VAPOR RECOGNITION WITH SURFACE ACOUSTIC WAVE SENSOR ARRAYS

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Introduction

Arrays of polymer-coated surface-acoustic-wave (SAW) vapor sensors were first reported in the 1980's [1-2] and have been the subject of intensive research and development efforts over the past decade [3,4]. Our primary interest in SAW sensor arrays stems from the potential for incorporating them into miniaturized instrumentation for assessing human exposures to toxic organic vapors encountered in the workplace and in the general environment. Toward this end we have explored various fundamental aspects of sensor-array design and operation, developed and tested prototype instruments and sub-systems for personal exposure monitoring and exhaled breath monitoring, and we are currently assessing the performance of such instruments for field testing the permeation resistance of chemical protective clothing for emergency responders and for assessing indoor air quality where dozens of organic compounds can be encountered at low-part-per-billion exposure levels.

Regardless of the specific application, a number of issues have arisen in the course of this research that might be considered generic to the development of SAW sensor arrays and associated instrumentation for organic vapor analysis. Among these are 1) designing the array for optimal selectivity through strategic coating selection; 2) assessing the limits of detection, recognition, and discrimination; 3) determining the minimum number of sensor required for a given analysis; 4) miniaturization; and 5) incorporating sample capture, preconcentration, and separation stages with the array to enhance analytical performance. In this presentation, we will highlight some of the work we have done to address these issues.

Background

In the SAW sensor, radio-frequency mechanical (acoustic) waves are generated within a piezoelectric substrate that has been coated with a chemically sensitive (e.g., polymer) film. The acoustic waves are launched and received by a pair of interdigital transducers (IDTs) on the device surface. A feedback amplifier connecting the IDTs permits sustained oscillation at a frequency determined by the device structure. Small changes in the mass and/or viscoelastic properties of the coating film caused by interactions with gases or vapors result in a change of the acoustic wave velocity, which can be measured indirectly as a change in wave frequency using digital frequency counting electronics.

When coated with absorbent thin films, these sensors can provide rapid, reversible responses, which vary in proportion to the vapor concentration over fairly wide ranges. When assembled into arrays of differently coated sensors, they offer sensitivity to a wide range of analytes, simultaneous multicomponent analysis, and analyte recognition rather than mere detection. These analytical features are not found in current portable instrumentation.

Correlating array response patterns with vapor identities requires statistical pattern recognition techniques or trained neural networks. For most of our work, we have employed extended disjoint principal components regression (EDPCR) for vapor recognition and quantification [5]. It can be applied to individual vapors or vapor mixtures of arbitrary complexity, and can yield the identity and quantity of the component vapors from multi-vapor

composite response patterns. Since responses to mixtures are invariably equivalent to the sums of the component-vapor responses with polymer-coated SAW sensors, it is possible to model mixture responses as linear combinations of individual vapors.

In several of our recent studies, we have found it useful to combine EDPCR with Monte Carlo simulations to assess array performance [6-9]. Using the calibrated responses for all vapors and sensors in a given data set together with modeled responses to mixtures, the Monte Carlo procedure is used to superimpose error on the response values to simulate the types of systematic and random variations expected from factors such as baseline noise, pump flow rate variations, sensor sensitivity, and small changes in background water vapor levels of captured samples. Samples from the population of error-enhanced responses are treated as "unknowns" that are assigned identities by comparison with calibrated (or modeled) response patterns using EDPCR. This is performed iteratively (e.g., >500 trials per vapor or vapor mixture) to yield statistical estimates of the nature and extent of errors in recognition and discrimination of the vapors under consideration.

This type of data analysis can reveal how many sensors are needed for a particular vapor mixture discrimination, what is the best subset of sensors to use, which vapors (if any) are most likely to present problems in discrimination, and the likelihood of such recognition errors. The influence of vapor concentration can also be examined. This is a very powerful tool for designing SAW sensor arrays and predicting performance as illustrated below.

Array Design - Coating Selection Strategies

Chemical diversity in sensor arrays can be achieved by selecting sets of coating materials having chemical structures that span the entire range of possible non-bonding interactions with the analyte vapors of interest. Isotropic functionalized polymers with glass transition temperatures below ambient temperature represent the class of sensor coatings for which relationships between structure, properties, chemical interactions, and array performance have been most thoroughly investigated. They generally form adherent coating films that can be deposited reproducibly by simply spray-coating or solvent casting.

The most rational approach to selecting polymeric coatings for a chemical diverse vapor sensor array entails the use of linear solvation-energy relationships (LSER), which draw upon the analogy between sensor responses to vapors and their retention in the stationary phase of a gas chromatographic (GC) column [10-13]. The LSER approach considers vapor sorption systematically in terms of contributions attributable to dispersion, dipolarity, polarizability, and hydrogen-bond acceptance and donation. An array of SAW sensors, each coated with a polymer whose functionalities give rise to interactions associated predominantly with one of these LSER components, should provide the diversity required for generalized organic vapor analysis where responses rely on equilibrium sorption.

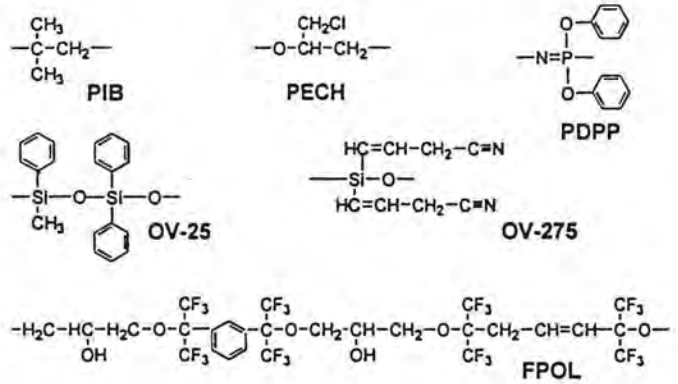

Figure 1. A chemically diverse set of polymeric SAW sensor coatings [8].

We have found the polymers shown in Figure 1 to be broadly applicable to the problem of organic solvent vapor recognition, and have employed these or subsets of these as SAW sensor coatings in our work. They span most of the interactions embodied in the LSERs. They form stable thin films and yield highly reproducible responses to vapors.

The Limit of Recognition

The two most important output parameters from SAW sensor arrays are the response pattern, which provides qualitative information, and the response sensitivity, which determines the limit of detection (LOD). The latter is used to define the operating limit in the low concentration range, under the implicit assumption that if a vapor can be *detected* it can be *identified* and *differentiated* from other vapors by its response pattern. We examined this assumption using a database of responses to 16 vapors from an array of four polymer-coated SAW sensors using Monte Carlo simulations and EDPCR [7]. Analyses were restricted to individual vapor recognition. Simulations were performed within a series of steadily decreasing concentration intervals for all of the vapors. Not surprisingly, the ability to recognize a vapor from its response pattern decreases with decreasing vapor concentration. However, it was found that the concentration at which errors in vapor recognition become excessive is well above the calculated LOD in most cases, despite the LOD being based on the least sensitive sensor in the array. On the basis of results such as these, we have suggested the adoption of a 'limit of recognition' (LOR), defined as the concentration below which a vapor can no longer be reliably recognized from its response pattern, as an additional criterion for evaluating the performance of sensor arrays.

Figure 2 shows results for toluene, where the shaded regions within an interval represent the fraction of cases where toluene was incorrectly identified as one of the other 15 possible vapors in the training set. Note that the statistically estimated recognition rate (1000 iterations for each interval) declines to about 50% at the LOD of 9 mg/m^3. The LOR (i.e., the lower limit of the concentration interval within which the correct recognition rate first declines to 95%) is at about 2.7 times the LOD concentration, or 24 mg/m^3. The most common error in recognition was where toluene was identified as either benzene or m-xylene, but there were several other types of recognition errors.

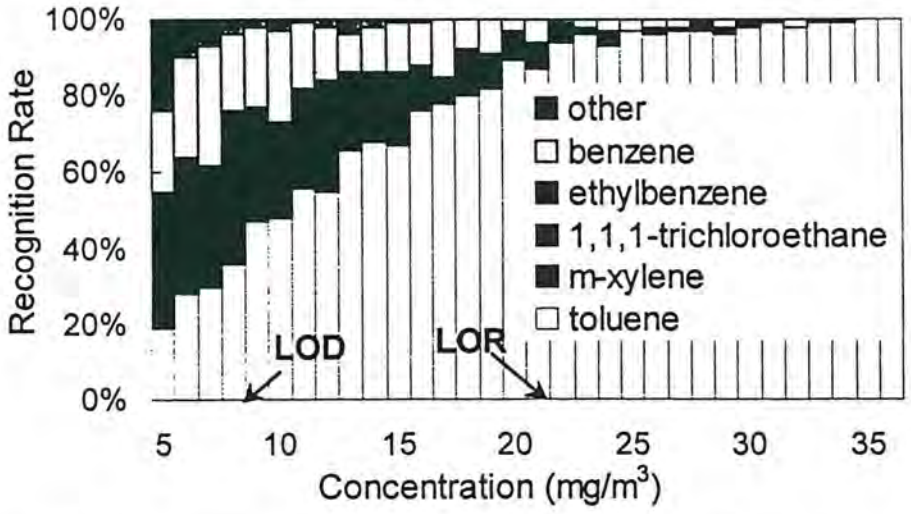

Figure 2. Plot of recognition rate versus concentration for toluene, illustrating how the limit of recognition (LOR) can be greater than the limit of detection (LOD) [7].

Minimum Array Size and Mixture Analysis

In a follow up study, we performed a comprehensive analysis of vapor recognition as a function of the number of sensors in a SAW sensor array [8]. Another data base of responses was generated for 16 vapors and various mixtures from six SAW sensors coated with the materials shown in Figure 1. In this case, the data were processed with the EDPCR/Monte Carlo method to derive estimates of vapor recognition rates as a function of the number of sensors in the array (up to six), the nature of the polymer sensor coatings employed, and the number and concentration of vapors being analyzed (up to mixtures of six vapors).

Results demonstrate that arrays of as few as 2-3 sensors can recognize individual vapors from a set of 16 possibilities with very low error. Furthermore, arrays of 3-6 sensor provide comparable results. Analyses also showed that individual-vapor recognition hinges more on the similarity of the vapor response patterns than on the total number of possible vapors considered.

Vapor mixtures were also analyzed for specific 2-, 3-, 4-, 5-, and 6-vapor subsets where all possible combinations of vapors within each subset were considered simultaneously. Representative results are shown in Figure 3. Very high recognition rates could be achieved for mixtures of up to four vapors using the same number of sensors as vapors in the subset. Lower recognition rates were generally found for mixtures that included structurally homologous vapors. Acceptable recognition rates could not be obtained for the 5- and 6-vapor subsets examined, undoubtedly due to the large number of vapor combinations possible in subsets of these sizes (i.e., 31 and 63, respectively). Importantly, *increasing the number of sensors in the array did not improve performance significantly for any of the mixture analyses*, suggesting that for SAW sensors and other sensors whose responses rely on equilibrium vapor-polymer partitioning, large arrays are not necessary for accurate vapor recognition and quantification.

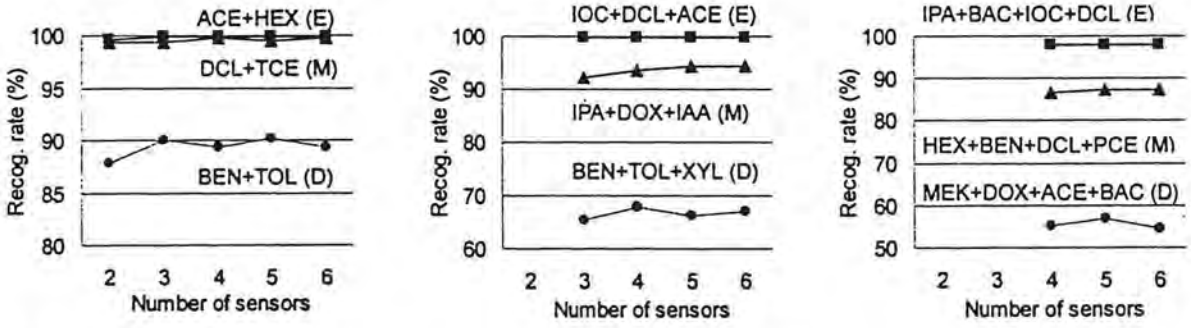

Figure 3. Average recognition rates for selected subsets of 2, 3, and 4 vapors as a function of the number of sensors in the array. The designations E, M, D indicate subsets expected to be easy, moderate, and difficult discrimination problems, respectively.

Shape-Selective Sensor Coatings

As demonstrated in the preceding study, homologous and structurally similar vapors represent the most difficult discrimination problems due to the similarity of partitioning into all of the sensor coatings. Attempts to augment the discrimination power of an array for such vapors by use of coating materials that are size- or shape-selective have been explored by a number of researchers with varying success [14-19].

In an earlier study we showed evidence for shape selectivity using a thermotropic liquid crystal (LC) coating, but found that the material slowly evaporated from the surface of

the sensor [14]. We therefore explored two less volatile anisotropic materials: a low-molecular-weight cyanobiphenyl LC and a side-chain liquid crystalline polymer (SCLCP). Both the LC and SCLCP exhibit room temperature smectic mesophases, and the LC also has a nematic phase between 33 and 41°C. Temperature, electric-field, and pretreatment with self-assembled monolayers (SAM) consisting of either a methyl-terminated (Me-SAM) or carboxylic acid-terminated (COOH-SAM) alkane thiol anchored to a gold layer in the delay path of the sensor were explored as means of affecting the alignment and selectivity of the LC and SCLCP films. Responses to the following pairs of isomeric organic vapors were measured: n-octane and iso-octane; p-xylene and m-xylene; and 4-methylstyrene and α-methylstyrene. Responses from SAW sensors coated with isotropic polymers (PIB and OV-275) were collected for reference.

Linear response isotherms were observed at low vapor concentrations, and the SCLCP exhibited consistently higher ratios of sensitivities (rod-like:non-rod-like isomer) at 25°C than the LC (Table 1), with sensitivity ratios ranging from 1.17 to 1.68 for the SCLCP and 0.92 to 1.37 for the LC. The SAM pretreatment did not significantly affect the LC or SCLCP selectivity. Curiously, positive frequency shifts were observed in response to all vapors for the LC on the Me-SAM, indicating a predominance of film stiffening vs. mass loading. FTIR-ERS characterization of the LC coating films provided insight into the vapor-coating dynamics. Operating the sensor in the LC nematic temperature range gave larger, but slower responses and did not affect selectivity. Selectivities were retained above the isotropization temperature for the LC on the Me-SAM, suggesting surface-induced retention of alignment. Reversible LC smectic-nematic phase transitions induced at high vapor concentrations resulted in dramatic increases in sensitivity and selectivity. Attempts to affect alignment by pre-exposure application of an electric field were unsuccessful.

Table 1. Sensitivity ratios (rod-like to non-rod-like isomer) for two isotropic coatings (PIB, OV-275) and the LC and SCLCP as a function of SAM pretreatment.

		SAW Sensor Coating							
Isomer Pair		PIB	OV-275	K24 LC -------	K24 LC Me-SAM	K24 LC COOH-SAM	SCLCP -------	SCLCP Me-SAM	SCLCP COOH-SAM
p-Xylene/	ratio	1.00	1.05	1.14	1.01	0.92	1.17	1.18	1.18
m-Xylene	std. dev.	NA	0.03	0.05	0.06	0.09	0.01	0.00	0.02
	n	NA	19	8	15	12	8	2	8
n-Octane/	ratio	1.00	0.74	1.02	1.05	1.10	1.27	1.65	1.68
iso-Octane	std.dev.	NA	0.06	0.11	0.13	0.01	0.07	0.08	0.09
	n	NA	8	8	4	2	8	2	6
4-Me-styrene/									
α-Me-styrene	ratio	1.00	1.15	1.31	1.35	1.37	1.47	1.44	1.45
	std.dev.	NA	0.02	0.16	0.21	0.11	0.02	0.05	0.05
	n	NA	15	13	16	13	8	6	13

PIB ratios were adjusted to a value of unity, and all other sensitivity ratios were adjusted accordingly to account for small changes in bubbler temperatures and/or saturation between tests of isomeric vapors.

Preconcentration

Where measurement of low concentrations of organic vapors in the ambient environment are required, preconcentration via a bed of a hydrophobic granular porous polymer can be useful. In addition to increasing sensitivity and reducing limits of detection (LOD), preconcentration can provide immunity from baseline drift as well as a degree of water-vapor compensation [9,21,22]. It has also been shown that elution times of desorbed peaks can vary and that this can be used to enhance vapor recognition and discrimination [9,23].

With a view toward miniaturization, a preliminary evaluation of two porous-layer open tubular (PLOT) capillary traps as vapor mini-preconcentrators for a series of organic vapors was conducted. Short (1-cm) sections of commercial PLOT-Q and PLOT-S capillary (≤ 320-μm i.d.) having 8-μm-thick wall coatings of styrene-divinylbenzene copolymer and divinylbenzene-vinylpyridine copolymer, respectively, were fitted with a metal sleeve for rapid thermal desorption of preconcentrated vapor samples, and tested using a downstream 97-MHz PIB-coated SAW sensor enclosed in flow-through cell of low dead volume. Calibrated responses to four organic vapors were collected with and without preconcentration. Increases in sensitivity of 2-24 fold and LODs of < 10 ppm were achieved by preconcentrating just 1 mL of sample air. Interestingly, for toluene and xylene the response profiles and sensitivities were the same for the PLOT-Q and PLOT-S traps, while for the more polar vapors, MEK and TCE, they were quite different. Thus, information from a sensor array can be augmented with information on elution time and differential sensitivity from two traps to assist in vapor discrimination.

Integrated Sensor Arrays and Microanalytical Systems

For polymer-coated sensor arrays it is feasible to consider sample reductions because responses depend on partitioning between a mobile phase and a stationary phase (sensor coating) rather than on total mass. As just described, it is possible to achieve low-ppm detection limits with just a 1 mL air sample if dead volumes are minimized.

We have just completed preliminary testing of a prototype instrument employing an integrated array of six polymer-coated flexural plate wave (FPW) sensors and an adsorbent preconcentrator (PCT) [24]. In the FPW sensor, the active region on which the acoustic waves travel in the FPW device is a membrane whose thickness is much smaller than the acoustic wavelength. As a result, wave energy is present at both the front- and back-side of the membrane and the entire membrane undergoes mechanical flexure.

The array of six FPW sensors shown (inverted) in Figure 4 has a total dead volume of only 20 μL. Responses to thermally desorbed samples of several vapors and vapor mixtures were analyzed. LODs as low as 0.3 ppm were achieved from a 60-sec (34 cm^3) air sample. Tests at different flow rates suggest that the kinetics of vapor sorption in the sensor coating films may limit responses at higher flow rates. Vapor recognition for individual vapors and selected mixtures was evaluated using independent test data and the Monte Carlo/EDPCR approach described above. This is the first report of an integrated FPW vapor sensor array.

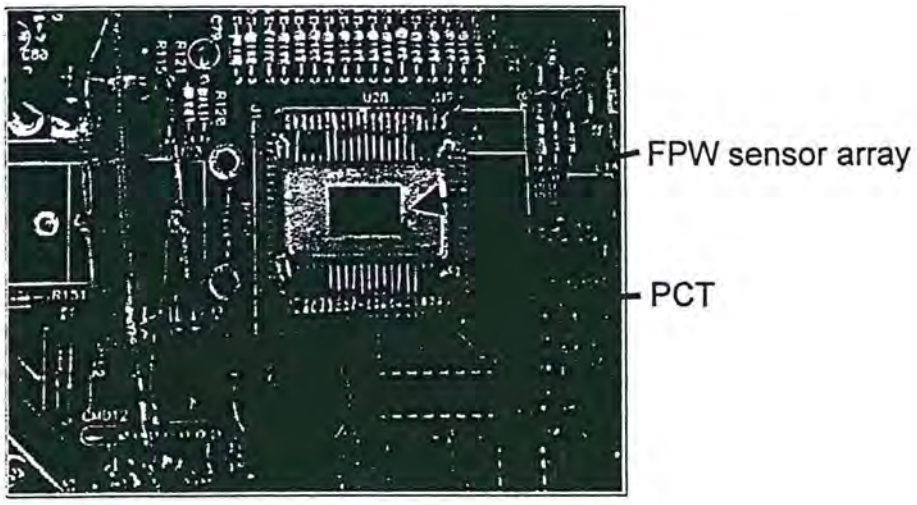

Figure 4. Integrated array of six FPW sensors and adsorbent preconcentrator (PCT) [24].

Frye-Mason et al. have developed an ultraminiature hybrid system comprising a planar single-stage sample preconcentrator, an etched-channel separation stage (gas chromatographic column), and an array of four 389-MHz SAW sensors as the detector [25,26]. These components, along with a separate miniature valve and diaphragm pump and the associated data acquisition and control electronics are being assembled into a palm-sized module occupying about ~10 in^3. The preconcentrator is an etched SiN membrane with a sol-gel adsorbent layer and an embedded heater that can heat the membrane to 200 °C in less than 10 msec using only 100 mW of power. Adsorbed target vapors are released into a concentrated and rapid pulse (<200 msec peak width at half max). The micromachined separation stage (gas chromatographic column) consists of a Si chip (~ 1 cm^2) with a 1.5-meter long spiral etched channel that is narrow (~ 50 μm) but deep (~ 400 μm). The detector is an integrated array of four 389-MHz SAW sensors fabricated on a single quartz chip having a total dead volume of 1-2 μL.

We are working with this group to test various sub-components of this microanalytical system, including the detector module. Figure 5a shows a picture of the 389-MHz SAW-sensor-array detector module with inlet and outlet capillaries and Figure 5b shows a chromatogram obtained using a conventional GC capillary column with the array as detector (output from only one of the working sensors is shown) for a mixture of six vapors, each at ~ 100 ppm, in a 250-μL sample of humid air. Limits of detection vary with each sensor. For this sensor, detection limits for MEK are below 1 ppm, while those for the other vapors range from about 1-5 ppm.

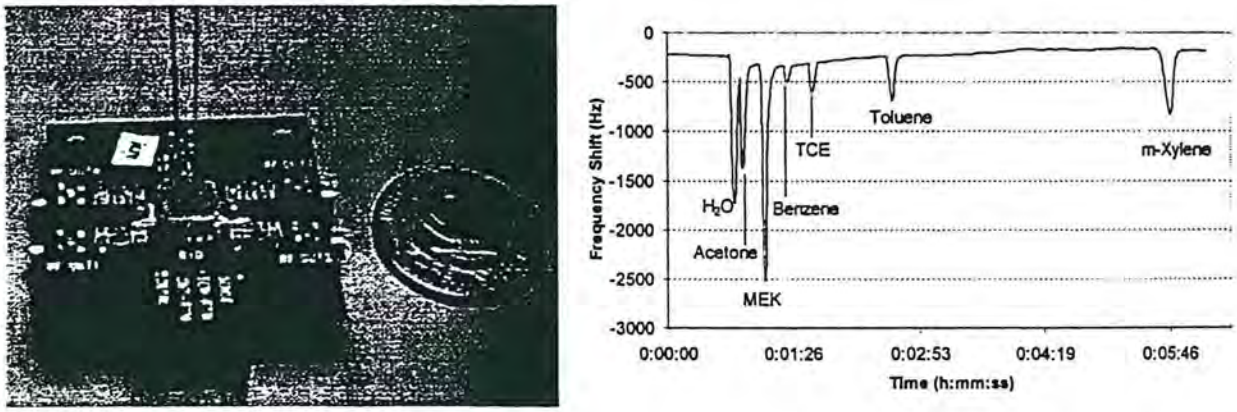

Figure 5. Response profiles from a 250-μL air sample containing 6 vapors injected into the GC/SAW-sensor-array system (data shown for only one of the working sensors).

Concluding Remarks

Using statistical tools we have developed, it is possible to predict the limits of detection, recognition, and discrimination of a SAW sensor array on the basis of limited calibration data. These can be used to guide sensor design efforts and to optimize the size and coating selection of an array for particular applications or for generalized vapor analysis. As illustrated above, an array of just 2-6 sensors is large enough for accurate vapor recognition in many cases. Even for problem cases, adding more sensors to the array is not likely to improve discrimination. Results also indicate that analyzing mixtures of more than four components will not be possible with polymer-coated stand alone SAW sensor arrays due to the complexity of the discrimination problem. Miniaturized systems that incorporate preconcentration and separation stages with integrated SAW or FPW sensor arrays can provide highly sensitive analysis of more complex vapor mixtures.

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Appendix 2

E. T. Zellers, "Vapor Recognition with Surface Acoustic Wave Sensor Arrays," Proceedings of the 4th Annual East Asian Conference on Chemical Sensors, Hsinchu, Taiwan, November 23-26, 1999, pp. 10-20.