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Exploiting Cross-sensitivity by Bayesian Decoding of Mixed Potential Sensor Arrays

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Summary (<75 words)

LANL mixed-potential electrochemical sensor (MPES) device arrays were coupled with advanced Bayesian inference treatment of the physical model of relevant sensor-analyte interactions. We demonstrated that our approach could be used to uniquely discriminate the composition of ternary gas sensors with three discreet MPES sensors with an average error of less than 2%. We also observed that the MPES exhibited excellent stability over a year of operation at elevated temperatures in the presence of test gases.

Technical Report

Introduction

Finding specific chemical signatures amongst a background of ordinary substances– a trace explosive signature, an illegal narcotic, a chemical agent intended to kill our soldiers on the battlefield, or civilians in our cities – remains a daunting task. Dogs can seem to handle this proverbial "needle" quite well, but what man's best friend does so well has eluded the sensor industry. Science's best solution to date is devices that use large numbers of inexpensive sensor elements (typically resistive or polymer) in conjunction with pattern recognition methods: commercial instruments based on these principles are available. However, there are significant shortcomings with the performance and capabilities of these sensor constructs, as well as significant limitations to the pattern recognition methods used to extract a meaningful signal from the data because these devices target generic applications requiring significant calibration to obtain qualitative results. The sensors at the heart of these systems are prone to drift and irreversible poisoning, blocking their use in simple, yet harsh, energy-related tasks such as monitoring vehicle emissions or smokestack pollutants. We proposed to use a special class of ceramic solid-state electrochemical sensors that are intrinsically inexpensive, durable, and stable. Nobody has ever attempted to create a sensor array using these devices before. Their robustness opens the possibility of detecting a great number of gas chemistries under conditions that would quickly destroy other types of electronic noses. Our highly innovative and original solution to the specificity problem is to create a new gas sensor technology that marries unique sensor design created at LANL with a recently--developed, advanced Bayesian inference treatment of the physical model of relevant sensor-analyte interactions. Our approach is designed to quantitatively decode complex mixtures with fidelity greater than present technology can deliver. Our methods will solve the major shortcomings of the electronic nose concept.

Benefit to National Security Missions

The concept described in this project has the potential to provide low-cost, robust, easily deployable gas-phase quantitative discriminatory sensing capabilities that do not exist today. The broad implications of this work directly support the Revolutionize Measurements aspect of the Science of Signature pillar, and the applications specifically targeted by the proposed work directly address key Energy and National Security concerns. There are presently no low-cost and durable sensors to control and monitor the vehicle emissions systems on today's Selective Catalytic Reduction (SCR) and Exhaust Gas Recirculation (EGR) pollution control technologies comparable to the automotive lambda sensor. Although exact details are understandably kept secret by the pertinent Federal Agencies, the explosives screening technologies employed at critical facilities and used on the battlefield are routinely rendered ineffective because of the presence of complex, natural and human-created background interferences. The proposed research has the ability to create a unique capability at Los Alamos National Laboratory (LANL) by supporting the development of inexpensive and portable systems for use both by civilian first

responders and as dedicated screening systems at airports, federal buildings, cargo containers, etc.

Results

Initial efforts on this project focused on developing a robust experimental set-up for extensive data collection and establishing the data set requirements to feed into the proof of concept model development work at Rutgers University. LANL performed extensive modification to an existing sensor test station to enable the collection of the appropriate volume and quality of data needed for the model development work. A multi-mass flow controller manifold was built and automated with a lab-view based control and data collection program. This system is capable of automated data collection from multiple sensors in the presence of 4 distinct test gases.

LANL initiated the sensor testing with the low-risk activity of looking at the concentration of analyte species where background interferents are known and quantifiable — relevant to vehicle emissions monitoring (Energy Security). For this test Nitrogen oxide (NO) was chosen as the analyte species with Nitrogen dioxide (NO_2), Ammonia (NH_3) and Propane (C_3H_8) serving as the background interfering species. The first set of experiments involved the use of two distinct mixed-potential thin film sensors, one having a Lanthanum chromite (LSC) sensing electrode and the other using gold (Au) as the sensing electrode. Both sensors had a Platinum (Pt) reference electrode and yttria stabilized zirconia (YSZ) electrolyte. These sensors were specifically chosen as prior work had determined that the Au electrode had preferentially sensitivity to NH_3 while the LSC electrode had preferentially selectivity to either C_3H_8 or NOx depending on the mode of operation. The two operational modes selected were "un-biased": where the voltage was measured at zero current, and "biased": where the voltage was measured at a fixed positive current bias.

The Au and LSC based sensors were tested in our newly modified test stand using various binary pairs of analyte/interferent gases at various mixing ratios (α). Five distinct αs varying from 0 to 4 were selected for the 3 binary pairs (NO/C_3H_8, NO/NO_2 and NO/NH_3). A total of 125 combinations of these mixing ratios were measured for 12 distinct concentration of NO leading to 1500 distinct data points being recorded for the Bayesian model validation. The data was recorded simultaneously on both sensors at each gas compositions in order to accelerate data collection. This data was then analyzed by Dr. Morozov at Rutgers. Both linear and non-linear models were considered, with the non-linear model providing the best fit to the data. This is not surprising since the non-linear model accounts for the saturation of the sensor response at high analyte concentrations.

The preliminary model was able to predict the αs within 20% when using just the NO/C_3H_8 mixtures. However, this data set was insufficient to predict the NO/NO_2 ratios with confidence, as well as absolute values of NH_3 above a threshold concentration where the sensors exhibited saturation in response with increasing concentration. These initial results were presented in an

invited talk titled "Quantitative Decoding of Complex Gas Mixtures for Environmental Monitoring Using Mixed Potential Sensor Arrays" at the 227th meeting of the Electrochemical society by Dr. Cortney Kreller.

The feedback from Rutgers indicated the need for additional sensors with varied response characteristics from the initial two sensors tested. Rutgers also advised LANL on modified mixing ratios tailored to each interferent species in order to provide a more robust model training set. In response, we chose to incorporate two additional discreet sensors into our data collection array. Prior work established that not only the sensing electrode material, but also the sensor geometry (i.e. the electrochemically active area) could be used to tune sensor selectivity and sensitivity. We therefore chose to incorporate sensors using the LSC sensing electrode with YSZ/LSC geometric surface areas of 0.8, 0.34 and 0.22 mm^2 with the Au sensing electrode based device comprising the fourth sensor in the array. Additionally, the range of αs selected also allowed us to probe the region low concentrations of analyte species in the presence of much larger concentrations of interferent species (Chemical signatures-Homeland Security).

Data for binary and ternary mixtures of test gases NO/NO$_2$/C$_3$H$_8$ were collected and supplied to our collaborators at Rutgers. There they developed a model based on the well-established Butler-Volmer equation describing electrochemical reaction rates. They first trained this model on the C$_3$H$_8$/NO mixtures, as before and, as shown in **Figure 1**, found an accuracy of > 10% in predicting mixtures when utilizing the data from only a single sensor, a two-fold improvement in the accuracy over the previous work. The accuracy was >5% when the voltage output from two sensors was utilized. The modeling was also used to ascertain the minimum number of training sets required to obtain a model of sufficient fidelity. **Figure 2** shows the predictions for α for the binary mixture C$_3$H$_8$+NO using the Au sensor only for different sized training sets (number of C$_3$H$_8$ runs). The α's used for prediction are picked so as to distribute them as evenly as possible in the range alpha = 1 to alpha = 5.2. This analysis showed that while there was a very gradual decrease in accuracy going from 9 to 5 training sets, the error introduced by this reduction was quite small. The error then increased dramatically when the number of training sets was reduced to 4 as a result of the quadratic nature of the model. This result was very encouraging as decreasing the model training procedure would streamline the implementation of the MPES arrays into their desired application field. However, it should be noted that these results are for this case in particular and will change according to sensor used and gases present (e.g. Cr sensors need more αs to be calibrated accurately).
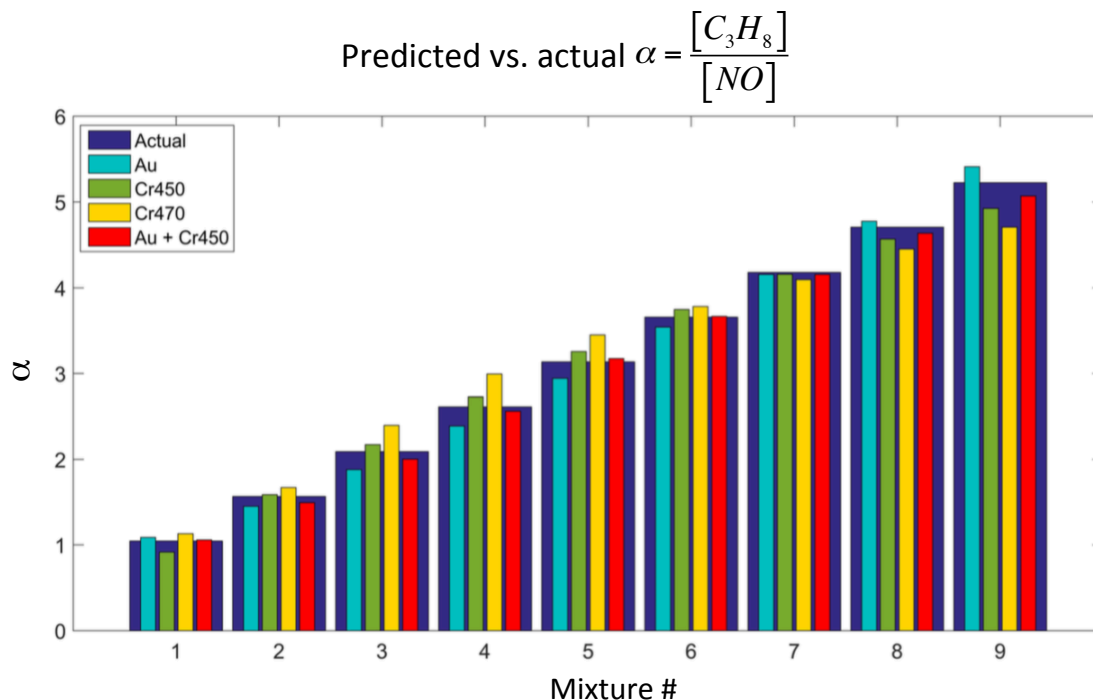
Figure 1. Predicted verses actual alpha as a function of mixture number (increasing NO concentration) using sensor response from each individual sensor as well as the output of two sensors.
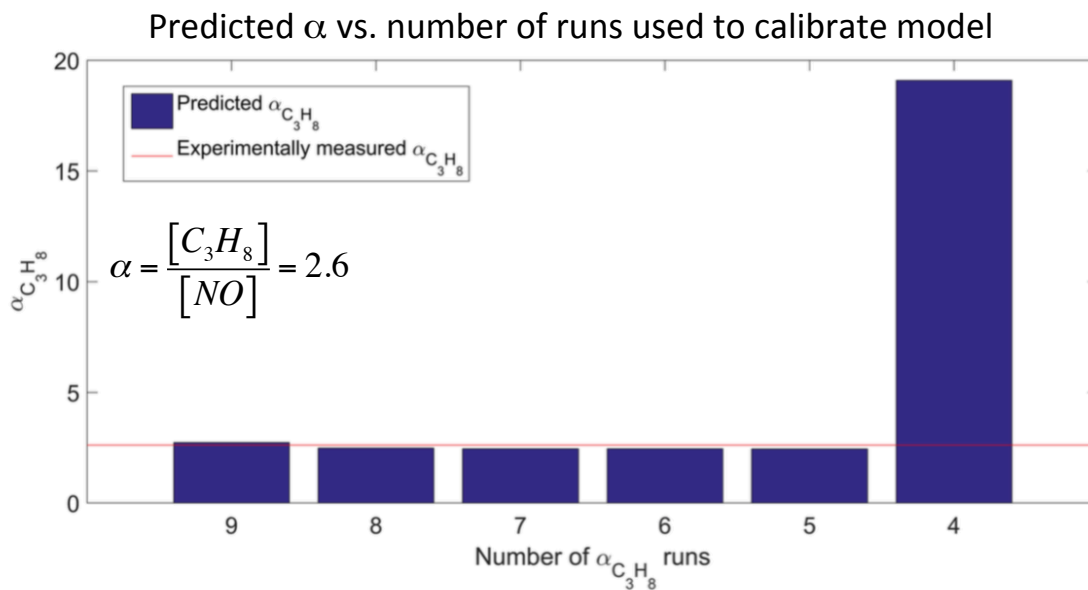

Figure 2. Predicted alpha verses number of runs used to calibrate model for binary mixture of a=[C_3H_8]/[NO]=2.6.

Rutgers Graduate student Unab Javed presented an invited talk on this work at the 2nd International Conference on Sensors Engineering and Electronics Instrumental Advances (SEIA'

2016). LANL postdoc Kannan Ramaiyan presented this work at the 230th Meeting of The Electrochemical Society (10/2016) as well as two invited talks at the iSAEST-11 and the IUMRS-ICYRAM conferences in December 2016.

The work was subsequently extended to include ternary mixtures including NH_3. For the two-gas and three-gas mixtures, the ratios of gases with respect to NO was fixed and [NO] was increased from 20ppm to 220ppm with the alpha ranges:

$$\alpha_{C_3H_8} = \{1.0, 1.6, 2.1, 2.6, 3.1, 3.7, 4.2, 4.7, 5.2\},$$
$$\alpha_{NO_2} = \{0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0\},$$
$$\alpha_{NH_3} = \{0.2, 0.5, 0.7, 1.3, 1.5, 1.8, 2.0, 2.2\}.$$

We worked with 3 binary gas data sets: $NO+NH_3$, $NO+C_3H_8$ and $NO+NO_2$, 24 mixtures in total; and 1 tertiary data set: $NO+NO_2+C_3H_8$. The tertiary data set consists of 61 mixtures (63 mixtures with C_3H_8 and NO_2 ratios minus two sets excluded due to limited data). Thus our data set comprises 85 tertiary and binary mixtures. For each mixture with fixed a's, volt- age readings at 10

Figure 3. A plot of the voltage response (in volts) of three sensors: Cr450, Au475 and H545. Shown are the readings taken at all a's and [NO] concentrations for the binary and tertiary mixtures. The regions are defined in the main text.

different NO concentrations are recorded. A reading at each NO concentration consists of 30 independent data points, which are split evenly into a training set and a test set. The experimental data set is shown in Figure 3. The regions highlighted describe the splitting of the tertiary mixtures into the following: (i) pre-jump for C_3H_8 and NO_2, (ii) post-jump for C_3H_8, pre-jump for NO_2, (iii) pre-jump for C_3H_8, post-jump for NO_2, (iv) post-jump for C_3H_8 and NO_2. These "jumps" occur at a constant concentration in every sensor, and they are independent of the electrode used and the temperature of the sensor. However, their physical cause is currently unclear. The reader will note how cleanly the data is split into the different regions. As there is minimal overlap, it is possible, just from the voltage measurements of the 4 sensors, to classify which region the mixture belongs to.

We created a model capable of predicting either relative or absolute concentrations of each gas of interest in complex mixtures of unknown composition. The model is guided by fundamental
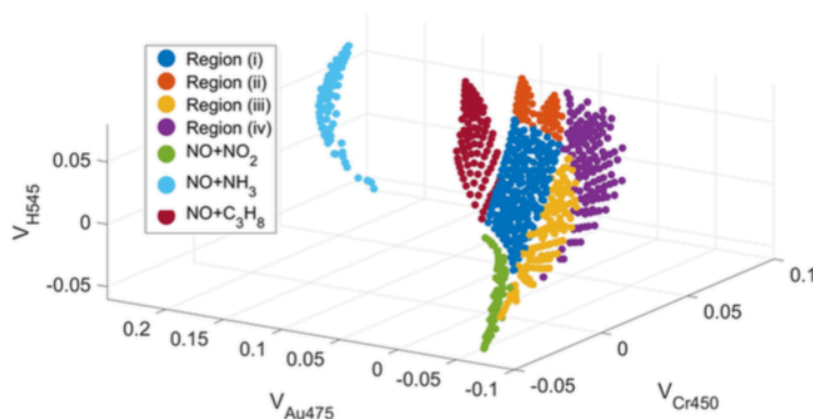
principles of gas-sensor interactions, but also includes empirical extensions which account for the observed non-linearities in the data, including abrupt voltage jumps at certain threshold concentrations of analyte gases. The parameters of the model are trained on a set of mixtures and then the calibrated model is deployed to predict gas concentrations.

Our model can simultaneously detect the relative concentrations of C_3H_8, NH_3 and NO_2 with respect to NO in an extensive set of mixtures, with a maximum error of 14% and the average error of 1.83%. Furthermore, we are able to predict the total concentration of each gas in two- and three-gas mixtures with the average error of 3.23%. We also check the robustness of the model performance when it is trained using either fewer mixtures or fewer sensors. On average, the system performs well even if it is trained on fewer mixtures, with the average errors of all parameters ~4.3% in absolute concentration predictions. The accuracy of predictions is similar for mixtures removed from and retained in the training dataset, implying that our model is capable of interpolating the training data.

Setup		Misclassified mixtures
Predict α's, full data		0/85
Predict α's and $[NO]_{ref}$, full data		0/85
Predict α's and $[NO]_{ref}$, reduced data	$\alpha_{C_3H_8}$ set reduced	0/85
	α_{NO_2} set reduced	0/85
Predict α's and $[NO]_{ref}$, 3 sensors	Cr450, Au475, Cr470	0/85
	Cr450, Au475, H545	0/85
	Cr450, Cr470, H545	1/85
	Au475, Cr470, H545	0/85
Predict α's, 2 sensors	Cr450, Au475	1/85
	Au475, Cr470	1/85
	Cr470, H545	1/85
	Cr450, Cr470	2/85
	Cr450, H545	0/85
	Au475, H545	2/85
Predict α's and $[NO]_{ref}$, 2 sensors	Cr450, Au475	0/85
	Au475, Cr470	1/85
	Cr470, H545	1/85
	Cr450, Cr470	0/85
	Cr450, H545	1/85
	Au475, H545	2/85

Table 1. Table showing the number of misclassified mixtures for each calibration/prediction setup.

Our approach is also robust to removing the output of one sensor from both training and test datasets, yielding the 7.2% average error for predicting absolute concentrations. In all of these cases, there is only one instance of misclassifying a mixture into incorrect binary/tertiary type

(Table 1). With two sensors removed from consideration, the accuracy of predictions begins to suffer, but most mixtures are still classified correctly.

Overall, we conclude that our model is capable of predicting gas concentrations in complex mixtures with high accuracy. The flexibility of our approach is that it is based on physical principles of gas-sensor interactions and is thus not gas- or chemical reaction-specific. Depending on the situation, if other mixtures need to be considered and other gases need to be added, our framework can be easily expanded to accommodate them. This work was submitted to *Sensors and Actuators B* in the summer of 2017 and an invited talk is being given by Kannan Ramaiyan at the 232nd meeting of The Electrochemical Society. A publication is currently in preparation regarding the quaternary mixtures.

An additional result of this study was the verification of the long-term durability and stability of the MPES devices. During the iterative data collection process, the sensors were at operating temperature and exposed to test gases nearly continuously for almost a year. During this time, single test gas calibration checks were periodically performed. A subset of these calibration tests are shown for the LSCr-470 sensor exposed to C_3H_8 and the Au sensor exposed to NH_3 in **Figure 4**. Overall, the sensor response is incredibly stable. There was a building-wide power outage between day 158 and 287 that appeared to shift the operating temperature of the Cr sensor (an abrupt shift in the sensitivity curve is evident). However, it was determined that the power outage corrupted the control electronics. Stable sensor operation was recovered after the incident.
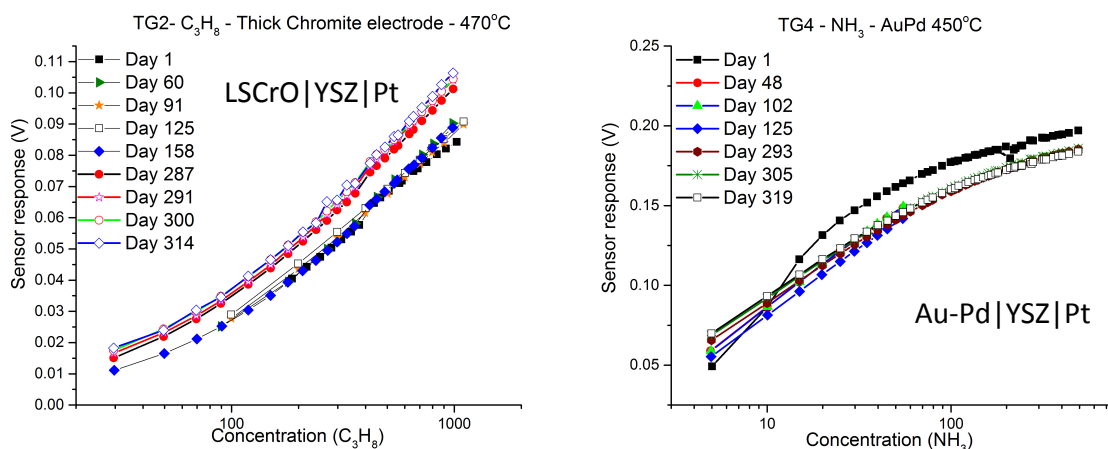

Figure 4. Plot of C_3H_8 single gas calibration curves on LSCr-470 sensor (left) and NH_3 single gas calibration curve on Au sensor (right) over the course of ~320 days.

The non-specific metal-oxide (MOX) or electrochemical (EC) sensor elements used in commercially available E-Nose devices on the market today are prone to drift and therefore require frequent calibration by a knowledgeable end user, precluding their use in remote or set-

and-forget applications. They are also prone to irreversible poisoning and cannot withstand simple, yet harsh, energy-related tasks such as monitoring vehicle emissions or smokestack pollutants. The data-set shown in **Figure 4** underscores one of the key benefits of using LANL MPES gas sensor technology: they are intrinsically durable and after a single mission-specific calibration in a laboratory setting, may be deployed in both remote and harsh conditions to provide quantitative and reliable analysis.
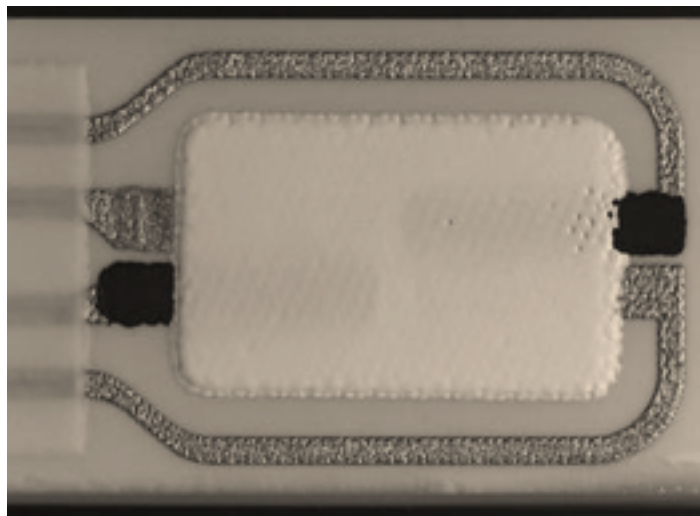

Figure 5. Photograph of 4-electrode MPES array in automotive stick sensor configuration

After establishing predictive algorithms based on the response of discreet MPES sensors, the next step was to fabricate single platform MPES arrays. The computational framework established from the discreet sensor indicated that using multiple electrodes of the same material but with different electrochemical active area provides sufficient fidelity for the computational discrimination of various analyte species. This is highly advantageous from a fabrication standpoint where utilizing many different materials would require consideration of varying substrate/electrode thermal expansion properties, as well as multiple targets and depositions. This discreet sensor testing also showed that tuning the unique cross-selective sensor element response via temperature was an additional option. Based on these results, we worked with ESL Electroscience to design and fabricate two distinctly different single-platform MPES arrays via the commercially viable high-temperature ceramic co-fire (HTCC) approach. The first design maintains the automotive stick sensor configuration but employs three different working electrodes, two LSCr and on Au, and a common Pt pseudo reference electrode. A photograph of the sensor element portion of the sensor is shown in **Figure 5**. This MPES array is designed for all of the sensor elements to operate at a single temperature, but variation in electrode composition and the geometry of the LSCr electrodes will yield unique responses. Additionally, one of the LSCr electrodes may be operated in biased mode to provide a more pronouncedly different cross interference response. The shape of the platform renders it ready for immediate application in vehicle emissions monitoring applications. The second design is shown in **Figure 6**. A gradient in
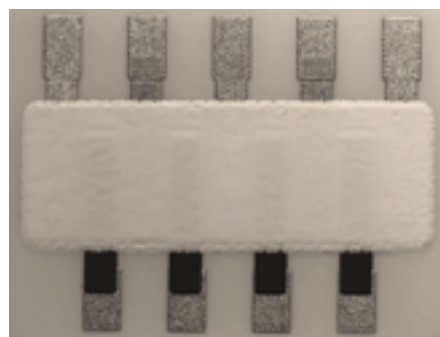

Figure 6. Photograph of temperature gradient device.

temperature across the device is made possible by using an integrated heater with varying serpentine loops across the backside of the substrate. The MPES array consists of alternating pairs of Au and LSCr electrodes with a common Pt pseudo reference electrode within each temperature zone. The temperature gradient, MPES array concept is the most flexible design as multiple operating parameters may be tuned at once to achieve desired sensitivity and selectivity of each sensor element.

Both of these devices were tested under binary and ternary mixtures. While the data collection time was much shorter than that employed in the discreet sensor testing (<1 month), the voltage response of the individual sensing elements exhibited stable calibration curves to single gas exposures. Rutgers graduate student Unab Javed is analyzing this data set as part of her Ph.D. thesis to determine if the model established for the discreet sensors can be readily extended to the single-platform arrays.

Conclusion

Our proposed end goal of this LDRD project was to demonstrate a versatile, standalone device that after a single mission-specific calibration in a laboratory setting may be deployed in both remote and harsh conditions to provide quantitative analysis of chemical signatures against large and unknown environmental backgrounds. The Bayesian analysis also guided our development of single platform MPES arrays by identifying what parameters (both operational and material) yielded sufficiently discriminating responses to develop predictive algorithms and also by informing the number of sensors in the array required to successfully discriminate the target species from one another, as well as against additional background interferents. Our discreet sensor testing successfully demonstrated the concept of using stable and robust LANL MPES devices in single mission-specific training. We also successfully used Bayesian inference methods to develop predictive algorithms of the sensor response to complex gas mixtures. Using the raw voltage response from three discreet MPES devices, the predictive algorithms were able to discern the composition of 3 gas mixtures with an average error of less than 5%. The experimental data set and predictive algorithms were extended to include NH_3. Our model can simultaneously detect the relative concentrations of C_3H_8, NH_3 and NO_2 with respect to NO in an extensive set of mixtures, with a maximum error of 14% and the average error of 1.83%. Furthermore, we are able to predict the total concentration of each gas in two- and three-gas mixtures with the average error of 3.23%. We also showed that the discreet LANL MPES devices exhibited exceptional stability over almost a year of operation at elevated temperature and exposed to test gas environments. This data shows that the LANL MPES devices are intrinsically durable and after a single mission-specific calibration in a laboratory setting, may be deployed in both remote and harsh conditions to provide quantitative and reliable analysis.

The modeling was also used to inform the designs of two novel single platform MPES arrays. These arrays were shown to give desired sensing characteristics and yield stable performance over a month of testing. The final goal is to show that the predictive algorithms established for

the discreet sensors can be extended to the single platform arrays. This work is being completed by Unbar Javed at Rutgers as part of her Ph.D. thesis work.

Publications

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