Detection of volatile organics using a surface acoustic wave array system

R. W. Cernosek[*,a], W. G. Yelton[a], C. W. Colburn[a], L. F. Anderson[a], A. W. Staton[a],
G. C. Osbourn[b], J. W. Bartholomew[b], R. F. Martinez[b], A. J. Ricco[c], and R. M. Crooks[d]

[a]Sandia National Laboratories, Microsensor Research & Development Dept., Albuquerque, NM

[b]Sandia National Laboratories, Vision Science & Pattern Recognition Dept., Albuquerque, NM

[c]ACLARA Biosciences, Inc., Mountain View, CA

[d]Texas A&M University, Dept. of Chemistry, College Station, TX

ABSTRACT

A chemical sensing system based on arrays of surface acoustic wave (SAW) delay lines has been developed for identification and quantification of volatile organic compounds (VOCs). The individual SAW chemical sensors consist of interdigital transducers patterned on the surface of an ST-cut quartz substrate to launch and detect the acoustic waves and a thin film coating in the SAW propagation path to perturb the acoustic wave velocity and attenuation during analyte sorption. A diverse set of material coatings gives the sensor arrays a degree of chemical sensitivity and selectivity. Materials examined for sensor application include the alkanethiol-based self-assembled monolayers, plasma-processed films, custom-synthesized conventional polymers, dendrimeric polymers, molecular recognition materials, electroplated metal thin films, and porous metal oxides. All of these materials target a specific chemical functionality and the enhancement of accessible film surface area. Since no one coating provides absolute analyte specificity, the array responses are further analyzed using a visual-empirical region-of-influence (VERI) pattern recognition algorithm. The chemical sensing system consists of a seven-element SAW array with accompanying drive and control electronics, sensor signal acquisition electronics, environmental vapor sampling hardware, and a notebook computer. Based on data gathered for individual sensor responses, greater than 93%-accurate identification can be achieved for any single analyte from a group of 17 VOCs and water.

Keywords: chemical sensor, SAW device, sensor array, pattern recognition, VOC detection

1. INTRODUCTION

Traditional approaches to chemical sensing use single devices with distinct functionality to detect one analyte.[1] This usually works well in environments with few interferences to the target species or for detector-analyte combinations that are highly specific. The disadvantages of these sensors are (1) that isolated or interference-free chemical environments rarely exist or are not of high interest for most applications, (2) design and implementation for extreme specificity can be difficult and expensive, and (3) many different sensors are required to detect even a few analytes, adding to the complexity and cost. An alternate approach to chemical sensing is to develop an array of low-cost devices each with varying sensitivity and partial selectivity to many target analytes, and then utilize pattern recognition to discriminate among the analytes and determine concentrations of each.[2] This technique offers a high degree of detection accuracy and efficiency and can be adapted to a wide range of applications such as industrial process monitoring, environmental monitoring and remediation, and explosive and drug detection.

An excellent, universal platform for chemical sensors is the surface acoustic wave (SAW) device.[3-6] SAW sensors provide high sensitivity for vapor phase molecules and are readily configured for array sensing. Because of their planar geometry, the SAW devices also are easy to coat with sensitive interface layers. Large libraries of material coatings for SAW sensing applications have been developed through this work as well as earlier efforts,[3,4,6,7] providing a foundation for array systems. Recently, a new visual empirical region-of-influence (VERI) pattern recognition technique has been evaluated for use with the SAW chemical sensor arrays.[2,8,9] It has proven to be very accurate in discriminating among large numbers of analytes that

*Correspondence: P. O. Box 5800, MS 1425, Albuquerque, NM 87185-1425; Voice: (505)845-8818; Fax: (505)844-1198; Email: rwcerno@sandia.gov

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are chemically similar. Another strength of the VERI recognition technique is its utility in array selection and optimization from large sensor libraries.[10]

Many of the applications calling for chemical sensors focus on the detection of volatile organic compounds (VOCs) because they are readily encountered in numerous environments. Some VOCs are listed as environmental pollutants or workplace hazards that could lead to severe health problems. Thus, monitoring is required to determine concentrations and document regulatory compliance. Certain VOCs also can signify illegal or surreptitious activity, and government agencies (e.g., law enforcement) have needs to detect these activities and take appropriate action.

The SAW chemical sensor array system being developed attempts to satisfy some of these needs. The system is a culmination of the development work on SAW platforms, sensor coating materials, and VERI pattern recognition techniques. Evaluations of the component and system characteristics show that it possesses many of the desirable properties of a chemical detector: it is sufficiently sensitive to determine analyte concentrations at relevant levels, it can identify analytes from a large target list with a high degree of accuracy, it has rapid response for timely determination of information, it is insensitive to ambient temperature and humidity, it is portable and uses low power making it suitable for field applications, and it can be produced at low cost. Additionally, the system configuration is universal, requiring only a new SAW device array for different applications.

This paper begins with brief descriptions of the research and development of the SAW chemical sensor technology followed by details of the prototype sensing system. The paper presents, in order, discussions of the SAW sensor platform, the coating materials used for chemical sensing, the test analytes and laboratory procedures for sensor response characterization, the VERI pattern recognition algorithm and large sensor array optimization, the chemical sensor array system hardware and operation, and the expected system performances.

2. SAW DELAY LINE SENSORS

A schematic of the typical SAW sensor is shown in Figure 1. The substrate is ST-cut, X-propagating quartz with two inter-digital transducers (IDTs) patterned on the surface. Application of an alternating voltage to the input IDT generates a strain in the underlying quartz due to its piezoelectric properties. This strain launches a surface acoustic wave that travels along the substrate surface and is converted back to an electrical signal by the output transducer. A chemically sensitive and selective film placed in the SAW propagation path acts to perturb the wave velocity, v, and the attenuation, α, upon interaction with a gaseous species. Using the SAW device as the feedback element of an oscillator circuit (as configured in Figure 1), changes in wave velocity can be accurately monitored from the resulting shift in oscillator frequency, f. Alternately, the SAW device can be directly driven at a continuous single frequency and the phase shift, φ, measured.

The relative frequency or phase changes are proportional to relative velocity changes: $\Delta f/f_0 = \Delta\varphi/\varphi_0 = \kappa\Delta v/v_0$, where f_0, φ_0, and v_0 are the unperturbed frequency, phase, and velocity, and κ is the fraction of the wave path covered by the coating material. For the SAW devices used in these investigations, $f_0 \approx 97$ MHz. Wave attenuation or device insertion loss can be evaluated by comparing the RF power levels before and after the SAW device. Changes in insertion loss are represented as a normalized attenuation shift ($\Delta\alpha/k$), where $k = 2\pi/\lambda$ is the wavenumber and λ is the acoustic wavelength (~ 32 μm). Typical SAW delay line propagation lengths are $\sim 400\lambda$.

Frequency changes in SAW chemical sensors occur due to mass sorption in the film or a change in its viscoelastic properties.[11] Attenuation is dependent only on the viscoelastic properties since moving mass dissipates no power. The independence of these two sensor responses can be utilized for molecular identification if the viscoelastic component is large, as in some polymer films.[12] However, many sensor materials are relativity rigid, exhibiting low viscoelasticity, and thus cannot be used effectively for direct identification. This feature, coupled with the higher noise levels associated with attenuation measurements, leads to
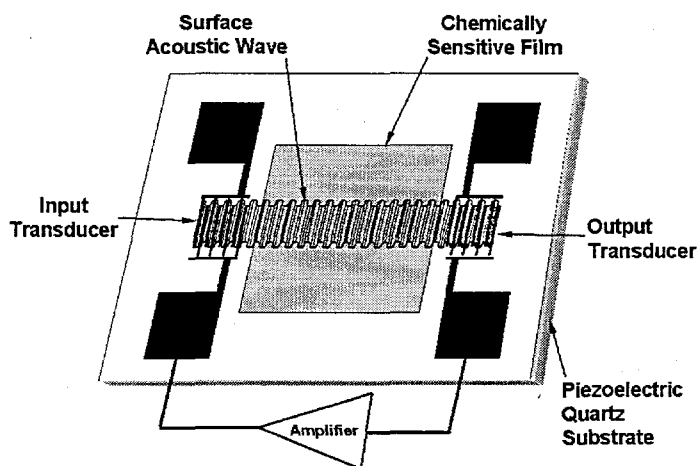

Figure 1. Schematic of a surface acoustic wave delay line chemical sensor configured as the control element in a simple oscillator.

the use of frequency shift measurements only in most chemical sensing systems. Pattern recognition from an array of sensor responses is then utilized for chemical discrimination. In SAW sensors dominated by mass sorption in the surface coating, the relative frequency shift is given by $\Delta f/f_0 = -c_m f_0 \Delta(m/A)$, where c_m is the coefficient of mass sensitivity, and $\Delta(m/A)$ is the change in areal mass density.[5] Frequency measurements using SAW devices can be very sensitive, as stability over a short interval (several seconds) is typically 1 Hz or better.[6] This measurement precision allows for mass determinations in the range of 100 pg/cm^2.

3. SENSOR COATINGS

The coating material between the SAW transducers provides the interface that defines the chemical sensitivity and selectivity. A foremost property of the interface material is its compatibility with the propagating surface wave. It must be capable of deposition as a thin film – usually less than a micrometer thick – and have low acoustic loss at the SAW operating frequency. Rapid and reversible responses also are required to produce sensors that relate information in real time and that can be utilized repetitively at low cost. Since it is desirable to produce an array of coated SAW sensors, each coating also should respond uniquely to the analytes of interest. Thus, diversity in the coating materials is a key to producing an optimized sensor array. Fortunately, significant fundamental research and development has produced a large and diverse collection of SAW interface materials. A good summary of these can be found in Ref. 5, Chap. 5.

Table 1 lists the sensor film library assembled for this work. Coating materials are sorted into six classes: polymers, molecular recognition materials, high-surface-area films, dendrimers, self-assembled monolayers, and plasma-processed films. One material, the polymer chirasil-val, actually spans two classes since it also provides molecular recognition. Focused research in these material classes is an ongoing effort, so the list in Table 1 is simply a snapshot in time. Moreover, the materials are only a small fraction of those available and are chosen as candidate films for detecting the target analytes discussed in Section 4.

3.1. Polymers

Early work with SAW chemical sensors utilized conventional and modified polymers as coating materials.[3,4] These materials still play a significant role in sensor film development, though custom-synthesized polymers are becoming more common to improve functionality.[13] Vapor-phase molecules partition readily into bulk polymers based on the solubility of that polymer in the organic compound. Polar (nonpolar) polymers have an affinity for polar (nonpolar) solvents; manipulating the hydrogen bonding capability modifies the affinity. Sorption of volatile organics in polymers often can be treated as a pure mass increase, thus making this class of materials one of the most studied for SAW chemical sensors.

3.2. Molecular Recognition Materials

Molecular recognition materials target a higher level of specificity for preferred molecule size, shape, and function.[7,14] These materials are not designed for absolute specificity as with biological systems since reversibility is a necessary property of the sensor response. Intermolecular interactions are achieved by incorporating weak chemical binding – metal coordination, cage compound inclusion, and π-stacking – that exceeds simple physisorption on the film surfaces. Included with these materials are compounds with chiral functionality required for detection of enantiomers. Development of the molecular recognition materials includes use of FTIR spectroscopy along with SAW analysis to fully characterize the films during vapor sorption.[14]

3.3. High-Surface-Area Films

Improved detection sensitivity is gained by using thin coatings with extremely high accessible surface areas. These materials increase the potential vapor sorption sites. Recent investigations have explored electrodeposited metals and electrochemically prepared metal oxides as high-surface-area thin films.[15,16] Mass-transport-limiting deposition of transition metals produces highly dendritic crystal growth on the SAW device surfaces. The high-area films scatter light with such great efficiency, they appear "black." Copper oxide coatings begin with a copper layer that is then oxidized using chemical conversion. Aluminum oxide films are produced by anodizing a vapor-deposited aluminum layer. Alumina pore size is controlled by the anodizing potential. Many of the metal and metal oxide films have surface areas greater than 100 times larger than the bare quartz surface.

3.4. Self-Assembled Monolayers

Self-assembling monolayers (SAMs) of *n*-alkanethiols are formed on gold surfaces from the liquid phase.[7,17,18] The hydrocarbon chain lengths vary from 2 to 16, with significant ordering for the longer-chain molecules. Chemical functionality occurs in the terminal groups, which can be manipulated either prior to surface immobilization or by chemical reaction after layer attachment. Acid terminal groups react with vapor-phase molecules through hydrogen bonding or proton transfer. A bilayer terminal group can be formed by deprotonating a bound mercaptoundecanoic acid (MUA) group and

Table 1. Chemical sensor coating materials arranged by class

Material Class	Sensor Films
polymers	*poly(isobutylene), PIB* *poly(epichlorohydrin), PECH*[#] *poly(dimethylsiloxane), PDMS, SE30*[#] poly(N-vinylpyrrolidine), PNVP *chirasil-val* (chiral amide-function polymer)
molecular recognition materials	*nickel camphorate* (coordinated Lewis bases) *nickel phthalocyanine* (aromatics via π stacking) *cyclodextrins* and calixarenes (molecular buckets)
high-surface-area films	*black platinum*[#] *(two processes)* *black gold*[#] *(two processes)* *black nickel* *black palladium* *copper oxide*[#] (conversion films, *two processes*) *aluminum oxide* (*anodize in sulfuric acid at two potentials,* *anodize in oxalic acid, anodize in phosphoric acid*)
self-assembled monolayers (SAMs)	*$HS(CH_2)_{15}CH_3$, C-16 thiol monolayer* (two substrate treatments) $HS(CH_2)_2SO_3H$ $HS(CH_2)_9CN$ $HS(CH_2)_9NH_2$ $HS(CH_2)_{10}COOH$, mercaptoundoenoic acid, MUA $HS(CH_2)_{10}\ COO^-/(Cu^{2+})_{0.5}$ $HS(CH_2)_{10}\ COO^-/(Ni^{2+})_{0.5}$ $HS(CH_2)_{10}\ COO^-/(Fe^{2+})_{0.5}$ $HS(CH_2)_{10}\ COO^-/(Zr^{2+})_{0.5}$
dendrimers	*G4 poly(amidoamine), OH + 2.5% C-6(CH$_3$) terminal group* *G4 PAMAM, OH + 21% C-6(CH$_3$) terminal group* *G4 PAMAM, OH + 61% C-6(CH$_3$) terminal group* *G4 PAMAM, 100% NH$_2$ terminal group* *G4 PAMAM, OH + 20.3% C-12(CH$_3$) terminal group* *G4 PAMAM, OH + 20.9% C-2 phenyl terminal group* *G4 PAMAM, 45% AEEA terminal group*[#] *G4 PAMAM, 48% OH + 52% NH$_2$ terminal group*
plasma-processed films	plasma-grafted acrylic acid, PGAA (two thicknesses) PIB/PGAA (two thicknesses) eugenol (phenol derivative) poly(vinyl acetate), PVA poly(allylamine), PALA poly(N-vinyl formamide), PNVF
none	*bare quartz*[#]

The 29 *italicized sensor films* are those used in the large array optimization investigations.

[#]These seven sensor films were selected for use in the prototype system array. Only one each of the high-surface-area films is used.

substituting different metal ions. Some of the metal-carboxylate interfaces show a strong affinity for select organophosphorous compounds.[7] The SAMs also can be utilized as a base or adhesion layer to form more complex bilayer structures.

3.5. Dendrimers

The dendrimers utilized here are polymers prepared by repetitive branching from an ethylenediamine core, with amidoamine branch units and primary-amine or hydroxyl terminal groups.[7] Fourth-generation (G4) poly(amidoamine) (PAMAM) dendrimers have a diameter of ~ 4.5 nm, and while they are relatively sterically crowded on the exterior, they are somewhat hollow in the interior. A feature of the dendrimers is that both the interior and exterior can be modified for target specificity. For example, the terminal groups are functionalized via epoxidation, amidation, or esterification with different exoreceptors to create the desired chemical affinity. A large number of terminal combinations are possible, leading to diverse coating

characteristics.[9] Dendrimers can be immobilized on SAW device surfaces directly on a gold layer or as a bilayer with intermediate alkanethiol SAM.[7]

3.6. Plasma-Processed Films

Plasma-polymerization and plasma-grafting processes produce thin organic films with a wide range of functionality.[1,19] Many different monomers can be polymerized using RF plasmas. The resulting polymers tend to be highly cross-linked due to the excess of free radicals in the plasma discharge. Altering cross-link density controls the film sensitivity and response time. Plasma-grafted polymers are a new class of polymeric materials with a more open and permeable matrix.[19] Composites can be formed by depositing a base layer of a plasma-polymerized film followed by a plasma-grafting of a second material. The result is a dendritic permeable thin film with a desired functionality produced at the base.

4. CHEMICAL ANALYTES AND SAW SENSOR TESTING

The development of SAW chemical sensors focuses on the detection of volatile organic compounds (VOCs). Individual analytes are chosen because they represent
- common industrial solvents
- pesticides and fertilizers
- various environmental pollutants
- relative humidity.

A list of the test analytes is given in Table 2, grouped according to chemical class. This 18-analyte set represents most of the major classes of VOCs plus water. Species such as chlorobenzene belong to both the chlorinated and aromatic hydrocarbon classes, while the mixture kerosene is primarily aliphatics and aromatics. The analytes cover a wide range of volatility and span the entire solubility spectrum, including both nonpolar (aliphatics) and highly polar molecules (alcohols and water).

Table 2. List of chemical analytes arranged by class

Chemical Class	Compounds Studied
aliphatic hydrocarbons	Cyclohexane
	hexane
	iso-octane
	kerosene[†]
aromatic hydrocarbons	*benzene*
	toluene
	chlorobenzene
chlorinated hydrocarbons	carbon tetrachloride
	tricholoroethylene (TCE)
alcohols	*methanol*
	1-propanol
	pinacolyl alcohol (2,2-dimethyl-3-butanol)
ketones	*acetone*
	methyl isobutyl ketone (MIBK)
organophosphorus compounds	dimethylmethylphosphonate (DMMP)
	diisopropylmethylphosphonate (DIMP)
	tributyl phosphate (TBP)
water	*water*

[†]Kerosene is typically a mixture of *n*-dodecane, several alkyl derivatives of benzene, naphthalene, and a pair of tetrahydronaphthalenes (Windholz, M., Ed., *The Merck Index*, 10th ed., Merck & Co.: Rahway, NJ, 1983)

The eight *italicized analytes* constitute the subset group used in array testing.

This group of 18 analytes is used for the majority of testing; other chemical species are added for studies of selected films, particularly the molecular recognition materials where enantiomer discrimination is important.[14] An eight analyte subset of the larger group, shown as the italicized species in Table 2, is used for some sensor array characterizations. This group consists of one analyte from each VOC class plus chlorobenzene and water.

Each coated SAW device is placed in a temperature controlled test environment and exposed to the individual analytes over the concentration range 0.1 to 80% of saturated vapor pressure (p_{sat}). SAW device frequency shifts and attenuation changes are recorded at 220 points over the concentration range. This large array of data points is needed since pattern recognition results are generally valid only when the number of data points is several times greater than the number of sensor elements in an array. Thus, for analysis of large sensor arrays a significantly large data point array must be acquired.

Because the vapor pressures of the VOCs are widely distributed, the various analyte concentrations could range from less than 1 ppm to greater than 100,000 ppm by volume. Over this large range, the sensors exhibit varying types of sorption characteristics and many are not linear. Figure 2 shows the adsorption branch isotherms for six high-surface-area metal and metal oxide-coated sensors when exposed to diisopropylmethylphosphonate (DIMP). All responses decrease monotonically (negative frequency shifts) with increasing vapor concentration and all are nonlinear. Since the oxide films typically have the greatest accessible surface area, they show the largest response magnitudes, especially at the higher concentrations.

5. PATTERN RECOGNITION AND ARRAY OPTIMIZATION

Since the individual SAW sensors are designed to partially respond with differing sensitivities to the 17 VOCs and water, high accuracy pattern recognition is needed to discriminate and quantify the analytes.

5.1. VERI Pattern Recognition

The visual empirical region of influence (VERI) clustering technique implements pattern recognition modeled after human perception.[20] VERI is a nonparametric, nonstatistical pattern recognition technique that is applicable to any kind of sensor responses. The region of influence clustering method extends to multi-dimensional analysis where each dimension is one sensor response. Dual output responses from a single SAW sensor can be introduced as two dimensions in the analysis. VERI clustering also provides a means for detecting both outlier points in data sets and unreliable or multiply matched points among data classes. Recently, VERI pattern recognition analysis has been applied to response data from SAW sensor arrays.[2,8,9]

Training sets for the VERI algorithm are derived from the analyte sorption isotherms described in the previous section and illustrated in Figure 2. It is important that sensor responses for training set data are acquired over the analyte concentration range expected in use; VERI has no means of interpolation or extrapolation, working only with the data provided. Since it is
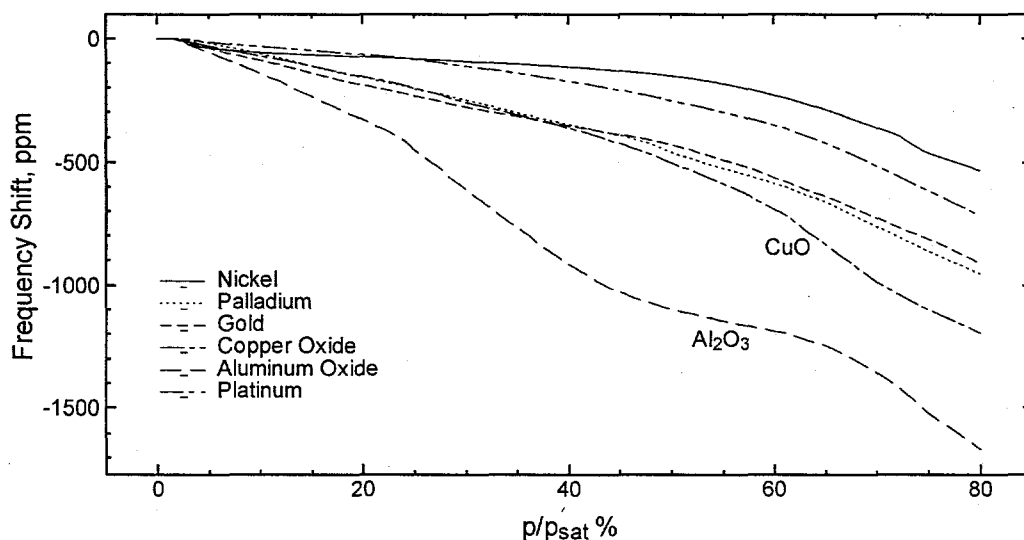

Figure 2. Adsorption branch DIMP isotherms for six high-surface-area metal and metal oxide films on SAW devices. DIMP concentrations range from 0.1 to 80% p_{sat} which correspond to 0.92 to 598 ppm by volume at 20 °C. Frequency shifts are given in ppm, where 1ppm = 97 Hz.

common for coated SAW devices to yield responses with widely varying magnitudes – both among the different sensors as well as for a single sensor exposed to different analytes, the algorithm first scales each sensor data set so the largest training response is unity. VERI clustering is then applied to assign class membership. One of the processing steps is a leave-one-out analysis of each response in every training data set. By holding out one response, the algorithm examines each point as if it is an unknown or new measurement and evaluates whether class overlaps exist (clustering with points from another analyte class) and whether classes are adequately sampled.[20] Points that do not cluster properly (incorrect, in multiple classes, or as outliers) are flagged so that these volumes of the multi-dimensional space are known for subsequent pattern recognition. Once the leave-one-out calculations are complete, VERI pattern recognition can be implemented on unknown samples.

An essential ingredient for successful pattern recognition development is inclusion of training data that represents the expected variability of sensor responses. Addition of variability to the data spreads out the array response patterns for each analyte, and can mimic changes in response magnitude over the sensor lifetime. Increasing the variability ultimately causes response patterns of differing analytes to overlap and become indistinguishable. The most robust arrays are those that exhibit the greatest performance for large added response variability to all sensors. The variability model used by VERI assumes sensors lose response sensitivity with time, so that future responses are related to the initial response reduced by a multiplicative constant (independent of analyte).[8] Since relative aging rates are not known for the different SAW films, a simulated data set is created for each analyte by adding random values of sensitivity loss to each sensor. The sensitivity loss is bound by a chosen ceiling value for all analytes in the data set, and thus controls overall array variability. Array discriminating performance is then evaluated for increasing levels of sensitivity loss.

5.2. Chemical Sensor Array Optimization

Optimal selection of sensors for various array applications is desirable to minimize cost and to maximize performance. The VERI pattern recognition technique is particularly well suited for implementing the combinatorial inspection tasks necessary for the array optimization.[8,20] Large libraries of training set data gathered on coated SAW sensors can be evaluated, and the top performing arrays identified. The 29 sensor films listed in italics in Table 1 were all exposed, under similar controlled test conditions, to the full 18-analyte set given in Table 1. Combinations of SAW sensors using these films were inspected using VERI for arrays of 2 to 29 devices.[10]

The full combinatorial comparison for all 29 available sensors is not feasible because there are too many sensor combinations to examine in a reasonable computing time. The fewest number of array combinations occur at the limits of small arrays (using only a few sensors) and large arrays (using all but a few sensors), and is largest for array sizes that use half of the available sensors (14 and 15 sensors). All array combinations for 5 or fewer sensors and 25 or more sensors were examined. For arrays of intermediate size, a technique called the "upper band" optimization was used to find small groups of candidate arrays that give the best performance.[10] The exact results for the top performing arrays with 5 sensors provide the basis for a good candidate set of arrays with 6 sensors. The chemical selectivities of these candidate arrays with N+1 sensors are then evaluated using VERI, and the upper band of these arrays are then used to build arrays with N+2 sensors, and so on up to arrays of 14 sensors. Similarly, exact results of the top band from the 25 sensor arrays are used to find candidate arrays of 24 sensors by removing one at a time. This process is followed to find top performing arrays down to 15 sensors.

The results of array optimization for the 29 SAW sensors are summarized in Figure 3.[10] Response maximum sensitivity losses were set at 20% and 35%. The plots give the percentage of correctly identified analytes for the best performing array (or arrays) as a function of the number of sensors in the array. For 20% maximum sensitivity loss, many array sizes yield 100% chemical selectivity. It is clearly necessary to have an array that is not too small for this case; however, arrays with as few as six SAW sensors have essentially perfect performance. For the larger value of response variability (35%), it is easier to identify the arrays that provide the best analyte discrimination, since all of the arrays fall below 100% selectivity. Arrays in the range of 8-15 sensors are best for this set of 18 analytes. At larger array
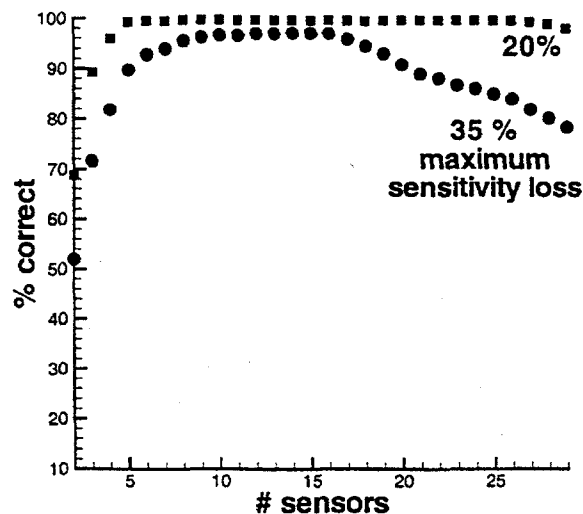

Figure 3. Chemical recognition performance on all 18 analytes for the best sensor array combination as a function of array size and with sensitivity losses of 20% and 35%.

sizes, the added effect of variability in the additional response channels dominates, so that chemical selectivity decreases with array size and potential false identification rates are expected to increase.

Following this large array optimization evaluation, the top 20 best-performing array combinations of six and seven devices were inspected. Not surprising based on the analysis, many of the same sensor films appear in each array combination. Using this information, six candidate films, along with a bare quartz surface, were selected for preparation of a 7-device SAW sensor array. (See Table 1 for the film list.) This group of sensors is considered near-optimal since not all the material coatings could be reproduced readily.

6. THE CHEMICAL SENSOR ARRAY SYSTEM

Based on the SAW platform development, sensor coating material investigations, and VERI pattern recognition array optimization, a prototype chemical sensor array system has been designed and assembled. Figure 4 is a general schematic of the system, while Figure 5 shows several photographs of the hardware. The heart of the system is the 7-device SAW array similar to the one shown in Figure 5(b). Coating materials for the seven SAW devices are noted in Table 1: the polymers PDMS (SE30) and PECH, a 4th generation PAMAM dendrimer with 45% AEEA terminal group substitution, the high-surface-area metals Au and Pt, the high-surface-area oxide CuO, and an uncoated SAW. The bare device can be used as a reference, though its response often participates in the chemical discrimination. The sensor array is contained in a sealed, temperature-controlled test case with electrical connections and gas flow ports. The array header is fully removable from the test case allowing sensor arrays to be customized for particular field applications. Test case temperature can be designated by the user, but typically, it is set at 45 °C to prevent condensation on the SAW device surfaces. A small diaphragm pump pulls vapor samples from the designated environment through the test case cavity. Periodically, the vapor stream is switched to a non-analyte containing state (scrubbed input) using a three-way valve, allowing sensor baseline to be recorded.

Individual sensor responses are interrogated using a continuous wave frequency source (operating at 97 MHz) and an I & Q (in-phase and quadrature-phase) demodulation scheme.[21] This technique compares the SAW phase delay and amplitude shift to reference values from the source and generates two dc voltages. The two voltages are processed later to reconstruct sensor amplitude and phase. Though this technique differs from the frequency shift and insertion loss measurements used in the lab, the extracted sensor information is equivalent. A pair of RF multiplexers located next to the array test case sequentially selects each of the seven devices and allows recording of individual responses. Scan time for all seven sensors is ~ 1.6 seconds. The sensor voltages and other system parameters, such as test case temperature, are recorded using a microprocessor-controlled data acquisition sub-system located on the system motherboard. This microprocessor unit also has an RS-232 serial port for communicating with the system notebook computer and both digital and analog output ports for implementing control commands (e.g., turning on the pump or switching the three-way valve) through the mother board. The remaining electronic hardware provides battery or wall-plug power, power supply conditioning, and a variety of support functions.

The system utilizes a Windows-based notebook computer for system control, real-time data display, data storage, and pattern recognition algorithm implementation. The software contains a shell routine, written in the Hewlett Packard virtual engineering environment (HPVEE), to perform the majority of system operations and provide the graphical user interface. Several control function modules are written in Visual C^{++}. Pattern recognition training sets are generated by following a controlled sequence of stepped isotherms (switching the analyte on and off at
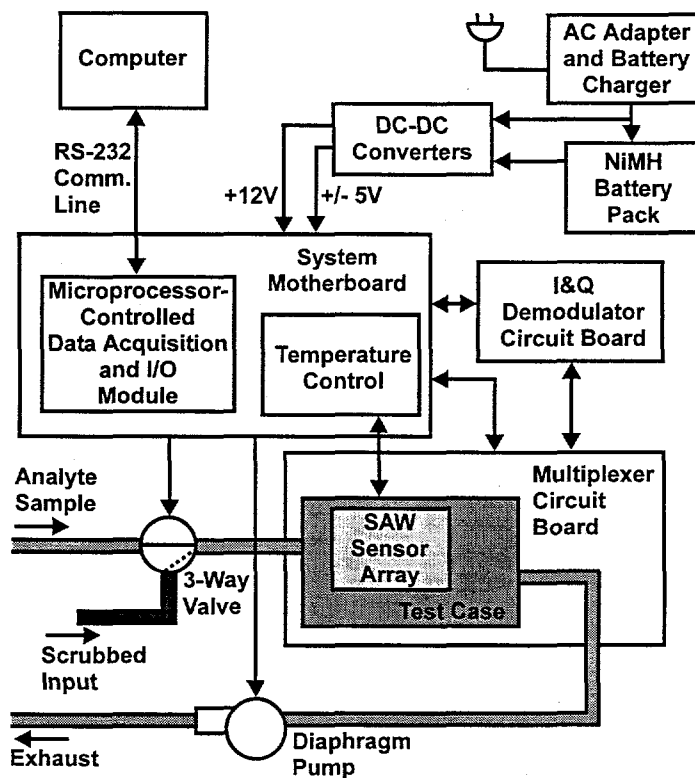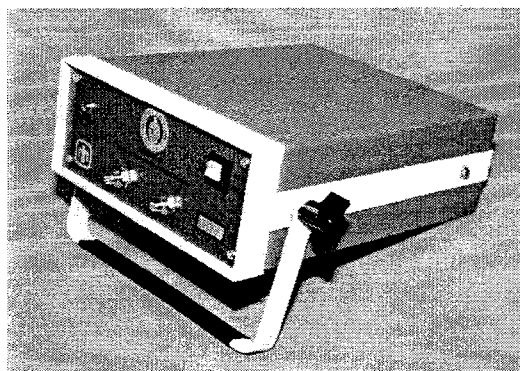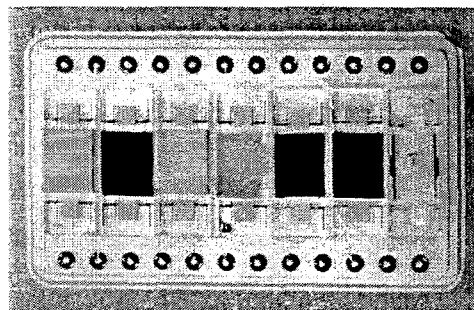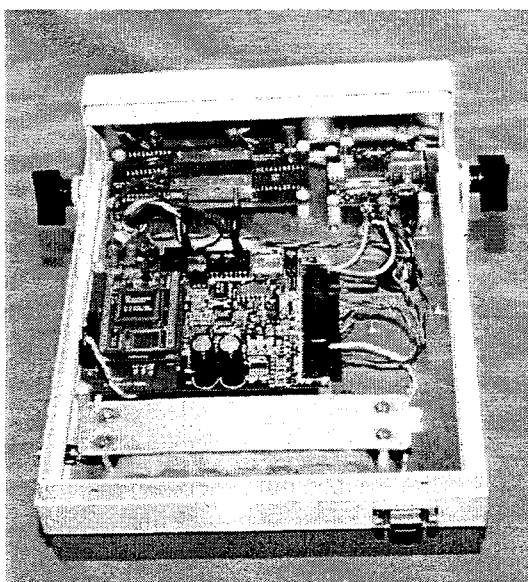

Figure 4. Schematic of the chemical sensor array system. The vapor flow path for analyte sampling and reference gas (scrubbed input) is shown as the shaded elements.
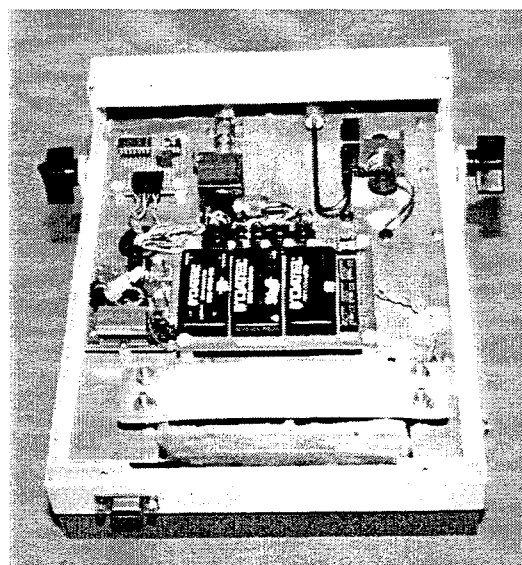
Figure 5. Photographs of the chemical sensor array system. (a) Exterior view of the enclosure. Enclosure dimensions are 8.2" wide × 3.5" tall × 10.7" deep. Vapor sampling ports, input and exhaust, are at the lower center of the front panel. (b) The 7-device SAW sensor array bonded in a 24-pin carrier header. The header footprint is 1.25" × 0.7". (c) Top section of the system interior. The SAW array test case is shown in the upper left; the I & Q demodulator circuit board is at upper right; the system motherboard is located in the center; and the NiMH battery pack is at the interior rear. The microprocessor-controlled data acquisition subsystem is a daughter board at the left side of the motherboard. On the back plate is the serial communications connector. (d) Lower section of the system interior. The diaphragm pump is at the upper right; the three-way sampling valve is at upper center; battery charging control and indication circuits are at center and upper left; and the DC-DC converter board is in the center just above the battery pack.

discrete concentrations as compared to continuous increases as in Figure 2). Subsequent data acquisition during environmental sampling follows a similar user-defined on-off sequencing.

7. DISCUSSION OF SENSOR SYSTEM PERFORMANCE

This prototype sensor system is designed to identify unknown chemical analytes from a specified set and then indicate the constituent concentrations. The long-term goal is to discriminate among several analytes in a mixture, identifying and quantifying each. Initially, the system is being trained to identify any of the eight analytes in the subset group listed in Table 2. Generation of the training data involves exposing the sensor array to a wide concentration range (0 to 80% p_{sat}) of each individual analyte, followed by exposure to binary combinations of the seven VOCs with water. Each component concentration in the binary mixtures is varied from 0 to 80% p_{sat}. This procedure is being implemented since the envisioned system demonstrations will involve sampling of VOCs from the environment in the presence of unknown, but widely varying, relative humidity.

At this writing, the training operation for the first system demonstrations is not fully complete. Thus, recognition performance in field environments is still unknown. In the interim, it is useful to investigate the expected system performance based on existing sensor library information and the VERI pattern recognition leave-one-out process. Such investigations assume that coated SAW devices in the prototype array will respond similarly to their predecessors and that array selectivity will be nearly identical. Introducing variability in the existing library sensor responses during VERI evaluation is one way to accommodate any expected differences, though this is not a recommended substitute for pattern recognition based on precise training data.

The expected performance of the 7-device SAW sensor array is shown in Figure 6 for both the complete 18-analyte test set and the 8-analyte subset. When maximum sensitivity loss is 20% (the minimum value plotted in Figure 6), array discriminating ability is greater than 94% accurate for all 18 analytes and greater than 96% accurate for eight analytes. Thus, for variabilities up to 20%, the performance of this sensor array is almost as good for the full analyte set as for the subset. As the maximum sensitivity loss increases, the array discriminating ability decreases sharply, with worse performance for the larger analyte set as expected. It is noted that a strength of the VERI clustering technique is its ability to separate data points that occupy regions of class overlap from those that cluster with the wrong class. As seen in Figure 6, essentially all data points that are not correctly identified cluster with multiple classes. As the class overlap increases with the larger data variabilities, more data points occupy these regions. An additional investigation looked at the performance of a 6-device array that eliminated the bare SAW device leaving the six coated devices. Results were essentially identical to those shown in Figure 6, indicating that the bare device does not influence the discriminating ability of this array.

Further details of the array performance evaluation are shown in Figure 7 where selectivity for each of the eight individual analytes is indicated. As the maximum sensitivity loss increases, discrimination of five analytes remains high (greater than 94%), but three chemicals – TCE, benzene, and chlorobenzene – become more difficult to distinguish. This feature results from the chemical similarity of chlorobenzene to both the aromatic hydrocarbon, benzene, and the chlorinated hydrocarbon, TCE. The sensor array provides responses that cluster properly for the exact training data (i.e., small variability) but that overlap significantly for larger variability. The other five analytes are from different chemical classes, and thus sensor responses remain highly independent. A similar analysis for the 7-device array and all 18 analytes indicates that many more compounds become increasingly more difficult to distinguish as the maximum sensitivity loss increases. The aliphatic, aromatic, and chlorinated hydrocarbons all elicit relatively poor array selectivity at higher variability, while the alcohols, the organophosphorous compounds, and water are easily discriminated. These results are not surprising since the analytes in the first group comprise VOC classes which contain compounds that are very similar chemically, while the analytes in the latter group comprise classes with more dissimilar compounds or those with a high degree of polarity. Designing sensors for the latter group is much easier. One encouraging aspect of these findings is that small sensor arrays may have a difficult time discriminating among some common solvents that appear chemically similar, but should easily be able to tell the difference between more-complex, toxic molecules.
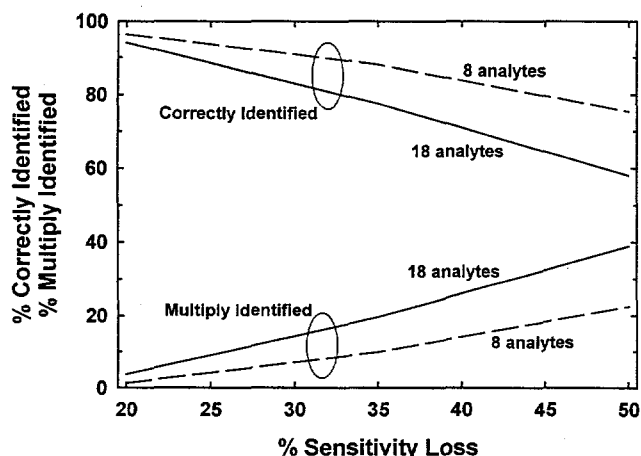

Figure 6. Performance of the 7-device SAW array in discriminating among 18 different analytes and an 8-analyte subset. The percentage of correctly identified analytes drops as sensor sensitivity loss increases. Note that plots begin at 20% sensitivity loss to better observe degradation effects.
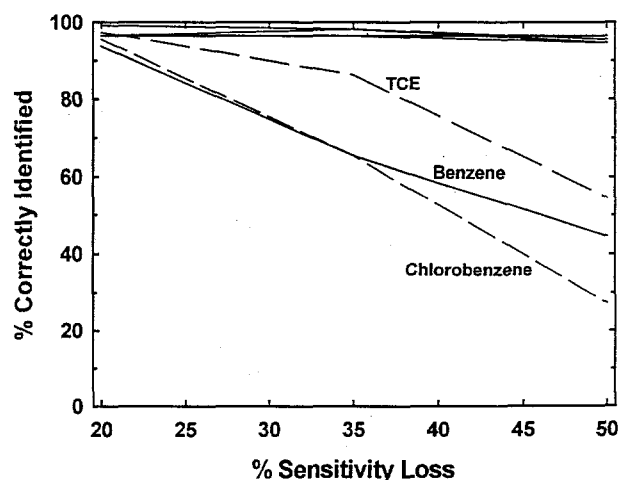
Figure 7. Discriminating capability of the 7-device SAW array for the individual chemicals in the 8-analyte set. The curves grouped at the top of the plot are responses for acetone, DIMP, water, methanol, and iso-octane.

As a result of these 7-device array evaluations, the prototype chemical sensing system is expected to perform quite well in its initial demonstrations with eight analytes. Subsequent operating performance with significantly larger analyte sets and with multi-compound mixtures will depend on the adequacy and precision of the training data sets gathered for VERI cluster analysis. If the sensor responses are expected to lose significant sensitivity during their lifetime, the array performance also will degrade accordingly.

8. CONCLUSIONS

Sensing systems utilizing SAW device arrays with diverse chemical interface materials and vision-based pattern recognition have many desirable characteristics. Measurement sensitivities are very good and accurate discrimination among VOCs and water has been demonstrated. Significant development efforts to refine the SAW chemical sensor technology and the VERI clustering algorithms have culminated in a prototype sensing system incorporating a 7-device SAW array. The system is portable providing the capability for on-site environmental sampling with rapid analyte determination.

The exact performance specifications for the prototype SAW chemical sensing system will depend on adequacy of training data gathered for the target analytes. Expected performance of the present system is greater than 96% selectivity among seven VOCs and water when sensor sensitivity loss does not exceed 20%. Selectivity among a larger set of 17 VOCs and water is only slightly lower at 93%, mostly due to the interference created by chemically similar analytes. For higher percentages of maximum sensitivity loss (sensor variability), performance degrades due to increased clustering overlap among classes as the data points spread out. This reinforces the need to properly identify all the anticipated sensor responses during training and to adequately predict sensor variabilities so that VERI clustering will maximize recognition of unknown analytes.

Evaluation of a large SAW chemical sensor coatings library during system development has provided direction for future research. Degradation in sensor array selectivity for certain classes of VOCs, namely the aliphatic, the aromatic, and the chlorinated hydrocarbons, indicates that greater diversity among coating materials might lead to more robust array performance. New materials can be added to the library, while existing materials can be studied to understand response degradations and improve stability. For large target analyte groups, it appears that identifying individual analytes by their chemical class is easier than discriminating among species within a class. Thus, sensor arrays and recognition algorithms could be implemented to inspect responses hierarchically instead of as a single large group.[10] Small subarrays would first sort analytes by broad class (e.g., distinguish alcohols from aliphatic hydrocarbons), followed by analysis of other small subarrays to distinguish the members of each class. Such hierarchical analysis becomes more important as the analyte list expands or the complexity of the chemical environment increases.

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