(2)

Naval Research Laboratory
Washington, DC 20375-5000

NRL Memorandum Report 6829

Surface Acoustic Wave Vapor Sensors Based on Resonator Devices

JAY W. GRATE AND MARK KLUSTY*

Surface Chemistry Branch
Chemistry Division

May 23, 1991

20030207006

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
1991 May 23

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
Surface Acoustic Wave Vapor Sensors Based on Resonator Devices

5. FUNDING NUMBERS
61-1639-E1

6. AUTHOR(S)
Jay W. Grate and Mark Klusty*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Chemistry Division
Naval Research Laboratory
Washington, DC 20375-5000

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL Memorandum Report 6829

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Technology
Naval Surface Warfare Center
Dahlgren, VA 22448-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
*Present address: Microsensor Systems, Inc., 6800 Versar Center Springfield, VA 22151

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Surface acoustic wave (SAW) devices fabricated in the resonator configuration have been utilized as organic vapor sensors and compared with delay line devices more commonly used. The experimentally determined mass sensitivities of 200, 300, and 400 MHz resonators and 158 MHz delay lines coated with Langmuir-Blodgett films of poly(vinyl tetradecanal) are in excellent agreement with theoretical predictions. The responses of LB- and spray-coated sensors to various organic vapors were determined, and scaling laws for mass sensitivities, vapor sensitivities, and detection limits are discussed. The 200 MHz resonators provide the lowest noise levels and detection limits of all the devices examined.

14. SUBJECT TERMS
Surface acoustic wave, resonator, vapor sensor

15. NUMBER OF PAGES
44

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
Unclassified	Unclassified	Unclassified	Unlimited

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

CONTENTS

SURFACE ACOUSTIC WAVE VAPOR SENSORS BASED ON RESONATOR DEVICES

INTRODUCTION

Interest in the use of surface acoustic wave (SAW) devices as chemical sensors increased rapidly during the past decade. Wohltjen first reported this method of chemical detection in 1979, and now several general articles and reviews have appeared (1-8). The SAW device responds to changes in the mass on its surface with a shift in frequency, and is most frequently used in gas phase sensing applications. A thin overlayer of a chemically selective material serves to collect and concentrate analyte molecules at the sensor's surface by sorption. The sensitivity of this type of sensor is dependent on the amount of vapor sorbed and the SAW transducers inherent ability to respond to the physical changes in the overlay film caused by vapor sorption. We define sensitivity as the incremental change in signal occurring in response to an incremental change in analyte concentration. The detection limits achievable depend on the vapor sensitivity and on the noise of the sensor's signal.

The vast majority of investigations of SAW chemical sensors have used SAW devices fabricated in the delay line configuration. Indeed, a review by D'Amico and Verona specifies the types of SAW devices utilized, and all those for chemical sensing were delay lines (4). An alternative SAW device configuration is the resonator. Whereas the delay line consists of metallized interdigital transducers on the ends of a planar piezoelectric substrate, the resonator has metallized interdigital transducers placed centrally on the planar device inside a resonant cavity defined by microfabricated reflectors. These two configurations are compared in Figure 1.

Manuscript approved April 2, 1991.

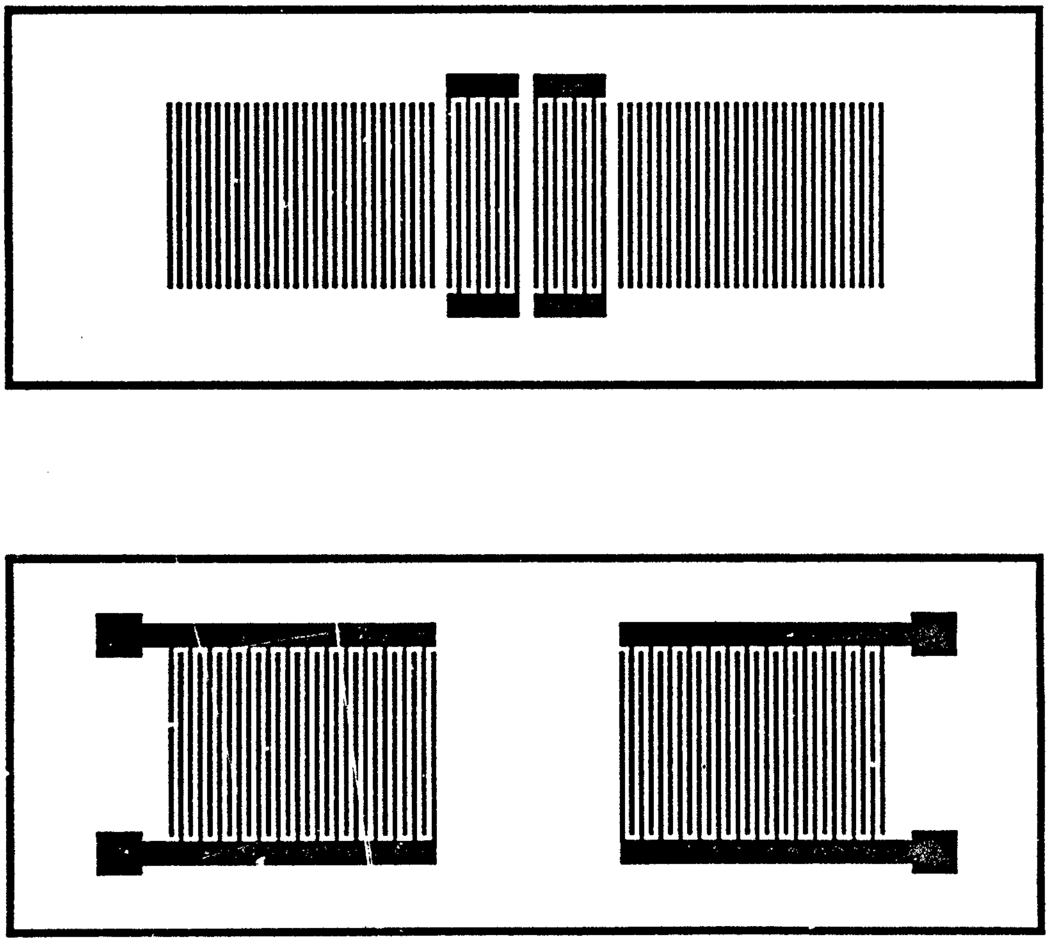

Figure 1. Schematic diagram comparing SAW resonator and SAW delay line devices.

We became interested in SAW resonator devices because of the possibility that chemical sensors based on these devices might have lower noise levels and hence yield lower detection limits than similarly coated devices based on delay lines. Bare SAW resonator devices have narrower bandwidths and higher Q values than delay lines, which results in lower noise levels (7,9). It remained to be established, however, whether resonator devices would tolerate soft organic coatings on their surfaces, and whether lower noise levels would be maintained after a coating had been applied.

To our knowledge, the first use of a SAW device in the resonator configuration for chemical detection was reported by Martin et al. (10). These authors prepared ZnO-on-Si resonators for organic vapor detection. The porous ZnO layer served as both the piezoelectric material and as the sorbent medium. No separate sorbent overlayer was applied. More recently 200 MHz quartz SAW resonators for analytical applications have been developed by Bowers et al. (11-13). These authors had investigated SAW delay lines for use in a cascade impactor for the collection and measurement of aerosols(14), and then developed their resonator-based system in order to improve baseline stability. They have also briefly reported the use of resonator devices with sorbent coatings as gas sensors (13).

In this paper we report the results of our investigations of 200, 300, and 400 MHz quartz SAW resonators for organic vapor detection, with emphasis on the performance of the 200 MHz devices. Soft organic coatings have been applied by both the Langmuir-Blodgett (LB) method and by spray-coating techniques. Mass sensitivities, vapor responses, and noise levels of these sensors are evaluated. In addition, scaling laws for SAW sensors are reconsidered. We demonstrate that increasing device frequencies and mass sensitivities does not necessarily lead to improved vapor detection limits.

EXPERIMENTAL SECTIONS

Materials. Poly(vinyl tetradecanal) was prepared from poly(vinyl alcohol) (J.T. Baker Chemical Co.) and tetradecanal (Pfaltz and Bauer, used as received) using HCl as the catalyst, using the procedures described in reference 15. (The properties of poly(vinyl acetals) in general are described in reference 16.) The product is a clear rubbery material with a glass transition temperature of 5°C. A density of 0.96 g/mL was determined by flotation in methanol / water mixtures.

The liquid organic solvents used to generate vapor streams were commercial chemicals of 99% or greater purity, except nitromethane (Fisher certified ACS, Assay 95.4%).

Saw Resonators and Oscillators. During the course of this study, we examined two port SAW resonators from Microsensor Systems, Inc. (Springfield, VA) and Femtometrics (Costa Mesa, CA). In each case, the resonators were originally manufactured by SAWTECH, INC. (Orlando, FL) on ST-cut quartz with aluminum metallization and a thin silicon dioxide overcoat. Each resonator is on a separate quartz chip. We began the study with resonators from Microsensor Systems, and unless otherwise noted, data in this paper are from these devices. Toward the completion of our study, we had the opportunity to examine a resonator system from Femtometrics.

200, 300, and 400 MHz resonators from Microsensor Systems were mounted on 4 pin round TO-6 headers, one resonator chip per header. Electrical connections were made via gold wire bonds. The oscillator boards for each frequency device were identical except for the tuning inductors. The boards contained two sockets for SAW resonators, an oscillator circuit for each of these resonators, and a mixer circuit to provide the difference in frequency between the two. This configuration is shown schematically in Figure 2. It is directly analogous to the configuration used for dual SAW delay lines, except that the resonators are packaged separately. One resonator serves as a constant reference frequency; a lid was epoxied onto the reference device to seal it from the atmosphere. The second resonator is the sampling device. Changes in the frequency of the sampling sensor can be followed from its frequency directly, or from the low frequency difference signal provided by the mixer circuit. We normally monitored the difference frequency.

The resonator devices on the Microsensor Systems oscillator boards are separated by 4 cm, center to center. Their temperatures were controlled in our laboratory using a single brass heat sink clamped against the lids of both devices. Water from a refrigerated circulating water bath circulated through the brass heat sink. All experiments were conducted at 25°C. Temperatures were monitored with a Cole Parmer Thermister Thermometer (Model N-08502-16) and YSI 427 small surface probes.

200 MHz resonators from Femtometrics were mounted on 6 pin rectangular headers, two SAW resonators per header. (The 200 MHz resonators from Femtometrics and Microsensor Systems are the same SAWTECH chip; however these two vendors package them differently.) One resonator serves as the reference and the other as the sampling device. A circuit board with two oscillator circuits and a mixer circuit drives the devices. We monitored the difference frequency. The Femtometrics configuration for the 200 MHz resonators is shown in Figure 3. This system has been described previously (11-13).

SAW Delay Line Devices. The 158 MHz SAW dual delay line devices and oscillators used in this study were described in detail in reference 17 and are also reported in references 14, 18, and 19. These SAW devices have two delay lines on one ST-cut quartz chip, mounted on a TO-8 header. The interdigital transducers are aluminum and they are covered with a thin protective layer of silicon dioxide. The oscillator circuitry allows the individual delay line frequencies and their difference frequency to be monitored. Power (5 VDC) was supplied by a Micronta adjustable dual-tracking DC power supply. In this study, both delay lines were coated with poly(vinyl tetradecanal) and the individual frequency of one delay line was monitored. Thus, it was operated as a single delay line device. The device was covered and sealed with a nickel-plated lid with two stainless steel tubes for gas flow inlet and outlet.

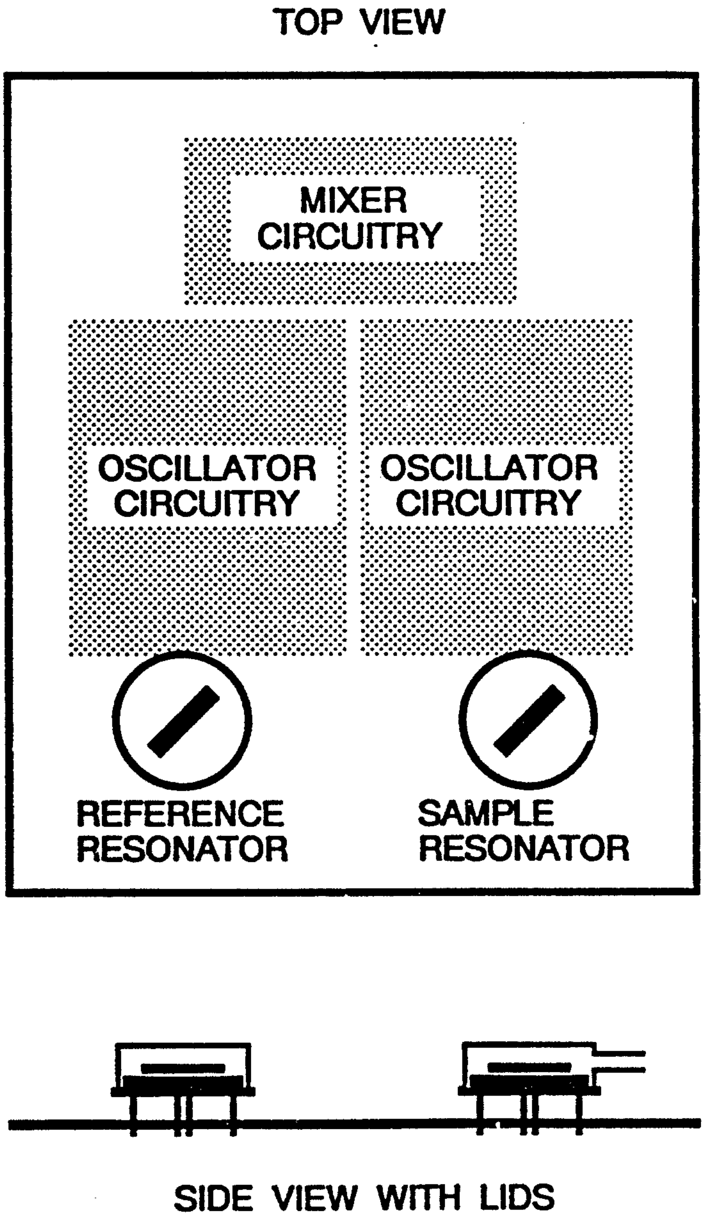

Figure 2. Schematic diagram of the Microsensor Systems dual SAW oscillator board with separately packaged SAW resonators.

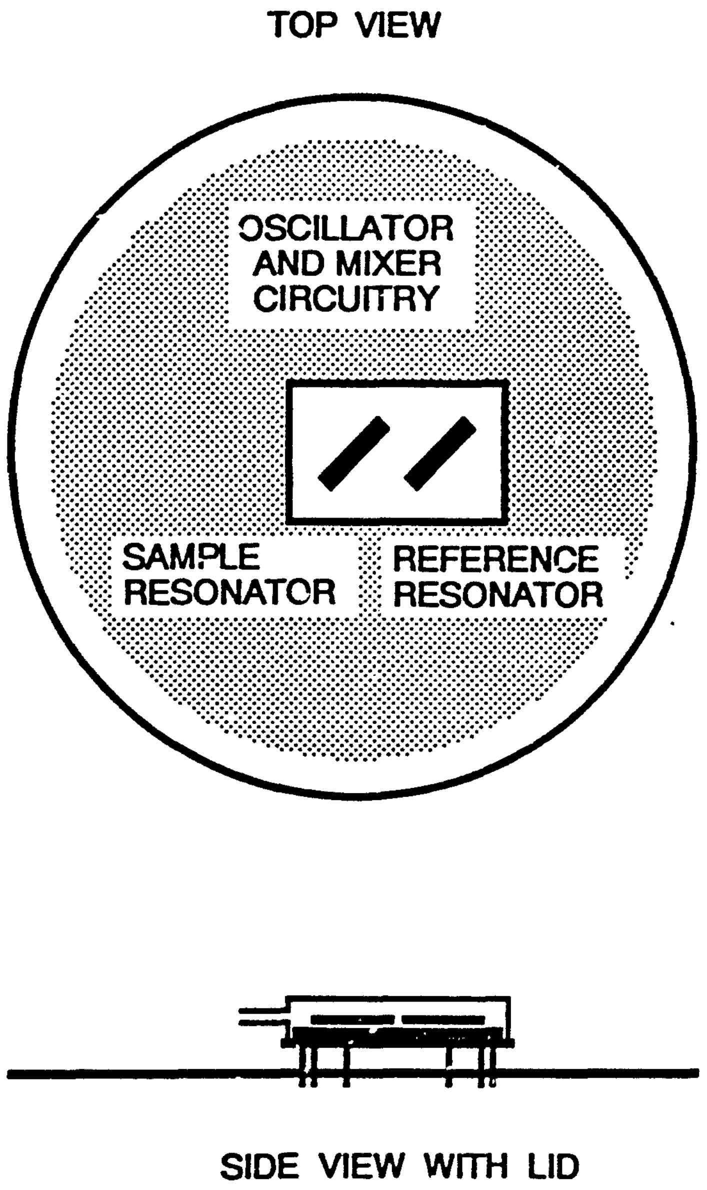

Figure 3. Schematic diagram of the Femtometrics dual SAW oscillator board with two SAW resonators mounted on one header.

Frequency Data Collection. Frequency measurements were made using Phillips PM6674 frequency counters with TXCO, transferring the data to a microcomputer using the IEEE-488 bus. Low frequency difference signals from the mixer circuits of SAW resonator oscillators were collected at a resolution of 0.02 Hz or less. Individual delay line frequencies were collected from the coated 158 MHz dual delay line sensors: these data were collected at 2 Hz resolution. Routine noise measurements were typically determined from frequency data collected for 4 min at 10 points per min. The noise was taken as the standard deviation of the residuals of the linear least squares line through the data. Usually, several such measurements were conducted consecutively. During vapor exposure experiments, baseline noise was determined using baseline frequency data collected at 5 points per min for 10 min prior to vapor exposure

Spray-coated Polymer Films. Spray-coated films were applied using an airbrush supplied with compressed dry nitrogen and a dilute solution of the polymer in HFLC-grade chloroform (Aldrich). The polymer was applied over the entire surface of the sampling SAW sensor. The SAW frequency was monitored during deposition; the change in frequency provides a measure of the amount of material applied. To begin coating, the airbrush was placed several inches away from the SAW device and spraying was initiated with the nozzle directed away from the device. Then the spray was passed over the device several times, followed by a pause to observe the change in frequency. This process was repeated many times until the desired frequency change was obtained.

Spray-coated films were examined by optical microscopy with a Nikon Optiphot M microscope using reflected light Nomarski differential interference contrast.

Langmuir-Blodget Film Deposition. The Langmuir trough used to deposit poly(vinyl tetradecanal) films on the SAW resonators was the same trough used in previous studies (20-22); details can be found in reference (23). Water used as the subphase was triply distilled, with the last two distillations from an all-quartz still. Solutions of poly(vinyl tetradecanal) were prepared in chloroform at precisely known concentrations near 0.5 mg/mL. The surface mass density of poly(vinyl tetradecanal) was determined from film pressure vs. area isotherm

(25°C) measurements; repeated determinations gave a value of 156 ng/cm^2 area density at 20 dynes/cm surface pressure.

Films were applied to the 200, 300 and 400 MHz SAW resonators mounted on the TO-6 headers by the vertical dipping technique at 20 dynes/cm surface pressure. The first layer was applied beginning with the device submerged. The dipping velocity was 4.2 x 10^{-4} m/s, with the device being coated allowed to dry in air for 5 min after each down-up cycle. During film transfer, the area of the film on the trough surface decreases in proportion to the area of the device being coated. Care was taken to monitor these surface area changes closely to be sure the film transfer was proceeding effectively. When anomalies were observed, the dipping was discontinued and no further dipping or frequency measurements were made on that device.

When resonators were coated for the mass sensitivity studies described below, the LB coating process was interrupted periodically for intermediate frequency measurements before the final numbers of layers were reached. In preparing resonators for vapor sensitivity studies, the desired total number of LB layers were applied to initially bare devices with no interruptions for intermediate frequency measurements. The 158 MHz dual delay line device on the TO-8 header was coated similarly. Both delay lines were covered by the film.

Mass Sensitivity Determinations. The device to be coated was placed in the sample socket of the oscillator board with a sealed reference device in place. A lid with gas inlet and outlet tubes was placed on the sample device and the thermostatted (25°C) heat sink was clamped into position. Dry nitrogen flowed over the device at 120 mL/min. After a period for warm up and temperature stabilization, the difference frequency was recorded. In addition, noise measurements were performed by collecting frequency data, usually at six second intervals for four minutes (≈40 points). Five such sets of data were collected consecutively and the noise for each set was determined as described above.

The sample device was removed and a predetermined number of LB layers of poly(vinyl tetradecanal) were applied. The device was returned to the oscillator board and allowed to stabilize for at least an hour. Frequency and noise measurements were made as just described. The device was returned to the LB trough and additional layers added. If no difficulties were encountered in adding these layers, frequency and noise measurements were made again, and the process was continued. If anomalies were observed during deposition, the process was started anew with a bare device. When excessive layers were applied, the devices would not oscillate.

It was found that long delays (> a day) after frequency measurements on a deposited film resulted in difficulties when efforts were made to apply additional layers. When freshly deposited, these multilayers are organized with the outer surfaces of odd numbered layers being hydrophobic. It is likely that the layers of this elastomeric material slowly disorganize by thermal segmental chain motion, altering the properties of the outermost surface to which subsequent layers must transfer.

Vapor Exposure Experiments. Vapor streams were generated from bubbler sources and diluted using a Microsensor Systems VG-7000 vapor generation instrument. The bubblers were maintained at 15°C in machined aluminum blocks with inlets and outlets for water from a refrigerated circulating water bath. The carrier gas for bubbler vapors was dry nitrogen supplied to the bubblers at 120 mL/min with electronic flow controllers. The saturated bubbler vapor streams were diluted by the VG-7000 using a pulse-width modulation method which we describe in detail in reference 24. The experiments in this paper were all conducted with the saturated(at 15°C) vapor streams diluted by a factor of 4. Finally, the instrument output can be either the diluted vapor stream or clean carrier gas, each at a flow rate of 120 mL/min.

Saturated vapor streams were calibrated gravimetrically by trapping the vapor in tared glass tubes containing activated charcoal and molecular sieves in series. These calibrations were in agreement with vapor concentrations calculated from published vapor pressures and the ideal gas law.

The VG-7000 was connected to a Macintosh computer with a serial communications line. We delivered commands for each experiment using a communications program (Smartcom II); sequences of experiments were programmed using the macro or "autopilot" capabilities of this program.

Sensor exposure experiments were carried out by first generating and equilibrating a vapor stream for 45 min while delivering clean carrier gas to the sensor. Vapor was then delivered to the sensor for 5 min, followed by 10 min of clean carrier gas for sensor recovery, another 5 min of vapor to check response reproducibility, and another 10 min of clean carrier gas. Thus each experiment takes 75 min. Sensor frequency data were collected every 12 sec beginning 10 min prior to the first vapor exposure. The two consecutive exposures were quite reproducible. Poly(vinyl tetradecanal)-coated sensors responded to >90% of steady-state response within two data points after the beginning of a vapor exposure, and recovered in a similar period of time when the vapor stream was replaced with clean carrier gas. The numerical data reported in the tables are taken from the frequency shifts observed during the first exposure.

Before each 75 min experiment described above, a 75 min control experiment was run to insure that no residual vapors were present in the instrument that could cause a sensor response. The carrier gas flows and timing of the control experiment were identical to those of the subsequent vapor experiment, except that the bubbler was bypassed. The 45 min equilibration time served to flush out any traces of vapor which may have adsorbed to tubing walls during the previous experiment. Following the sensor frequency during the subsequent 'vapor'/clean carrier gas output cycles provided an experimental determination that the system is adequately flushed. If the sensor frequency shifts were absent or negligibly small, then the response in the subsequent experiment was certain to be due to the vapor from the bubbler selected.

As a further quality check, a 158 MHz dual delay SAW vapor sensor whose response characteristics are well-known to us was always placed in series after the experimental sensor and its responses were monitored. The consistent responses of this sensor from data set to data set confirmed that the programmed vapor streams were being generated and delivered.

RESULTS AND DISCUSSION

Mass Sensitivities. We will define mass sensitivity as the incremental signal change in response to an incremental change in the mass per unit area on the SAW device surface. The signal change is a shift in the frequency of the oscillator expressed in Hz or kHz. We determined the mass sensitivities of our devices by applying thin polymer overlayers of known mass per unit area by the LB technique. The effect of a thin non-conducting overlay film of thickness h and density ρ on the frequency of a SAW device has been described by Wohltjen (2) as

$$\Delta f_s = (k_1 + k_2) F^2 h \rho - k_2 F^2 h (4 \mu / V_R^2) [(\lambda + \mu)/\lambda + 2\mu)] \qquad (1)$$

In this equation, F is the fundamental resonant frequency of the oscillator, and Δf_s is the change in frequency caused by the film. The constants k_1 and k_2 are material constants for the piezoelectric substrate, and V_R is the Rayleigh wave velocity in that substrate. The parameters λ and μ describe the physical properties of the overlay film material, being the Lame' constant and the shear modulus, respectively.

The first term in eq 1 represents the mass sensitivity, and is often simplified to

$$\Delta f_s = (k_1 + k_2) F^2 m / A \qquad (2)$$

The film mass per unit area, m / A, replaces h / ρ; both terms have the same units. This equation shows that the absolute mass sensitivity of the SAW device depends on the physical properties of the piezoelectric substrate and on the square of the operating frequency. The theoretical calculation of mass sensitivities is straightforward.

The second term in eq 1 represents the effect of film stiffness on device frequency. For soft materials, e.g. with $\mu = 10^7$ dynes/cm^2 or less and densities near 1 g/cm^3 (values typical of rubbery amorphous polymers), this term is negligible relative to the first and mass sensitivity alone (eq 2) is sufficient to describe the effect of the film. For stiffer materials with $\mu = 10^{10}$ dynes/cm^2 and densities near 1 g/cm^3 (values typical of glassy amorphous polymers), the second term is 10 to 15% of the absolute value of the first term. It is likely that amorphous polymers above their static glass transition temperatures appear to be stiffer than 10^7 dynes/cm^2 under the dynamic operating conditions present on the SAW device surface. Periodic strains induced by acoustic waves coupled into the polymer layer at high frequencies may raise the temperature at which the polymer chains relax (1,25). If this is the case, then the polymer will appear to be stiffer than a static rubbery material, but its dynamic stiffness will likely not be greater than that of a polymer glass. Ignoring the second term when calculating the effect of a rubbery polymer layer on the SAW frequency may introduce an error which is unlikely to exceed 10-15%.

For our experimental determination of device mass sensitivities we selected the LB method to apply continuous thin films to the device surfaces. The Langmuir-Blodgett (LB) method is well suited to the application of thin organic films one layer at a time, and provides an experimental measure of the mass per unit area of the film (26,27). The material we required for these studies and following experiments on vapor sorption had to meet three requirements. First, the material had to be suitable for deposition by the LB method so that it could be reliably applied in layers of known mass per unit area. Second, we desired a polymer which was well above its static glass transition temperature at room temperature so that the contribution of the second term in eq 1 would be minimal, and we could then compare our experimental results with theoretical results calculated according to eq 2. Third, the material needed to be a reasonable sorbent for organic vapors, and rapid vapor diffusion into the material was desirable. The third requirement also suggests the choice of a polymer above its static glass transition temperature.

Oguchi et al. have demonstrated in very thorough studies that poly(vinyl acetals) with linear aliphatic side chains are well suited for LB deposition (15). These polymers are prepared by acetalization of poly(vinyl alcohol) with linear aldehydes under acid catalysis as shown in Figure 4 (15,16). The reaction leaves some of the polymer hydroxyl groups unreacted; acetalization is typically 70-95%. When the material is applied to the LB trough the residual hydroxyl groups can

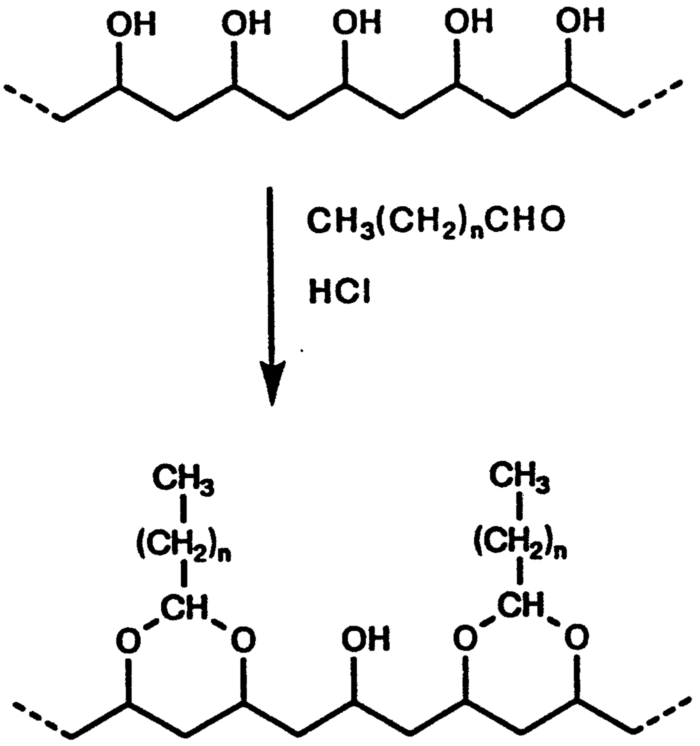

Figure 4. Synthesis and structure of poly(vinyl acetals). In this study, poly(vinyl tetradecanal), $n = 12$, was used for mass sensitivity calibrations and as the sorbent layer in vapor response experiments.

interact with the aqueous subphase. Oguchi et al. found that LB layers of poly(vinyl acetals) could be easily deposited onto various substrates when the side chains were derived from linear aldehydes with four or more carbons.

The glass transition temperatures of poly(vinyl acetals) decrease with increasing chain length of the starting aldehyde. For lengths longer than about eight carbons, the transitions occur at or below room temperature. Oguchi et al. obtained materials with glass transition temperatures of 25, 21.5, 13, 3 and 5°C from octanal, decanal, dodecanal, tridecanal, and tetradecanal, respectively. We therefore selected LB films of poly(vinyl tetradecanal) for our mass sensitivity studies.

LB layers of poly(vinyl tetradecanal) were applied to the 200, 300, and 400 MHz SAW resonators as described in the Experimental section. The frequency shifts observed with the applications of these layers are given in Table 1 and plotted in Figure 5. These results show quite clearly that the frequency shift increases linearly with the number of deposited layers, and that the sensitivity to these layers increases with device frequency. The slopes of the lines give the mass sensitivities in Hz per layer. These values are converted to absolute mass sensitivities in Hz per ng using the surface density of 156 ng cm^{-2} per layer, determined experimentally. The results are given in Table 2 and compared with the predictions of eq 2 (using values of -8.7×10^{-8} and -3.9×10^{-8} for k_1 and k_2, respectively) (17,28). The agreement is excellent.

We also have single mass sensitivity determinations for each of two SAW delay lines. These data were obtained when the entire surface of a dual delay line device was coated with LB multilayers for vapor exposure experiments. Application of 49 LB layers produced frequency shifts of 247 kHz on each delay line, which gives a mass sensitivity of 5040 Hz/layer or 32.3 Hz per ng/cm^2. The theoretical mass sensitivity according to eq 2 is 4910 Hz per layer or 31.5 Hz per ng/cm^2. Again, the agreement between experiment and theory is excellent.

Table I. Shifts in SAW Resonator Frequencies in Response to Mass-Loading with Langmuir-Blodgett Layers of Poly(vinyl tetradecanal)

200 MHz			300 MHz			400 MHz		
#[a]	Layers[b]	-Δf_s, Hz[c]	#	Layers	-Δf_s, Hz	#	Layers	-Δf_s, Hz
21	11	78000	31	1	18240	41	1	35700
22	21	173300	32	11	197100	42	11	354160
"	31	260700	33	15	274800	"	15	467580
"	41	342700	"	25	433560	"	19	575420
23	11	91400	34	31	555210	43	7	204680
"	21	172800	35	15	259170			
24	41	325720						
"	55	447550						
"	69	562590						
25	31	243030						

[a] Device number.

[b] Number of LB layers applied.

[c] Shift in frequency due to the LB layers.

Table II. **Comparison of Experimental and Calculated Resonator Mass Sensitivities**

Device Frequency MHz	Shift per LB Layer Hz/layer		Shift per Mass per Unit Area Hz/ng/cm^2	
	Exp.	Calc.	Exp.	Calc.
200	8140	7860	52.2	50.4
300	17700	17690	114	113
400	30800	31450	197	202

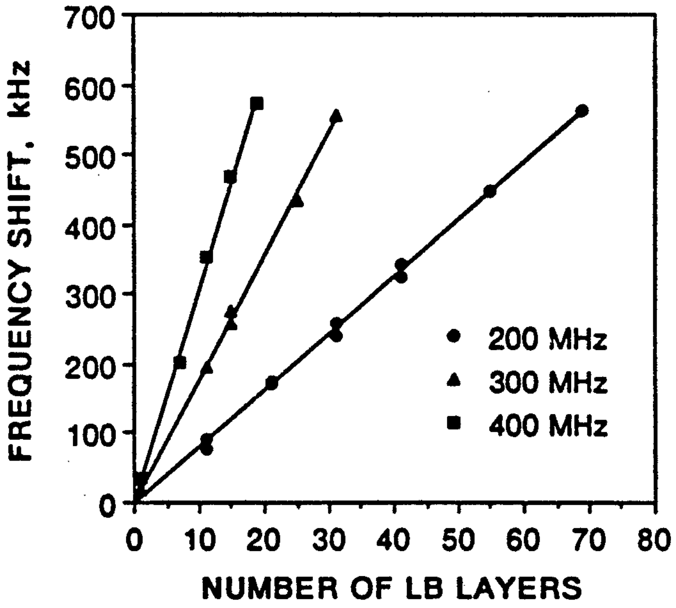

Figure 5. Frequency shifts observed as a function of the number of LB layers applied to the surfaces of 200, 300, and 400 MHz SAW resonators.

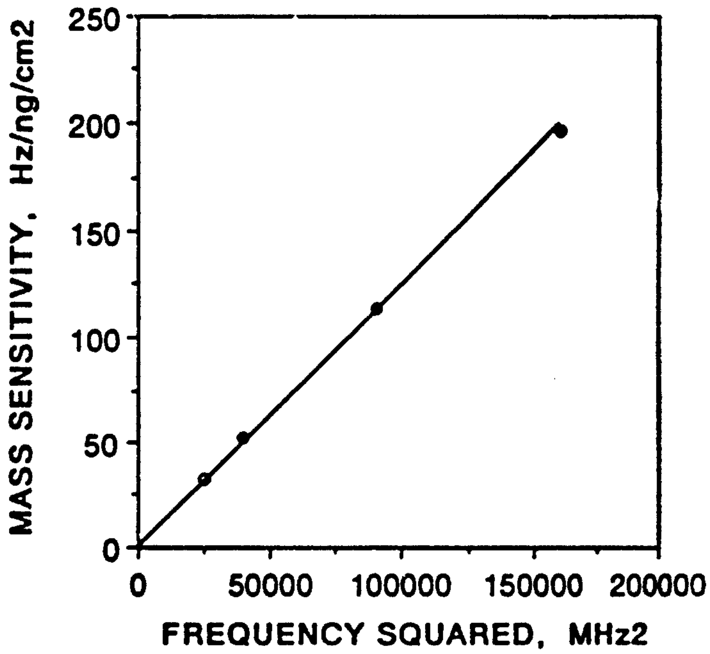

Figure 6. Experimentally determined mass sensitivities of the 158 MHz SAW delay line device (open circle) and the 200, 300, and 400 MHz SAW resonator devices (filled circles) as a function of device frequency squared.

Our results confirm or re-confirm a number of aspects of eqs 1 and 2, and show that they apply equally well to delay line and resonator devices. The increase in sensitivity with the square of device frequency is apparent in the data (the 400 MHz device has four times the mass sensitivity of the 200 MHz device) and is further illustrated in Figure 6, where mass sensitivities are plotted as a function of F^2. The quantitative validity of eq 2 in predicting mass sensitivity when stiffness effects are minimized is demonstrated. The very close agreement re-emphasizes the role of the SAW device as a mass detector. Although SAW devices are widely recognized to be mass detectors, the relative importance of stiffness effects is debated from time to time. Our results show unambiguously that when a soft elastomeric material is applied as the sorbent overlayer, and the frequency is taken as the sensor's response, stiffness effects can be negligible.

In a previous study Wohltjen et al. applied mixed LB films containing stearyl alcohol and copper tetrakis(cumylphenoxy)phthalocyanine to SAW delay lines in order to test the prediction of eq 2 that the frequency shift obtained in response to a given mass-loading increases with the square of the SAW oscillator frequency (20). This prediction was confirmed using delay lines operating at 31, 52, and 112 MHz. However, the experimentally observed mass sensitivities differed significantly from those predicted by eq 2. It was suggested that the film stiffness must be playing a role in the observed results, but the actual modulus of the mixed films was not known. Both components of these mixed films were solids. Our approach using a soft organic polymer carefully selected according to the criteria above gave excellent agreement between experimental and theoretical results.

Vapor sensitivities. In our discussion of vapor sensitivities we will define the response of the sensor to a vapor as the frequency shift (in Hz or kHz) observed when the sensor reaches its steady state or "equilibrium" response. We define vapor sensitivity exactly as sensitivity is defined in the Introduction, i.e. as the incremental change in signal in response to an incremental change in analyte concentration, where the analyte concentration refers to the vapor concentration in the gas phase. It should be noted that vapor sensitivity is not at all identical to mass sensitivity. Mass sensitivity depends on the fundamental properties of the piezoelectric device, whereas vapor sensitivity depends on additional factors that influence the mass of vapor per unit area that is collected on the device surface. Consequently the vapor sensitivity must depend on the amount of sorbent coating material on the surface (loosely referred to as the coating thickness) and the strength with which it sorbs vapors.

We will discuss factors influencing the choice of coating thickness in detail below. The strength of sorption is dependent on the choice of the sorbent material and the sensor's operating temperature. At any particular temperature for a given polymer and vapor, the strength of sorption is quantified by the partition coefficient, K, which is the ratio of the concentration of the vapor in the sorbent phase, C_s, to the concentration of the vapor in the gas phase, C_v.

$$K = C_s / C_v \qquad (3)$$

The vapor sensitivity is therefore determined primarily by three factors, the coating thickness, the partition coefficient, and the response of the device to the changes in the physical properties of the film that occur during sorption. When the response of the device is primarily gravimetric, as is usually assumed to be the case, then the third factor in vapor sensitivity is simply the mass sensitivity of the device. If vapor sorption causes viscoelastic changes in the film material which significantly contribute to the frequency response, then this will be an additional factor influencing the sensitivity. A full understanding of the viscoelastic properties of polymers on planar acoustic device surfaces and the effects of vapors on those properties are current areas of investigation (25,29). When the viscoelastic effect is significant, it will be dependent on the concentration of vapor molecules in the sorbent phase, and will therefore also be a function of the partition coefficient.

In principle, the greater the amount of sorbent coating applied to the SAW device, the greater the vapor sensitivity of the sensor because more vapor is collected at its surface. For example, if one compares two identical SAW devcies coated with different absolute thicknesses of polymer (in nm) and exposed to the same gas phase vapor concentration, the sensor with the thicker polymer layer will collect more mass and respond with a larger change in signal. Hence it will have greater vapor sensitivity. Alternativly, consider two devices with the same polymer layers at the same absolute thicknesses exposed to the same gas phase vapor concentration where one device is fabricated to operate at twice the frequency of the other. In this case both devices collect the same amount of vapor per unit area by sorption into their polymer layers, but the higher frequency device has four times the sensitivity to the mass per unit area of the device, and hence four times the vapor sensitivity.

Unfortunately, one cannot coat high frequency devices with the same absolute thicknesses of sorbent material as lower frequency devices, so vapor sensitivities do not rise with the square of the operating frequency. Identical coating thicknesses cannot be maintained as device frequency rises because the energy of the acoustic waves is partially dissipated into the film material and attenuation increases as frequency increases (2). When SAW devices are operated in oscillator circuits, the signal is lost when the acoustic losses exceed the gain of the feedback oscillator. It follows that the coating thickness that can be applied without quenching oscillation will decrease as the device frequency is increased. This principle was noted previously in a study by Snow and Wohltjen using 31 MHz SAW delay lines (30). These authors suggested a guideline for coating thicknesses, i.e. that coating thicknesses approximate 1% of the acoustic wavelength, which implicitly recognizes that as frequencies increase and acoustic wavelengths decrease, coating thicknesses must decrease.

With the circuits and resonator devices in this study, we have found that coating thicknesses producing more than 500 to 600 kHz of frequency shift damp out the oscillator. This limit is consistently observed whether the coating material is applied by spray-coating or the LB method, and it is independent of resonator frequency. Similar limits have been observed in our laboratory using SAW delay lines of various frequencies. Therefore, we routinely select ca. 250 kHz as an appropriate coating "thickness" for our SAW vapor sensors.

It must be noted that the coating mass per unit areas corresponding to 250 kHz, and therefore the absolute coating thicknesses in nm, vary with the device frequency. Some comparisons are given in Table III where mass per unit areas are calculated according to eq 2 and a film material density of 1 g/cm^3 is assumed. These calculations show that 250 kHz of film on a 400 MHz device is only one fourth the absolute thickness of a 250 kHz film on a 200 MHz device, assuming the material is evenly distributed. With this in mind, our results for maximum coating thicknesses indicate that higher frequency devices tolerate less coating in absolute terms than lower frequency devices. This is consistent with the fact that attenuation increases with frequency (2). A consequence of this trend is that although higher frequency devices have greater mass sensitivities, the use of thinner coatings as frequencies are increased will result in less vapor being sorbed at the surface. The two trends counteract one another.

One can predict, based on eqs 4 and 5 below (17,31), that if SAW sensors of various frequencies are all coated with the same material to the same degree of frequency shift, then their vapor sensitivities should be identical.

$$\Delta f_v / \Delta f_s = m_v / m_s \qquad (4)$$

$$\Delta f_v = \Delta f_s C_v K / \rho \qquad (5)$$

In these equations the frequency shift caused by the sorption of vapor of mass per unit area m_v is given by Δf_v. Similarly, m_s is the mass per unit area of the coating causing Δf_s in frequency shift. C_v and K are the concentration of the vapor in the vapor phase and the partition coefficient as before. The density of the coating material is given by ρ. Both expressions give the frequency shift due to the mass of vapor sorbed as a fraction of the amount of coating expressed as a frequency shift. The device operating frequency does not appear in the equations.

Table III. Mass per Unit Areas and Film Thicknesses Corresponding to 250 KHz on SAW Devices of Various Frequencies

Device Frequency MHz	$-\Delta f_s$[a] kHz	Film Mass per Unit Area[b] $\mu g/cm^2$	Film Thickness[c] nm
158	250	7.95	79.5
200	250	4.96	49.6
300	250	2.20	22.0
400	250	1.24	12.4

[a] Freqency shift caused by the application of the film.

[b] Calculated from eq 2.

[c] Calculated assuming a film material density of 1 g/cm^3.

The responses of poly(vinyl tetradecanal)-coated 200, 300, and 400 MHz SAW resonator sensors to a selection of organic vapors were determined as described in the Experimental Sections. Results for similarly coated 158 MHz SAW delay lines were also determined for comparison. Both LB and spray-coated films were investigated. In accordance with the rationale above, coating thicknesses were in the range of 200 - 275 kHz. The responses to vapors were normalized to 250 kHz of coating to simplify comparisons, and the results are reported in Table IV. (The actual kHz of coating on the sensors appear in the column headings.)

The first two columns of responses in Table IV are for two SAW delay lines on the same quartz chip. These two delay lines were coated by the LB method at the same time, but vapor response data were recorded in separate data sets. The largest responses (i.e. to 1,2-dichloroethane and toluene) agree to within less than 2%. Responses for the remaining vapors differ by ca. 10% (i.e. +/- 5% from the average). Variation among the entire set of sensors is somewhat greater, as one might expect, and again the largest responses are the most consistent. Excluding the two vapors giving the weakest responses, the ranges are +/- 20% or less, dropping to +/-15% for the two vapors giving the largest responses. Considering standard deviations instead of ranges, values of +/- 20% or less are obtained for all vapors except nitromethane, dropping to +/- 11% for 1,2-dichloroethane and toluene. There is a small but consistent increase in response with frequency which we will discuss below and which contributes to the variations from sensor to sensor. Nevertheless, overall the responses are similar and the prediction above that sensors with the same kHz of coating will give the same responses is confirmed.

The responses of the sensors were largely independent of the coating application method. This point is illustrated in the bar graphs in Figure 7, where the responses of LB and spray-coated 200 and 400 MHz resonators are compared. This is a significant result since the film morphologies are not the same, and equations modelling SAW sensor responses usually assume a uniform overlay film. The spray-coated films of poly(vinyl tetradecanal) are actually discontinuous at the thicknesses applied on these high frequency devices. They appear primarily as small circular domains with raised edges, as if the polymer deposited preferentially at the perimeter of aerosol

Table IV. Responses of Poly(vinyl tetradecanal)-coated SAW Vapor Sensors to Organic Vapors.

Freq., MHz		158	158	158	200	200	300	400	400
SAW Type		Delay[a]	Delay	Delay	Res[b]	Res	Res	Res	Res
Film Type		LB(49)[c]	LB(49)	Spray	LB(31)	Spray	LB(15)	LB(7)	Spray
kHz Coating		247	247	247	243	253	259	205	254
Vapor	Concn mg/m^3	Responses Normalized to 250 kHz of Coating Hz							
isopropanol	17520	2799	2609	1718	2084	1757	2466	2764	2452
isooctane	44980	9296	10088	8570	8874	8561	10644	12526	12760
nitromethane	16450	2079	2241	1386	1508	1285	2539	1911	1914
1-butanol	3768	3425	3811	2673	3146	2757	3869	4149	4069
1,2-dichloroethane	65080	13713	13547	10865	12040	11485	14008	14483	14150
toluene	21220	17289	17458	14745	15784	15316	18135	19603	19669
2-butanone	53380	n.m.[d]	n.m.	5569	6311	5713	8151	8796	7986

[a] Delay line configuration.

[b] Resonator configuration.

[c] Langmuir-Blodgett film, number of layers in parentheses.

[d] Not measured.

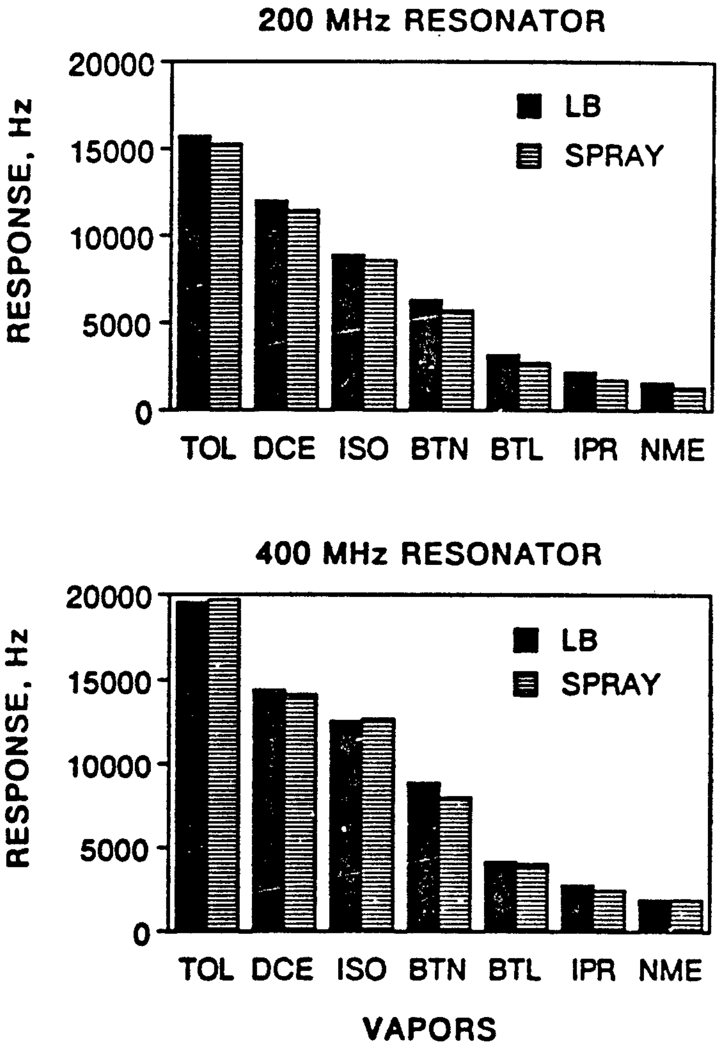

Figure 7. Comparisons of the vapor responses of LB and spray-coated 200 and 400 MHz SAW resonator sensors to a variety of organic vapors: toluene (TOL), 1,2-dichloroethane (DCE), isooctane (ISO), 2-butanone (BTN), 1-butanol (BTL), isopropanol (IPR), and nitromethane (NME).

droplets that landed on the surface. On the 200 MHz devices, these structures are quite numerous and overlapping. The structures are of the same size on the 400 MHz devices, but less numerous. The LB films, by contrast, are deposited as continuous thin films and are featureless under the optical microscope. Our results show that spray-coated films of soft rubbery materials can provide the same sensor performance as thin continuous films. This validates our use of spray-coated films in previous studies (17,18,31).

In Figure 8, we compare the responses of the LB-coated 200, 300, and 400 MHz sensors. A small systematic increase in response with frequency is observed for six of the seven vapors tested, with the 400 MHz sensor responses being 20 to 30% higher than the 200 MHz sensor responses. By examining the data from the spray-coated sensors in Table IV, it can again be seen that responses increase somewhat with device frequency for most vapors. The spray-coated 400 MHz sensor responses are 30 to 50% higher than the spray-coated 200 MHz sensor responses. (All things considered, the responses of the LB-coated 158 MHz delay line sensors are anomalously high, both in comparison to the spray-coated 158 MHz delay line sensor and in comparison with the trends among the higher frequency LB-coated resonators.)

The increase in response with increasing frequency can be considered a secondary effect relative to the overall similarity in response levels, but the effect may be real. If so, it can be rationalized by considering interfacial adsorption processes in addition to the bulk absorption of vapor into the film material. Vapor is likely to be adsorbed at the polymer/solid interface, the gas/polymer interface, and if bare surface is exposed, at the gas/solid interface. When coating films are thick (in nm), the effects of interfacial adsorption will be negligible if the film is a good sorbent. However, as sensor frequencies increase, the effects of adsorption processes will increase since the sensitivities to mass per unit area increase. At the same time, the volume of the coating is decreasing as absolute film thicknesses decrease. Both these trends work to increase the sensitivity to interfacial adsorption processes.

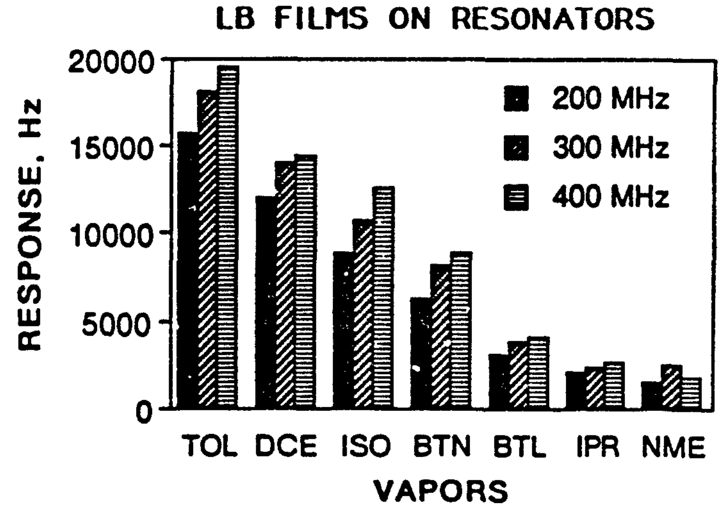

Figure 8. Comparisons of the vapor sensitivities of LB-coated 200, 300, and 400 MHz SAW resonator sensors to a variety of organic vapors: toluene (TOL), 1,2-dichloroethane (DCE), isooctane (ISO), 2-butanone (BTN), 1-butanol (BTL), isopropanol (IPR), and nitromethane (NME).

Note that in the extreme case where interfacial adsorption is the main effect, vapor sensitivities would be governed by device mass per unit areas. The responses of the 400 MHz sensors would then be 400% greater than those of the 200 MHz sensors. This magnitude of increase in vapor sensitivity with frequency was not observed, so it can be concluded that the principle mechanism for sensor response is bulk absorption of vapor into the film material.

Noise and Detection Limits. The noise levels of the SAW resonators were determined repeatedly while monitoring frequencies during mass sensitivity studies, and also from sensor baseline frequency data during vapor response experiments. Additional experiments were conducted on 200 MHz resonators to determine environmental factors which influenced the noise levels. We found no difference in the noise performance of the 200 MHz SAW resonators and oscillators supplied by Microsensor Systems and Femtometrics. This suggests that the limiting factor in the noise was the quartz resonator chip itself (both vendors use the same chip from SAWTEK) rather than the oscillator electronics.

We found that thermal conditions played a key role in determining 200 MHz resonator noise levels. Resonator temperatures are influenced by ambient conditions and the heat generated by the oscillator electronics. The lowest noise levels were observed when the bare resonators and oscillators were allowed to come to their own thermal equilibrium in a draft-free enclosure. Under these conditions, sensor temperatures stabilized near 35°C and noise levels were as low as 0.2 Hz. However, any change that perturbs the heat flow increases the noise. With gas flow over the sensor and a thermostatted heat sink on the sensor lid actively regulating the temperature, the best noise levels we observed were 1 to 2 Hz. Typical noise levels under these conditions were in the 2 to 6 Hz range, regardless of the presence or absence of a coating. Nor were any trends observed as the amount of coating was varied in the mass sensitivity studies. During vapor response experiments, baseline noise levels were in the 3 to 10 Hz range. Thus, we conclude that these devices are capable of very stable operation under ideal conditions, but that thermal effects significantly influence the noise in practical use. Neither the presence or the absence of a coating nor its thickness were important determinants of noise levels under practical operating conditions in our laboratory.

The 300 and 400 MHz resonators were noisier than the 200 MHz devices. Typical noise levels on the 300 MHz device were in the range of 15 to 40 Hz during mass sensitivity studies, and 26 to 55 Hz during vapor response experiments. With 400 MHz resonators typical noise levels were 8 to 25 Hz during the mass sensitivity studies and 15 to 40 Hz during the vapor response experiments. One would expect that absolute noise levels would increase with device frequency. Thus, if the stability were 1 part in 10^8, the noise levels would be 2, 3, and 4 Hz on the 200, 300, and 400 MHz devices respectively. In our experiments, the lowest frequency resonator was certainly the most stable, but the 300 MHz resonator was noisier than the 400 MHz resonator.

A convenient scaling law for SAW delay lines has been that the noise levels can be approximated as 1 part in 10^7 (2), or 16 Hz on the 158 MHz device . In fact, this is a typical noise level for this device in our laboratory. The LB-coated 158 MHz SAW sensors in this study had noise levels in the range of 10 to 25 Hz during vapor response experiments, while the spray-coated device had noise in the 5 to 7 Hz range during most experiments. The latter noise levels are the best that can be achieved with these devices, in our experience. The worst noise levels we have seen are in the 30 to 40 Hz range. Bowers and Chuan report noise levels of 1 part in 10^7 for these 158 MHz SAW delay lines, while Rezgui and Alder have reported noise levels of 5 Hz (14,19).

We can then conclude that the 200 MHz resonators have the lowest noise levels of all the devices examined in this study. Typical noise levels around 5 Hz, with the potential for noise levels of 1 Hz or less if the sensor thermal environment is very stable, are an improvement over typical levels around 16 Hz on the 158 SAW delay lines. Moreover, the worst noise levels on the 200 MHz resonator are well below the worst levels observed on the delay lines. Since all devices with the same kHz of coating have approximately the same vapor sensitivities when absorption is the principle sorption mechanism, the lowest detection limits will be achieved with the lowest noise device. Thus, detection limits on the 200 MHz resonator are about three times lower than on the

158 MHz delay line. Taking the response of the poly(vinyl tetradecanal)-coated 200 MHz resonator to toluene vapor as an example, one would project a detection limit of ca. 20 mg/m^3 (ca. 5 ppm) at a signal-to-noise ratio of three.

Final Remarks. Our main objective in beginning this study was to determine if SAW resonators could be used as vapor sensors with soft organic coatings applied, and if they would offer any advantages in terms of lower noise levels. Our experiments have established that they are useful for this purpose, and that the 200 MHz resonators investigated do have lower noise levels than the 158 MHz devices we have used in the past.

In the course of this study, we have also re-examined SAW scaling laws as they apply to vapor sensors with soft sorbent coatings. The usual statement that SAW sensitivity increases with the square of the device frequency applies to the mass sensitivities of the bare devices, but does not necessarily apply to the vapor sensitivities of coated devices or their detection limits. For a given sorbent coating and vapor at a fixed temperature, SAW vapor sensitivity will depend on the sorbent coating thickness as well as the mass sensitivity, and vapor detection limits will also depend on the noise. In order to understand vapor sensor scaling laws, one must consider the effect of device frequency on all three factors. Mass sensitivity increases with F^2, as is well established in theory and experimentally verified in this study. Noise is typically described as increasing linearly with F (2). Then one can consider two cases for coating thicknesses. If coating thicknesses decrease with F^2, as we investigated experimentally , absolute vapor sensitivities remain constant with frequency. The effects of operating frequency on mass sensitivity and coating thicknesses cancel one another out exactly. Vapor detection limits actually become less favorable at higher operating frequency because of increasing noise levels.

Alternatively, one can consider the case where coating thicknesses decrease linearly with F. Comparing 200 and 400 MHz resonators, for example, the 400 MHz device would have four times the mass semsitivity but one half the coating thickness, and hence twice the absolute vapor sensitivity. In this case, vapor sensitivity increases linearly with F. However, if noise levels also increase linearly with F, then vapor detection limits will be constant with frequency.

It can be seen that because attenuation increases with frequency, and coating thicknesses must decrease accordingly, vapor sensitivities and detection limits cannot be equated with mass sensitivities and detection limits. Detection limits are not improved by using higher frequency SAW devices in either of the cases examined above. Indeed, detection limits may be degraded by higher SAW operating frequencies in the first case.

Our analysis has not considered response times so far, and this factor can favor higher frequency devices. Higher frequencies lead to thinner coatings and faster response times under conditions where vapor diffusion is the limiting factor in sensor response. This was not a concern in our studies since all vapors diffused quite rapidly in the poly(vinyl tetradecanal) films and sensor response times were indistinguishable under our experimental conditions. With other coatings and vapors, however, this could become an important factor. Higher frequencies also lead to smaller devices and lower costs, which may also be factors in some applications. In addition, the trend that higher frequency devices give higher noise levels is not a hard and fast rule. Device designs change as frequencies change, and this will also effect noise levels. At the moment, the 200 MHz SAW resonator provides the best detection limits we can achieve with a SAW device and response times are quite rapid when soft elastomeric polymers are chosen as the coating material. It is our SAW device of choice when detection limits are of prime importance.

We also prefer having the coated SAW resonator and the reference resonator on separate quartz chips. In this configuration there is no possibility of cross-talk directly between two devices on the same chip, as has been observed on the 158 MHz devices (14). In addition, coating the sensor without contaminating the reference is simplified. The main purposes of the dual delay line SAW configuration have been to obtain a low frequency difference signal and provide temperature compensation. Low frequency difference signals are still obtained with the devices on separate chips. Temperature compensation, if perfect (which it never is) only compensates for the frequency drift of the bare devices. Thermal expansion of the polymer on a vapor sensor also induces a temperature drift which remains uncompensated, and the sorption of vapors is highly temperature dependent (17). Therefore, we find that little is lost by separating the reference and sensor chips, and much is gained by actively thermostatting the sensors. Very precise control of the sensor thermal environment would likely reduce noise levels and improve detection limits.

The ultimate objective of SAW sensor development is in real world detection applications. In this case, the detection limits of importance are actually the detection limits where other vapors which may appear in the background do not interfere with accurate measurements of analyte concentrations or cause false alarms. This consideration demands that selectivity be achieved, a topic not considered in this paper. Selectivity with SAW resonators will be achieved by the same methods used with SAW delay lines and quartz crystal microbalances, namely: the development of selective sorbent materials, the use of sensor arrays with pattern recognition, and pre-separation or pre-concentration methods (2-8,17,18,32-35). Thus the requirements of real world applications will be met by integrating individual SAW vapor sensors into complete detection systems.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Hank Wohltjen and Bill Bowers for helpful discussions on SAW resonators, and Bill Bowers for the loan of one of his resonator systems.

This work was supported by the Office of Naval Technology / Naval Surface Warfare Center, Dahlgren, VA.

REFERENCES

1. Wohltjen, H.; Dessy, R.E. *Anal. Chem.* 1979, *51*, 1458-1475.

2. Wohltjen, H. *Sens. Actuators* 1984, *5*, 307-325.

3. Ballantine, D.S., Jr.; Wohltjen, H. *Anal. Chem.* 1989, *61*, 704A-715A.

4. D'Amico, A.; Verona, E. *Sens. Actuators* 1989, *17*, 55-66.

5. Nieuwenhuizen, M.S.; Venema, A. *Sensors and Materials* 1989, *5*, 261-300.

6. Fox, C.G.; Alder, J.F. *Analyst* 1989, *114*, 997-1004.

7. Bastiaans, G.J. *Chemical Sensors*; Edmonds, T.E. Ed.; Blackie: Glasgow and London, 1988, 295-319.

8. Grate, J.W.; Abraham, M.H. *Sens. Actuators* 1991, in the press.

9. Parker, T.E.; Montress, G.K. IEEE Trans. Ultrason., Ferroelectrics, Freq. Contr. 1988, 35, 342-364.

10. Martin, S.J.; Schweizer, K.S.; Ricco, A.J.; Zipperian, T.E. *Proc. 3rd Int. Conf. Solid-State Sens. Actuators - Transducers '85* 1985, 71-73.

11. Bowers, W.D.; Chuan, R.L. 198th National Meeting of the American Chemical Society, Miami Beach, FL, Sept. 10-15, 1989.

12. Bowers, W.D.; Chuan, R.L. Proc. SPIE 1990 Int. Symp. on Opt. and Optoelectronic Appl.Sci. and Eng., San Diego, CA, July 8-13, 1990.

13. Bowers, W.D.; Duong, R.; Chuan, R.L. *Rev. Sci. Instrum.* 1991, in the press.

14. Bowers, W.D.; Chuan, R.L. *Rev. Sci. Instrum.* 1989, *60*, 1297-1302.

15. Oguchi, K.; Yoden, T.; Kosaka, Y.; Watanabe, M.; Sanui, K.; Ogata, N. *Thin Solid Films* 1988, *161*, 305-313.

16. Lindemann, M.K. in Encyclopedia of Polymer Science and Technology, Vol. 14, John Wiley and Sons, Inc.: New York, 1971 ; pp 208-239.

17. Grate, J.W.; Snow, A.; Ballantine, D.S., Jr.; Wohltjen, H.; Abraham, M.H.; McGill, R.A.; Sasson, P. *Anal. Chem.* 1988, *60*, 869-875.

18. Rose-Pehrsson, S.L.; Grate, J.W.; Ballantine, D.S., Jr.; Jurs, P.C. *Anal. Chem.* 1988, *60*, 2801-2811.

19. Rezgui, N.; Alder, J.F. *Analytical Proceedings* 1989, *26*, 46-48.

20. Wohltjen, H.; Snow, A.W.; Barger, W.R.; Ballantine, D.S. *IEEE Trans. Ultrason., Ferroelectrics, Freq. Contr.* 1987, *UFFC-34*, 172-177.

21. Grate J. W.; Klusty, M.; Barger, W. R.; Snow, A.W. *Anal. Chem.* **1990,** *62*, 1927-1934.

22. Grate J. W.; Rose-Pehrsson, S.; Barger, W. R. *Langmuir* 1988, *4*, 1293-1301.

23. Barger, W. R.; Snow, A. W.; Wohltjen, H.; Jarvis, N.L. *Thin Solid Films* 1985, *133*, 197-206.

24. Grate, J.W.; Klusty, M. NRL Memorandum Report 6762, 1990.

25. Martin, S.J.; Frye, G.C. *Appl. Phys. Lett.* 1990, *57*, 1867-1869.

26. Gaines, G.L. *Insoluble Monolayers at Liquid Gas Interfaces*, Interscience: New York, 1966.

27. Sugi, M. *J. Mol. Electronics* 1985, *1*, 3-17.

28. *Microwave Acoustics Handbook, Vol. 2, Surface Wave Velocities - Numerical Data*; Slobodnik, A.J., Jr. Demonico, R.T., Donway, E.D., Eds.; Air Force Cambridge Research Laboratory, Feport No. AFCRL-TR-74-0536, Oct. 1974, p.197.

29. Grate, J.W.: Wenzell, S.W.; White, R.M., unpublished results.

30. Snow, A.; Wohltjen, H. *Anal. Chem.* 1984, *56*, 1411-1416.

31. King, W.H. *Anal. Chem.* 1964, *36*, 1735-1739.

32. Ballantine, D.S., Jr.; Rose, S.L.; Grate, J.W.; Wohltjen, H. *Anal. Chem.* 1986, *58*, 3058-3066.

33. Kindlund, A.; Sundgren, H.; Lundstrom, I *Sens. Actuators* 1984, *6*, 1-17.

34. Grate, J.W.; Klusty, M.K.; Rose-Pehrsson, S.L.; Wohltjen, H. presented at the 199th National Meeting of the American Chemical Society, Boston , MA, April 22-27, 1990.

35. Carey, W.P.; Beebe, K.R.; Kowalski, B.R. *Anal. Chem.* 1987, *59*, 1529-1534.

APPENDIX I

If it is assumed that the sole contributor to the response of a SAW vapor sensor is mass loading, it is possible to calculate partitiion coefficients, which we denote K_{SAW}, from the observed frequency shifts. These are tabulated as logs in Table V, using the data from Table IV and equation 5. The assumption that sensor responses are entirely due to mass-loading is not necessarily correct.

Table V. Responses of Poly(vinyl tetradecanal)-coated SAW Vapor Sensors to Organic Vapors Expressed as Log K_{SAW}.

	Freq., MHz	158	158	158	200	200	300	400	400
	SAW Type	Delay[a]	Delay	Delay	Res[b]	Res	Res	Res	Res
	Film Type	LB(49)[c]	LB(49)	Spray	LB(31)	Spray	LB(15)	LB(7)	Spray
	kHz Coating	247	247	247	243	253	259	205	254
Vapor	Concn mg/m^3	Responses Expressed as Log K_{SAW}							
isopropanol	17520	2.79	2.76	2.58	2.66	2.59	2.73	2.78	2.73
isooctane	44980	2.90	2.94	2.86	2.88	2.86	2.96	3.03	3.04
nitromethane	16450	2.69	2.72	2.51	2.55	2.48	2.77	2.65	2.65
1-butanol	3768	3.54	3.59	3.44	3.51	3.45	3.60	3.63	3.62
1,2-dichloroethane	65080	2.91	2.90	2.81	2.85	2.83	2.92	2.93	2.92
toluene	21220	3.50	3.50	3.43	3.46	3.44	3.52	3.55	3.55
2-butanone	53380	n.m.[d]	n.m.	2.60	2.66	2.61	2.77	2.80	2.76

[a] Delay line configuration.

[b] Resonator configuration.

[c] Langmuir-Blodgett film, number of layers in parentheses.

[d] Not measured.