FINAL PERFORMANCE REPORT

Project Title

Selective Real-Time Detection of Olefin Gases and Vapors

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Sponsor

National Institute for Occupational Safety and Health
of the Centers for Disease Control

Grant R01-OH02663

Date

March 30, 1993

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO.

2.

PB93-217115

4. Title and Subtitle Selective Real-Time Detection of Olefin Gases and Vapors

5. Report Date 1993/03/00

6.

7. Author(s) Zellers, E. T.

8. Performing Organization Rept. No.

9. Performing Organization Name and Address Department of Environmental and Industrial Health, School of Public Health, University of Michigan, Ann Arbor, Michigan

10. Project/Task/Work Unit No.

11. Contract (C) or Grant(G) No.
(C)
(G) R01-OH-02663

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Coated surface acoustic wave (SAW) chemical sensors were developed for the selective measurement of toxic olefins and dienes. Specific attention was given to styrene (100425), ethyl-acrylate (140885), 1,3-butadiene (106990), acrylonitrile (107131), beta-chloroprene (126998), vinyl-chloride (75014), and vinylidene-chloride (75354). The device as constructed consisted of a piezoelectric substrate with two sets of interdigitated metal-electrode transducers deposited on the surface. The coating reagents used were all members of a class of square planar platinum olefin pi coordination complexes of the general formula trans-PtCl2(olefin)(amine). They were designed to react via substitution of the initially bound olefin with certain olefins and dienes, forming stable products. By monitoring the rate of frequency change of the SAW sensor, the steady state rate of mass change accompanying the olefin substitution reaction could be measured, allowing real time monitoring of air levels of the analyte. Each of the target compounds was measurable using this general approach, with the exception of vinylidene-chloride. A prototype battery powered field instrument was designed and constructed which provided real time measurement of olefin and diene vapor concentrations, coating regeneration functions, and data logging capabilities.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Grant, Grant-Number-R01-OH-02663, End-Date-11-30-1992, Grants-other, Chemical-analysis, Gas-detectors, Air-quality-monitoring, Sampling-equipment, Vapor-detectors, Chlorinated-hydrocarbons, Chemical-agent-detectors

c. COSATI Field/Group

18. Availability Statement

19. Security Class (This Report)

21. No. of Pages 138

22. Security Class (This Page)

22. Price

(See ANSI-Z39.18)

See Instructions on Reverse

OPTIONAL FORM 272(4-77)
(Formerly NTIS-35)
Department of Commerce

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ABSTRACT

This report describes a series of investigations concerned with the development of coated surface acoustic wave (SAW) chemical sensors for the selective measurement of toxic olefins and dienes. This work was motivated by the need for improved sensor technology in compact direct-reading industrial-hygiene monitoring instruments for members of this class of air contaminants. Due to the presence of other organic-vapor contaminants in industrial settings where these chemicals are used, real-time measurement with current portable direct-reading instruments is often not possible. The project has focused on the following target analytes: styrene, ethyl acrylate, 1,3-butadiene, acrylonitrile, β-chloroprene, vinyl chloride, and vinylidene chloride. These chemicals were chosen due to their potential carcinogenic, neurotoxic, and/or adverse-reproductive health effects. Additional olefins were examined either as potential interferents or as part of systematic studies of how the structural features of the analytes and/or sensor coating materials affect sensor responses.

The SAW device consists of a piezoelectric substrate with two sets of interdigitated metal-electrode transducers deposited on its surface. The transducers serve to launch and receive electrically generated acoustic waves along the surface of the substrate. Changes in the properties of the acoustic waves, caused by physical or chemical changes at the surface of the device, can be measured very accurately. Depositing a thin film of a chemically sensitive coating material onto the substrate surface can render the SAW device selectively responsive to certain gases and vapors. In the application here, SAW devices were used as the frequency controlling elements of feedback oscillator circuits. Devices having oscillation frequencies in the range of 30-60 MHz were fabricated and tested. The interaction between gas-phase analytes and the sensor coating causes a change of deposited mass at surface of the sensor which, in turn, alters the oscillation frequency. The measured change of frequency can then be related to the air concentration of the analyte.

A large number of surface coatings have been synthesized and tested for their selectivity and sensitivity to each of the target analytes. The coating reagents employed were all members of a class of square-planar platinum-olefin π-coordination complexes of the general formula trans-$PtCl_2$(olefin)(amine) designed to react, via substitution of the initially bound olefin, with certain olefin(s) and dienes to form stable products. The steady-state rate of mass change accompanying the olefin-substitution reaction was determined by monitoring the rate of frequency change (ie., response) of the SAW sensor, which allowed real-time monitoring of analyte air concentrations.

With the exception of vinylidene chloride, all of the target analytes could be measured using this general approach. The sensitivity and selectivity varied with the analyte and the structure of the reagent complex employed. Real-time measurement of styrene, ethyl acrylate, vinyl acetate and several butene isomers at low-ppm concentrations in the presence of each of several industrially relevant non-olefin solvent vapors was achieved using a 30-MHz SAW sensor coated with a mixture of trans-$PtCl_2$(ethylene)(pyridine) and poly(isobutylene) (PIB). The PIB served as a matrix in which the reagent was dispersed in order to

improve the uniformity and adhesion of the coating films. In all cases post-exposure regeneration of the reagent was possible by treatment with ethylene, in situ, permitting repeated use of the same sensor coating. Selectivity for the target olefins in the presence of certain other olefin gases and vapors was also achieved and could be attributed to steric and electronic factors favoring the target olefins.

A systematic investigation of steric factors affecting the olefin-substitution reactions revealed a remarkably high degree of selectivity for unhindered olefins. For example, ethyl acrylate could be monitored without interference from its more hindered isomers methylmethacrylate and methylcrotonate. Similarly, the response to styrene was about 8-10 times larger than that for α-methylstyrene and indene. Testing of various butene isomers showed that 1-butene could be monitored without interference from isobutylene and gave a significantly larger response than either cis- or trans-2-butene. Replacing pyridine with 2-methylpyridine and 2,6-dimethylpyridine in the reagent complex led to a progressive decline in response for the olefins examined. The steric effect thus appears to be quite general and similar selectivity would be expected for other less-hindered olefins in the presence of their more hindered structural analogues.

Electronic factors were also examined by systematically varying the substituents on the olefin analyte, the initially bound olefin and the amine ligand in the complex. For a given reagent complex, olefin analytes with electron donating substituents generally gave larger responses. The inability to detect vinylidene chloride is attributed to the presence of the two strongly electron-withdrawing chlorine atoms on the double bond, which precludes complexation with Pt. For a given analyte, changing the substituents on the pyridine ligand gave maximum responses at intermediate degrees of amine basicity. Changing the initially bound olefin had a dramatic effect on sensor responses, the pattern of which varied with the nature of gas-phase olefin or diene.

1,3-butadiene could not be measured with the $PtCl_2$(ethylene)(pyridine) complex. However, use of the related reagent $PtCl_2$(1-hexene)(pyridine) coated on a 30-MHz SAW device permitted selective measurement of 1,3-butadiene with a limit of detection (LOD) of about 100 ppb in one minute. Use of a 60-MHz sensor instead of a 30-MHz sensor decreased the LOD for 1,3-butadiene to 24 ppb. In this case there is a 2-for-1 ligand exchange involved, with formation of the bridged Pt:butadiene complex $[PtCl_2(pyridine)]_2$(butadiene), which effectively amplifies the sensor response. No interference was seen from several industrially relevant non-olefin gases and vapors, and repeated regeneration of the reagent was possible by brief exposure to 1-hexene. The response to 1,3-butadiene was independent of relative humidity over the range of 5-80%, and independent of temperature from 25-35°C.

Certain olefins could also be measured with the 1-hexene complex, but only at concentrations higher than that of 1,3-butadiene. Acrylonitrile and vinyl chloride could be detected at levels of about 3 and 30 ppm, respectively, using the 1-hexene complex whereas they could not be detected at any concentration using the corresponding ethylene complex. Interestingly, ethyl acrylate did not react with the 1-hexene complex whereas it reacted quite readily with the ethylene complex. Chloroprene could also be measured with the 1-hexene complex, but only at concentrations above 100 ppm. Vinylidene chloride, dichloroethylene and trichloroethylene neither reacted nor interfered with the responses of the other analytes. Replacing pyridine by 2,6-dimethylpyridine in the 1-hexene complex precluded reaction by the relatively large styrene due to steric hindrance, but still allowed sensitive detection of acrylonitrile and 1,3-butadiene. These results demonstrate the ability to predictably alter the sensitivity and selectivity of the sensor through subtle modifications in the structure of the sensor coating. This, in turn, leads to a high degree of versatility in the use of these reagent-coated SAW sensors for solving industrial hygiene monitoring problems involving this class of air contaminants.

A prototype battery-powered field instrument employing a dual 60-MHz SAW sensor configuration has been designed and constructed. The instrument provides real-time measurement of olefin and diene vapor concentrations, coating-regeneration functions, and datalogging capabilities. Laboratory testing of the instrument is currently being completed. Instrument performance is being examined with respect to response time, sensitivity, limits of detection, dynamic range, selectivity, ambient temperature and humidity effects, and multiple exposure/regeneration cycling.

SIGNIFICANT FINDINGS

General Findings

1. SAW sensors coated with reagents of the general formula $PtCl_2$(olefin)(amine) can be used to measure several olefins and dienes at concentrations below currently accepted (or proposed) occupational exposure limits. In general, responses are not affected by the presence of organic solvent vapors typically found together with the target olefins/dienes in industrial environments, even when the solvent vapors are present at much higher relative concentrations. This degree of selectivity is not generally possible with commercial organic vapor monitors.

2. In addition to obtaining selectivity for olefins in the presence of non-olefin interferences, it is possible to obtain selectivity for certain olefins in the presence of other olefins using these reagent-coated SAW sensors. Both steric and electronic structural features in the reagent and the target analytes appear to be important.

   Subtle differences in the steric properties of olefins can be used to advantage in achieving a high degree of selectivity for relatively unhindered olefins in the presence of their more hindered structural analogues and isomers using the reagent $PtCl_2$(ethylene)(pyridine) as the sensor coating. Positional isomers can be completely discriminated in certain cases and appreciable differences in response are seen even for geometric (cis/trans) isomers. The consistent trend observed across three series of olefins (e.g., butenes, acrylates and aromatic olefins) indicates that the steric effects are quite general. Thus, similar molecular selectivity would be expected within other groups of olefins. Replacing pyridine by 2-methylpyridine and 2,6-dimethylpyridine in the reagent complex progressively reduces the sensor response, again, due to the influence of steric factors.

   Electronic structural features of the analytes and coating reagents also affect the sensor response. In general, olefins and dienes having electron-withdrawing substituents on the double-bond carbons react at a low rate or not at all, whereas olefins with electron-donating substituents react quite rapidly. This permits selective measurement of the latter in the presence of the former. Replacing ethylene by other olefins in the reagent complex leads to large changes in response, the pattern of which depends on the target analyte.

   The combination of steric and electronic factors affecting sensor responses with this class of reagent coatings can be used to achieve selectivity either with individual sensors or with an array of differently coated sensors.

3. Sensor responses to the olefin analytes examined showed a positive Arrhenius temperature dependence, the strength of which varied with the analyte. While this leads to a requirement for careful temperature control in order to maintain calibration, it also suggests an additional means for obtaining selectivity: use of a simple sensor array comprising as few as two sensors coated with the same reagent, but operated a different temperatures, could provide selectivity based on differences in activation energy between different reacting olefins.

4. As expected with reagent SAW sensor coatings, continued exposure leads to an eventual decline in response due to the consumption of the reagent. A key feature of the class of reagents used here, however, is their capability for post-exposure regeneration, in situ, by brief treatment with the initially complexed olefin. This permits repeated use of the coating and extends the service life of the sensor.

5. This work highlights several advantages of reagent SAW sensor coatings over sorptive-polymer sensor coatings for measurement of this class of organic compounds. In addition to the unusually high selectivity obtained, the reagent coatings allow detection of low concentrations of gases which have small polymer/air partition coefficients and, consequently, low responses with polymer-coated sensors. Increasing the temperature of the reagent-coated sensor generally leads to increased sensitivity (and selectivity, in some cases) whereas increasing the temperature of polymer-coated sensors decreases sensitivity. This adds a measure flexibility to the reagent-coating approach. Finally, increasing the operating frequency of the sensor increases the sensitivity of responses using the reagent coating, in contrast to polymer-coated sensors.

6. It has also been shown by this research that the SAW sensor can be a useful probe of fundamental kinetic and thermodynamic parameters of chemical reactions. It is possible to derive from the SAW sensor responses data on rate constants, the applicability of different rate law models, activation energies and equilibrium constants.

Specific Findings

1. SAW sensors coated with $PtCl_2$(ethylene)(pyridine) dispersed in a poly(isobutylene) matrix can be used to measure styrene and ethyl acrylate vapors selectively at concentrations below their current permissible exposure limits. Following exposure to these vapors the reagent coating can be regenerated repeatedly, permitting repeated use of the coating and extended service life for the sensor. The sensor response exhibits a positive Arrhenius temperature dependence, which allows control over the sensitivity: higher operating temperatures permit lower detection limits and higher sensitivity. Limits of detection in the low- or sub-ppm range have been achieved at modest operating temperatures of 30-40°C. The limit of detection decreases as the square of the

sensor operating frequency. Since sensors operating in the range of several hundred MHz can be constructed, detection in the low-ppb range appears feasible.

2. In addition to selectivity in the presence of non-olefin organic solvent vapors, excellent selectivity for styrene and ethyl acrylate was also obtained in the presence of other olefins: no effect on the responses to these vapors was observed upon co-exposure to acrylonitrile, vinyl chloride, vinylidene chloride, tetrachloroethylene, and methylmethacrylate (note: that methylmethacrylate is an isomer of ethyl acrylate). For styrene, an 8-10 fold higher relative response was also obtained in the presence of alpha-methylstyrene and indene. However, 1,3-butadiene did cause a reversible suppression of the styrene response using the $PtCl_2$(ethylene)(pyridine) complex, even though the sensor does not respond to 1,3-butadiene itself with this coating (see below). For ethyl acrylate, high selectivity was also obtained in the presence of the structurally similar chemicals methyl acrylate and methylcrotonate.

3. The inherent selectivity of the $PtCl_2$(ethylene)(pyridine) reagent coatings for sterically unhindered olefins was further demonstrated within a series of isomeric butenes. It was possible to monitor 1-butene without interference from isobutylene, and responses to cis- and trans-2-butene were significantly lower than those for 1-butene. Both cis-and trans-2-butene could be monitored without interference from isobutylene, as well.

4. Although acrylonitrile, vinyl chloride, and chloroprene could be measured at levels of 3, 30 and 100 ppm, respectively, other olefins would also react at similar or lower concentrations. Thus, it does not appear possible to achieve selective detection of olefins having strongly electronegative substituents on the double bond in the presence of other reactive olefins. However, complete selectivity in the presence of non-olefin gases and vapors would still be expected.

5. Through the combination of a high reaction rate and a mass-amplifying 2-for-1 ligand exchange process, highly sensitive measurement of 1,3-butadiene gas has been achieved using a SAW sensor coated with trans-$PtCl_2$(1-hexene)(pyridine). Detection at levels below the recently proposed Permissible Exposure Limit of 2 ppm was demonstrated. The ability to adjust the sensitivity and selectivity through changes in the Pt ligands was also demonstrated.

6. Several practical advantages can be cited for this approach to 1,3-butadiene measurement. High sensitivity is obtained at relatively low sensor operating frequencies which simplifies circuit design and radio-frequency shielding requirements. While the detection limits obtained using a 30-MHz sensor are adequate for monitoring butadiene in the range of the recently proposed occupational exposure limit of 2 ppm, the sensitivity can be further increased by increasing the sensor operating frequency:

data collected using a 60-MHz sensor confirm that the sensitivity increases as the square of the operating frequency, consistent with theoretical expectations. Since SAW devices operating at several hundred MHz can be fabricated, detection of sub-ppb concentrations of 1,3-butadiene appears feasible. The sensor response is independent of relative humidity, which obviates the need to monitor and compensate for changes in ambient water vapor concentrations. The sensor response is also independent of temperature in the range of 25-35°C and while some degree of temperature control is still needed to avoid thermal drift in the SAW oscillator frequency, maintaining an exact set point is not necessary as is the case with polymer coatings or other reagent coatings whose interactions with gases and vapors are strongly temperature dependent. The coating reagent is easy to synthesis and stable in air for several months. In addition, the sensor response is independent of the amount of coating deposited on the surface. Thus, tolerance limits on coating application procedures are relaxed.

7. A high degree of selectivity for 1,3-butadiene was obtained in the presence of many potential industrial co-contaminants. Most non-olefin gases and vapors did not interfere at all with the response to butadiene and although responses to several olefins were observed they interfered with the 1,3-butadiene response only at higher relative concentrations. Since 1,3-butadiene is the major component of most industrial process mixtures containing these other chemicals, quantification of 1,3-butadiene should be possible in most practical situations.

8. The primary limitation of this approach is the service life of the reagent. Although several hours of operation are possible at concentrations below 1 ppm of 1,3-butadiene, the effective service life progressively declines as the 1,3-butadiene concentration increases. The reagent can be regenerated rapidly and repeatedly, however, by brief in situ exposure to 1-hexene vapor. In practice, one could simply monitor the total frequency shift over time and initiate a regeneration cycle periodically to maintain the response characteristics of the sensor. The prototype instrument being constructed incorporates this operating feature.

9. A working compact battery-powered prototype field instrument has been constructed that employs the coatings described above. The instrument utilizes a dual 60-MHz SAW sensor configuration and incorporates automated sample measurement, baseline check, and regeneration cycles, as well as data display, averaging and storage functions.

PUBLICATIONS RESULTING FROM THE PROJECT

1. E. T. Zellers, R. M. White, and S. M. Rappaport, "Use of a surface-acoustic-wave sensor to characterize the reaction of styrene vapor with a square-planar organoplatinum complex," Anal. Chem., 62, 1222-1227 (1990).

2. E. T. Zellers, N. Hassold, R. M. White, and S. M. Rappaport, "Selective real-time measurement of styrene vapor using a surface-acoustic-wave sensor with a regenerable organoplatinum coating," Anal. Chem., 62, 1227-1232 (1990).

3. E. T. Zellers, S. J. Patrash, and G. Zhang: "Selective measurement of organic vapors using SAW sensors with reactive or sorptive coatings: steric, electronic, and solubility factors", Proceedings 6th Internat. Conf. Solid-State Sensors and Actuators - Transducers '91, San Francisco pp. 998-1001 (June, 1991).

4. E. T. Zellers, G. Zhang: "Steric factors affecting the discrimination of isomeric and structurally related olefin gases and vapors with a reagent-coated surface acoustic wave sensor." Anal. Chem. 64:1277-1284 (1992).

5. G. Z. Zhang and E. T. Zellers*: "A coated surface acoustic wave sensor employing a reversible mass-amplifying ligand substitution reaction for real-time measurement of 1,3-butadiene at low- and sub-ppm concentrations," Anal. Chem. 65 (May 15, 1993).

6. E. T. Zellers and G. Z. Zhang: "The influence of substituent and ligand electronic factors on the measurement of gas phase olefins using a surface-acoustic-wave oscillator coated with trans-$PtCl_2$(olefin)(amine) complexes," Analy. Chim. Acta (in press).

7. D. S. Ballantine, S. J. Martin, R. M. White, A. J. Ricco, E. T. Zellers, G. Frye: Acoustic Wave Sensors: Theory, Design, and Physicochemical Applications, Academic Press (in review).

8. E. T. Zellers and G.Z. Zhang: A portable field instrument employing a coated surface acoustic wave sensor for selective measurement of olefins and dienes - laboratory performance tests. Applied Occup. Environ. Hyg. (in preparation).

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CHAPTER 1

Use of a Surface-Acoustic-Wave Sensor to Characterize the Reaction of Styrene Vapor with a Square-Planar Organoplatinum Complex

Abstract

A coated surface-acoustic-wave (SAW) sensor is used to probe the reaction of styrene vapor with the square-planar platinum-ethylene π-complex, trans-$PtCl_2$(ethylene)(pyridine). A dual-SAW delay-line oscillator configuration is employed: one oscillator is coated with a solvent-cast film of the solid platinum-ethylene complex dispersed in a poly(isobutylene) matrix, and the second oscillator is coated only with polymer. Absorbed styrene vapor displaces ethylene to form the stable styrene-substituted complex, trans-$PtCl_2$(styrene)(pyridine), causing a decrease in the oscillator frequency from the increase of mass on the surface of the sensor. For short-term exposures, there is a linear relationship between the logarithm of the rate of frequency change and the logarithm of the styrene vapor concentration, consistent with a power-law kinetic model for the heterogeneous trapping reaction. Deviation from this relationship above 300 ppm at 25°C is attributed to the onset of multilayer adsorption of styrene at the surface of the trapping reagent. The sensor response exhibits an Arrhenius temperature dependence permitting estimation of the thermal activation energy for the olefin-substitution reaction. Calculated detection limits of 3 and 0.6 ppm of styrene vapor are achieved for operation at 25 and 40°C, respectively.

INTRODUCTION

Research on coated surface-acoustic-wave (SAW) chemical sensors has focused primarily on the detection of gas-phase analytes. By varying the nature of the surface coating, SAW sensors have been developed for a number of organic and inorganic gases and vapors (1-10). Like other ultrasonic-oscillator sensors, such as the bulk-acoustic-wave (BAW) (11) and Lamb-wave (12) sensors, the coated-SAW sensor responds to changes in the physical properties of the coating on the sensor surface. Advantage has been taken of this feature not only for gas and vapor monitoring applications but also for characterizing the physicochemical properties of the coating materials. For example, coated-SAW sensors have been used to examine the thermodynamics of water-vapor sorption in hygroscopic polymers (13), thermally induced phase transitions in organic polymers (14,15), vapor diffusion coefficients in thin films of polyimide, and surface areas of microporous inorganic sol-gel films (16). Partition coefficients of various organic vapors into an oligomeric stationary phase deposited on the surface of a SAW sensor have also been reported (17).

In the course of our investigations into reagent-based SAW-sensor coatings for olefin gases and vapors, we have found that the sensor responses can be used to obtain fundamental information about the nature of the heterogeneous trapping reaction between the coating and the analyte vapor. The sensor coating used here consists of a mixture of the solid reagent trans-

$PtCl_2$(ethylene)(pyridine), and the amorphous rubbery polymer poly(isobutylene) (PIB). Reaction between this reagent and absorbed styrene vapor results in a continuous concentration-dependent change in the output frequency of the sensor.

The trapping reagent is one member of a class of square-planar platinum-olefin π-complexes of the general formula, trans-$PtCl_2$(olefin)(amine), whose ligand-substitution behavior has been studied extensively (18-23). In the case of nucleophilic attack by olefins, reversible substitution of the initially bound olefin occurs with retention of the spatial configuration of the ligands in the olefin-substituted product. For complexes where the amine is pyridine or a substituted pyridine, olefin-substitution reactions proceed under mild conditions via an associative bimolecular transition state (21,22).

In this paper, we show how the SAW sensor can be used to characterize the kinetics and thermodynamics of the vapor-coating interactions. The companion paper that follows describes the performance of the sensor as an environmental monitor for styrene, and examines the effects of humidity and other relevant industrial co-contaminants on the response to styrene, as well as the regeneration the trapping reagent.

Sensor Design and Operation. Since details of the design and operation of the coated-SAW chemical sensor have been described elsewhere (24), only the salient operating features are given here. The SAW delay-line oscillator consists of a polished piezoelectric substrate having a pair of evaporated-metal interdigital transducers (IDT) deposited on its surface and connected via an external feedback amplifier. Application of a voltage to the input IDT results in oscillation at a frequency whose value is determined by the velocity of the wave in the substrate, the distance between the IDTs, and the spacings of the IDT electrodes.

Eq 1 gives an approximate expression for the change of the oscillator frequency upon deposition of a thin, non-conducting, low-modulus, isotropic coating film (24, 25),

$$\Delta f = (k_1+k_2)f_o^2 h\rho = (k_1+k_2)f_o^2 m/a \qquad (1)$$

where Δf is the change of frequency, k_1 and k_2 are negative substrate-dependent constants of the order 10^{-8} (m^2/kg-s), f_o is the resonant frequency (Hz), ρ is the density of the coating film (kg/m^3), h is the coating film thickness (m), and m/a is the mass per unit area of the coating film (kg/m^2). This relationship can be used to estimate the initial mass or thickness of the coating film deposited on the oscillator and to monitor subsequent changes of the coating mass due to interactions with a gas or vapor. For a 30-MHz oscillator on ST-quartz with an active area of 1.5 cm^2, such as that used here, eq 1 predicts a change of about 840 Hz for every μg change of surface mass.

EXPERIMENTAL SECTION

Reagent Synthesis. All starting materials and solvents were of reagent grade or higher purity and were used without further purification. Melting points were determined using a Mettler FP-52 Hot Stage with an optical microscope. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer 775B IR spectrophotometer.

The trapping reagent, trans-$PtCl_2$(ethylene)(pyridine), was synthesized by a known procedure (21) involving the addition of pyridine (Aldrich) to an aqueous solution of Zeise's salt, $KPtCl_3$(ethylene) (Alfa). The solid precipitate was recrystallized from methylene chloride/petroleum ether, m.p.=112°C (dec); elemental analysis, percent found (theor.): C, 22.5(22.5); H, 2.5(2.4); N, 3.7(3.7). The corresponding styrene-substituted compound was synthesized by adding a 4-fold excess of styrene (Aldrich) to a methylene chloride solution of $PtCl_2$(ethylene)(pyridine) followed by refluxing for 10 minutes (19). The solid styrene complex was isolated in pure form by the addition of excess petroleum ether (m.p.=124°C). Both of the complexes are yellow crystalline solids that are soluble in polar organic solvents such as methylene chloride, chloroform, acetone and toluene.

Apparatus. The sensor and associated measurement equipment are shown schematically in Figure 1. Two matched 30-MHz SAW devices were fabricated on a 2-inch ST-quartz wafer (Valpey-Fischer). Each IDT consisted of 50 pairs of evaporated Au/Cr electrodes (2600 Angstoms thick) having equal widths and spaces of 25 μm and an acoustic aperture (i.e., the overlap length of the electrodes which defines the width of the acoustic wave) of 6000 μm. The distance between the IDT centers was approximately 2 cm, resulting in an active area of 1.5 cm^2 for each device. Variable series inductors were used as tuning elements to cancel the reactive (i.e., capacitive) component of the impedance in each IDT. Two cascaded LM733 amplifiers provided the gain necessary to maintain oscillations in each device. The signals from the oscillators were passed through a mixer and low-pass filter (LPF) to obtain the difference frequency, which was monitored with a digital frequency counter (Hewlett-Packard 5384A) and logged on a personal computer (Commodore 64 or Hewlett-Packard Vectra) via an IEEE-488 interface. Frequency measurements were collected every 6 s with a resolution of 1 Hz.

The sensor was mounted in a cylindrical stainless-steel chamber having an internal volume of 0.24L and equipped with gas inlet and outlet ports. Electrical connections were made using coaxial (BNC) connectors through tapped fittings in the floor of the chamber. Heating tape wrapped around the exposure chamber and the immediate foreline was used to control the chamber temperature, and a thermocouple was used to monitor the temperature at the surface of the sensor. Dynamic (i.e., continuous flow) test atmospheres of the solvent vapors were generated by passing nitrogen gas through a fritted-glass bubbler containing the liquid solvent and then into a metered dilution-air stream. After passing through a length of tubing to ensure adequate mixing, the air stream was divided, with a portion being directed to the exposure chamber and the remainder passing through an infrared gas analyzer (Foxboro, MIRAN 1A) used for verification of solvent vapor concentrations. A calibrated rotameter was used to maintain a flow of 8 L/min through the exposure chamber, corresponding to a theoretical mixing time of 8 s (26). Dilution-air flow, temperature, and relative humidity (RH) were controlled with a Miller-Nelson Research HCS 301 control unit.

Coating-Film Deposition. We found that combining the solid complex with the amorphous, rubbery polymer, poly(isobutylene) (PIB, T_g = -65°C, Scientific Polymer Products) resulted in more uniform coating films and more consistent results than those obtained using the solid complex alone. Several coating deposition techniques were examined including sublimation (of the platinum-ethylene complex), spraying, dipping, painting, and solvent casting. Solvent casting gave the best uniformity and reproducibility of films as judged by visual and microscopic inspection. The resulting films consisted of roughly cubic crystals of the complex dispersed randomly throughout the polymer film (Figure 2). Solutions containing 6 mg/mL of each component in 3:1 toluene:hexane were applied to the sensor surface using a micropipette, and the mass deposited was estimated using the net frequency shift of the oscillator upon evaporation of the casting solvent (via eq 1).

From the estimate of deposited mass, nominal coating thicknesses could be calculated using the mean of the densities for each of the components (918 and 2400 kg/m^3 for the PIB and the platinum-ethylene complex, respectively). Thicknesses ranging from about 1-2.5 μm, corresponding to coating masses of 240-590 μg (120-295 μg of $PtCl_2$(ethylene)(pyridine)), could be obtained by multiple solvent castings. For the experiments described below, coating thicknesses typically ranged from 1.8-2 μm. The reference device was coated with an equivalent thickness of PIB so that measuring the difference frequency would cancel the response due to sorption and desorption of vapors by the polymer on the sensing oscillator.

VAPOR-COATING INTERACTIONS

The principal interactions occurring between styrene and the trans-$PtCl_2$(ethylene)(pyridine)/PIB sensor coating film are depicted in Figure 3. Upon exposure to a given styrene-vapor concentration, the coating film (on each oscillator) sorbs styrene to an extent determined by the equilibrium air/film partition coefficient, K. The sorbed styrene then reacts with the platinum-ethylene complex at a rate determined by the effective styrene concentration at the surface of the solid and the rate constant for the reaction, k. The reaction results in the formation of the corresponding platinum-styrene complex, trans-$PtCl_2$(styrene)(pyridine), and evolution of ethylene gas. While the olefin substitution reaction is reversible, the combination of an excess of styrene and the release of volatile ethylene from the film drives the equilibrium to the right.

As the styrene reacts with the complex, the equilibrium concentration of free styrene in the polymer decreases proportionally, causing more styrene to be sorbed by the polymer. Since styrene (MW = 104) is heavier than ethylene (MW = 28) there is a continual increase of surface mass and, consequently, a continual reduction of the frequency of the SAW oscillator. By measuring the difference frequency of the two oscillators the initial response (i.e., mass increase) due to polymer sorption of styrene (and other solvent vapors), which can be several hundred Hz in magnitude, is effectively cancelled and the measured frequency shift is due only to the chemical reaction.

Since the sensor frequency shift is directly proportional to changes of coating mass, the rate of change of frequency should be directly proportional to the rate of reaction of styrene vapor with the platinum-ethylene complex. Furthermore, since there is 1:1 stoichiometry of all reactants and products, the steady-state reaction rate can be given in any of the following equivalent forms

$$\text{rate} = -dN_{Pt\text{-}eth}/dt = -dN_{sty}/dt = dN_{Pt\text{-}sty}/dt = dN_{eth}/dt \qquad (2)$$

where N is the number of moles and the subscripts refer, respectively, to the platinum-ethylene complex, styrene, the platinum-styrene complex, and ethylene.

The rate of frequency change resulting from a given rate of mass change on the surface of the sensor can be expressed as

$$df/dt = Cdm/dt \tag{3}$$

where $C = (k_1+k_2f_o)/a$ from eq 1.

At steady-state, there is a continual change of mass at the device surface as styrene replaces ethylene in the complex. Thus, the rate of frequency change can be written as

$$df/dt = C(dm_{sty}/dt-dm_{eth}/dt) = C(MW_{sty}dN_{sty} - MW_{eth}dN_{eth})/dt \tag{4}$$

where m_i and MW_i refer, respectively, to the mass and the molecular weight of the i-th species.

From the equivalent rate expressions in eq 2, we have $dN_{eth}/dt = -dN_{sty}/dt = -dN_{Pt-eth}/dt$. Thus,

$$df/dt = -C(MW_{sty}-MW_{eth})dN_{sty}/dt = C'dN_{Pt-eth}/dt \tag{5}$$

which shows the proportionality between the rate of the trapping reaction and the rate of frequency change of the sensor.

Provided that the rate-limiting step is the first-order reaction with styrene, the rate of frequency change depends on the instantaneous styrene air concentration. The net frequency shift measured after exposure is also related to the integrated exposure level (i.e., concentration x time); however, the primary focus of the discussions that follow is on the use of the sensor output to probe the dynamics of the trapping reaction.

RESULTS AND DISCUSSION

Verification of Reaction Products. IR spectrophotometry was used to document formation of the styrene-substituted product. A squalane mull of $PtCl_2$(ethylene)(pyridine) was applied to a KBr plate and exposed to about 100 ppm of styrene over several hr at room temperature. The sample was periodically removed from the exposure chamber to record the IR spectrum and compare it to the spectra of authentic samples of each complex. The gradual emergence of absorbances at 1000, 580, and 540 cm^{-1} (corresponding to the platinum-styrene complex) along with a concommitant reduction in the strength of absorbances at 1035 and 960cm^{-1} (corresponding to the platinum-ethylene complex) confirmed that the reaction was proceeding. Complete conversion of the sample was indicated after several hours of exposure.

Polymer Sorption. Initial tests were performed to characterize the response to styrene of a single SAW oscillator coated only with PIB (~2 μm). Exposure to a given styrene concentration resulted in a rapid negative frequency shift followed by re-establishment of stable (lower) frequency corresponding to the equilibrium mass of styrene sorbed by the polymer. Upon removal of styrene from the atmosphere the frequency recovered to the pre-exposure value. The initial response of the sensor upon introduction or removal of styrene was very rapid, with large frequency shifts being observed within 6 s. The time required to reach the equilibrium frequency shift (response or recovery) ranged from about 15-90 s for styrene vapor concentrations of 5-700 ppm, respectively.

Exposure of the PIB-coated oscillator to styrene concentrations from 5-700 ppm at temperatures of 15, 25, 32, and 40°C yielded a series of linear sorption isotherms, indicating that the concentration of styrene in the polymer is proportional to its air concentration. As expected, the frequency shift for a given styrene concentration decreased with increasing temperature. Since the response of the sensor is proportional to deposited mass, the ratio of the mass of styrene sorbed to the mass of polymer on the device is equal to the ratio of the frequency shifts due to these quantities (17). The slope of the isotherm at each temperature is therefore proportional to the air/polymer partition coefficient. Using this relationship, an Arrhenius plot of the data yields a value of -9.9 kcal/mole for the heat of sorption (ΔH_s), which is considered typical of vapor sorption in organic polymers (27).

Sensor Response Curves. A plot of the rate of frequency change versus styrene concentration for the trans-$PtCl_2$(ethylene)(pyridine)/PIB-coated sensor at 25°C is shown in Figure 4a. Each point represents the mean response for exposures of 10-20 min duration at each concentration. The time required to establish a steady-state rate of frequency change ranged from about 30-180 s for styrene concentrations from 5-700 ppm, respectively.

The response to styrene increases over the entire concentration range. Up to 300 ppm there is a continual decrease in sensitivity (Hz/ppm-min) with increasing concentration in accordance with the heterogeneous nature of the reaction which involves only a limited number of reactive surface sites on the trapping agent. Above 300 ppm, the sensitivity increases slightly, giving rise to the inflexion point seen in Figure 4a. In contrast, responses at 32 and 40°C are monotonic over the entire concentration range and the sensitivity steadily decreases with increasing concentration, as shown in Figure 4b. The increase in sensitivity observed for the higher concentrations at 25°C can be explained in terms of the vapor-solid reaction kinetics as discussed in the next section.

The shapes of the response curves shown in Figure 4 are highly reproducible. Variations of up to 30% in the sensor response value for a given styrene concentration have been observed between different coatings, which is attributed to differences in both the mass of coating deposited and the surface area of the solid trapping reagent. However, with careful solution preparation and deposition we have achieved responses differing by less than 6% for replicate coatings within the concentration range of 5-600 ppm for operation at both 25 and 40°C.

Long-term aging effects have not been examined, although both the platinum-ethylene complex and the platinum-styrene complex solids were stored in capped vials exposed to air for over three months with no signs of decomposition. For a number of exposure experiments, the same coating was used repeatedly over the course of several days with no change in response.

Comparison with Theoretical Gas-Solid Reaction Models. Since the rate of frequency change is proportional to the rate of reaction of styrene with the platinum-ethylene complex, it is possible to compare the sensor response to theoretical models of gas-solid reactions. For the short-term exposures considered here it is assumed that the surface area of the solid particle does not change significantly over the course of reaction and the reaction can be considered catalytic. Furthermore, it is assumed that the rate-limiting step of the overall vapor-coating interaction is the reaction at the solid surface.

The Langmuir-Hinshelwood (LH) and power-law models have been used successfully in describing the kinetics of a broad range of gas-solid reaction systems (28,29). The LH model assumes that gas adsorption follows a Langmuir isotherm and the power-law model assumes a Freundlich adsorption isotherm. Both models assume that the surface reaction is first-order with respect to the reactant gas (styrene, in this case), and that the surface coverage asymptotically approaches a monolayer with increasing gas concentration.

The LH expression for the reversible gas/solid reaction considered here is (28)

$$r_{Pt} = (kK_{sty}p_{sty} - p_{eth}/K_e)/(1 + K_{sty}p_{sty} + K_{eth}p_{eth}) \tag{6}$$

where r_{Pt} is the rate of reaction of the platinum-ethylene complex, k is the reaction rate constant , K_{sty} and K_{eth} are the equilibrium adsorption constants for styrene and ethylene, respectively, p_{sty} and p_{eth} are their partial pressures, and K_e is the equilibrium constant for the overall reaction. For our system the partial pressure of ethylene is very small compared to the partial pressure of styrene, so that eq 6 can be reduced to

$$r_{Pt} = kK_{sty}p_{sty}/(1 + K_{sty}p_{sty}) \tag{7}$$

Rearranging eq 7 into the following form allows comparison of the data with the model using linear regression analysis:

$$p_{sty}/r_{Pt} = 1/kK_{sty} + p_{sty}/k \tag{8}$$

Since p_{sty} is proportional to the styrene vapor concentration in ppm (ppm_{sty}) and r_{Pt} is proportional to the sensor response, plotting ppm_{sty} versus ppm_{sty}/response should yield a straight line (note: the concentration of styrene in the polymer phase of the coating is also proportional to the styrene vapor concentration, as discussed above).

The power-law kinetic expression for a reaction that is first-order in styrene is (29)

$$r_{Pt} = Fp_{sty}^{1/n} \tag{9}$$

where F is a combined reaction-rate/adsorption constant and n is a constant >1. Adherence to this model is indicated if there is a linear relationship between the logarithm of the rate (sensor response) and the logarithm of p_{sty} (ppm_{sty}).

Table I presents linear-regression correlation coefficients (r^2) obtained from fitting the data shown in Figure 4b to each of the rate models (i.e., eqs 7 and 9). Also presented in Table I are the ranges of error resulting from using the models to predict the sensor response for a given styrene concentration. At 25°C, the correlation with the LH model is rather poor ($r^2 = 0.195$), reflecting the sensitivity of the model to the assumption of a Langmuir adsorption isotherm. The correlation with the power-law model is much better ($r^2 = 0.869$), but rather large errors are still encountered between the observed and expected values (percent error = 12-47%). Restricting consideration to concentrations ≤300 ppm (values in parentheses in Table I) improves the fit of the data to both models. At the higher temperatures the correlations with both models are quite good over the entire concentration range examined (note: it is not unusual to find, as we do here, similar correlations with both models since they predict curves of similar shape (30)). Overall, the data appear to fit the power-law model better than the LH model. Errors of less than 15% are obtained using the power-law model to predict the sensor responses, with the exception of high concentrations measured at 25°C.

Both of the models predict that the reaction rate should increase with increasing gas partial pressure, asymptotically approaching a limiting value as the surface coverage approaches a monolayer. The deviation from this behavior observed above 300 ppm at 25°C is most likely due to the onset of multilayer styrene adsorption at the reagent surface. The lower activation energy required for reaction with styrene molecules in these subsequent layers would explain the higher-than-expected reaction rate. That we do not see this behavior at higher temperatures is consistent with this explanation since multilayer adsorption would be expected to diminish at higher temperatures for a given styrene concentration. Slower diffusion of styrene within the solid at 25°C may also be affecting the overall reaction rate and contributing to the lack of fit to the models.

Activation Energy. For a given styrene concentration, there is a positive-exponential (Arrhenius) dependence of the response on temperature. Figure 5 shows Arrhenius plots for exposure to 50, 150, and 300 ppm of styrene at temperatures ranging from 15-40°C. The curves are all linear (linear-regression r^2 values range from 0.973-0.999) and from their slopes a mean thermal activation energy of 22.8 ±0.3 kcal/mole is obtained. Studies of similar reactions in solution, where the olefins involved were substituted butenes, yielded values of 13-20 kcal/mole (22). While the agreement with these previous data is quite good, the slightly higher value measured for our system may reflect the positive temperature dependence of diffusion of the styrene (or ethylene) in the solid trapping agent. Apparently, transport of the styrene through the polymer is fast relative to the chemical reaction since the response (reaction rate) increases with increasing temperature even though equilibrium polymer sorption decreases.

Limit of Detection. The lower detection limit for the sensor was determined by extrapolation from the responses measured at 5 ppm. We define the detection limit as 3σ/sensitivity, where σ is the standard deviation of the noise (31). Using the measured sensitivity of 4 Hz/ppm-min at 5 ppm and a value for σ of 4 Hz/min (measured before and after exposure), a detection limit of 3 ppm is obtained for operation at 25°C. This is considered a conservative (high) estimate since the slope of the response curve is probably slightly higher than that measured at 5 ppm. If the data collected at 40°C are used instead, a detection limit of 0.6 ppm is obtained.

CONCLUSIONS

We have shown that the coated-SAW sensor can serve as a useful probe of vapor-solid reactions. The output from the sensor has been used to calculate the heat of sorption of styrene in poly(isobutylene) and the activation energy for the reaction of styrene vapor with trans-$PtCl_2$(ethylene)(pyridine). The direct relationship between the sensor response and the rate of the trapping reaction also enables a comparison of sensor response data with theoretical kinetic models. For the heterogeneous olefin-substitution reaction studied here, a better correlation was found with a power-law kinetic model than a Langmuir-Hinshelwood model as indicated by the linear relationship between the logarithm of the sensor response and the logarithm of the styrene vapor concentration for operation above room temperature. Deviation from this relationship observed at 25°C for styrene concentrations exceeding 300 ppm is attributable to the onset of multilayer adsorption of styrene at the surface of the solid trapping agent.

In addition to characterizing the vapor-coating interactions, direct measurement of styrene vapor from 5-700 ppm has been demonstrated. The calculated detection limits of 3 ppm (25°C) and 0.6 ppm (40°C) are quite low considering the modest operating frequency of the sensor (30 MHz). Further improvements in sensitivity would be expected with SAW devices operating at higher frequencies. The strong temperature dependence observed underscores the need for careful thermostatting of the sensor during operation. At the same time, this factor provides a means for controlling the reaction rate and the sensitivity to a given styrene vapor concentration.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Andrew Waterhouse for valuable discussions during the early stages of this work and Dr. Juan Goicolea for his assistance during the electrical characterization of the sensor.

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Figure Captions

Figure 1. Schematic diagram of dual-SAW sensor and associated measurement equipment.

Figure 2. Photomicrograph (1,000X) of the trans-$PtCl_2$(ethylene)(pyridine)/PIB sensor coating.

Figure 3. Interactions between the sensor coating and styrene vapor.

Figure 4 a) Plot of the rate of frequency change (response) versus styrene concentration for operation at 25°C and 50% RH. b) Plot of the rate of frequency change (response) versus styrene concentration for operation at 25°C (lower curve), 32°C (middle curve) and 40°C (upper curve) (5% RH). Each point represents the mean response measured for 10-15 minutes at each concentration.

Figure 5. Arrhenius plot of the sensor response at the indicated concentrations for temperatures ranging from 15-40°C.

List of Tables

Table I. Linear-regression correlation coefficients (r^2) and ranges of error obtained by fitting experimental data from Figure 4b to the LH and power-law kinetic models.[a,b]

	LH Model		Power-Law Model	
	r^2	error	r^2	error
25°C	0.195	-----	0.869	12-47%
	(0.832)	10-56%	(0.961)	6-15%
32°C	0.929	7-46%	0.993	0-7%
40°C	0.978	4-29%	0.984	4-11%

[a] Error values were calculated as (Observed-Predicted)/Predicted x 100 using predicted sensor response values obtained from the linear regression model at each temperature.

[b] Values in parentheses are for a styrene concentration range of ~10-300 ppm. All other values are for a styrene concentration range of ~10-620 ppm.

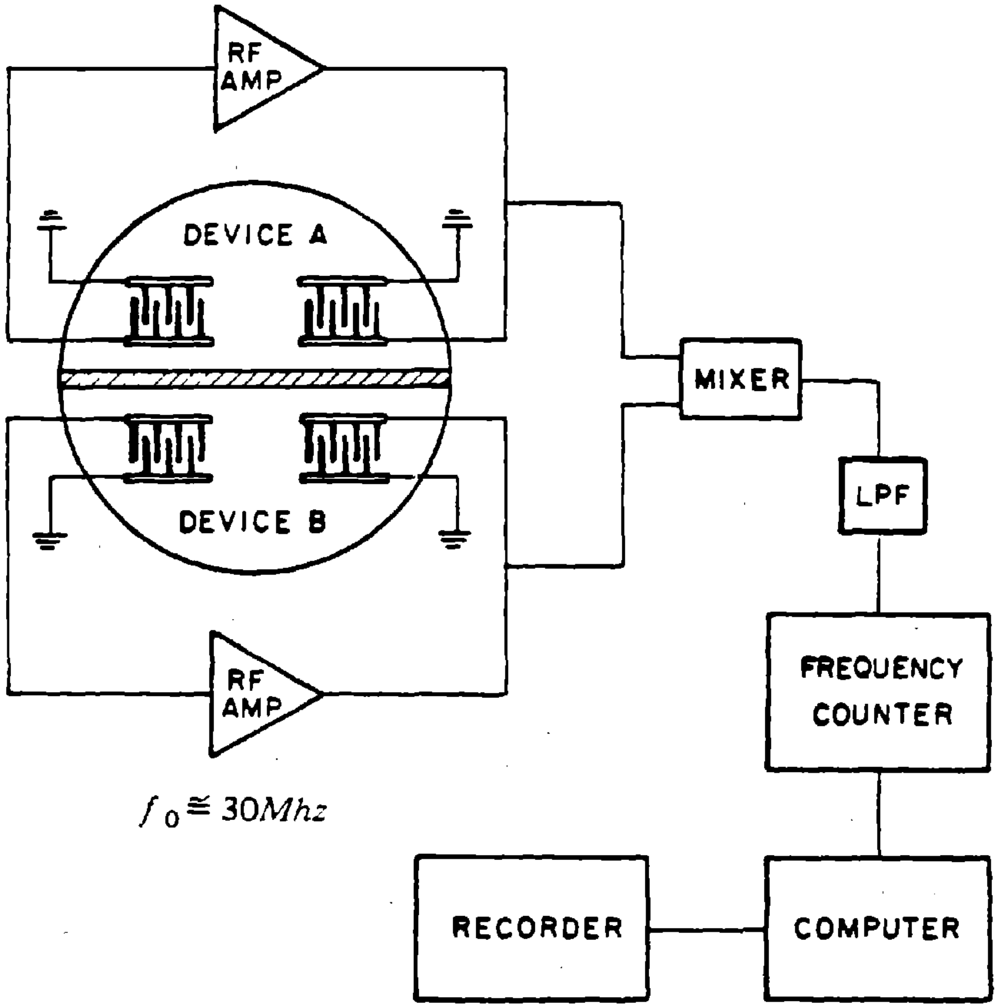

RF AMP
DEVICE A
MIXER
LPF
DEVICE B
RF AMP
FREQUENCY COUNTER
$f_0 \cong 30Mhz$
RECORDER
COMPUTER

Figure 1

Figure 2

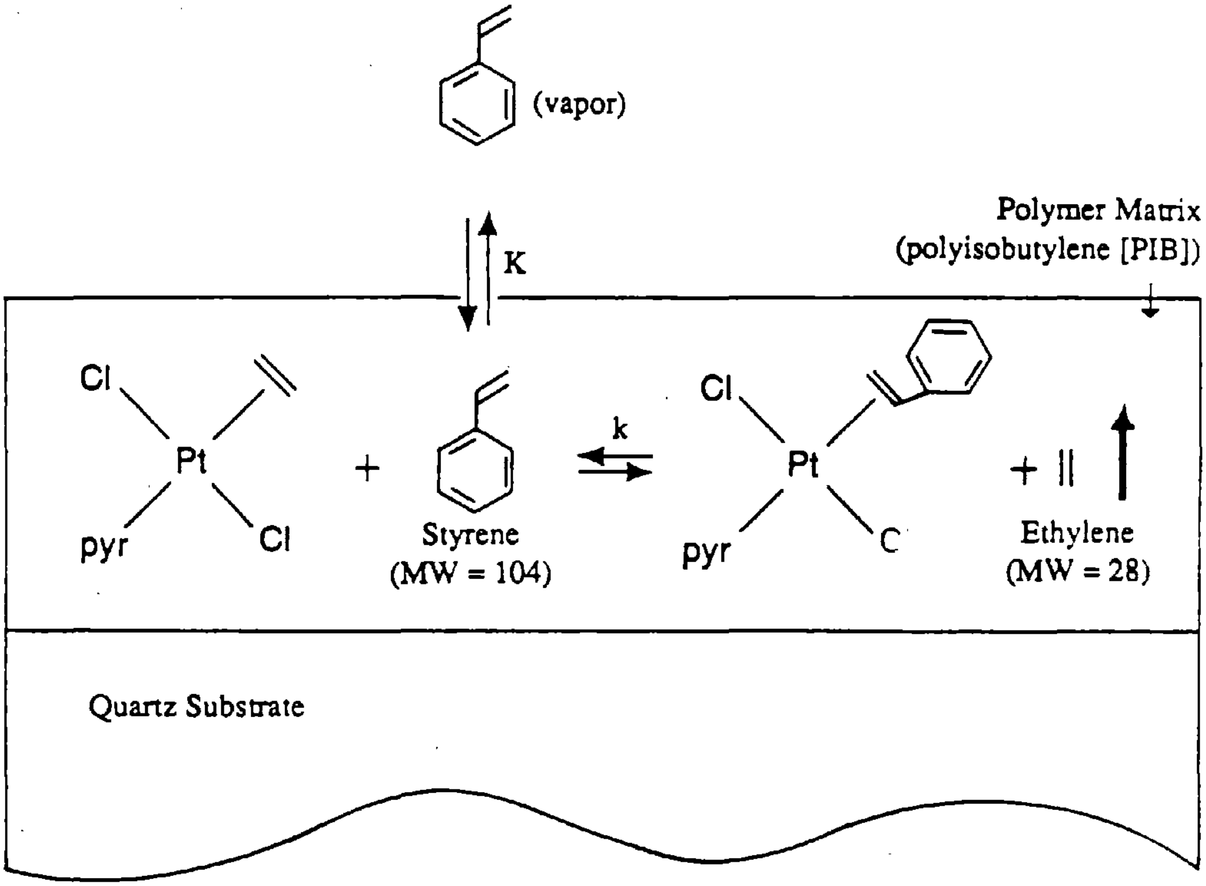

(vapor)
K
Polymer Matrix
(polyisobutylene [PIB])
Cl
Pt
pyr
Cl
+
k
Styrene
(MW = 104)
Cl
Pt
pyr
C
+
Ethylene
(MW = 28)
Quartz Substrate

Figure 3

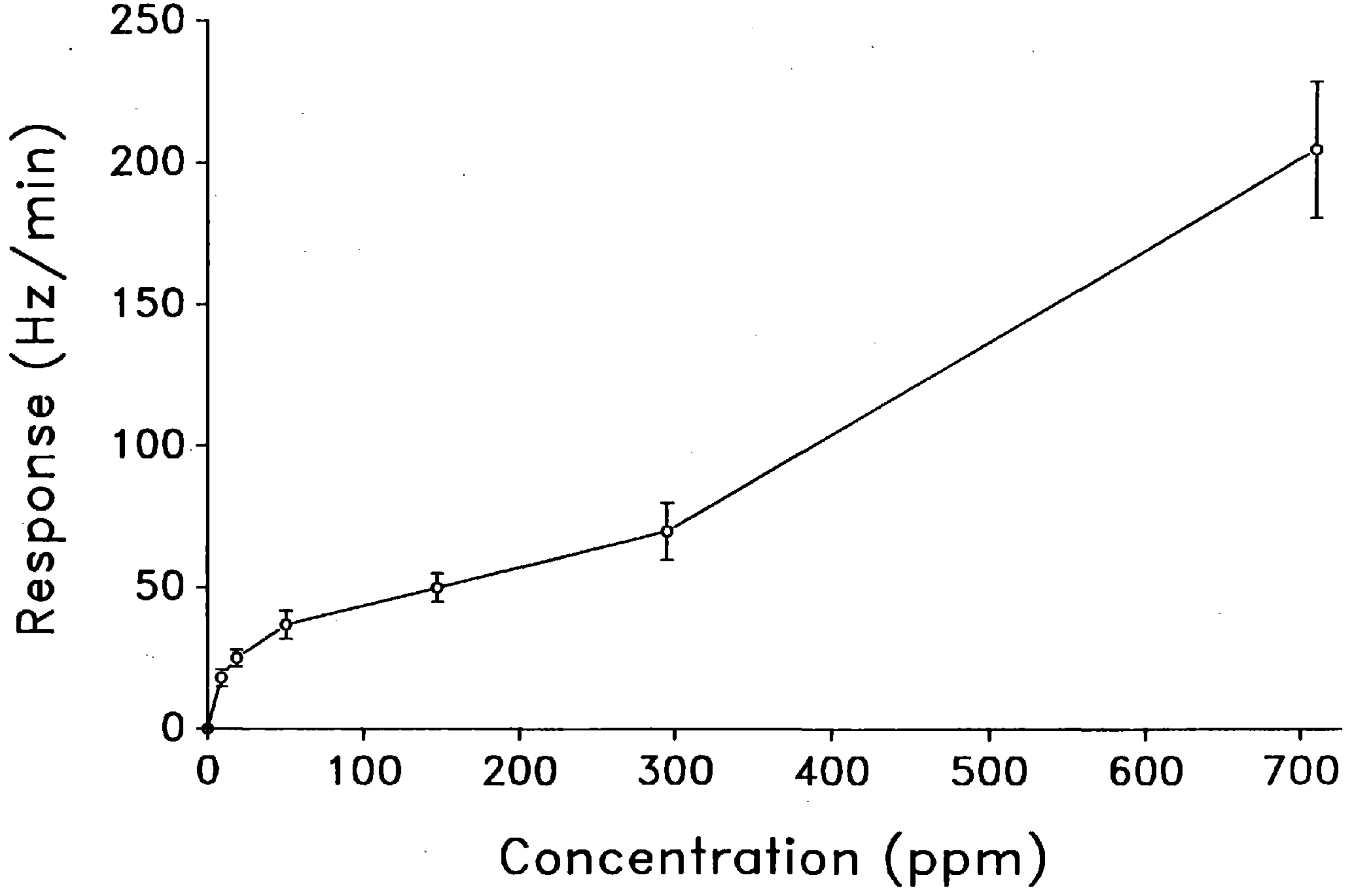
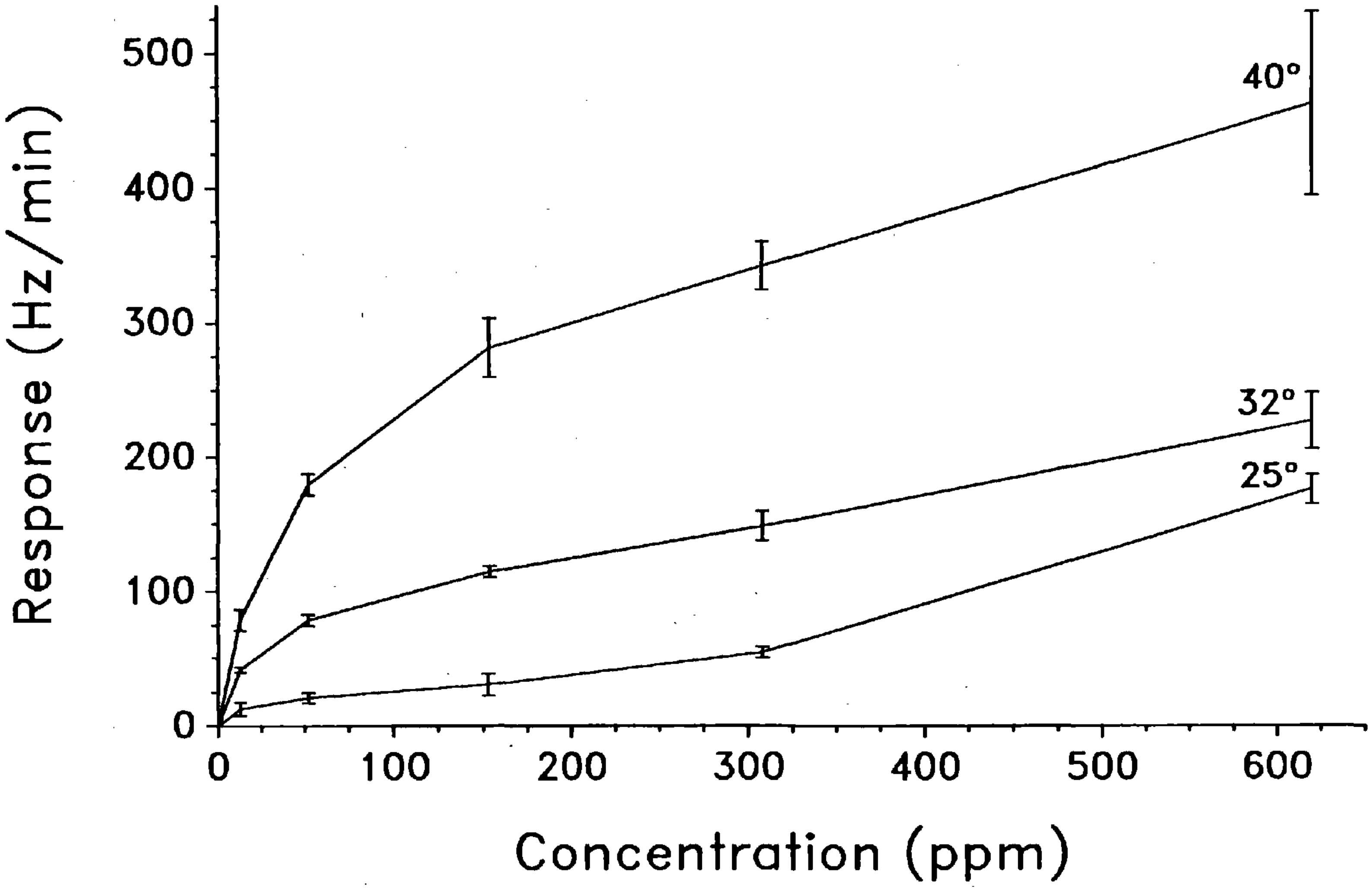

Response (Hz/min)
250
200
150
100
50
0
0
100
200
300
400
500
600
700
Concentration (ppm)

Figure 4a



40°
32°
25°
Response (Hz/min)
0
100
200
300
400
500
0
100
200
300
400
500
600
Concentration (ppm)

Figure 4b

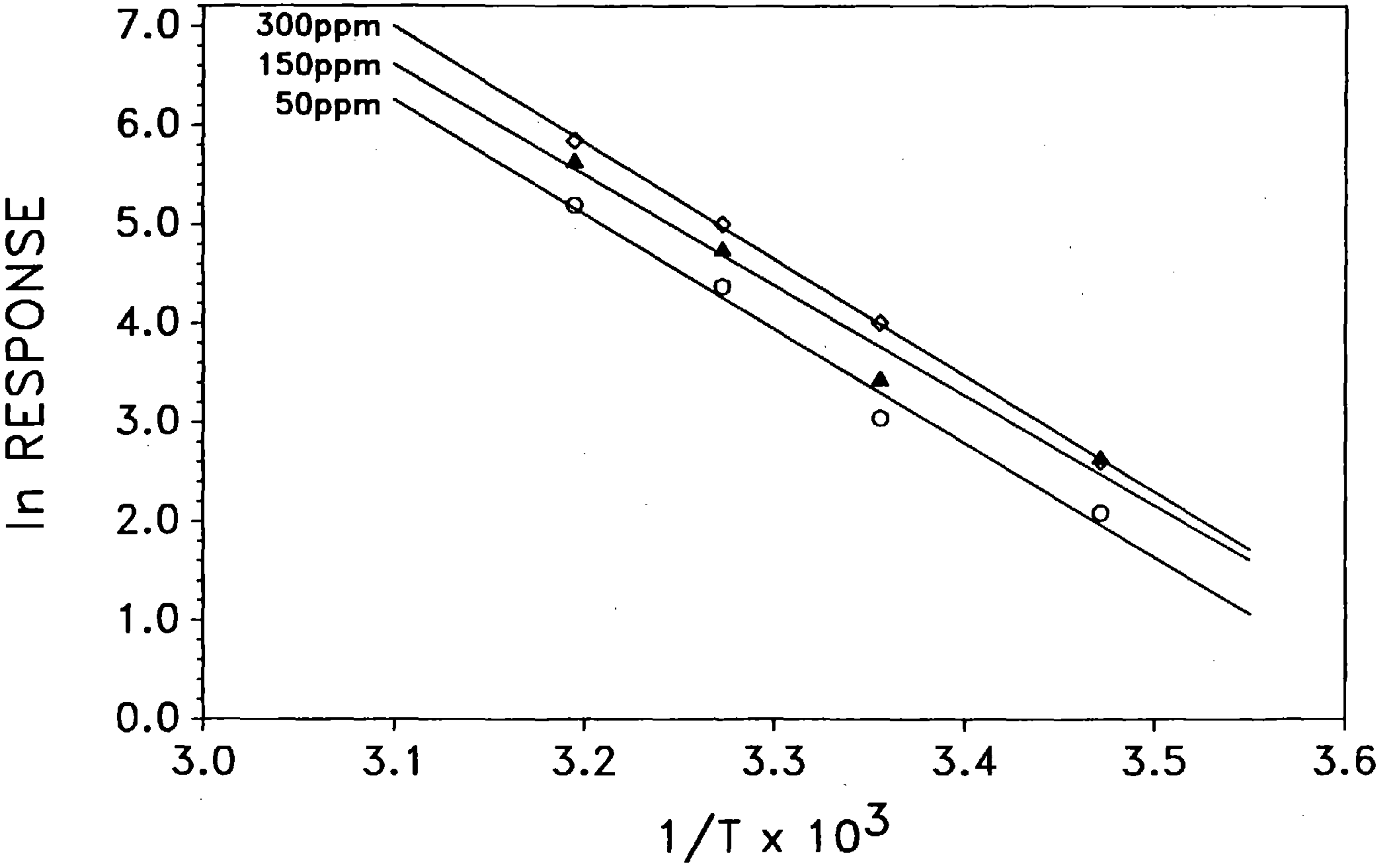

300ppm
150ppm
50ppm
ln RESPONSE
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.0
3.1
3.2
3.3
3.4
3.5
3.6
1/T x 10^3

Figure 5

CHAPTER 2

Selective Real-time Measurement of Styrene Vapor Using a Surface-Acoustic-Wave Sensor with a Regenerable Organoplatinum Coating

Abstract

The performance of a coated surface-acoustic-wave (SAW) sensor for monitoring styrene vapor is investigated. The effects of several organic co-contaminants and atmospheric humidity are described, and regeneration of the sensor coating is demonstrated. The dual-SAW delay-line oscillator employs a reagent coating of trans-$PtCl_2$(ethylene)(pyridine) to trap styrene via ethylene substitution. The rate of change of the sensor frequency is used to provide real-time measurement of styrene vapor concentrations. No effect on the response to styrene is observed upon simultaneous exposure to each of several olefin and non-olefin solvent vapors used with styrene in industrial processes. Butadiene, however, presents a reversible negative interference by successfully competing with styrene for reaction with the trapping agent. The response to styrene exhibits a moderate positive humidity dependence. Following prolonged exposure, the original complex can be regenerated in situ by exposure to ethylene gas, permitting repeated use of the sensor. An emphasis is placed on the application of the sensor to workplace air-monitoring.

INTRODUCTION

Styrene is used principally for the industrial-scale production of polymer resins and thermoplastics, often in combination with other vinyl monomers such as acrylonitrile, butadiene, or various acrylates (1). While industrial surveys have shown that exposure to these monomers during polymer production is minimized by the use of closed reactor systems, transient releases can occur during transfer to and from storage vessels and during maintenance operations (2). Subsequent processing of polymer materials can also result in exposure to residual monomers (3).

Exposure to styrene is also encountered in the fiber-reinforced plastics (FRP) industry (2). In a typical FRP operation, the viscous resin-laden fiber material is sprayed onto a product mold and then manually rolled out to remove entrapped air. The resin contains a high percentage of styrene, along with curing agents, binders, and other volatile solvents that off-gas during this process. The most common air contaminants found in the FRP workplace along with styrene are aromatic hydrocarbons (e.g., ethylbenzene and toluene), chlorinated hydrocarbons (e.g., methylene chloride), and aliphatic ketones (e.g., acetone and 2-butanone) (2).

Occupational exposure to styrene vapor has been associated with impairment of the central and peripheral nervous systems as well as irritation of the eyes, skin, and upper respiratory tract (1,2,4). Styrene is also weakly mutagenic in vitro and in vivo (1,5), presumably due to metabolic transformation to styrene-7,8-oxide followed by DNA alkylation (6). These data, coupled with findings of increased frequencies of chromosomal aberrations (7,8) and sister chromatid exchanges (9) in the lymphocytes of styrene-exposed workers, suggest the possibility of styrene genotoxicity.

The recently revised Occupational Safety and Health Administration (OSHA) limits for styrene are 50 parts-per-million (ppm) based on an eight-hour time-weighted-average (8-hr TWA), and 100 ppm for short-term exposures (15-min TWA) (10). Similar workplace exposure limits are recommended by both the American Conference of Governmental Industrial Hygienists (ACGIH) (11) and the National Institute for Occupational Safety and Health (NIOSH) (2) to protect against the irritant and narcotic effects of styrene exposure.

Given the acute toxicity of styrene, it is desirable to measure workers' exposures continuously. Unfortunately, currently available portable direct-reading instruments lack the degree of selectivity necessary to discriminate between styrene and most of the potentially interfering gases and vapors mentioned above. Thus, a coated surface-acoustic-wave (SAW) chemical sensor was developed to measure styrene vapor continuously in the industrial environment.

The small size, simple design, and excellent sensitivity of this sensor, coupled with the ability to adjust the sensitivity and selectivity (by judicious choice of a chemically sensitive coating layer), make this device attractive for incorporation into miniaturized air-monitoring instrumentation. A wide variety of chemicals have been detected using coated-SAW sensors (12), and detection limits in the part-per-billion concentration range have been reported by several authors (13-15). However, only limited testing of selectivity in the presence of relevant interferences has been performed (16). The effects of other environmental variables, such as ambient temperature and humidity, which are critical to the ultimate performance of the sensor in field applications, have also received little attention.

In the preceding paper we showed that a SAW sensor coated with a mixture of trans-$PtCl_2$(ethylene)(pyridine) and poly(isobutylene) (PIB) could provide real-time measurement of styrene vapor over a concentration range of 5-700 ppm, with a calculated detection limit of 0.6 ppm (17). The sensor response is based on the increase of the mass of the coating accompanying the displacement of ethylene from the solid platinum-ethylene π-complex and formation of the corresponding styrene complex, trans-$PtCl_2$(styrene)(pyridine). The sensitivity to styrene was found to increase with increasing temperature according to an Arrhenius relationship.

In this paper, we present the results of laboratory experiments designed to assess the performance of this sensor as a real-time monitor of styrene vapor. The effects of ambient humidity and other solvent vapors on the response to styrene are investigated and the ability to repeatedly regenerate the coating reagent by treatment with ethylene is demonstrated.

COATING SELECTION CONSIDERATIONS

Selectivity and reversibility are often competing characteristics of a chemical sensor. In the SAW sensor these characteristics are a function of the type of interaction occuring between the analyte gas or vapor and the coating film deposited on the surface of the sensor. While low-energy, spontaneously reversible interactions, such as physical adsorption or absorption, are desirable for extended sensor operation, they generally lack a high degree of selectivity. Higher-energy interactions, such as chemical-bond formation, are more selective but also tend to be less reversible. Sensor coatings designed for this type of interaction would eventually become saturated.

The use of sensor arrays coupled with pattern recognition analysis has been explored as a way to achieve a high degree of selectivity using reversible sensor-analyte interactions (16,18). In this case, the different sensor coatings need only be partially selective as long as the pattern of responses from the array permits discrimination of the target analyte(s) from potentially interfering chemicals. However, the ultimate discriminating power of the array will still depend on the selectivity of the individual sensors, particularly where mixtures of structurally similar chemicals are involved.

The approach taken in designing chemically sensitive sensor layers will be influenced by the constraints of the particular application. For workplace monitoring over a single workshift it is feasible to consider non-reversible interactions since the sensor could be replaced or regenerated between sampling periods. For long-term continuous monitoring, reversibility may be a more important consideration.

With the sensor coating employed here, styrene is trapped as a stable product. As a result, the trapping reagent is eventually depleted. However, regeneration of the original trapping reagent is possible, permitting repeated use of the sensor.

EXPERIMENTAL SECTION

Detailed descriptions of the reagent synthesis, sensor fabrication, data aquisition system, test-atmosphere generation apparatus, and coating-deposition method have been presented in the preceding paper (17). Only procedures specific to this series of experiments are presented here.

Synthesis. The butadiene-substituted complex, $[PtCl_2(pyridine)]_2$(butadiene), was prepared by passing butadiene gas (Matheson) through a refluxing solution of trans-$PtCl_2$(ethylene)(pyridine) in methylene chloride for 45 min. Addition of petroleum ether to the cooled solution yielded an orange-yellow precipitate; m.p.=134°C (dec); elemental analysis, found (calculated for bridging-olefin structure): C, 22.7(22.6); H, 2.2(2.3).

The polymer-bound complex, $PtCl_2$(ethylene)(poly(4-vinylpyridine) (nominal formula), was prepared by adding a solution of 34 mg (0.34 mmole based on 4-vinylpyridine) of poly(4-vinylpyridine) (Scientific Polymer Products) in aqueous ethanol to a stirred solution of 200 mg (0.54 mmole) of $KPtCl_3$(ethylene) (Alfa) in aqueous ethanol. A flocculent yellow-white precipitate formed upon addition of the polymer solution. The supernatant was removed following centrifugation and the solid was rinsed twice with ethanol and dried in air. The solid was soluble in methylene chloride and chloroform. No further structural characterization was performed.

Test-Atmosphere Generation. Solvent vapors were generated by passing nitrogen through a bubbler containing the liquid solvent and then into a metered dilution-air stream. For butadiene, vinyl chloride, and vinyl bromide, a syringe pump was used to introduce the pure gas into the air stream. The flow rate, temperature, and relative humidity (RH) of the dilution air were controlled using a Miller-Nelson Research Model HCS-301 Controller.

An infrared gas analyzer (Foxboro, MIRAN 1A) was used for continuous verification of gas/vapor concentrations. For experiments involving simultaneous exposure to styrene and each of the other contaminants, the gas analyzer was calibrated for each component of the mixture individually at a wavelength where both chemicals exhibited strong IR absorbance. After establishing a constant concentration of styrene vapor, the second contaminant was introduced and the increase in the IR absorbance was used to determine the concentration of the second component.

Trapping Agent Regeneration. Following exposure to styrene, the trans-$PtCl_2$(ethylene)(pyridine) was regenerated by exposing the sensor to pure ethylene. The difference frequency decreased rapidly upon initial exposure to ethylene, corresponding to replacement of ethylene for styrene in the complex. Exposure was continued until no further decrease in frequency was observed, which typically required 25-40 min.

RESULTS AND DISCUSSION

Selectivity. The selectivity of the sensor was investigated for both simultaneous and sequential exposures to styrene and each of several other gases and vapors used with styrene in industrial processes. For most experiments a styrene concentration of 50 parts-per-million (ppm) was used, corresponding to the Occupational Safety and Health Administration (OSHA) limit for occupational exposures (10). The concentrations of the other vapors tested were all well in excess of their respective OSHA exposure limits (10). The other chemicals examined included toluene, ethylbenzene, 2-butanone, methylene chloride, acrylonitrile, butadiene, methyl acrylate, methylmethacrylate, vinyl acetate, vinyl chloride, and mesityl oxide.

All of the potential interferences were absorbed by the coating film as indicated by an initial negative shift in the frequency of the single oscillator upon exposure, and a corresponding positive frequency shift upon removal from the atmosphere. These signals were effectively masked by measuring the difference frequency with the reference device coated with PIB. No further change of frequency was observed for exposure to these chemicals, with the exception of butadiene, vinyl acetate and methyl acrylate. In all cases, the response to styrene was the same before and after exposure to these chemicals.

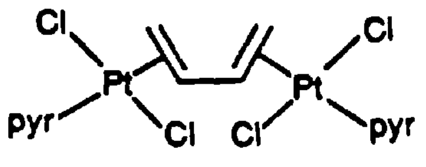
Exposure to methyl acrylate from 50-900 ppm yielded responses ranging from 3-28 Hz/min, respectively. For vinyl acetate, exposures ranging from 10-275 ppm yielded responses ranging respectively from 2-30 Hz/min (19). Curiously, butadiene exposure caused a *decrease* in the difference-frequency signal (i.e., an increase in the single oscillator frequency). Exposure to 30 ppm of butadiene caused an initial response of -22 Hz/min (averaged over 15 min), however, the response declined to negligible values after only 45 min of exposure. Raising the butadiene concentration had no effect on the response. A more detailed discussion of the interaction of butadiene with the sensor coating is provided below.

To further examine the selectivity for styrene, the coated sensor was exposed simultaneously to styrene and each of the chemicals listed above. As shown in Table I, with the exception of butadiene, the presence of these other gases and vapors did not affect the response to styrene. The lack of interference by the non-olefin and non-reactive olefin vapors might have been expected, but does provide evidence for an S_N2 (i.e., non-solvent-assisted) mechanism for the reaction with styrene, as reported for similar olefin-substitution reactions in solution (20-23). Remarkably, neither vinyl acetate nor methyl acrylate affected the response to styrene, even though they react individually with the trapping agent. This indicates that styrene is exclusively favored in the competition for reaction with the solid.

The selectivity for styrene may be explained by considering the nature of the platinum-olefin bond in these complexes. Bonding between the olefin and the platinum involves donation of electron density from the π-cloud of the olefin to the metal d-orbitals via a σ-bond, as well as back-bonding from the metal to the olefin via a π-bond (20). The energies and overlaps of the involved orbitals will determine the strength of the platinum-olefin bond. Meester et al., have determined approximate energies for the highest-occupied and lowest-unoccupied platinum d-orbitals in several $PtCl_2$(olefin)(pyridine or NH_3) complexes based on spectroscopic data (24). A comparison of these energies with those of the corresponding free-olefin orbitals is shown in Figure 1 for several of the olefins studied here. For the unoccupied orbitals, there is no discernable correlation between the relative reactivities and the relative energies of olefin and platinum orbitals involved: energy differences for styrene, methyl acrylate and acrylonitrile are all < 0.7eV, and that of vinyl acetate is > 1.4 eV. For the occupied orbitals, however, styrene has the closest energy match followed in order by vinyl acetate, methyl acrylate and acrylonitrile.

Apparently, the σ-bond interaction is more important in determining the relative reactions rates (and product stabilities) for these olefin substitution reactions. This is consistent with our previous results where preferential reaction with vinyl acetate was observed in the presence of methyl acrylate (19). The failure of vinyl chloride to react or interfere with the response to styrene is most likely due a combination of poor orbital overlap and the presence of the strongly electron-withdrawing chlorine substituent on the double bond. For methylmethacrylate and mesityl oxide, the additional steric hindrance from the methyl groups on the double bonds undoubtedly contributes to their lack of reactivity.

As noted above, exposure to butadiene caused an initial increase in the single oscillator frequency (decrease in the difference frequency), which corresponds to a decrease in the mass/area of the coating (see eq 1 in reference 17). To further investigate the product of reaction with butadiene, a sample of the butadiene-substituted complex was synthesized by reaction with the $PtCl_2$(ethylene)(pyridine) complex in solution (see Experimental Section). Elemental analysis of the product is consistent with the bridged structure shown below, wherein each double bond is coordinated to a separate platinum moiety (note: the butadiene configuration may be cis or trans). Similar bridged structures involving butadiene complexes with platinum and palladium have been reported (25).



Since there is a negligible net mass difference accompanying the substitution reaction, the increase in the single-oscillator frequency observed upon exposure to butadiene is attributed to a slight decrease in the density incurred upon formation of the butadiene complex (note: an increase in the elastic stiffness of the coating would also cause an increase in frequency; however, this outcome seems unlikely given the low modulus of the PIB in the coating). That the response to butadiene declines rapidly may reflect either an unfavorable competition with ethylene or conformational constraints encountered within the solid complex.

Results of additional tests of the effect of butadiene on the response to styrene are shown in Figure 2 for exposure at 40°C to 5 ppm of styrene and various concentrations of butadiene. The steady-state response decreases as the butadiene concentration increases. At 136 ppm of butadiene the reaction with styrene is completely blocked. Removal of butadiene leads to a recovery of the initial response obtained for styrene alone. Thus, displacement of butadiene from the complex by styrene appears to proceed at a rate similar to that for ethylene.

Attempts to monitor butadiene using trans-$PtCl_2$(styrene)(pyridine) as the coating reagent gave a response that was independent of concentration: for exposures ranging from 16-150 ppm of butadiene, a constant response of -20 Hz/min (15-min average at each concentration) was observed (note: in this case a decrease in the difference frequency is expected because styrene is displaced by the lighter butadiene).

Humidity Effects. The effects of humidity on the sensor were examined with and without styrene present. Initial tests involved monitoring the single coated-oscillator output with no styrene present during a series of step-changes of relative humidity (RH) over the range of 5-80% RH (25°C). For each change of RH, the sorption of water vapor caused an abrupt decrease in the frequency over the first few minutes followed by re-establishment of a stable frequency, as observed for the non-reactive organic vapors described above. From 5-60% RH a net frequency shift of only -370 Hz was observed, corresponding to a relatively small uptake of water vapor by the coating. Increasing the RH from 60 to 80% resulted in a significantly larger frequency shift (~-560 Hz) than observed at lower RH values. Similar non-linear sorption behavior has been reported for a polyimide-coated SAW sensor upon exposure to water vapor, although the frequency shifts obtained were about two orders of magnitude larger than those seen here (26). Upon returning to 5% RH the baseline oscillator frequency returned to the pre-exposure value, confirming the reversibility of water-vapor sorption.

The effect of humidity on the response to styrene was also examined at 25°C for RH values ranging from 5-80%. Figure 3 summarizes the results of several experiments involving a sequence of exposures to styrene at 5, 50, and then 80% RH (solid line in Figure 3), followed by re-exposure at 50% and then 5% RH (dashed line in Figure 3). For each change of RH level in the exposure series, the sensor was allowed to equilibrate for several minutes before being exposed to styrene. Responses are presented relative to the initial response at 5% RH, and each point represents the mean relative response for exposures of 15-30 min duration at each of several styrene concentrations in the range of 10-600 ppm. Relative responses are in the ratio 1:1.6:2.2 for operation at 5, 50, and 80% RH, respectively. As shown, no significant hysteresis is observed. The lower response observed upon returning to 5% RH is within experimental error and is attributed to a slight reduction in the surface area of the trapping reagent accompanying repeated exposure to styrene (see below).

The most likely explanation for the observed humidity dependence is an increase in the olefin-substitution reaction rate due to the solvation effect of adsorbed water. Although there are no ionized species involved in the reaction, water would be expected to stabilize the polar pentacoordinate transition state to a greater extent than the square-planar reactant complex. Adsorbed water might also facilitate diffusion of styrene into the solid. Note that the ratio of responses to styrene at 50 and 80% RH (~1.4) parallels the ratio of water vapor uptake by the coating at these RH levels.

An alternative explanation for the increased response is the establishment of an additional, solvent-assisted reaction pathway involving surface-adsorbed water. A similar mechanism was postulated to describe olefin-substitution reactions of trans-$PtCl_2$(ethylene)(4-X-aniline) complexes in non-coordinating solvents upon addition of traces of ethanol (23) - a reduction in the degree of bimolecular substitution of the bound olefin was suggested as resulting from initial displacement of the olefin by ethanol. If water were displacing ethylene in our complex, however, one would also expect to see a continual decrease in the single-oscillator response at high humidity, which was not observed. Furthermore, interference by other olefins and non-olefins would have been expected if a solvent-assisted mechanism were important. Thus, while this mechanism cannot be ruled out completely, any competition between water and ethylene for coordination to the platinum clearly favors the latter.

Coating Regeneration. As expected, the sensitivity gradually declines upon continued exposure styrene due, in part, to depletion of the unreacted trapping agent. While for low styrene concentrations (i.e., 10 ppm) there was no measurable decline in response over 8 h of continuous exposure, at 50 ppm the response declined by about 20% after 4 h, and at 300 ppm the response declined by about 75% after 4 h. Increasing the amount of coating material initially deposited on the device did not alter the decline in response. Given the apparent dependence of the reaction on the available surface area of the trapping agent (17), this result was not unexpected.

Treatment with pure ethylene gas resulted in release of styrene and regeneration of the original complex (note: the structure of the regenerated complex was confirmed by IR spectrophotometry in a separate series of experiments). Table 2 shows a series of responses (15-30 min averages) measured at 25 and 38°C that demonstrates the regenerability of the coating reagent. The first column in Table 2 presents responses for the original coatings at each temperature and illustrates the decline in sensitivity upon re-exposure to styrene. Values presented in columns 2-4 were obtained following successive regeneration/exposure cycles. As shown, the responses of the regenerated coatings were virtually the same as those for the original coatings.

Regeneration following prolonged exposure, however, gives a response that is initially higher than that for the initial coating. Figure 4 shows this effect for exposure at 25°C to 50 ppm of styrene followed by regeneration and re-exposure. The response of the original coating remained essentially constant for several hours, dropping to about 80% of the initial response value after 4 h. In this case, the response of the regenerated coating was initially 28% higher than that of the original coating. After several min, however, the regenerated-coating response returned to that of the original coating. Similar results are obtained for exposure at 40°C.

We speculate that reaction with styrene causes an expansion of the crystal lattice of the platinum-ethylene complex that persists after regeneration. This would increase the accessible surface area as well as facilitate diffusion through the solid during the initial phases of the subsequent exposure. Apparently, this effect is not significant at low conversion levels but becomes more important as more of the reagent reacts.

For longer exposures the assumption of catalytic behavior, made in the previous paper for comparison with theoretical rate models (17), is clearly no longer valid. As the reaction proceeds, the styrene, as well as the evolved ethylene, must diffuse through an increasingly thick layer of the product platinum-styrene complex. In addition, the ethylene may react with the product layer as it diffuses out of the solid. Thus, the gradual reduction in the sensor response may result from a combination of these phenomena and a net reduction in reactive surface area of the platinum-ethylene complex. Under these conditions, the so-called unreacted-core model described by Levenspiel (27) may be more appropriate for describing the trapping reaction. This model depicts the gas-solid reaction as proceeding from the outer surface of the solid inward, with production of a progressively thicker product shell (the platinum-styrene complex in this case) around a shrinking core of unreacted starting material. The use of this model to predict the behavior of the sensor for prolonged styrene exposure is currently being explored.

An alternative approach being investigated involves the polymer-bound reagent $PtCl_2$(ethylene)(poly(4-vinylpyridine)) as the sensor coating. Preliminary experiments using an uncharacterized sample of this reagent yielded a sensor response of 50 Hz/min for exposure to 50 ppm of styrene, although the response declined fairly rapidly for the thin films examined. Regeneration with ethylene provided a response equivalent to that of the original coating.

CONCLUSIONS

Selective measurement of styrene vapor in the ppm concentration range has been achieved using a SAW sensor coated with a mixture of trans-$PtCl_2$(ethylene)(pyridine) and poly(isobutylene). With the exception of butadiene, which causes a reversible negative interference, co-exposure to each of several relevant olefin and non-olefin interferences does not affect the response to styrene. The high degree of selectivity obtained represents an improvement over portable direct-reading instruments currently used for monitoring styrene in the industrial environment.

Preferential reaction with styrene in the presence of other olefins is consistent with the similarity in the energies of the bonding orbitals of platinum and styrene. The steric properties of the attacking olefin also appear to affect the reactivity with the trapping agent. Furthur research is needed to determine whether other olefins can be detected selectively based on the size or electron-withdrawing/donating strengths of the olefin substituents. The influence of steric and electronic factors also suggests that altering the substituents on the pyridine and/or ethylene ligands of the trapping agent could be used to adjust the selectivity of the sensor.

Increasing atmospheric humidity from 5-80% roughly doubles the response to a given styrene concentration. In practice, a means for monitoring or eliminating ambient humidity would be needed. It should be noted that conventional photoionization detectors exhibit a stronger humidity dependence (28), requiring the use of a scrubber to eliminate water vapor upstream from the sensor. A similar technique might employed for the sensor described here.

At present, the operating time of the sensor is limited by the gradual depletion of the trapping reagent in the coating. The decline in the sensor response over time is apparently related to both the reduction in active surface area and the mass-transfer resistance associated with diffusion of styrene and ethylene through an increasingly thick solid product layer. The trapping reagent can be regenerated after exposure to styrene by treatment with ethylene gas, in situ. For relatively short-term exposures, multiple regenerations are possible with retention of the original coating response characteristics. For prolonged exposure, however, the regenerated coating exhibits initially higher sensitivity than the original coating which is attributed to an expansion of the crystal lattice in the outer layer of the solid following styrene exposure. The use of a polymer-bound trapping reagent with active sites distributed along the polymer backbone may have several advantages over the use of a discrete solid trapping reagent. Preliminary results using a poly(4-vinylpyridine) analogue of the platinum-ethylene π-complex demonstrate the feasibility of this approach.

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Table I. Sensor response for exposure to approximately 50 ppm of styrene with and without other co-contaminants present at the indicated concentrations.[a]

Trial	Co-contaminants	Response (Hz/min) to ~50 ppm styrene mean (s.d.)
1	styrene	43(8)
	styrene + 2-butanone (300ppm)	44(6)
2	styrene	46(3)
	styrene + dichloromethane (350ppm)	45(6)
3	styrene	48(6)
	styrene + ethylbenzene (250ppm)	49(4)
4	styrene	47(5)
	styrene + toluene (300ppm)	50(6)
5	styrene	40(5)
	styrene + acrylonitrile (120ppm)	42(5)
6	styrene	48(3)
	styrene + methyl acrylate (800ppm)	45(3)
7	styrene	52(4)
	styrene + methylmethacrylate (200ppm)	53(4)
8	styrene	53(5)
	styrene + mesityl oxide (140ppm)	52(5)
9	styrene	50(4)
	styrene + vinyl acetate (135ppm)	51(3)
10	styrene	46(8)
	styrene + vinyl chloride (65ppm)	42(8)
11	styrene	42(9)
	styrene + butadiene (30ppm)	11(3)

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[a] T = 25°C, RH = 50%.

Table II. Response to styrene at 25 and 38°C (20% RH) of original coatings and multiple regenerated coatings.[a]

	Response (Hz/min)			
styrene concentration	original coating	1st regen	2nd regen	3rd regen
initial exposure (25°C)				
10 ppm	17	18	20	21
230 ppm	36	32	32	30
625 ppm	89	87	86	81
re-exposure (25°C)				
10 ppm	6	6	8	11
230 ppm	24	22	22	20
625 ppm	58	53	54	48
initial exposure (38°C)				
3 ppm	31	32	31	32
8 ppm	51	61	52	56
50 ppm	109	114	94	95
re-exposure (38°C)				
3 ppm	20	19	18	23
8 ppm	34	31	34	29
50 ppm	50	56	59	54

[a] Each value represents the mean response for exposures of 15-30 min duration.

Figure Captions

Figure 1. Comparison of approximate energy levels of the highest-occupied orbitals (----) and lowest-unoccupied orbitals (- - -) of free olefins and platinum in trans-$PtCl_2$(olefin)(pyridine or NH_3). ST-styrene, VA-vinyl acetate, MA-methyl acrylate, AN-acrylonitrile . Adapted from reference 24 with permission.

Figure 2. Response to 5 ppm of styrene at 40°C with varying concentrations of butadiene. Each point represents the mean response for exposures of 10 min duration.

Figure 3. Relative response to styrene at 25°C for relative humidities (RH) ranging from 5-80%. Solid line is for increasing RH and dashed line is for decreasing RH. Each point represents the mean relative response for exposures ranging from 10-620 ppm.

Figure 4. Relative response to 50 ppm of styrene for original coating (○) and regenerated coating (△) for continuous 4-h exposures. Each point represents the mean relative response determined at 15-min intervals.

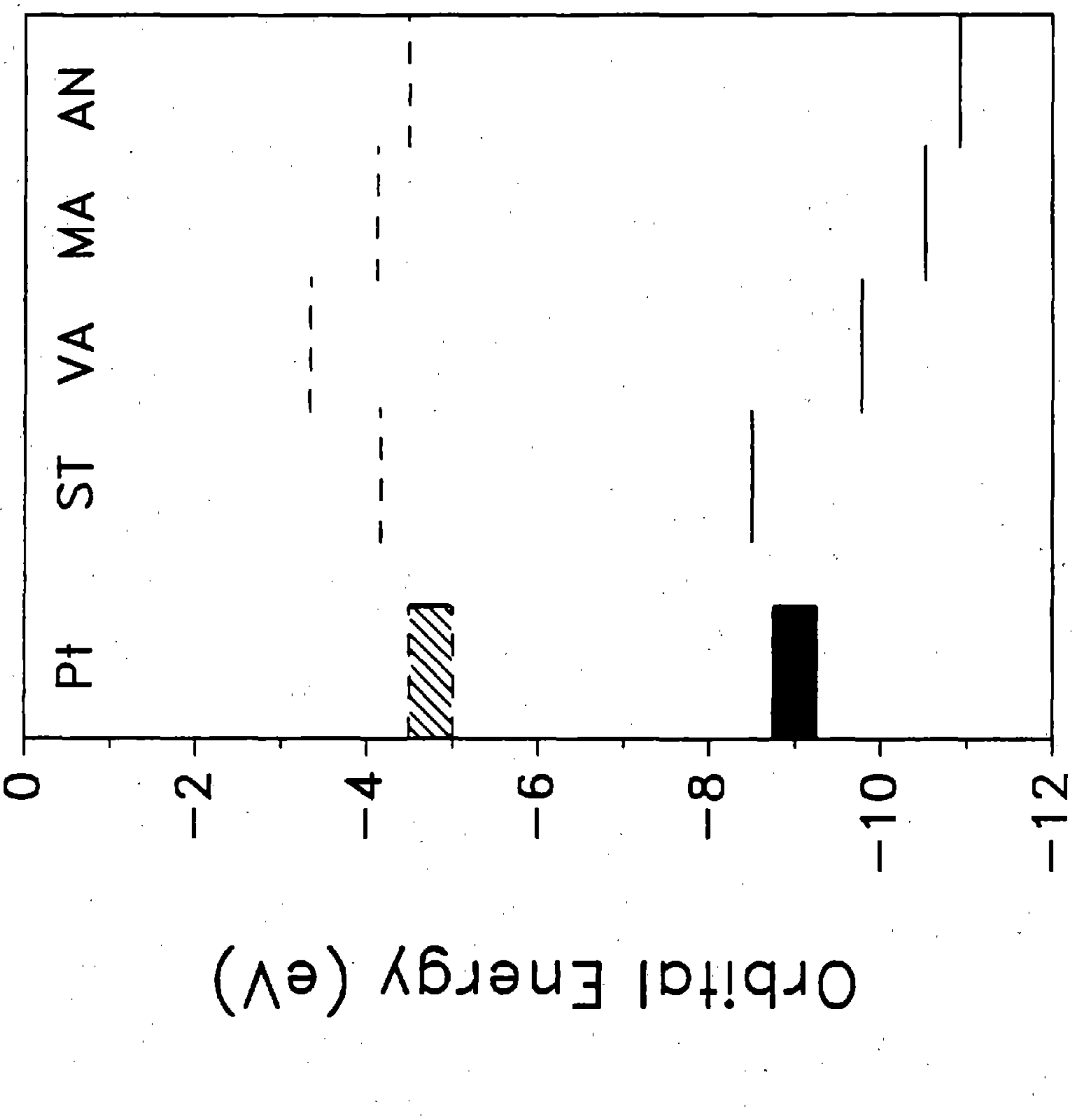


Figure 1

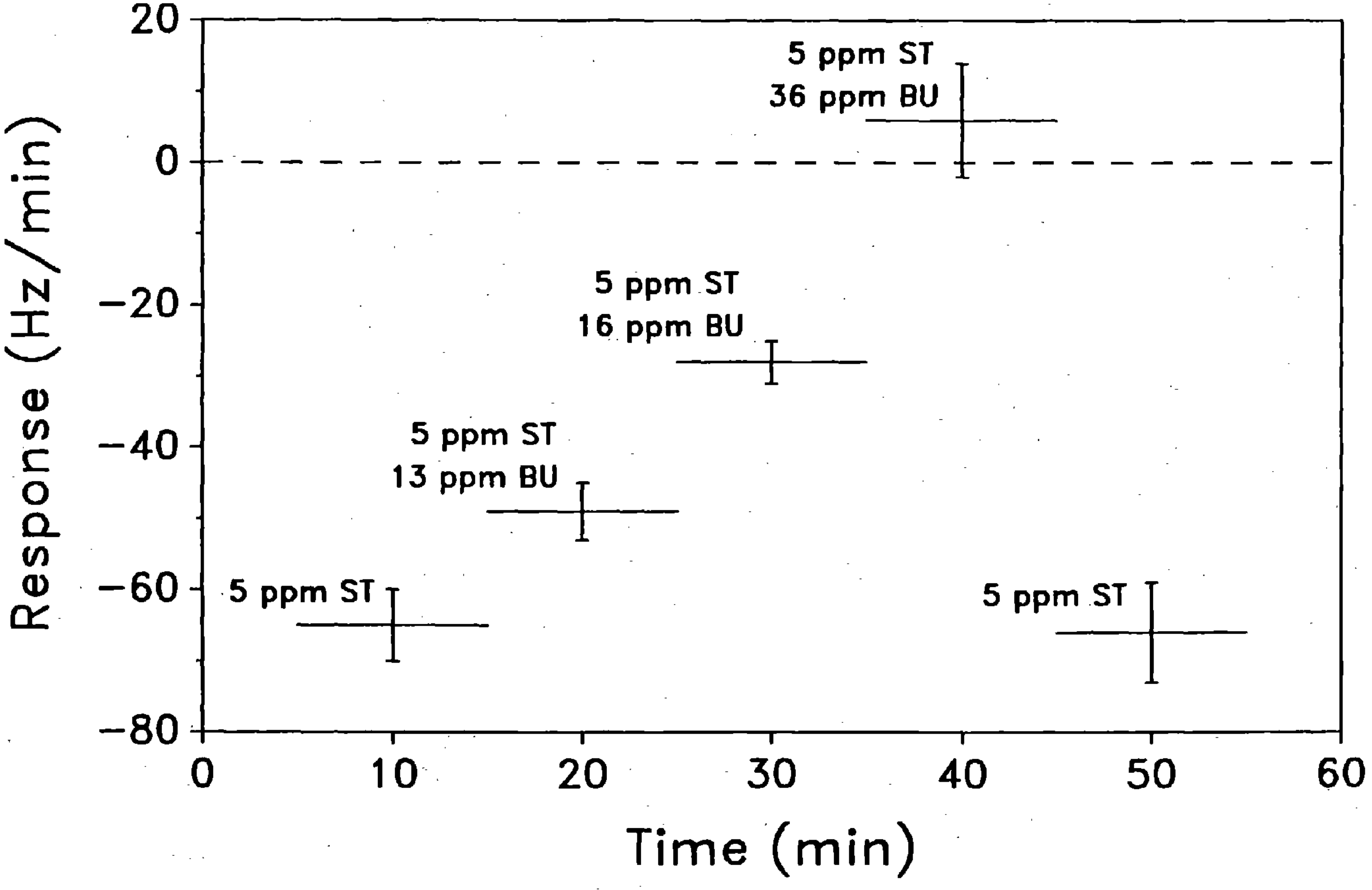

5 ppm ST
36 ppm BU
5 ppm ST
16 ppm BU
5 ppm ST
13 ppm BU
5 ppm ST
5 ppm ST
20
0
−20
−40
−60
−80
0
10
20
30
40
50
60
Response (Hz/min)
Time (min)

Figure 2

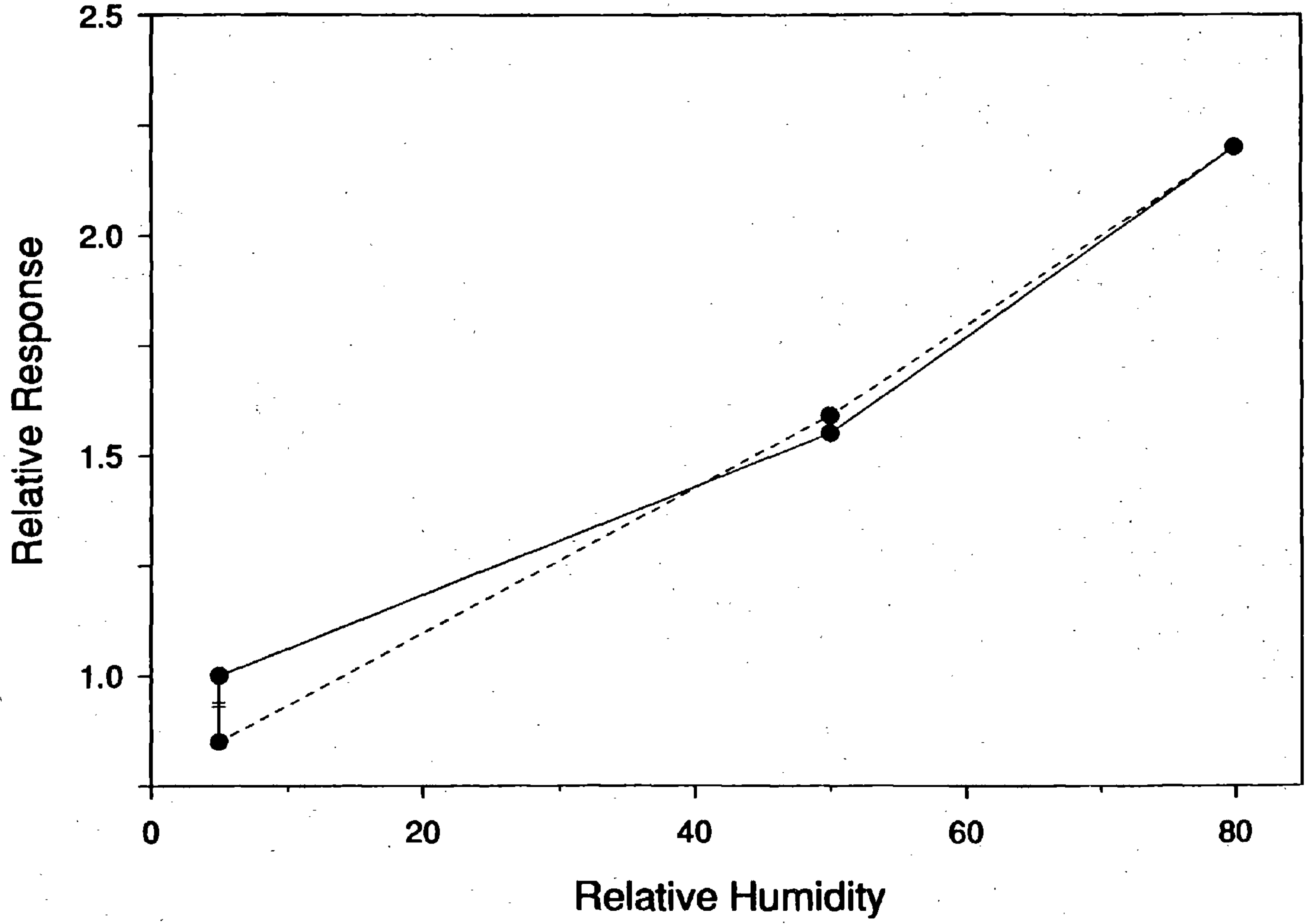
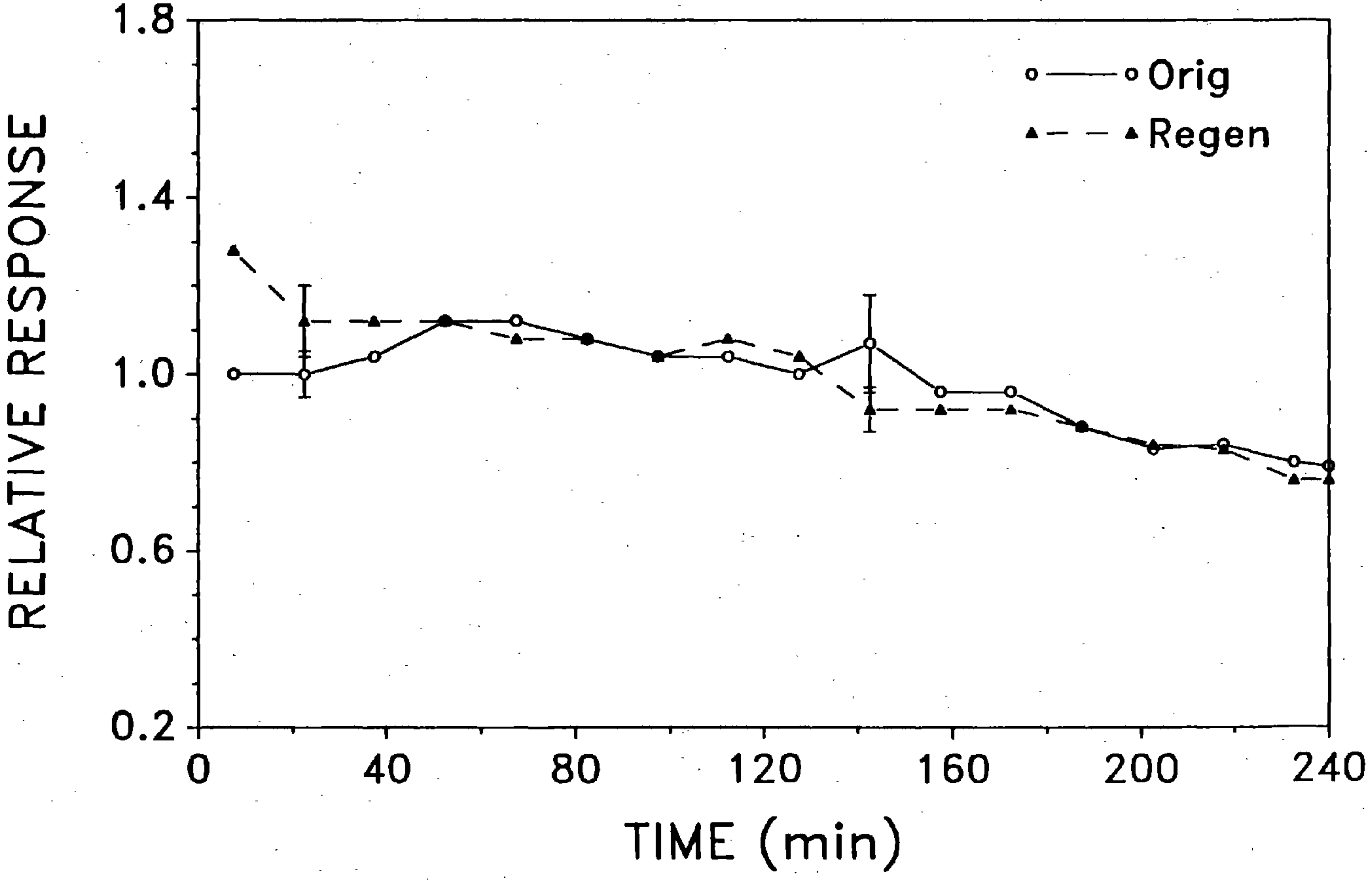


Figure 3



1.8
1.4
1.0
0.6
0.2
RELATIVE RESPONSE
0
40
80
120
160
200
240
TIME (min)
Orig
Regen

Figure 4

CHAPTER 3

Steric Factors Affecting the Discrimination of Isomeric and Structurally Related Olefin Gases and Vapors with a Reagent-Coated Surface-Acoustic-Wave Sensor

Abstract

An investigation of steric factors affecting the olefin-olefin selectivity of a surface-acoustic-wave (SAW) sensor coated with reagents of the general formula trans-$PtCl_2$(ethylene)(substituted-pyridine) is described. Detection is based on the mass increase accompanying replacement of ethylene by other gas-phase olefins to form the corresponding olefin-substitution products. Selectivity depends on the relative reaction rates of the different olefins. Within series of structurally similar butenes, acrylates and aromatic olefins unusually high selectivity is observed for the less hindered olefins and complete discrimination of isomers is achieved in certain cases. Replacing pyridine by 2-methylpyridine and 2,6-dimethylpyridine in the reagent complex progressively reduces the sensor response. Sensitivities increase with increasing temperature and limits of detection ranging from about 2-70 μg/L are achieved with modest heating (30-40°C) using a 30-MHz SAW oscillator. Initial results with a 52-MHz sensor show a 3.4-fold increase in sensitivity compared to the 30-MHz sensor in rough agreement with theory.

INTRODUCTION

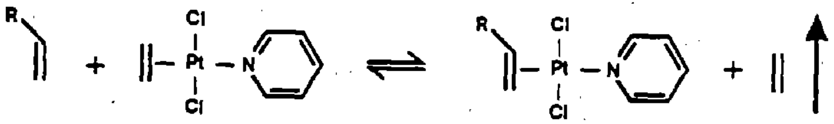
The surface-acoustic-wave (SAW) chemical sensor has emerged as a useful tool for the characterization of thin films (1,2) and the measurement of atmospheric gases, vapors and aerosols (3-5). The analytical versatility of the SAW sensor stems largely from the generic nature of its predominant transduction mechanism, i.e., its sensitivity to surface mass changes. For the case of gas and vapor measurements, this feature, coupled with the ability to adjust the response of the sensor through the use of different surface coatings, results in a broad range of detectable analytes (3).

We are primarily interested in the development of SAW sensors for environmental and industrial monitoring of toxic organic gases and vapors whose moderate-to-low reactivity can preclude direct or selective measurement by other sensor technologies. To date, the most common approach to measuring organic vapors with SAW sensors has been to use a sorptive polymer coating to concentrate the vapor(s) near the sensor surface (3,6-8). The partition coefficient of the vapor, which reflects the magnitude of the sensor response at a given vapor concentration, will depend on the strength of the solubility interactions between the vapor and the polymer (8,9). By use of an array of SAW sensors coated with polymers of different structures and solubility properties, a collective response pattern can be obtained that is characteristic of a given type of vapor

(6,10). Discrimination between the components of simple vapor mixtures is also possible (11).

Due to the low energies associated with these solubility interactions, however, there is a limit to both the sensitivity and selectivity achievable with this approach. Thus, structural isomers and homologues with very similar solubility properties will not be easily discriminated. In addition, most organic gases and many volatile solvents have very low partition coefficients at ambient temperatures (12). As a result, detection limits for these compounds using polymer-coated SAW sensors can be rather high. For detection in the range of many environmental and occupational health standards, this approach may not provide adequate sensitivity without sample preconcentration (13).

We recently reported the selective measurement of vinyl acetate (14) and styrene (15,16) vapors using a SAW sensor coated with the Pt-olefin π-complex trans-$PtCl_2$(ET)(pyr) (ET = ethylene, pyr = pyridine). The trapping reaction is shown in general form by eq 1, where R represents the substituent on the target olefin:



(1)

The rate of frequency change was related to the olefin vapor concentration by means of a power-law kinetic model and real-time measurement of olefin vapor concentrations was possible. In addition, the initial trapping reagent was regenerable following exposure by treatment with ET in situ. Complete selectivity in the presence of non-olefin organic vapors was observed. High selectivity in the presence of certain other olefins was also observed and was tentatively attributed to steric and electronic factors that favored reaction with the target olefins.

This paper describes a more systemmatic study of the influence of steric factors on the rates of olefin substitution reactions in complexes of the general formula trans-$PtCl_2$(ET)(R_n-pyr) (R = -H or -CH_3, n = 1-3) and the corresponding selectivity obtained when these coatings are used in SAW sensors for measuring the concentrations of various olefin gases and vapors. The response of a 30-MHz SAW sensor coated with trans-$PtCl_2$(ET)(pyr) to vapors of ethyl acrylate (EA) is first characterized over a range of concentrations and temperatures. Data are presented confirming the selectivity for EA in the presence of several non-olefin organic vapors. Then, for series of acrylate (including EA), butene, and aromatic-olefin isomers and derivatives, the effects of steric hindrance in both the reagent coating and olefin analytes on the olefin-olefin selectivity of the coated-sensor are described. Sensitivities and limits of detection (LOD) using this type of reagent coating are compared to those obtained using a sorptive polymer coating of poly(isobutylene) (PIB). Preliminary results obtained with a 52-MHz reagent-coated SAW sensor are also presented to demonstrate the effect on sensitivity of increasing the sensor operating frequency.

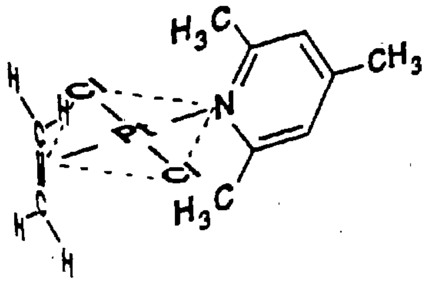
Sensor Configuration and Trapping Reaction. As in most reported chemical sensing applications (3), we use the coated-SAW device as the frequency controlling element in a feedback oscillator circuit and monitor the oscillation frequency. The response of the SAW oscillator to changes of surface mass can be described by the following approximate expression (17):

$$\Delta f = K f_o^2 \Delta m/a \qquad (2)$$

where Δf is the frequency change (sensor response), K is a negative substrate constant , f_o is the initial operating frequency, and $\Delta m/a$ is the change of mass per unit area caused by deposition of the coating film and by subsequent interactions of the coating with a gas or vapor.

In the coating reagents, bonding between ET and Pt(II) occurs through donation of electron density from the filled p_π-orbital of the ET to the Pt via a σ bond as well as through back-bonding from the filled orbitals on the Pt to the antibonding π^* orbitals of the ET via a π bond (18). Similar σ and π bonding interactions occur between Pt and pyr. The strength of the Pt-ligand bonds will depend on the relative energies and overlaps of the orbitals involved. One consequence of the trans configuration of these ligands is that substituents on pyr can affect the bonding to ET (and vice-versa). This, in turn, can affect the susceptibility of the complex to nucleophilic attack by other olefins. Both steric and electronic factors can be important and although it is often difficult to completely separate the influences of these factors, an attempt has been made here to focus on systems where steric factors are predominant. An investigation of substituent-related electronic factors affecting the responses of these complexes as SAW-sensor coatings is currently being performed and will be the topic of a separate report.

Crystallographic studies of Pt(II)-ET complexes have shown that the C=C bond axis is nearly perpendicular to the Pt-Cl-N-Cl plane (19). The angle between the pyr ring and this plane can vary significantly with different pyr substituents. For the 4-methylpyridine (4-Mepyr) complex this angle is 50°, whereas for the 2,6-dimethylpyridine (2,6-Me_2pyr) and the 2,4,6-trimethylpyridine (2,4,6-Me_3pyr) complexes this angle is about 90°:



Interestingly, the C=C, Pt-N and (C=C)-Pt bond lengths are nearly identical in these three structures. Although no crystallographic data are available for the 2-methylpyridine (2-Mepyr) complex, one would expect some intermediate value for the ring-plane angle.

Olefin-substitution reactions proceed by an associative pathway (18). Attack by the entering olefin occurs from above or below the Pt-Cl-N-Cl plane and the two olefins and the pyr comprise the base of the trigonal bipyramidal transition state. It is not difficult to envision how substituents in the 2- and 6- positions on the pyr ring would inhibit the reaction through crowding in the transition state. Similar crowding would be expected for olefins having bulky substituents on the double-bonded carbons.

Miya et al. (20), reported a significant decrease in the olefin substitution rate with trans-$PtCl_2$(2-methyl-2-butene)(pyr) for more sterically hindered olefins, but only a few olefins were examined in that report. Additional evidence of steric effects is found in studies of exchange rates between free and bound ET in solutions of trans-$PtCl_2$(ET)(R_n-pyr) where the activation energies for the exchange process were in the order 2,4,6-Me_3pyr > 2-Mepyr > 4-Mepyr ~ pyr (21,22). Thermodynamic studies have revealed a consistent trend toward lower equilibrium formation constants for more hindered olefins in Pt(II)-olefin complexes (19,23) as well as in olefin complexes of Ag(I) (24), Rh(I) (25), and Pd(II) (26). In the case of the Pt(II)-olefin complexes, NMR (27) and x-ray (23,28) data have revealed that substituents on the olefin double bonds are invariably bent away from the metal (i.e., out of the C=C plane) presumably to minimize repulsions between the olefin substituents and either the metal or the adjacent ligands.

The goal of the work described in this paper was to determine the extent to which steric factors could be exploited to obtain selectivity for unhindered olefins in the presence of hindered olefins with these reagents coated on a SAW sensor.

EXPERIMENTAL SECTION

Sensor Coatings. All synthetic reagents, gases and solvents were 97% or higher purity and were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were obtained with a Perkin-Elmer 775B Spectrophotomer using thin-film samples deposited on KBr discs. Particle-size analyses were performed using an Olympus Model BHA optical microscope according to established methods (29).

Coating reagents, trans-$PtCl_2$(ET)(R_n-pyr), were synthesized by the addition of one equivalent of the amine to a stirred aqueous solution of $KPtCl_3$(ET) (Aldrich) at room temperature (30). The solid precipitates which formed immediately were isolated, rinsed with water, dried and then recrystallized from a minimum of methylene chloride by addition of hexane to the cloud point. The resulting products were typically yellow crystalline solids soluble in moderately polar organic solvents (e.g., methylene chloride and toluene). The 2-Mepyr complex would often precipitate as an oil that could be eventually crystallized following slow evaporation of the solvents. trans-$PtCl_2$(ethyl acrylate)(pyr) and trans-$PtCl_2$(methyl acrylate)(pyr) were prepared from methylene chloride solutions of the corresponding ET complex by adding an excess of the acrylate and refluxing for 1 hr. Both acrylate complexes were isolated as viscous yellow oils by addition of hexane. The products could not be recystallized but did become semi-solid on standing for several days. Table 1 lists the reagents investigated along with the corresponding melting points and elemental analyses.

Previous work showed that combining the Pt-olefin complexes with the amorphous rubbery polymer PIB resulted in more uniform and adherent coating films than those obtained using the solid complexes alone (15). Films were deposited by solvent casting from solutions containing 6 mg/mL of each component in 2:1 toluene:hexane. The amount deposited was estimated by eq 2 from the net frequency shift after evaporation of the casting solvent. Frequency shifts due to the coating films were typically in the range of 280 ± 30 kHz. It has also been shown previously that coating the reference SAW device with PIB and measuring the difference frequency between the two sensors masked the response due to sorption and desorption of vapors by the polymer on the sensing oscillator (15). For measurements described here only the single-oscillator output was monitored and the steady-state response was determined after establishment of sorption equilibrium at a given olefin concentration.

Apparatus. Most experiments were performed using a 30-MHz SAW oscillator (active area = 1.5 cm^2) fabricated on an ST-quartz substrate (Valpey-Fischer, Hopkinton, MA). Additional experiments were performed using a 52-MHz SAW oscillator (active area = 0.63 cm^2) purchased from Microsensor Systems, Inc. (Springfield, VA). Sensor frequencies were monitored with a digital frequency counter (Hewlett-Packard Model 5384A) and logged on a personal computer via an IEEE-488 interface. Frequency measurements were collected every 10 s with a resolution of 1 Hz and the net 1-min frequency shifts were averaged over a given exposure interval.

The sensor was placed on a Teflon^R pedestal in a 240-cm^3 stainless-steel exposure chamber wrapped with heating tape to control the temperature. A thermocouple was used to monitor the temperature at the surface of the sensor. Test atmospheres of the vapors were generated by passing nitrogen gas through a bubbler containing the liquid solvent and then into a dilution-air stream. For the gases investigated, a syringe pump was used to meter the gas into the dilution stream. Dilution-air flow and temperature were controlled with a Miller-Nelson Research HCS 301 control unit and the relative humidity was maintained below 10%. Part of the contaminated air stream was directed through the exposure chamber and the remainder through an infrared gas analyzer (Foxboro, MIRAN 1A) used for continuous monitoring of solvent vapor concentrations. The exhaust from both streams was then vented to a fume hood. At the flow rates used, the theoretical mixing time in the exposure chamber was 8 s (31). For binary-mixture exposures the infrared gas analyzer was calibrated for each component of the mixture at a common absorbance wavelength. Following establishment of a constant concentration for the initial component, the second component was introduced and the increase in absorbance was used to determine its concentration.

RESULTS AND DISCUSSION

Response to Ethyl Acrylate. Figure 1 shows the response of the sensor coated with trans-$PtCl_2$(ET)(pyr) to EA as a function of concentration and temperature. Each point on the curves represents the mean steady-state rate of frequency change observed at each concentration. Exposures were limited to 20 minutes at each concentration to avoid any significant depletion of the reagent (see below). The standard deviations around each point ranged from 1-3 Hz/min at low concentrations to about 6 Hz/min at the higher concentrations. Results were quite reproducible, with differences of less than 10% being observed at a given concentration for duplicate coating films. Response times and recovery times ranged from about 20-45 s.

The non-linear response vs. concentration curves presented in Figure 1 are typical of those observed for all of the olefins tested and reflect the heterogeneous nature of the gas-solid trapping reaction which is the rate-limiting step in the overall interaction of the olefins with the sensor coating. For a given temperature a plot of log concentration vs. log response gave a straight line ($r^2 > 0.998$) in accordance with a power-law kinetic model (32). Linear regressions of Arrhenius plots at several different concentrations ($r^2 > 0.994$) yielded a mean thermal activation energy of 21.9 ± 2.4 kcal/mole. This value is close to that determined from similar experiments with styrene (22.8 kcal/mole) (15) and those previously reported for analogous olefin-substitution reactions studied in solution (13-20 kcal/mole) (20). LODs were defined as $3s_n$/sensitivity, where s_n is the standard deviation of oscillator noise measured each minute for 10-15 minutes before and after exposure and the sensitivity is the slope of the response curve at low concentrations. LODs ranged from 102 µg/L at 25°C to 22 µg/L at 40°C.

A persistent drift in the post-exposure baseline was observed following exposure to EA at 40°C. To determine whether the complex was hydrolyzing or otherwise decomposing, a thin film of the complex was deposited on a KBr plate and exposed to air at 40% RH at 40°C for several hours. IR spectra taken before and after exposure of the sample were indistinguishable. If hydrolysis to acrylic acid or polymerization of the EA were occurring it was evidently at a very low rate. Our previous studies suggested that the olefin substitution reaction can cause slight changes in the packing density of the solid. It is possible that subtle post-exposure structural relaxations could be responsible for the observed drift. Despite the baseline drift, the response to EA did not change upon repeated exposure. Lowering the temperature to 30°C eliminated the post-exposure drift but raised the LOD to 67 µg/L.

Table II presents the results of simultaneous exposure to 800 µg/L of EA and each of several non-olefin organic solvent vapors at 30°C. As shown, there were no effects on the response to EA even at the high interferent concentrations tested. These results were not unexpected since the interfering vapors cannot react with the trapping agent. A high degree of selectivity for EA in the presence of other acrylates was also observed and is discussed below in the context of steric effects.

For continuous exposure to 1100 µg/L of EA, the sensor response remained constant (within 5%) for over two hr and then began to gradually decline, reaching about 70% of the initial response after four hr. This reflects the depletion of the reagent and, possibly, the added diffusional resistance associated with an increasingly thick product layer around a core of unreacted reagent (16,33). Regeneration of the reagent by exposure to pure ET was only partially successful after such prolonged exposure - the sensor response for the regenerated coating was considerably lower than that for the fresh coating. For repeated exposures of shorter duration (~1.5 hr at 200-4800 µg/L), however, regeneration yielded responses that were within 7% of those for the fresh coating.

Steric Effects of Attacking Olefins. The effect of olefin steric hindrance on the response of the trans-$PtCl_2$(ET)(pyr)-coated sensor was examined for three series of olefins in which the number and/or geometry of substituents adjacent to the olefin double bond were varied. Experiments were performed by exposing a freshly coated sensor to each of the olefins individually over a range of concentrations. Additional experiments were then performed for certain binary olefin mixtures. As above, the duration of exposure at a given olefin concentration ($\leq$ 20 minutes) was limited to avoid reagent depletion: relative standard deviations at a given concentration were invariably below 10%. Continued exposure at high concentrations, however, did lead to a reduction in response. The reproducibility of responses to a given olefin for different coating films was similar to that described above for EA.

Acrylate Series. The first series consisted of the isomers EA, methyl crotonate (MC) and methylmethacrylate (MMA), as well as methyl acrylate (MA). As shown in Figure 2a the responses were in the order EA > MA >> MC > MMA (exposure temperature = 30°C). The greater response for EA compared to MA is due in part to its slightly higher mass (i.e., for the same rate of reaction, substitution of ethylene by EA would produce a larger frequency shift). However, this factor alone does not account for the observed difference in sensitivity. Since the steric environment of the double bond is similar in each of these olefins, the difference in response (i.e., reactivity) probably has an electronic origin. A previous report on the MA-complex showed that the carbonyl group is not involved in the bonding to Pt (34), and our own IR spectra confirm this. Nevertheless, conjugation of the double bonds with the carbonyl groups will cause some electron delocalization of the olefin π cloud in both compounds. The increased reactivity found with EA is assumed to arise from the subtle difference in the field/inductive effects of the methyl and ethyl esters (35).

The responses for EA and MA were much higher than those for the remaining acrylates, MC and MMA. MC gives a low concentration-dependent response but the response to MMA could not be differentiated from the baseline noise. In MMA, the pendant methyl group and the ester group are on the same carbon atom of the double bond. In MC, the olefin substituents are on different carbon atoms. Thus, it appears that vicinal substitution presents less steric hindrance than geminal substitution in the formation of the Pt-olefin complexes. Differences in the rates of diffusion of the vapors into the surface of the solid reagent would also contribute to the observed order of responses, since the more highly branched MMA and MC would be expected to have smaller diffusion coefficients than the other acrylates. The potential role of diffusional effects is discussed in more detail in the next section.

Co-exposure to EA and MMA did not affect the response to EA, even up to a concentration ratio of 2:1 (MMA:EA). MC only affected the response to EA at relatively high MC concentrations: an increase of about 13% in the response to 2000 μg/L of EA was observed upon co-exposure to 5000 μg/L of MC (note: analogous results were obtained for the complex where 4-Mepyr was the amine ligand). Similarly, co-exposure to MA and MMA did not affect the response to MA. The response to MA increased by about 20%, however, upon introduction of an equivalent concentration of MC.

Co-exposure to EA and MA revealed a preferential response to EA. At equivalent concentrations, MA did not affect the response to EA. But at a concentration ratio 2:1 (MA:EA) the response increased by 30% due to MA. The combined response was somewhat less than the sum of the individual responses measured at the same concentrations. To further probe this issue, coatings of trans-$PtCl_2$(EA)(pyr) and trans-$PtCl_2$(MA)(pyr) were tested for reactivity toward MA and EA, respectively. No response was observed for either combination at concentrations as high as 4800 μg/L indicating that these olefins are competing for displacement of ET from its complex and are not displacing each other.

It should be mentioned that this is the first report of the complex trans-$PtCl_2$(EA)(pyr), although the corresponding MA complex is known (34). That olefins with electron-withdrawing ester substituents can so readily displace ET by nucleophilic attack on Pt is quite remarkable, particularly in light of our previous results showing that electron deficient olefins (e.g., vinyl chloride, acrylonitrile) do not react with trans-$PtCl_2$(ET)(pyr) (16).

Butene Series. Responses of the trans-$PtCl_2$(ET)(pyr)-coated sensor to the butenes and substituted butenes examined were in the order 1-butene (1-B) > cis-2-butene (cis2B) > trans-2-butene (trans2B) >> isobutylene (isoB) ~ 2,3-dimethyl-2-butene (DMB), as shown in Figure 2b for exposure at 40°C. No responses were observed for the latter two olefins at concentrations up to 2200 μg/L. Limits of detection for the former three olefins ranged from 15 μg/L for 1-B to 45 μg/L for trans2B and response times were < 30 s.

The order of responses follows the same trend as that observed for the acrylates, with increases in methyl substitution on the double bond leading to decreases in the rate of reaction. Comparison of the results for isoB and either cis2B or trans2B shows that, again, geminal substitution results in significantly lower reactivity than vicinal substitution.

The difference in responses between cis2B and trans2B is consistent with the general finding that cis isomers form more stable metal-olefin complexes than trans isomers (19), which can ascribed to two effects. First, cis olefins are generally more strained than trans olefins, as indicated by their higher heats of hydrogenation (36), and coordination with the metal relieves the strain because the bond order is lowered (i.e., the C=C bond length is increased and takes on slightly more sp^3 character). Second, the metal-olefin bonds are stronger in the case of cis isomers owing to the ability for rotation about the C=C axis to minimize repulsive nonbonded interactions between the methyl substituents and the other ligands (e.g., the Cl atoms in the Pt complexes considered here) (28). For trans isomers, additional rotation about the olefin-Pt bond axis is necessary to relieve these interactions with a resultant reduction in overlap between the filled d orbitals of the Pt and the π^* orbitals of the olefin. This reduces considerably the overall bond strength (19). For isoB, neither type of rotation would lead to significant reductions in these repulsive interactions with the Cl ligands in the complex, hence the lack of response for this isomer.

Addition of isoB at concentrations up to 2200 μg/L to atmospheres of 200-1000 μg/L of 1-B, cis2B, or trans2B did not affect the responses to the latter olefins. Co-exposure to cis2B and trans2B gave a response that was roughly equal to the sum of the individual responses at a given concentration. Addition of either cis2B or trans2B to an atmosphere of 1-B also caused an increase in response, but there was an apparent preference for the 1-B. From a practical standpoint, although monitoring 1-B, cis2B or trans2B in the presence of isoB (and probably DMB) would be possible, discrimination of the former three isomers in the presence of each other would not be possible with a single sensor.

Aromatic Olefin Series. The aromatic olefins examined gave the following order of responses with the trans-$PtCl_2$(ET)(pyr) coating: styrene (ST) > trans-β-methylstyrene (βMeST) > indene (IN) ~ α-methylstyrene (αMeST). Figure 2c shows the response curves for these vapors at 40°C. Here again, the geminally substituted αMeST gives a lower response than its vicinally substituted βMeST isomer. The low response for IN is contrary to expectations based on steric factors, since the cis configuration of IN is less sterically hindered than the trans configuration of βMeST. Based on the NMR and x-ray data cited previously (see Introduction Section), we speculate that the rigidity of the IN structure reduces the extent to which the substituents on the double bond can bend away from the Pt or the Cl ligands. The greater repulsion would destabilize both the transition state and the product.

Responses to αMeST were observed to decline by several percent even over the short exposure periods of 15-20 minutes at a given concentration. These results suggest that diffusional resistance in the solid reagent may be more important for this molecule. This is further supported by the observation that the difference in responses between ST and αMeST showed a marked temperature dependence. At 25°C the ratio of responses to 200 μg/L of each vapor (for separate exposures) was only about 3:1 (ST:αMeST), but at 40°C this ratio increased to about 10:1. To the extent that the reaction is limited by diffusion of the vapors into the solid reagent, there would be a smaller temperature dependence for the overall response since diffusion generally involves a lower activation energy than chemical reaction. That diffusional effects are more important in the interaction with αMeST is consistent with its lower reactivity and more highly branched structure. This factor enhances the selectivity for styrene. Co-exposures to equivalent air concentrations of styrene and αMeST gave responses that were only 5-10% higher than the responses to styrene alone.

trans-$PtCl_2$(ET)(R_n-pyr). To further investigate the effects of steric hindrance, several of the olefins were exposed to the sensor coated with complexes having 2-Mepyr, 2,6-Me_2pyr, or 2,4,6-Me_3pyr ligands trans to the ET. To account for the slight electron donating effect of the methyl substituents, the complex with a 4-Mepyr ligand was also included in this series. Substitution in the 4-position allows resonance interaction through the aromatic ring (as with the 2-methyl isomer) but does not exert any steric influence.

Figure 3 shows the sensor response to EA at 30°C with coatings of the different complexes. The pattern of responses is consistent with the progressive increase in steric hindrance. Thus, the 2-Mepyr complex exhibits considerably less sensitivity than the pyr and 4-Mepyr complexes. Remarkably, adding a second methyl group at the 6 position of the pyridine (i.e., 2,6-Me_2pyr) completely precludes reaction. Similarly, no response was obtained with 2,4,6-Me_3pyr as the trans ligand. The dramatic difference is attributed to the exclusion of EA attack from both above and below the square plane for the 2,6-Me_2pyr and 2,4,6-Me_3pyr complexes. In addition, to the extent that the 2-Mepyr ring is rotated toward the square plane (see Introduction Section), the steric hindrance from the 2-methyl group would be reduced. For 2,6-Me_2pyr and 2,4,6-Me_3pyr the rings are perpendicular to the square plane and the pendant methyl groups would exert more steric influence.

Similar orders of response were observed for MA and MC. None of the complexes gave responses to MMA. Contrary to expectations, use of the 2-

Mepyr complex did not enhance the selectivity for the unhindered EA and MA relative to the more hindered MC. That is, the ratios of responses of the former acrylates to the latter were reduced for the 2-Mepyr complex. We also noted somewhat poorer reproducibility with this reagent.

Results for the butene series were similar to those for the acrylate series. For the relatively unhindered 1-B and cis2B the responses decreased in the order pyr > 4-Mepyr > 2-Mepyr >> 2,6-Me_2pyr, with no response being observed for the latter complex. Interestingly, at low concentrations of trans2B, the 2-Mepyr complex gave responses that were slightly higher than those for the pyr and 4-Mepyr complexes. The slope of the 2-Mepyr response curve was quite shallow, however, and responses at higher trans2B concentrations were lower than those for the pyr and 4-methylpyridine complexes. Use of the 2-Mepyr complex also reduced the differences in responses between 1-B, cis2B and trans2B. In fact, responses to the cis and trans isomers could not be differentiated with this reagent.

The aromatic olefins showed response trends similar to those just described. ST and βMeST gave the following overall order of responses: pyr > 4-Mepyr > 2-Mepyr >> 2,6-Me_2pyr ~ 2,4,6-Me_3pyr. However, at low vapor concentrations of both ST and βMeST responses with the 2-Mepyr complex were similar to those for the pyr and 4-Mepyr complexes. At higher vapor concentrations higher responses were obtained with the latter complexes. For αMeST and IN the responses with the 2-Mepyr complex, while still quite low, were consistently higher than those for the pyr and 4-Mepyr complexes over the entire concentration range examined. No responses were observed for any of the aromatic olefins with the 2,6-Me_2pyr or the 2,4,6-Me_3pyr complexes.

The results for the 2-Mepyr complex reveal a consistent trend across all three series of olefins: the more hindered olefins give responses that are higher than expected. For most of the olefins this effect is seen only at low concentrations, while for IN and αMeST this effect extends over a fairly large concentration range. These results support the notion that diffusional resistance may be an important covariable affecting the responses to certain vapors.

Microscopic inspection of the 2-Mepyr-complex coating films showed that it formed a mixture of solid crystals and oil droplets, consistent with the difficulty encountered in recrystallizing the reagent following synthesis. The other reagents formed solids in all cases. For olefins whose interactions with the reagent are limited by the rate of reaction, the physical state of the reagent would be less critical. But for olefins whose interactions were at least partly diffusion-limited the physical state would be important since diffusion rates would be higher into an oil than into a solid. For the least hindered (and most diffusive) olefins the responses to the 2-Mepyr complex were consistently lower than for the pyr and 4-Mepyr complexes indicating that the chemical reaction is rate-limiting. For the more hindered olefins, which would have lower diffusion coefficients due to higher branching, diffusion into the reagent complexes becomes increasingly important in the rate of the overall interaction. This leads to the initially higher responses for the partially-liquid 2-Mepyr complex relative to the solid pyr and 4-Mepyr complexes even though the reaction rates are higher for the latter complexes. As the olefin concentration increases at the surface of the reagents, the relative influence of diffusional effects declines and the reaction rates predominate for all but the least diffusive vapors (i.e., IN and αMeST).

Particle Size. With the exception of the 2-Mepyr complex, responses obtained for successive coatings of the same reagent were quite reproducible at the low concentrations examined. The amount of coating deposited affected the capacity (i.e., service life) but had little effect on responses for short-term exposures. The somewhat poorer reproducibility with the 2-Mepyr complex is consistent with its variable composition as discussed above.

Given the heterogeneous nature of the trapping reactions, we considered the possibility that particle size might be contributing to some of the differences observed between the coating reagents (notwithstanding the results for the 2-Mepyr complex). Investigations of this issue were hampered by differences in the morphologies of the reagents in the coating films: although the methyl-substituted-pyr complexes generally precipitated at discrete nucleation sites on the surface of the sensor, the pyr complex formed a mixture of discrete crystals and intricate crystalline networks. As a result, the distribution of particle sizes could not be accurately determined by microscopic analyses for coating films of the pyridine complex.

For the remaining complexes the size distributions of the solid particles (or solid/oil mixtures, in the case of the 2-Mepyr complex) were all approximately lognormal, i.e., skewed toward smaller diameters. The 2- and 4-Mepyr complexes gave similar geometric mean diameters (d_g) of about 4 μm, whereas the remaining complexes gave d_g values ranging from 1.1-1.4 μm. For similar deposited masses, smaller particle sizes would lead to a larger total surface area for reaction. If surface area were a predominant factor, the latter complexes would have given higher responses. For the 4-Mepyr complex an additional experiment was performed to compare a solvent-cast coating to a coating applied with an air brush. The former gave a d_g of 4.3 μm and the latter gave d_g of 1.2 μm, yet the responses to EA were nearly identical. From these data and estimates of the amount of reagent consumed it is apparent that at the relatively low olefin concentrations examined there is an excess of reagent surface area available for adsorption/reaction.

Polymer Sorption vs. Chemical Reaction. The advantage of using these reagent coatings to improve selectivity are clear from the data just presented. It should also be stressed that this approach can have advantages in terms of sensitivity compared to the more common approach of using a polymer-coated sensor where equilibrium sorption determines the sensor response. This is particularly true for more volatile compounds and can be illustrated by comparison of the responses to 1-B using the trans-$PtCl_2$(ET)(pyr) coating and a coating of PIB alone.

Several factors must be considered in order to make a fair comparison between these coatings. One factor is the affinity of the polymer for 1-B. Given the similarity in the structures of 1-B and PIB, the solubility interactions should be quite strong and the polymer/air partition coefficient for 1-B in PIB should be relatively high. That is, polymers containing polar functional groups would probably interact less with 1-B than would PIB. Another factor is the exposure temperature. Since sorption decreases exponentially with increasing temperature, operating a polymer-coated sensor at elevated temperatures would decrease the sensitivity and increase the LOD. A temperature of 25°C is suitable for most practical air monitoring applications (note: cooling to sub-ambient temperatures is possible but can lead to problems such as condensation of atmospheric humidity). Finally, for a given partition coefficient the sensor response will increase linearly with the amount of coating deposited (37). In practice, however, there is a limit to the amount of coating that can be applied without completely dampening the oscillator. Typical coatings reported in the literature (6,37) are on the order of a few percent of the acoustic wavelength in nominal thickness, which corresponds to frequency shifts of 200-300 kHz for polymers having densities near 1 g/cm^3.

With these factors in mind, a coating of 250 kHz of PIB was used and the response to 1-B was determined at a temperature of 25°C. Exposure to several concentrations in the range of 250-4600 μg/L resulted in a linear sorption isotherm having a slope (i.e., sensitivity) of 0.008 Hz/μg/L and a corresponding limit of detection of about 374 μg/L (note: at 40°C the LOD was well above 1000 μg/L). The sensitivity using the pyr complex decreases slightly with increasing concentration (i.e., the response isotherm is concave downward, see Figure 2b) but at low concentrations it is nearly constant: a value of 0.21 Hz/μg/L/min was obtained for 1-B at 40°C. The LOD was about 15 μg/L, as mentioned above. Thus, the reagent-coating provides about a 25-fold sensitivity and detection limit advantage for 1-B.

The relatively poor sensitivity of the PIB coated sensor to 1-B arises from its low molecular weight and high volatility. For higher-molecular-weight (and less-volatile) compounds, responses using polymer-coated sensors generally increase. The sensitivity of the PIB-coated sensor to ST, for example, was about 1 Hz/μg/L at 25°C. The corresponding value for the pyr complex was 2.2 Hz/μg/L/min. Although the reagent coating still provides higher sensitivity, the difference is much smaller than for 1-B.

Sensor Operating Frequency. From eq 2 it can be seen that the mass sensitivity of the SAW device increases with the square of the operating frequency. According to this equation, using a SAW oscillator that operates at twice the frequency should lead to a four-fold increase in mass sensitivity. However, the sensitivity to vapors will not necessarily increase proportionally. For polymer coatings the response to the vapor is dependent on the amount of polymer on the device. As just mentioned, there is a limit to the amount of coating that can be tolerated without loss of oscillation. This limit will decrease as the frequency of the SAW device increases (and the acoustic wavelength decreases). Grate and Klusty recently examined this issue and found for SAW devices operating at frequencies ranging from 158-400 MHz that if a polymer coating causing the same frequency shift is used on these devices the sensitivity to organic vapors is the same regardless of the operating frequency (37). Their report also confirmed that vapors penetrate into the bulk of the polymer film rather than adsorbing at the surface.

In contrast to the case of polymer coatings, for the reagent coatings used here the responses involve interfacial phenomena. As a result, increases in sensor frequency should lead to increases in sensitivity. From preliminary tests of a 52-MHz sensor having acoustic dimensions similar to the 30-MHz device (i.e., similar active areas as measured in terms of the acoustic wavelength) the sensitivity to EA using the pyr-complex was found to be about 3.4 times that of the 30-MHz device over the concentration range of 200-1200 μg/L. According to eq 2, an increase of

$52^2/30^2 = 3$ would be expected theoretically, which is in reasonable agreement with the data.

CONCLUSIONS

The use of a SAW sensor coated with reagents of the general formula trans-$PtCl_2$(ethylene)(substituted-pyridine) for real-time measurement of various olefin gases and vapors has been described. It has been shown that subtle differences in the steric properties of olefins lead to a high degree of selectivity for the relatively unhindered olefins. Positional isomers can be completely discriminated and appreciable differences in response are seen even for geometric (cis/trans) isomers. The consistent trend observed across three series of olefins indicates that the steric effects are quite general. Thus, similar molecular selectivity would be expected within other groups of olefins.

As shown here for ethyl acrylate, and previously for styrene (16) and vinyl acetate (14), use of Pt-olefin π-complexes as SAW sensor coatings provides responses to olefins that are unaffected by the presence of a range of non-olefin organic vapors. These findings thus also appear to be general. While not unexpected, the practical significance of these results should not be underemphasized since this degree of selectivity is not generally possible with commercial organic vapor detectors.

The ability to regenerate the reagent complex by exposure to ethylene gas was demonstrated following exposure to ethyl acrylate. For prolonged exposure, the response of the regenerated coating was lower than that of the original coating owing, presumably, to structural changes within the reagent solid. For short-term exposures, however, the regenerated-coating responses were the same as the original coatings. In practice a means for periodic regeneration would be necessary to maintain the initial calibration for extended monitoring periods.

This work highlights several advantages of reagent SAW sensor coatings over sorptive-polymer coatings for measurement of this class of organic compounds. In addition to the unusually high selectivity obtained, the reagent coatings allow detection of low concentrations of gases which have small polymer/air partition coefficients and therefore low responses with polymer-coated sensors. Increasing the temperature of the reagent-coated sensor leads to increased sensitivity (and selectivity, in some cases) whereas increasing the temperature of polymer-coated sensors decreases sensitivity. This adds a measure flexibility to the reagent-coating approach. Finally, increasing the operating frequency of the sensor increases the sensitivity of responses using the reagent coating, in contrast to polymer-coated sensors.

The influence of electronic factors was apparent in some of the results obtained in this study. A more systemmatic investigation of substituent-related electronic factors is currently being performed and preliminary results indicate very large differences in response depending on the electron-withdrawing/donating strengths of substituents on both of the olefins and the pyridine-ligand in the complex. Once the influence of these factors are more completely characterized it may be possible to modulate both steric and electronic effects by judicious choice of ligands in the complex to provide even greater control over the response selectivity of the sensor.

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Figure Captions

Figure 1. Response to ethyl acrylate from 25-40°C using trans-$PtCl_2(ET)(pyr)$ coating.

Figure 2. Responses using trans-$PtCl_2(ET)(pyr)$ coating for series of a) acrylates at 30°C; b) butenes at 40°C; and c) aromatic olefins at 40°C.

Figure 3. Responses to EA at 30°C using trans-$PtCl_2(ET)(R_n\text{-pyr})$ coatings ($R = -H, -CH_3$; $n = 1\text{-}3$).

Table I. Analytical Data for trans-PtCl$_2$(Olefin)(Amine) Complexes

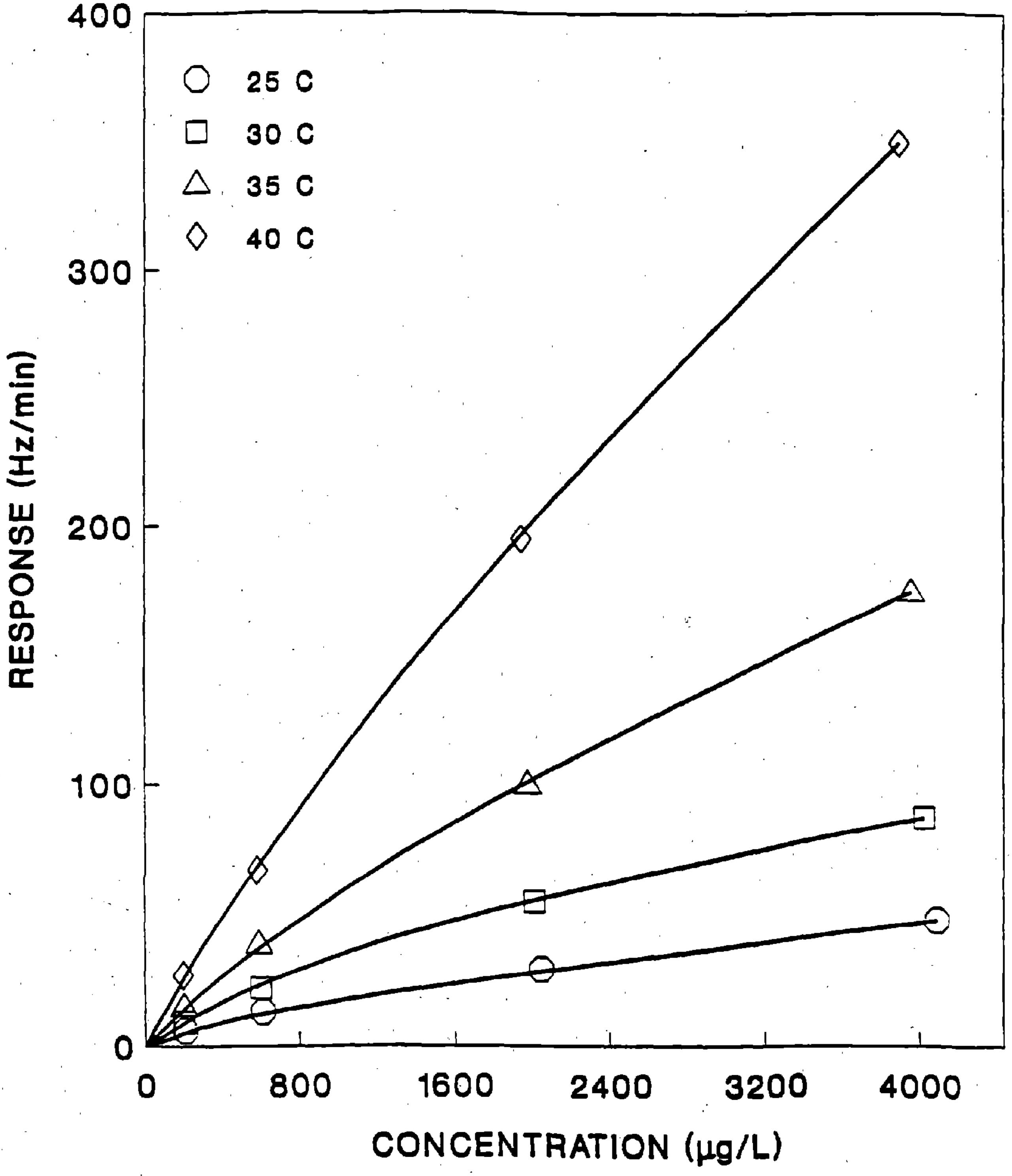
			elemental analysis					
			found, %			theoretical, %		
olefin	amine	m.p.[a]	C	H	N	C	H	N
ET	pyr	112	22.50	2.50	3.70	22.53	2.43	3.75
ET	2-Mepyr	97	24.82	2.86	3.62	24.88	2.84	3.75
ET	4-Mepyr	118	24.82	2.86	3.62	24.90	2.90	3.60
ET	2,6-Me$_2$pyr	155	26.94	3.27	3.49	26.89	3.30	3.46
ET	2,4,6-Me$_3$pyr	151	28.93	3.64	3.37	29.10	3.70	3.30
EA	pyr	-[b]	26.98	2.94	3.15	27.08	3.13	2.94
MA	pyr	-[b]	25.07	2.57	3.25	24.32	2.69	3.30

[a] All compounds melted with decomposition.
[b] Not determined.

Table II. Response to EA in the Presence of Other Solvent Vapors Using trans-$PtCl_2$(ET)(pyr) Coating

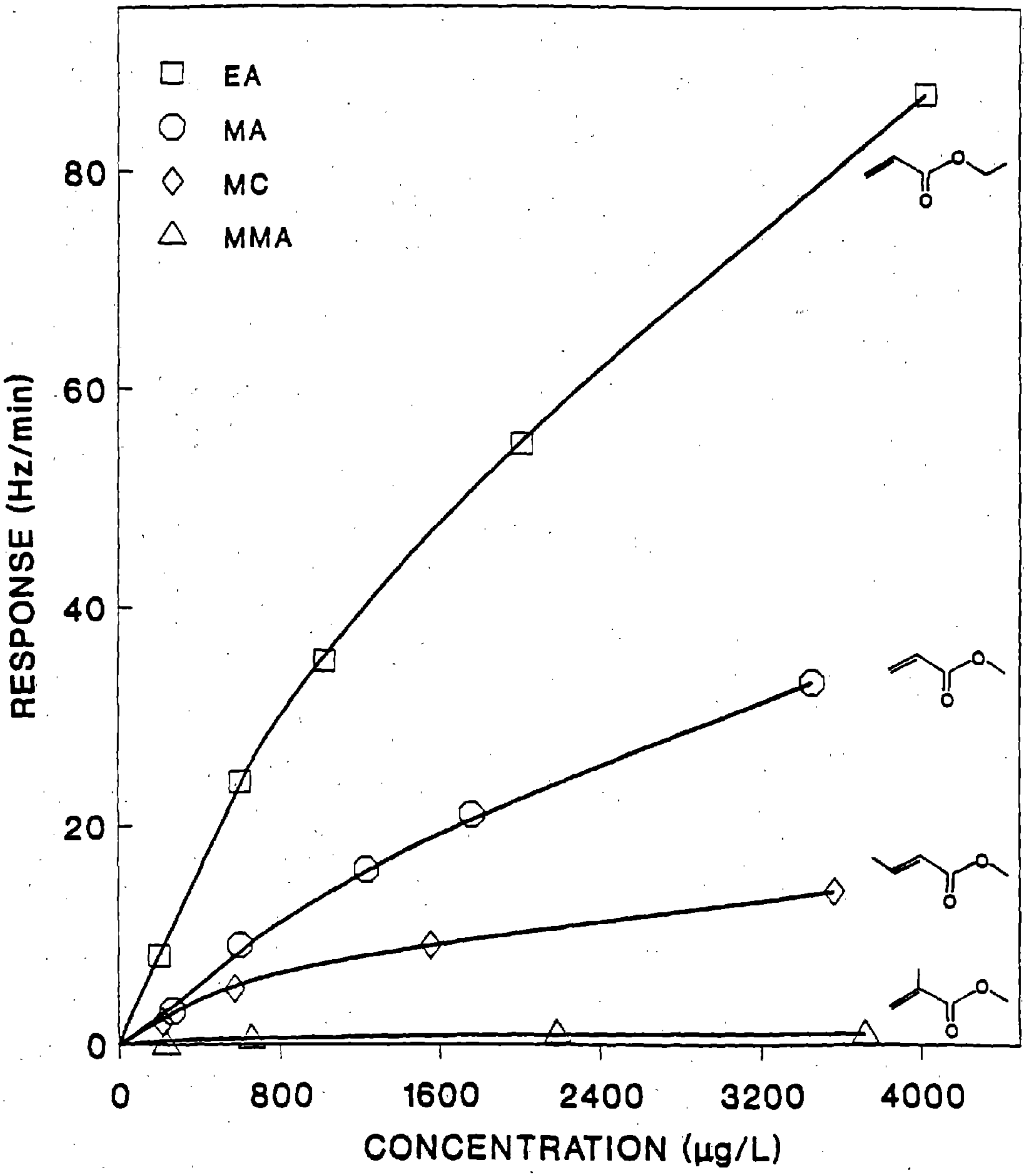
interferent	conc, μg/L	mean response (std dev) to 800 μg/L of EA[a], Hz/min
--	---	29 (1)
Hexane	3600	27 (2)
Toluene	3800	31 (2)
Tetrahydrofuran	3200	29 (1)
Ethyl Acetate	4100	30 (3)
Chloroform	6900	29 (2)
Acetone	4000	28 (3)
Methanol	1400	27 (3)

[a] 15-20 minute exposure.



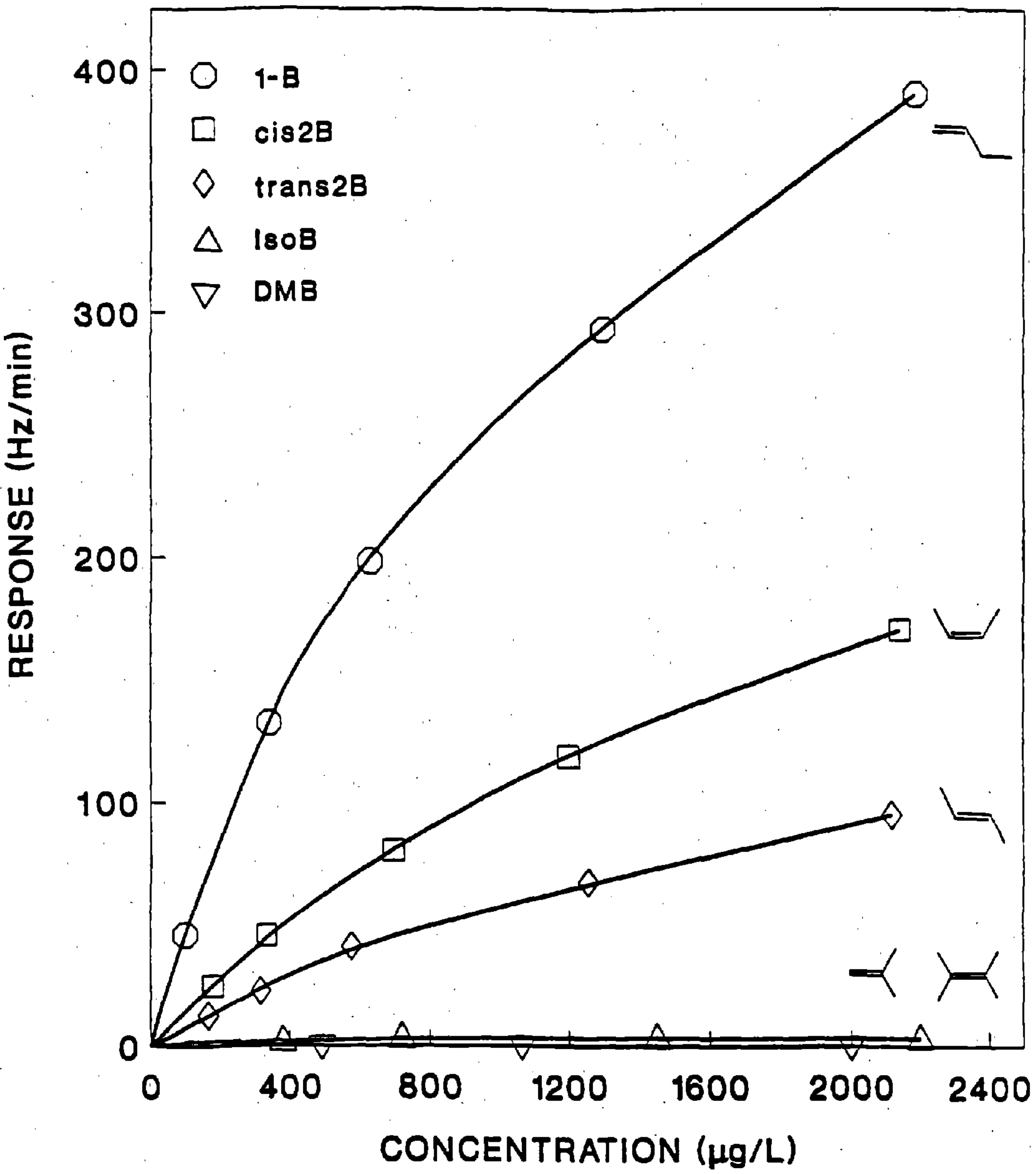
400
300
200
100
0
RESPONSE (Hz/min)
0
800
1600
2400
3200
4000
CONCENTRATION (µg/L)
○ 25 C
□ 30 C
△ 35 C
◇ 40 C

Figure 1



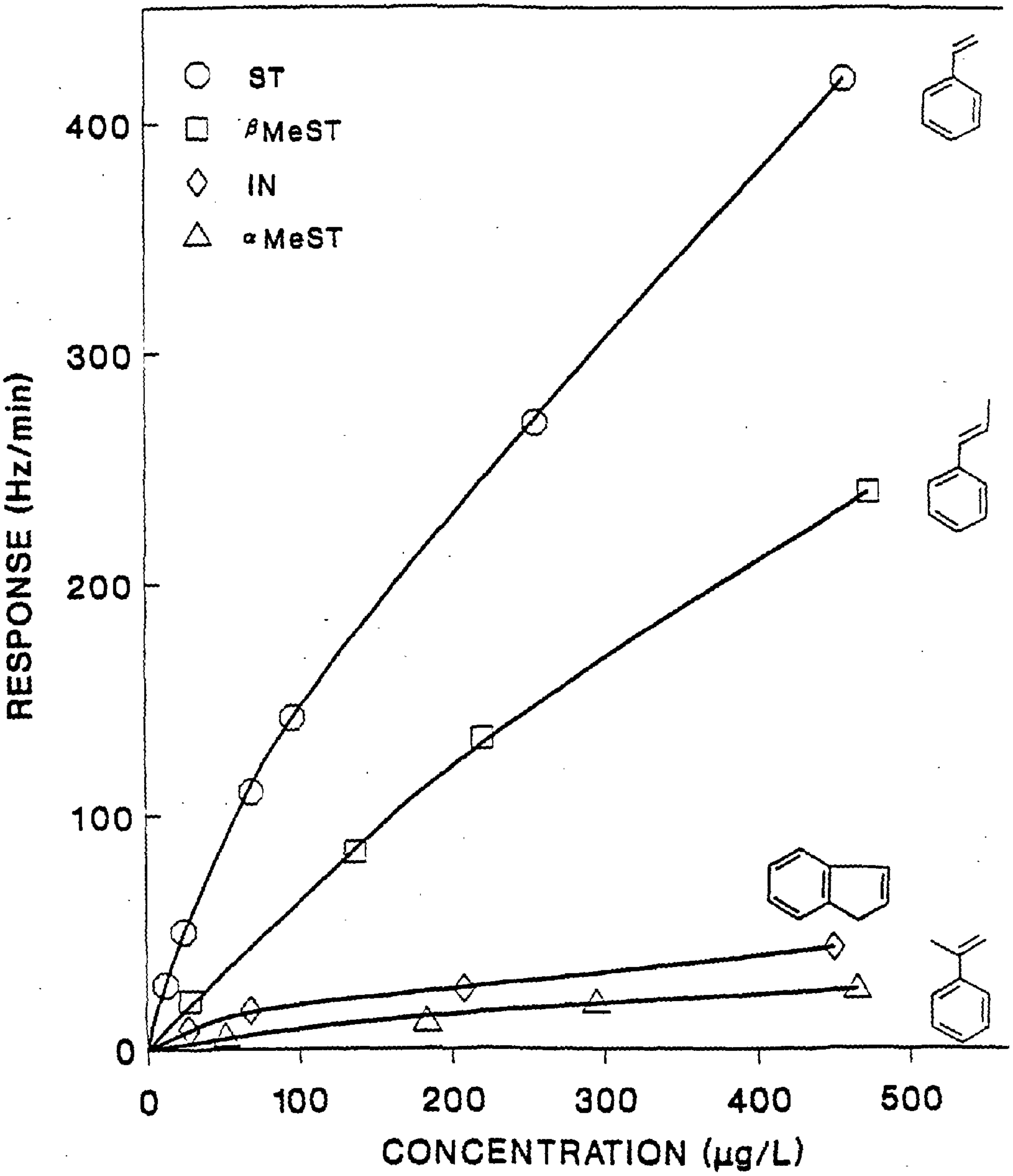
□ EA
○ MA
◇ MC
△ MMA
RESPONSE (Hz/min)
0
20
40
60
80
0
800
1600
2400
3200
4000
CONCENTRATION (µg/L)

Figure 2a



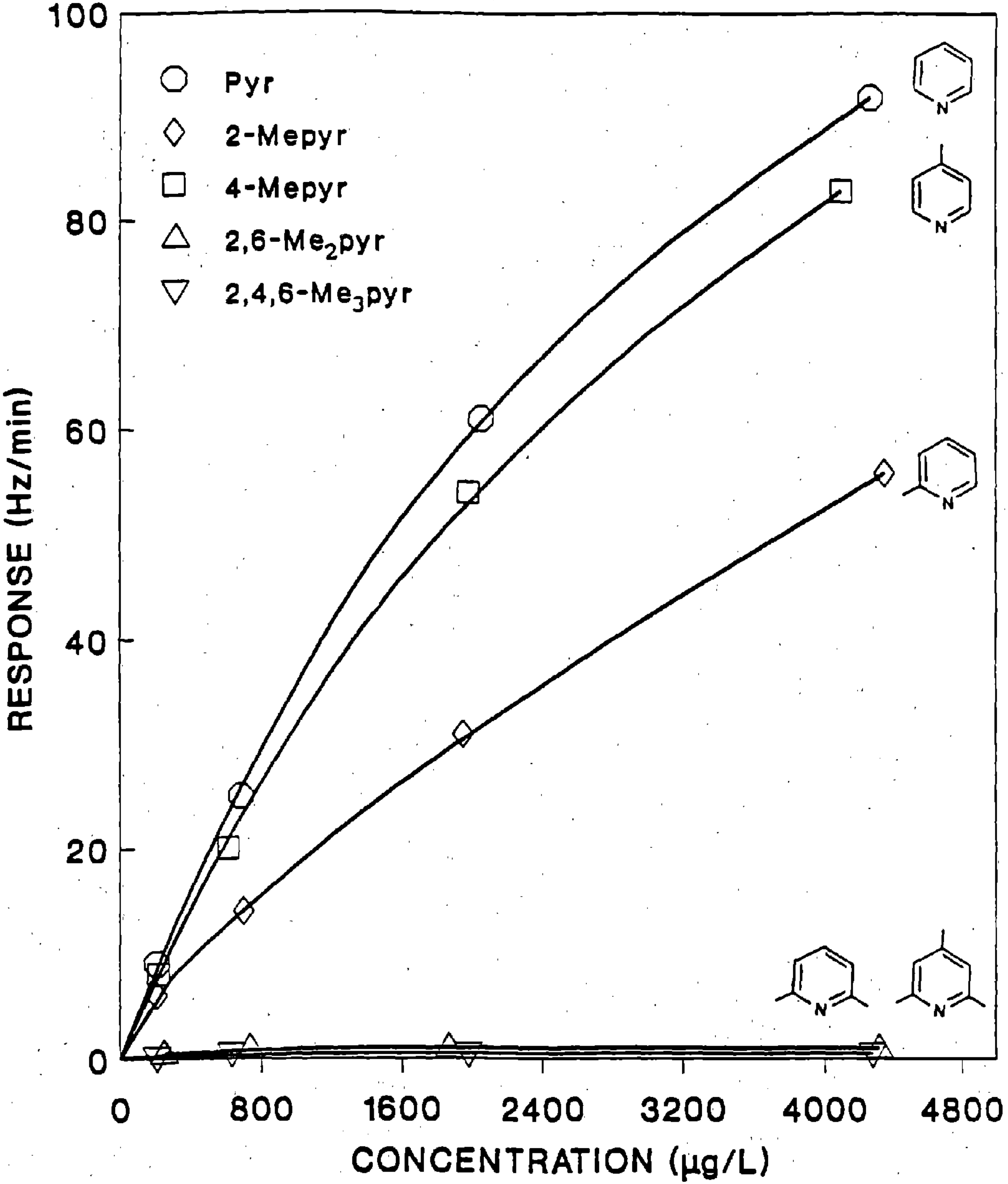
400
300
200
100
0
RESPONSE (Hz/min)
0
400
800
1200
1600
2000
2400
CONCENTRATION (µg/L)
○ 1-B
□ cis2B
◇ trans2B
△ IsoB
▽ DMB

Figure 2b



○ ST
□ βMeST
◇ IN
△ αMeST
RESPONSE (Hz/min)
0
100
200
300
400
CONCENTRATION (µg/L)
0
100
200
300
400
500

Figure 2c



100
80
60
40
20
0
RESPONSE (Hz/min)
0
800
1600
2400
3200
4000
4800
CONCENTRATION (µg/L)
○ Pyr
◇ 2-Mepyr
□ 4-Mepyr
△ 2,6-Me₂pyr
▽ 2,4,6-Me₃pyr
N
N
N
N
N

Figure 3

CHAPTER 4

The Influence of Substituent and Ligand Electronic Factors on the Measurement of Gas Phase Olefins Using a Surface-Acoustic-Wave Oscillator Coated with trans-$PtCl_2$(olefin)(amine) Complexes

Abstract

Certain olefin gases and vapors can be measured selectively at low concentrations using surface acoustic wave (SAW) sensors coated with reagents of the general formula trans-$PtCl_2$(olefin)(amine). The sensor response depends on the steady-state rate of mass change associated with substitution of the initially complexed olefin by the free olefin analyte. This paper examines the effects of changes in the electronic nature of substituents on the free olefin and the olefin and amine ligands in the complex on the sensitivity and selectivity obtained with this class of SAW sensor coatings. For a given reagent, higher reaction rates are generally observed with electron-donating substituents on the double bond of the free olefin. For a given free olefin, varying the 4-substituent of the pyridine ligand in $PtCl_2$(ethylene)(4-X-pyridine) gives a maximum response at an intermediate degree of amine basicity. Replacing pyridine by aniline, pyridine N-oxide or the 4-substituted derivatives of these ligands results in reduced responses for the olefins tested. Changing the initially complexed olefin leads to large changes in response, the pattern of which varies with the nature of the free olefin. Results demonstrate the potential for controlling the response of SAW sensors through subtle structural modifications of these coating reagents.

INTRODUCTION

Olefins comprise an industrially important class of organic compounds used primarily in the production of polymers. Adverse health effects ranging from mild respiratory tract irritation to cancer and birth defects have been associated with exposure to different olefins in humans and test animals [1]. As a result, regulatory exposure limits have been established to minimize the risk of injury and disease in production workers and the general population [2-3]. Ensuring compliance with such standards requires accurate monitoring of these compounds in the atmosphere, often in the presence of other air contaminants. Unfortunately, portable instruments suitable for routine monitoring of personnel exposures to olefin gases and vapors are limited by a lack of sensitivity and/or selectivity [4].

Surface acoustic wave (SAW) sensors and sensor arrays have the potential to address these shortcomings by providing selective measurement of a broad range of organic gases and vapors [5,6]. In the SAW sensor, a high-frequency mechanical wave is generated along the surface of a piezoelectric substrate which has been coated with a chemically sensitive film. The most common configuration used for sensing applications employs the SAW device as the frequency controlling element in an oscillator circuit. A feedback amplifier is incorporated between the input and output transducers of the device, resulting in oscillation at a fixed frequency, f_o. Small changes in the physical properties (e.g., mass) of the coating film result in a change of the velocity of the propagating wave, and hence of the oscillator frequency [6].

The following approximate expression can be used to relate the change of the SAW oscillator frequency to changes of deposited mass at the surface of the sensor [7]:

$$\Delta f = K_s f_o^2 \Delta m/a \tag{1}$$

where Δf is the change of frequency (Hz), K_s is a negative substrate-dependent constant (m^2/kg-sec), f_o is the oscillation frequency of the uncoated device (Hz), and $\Delta m/a$ is the change of coating mass per unit area (kg/m^2). This relationship allows one to estimate both the amount of coating deposited on the sensor and the changes in the coating mass resulting from subsequent interactions with gas-phase analytes.

In attempting to design sensor coatings that will respond to olefins, advantage can be taken of the ability for the C=C functional group to coordinate, often reversibly, to various transition metal compounds [8,9]. In this way selectivity for olefins in the presence of non-coordinating non-olefin organic vapors would be expected. The more difficult problem is to obtain selectivity for a given olefin in the presence of other olefins.

In a series of recent papers we have shown that a number of olefins can be measured selectivity in the presence of industrially relevant non-olefin organic solvent vapors and structurally similar olefin gases and vapors using SAW oscillators coated with the reagent complex trans-$PtCl_2$(ethylene)(pyridine) and related complexes [10-13]. The reaction is shown below in general form:

$$\text{trans-PtCl}_2(\text{OL}_1)(\text{AM}) + \text{OL}_2 \rightleftharpoons \text{trans-PtCl}_2(\text{OL}_2)(\text{AM}) + \text{OL}_1 \tag{2}$$

where OL_1 and OL_2 represent the initially complexed and free olefins, respectively, and AM is the trans-amine ligand. A useful property of this class of reagents is the capability for regeneration following exposure to the target olefin by brief exposure to the initially complexed olefin which drives the olefin-exchange reaction in the reverse direction.

Results from our earlier studies suggested that the selectivity observed for the target olefins in the presence of other olefins could be attributed to electronic and steric factors [11,12]. The importance of steric factors was investigated in a subsequent study where it was shown that bulky substituents on the gas-phase olefin or on the pyridine ligand (i.e., in the 2 or 6 positions on the pyridine ring) dramatically reduced the rate of the substitution reaction and permitted the measurement of less sterically hindered olefins in the presence of their more sterically hindered isomers and structural analogues [13]. The influence of the electronic structural features of the free olefins and the ligands in the Pt-olefin complex has not yet been systematically explored.

The coating reagents investigated here are examples of square-planar metal-olefin π-complexes which have amine and olefin ligands in a trans configuration about a central Pt(II) atom [8,14]. The olefin is bound to Pt via a σ bond, involving donation of electron density from the olefin π cloud to the Pt, as well as by a π bond, involving back-bonding from the metal to the antibonding orbitals of the olefin. The relative importance of each of these bonding interactions depends on the overlaps and energies of the respective orbitals on the metal and the olefin, though it is generally accepted that the σ bond is predominant [15].

Both the rates and mechanisms of olefin-substitution reactions in these complexes are affected by the amine ligand [16,17]. The σ-bond strength of the amine is determined primarily by its basicity. In addition, where the amine has low-lying vacant p orbitals, as in pyridine and pyridine N-oxide, back-bonding from the metal is possible. This interaction does not occur with aniline due to the unavailability of accepting orbitals. The competitive donation (via σ bonding) and acceptance (via π bonding) of electron density between between the amine and olefin can thus affect the overall reactivity of the complex. When a free olefin reacts it replaces the initially bound olefin without disrupting the spatial configuration of the other ligands. Where the amine is pyridine or pyridine N-oxide the reaction proceeds exclusively through a pentacoordinate associative transition state [16]. Where the amine is aniline both solvent-assisted and associative pathways are observed [17].

In the study described here, we examine the effect of substituents on the free olefin and the amine and olefin ligands in the complex on the relative reactivities of the complexes and the extent to which such effects might be used to adjust the sensitivity and selectivity of a SAW sensor having these complexes as coatings. Coating reagents examined included $PtCl_2$(ethylene)(AM) (AM = pyridine, aniline, pyridine N-oxide and their 4-substituted derivatives) and $PtCl_2(OL_1)$(pyridine) (OL_1 = 1-butene, 1-hexene and 1-octene).

The sensor response at steady-state is a function of the change of mass accompanying the olefin substitution and it will therefore depend on the gas-phase olefin concentration. Furthermore, since there is a 1:1 stoichiometry between reactants and products, the rate of frequency change of the sensor, df/dt, will depend on the steady-state reaction rate according to the following equation [11]:

$$df/dt = -C(MW_2 - MW_1)dN/dt \qquad (3)$$

where MW_1 is the molecular weight of the free or initially complexed olefin, N is the number of moles of each olefin involved in the reaction and C is a constant. Thus, for equivalent reaction rates, the greater the MW difference between the attacking and leaving olefin, the greater will be the sensor response.

EXPERIMENTAL SECTION

Most of the starting materials, solvents and gases were obtained from Aldrich, Milwaukee, WI and were used without further purification, with the exception of pyridine N-oxide which was purified by fractional distillation. Ethylene, vinyl chloride and vinyl bromide gases were obtained from Matheson Gas Products, Secaucus, NJ. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Particle size distributions were determined according to established methods [18] using an Olympus Model BHA optical microscope.

trans-$PtCl_2$(ethylene)(amine) reagents were synthesized by the addition of 1 molar equivalent of the amine to a stirred aqueous solution of $KPtCl_3$(ethylene) (Zeise's salt) at room temperature [14]. The crude solid precipitates which formed were recrystallized after air drying from a minimum of dichloromethane by adding an excess of hexane or petroleum ether. All of the products were isolated as yellow crystalline solids.

Conversion of the ethylene complexes to the corresponding olefin-substituted reagents was performed by combining the ethylene complex with an excess of the olefin in dichloromethane and refluxing for 1-2 hr. These products were isolated and recrystallized as described above. In the case of $PtCl_2$(1-hexene)(pyridine) and $PtCl_2$(1-octene)(pyridine), the products were difficult to recrystallize and were generally isolated as viscous oils. The former complex could be obtained as a low-melting solid upon repeated recrystallizations. The complexes investigated are listed in Table 1 along with the corresponding melting points and elemental analyses.

Combining the Pt-olefin complexes with the amorphous rubbery polymer, poly(isobutylene) (PIB, Scientific Polymer Products, Ontario, NY) improved the coating uniformity and response reproducibility relative to the use of the solid complexes alone. Films were deposited on the entire active area of the sensor either by solvent casting or spray-coating from solutions containing approximately 6 mg/mL of each component in 2:1 toluene:hexane. The mass deposited was estimated from the net frequency shift via Eq. 1 after evaporation of the casting solvent. For all experiments described here, the frequency shift due to the coating film was in the range of 200-400 kHz, corresponding to deposited masses of 260-520 μg.

It has been shown that the reference device can be coated with an equivalent amount of PIB so that measuring the difference frequency would cancel the transient responses due to physical sorption and desorption of vapors by the polymer component of the reagent-coated sensor [10,12]. Therefore measurements collected for this study were made using a single oscillator and the response was determined after allowing a short time for equilibration: this typically required from 30-90 s owing to mixing in the chamber and to establishment of steady-state reaction conditions within the sensor coating.

A 30-MHz ST-quartz SAW oscillator with Au-on-Cr metallization and an active of 1.5 cm^2 was used for all tests [11]. Series inductors were used as tuning elements and two LM733 amplifiers provided the gain necessary to maintain oscillations in the SAW device. The sensor frequency was monitored with a digital frequency counter (Hewlett-Packard 5384A) and monitored with a personal computer via an IEEE-488 interface. Signals were collected every 10 s at a resolution of 1 Hz and the net 1-min frequency shifts were averaged over the exposure interval at a given olefin concentration to yield the rate of frequency change in Hz/min.

The sensor was placed in a stainless-steel chamber equipped with gas inlet and outlet ports. Electrical connections were made using coaxial cables and connectors in the bottom of the chamber. The chamber was wrapped with heating tape to control the temperature and a thermocouple was used to monitor the temperature at the surface of the sensor. Known concentrations of the olefin vapors were generated by bubbling N_2 gas through a flask containing the liquid solvent and then into a dilution-air stream. For gaseous olefins a syringe pump was used to introduce the pure material into the air stream. The contaminant stream was divided between the sensor exposure chamber and a calibrated infrared gas analyzer (MIRAN 1A, Foxboro, Bridgewood, CT) used for continuous monitoring of solvent vapor concentrations. Dilution-air flow and temperature were controlled with a Miller-Nelson Research HCS 301 control unit. The relative humidity was maintained at 5 ± 3% for all experiments.

RESULTS AND DISCUSSION

Free-Olefin Substituent Effects

Our current and previous [10-13] tests of the SAW sensor coated with $PtCl_2$(ethylene)(pyridine) have revealed two general features of the sensor responses to olefin gases and vapors: they vary non-linearly with the olefin concentration and they exhibit a positive Arrhenius temperature dependence. Responses to styrene, ethyl acrylate and vinyl acetate as a function of concentration and temperature are shown in Figs. 1 a and b, respectively. These data are representative of the those obtained with other reactive olefins. Each point on the curves represents the average rate of frequency change obtained at a given concentration over a period of 10-30 min. Responses are generally quite constant at a given concentration for such exposures. However, prolonged exposure leads to an eventual decline in response as the reagent becomes depleted. This occurs more rapidly at higher concentrations. With careful deposition technique, intercoating response variations can be maintained below 10%.

The downward concavity in the response curves is a consequence of the heterogeneous reaction between the gaseous olefin and the solid reagent which is the rate-limiting step in the overall analyte-coating interaction. Log-log plots of the sensor response versus concentration yield straight lines in accordance with a pseudo-first-order (with respect to the olefin) power-law kinetic model for the reactions [19]. For certain olefins, diffusional resistance within the reagent may also play a role in the overall interaction [13]. As mentioned above, regeneration of the $PtCl_2$(ethylene)(pyridine) is possible following exposure to the olefins shown in Fig. 1 and for several other olefins. However, this issue is not examined in detail in this paper.

The Arrhenius plots in Fig. 1b show that the slopes of the lines for styrene and ethyl acrylate are quite similar, indicating a similar activation energy for reaction. The slope for vinyl acetate is significantly smaller. This suggests a possible scheme for enhancing selectivity between certain olefins by the use of a simple sensor array where all the sensors are coated with the same reagent: the ratios of responses of two or three sensors operating at different temperatures should allow discrimination on the basis of activation energies.

In Table 2, responses from the sensor coated with $PtCl_2$(ethylene)(pyridine) are summarized for exposure to each of several different olefins. The limit of detection (LOD) is defined as the concentration corresponding to 3s/sensitivity, where $s = 1$ Hz is the typical standard deviation of the 1-min frequency shifts measured before and after exposure. The sensitivity, in Hz/(μg/L)-min, is based on the slope of the response curve at the lowest measured concentration for each olefin. The rate of reaction shown in Table 2 was determined from Eq. 3 assuming a nominal free-olefin concentration of 1 μg/L. This latter measure accounts for the differences in mass change accompanying ethylene substitution.

An obvious trend in reactivity is observed between the groups listed in Table 2: olefins with strongly electron-withdrawing groups attached to the double bond (e.g., vinyl chloride, vinyl bromide, vinylidene chloride, trichloroethylene, acrylonitrile) do not react while those with moderately electron-withdrawing substituents (e.g., ethyl acrylate, methyl acrylate and vinyl acetate) or electron-donating substituents (e.g., aromatic olefins and alkenes) generally react quite readily. This inherent selectivity allows measurement of the reactive olefins in the presence of the non-reactive olefins even where the latter are present in large excess [11-13].

Within a given class of olefins, both steric and electronic factors appear to govern the relative reactivities. In the absence of such effects, sensitivity would be proportional to the difference in MW between each olefin and ethylene. This is clearly not the case. Within the aromatic olefin group, the lower response for β-methylstyrene compared to styrene and the isomeric 4-methylstyrene can be attributed to the steric hindrance associated with the methyl group on the pendant double bond. The lower response for indene, however, is less easily explained. One would expect indene to give a higher response since the substituents on the coordinating double-bond are in a cis configuration. The anomolously low indene reactivity is apparently due to its fused ring structure. Upon coordination, the double bonded carbons in most olefins acquire some sp^3 character with a commensurate change occuring in the bond lengths and bond angles in the molecule. In addition, the substituents on coordinated olefins are bent back away from the Pt atom to minimize repulsive non-bonded interactions with the Pt or the other ligands [9]. The inflexibility of the indene ring would inhibit such structural adjustments and destabilize the transition state for the reaction.

The increase in sensitivity observed in the series styrene, 4-methylstyrene and 4-chlorostyrene is much greater than expected from the MW differences alone, and can be attributed to the electronic influence of the 4-substituent (see Fig. 2). Interestingly, the addition of either an electron withdrawing or donating group enhances the reaction rate relative to styrene. These results are consistent with those reported for the relative thermodynamic stabilities of 4-substituted-styrene complexes of Pt(II) in solution [20]. But they are in contrast to that expected from C^{13}-NMR data reported on a series of styrene complexes where it was found that the coupling constants between Pt and the olefinic carbons increased with the electron-donating strength of the 4-substituent of styrene [21,22]. It is known, however, that the coupling constant is insensitive to the strength of the π back-bonding in these complexes [21].

With respect to the alkenes and cycloalkenes in Table 2, the trend in reactivity among the butene isomers (i.e., 1-butene > cis-2-butene > trans-2-butene > isobutylene) can be ascribed to steric factors. The high reactivity of 1-hexene and low reactivity of cyclohexene were both unexpected. As shown below, use of the 1-hexene complex as the reagent coating leads to higher sensitivity for several olefins than its lower-homologue complexes. Cyclohexene adopts a so-called half-chair configuration where the methylene groups attached to the double bond are cis [23]. One would therefore expect the double bond to be relatively accessible for coordination, analogous to the case of cis-2-butene. Unlike indene, structural adjustments accompanying cooordination to Pt would be relatively facile for the six-membered cyclohexene ring. While the low cyclohexene response is not completely understood, in light of the relatively high reactivity of 1-hexene and the results for indene relative to the other aromatic olefins, a high degree of selectivity against cyclic olefins is apparent.

The relative reactivities of vinyl acetate and ethyl acrylate are similar (see Fig. 1). This follows from the similarity in the electron-withdrawing strength of the ethoxycarbonyl and acetoxy groups as reflected in their Hammet σ_p and σ_m constants [23]. Surprisingly, methyl acrylate is less reactive than both vinyl acetate (an isomer of methyl acrylate) and ethyl acrylate at all concentrations. Since steric factors can be ruled out, apparently there is a subtle difference in the electronic influence of the methyl and ethyl esters in the acrylates on the olefin double bond. It has been shown previously that the response to vinyl acetate is not affected by equivalent concentrations of methyl acrylate upon coexposure [11]. Methyl acrylate, however, will interfere with the response due to ethyl acrylate [13]. Notably, methylmethacrylate does not react to any measurable extent due to the steric hindrance of the additional methyl group on the olefin carbon.

In the absence of significant steric effects, the reactivities of the various olefins can be considered in terms of their orbital energies. As stated above, the Pt-olefin bond strength depends on the contribution of both σ-type and π-type bonding. Meester et al. studied the bonding properties of a similar series of trans-$PtCl_2$(ethylene)(amine) complexes and determined approximate energy levels for the highest-occupied and lowest-unoccupied Pt orbitals in these complexes based on spectroscopic data [24]. Fig. 3 presents a comparison of these energies with those of the corresponding orbitals of several of the free olefins tested here (data for the remaining olefins were not available). The trend in relative energies of the occupied orbitals follows that of the observed reactivities, with the exception of vinyl chloride. That is, those olefins with closer occupied-orbital energy matches to Pt are generally more reactive. The relative energies of the unoccupied orbitals do not follow this trend. These data support the view that the σ-bonding interaction is relatively more important than the π back-bonding interaction in determining the reaction kinetics of these complexes.

$PtCl_2$(ethylene)(4-X-pyridine)

Fig. 4 shows the sensor response to ethyl acrylate using the coating reagents $PtCl_2$(ethylene)(4-X-pyridine), where X = $N(CH_3)_2$, CH_3, H, Cl, and CN. Once again, each point represents the mean rate of frequency change measured over 10-30 min at a given concentration. Similar series of exposures were performed with vinyl acetate and styrene. Representative responses are shown in Fig. 5 for individual exposures to 2000 μg/L of ethyl acrylate and vinyl acetate at 30°C and 400 μg/L of styrene at 40°C. The responses have been normalized separately for each of the olefins to the coating providing the highest response.

For styrene and vinyl acetate the pyridine complex gives the highest response, whereas for ethyl acrylate the highest response is observed with the 4-chloropyridine complex. The 4-hydroxypyridine and 4,4'-nitrobenzylpyridine complexes were also tested and found to give no reaction. Although these olefins could be identified based on the collective response patterns, the trends in the sensor responses shown in Fig. 5 are fairly similar, with a peak in reactivity occuring at an intermediate degree of amine basicity. The patterns for a given olefin will vary somewhat with concentration because the responses do not increase at exactly the same rate with concentration. However, the same order of responses is maintained over a wide range of concentration. None of the 4-substituted pyridine complexes responded to vinyl chloride, vinyl bromide, vinylidene chloride or acrylonitrile.

The response patterns observed are different than what would have been expected based on solution-phase kinetic studies of similar complexes. The rates of olefin substitution in the complexes $PtCl_2$(2-methyl-2-butene)(4-X-pyridine) [16] and $PtCl_2$(styrene)(4-X-aniline) [17] increased markedly with the electron-withdrawing strength of X. In the former case, the order of reactivity was X = CN > Cl > H > CH_3 > NH_2 and a linear relationship was observed between the log of the rate constant and the Hammett σ_p constant of X. It has also been shown that the C^{13}-NMR chemical shifts of the olefinic carbons and the Pt-(C=C) coupling constants also decrease in the same order, although the correlations are rather weak [22].

The reaction orders we observe are similar to the thermodynamic stabilities of olefin complexes in chloroform solution reported by Shupack and Orchin where substitution of styrene by 1-dodecene in a series of trans-$PtCl_2$(styrene)(4-X-Pyridine N-oxide) showed a minimum value of the equilibrium constant for X=H followed closely by the complex where X=Cl [25]. Raman and IR data indicate that the strength of the Pt-ethylene bond in a series of $PtCl_2$(ethylene)(4-X-pyridine) complexes is not strongly affected by changes in the electron-withdrawing/donating strength of X [26]. For the same series of complexes, however, the Pt-N bond strength passes through a minimum at X=H [27].

The influence of X observed here can be rationalized broadly in terms of the relative strengths of the σ and π bonding of the substituted pyridines. For pyridines with strongly electron donating groups, the Pt-N σ bond is stronger and the Pt-ethylene π bond is also stronger, leading to a stabilization of the ethylene complex toward substitution by the attacking olefins. For complexes having electron-withdrawing pyridine 4-substituents, apparently the Pt-N π bond is strenthened and the Pt-ethylene σ bond is also strengthened, again, leading to stabilization of the ethylene complex. Only at intermediate degrees of electron withdrawal/donation by the pyridine substituents is displacement of the ethylene favorable for these olefins.

Particle Size

One potential mitigating factor affecting the observed sensor responses is the particle size distributions of the solid reagents when deposited on the sensor. The active surface area of the solid Pt-olefin complex could affect the reactivity with the gas-phase olefin. In order to investigate this factor, the size distributions of the reagents in the coating films were characterized. While the morphologies of the deposited solids varied from reagent to reagent, approximate values of the mean diameters and surface areas could be obtained using a projected area method and assuming spherical particles. Table 3 provides summary statistics of the particle size distributions measured for several coating films of each of the reagents tested. The values for the pyridine complex are viewed with skepticism because the morphology of this reagent was particularly variable. The data shown in Table 3 were obtained using films deposited directly on the sensor that were subsequently exposed to one of the olefins.

While there is some variation in the mean particle diameters and calculated surface areas, the differences could not account for the observed differences in reactivity. The densities of the complexes may also be important, since the free olefin must diffuse into the reagent during reaction. This factor was not investigated, but is not likely to differ greatly between these complexes.

$PtCl_2$(ethylene)(4-X-aniline, 4-X-pyridine N-oxide)

Complexes having other trans-amine ligands were then deposited on the sensor and tested for their responses to ethyl acrylate at 30°C. In all cases, ethylene was the initially complexed olefin. It had been determined previously that the complex having NH_3 as the amine ligand showed no reactivity toward styrene, so this complex was not tested further with ethyl acrylate. Where the amine was 4-X-pyridine N-oxide, responses were in the order X = H > CH_3 > Cl and in all cases were significantly lower than those for the corresponding pyridine complexes. As mentioned above, the maximum response for X=H is consistent with the trend in the thermodynamic stability of 4-X-pyridine N-oxide complexes of styrene [25]. For the 4-X-aniline series, responses were in the order CH_3 > H > Cl and were greater than those for the corresponding pyridine N-oxides but less than those for the pyridine series. Although thermodynamic data on the aniline complexes were not available, the kinetic study cited above [17] indicated a trend opposite to that observed here, i.e., substitution rates generally increased with the electron-withdrawing strength of X. It was found for the aniline complexes, and to a lesser extent for the pyridine N-oxide complexes, that the sensor responses decreased rapidly at a given ethyl acrylate concentration within a few minutes of exposure.

$PtCl_2$(olefin)(pyridine)

Attempts to prepare complexes where OL_1 = vinyl chloride and trichloroethylene were unsuccessful. However, complexes of 1-butene, 1-hexene and 1-octene, with pyridine as the trans-amine ligand, could be prepared easily and allowed a systematic examination of the effect of progressively longer alkyl side chains on the olefin substitutional lability. Results of exposure to three different free olefins are summarized in Fig. 6 and Table 4. For exposure to ethylene, there is a steady increase in response with increasing alkyl chain length and all frequency shifts are positive because of the loss of mass from the coatings. As shown in Table 4 the response ratios are 3:2:1 for the 1-octene, 1-hexene, and 1-butene complexes, respectively, in agreement with the ratios expected based on the mass differences alone. Thus, there does not appear to be any difference due to electronic factors. In contrast, with ethyl acrylate the response pattern is quite different. The ethylene and 1-butene complexes show about the same responses, which indicates that the latter reagent is reacting at a higher rate since the net mass change is smaller. The 1-octene complex gives a large response, indicating an even higher reaction rate because of the similarity in MW between ethyl acrylate and 1-octene. In contrast to ethylene and 1-butene complexes, the response using the 1-octene complex is positive because there is a net mass loss from the surface upon reaction with ethyl acrylate. Surprisingly, ethyl acrylate did not react to any measurable extent with the 1-hexene complex. The reason for this is not clear. When acrylonitrile is exposed to each of these coatings, no responses are observed for the ethylene or 1-butene complexes, but large responses in the ratio of about 2:3 are obtained using the 1-hexene and 1-octene complexes, respectively (positive responses are obtained for these coatings, again, because of the net loss of mass from the sensor surface). Vinyl chloride gives small concentration dependent responses with the 1-hexene and 1-octene complexes, but vinylidene chloride could not be detected with any of the sensor coatings investigated.

Additional tests involving exposure to the butene isomers were performed using the 1-hexene complex coating. The LODs at 25°C are 1.58, 1.74, 5.31, and 49.2 μg/L for 1-butene, cis-2-butene, trans-2-butene and isobutylene, respectively. Comparison of these results with those in Table 2 shows that the 1-hexene complex is much more sensitive to these compounds than the ethylene complex.

CONCLUSIONS

The results presented here demonstrate the ability to adjust the selectivity and sensitivity of SAW sensors toward various olefin gases and vapors through subtle changes in the electronic structural features of the reagent coatings. The inherent selectivity for relatively electron-rich olefins arises from the apparent predominance of σ-bonding interactions between the olefin and Pt, though the trends observed in the data suggest that back-bonding is also important. The exceptional behavior of several olefin-complex combinations, however, indicate that the dynamics of these reactions cannot be fully rationalized in terms of simple variations in σ and π bonding strength alone. Still, advantage can be taken of the observed selectivities. The remarkably high response to 1-hexene relative to 1-butene and cyclohexene using $PtCl_2$(ethylene)(pyridine) and the ability to measure electron-deficient olefins by extending the alkyl side chain of the initially complexed olefin are particularly noteworthy.

The patterns of response as a function of the amine ligands in these complexes differ from those expected from previous solution-phase kinetic studies and NMR data on these and similar complexes. In contrast, fairly consistent correlations are found with thermodynamic stability data for similar systems which suggests the possibility of pseudo-equilibria being established at or just beneath the surface of the reagents even under dynamic exposure conditions.

In some practical situations, use of a single SAW sensor coated with one of the reagents studied here could provide sufficient selectivity in the presence of non-olefins or certain other (non-reactive) olefins. The use of a simple sensor array comprising as few as two sensors coated with the same reagent complex, but operated a different temperatures, could provide selectivity based on differences in activation energy between different reacting olefins. Finally, an array of sensors having different reagent coatings could provide discrimination between a wider range of olefins on the basis of differences in steady-state response.

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Figure Captions

Figure 1. Response of the $PtCl_2$(ethylene)(pyridine)-coated SAW sensor to (□) styrene, (△) ethyl acrylate and (◇) vinyl acetate as a function of (a) concentration at 40°C; and (b) temperature at a fixed air concentration for each olefin. Each point represents the average response for a 10-30 min exposure.

Figure 2. Response of the $PtCl_2$(ethylene)(pyridine)-coated SAW sensor to (◇) 4-chlorostyrene, (△) 4-methylstyrene and (□) styrene at 40°C. Each point represents the average response for a 5-10 min exposure.

Figure 3. Energy-level comparison of highest-occupied (—) and lowest unoccupied (---) orbitals for several free olefins and Pt in $PtCl_2$(ethylene)(amine); ST = styrene, 1B = 1-butene, C2B = cis-2-butene, T2B = trans-2-butene, 1H = 1-hexene, VC = vinyl chloride, MA = methyl acrylate, AN = acrylonitrile.

Figure 4. Response to ethyl acrylate of the SAW sensor coated with $PtCl_2$(ethylene)(4-X-pyridine), where X = (◇) $N(CH_3)_2$, (○) CH_3, (△) H, (□) Cl, (▽) CN. Each point represents the average response from a 10-30 exposure.

Figure 5. Normalized responses to a given concentration of styrene, ethyl acrylate and vinyl acetate as a function of the Hammett σ_p constant of X for the $PtCl_2$(ethylene)(4-X-pyridine)-coated sensor.

Figure 6. Normalized responses to ethylene (ET), ethyl acrylate (EA) and acrylonitrile (AN) as a function of OL_1 for the $PtCl_2(OL_1)$(pyridine)-coated sensor where OL_1 = ethylene, 1-butene, 1-hexene or 1-octene (note: with the exception of EA reacting with the ethylene and 1-butene complexes, all responses are positive since there is a net loss of mass from the sensor coatings).

TABLE 1. Analytical data for the trans-$PtCl_2(OL_1)(AM)$ reagents

Complex	m.p. (°C)	Calc %C	Calc %H	Calc %N	Found %C	Found %H	Found %N
	OL_1 = ethylene AM = 4-X-pyridine						
X							
$-N(CH_3)_2$	124	25.97	3.39	6.73	26.01	3.44	6.68
-OH	122	21.61	2.33	3.60	21.64	2.35	3.57
$-CH_3$	117	24.82	2.86	3.62	24.90	2.90	3.60
-H	112	22.53	2.43	3.75	22.50	2.50	3.70
-Cl	120	20.63	1.98	3.44	20.80	2.00	3.40
-CN	145	24.13	2.03	7.04	24.01	1.92	6.98
	OL_1 = ethylene AM = 4-X-aniline						
X							
-H	110	22.53	2.43	3.75	22.50	2.50	3.70
$-CH_3$	114	26.94	3.27	3.49	26.82	3.26	3.67
-Cl	116	22.79	2.39	3.32	22.64	2.39	3.23
	OL_1 = ethylene AM = 4-X-pyridine N-oxide						
X							
-H	146	21.61	2.33	-	21.67	2.33	-
$-CH_3$	147	23.83	2.75	-	24.29	2.82	-
-Cl	165	19.85	1.90	-	19.77	1.82	-
	AM = pyridine						
OL_1							
Ethylene	112	22.53	2.43	3.75	22.50	2.50	3.70
1-Butene	106	26.94	3.27	-	26.77	3.33	-
1-Hexene	40	30.77	3.99	-	30.58	3.99	-
1-Octene	-	34.14	4.63	-	34.15	4.77	-

TABLE 2. Limit of detection, sensitivity and molar reaction rate for various free olefins with trans-$PtCl_2$(ethylene)(pyridine) coatings at 40°C

Free olefin	ΔMW[a] (g/mol)	LOD (μg/L)	Sensitivity (Hz/(μg/L)-min)	Reaction rate[b] (pmol/min)
4-Chlorostyrene	110.6	0.38	-8.0	95
4-Methylstyrene	90.1	0.65	-4.7	68
Styrene	76.1	1.4	-2.1	37
β-Methylstyrene	90.1	4.1	-0.7	11
1-Butene	28.1	15	-0.21	9.7
cis-2-Butene	28.1	20	-0.15	7.2
trans-2-Butene	28.1	45	-0.07	3.1
Isobutylene	28.1	ND[c]	----	---
1-Hexene	56.1	1.0	-2.9	68
Cyclohexene	54.1	106	-0.03	0.7
Vinyl acetate	58.0	16	-0.19	4.3
Ethyl acrylate	72.1	22	-0.14	2.5
Methyl acrylate	58.0	62	-0.05	1.1
Vinyl chloride	34.5	ND	ND	ND
Vinyl bromide	78.9	ND	ND	ND
Vinylidene chloride	68.9	ND	ND	ND
Trichloroethylene	103.3	ND	ND	ND
Acrylonitrile	25.0	ND	ND	ND

[a] Difference in molecular weight between free olefin and ethylene
[b] Calculated at a nominal free-olefin concentration of 1 μg/L
[c] Not detected

TABLE 3. Geometric mean particle size and reagent surface area of deposited trans-$PtCl_2$(ethylene)(4-X-pyridine) coating reagents

X	Geometric mean diameter (μm)	Coating freqency shift (kHz)	Reagent surface area[a] (mm^2)
$-NH_3$	1.10	272	11.2
-OH	1.23	254	16.1
$-CH_3$	1.23	274	13.1
-H	1.17	247	16.5
-Cl	1.00	269	14.9
-CN	1.37	234	22.6

[a] Determined assuming approximately spherical particles within the coating.

TABLE 4. Comparison of sensor responses to each of several free olefins using different trans-$PtCl_2$(olefin)(pyridine) coatings

Initially complexed olefin	ΔMW (g/mol)	ΔMW ratio	Sensitivity[a] (Hz/(μg/L)-min)	Sensitivity ratio
Free olefin = ethylene				
Ethylene	0.0	-	-	-
1-Butene	28.0	1.0	0.64	1.0
1-Hexene	56.1	2.0	1.4	2.2
1-Octene	84.1	3.0	2.1	3.1
Free olefin = ethyl acrylate				
Ethylene	72.1	6.0	-0.031	0.5
1-Butene	44.0	3.6	-0.040	0.6
1-Hexene	16.0	1.3	ND	-
1-Octene	-12.1	1.0	0.064	1.0
Free olefin = acrylonitrile				
Ethylene	25.0	8.3	ND	ND
1-Butene	3.0	1.0	ND	ND
1-Hexene	-31.1	10.3	0.21	1.0
1-Octene	-59.1	19.7	0.34	1.6

[a] Evaluated at 50 μg/L for ethylene (30°C), 1000 μg/L for ethyl acrylate (30°C) and 300 μg/L for acrylonitrile (25°C).

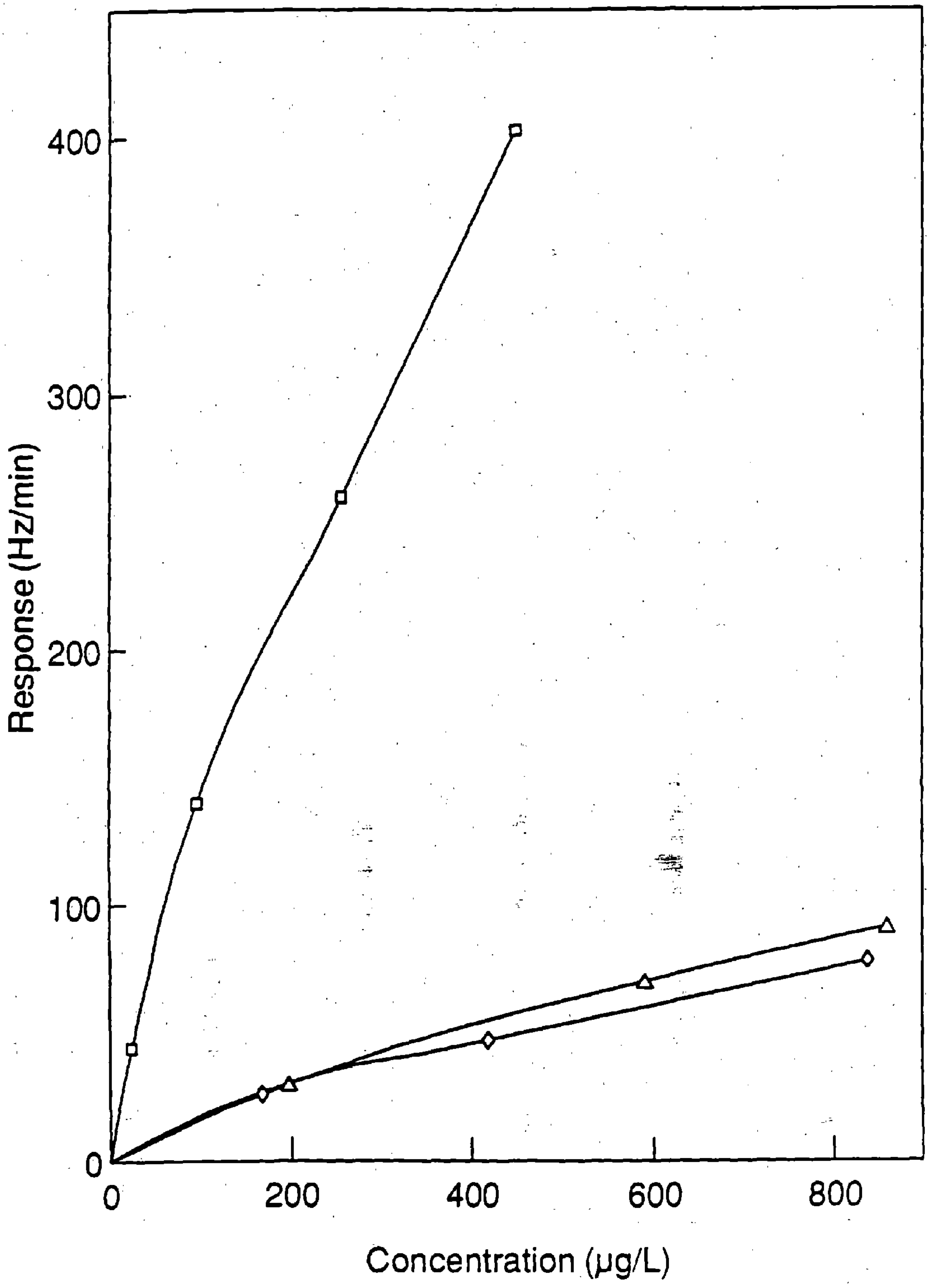

Response (Hz/min)
400
300
200
100
0
0
200
400
600
800
Concentration (µg/L)

Figure 1a

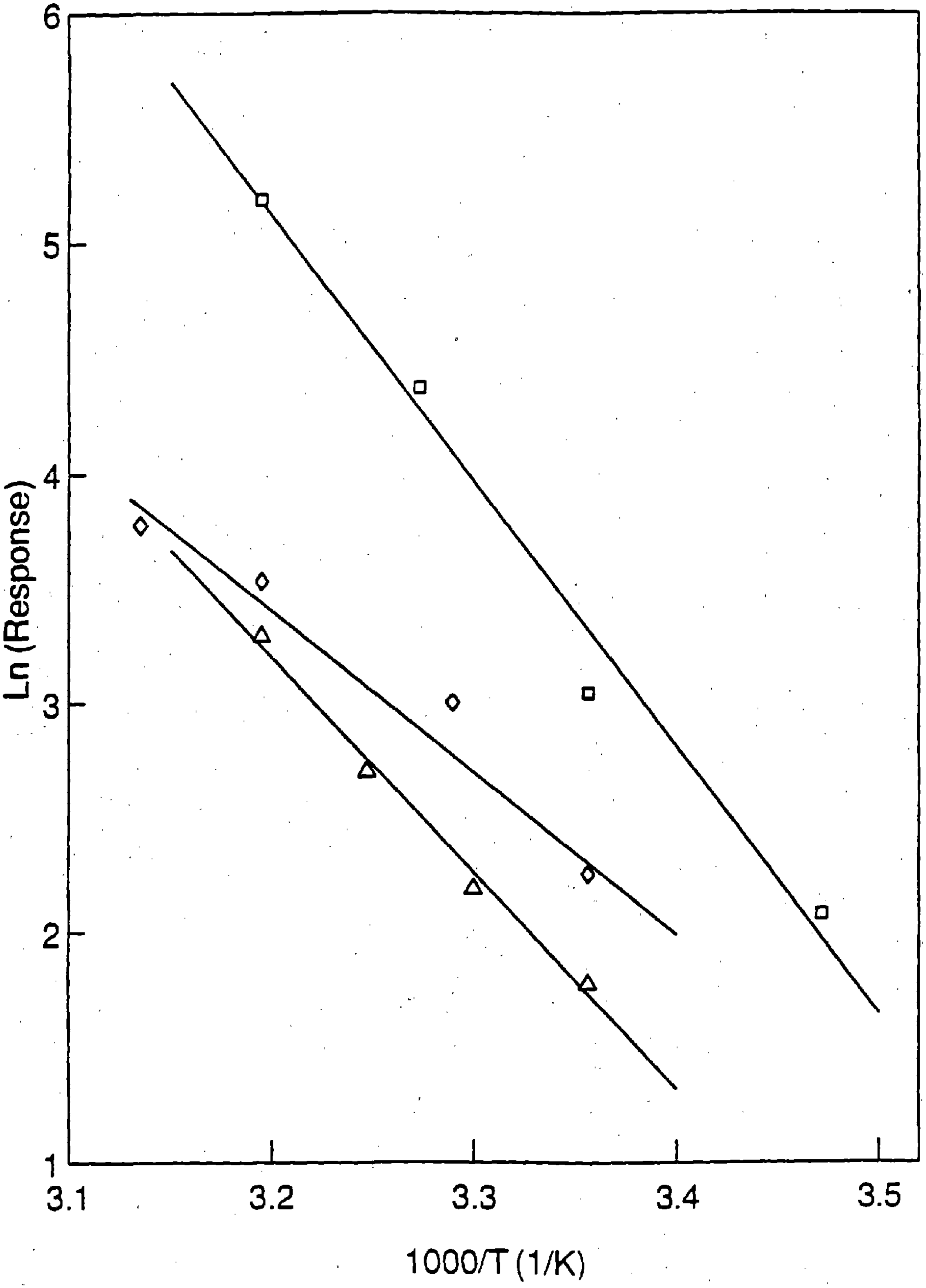


Figure 1b

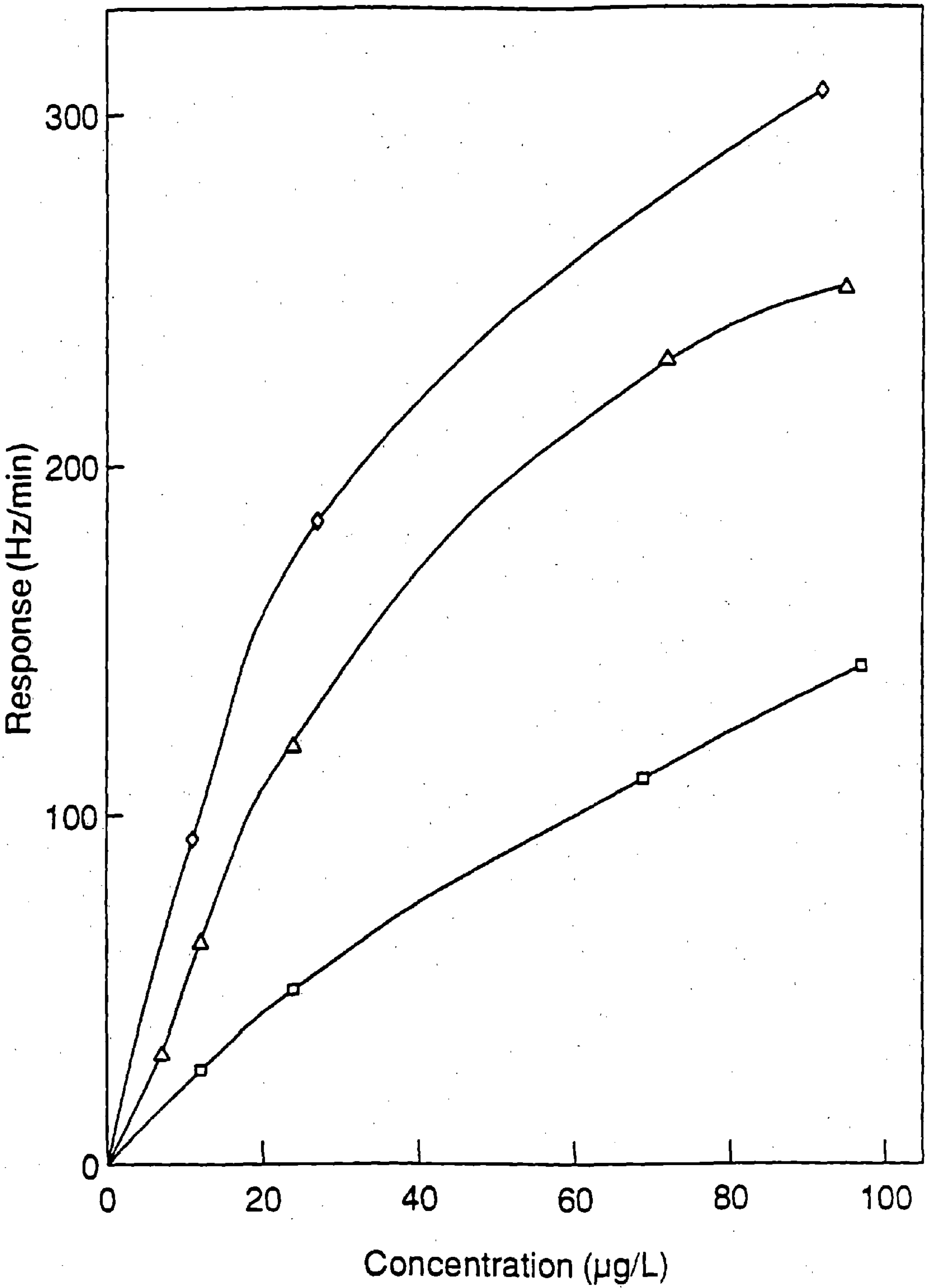

Response (Hz/min)
300
200
100
0
0
20
40
60
80
100
Concentration (µg/L)

Figure 2

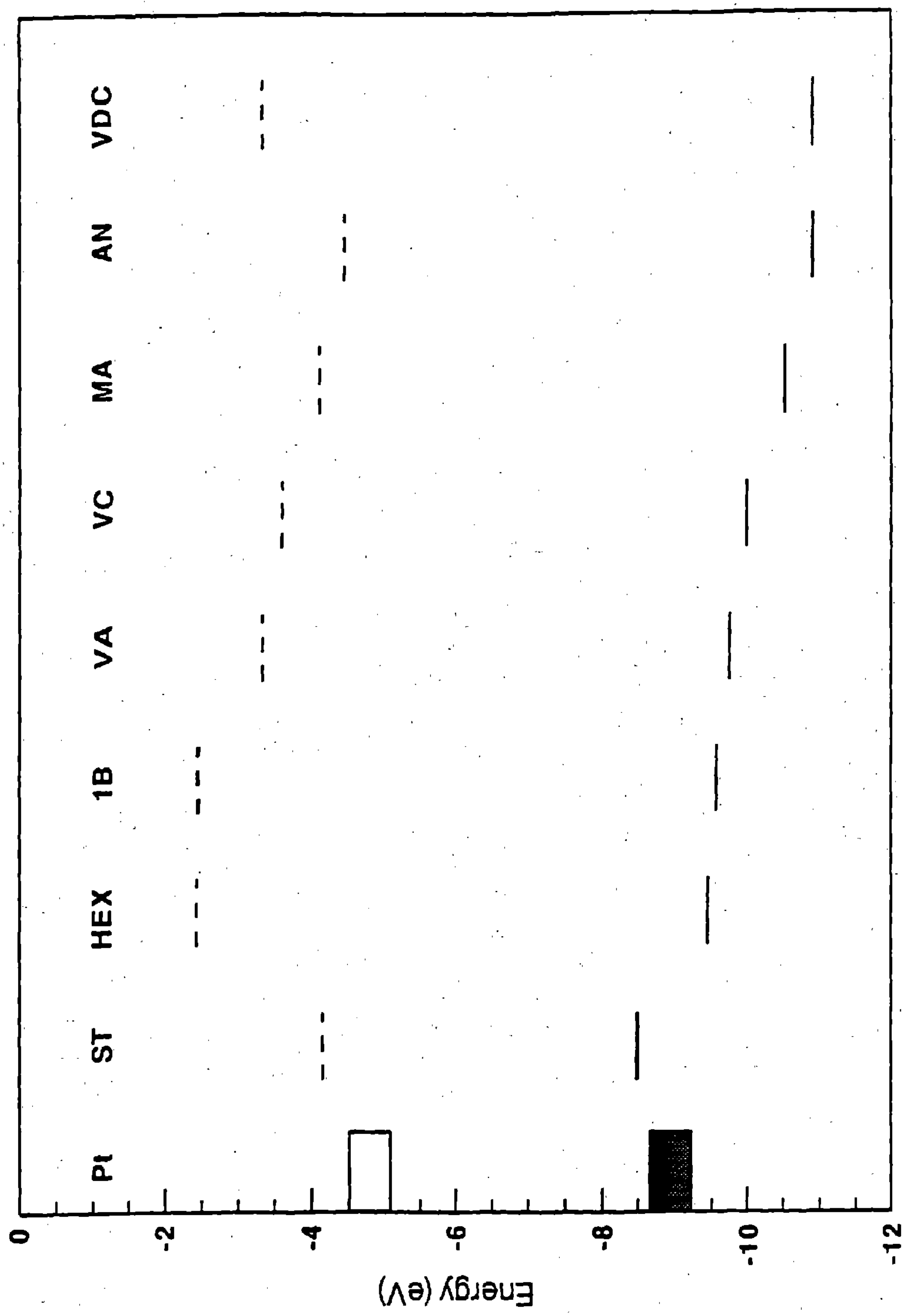
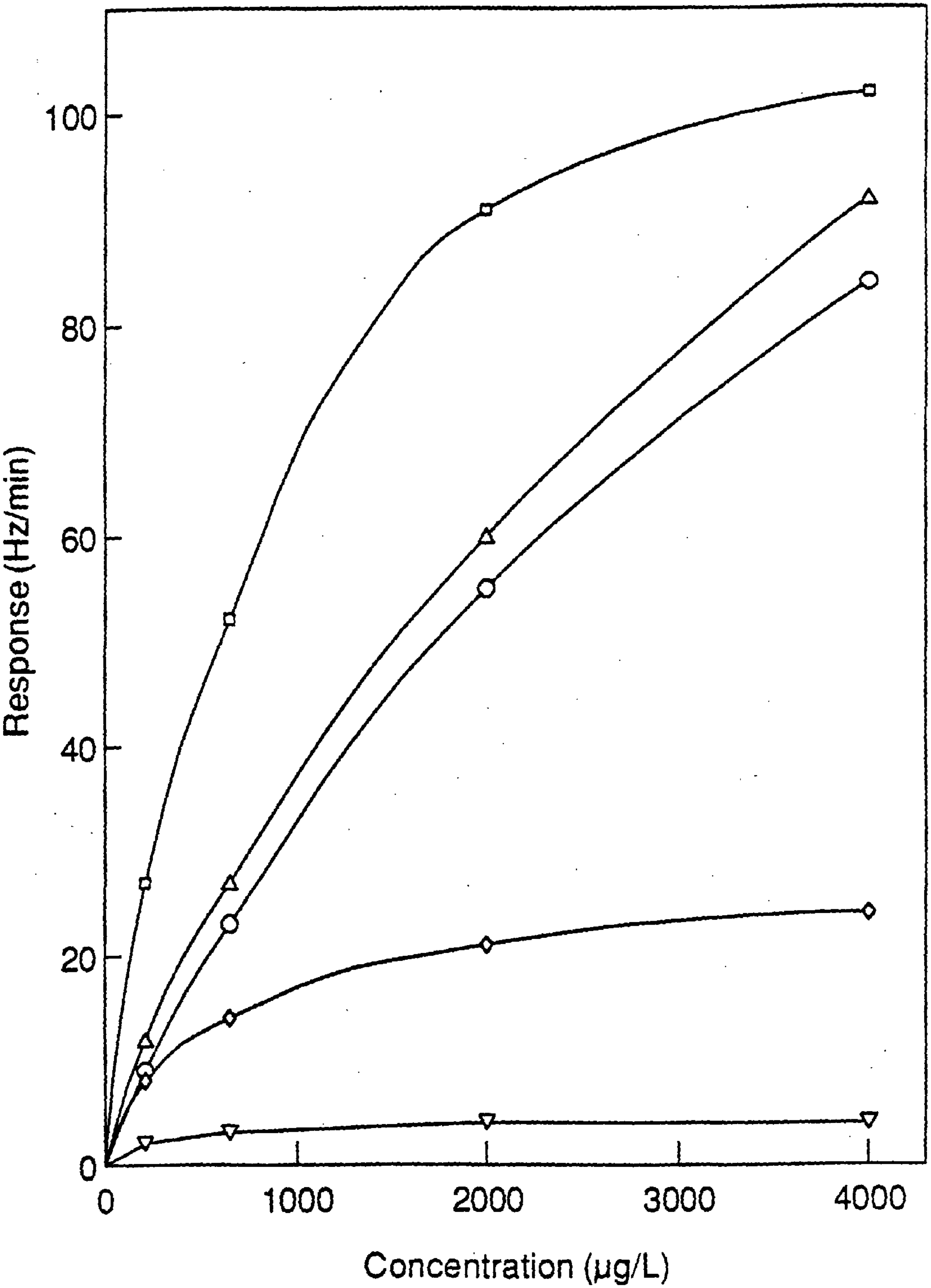
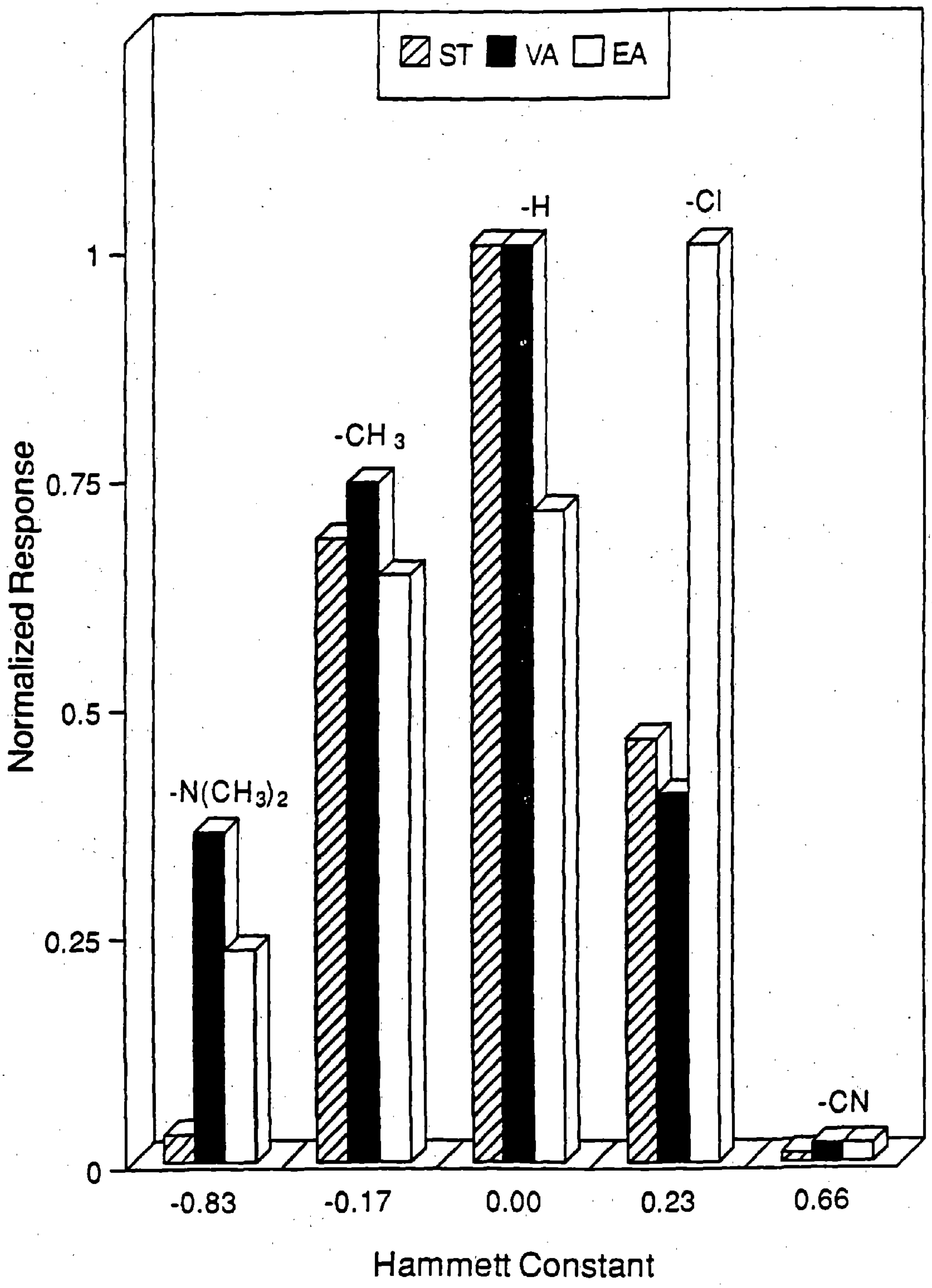


Figure 3



Response (Hz/min)
0
20
40
60
80
100
0
1000
2000
3000
4000
Concentration (µg/L)

Figure 4



▨ ST ■ VA ☐ EA
Normalized Response
0
0.25
0.5
0.75
1
-N(CH₃)₂
-CH ₃
-H
-Cl
-CN
-0.83
-0.17
0.00
0.23
0.66
Hammett Constant

Figure 5

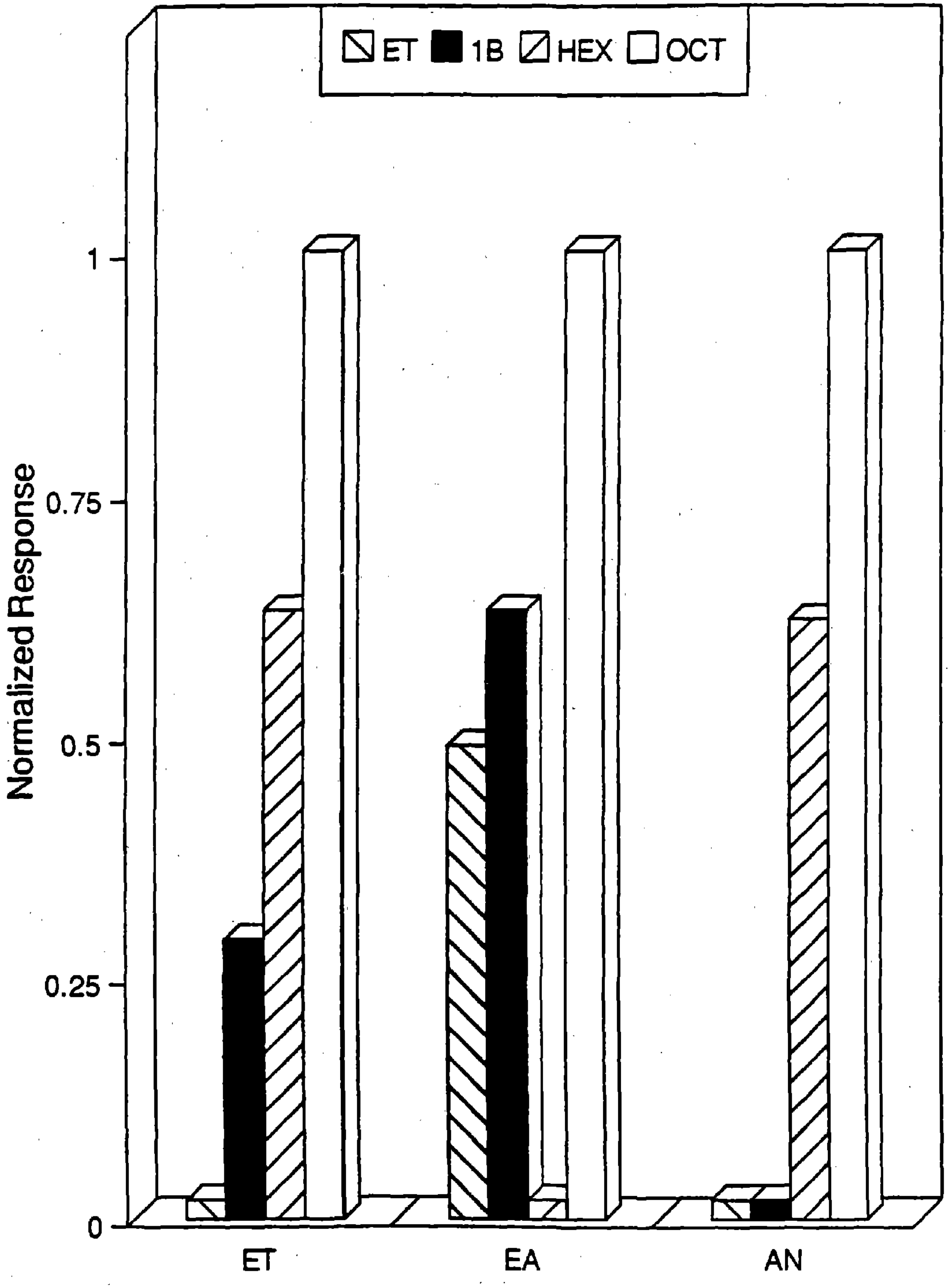


Figure 6

CHAPTER 5

A Coated Surface Acoustic Wave Sensor Employing A Reversible Mass Amplifying Ligand Substitution Reaction for Real-Time Measurement of 1,3-Butadiene at Low- and Sub-ppm Concentrations

Abstract

Real-time measurement of 1,3-butadiene gas using a surface-acoustic-wave (SAW) sensor coated with the square-planar Pt(II)-olefin π-complex $PtCl_2$(1-hexene)(pyridine) and related complexes is described. Amplification of the sensor response results from displacement of two 1-hexene molecules by each butadiene molecule and formation of the bridged complex $[PtCl_2(pyridine)]_2$(1,3-butadiene). Using a 30-MHz SAW oscillator, the rate of frequency change is linearly related to the butadiene air concentration from 150 ppb to ≥13 ppm and a calculated detection limit of 101 ppb is obtained. Using a 60-MHz oscillator, the detection limit is reduced to 24 ppb. No effect on the sensor response is observed with changes in relative humidity from 5-80% or changes in temperature from 25-35°C. No interference is observed from several industrially relevant non-olefin organic gases and vapors. Responses are obtained for several olefins but they interfere with the response to butadiene only at higher relative concentrations. The reagent can be regenerated repeatedly by brief exposure to 1-hexene vapor with retention of the original response characteristics upon subsequent exposure. The potential for using this sensor to monitor occupational 1,3-butadiene exposures is discussed in light of the recently proposed occupational exposure limit of 2 ppm.

INTRODUCTION

1,3-Butadiene is a major feedstock chemical for the production of polymeric resins and elastomers. It is classified as a suspected carcinogen, as well as a possible teratogen and reproductive hazard.[1,2] According to the National Institute for Occupational Safety and Health (NIOSH), approximately 65,000 workers are potentially exposed to butadiene each year in the U.S. alone.[2] Recognition of the health hazard of butadiene exposure has led to a recent proposal by the Occupational Safety and Health Administration (OSHA) to lower the Permissible Exposure Limit (PEL) from 1000 ppm to 2 ppm with an associated Action Level of 1 ppm.[1] This, in turn, has required a reassessment of sampling and analytical methodologies used for compliance determinations.

Lunsford et al.[3] reported several shortcomings associated with the standard NIOSH method of sampling and analysis for butadiene which entails collection on 100 mg of activated charcoal followed by solvent desorption and gas chromatographic analysis.[4] These include rapid saturation of the carbon bed, instability of adsorbed butadiene, variations in desorption efficiency, and poor chromatographic resolution of butadiene from other light hydrocarbons in collected samples. Modified sampling methods employing larger charcoal beds[3] or charcoal impregnated with 4-tert-butylcatechol[5] have been developed to increase the breakthrough volume and sample stability, but refrigeration of collected samples is still recommended. Chromatographic resolution of butadiene from potential co-contaminants was possible by means of an alumina-coated capillary column preceded by a backflushable pre-column to remove high-boiling and polar contaminants.[3] Use of such methods for routine compliance monitoring is thus rather cumbersome and labor/capital intensive.

Surveys of butadiene monomer and polymer production facilities, most of which are open-air plants, indicate that the vast majority of average daily exposures are currently below the proposed PEL and that highest exposures occur during short periods associated with quality control sample collection/analysis or loading/unloading of cargo vessels.[1,6] The primary source of fugitive emissions to the ambient atmosphere, however, is leakage from process equipment seals.[7] These findings point to the need for continuous monitoring of both personnel exposures and potential leak sources along the production line.

The selection of an appropriate continuous monitor is problematic. Portable direct-reading instruments employing photoionization detectors can measure sub-ppm levels of butadiene and are of suitable size for periodic leak-source surveys, but they are inherently nonselective and cannot differentiate between butadiene and a number of other relevant unsaturated solvents and monomers. Field infrared gas analyzers are also subject to interferences from unsaturated co-contaminants which have absorbance maxima that coincide with those of butadiene. Transportable gas chromatographs have the potential for greater selectivity, but difficulty with peak resolution would be expected in light of the report by Lunsford et al..[3] In any case, the size and cost of these types of instruments preclude their use for routine monitoring of personnel exposures. Thus, there is a need for low-cost miniaturized instrumentation for monitoring butadiene selectively in the low- and sub-ppm concentration range in the occupational environment.

An increasing number of reports have appeared over the past several years on the application of microfabricated surface-acoustic-wave (SAW) sensors to the measurement of gases and vapors.[8] The small size and simple design of the SAW device and associated electronics, coupled with the potential for sensitive and selective organic gas/vapor measurement, favors consideration of this particular sensor technology for the applications of interest here.

The detection mechanism most often employed in the coated SAW sensor involves the change in mass and, in certain cases, the elastic properties of a chemically sensitive sensor coating film that accompanies interaction of the coating with gas-phase analytes. The nature of the coating material is therefore a key factor governing the sensor response characteristics.

The amount of coating on the sensor surface can be estimated by eq 1 from the net frequency shift, Δf_c (Hz), measured before and after deposition:[9]

$$\Delta f_c = (k/a) f_o^2 \Delta m_c \qquad (1)$$

where k is a negative substrate constant ($= -1.26$ cm^2-s/μg), a is the active area of the SAW device (cm^2), f_o is the uncoated sensor operating frequency (MHz) and Δm_c is the mass of the coating (μg). The sensor response, Δf_a, due to the mass of gas-phase analyte added to the coated sensor upon exposure, Δm_a, can be described by eq 1 as well, by substituting Δf_a and Δm_a for Δf_c and Δm_c, respectively. Δm_a then can be related to the air concentration of the analyte, C_a, by whatever isotherm equation is appropriate for the particular coating-analyte interaction involved (e.g., surface adsorption, bulk sorption, chemical reaction, etc.).

In most reports on the use of SAW sensors for measuring organic vapors, a polymer is used as the sensor coating and vapors are reversibly concentrated at the sensor surface by bulk sorption. For this particular case, the amount of vapor sorbed by the polymer coating at equilibrium will depend upon the amount of polymer initially deposited on the sensor, as reflected by Δf_c, and Δf_a can be related to C_a by means of the following approximate expression:[10]

$$\Delta f_a = \Delta f_c C_a K/\rho_c \qquad (2)$$

where K is the apparent partition coefficient and ρ_c is the density of the coating material. It has been reported that the apparent partition coefficient determined from SAW sensor responses can be significantly larger than that determined under similar conditions by gas chromatography, owing to the sensitivity of the SAW device to changes in the polymer modulus accompanying vapor sorption.[11] However, eq 2 was still found to describe the response isotherms accurately for a given polymer coating if K was determined from the SAW responses.

Because of the low energy of sorptive vapor-polymer interactions, many vapors will partition into a given coating film, with the magnitude of the apparent K being a function of the volatility of the vapor and its solubility in the coating material.[12-14] In order to obtain selectivity with this approach, it is generally necessary to use an array of differently coated sensors whose collective response pattern can be correlated with a given vapor or class of vapors.[15-17] Unfortunately, for many common organic gases and vapors K is relatively small and sample preconcentration would be necessary for measurement in the vicinity of many occupational exposure limits.[16,18]

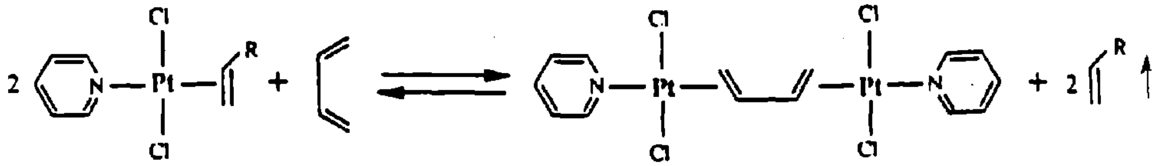
The alternative approach of using SAW sensor coatings capable of specific chemical reactions with certain gases and vapors offers the potential for improved sensitivity and selectivity. In the case of unsaturated organic compounds, such as olefins and dienes, the reactivity of the double bonds can be utilized in the design of sensor coatings. An example of this approach was reported by Snow and Wohltjen who used a SAW sensor coated with poly(ethylene maleate) to detect cyclopentadiene by means of a Diels-Alder reaction.[19] Although a detection limit of only 200 ppm was reported, high selectivity for cyclopentadiene was obtained by virtue of the fact that other common solvent vapors, while physically sorbed into the polymer backbone, did not react chemically with the dienophilic maleate double bond in the polymer. The tradeoff for this degree of selectivity is the gradual consumption of the reagent with continued exposure - attempts to regenerate the coating thermally by a retro Diels Alder reaction were not successful.

We have found that highly selective and sensitive measurement of various olefins is possible by use of SAW sensors coated with reagents of the general formula trans-$PtCl_2$(olefin)(amine) which can undergo olefin substitution reactions under mild conditions without interference from non-olefin organic vapors.[20-23] Since the rate of olefin substitution depends on the gas-phase olefin concentration and the rate of mass change in the reagent is proportional to the reaction rate, real-time monitoring of olefin concentrations is possible by measurement of the instantaneous rate of frequency change (via eq 1):

$$df_a/dt = (k/a) f_o^2 dm_a/dt \qquad (3)$$

In addition, a general feature of this class of reagents is their post-exposure regenerability by brief treatment with the initially complexed olefin.

With butadiene, both double bonds are available for coordination to Pt. Olefin substitution would result in formation of a 2:1 Pt:butadiene bridged complex:



(4)

The reactions of butadiene with K_2PtCl_4,[24-26] $Pt_2Cl_4(Ph_3P)_2$[27] and benzonitrile-$PdCl_2$[25] have been shown to yield analogous bridged complexes, and in a previous report we showed that combining butadiene with a solution of trans-$PtCl_2$(ethylene)(pyridine) in refluxing dichloromethane also produced a bridged 2:1 complex.[21] Use of the latter reagent as a SAW sensor coating for butadiene, however, was unsuccessful. In subsequent studies of this class of reagents it was demonstrated that replacing ethylene with other olefins or replacing pyridine with various substituted-pyridines in the complex can markedly alter the rate of olefin substitution.[22,23]

In this paper we explore the use of SAW sensors coated with several Pt-olefin complexes for measuring low concentrations of butadiene gas. After describing results of initial screening experiments using several different types of SAW sensor coatings, a focus is placed on the sensor performance using coatings of trans-$PtCl_2$(1-hexene)(pyridine) and related complexes which show high sensitivity toward butadiene. Topics addressed include the characterization of the trapping reaction, sensitivity and reproducibility of sensor responses, regenerability of the coating reagent, selectivity, humidity and temperature effects, sensor operating frequency, and the potential for real-time monitoring of butadiene in industrial environments.

EXPERIMENTAL SECTION

Reagent Syntheses. All reagents and solvents were >96% pure and were used without further purification. Vinyl chloride was obtained from Matheson Gas Products, Secaucus, NJ. 2-Chloroprene (2-chloro-1,3-butadiene, 50% in xylene) was obtained from Alfa Products, Ward Hill, MA. Poly(ethylene maleate) was provided by Dr. A. Snow of the Naval Research Laboratory and was prepared using a procedure described previously.[19] All other chemicals were obtained from Aldrich, Milwaulkee, WI. Infrared spectra were recorded on a Perkin-Elmer 281B IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

trans-$PtCl_2$(olefin)(amine) complexes were synthesized in two steps according to established methods.[28] The first step entailed adding one equivalent of the amine (i.e., pyridine or substituted-pyridine) to a stirred aqueous solution of Zeise's salt to form the corresponding trans-$PtCl_2$(ethylene)(amine) which precipitated from solution. After isolation and recrystallization from dichloromethane/hexane, the ethylene was replaced by dissolving the complex in dichloromethane, adding an excess of the desired olefin or diene and then refluxing for 1-2 hr. For preparing complexes with butenes and butadiene, an ice-water bath was used to first condense an excess of the gaseous reactants in the reaction flask followed by continuous bubbling through the solution over the course of the reaction period. After cooling to room temperature, the solvent and unreacted olefin were evaporated under reduced pressure. The products were subsequently taken up in a minimum of dichloromethane and recrystallized by addition of hexane. The trans-$PtCl_2$(1-hexene)(4-X-pyridine) and trans-$PtCl_2$(1-octene)(pyridine) complexes were recovered as viscous oils that tended to form amorphous semi-solid masses on standing. The former (X = H) could be recovered as a low-melting crystalline solid (m.p. = 40°C) but only after repeated attempts at recrystallization. Elemental analyses are listed in Table I. All products were stored in air in sealed vials prior to use.

Apparatus. Most of the experiments described here employed a 30-MHz SAW oscillator with an active area of 1.5 cm^2 whose design has been described previously.[29] Additional tests were peformed using a 60-MHz SAW oscillator fabricated in-house on a 2.5 x 1.0 cm ST-quartz substrate (Valpey-Fischer, Hopkinton, MA). Each interdigital transducer (IDT) consisted of 50 pairs of evaporated Au-on-Cr microelectrodes having equal widths and spaces of 13 μm and an acoustic aperture of 0.27 cm. The distance between IDT centers was 1.2 cm and the overall active device area was approximately 0.36 cm^2. Variable series inductors were used as impedance matching elements (50 ohm) for each IDT and a pair of LM733 amplifiers was used to complete the oscillator circuit. The frequency of each SAW device was monitored with a digital frequency counter (Hewlett Packard 5384A) and logged on a personal computer. Data aquisition software was written in-house.

The sensor was mounted inside a stainless steel exposure chamber (0.24 L) and exposed to test atmospheres of the analytes in air at a flow rate of 8 L/min. The chamber temperature was controlled externally using heating tape and monitored by a thermocouple mounted near the surface of the sensor.

Test atmospheres were generated by introducing the analytes into a metered dilution-air stream: for gases a precision syringe pump equipped with a gas-tight syringe was used as the analyte source, and for vapors N_2 was passed through a fritted bubbler containing the liquid analyte. The flow rate, temperature and relative humidity of dilution air were controlled by a Miller-Nelson Research Model HCS-301 control unit. Unless otherwise indicated, exposure tests were performed at 25°C and ~5% RH. Gas and vapor concentrations were continuously monitored with either an infrared spectrophotometer (MIRAN-1A gas analyzer, Foxboro, East Bridgewood, MA) or a photoionization detector (HNu Systems, Newton, PA) placed in parallel with the exposure chamber.

Coating Deposition. In consideration of coating adhesion and uniformity, the Pt-olefin reagents were combined with polyisobutylene (PIB) and spray coated onto the sensors from solutions containing 6 mg/mL of each component in 2:1 toluene/hexane. As discussed below, PIB does sorb butadiene reversibly, but measurable signals were obtained only at relatively high concentrations. Thus, the response due to equilibrium vapor sorption at a given concentration did not interfere with the response due to chemical reaction over the concentration range of interest. For less-volatile solvents, tested here as potential interferences, the signals due to PIB sorption and desorption could be masked by use of a reference sensor coated with only PIB as shown previously.[20,21]

The deposited coating mass was determined by eq 1 from the Δf_c value obtained after evaporation of the carrier solvent. For the 30-MHz oscillator the mass sensitivity is approximately 760 Hz/μg and for the experiments performed here Δf_c ranged from about 45-250 kHz, corresponding to deposited masses of 60-330 μg. For the 60-MHz oscillator, with a mass sensitivity of 12.6 kHz/μg, Δf_c ranged from 400 - 600 kHz (32-48 μg).

RESULTS AND DISCUSSION

Selection and Initial Testing of Coating Materials.

Representatives from three classes of materials were investigated initially as potential sensor coatings: one sorptive polymer, four Diels-Alder dienophiles, and several Pt-olefin complexes. Coating stability and sensitivity were used as the primary selection criteria.

PIB was selected as the sorptive coating because it is a non-polar rubbery amorphous polymer that would be expected to sorb butadiene rapidly and reversibly. In addition, the partition coefficient for this polymer would be relatively large compared to other polymers containing more polar functional groups.[12,13] A coating of 200 kHz of PIB was applied to the 30-MHz SAW device and responses were recorded for eight concentrations ranging from 30-9300 ppm. Sorption equilibrium was established quite rapidly (< 20 s) at all concentrations and the sorption isotherm was linear ($r^2 = 0.998$), however, the calculated limit of detection (LOD) was only 220 ppm. This LOD is based on a criterion of $3\sigma = 3$ Hz, where σ is the standard deviation of 1-min baseline frequency shifts measured for 5-10 minutes before and after exposure. This level of sensitivity is clearly inadequate for monitoring butadiene at typical workplace concentrations. Although slightly greater sensitivity could be obtained by applying more coating to this sensor, for Δf_c > 250-270 kHz the oscillator generally became unstable or would cease to oscillate.

Attempts to use reagent coatings capable of Diels-Alder cyclization reactions with butadiene[30] were largely unsuccessful. The dienophiles maleic anhydride, N-phenyl maleimide and 1,4-benzoquinone did not form stable coating films on the sensor. Coatings of poly(ethylene maleate) were stable, but the sensitivity to butadiene was quite poor: for three separate coatings, 1500 ppm was barely detectable using the 30-MHz device. Increasing the temperature to 40°C did not significantly increase the response. Therefore, no further testing of this coating material was performed.

Several different Pt-olefin complexes were then examined. For coatings of trans-$PtCl_2$(OL)(pyridine) where OL = styrene, ethylacrylate, methylacrylate, ethylene, 1-butene or cis-2-butene, little or no response was observed for butadiene concentrations as high as several hundred ppm. For OL = 1-hexene or 1-octene, however, the response to butadiene was quite large as shown in Figure 1. Data for the corresponding 1-butene and ethylene complexes are included in Figure 1 for comparison. The concentration range of 150 ppb to 3 ppm covers the most relevant range for occupational exposure monitoring. Discussions about dynamic range are provided below.

Each point on the response curves represents the average steady-state rate of frequency change (Hz/min) measured at a given concentration over a period of 5-20 min. Response and recovery times were in the range of 5-10 s, which is comparable to the theoretical mixing time for the chamber and indicates rapid attainment of steady-state conditions within the coatings. The responses shown in Figure 1 for the 1-octene complex represent the averages from two separate coating films. Responses for the 1-hexene complex are the averages from eight different films. In the latter case, Δf_c values ranging from 50 to 205 kHz were used to examine the effect of the initial coating mass on the sensor response. For a given coating film, the responses were remarkably constant over each exposure period at a given concentration, with relative standard deviations typically < 1 Hz/min at the lower concentrations and only 6-7 Hz/min at the highest concentration. Inter-coating response variations were also quite low, with standard deviations of 2-16 Hz/min for the 1-octene complex and 2-6 Hz/min for the 1-hexene complex.

The fact that responses for the 1-hexene complex were independent of the amount of coating initially deposited on the sensor is consistent with eq 3 and with the interaction model presented previously for this class of reagent coatings[29] where pseudo-first-order kinetics with respect to butadiene can be assumed because there is an excess of reagent on the sensor relative to the amount of butadiene adsorbed at the gas-reagent interface at steady-state. Since the interaction is confined initially to the outer surface of the reagent and the reagent is already present in excess, increasing the thickness of the reagent layer or the average reagent particle size within the coating film would not be expected to increase the reaction rate.

Increases in the sensor frequency, corresponding to net losses of mass from the coatings, are observed for both the 1-hexene and 1-octene complexes, which would be expected (see eq 3) from the substitution of two heavier 1-hexene or 1-octene ligands by a single lighter butadiene molecule. The response curves are linear ($r^2 > 0.99$) and average sensitivities of 0.030 and 0.068 Hz/ppb-min and LODs of 101 and 44 ppb are obtained for the 1-hexene and 1-octene complexes, respectively.

It can be shown that the rate of the SAW frequency change is directly proportional to the rate of reaction for these complexes.[29] In order to compare the reactivity of one complex to another, however, account must be taken of the difference in mass change associated with each olefin-substitution reaction. The average ratio of responses for the 1-octene and 1-hexene was 2.3 ± 0.1. If the difference in responses was due only to the mass difference between the ligands being replaced then the response ratio would be 1.5. The slightly higher ratio actually observed can be attributed therefore to a higher reaction rate for the 1-octene complex.

The lack of response for the ethylene and 1-butene complexes may be due either to a failure to react under the conditions of exposure or to reaction with no net mass change. Note that reaction of butadiene with the ethylene complex to form the 2:1 bridged complex would result in a negligible mass change in the coating and would go undetected. Similarly, if the 1-butene complex reacted to form a 1:1 complex with butadiene, this would also yield a negligibly small mass change. To probe this issue, a simple experiment was conducted by depositing thin films of the 1-butene and ethylene complexes on separate glass slides and exposing them to a stream of pure butadiene for 45-60 min. The melting points of these samples were then measured and found to be identical to those of the starting complexes (Table I), indicating that the complexes do not react with the butadiene to any significant extent under actual exposure conditions. It is interesting to note, however, that in previous testing of styrene vapor responses using coatings of the ethylene complex, the presence of relatively high concentrations of butadiene reduced the response to styrene significantly.[21] Apparently, while butadiene cannot displace ethylene from the ethylene complex, it can enter the coordination sphere of the Pt in the complex and thereby inhibit the reaction with styrene.

The order of reactivities observed here on going from ethylene to 1-octene suggests that increases in the alkyl chain length of the initially complexed olefin reduces the strength of the Pt-olefin bond and increases the lability of the olefin toward substitution. Data reported on the NMR coupling coefficients between Pt and the double-bond carbons as well as the change in chemical shift of the olefinic carbons upon complexation in similar complexes[31-32] suggest that ethylene is indeed bound more tightly than its higher homologues, but little difference is seen in the Pt-C coupling coefficients or olefinic-carbon chemical shift changes between 1-propene, 1-butene, cis- and trans-2-butene, and 1-hexene (data on higher homologues were not available). Thus, the abrupt increase in reactivity between the 1-butene and 1-hexene complexes seen here is not fully consistent with expectations based on NMR data. We have, however, found similar inconsistencies in studies of other olefin-substitution reactions with this class of reagents.[23]

Another factor that must be considered is the physical state of the reagent. Examination of the coating films by polarized-light microscopy showed the 1-hexene and 1-octene complexes to be randomly dispersed oils or amorphous solids when deposited on the sensor with or without PIB, whereas the ethylene and 1-butene complexes are both crystalline solids. It is possible that the mobility of both the butadiene and the reagents themselves are greater for the 1-hexene and 1-octene complexes because of the lack of long range crystalline order and that this contributes to the reactivity. This is accordant with expectations of some conformational constraints associated with the trapping reaction, since formation of the bridged diene complex requires the presence of two Pt-olefin moieties in close proximity. It could also account for the ability to synthesize the 2:1 Pt-butadiene complex from the Pt-ethylene complex in solution but not in the solid state.

Aging effects were then explored for the 1-hexene and 1-octene complexes. Coatings prepared from freshly synthesized samples of the 1-octene complex gave similar responses for only 2-3 days after which the responses progressively declined over the remainder of a one week period. IR spectra of the reagent showed no evidence of decomposition after standing in air for this period of time, but a small amount of insoluble white residue was observed in solutions of this material and upon removing some of the later films. Loss of 1-octene accompanied by Cl-bridged dimer formation, which has been reported for bis-(1-octene) complexes of $PtCl_2$,[33] could account for the observed behavior and would not lead to significant changes in the IR spectrum. Coatings of the 1-hexene complex provided reproducible responses when prepared from samples that were less than 2-3 months old. Beyond this time a reduction in response was observed, although even for aged samples exposure at a given concentration gave stable responses. As a result, all experiments were restricted to 1-hexene complex samples that were < 2 months old.

Earlier investigations had shown that the reactivity of this class of reagents toward several gas-phase olefins was not only a function of the complexed olefin, but also of the substituents on the trans-pyridine ligand.[13,22,23] For the complexes trans-$PtCl_2$(ethylene)(4-X-pyridine), increases in either the electron withdrawing or donating strength of X led to decreases in response relative to X = H. Tests performed in this study using trans-$PtCl_2$(1-hexene)(4-X-pyridine) (X = Cl or CH_3) showed the same trend in responses to butadiene (Figure 2). The relative sensitivities were 1, 0.75 and 0.60 for X = H, Cl and CH_3, respectively. Thus, there was no apparent advantage to using the substituted-pyridine complexes.

Product Characterization. Formation of the 2:1 Pt-butadiene complex according to eq 4 yields an effective amplification of the sensor response because of the loss of two 1-hexene molecules for every butadiene molecule reacted. The concept of mass amplification in the measurement of gases using piezoelectric sensors was first described by Alder et al., who used a coating of bis(pentan-2,4-dionato)nickel to detect HCN gas with a bulk-wave piezoelectric crystal sensor.[34] In that case the lighter HCN displaced the heavier diketone ligand thereby amplifying the mass change relative to the mere addition of HCN. Unfortunately, the complex was hydrolytically unstable and responses were not reproducible. Other reports have explored this concept with enzyme-catalyzed reactions using bulk-wave piezoelectric sensors in solution-phase analyses.[35]

Several experiments were performed to confirm the formation of the 2:1 bridged complex. First, butadiene was reacted with the 1-hexene complex in refluxing dichloromethane solution. Elemental analysis of the isolated product gave results that agreed closely with theory and with values obtained from the product of solution-phase reaction of butadiene with the ethylene complex (see Table I). The melting points of the products derived from the ethylene and 1-hexene complexes were also in agreement. Note that the melting point of 134°C corresponds to the temperature at which significant discoloration and morphological changes in the solid samples are observed. With further heating, the samples eventually show evolution of gas and formation of a black tar. This occurs over the range of 160-170°C for the products derived from both the ethylene and 1-hexene complexes.

To determine whether the bridged Pt-butadiene complex is also formed on the sensor surface under actual exposure conditions, a spray-coated film of the 1-hexene complex was deposited on a glass slide and then exposed pure butadiene gas for 40 min. The post-exposure melting point (134°C) matched that of the authentic sample of the Pt-butadiene complex prepared from solution.

A 105-kHz coating of the 1-hexene complex (1:1 ratio with PIB) was then deposited on the SAW device and exposed to 750 ppb of butadiene until no change in the frequency was observed, which required about 10 hr. The plot of frequency shift versus time is shown in Figure 3. The total frequency shift was 6500 Hz. Since the 1-hexene complex accounts for 50% of the coating mass, this would correspond to 52.5 kHz out of the total Δfc. Conversion to the 2:1 Pt-butadiene complex results in a calculated total mass change of 13.3%, or 6900 Hz. The small difference (-6%) can be attributed to slight errors in the preparation of the solution used to deposit the coating film.

Additional indirect evidence for the 2:1 Pt-butadiene complex is found in the relative sensitivity to butadiene versus each of several butene isomers. Butene:butadiene sensitivity ratios of 0.14, 0.14, 0.05, and 0.004 are found for 1-butene, cis-2-butene, trans-2-butene and isobutylene, respectively, even though there is little difference in molecular weight. While electronic factors (i.e., orbital symmetries and overlaps) and steric factors undoubtedly contribute to this order of responses,[22] formation of a 2:1 complex would certainly help to account for the much larger response to butadiene.

Service Life and Dynamic Range. Referring again to Fig. 3, it can be seen that the rate of the frequency increase is constant up to a net frequency shift of about 1550 Hz which corresponds to 24% of the 6500 Hz total frequency shift observed. Beyond this point the response rate declines continuously and is no longer proportional to the butadiene concentration. This point can be used to define the effective service life of the coating. Analogous experiments involving exposures of 1250 ppb (Δf_c - 50 kHz), 1500 ppb (Δf_c - 110) and 600 ppb (Δf_c - 205 kHz) gave constant rates of frequency change until

20-23% of the total frequency shift was reached, supporting the concept that the service life is a function of the total amount of coating on the sensor. The times required to reach these points were 16, 35 and 165 min, respectively.

However, increasing the exposure concentration led to more rapid decreases in the effective service life. We found, for example, that the responses to 8.5 ppm (Δf_c = 160 kHz) and 13.5 ppm (Δf_c = 215 kHz) of butadiene declined significantly (i.e., by > 10%) at only 15, and 11% of the total possible frequency shift, respectively, and that the corresponding service lives were only 6 and 3.5 minutes. At the same time, it must be appreciated that the average responses at these higher concentrations were extremely high: 255 ± 6 Hz/min and 461 ± 24 Hz/min.

We believe that the concentration dependence of the service life can be attributed to the reversibility of the olefin substitution reaction (see eq 4). The overall trapping interaction involves surface adsorption and then diffusion of the butadiene into the coating reagent. Chemical reaction leads to formation of free 1-hexene which must then diffuse out and desorb. As the reagent is consumed, there is an increase in the pathlength through which the butadiene and 1-hexene must diffuse. The free 1-hexene may also react with freshly formed Pt-butadiene moieties as it diffuses out of the reagent. At all concentrations, the butadiene trapping reaction initially appears to be rate-limiting, but as the reagent is consumed diffusional resistance and/or the reverse reaction become more significant. The reason why this occurs at a lower conversion percentage for higher butadiene concentrations is due to a greater build up of 1-hexene within the reagent accompanying the higher reaction rate.

Thus, the definition of the dynamic range must incorporate considerations of the length of exposure. Most of the experiments performed have been confined to butadiene concentrations from 150 ppb to 13 ppm and the sensor response is linear over this range (r^2 = 0.994). Higher concentrations can be measured, however, the ability to maintain a constant rate of frequency change becomes a limiting factor. In any case, we are most interested in the lower concentrations for industrial monitoring applications. Furthermore, although the service life is limited, it is possible to regenerate the coating reagent as discussed in the next section.

Reagent Regeneration. An important attribute of this class of reagents is the capability for rapid chemical regeneration, in situ, which has been demonstrated in previous reports on the measurement of olefins using trans-$PtCl_2$(ethylene)(pyridine).[19-21] Initial tests of the regeneration of the 1-hexene complex were performed by exposing coatings of different Δf_c values to high concentrations of butadiene until no further frequency shifts were observed. The net frequency shift was recorded and then 1-hexene was introduced to the atmosphere at concentrations ranging from 800-1200 ppm. A rapid decrease in frequency occured in all cases and a stable frequency was once again recovered after a few minutes. The coating was then reexposed, regenerated and exposed a third time. The results presented in Table II for three different initial coating masses (i.e., $\Delta f_c \simeq 50$, 100, and 200 kHz) demonstrate the highly reproducible responses and the remarkably close agreement with the theoretical values assuming formation of the 2:1 complex.

Results of further tests of coating regenerability are shown in Table III for repeated exposures to 500 ppb of butadiene (Δf_c = 100 kHz). Each 75-min exposure period was followed by a 5-min regeneration with 1-hexene. The net exposure frequency shift corresponds to 18% of the total possible frequency shift. This cycle was repeated five times and, as shown in Table III, there was no difference in the sensor response. In all cases the frequency shift on regeneration was equal in magnitude to that on exposure. If the regeneration were not successful, a decline in response would have been expected during the second exposure cycle. The standard deviations around the means were all ≤ 2 Hz/min demonstrating that the reaction rate does not decline over this interval.

Selectivity. The selection of interferences to examine was based primarily, though not exclusively, on considerations of air contaminants potentially encountered with butadiene in the industrial environment. According to industry surveys performed by NIOSH[6] and others,[1] occupational exposures to butadiene are of most concern in monomer and polymer production facilities - no measurable exposures were found in surveys of typical end-use industries such as tire and rubber-hose production.

Crude butadiene can be isolated from the so-called "C_4 co-product stream" created during thermal/catalytic cracking processes designed to produce ethylene from petroleum feedstock. The C_4 co-product typically contains from 37-47% butadiene as well as the following gases: isobutylene (25%), 1-butene (15%), trans-2-butene (6%), cis-2-butene (5%), butanes (5%), and traces of C_3 and C_5 hydrocarbons.[36] In certain plants, this stream is passed through a dehydrogenation reactor to convert residual butane and 1-butene to butadiene. Purification of the butadiene is performed by counter current extraction either with cuprous ammonium acetate or solvents such as acetonitrile. Butadiene can also be produced industrially by the condensation of ethanol.[36]

Most of the butadiene produced in the U.S. is used to make polybutadiene or styrene-butadiene rubber with smaller fractions allocated to production of chloroprene (and ultimately polychloroprene), nitrile rubber (acrylonitrile-butadiene copolymer) and ABS resins (terpolymer of acrylonitrile, styrene and butadiene).[1,37] Polymerization is typically performed using an aqueous emulsion process, although solution polymerization in aliphatic or aromatic hydrocarbon solvents is also practiced.

Due to the flammability of butadiene, all reactions are carried out in closed reactor systems which effectively minimizes routine exposure levels from the processing equipment. As stated above, sampling surveys indicate that the majority of industrial exposures are below 2 ppm.[1,6] Higher exposures have been encountered during quality control procedures and vessel transfers, but recognition of this has led to engineering and work practice modifications that reduce levels encountered during these activities.[1]

Table IV summarizes the results of experiments involving co-exposure to 900 ppb of butadiene and each of several potential co-contaminants. As expected, butane, ethanol, benzene, hexane, acetone, and dichloromethane do not react or interfere even when present in large excess. Acetonitrile, however, reduces the response to butadiene by about 4 Hz/min regardless of the acetonitrile concentration. Exposure to acetonitrile alone also produces a response of -4 Hz/min that is independent of concentration. It is known that acetonitrile can coordinate to Pt through its nitrile group.[38,39] The results obtained here indicate that it is not displacing any other ligand but rather adding to the Pt presumably to form a pentacoordinate Pt complex.[40,41] The fact that the acetonitrile causes a decrease in frequency means that it could be differentiated from butadiene and the fact that the interference is small and does not increase with increasing acetonitrile concentration means that it would only lead to significant measurement error (i.e., >10%) at relatively low butadiene concentrations (i.e., below ~ 1.3 ppm).

For the olefins examined, varying degrees of reactivity and interference were observed. Vinylidene chloride neither reacts with the complex nor interferes with the response to butadiene, even at high concentrations. Co-exposure of butadiene and chloroprene at relatively high chloroprene concentrations also did not affect the response to butadiene. Chloroprene can be measured with this reagent, but the LOD is about 100 ppm and the sensitivity is quite low. It should be noted that the chloroprene test atmospheres were generated using a solution of chloroprene in xylene, but the xylene concentration was determined to be below about 2 ppm in all cases. Vinyl chloride did not interfere at low concentrations, but above 30 ppm it showed a small positive effect on the butadiene response that increased with the vinyl chloride concentration. Comparison of these results to those for vinyl chloride alone indicates that the combined response to butadiene and vinyl chloride is additive.

As mentioned above, 1-butene, cis-2-butene, trans-2-butene and isobutylene can also be measured with this reagent coating but the sensitivities are much lower than for butadiene. Co-exposure to butadiene and equivalent concentrations of either 1-butene or cis-2-butene had no measurable effect on the butadiene response, but an increase in response was observed with increases in the concentrations of these co-contaminants. For trans-2-butene and isobutylene, significant interference was observed only at concentrations several times that of butadiene. As with vinyl chloride, responses to butadiene and the butene isomers are roughly additive. From a practical standpoint, since butadiene is invariably present in much higher concentrations than the butenes in the butadiene production stream, the likelihood of their causing significant interference with butadiene exposure measurements is quite low.

Acrylonitrile caused a progressive enhancement in response above about 2 ppm and styrene caused a progressive suppression at concentrations above 1 ppm. Although these interferences are of some concern, as with the co-contaminants encountered in butadiene production processes, concentrations of styrene and acrylonitrile are lower than that of butadiene in most copolymerization reaction formulations.[36] Releases from reactor vessels would therefore also be rich in butadiene. Available data on styrene-butadiene production facilities confirm that the average styrene concentration is less than that of butadiene in the workplace environment.[42] Thus, in practice the interferences from these compounds are likely to be minimal.

The presence of higher styrene concentrations could be detected by the use of a simple two-sensor array: one coated with the 1-hexene complex and one coated with the ethylene complex. From Table IV it is seen that up to a styrene:butadiene concentration ratio of five or more, the 1-hexene complex still gives a positive frequency shift which reflects the presence of butadiene. Although butadiene progressively reduces the response to styrene using a coating of the ethylene complex,[21] the response to styrene predominates when the butadiene concentration is relatively lower. Therefore, when styrene is present in excess, there will be a negative fequency shift observed from the sensor coated with the ethylene complex, while if styrene is not present there will be no response from this sensor because it does not respond to butadiene alone.

Another approach to the styrene interference problem was also investigated. Previous results had shown that styrene would not react with the reagent trans-$PtCl_2$(ethylene)(2,6-dimethylpyridine) because of steric hindrance.[22] It was thought that the interference from styrene here might be reduced or eliminated by use of the more hindered reagent trans-$PtCl_2$(1-hexene)(2,6-dimethylpyridine) as the sensor coating. Figure 4 shows the responses for separate exposures to butadiene and styrene using this reagent coating. The sensitivity to butadiene is lower than that observed for the less hindered trans-$PtCl_2$(1-hexene)(pyridine) but it is still quite good (0.023 Hz/ppb-min). No response was observed with styrene even at concentrations as high as 150 ppm. Thus, it appears that the styrene is effectively precluded from reaction by steric hindrance. Unfortunately, co-exposure to butadiene and styrene still resulted in a reduction in the butadiene response: apparently, as described above, styrene can enter into the coordination sphere of the Pt even though no net displacement of 1-hexene occurs. It was also found that the trans-$PtCl_2$(1-hexene)(2,6-dimethylpyridine) complex could not be regenerated following butadiene exposure.

Humidity and Temperature Effects. The response to butadiene using trans-$PtCl_2$(1-hexene)(pyridine) was then examined at relative humidities (RH) ranging from 5-80%. As shown in Table V, there was no effect on the sensor response. This in accordance with experimental evidence of an associative pathway for olefin-substitution reactions with this class of reagents,[28] but is in contrast to results obtained for reaction of styrene with the ethylene complex which showed a two-fold increase in response over this range of RH.[21] It was postulated in that study that the adsorbed water was facilitating the diffusion of the styrene into the reagent or possibily stabilizing the transition state of the reaction. That this effect is not seen for butadiene follows from its low water solubility, higher diffusion rate into the reagent and higher reaction rate: the molar reaction rate of butadiene with the 1-hexene complex at 25°C is about 15 times that of styrene with the ethylene complex.

Perhaps the most surprising result obtained in this study is the lack of a strong temperature dependence. The response to butadiene is independent of temperature from 25-35°C, increasing somewhat at 42°C (Table VI). This behavior is quite different from the Arrhenius temperature dependence observed previously with sensor coatings of the ethylene complex exposed to each of several olefins.[20,22,28] If the interaction between butadiene and the reagent were limited by the diffusion rate of either the butadiene or 1-hexene through the reagent, alone, or by the rate of the substitution reaction, then an Arrhenius temperature dependence would be expected. The reason why this is not observed is not completely clear. While the increase in temperature would necessarily increase the diffusion and reaction rates of butadiene, the effects of this would be offset by similar increases in the diffusion and reaction rates of the free 1-hexene. The nature of the temperature effect also supports the notion of some conformational dependence for the reaction. The increase in response occurs at a temperature just above the melting point of the 1-hexene complex. Although the complex appears to be amorphous by microsopic examination of the coating films, there is likely to be some degree of short-range order within the domains of the reagent that is disrupted above the 40°C melting point.

Sensor Operating Frequency. According to eq 3, the mass sensitivity of the SAW sensor should increase as the square of the operating frequency, f_o. This, in turn, should lead to an increase in sensitivity toward butadiene when using reagent coatings, such as those used here, where interfacial coating-analyte interactions prevail.[22] This is in contrast to what occurs for bulk vapor sorption in polymer-coated SAW sensors. In the latter case, responses are described by eq 2 and increases of f_o do not necessarily lead to increases in sensitivity because for a given value of Δf_c the amount of polymer coating on the sensor varies inversely with f_o.[43] Figure 5 compares the responses to butadiene for the 30-MHz and 60-MHz devices coated with 1-hexene complex. The average response ratio was 4.2 ± 0.1 which agrees very well with the theoretical ratio of 4.0. Interestingly, we saw no increase in the baseline noise level with the higher frequency device. Using the 60-MHz sensor a limit of detection of 24 ppb is calculated for butadiene. Testing was also performed using the 60-MHz device coated with freshly prepared samples of the 1-octene complex and an LOD of 12 ppb was obtained, which is also about four times lower than that determined for the 30-MHz sensor with this coating.

CONCLUDING REMARKS

Through the combination of a high reaction rate and a mass-amplifying 2-for-1 ligand exchange process, highly sensitive measurement of butadiene gas has been achieved using a SAW sensor coated with trans-$PtCl_2$(1-hexene)(pyridine). The ability to adjust the sensitivity and selectivity through changes in the Pt ligands has also been demonstrated.

Several practical advantages can be cited for this approach to butadiene measurement. High sensitivity is obtained at relatively low sensor operating frequencies which simplifies circuit design and radio-frequency shielding requirements. While the detection limits obtained using a 30-MHz sensor are adequate for monitoring butadiene in the range of the recently proposed occupational exposure limit of 2 ppm, the sensitivity can be further increased by increasing the sensor operating frequency: data collected using a 60-MHz sensor confirm that the sensitivity increases as the square of the operating frequency, consistent with theoretical expectations. Since SAW devices operating at several hundred MHz can be fabricated, detection of sub-ppb concentrations of butadiene appears feasible.

The sensor response is independent of relative humidity, which obviates the need to monitor and compensate for changes in ambient water vapor concentrations. The sensor response is also independent of temperature in the range of 25-35°C and while some degree of temperature control is still needed to avoid thermal drift in the SAW oscillator frequency, maintaining an exact set point is not necessary as is the case with polymer coatings or other reagent coatings whose interactions with gases and vapors are strongly temperature dependent. The coating reagent is easy to synthesis and stable in air for several months. In addition, the sensor response is independent of the amount of coating deposited on the surface. Thus, tolerance limits on coating application procedures are relaxed.

A high degree of selectivity for butadiene is obtained in the presence of many potential co-contaminants found in the industrial environment with butadiene. Most non-olefin gases and vapors do not interfere at all with the response to butadiene and although responses to several olefins are observed they interfere with the butadiene response only at higher relative concentrations. Since butadiene is the major component of industrial process mixtures, these should not pose a significant problem in attempting to quantify butadiene concentrations in most practical situations.

The primary limitation of this approach is the service life of the reagent. Although several hours of operation are possible at concentrations below 1 ppm, the effective service life progressively declines as the butadiene concentration increases. The reagent can be regenerated rapidly and repeatedly, however, by brief in situ exposure to 1-hexene vapor. In practice, one could simply monitor the total frequency shift over time and initiate a regeneration cycle periodically to maintain the response characteristics of the sensor. Work is currently underway on a prototype instrument that incorporates this operating feature.

ACKNOWLEDGMENT

The authors would like to express there sincere appreciation to Dr. Tin Su Pan for writing the data aquisition software used in this study, Dr. Arthur Snow for providing a sample of poly(ethylene maleate), Ms. Terry Hull for assistance in the fabrication of SAW devices and Mr. Ron Hartica for assistance in the electrical characterization of the 60-MHz SAW devices. This work was funded by Grant No. R01-OH02663 from the National Institute for Occupational Safety and Health of the Centers for Disease Control.

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Table I. Melting Points and Elemental Analyses of Reagents and Products.

olefin[a]	amine[a]	m.p. °C	Calc. C%	Calc. H%	Anal. C%	Anal. H%
ethylene	pyridine	113	22.53	2.43	22.50	2.50
1-butene	pyridine	106	26.94	3.27	26.77	3.33
1-hexene	pyridine	40	30.77	3.99	30.58	3.99
1-octene	pyridine	---[b]	34.14	4.63	34.15	4.77
1-hexene	4-chloropyridine	---[b]	28.49	3.48	28.75	3.58
1-hexene	4-methylpyridine	---[b]	32.51	4.32	32.78	4.37
1-hexene	2,6-dimethylpyridine	---[b]	34.14	4.63	34.27	4.92
(1,3-butadiene)[(PtCl$_2$)(pyridine)]$_2$[c]		134	22.59	2.17	23.09	2.23
(1,3-butadiene)[(PtCl$_2$)(pyridine)]$_2$[d]		134	22.59	2.17	22.89	2.17

[a] these compounds have the general formula trans-PtCl$_2$(olefin)(amine).

[b] not determined

[c] synthesized from PtCl$_2$(1-hexene)(pyridine)

[d] synthesized from PtCl$_2$(ethylene)(pyridine)[21]

Table II. Regeneration following exhaustive exposure to butadiene.

Δf_c (kHz)	46.5	101.5	205.2
mass of reagent (μg, from eq 1)	17.8	38.8	78.4
Calc. Δf for 2:1 complex (Hz)	3095	6750	13646
Exper. Δf_a (Hz)[a]	3081 (37)[c]	7076 (158)	12891 (310)
Exper. Δf_a (Hz)[b]	-3095 (44)	-7185 (92)	-12935 (337)
% difference[d]	0.2	-6	-5

[a] net frequency shift for exhaustive butadiene exposure.
[b] net frequency shift for regeneration with 1-hexene.
[c] values in parentheses are standard deviations (n = 3).
[d] calculated as [(Exper. Δf - Calc. Δf)/Calc Δf] x 100, where Exper. Δf_a is the average absolute Δf_a of the exposure and regeneration cycles.

Table III. Multiple regenerations of $PtCl_2$(1-hexene)(pyridine) following repeated exposure to 500 ppb of butadiene.

regeneration cycle	mean response (s.d.) Hz/min[a]
0 (fresh coating)	16 (1)
1	16 (1)
2	15 (1)
3	16 (2)
4	15 (1)
5	15 (1)

[a] based on butadiene exposures of about 75 minutes for each cycle. Regeneration cycle involved a 5-min exposure to about 800 ppm of 1-hexene.

Table IV. Responses for co-exposure to 900 ppb of butadiene and each of several co-contaminants.

co-contaminants	concentration ppm	mean response (s.d.) Hz/min
------	----	28 (1)
butane	2300	27 (2)
ethanol	900	29 (2)
dichloromethane	1300	27 (2)
acetone	1000	29 (1)
benzene	1100	29 (2)
hexane	1500	27 (1)
acetonitrile	55	24 (1)
	180	23 (2)
	260	24 (2)
vinylidine chloride	1100	27 (1)
vinyl chloride	30	29 (2)
	95	35 (2)
	250	39 (2)
2-chloroprene	20	27 (2)
	35	28 (2)
1-butene	0.9	28 (1)
	1.3	34 (2)
	3.2	45 (3)
cis-2-butene	0.9	29 (2)
	1.3	34 (1)
trans-2-butene	0.9	28 (2)
	1.3	29 (1)
	3.2	32 (1)
isobutylene	5	29 (1)
	9	29 (2)
	48	35 (2)
	100	39 (2)
acrylonitrile	2	33 (2)
	6	38 (2)
styrene	1	27 (1)
	2	25 (2)
	5	19 (3)

Table V. Humidity Effects[a]

RH (%)	mean response (s.d.) Hz/min
5	21 (1)
20	23 (2)
40	22 (2)
60	21 (1)
80	20 (2)

[a] Butadiene concentration = 750 ppb. Based on a 15-20 min exposure at each RH level.

Table VI. Response to butadiene as a function of temperature.

	butadiene concentration (ppb)			
T(°C)	500	750	1500	2500
25	16 (1)	23 (1)	41 (3)	79 (5)
30	16 (0)	22 (1)	45 (1)	84 (2)
35	17 (2)	24 (1)	43 (2)	82 (2)
42	23 (3)	32 (3)	55 (3)	89 (3)

[a] Responses are in Hz/min (s.d.). Duplicate tests were performed at each temperature except 42°C where n=4.

Figure Captions

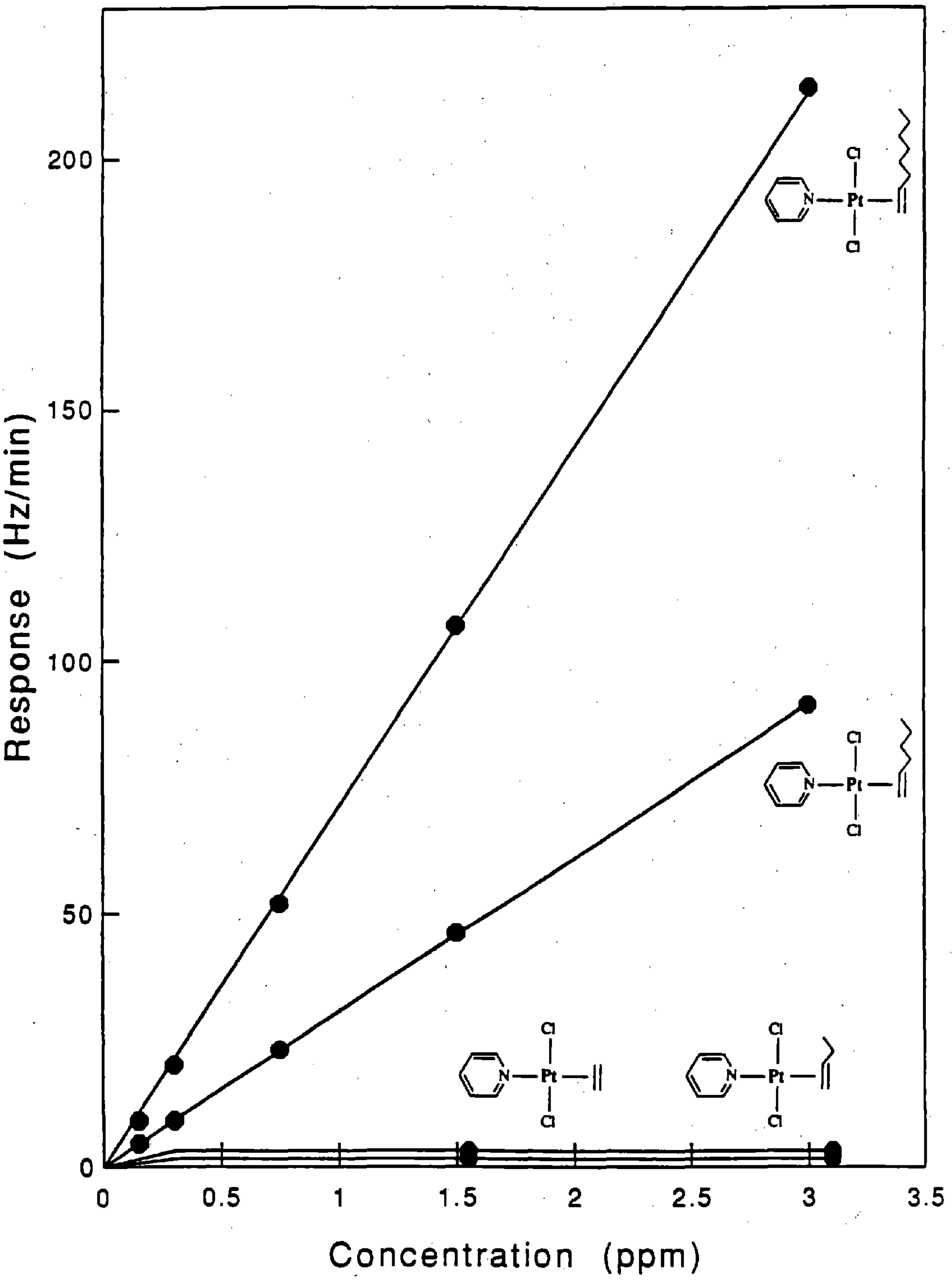
Figure 1. Sensor response to butadiene using a series of $PtCl_2(OL)(pyridine)$ coatings (OL = ethylene, 1-butene, 1-hexene and 1-octene).

Figure 2. Sensor response to butadiene as a function of the 4-substituents on the pyridine ligand in $PtCl_2$(1-hexene)(4-X-pyridine) (X = H, CH_3, Cl).

Figure 3. Frequency vs. time curve for exhaustive exposure to 750 ppb of butadiene.

Figure 4. Responses to butadiene and styrene using $PtCl_2$(1-hexene)(2,6-dimethylpyridine) coating.

Figure 5. Responses to butadiene using $PtCl_2$(1-hexene)(pyridine) coatings on 30-MHz and 60-MHz SAW devices.



Response (Hz/min)
0
50
100
150
200
Concentration (ppm)
0
0.5
1
1.5
2
2.5
3
3.5
Cl
N
Pt
Cl

Figure 1

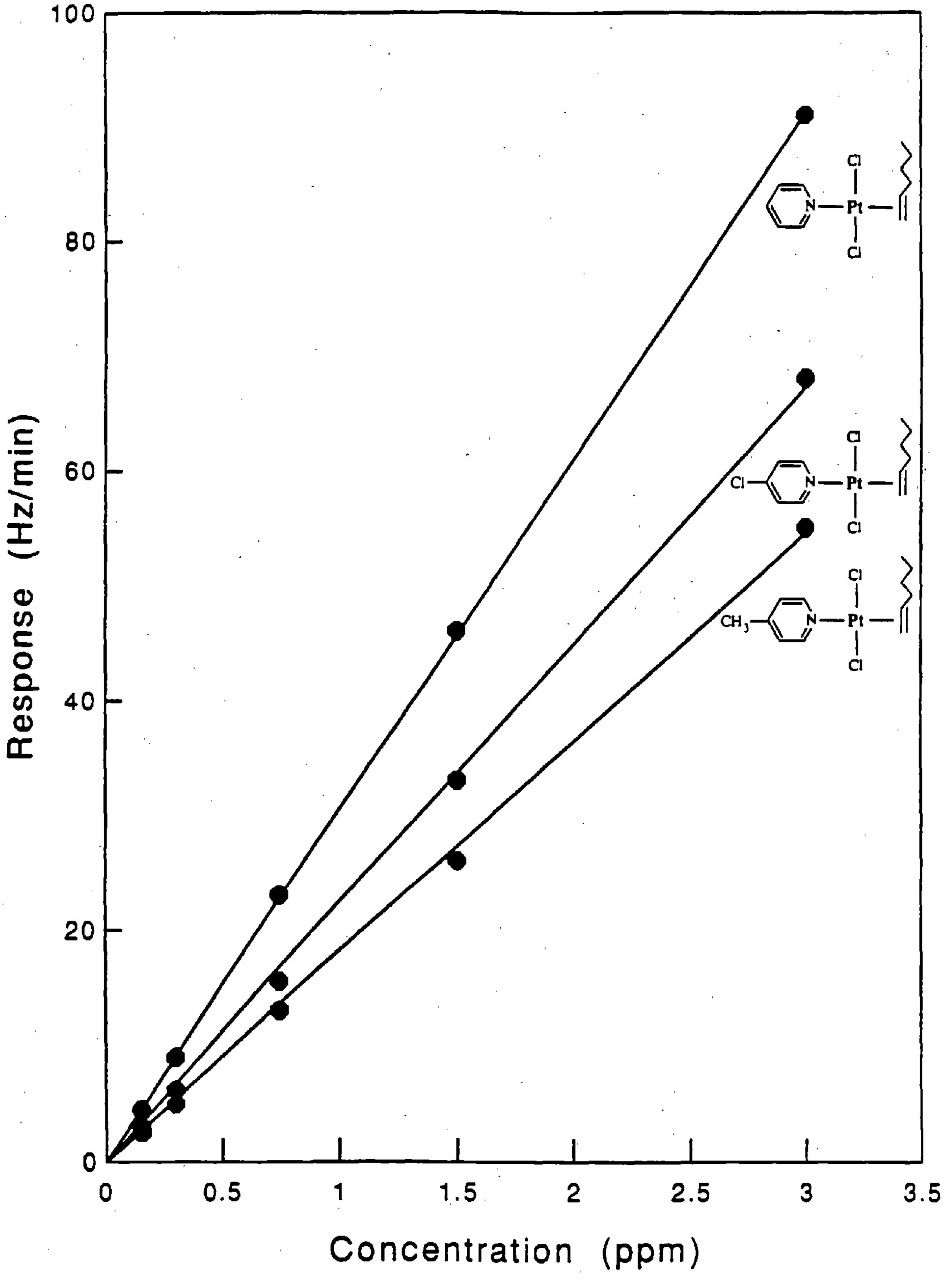

100
80
60
40
20
0
Response (Hz/min)
0
0.5
1
1.5
2
2.5
3
3.5
Concentration (ppm)
Cl
N
Pt
Cl
Cl
Cl
N
Pt
Cl
Cl
CH3
N
Pt
Cl

Figure 2

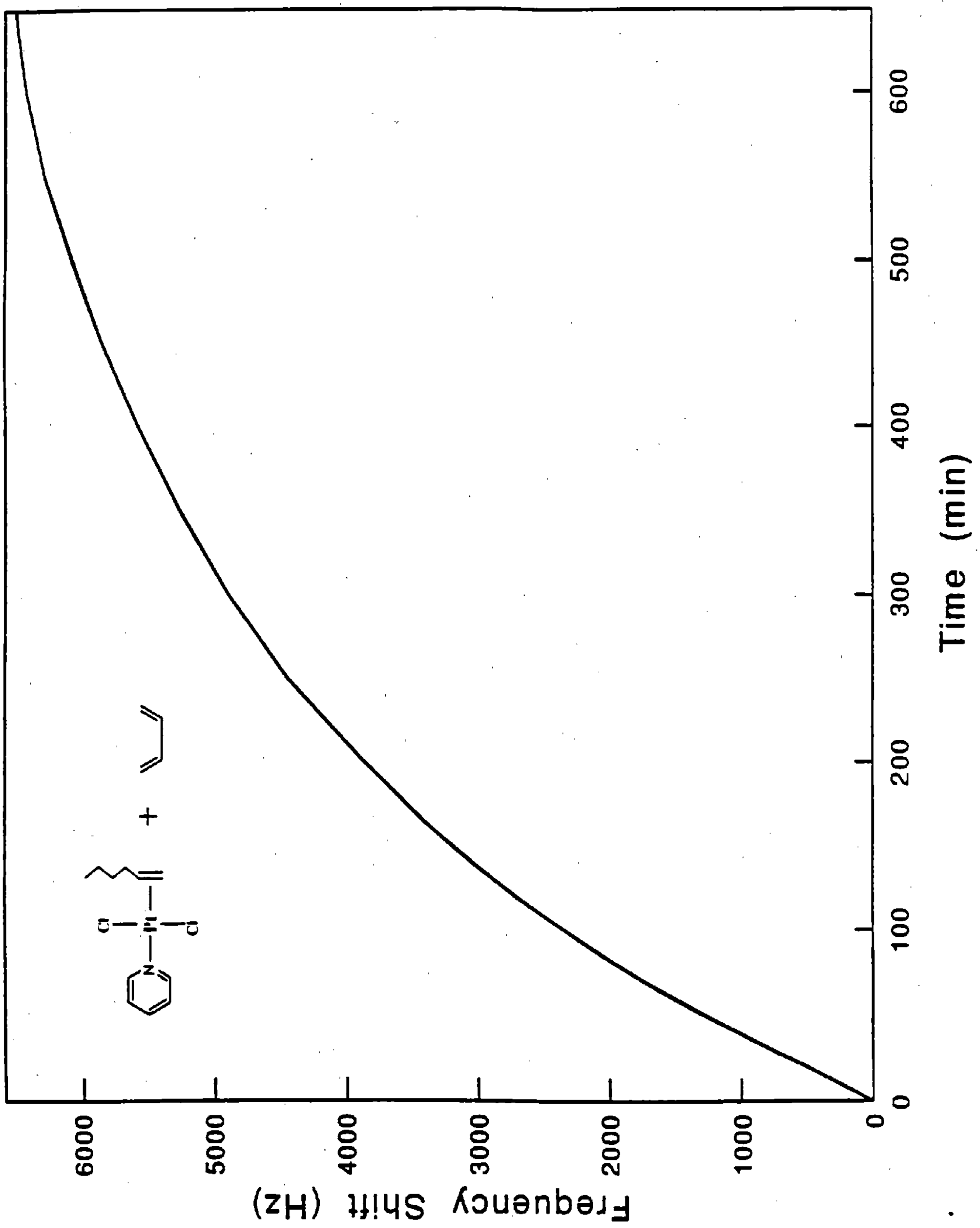

Frequency Shift (Hz)
0
1000
2000
3000
4000
5000
6000
Time (min)
0
100
200
300
400
500
600
Cl
Cl
N
+

Figure 3

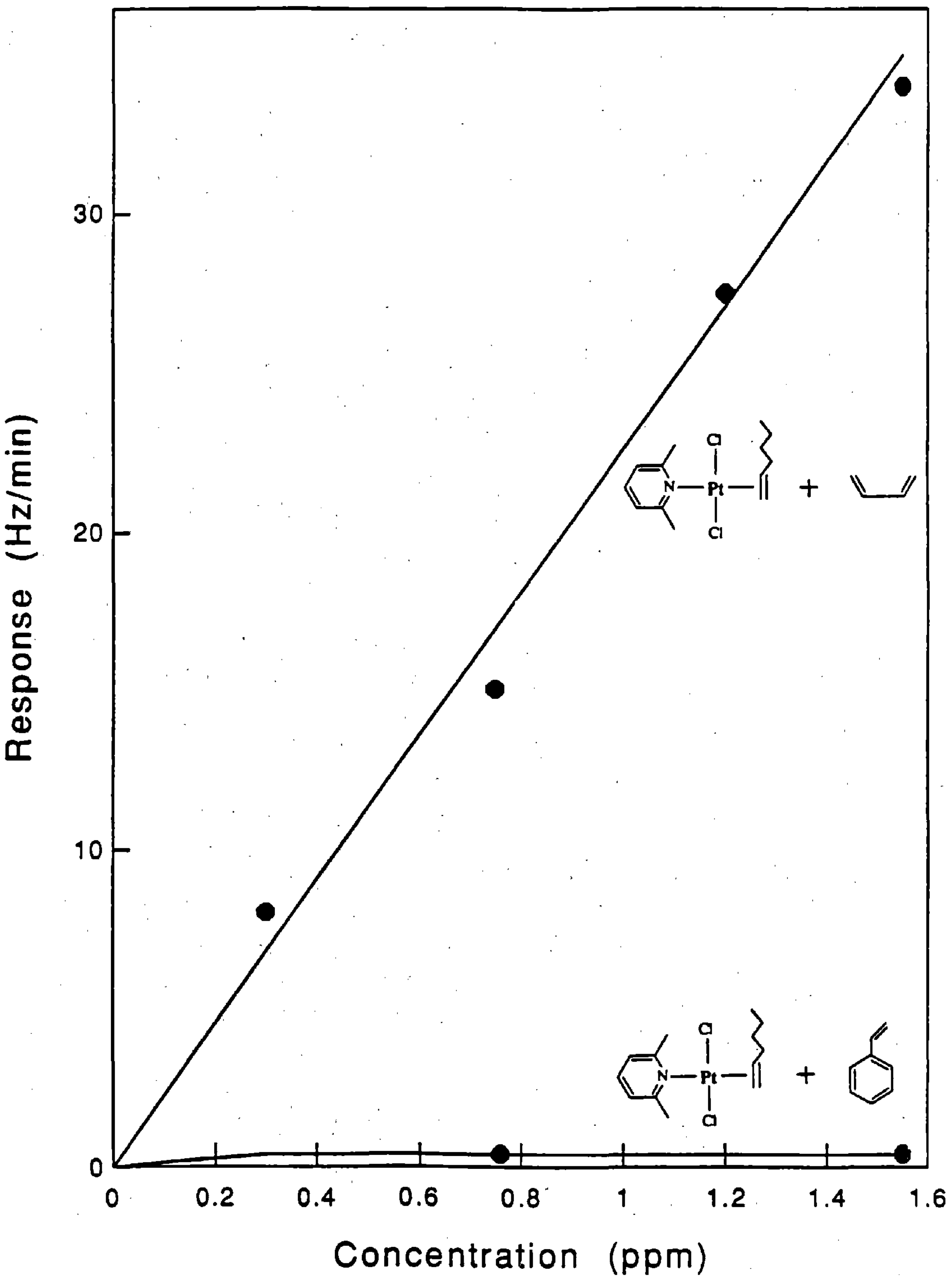

Response (Hz/min)
0
10
20
30
Concentration (ppm)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Cl
N
Pt
Cl
+
Cl
N
Pt
Cl
+

Figure 4

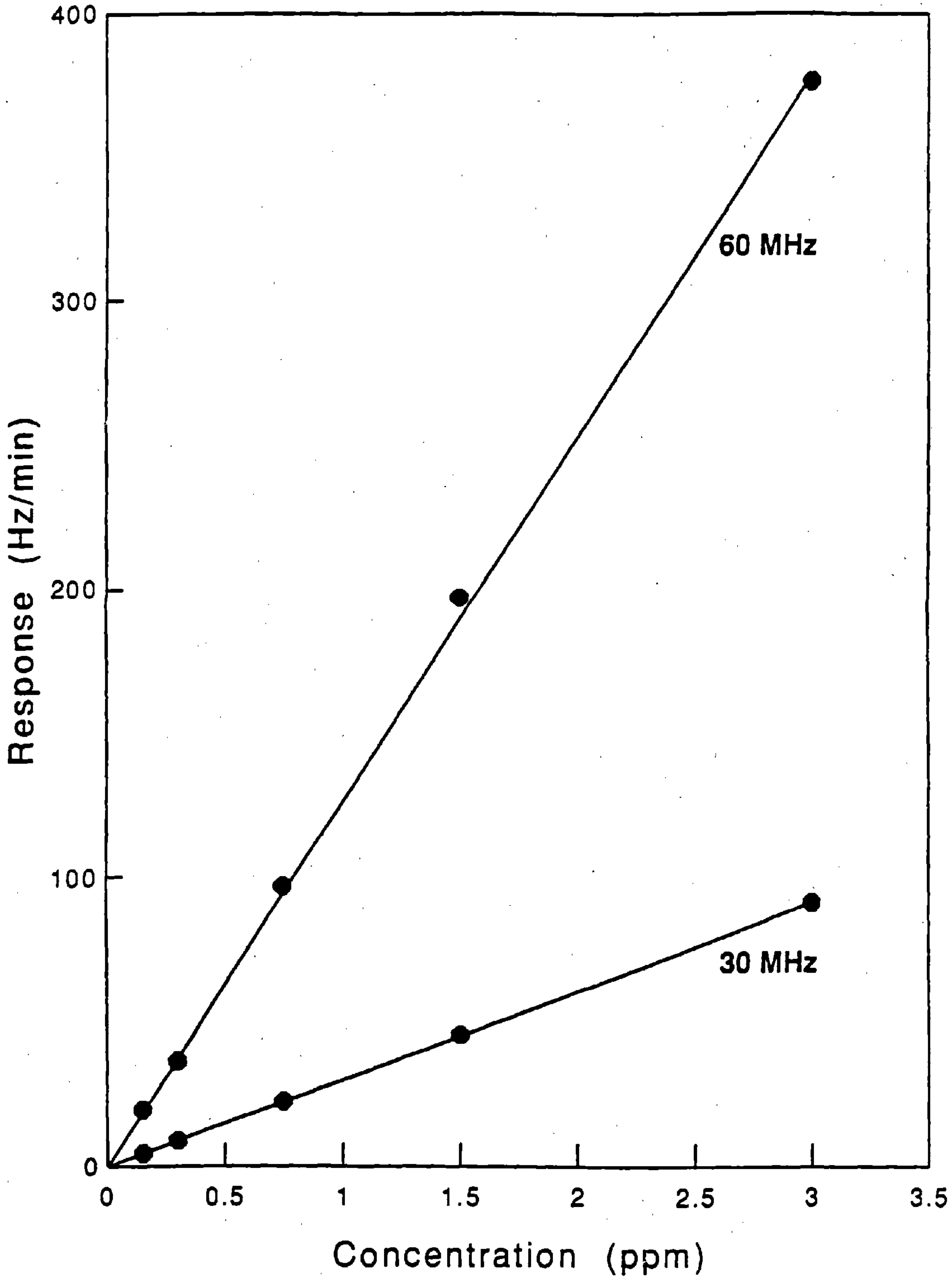

400
300
200
100
0
Response (Hz/min)
0
0.5
1
1.5
2
2.5
3
3.5
Concentration (ppm)
60 MHz
30 MHz

Figure 5

CHAPTER 6

Design and Preliminary Testing of a Prototype Field Instrument for Monitoring Olefin and Diene Air Concentrations

Abstract

The design and operation of a portable prototype instrument employing two 60-MHz SAW sensors is described, along with preliminary results of laboratory performance testing. Results obtained to date demonstrate the capability for real-time measurement of 1,3-butadiene gas at low- and sub-ppm concentrations with the instrument. Repeated in-situ regeneration of the reagent used as the SAW sensor coating has also been performed automatically. Response data are displayed on the readout panel of the instrument and stored for the purpose of documenting air concentration profiles over time.

INTRODUCTION

The instrument described in this chapter has been designed for use with SAW sensors employing the coatings described in the preceding chapters. It is intended to serve as a protoype to determine whether the capabilities of the sensors demonstrated in the preceding chapters can be realized in a field-deployable instrument. The instrument has been constructed and preliminary testing has been performed to demonstrate certain functions. Testing is still in progress and will be completed in the near future.

INSTRUMENT DESCRIPTION AND PRELIMINARY TESTING

General Description

The instrument was constructed in collaboration with researchers at Microsensor Systems, Inc. (Bowling Green, KY) according to our design specifications. It has overall dimensions of 13.5" x 8.5" x 5.7" and weighs about 2 lbs. Two matched 60-MHz SAW oscillators, which were fabricated at the University of Michigan Microfabrication Laboratory, are utilized (see Chapter 5 for description). The instrument incorporates an Intel 8052AH microcomputer which is used to control valve sequencing and the collection, display, processing and storage of sensor response data. The instrument can be powered externally or with the on-board 6V (8 amp-hr) rechargeble battery pack.

The front panel consists of an LCD digital readout and a keypad for selecting functions. The back panel contains an RS-232 communications port and several pneumatic connection ports for sample handling. Figure 1 provides a diagram of the back panel. A carrying strap on the outside of the instrument chassis facilitates transport.

Within the instrument, the sensors are housed in a stainless-steel chamber having outer dimensions of 3.5" x 2.5" x 0.5" and an internal volume of approximately 4 cm^3. The chamber was constructed in-house. Electrical connections are made via integrated-circuit (IC) pins inserted through the floor of the chamber. The pins are held in place and electrically isolated from the chamber using Delrin^R cylinders that were press-fitted through clearance holes drilled in the chamber floor. The chamber can be reversibly plugged into a set of IC sockets arranged on a PC board within the instrument. The sensors are situated in parallel on the floor of the chamber and connected to the IC pins using low-temperature solder.

The top cover of the chamber is equipped with machined inlet and outlet fittings to permit gas flow over the sensors. The top and bottom sections of the chamber are sealed with a Teflon^R gasket and clamped together with a set of six bolts. All gas handling components of the instrument are constructed of Teflon^R or stainless steel. Three Teflon^R solenoid valves are used to direct air flow to the sensor chamber. Air flow is provided by a small diaphragm pump capable of producing air flows of 200 cm^3/min through the system.

Pneumatic system

The instrument operates in three different modes, depending on the function desired. Each mode has a configuration of valve settings and corresponding flow paths. These are illustrated in Figures 2-4. In Baseline Mode (Fig. 2), valve 1 is in the "on" position and valves 2 and 3 are "off". In Sampling Mode (Fig. 3), valves 1-3 will all be in the "off" position. In Regeneration Mode (Fig. 4), valves 1-3 are in the "on" position.

An activated carbon scrubber, mounted on the outside of the instrument, is used to filter the incoming air in Baseline Mode. During Sample Mode, air is drawn directly through the sensor chamber. During Regeneration Mode, air is passed over the regenerating chemical reservoir and then to the sensor chamber. The regeneration chemical is either 1-hexene or ethylene. For the 1-hexene, a small vial containing an absorbent filter material soaked in the liquid is used. Filtered air flows directly over this source, becomes saturated with the vapor, and then passes to the sensor chamber. The exhaust then passes through another filter before returning to the pump. For the case of regeneration with ethylene gas, a regulated lecture bottle will be used as the source. Future models of the instrument will require a smaller source, which can be housed within the instrument chassis.

Temperature control and monitoring

A resistive heater has been mounted in a recessed cavity on the bottom of the sensor chamber. The heater is capable of reaching 65°C (nominal) and to bring the surface temperature of the sensors to as high as 40°C. The heater is operated continuously while the instrument is on. The actual sensor temperature can be reduced by elevating the sensor above the chamber floor slightly, for example, by inserting thermally insulating polymer sheets beneath the sensors (note: the sensor will operate at a fixed temperature for a given analyte). This approach has been used to reduce the sensor temperature to 25°C for the 1,3-butadiene exposure testing described below. A thermocouple has been mounted to a pair of IC pins within the sensor chamber, with the sensing element resting on the surface of one of the sensors. Temperature readings are made with a voltmeter connected to the external terminals of the IC pins (note: the voltmeter will not be necessary after initial laboratory testing). The combination of a precision heater and continuous flow over the sensors results in a constant sensor temperature, as evidenced by near-zero baseline drifts over time. Operation at elevated temperatures is currently being examined.

Software

The microcomputer controls all instrument functions. Software has been written in MCS-52 BASIC to implement the collection, display, storage, and output of data and the switching of valves for each of the three operating modes. The duration of each mode is selectable at the start of run. All experiments to date have been performed via direct interface with a personal computer, but the capability for control from the on-board keypad has been included in the software routines. Ultimately, the final program will be stored in the instrument's EPROM and all options and commands will be input through the instrument keypad. The capability for converting frequency signals to air concentrations has also been incorporated into the software program. The calibration equation corresponding to a given target analyte at a given sensor operating temperature can be selected at the start of a run. There is sufficient memory available for storage of 1-min concentration readings over the course of an 8-hr period. The ability to store and retrieve such a large data set has not yet been fully verified.

Signal processing

Signals from the sensors are passed through feedback oscillation circuitry on the PC board underlying the sensor chamber. Frequency signals are tapped from this circuit and passed to a radio-frequency signal processing module on a separate board within the instrument. This module collects the frequency signals from each sensor and employs a mixer and low-pass filter to obtain a difference frequency, which is then read by a frequency counter. The measured rate of frequency change can be sampled and displayed every four seconds along with the corresponding air concentration in parts-per-million. The net 1-min frequency readings (or air concentrations) are stored and can also be displayed. These data can be subsequently retrieved by uploading to a personal computer (via the RS-232 interface) in order to construct retrospective profiles of air concentrations versus time.

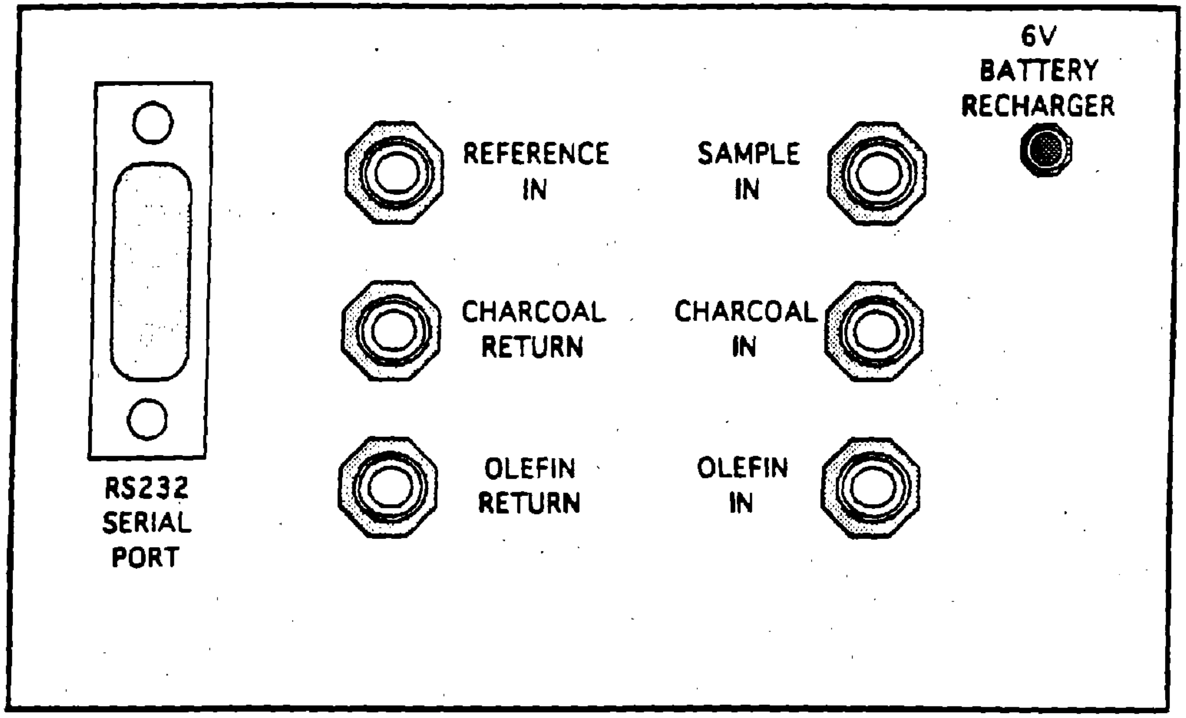
Preliminary performance testing

The instrument has been successfully tested for execution of all modes of operation and repeated cycling through these modes. All gas flows and switching cycles have been verified. Data collection, transfer, and display functions have been verified also.

Initial exposure tests have been performed using 1,3-butadiene as the test analyte and coatings of $PtCl_2$(1-hexene)(pyridine) dispersed in poly(isobutylene) on the working sensor at 25°C. The reference sensor has been coated with a thin film of poly(isobutylene) to cancel any possible responses due to reversible polymer sorption of potential vapor interferents (see Chapter 5). Responses are comparable to those obtained in previous tests. Multiple exposure/regeneration cycles have been performed successfully. Testing of responses time, sensitivity, selectivity, ambient temperature and humidity effects, and dynamic range are currently in progress. Similar testing will be performed for styrene and ethyl acrylate using the $PtCl_2$(ethylene)(pyridine) coating.

CONCLUDING REMARKS

Results obtained to date on the operation of the portable SAW-sensor based instrument support the feasibility of this approach to monitoring olefins and dienes in real time. The successful completion of the laboratory validation phase of the project will permit an extension of this research on SAW sensor technology to field tests of instrument performance in actual working environments.


6V
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RS232
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Figure 1

BASELINE MODE

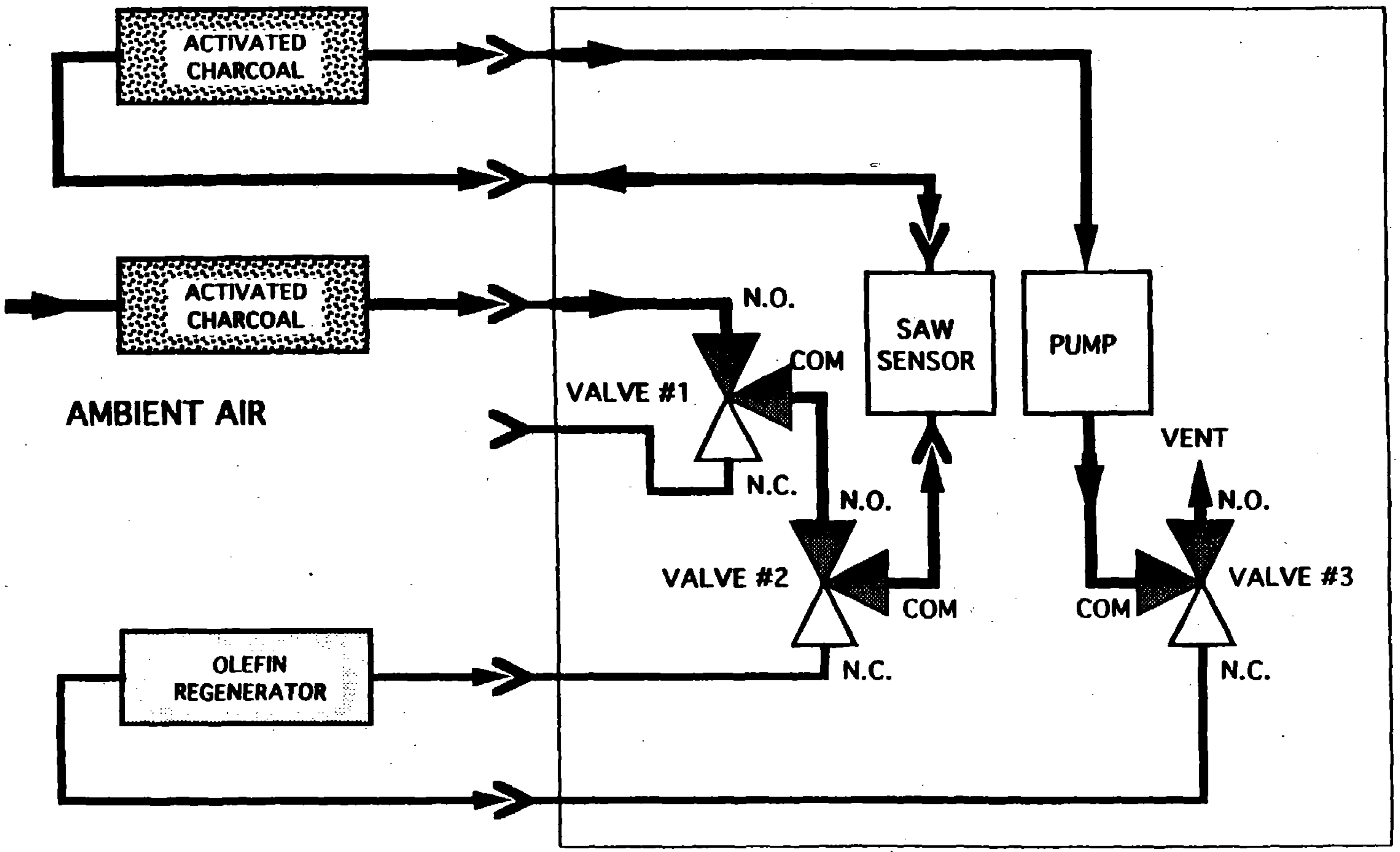

Figure 2

SAMPLE MODE

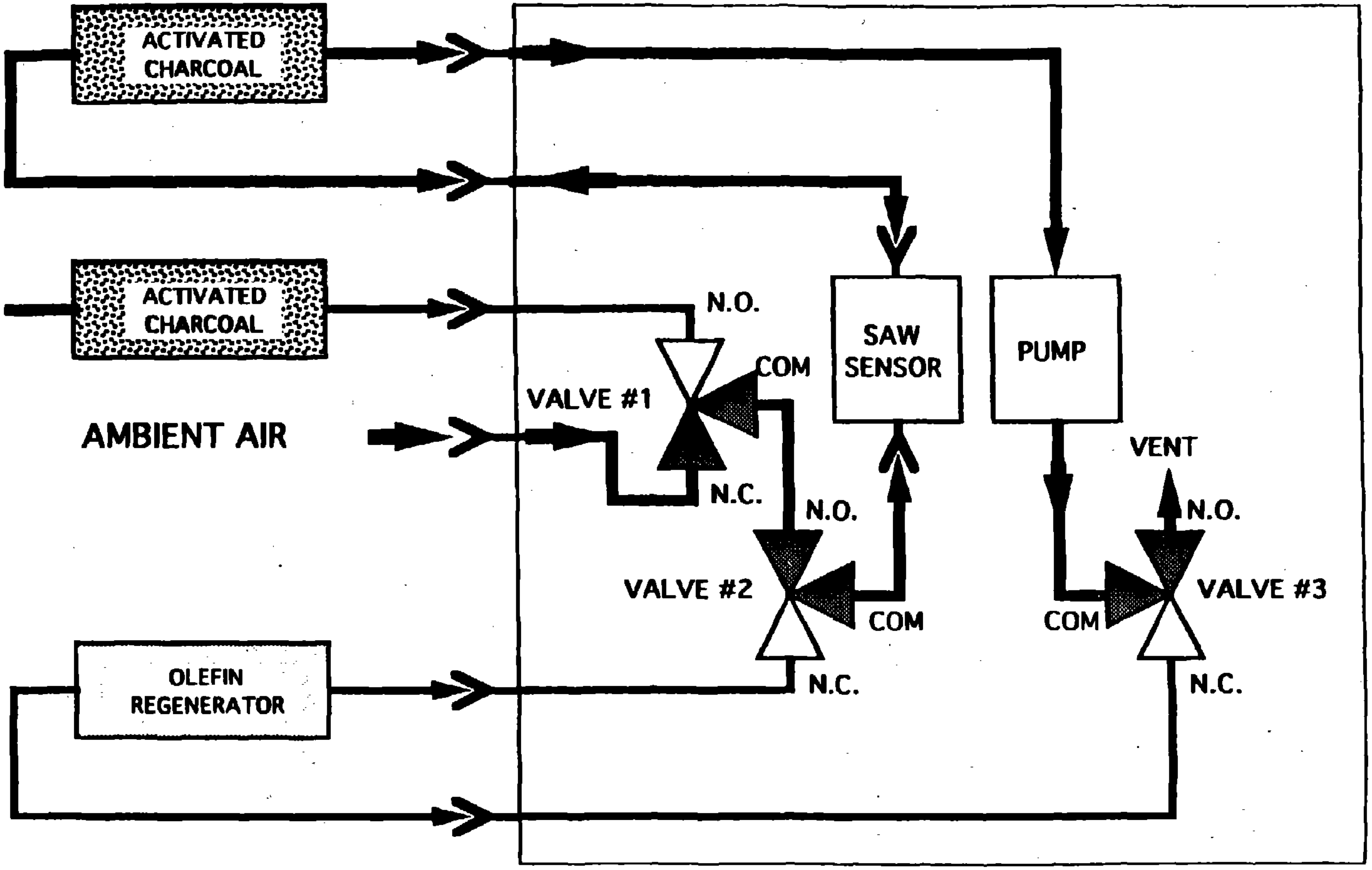

Figure 3

REGENERATE MODE

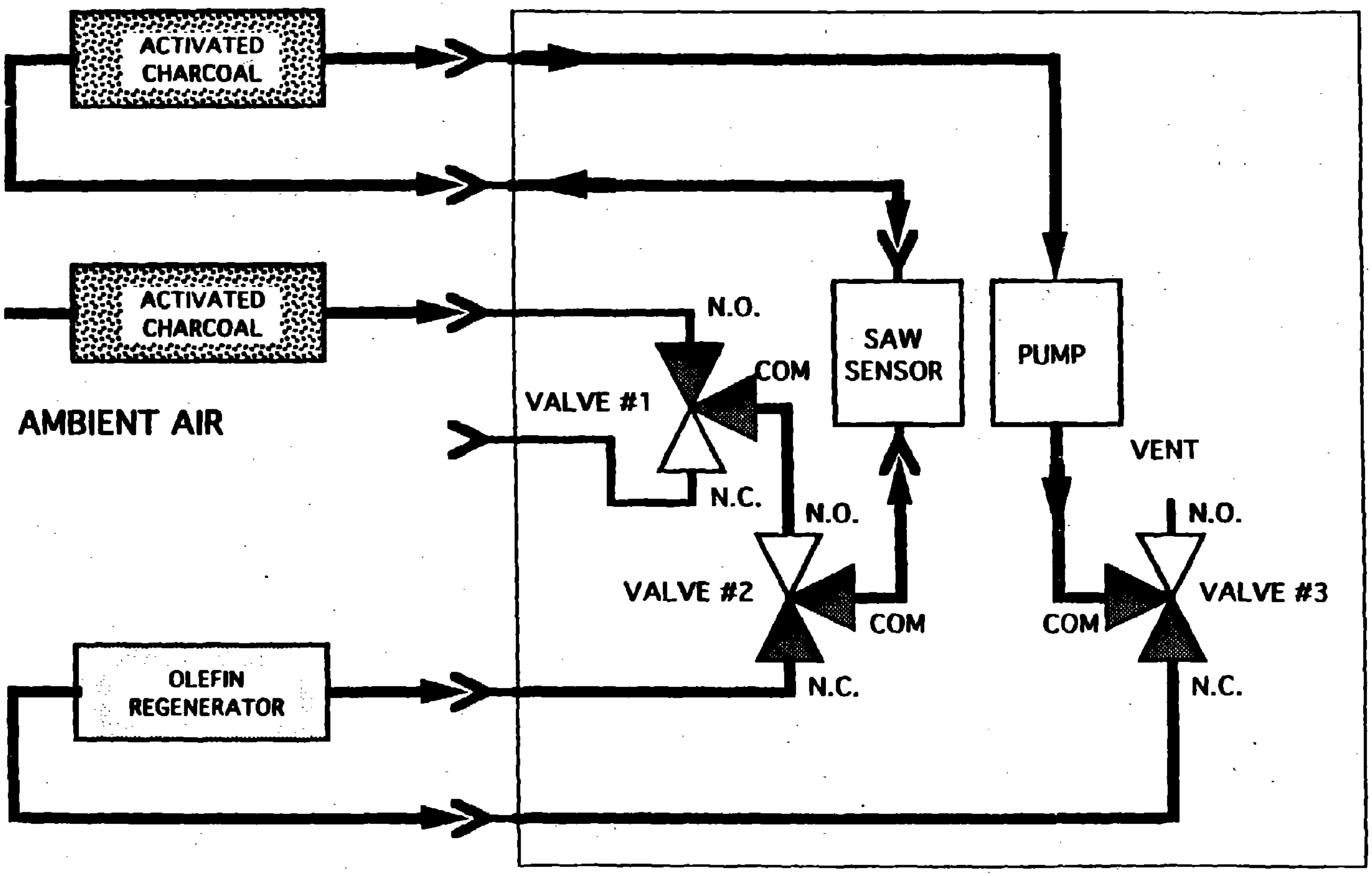

Figure 4