

RESULTS FROM THE SPACE SHUTTLE STS-95

ELECTRONIC NOSE EXPERIMENT

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ABSTRACT

A miniature **electronic nose** in which the sensing media are insulating polymers loaded with carbon black as a conductive medium has been designed and built at the Jet Propulsion Laboratory. The ENose has a volume of 1700 cm³, weighs 1.4 kg including the operating computer, and uses 1.5 W average power (3 W peak power). This ENose was used in a **demonstration experiment** aboard STS-95 (October, 1998), in which the ENose was operated continuously for six days and recorded the sensors' response to the air in the mid-deck. The ENose was designed to detect ten common contaminants in space shuttle crew quarters air. The experiment was controlled by collecting air samples daily and analyzing them using standard analytical techniques after the flight. Changes in humidity were detected and quantified; neither the ENose nor the air samples detected any of the contaminants on the target list. The device is microgravity insensitive.

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 in closed environments such as the space shuttle, the space station, and planned human habitats on Mars or the Moon. At present, air quality from the space shuttle is determined on the ground after a flight by collecting samples and analyzing them 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 levels which have the potential to be harmful to crew health, generally single or tens of parts-per-million, 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 (ENose) which has been developed at JPL in collaboration with Caltech [1-4].

At present, the best real time, broad band air quality monitor available in space habitats is the human nose. It is limited by human factors such as fatigue, exposure to toxins, and inability to detect some compounds. Most existing chemical sensors are designed to detect specific molecules. Array-based sensing uses non-specific sensors in which the pattern and magnitude of response are used to identify and quantify the presence of contaminants. Array-based sensors are based on a biological model of "sniffing", detecting changes in odor, and can be trained to detect new patterns.

An electronic nose is such an array of non-specific chemical sensors, controlled and analyzed electronically, which mimics the action of the mammalian nose by recognizing patterns of response to

vapors. The sensors used in the device discussed here are 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 of which responds differently, 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 as well as to quality control in such wide fields as food processing and industrial environmental monitoring [5,6].

In the device designed and built for crew habitat air monitoring, a baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors is deconvoluted, and contaminants identified and quantified by using a set of software analysis routines developed for this purpose. The overall goal of the program at JPL/Caltech has been 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.

In a program to develop a miniature electronic nose, JPL has designed and built a device which uses the conductometric polymer and carbon sensing media developed at Caltech. This device was built and used in an experiment on the space shuttle in which air in the shuttle mid-deck was monitored continuously for 6 days and the data stored in memory. The data were analyzed after the landing and compared with independent analysis of air samples which had been taken daily during the ENose operation.

Table 1: Target compounds for electronic nose shuttle experiment and JPL limits of detection.

Compound	Detected on shuttle (ppm) ^[7]	SMAC (ppm) ^[8,9] 1hr	JPL Detection Limit (ppm)
alcohols			
methanol	< 1	30	5
ethanol	.5 - 5	2000	50
2-propanol	.4 - 4	400	50
ammonia	0	30	20
benzene	< .1	10	10
formaldehyde	0	.4	15
Freon 113	.1 - 1	50	20
indole	0	1	0.03
methane	1 - 10	5300	3000
toluene	.4 - 4	16	15

The ENose experiment on STS-95 was designed to monitor the air for the presence of ten compounds at or above the Spacecraft Maximum Allowable Concentration (SMAC) for each compound. The ten compounds and their SMACs are listed in Table 1. These compounds were selected based on their having been previously found in analysis of shuttle air. Also listed in the table is the detection limit for that compound in the current version of sensors and device at JPL.

THE ELECTRONIC NOSE

The ENose prototype developed and built at JPL has the dimensions 18.5 cm x 11.5 cm x 8 cm (1700 cm³). It weighs 1.4 kg with the control computer, and uses 1.5 W average power and 3 W peak power. The device is controlled by an HP200-LX palm-top computer. Data are collected through a

circuit designed for the purpose and stored in flash memory in the HP200LX. A sketch of the ENose set-up is shown in Figure 1.

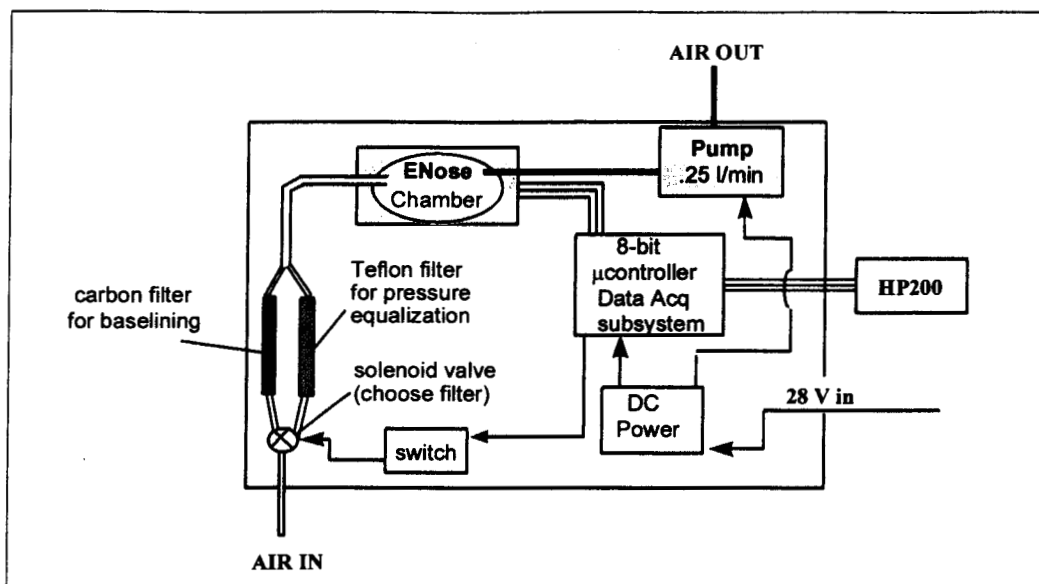


Figure 1: Sketch of JPL ENose flown on STS-95

Sensors: The sensors in the ENose are polymer films which have been loaded with a conductive medium, in this case carbon black. A baseline resistance of each film is established; as the constituents in the air change, the films swell or contract in response to the new composition of the air, and the resistance changes. In the JPL ENose, sensing films were deposited on co-fired ceramic substrates which were provided with eight Au-Pd electrode sets. A sketch of the sensor substrate is shown in Figure 2.

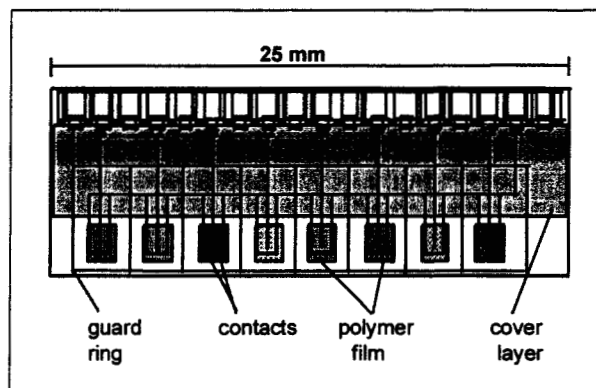


Figure 2: Sensor substrate

The polymers used in the ENose flight experiment were selected by statistical analysis of responses of these films to the target compounds. Data for the statistical analysis were provided by Caltech. The polymers used in the STS-95 flight experiment were:

- Poly(2, 4, 6-tribromostyrene), 66%
- Poly(4-vinylphenol)
- Poly(ethylene oxide)
- Polyamide resin
- Cellulose triacetate
- Poly(2-hydroxyethyl methacrylate)
- Vinyl alcohol/ vinyl butyral copolymer, 80% vinyl butyral
- Poly(caprolactone)

Poly(vinylchloride-co-vinyl acetate)
 Poly(vinyl chloride-co-vinyl acetate) 10%vinyl acetate
 Poly(vinyl acetate)
 Poly(N -vinylpyrrolidone)
 Styrene/isoprene, 14/86 ABA Block copolymer
 Poly(vinyl stearate)
 Methyl vinyl ether/ maleic acid 50/50 copolymer
 Hydroxypropyl methyl cellulose, 10/30

Protocols for depositing these polymers have been previously published [3,4]. Because most of the polymer film resistances are very sensitive to changes in temperature [10], heaters were included on the back of substrates to provide a constant temperature environment.

Mechanical Design: To monitor air quality, flowing air (.25 L/min) is pumped from the room into the sensor chamber of the ENose using a Thomas model X-400 miniature diaphragm pump. The air is directed either through an activated charcoal filter, put in line to provide clean air baseline data, or through a dummy Teflon bead filter, put in line to provide a pressure drop similar to the charcoal filter. Solenoid valves are programmed to open the path to the charcoal filter and provide 15 minutes of clean air flow every 3.5 hours; otherwise, the air is directed through the Teflon bead filter. Air then enters the glass enclosed sensor head chamber where resistance is measured.

Data Acquisition: The air is monitored by measuring the sensor voltage at a known, provided current and converting it to resistance. Data acquisition and device control are accomplished using a PIC 16C74A microcontroller. The Hewlett Packard HP 200 LX palm top computer is programmed to direct the microcontroller to open or close the solenoid valve which controls access to the charcoal or Teflon filter and to record sensor resistance. Typical resistance change for 10-50 ppm of contaminant is on the order of 2×10^{-4} (200 ppm resistance change), and may be as small as 1×10^{-5} .

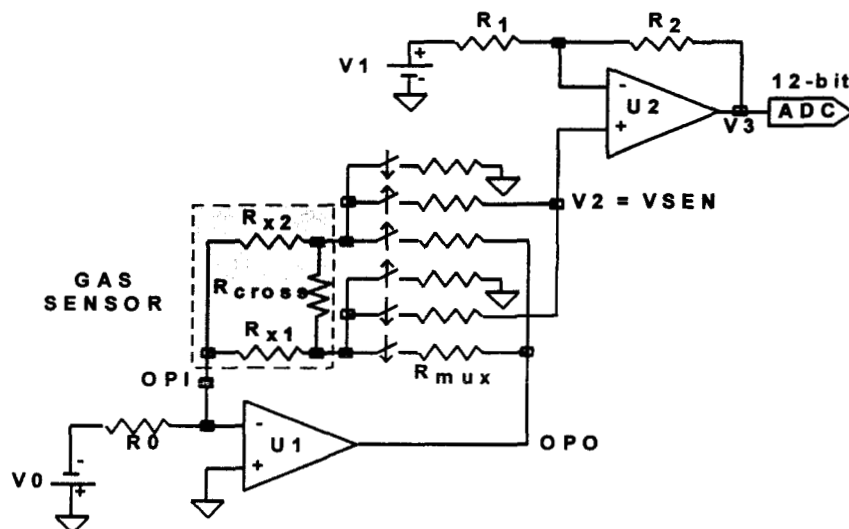


Figure 3: 12 Bit Dual Offset Nulling Amplifier

The resistance measurement circuitry designed for the ENose is shown in Figure 3. It is designed to allow the measurement of film resistance changes as 1 in 10^5 , to eliminate cross talk between sensors, and to minimize pin count. The architecture of the sensor substrate, the shaded region in Figure 3, indicates that one side of each sensor, R_{x_i} is connected to a common node which is connected to the input terminal of Operational Amplifier U1. Resistance caused by cross-talk which was not by bridging, R_{cross} , is eliminated by grounding the sensor nodes on either side of the sensor under test. This feature became unnecessary as sensor development proceeded, but it was not removed from the circuit. Detection of changes in resistance of 1 in 10^5 was achieved by nulling the V_{SEN} signal to within 12 bit resolution by way of V1, and amplifying the remainder with Op Amp U2, a follower with gain. The amplified remainder is digitized with a 12 bit Analog-to-Digital Converter (ADC) and signal averaged 8 times. The reported resistance change has the equivalent of 18-20 bit resolution.

Data Analysis: Data analysis for this experiment were done after the flight, using software developed for the purpose. Data analysis development for this experiment focused on development of a data analysis method that can correctly identify and accurately quantify a gas event off-line, of single or mixed gases. The routines developed can be modified to provide real-time or quasi-real time analysis.

Data analysis is intended to identify and quantify compounds on the target list at the 1 hour SMAC level. Laboratory tests show 80 - 90% accuracy in identification and quantification at the +/- 50% level. This degree of quantification is sufficient for toxicological purposes. Mixtures of two or three compounds on the list can also be identified and quantified, with somewhat lower confidence. Gas events from compounds not in the training sets or from mixtures of several target compounds will be classified as unknown.

The data analysis routines developed included several steps. Upon receipt of the data, which are stored as Resistance vs. Time, high and low frequency noise are removed by filtering. High frequency noise is largely caused by the responses of the sensing films. Low frequency noise appears in the data as baseline drift, and is largely caused by humidity, temperature and pressure changes in the monitored atmosphere. Baseline drift which is not removed by high or low frequency filters is removed by constructing a piece-wise baseline and subtracting it from the data.

Once the baseline of the data is treated, events are identified and patterns for each event generated for use in pattern recognition routines. Because the responses of the array are not linear outside of relatively small concentration ranges, the technique used in this step is the Levenberg-Marquardt Non-linear Least Squares Method (LM-NLS) [11].

LM-NLS is an iterative damped least-square method. LM-NLS tries to find the best-fit parameter vector \mathbf{x} from an observation vector \mathbf{y} , which is related to \mathbf{x} through a known linear or nonlinear function, $\mathbf{y}=\mathbf{f}(\mathbf{A},\mathbf{x})$, e.g. $\mathbf{y}=\mathbf{A}_1\mathbf{x}+\mathbf{A}_2\mathbf{x}^2$, where \mathbf{A}_1 and \mathbf{A}_2 are system characteristics obtained from training data. This method begins from a given starting point of \mathbf{x} , calculates the discrepancy of the fit as

$$residual = (computed-observed)/\sigma$$

and updates with a better-fitted parameter \mathbf{x} at each step.

FLIGHT EXPERIMENT

Design: The ENose flight experiment was designed to provide continuous (*i.e.* data points every 30 seconds) monitoring of the air in the mid-deck of the orbiter. The ENose response was recorded over 6 days. In order to confirm that the ENose was operating, a crew member would check the operating LEDs on the side of the unit daily to determine that the unit was operating and not in a reference cycle, collect a daily air sample in a grab sample container, and provide a “event” or daily marker by exposing the inlet of the unit to a 2-propanol wipe.

After the flight the GSC air samples were returned to Johnson Space Center for post-flight analysis using GC-MS, and the ENose unit was returned to JPL. The monitoring data saved in the ENose were analyzed using the software routines developed, and the unit was calibrated to confirm that the sensor responses had not changed. After both JSC and JPL analyzed the data, the two teams met for a data review.

Results: Observation of the Resistance vs. Time data that were returned from STS-95 showed that there were several gas events in addition to the daily marker. The daily marker had been added to the experiment so that operation of the device over the entire period could be confirmed. The initial work done with analysis confirmed that the events identified as daily propanol markers by visual examination and comparison of crew log times with the time of the event were indeed the propanol wipes.

Software analysis identifies all events which were not propanol wipe events as humidity changes. Most of those changes can be well correlated with the humidity changes recorded by the independent humidity measurements provided to JPL by JSC. The events are not completely correlated in time because the humidity sensor was located on the stairway between the mid-deck and the flight deck, and the ENose was located in the mid-deck locker area near the air revitalization system intake. Those events identified as humidity changes but not correlated with cabin humidity change are likely to be caused by local humidity changes; that is, changes in humidity near the ENose which were not sufficient to cause a measurable change in cabin humidity. Figure 4 shows the correlation of cabin humidity with ENose response in several cases.

Figure 5 shows the similarity between the pattern for particular events in Figure 4, and compares them with the pattern recorded in training sets for humidity change. Note that the daily marker event from Figure 4, which is a spike seen at time 306.95, is a combination of 2-propanol wipe and humidity change. The marker was made in a time of rising humidity in the cabin. Software analysis of the flight data did not identify any other target compounds, as single gases or as mixtures.

The independent analysis of collected air samples, in which the samples were analyzed at Johnson Space Center by GC-MS, confirmed that no target compounds were found in the daily air samples in concentrations above the ENose detection threshold. There were no compounds that the ENose would have indicated as unidentified events present in the air samples.

The correlation between the ground training and in-flight response patterns for both the 2-propanol wipe and humidity change shows that the operation of the ENose is microgravity insensitive, and thus can be used in a space-based application without further accounting for in microgravity effects.

CONCLUSIONS

While the hope in an experiment such as this one is that there will be several events which test the ability of the device, such events would certainly be anomalous events in the space shuttle environment. It is not surprising that the only changes the ENose saw were humidity changes, and it is because events were not expected that the experiment included the relatively uncontrolled daily marker events. The ENose experiment is judged a success on four counts:

1. the daily marker was identified and quantified
2. humidity events were identified and quantified
3. that unremarkable events such as a crew member passing by were not recorded
4. the crew reported no events that would be expected to induce a response in the ENose.

Further work with the ENose should take in to account the limitations of the experiment done in this program. The experiment was controlled to the extent that daily air samples were taken and daily confirmation of the device's operation was made; however, if an event occurred several hours before the air sample was taken, then the ENose would have been the only detection system. Truly testing the ENose as an incident monitor will require controlled release of target compounds, mixtures of target compounds, and unknowns. This scenario is not a likely one for use in a flight environment, as it will pose risk to crew health. Thus, the logical next step for testing the ENose as an incident monitor for crew-habitat in spacecraft will be extensive ground testing in a habitat-like environment where controlled releases of contaminants can take place.

ACKNOWLEDGMENTS

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

Research was supported by NASA Code UL. The authors thank Dr. John James of JSC and Dr. Thomas Limero of Wyle Laboratories for providing copies of the GSC analysis.

REFERENCES

1. M.S. Freund and N.S. Lewis, *Proc. National Academy of Science*, **92**, 2652, (1995).
2. M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs and N.S. Lewis, *Chem. Materials*, **8**, 2298 (1996).
3. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zec, and J. Graf, *Proceedings of the 27th International Conference on Environmental Systems*, Society of Automotive Engineers, (1997).
4. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, B. Lau, D. Karmon and S. Jackson, *Proceedings of the 28th International Conference on Environmental Systems*, Society of Automotive Engineers, (1998).
5. H.V. Shurmer and J.W. Gardner, *Sensors and Actuators*, **B8**, 8, (1992).
6. J.W. Gardner, T.C. Pearce, S. Friel, P.N. Bartlett and N. Blair, *Sensors and Actuators*, **B18-19**, 240, (1994).
7. J.T. James, *et al.*, *Aviation, Space Environ. Med.*, **65**, 851 (1994).

8. *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).
9. *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).
10. M.G. Buehler and M.A. Ryan. *Proc. SPIE Conf. on Electro-Optical Tech. for Chemical Detection*, (April, 1997).
11. M. Lampton, *Computers in Physics*, **11**, 110 (1997).

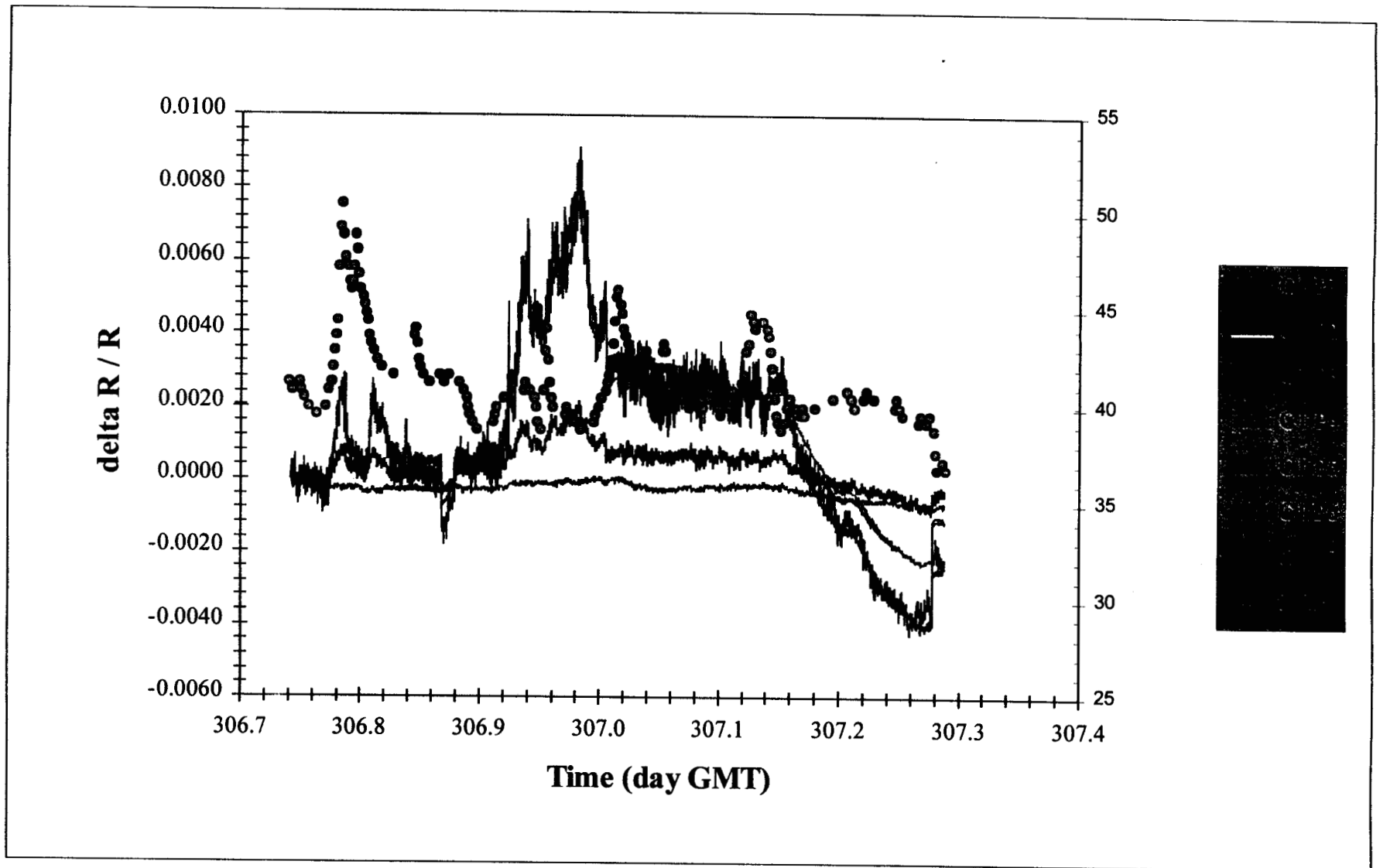


Figure 4: STS-95 Shuttle Data. Circles are the plot of independent humidity measurements in the stairway from mid-deck to flight deck. The solid traces are polymer responses and correspond to positions on the sensor chips.

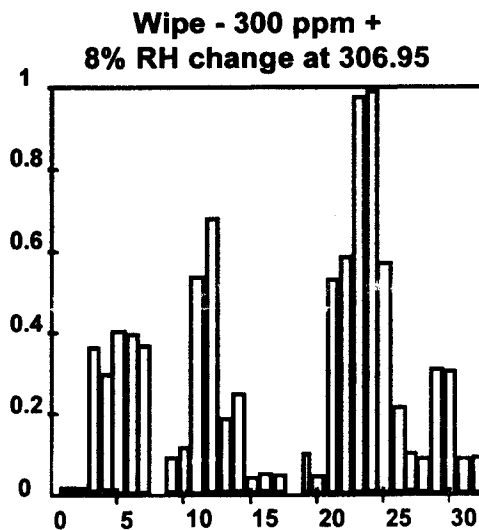
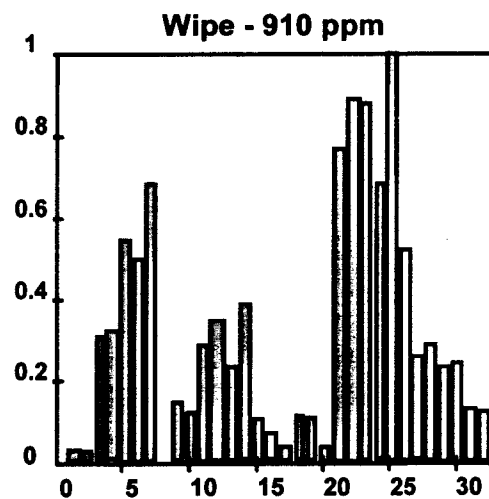
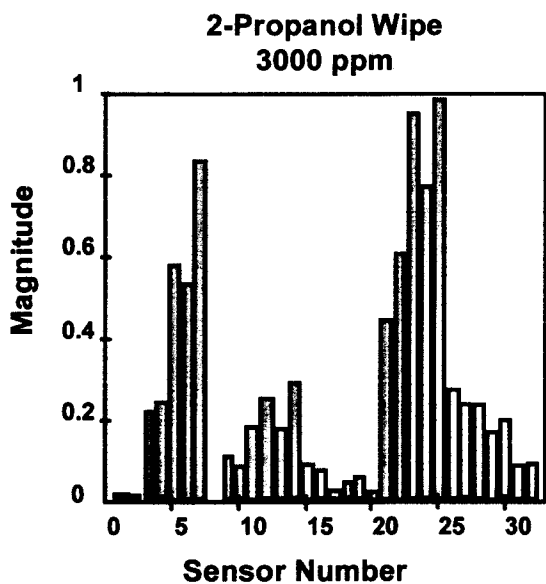
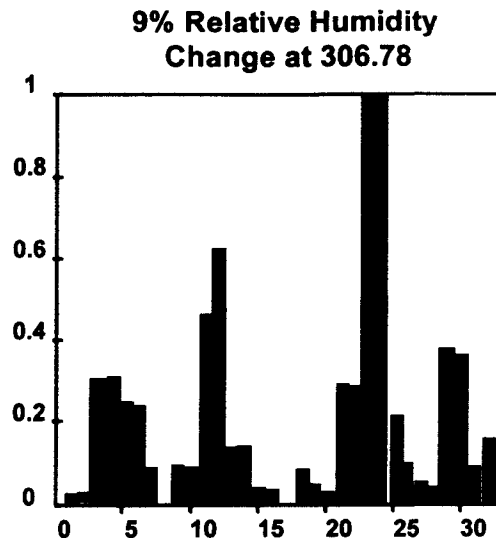
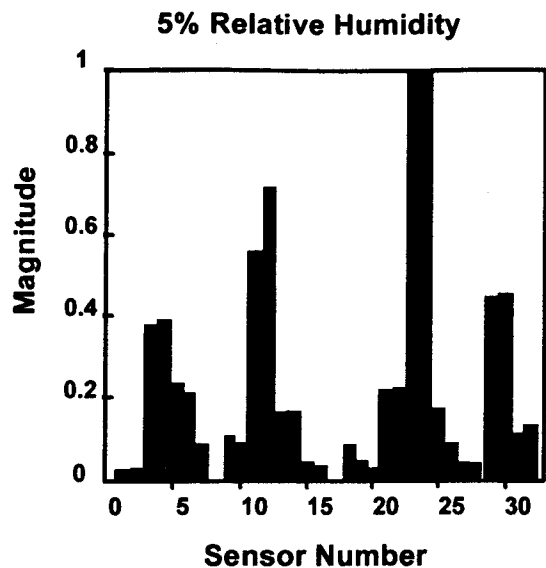


Figure 5: Signature or fingerprint patterns of sensor response to humidity and 2-propanol wipe.

Left side: Training sets

Right side: Flight data. The daily marker shown in Figure 4 at 306.95 was wipe plus humidity.