Rapid Analysis, Self-Calibrating Array for Air Monitoring

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Human space missions have critical needs for monitoring and control for life support systems. These systems have monitoring needs that include feedback for closed loop processes and quality control for environmental factors. Sensors and monitoring technologies assure that the air environment and water supply for the astronaut crew habitat fall within acceptable limits, and that the life support system is functioning properly and efficiently. The longer the flight duration and the more distant the destination, the more critical it becomes to have carefully monitored and automated control systems for life support. Past experiments with the JPL ENose have demonstrated a lifetime of the sensor array, with the software, of around 18 months. The lifetime of the calibration, for some analytes, was as long as 24 months. We are working on a sensor array and new algorithms that will include sensor response time in the analysis. The preliminary array analysis for two analytes shows that the analysis time, of an event, can be dropped from 45 minutes to less than10 minutes and array training time can be cut substantially. We will describe the lifetime testing of an array and show lifetime data on individual sensors. This progress will lead to more rapid identification of analytes, and faster training time of the array.

Nomenclature

R	=	sensor resistance
$\Delta R/R_0$	=	normalized sensor response
RASCal	=	Rapid Analysis, Self Calibrating

I. Introduction

A. Sensor Arrays

Sensor arrays, often called electronic noses, have been studied and put in to use for a myriad of applications, including medical diagnostics[1,2], quality and process control for food[3], fire detection in human habitats[4], and other types of event detection in human habitats[5-13]. Sensor arrays, have traditionally, been comprised of any number of sensors, nearly always of the same type of sensor and same type of transducer, e.g. all metal oxide sensors, all polymer sensors or all colorometric sensors. Most of the analysis approaches focus on classification and identification of the analytes of interest.

The JPL Electronic Nose (ENose) began as a demonstration of a sensor array for monitoring space cabin air on space shuttle mission STS-95 in 1998[5,]. Later developments include expanding number and type of analytes detectable[6,8], improving sensor array reproducibility[6], including near real-time analysis[9,12,13], and many other capabilities. Unlike, most sensor array analysis approaches, the JPL ENose included quantification as well as identification.[14] This culminated in a successful demonstration of the 3rd Generation ENose aboard the International

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Space Station; this involved more than 3200 hours (> 6 months) of continuous operation aboard the US Lab on the ISS[9,13]. Chemical species were quantified, generally, in the parts-per-million range; some targeted species were detected in the parts-per-billion range. Analysis of the Third Generation JPL ENose monitoring data on ISS showed the short term presence of low concentrations of alcohols, octafluoropropane and formaldehyde as well as frequent short term unknown events. "Unknown" refers to the chemical species outside the set of target analytes.

As applications for sensor arrays expand, sensor groups look toward extending the capabilities of sensor arrays, by adapting and improving both sensor hardware and software approaches. While using only one type of sensor can limit the chemical families of detectable analytes, development of hybrid arrays can greatly increase the number and type of detectable analytes in one system[8,11,15]. Software approaches can be used to determine direction of an analyte and improve speed and accuracy of array analysis.

B. JPL Electronic Nose

The JPL ENose was developed to be a fully operational system designed to fill the gap between an alarm which sounds at the presence of any chemical compounds with little or no ability to distinguish among them, and an analytical instrument able to distinguish all compounds present but with no real-time or continuous event monitoring ability. The specific analysis scenario targeted for this development is one of leaks or spills of specific compounds. It has been shown in analysis of samples taken from space shuttle flights and the International Space Station (ISS) that, in general, air is kept clean by the air revitalization system and contaminants are present at levels significantly lower than the Spacecraft Maximum Allowable Concentrations (SMACs)[16]. The JPL ENose has therefore been developed to detect targeted chemical species released suddenly into the breathing environment; the sensing system in the JPL ENose is a chemical sensing array made up of 32 semi-selective conductometric sensors.

Three generations of the JPL ENose have previously been shown to be able to detect, identify and quantify of a variety of organic analytes, as well as ammonia, hydrazine elemental mercury and sulfur dioxide[5-13]. The first generation ENose was tested in the laboratory and subsequently on Space Shuttle flight STS-95 in 1998 for six days, and was shown to detect, identify and quantify nine volatile organic compounds as well as ammonia, all at the 1-hour SMAC levels, and water against a breathing-air background[5]. The second generation ENose was tested in the laboratory and shown to detect, identify and quantify 20 volatile organic compounds as well as ammonia, all at the 24-hour SMAC levels, and water against an air background. In these two generations of the JPL ENose, the 32 sensors in the array were all polymer-carbon composite conductometric sensors. Lifetime was established during the Second Generation ENose research effort as being approximately 15-18 months, where lifetime is the period during which overall array response to a single stimulus does not change more than 10%. This lifetime addresses the identification and quantification capability of the array as a whole and does not address lifetime of any one particular sensor. The third generation ENose was developed for demonstration and testing on board the ISS. For this application, the target analytes included eight organic and three inorganic species at the 24-hour SMAC levels. The species which were new to the third generation JPL ENose were elemental mercury and sulfur dioxide[9,10]. In order to expand the detection capabilities of the array, a hybrid array approach was taken and one sensor substrate (eight sensors) was replaced with a microhotplate substrate. The microhotplate platform is compatible with metal oxides and other sensors that require a more extensive heating capability than was previously available on the JPL ENose platform. During the ISS demonstration, the ENose operated continuously for over six months; it detected and identified multiple events, including one instance of ethanol and several of Freon 218, formaldehyde and methanol. Upon return to earth and to JPL, the ENose continued to operate properly and further lab testing verified that deliveries of ethanol, formaldehyde and methanol were identified and quantified correctly. The post-flight verification took place more than 24 months after the ENose was originally trained, thus demonstrating that an array lifetime over 18 months is possible[13].

Subsequent JPL ENose work examined pre-combustion event markers by testing the ENose alongside a particle counter and an Industrial Scientific ITX gas monitor[10]. Wire samples were heated from room temperature to 500 °C while simultaneous measurements were made for particle releases and off-gassing products. As the wires were heated, particles, water, CO, and HCl were the primary species detected by the three instruments. The water was easily identified by the ENose, but the CO proved more challenging. More recently,in the interest of adding capabilities to the JPL ENose as well as addressing the challenge of detecting carbon monoxide, we developed and tested polymer-based sensors capable of detecting carbon monoxide[11].

C. Rapid Analysis, Self Calibrating Array

Long duration exploration human space missions have critical needs for monitoring and control for life support systems. Sensors and monitoring technologies assure that the air environment and water supply for the astronaut crew habitat fall within acceptable limits, and that the life support system is functioning properly and efficiently. In

addition to enduring the rigors of space flight, the sensors will need to have extended lifetimes. The lifetime refers to both the physical operational life and functioning of the sensor as well as the calibration of the instrument that controls the sensor. The longer the flight duration and the more distant the destination, the more critical it becomes to have systems that are small, low power, adaptable, and have few consumables.

Past experiments with the JPL ENose have demonstrated a lifetime of the sensor array, with the software, of around 18 months. The lifetime of the calibration, for some analytes, was as long as 24 months. We are working on a sensor array and new algorithms that will include sensor response time in the analysis. Previous approaches to training the JPL ENose included training libraries where the sensors were exposed to different analytes and allowed to establish equilibrium. Most sensors demonstrate different time dependent behavior and by analyzing the transients of metal oxide sensors[17] Muezzinoglu et al. demonstrated it is possible to both shorten the time to analyze an event. Sensors also show time dependent behavior, or drift, over much longer time periods. Using an array of metal oxide sensors, and three years of data on the array, Vergara et al. demonstrated improved sensor array analysis using time drift compensation.[18]

By combining a hybrid sensor array approach, developed in earlier JPL ENose work, with additional analyses approaches (including short and long term time dependent sensor behavior) we are working towards an array that will provide faster analysis and be capable of self-correcting for long-term drift. Such an array would be highly desirable for long duration space exploration.

In this paper we will show preliminary data demonstrating the improved time response of a sensor array, using transient sensor information to identify and quantify ethanol and propanol. We will also show some long term sensor response to ethanol.

II. Experimental

D. Sensor Array

For these experiments we tested an array that was made in June 2007. More detail about the fabrication of sensors and sensor substrates can be found in previous publications. The polymers used for this sensor array are listed in Table 1. Each column lists the polymer and, in parentheses, the carbon black weight percent.

Table 1. Polymers used for sensor array testing.

Substrate A	Substrate B	Substrate C	Substrate D
poly(4-vinyl phenol) (15)	poly (2,2,2-trifluoroethyl methacrylate) (15)	polyamide resin (15)	poly-4-vinyl pyridine/poly-4-vinyl pyridinium propylamine chloride, 50/50 (EYN2) (10)
poly(4-vinyl phenol) (20)	poly (2,2,2-trifluoroethyl methacrylate) (20)	styrene/isoprene, 14/86 ABA (15)	EYN2 (10)
poly(4-vinyl phenol) (20)	poly(t-butylaminoethyl methacrylate) (20)	vinyl alcohol/vinyl butyral, 20/80 (12)	poly-4-vinyl pyridine/poly-4-vinyl pyridinium propylamine chloride, 70/30 (EYN7) (10)
poly(2,4,6-tribromostyrene), 66% (10)	poly(t-butylaminoethyl methacrylate) (20)	ethylene-propylene diene terpolymer (15)	EYN7 (10)
poly(2,4,6-tribromostyrene), 66% (10)	poly(ethylene-co-acrylic acid), 80/20 (10)	poly(4-vinyl phenol) (15)	EYN2 (10)
poly(2,4,6-tribromostyrene), 66% (15)	polystyrene (12)	poly(4-vinyl phenol) (20)	EYN2 (10)
poly(styrene-co-maleic acid) (15)	soluble polyimide, Matrimid (12)	poly(t-butylaminoethyl methacrylate) (20)	EYN7 (10)
poly(styrene-co-maleic acid) (15)	ethyl cellulose (12)	poly(t-butylaminoethyl methacrylate) (20)	EYN7 (10)

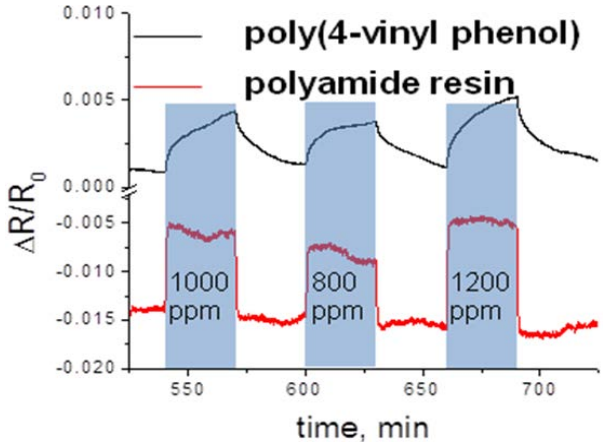

Figure 1. Exposure of poly(4-vinyl phenol) and polyamide resin sensors to 1000, 800, and 1200 ppm of ethanol.

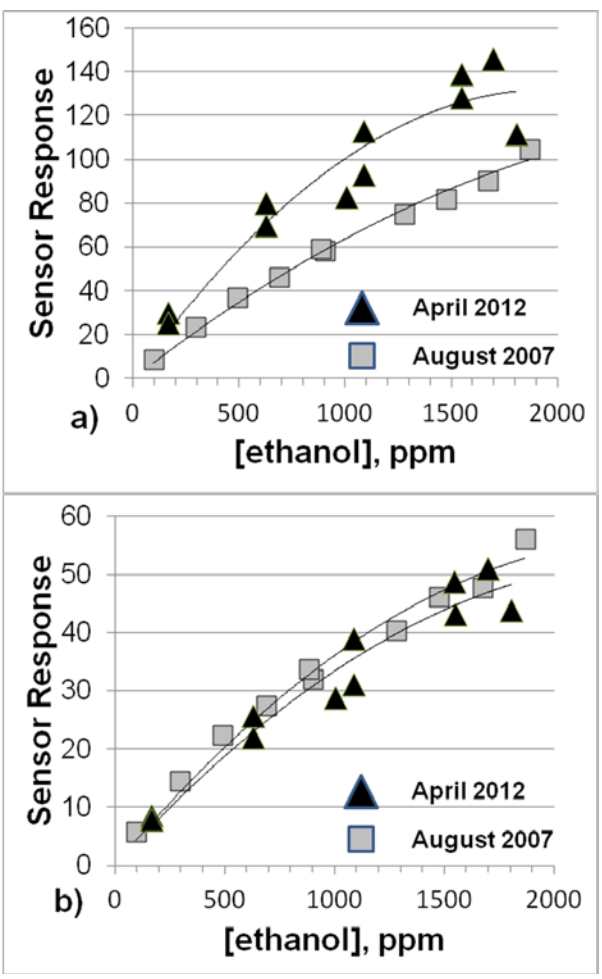

Figure 2. Sensor responses to ethanol over almost 5 years. a) poly(4-vinyl phenol), b) poly(2,4,6-tribromostyrene), 66%

E. Gas Handling System

For these experiments, to deliver clean air as well as analytes to the sensors for testing, we used a gas handling system built in our laboratory. The gas handling system is run on house air that is filtered to clean and dehumidify it. The flow of the air is controlled by a series of mass flow controllers, valves, and check valves. The air delivered to the sensors can then be humidity controlled: a fraction of the air is bubbled through water and remixed with dry air. To introduce ethanol, toluene or other volatile organics as an analyte, a small fraction of clean, dry air is passed through a bubbler and mixed with the clean air. As with the humidity, the analyte concentrations are calculated and controlled using a LabVIEW program. All of these experiments were performed using air with 10,000 ppm of water in air.

F. Array Testing

The sensors were placed in our test chamber and were exposed, alternately, to clean humidified air and humidified air containing ethanol, 2-propanol or toluene. After allowing the sensors to equilibrate in clean humidified air, the sensor exposures alternate between analytes at varying concentrations and 60 minutes of clean air. The exposure length for the analytes varied. In order to determine whether transients could improve our analysis time, exposures ranged from 3 minutes to 45 minutes. To look at some sensor lifetime drift, only longer exposure data was used, where the sensors were allowed to come to equilibrium with the analyte. All of the tests were run with a water background of 10,000 ppm H_2O. The sensor substrates were held at 28°C. Our testing chamber and device electronics can test 32 sensors concurrently: three substrates with eight Au-Pd electrodes each and one substrate with eight microhotplates. More detailed descriptions of the device operation can be found elsewhere[5-9].

Sensor data is measured as resistance versus time and the data is plotted as the normalized change in resistance, $\Delta R/R_0$, where ΔR is (R_t-R_0), R_0 is the resistance at the start of an experiment and R_t is the resistance at time t; the response of two different polymer-carbon black sensors to varying concentrations of ethanol can be seen in Fig. 1. In addition, these sensors highlight a variation in temporal response; the poly(4-vinyl phenol) (PVP) takes longer to reach equilibrium, and longer to return to baseline. Previous JPL ENose training would have to train

to the slowest sensor to get good equilibrium data for the entire array.

III. Results and Discussion

G. Polymer Sensor Response to Ethanol Over Time

Figure 2 shows two individual sensor responses to ethanol over time. The data were taken nearly 5 years apart. The curves are a quadratic fit, forced through the origin; the coefficients calculated in the fit are used in the original ENose analysis software[14]. For the PVP sensor, the linear coefficient increased by 75%; at the same time, the coefficient for the tribromostyrene sensor decreased by less than 10%. Surprisingly, the PVP sensor actually showed an increased response to ethanol, as did some of the other sensors, including the polyamide resin. One polymer film that showed some decreased sensitivity was the poly(t-butylaminoethyl methacrylate) sensor. Since we do not have a full training set for this array, it is not possible to say whether a these changes will be characteristic of each sensor, e.g. PVP may become more sensitive to additional analytes and less sensitive to others.

H. Time-dependent Sensor Features

In order to look at time dependent responses of the sensor, additional data was taken on the array where analyte exposure was not always allowed to equilibrate. Several approaches were used to identify and calculate useful features in the sensor array, with the emphasis on the sensor transients for faster analysis purposes.The trade-off between the occurrence time of the transient feature and the amount of information it conveyed for the prediction task was examined. This analysis selected the optimum transient features for each sensor type in the array and, at the same time, minimized the duration of measurements that are required to design the prediction system.

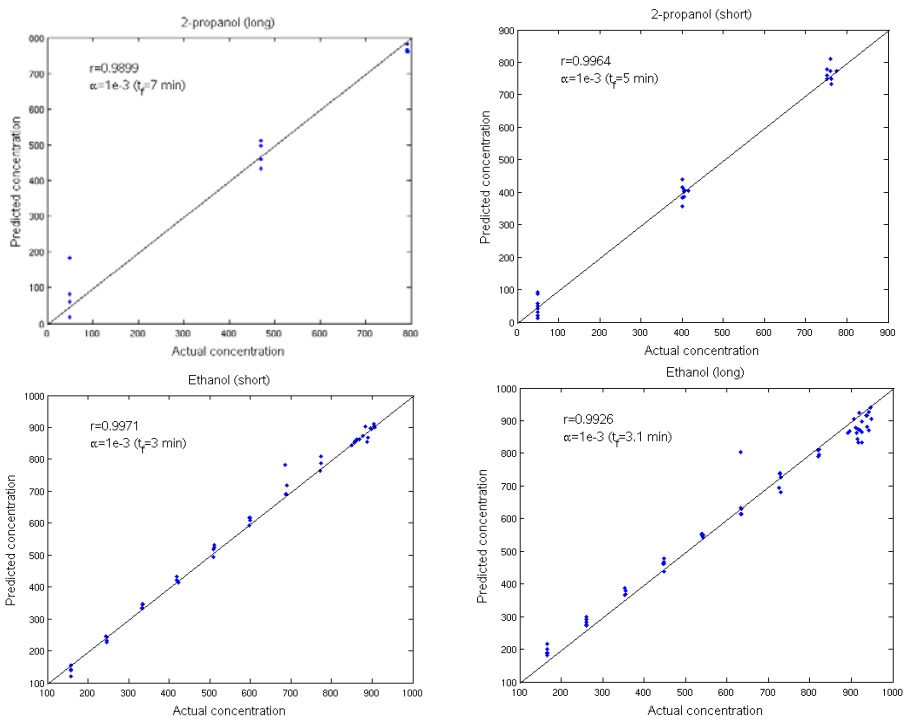

Figure 3. Performance in gas concentration estimation for two different gases using an optimized feature. The axis are in units of particle per millions and r is the Pearson correlation which is very close to 1.

We could show it both on regression and in classification. Figure 3 shows how the time dependent features can be used for analysis and still get good identification and quantification. The gas concentration estimation can achieve very good performance despite reducing the sampling period to 3 minutes. The exponential moving average feature[17] can be optimized to capture the most relevant characteristics of the transient sensor response.

IV. Conclusions

The preliminary data on the individual lifetime of sensor responses is surprising. It was anticipated that the polymer sensors would decrease in sensitivity since their primary mechanism of response is film "swelling"; we predicted that as the films aged they would become less flexible and, therefore, less responsive. While this appears to be the case for some sensors, it is clearly not the case for all. It is difficult to predict how these changes will manifest in the recalibration of the array. Ideally it would be possible to recalibrate one or a few select analytes, and that recalibration would be sufficient to predict the recalibration for all the analytes. Future work will include analysis of additional arrays with more extensive analyte data.

The time dependent analysis of the array is very promising. Being able to extract features in the sensors within the first 10 minutes of an event means that training time can be shortened significantly. In addition, the analysis during array operation will be able to identify an event more quickly.

Acknowledgments

The research reported in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration and supported by the ARREM Program, AES, NASA.

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