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Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose

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ABSTRACT

An Electronic Nose is being developed at JPL and Caltech for use in environmental monitoring in the International Space Station. The Electronic Nose (ENose) is an array of 32 polymer film conductometric sensors; the pattern of response may be deconvoluted to identify contaminants in the environment. An engineering test model of the ENose was used to monitor the air of the Early Human Test experiment at Johnson Space Center for 49 days. Examination of the data recorded by the ENose shows that major excursions in the resistance recorded in the sensor array may be correlated with events recorded in the Test Logs of the Test Chamber.

INTRODUCTION

The ability to monitor the constituents of the breathing air in a closed chamber in which air is recycled is important to NASA for use closed environments such as the space shuttle and the space station. At present, air quality is determined after the fact by collecting samples and analyzing them on the ground in laboratory analytical instruments such as a gas chromatograph-mass spectrometer (GC-MS). The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at part-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. Such an instrument is the Electronic Nose now under development at JPL and Caltech [1,2].

An electronic nose is an array of conductometric chemical sensors which change resistance when exposed to vapors. The sensors are not specific to any one vapor; it is in the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be identified by the pattern of response of the array. Electronic Noses have been discussed by several authors, and may be applied to environmental monitoring and quality control in such wide fields as food processing, and industrial environmental monitoring [3,4]. A baseline of "healthy air" is established, and deviations from that baseline are recoded as changes in resistance of the sensors. The pattern of distributed response of the sensors may be deconvoluted, and contaminants identified and quantified by using a software analysis program such as pattern recognition and/or neural network.

The overall goal of the program at JPL/Caltech is the development of a miniature sensor which may be used to monitor the breathing air in the International Space Station, and which may be coordinated with the environmental control system to solve air quality problems without crew intervention. Progress to that goal will depend On the success of this portion of the Electronic Nose program, which is the development of a prototype system which will be the subject of an experimental test during a space shuttle fight in 1998.

The Electronic Nose (ENose) now under development at JPL and Caltech is designed to monitor for common contaminants in space shuttle air. The ENose is not intended to be an analytical instrument such as a GC-MS, although it is being developed with the capacity to identify a limited number of contaminants and metabolic products and to quantify them within 10-20% of their concentration. The goal of this portion of the program is to develop the ability to detect the 12 target compounds listed in Table 1 at levels approximately 1/2 the SMAC (Spacecraft Maximum Allowable Concentration) levels. For most compounds, SMACS are in the single to tens of parts-per-million (ppm) regime. Success of the ENose to detect and quantify contaminants will be confirmed by traditional analyses of air samples with GC-MS.

In the experiment described in this paper, an early developmental model of the ENose was attached to the air recycling line of the Early Human Test Experiment at NASA-Johnson Space Center in January

Compound	Detected on shuttle (ppm) [51	SMAC (ppm) lhr / 7day [6,7]
alcohols		
methanol	< 1	30/ 7
ethanol	. 5 - 5	—
2-propanol	. 4 - 4	400 / 60
methane	1-1o	5300 /5300
ammonia	0	3 0 / 0
benzene	< .1	10/ 0.5
CO_2	320	13000 /700
formaldehyde	0	.4/ 0.4
Freon 113	.1-1	50 I 50
hydrazine	0	4 / . 0 4
indole	0	1 I .05
toluene	. 4 - 4	16/ 16

Table 1: Target compounds for electronic nose shuttle experiment

1997. This experiment offered an earfy opportunity to determine some of the operating parameters of the ENose and to observe its operation in a closed environment similar to that of the space shuttle or space station. The version of the ENose used in this experiment was an early developmental model, and the analytical software for identification and quantification of contaminants is not yet completed; thus, only qualitative interpretations of events can be made.

EXPERIMENTAL

The Electronic Nose Engineering Development Model: JSC Experiment

An engineering development model of an electronic nose was fabricated at JPL and plumbed in to the air revitalization line of the Early Human Testing Chamber (EHT) at NASA-Johnson Space Center for 49 days in early 1997. Air which was to be recycled in the EHT Air Revitalization System (ARS) was heated to 30-34 "C before being passed through the electronic nose chamber. After leaving the ENose chamber, the air was directed to the ARS. The air which passed through the ENose chamber bypassed the EHT testing equipment, then rejoined the air stream to be revitalized.

Presence of a contaminant in air is measured as a change in resistance in the polymer films. Sensor response is expressed as a ratio of resistance at time t=t to resistance at time t=O (deltaR/R). The electronic circuit for data acquisition has been previously described in detail[9]. Data were acquired on a personal computer using a program written for this purpose in LabView.

Design of Sensor Head The sensor head of the Electronic Nose used in this experiment consisted of 32 sensor positions arranged on 4 substrates, each with 8 sensor positions. The substrates were made using hybrid microelectronic cofired ceramic (alumina) processes. Electrodes and contacts were deposited as thick films using screen printing. The substrate layout and fabrication has been discussed in detail elsewhere [8].

In the EHT model, 24 polymeric sensors were made by depositing a solution of polymer mixed with carbon black to make a film 1 - 5 microns thick in contact with gold electrodes. 12 polymers were used in this experiment, four on each of three chips. Each polymer was deposited in 2 positions on each chip. The fourth chip position was occupied by resistors included in the ENose sensor head for electronic reference. A thermistor was included on the sensor head for temperature monitoring. The 12 polymers used are:

A poly(4-vinylphenol)
B poly(styrene-*co*-allyl alcohol)
C poly(vinylchloride-*co*-vinyl acetate)
E polyvinyl acetate)
H polystyrene)
I poly(styrene-*co*-maleic anhydride)
J poly(sulfone)
K poly(methyl methacrylate)
M polyvinyl butyral)
P poly(ethylene-*co*-vinyl acetate)
Q polyethylene oxide)

Deposition of Films 160 mg of each polymer was dissolved in 15 mL of organic solvent. Solvents include tetrahydrofuran (THF), acetone, methylene chloride, toluene or a mixture of solvents. 40 mg of carbon black was added to the solution, and dispersed by sonication. 1- 3 μL of solution was pipetted onto the sensor area and allowed to dry in air. The resistance of the resulting films was in the range 1 -100 kΩ. Solution

was added in increments of 1 μL until the desired resistance was reached. The use of polymer films as sensing media in an electronic nose has been discussed in detail by several authors, including the Caltech group working with JPL on this project [1-4].

ENose System The ENose developmental system used in this experiment is shown in the diagram in Figure 1.

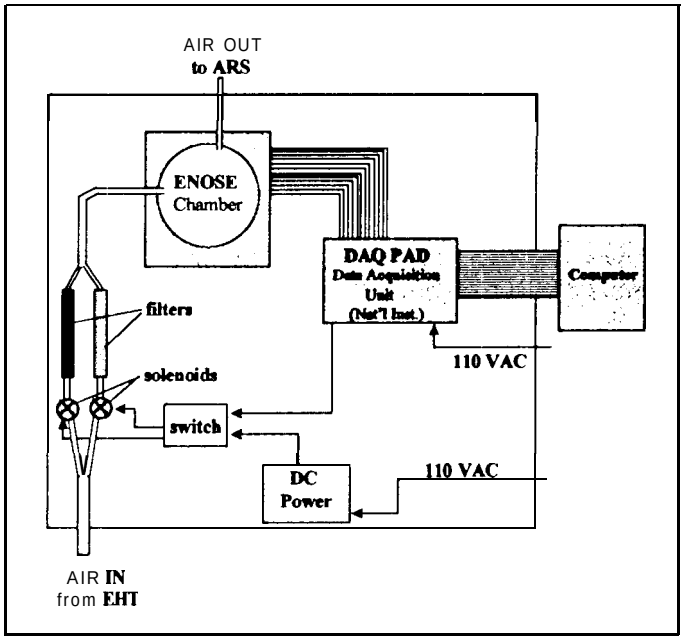

Figure 1: Diagram of ENose system used in EHT experiment

Flowing air (.25 L/min) was taken from the slipstream exiting the EHT chamber, and directed into the ENose system. The air, which had been heated to 30-34 "C for EHT testing purposes, was directed either through an activated charcoal filter, put in line to provide clean air baseline data, or though a dummy glass fitter, put in line to provide a pressure drop similar to the charcoal filter. Solenoid valves were programmed to open the valve to the charcoal filter and provide 30 minutes of clean air flow every four hours; otherwise, the air went through the glass filter. Air then entered the glass enclosed sensor head chamber where resistance was measured every 30 seconds, and then left the ENose system to enter the air revitalization system of the EHT.

The experiment was controlled using a personal computer and a National Instruments DAQPad. The DAQPad sent commands to the solenoids to open and close, and acquired resistance data from the sensors by measuring the voltage at a current provided by the DAQPad.

A sketch of the sensor chip is shown in Figure 2. Each chip consists of eight sensors approximately 1.5 mm x 2 mm. Polymer films were deposited on the sensor positions as described above.

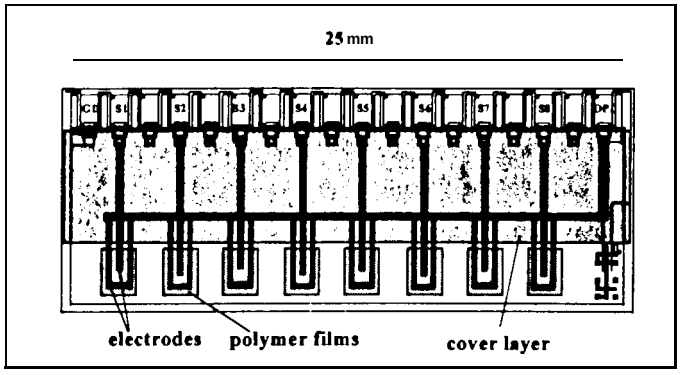

Figure 2: Sketch of the ceramic substrate chip containing eight sensors

Data Analysis The goal of the ENose development is construction of an air quality monitor capable of identifying the target compounds in Table 1 at less than SMAC levels. To accomplish this goal, data analysis software which recognizes the patterns of response of the target compounds is being developed. This software has not been completed, so the data from the EHT experiment maybe used only qualitatively.

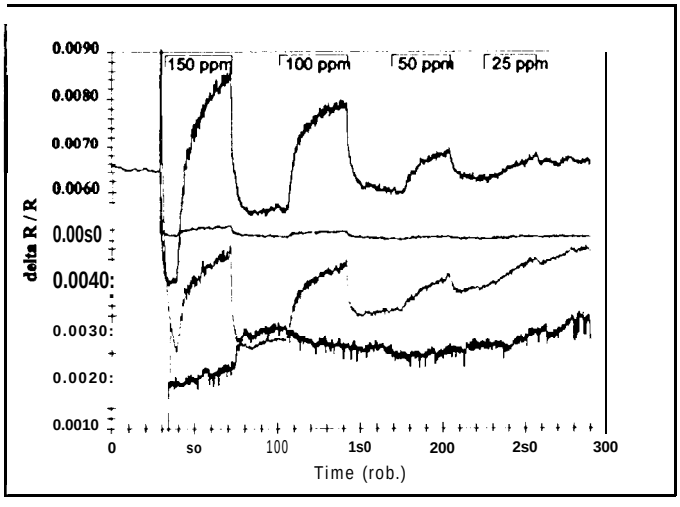

Figure 3: Partial training set for ENose analysis software development. Methanol response of 4 polymers.

ENose data analysis development requires recording training sets of polymer response at the concentrations desired. A sample of a partial training set is shown in Figure 3, where response of 4 polymers to 150, 100, 50 and 25 ppm methanol in air is plotted against time. As may be seen in this figure, different polymers have different magnitudes of response to methanol; polymer Q responds very weakly whereas polymer A has a very strong response. It is these differences which allows identification of compounds; each compound has a unique pattern of response, and

magnitude of *response* may be correlated to concentration of compound. The response to a mixture of compounds has been shown in most cases to be the linear combination of the response to the individual compounds [10].

ENOSE RESPONSE IN EHT

Responses of the ENose have been correlated to several events recorded in the test logs of the EHT. Two of the most notable correlations are shown in Figures 4 and 5.

In Figure 4, spiking in CO_2 levels, as determined by $C0_2$ measurements made by on line monitoring of the air to be recycled correlates in time with spikes in ENose sensor response. The magnitude of response for different polymers was different; as shown in the figure, Polymer E responds strongly and Polymer C rather weakly to the changes.

CO_2 concentration fluctuated between .46% and .60% as a percent of chamber air (measured by GC); this is reflected as a fluctuation of a similar magnitude in the most responsive polymer (E). On those days in which CO_2 spiking is not found in the EHT measurements, spiking is not found in the ENose data.

Figure 5 shows significant change in sensor resistance when the EHT chamber door was opened to the outside and untreated air was allowed to enter the chamber. The event in Figure 4 which begins about 8:00 may be correlated to the JSC Test Director Log entry at 8:03 AM (3/1 4/97).

Transfer in of Dr. Z and a blood draw technician through outerlock door. Mylar *screen implemented to secure air integrity.*

Subsequent rises in sensor resistance correlate with opening the EHT chamber, and a fall in response correlates with closing the EHT chamber. In spite of the use of a Mylar screen, there was substantial change in constituents in chamber air at the time the outerlock door was opened. There is no independent analysis of the air constituents at that time, so it is possible only to observe the change and correlate it with events recorded in the logs. As the identification software is not yet complete, the sensor responses to opening the chamber cannot be deconvoluted to identify the mixture of compounds inducing for the response.

Several other events recorded in the logs or the on line monitoring of the EHT were correlated with response in the ENose, such as change in humidity, water spills and crew report of an odor in the shower area.

CONCLUSIONS

Operation of the E Nose for 49 days in the JSC EHT experiment air stream showed that the polymer sensors will respond to events in the breathing air environment. The observation of ENose sensor spiking in temporal correlation with GC observed $C0_2$ spiking is especially encouraging for use of the ENose in environmental monitoring. The magnitude of $C0_2$ rise was not sufficient to be a danger to crew members, but the ENose was able to observe the rise, and thus could be used to monitor and quantify the $C0_2$ levels in an enclosed space.

As maybe seen in both Figures 4 and 5, there is little baseline drift over the period of 12 hours. As the sensor is zeroed on clean air provided by the carbon filter, moderate baseline drift, defined as a change over time in the resistance of the polymer in the presence of the same atmosphere, will not affect the operation of the device. However, comparison of the responses of the polymers to cleaned air show that the carbon filter was not sufficiently large to give good cleaning for 49 days. The limit of the filter used is about 15 days of continuous operation. Future investigations will include filter materials capable of longer term operation.

Careful study of the data curves in Figure 4 show a cycling which corresponds to the carbon fitter on-off cycle. Temperature measurements showed that turning on the valve to direct air through the carbon fitter heated the air by 1-2 'C. Many of the polymers are strongly responsive to temperature changes of 1-2 'C. Future work also focus on calibration of the temperature response as data which must be included in the data analysis software and on design of a system which is not highly responsive to temperature changes in the environment.

Figure 5, which shows the response of the sensor to outer door activity, shows that the ENose will respond to leaks in a chamber. Further development of the data analysis software and the low concentration monitoring capacity of the device will lead to a miniature instrument for environmental monitoring and earfy detection and identification of changes in environmental constituents.

Development of the low concentration monitoring capacity of the ENose will be accomplished by improving the polymer response and by diminishing the noise in the electronics response. Polymer response improvement includes development of application methods and determination of optimum carbon loading and film thickness.

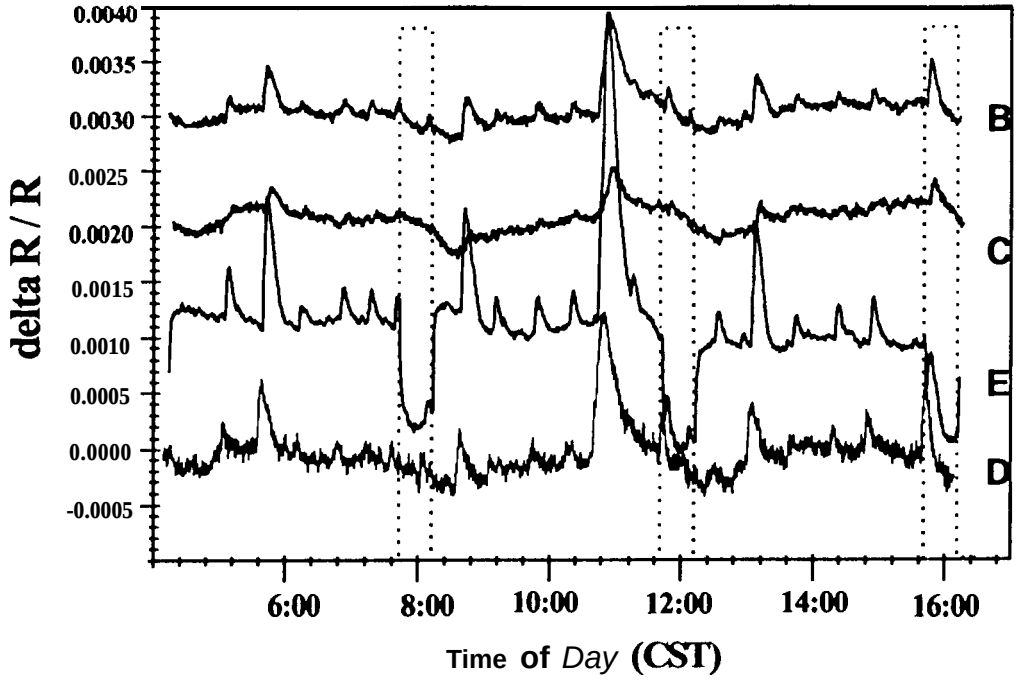

Figure 3: Spiking in EHT air CO_2 levels maybe correlated to spikes in Enose sensor response at the same time. Dotted vertical lines show the 30minute reference cycle with a corresponding dip in sensor response.

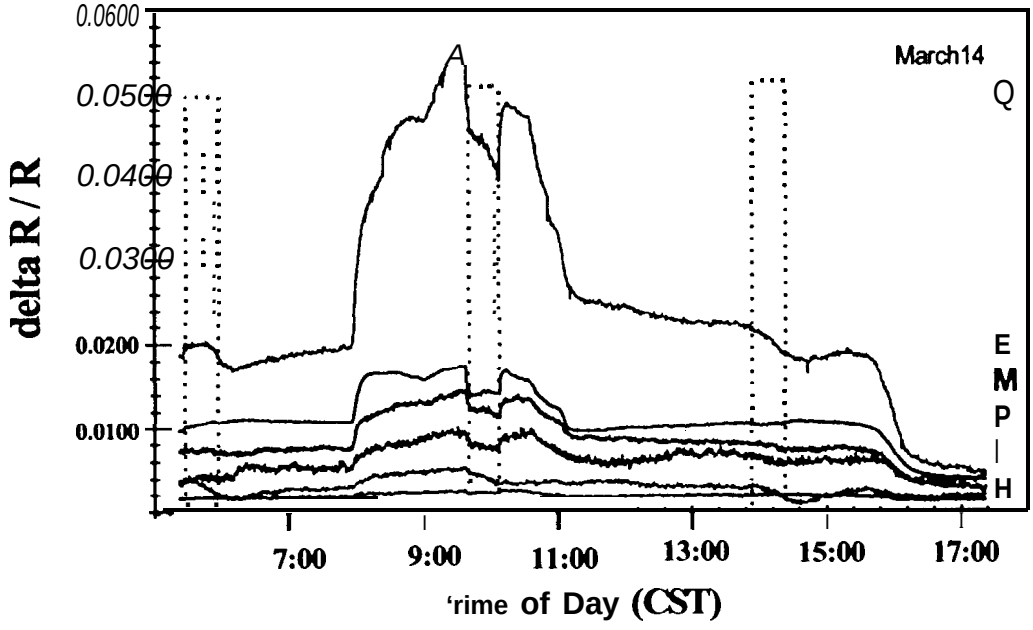

Figure 4: When the EHT chamber door was opened, there is significant change in resistance in Enose sensors. Dotted vertical lines show 30 minute reference cycles with a corresponding dip in sensor response.

The goal of this portion of the ENose development program is demonstration of the ability of the device to recognize and quantify the 12 contaminants listed in Table 1. It is intended that a demonstration experiment be performed with the ENose on a Shuttle flight in 1998. Demonstration of the ENose's ability to detect leaks and unusual events in the JSC EHT experiment shows that with development of analysis software, it will be possible to build a miniature environmental monitoring device.

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