Detection of Hydrazine and Monomethyl Hydrazine Using Electronic Noses

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Abstract: Two electronic noses, the Cyranose™ electronic nose and the electronic nose developed at the Jet Propulsion Laboratory (JPL Enose), have been tested to determine their utility for detecting hydrazine and monomethyl hydrazine (MMH). The devices were exposed to concentrations of hydrazine from 0.5 to 52 ppm (parts per million), and 14 ppm and 1 ppm MMH. The Cyranose sensors respond to hydrazine at 52 ppm and 18 ppm; the JPL ENose sensors respond to hydrazine at 3 ppm. The response of the Cyranose to 1.1 ppm hydrazine was not measurable; the response of the JPL ENose sensors to 0.5 ppm was evident but was obscured by a humidity change. The Cyranose sensors responded to 14 ppm and 1.1 ppm MMH; the JPL ENose was not tested for response to MMH.

Introduction: Both the electronic nose developed at the Jet Propulsion Laboratory (JPL Enose) and the Cyranose™ electronic noses have been developed around an array of sensors made of polymer-carbon composite films. Response of each sensor to change in the composition of the gaseous environment is recorded as a change in DC resistance; responses are used to detect and identify a variety of chemical vapors or classes of vapors by creating a fingerprint of each vapor [1]. We are assessing and evaluating the reliability of several commercial-off-the-shelf (COTS) electronic noses as well as the JPL ENose and their respective advanced electronic packages in various environments. The goal of this work is to determine whether these technologies are candidates for use in future NASA projects and missions and to ensure the safety of personnel aboard the International Space Station (ISS).

Air contaminant monitoring in a closed environment, for example, the Space Shuttle, ISS and future manned flight projects, is essential to the safety and health of astronauts. Air quality in the shuttle is now determined by collecting samples during flight and analyzing them after landing using laboratory analytical instruments and by crewmember observation. An inexpensive, lightweight, low-power, device capable of identifying contaminants at levels below their Spacecraft Maximum Allowable Concentrations (SMACs) in real time would greatly contribute to NASA's projects by providing real time monitoring for changes in the composition of the air, accompanied by identification and quantification of contaminants with minimal crew interaction.

Devices such as electronic noses can be used to monitor air quality in the cabin of the space shuttle as a part of the Integrated Vehicle Health Management (IVHM) project and other related NASA projects. An experiment using the JPL ENose was conducted on STS-95 in 1998; its response was found to be micro gravity insensitive and events detected during the experiment could be separated and deconvoluted [2]. This report focuses on response of the sensors in the JPL ENose to hydrazine and in the Cyranose and to hydrazine and monomethyl hydrazine.

Hydrazine is a colorless, corrosive and highly toxic compound used in aerospace propulsion and power systems and currently used in the Space Shuttle system as a fuel for the auxiliary power units. Propellant plumes surrounding the orbiting Space Shuttle may include hydrazine and other toxic compounds, and such compounds may be brought into the human habitat of spacecraft by condensing in or on materials, which are brought in to the spacecraft. A monitor, which is capable of detecting and quantifying hydrazine would be useful both in the airlock and in the crew habitat of a spacecraft, as part of the system to ensure crew health. Electronic noses are being evaluated for their capability to detect hydrazine and monomethyl hydrazine against the humidified air background of the human habitat in spacecraft.

The concentrations of hydrazine compounds, which must be detected, are shown in Table 1. The testing program described here has as its goal identification of devices, which are capable of detecting toxic compounds at 50% of the allowed exposure level. Spacecraft Maximum Allowable Concentration (SMACs) is levels set by NASA for crew exposure. They are shown in Table 1 as parts-per-million (ppm) in a background of 1 atm air. OSHA and Threshold Limit Values are shown for comparison.

Table 1: Airborne exposure limit

	SMAC [5]	**SMAC** [5]	**TLV** [3]	**OSHA** [4]
Hydrazine	4 ppm/1 hr	0.04 ppm/7 days	0.01 ppm (10 ppb)	1 ppm.
Monomethyl hydrazine	0.002 ppm/1 hr	0.002 ppm/7 days	0.01 ppm (10 ppb)	--

Electronic Noses: In this test apparatus, humidity of the background air is controlled; temperature is not controlled. Figure 1a shows a photo of the Cyranose, and the sensor array employed in the Cyranose, and figure 1b shows the JPL ENose and its sensor array.

<u>Testing the Cyranose™</u>

The Cyranose was turned on with a baseline purge (zero air, or clean air), which is represented as the unchanging response in the initial part of Figure 2. The baseline showed no significant change in sensor resistance for all 32 sensors if the environment did not change. Hydrazine was injected into the inlet of the Cyranose. Three concentrations of hydrazine (52, 18, 1.1 ppm) were used in this test. Response of the Cyranose was recorded for these concentrations of hydrazine as a function of time in seconds. Similar tests were performed for 14 ppm and 1 ppm of monomethyl hydrazine using a test set-up similar approach.

<u>Testing the JPL ENose</u>

The JPL ENose was exposed to concentrations of hydrazine ranging from 17 to 0.5 ppm using a test setup similar to the same approach used above. Tests were not done with monomethyl hydrazine. Response of the sensors was recorded at intervals of 2 seconds.

Results And Discussion

Cyranose

At the onset of injecting hydrazine (52 ppm) DC resistance in several of the sensors rose markedly with respect to the baseline resistance. There was moderate response for 18 ppm hydrazine and no measurable response to 1.1 ppm of hydrazine. Cyranose sensors responded to hydrazine at concentrations of 18 ppm and higher.

Figure 3 shows the response of the Cyranose sensors to various concentrations of monomethyl hydrazine. There was significant response for 14 ppm monomethyl hydrazine and a moderate response for 1 ppm. Cyranose sensors respond to MMH at concentrations greater than 1 ppm.

The responses recorded for each sensor to the injection of these concentrations of hydrazine and monomethyl hydrazine are unprocessed data; this experiment has shown that several of the sensors respond to the presence of these compounds. The device as currently available is not calibrated or trained to identify to these compounds, but there is no reason to expect that calibration to these compounds cannot be done. The compound recognition software used in the Cyranose, as currently available, does not quantify the compounds it detects.

JPL Enose

When the JPL ENose was exposed to hydrazine, the DC resistance of several of the sensors rose significantly. The local ambient pressure and the gas flow rate changed significantly when the valve to the hydrazine reservoir was opened to add hydrazine to the airflow; these changes could account for the change in the sensor resistances. Tests of response to changes in pressure and flow rate in the absence of hydrazine are shown in figure 4a. Figure 4b shows the response of 6 JPL ENose sensors in the presence of hydrazine; if flow rate and in the absence of hydrazine the sensor resistance returns to baseline. In the presence of hydrazine, the sensor resistance remains high until the hydrazine flow is turned off; thus it can be concluded that the persistent change in sensor resistance upon exposure to hydrazine was caused by response to hydrazine. The substantially different size and shape of the response curves aid in identification of analytes.

As can be seen in Figure 4, sensors in the JPL ENose respond to the presence of 3 ppm hydrazine. The sensors also responded to the presence of 0.5 ppm hydrazine, but the response is small and close to the size of the noise and was obscured by a large response to a sudden change in humidity. Using baseline correcting procedures such as low frequency filtering and noise reduction techniques such as high frequency filtering, and correcting for flow change effects, it has been possible to determine a fingerprint for the JPL ENose response to hydrazine at 0.5 ppm, as shown in figure 5. Also shown in figure 5 are flow corrected fingerprints for 3 and 5 ppm hydrazine.

Using the software designed for the JPL ENose for compound identification and quantification [6], this device can be trained to identify and quantify the presence of hydrazine in air at concentrations at least as small as 0.5 ppm.

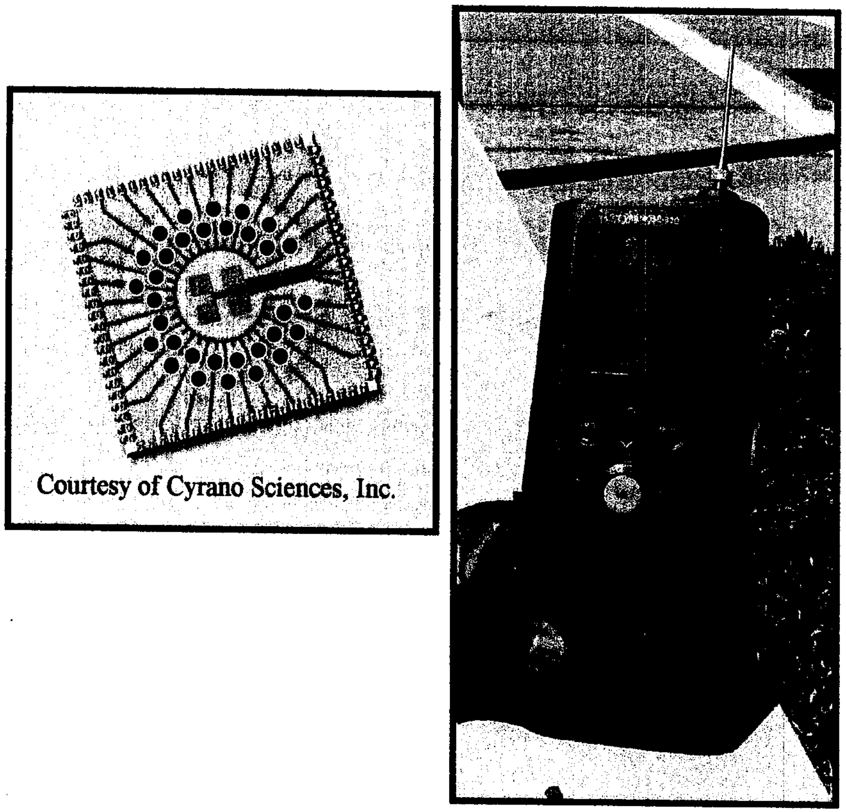


Figure 1a:Cyranose 320 hand-held device and the 32-sensor array used in the device

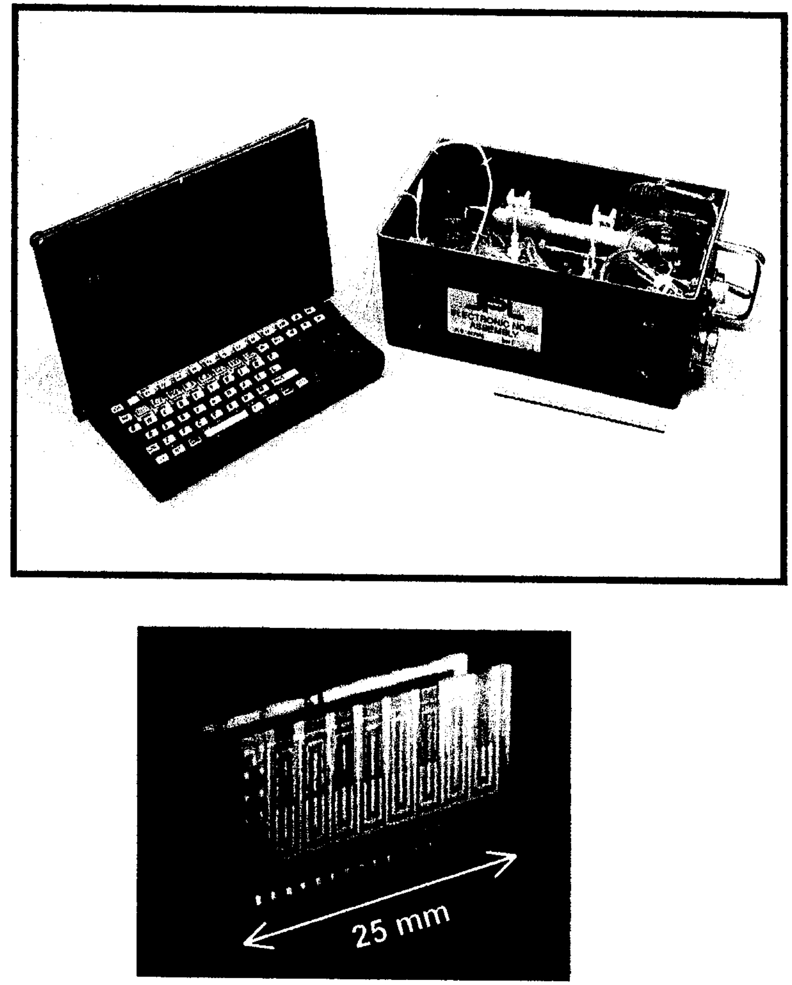


Figure 1b: JPL ENose used in Space Shuttle experiment, and a sensor substrate. Four substrates are used in the device to make a 32-sensor array.

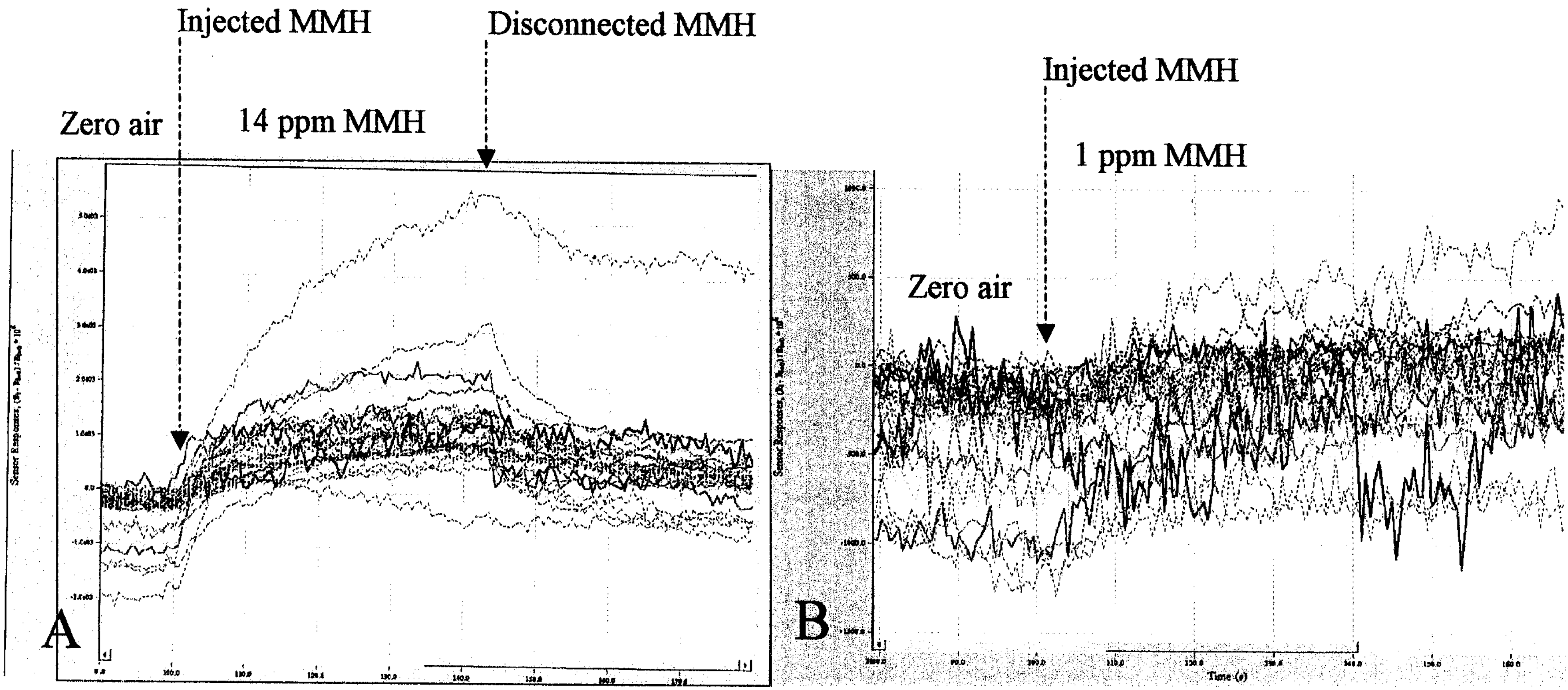


Figure 3: Response of the Cyranose (consists of 32 conducting polymer sensors) to 14 ppm and 1 ppm, of Monomethylhydrazine (MMH). Each curve is a response from one of the sensors.

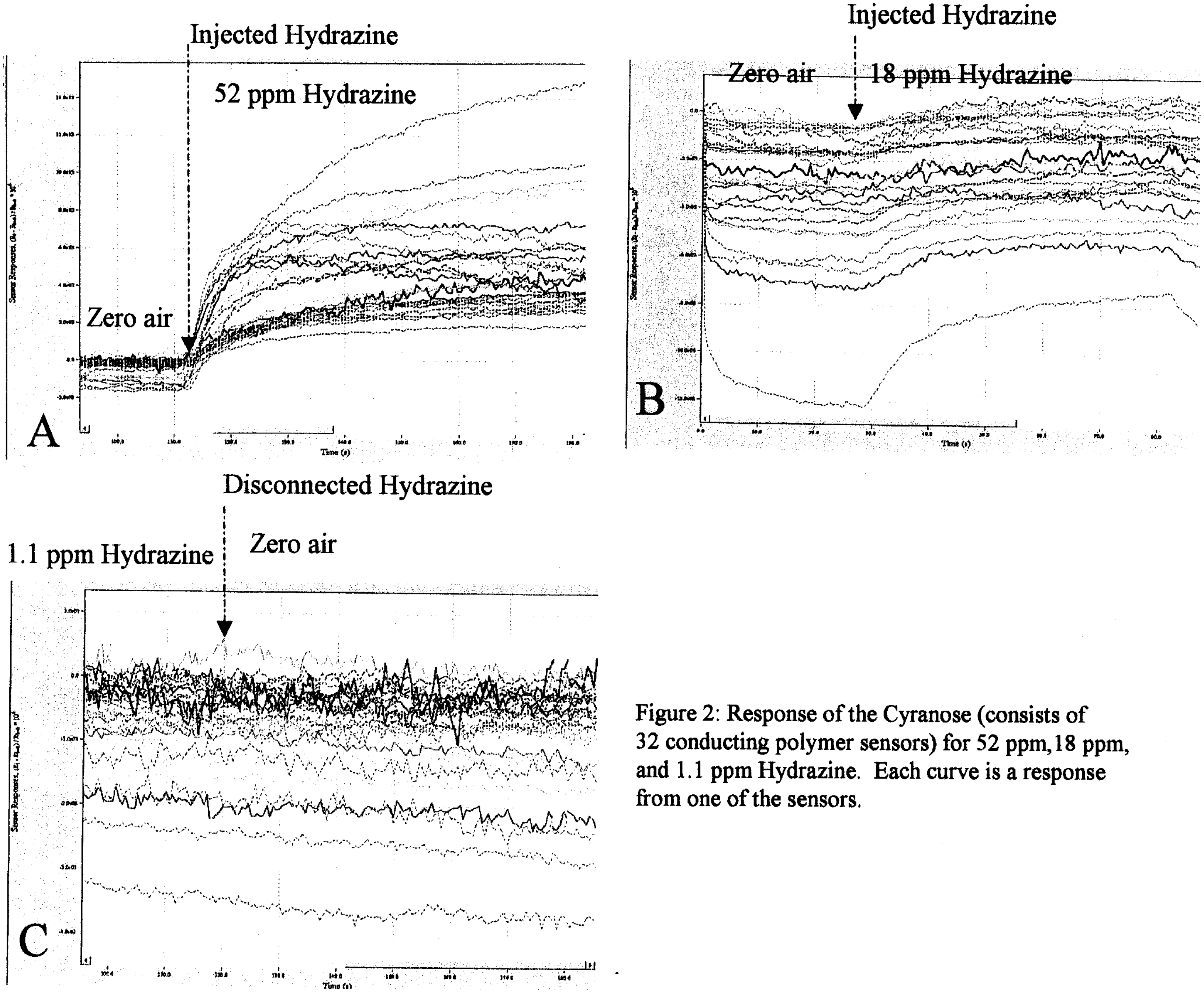


Figure 2: Response of the Cyranose (consists of 32 conducting polymer sensors) for 52 ppm, 18 ppm, and 1.1 ppm Hydrazine. Each curve is a response from one of the sensors.

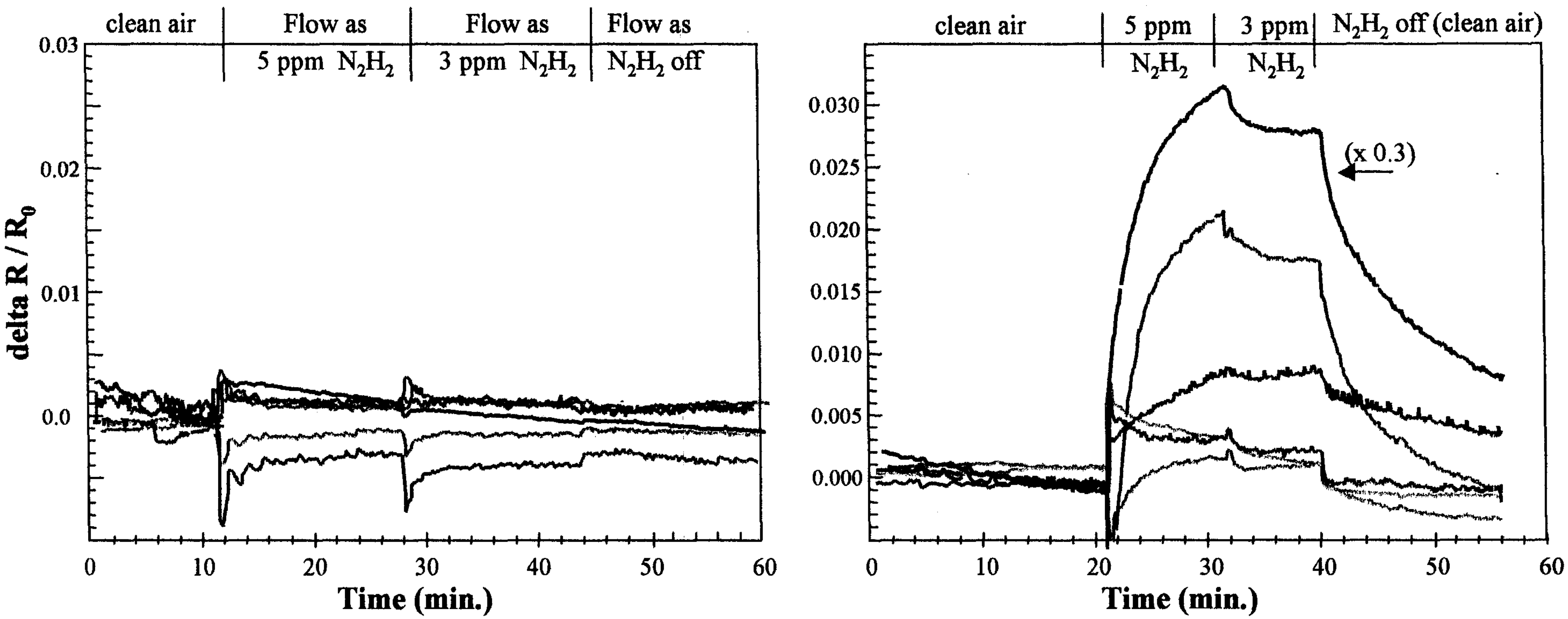
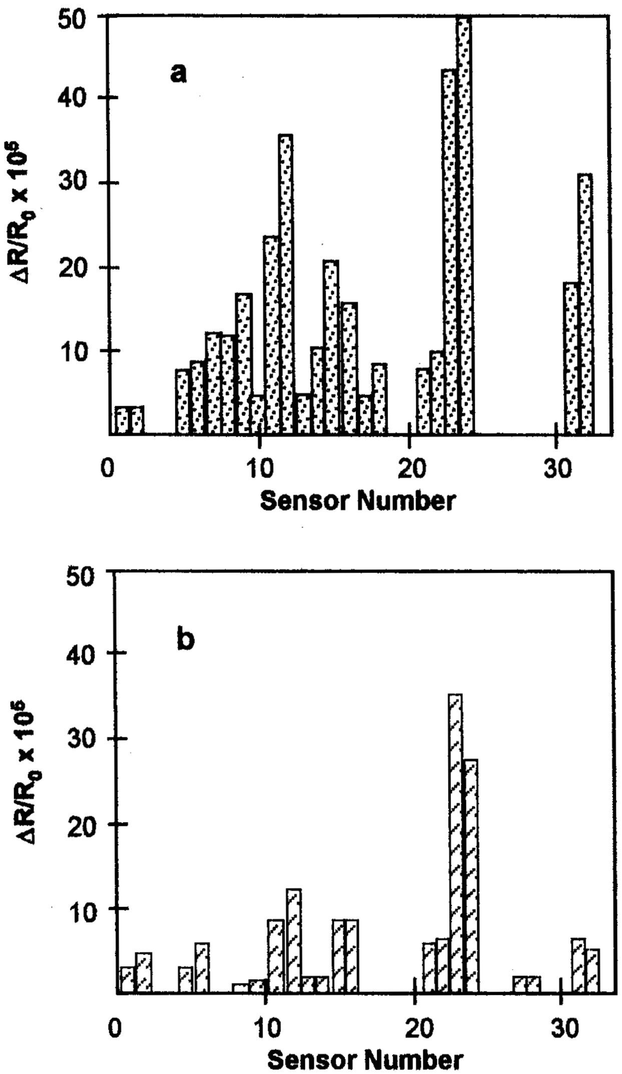


Figure 4: (a) Response of 6 sensors from the JPL ENose to change in flow rate and pressure in clean air (without hydrazine)
(b) Response of 6 sensors to 5 and 3 ppm hydrazine. Large rises or dips in sensor response when hydrazine concentration is changed are caused by changes in the air flow rate and pressure.



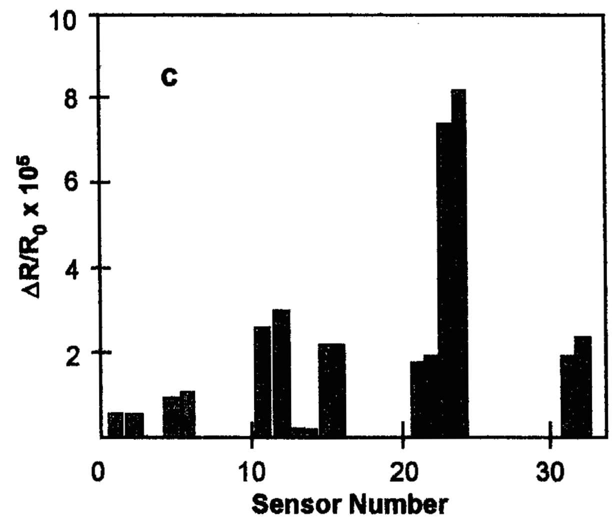


Figure 5: Fingerprint pattern of response of the 32 sensor array in the JPL ENose to hydrazine, after baseline correction and correction for response to flow rate changes. (a) 5 ppm hydrazine; (b) 3 ppm hydrazine; (c) 0.5 ppm hydrazine.