

Ground Validation of the Third Generation JPL Electronic Nose

M. A. Ryan, A. V. Shevade, A. K. Kisor,
K. S. Manatt, M. L. Homer, L. M. Lara and H. Zhou

Jet Propulsion Laboratory, California Institute of Technology

Copyright © 2008 SAE International

ABSTRACT

The Third Generation ENose is an air quality monitor designed to operate in the environment of the US Lab on the International Space Station. It detects a selected group of analytes at target concentrations in the ppm regime at an environmental temperature range of 18 - 30 °C, relative humidity from 25 - 75% and pressure from 530 to 760 torr. The abilities of the device to detect ten analytes, to reject confounders as "unknown" and to deconvolute mixtures of two analytes under varying environmental conditions has been tested extensively in the laboratory. Results of ground testing showed an overall success rate for detection, identification and quantification of analytes of 87% under nominal temperature and humidity conditions and 83% over all conditions.

INTRODUCTION

The JPL Electronic Nose [1-5] is an event monitor designed and built for near real time air quality monitoring in crew habitat aboard the space shuttle/space station. This is an array-based sensing system which is designed to run continuously and to monitor for the presence of selected chemical species in the air at parts-per-million (ppm) to parts-per-billion (ppb) concentrations.

There have been three phases of development of the JPL Electronic Nose. In the first phase, a device capable of detecting, analyzing and quantifying ten analytes at the 1-hour Spacecraft Maximum Allowable Concentration (SMAC) was developed. This device was tested successfully in 1998 on Space Shuttle flight STS-95 [4]. In the second phase, the ENose was miniaturized and the capabilities were significantly expanded to include 21 analytes and detection at varying humidity and temperature. The Second Generation ENose was tested extensively on the ground and was demonstrated to be able to detect, identify and quantify the 21 analytes at or below their 24-hour SMACs [6]. In preparation for an upcoming, six-month technology demonstration aboard the International Space Station (ISS) in 2008-09, the JPL ENose team is

developing a Third Generation ENose which is designed to monitor spacecraft cabin air quality in near real-time.

Development of the Third Generation JPL ENose has required two major areas of development. One area is the design and fabrication of an interface unit which will allow the ENose to be operated through the EXPRESS Rack (EXpedite The PROcessing Of Experiments To Space Station) on the ISS for a six-month technology demonstration experiment. The second area of development includes the sensing platform and the data analysis software. Using the Second Generation ENose as a base, the sensing materials, sensor substrate, and data analysis routines are being expanded in order to include the ability to detect additional inorganic species, mercury and sulfur dioxide, and to provide quasi-real time data analysis. The design and development of the 3rd Generation ENose has been discussed in detail elsewhere [7,8].

This paper will focus on extensive laboratory testing of the capabilities of the 3rd Generation Electronic Nose (ENose) under a variety of environmental conditions.



Figure 1: The Third Generation ENose. The Sensor Unit is enclosed in the Interface Unit, which will be connected to the ISS EXPRESS Rack

THE THIRD GENERATION JPL ENOSE

The ENose was tested for response and ability to identify and quantify eleven chemical species, shown in Table 1. A quantification is considered to be correct if the concentration value reported by the ENose data analysis software is $\pm 50\%$ of the independently measured concentration of the species. The error range of $\pm 50\%$ in quantification is based on the approximate range with which the Spacecraft Maximum Concentrations (SMACs) are set; toxicities are not well known for most chemical species, and SMACs are set very conservatively.

Success rate in analyte identification and quantification is the number of correctly identified and quantified deliveries of analyte, minus the number of false negatives and false positives, divided by the number of deliveries of analyte. A false negative is failure to detect the delivery and presence of a targeted chemical species. A false positive is a report of the presence of a chemical species when it was not present. Misidentification of a targeted species, for example identifying propanol as methanol, or identifying a confounder as a targeted species, is considered to be a false positive.

Table 1: Analyte List and Target Detection

Concentration; mg/m^3 is a pressure independent unit; ppm is for 1 atm.

	ANALYTE	QUANT. TARGET (mg/m^3)	QUANT. TARGET (ppm)
TIER 1	Ammonia	3.5	5.0
	Mercury	0.080	0.010
	Sulfur Dioxide	3.0	1.0
TIER 2	Acetone	500	200
	Dichloromethane	35	10
	Ethanol	940	500
	Freon 218	150	20
	Methanol	13	10
	2-Propanol	240	100
	Toluene	60	16
TIER 3	Formaldehyde	0.12	0.10

The chemical species in Table 1 are divided into three tiers, based on the importance to NASA Habitability and Environmental Factors Office in detecting these species. Formaldehyde was classified as Tier 3 because its identification and quantification was a goal, not a

requirement for this program; however, formaldehyde was treated as a Tier 2 analyte for ease of testing.

ENVIRONMENTAL CONDITIONS

The environmental conditions under which testing was done were defined according to conditions which can be expected in the US Lab on the ISS. Background air composition was based on allowed ISS atmospheric concentrations of water, carbon dioxide and methane. Relative humidity (RH) may vary from 25-75% at temperatures of 18°C - 30°C , CO_2 concentration may be as much as ~ 15 mm Hg partial pressure and CH_4 may be several hundred ppm). Atmospheric pressure in the ISS may vary from 538 - 760 torr (10.4 to 14.7 psi) and may rise for brief periods (minutes) as high as 830 torr (16 psi).

Temperature may vary over the range $18 - 30^\circ\text{C}$ (66 to 86°F). Nominal conditions are 760 torr, temperature $21 - 23^\circ\text{C}$ and relative humidity 30-40%. Testing was done under all conditions, but not all concentrations of all analytes were tested under all conditions. For repeatability in testing, water content was controlled as ppm water rather than as relative humidity. Nominal conditions on orbit in ISS correspond approximately to $21 - 22^\circ\text{C}$, 10,000 ppm water, and atmospheric pressure.

TRAINING SETS

As the ENose is an array-based chemical sensor device, before it can be used as an air quality monitor, training sets must be acquired. Based on the training sets, the patterns of array response to targeted analytes under specified conditions are included in the data analysis algorithm.

Data from the ENose are recorded for each individual sensor as resistance versus time. Because the ENose is designed to function as an event monitor, the data are analyzed as change in resistance vs. time. Individual sensor resistances are recorded simultaneously, with a point being taken every twenty seconds. While it would be possible to take data more or less frequently than three times a minute, this data rate has been established as an optimum rate to show fairly rapid changes in the environment without overwhelming computer memory with data. Our data analysis approach defines an "event" as a change in the composition of the environment which lasts longer than ten minutes, or thirty points at the standard data rate, in part because events of duration shorter than ten minutes cannot practically be addressed or mitigated using either breathing apparatus or clean-up techniques. The data analysis algorithm needs about ten points ($\sim$ three

minutes) to establish that resistance has changed significantly. Based on the data rate and needs of the data analysis algorithm, training sets are established using vapor deliveries, or events, of 30-45 minutes duration.

The data analysis algorithm is a Levenberg-Marquart non-linear least squares fitting approach to deconvolution of change in resistance across the sensing array into identification and quantification of the analyte causing response in the sensors. The analysis approach has been discussed in detail previously [9].

Training sets were established for the eleven analytes in Table 1. The environmental conditions for the training sets vary only in water content. Because there is temperature control in the sensing chamber in the ENose, the environmental temperature does not influence the temperature at which analytes are detected, identified and quantified. Detection temperature is held at 25-27°C for all training sets. Detection temperature rises above 27°C only when environmental temperature approaches 30°C, the maximum temperature for ENose operation, in which case detection temperature will be 27-28°C. The relative humidity of the environment will be altered if the temperature of the sensing chamber is different from the temperature of the environment, so for training sets, the humidity is regulated as ppm water. Training sets were made in a background of filtered house air with water concentrations of 5000, 10,000, 15,000 and 20,000 ppm. These concentrations correspond roughly to 20%, 40%, 60% and 80% relative humidity at 21°C, and cover the specified range of humidities for the specified range of temperatures.

Initial training sets where pressure was varied showed that the sensor resistance changes with respect to the presence of analyte were not dependent on environmental pressure, so a complete set of varied pressure training sets was not made.

In designing training sets, the range of analyte concentration to which sensors are exposed is set at 1/3 to 3 times the target concentration. This range is divided into 10-12 concentrations, and the sensor array exposed to those concentrations at each water content. A total of 1599 different analyte exposures were made to establish the training sets; 325 for Tier 1 compounds and 1274 for Tiers 2 & 3. The exposures were divided approximately equally among four humidity levels, although there was a larger number at the two lowest humidities in both sets, Tier 1 and Tiers 2 & 3. Formaldehyde, the one Tier 3 compound, had the fewest exposures, as it was a goal rather than a requirement in this program.

Training sets give insight into the conditions under which the ENose operates best, which conditions cause difficulties in identification and quantification, and allow calculation of performance as accuracy of identification and quantification, number of false negatives and number of false positives using a large number of trials.

Training sets can be used to judge the accuracy of the identification and quantification algorithm even though they are used to establish the coefficients. Accuracy of the algorithm has been computed using half the data to establish the algorithm and coefficients and the other half to test the application, and using all the data for both functions. The statistical difference in results is insignificant. In the success rates for identification and quantification shown below, all the data are used for both functions.

SUCCESS RATES

Tables 2 and 3 summarize the identification and quantification accuracy results based on training sets. In these data, success in detection signifies that the analyte was detected, identified correctly, and quantified within +/- 50% of the measured delivered concentration of analyte. An "event" is defined as a change in environment caused by the presence of a targeted species. A false positive is detection of an "event," either where there was no event, or mis-identification of an event (e.g. identification of toluene as methanol.) A false negative is failure to identify that an event has happened, without respect to identification or quantification.

As can be seen from both Tables 2 and 3, accuracy in identification of analytes is best at nominal humidity conditions, approximately 10,000 ppm water (30-40% RH). The overall success rate for identification and quantification is better when the water content of the air is not at its highest; for Tier 1 species, the overall success rate at nominal temperature and humidity is 93%, and for Tier 2 the overall success rate at nominal conditions is 85%.

At conditions of 50-60% relative humidity with environmental temperature above 21-22°C, the increased water absorbed by polymer based sensors lowers the sensor responses to other vapors. In addition, high water content in polymer based sensors can result in dissolution of some Tier 2 compounds, particularly oxygen-containing compounds, which will result in a different type of capture of analyte molecules in the sensing film. At high humidity, overall success rate for Tier 1 species falls to 82% and to 74% for Tier 2 species. Sensors for mercury are inorganic, and so are not significantly affected by humidity; the fall in success with humidity for Tier 1 species is caused by a slight fall in success with ammonia and a significant fall in success for SO₂. With Tier 1 species, lower, but not zero, humidity tends to be better for sensing, especially with SO₂, which reacts with water to form sulfuric acid. Sensor response to ammonia falls off with humidity as it does for the organic species in Tier 2; it is the same polymer sensors which are used to detect and quantify organic compounds that are used in sensing ammonia.