Faster Array Training and Rapid Analysis for a Sensor Array Intended for an Event Monitor in Air

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Environmental monitoring, in particular, air monitoring, is a critical need for human space flight. Both monitoring and life support systems have needs for closed loop process feedback and quality control for environmental factors. Monitoring protects the air environment and water supply for the astronaut crew and different sensors help ensure that the habitat falls within acceptable limits, and that the life support system is functioning properly and efficiently. The longer the flight duration and the farther the destination, the more critical it becomes to have carefully monitored and automated control systems for life support. There is an acknowledged need for an event monitor which samples the air continuously and provides near real-time information on changes in the air. Past experiments with the JPL ENose have demonstrated a lifetime of the sensor array, with the software, of around 18 months. We are working on a sensor array and new algorithms that will incorporate transient sensor responses in the analysis. Preliminary work has already showed more rapid quantification and identification of analytes and the potential for faster training time of the array. We will look at some of the factors that contribute to demonstrating faster training time for the array. Faster training will decrease the integrated sensor exposure to training analytes, which will also help extend sensor lifetime.

Nomenclature

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

I. Introduction

MONITORING an air quality event (e.g. a chemical spill or precombustion smoldering) as it evolves requires the ability to monitor air on a time scale faster than the event and the ability to detect the event analyte at the concentration of interest. Event monitors are designed to detect unusual or atypical air composition, which may indicate a leak or spill while trace gas monitors are designed to periodically monitor the concentrations of potential contaminants known to be present in the air. Daily or weekly sampling of the air for trace detection may indicate a

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long-term change (days, weeks, or months) in baseline air composition but miss an event that has taken place on the time scale of hours and dispersed. Both long- and short-term changes in air composition may be indicative of a problem in the spacecraft and so event monitoring and trace gas monitoring serve complementary purposes.

Experimental investigations reported for spacecraft air quality monitoring applications include both event monitors and trace gas monitors.[1-5] Devices for monitoring have been tested on the MIR space station, the Space Shuttle, and on the International Space Station (ISS). Two sensing arrays were combined to make an experimental event monitor that was operated on the MIR space station for 40 days within a six month period and again for several days more than a year later[1]. In that experiment, data were downloaded and analyzed after the monitoring period; the device was able to detect changes in the composition of the air and changes were correlated to recorded events. The European Space Agency (ESA) sponsored an ISS test of a sensor array event monitor composed of metalloporphyrin coated crystals in a QCM array device[2]. That device was operated in several experiments over a period of nine days, the data was analyzed afterward; the test demonstrated microgravity operation. NASA's Volatile Organics Analyzer (VOA) is a trace gas monitor composed of a gas chromatograph-ion mobility spectrometer[3]. The VOA was operated intermittently on the ISS for several years. It was designed to detect several tens of constituents in the air with samples taken once a day, and included on-board data processing. The ESA-sponsored Analysing Interferometer for Ambient Air (ANITA) is a trace-gas monitor based on a Fourier transform infra-red spectrometer[4]. ANITA operated on-board the ISS for one year, taking a sample once every 40 minutes, with on-board, near real time data analysis. This device was also able to detect and identify changes in the atmosphere on ISS. Finally, the Vehicle Cabin Air Monitor (VCAM) is another trace gas monitor that was tested on the ISS. VCAM was designed to measure ppb-to-ppm levels of volatile trace-gas constituents as well as nitrogen, oxygen, argon, and carbon dioxide. in a space vehicle or station. It is designed to operate roughly once per day.

The JPL Electronic Nose (ENose), a 32 sensor array, was first demonstrated for monitoring space cabin air on space shuttle mission STS-95 in 1998[6]. Some of the later developments of the ENose include expanding number and type of analytes detectable[7,8], improving sensor array reproducibility[7], including near real-time analysis[9-11]. Unlike most sensor array analysis approaches, the JPL ENose included quantification as well as identification.[12] All of this development work culminated in a successful demonstration of the 3rd Generation ENose aboard the ISS. The demonstration involved more than 3200 hours (> 6 months) of continuous operation aboard the US Lab on the ISS[9,11]. 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. 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[11].

We are working on a sensor array and new algorithms that will include sensor transients or 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. Muezzinoglu et al. analyzed the transients of metal oxide sensors[13] and demonstrated it is possible to shorten the time to analyze an event. We used this same approach, with the JPL Rapid Analysis, Self-Calibrating (RASCal) Array, to demonstrate it was possible to use time features to shorten the identification of some analytes to under 10 minutes.[14] 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 discuss some of the time-dependent behavior of the polymer-carbon composite sensors in the ENose array, and show preliminary data demonstrating the improved time response of a sensor array, using transient sensor information to identify and quantify ethanol and propanol.

II. Improving Array Response Time

Array response time is the time it takes to correctly identify and quantify an analyte event. Individual sensor response time (evidence that sensor is responding to stimulant) may be fast, but the analysis software will determine the array response time. Using the 3rd Generation JPL ENose, monitoring for an event, involves three steps: establishing a baseline for all sensors, identifying an event onset, and consistent identification/classification of the

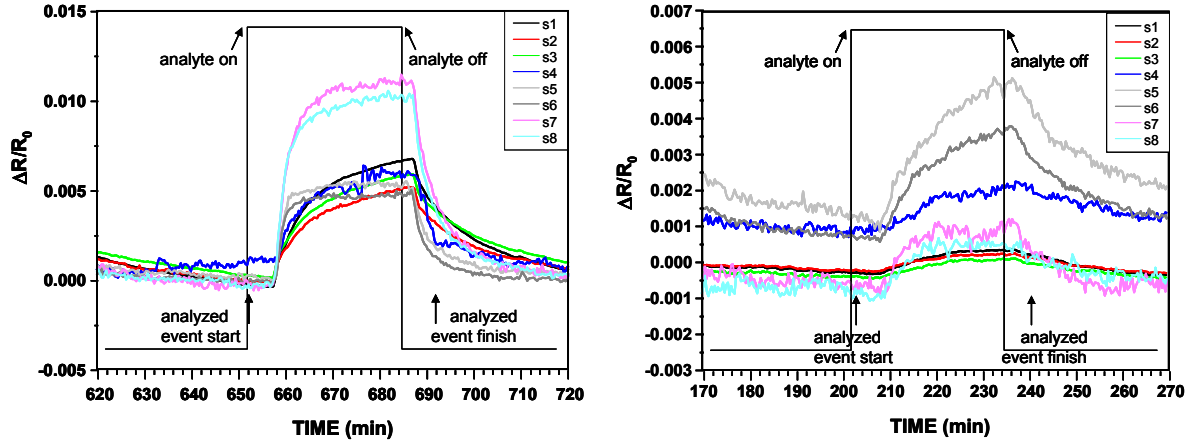

Figure 1. (left) Response of 8 polymer-carbon composite sensors to 1083 ppm ethanol (right) Response of same 8 sensors to 37 ppm of toluene

event. The focus for improvement is the time to identify and quantify the event after onset. The goal for the 3rd Generation JPL ENose ISS technology demonstration was <40 minutes. The data analysis approach uses a Levenberg-Marquart non-linear least squares fit to deconvolute changes in sensor resistance across the sensing array into identification and quantification of the analyte in question. The actual demonstrated response time was 20-30 minutes, depending on the analyte[11]. The current goal for RASCal is < 10 minutes.

Figure 1 shows the monitoring response of the same eight sensors during two different events. The left-hand graph shows the response to 1083 ppm of ethanol while the right-hand side shows the response to 37 ppm of toluene. Both plots are overlaid with a step function that indicates the timing of the event, which lasts for 35 minutes. The eight sensors shown have a much sharper time response to ethanol compared to toluene. Most of the sensors reach equilibrium or plateau within 15 minutes of the onset of the ethanol event. The sensor response to toluene is more varied; sensors five and six do not plateau within the time of the event whereas sensor seven does. For both events the 3rd Generation JPL ENose data analysis software correctly identifies and quantifies the analyte in 20 minutes. In order to calibrate (train) this array to toluene, the training events were run for longer than 35 minutes in order to allow the sensors to come to equilibrium.

III. Experimental

A. Sensor Array

For these experiments we continued tested an array that was made in June 2007. More detail about the polymers in the array can be found in reference 14. In addition, further discussion of the fabrication of sensors and sensor substrates can be found in previous publications.

B. Gas Handling System

For these experiments we used a gas handling system built in our laboratory to deliver clean air as well as analytes to the sensors for testing,. The background gas is house air that is filtered to clean and dehumidify it. A series of mass flow controllers, valves, and check valves are used to control the flow of air and to mix the air to desired humidity and analyte levels. A fraction of the cleaned and dried 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.

C. Array Testing

The sensors were placed in our ENose test chamber and clean humidified air was flowed over the sensors. The sensors were exposed to analytes by alternately flowing clean 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, analyte 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. Ethanol, 2-propanol, and toluene were chosen because these were three of the main analytes used to do preliminary testing and optimization on generation 3 sensor arrays[15].

The water concentration for all of the tests was held at 10,000 ppm H_2O. The sensor substrates were held at 28°C. The 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[6-10].

The sensor data is measured and stored as resistance versus time and for the purposes of viewing here, 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; this data is not smoothed or filtered. For training and analysis, for the 3rd Gen ENose, the normalized change in resistance is used as the response, but the baseline may be corrected for drift.

The response of several different polymer-carbon black sensors to varying concentrations of ethanol can be seen in Fig. 2. Individual sensors have different time responses depending on the sensing material and analyte. The time to equilibration for different sensors ranges from as short as two minutes to longer than half an hour. These temporal variations are illustrated in Figure 2. In some cases the time response (Fig. 2, top) will look similar for several sensors. In other cases the time dependence is very different (Fig. 2, bottom); one sensor shows a very sharp turn-on, almost like a step function, whereas the other shows a very slow rise over time. These two sensors highlight a variation in temporal response; the poly(4-vinyl phenol) (PVP) takes longer to reach equilibrium, and longer to return to baseline. JPL 3rd Generation ENose training had to train to the slowest sensor to get good equilibrium data for the entire array.

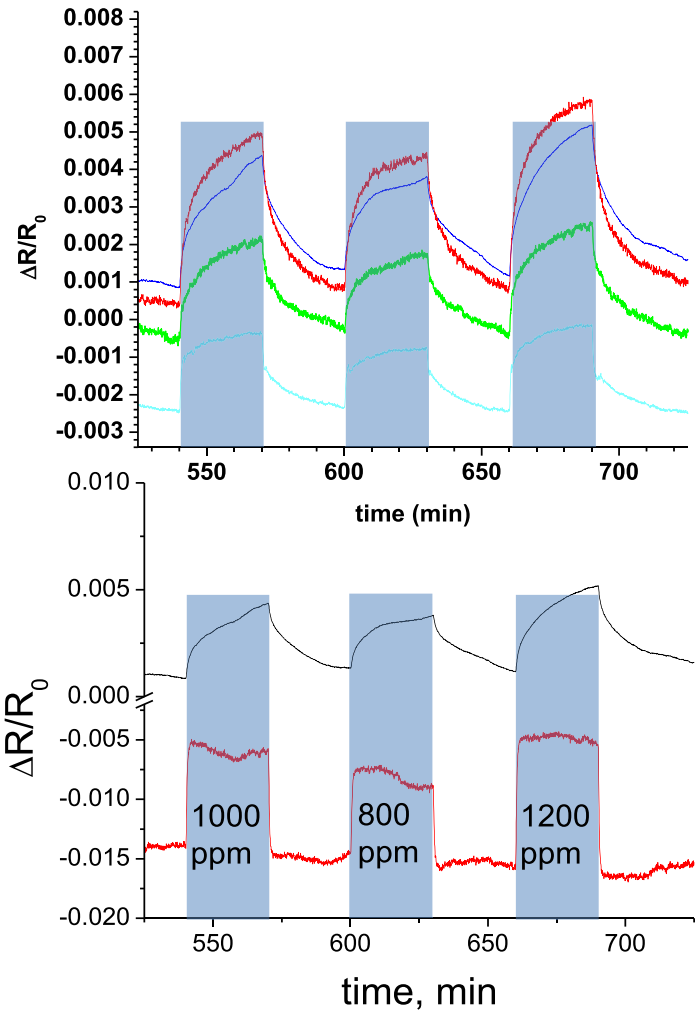

Figure 2. Response of different polymer-carbon composite sensors to 1000, 800, and 1200 ppm of ethanol. (top) Four sensors that show similar responses to ethanol (bottom) poly(4-vinyl phenol) and polyamide resin (red) sensor responses to ethanol.

IV. Results

In order to determine whether we could take advantage of the temporal features in the 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.

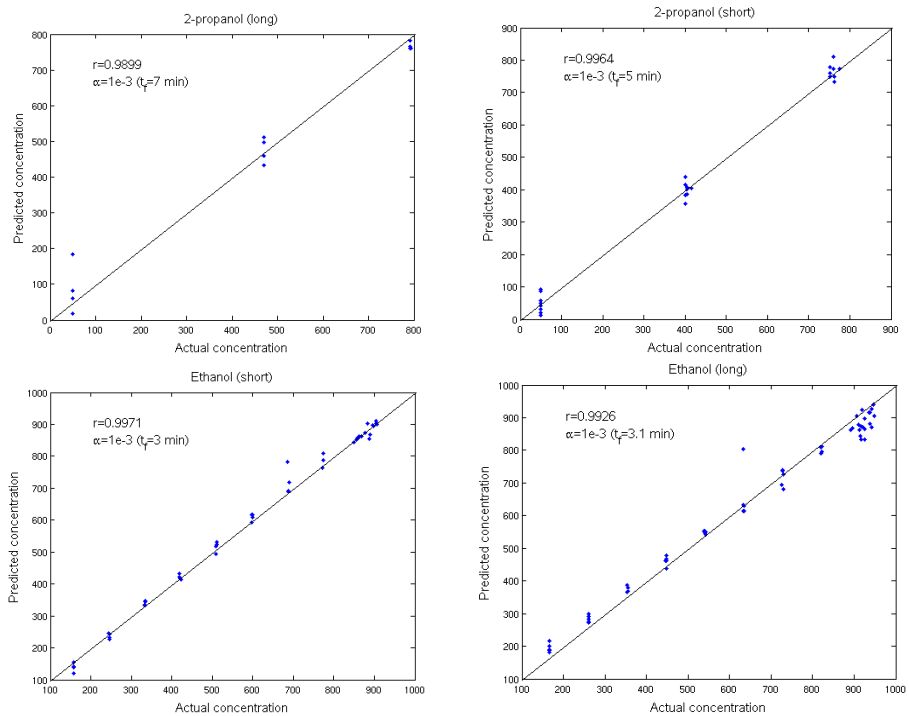

Figure 3. Performance in gas concentration estimation for ethanol and 2-propanol using an optimized feature. The axes are in units of parts per million and r is the Pearson correlation, which is very close to 1.

Using our algorithms for gas discrimination and gas estimation of the concentration[16] we could show the feature selection works both on regression (gas concentration estimation) and in classification (discrimination). Figure 3 shows how the time dependent features can be used for analysis and still get good identification and quantification. The gas concentration estimation is very good even though the sampling period has been reduced to three minutes. The exponential moving average feature[13] can be optimized to capture the most relevant characteristics of the transient sensor response.

V. Conclusions

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.

The interaction between the analytes and the sensing films, has been modeled[11, 17] under equilibrium conditions. In addition, some of these descriptors have been used to model sensor response.[18] While the current transient analysis identifies features in the sensors, it is not currently tied to each sensor by a chemical process like diffusion. Future work will focus on relating the transient analysis to the physical and chemical properties of the sensing films, possibly through diffusion and/or kinetics.

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