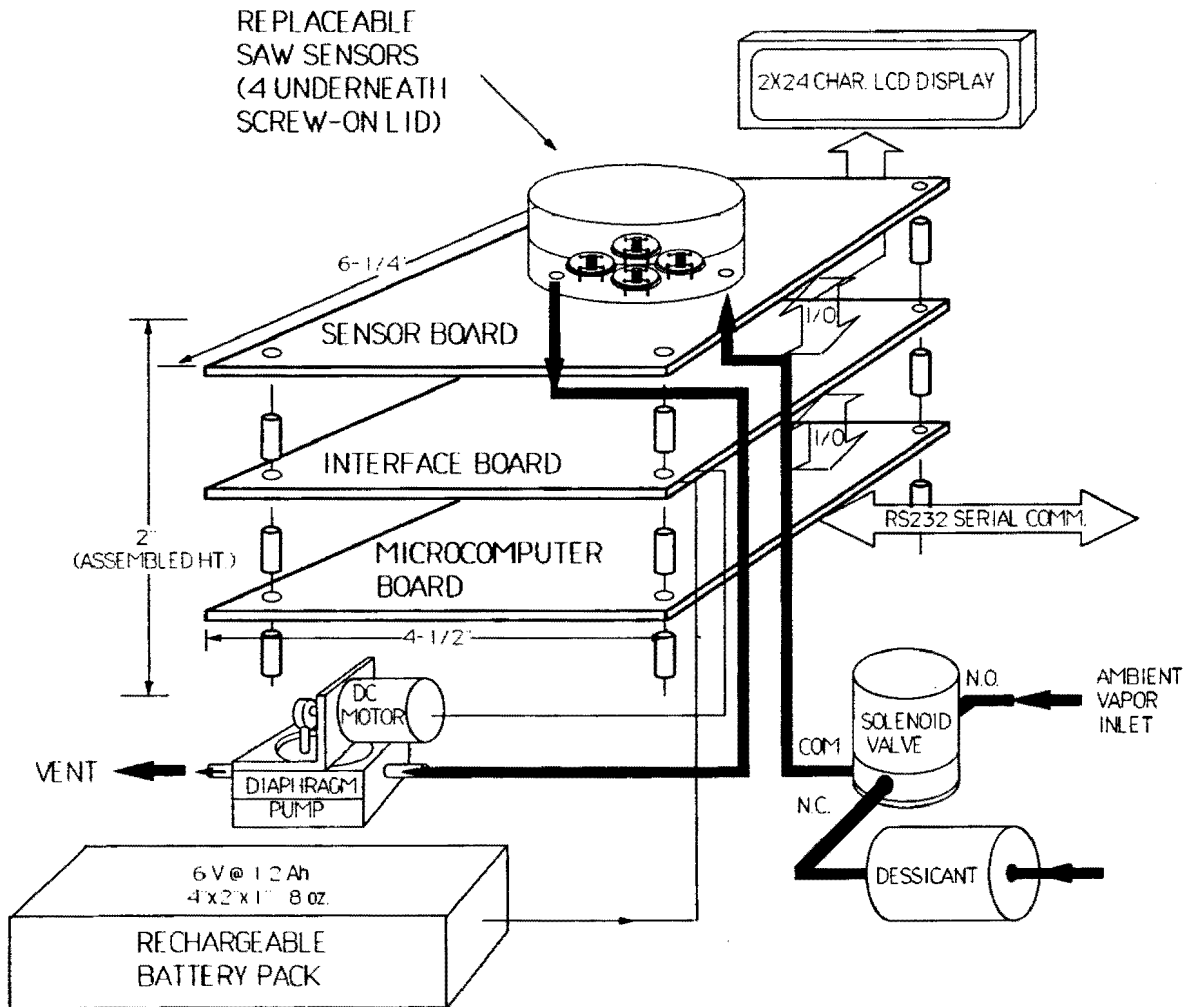4"x2"x1" 8 oz.

RECHARGEABLE
BATTERY PACK

Figure 1. Pictorial Layout of SAW Array Personal Exposure Monitor

3. Screening and Selection of Coatings for SAW Test and Evaluation

The following criteria were established to define a successful candidate material: (1) that a coating give a frequency shift equivalent to a 100:1 signal to noise ratio when exposed to the toxic gas at a concentration of approximately 100 ppm for 1 minute or less; and (2) that the coating react irreversibly with the test gas. With a baseline noise level of approximately 15 Hz, a 100:1 signal to noise ratio would be equivalent to a frequency shift on the order of 1500 Hz. Thin film coatings showing less response would not have sufficient sensitivity nor capacity to be useful in field monitoring applications.

A calibrated cylinder of each of the test gases (NO_2, SO_2, HCl, H_2S, NH_3) in air was obtained from the Scott Specialty Gas Co. The concentration of each gas source was:

Toxic Gas	Source Concentration
HCl	103.3 ppm
NH_3	106.5 ppm
H_2S	100.6 ppm
NO_2	108.0 ppm
SO_2	102.5 ppm

By simple dilution of the compressed gas with clean, dry, zero air, a steady state concentration at any value less than 100 ppm could be easily prepared. A constant gas flow rate of 200 cc/min was maintained. A valve was arranged so that clean air, or a known concentration of the specific test gas, could be alternately delivered to the sensor. A lid with 1/8" gold gas inlet and outlet tubes was placed over the device and was connected to the output of the gas dilution chamber. The frequency output of the dual delay lines could be monitored using a small frequency counter.

In the tests, a coated SAW device was first exposed to clean, dry air at 200 cc/min to obtain a steady baseline frequency. The valve was then turned to expose the sensor to a known concentration of the toxic gas, at the same flow rate, for a pre-determined period of time. The sensor was then exposed once again to clean, dry air to establish a new baseline. If the clean air baseline, after exposure to the toxic gas, was significantly different from the initial clean air baseline, it was assumed the change in frequency was due to an increase in coating mass resulting from the irreversible reaction with the challenge gas. If there was no significant change in SAW frequency, the device was exposed to higher gas concentrations for longer periods of times. If there was still no permanent change in baseline, it was assumed there was no reaction and that the coating, in its present form at least, was ineffective. All tests were performed with dry air, unless otherwise specified in the text.

The results of the initial screening tests are given in Table 2. They show that for each toxic gas there was at least one coating that gave an acceptable response. However, in several instances there were rather unexpected results. For example, NO_2 did not appear to react at all with 2,4 Dinitrophenyl hydrazine unless there was a relatively high

moisture content ($\approx$ 80% RH) in the carrier gas. It was also surprising that H_2S did not react readily with the lead acetate coating, even though we have observed this surface reaction in a previous study. Copper sulfate seemed unreactive initially, however, after repeated cycling it did react to give a very large and permanent frequency shift. The reaction, or lack of it, in each case may depend to a large extent upon the amount of water present in the film.

Table 2. Results of Initial Coating Screening Test
(Thickness of all coatings approx. 250 Hz)

Coating	Gas	Conc./Time	Δf (Hz)	Stable Reaction
Diphenylbenzidine	NO_2	50 ppm/60 s.	900	No
2,4, Dinitrophenyl hydrazine	NO_2	50 ppm/60 s.	2,800	Yes
o-Toluidine	NO_2	50 ppm/60 s.	<100	---
TEDA	SO_2	50 ppm/60	1,000	Yes
Na[HgCl2]	SO_2	50 ppm/60 s.	---	---
Pb(C2H3O2)2**	H_2S		---	---
CuSO4***	H_2S	50 ppm/60 s.	2,000	Yes
Ninhydrin	NH_3	50 ppm/ 60 s.	100	---
CoCl2	NH_3	50 ppm/ 20 s	2,700	Yes
PVP	HCl	(known to react)		

*   Reacted only in presence of high RH
**   Reacted in a previous study, but now
***   Reaction occurred after repeated H_2S exposure

Based on the results of Table 2, the following coatings were selected for more careful evaluation. 2,4 Dinitrophenyl-hydrazine was not used for NO_2. Rather TEDA was used for both SO_2 and NO_2.

Coating Material	Toxic Gas
Polyvinylpyridine (PVP)	HCl
Triethylenediamine (TEDA)	NO_2 and SO_2
Copper sulfate (CuSO4)	H_2S
Cobaltous chloride (CoCl2)	NH_3

TEST AND EVALUATION OF SAW SENSORS AS MONITORS FOR TOXIC GASES

1. Coating of SAW Sensors

The coating procedure used was the same as described above. Both SAW delay lines on each device were coated simultaneously, and the amount deposited was measured and recorded. The identification number of each device and the coating mass (in terms of frequency shift, Δf) are given in Table 3. The coatings applied are very thin, on the order of a micron or so in thickness, on the average.

2. Evaluation of SAW Sensors as Monitors for Toxic Gases

The frequency difference, Δf, of each SAW device being tested was input to a Apple Macintosh computer where the data was collected and displayed. The test system evaluated

77

only one sensor at a time against a single toxic gas. Even though each of the coating materials being tested could very likely react with more than one gas, binary gas mixtures and interference studies were not included in this preliminary investigation. Interference studies will be a part of the follow-on study, using multiple sensor arrays and other techniques to address the problem of sensor specificity.

The gas dilution chamber was again used to deliver known concentrations of each test gas to the SAW sensors at a constant flow rate of 200 cc/min at ambient pressure, and a constant "baseline" frequency established for each SAW device by exposing it to a clean, dry air stream. Once a constant baseline frequency was established, the sensor was exposed to a predetermined "dose" of the selected toxic gas. The size of the dose could be varied from 10 to 100 ppm over any selected time interval. After exposure to the toxic gas, the sensor was again exposed to clean, zero air until a new baseline frequency was established. The difference between the initial baseline and the final baseline was taken as the frequency shift due to the irreversible reaction of the toxic gas with the coating material. The magnitude of this frequency shift could be correlated with the amount of toxic gas interacting with the sensor.

The intent of the tests was to quickly look for order of magnitude changes in frequency and general reproducibility of performance when exposed to moderate changes in gas concentrations; i.e., to identify coatings that could be used in a more comprehensive follow-on development program. This study did not include a careful characterization of each coating reaction. In any event an accurate characterization of the surface reactions would be difficult without a more careful control of trace water, both in the hygroscopic coating materials and the gas delivery system.

3. Exposure of NH3 to CoCl2 Coated SAW Sensor

The SAW devices were at ambient temperature and thus subject to the room temperature fluctuations ($\approx 25^\circ$ +/- 1 C). Although a reference SAW device was used to compensate for both temperature and pressure changes, the compensation is not exact, and may have caused some small, random drift in device background frequency. These slow changes occurred in cycles of many minutes and thus did not adversely effect the measurements. Even though a number of the coating materials have a small volatility, the signal drift reflected "apparent" increases as well as decreases in weight. Thus volatility did not have a measurable effect on the measurements. Once a device was equilibrated with the laboratory environment (temperature and pressure) the slow baseline drift was usually on the order of ± 50 Hz. In addition to temperature changes and the possibility of volatility, the baseline drift may also be due in part to changes in gas flow rate (due to changes in flow through the non-precision needle valve used to set the flow rate). Even with the small observed background drift, the following data show that system performance was excellent and clearly able to detect and monitor changes in

SAW frequency upon exposure to the challenge gases. Sensor drift will be corrected for in the follow-on Personal Monitor development program.

An example of data for the exposure of ammonia to the CoCl2 coated SAW devices is shown in Figures 1. An exposure of 20 ppm NH3 for 20 seconds was selected for testing the CoCl2 coated sensors. When the NH3 was introduced, there was a large initial decrease in SAW frequency followed by a rapid increase. Each point on the curve corresponds to a 2 second time interval. After 20 seconds, when the clean air at 200 cc/min was again introduced, Δf continued to increase through a small maximum and then level off to a new, higher, baseline value. The initial negative "spike" in the Δf vs time plot may be due in part to disruption and re-establishment of a constant gas flow rate, while the subsequent increase in Δf most probably results from both adsorption and reaction of the NH3 with the CoCl2 coating. The maximum may result from a more gradual desorption of non-reacted NH3 from the coating. The equilibrium frequency shift values for all devices are shown in Table 4.
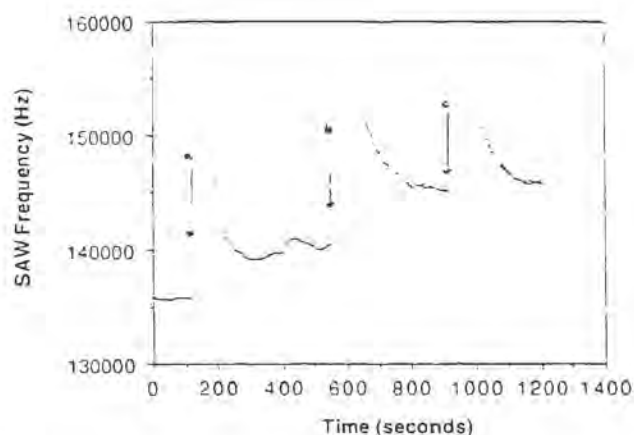

Figure 1. Frequency Shift (Hz) vs. Time for Repeat Exposure of CoCl2 Coated SAW Device (9024-11) to 20 ppm NH3 for 20 Sec.

Table 3. Thickness of SAW Device Coatings

Coating Material	Device Number	Coating Thickness (KHz) Side "A"
PVP	9024-1	255
	9024-2	198
	9024-3	198
CuSO4	9024-7	149
	9024-8	150
	9024-9	196
CoCl2	9024-10	136
	9024-11	112
	9024-12	106
TEDA	9024-4	149
	9024-5	178
	9024-6	300

Table 4. Frequency Shifts for CoCl₂ Coated SAW Devices Upon Repeated Exposure to 20 ppm NH₃ for 20 seconds

Table 4. Frequency Shifts for $CoCl_2$ Coated SAW Devices Upon Repeated Exposure to 20 ppm NH_3 for 20 seconds

Device Number	Exposure	Frequency Shift
9024-10	a. - d.	(dose optimization test)
(Coating 112 KHz)	e.	1,200 Hz
	f.	0 Hz
9024-11	a.	4,000 Hz
(Coating 136 KHz)	b.	4,000 Hz
	c.	1,000 Hz
9024-12	a.	2,600 Hz
(Coating 106 KHz)	b.	2,000 Hz
	c.	1,200 Hz
	d.	1,600 Hz
	e.	2,000 Hz
	f.	0 Hz

From the data in Table 4 it is evident that $CoCl_2$ coated SAW devices show large (Kilohertz), irreversible shifts in frequency when exposed to small doses of ammonia, and that with continued exposure the coatings saturate as expected. Even allowing for the variation is response of the different sensors, the sensitivity of the $CoCl_2$ coatings, i.e., those with some residual capacity, is on the order of 5 to 10 Hz/ppm/sec. Considering that the background noise level of the SAW sensors is on the order of 15 Hz, a ten seconds exposure of a sensor to 1 ppm NH_3 would give a signal of better than 50 Hz, at least three times the background noise. Thus the $CoCl_2$ coatings have more than enough sensitivity to detect ammonia at concentrations below the OSHA Exposure Limit of 50 ppm NH_3 for an 8 hour weighted average.

4.   Exposure of $CuSO_4$ Coated SAW Sensor to H_2S Gas

The test procedure was essentially the same as described above. Typical results are shown in Figure 2 for device 9024-7. H_2S shows a decrease in SAW frequency with exposure rather than an increase in Δf as observed with the reaction of NH_3 with the $CoCl_2$. Also, there was no initial "spike" in Δf when the challenge gas was introduced. Upon repeated exposure, the frequency shifts became progressively smaller, due to saturation of the reactive sites of the $CuSO_4$ coating.

The Δf values for the $CuSO_4$ coated sensors 9024-7 and 9024-8 are given in Table 5. SAW device 9024-9 apparently became defective during the coating process. SAW device 9024-7 was exposed five times to 20 ppm of H_2S for 20 seconds. With the initial dose of H_2S, Δf decreased by 1,400 Hz. The second exposure decreased Δf by only 400 Hz. Subsequent doses caused essentially no further change in Δf. Thus the $CuSO_4$ coatings were essentially saturated by a single 20 ppm dose of H_2S for 20 seconds.
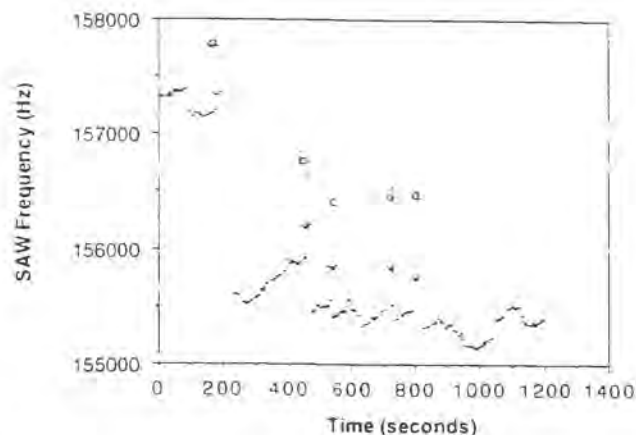

Figure 2. Frequency Shift (Hz) vs. Time for Repeat Exposure of CuSO4 Coated SAW Device (9024-7) to 20 ppm H2S for 20 Sec.

Table 5. Frequency Shifts for $CuSO_4$ Coated SAW Devices Upon Exposures to 20 ppm H_2S for 20 seconds

Device Number	Exposure	Frequency Shift
9024-7	a.	1,400 Hz
(Coating 149 KHz)	b.	400 Hz
	c.	100 Hz
	d.	0 Hz
	e.	0 Hz
9024-8	a.	1,400 Hz
(Coating 150 KHz)		
9024-9	(device defective after coating)	
(Coating 196 KHz)		

Thus the $CuSO_4$ coated SAW devices, like the $CoCl_2$ coated devices, do give large (KHz), irreversible shifts in frequency when exposed to small doses of an appropriately reactive gas, and that with continued exposure the coatings saturate as expected. The sensitivity of a newly prepared $CuSO_4$ coating is on the order of 3 to 4 Hz/ppm/sec. With background noise on the order of 15 Hz, a ten second exposure to 1 ppm H_2S would give a signal of around 30 to 40 Hz, equivalent to a signal to noise ratio of 2:1. The detection limit of this coating is thus also is well below the OSHA Exposure Limit of 20 ppm H_2S for an 8 hour weighted average.

5.   Exposure of TEDA Coated SAW Sensor to SO_2 Gas

The procedure used to test the TEDA coated SAW sensors with SO_2 was the same as described above. Typical results are shown in Figure 3 for device 9024-6. The results for device 9024-5 were similar. SAW device 9024-4 was reserved for testing with NO_2, which was expected to react with TEDA in much the same way as SO_2. A rather unexpected behavior was observed when the TEDA coated devices were initially exposed to SO_2. For the first few

exposures of 20 ppm SO₂ (20 seconds), the coatings did not respond significantly. After several repetitions, however, the coatings did begin to respond with positive shifts in Δf with the continuing exposure. Thus it appears there was a "conditioning" period, after which the coatings began to respond. The "conditioning" must be associated with some chemical change in the coatings upon exposure to the test gas, or to the zero air, most likely involving associated water. As each device, after being coated, was covered with a close fitting lid (but not hermetically sealed) and stored in a ≈ 10% RH environment, they must have adsorbed some water vapor (or perhaps another ambient gas) which was subsequently desorbed from the coatings by the dry (< 1% RH) zero air and/or the dry sample (SO₂) air. This "conditioning" or "ageing" effect was not further explored at this time, but will of necessity be investigated in the follow-on study in order to provide coatings that behave predictably and reproducibly.
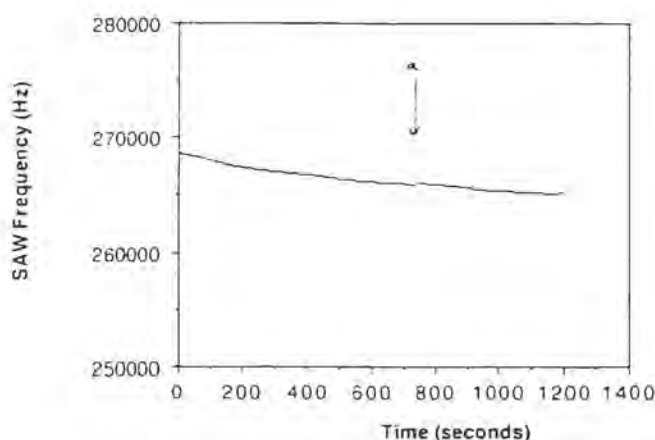

Figure 3(a). Frequency Shift (Hz) vs. Time for Repeat Exposure of TEDA Coated SAW Device (9024-6) to 20 ppm SO₂ for 20 Sec. (First exposure, a)
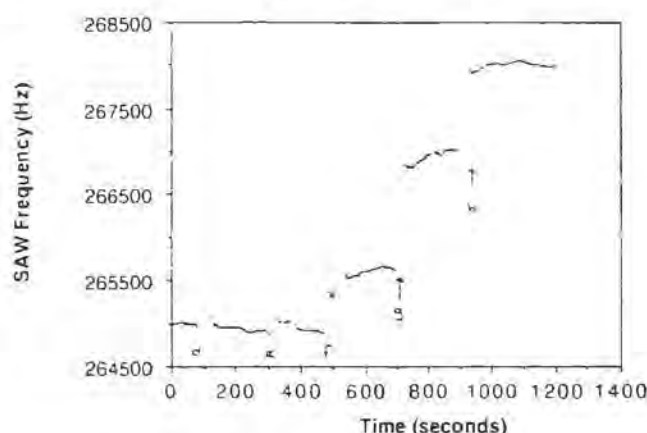

Figure 3(b). Frequency Shift (Hz) vs. Time for Repeat Exposure of TEDA Coated SAW Device (9024-5) to 20 ppm SO₂ for 20 Sec. (Exposures d to h)

After the initial induction period, the frequency shift vs time plot in both Figure 3(b) shows an increase in the SAW baseline with each 20 second dose of SO₂, after the initial "spike" in Δf. Device 9024-5 was allowed to stand in the test apparatus for approximately two hours with continuous exposure to zero air, before the run. Even so, it wasn't until exposure f that the device began to respond. Somewhat similar behavior was observed for device 9024-6, however the conditioning period was much shorter. For both device 9024-5 and 9024-6, once the coatings became reactive, the shifts in frequency were regular and irreversible.

The frequency shifts are given in Table 6. The data clearly show the induction period during which there was no effect of SO₂ exposure, and the subsequent increases in Δf when reaction began to occur. If we assume an average response of 1,200 Hz for device 9024-5 and 1,800 Hz for device 9024-6, the sensitivities are approximately 3 and 4.5 Hz/ppm/sec, respectively. The coating on device 9024-6 was a third again the mass of the coating on 9024-5 (300 KHz to 178 KHz), thus one would expect the sensitivity to SO₂ to be a third again as high, which was observed. Thus the two coated devices had essentially equivalent sensitivities.

Table 6. Frequency Shifts for TEDA Coated SAW Devices Upon Repeated Exposure to 20 ppm SO₂ for 20 seconds

Device Number	Exposure	Frequency Shift
9024-5	a.	0 Hz
(Coating 178 KHz)	b.	0 Hz
	c.	0 Hz
	d.	0 Hz
	e.	0 Hz
	f.	800 Hz
	g.	1,400 Hz
	h.	1,000 Hz
9024-6	a.	0 Hz
(Coating 300 KHz)	b.	0 Hz
	c.	200 Hz
	d.	1,600 Hz
	e.	2,000 Hz
	f.	1,800 Hz

With sensitivities of about 3 to 4 Hz/ppm/sec, depending upon coating thickness, and a background noise level of 15 Hz for the SAW devices, the sensors should ultimately detect concentrations of SO₂ as low as 1 ppm within 10 seconds at a signal to noise ratio of about 2:1. With this sensitivity, these coatings should easily detect SO₂ at or below the OSHA Exposure Limit of 5 ppm SO₂ for an 8 hour weighted average.

6. Exposure of TEDA Coated SAW Sensor to NO₂ Gas

It was anticipated that TEDA would respond to NO_2 in much the same manner as to SO_2; however, the data for the one available sensor showed quite different behavior. First, no conditioning period was observed. The first 20 second dose of 20 ppm NO_2 gave a relatively small but definite increase in SAW frequency which apparently saturated the sensor, as no further increase in Δf was observed with additional exposure to NO_2. The frequency shift data are given in Table 7. The baseline shift of approximately 350 Hz for an exposure of 20 ppm NO_2 for 20 seconds, is equivalent to about 1 Hz/ppm/sec, well below the sensitivity to SO_2. With a sensitivity of approximately 1 Hz/ppm/sec, and a background noise level of 15 Hz, the TEDA coated sensors would have to be exposed to 1 ppm NO_2 for over 30 seconds to give a 2:1 signal to noise ratio. In addition, the film apparently has a very low capacity for NO_2 (i.e., saturating at a very low exposure concentration). TEDA is therefore of only marginal utility as a dosimeter coating for NO_2.

Table 7. Frequency Shifts for TEDA Coated SAW Devices Upon Repeated Exposure to 20 ppm NO₂ for 20 seconds

Device Number	Exposure	Frequency Shift
9024-4	a.	350 Hz
(Coating 149 KHz)	b. - g.	0 Hz

7. Exposure of PVP Coated SAW Sensors to HCl Gas

Device 9024-1 was given 5 separate exposures to 20 ppm of HCl for 20 seconds, over approximately a 30 minute period, with no apparent reaction of the HCl with the PVP. We know from previous studies that surface films of PVP do react with HCl, thus the lack of response must be similar to the "conditioning" period observed for SO_2 gas on TEDA. To accelerate the reaction, the PVP coated device 9024-1 was exposed to a higher concentration of HCl (100 ppm) for 2 minutes. The result was a very large increase in Δf, over 30,000 Hz in the 2 minute period, as shown in Table 8. A second large dose (100 ppm over a 60 second period) further increased Δf by only 4,800 Hz, indicating that the PVP coating was approaching saturation. The estimated sensitivity, based on the 30,000 Hz shift is about 3 Hz/ppm/sec.

Device 9024-2 was exposed to repetitive doses of HCl at a concentration of 25 ppm for 20 seconds. The results given in Table 8 indicate no conditioning period was needed. The very first exposure gave an increase of about 900 Hz and appeared to be stable with time. Subsequent exposures also increased Δf, until the film began to saturate. Sensitivity based on the initial exposure is about 2 Hz/ppm/sec. Device 9024-3 did require a conditioning period when exposed to 25 ppm HCl for 20 seconds. HCl exposures were increase to 50 ppm for 30, 60 and 90 seconds, before an increase in Δf was observed. With the final exposure, a frequency increase of approximately 6,400 Hz was observed.

Table 8. Frequency Shifts for PVP Coated SAW Devices Upon Repeated Exposure to HCl

Device Number	Exposure	Frequency Shift
9024-1	a.(20 ppm 20 sec)	0 Hz
(Coating 255 KHz)	b.(20 ppm 20 sec)	0 Hz
	c.(20 ppm 20 sec)	0 Hz
	d.(20 ppm 20 sec)	0 Hz
	e.(20 ppm 20 sec)	0 Hz
	f.(100 ppm 120 sec)	30,000 Hz
	g.(100 ppm 60 sec)	4,800 Hz
9024-2	a.(25 ppm 20 sec)	900 Hz
(Coating 198 KHz)	b.(25 ppm 20 sec)	600 Hz
	c.(25 ppm 20 sec)	400 Hz
	d.(25 ppm 20 sec)	600 Hz
	e.(25 ppm 20 sec)	400 Hz
	f.(25 ppm 20 sec)	200 Hz
9024-3	a.(25 ppm 20 sec)	0 Hz
(Coating 198 KHz)	b.(25 ppm 20 sec)	0 Hz
	c.(25 ppm 20 sec)	0 Hz
	d.(50 ppm 30 sec)	0 Hz
	e.(50 ppm 60 sec)	0 Hz
	f.(50 ppm 90 sec)	6,400 Hz

The sensitivities of the PVP coated SAW devices were in the range of 1 to 3 Hz/ppm/sec. Device 9024-1, with the greatest apparent sensitivity (3 Hz/ppm/sec), had the highest coating mass, as would be expected. Thus the results for the three devices are consistent. With a sensitivity of 1 to 3 Hz/ppm/sec, a sensor would have to be exposed to 1 ppm HCl for 10 to 30 seconds to give a 2:1 signal to noise ratio. The PVP films do appear to have a high capacity for HCl, as evidenced by the 30,000 Hz shift for device 9024-1. Considering that the OSHA Exposure Limit is 5 ppm HCl for an 8 hour weighted average, the PVP coating should be considered a good candidate for further development as a coating for monitoring acid gases.

CONCLUSION

In the evaluation of the various SAW coatings it was found that for each toxic gas, except NO_2, a relatively large, easily measured SAW response was observed when an appropriate coating was exposed small concentrations. The measured sensitivities show that each toxic gas studied (except NO_2) could be detected by a SAW sensor well below the "action level" set by OHSA, when monitored for a period of one minute or less. The candidate coatings, toxic gases, and the respective OSHSA exposure limits, are:

Candidate Coating	Toxic Gas	OSHA Exposure Limit - 8 hour Weighted Ave.
polyvinylpyridine (PVP)	HCl	5 ppm
triethylenediamine (TEDA)	NO_2 and SO_2	5 ppm
copper sulfate ($CuSO_4$)	H_2S	20 ppm
colbaltous chloride ($CoCl_2$)	NH_3	50 ppm

The study thus successfully achieved it's objective of demonstrating that: (1) the SAW sensors and necessary support electronics can be appropriately miniaturized;

(2) a number of successful coatings are readily available and others can certainly be identified in the literature, or developed, for additional toxic gases; and (3) SAW sensors are sufficiently sensitive to meet OHSA requirements, at least for the toxic gases selected for this demonstration study. A number of technical problems and/or potential limitations of the technology were identified and approaches suggested for their solution. Based on the results of this program, we conclude that a prototype Surface Acoustic Wave Personal Monitor for Toxic Agents could be readily developed in a follow-on program. In addition to use as a Personal Monitor, such a small, sensitive and rugged solid state instrument could possibly find other applications in the field screening for toxic chemicals. In all applications however, the usefulness of SAW sensors will increase with the continued development of more sensitive and selective device coatings.

REFERENCES

1. H. Wohltjen and R.E. Dessy, "Surface Acoustic Wave Probe for Chemical Analysis I. Introduction and Instrument Design", Anal. Chem., 51(9), 1458-1464 (1979).

2. H. Wohltjen and R.E. Dessy, "Surface Acoustic Wave Probe for Chemical Analysis II. Gas Chromatography Detector", Anal. Chem., 51(9), 1465-1470 (1979).

3. H. Wohltjen and R.E. Dessy, "Surface Acoustic Wave Probe for Chemical Analysis III. Thermomechanical Polymer Analyzer", Anal. Chem., 51(9), 1 470-1475 (1979).

4. H. Wohltjen and H. Ravner, "The Determination of the Oxidative Stability of Several Deuterated Lubricants by an Electronic Gas Sensor", Lubrication Engineering, 39(11), 701-705 (1983).

5. (Invited) H. Wohltjen, "Chemical Microsensors and Microinstrumentation", Analytical Chemistry, 56(1), 87A-103(1984).

6. H. Wohltjen, "Mechanism of Operation and Design Considerations for Surface Acoustic Wave Vapor Sensors", Sensors and Actuators, 5 (4), 307-325 (1984).

7. H. Wohltjen, W. R. Barger, A. W. Snow, and N. L. Jarvis, "A Vapor Sensitive Chemiresistor Fabricated with Planar Microelectrodes and a Langmuir-Blodgett Organic Semiconductor Film", IEEE Trans. on Electron Devices, ED-32, No. 7, 1170-1174 (1985).

8. W.R. Barger, J.F. Giuliani, N.L. Jarvis, A.Snow, and H. Wohltjen, "Chemical Microsensors- A New Approach for the Detection of Agro Chemicals", Environ. Sci. Health, B20(4), 359-371 (1985).

9. W.R. Barger, A.W. Snow, H. Wohltjen, and N. L. Jarvis, "Derivatives of Phthalocyanine Prepared for Deposition as Thin Films by the Langmuir-Blodgett Technique", Thin Solid Films, 133, 197 206 (1985).

10. A.W. Snow, W.R. Barger, M. Klusty, H. Wohltjen, and N.L. Jarvis, "Simultaneous Electrical Conductivity and Piezoelectric Mass Measurements on Iodine-Doped Phthalocyanine Langmuir-Blodgett Films", Langmuir, 2, 513-519 (1986).

11. D.S. Ballantine, S.L. Rose, J.W. Grate, and H. Wohltjen, "Correlation of SAW Coating Responses with Solubility Properties and Chemical Structure Using Pattern Recognition", Anal. Chem. 58, 3058 (1986).

12. G. S. Calbrese, H. Wohltjen, and M.K. Roy, "Surface Acoustic Wave Devices as Chemical Sensors in Liquids", Anal. Chem. 59, 833 (1987).

13. J. W. Grate, A. W. Snow, D. S. Ballantine, Jr., H. Wohltjen, M. H. Abraham, R. A. McGill, and P. Sasson, "Determination of Partition Coefficients from Surface Acoustic Wave Vapor Sensor Responses and Correlation with Gas-Liquid Chromatographic Partition Coefficients", Anal. Chem. 60, 869 (1986).

DISCUSSION

WILLIAM BOWERS: You showed some data on individual sensor responses for single exposures. Have you done any interference effects on some of these? I am glad to see you're going to resonators now.

N. LYNN JARVIS: We did no interference studies in this particular program. You could probably tell that many of the coatings used would respond to more than one vapor. These were not selective coatings in that sense. Selectivity is much more difficult to get. That's why we end up using an array of sensors to get the selectivity. Resonators are much, much nicer.

MICHAEL CARRABBA: When you put the coating on these SAW devices, and the coating goes over electrodes, is the area on the whole surface sensing the weight or is it just the area between the electrodes, or the area on the electrodes?

N. LYNN JARVIS: The whole area surface senses the weight. The wave will cover most of the surface. Most of the surface is sensitive and you get a response.

PHILLIP GREENBAUM: Have you tried attaching antibodies to these? And if not, do you think that would be a problem?

N. LYNN JARVIS: We have not and you could certainly attach them. The problem is that antibodies are very large, and you're trying to attack very small molecules with the antibody. You may get a very small signal i.e., the change in weight is very small. Sensitivity might be fairly low in this case. It would not be a way we would probably choose to go with these particular sensors. There are probably better sensors for that.

MAHADEVA SINHA: Are these things disposable once you use them? After a certain while do you throw them out?

N. LYNN JARVIS: Yes. In this system, once a sensor is used up, we propose to it throw it away and plug in a new one.

MAHADEVA SINHA: You talked about the reversibility of some of the reactions. What did you mean by that?

N. LYNN JARVIS: There are two ways you can go with a coating on a SAW device. You can use coatings where the vapors absorb onto the coating, depending on solubility characteristics and other factors. They will absorb when the vapor is present. When the vapor challenge is removed, it desorbs again from this polymer and is removed. So it's a completely reversible system with certain vapor coating combinations. You can use a coating where there is no chemical reaction. However, if you have a chemical reaction, then it is completely irreversible, which is what we're looking for in this particular application. In some applications you want reversibility; in some you don't, depending on the intended use.

EDWARD POZIOMEK: In your last viewgraph and also in your comments you mentioned the possibility of the wide applications to environmental measurements, and you said something about putting a SAW down a well. Perhaps you could comment on the state of this SAW technology for use in liquids, because the applications presented here were for vapors or for gases.

N. LYNN JARVIS: If we put a sensor in a well, it would have to be within the well headspace to be monitored, not the liquid. The technology for SAWs in liquid is very poorly developed, and is just barely beginning. We know of no really effective way to monitor using a SAW in solution.

Second International Symposium

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

Symposium Proceedings

SECOND INTERNATIONAL SYMPOSIUM

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

CO-SPONSORS

U.S. Environmental Protection Agency

U.S. Department of Energy

U.S. Army Toxic and Hazardous Materials Agency

U.S. Army Chemical Research, Development and Engineering Center

U.S. Air Force

Florida State University

National Environmental Technology Applications Corporation

National Institute for Occupational Safety and Health