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TECHNICAL NOTE

CRIMINALISTICS

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Detection and Classification of Ignitable Liquid Residues Using a Fluorescence-Based Vapor-Sensitive Microsphere Array*

ABSTRACT: This paper describes the application of microsphere vapor sensing arrays to the detection of ignitable liquid (IL) vapors as both pure vapors and as residues (ILRs) on simulated fire debris samples. The temporal fluorescence response profile of the microsphere array generated a reproducible pattern unique to each analyte that could be used to classify subsequent sensor responses. This system, together with a support vector machine pattern recognition algorithm, was used to address several different IL and ILR classification scenarios. High classification accuracy (98%) was maintained over more than 200 vapor responses and the array was able to identify ILs when presented to the pattern classification algorithm within a dataset containing 11 other volatile compounds. Both burned and unburned IL treated samples were classified correctly greater than 97% of the time. These results indicate that microsphere vapor sensing arrays may be useful for the rapid identification of ILs and ILRs.

KEYWORDS: forensic science, ignitable liquid detection, artificial nose, microsensor array, pattern recognition, fluorescence

In 2006, there were approximately 31,000 intentionally set structure fires in the United States that resulted in the loss of several hundred lives and approximately $755M in property damage (1). Investigating a fire scene in an effort to determine whether the fire was deliberately set and if an ignitable liquid residue (ILR) is present poses several analytical challenges. The scene itself can encompass a wide area and comprise a large amount of debris, all of which must be examined and screened. Frequently, ILR containing debris is weathered due to exposure for extended periods to the ambient environment after the fire has been extinguished and it may be contaminated by the many people who, out of necessity, must track through the scene. Throughout the course of their inquiry, fire investigators consider numerous factors when formulating a hypothesis and drawing conclusions about the cause of a fire, one of which is whether or not an ILR is present. This aspect of the overall investigation can be determined from both scene analysis and chemical analyses performed in the laboratory.

When examining a fire scene for the presence of an ILR, methods that are capable of screening large areas in a reasonable amount of time without sacrificing specificity are preferred. Ideally, samples collected from areas of the fire scene where the concentration of ILRs is perceived to be high can increase the likelihood that meaningful results will be obtained when the samples are analyzed in the laboratory. One method of identifying areas of a scene containing an ILR is the use of canines trained to sniff and signal whether an ILR is present. Under ideal conditions, these canines together with their handlers, are estimated to identify the presence or absence of a target analyte correctly upwards of 90% of the time (2,3). Accelerant detection canines have demonstrated target compound sensitivities under laboratory conditions in the 10 parts-per-billion (ppb) range and as low as a 100 parts-per-trillion (ppt) (4). They can be trained to discriminate several vapors of interest and can reliably search for these compounds over a period of 30–120 min (5). Despite these impressive characteristics, the cognitive and physiological processes that underlie canine olfaction remain poorly understood and these methods lack an objective, quantifiable measure by which to express a conclusion. Nonstandardized training protocols, combined with the genetic proclivities of the animal, often lead to varied performance among units. The accuracy of canine/handler teams in the field is further affected by fatigue, the health and temperament of the canine at the time of the search, as well as the handler's interpretation of the canine's response (6). These factors add subjectivity to the interpretation of a positive canine response. Challenges regarding the admissibility of confirmatory identifications based solely on canine reactions have been presented in court (7). Furthermore, these animals and their handlers require a lengthy period of specialized training before they are qualified to work in an investigation and frequent follow-up training is necessary to monitor the competence of the team. Despite these shortcomings, dog/handler teams continue to provide the best means currently available to screen for ILRs at the scene of a fire.

Handheld, portable, instrumental alternatives to dog/handler teams for fire investigations are combustible gas leak detectors or "sniffers," which have seen limited use. Several formats of these devices employ a single vapor-sensitive element, most commonly an electrochemical transducer, and are broadly responsive to any type of combustible vapor. Recently, two of these instruments were evaluated for the detection of ILRs from simulated fire debris samples under several conditions (8). Only one of the two instruments

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tested was deemed suitable for field use. Its performance, however, was hampered by an inability to consistently distinguish between ILR positive and ILR negative samples. Because these instruments are broadly responsive to combustible vapors, background vapors generated from the substrate as a result of pyrolysis can be a source of false positive readings. A few jurisdictions have employed these devices; however, due to their inferior sensitivity compared to canines, susceptibility to false positive readings, and short sensor lifetime, these devices have not found widespread use.

One emerging technology that may, with continued study, address some of the shortcomings of other methods for ILR identification in the field are multi-sensor vapor detectors, commonly referred to as "artificial noses." In contrast to the single-element vapor-sensitive devices described above, artificial noses designed on the principles of mammalian olfaction, employ an array of semiselective cross-reactive sensing elements that generate a response pattern when they encounter analyte vapors. Pattern recognition algorithms enable these multidimensional responses to be analyzed and processed *in toto* as an aggregate signal encoding a particular vapor. Upon exposure of the array to an unknown analyte, stored response patterns to known analytes can be used to classify the response. Because of the cross-reactive nature of the sensor array and the large number of unique vapor-specific patterns it can generate, it is possible to detect many more analytes than there are sensors. Depending on how the system is trained, these devices can be configured to detect a subset of vapors particular to a specific analytical problem or they can be more broadly implemented to identify a wider range of analytes.

Several artificial nose platforms have been developed (9) that employ a range of different sensing mechanisms such as surface acoustic wave (SAW) resonators (10–12), polymer or low-volatility small molecule chemiresistors (13,14), cantilevers (15), calorimeters (16), metal-oxide semiconductors (17), and colorimetric sensors (18). The artificial nose system developed in our laboratory is a fluorescence-based system consisting of tens of thousands of silica microspheres (3–5 μm in diameter) that have a solvatochromic fluorescent dye adsorbed or covalently attached to their surface (19). Several different sensor types can be generated by varying the chemical functionality and/or dye present on the sensor surface. The sensors are distributed into complementary sized microwells that have been chemically etched into one face of an imaging fiber-optic bundle (20). The sensors are excited with light and the fluorescence responses are monitored through the non-etched end of the fiber using conventional fluorescence imaging equipment. Changes in the local environment surrounding the sensor due to vapor exposure are reported as a change in the position and/or intensity of the fluorescent wavelength maximum of the dye. Multiple factors including the surface functionality of the microsphere, the solvatochromic dye, as well as the polarity and degree with which the analyte vapor partitions into the sensor surface, influence the final sensor response. The use of microspheres as the sensor substrate enables billions of nearly identical sensing elements to be produced easily in a single step (21). Sensors from individual bead stocks are combined to form a mixture that can be used to fabricate thousands of arrays. Because the sensors respond with a high degree of uniformity, stored responses collected on one array or from an area within an array are easily transferred to subsequent arrays, thereby eliminating the need for successive retraining (22). We have previously demonstrated the application of this system to detect volatile organic compounds (VOCs) and bacteria (23), explosives (24,25), and nerve agents (26).

Herein, we present the results of an exploratory study into ILR detection designed to examine the ability of this fluorescence-based artificial nose system to distinguish between three classes of ignitable liquids (ILs) in both burned and unburned samples. We did not attempt, at this stage of the research, to determine the IL and ILR detection limits of the system, validate the method for routine analysis, or demonstrate field portability. Typical fire debris sample containers were modified for use on our laboratory-based system. Several samples consisting of liquid ILs, ILs applied to a substrate, and substrates treated with an IL and burned were tested and the responses processed using a support vector machine (SVM) pattern recognition program. The problem posed in this study is a straightforward classification query that remains challenging due to the complex background and unpredictable concentrations that inevitably occur as a result of sample combustion. Furthermore, we wanted to evaluate the performance of the system under several classification scenarios ranging from simple, such as whether or not an ILR is present on simulated fire debris, to complex, such as identifying not only the presence but also the class of ILR. We also examined the specificity of the array for ILs presented within the context of a wide range of diverse chemical vapors.

Materials and Methods

Sensor and Array Fabrication

The microbead chemical sensors utilized in this study were prepared in the same manner as those described previously (22) and are listed in Table 1. Briefly, three different 10 mg portions of 3–5 μm silica microbeads, each possessing a different surface functionality, were stirred for approximately 3 h in 1 mL of a 1 mg/mL solution of the solvatochromic dye Nile Red in toluene. The sensors were filtered and dried at 60°C overnight. A portion of each dried single sensor stock was combined into a mixture that was used to prepare the sensor arrays.

Sensor arrays were fabricated by chemically etching the polished surface of a 2 mm imaging fiber-optic bundle (Schott North America, Elmsford, NY) to produce an array of 50,000 microwells (27). The cores of the imaging fiber (4.5 μm diameter) are preferentially etched during this process and hence the diameter of the core defines the diameter of the microwell. An aliquot of the dry bead mixture is placed on the microwell array and gently tapped with a glass coverslip to distribute the mixture across the etched surface. The sensor beads randomly assemble into the microwells, one sensor per well. Excess beads are removed using a blast of air from a compressed-gas duster.

Imaging System

The imaging system has been described in detail elsewhere (22). It consists of an Olympus BX epi-fluorescence microscope equipped with a 75-W xenon excitation source (Ludl, Hawthorne, NY), and automated excitation, emission, and dichroic filter wheels. A Sensicam QE CCD camera (Cooke Corporation, Auburn Hills, MI) combined with a 20× (0.50 NA) objective and a 0.5× intermediate lens were used to image the array and collect sensor responses. Sensors were excited at 530 nm, the absorption maximum of Nile Red, and the emission was monitored at 640 nm. The

TABLE 1—*Microsphere sensor materials.*

Sensor Name	Bead Size (μm)	Bead Surface Functionality
Selectosil	5	Strong cation exchange
Chirex	5	Chiral
Alltech	5	C4

intensity of the excitation light was attenuated through the use of neutral density filters positioned in the optical path in front of the array as necessary to maintain the average sensor fluorescence intensity at the grayscale midpoint of the CCD camera.

Vapor Generation and Delivery

Analyte vapors were prepared and presented to the array using an eight-channel computer-controlled gas delivery system (GDS8) (Sensor Research and Development, Orono, ME). Each of the GDS8 lines (seven analyte channels and one ultra-zero air) utilized a mass flow controller and solenoid valves to maintain constant flow rates and allow easy switching between single and multiple analyte lines.

Sample vapors were presented to the array as dilutions of either a saturated vapor stream or sample headspace. Saturated vapor flows were generated by passing a stream of ultra-zero air (Total Hydrocarbon Content [THC] <0.1 ppm, Airgas East, Cambridge, MA) through a 120 mL glass bubbler (Ace Glass, Vineland, NJ) filled with the desired liquid organic compound. To ensure that a constant concentration of analyte vapor was maintained in the saturated vapor stream, the bubblers were periodically checked to verify that the level of liquid had not changed. Headspace vapors were collected from simulated fire debris samples housed in clean, dry metal fire debris cans (1 pint, Lynn Peavey, Lenexa, KS). To facilitate connection of the fire debris cans to the GDS system, two holes were punched on opposite sides of the lid and fitted with through-wall couplers (1/8 inch outer tube diameter, McMaster-Carr, Atlanta, GA). One connection was used for the positive pressure ultra-zero air line and the second connection was used to collect the flow from the sample headspace and deliver it to the sensor array (Fig. 1). All sample containers were maintained at a constant temperature of 25°C throughout these experiments. The samples were kept in sealed fire debris cans between analysis times. Both of the inlets to the container remained connected to the GDS lines. These lines are regulated by a solenoid valve that is closed except during times of vapor sampling, ensuring that sample vapors did not escape to the ambient environment.

The sample vapor stream emerging from the sample container was directed to a mixing manifold where it was diluted with ultra-zero air before being pulsed to the array. The fiber-optic sensor array was oriented such that the surface containing the sensors was perpendicular to the direction of vapor flow and positioned at the terminus of the vapor delivery line. A solenoid valve positioned directly behind the output of the vapor delivery line was used to alternate between a constant flow rate of 200 standard cubic centimeters per minute (sccm) of ultrapure nitrogen (THC <0.5 ppm, Airgas East) or the analyte vapor. Flow rates were fixed at 100 sccm of analyte vapor and 100 sccm of diluent ultra-zero air to produce a combined flow to the sensors of 200 sccm. Each analyte vapor was pulsed to the array for 0.8 sec. Following vapor presentation, the GDS lines and mixing manifold were purged with ultra-zero air for 45 sec, followed by an additional 30 sec purge during which ultra-zero air was flowed through the vapor delivery lines to the sensor array. Sensors were maintained under ultrapure nitrogen before and after all vapor exposure and purge sequences as well as periods during which data collection had ceased. The order in which analyte vapors were presented to the array was completely randomized for each data collection block, with each block typically consisting of 28 analyte vapor exposures (7 vapors × 4 repeats).

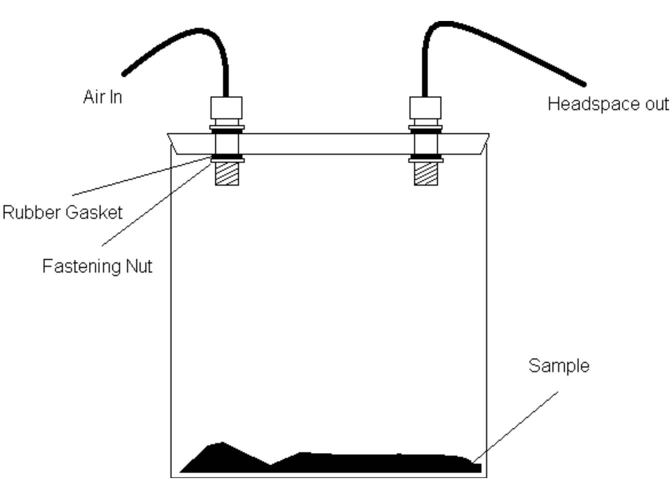

FIG. 1—*Schematic showing the container modification used to collect the sample headspace. Metal pass-throughs with a rubber gasket on either side were inserted into the lid of a metal arson can. Airtight seals were made by tightening the fastening nut on either side of the lid. Headspace vapors were sampled by passing ultra-zero air into the container through one connection, collecting the flow at the other connection, and delivering it to the sensor array.*

Sample Preparation

Analyte vapors were prepared from liquid samples of ethanol, dimethyl methylphosphonate (dmmp), p-xylene, ethyl acetate, chloroform, benzaldehyde, benzene, isopropanol (all of which were obtained from Sigma-Aldrich, St. Louis, MO), acetone (Fisher Scientific, Pittsburgh, PA), and water (in-house, deioinzed). Each liquid organic compound was used without further purification. Regular unleaded gasoline, diesel fuel, and Gulflite™ odorless charcoal starter were obtained locally and used without further purification for the preparation of IL vapors. IL samples were generated from the pure liquid and ILR samples were generated from simulated fire debris samples. The substrate for the simulated fire debris samples was nylon indoor carpet that had recently been removed from an active residence. Twenty milliliters of an IL was added to a 7.6 × 7.6 cm cutting of carpet, placed in a metal fire debris can, ignited with a butane lighter and burned in air, outdoors, until moderate charring of the substrate was observed. In total, the burn time was *c.* 3–4 min. The samples were extinguished via oxygen deprivation, cooled to ambient temperature, checked to ensure they were not smoldering, and the lid was sealed. Both GDS connection inlets were capped with an airtight rubber septum to prevent any headspace vapors from escaping to the ambient environment.

Data Collection

The imaging and vapor delivery systems were completely integrated, enabling synchronous control of the analyte delivery and image acquisition sequences. Sensor responses were acquired by recording a series of images before, during, and after the analyte vapor pulse. Each image was acquired using 100 ms exposure time and each 2 sec vapor response sequence consisted of four frames recorded prior to the vapor pulse, eight frames during the vapor pulse, and eight frames after the vapor pulse. 4 × 4 binning was used throughout data collection. The sensors were exposed to the excitation light only during image acquisition to minimize photobleaching of the fluorescent dye.

Data Analysis

The fluorescence intensity of each sensor as a function of time was extracted from each response movie using image processing software (IP Lab version 3.7.1; BD Biosciences, Rockville, MD). The response plots were imported into custom-designed software where they were normalized and grouped according to sensor type. Sensor-to-sensor variation in raw fluorescence intensity was processed by subtracting the value of the first time point in each sensor response sequence from every subsequent point. Every initial-value-subtracted point in the sequence was then divided by the maximum intensity value in the sensor response series. This process produces normalized responses that have a maximum intensity value between −1 and 1 and are virtually identical in shape for a given bead type. All replicate responses from the same sensor type within the array were averaged to increase the signal-to-noise ratio, and the averaged responses were concatenated according to bead type to produce an array super-response for a single vapor exposure (21). The super-responses for a dataset were compiled, formatted, and imported into Weka version 3.4.12 data mining software (University of Waikato, New Zealand). Classification of the super-responses was performed using a SVM algorithm and the algorithm was tested using 10-fold cross-validation.

Results and Discussion

Array Fabrication and Registration

The vapor sensing array is fabricated from an etched fiber-optic bundle and contains tens of thousands of individual vapor-sensitive microsensors. The microsensor fabrication procedure can be performed in parallel and offers a rapid method by which to produce billions of similarly responding vapor sensors. Three different types of microsensor beads were combined into a mixture that was randomly distributed into the microwells of the etched fiber-optic array. The identity of each vapor-sensitive microsphere within the array was ascertained by examining its intrinsic response to a predetermined vapor pulsed to the array immediately following fabrication (21,22). Custom-designed software is used to assign an individual sensor response to one of the three sensor types used to fabricate the array based on comparison to stored sensor responses. Due to the self-encoding character of the sensors and the high sensor-to-sensor response reproducibility, there is no need for a separate sensor encoding chemistry. Thousands of arrays fabricated from the same sensor mixture can be prepared.

Array Response to ILs

Three types of petroleum-derived ILs were selected based on the different distillation fractions they represent using current ASTM classification guidelines (28) and because they are frequently encountered during fire investigations (29). Regular unleaded gasoline was selected to represent this stand-alone class and odorless charcoal lighter fluid and diesel fuel were chosen to represent medium and heavy petroleum distillates, respectively. While these three classes do not comprise the entire family of ILs, the boiling point range spanned should provide a good estimate of the extent of flammable and combustible liquid mixtures to which the system is sensitive and the accuracy with which it is able to designate a particular class. To examine if the array responded uniquely to each

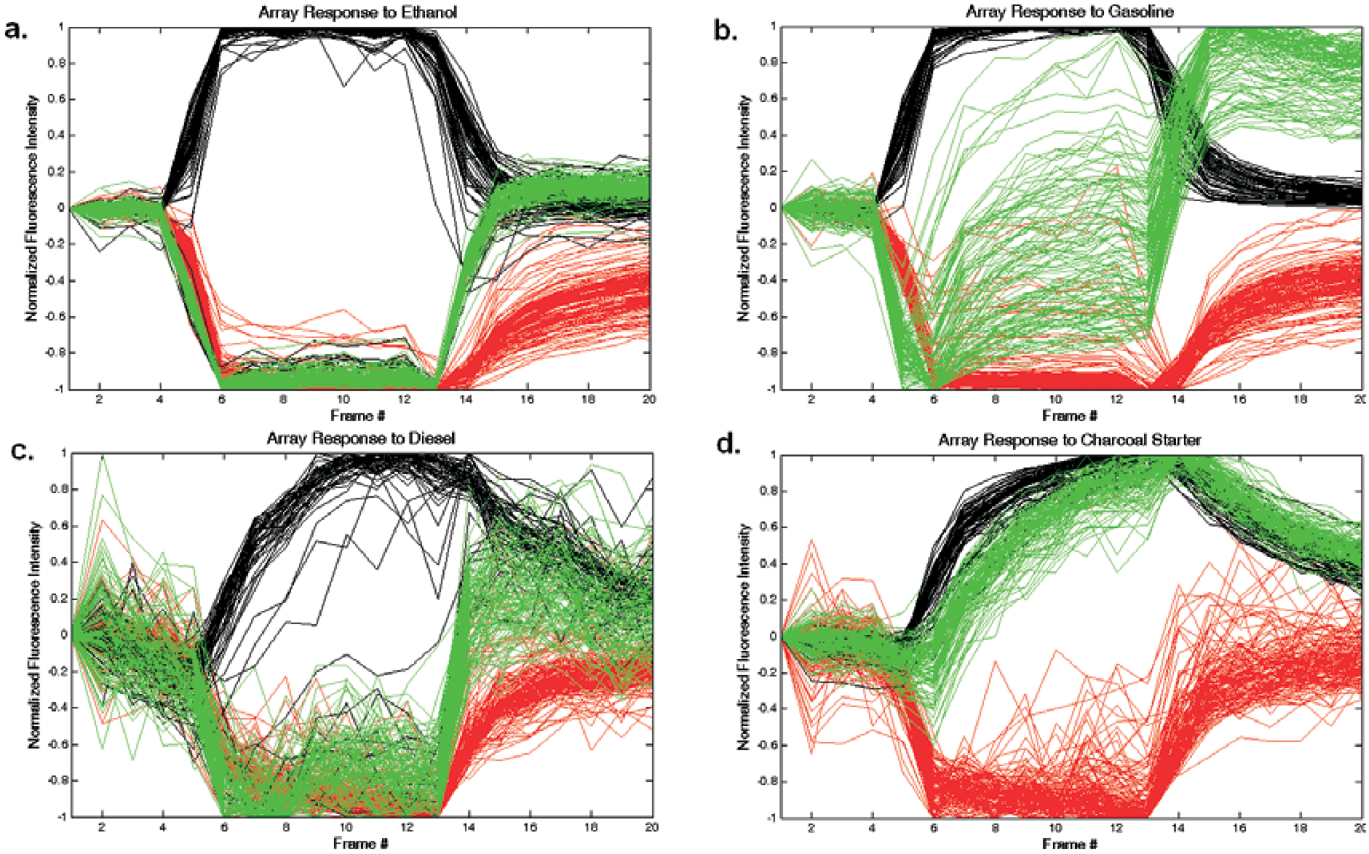

FIG. 2—*Temporal fluorescence responses of approximately 300 microsphere sensors to (a) ethanol, (b) regular unleaded gasoline, (c) diesel fuel, and (d) Gulflite™ odorless charcoal starter. The responses were obtained when the vapor was presented at 50% of its saturated vapor pressure at 25°C. The three sensor types displayed in these plots are Alltech (red), Chirex (green), and Selectosil (black). Sensor responses exhibiting a high level of noise (less than 10% of the total array responses) have been removed for clarity. These array responses, including those with a high level of noise, are subsequently averaged according to sensor type and the averaged responses are processed using pattern recognition software.*

of these mixtures, analyte vapor streams of each IL were prepared from pure liquid samples housed in 120 mL glass bubblers. Typical array responses to ethanol, diesel fuel, charcoal starter, and regular unleaded gasoline are presented in Fig. 2. Each plot displays approximately 300 normalized sensor responses and these individual responses are further grouped according to sensor type. Significant variations in individual sensor responses within the group are relatively low and are essentially eliminated when all the individual responses for a given sensor type are averaged prior to processing by the pattern recognition program. These plots are useful for highlighting the diversity of sensor responses that the array generates for a particular vapor, although it must be recognized that the visual representation does not capture some of the features used by the SVM algorithm. The sensor with the most dramatic change in response between the vapors is Chirex, while the remaining two sensors exhibit only subtle changes. Examined collectively, the combination of these three nonspecific sensor responses comprises a multidimensional signal that is the basis for analyte identification in this artificial nose system.

Identification of ILs in a Diverse Set of Vapors

One way to determine the ability of an artificial nose to discriminate a large set of vapors is by processing the responses with a pattern recognition algorithm and evaluating the model using cross-validation. The classification accuracy calculated from the cross-validation experiment provides an estimate of the predictive power of the system to discriminate new data. Our previous studies have utilized the instance-based learning algorithm k-nearest neighbor (k-NN) in conjunction with 10-fold or leave-one-out cross-validation to characterize the performance of the system to a particular problem. In this study, we utilize a different algorithm, a SVM, to classify sensor responses. SVMs are computationally similar to linear models but they differ in that they incorporate a maximum margin hyperplane, rather than a line, as the class separator in feature space. The maximum margin hyperplane represents the decision boundary that provides the largest magnitude of separation between two distinct classes. SVMs determine the location of this hyperplane not by using every instance in a particular class, but rather by selecting the specific instances that actually define the maximum distance between two distinct classes. By focusing on these critical instances, known as the support vectors, SVMs can decrease the computational complexity of the algorithm and clearly define the optimal separation between two particular classes. SVMs iteratively calculate the maximum margin hyperplanes for each pair of classes within a dataset and compile them into a mathematical model that fully describes the entire dataset. Often, two classes are separated by a nonlinear boundary. While this nonlinearity would provide a problem for conventional linear models, SVMs contain a provision that enables data to be transformed nonlinearly prior to calculating the maximum margin hyperplane. While computationally more involved than simple linear models or instance-based methods, SVMs have consistently provided superior classification accuracy with our artificial nose data, hence we utilize them here.

Cross-validation evaluates the predictive ability of a classifier by partitioning the dataset into n equal parts (n is a user-defined number) and then builds a predictive model using $n - 1$ portions of the data as a training set with the pattern recognition algorithm. The remaining data are used to test the model built on the training data. This train/test procedure is repeated until each partition has served as the test data once. In this way, every instance in the dataset has served as an unknown sample one time. In this study, we employ 10-fold cross-validation because it reduces the time required to carry out the calculation while maintaining the statistical relevance of the classification score (30).

We applied these procedures to a dataset of array responses to 14 different vapors, three of which were the ILs selected for this study, presented to the array at 50% of their saturated vapor pressures. We evaluated the ability of the system to distinguish ILs collectively, as well as individually, from a larger set of chemically diverse analytes. Sensor responses were classified using an SVM and the classification score for this dataset is displayed as a confusion matrix in Table 2. The classification score, expressed as a percentage of correct identifications, is presented at the top of the table. The confusion matrix expresses the classification accuracy for each individual vapor, listing its true identity on the vertical axis and the identity assigned to it by the classification algorithm on the horizontal axis. The scores for this dataset were calculated using concatenated three-sensor super-responses and the vapor identities were classified with 98% accuracy indicating that the system performs well when challenged with diverse vapors. This high classification accuracy includes 252 vapor exposures, collected over the course of 2 days, underscoring the

TABLE 2—*Support vector machine 10-fold cross-validation classification score and confusion matrix for the dataset containing concatenated three-sensor super-responses to 14 chemical vapors.*

	Classified As													
Actual Compound	etoh	air	dmmp	pxyl	etace	ace	chlor	wat	gas	Beald	benz	gulf	diesel	iso
Correctly Classified Instances: 247 (98.4172%).														
Incorrectly Classified Instances: 4 (1.5873%).														
etoh	18	0	0	0	0	0	0	0	0	0	0	0	0	0
air	0	18	0	0	0	0	0	0	0	0	0	0	0	0
dmmp	0	0	18	0	0	0	0	0	0	0	0	0	0	0
pxyl	0	0	0	18	0	0	0	0	0	0	0	0	0	0
etace	0	0	0	0	18	0	0	0	0	0	0	0	0	0
ace	0	0	0	0	0	18	0	0	0	0	0	0	0	0
chlor	0	0	0	0	0	0	18	0	0	0	0	0	0	0
wat	1	0	0	0	0	0	0	17	0	0	0	0	0	0
gas	0	0	0	0	0	0	0	0	18	0	0	0	0	0
beald	0	0	0	0	0	0	0	0	0	18	0	0	0	0
benz	0	0	0	0	1	0	0	0	0	1	16	0	0	0
gulf	0	0	0	0	0	0	0	0	0	0	0	18	0	0
diesel	0	0	0	0	0	0	0	0	0	0	0	0	18	0
iso	1	0	0	0	0	0	0	0	0	0	0	0	0	17

etoh, ethanol; dmmp, dimethyl methylphosphonate; pxyl, p-xylene; etace, ethyl acetate; ace, acetone; chlor, chloroform; wat, water; gas, regular unleaded gasoline; beald, benzaldehyde; benz, benzene; gulf, gulflite odorless charcoal lighter; iso, isopropanol.

reproducibility of the sensor responses. The IL samples were distinguished from all the other vapors and correctly assigned to their respective classes. The four misclassifications can all be ascribed to either the close chemical similarity between the confused vapors or random instrumental error. The absence of a large number of confusions for any single vapor class points to random instrumental error; however, confusion due to a high degree of chemical similarity has been seen in other datasets and cannot be completely ruled out here. The single misclassification of isopropanol with ethanol demonstrates that two vapors with comparable physical and chemical properties can be confused. Regardless of the type of error leading to the misclassifications in this dataset, the relatively low percentage of vapors that were misclassified does not represent any significant problem with the overall classification accuracy of the system.

Headspace Collection

Metal fire debris cans were selected as containers for headspace samples and for simulated fire debris due to their common use as packaging for fire debris evidence (29). Pint-sized cans were modified to enable connection to the GDS and thereby facilitate direct sampling of the headspace within the container. Soap bubble tests confirmed that there was no air leakage from either the line connections or the lid seal of the cans. A comparison of sensor responses to air passed through a bubbler and air passed through the modified metal fire debris can confirmed that the container and the additional hardware did not elicit any background sensor response other than what was typical for ultra-zero air.

Classification of Simulated Fire Debris Samples

One of the central questions posed in this study is whether or not the array would maintain its classification accuracy when challenged to classify ILRs that are present on a substrate following combustion. It is widely known that the composition of various flammable liquid mixtures becomes skewed toward high boiling point compounds as a result of evaporation during the burning process. Additionally, the combustion of various substrates has been shown to produce volatile pyrolysis products that are chemically similar to the aromatic hydrocarbons found in some IL formulations (31). This high degree of chemical similarity can elicit a false positive response from field devices or laboratory-based instrumentation (32). Several samples were prepared in a manner that approaches conditions present at the scene of a fire and were tested with our system. The samples tested in this dataset are listed in Table 3. Worn indoor carpet was selected as a substrate due to its high frequency of occurrence as fire debris evidence (29) and because it has been shown to generate background vapors that often interfere with ILR vapor measurements (31,32).

A preliminary dataset of 28 array responses to the simulated fire debris samples and controls was collected and processed using an SVM classification algorithm. The classification scores and confusion matrices for both two and five class problems are given in Table 4. The two class problem, a simple determination of whether or not an ILR is present in the sample without regard to class, was answered without error. All samples, including the pure ILs, were included in this dataset. The perfect classification score obtained for this dataset indicates that this low level inquiry can be solved with a high level of confidence.

TABLE 3—*Composition of simulated fire debris samples used in this study.*

	Sample Composition
1	Substrate + gasoline (20 mL)—burned
2	Substrate + charcoal starter (20 mL)—burned
3	Substrate + diesel (20 mL)—burned
4	Substrate—burned (no IL)
5	Substrate—not burned (no IL)
6	20 mL charcoal starter liquid
7	20 mL gasoline liquid

A more challenging query assigns the class of the particular ILR that is identified in a sample. The dataset used to evaluate this five class problem omitted the pure liquid samples and contained only ILR positive and negative simulated fire debris samples, as well as a sample of unburned, non-IL treated carpet. The result of this classification is presented as the five class problem of Table 4*b*. The classification score was 90% with only two misclassifications. These errors occurred between samples 4 and 5—the two negative controls that did not contain an ILR. Importantly, all of the simulated fire debris samples containing an ILR were correctly identified and the ILR was correctly assigned to its proper IL class. If the negative samples are grouped together as a general "ILR negative" class, the classification score for this dataset is also 100%.

The ability of the array to maintain its high classification ability over an extended sampling period was examined by exposing it to the same seven samples on multiple days. The responses collected in this dataset were obtained over a 4-day period, with the array stored under nitrogen in between periods of data collection and overnight. The order in which the samples were presented to the array was completely randomized. These results, framed as a four class query, with all of the ILR negative samples grouped together, are presented in Table 5 and clearly demonstrate that the instrument is able to maintain excellent classification accuracy for extended periods of time without retraining.

Conclusion

This paper reports the use of fluorescence-based vapor-sensitive arrays to detect three types of ILs and ILRs from simulated fire debris samples. The aim of the present study was designed to examine if our system could be used to discriminate common ILs from a larger

TABLE 4—*Classification accuracies and confusion matrices for simulated fire debris presented as (a) two* and (b) five† class classification problems.*

		Classified As	
(a)		ILR Absent	ILR Present
Correctly Classified Instances: 28 (100%).			
Incorrectly Classified Instances: 0 (0%).			
Actual	ILR Absent	8	0
	ILR Present	0	20

		Classified As				
(b)		Burnt Substrate	ILR Gas	ILR Gulflite	ILR Diesel	Air
Correctly Classified Instances: 18 (90%).						
Incorrectly Classified Instances: 2 (10%).						
Actual	Burnt Substrate	3	0	0	0	1
	ILR Gas	0	4	0	0	0
	ILR Gulflite	0	0	4	0	0
	ILR Diesel	0	0	0	4	0
	Air	1	0	0	0	3

*Samples 1–7 from Table 3.
†Samples 1–5 from Table 3.

TABLE 5—*Classification accuracies and confusion matrices for array responses to simulated fire debris samples.**

	Classified As			
Actual	ILR Gas	ILR Gulflite	ILR Diesel	ILR Negative
Correctly Classified Instances: 117 (97.5%).				
Incorrectly Classified Instances: 3 (2.5%).				
ILR Gas	24	0	0	0
ILR Gulflite	0	24	0	0
ILR Diesel	0	0	24	0
ILR Negative	0	0	3	45

*Samples 1–5 are shown. Samples 4 and 5 are grouped together under the class ILR negative.

class of VOCs and to examine if the system could maintain its classification accuracy when challenged with complex samples. Two ILs representing high and medium petroleum distillates as well as gasoline were used for the preparation of vapor samples. Analyte vapors were presented as both pure ILs and simulated fire debris samples, where a substrate was treated with an IL and burned. Each IL was shown to produce a unique pattern response upon exposure to the microsphere array. These response patterns were used to distinguish IL vapors from a library of other vapors with high classification accuracy over more than 200 vapor exposures. Simulated fire debris samples, both with and without ILRs, were classified with greater than 97% accuracy. The system was able to detect and correctly identify the class of ILR from the closed set of vapors used in this study when it was present in a sample. These results demonstrate the possibility of using vapor-sensitive microsphere arrays to detect ILs and ILRs. Following additional studies to better characterize the range of ILs to which the system is sensitive and to further challenge the system with more realistic simulated fire debris, this platform may also prove useful for field measurements. Efforts to miniaturize the instrumental apparatus are currently underway.

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