

Micropatterned Polymeric Gratings as Chemoresponsive Volatile Organic Compound Sensors: Implications for Analyte Detection and Identification via Diffraction-Based Sensor Arrays

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Micropatterned polymeric diffraction gratings have been fabricated and evaluated as volatile organic chemical sensors. When operated under nonresonant conditions, sensor elements were found to respond in a rapid (response time 5–15 s) and reproducible fashion to each analyte investigated. Relative response magnitudes were found to be in qualitative agreement with those obtained via surface acoustic wave techniques. Preliminary limits of detection as determined by investigations with micropatterned polyepichlorohydrin, polyisobutylene, and polybutadiene gratings, respectively, were found to be 8, 11, and 7 ppm for toluene, 25, 258; and 72 ppm for methyl ethyl ketone; 41, 102, and 34 ppm for chloroform; and 460, 60, and 59 ppm for hexane. While generally less than 1 order of magnitude higher than those observed for identical polymer/analyte combinations in SAW studies, the observed limits of detection were at or below governmental standards (OSHA-PEL and NIOSH-REL) for each analyte evaluated. These diffraction-based sensors show promise for integration into an array-based sensor system, providing simultaneous identification and quantification of unknown analytes and simple analyte mixtures.

The design of chemical and biological sensors to detect analytes in both atmospheric and aquatic environments is of obvious interest for reasons of human health and environmental quality. To this end, there are two distinct considerations that must be addressed in the design of appropriate sensing methodologies. The first is that target molecules must be localized into or onto the sensing framework by either chemical or physical means, including but not limited to covalent, ionic, van der Waals, or hydrogen-bonding interactions with a “receptor” medium. The second is that these binding events must be converted into an externally observable signal. After initial sensor design, further developments of viable systems must address considerations such as appropriate limits of detection, dynamic range, and time response before gaining practical utility.

Recently, a new transduction methodology based upon analyte modulation of the intensity of diffracted light produced by

micropatterned receptor platforms has been reported.^{1–6} Micropatterning of a “receptor” material, regardless of atomic or molecular structure, into a periodic array on the length scale of the wavelength of visible light results in the creation of a visible-region diffraction grating. This occurs because of a periodic contrast in the index of refraction between the patterned lattice and the surrounding media, typically air or water. If the lattice specifically or nonspecifically interacts with a target analyte, either adsorbing onto the surface or internalizing within the lattice, the refractive index contrast will change, resulting in a measurable modulation in the diffracted light intensity. This transduction mechanism has successfully been demonstrated in the sensing of various volatile organic compounds^{2,4,5} as well as aqueous phase metal ions.⁵ Additionally, we have introduced a strategy by which large signal amplification can be achieved by fabricating gratings from materials displaying dynamic absorption behavior at wavelengths coincident with the diffraction measurement probe wavelength.² This advance also supplies some degree of chemical specificity, because not all signals are amplified equally.

More generally, there are two approaches by which chemically selective sensing can be achieved. The first relies upon the synthesis of specific receptor molecules designed to bind or ligate the desired analyte selectively. This approach has yielded extremely selective sensors that display measurable responses only in the presence of the specific chemical or biochemical target for which they are designed. Moreover, if the analyte/receptor binding constant is large, low detection limits can be achieved. However, the specific-receptor approach often entails tedious or difficult synthetic chemistry, and the resulting sensor is limited in applicability to a single analyte or family of analytes.

The second approach makes use of multiple sensor elements, each displaying broad responsiveness, but with differing degrees of response to any one analyte. The responses from an array of

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these moderately selective sensors can then be analyzed collectively via pattern recognition techniques, allowing for the identity of an unknown target to be determined.⁷ We have focused on the second approach here.

A general class of materials amenable to the diffraction methodology and fitting the outlined sensitivity and selectivity requirements are polymeric materials.⁸ Much effort has been put into the design, synthesis, and evaluation of chemically sensitive polymers for use in vapor sensing via other transduction mechanisms.^{9–19} Moreover, the chemical tailorability and relative ease of synthesis of many polymers have led to the commercial availability of a large number of potentially useful sensor materials. As a guide for material selection, we turned to the polymer coating-based surface acoustic wave (SAW) sensing literature, choosing to confine our initial studies to polymers that displayed well-defined and characterized sorption properties.^{20,21} Here, we present preliminary results obtained from the evaluation of three polymers configured as chemoresponsive diffraction gratings and evaluated against a representative set of four volatile analytes over environmentally relevant concentration ranges. The three polymers, polyepichlorohydrin, polyisobutylene and polybutadiene, were exposed to toluene, methyl ethyl ketone, chloroform, and hexane over a concentration range of 0–50 g/m³.

EXPERIMENTAL SECTION

Materials. The structures of the three polymers used in this study are shown in Figure 1 along with their abbreviations. Polyepichlorohydrin (average M_w = 700 000), polyisobutylene (average M_w = 500 000), and polybutadiene (M_w = 2 000 000–3 000 000, 98% cis) were obtained from Aldrich Chemical and used without further purification. Organic solvents used for micropatterning and vapor generation were similarly obtained from commercial sources and used without further purification. 2-Butanone (methyl ethyl ketone, MEK) and hexane (HEX) were obtained from Aldrich and were ACS certified and 95+% anhydrous, respectively. ACS grade chloroform (CHCl₃) and toluene (TOL) were purchased from Fisher Scientific.

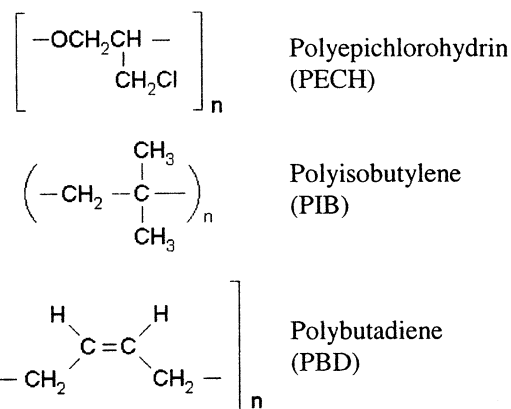


Figure 1. Structures and abbreviations of polymers micropatterned into chemoresponsive diffraction gratings.

Grating Fabrication. Micropatterned polymeric diffraction gratings were fabricated via the micromolding in capillaries²² technique with details having been described extensively.^{2,5} Briefly, candidate polymers were dissolved in an appropriate solvent, 0.3 g polymer into 100 mL solvent, and a droplet of the solution was placed next to a freshly prepared poly(dimethylsiloxane) stamp on a clean glass microscope slide. The stamp employed features of $5 \times 5\text{-}\mu\text{m}$ squares separated by $5\text{-}\mu\text{m}$ channels having a depth of 180 nm, as dictated by the lithographic master used to create the stamp. A small weight, $\sim 5\text{ g/cm}^2$, was placed on top of the stamp to ensure conformal contact with the surface. Upon evaporation of the solvent, the stamp was removed, leaving the micropatterned film. The quality of the polymer gratings was investigated using a Digital Instruments Nanoscope III atomic force microscope (AFM) operating in contact mode at a scan rate of 1 Hz or a Molecular Imaging PicoSPM operated in magnetic AC (MAC) mode at a resonance frequency of $\sim 55\text{ kHz}$ and scan rate 3 Hz.

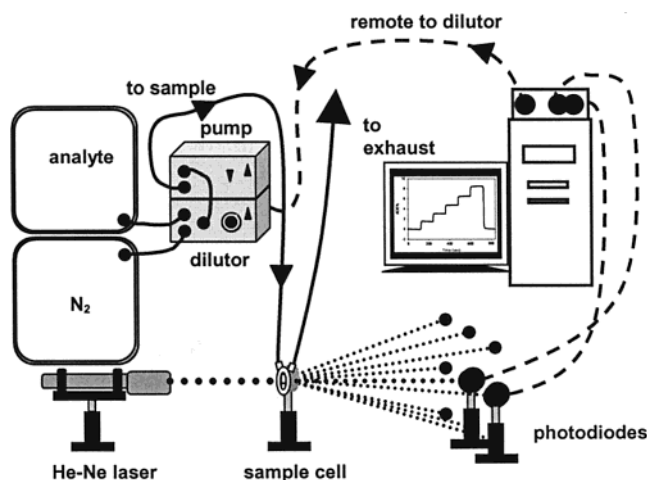
Vapor Generation. Vapor samples of fixed concentration (50 g/m³) were prepared by injection of a measured volume of liquid sample into an $\sim 40\text{-L}$ vapor dilution bag (2-mil Tedlar, Pollution Measurement Corporation, Oak Park, IL), followed by inflation with dry N₂ to a known volume with a calibrated pump. Sample bags were always prepared the day of use and were allowed to equilibrate for at least 1 h. The resulting 50 g/m³ bags, the highest investigated concentrations, were used as “stock” vapors for obtaining lower concentrations via controlled dilution.

Diffraction Measurements and Data Analysis. A schematic of the instrumentation used in the diffraction experiments is shown in Scheme 1. The laser used was a Melles-Griot 25-LGP-909-249 stabilized helium–neon gas laser ($\lambda = 632.8\text{ nm}$). Vapors of known concentrations were obtained by dilution of the “stock” sample bags with dry N₂ using a model 1010 Precision Gas Diluter (Custom Sensor Solutions, Inc., Naperville, IL). The model 1010 was remotely controlled via a custom LabView program, affording excellent control over timing and precision of mixing ratios. Known concentrations of vapors were then delivered to the grating, housed in a home-built small-volume Teflon cell ($\sim 5\text{ mL}$) with a TorrSeal adhered quartz window, using a model 1011 gas sample pump (Custom Sensor Solutions, Inc.) and Bev-A-Line IV

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Scheme 1. Illustration of Experimental Setup



chemical-resistant tubing (Cole-Parmer, Vernon Hills, IL). Silicon photodiodes were used to measure the intensities of the diffracted ($I_{1,0}$) and transmitted ($I_{0,0}$) beams. (The indexes refer to diffraction orders in each of two directions.) Diode signals were amplified as needed by home-built voltage-following op-amps and digitized by a custom LabView interface at a rate of 100 Hz. Data treatment consisted of performing a 100-point floating average on the raw diode voltages to compensate for high-frequency laser power fluctuations, followed by ratioing of the diffracted and undiffracted signals to obtain an operational diffraction efficiency (DE).

$$DE = \frac{I_{1,0}}{I_{0,0}} \quad (1)$$

The modulation in diffraction efficiency upon exposure to analyte was then determined by normalizing the diffraction efficiency following exposure to analyte (DE_{analyte}) to that before exposure (DE_0).

$$\Delta DE\% = \left(\frac{DE_{\text{analyte}} - DE_0}{DE_0} \right) \times 100\% \quad (2)$$

$\Delta DE\%$ values at discrete concentrations were obtained by averaging the appropriate signal after stabilization, following the concentration increment.

RESULTS AND DISCUSSION

Grating Characterization. A representative AFM image, shown in Figure 2, reveals a highly periodic polymeric film having thickness of 160 ± 5 nm over the investigated region. Multiple large-area scans verified the micropattern integrity and consistency of feature height within individual gratings. However, thicknesses measured for other gratings ranged from 100 to 180 nm, but again with variations of only a few percent for any given grating. Thickness variations are functionally significant because diffraction efficiencies vary with optical path length. The gratings used here are well approximated as "thin" gratings; the diffraction efficiencies for these are directly proportional to the square of the grating path length, d , and the square of the difference in refractive index, Δn , between the chemoresponsive lattice and the surrounding

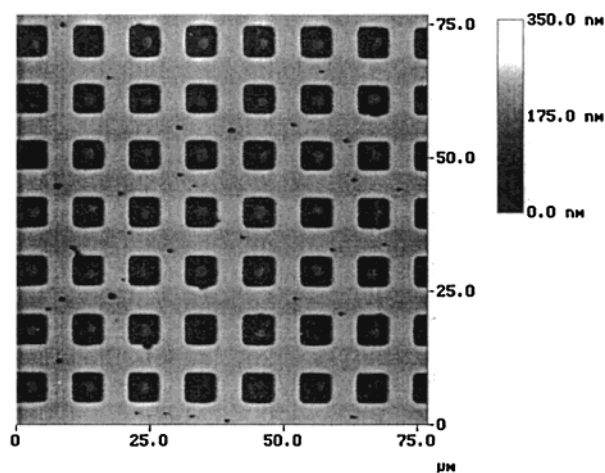


Figure 2. Atomic force microscope (AFM) image of a representative polymer grating. The grating shown is made of PECH and is 160 ± 5 nm thick.

medium, $\Delta n = n_{\text{lattice}} - n_{\text{medium}}$, at a constant probe wavelength, λ .²³

$$DE_{1,0} = 0.1012 \left(\frac{\pi d \Delta n}{\lambda} \right)^2 \quad (3)$$

Inserting this expression into eq 2, the measured $\Delta DE\%$ can be quantitatively expressed in terms of the change in grating refractive index,

$$\frac{\Delta DE\%}{100\%} = \frac{(\Delta n')^2}{(\Delta n_0)^2} - 1 \quad (4)$$

where $\Delta n'$ is the index contrast upon analyte exposure, and Δn_0 is the initial index contrast, before exposure.

Chemoresponsive Diffraction Measurements. The time-resolved diffraction behaviors of gratings fabricated from three polymers were observed upon exposure to four chemically dissimilar analytes. In each case, upon exposure to analytes, the refractive index of the micropatterned lattice was modulated, resulting in increases in the measured diffraction efficiency. Figure 3 shows representative time-resolved responses for gratings fabricated of polyepichlorohydrin, polyisobutylene, and polybutadiene exposed to 2-butanone (MEK), *n*-hexane (HEX), chloroform (CHCl_3), and toluene (TOL) over a range of concentrations.

As can be seen from Figure 3, polymer gratings exhibit different signal magnitudes upon exposure to different analytes over a constant concentration range. The analyte response pattern is unique to each of the investigated polymers. TOL generates the largest signal with PECH, followed by MEK, CHCl_3 , and HEX, respectively. For the PIB grating, TOL again engenders the largest response, followed by HEX, CHCl_3 , and MEK, respectively. The signal magnitudes for PBD gratings are ordered as follows: TOL > MEK \approx HEX \approx CHCl_3 .

The data in Figure 3 can also be plotted as a function of vapor concentration, yielding uptake isotherms unique to specific

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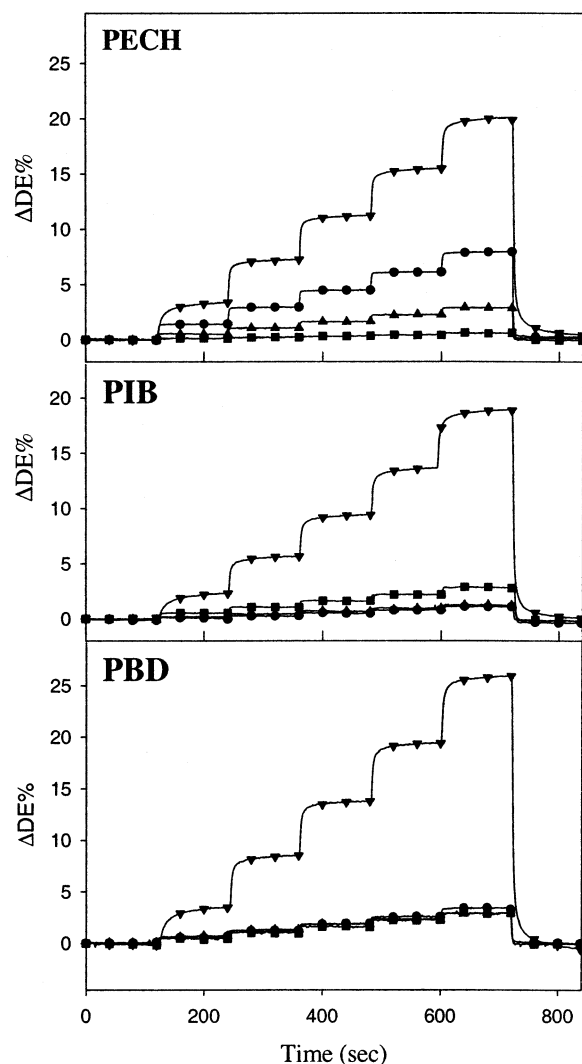


Figure 3. Diffraction responses for PECH, PIB, and PBD gratings upon exposure to increasing concentrations of MEK(●), HEX(■), CHCl₃(▲), and TOL(▼). The concentration profile consists of 10 g/m³ increases of analyte every 2 min, followed by a purge with dry N₂.

polymer/analyte combinations. These uptake isotherms are shown in Figure 4. The dispersion of the responses to different analytes clearly is dependent on the chemical identity of the polymer used. PECH, for instance, gives distinctly unique responses to each of the four analytes, whereas PIB responds differentially to TOL, HEX, and either MEK or CHCl₃, which have virtually indistinguishable responses. PBD proved to be the least effective polymer for differentiating analytes, because only the TOL response was distinguishable from HEX, MEK, and CHCl₃ response uptake isotherms. Regression lines for isotherms were obtained by fitting data to a second-order polynomial according to eq 3, with the constraint that the *y* intercept be 0 at zero concentration.

Of vital importance in a vapor detection system is the reproducibility and time response of the sensor. Figure 5 shows the time-resolved diffraction response of a PECH grating upon repeated exposure/purge cycles of 50 g/m³ MEK/dry N₂. The sensor reproduces the initial response upon repeated cycling, although a very small systematic decrease with increasing cycle number is observed. Additionally, gratings were shown to preserve this reproducibility upon cycling through multiple stepped con-

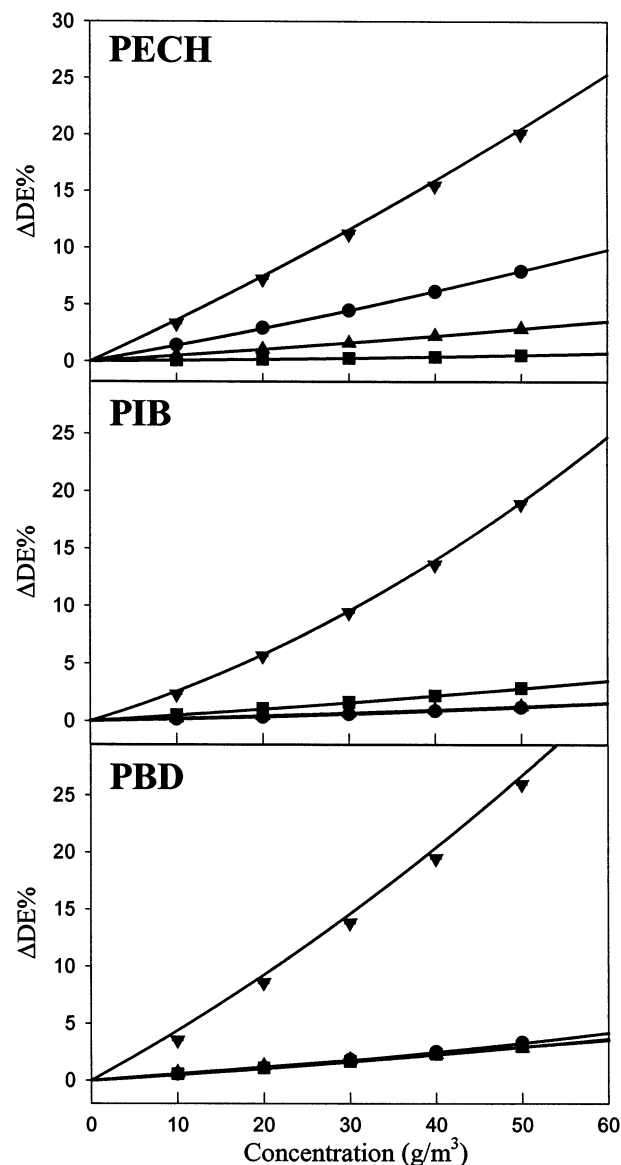


Figure 4. Uptake isotherms obtained by plotting the data in Figure 3 as a function of analyte concentration. Regression lines were generated by fitting data to a second-order polynomial, according to eq 3. Responses from PECH, PIB, and PBD gratings upon exposure to increasing concentrations of MEK(●), HEX(■), CHCl₃(▲), and TOL(▼). Note: Error bars for data points are smaller than the data symbols.

centration cycles, analogous to those shown in Figure 3. In most cases examined here, the sensor has reached its full response level within 15 s, the minimum time possible with our current vapor delivery system.²⁴ Because of the short path lengths (film thicknesses) used, 100–200 nm, faster response times might realistically be achieved with a faster vapor delivery system.

One other interesting feature of the polymeric grating-based sensor system is that signals for mixtures of several different analytes are found to behave as sums of the isolated component

(24) The vapor mixing system employed has a rather large mixing chamber that slows instrument response times. Another factor leading to artificially slow response is a weak, though significant, interaction between the studied vapors and the walls of the delivery tubing. Therefore, equilibrium had to be reached along the entire tubing interior before vapor reached the chemoresponsive grating.

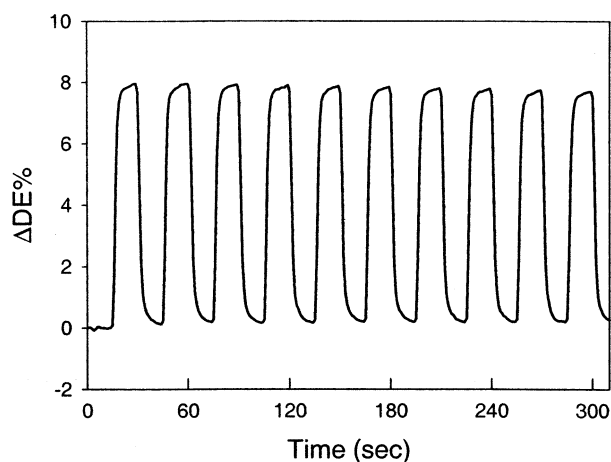


Figure 5. Cycling behavior of chemoresponsive polymer diffraction gratings. The PECH grating was subjected to alternating 15-s analyte/purge cycles with 50 g/m³ MEK/dry N₂.

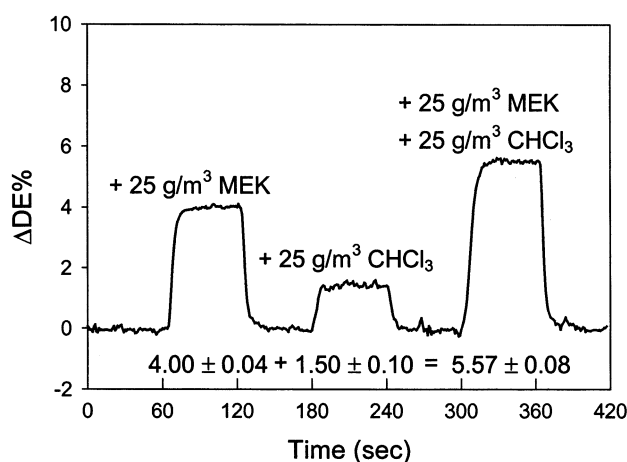


Figure 6. Diffraction response of a PECH grating exposed to a mixture of two analytes of known concentration. The grating was first separately exposed to "neat" MEK and CHCl₃ both at 25 g/m³, followed by the simultaneous exposure to both analytes, each at 25 g/m³.

responses. An example is shown in Figure 6, where a PECH grating was separately exposed to 25 g/m³ of MEK and 25 g/m³ CHCl₃, followed by the concurrent delivery of 25 g/m³ of both analytes. At a single concentration, the resulting signal agrees within experimental error with the sum of the separate signals. However, more complex mixtures would likely need to be considered as linear combinations of the observed *nonlinear* uptake functions.

Comparison to Acoustic Wave Measurements. A large body of work exists detailing the use of polymer-coated acoustic wave sensors for vapor detection,^{9,13,25–31} in part because these

techniques deliver exceptional signal-to-noise ratios and low limits of detection relative to most other applicable signal transduction methods. A majority of this work has focused on using thickness shear mode (TSM) and surface acoustic wave (SAW) devices with a large number of chemically sensitive polymer coatings.^{15,25,32} The transduction mechanism of these devices lies in the frequency decrease of an oscillating piezoelectric material upon mass loading, first with polymer film and then with sorbed vapors, although other factors have been shown to contribute to the observed responses.^{21,26,33}

Since the diffraction-based transduction methodology relies upon detection of refractive index changes concurrent with vapor localization within the polymer film, we set out to compare our sensor response patterns with those observed via SAW devices for identical polymer/analyte combinations. The acoustic wave study from which we will draw comparisons describes the polymer/analyte combination in terms of apparent partition coefficients, K_{app} .²¹

$$K_{app} = \frac{\Delta f_{V(SAW)} \rho_S}{4 \Delta f_S C_V} \quad (5)$$

where $\Delta f_{V(SAW)}$ is the change in oscillation frequency caused by analyte sorption, ρ_S is the density of the polymer coating, Δf_S is the film contribution to oscillation frequency modulation in the absence of analyte, and C_V is the analyte concentration in the vapor phase. If mass changes are the only contributions to the frequency change, K_{app} can be expressed as the true partition coefficient, K ,

$$K = \frac{C_S}{C_V} \quad (6)$$

where C_S is the analyte concentration localized in the sorbent layer. A numerical partition coefficient is difficult to extract from the observed diffraction responses, because the effects of polymer swelling changes are not known.³⁴ To overcome this, the linear component of the nonlinear regression analysis (Figure 4) was evaluated against reported SAW frequency changes for specific polymer/analyte interactions, allowing for qualitative comparison of the two techniques. For ease of evaluation, the diffraction-based values were normalized to reported $K_{app}(SAW)$ values for each polymer grating at the respective value for hexane exposure. The results of the comparison between diffraction-based and acoustic wave measurements are graphically displayed in Figure 7. As can be seen, the normalized diffraction responses are in qualitative agreement with SAW-based results, especially for PIB and PBD. Response behavior for the PECH grating shows the largest deviation from $K_{app}(SAW)$; however, even here, the ordering of scaled responses to the four analytes is the same for the two transduction methods. One possible reason for the observed disparities is the occurrence of polymer modulus changes upon

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(34) eq 4 neglects any swelling-induced change in grating path length. An AFM study with a representative analyte/polymer pair (toluene/PECH) yielded no detectable dimension change.

Table 1. Comparison of Diffraction and SAW Obtained Detection Limits for Polymer/Analyte Combination, and Evaluation against the Governmental Standard Concentrations, OSHA-PEL and NIOSH-REL

| analyte | LOD | | | SAW PECH (ppm) | SAW PIB (ppm) | OSHA PEL (ppm) | NIOSH REL (ppm) |
|-------------------|------------|-----------|-----------|----------------|-------------------|----------------|-----------------|
| | PECH (ppm) | PIB (ppm) | PBD (ppm) | | | | |
| MEK | 25 | 258 | 72 | 2.76 | 2.95 | 200 | 300 |
| HEX | 460 | 60 | 59 | 22.7 | 1.21 | 500 | 50 |
| CHCl ₃ | 41 | 102 | 34 | 8.97* | 6.54 ^a | 50 | 2 |
| TOL | 8 | 11 | 7 | 1.37 | 0.52 | 500 | 150 |

^a SAW LOD value was not reported for chloroform in ref 19; therefore, the value obtained for dichloromethane has been listed.

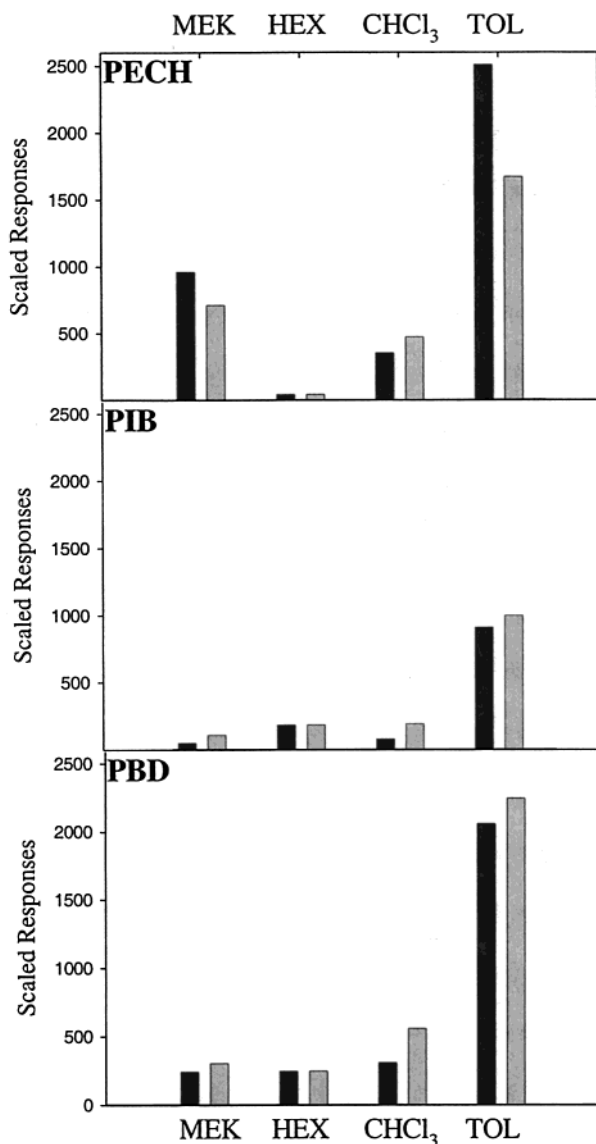


Figure 7. Graphical comparison of diffraction response to that obtained from a SAW device. For comparison, the linear component of the regression from Figure 4 was scaled to $K_{app}(\text{SAW})$ values for each polymer grating. Diffraction-based responses are represented by black bars and SAW values, by gray bars.

vapor absorption. Modulus changes can provide substantial contributions to SAW signals, but should not directly affect grating-based measurements.

Implications for Array-Based Sensors. Several studies have reported on polymer-array-based sensing using acoustic wave transduction techniques.^{15,19,27,32,35} On the basis of the ability to

fabricate an array of diffraction-based gratings using a set of chemically diverse polymers, we suggest the applicability of this methodology to simultaneous analyte identification and quantification. The good agreement between diffraction and SAW-based analyte response patterns in Figure 7 suggests that the large existing body of SAW data can be used as a reasonably accurate preliminary guide for nonresonant chemoresponsive grating array design. Indeed, this is one focus of continuing work. Although unlikely to be true for all candidate polymers, the theoretically well-described second-order polynomial behavior in Figure 4 for signal magnitude versus analyte concentration suggests that sensor array training at just a few standard vapor concentrations will permit accurate identification of unknown compounds over a reasonable dynamic range. Accurate data fitting, of course, also implies that gratings can be used to determine volatile analyte concentrations using a calibrated quadratic function. Additionally, since diffraction-based responses for component mixtures appear to be linear combinations of individual analyte responses, identifying and quantifying unknown mixtures is a real possibility with an expanded number of array elements.

Analytical Applications. Limits of detection (LOD) for the polymer-based diffraction sensor were calculated as three times the standard deviation of the sensor baseline. Under routinely observed noise levels, these limits were evaluated against detection limits obtained on a SAW device.¹⁹ The limits are also compared with governmental guidelines: OSHA Permissible Exposure Limits (PEL) and NIOSH Recommended Exposure Limits (REL).³⁶ Results for PECH, PIB, and PBD gratings are listed in Table 1.

From the table, at least one of the polymeric grating sensors is able to detect each analyte below OSHA-PEL limits. The detection limits of certain analytes are highly variable, corresponding to the polymer/analyte interactions of each pair, thus limiting the LODs for the polymer materials used in this work. For the sake of comparison, the refractive index sensitivity of an average grating is on the order of 5×10^{-5} refractive index units (RIU). For reference, this refractive index sensitivity is comparable to or exceeds those of other refractive index techniques, such as surface plasmon resonance spectroscopy (SPR),³⁷ localized surface plasmon resonance spectroscopy (LSPR)³⁸ coated optical fibers,³⁹ and porous silicon-based sensors.^{40–42}

Although many of the presently reported LODs are ~ 1 order of magnitude higher than those obtained on SAW devices, work

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on grating geometry optimization together with chromophoric dye-doping (resonance amplification behavior²) should result in substantial sensitivity enhancements for the diffraction-based system. Additionally, as discussed elsewhere, resonance amplification is capable of engendering enhanced *selectivity* at the read-out phase of the chemical sensing process.

CONCLUSIONS

Micropatterned polymeric diffraction gratings have been evaluated as volatile organic chemical sensors. These sensor elements were found to respond in a rapid and reproducible fashion to each analyte in a four-member set. The relative magnitudes of responses differed for different polymeric materials, but showed good qualitative agreement with responses reported for surface acoustic wave measurements. It seems clear that together with additional elements, these polymeric gratings could be assembled into an array-based sensor system, affording simultaneous identification and quantification of unknown analytes and simple analyte

mixtures. Although detection limits appear satisfactory for some analytes, lower limits are clearly needed for others. At this stage of development, limits of detection with nonresonant chemoresponsive gratings are on the order of one magnitude poorer than those observed with SAW devices. With these issues in mind, current work is directed toward *resonant* diffraction behavior using dye-doped polymers, as well as intrinsically chromophoric polymers. With other grating materials, selective signal amplification of as much as 3500 \times has been reported under resonant conditions.²

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