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Chemically Selective Coated Quartz Crystal Microbalance (QCM) Array for Detection of Volatile Organic Chemicals

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ABSTRACT

Liquid flow cells have been fabricated to prepare an array of QCMs operating simultaneously for detection and identification of VOCs in water. Two signals, a frequency response and a damping voltage response, were obtained per resonator. A blank QCM was used as a reference to account for changes in liquid density and viscosity. Nine different polymer coatings applied using a spin coat technique have been examined for VOC response under liquid flow conditions. A matrix of three classes of VOCs were examined for each coating with four chemicals in each class. The three classes of VOCs are polar, nonpolar and chlorinated. A pattern recognition technique, called visually empirical region of influence (VERI), was used to cluster the responses in n-dimensional space. Chemicals within a class varying by only one methyl group (e.g., toluene and xylene) are easily discriminated using only two different coatings with three different QCM responses. All chemicals were easily separated and detected with a total of 5 films and 6 responses with >99% accuracy.

Keywords: quartz crystal microbalance (QCM), thickness-shear mode (TSM) resonator, volatile organic compound (VOC), visually empirical region of influence (VERI).

1. INTRODUCTION

The large number of chemically contaminated sites and the high cost for restoration present the need for economical, low power, sensitive and specific chemical sensors. Applications for these sensors are often centered around detection of contaminants in water, for example, monitoring of contamination in groundwater and in process, recycle, and waste streams. Quartz crystal microbalances (QCMs) are well suited for these applications since they are rugged, low power, and easily miniaturized. Moreover, QCMs may potentially be adapted for many different uses by developing coatings that respond to different target molecules, adding to their versatility[1-3].

QCMs are piezoelectric thickness-shear-mode resonators where the resonant frequency has long been known to vary linearly with the mass of rigid layers on the surface when the device is in contact with air[4]. These devices were also determined to be sensitive to changes in mass in contact with liquids[5,6]. Liquid properties, such as liquid density and viscosity, can also affect QCM response[7-10]. These effects are important since liquid properties may change slightly as an analyte spike passes a device. However, at low analyte concentrations, very small changes in liquid physical properties generally occur. This can be verified by a lack of any detectable changes with an uncoated reference QCM.

Compressional wave effects arising due to the unequal surface displacement of the QCM have been identified as a possible source of error for liquid sensing experiments[11-13]. The use of these compressional waves to enhance the signal has not been reported. Responses due to compressional resonance can enhance the signal provided a change in film thickness occurs[13]; however, the resulting responses are nonlinear. We should be able to use these nonlinear responses due to the pattern recognition data analysis. The liquid cavity cell thickness was not determined for these experiments. A tunable cell would provide an opportunity to maximize the compressional response for each signal. Since the compressional wavelength is

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affected by changes in the liquid density, the temperature was kept constant. At the low concentrations used in this study, changes in density of the solutions relative to that of pure water should not be significant enough to affect the resonance condition.

Developments in QCM sensor technology have progressed in the area of gas phase analysis since the first report in 1964, where King used a QCM as a gas chromatograph sorption detector[14]. Since then, a series of reports of other detection schemes for different gas phase analytes have appeared in the literature[15]. These reports describe the use of a variety of coatings with chemically selective sorption properties for detection of target analytes.

Chemical recognition using selective coatings on QCMs has been explored to a much smaller extent for liquid-phase sensing than for gas-phase sensing. Very few cases of chemically selective coated QCMs for liquid phase detection have been reported. Lasky and Buttry developed a glucose sensor by immobilizing hexokinase in a poly(acrylamide) matrix onto the surface of the QCM[1]. Cox et al. immobilized high-surface-area silica particles derivatized with metal specific ligands on the QCM to measure trace uranium in water[2]. Auge et al. used a cholesteryl layer for detection of the surfactant N9[3]. Despite these research efforts, an array of coated QCM sensors for liquid-phase sensing has not yet been reported. This study focused on using a QCM array for the detection of volatile organic compounds (VOCs) in water. The array of QCMs was coated with different polymers that have only partial selectivity and respond in some way to all compounds. The pattern of responses from this sensor array can be analyzed using chemometrics or pattern recognition techniques to identify the chemical being detected and determine its concentration[16,17]. In this study, a new pattern recognition technique, capable of handling nonlinear and even non-monotonic responses, was applied to the data[18,19].

Pattern recognition (PR) analysis has been carried out to: (1) identify the individual chemicals from the array responses and subsequently quantify the chemical concentrations, (2) determine which subsets of the 18 sensor signals provide the best chemical recognition performance, and (3) determine the robustness of chemical recognition with artificially added sensitivity drifts. A new PR method, called visually empirical region of influence (VERI), was used here[18,20,21]. VERI-PR has proved useful for handling diverse PR problems in chemical sensing and multispectral image classification. VERI-PR exhibits several useful properties: the ability to handle complex sensor signals (nonlinear, nonmonotonic); PR results are determined entirely by the training data, i.e. no user-supplied threshold adjustments or computations are required; and class volumes for each chemical class are bounded, so that unexpected chemicals (outside of the training set) are typically classified as unknown rather than spuriously identified as one of the training set chemicals. VERI is also able to identify overlapping and touching class volumes automatically (i.e., chemicals which give similar array responses and are likely to be incorrectly identified by a PR analysis), and is thus useful for directly comparing the ability of different sensor combinations to distinguish the chemicals of interest.

2. EXPERIMENTAL

Quartz Crystal Microbalance - The AT-cut quartz crystals used in this study were purchased from Maxtec (Torrance CA) having a diameter of 25.4 mm and a thickness of 0.33 mm. They were patterned with two concentric gold-on-chrome electrodes having a wrap around geometry that allows both ground and radio frequency (rf) connections to be made to one side. The larger 12.9-mm diameter electrode, used to contact the fluid, functioned as the ground electrode. The smaller 6.6-mm diameter electrode on the opposing side was used to provide the rf signal. The different electrode sizes were used to minimize electrical fringing fields that may potentially arise between the electrodes through the crystal. Application of a voltage to the two electrodes produces a strain in the surface of the QCM along the cut of the crystal. An oscillator circuit providing an alternating voltage will produce a fundamental frequency of 5 MHz for this particular crystal diameter and thickness.

Flow Cell and Oscillator - Figure 1 shows one of the four flow cells used in this study. This stainless steel flow cell housed the QCM between a nitrile o-ring on the liquid side and a polycarbonate (Lexan) spacer on the opposite side where electrical contacts were made via spring-loaded pogo pins. The oscillator board (connected to the cell with an SMB connector) provided two output signals, the peak series resonance frequency and a voltage proportional to the resonance magnitude (indicates wave damping)[22].

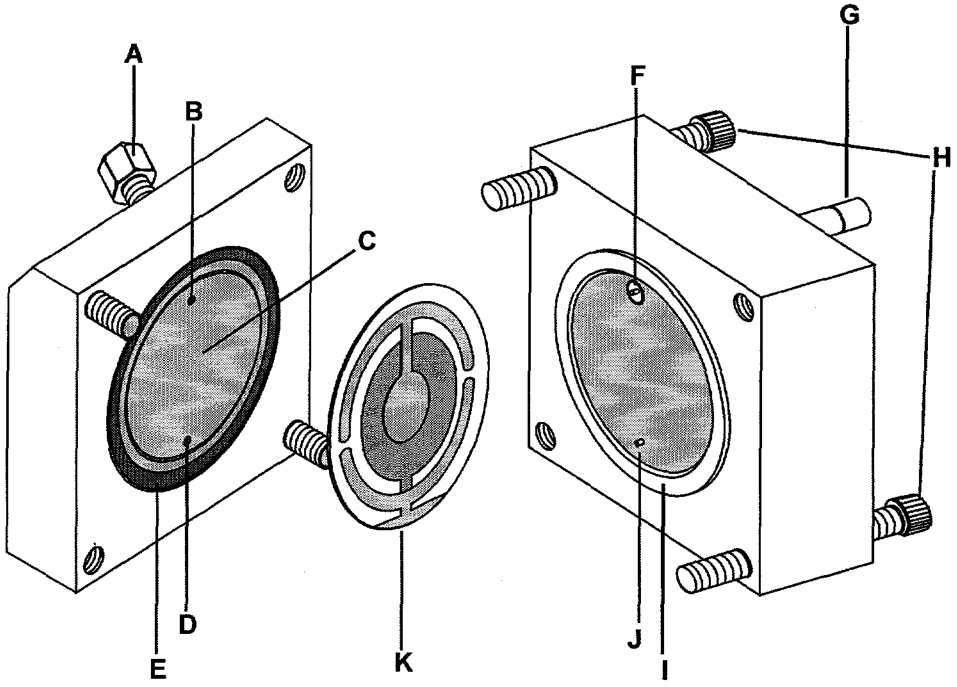

Figure 1. QCM liquid flow cell: (A) Zero dead volume tube connector, (B) Liquid exit port, (C) Liquid cavity, (D) Liquid inlet port, (E) O-ring, (F) Pogo pin rf-contact, (G) SMB rf-connector, (H) Socket Head Cap Screws, (I) Polycarbonate spacer, (J) Pogo pin ground contact, and (K) coated QCM sensor.

Gas bubble trapping in the QCM cell or directly on the surface of the QCM has been found to interfere with QCM measurements. However, degassing of the test solutions was not done due to possible changes in concentration of the stock solutions by sparging of the VOCs. To minimize any anticipated problem of gas bubble trapping, the flow cells were constructed so that the liquid cavity created from the sealed QCM was positioned in a vertical direction in order to force gas bubbles through the cell. In addition, the liquid flow cell was designed to aid in bubble removal by setting the liquid outlet port at a 45-degree angle up from the surface of the QCM. This design provided a smooth flow of fluid across the QCM surface, sweeping gas bubbles through the cell without trapping them.

Test System - The experimental setup consisted of an Eldex Model 9600 programmable pump for dilution, mixing and delivery to the sensors. A Hewlett-Packard (HP) 3488A Switch/Control Unit was used to switch between two HP 5384A Dual Input Frequency Counters and an HP 3457A Multimeter. The multimeter had the ability to read 9 voltages; 3 voltages from the Eldex supplied the concentration profile and one voltage from each oscillator circuit provided the damping voltage measurement related to the energy loss of the QCM. The instrumentation was computer controlled with a program written in HP-Instrument Basic.

Coatings - Table 1 shows the polymers and films used for the QCM array. The coating procedure was optimized for each polymer by visual inspection for uniformity and reproducibility of the film. The standard procedure was to first spin coat the film onto the QCM surface and then heat the coated QCM in an oven to drive off remaining solvents. Two of the films, the Poly 3/15 Fox polyol and the Poly(isobutylene)-Carbosieve, required a surface derivatization step to keep the films from delaminating. An octadecane thiol (C18SH) self-assembled monolayer (SAM) was used in both cases to enhance adhesion of the film to the device surface.

Table 1 Polymer coatings and conditions used to prepare coatings for sensor array.

Coating	Company	Coating Procedure	Solution
Poly(isobutylene)	Aldrich	2000 rpm for 30 s, 10 min. at 40C	0.01 g/ml in chloroform
Ethyl Cellulose	Aldrich	2000 rpm for 30 s, 10 min. at 45C	0.01 g/ml in 80% toluene and 20% ethanol
Poly(vinyl acetate)	Aldrich	2000 rpm for 30 s, 5 min. at 45C	0.01 g/ml in toluene
Poly 3/15-FOX polyol	Gencorp Aerojet	1000 rpm for 30 s, 5 min. at 100C, C18SH SAM Coated	0.01 g/ml in hot tetrahydrofuran (THF)
Poly(epichlorohydrin)	Scientific Polymer Products, Inc.	1000 rpm for 30 s, 5 min. at 100C	0.02 g/ml in methyl ethyl ketone (MEK)
Poly(isoprene), *trans*	Aldrich	10 drops at 1500 rpm for 60 s, 5 min. at 100C	0.008 g/ml in 50% cyclohexane, 50% chloroform
Poly(diphenoxy-phosphazene)	Scientific Polymer Products, Inc.	1500 rpm for 60 s, 5 min. at 100C	5% by weight in chlorobenzene
Poly(isobutylene)-Carbosieve S-III	Aldrich Supelco	C18SH SAM coated surface, 1 drop of PIB solution, imbedded Carbosieve particles	PIB 0.01 g/ml in chloroform
OV-215	Ohio Valley Specialty Chemicals	10 drops at 1000 rpm for 90 s, 5 min. at 100C	0.02 g/ml in acetone

Chemicals - The test matrix for these experiments consisted of three classes of organic chemicals: polar, nonpolar, and chlorinated. Four chemicals from each of these classes were tested. The polar compounds studied were acetone, isopropanol, ethylene glycol, and ethyl acetate. The nonpolar compounds used in this study were p-xylene, toluene, cyclohexane, and n-pentane. The chlorinated hydrocarbons were carbon tetrachloride, chloroform, trichloroethylene (TCE) and tetrachloroethylene (PCE). All chemicals were of certified grade or better and obtained from Fisher, excluding PCE that was 99.8% from Sigma-Aldrich.

For the nonpolar and chlorinated groups, stock solutions were prepared by adding an excess of the chemical to a water bottle to prepare a saturated solution (the excess chemical maintained the solution at saturation). The ppm concentrations of the stock solutions were calculated by using literature values for their solubility constants in water[23]. For the polar compounds, which were less volatile and more likely to remain at a constant concentration for a reasonable time period, 1% by weight (10,000 ppm) stock solutions were prepared. Deionized water was used for both the stock solutions and the diluent stream.

Liquid Challenges: The experimental setup for exposing the QCMs to liquid challenges involved using four cells in series. The first cell in line always contained an uncoated QCM that provided a reference to changes in density or viscosity of the solution. The next three cells in the array housed polymer coated QCMs (Table 1). A typical run was started by pumping deionized (DI) water through the cells at a rate of 5 ml/min. A stable frequency and damping voltage response vs. time was first established for a 15-minute time interval. This DI water baseline was then followed by a series of 5-minute concentration challenges with solutions of various dilutions of stock bottles contaminated with known concentrations of a single VOC. These challenges were spaced by 15-minute intervening flows of DI water in order to allow the QCMs to reestablish stable baselines. The challenges were in order of increasing concentration (1, 5, 10, 15, 25, and 50% of the stock solutions). Consequently, a concentration profile, as seen in Figures 3, was generated.

3. RESULTS AND DISCUSSION

Description of Array Data: The oscillator circuit used to take these QCM data provides two separate responses: a frequency response and a feed back voltage. The frequency response is seen as a change in frequency caused by a perturbation to the film. The most common perturbation is partitioning of the chemical from solution onto the coating causing mass loading. Chromatographic separations rely on the partitioning of chemicals from a mobile phase (either liquid or gas) into a chemically-selective stationary phase, in order to impart a separation. This same partitioning into a stationary phase is used to provide an increased concentration of an analyte on a sensor surface. Figure 2 (top) shows a typical frequency response from a liquid challenge experiment. A fast negative change in frequency was seen as chloroform partitioned into the poly(vinyl acetate) (PVA) film during each of the five 300-second concentration hits. The frequency quickly recovered back to its initial value after each liquid challenge. The right y-axis shows the concentration profile for chloroform from 77-3900 ppm (dotted line). The PVA coated device responded rapidly and reproducibly to the chloroform exhibiting negative frequency shifts corresponding to the concentration profile (solid line). The reference uncoated QCM (dashed line), does not show a change in frequency even at the highest chloroform concentration.

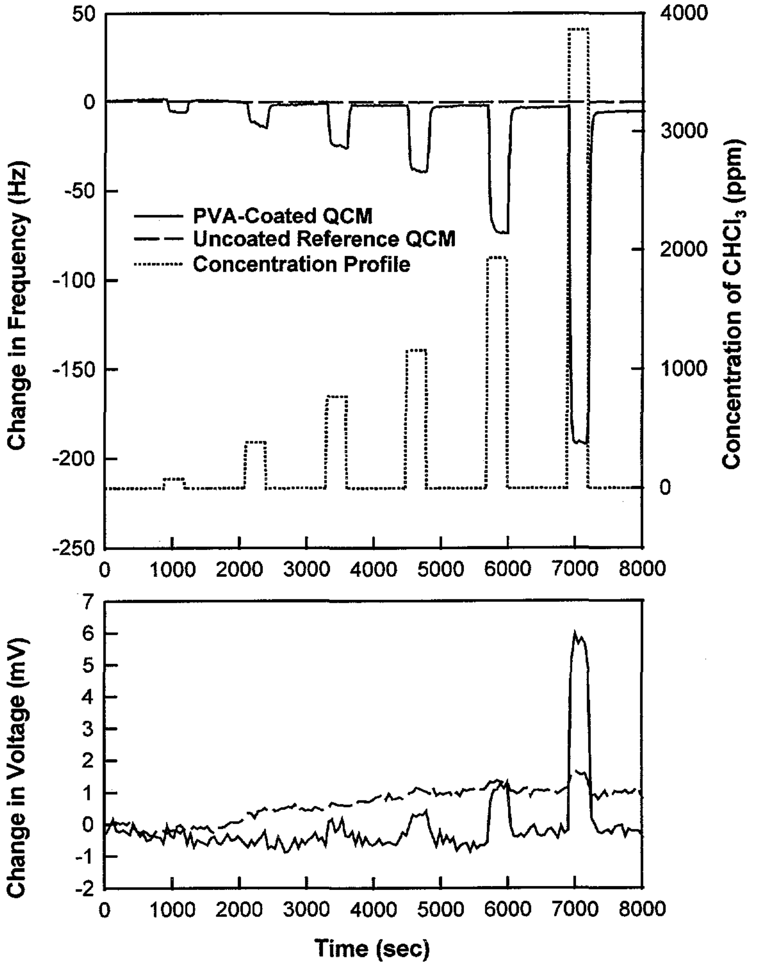

Figure 2. Top graph shows frequency response for a poly(vinyl acetate)-coated QCM (solid line) and an uncoated reference QCM (dotted line) to the indicated concentration profile of chloroform (dashed line). Bottom graph shows the damping voltage response.

The second signal from the QCM, the damping voltage, is shown in the bottom half of Figure 2. The damping voltage is a second feedback loop from the oscillator that varies the amplifier gain to maintain a constant oscillation level. This damping voltage is proportional to the total motional resistance[22]. The voltage response from the PVA-coated QCM is shown by the solid line. This damping voltage response was less sensitive than the frequency response (i.e., no signal at < 800 ppm of chloroform). The uncoated resonator (dashed line) shows a small voltage response to only the highest concentration of chloroform. This change, most likely related to the change in density and viscosity of the solution, was subtracted from the coated QCM responses when calculating the total chemical response.

Other perturbations that can occur due to a liquid challenge experiment are film swelling or shrinkage, changes in modulus, and/or compressional effects. These different effects can cause variations in responses that give rise to both positive and negative frequency and voltage responses. Figure 3 shows a response pattern for all the different coatings to 26 ppm of cyclohexane. The frequency responses are shown on the left hand side. The responses being due solely to mass loading induced by chemical uptake is inconsistent with the fact that some of these responses are positive. This indicates that additional perturbation mechanisms must be active for at least some of the coated QCMs. The damping voltage responses are shown on the right hand side of Figure 3 and correspond to the respective frequency change.

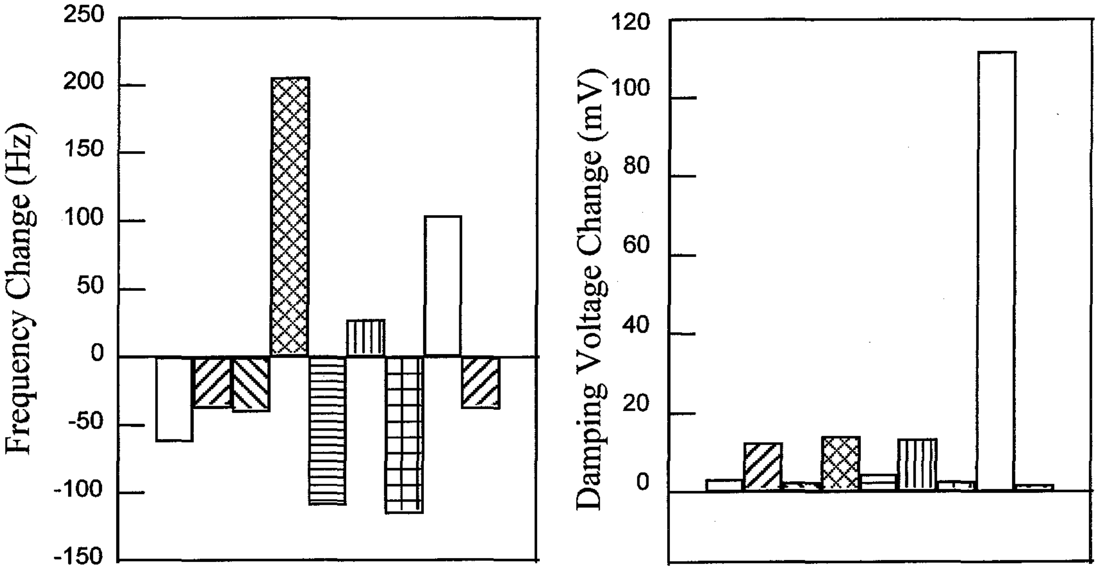

Figure 3. Frequency (left) and damping voltage (right) responses for 9 different polymer coatings to a concentration of 26 ppm cyclohexane. The coatings from left to right are: ethyl cellulose, poly(vinyl acetate), poly(isobutylene), poly 3/15 FOX polyol, OV-215, poly(isoprene), poly(diphenoxyphosphazene), and poly(isobutylene) - carbosieve.

An array of sensors must use some form of pattern recognition to separate and discern data generated by the array. Several different methods of chemometric analysis have been applied to sensor arrays[16]. However, these methods do not accurately take into account nonlinear responses such as observed with some of our QCM sensors. We therefore turned to a new pattern recognition technique, called visually empirical region of influence, that will be briefly outlined. The first step was to take the data (we had six points in each data set) and generate a smooth curve fit using any function that arbitrarily fits the best. For most of our data sets, at least a second order function was required to fit the data. Based on the smooth curve fit, large numbers of random points were generated (ca. 400) to add to the function to simulate the typical noise of the sensor (3 Hz for frequency and 0.2 mV for the damping voltage for the QCM system used in this study). Since a large number of points are used as the “class”, a training set was generated by reducing the 400 points to 40. This was done by examining which points in the class are best used to represent the whole class

Training data and test data for all chemicals were interpolated from a smooth spline fit to the raw sensor responses. Two types of noise were added back to the data: estimated measurement noise (3.0 Hz for the frequency signals and 0.3 mV for the damping voltage signals) and artificial drift of the sensor sensitivities to mimic long-term aging effects. Drift for each array response was produced by reducing the sensitivity of each sensor response from unity by an independent random factor in a specified range. The three sensitivity drift ranges were: no reduction, 0% to 16%, and 0% to 50%. Separate training data sets and test data sets were produced for each drift range. The simulated drift results provide an indication of the robustness of the chemical recognition under extended use.

A "leave-one-out" analysis[21] was carried out on the training data for all possible arrays made up of six or fewer sensors (twelve or fewer signals), so that the chemical recognition performance of all such arrays could be compared. Leave-one-out analyses provide the best use of the available training data while avoiding the bias associated with including the classification results of data points that are present in the training set. The VERI method is efficient enough that all of these arrays can be explicitly examined using SPARC workstation hardware. This more computationally intensive approach has some advantages over the commonly-used principal components analysis (PCA). PCA computations provide useful qualitative insights and are often the best guidance for signal selection from among very large numbers of potential signal combinations, but they are not guaranteed to provide the best choice of signals for distinguishing classes[24]. The VERI leave-one-out results were obtained for training data with no sensitivity drift. The results (not shown) indicated that the best percent accuracy of the chemical recognition without added drift was in the high 80s for the best three signal arrays, in the mid-to-high 90s for the best four and five signal arrays and in excess of 99% for the best arrays with six or more signals. Figure 4 illustrates the relatively good separation of the different chemical classes achievable using only three sensor signals (the maximum number that can be effectively represented in two dimensions). The large spread in the data for IPA and acetone is due to weak, noisy responses from the PIB-carbosieve frequency shifts.

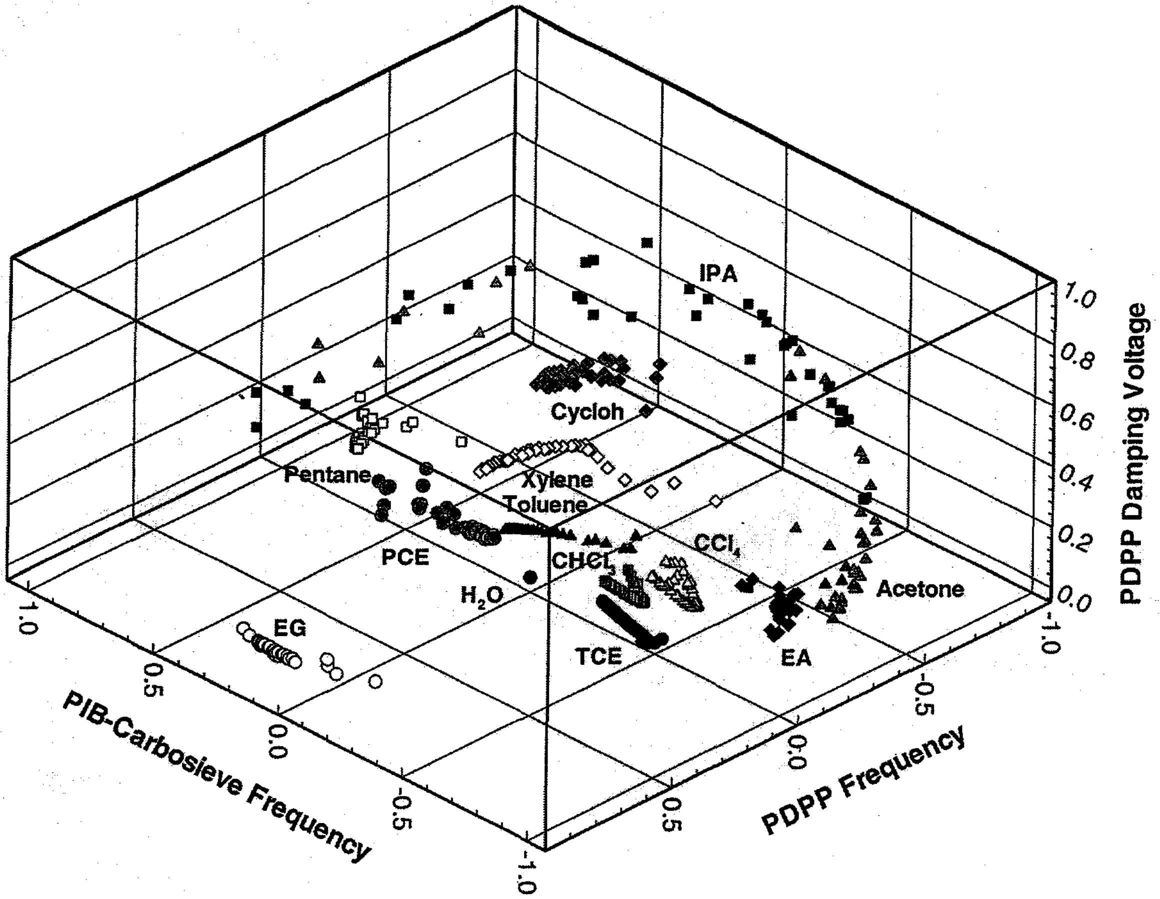

Figure 4. 2-dimensional visualization of separation and identification of 12 chemicals from three different classes using VERI technique. Data were equalized and normalized.

The PR analyses of data with up to 16% and 50% sensitivity drifts were carried out on an array with six signals obtained from five sensor films (polyvinyl acetate, PIB, FOX, epichlorohydrin, PDPP). The frequency response was used for all five sensors while the damping voltage was used only for the PDPP-coated QCM. The results indicate that better than 98% (88%) correct chemical recognition is maintained for the 16% (50%) drifts, respectively. These results indicate a good degree of robustness for these sensor films.

Complimentary to a sensor system that relies on partitioning of an analyte into a polymer coating, we were able to predict sensor responses of the polymer coated QCMs using a Linear Solvation Energy Relationship (LSER)[25] and Henry's Law constants[26]. LSER was first applied to partitioning of analytes into polymer coatings on surface acoustic wave (SAW) devices in air[25]. Thus, it provides predictions of the gas-polymer partition coefficient $K_{gp} = C_p/C_g$ where C_p is the concentration of the analyte in the polymer coating and C_g is the concentration of the vapor in the gas phase. The Henry's Law constant H describes the gas-liquid equilibrium and is given by $H = C_g/C_l$ where C_l is the concentration of the analyte in the liquid phase. Making sure the concentration units are consistent, an estimate of the liquid-polymer partition coefficient K_{lp} can be obtained using $K_{lp} = C_p/C_l = K_{pv}*H$. Preliminary data show accurate predictions of the response trends for several of the polymers used in this study. However, these results are beyond the scope of this manuscript [27].

4. CONCLUSION

This work describes some of the first published results of a QCM sensor array in for liquid sensing. The array consisting of QCMs coated with 9 polymer coatings was used to detect 12 different VOCs from three different classes of chemicals. Rapid and reversible responses were observed. The individual sensors provided characteristic patterns of responses for each chemical. A pattern recognition technique called VERI was used to build a training set of data for each chemical response per coating. A minimal set of coatings needed to separate all responses was determined from these training sets. Five films and six responses were determined to be the minimum number of responses necessary to discern all chemicals with >99% accuracy.

5. ACKNOWLEDGMENTS

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