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DEVELOPMENT AND EVALUATION OF ON-LINE DETECTION TECHNIQUES FOR POLAR ORGANICS IN ULTRAPURE WATER

Gregory C. Frye*, Dianna S. Blair, Thomas W. Schneider†, Curtis D. Mowry, Chris W. Colburn, and
Robert P. Donovan

Sandia National Laboratories, P.O. Box 5800, MS-1425, Albuquerque, New Mexico 87185-1425

†Currently at Science Applications International Corporation, 1710 Goodridge Drive, McLean, Virginia 22102

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Gregory C. Frye received his Ph.D. in Chemical Engineering from the University of Washington before joining Sandia in 1987. At Sandia, his research has focused on using surface acoustic wave (SAW) devices to develop chemical sensors and characterization techniques for thin film materials. Development efforts have resulted in the fabrication and field testing of portable, real-time, on-line or *in situ* (down hole) environmental monitoring systems for volatile organic compounds (VOCs). These systems include SAW sensors, environmental sampling hardware, and associated electronics, microprocessors, and software. Phone: 505-844-0787, E-mail: gcfrye@sandia.gov

Dianna S. Blair joined Sandia in 1985, performing basic research in the areas of catalysis and surface science. After returning from graduate work at the University of Washington, where she received her Ph.D. in Chemical Engineering, her research has focused on detecting organic analytes in aqueous media. This research includes developing an evanescent fiber optic chemical sensor as well as evaluating and modifying commercial instrumentation for performing automated on-site analysis for environmental applications.

ABSTRACT

An on-line monitor that can perform rapid, trace detection of polar organics such as acetone and isopropanol in ultrapure water (UPW) is necessary to efficiently recycle water in semiconductor manufacturing facilities. The detection of these analytes is problematic due to their high solubility in water, resulting in low partitioning into sensor coatings for direct water analysis or into the vapor phase for detection by vapor phase analyzers. After considering various options, we have evaluated two conventional laboratory techniques: gas chromatography and ion mobility spectroscopy. In addition, optimizations of sensor coating materials and sample preconditioning systems were performed with the goal of a low cost, chemical sensor system for this application. Results from these evaluations, including recommendations for meeting the needs of this application, are reported.

Keywords: On-Line Monitor, Water Analysis, Gas Chromatograph, Surface Acoustic Wave, SAW, Purge and Trap, Adsorbent, Acetone, Isopropanol.

INTRODUCTION

The 1994 National Technology Roadmap for Semiconductors (NTRS) report [Semiconductor Industry Association, 1994] identifies a need for reducing water usage in semiconductor manufacturing. The NTRS has established a 1998 goal of reducing water usage per square meter of silicon by 50% (compared to the 1988 usage). One approach capable of significantly reducing water usage is recycling the waste water from rinse processes back into the ultrapure water system. While a number of semiconductor

manufacturers currently recycle at least a portion of their rinse water, the present impact of recycling on industry usage in the US remains far below its full potential. An important barrier to more widespread adoption of recycling is the perceived risk to be associated with this approach. This fear has historical basis in that early ventures into recycling sometimes resulted in huge product losses attributed to the buildup of organic impurities in the recycle loop. Therefore, an immediate objective of this work was to develop near real-time, on-line sensors of organic contaminants in water recycle loops, providing early warning of excursions or spikes in organic concentrations and enabling an operator or a control system to divert flow well before production upset. Since the decision process would ideally also consider the type of organic contaminant, speciating analyzers, rather than just monitors of total oxidizable carbon (TOC), would be preferred.

On the advice of a SEMATECH advisory board, this work focused on the detection of three species, or analytes of concern (AOCs), that pose particular problems for water recycling. These AOCs are acetone, isopropanol (IPA), and ethylene glycol. (Other identified potential analytes include chloroform, N-methyl pyrrolidone and surfactants in general.) The detection of these AOCs is problematic due to their high solubility in water. For example, the strong attractive forces between the AOCs and water result in a limited ability of sensor coatings to selectively partition these compounds from water for direct water analysis. This partitioning is needed to concentrate the analyte at or near the sensor surface for improved sensitivity. Furthermore, this solubility results in low Henry's Law constants (H) indicating limited vapor phase concentrations when performing headspace or purge-and-trap analysis. For example, a one ppm acetone or IPA water concentration results in an equilibrium vapor phase concentration of only 0.7 and 0.2 ppm, respectively, compared with values of 30 and 70 ppm, respectively, for chloroform and toluene [1].

BACKGROUND ON TECHNIQUE SELECTION

The following performance parameters were chosen as priorities in meeting this application. (1) Compatibility with on-line, or better yet, in-line operation to provide near real time information on changing composition in the recycle stream. (2) Rapid response times with less than 30 seconds being the present goal. (3) Limits of detection, even though they will probably vary with the species being detected, need to be on the order of low ppb; the current goal is 30 ppb. (4) Speciation, enabling identification of specific organic compounds, which is a capability not currently available in any on-line sensor, is likely to become an important parameter in the operation and control of future recycle systems. Sensors possessing this capability will be especially valuable in future recycle systems.

Before initiating the development efforts, a literature review and evaluation of published results was performed for both conventional laboratory techniques and various chemical sensor systems. In some cases, preliminary experiments were performed to evaluate capabilities. The following techniques were not pursued based on this evaluation: (1) Direct absorption spectroscopy was found to be unlikely to provide the necessary detection levels due to strong water absorption bands in the same spectral region as the AOCs. This is different from TOC analyzers based on infrared (IR) detection of CO₂ produced by catalytic conversion of organics, a common laboratory analysis technique that is becoming available as an on-line analyzer (Zellweger Analytics, Inc., League City, TX) (2) UV fluorescence is inappropriate since none of the AOCs have strong fluorescence behavior. However, complexing of the AOCs with fluorescent dyes is a potential area for future research. (3) Quartz crystal microbalance (QCM) sensors and evanescent fiber optic chemical sensors (EFOCS) were both found to have low detection levels due

to the poor partitioning of the AOCs from water into polymer coating materials. (4) Electrical and electrochemical sensors were determined to be unlikely to provide sufficient sensitivity for the AOCs (this is aside from TOC instruments, such as from Anatel (Boulder, CO) and Sievers Instruments, Inc. (Boulder, CO), which depend on coupling to catalytic conversion of the AOCs to CO₂ that is detected based on conductivity changes).

Based on these preliminary evaluations, the following six tasks were chosen to pursue for detecting organic contaminants on-line, at low concentrations (<30 ppb), and in near real-time (<30 s):

1. Customized, fast response commercial TOC analyzers based on catalytic conversion followed by conductivity or IR detection of the CO₂ produced.
2. Customized detectors based on commercial gas chromatography hardware.
3. Ion mobility spectrometers (IMS) adapted for water.
4. Sensor coatings optimized for enhancing selectivity/ sensitivity.
5. Sampling technologies for AOC analysis in water using vapor sensors.
6. Planar, crystalline waveguides with selective coatings based on attenuated total reflection in the mid-IR.

This paper discusses, in separate sections that follow, the results from Tasks 2, 4, and 5 above. The IMS, Task 3, is discussed in a separate paper by P. R. Rodacy *et al.* in this same volume.

GAS CHROMATOGRAPHY BASED SENSOR

On-line analysis of trace contaminants in water has been reported using a variety of sampling approaches with both mass spectrometric and flame ionization detection. Continuous measurement of trace contaminants, such as acetone, has been demonstrated using headspace mass spectrometry [2]. A detection limit of one ppm was reported.

Lower detection limits are possible using gas chromatography/flame ionization detection (GC/FID). The FID is commonly used due to its simplicity, relatively low cost, dynamic range and sensitivity. The research reporting combined GC/FID and automated on-line sampling have used two approaches: preconcentration and direct injection. Preconcentration methods previously examined include membrane separation, sorbent trapping, cryo-trapping and liquid-liquid extraction [3]. Contaminants have been extracted on-line with hollow fiber membranes and detected by GC/FID, with a reported detection limit for acetone of 61 ppb [4]. Sorbent and cryo-trapping have been applied for sampling acetone vapor but the trapping methodology increases the time between measurements to several minutes [5,6]. In direct injection methods, the simplest configuration utilizes an automated valve to sample the liquid flow, followed directly by injection into the GC. This has been demonstrated with two types of commercial valves, one measuring acetone [7] and the other measuring low molecular weight alcohols [8]. In each case, the sampling rate was dependent upon the chromatography required for analyte separation of a large number of contaminants.

The work reported here focuses on using the FID as a total organic carbon detector in UPW. Analyte speciation was also addressed using GC/FID technology to determine whether sample fractionation can be achieved in the time limit required for the application.

Experimental Setup: The work was performed using a Hewlett-Packard 5890 Series 2 gas

chromatograph operated in an isothermal mode, typically 50 °C, with both uncoated and Carbowax-coated capillary columns. The injector port, maintained at 150 °C, was operated in a split mode and helium carrier gas was used. The FID was heated to 250 °C to minimize sample deposition. The chromatograph was interfaced to a PC based computer and controlled using Turbochrom™ software (Perkin Elmer Corporation). The HPLC grade acetone and isopropanol were obtained from Fisher Scientific. All samples were prepared volumetrically using deionized and carbon filtered water. Samples were introduced into the GC using a 10 µl Hamilton syringe.

Results and Discussion: A relatively short length of uncoated capillary column, 0.3 m, was used between the injector port and the FID to provide a means for introducing the unfractionated sample directly onto the detector. Various sample sizes of 10 ppm acetone solution, < 1 µl, were then injected into the system. This arrangement produced a flame stability problem. The pressure burst accompanying sample introduction and the effect of water, cooling the flame temperature, resulted in chronic flame outs. Therefore, a short, 1 m, Carbowax-coated column was used in place of the uncoated column, eliminating this flame-out problem.

Sample size was examined with the injector operating at a 20:1 split ratio to determine optimal conditions. As shown in Figure 1, a fairly linear relationship was observed between sample size and integrated detector response for both compounds. The detector was clearly not saturated in its response even at 5 µl. However, at sample sizes greater than 1 µl it was observed that the column became saturated after repeated sample injections, resulting in a large detector signal caused by either column bleed or sample carryover. Furthermore, stability of system response to the analytes was evaluated at 2 and 3 µl. The relative standard deviation of the integrated peak area was observed to increase from 5.4% to 8.6% for acetone and from 8.1% to 13.5% for isopropanol when the sample size was increased from 2 to 3 µl. This could be due to cooling of the detector flame by the water and/or the pressure burst associated with the larger sample size. Therefore, it was determined that for sequential sample injections, smaller sample sizes were optimal due to column saturation and response variability.

As shown in Figure 2, sensitivity of the FID to acetone was examined by injecting 1 µl of a 100 ppb mixture at a split ratio of 2:1 into the GC configured with a 1 m Carbowax-coated capillary column. The system response time was less than 2 s after injection and was probably limited by software data acquisition and display. Blank water injections were also performed to determine detector response. As can be

seen, the detector exhibited a response that was approximately 25% of the analyte signal. Since purity of water at the low parts-per-billion contaminant levels can be considered an issue, it is still unclear how much of this water peak is due to the water and pressure pulse and how much is due to detection of residual contamination in the "uncontaminated" water. However, assuming the blank water was uncontaminated and the response was due to a perturbation of the detector by water, setting a threshold value for positive response at twice the detector signal resulting from water suggests the FID can provide detection limits of 60 ppb for both acetone and isopropanol. This limit may be lowered by signal averaging, since the signal-to-noise ratio is known to increase as the square root of the number of signals averaged.

As shown in Figure 3, speciation has been addressed with injection of a 10 ppm mixture of acetone and

isopropanol at a 20:1 split ratio fractionated using a 30 m Carbowax-coated capillary column. The total analysis time for this separation was 2.2 min with a peak separation of 42 s. Though this response time exceeds the targeted response time (<30 s), the relatively broad peak separation shown in Figure 3 indicates that the column could be shortened to provide faster response and still provide effective speciation for these two species.

Performance Metrics Assessment: As currently configured, with a 1 m column between injector and detector, the FID can detect acetone and isopropanol concentrations in UPW down to 60 ppb in less than 2 s. Sensitivity of the technique to other organic molecules is dependent upon the number of carbon-hydrogen bonds present in the molecule. In general, the more bonds, the more sensitive the technique. Inorganic materials, not being oxidizable, will not be detected using FID. However, potential residue left on the detector by these inorganic compounds could affect detector performance. Therefore, prototype performance in realistic waste water streams will be an important part of future evaluations.

SENSOR COATING OPTIMIZATION

Most chemical sensors consist of a sensor coating (chemical interface) made of a material that will selectively sorb the chemical of interest and a transducer for converting changes in the coating due to chemical uptake into measurable electrical signals [9]. Sensor coatings are often made from rubbery polymers due to the variety of chemical properties that can be customized and the rapid and reversible uptake of chemical species. Examples of transduction mechanisms include acoustic (mechanical probing or mass detection using a passing acoustic wave), optical (detecting changes in absorbance or fluorescence intensity in guided light), and electrical (probing changes in conductivity or charge with a microelectrode). Some sensors can be operated in contact with liquids while others are only useful for vapor detection. For example, with acoustic wave sensors, a QCM can be used as a mass sensor in water while the more sensitive SAW sensor is too highly damped by compressional wave generation into water [9].

Due to the inherent sensitivity limits of these techniques, low level detection requires that the analytes partition from the gas or liquid into a coating material. This concentrating of the analyte into the coating is typically quantified by a partition coefficient K , where K is the ratio of the concentration of the chemical in the coating material to that in the contacting gas or liquid medium [10-12]. Large K values indicate large uptake of the analytes into the coating and thus, more sensitivity and lower detection levels. Partitioning depends on: (1) the strength of the chemical interactions between the species to be detected and the coating material and (2) the tendency of the species to want to partition out (i.e., condense) of the gas or liquid matrix.

Focusing on the first point, increasing the chemical interaction between the species and the coating will increase the amount of uptake by the coating at a given concentration, resulting in larger sensor response. These interactions can be increased by choosing the coating material to complement the species to be detected. Chemical interactions between a coating material and a species to be detected can be modeled using linear solvation energy relationships (LSER) that take into account the chemical properties of the coating and the interacting species [10-12]. These interactions are broken into: hydrogen bond acidity and bond basicity, polarity, polarizability, and a combined parameter that includes a positive term due to the dispersion interactions that occur between all molecules and a negative term due to the loss of chemical interactions in the coating material when an interacting species entering the material forms a

"cavity." Based on published LSER parameters [12] for hundreds of chemicals and more than a dozen coating materials, estimated partition coefficients can be generated to select the optimal coating material for an application and to predict detection levels [10,11].

In looking at the magnitude of the LSER parameters for the AOCs, the parameters that show most promise for improved detection are the hydrogen bond acid and base terms. However, since water has such a large hydrogen bond acidity, a hydrogen bond base polymer would be a poor choice since it would detect the AOCs but would be even better at detecting water (for example, poly(ethylenimine), the strongest hydrogen bond base with published LSER parameters, makes an excellent humidity sensor). Thus, the material of choice is a polymer with a strong hydrogen bond acid potential. This is verified based on calculating K values using the LSER predictions where the best candidate (P4V) is also the material with the largest hydrogen bond acidity.

The second factor mentioned above that determines partitioning is the tendency of a species to "condense" out of the air or liquid matrix. For vapor analysis, this is related to volatility of a chemical as represented by its saturation vapor pressure. For analysis of analytes in water, this tendency is related to the strength of the interactions between water and the chemical and is correlated to the solubility of the analyte in water. In other words, species with low solubility tend to want to "get out" of the water and, thus, will partition well into a hydrophobic sensor coating, while species that are similar to water will show lower partitioning. This is important for the AOCs since they are all fully miscible with water and will show a low degree of partitioning. The LSER K predictions for vapor phase detection can be multiplied by Henry's Law coefficients, that quantify the partitioning of species from water to air, to predict K values for direct water analysis [13]. The three soluble AOCs have much lower H values than low solubility species like chloroform and toluene and will be difficult to detect directly from water. Experiments with the QCM and the EFOCS show that these predictions appear to be accurate and that low level detection by direct water analysis is beyond current sensor technology.

Experimental Setup: The goal of this work was to identify, synthesize, and evaluate new coating materials to provide improved sensitivity and selectivity for chemical sensors for the AOCs. Since SAW devices have been shown to be a sensitive and versatile (i.e., can act as a mass sensor and detect any species that is sorbed into the coating without requiring an optical or electrical property change) platform, it was chosen as the sensor for evaluating new sensor coatings. The SAW devices used in this study consisted of an ST-cut quartz substrate with a gold-on-chrome metallization photolithographically patterned to form two interdigitated transducers. Application of an alternating voltage to one transducer generates an alternating strain in the quartz substrate due to its piezoelectric nature. This strain field launches a surface acoustic wave that travels along the surface of the device, mechanically probing the coating properties (e.g., mass, viscoelasticity), before being converted back into an electrical signal by the second transducer. Changes in film properties result in changes in wave propagation properties, specifically wave velocity and attenuation (damping). The wave velocity response, detected as a frequency change when the device is used as the feedback element of an oscillator circuit, is generally the most sensitive and can be used to probe mass changes of tens of picograms in a sensor coating material [9].

Since SAW devices only operate in the vapor phase, all testing was done using an automated vapor generation system to generate known concentrations of various vapors. This test system uses mass flow

controllers to vary flow rates of a vapor stream (generated by passing nitrogen through a bubbler containing the solvent to generate a saturated stream or obtained using a calibrated gas cylinder) and a nitrogen mix-down stream. Dilutions from 0.1% to 98% of full scale can be generated. Automated valves switch between a nitrogen purge stream and this mixed stream to switch between "zero gas" and a known concentration of a given analyte. Because of difficulties generating ethylene glycol vapors, attributable to its low volatility, testing focused on challenging coated SAW sensors to acetone and IPA as target analytes and humidity as the key interferant. All solvents used were reagent grade or better and deionized water was used for humidity tests.

SAW devices were coated by spin casting from solutions containing the polymer. The following coatings were tested (the frequency in parentheses is the frequency shift due to the coating -- an indication of film thickness): (1) PIB: poly(isobutylene) from Aldrich, MW = 1,300,000, 1.5% solution in chloroform at 2000 rpm (370 kHz), (2) PVA: poly(vinyl acetate) from Aldrich, MW = 195,000, 2% solution in acetone at 2000 rpm (155 kHz), (3) PVPR: poly(vinyl propionate) from Aldrich, 5% solution in toluene at 2000 rpm (250 kHz), (4) a proprietary hydrogen bond acid polymer obtained courtesy of Jay Grate of Pacific Northwest National Laboratory (PNNL), 2% solution in chloroform at 1000 rpm (365 kHz), and (5) poly(4-vinylhexafluorocumyl alcohol) (P4V) synthesized in house according to a literature preparation [14], <1% solution in chloroform coated four times at 1000 rpm (80 kHz).

Results and Discussion: The results for the five different coating materials are given in Figure 4 for acetone, IPA, and water. For reference, the noise level for the current system is generally less than two Hz. Early in this study, two polymer films, PIB and PVA, that had been previously used for detecting non-polar organics, were tested. These devices do respond to the acetone and IPA but with relatively small signals. The PIB has the advantage of a very small water response. In addition, a total of eleven other commercially available polymers being tested for other applications were tested on SAW devices with ten chemical species including IPA and acetone. The best polymer for the AOCs turned out to be PVPR with enhancements in sensitivity over PIB of 8 and 5 for IPA and acetone, respectively. Data for PVPR, shown in Fig. 4, illustrate the improved detection of acetone and IPA while at the same time, the humidity sensitivity remains similar to PVA. Ethyl cellulose and poly(epichlorohydrin) (neither shown) also gave significant improvements for the AOCs. These improvements were significant; however, they were not sufficient to lower detection levels sufficiently for this application.

The results in Fig. 4 for the two strong hydrogen bond acids (P4V and the PNNL polymer) show a dramatic improvement (almost an order of magnitude) in response for acetone and IPA and a humidity response larger than for PIB but similar to (PNNL) or actually lower (P4V) than for PVA and PVPR. The P4V polymer is glassy, making it difficult to dissolve for coating (the coating tested was relatively thin and sensitivity may be improved if thicker coatings can be prepared). The glassy nature of P4V also results in slower responses (15-60 s to respond and >60 s to recover) that could worsen with thicker coatings. The PNNL polymer is rubbery and easy to dissolve and coat. Responses are fast and easily reversible (<10 s to respond and recover).

Chemical selectivity arises due to differences in the chemical interactions between the chemical and the coating material. The hydrogen bond interactions result in a larger response to the polar species of interest as compared with low polarity organics such as tetrachloroethylene and toluene. For chemical selectivity, the P4V was found to be the best, for example, the ratio of the response to acetone to the

response to tetrachloroethylene when both vapors are at 10% of saturation was 1.2 for PVPR, 5.5 for the PNNL polymer, and 29 for P4V. Regarding the goal of chemical discrimination, molecular identification can be performed with only partially selective coating materials based on using an array of sensors with different coatings. The pattern of responses from this array can be deconvolved using a pattern recognition scheme to identify and quantify one or more species that are causing the responses [15-16]. The large data base of chemical responses for coated SAW sensors (more than 15 coatings with ten chemical species) and the demonstration of multiple coatings with good detection of the AOCs but with different selectivity patterns will be useful in developing sensor systems to identify and quantify chemical species, including the AOCs.

Performance Metrics Assessment: The hydrogen bond acid polymers are showing significantly improved detection sensitivity. The response times of these coatings have been shown to be less than 10 s during both uptake and recovery for the PNNL polymer while the P4V responds more slowly. The differences in chemical response pattern with different coating materials can enable the use of arrays of differently coated sensors to obtain the desired chemical discrimination.

WATER SAMPLING METHODS

The goal of the sampling methods task is to increase the sensitivity of chemical sensor systems, enable the use of vapor sensors for water analysis, and minimize the effect of interferants, especially water vapor. The main technique being evaluated is to use an adsorbent preconcentrator to trap the species of interest from a large volume of sample and then thermally desorb them into a small gas volume. This results in a concentrated sample plug that produces a peak in sensor response that is easy to detect even when baseline drift is occurring (much like detecting gas chromatograph peaks). Detection levels for vapor phase sensors can be decreased by two to three orders of magnitude using this technique [17]. For water analysis, air purging of a water sample onto an adsorbent bed can be used to load the adsorbent. As discussed previously, this works best for weakly soluble species that have large Henry's Law constants making them easy to transfer into the vapor phase. For the polar AOCs that are fully soluble in water, this purging is less effective; however, acetone and IPA do provide reasonable gas phase concentrations (0.7 and 0.2 ppm in the vapor per ppm in the liquid, respectively) that can be used to load the adsorbent (ethylene glycol cannot be effectively dealt with using this technique due to its extremely low Henry's Law constant).

Experimental Setup: Adsorbent preconcentrators were fabricated using a 1/8" stainless steel tube. A small amount (30-50 mg) of either a carbon-based or polymeric adsorbent was packed on the inside. A resistive wire was wrapped around the tube to allow rapid heating, thermally desorbing the species from the trap for analysis. About 3 minutes per analysis was required, mainly due to heating and cooling times. The use in future systems of very thin wall tubing, thin wires with effective insulation (to minimize the amount of epoxy needed to prevent shorting), and small RTDs for temperature control and detection should result in a lower thermal mass, more rapid heating and cooling and, thus, a lower total analysis time.

The following adsorbents were tested: Tenax TA and Tenax GR from Scientific Instrument Services, Carbotrap, Carboxen 569 and 1001, and Carbosieve SIII from Supelco, Amberlite XAD-2 and XAD-4 from Aldrich, and XUS-43493.01 from Dow Chemical. To evaluate their utility to a variety of VOCs, tests were performed with isopropanol, acetone, methyl ethyl ketone, chloroform, tetrachloroethylene,

toluene, hexane, and water. These tests evaluated chemical uptake and holding at room temperature, desorption temperatures, and water uptake and release.

Results and Discussion: The adsorbent evaluations indicate that of the adsorbents tested, the two best adsorbents for the AOCs are Carboxen 569 and Dow XUS-43493.01 since they provided effective uptake of both acetone and IPA with reasonable desorption temperatures (the Carboxen 569 does require very high temperatures for some of the species tested, such as toluene and tetrachloroethylene). Both adsorbents have some water sensitivity, with the Dow XUS being the most problematic with significant times required to fully purge adsorbed water. Some tests were also performed with Tenax TA due to its very low water uptake; however, it has marginal uptake for acetone and IPA.

Initial trials involved directly adsorbing analytes from water, followed by a short air purge to remove the bulk of the water, and then thermal desorption into inert flowing gas onto a SAW sensor. Although this technique holds potential for detecting all of the AOCs (since ethylene glycol is not at all amenable to purge and trap), this technique requires significant optimization to minimize residual water from the adsorbent that interferes with detecting the organic signals.

Subsequent trials all focused on a simple purge and trap system where air was bubbled at 100 ml/min through a volume (100 ml in these tests) of contaminated water and then flowed through an adsorbent trap for a specific time (e.g., one minute). The trap was then purged briefly with dry air and then thermally desorbed onto the SAW sensor. Results from tests with uncontaminated water and with two contaminated water samples are shown in Figure 5. This plot shows the SAW sensor frequency response during the thermal desorption step. For the uncontaminated water, no response peak is observed; however, with only 10 ppb of toluene or 100 ppb of chloroform contamination, an easily detected peak is observed. Based on comparing these results to the baseline response, detection levels of about 30 ppb for chloroform and less than 3 ppb for toluene can be predicted. These values demonstrate detection of these lower solubility compounds at or below the range of interest for this project (desired detection limit of 30 ppb). This was accomplished with a total analysis time of only three minutes. The analysis time could be reduced, probably to less than one minute, based on lower thermal mass adsorbent beds (see experimental setup above) and shorter purge and desorption times. As expected, tests with soluble species such as acetone do not exhibit these low detection levels since these species are not easily purged from the water (the same issues that lead to poor partitioning into coatings) and these polar species are not held as well by many of the adsorbents. Optimization of these sampling systems to provide low level detection of the AOCs is an area of ongoing research.

Performance Metrics Assessment: Sampling systems can enhance sensitivity and selectivity but increase costs and add to response times. 30-60 s run times seem possible but the sensitivity gained will have to justify the sacrifice in response time. Limits of detection at or below the 30 ppb goal have been demonstrated for low solubility species (e.g., chloroform and toluene) but more work is needed to reach these levels for the water soluble AOCs.

CONCLUSIONS AND RECOMMENDATIONS

The goal of this work was to develop and demonstrate an on-line detector with the following ideal specifications: (1) capable of monitoring acetone, IPA, and ethylene glycol contamination in ultrapure

water, (2) a limit of detection at or below 30 ppb, (3) an analysis time of 30 s or less, (4) speciation of the contaminants, and (5) low cost. The analytes of concern have been shown to provide a particular challenge since their solubility in water results in poor partitioning into sensor coatings or into the vapor phase for analysis by vapor phase analyzers. An FID detector with a short Carbowax-coated column was found to provide a 60 ppb detection level for acetone and IPA with a 2 s analysis time using a 1 μ l sample injection. A longer column provided speciation of these two compounds in 2.2 min.

Chemical sensors with simple water sampling systems offer the promise of low cost and simple operation if the other specifications can be met. Coatings that provide more than an order of magnitude improvement in sensitivity for acetone and IPA (over more conventional coating materials) have been demonstrated on SAW sensors. Adsorbent preconcentrators can provide significant decreases in detection levels with improvements in chemical speciation. Current systems require several minutes but improvements should be possible to provide 30-60 s analysis times. The 30 ppb detection level has been demonstrated for chloroform and toluene but improvements are still required to enable this detection level for the polar species of concern for this application. Chemical speciation should be possible based on an array of sensors, the temporal separation of species desorbing from the preconcentrator, and a pattern recognition scheme for molecular discrimination and quantitation.

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Fig. 1: FID detector response to 10 ppm solutions of acetone and isopropanol of indicated sample sizes.

Fig. 2: FID detector response to sequential injections of 1 μ l samples, 2:1 split ratio, 100 ppb acetone in water and pure water samples, on 1 m Carbowax column.

Fig. 3: Chromatogram of 10 ppm acetone and isopropanol mixture. 2 μ l sample injected on 30 m Carbowax capillary column, 20:1 split ratio.

Fig. 4: Frequency shifts of five polymer-coated SAW devices as a function of acetone (a) and isopropanol (b) concentration and relative humidity (c). Coatings are P4V (▼), PNNL polymer (●), PVPR (■), PVA (◆), and PIB (▲). The low concentration data for PIB, PVA, and PVPR have been extrapolated from higher concentrations where significant responses were detected.

Fig. 5: Response of PIB-coated SAW device during thermal desorption of Tenax TA preconcentrator loaded by purging for one minute with uncontaminated water (dotted line) and with water contaminated with 100 ppb chloroform (dashed line) and 10 ppb toluene (solid line).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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