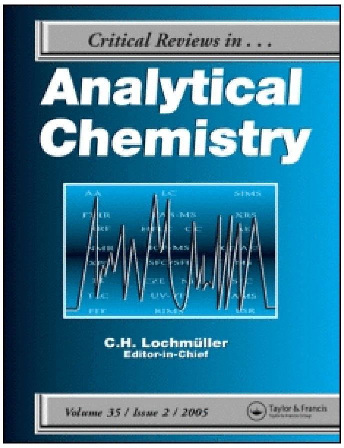

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The Development of New Microsensor Coatings and a Short Survey of Microsensor Technology

Alan R. Katritzky[a]; Rick J. Offerman[ab]
[a] Department of Chemistry, University of Florida, Gainesville [b] Tennessee Eastman Company, Kingsport

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The Development of New Microsensor Coatings and a Short Survey of Microsensor Technology

Alan R. Katritzky and Rick J. Offerman

Referee: Hank Wohltjen, Microsensor Systems Inc., Fairfax, Virginia

I. MICROSENSOR DEVICE CHARACTERISTICS

This review covers various aspects of microsensor technology with which we have been associated in our research program. Current work deals with the development of new coatings for use on surface acoustic wave (SAW) devices for both resistance and frequency-based measurements. The microsensor area is currently a small but rapidly expanding field that involves diverse disciplines, including synthetic and polymer chemistry, analytical chemistry, surface science, computer science, and electronic engineering. We have attempted to assist the reader by describing various other facets while highlighting the development of new microsensor coatings. These facets include the way in which the synthetic chemistry is guided by requirements of coating technology and surface science and notes on the use of sophisticated electronic devices and data manipulation techniques to evaluate the compounds synthesized.

Microsensor technology holds the promise of developing highly sophisticated chemical detectors, which can quickly, both quantitatively and qualitatively, analyze their immediate atmosphere for a wide variety of chemicals, in spite of potential interferences at extremely low levels. Currently, the area of this technology that has fallen behind in terms of sophistication is the development of new coatings for microsensor devices. The choice of coatings to date has been seemingly limited by the coatings that were commercially available. Often promising coatings could not be pursued further because other analogs were simply not available. We have attempted to "go the next step" on coating technology. Once a promising coating was identified, we were able to further modify its structure. The response of this new coating then provided new information for our knowledge base. This should allow all associated with microsensor technology the information necessary to devise and advance the fundamental science by helping to understand the mechanisms of frequency and resistance changes in microsensor coatings.

A. Definition and Mode of Action of Microsensors

A chemical microsensor can be defined as an extremely small device that detects contaminants in gases or liquids. Ideally, such a sensor would:

1. Show a response that varies with the nature and concentration of contaminants.
2. Show a response that is reversible for repeated cycles of exposure.

The mode of action of a chemical microsensor vapor detector depends on the following essentials:[1-3]

1. The presence of a thin film at a surface that reversibly adsorbs contaminants from the medium around the device.
2. The measurement of some physical property of the film that is altered by the adsorption of these contaminants.
3. Associated electronics that are used to amplify and interpret the signal.

B. Types of Microsensors[2-9]

Of the many types of microsensors that have been described, we note:

1. The chemiresistor[5,10]
2. The bulk-wave piezoelectric quartz crystal sensor[7]
3. The surface acoustic wave, or SAW, device[6,11,12]

The chemiresistors, as the name implies, are chemically sensitive devices that detect a change in the electrical resistance of a coating on the surface of a microsensor, a change that occurs when it is exposed to a vapor-borne challenge.[3]

The bulk-wave piezoelectric quartz crystal sensor indirectly measures mass changes of the coating on the surface of the device.[7] This change in mass causes changes in the resonant frequency of the device, and the frequency differences are measured. SAW devices are similar to bulk-wave piezoelectric devices in that the mode of detection is based on a mass change of the coating on the surface of the device, but the SAW device operates with waves of higher frequency and, consequently, with greater sensitivity.[6,11,12] SAW devices also possess several advantages over bulk-wave piezoelectric devices, including greater ease of coating, uniform surface mass sensitivity, and improved ruggedness.[3] Bulk-wave piezoelectric devices are the older of these two types of devices and have been known for about 25 years.[3,6,7,9,13] SAW devices are the more recent and more sensitive of the two, and this review concentrates on chemiresistor and SAW devices and their coatings.

Alan R. Katritzky received a D.Phil. degree from Oxford, England, and was on the faculty at the Universities of Cambridge and East Anglia in the U.K. before taking up, in 1980, his present position as Kenan Professor in the Department of Chemistry at the University of Florida in Gainesville. **Rick J. Offerman** received a B.S. degree from Upper Iowa University in Fayette and a Ph.D. degree from the University of Iowa in Iowa City. Dr. Offerman spent the years 1985 to 1987 as a Postdoctoral Fellow at the University of Florida in Gainesville. He is currently a chemist with the Tennessee Eastman Company in Kingsport.

C. Microsensor Arrays

The true potential of microsensors is realized when they are used in assemblies.[14-19] Thus, if we need to measure qualitatively and quantitatively for 100 contaminants:

1. A battery of 100 microsensors (if not degenerate) would easily enable this together with the possibility of screening out other common pollutants in air.
2. The signals can be fed into a microprocessor that can be programmed to give the results in a usable format using pattern recognition techniques (*vide infra*).
3. As new hazards appear, it would then be possible to adapt the pattern recognition software rather than the sensors themselves.

D. Potential Uses of Microsensors[2,3,8]

There are many potential uses of microsensors, and some of the most important are

1. Detection and quantitative analysis of various chemical agents
2. Monitoring levels of atmospheric pollution: SO_x, CO, C_nH_m
3. Industrial pollution: monitoring, qualitative and quantitative analysis
4. Ventilation control in any confined space
5. Potential for rapid analysis of quality of food by measurement of equilibrium atmospheres
6. Use of devices in a liquid environment[20]
7. Biomedical applications such as liquid phase immunosensors[21]
8. Determination of adsorption/desorption isotherms[22]

White[8] has reported on a scheme for classifying sensors by a number of characteristics, including measure and detection means, sensor conversion phenomena, technological aspects of sensors, sensor materials, and fields of application. The interested reader is referred to this report for a broad overview of other sensors and the burgeoning number of potential uses for sensors.

Some potential applications of microsensors that are already within limits attained are reviewed in Table 1, in terms of the coating utilized, the contaminant detected, and the level at which detection can be achieved.

Table 1
Applications of Microsensors[a]

Coating	Analyte	Level (ppm)
Phthalocyanine	Ammonia	0.5
FPOL	DMMP	0.03
WO_3	H_2S	0.01
UCON	NO_2	0.001
Carbowax	CO, SO_2, NH_3	30—300

[a] See text for associated references.

E. Microsensor Construction

A diagrammatic representation of a chemiresistor device is shown in Figure 1. This device is based on the detection of the change of the resistance of a coating placed over the interdigital electrodes of the device.[3,5] In practice this measurement can be made by simply connecting the device to a voltage source and an electrometer and exposing it to an analyte. Any change in resistance will appear as a change in current that can be recorded from the electrometer.

Figure 2 shows the general design for a chemiresistor, SAW, or bulk-wave piezoelectric device. The device is fabricated from a special cut of quartz that has gold interdigital electrodes lithographically plated on the surface.[1,9] In theory the device is coated with a compound that is sensitive and selective for the compound to be detected. When exposed to an analyte in vapor, the device responds by a change in resistance if used as a chemiresistor, or by a change in frequency if used as a resonant bulk piezoelectric or SAW device.[23]

Our own group currently employs the SD-52B SAW device that was purchased from Microsensor Systems, Inc., P.O. Box 90, Fairfax, VA. The associated electronics were also obtained there and are similar to those employed by W. R. Barger of the Naval Research Laboratory (NRL), Washington, D.C., to

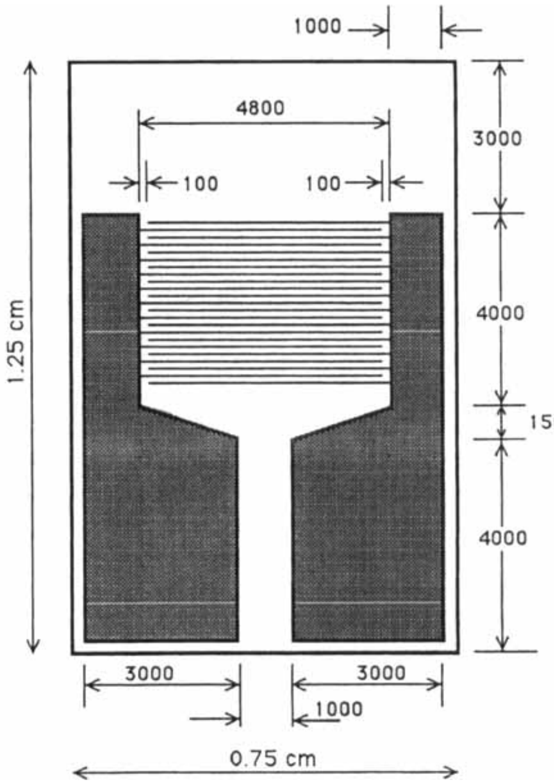


FIGURE 1. Chemiresistor device.

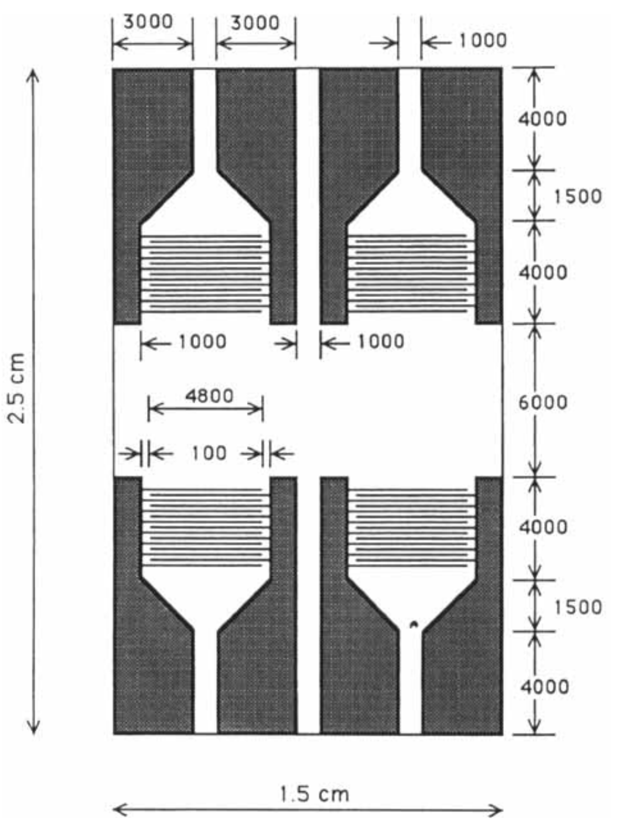


FIGURE 2. Surface acoustic wave device.

make possible interlaboratory collaboration with the systems in use there. This device (shown diagrammatically in Figure 2) allows simultaneous chemiresistor and SAW measurements to be carried out. Half of the device is devoted to SAW measurements, while one of the remaining interdigital arrays is utilized for chemiresistor measurements.

The dimensions of the device are shown in Figure 2 as 2.5 × 1.5 cm, but the devices can actually be made much smaller, having a total area as small as 10^{-4} cm^2. Therefore, it would be possible to attach a number of there devices, each specific for a different analyte, to a sensor pad and construct a sensor array that could analyze for a variety of compounds. Presently, a single device as shown in Figure 2 costs about \$250 to \$300. Higher frequency devices are available that are smaller and less costly, but they are also more fragile and difficult to coat.[24-26] Smaller devices would be more appealing in a sensor array, however, due to an overall reduction in the size of the device.

F. Microsensor Operation[6]

The operation of a SAW device is depicted in Figures 3 and 4. The device has gold interdigital electrodes lithographically fabricated onto the quartz. When a radio frequency voltage is applied to one end of the device, it generates a mechanical wave in the quartz substrate (Figure 4).[6] A selective coating is then applied to the surface of the device that changes the resonant frequency of the device. The frequency is measured by a frequency counter and the resistance by an electrometer. Typically, organic compounds are very poor conductors and show high resistances between the interdigital electrodes, however, some minimal conductivity is needed in chemiresistor coatings.

When the SAW device is exposed to a vapor challenge, the vapor dissolves in the selective coating, adding mass to the coating, thus changing the velocity of the mechanical wave in the quartz substrate and causing a frequency shift that is detected by the frequency counter (Figures 3 and 4). A chemiresistor measurement takes place between the interdigital electrodes where the vapor causes a change in the resistance of the coating that is detected by the electrometer (Figure 3).

The principles of operation of SAW devices have been described in detail,[6,27,28] but the devices are essentially mass sensitive detectors. They consist of a set of interdigital electrodes that have been microfabricated onto the surface of a piezoelectric crystal. When placed in an oscillator circuit, an acoustic Rayleigh wave is generated on the surface of the crystal. The characteristic resonant frequency of the device is dependent on transducer geometry and on the Rayleigh wave velocity. Small mass changes or elastic modulus changes on the surface perturb the wave velocity and are readily observed as shifts in this resonant frequency. The principle of these devices as detectors is that the frequency of vibration of an oscillating crystal is decreased by the adsorption of a foreign material on its surface. A gaseous pollutant is selectively adsorbed by a coating on the crystal surface, thereby increasing the mass on the crystal and decreasing the frequency of vibration. The decrease in frequency by perturbation of the coating can be described by Equation 1.[6,29]

$$\begin{aligned}\Delta f &= (\kappa_1 + \kappa_2)f^2h\rho' \\ &\quad - \kappa_2 f^2 h[4\mu'/V_R^2(\lambda' + \mu'/\lambda' + 2\mu')] \qquad (1)\end{aligned}$$

where Δf = the change in resonant frequency due to a perturbation in the wave velocity by the coating, κ_1 and κ_2 are material constants for the quartz substrate, f = the frequency of the SAW device, h = film thickness, ρ' = film mass density, μ' = shear modulus, V_R = Rayleigh wave velocity, and λ' = film Lamé constant. A simplified relationship between the resonant frequency of a SAW oscillator and the coating mass that neglects the effects of the elastic properties of the coating is given in Equation 2. The variables here are the same as in Equation 1. The quantity $h\rho'$ is simply the mass per unit area of the coating film, and variations in h or ρ' will cause a shift in the oscillator frequency.[6]

$$\Delta f = (\kappa_1 + \kappa_2)f^2h\rho' \qquad (2)$$

The extreme sensitivity of these devices makes them attractive as potential gas sensors. The 112-MHz dual SAW device, for

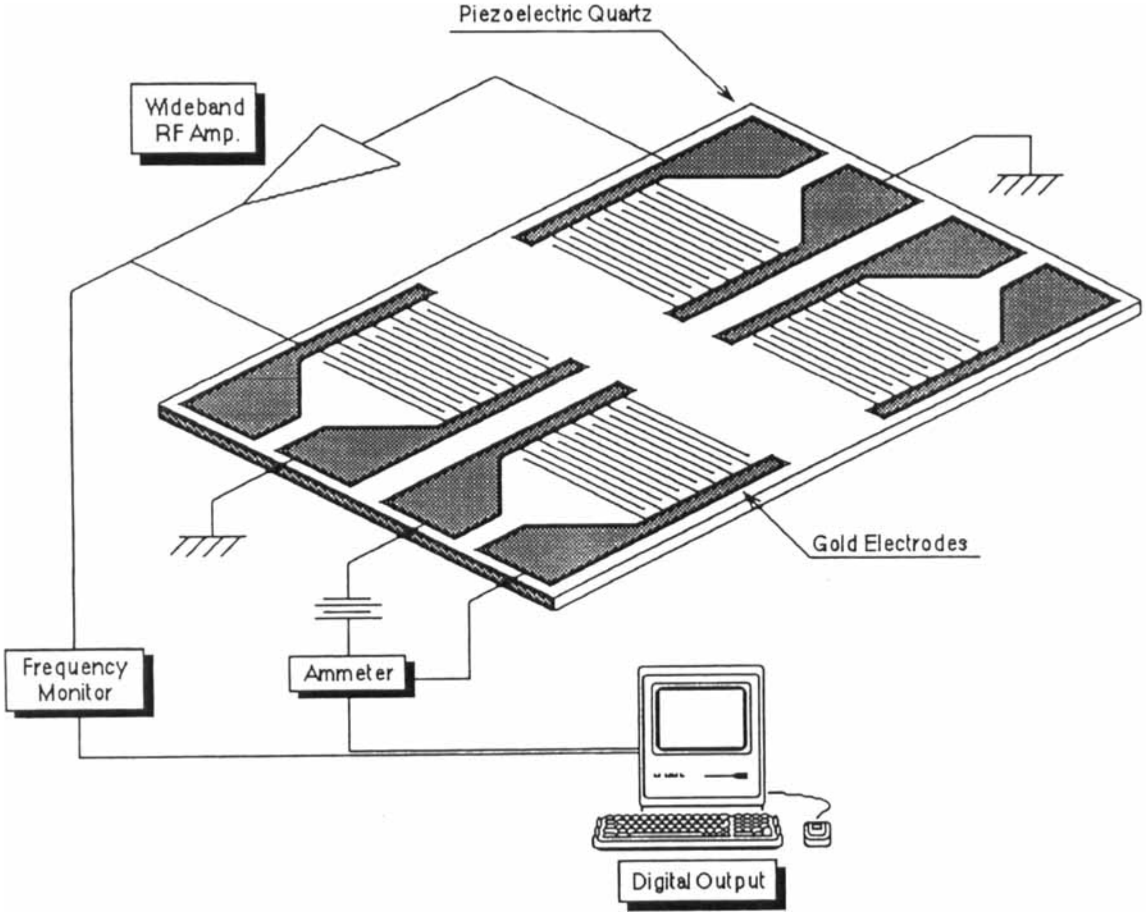


FIGURE 3. Dual 52-MHz SAW device used for simultaneous mass and conductivity measurements on thin films.

example, has a theoretical sensitivity of >17 Hz/ng/cm^2. Considering that the active area of the device covers 0.17 cm^2 and assuming a signal-to-noise ratio of three, this sensitivity results in a minimum detectability of about 0.2 ng.[6] Recently, a 290-MHz SAW device has been reported that may allow rapid detection of organic vapors at 100 ppb.[25] Wohltjen has estimated that a 3-GHz SAW device would have a minimum detectable mass change of 3×10^{-15} g.[6]

G. Microsensor Coatings

The requirements for a microsensor coating are as follows:

1. *Processible as a Uniform and Reproducible Film*

- The deposition technique must yield coatings with identical thickness and morphology reproducibly on many duplicate devices.
- The most precise technique to date is the Langmuir-Blodgett (L-B) multilayer transfer. This technique requires that film components be soluble in volatile organic solvents, be very insoluble in water, form monolayer films at the air/water interface, and transfer to the microelectrode substrate.[30-32]
- Other film deposition techniques producing coatings with uniform and reproducible thickness, and morphology should be equally applicable (e.g., spin casting, epitaxial growth, evaporation).

2. *Measurable Electrical Conductivity (for Chemiresistor Devices)*

Organic semiconductor films used in chemiresistor devices must have a measurable conductance to be useful. Interdigital electrode arrays on quartz typically exhibit an uncoated conductivity in the range of 10^{-15} to 10^{-16} S/cm under ambient conditions. Useful coatings must exhibit a conductivity significantly greater than this. Films having an intrinsic conductivity ranging from 10^{-10} to 10^{-9} S/cm display useful responses to vapors as chemiresistor coatings.[33,34] Moderately higher intrinsic conductivities would be beneficial. Ionic charge transport is undesirable in these devices as it would result in a device with a nonreversible response.

3. *Required Response to Vapors*

- Detectability — greater than 10 ppm
- Response time — less than 10 min

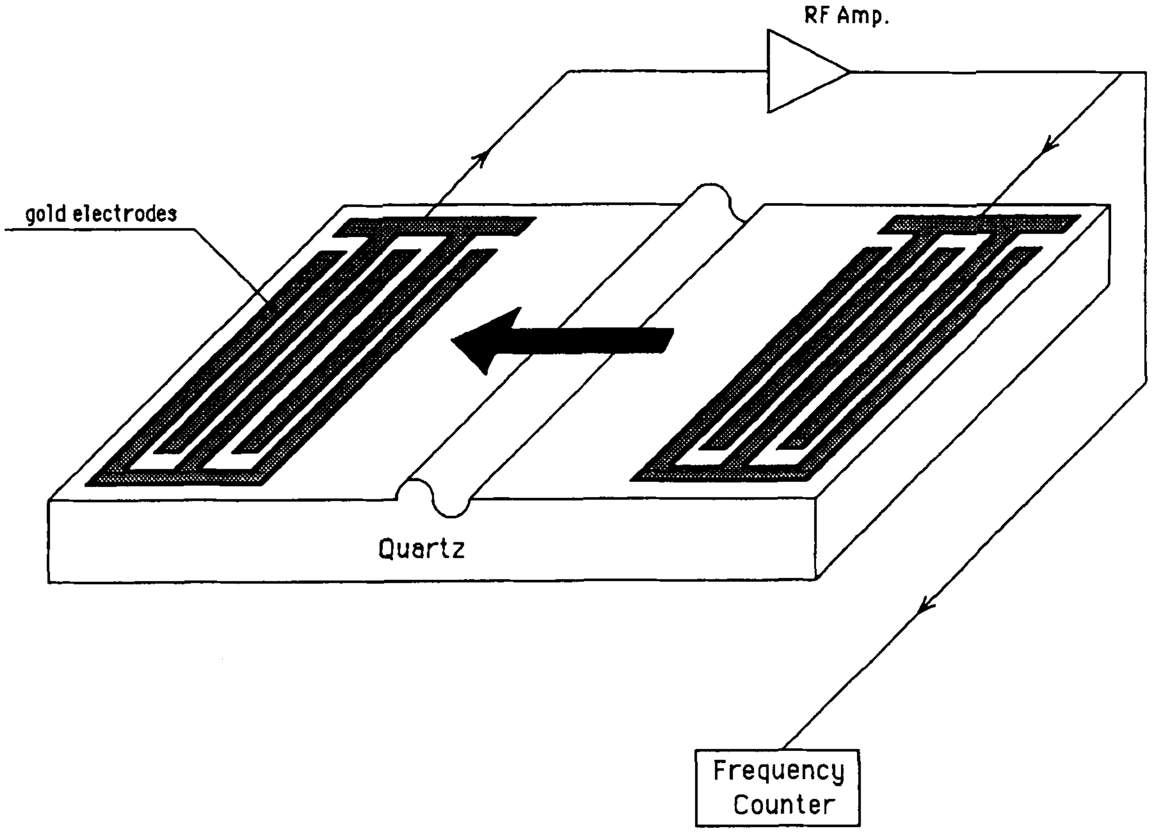


FIGURE 4. SAW sensor.

- Reversibility — greater than 90% recovery in 10 min
- Selectivity — 100:1 or better desirable
- Stability (adequate operational lifetime)

H. Methodology of Coating the Microsensor Device

Several techniques have been employed for coating microsensor devices. The first is a spin-coating[31] technique where the analyte is dissolved in a suitable organic solvent and placed on the surface of the device, the device is spun to spread the coating over the surface of the device, and the excess is spun off. This technique tends to be most useful for applying viscous polymer coatings. The second is a spray technique[23] where the analyte is again dissolved in a suitable organic solvent and airbrushed onto the surface of the device. This is a versatile method of applying coatings as most coatings can be applied in this manner. Additional techniques include sublimation, dip coating, evaporation, and condensation,[35] as well as those previously mentioned. Any of the aforementioned techniques for coating a microsensor device results in an amorphous coating on the device.

A more specialized coating technique is the L-B multilayer transfer, which can be utilized to apply the coating to the device in ordered monolayers.[23,30-32] Figure 5 shows a schematic representation of the L-B technique. The coating is placed on an aqueous surface where it forms an ordered monolayer. The device is then dipped into the aqueous layer, and, as it passes through the interface, the coating adheres to the device. Multiple passes through the monolayer build up multiple layers of the coating. The drawback here is that the coating must form a stable film on the aqueous layer and must readily transfer to the microsensor device. We have attempted to synthesize compounds that form stable films on aqueous surfaces so that they may be applied to microsensor devices via the L-B technique. This is not a necessary criterion for a good

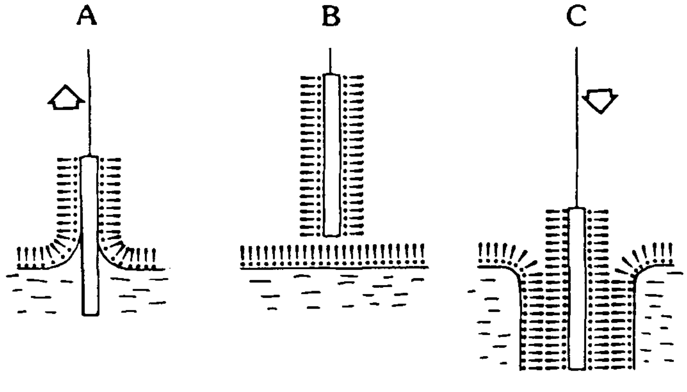


FIGURE 5. The Langmuir-Blodgett coating technique (figure from Reference 70).

microsensor coating, but studies on microsensor devices that are coated with ordered monolayers may help to understand coating-adsorbate interactions on the surface of the devices. This may be of particular interest in the case of chemiresistor devices where the vapor/coating interactions are not well understood.[33,34]

The method we have chosen to utilize for coating our devices has been the spray-coating technique. In this method the coating is dissolved in a suitable volatile organic solvent and simply airbrushed onto the SAW device (Figure 6). The frequency of the device is monitored and the coating is applied until a shift of ~50 kHz is seen. A mask is used to prevent overspray or damaging any of the electronic components. The spray technique is generally simple to do, fast, reproducible, and provides a more even coating than the spin-coating technique. It also requires much less sophisticated equipment than either the L-B technique or the spin-coating technique.

I. Microsensor Electronics and Vapor Generation System Employed in This Study

Figure 7 shows the electronic components used for carrying out computer-controlled simultaneous SAW and chemiresistor measurements. The apparatus includes a computer and peripherals that control the electrometer and frequency counter. These are connected to an oscillator box that contains the SAW device. The analytes are generated and passed through the oscillator box, over the surface of the SAW device, and the signals are then relayed to the computer where the results can be graphed.

The apparatus is shown assembled in Figure 7. (It is similar to those presently in use at NRL[95] and has been patterned after Barger's apparatus.) Other microsensor apparatuses have been reported as well.[36] An apparatus such as that in Figure 7 allows computer-controlled data acquisition to be carried out using an Apple IIE computer interfaced with an electrometer and to a frequency counter through an IEEE-488 interface. The computer and its peripherals are all commercially available, as are the other electronic devices. The oscillator box is commercially available from Microsensor Systems, Inc. (Fairfax, VA).

Figure 8 shows a schematic of a simple gas-handling system that can be employed with the microsensor coating testing apparatus. Nitrogen is used as the carrier gas, and attempts are made to minimize any problems associated with contamination by using only Teflon® and glass components. The Teflon® parts are high-performance liquid chromatography (HPLC) components purchased from the Ranin Instrument Co. (Mack Road, Woburn, MA, 01801-4628) or Cole-Parmer Instrument Company (7425 N. Oak Park Ave, Chicago, IL, 60648). The

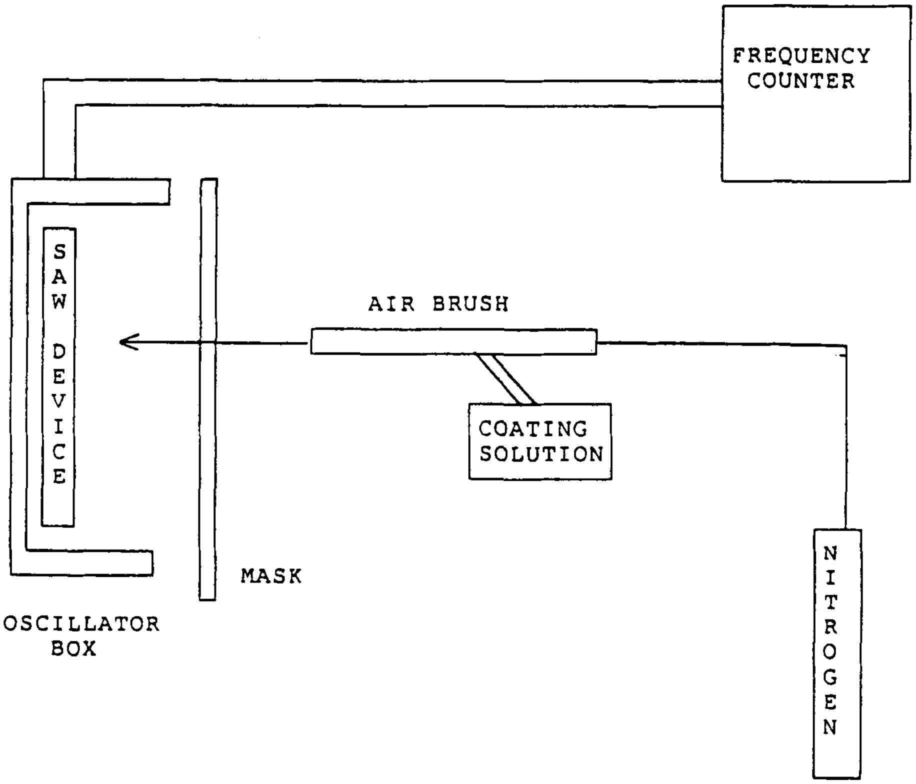


FIGURE 6. SAW coating system: the coating is sprayed on until a 50-kHz shift in the frequency of the device is seen.

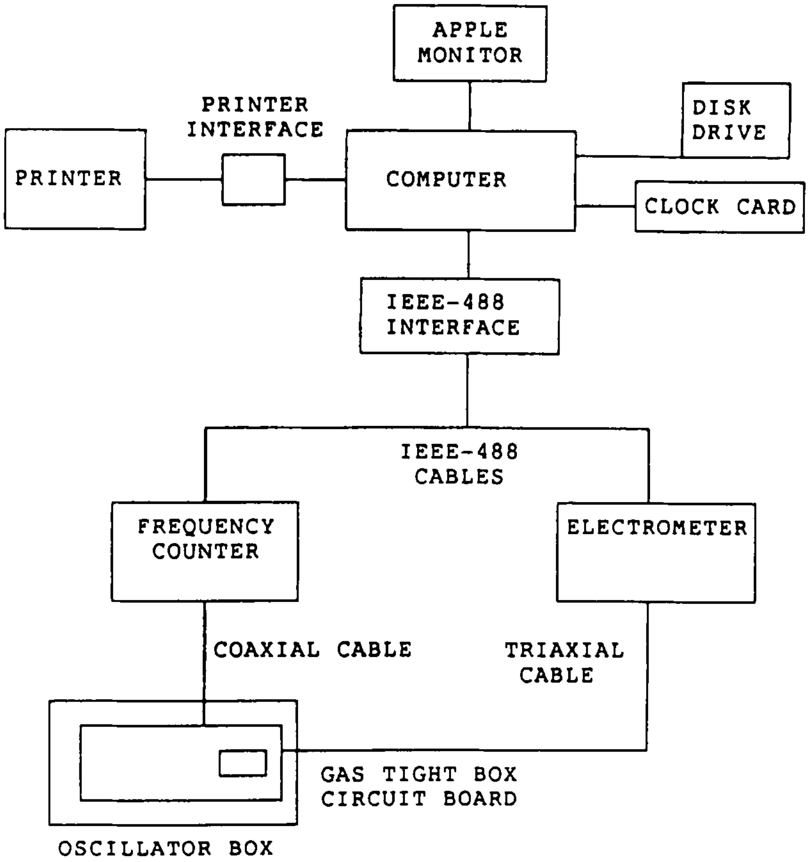


FIGURE 7. Electronic components of apparatus for testing the response of coatings on SAW and chemiresistor devices.

oscillator box is shown at the left. The gas-tight sampling box is milled from Teflon®, nylon, or Delrin®. The top of the box can be threated to make quick, easy connections with HPLC components. Vapors can be generated with a gas permeation tube at 0°C (by cooling in a Dewar), and nitrogen flow rates can be low (5 ml/min).

Figure 9 shows a schematic of an oscillator box. This device houses the sample chamber, the SAW device, and has the associated electronics for signal amplification. Brass-coated screws and platinum connectors (0.05-mm diameter) make the contact between the SAW device and circuit board.

II. COATINGS PREVIOUSLY USED FOR PIEZOELECTRIC MICROSENSORS AND REQUIREMENTS FOR NEW COATINGS

A. Compounds Previously Utilized as Microsensor Coatings

A number of compounds have been examined as microsensor coatings for bulk-wave piezoelectric, SAW, and, to a small extent, chemiresistor devices. However, no systematic approach has been taken to identify new microsensor coatings. A brief summary of the literature on coatings for microsensors is included to help acquaint the reader with some of the background material on coatings for these devices, the vapors detected by these coatings and devices, and to aid the reader to better understand the principles of how these devices work. Particular emphasis has been placed on the types of compounds that have been employed as coatings for these devices, as well as the types of vapors that they were able to detect and the concentration levels at which the vapors were detected.

The ultimate performance of a SAW device as a chemical sensor is critically dependent on the sensitivity and selectivity of the adsorbant coating applied to the surface of the piezoelectric crystal. No systematic investigation of adsorbant coatings on SAW devices has been reported, and references to responses of specific SAW coatings to specific vapors are few in number.[11,13,37,38] The most closely related sensor technology is the bulk piezoelectric crystal sensor, which has been recently reviewed.[10] Coatings that exhibit selectivity to specific vapors have been identified in some cases, but many coatings have been of ill-defined composition, and, until recently, selection has been largely empirical.[15,39-43] It is, therefore, essential to identify coatings for SAW devices that respond to vapors of interest, and to develop a rationale for the selection or design of such coatings.

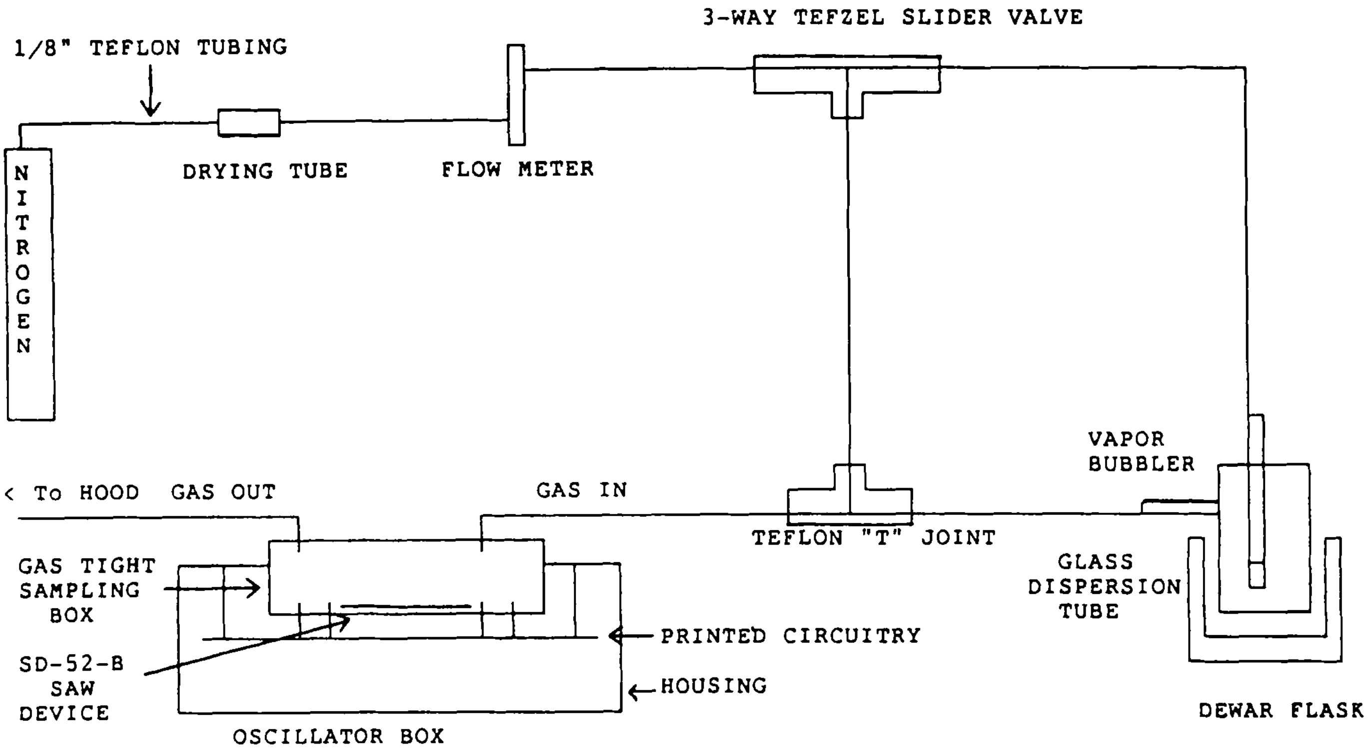


FIGURE 8. Vapor generation system for microsensor testing.

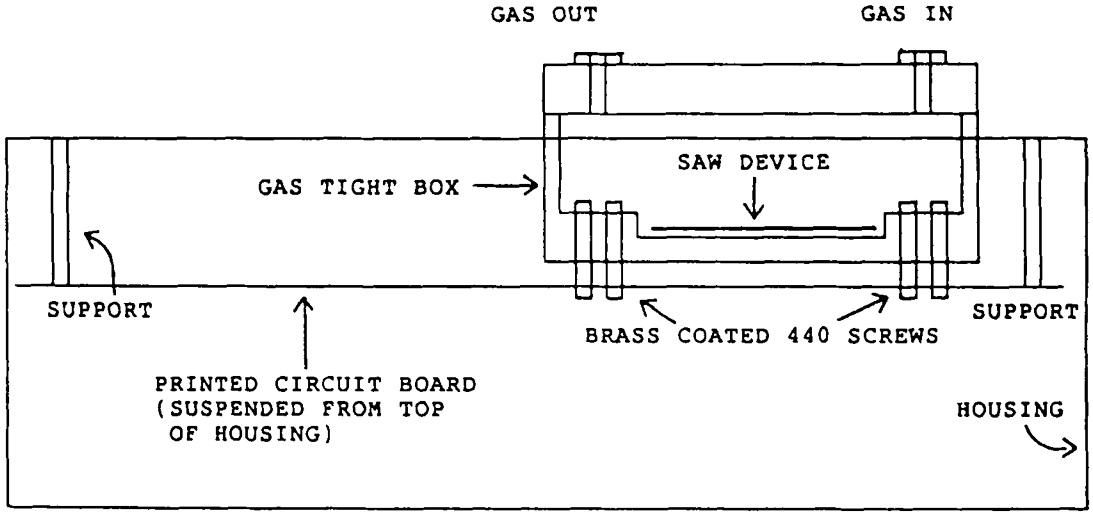


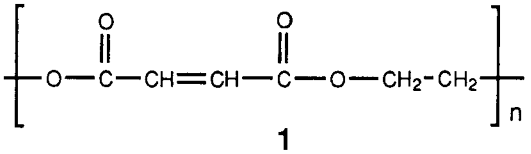
FIGURE 9. Oscillator box for microsensor apparatus.

The development of adsorbant coatings alone may not be sufficient for some applications of these devices. It is unlikely that any given material possesses sufficient selectivity to permit accurate detection and identification of a single chemical vapor of interest in the presence of multiple, unknown interferences. One approach to this type of analytical problem is the use of pattern recognition techniques in conjunction with an array of sensors of varying selectivity. This approach has been applied to vapor response data from electrochemical sensors[14-16,19] and to the selection of coatings for piezoelectric crystal sensors and is discussed later (*vide infra*).

1. SAW Device Coatings

This section deals with coatings that have been employed for use on SAW devices and the vapor challenges that have been employed in testing. The largest volume of work that currently exists on SAW coatings has been done at the NRL in Washington, D.C., and at the Chemical Research, Development, and Engineering Center (CRDEC) at Aberdeen Proving Ground in Maryland.

A variety of polymeric materials have been employed as coatings for SAW devices.[44] To date, the coatings that show the greatest response to vapor challenges include poly(ethylenemaleate) (PEM) **1**, which has been used for the detection of dimethyl methylphosphonate (DMMP) at 1.0 ppm. A fluorinated polymer (FPOL) **2** has been employed to detect DMMP at levels estimated as low as 0.03 ppm.[45] The FPOL incorporates CF_3 groups at regular intervals along a polymer backbone. Poly(epichlorohydrin) **3** has been utilized to detect DMMP at 15 ppm.



$$\left[-O-\overset{O}{\overset{\|}{C}}-CH{=}CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\right]_n$$

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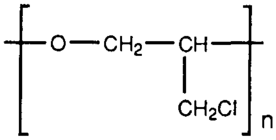

$$\left[-O-CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-\right]_n$$

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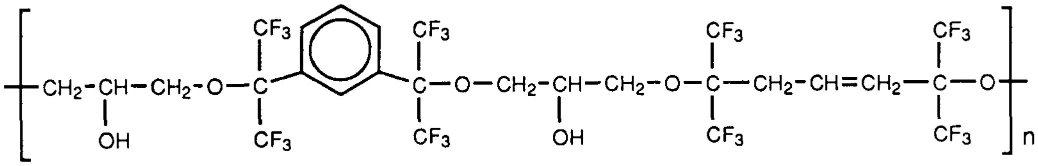

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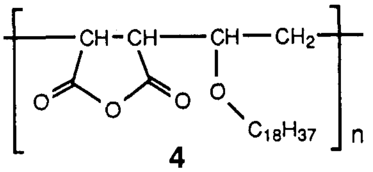

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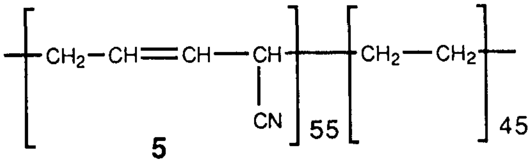

$$\left[-CH_2-CH{=}CH-\underset{CN}{\underset{|}{CH}}-\right]_{55}\left[-CH_2-CH_2-\right]_{45}$$

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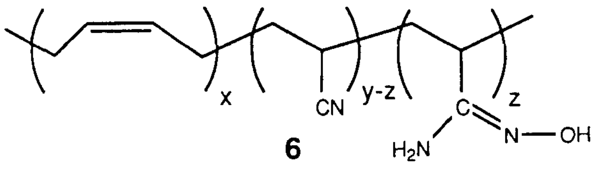

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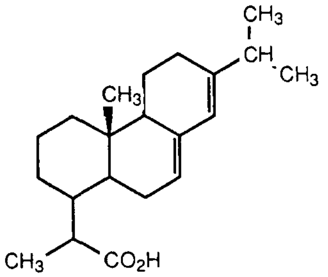

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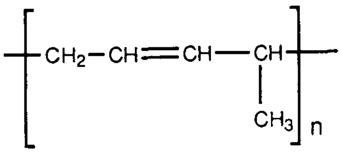
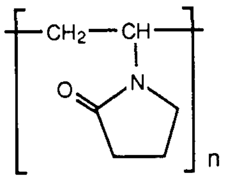


$$\left[-CH_2-CH{=}CH-\underset{CH_3}{\underset{|}{CH}}-\right]_n$$

8



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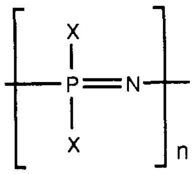


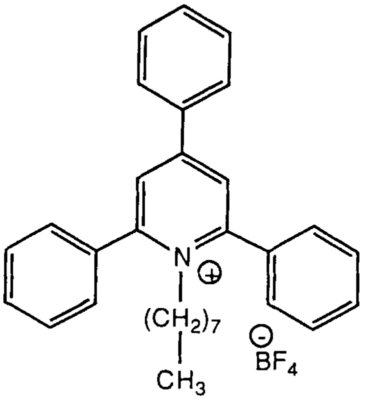
$$\left[-\underset{X}{\underset{|}{\overset{X}{\overset{|}{P}}}}{=}N-\right]_n$$

10

Additional polymer coatings that were examined include octadecyl vinyl ether maleic anhydride copolymer (OVERMAC) **4**; acrylonitrile butadiene copolymer (PBAN) **5**; poly(amidoxime) (PAOX) **6**;[46] abietic acid (ABACD) **7**; OV215, poly(isoprene) (PIP) **8**; poly(vinylpyrrolidone) (PVP) **9**; and polyphosphazines (PPZN1 and PPZN2) of general structure **10**. These coatings were tested against methanesulfonyl fluoride (MSF); *N,N*-dimethylacetamide (DMAC); and dimethyl methylphosphonate (DMMP) vapors. The fluoropolyol **2** was by far the most sensitive to all three vapors, while PEM **1** exhibited responses of about 50% of the magnitude of the fluoropolyol.[44] Reference 44 gives a good overview of the efficacy of these compounds in the detection of various vapors. Additional reports on the use of these compounds as SAW coatings have also been detailed. Using OV215 (a trifluoropropyl dimethyl silicon compound), DIMP (diisopropyl methylphosphonate) was detected at concentrations as low as 0.5 ppm.[37] Other reports on the use of PEM for vapor detection have also appeared with concentrations of DMMP as low as 1.6 ppm being detected.[29] Snow and co-workers have synthesized a number of polymer coatings that are PEM variants, but to date PEM remains as the most sensitive to DMMP vapor.[47]

Wohltjen and co-workers and Munavalli et al. have examined a number of pyridinium compounds as SAW coatings for the detection of DMMP vapor.[48-50] Their best results were obtained with compounds **11** and **12**, which were very sensitive to DMMP while at the same time relatively insensitive to water, ethanol, and toluene vapor. Small variations in the structures of **11** and **12** resulted in a loss of sensitivity for DMMP, however.

Additional heterocyclic systems that have been employed as SAW coatings are the vinyl(imidazole) systems such as **13** and **14**, which have been employed in the detection of MSF, DMMP, and DIMP.[51] Vetelino and co-workers[52] have reported on the use of a thin film WO_3 as a coating for the detection of H_2S in the presence of N_2 and CO at 10 ppb with excellent selectivity.



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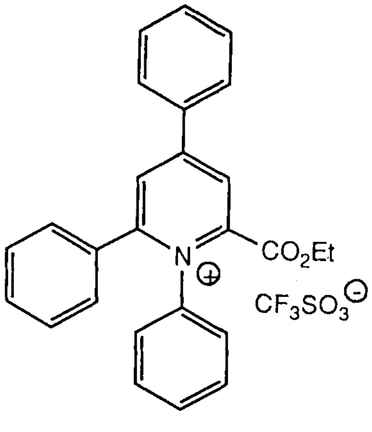

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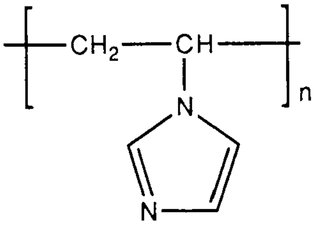
2. Bulk-Wave Piezoelectric Crystal Sensor Coatings

A related technology to SAW devices is the bulk-wave piezoelectric crystal sensor. As mentioned previously, this technology is somewhat older than that associated with SAW devices, although the principles are quite similar. A much wider variety of coatings and vapor challenges to the coatings have been examined, but, again, little in the way of a systematic approach to the development of new coatings has appeared in the literature. Since 1977, five reviews have appeared on the application of piezoelectric crystals to chemical analysis.[39,53-56]

Several types of Carbowax packings for gas chromatography columns have been tested as coatings for bulk-wave piezoelectric crystal devices. Carbowax 550 was used as coating for detecting toluene in the concentration range of 30 to 300 ppm in the presence of a number of inorganic vapors, such as CO, SO_2, NH_3, or NO_2.[57] Other organics such as benzene or alkylbenzenes did show significant interferences. Carbowax 1000 was used for the detection of explosives such as trinitrotoluene (TNT) based on the detection of mononitrotoluene (MNT) at concentrations as low as 1 ppb.[58] Carbowax 20M has been utilized in the detection of chloroform.

Coatings of undefined structure have also been employed as coatings for piezoelectric sensors. Karmarkar and Guilbault[59] used Ucon 75-H-90,000 and Ucon-LB-300X (lubricants of undisclosed structure) as coatings in the detection of NH_3 and NO_2 at the 1-ppb level. An acetone extract of soot from a pyrolyzed chloroaromatic or chloralkyl compound was used as a coating on a piezoelectric crystal for the detection of H_2S at concentrations as low as 1 ppm.[60] An example exists of an uncoated piezoelectric crystal that has been used to detect the organic phosphate DIMP with some success.[61]

The detection of organophosphorus derivatives is of interest because of their widespread use as pesticides. Coatings that have been utilized for the detection of organophosphorus compounds include 2-pyridylaldoxime methiodide (2-PAM) **15** and isonitrilobenzoylacetone (IBA),[62] $FeCl_3$,[63] copper chelates



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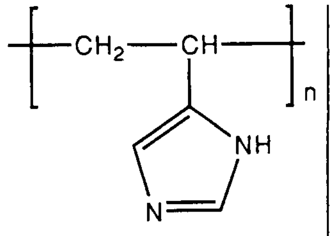

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of poly(vinylpyrrolidone) and poly(vinylbenzyl) chloride,[42,64] histidine hydrochloride,[65] and 1-*N*-dodecyl-3-(hydroximinomethyl)pyridinium iodide (3-PAD) **16**.[65] In certain instances the detection limits were quite low; for example, malathion could be detected at 1 ppm using a crystal coated with histidine hydrochloride **17**.[65]

Reports on the detection of a number of other vapors by a variety of coatings have also appeared. Morrison and Guilbault[41] reported on the detection of toluene diisocyanate (TDI) utilizing silicon-based coatings. They reported that TDI could be detected at 10 ppb with only minor interferences from ketones and alkylbenzenes. The authors examined a total of three coatings: Silicone Fluid FS-1265, Silastic LS-420, and high-vacuum silicone grease. FS-1265 exhibited the greatest sensitivity to TDI vapor. Guilbault and co-workers also examined coatings for the detection of ammonia[66] (L-glutamic acid hydrochloride **18** and pyridoxine hydrochloride **19**), SO_2[67] (various amines, including quadrol, triethanolamine, Amine 220, and Armeen 2S), and HCl[68] (trimethylamine hydrochloride and triphenylamine). Fog and Rietz[40] have utilized a polybutadiene crystal coating for the detection of ozone in the workplace at 10 ppb with little interference from nitrogen oxides, formaldehyde, CO, and phenol. Ito[69] has reported on a piezoelectric crystal humidity sensor that employs an epoxy resin as an amorphous polymer in its selective coating.

3. Chemiresistor Sensor Coatings Previously Reported

Only a few examples of chemisensor coating materials are reported in the literature. A number of phthalocyanines **20** have been employed as coatings for microsensor devices for use as SAW and chemiresistor coatings. The coatings were applied by the LB technique, in which ordered layers of phthalocyanines were applied to the SAW device, and by spraying-coating technique, where amorphous layers were applied.[5,23,31,33,70-73] These coatings have been employed in the detection of ammonia below 0.5 ppm as well as the detection of low levels of DMMP, SO_2, NH_3, and NO_2.

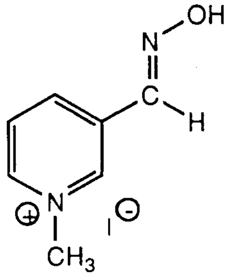
N-Eicosyl- and *N*-docosyl-pyridinium tetracyanoquinodimethane **21** have been reported to be sensitive to iodine vapor.[74,75]

B. New Materials for SAW Coatings

Particularly desirable additional requirements for useful new coatings include:

1. Adsorption capacity, i.e., maximal solubilities of the desired chemical agent(s)
2. Discrimination between the agent(s) of interest and ambient vapors

Barlow (University of Texas) has pointed out that the largest negative enthalpy of solution of an agent simulant (DMMP)



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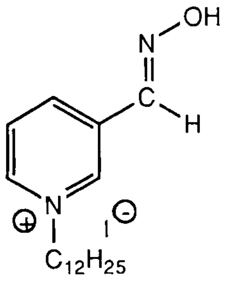

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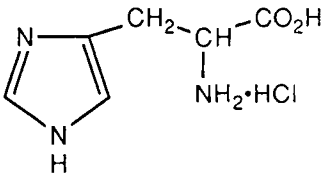

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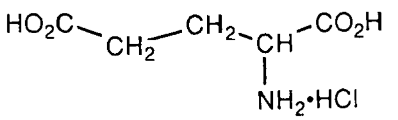

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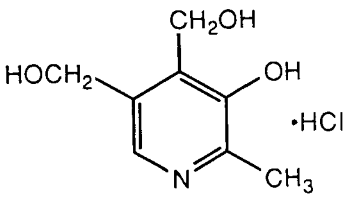

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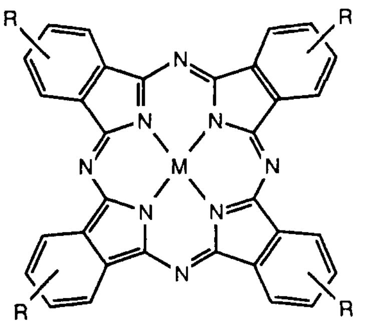
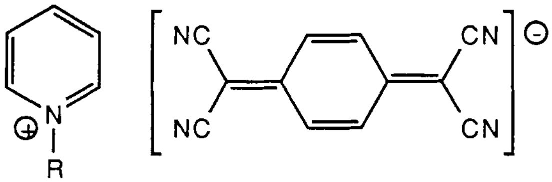


20 M = H_2, Mg, Co, Ni, Cu, Zn, Pd, Pt, Bi, Pb



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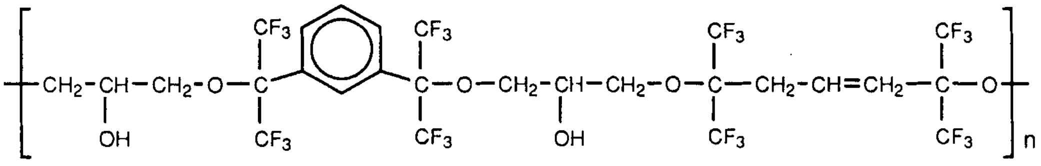
in a number of available solvents was in hexafluoroisopropanol (HFIP). HFIP has the largest alpha value (measure of hydrogen-bond donor acidity) of available solvents, and DMMP is a strong hydrogen-bond acceptor base.

Hence, it was suggested to incorporate $HO{-}C(CF_3)_2{-}$ groups into a copolymer of divinylbenzene and *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)styrene.[76] This copolymer should interact strongly with P=O bases and be a likely candidate for SAW coatings. Testing of this polymer **2** on a SAW device confirmed that, indeed, it was a very good SAW coating for DMMP detection. Sprague and co-workers[77] have synthesized analogs of this polymer **22** to **24** and have reported that the free hydroxyl groups of the polymer are necessary for maximum sensitivity in DMMP detection.

C. Chemometric Approach

Hirschfeld (Lawrence Livermore National Laboratory) and Kowalski (University of Washington) have used a chemometric approach of principal components analysis and pattern recognition.[15] Pattern recognition techniques were applied to frequency shift data obtained from 27 gas chromatography stationary phases using 14 analytes. The procedure allowed

Fpol Structure and Variants



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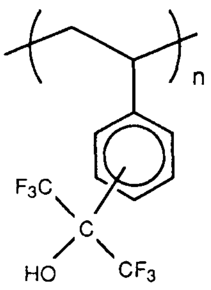

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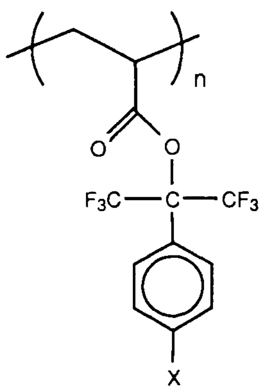
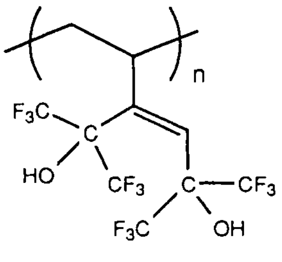


X = H, $C(CF_3)_2OH$

23



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the selection of seven coatings that provided the maximum level of analyte-discriminating ability.

Other factors (cost, reliability, etc.) are taken into consideration in the selection process while maintaining maximum analytical power with the fewest sensors.

D. Solubility Properties for Coatings[78-82]

It was desired to optimize:

1. The adsorption capacity (i.e., maximize solubility)
2. The discrimination between agent and interferent

The adsorption on SAW coatings is defined by Abraham et al.[82] in Equation 3:

$$AP = AP_o + S\pi^* + a\alpha + b\beta + l \log L_{16} \qquad (3)$$

Here AP = adsorption property, $S\pi^*$ = solvatochromatic parameter measuring molecular (dipolarity/polarizability), α and β measure solute-solvent hydrogen bond interactions, and $\log L_{16}$ = Ostwald solubility coefficient (gas-liquid partition coefficient).

E. Linear Solvation and Pattern Recognition Techniques

Snow and co-workers have suggested exposing a number of SAW coatings to a variety of vapors and then correlating the response with solubility properties.[49] The data are then treated by pattern recognition techniques[19,44,56,83-87] with the following results:

1. Sensors encode chemical information about vapors in numerical form.
2. Vapors with similar responses tend to "cluster" about a coating.
3. Multivariate statistics and numerical analysis are employed to investigate "clustering" and elucidate relationships.
4. This reduces interference effects and improves selectivity.

F. Potential for Future Development

Murday and co-workers[3] have summarized the present position and that expected in the year 2000 for both SAW and chemiresistor devices (Table 2). The sensor characteristics of these devices are totally dependent on the selective coating that is applied to the surface of the device.

III. DEVELOPMENT OF NEW MICROSENSOR COATINGS

A. General Objectives

Since the selectivity and sensitivity of chemical microsensors are almost wholly dependent on the coating, it is vitally important to continue the development of new coating materials. Some general criteria for the development of novel coatings are that they should:

1. Show superior selectivity to vapors
2. Show superior sensitivity to vapors
3. Form stable films on aqueous media
4. Transfer easily and reproducibly to SAW devices
5. Form coatings that show reversibility to uptake of vapors

In selecting candidates for these coatings our laboratory[88-92] has chosen a variety of structural compound classes, including:

1. Pyridine 1-oxides
2. Acridinium betaines
3. Pyridinium salts
4. Metal chelators
5. Other heterocyclic systems

Table 2
Present and Postulated Status of SAW and Chemiresistor Technology

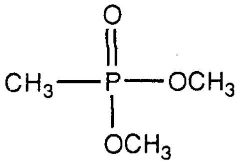
	SAW Device		Chemiresistor	
Device characteristics	**Present**	**Year 2000**	**Present**	**Year 2000**
Surface area (cm^2)	10^{-1}	10^{-4}	10^{-1}	10^{-4}
System volume (cm^3)	10	10^{-1}	10	10^{-2}
Power consumption (W)	1	10^{-1}	10^{-2}	10^{-5}
Sensor characteristics				
Detection limit				
(mg/m^3) DMMP in FPOL	0.05	0.0001	—	—
DMMP in PtPc	—	—	5	10^{-2}
Response time (s)	1—100	0.01—100	10—1000	1—100
Selectivity ratio				
DMMP vs. H_2O in FPOL	10,000:1	?	—	—
in PtPc	—	—	1000:1	?

B. Strategy

Our investigation was based on the following strategy:

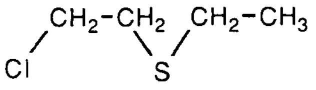
Synthesizing a variety of novel microsensor coatings for agent detection — The objectives for the synthetic work included the preparation of a variety of compounds, most of which are heterocycles. Originally, these compounds were to be sent for evaluation against background interferents at the NRL or to the Aberdeen Proving Ground for their effectiveness against various chemical agents. The results of the testing would then be used to guide the synthesis program. However, our collaborators did not want to spend large amounts of time to do elaborate testing on compounds that they were not sure would have utility as microsensor coatings. We set up our own microsensor coating testing apparatus to allow us to do preliminary screening on our (and other) compounds. In this way we were able to eliminate compounds from our synthetic work that did not show utility as microsensor coatings and to concentrate our synthetic efforts only on the most promising candidates.

Screening them against vapor challenges and sending promising candidates on for further testing — The compounds were tested against vapor challenges from a variety of chemical agents: DMMP **25** and chloroethyl ethyl sulfide **26** and water vapor. Only the more promising candidates were sent for further testing, such as suitability for use in L-B coatings or use for detection of other vapors.



$\mathrm{CH_3{-}P({=}O)(OCH_3){-}OCH_3}$

25



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Providing feedback for synthetic work and developing structure-utility relationships for agent detection — Our microsensor coating testing apparatus provided feedback into our synthesis program and helped guide us to make coatings with more desirable responses to phosphorus or sulfide-containing compounds. With enough data we may be able to develop structure utility relationships for agent detection to tell us what type of functionality we must build into our compounds to make them useful microsensor coatings.

The classes of compounds we chose to include in our study included various pyridines and other heterocyclic systems. Heterocycles were a logical starting point, as they had been previously identified as having utility as SAW coatings. For example, Wohltjen and co-workers and Munavalli et al.[48-50] had shown the utility of pyridinium salts as coatings for SAW devices for the detection of DMMP, while compounds **15** and **16** had also been identified as coatings for bulk-wave piezoelectric crystal sensors. Other heterocyclic systems have also been employed as microsensor coatings (see Section III.A). Abundant literature on the utility of phthalocyanines as both chemiresistor and SAW coatings (see Section III.A.3) prompted us to examine large planar heterocyclic systems (i.e., the acridinium betaines).

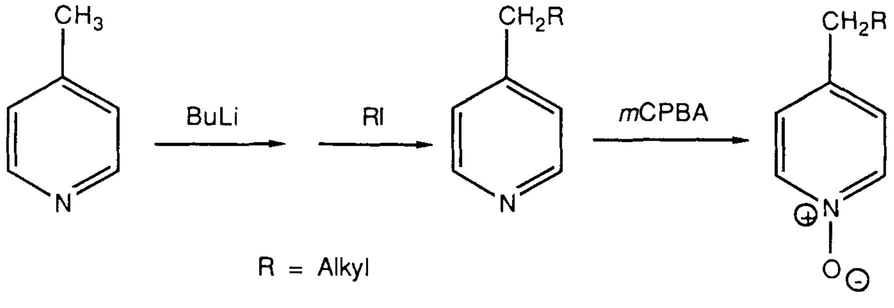
However, all of this synthetic work has been *exploratory* in nature. Without the fundamental knowledge of how the coatings interact with the analyte it is difficult to predict the response of a new coating when it is exposed to a vapor challenge. Especially for chemiresistor coatings, the mode of interaction between coating and analyte is particularly ambiguous. At this stage, it is important to identify new coatings and make alterations in the structures of known useful coatings to see what effect the structural modification has on the coating response. Only by this process, we believe, will we gain a better understanding of coating analyte interactions.

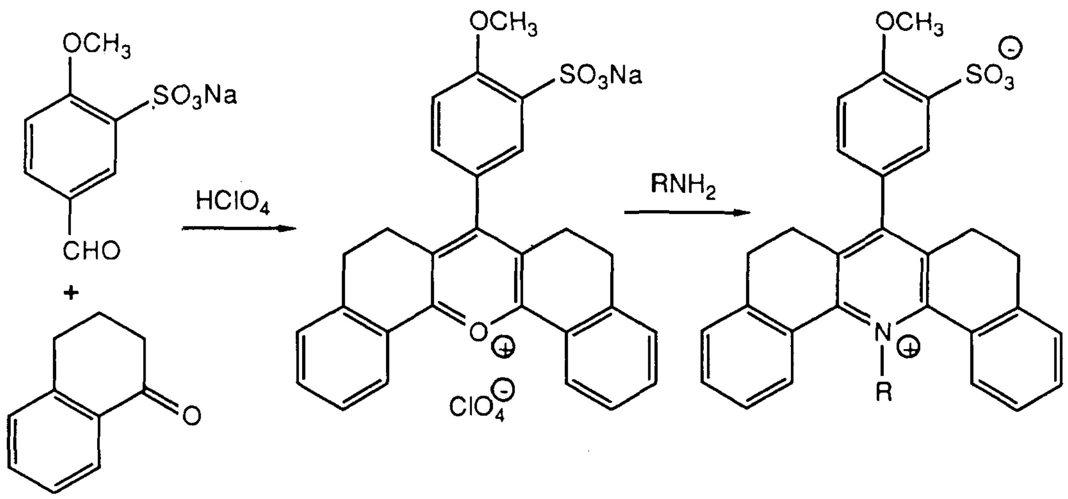
C. Pyridine 1-Oxide Synthesis[88]

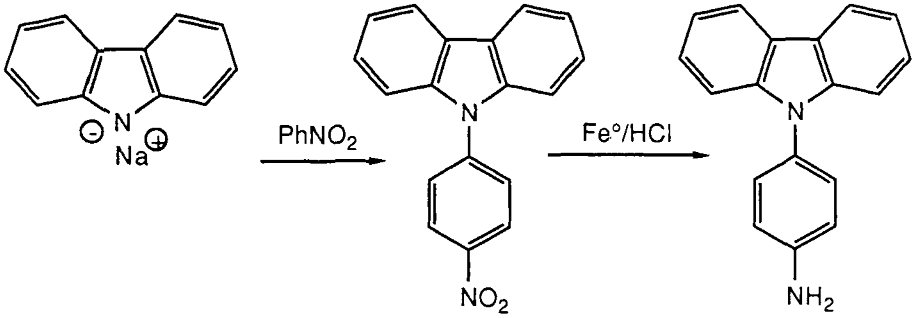
The synthesis of novel microsensor coatings included the preparation of pyridine 1-oxides that incorporated a long alkyl tail. These were prepared by the lithiation of 4-picoline and the subsequent reaction of the lithiopicoline to an alkyl iodide. The oxidation was effected by *m*-chloroperbenzoic acid in CH_2Cl_2.

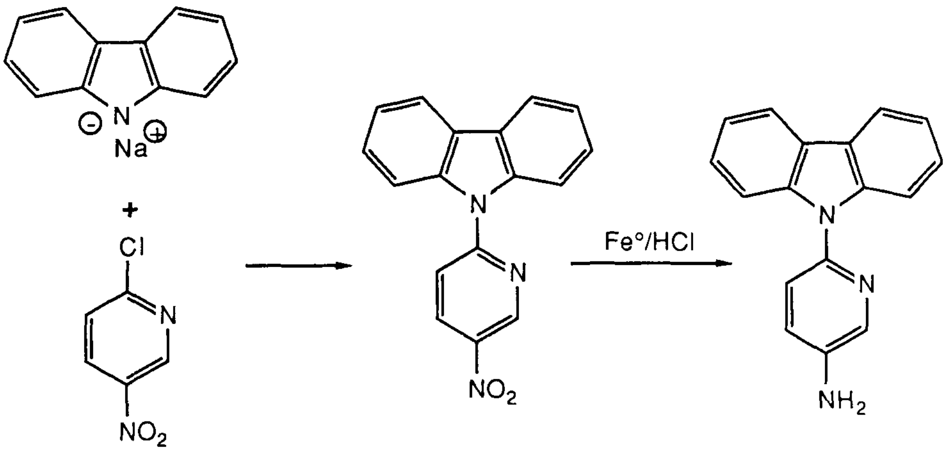
D. Preparation of Acridinium Betaines[89]

The betaines were prepared by the reaction of the known xanthylium salt with a variety of amines. In the case of the carbazole-derived compounds, these were prepared from the reaction of the sodium salt of carbazole with the corresponding nitro compound. The 1-substituted compound was then reduced with iron to form the corresponding amine.





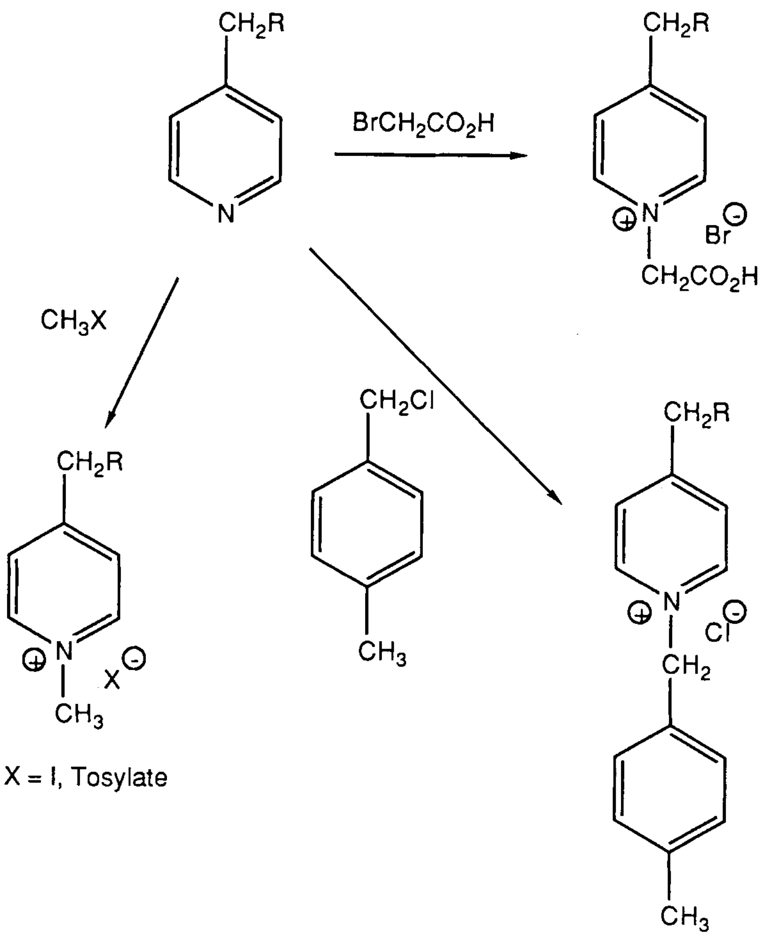




E. Synthesis of Pyridinium Salts[88]

A variety of pyridinium salts were prepared as well for use as microsensor coatings starting, in a number of cases, with the 4-substituted pyridines. These were alkylated with bromoacetic acid to form the corresponding pyridinium bromide and further neutralized with Na_2CO_3 to form the corresponding betaine. The *N*-alkylation of the 4-substituted pyridine was also effected with the *p*-methylbenzyl chloride to yield the 1-(*p*-methylbenzyl)pyridinium chlorides. A variety of *N*-methylated pyridinium salts with various counter ions were also synthesized. These compounds were prepared to test the effect of various counter ions on their utility as microsensor coatings.

Pyridinium compounds with extended conjugation were also prepared[88] to determine what effect extended conjugation may have on their utility as microsensor coatings. This was done by the initial alkylation of 4-hydroxybenzaldehyde with a long-chain alkyl iodide in refluxing absolute ethanol with K_2CO_3 as base. The resulting aldehyde was then allowed to react with 4-picolyllithium at −30°C to give the corresponding alcohol upon workup. This was dehydrated with acetic anhydride at



room temperature to give the alkene. The alkenes were then *N*-oxidized or *N*-alkylated to give the corresponding 1-oxides or pyridinium salts.

F. Synthesis of Pyridyl Ethers

The effect of other groups in the 4-position of the pyridine ring on the utility of these compounds as useful microsensor coatings was explored by the synthesis of pyridyl ethers of the type shown below.[88] These were prepared by the reaction of 4-chloropyridine with the benzyl alcohol in refluxing THF to give the pyridyl ether. This was then converted to either the 1-(carboxymethyl)pyridinium bromide with bromoacetic acid and then to the corresponding betaine, or it was methylated with methyl iodide to give the 1-methylpyridinium iodide.

G. Thiadiazole Synthesis

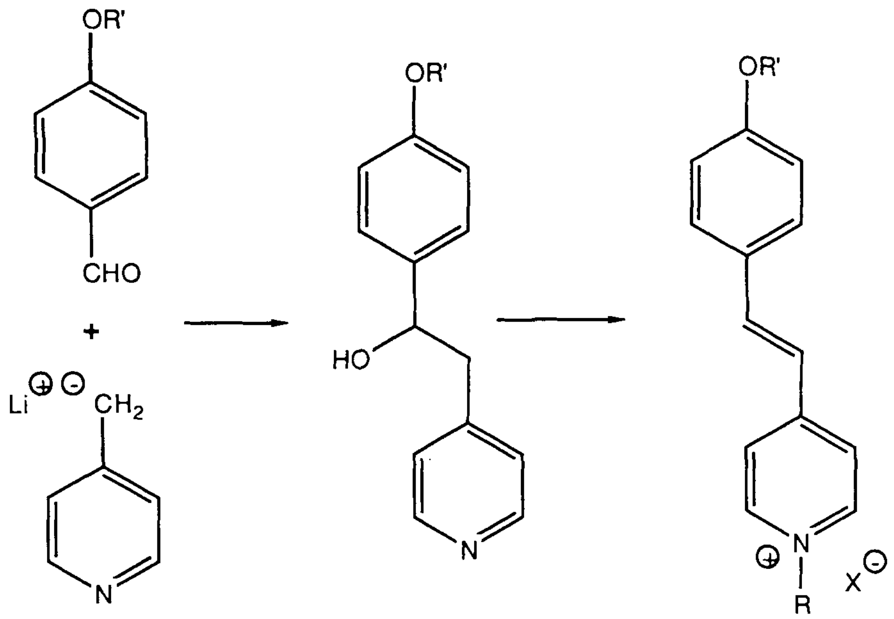
The search for new microsensor coatings has not been limited to pyridinium salts or pyridine-derived compounds. The preparation of sulfur-containing heterocycles has also been explored for their utility as microsensor coatings.[90] These heterocycles were prepared by the reaction of CS_2 with hydrazine in refluxing ethanol to give the thiadiazole. This was *S*-alkylated with alkyl iodides to give monoalkylated and symmetrical or unsymmetrical *bis*-alkylated products. The reaction of the monoalkylated thiadiazole with 1-chloromethylbenzotriazole resulted in the incorporation of a benzotriazole moiety into the heterocyclic system. Since the thione groups of thiadiazoles are known to interact with phosphites and phosphonates,[92] it is possible that the thiadiazoles will find utility as microsensor coatings. Depending on the type of interaction which occurs, however, the reversibility of the response may vary.

H. Synthesis Route to Metal Chelating Adducts

Since metal chelating compounds (i.e., phthalocyanines) have shown utility as chemiresistor coatings, a good approach to identifying new chemiresistor coatings is to synthesize other types of metal chelating systems and test them as microsensor coatings. One area that is currently being explored is the synthesis of copper cyanopyridine complexes as shown below from 2-cyanopyridine, copper chloride, and a variety of alcohols.[91] An additional synthetic route to metal complexes of the type shown below is underway.[93]

I. Film Formation of Heterocyclic Systems

The film-forming ability of a number of heterocyclic systems was studied by Katritzky and co-workers.[88,89,94] In general, they have reported that acridinium betaines (see Figure 10) formed stable films on aqueous media. The pyridine 1-oxide



R = Alkyl, -O$^-$

R' = $C_{12}H_{25}$, $C_{16}H_{33}$

(see Figure 11) formed a stable film, but only at film pressures lower than 10 dyn/cm.

IV. RESPONSE OF NEW COATINGS TO VAPOR CHALLENGES

A. Response of Pyridine 1-Oxides to DMMP

The response of tridecylpyridine 1-oxide to a DMMP vapor challenge in shown in Figure 12. The coating was sprayed onto a SAW device and exhibited a resistance of about 10^9 Ω. After exposure to iodine the resistance of the coating decreased to 10^5 Ω.[93] After an exposure to DMMP a small frequency change was seen, but a fairly large (approximately two orders of magnitude) change in resistance was seen. The conductivity of the film was on the order of 10 to 15 times that of the phthalocyanines, which have been employed as chemiresistor coatings. The 17-carbon adduct showed a similar response.

B. Response of Pyridinium Salts to DMMP

The responses of the compounds with extended conjugation to vapor challenges with DMMP are shown in Figure 13. As with the 1-oxide in Figure 12, the response as a SAW coating was minimal.[88] The response as a chemiresistor coating was also very poor. The resistance was greater than 200 GΩ and did not change through the lifetime of the run. Certainly, modifying the substituent in the 4-position of the pyridinium compound does markedly affect its utility as a chemiresistor coating. Unfortunately, in this instance the response was much worse, not better.

C. Pyridinium Betaine Vapor Response

Figure 14 shows the response of this tridecylpyridinium betaine as a chemiresistor coating to both DMMP and CEES.[88] The coating exhibited several positive attributes as a microsensor coating, including:

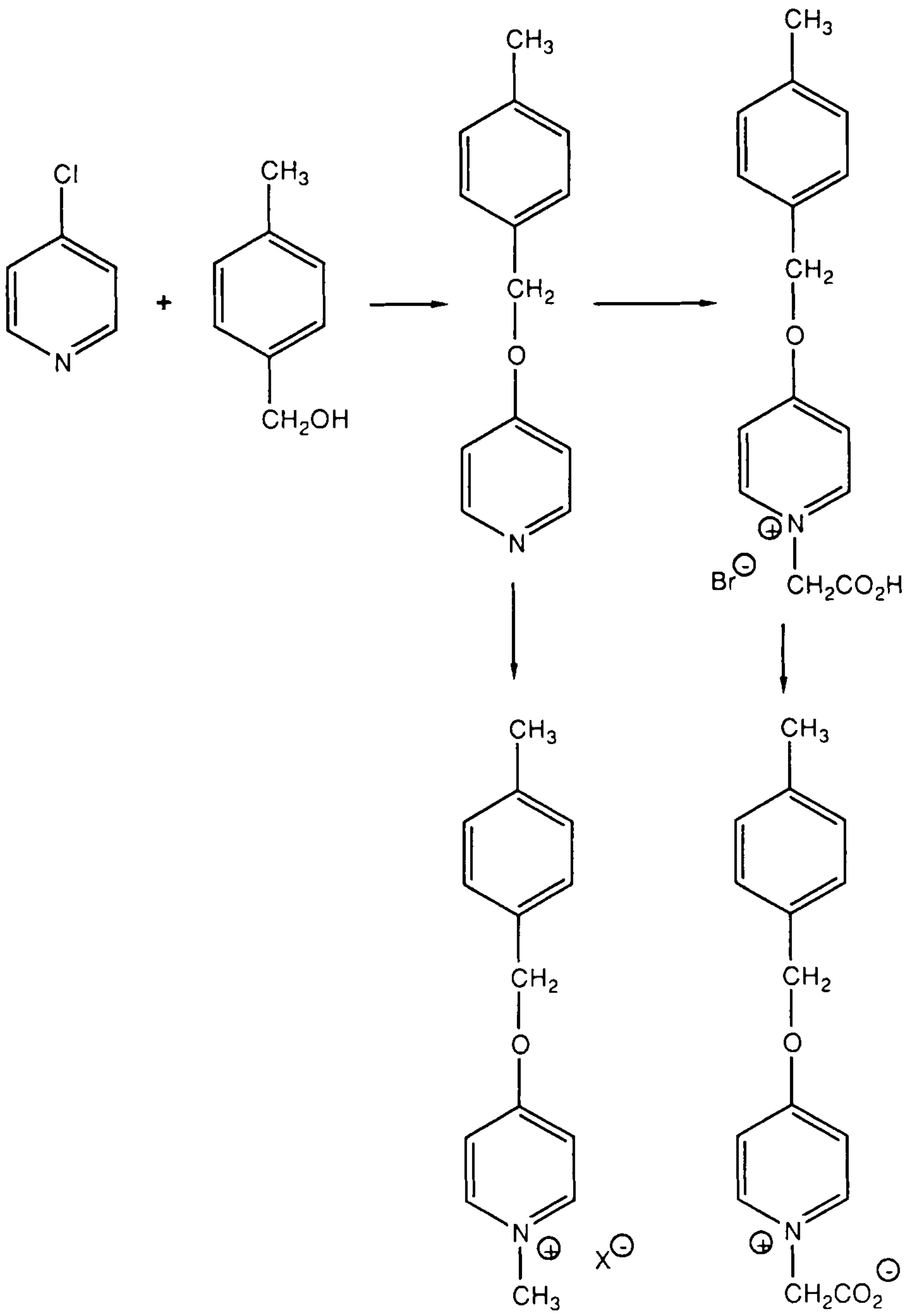
1. A rapid response to the vapor challenge
2. A large change in the resistance of the coating (two or greater orders of magnitude in each case)
3. A very rapid return of the resistance to baseline levels when the vapor challenge was removed

D. Response of Acridinium Betaines to Iodine Vapor

The acridinium betaines were coated on a SAW device via the L-B technique with the aid of a transfer promoter (stearamide), and 37 to 45 layers of the material could be applied with deposition ratios that ranged from 0.63 to 0.73. The coating exhibited a resistance of $\sim 10^{12}$ Ω, but after I_2 exposure the resistance dropped to $\sim 10^8$ Ω.[93]

E. Response of Pyridyl Ether Salts to CEES

Exposure of the 1-methyl pyridyl ether salt to CEES resulted in an extremely large change (4000 ×) in the resistance of the coating as shown below (Figure 15). The response was not completely reversible, however, as even after 100 min the resistance had not returned to baseline levels. As a SAW coating the response was extremely small (<1 kHz), which indicates a very low uptake of material into the coating and makes the



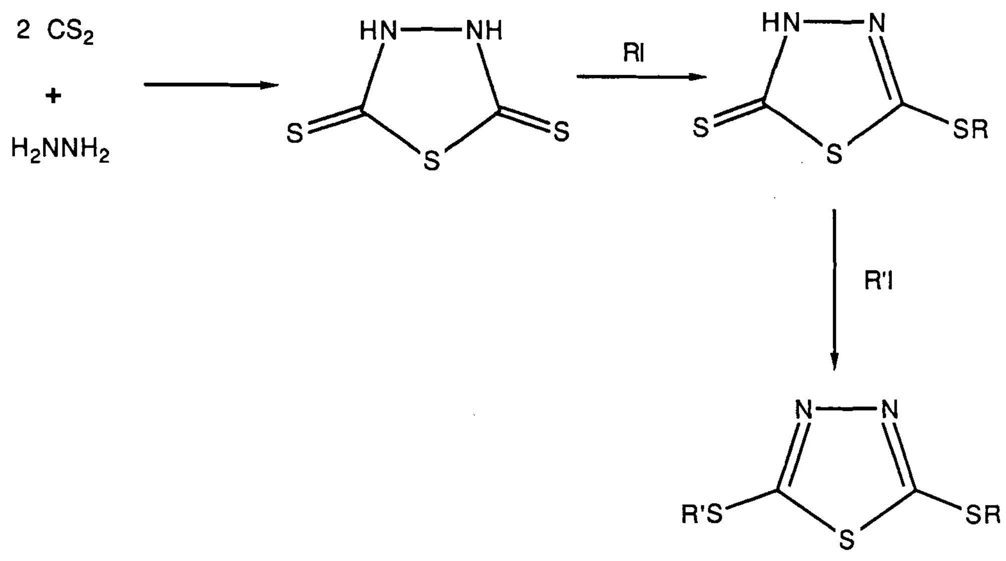
large response somewhat puzzling. Exposure of the coating to DMMP vapor (Figure 16) gave a response that was both qualitatively and quantitatively different. The resistance change was much smaller (30 ×) and nearly completely reversible.

F. Response of 1-Methyl Pyridinium Sulfonates to CEES

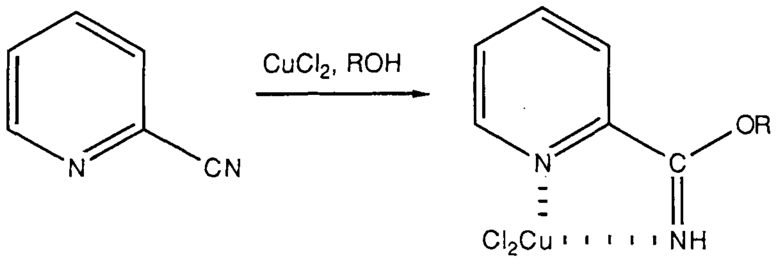
The sulfonate salt of the 4-octyl-1-methylpyridinium compound showed approximately a one order of magnitude change in resistance upon exposure to CEES vapor (Figure 17). In this case, as with some of the previous compounds, the resistance did not return to baseline levels after the vapor challenge was removed.

G. Response of 4-Hexadecyl Pyridinium β-Napthalenesulfonate to CEES

This coating also showed a large resistance change upon exposure to CEES (4000 ×). This coating showed little reversibility when the vapor response was removed. It also showed a low uptake of material into the coating (Figure 18).



R = Octyl, Dodecyl R' = Octyl, Dodecyl, Methylbenzotriazole



V. CONCLUSIONS AND FUTURE WORK

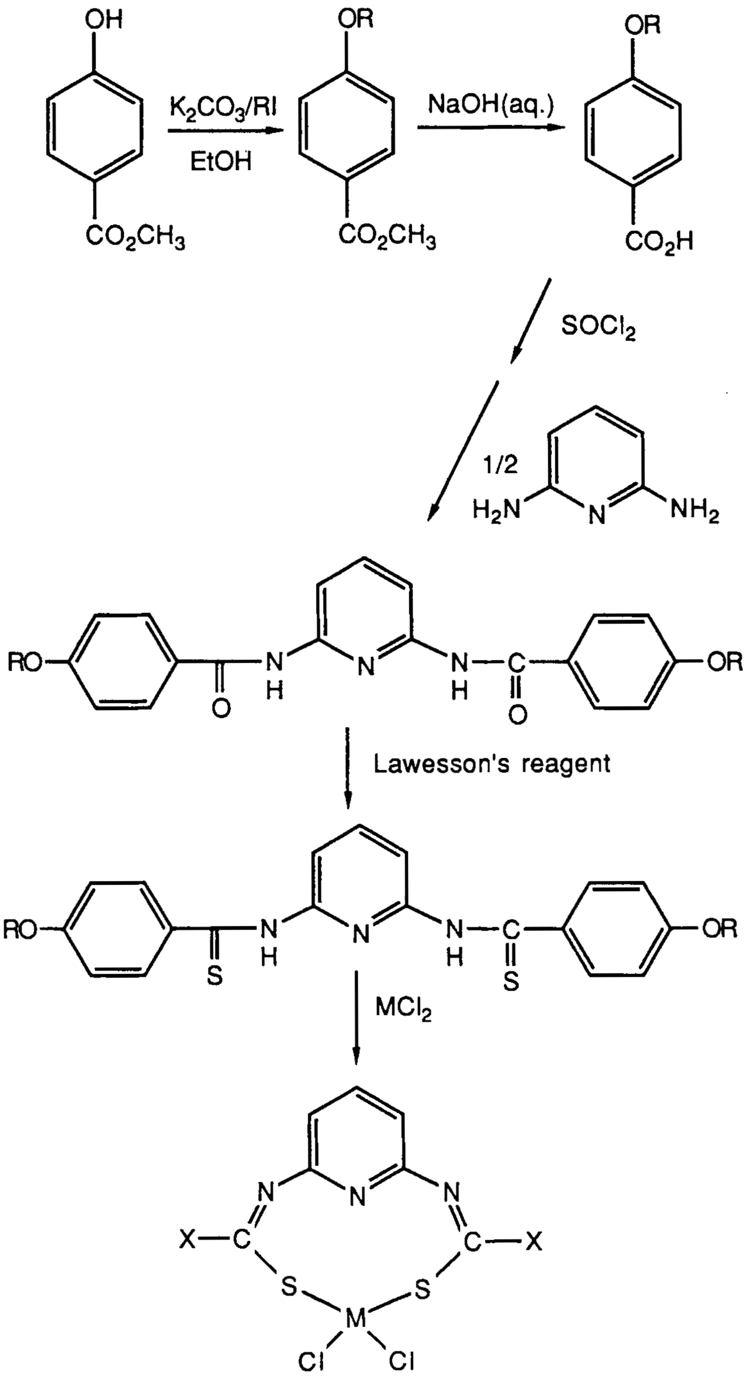
Microsensor technology is a fast-growing field that has the potential of providing a number of extremely sensitive and selective detectors for a wide variety of uses. The field is advancing on a number of fronts, with groups interested in a variety of aspects, including the development of new microsensor hardware, pattern recognition techniques to aid selectivity, and systematic approaches to designing new coatings through chemometric and synthetic means. Recent developments on the synthesis of microsensor coatings have resulted in a number of polymer coatings with good sensitivity.

We have examined a number of heterocyclic compounds as potential microsensor coatings for the detection of organophosphorus and organosulfur compounds. We have found that many of these compounds do show measurable responses as both chemiresistor and SAW coatings. We have also found, however, by examining a series of analogs such as pyridinium salts, that the response is highly dependent on the substituents on the heterocyclic ring. The counter ion of the pyridinium system also appears to affect the utility of these compounds as microsensor coatings. At present, we have no coherent theory to explain how the various factors affect the response of these materials as microsensor coatings. Additional studies in this area are warranted, and are underway, to determine the nature of substituent effects, to develop a model for the interaction of vapors and coatings, and to determine why such phenomena as reversibility or nonreversibility of responses occur.

All of this information contributes greatly to our knowledge of microsensors and may aid others in elucidating the mechanisms by which these microsensors are operating. This is particularly important in chemiresistor sensors as very little is known about the mechanisms by which these sensors operate.

Future work is this laboratory will be concerned with:

1. Continued synthesis of new pyridine 1-oxides and pyridinium betaines
2. Further development of metal complexes
3. Preparation of additional pyridinium salts
4. Preparation of derivatives of other heterocyclic systems
5. Testing of film-forming ability of these systems
6. Continued measurement of conductivity and frequency changes upon vapor exposure



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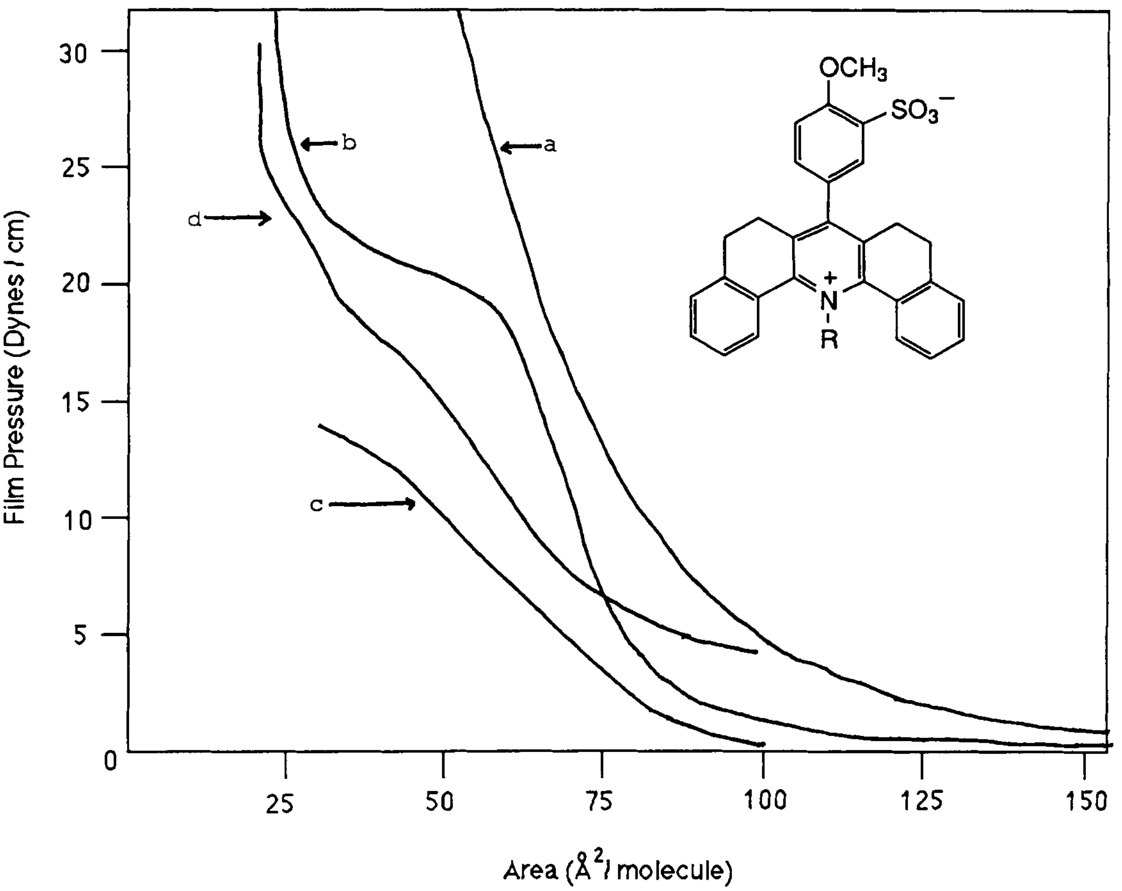

Generally Stable to > 20 dynes / cm

a) R = p-$C_{14}H_{29}$-phenyl
b) R = (Carbazol-1-yl)phenyl
c) R = n-Dodecyl
d) R = n-Octadecyl

FIGURE 10. Surface-area diagrams for acridinium betaines.

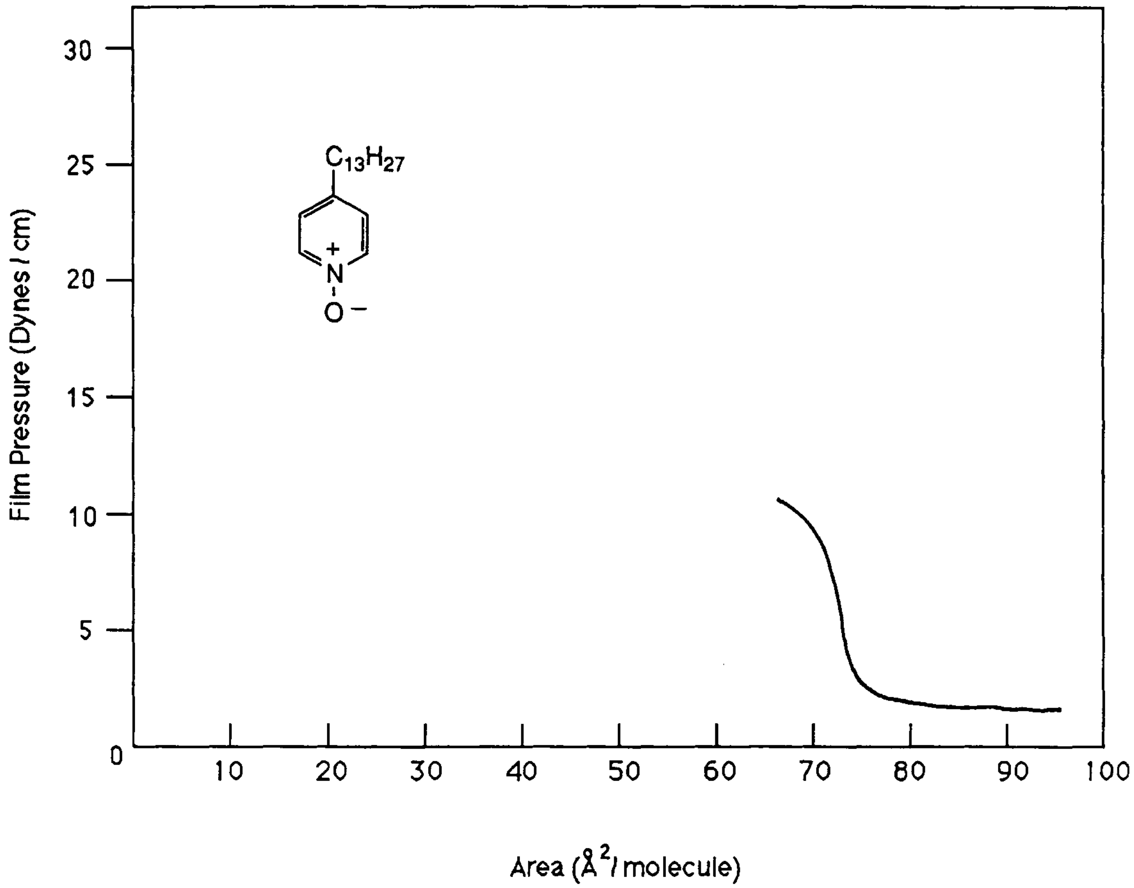

FIGURE 11. Surface-area diagram for tridecylpyridine 1-oxide.

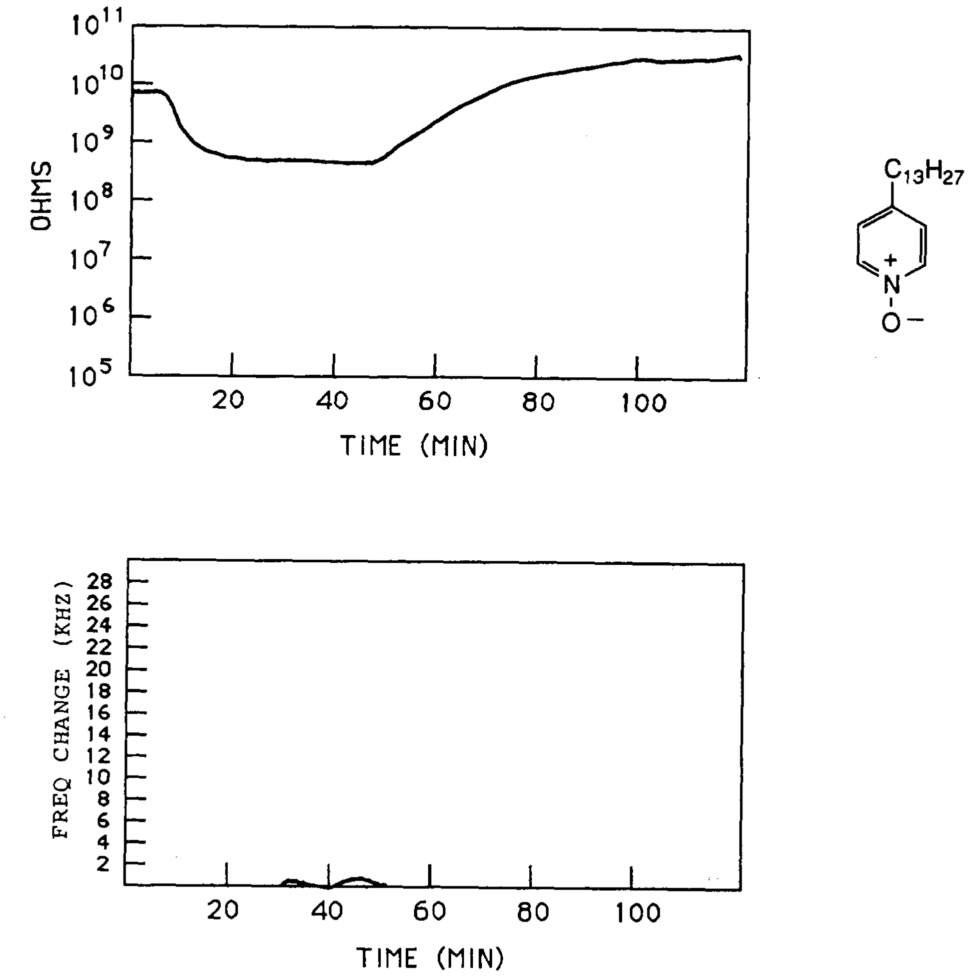

FIGURE 12. Response of tridecylpyridine 1-oxide to DMMP vapor as a chemiresistor showing a resistance change of 10 to 15 × and as a SAW coating showing only a minimal frequency shift in the device.

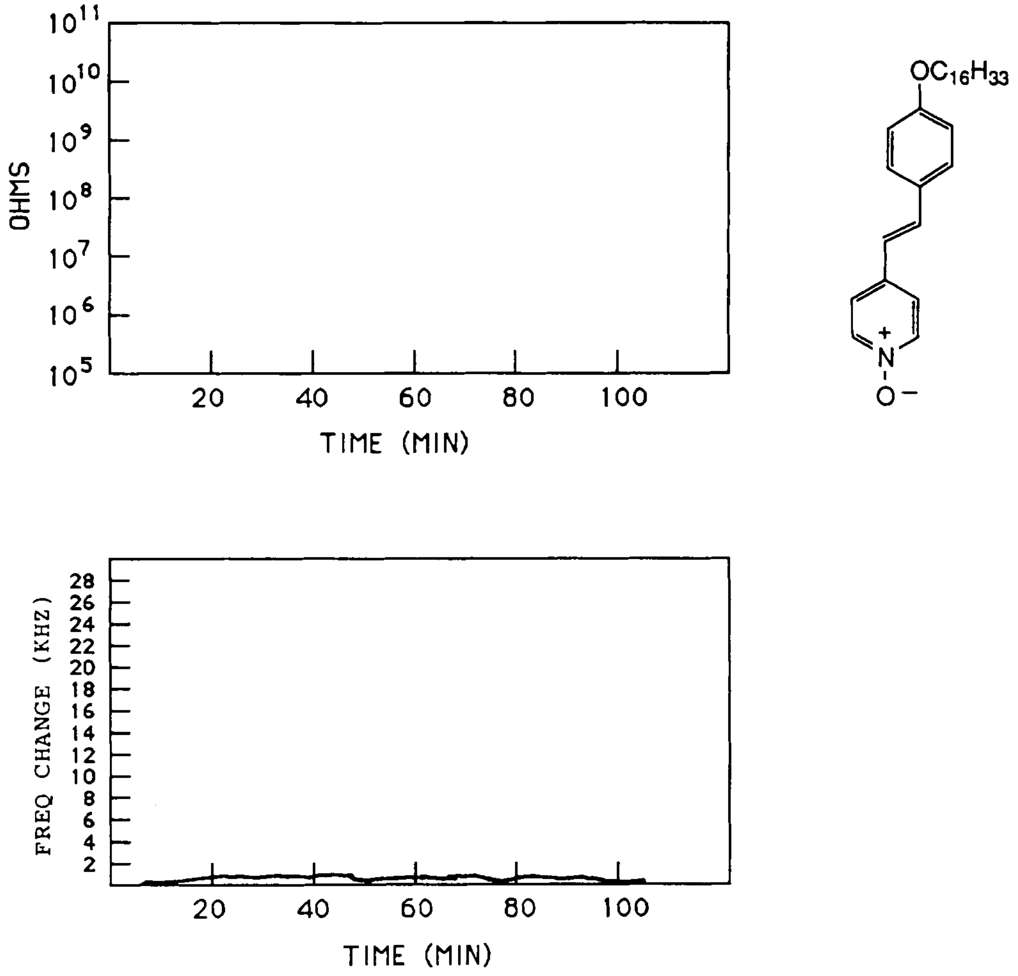

FIGURE 13. Response of pyridinium systems with extended conjugation to DMMP vapor as chemiresistor and SAW coatings. Note resistance >10'' Ω throughout exposure.

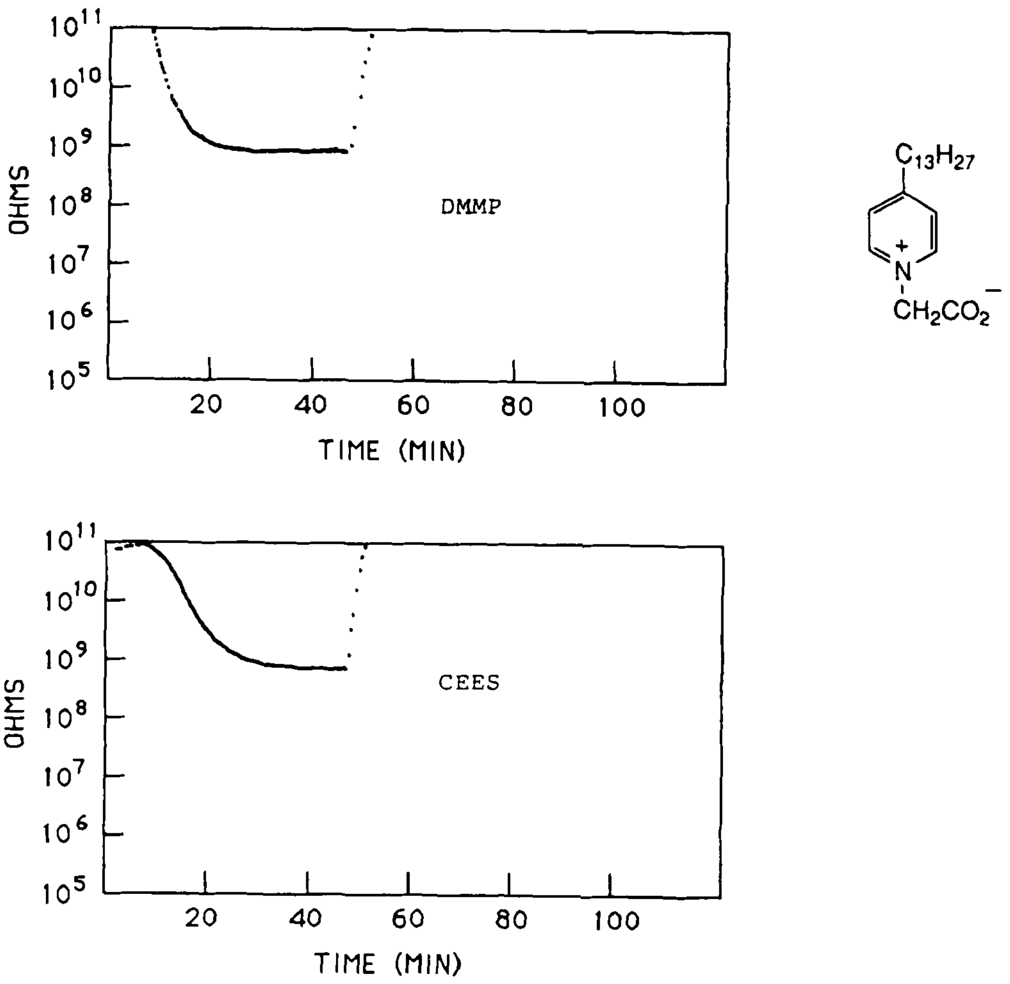

FIGURE 14. Response of tridecylpyridinium betaine as a chemiresistor coating to vapor challenges of DMMP and CEES.

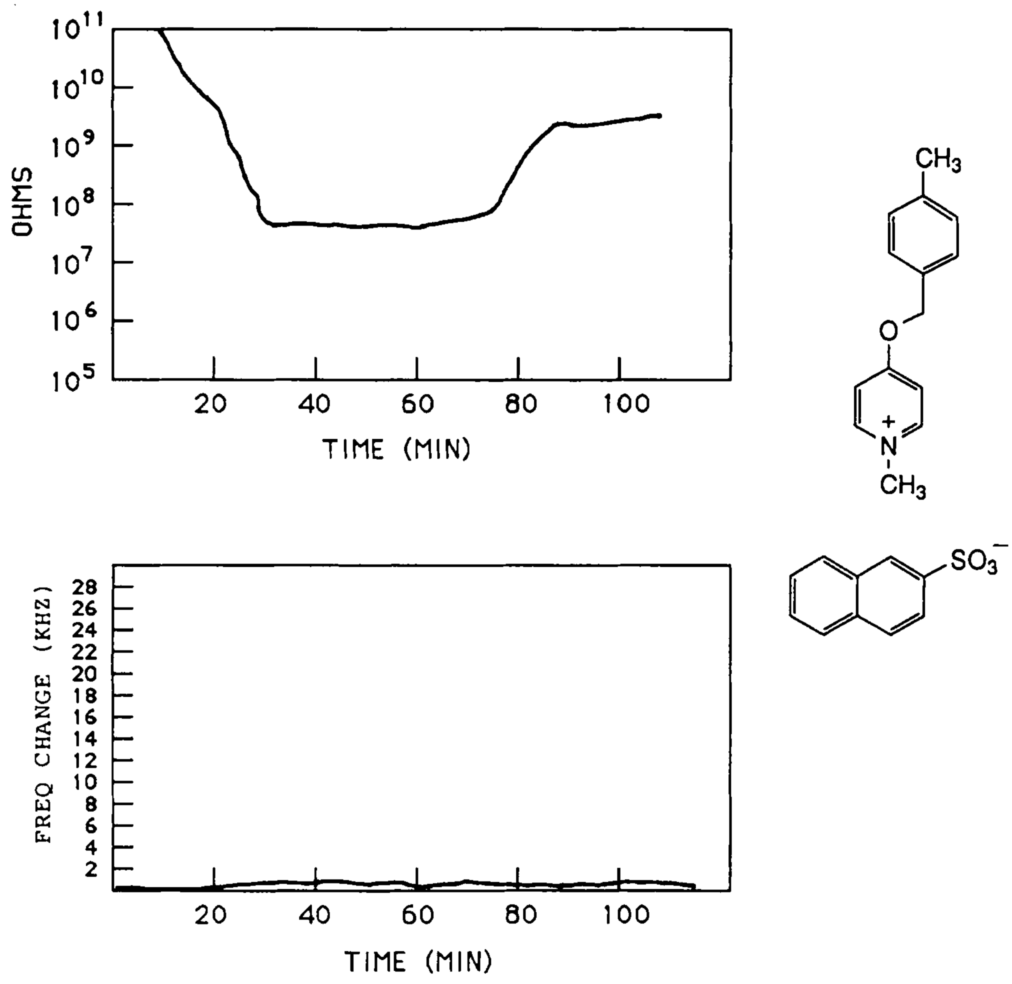

FIGURE 15. Response of pyridyl ether salts to CEES as a chemiresistor shows a resistance change of greater than three orders of magnitude. As a SAW coating only a small frequency shift is seen.

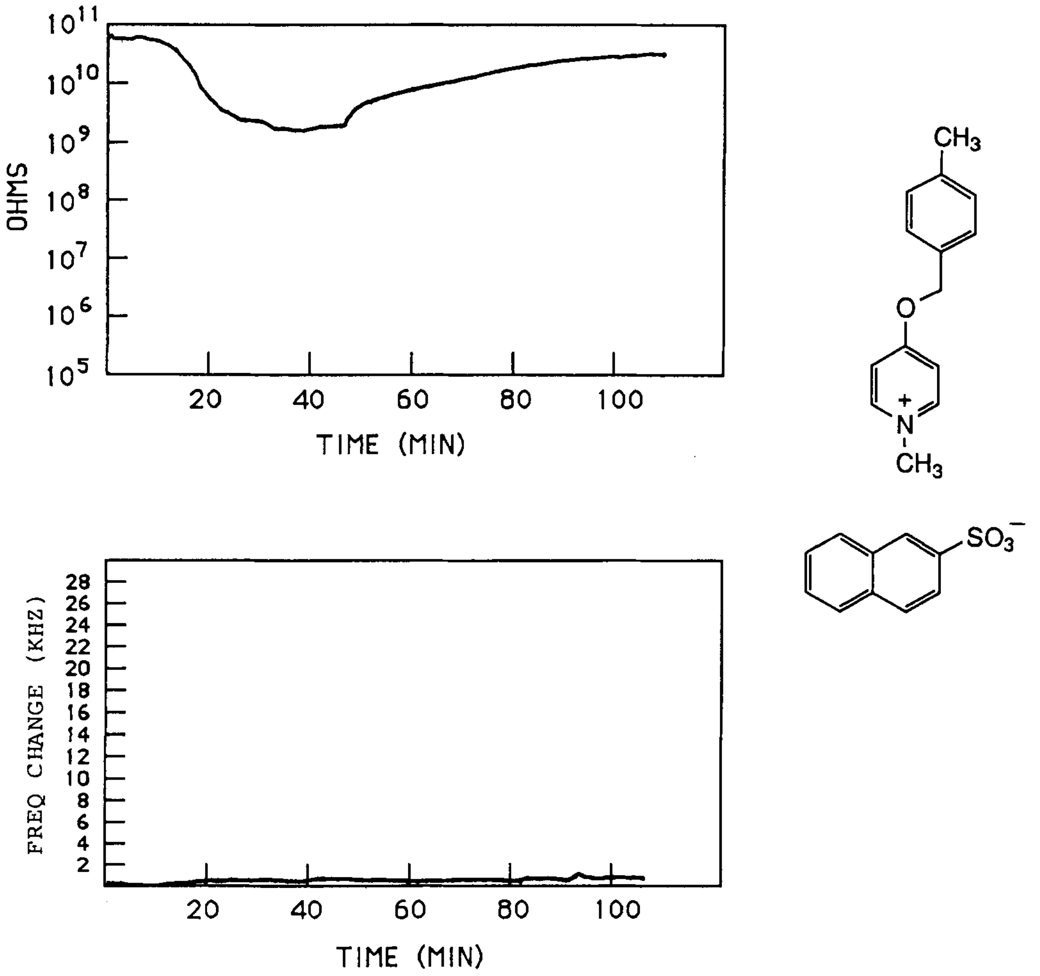

FIGURE 16. Response of pyridyl ether salts to DMMP showing a 15-fold change in resistance but a negligible frequency response.

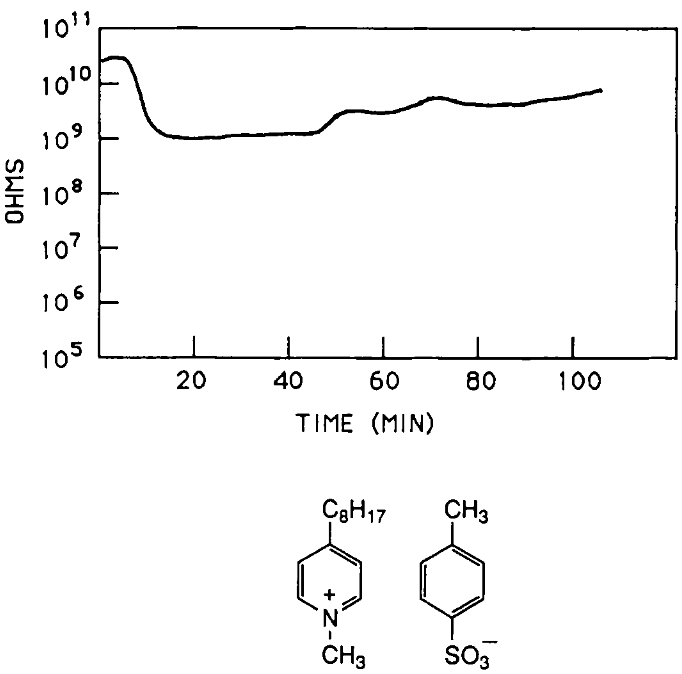

FIGURE 17. The chemiresistor response a of 1-methyl pyridinium sulfonates to CEES shows a rapid initial response but a lack of complete reversibility.

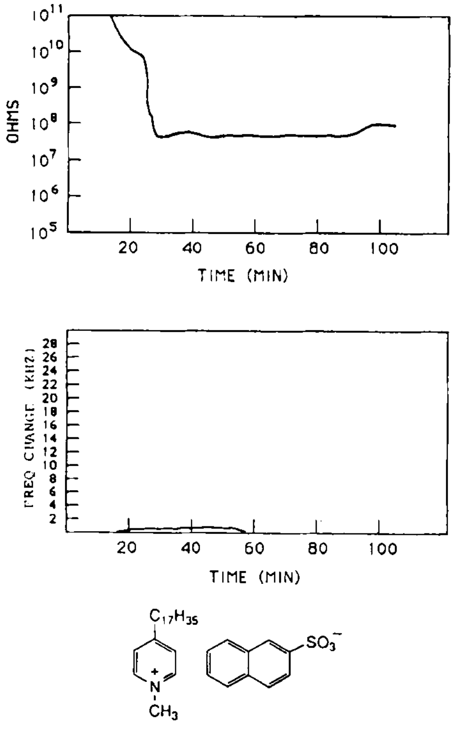

FIGURE 18. The chemiresistor response of 4-heptadecyl pyridinium B-naphthalenesulfonate to CEES shows a large change in the resistance of the coating which is irreversible while the mass uptake on the device, as measured by the frequency shift, is low.

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