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# A Portable Electronic Nose For Hydrazine and Monomethyl Hydrazine Detection

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## Abstract

The Space Program and military use large quantities Hydrazine (Hz) and monomethyl hydrazine (MMH) as rocket propellant. These substances are very toxic and are suspected human carcinogens. The American Conference of Governmental Industrial Hygienist set the threshold limit value to be 10 parts per billion (ppb). Current off-the-shelf portable instruments require 10 to 20 minutes of exposure to detect 10 ppb concentration. This shortcoming is not acceptable for many operations. A new prototype instrument using a gas sensor array and pattern recognition software technology (i.e., an electronic nose) has demonstrated the ability to identify either Hz or MMH and quantify their concentrations at 10 parts per billion in 90 seconds. This paper describes the design of the portable electronic nose (e-nose) instrument, test equipment setup, test protocol, pattern recognition algorithm, concentration estimation method, and laboratory test results.

Keywords: Electronic nose, space program, hypergolic fuel, pattern recognition, classification

## Introduction

An electronic nose<sup>[1]</sup> (e-nose) consists of an array of non-specific vapor sensors. In general, the sensor array is designed such that each individual sensor responds to a broad range of chemicals, but with a unique sensitivity relative to the other sensors. Different sensor types also have different analytic performances – for example, some sensors are more sensitive to specific vapors, while others are less prone to drift due to changes in ambient conditions (e.g., temperature, RH, pressure). Chemical identification is achieved by comparing the sensor response pattern of an unknown vapor to previously established patterns of known vapors. Many commercial e-noses can be trained to provide a level of quality for flavors and food products, diagnosis of certain diseases, detection of chemical spills, and other applications; however, none can quantify the concentrations. NASA at Kennedy Space Center (KSC) has assessed the sensitivity of several commercially available and developing e-noses. One very sensitive e-nose has been further developed as a hand-held instrument that is not only capable of identifying Hz or MMH vapors but also quantifying their concentrations at the 10 ppb level in 90 seconds. The hand-held instrument uses rechargeable battery that can last for 8 hours of continuous operation. It also uses a Palm Pilot instead of a laptop computer for reducing size and faster initial setup. The prototype unit has completed the lab test and is being field tested as a personnel safety monitor.

## Approach

A literature and market search for available e-noses was performed to identify instruments suitable for these applications. A number of compact commercial instruments were available in a moderate price range. In addition, several instruments that were not yet commercially available but were in an advanced

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stage of development were considered. A short series of tests were conducted to determine whether or not a specific instrument could meet the required sensitivities for HZ/MMH detection. One instrument that performed most favorably was tested further and pattern recognition and concentration prediction software were developed for it to achieve near 100% correctness in identification and 95% accuracy in concentration prediction.

## Experimental

### Vapor Generation—Calibrated Standards

Test vapors were generated using permeation devices (PD) and ovens (Kintek Model 360), as shown in Figure 1. The PDs were maintained at a constant temperature and were purged continuously with dry nitrogen at 100 cc/min. This gas stream was blended with 1.9L/min of dry clean air to generate 2.0 L/min of the vapor. Flows were verified prior to tests using flow meters (SKC Accuflow). In the "Zero" mode, the vapor stream through the PDs was not mixed with the 1.9L/min air stream, but rather was vented through a separate pneumatic line. This provided a source of non-contaminated air. Activation of a solenoid valve internal to the permeation oven allowed the purged vapor stream to mix with the clean air, thus generating the test vapors.

HZ and MMH vapor concentrations were verified using an impinger filled with 0.1M H<sub>2</sub>SO<sub>4</sub> to scrub a known volume of vapor. The HZ or MMH concentration in the resulting solution was determined by coulometric titration<sup>[2,3]</sup>.

Vapors from the permeation ovens either were used directly or were precisely blended with air from a temperature (T), humidity (RH) and flow rate (F) controller (Miller-Nelson Model HCS-40). Dilution factors up to 25 were conveniently obtained. Three ranges of RH values were typically used in testing—low (50%), medium (70%), and high (85%).

Earlier work has shown that stainless steel and other materials are incompatible with HZ or MMH vapors, especially at low concentrations<sup>[4]</sup>. The use of stainless steel tubing and fittings was kept to a minimum. All pneumatic lines were either Teflon or Bev-a-Line IV<sup>®</sup> tubing, which were shown to have minimal effect on these vapors, even in the low-ppb range.

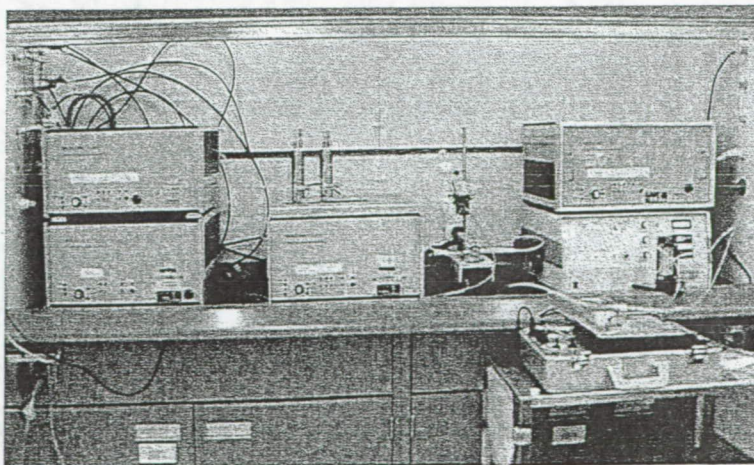


Figure 1 Basic Test Setup

## E-nose Instrumentation

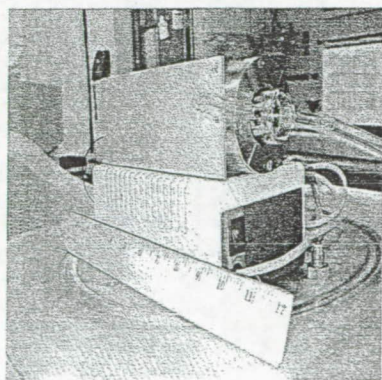
The various e-noses that were included in this study are provided in Table 1. MOS stands for metal-oxide semiconductor and PC stands for polymer composite. Either commercially available e-noses or pre-production models were used, and had to be lightweight and portable. The extent of evaluation was based first upon the ability to detect HZ and MMH vapors at the 10 ppb level. Instruments with sufficient sensitivity to vapors of interest were then subjected to more rigorous testing. This testing encompassed an assessment of the analytic performance of the instrument, an evaluation of the ability of a "trained" instrument to identify test vapors using the vendor supplied operating system, and the in-house development of identification algorithms to assess the information content of the raw data.

Table 1: E-nose instrumentation used in this study

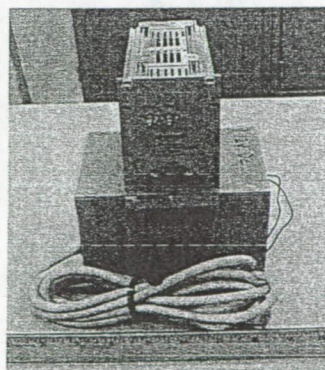
Instrument	Manufacturer	Array
i-Pen2	Air Sense	10 MOS
SamDetect	Daimler-Benz Aerospace	5 MOS
Cyranose	Cyranose Sciences	32 PC
KAMINA	Karlsruhe Research Center	38 MOS

## Hypergolic Fuels Tests

*Sensitivity Screening:* In the case of HZ and MMH, the ACGIH TLV standard of 10 ppb was selected. KSC has adopted the ACGIH standard for its operations. Several of the technologies showed reasonable sensitivity to ppm levels of HZ or MMH. Of the instruments tested, only the KAMINA and i-Pen (Figure 2) was able to respond to 10 ppb levels of HZ and MMH with a signal to noise ratio greater than 3. The responses of the KAMINA and i-Pen to 10 ppb HZ and 10 ppb MMH are displayed in Figures 3 and 4 respectively.



KAMINA



i- Pen

Figure 2 Vendor units for screening test.

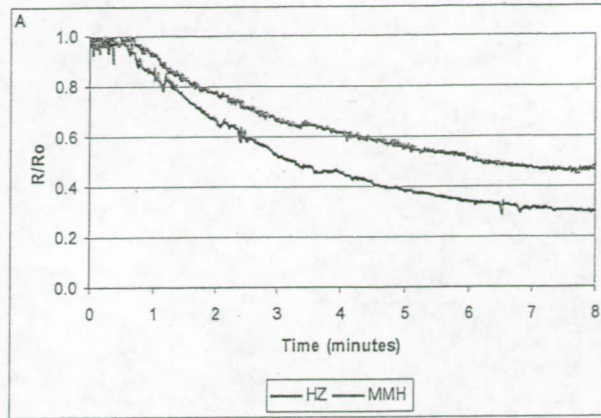


Figure 3: Response of the KAMINA to 10 ppb of HZ and MMH. The average of the 38 sensors are plotted as R/R<sub>0</sub> where R is the sensor response at any point in time and R<sub>0</sub> is the response of the sensor in clean air

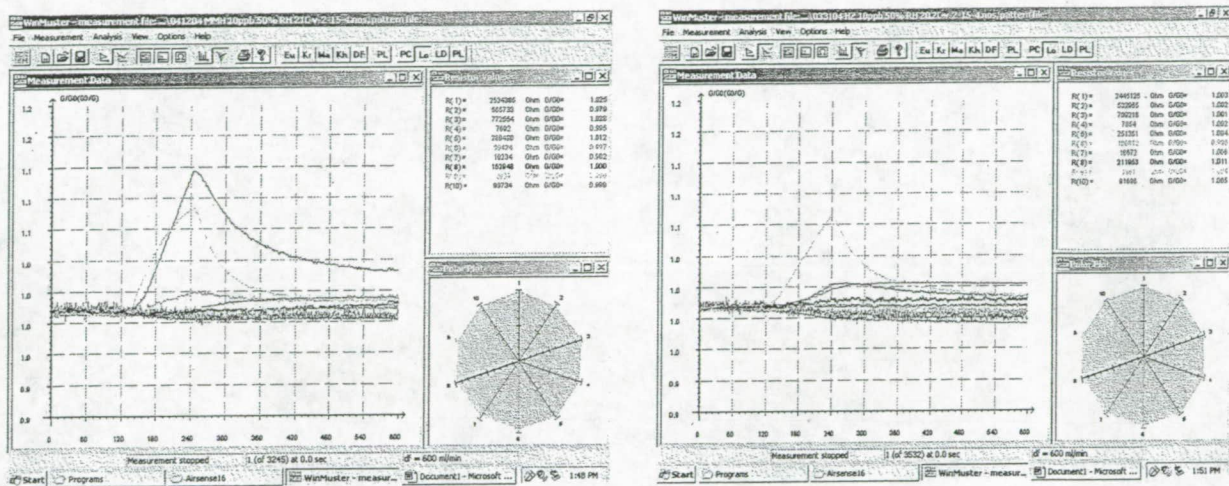


Figure 4: Response of the i-Pen to 10 ppb of MMH (left) and HZ (right). The 10-sensor response plot, the sensor values, and radial plot are shown.

### Prototype Design and Fabrication

Although both KAMINA and i-Pen met the 10 ppb detection limit requirement, i-Pen was selected for further development. This was because the signal from the i-Pen is less noisy and the vendor was willing to provide the communications protocols for the development of an e-nose interface with the Palm Pilot. The Lithium-Ion battery was selected after much research to provide at least 8 hours of continuous operation for the lowest weight. The filter consists of glass wool soaked in a 50% solution of sulphuric acid and water, suctioned to dampness, and dried at 60 degrees C. Figure 5 shows a schematic diagram of the prototype unit, and Figure 6 shows some photos of the unit.

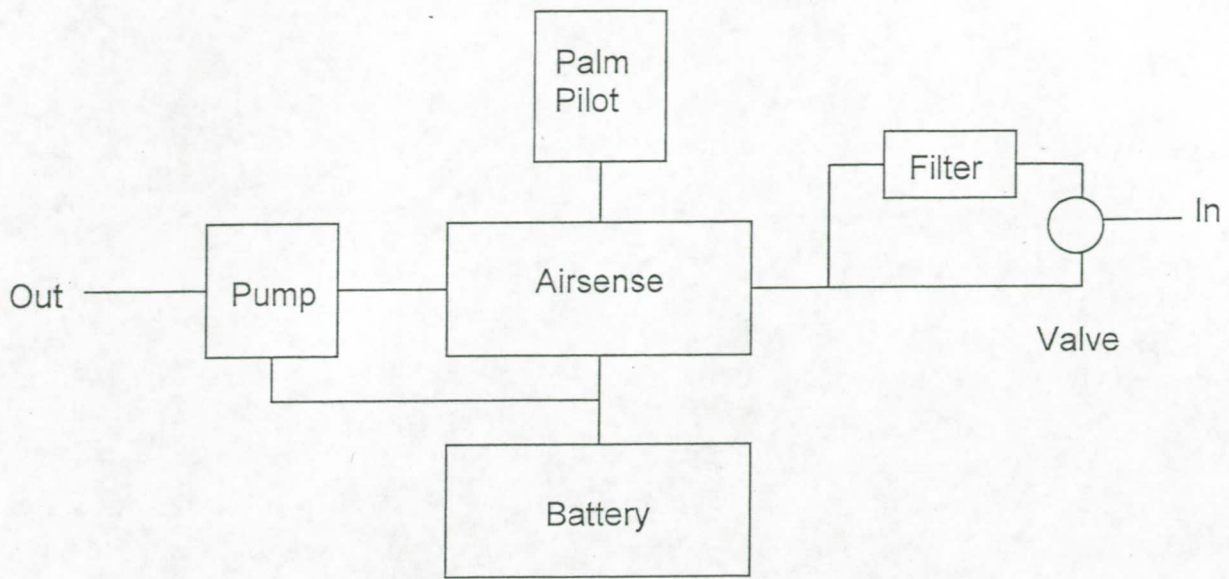


Figure 5 Prototype schematic

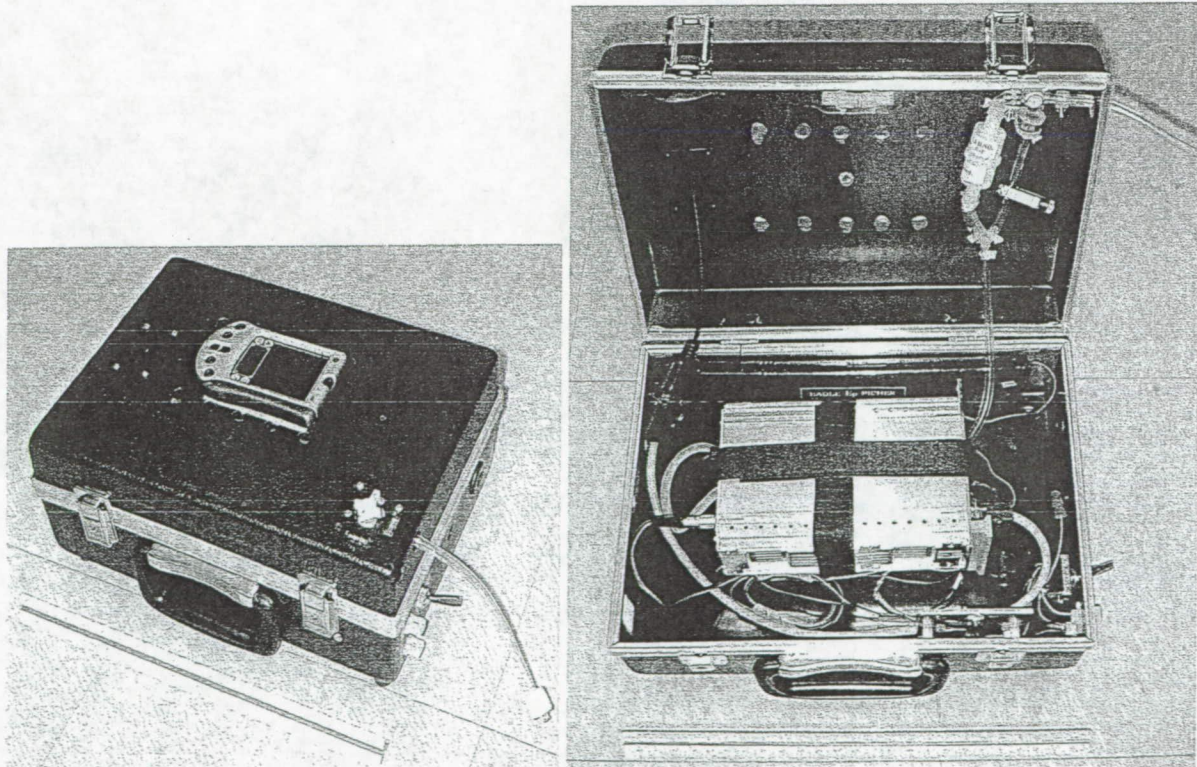


Figure 6 Prototype Unit.

## Training and Validation Testing

The i-Pen was trained using four concentrations of Hz and MMH vapors at three RHs. The nominal concentrations were 10, 50, 100, and 500 ppb. The RH values were 50%, 70%, and 85%. A lab computer was used to acquire the training data.

From the training data, a model was created using statistical pattern recognition algorithms developed in-house to ensure near 100% correctness in identifying the sample as Hz or MMH. Then algorithms were applied to quantify the concentration of the identified vapor. See the next section for details on the algorithms.

Validation data using Hz and MMH vapors at various concentrations and %RH were then gathered using the Palm Pilot, as it would be used in the field.

## Vapor Identification and Quantification Algorithms

Code was written for the Palm Pilot to implement a standard quadratic classifier<sup>[5]</sup>. Given class  $i$  with mean  $\mu_i$  and covariance matrix  $\Sigma_i$ , an unknown sample  $x$  is assigned to that class with the smallest value of

$$(x-\mu_i)^T \Sigma_i (x-\mu_i) + \ln(|\Sigma_i|)$$

After a class has been selected, the square of the Mahalanobis distance<sup>[5]</sup>  $(x-\mu_i)^T \Sigma_i (x-\mu_i)$  from the example to the estimated class is calculated, and compared to a predetermined threshold. If the example is too far from the class, the example is rejected as an unknown vapor.

To estimate the concentration, the model data was plotted to show sensor response as a function of concentration, as shown in Figure 7. This data was then fitted to the formula  $A(1 - e^{-Bx})$ , also shown in Figure 7, to find the least-squares values for the parameters A and B. This formula was determined to be appropriate because the sensor response should go to zero as the concentration goes to zero, and the sensor response should saturate at high enough concentrations. Other formulas with similar qualities were tested, but this one performed the best. When presented with an unknown sample, the inverse of this formula was then used to convert the sensor response for each of the ten sensors into a concentration estimation. Many different techniques were explored to convert the ten concentration estimates into a single value, including taking the mean, the mean weighted by the quality of the curve fit, and multiple linear regression, but it turned out that the estimate of one particular sensor was consistently the best.

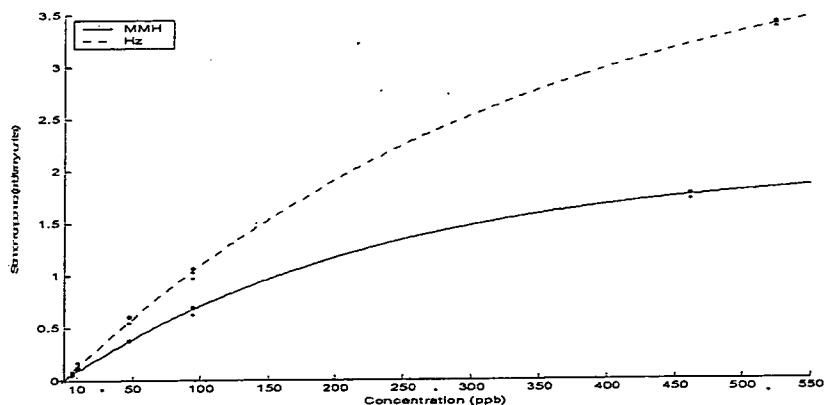


Figure 7 Concentration curve fitting (one sensor)

Results

The following trials were gathered using the prototype unit exactly as it would be used in the field. All tests were done at 70% RH. Note that 250 ppb vapors were not part of the training data.

Vapor	Std. Conc. (ppb)	Identified as	Conc. Reading (ppb)	%error
Hz	7.2	Hz	7	-2.7
Hz	7.2	Hz	8	11
Hz	7.2	MMH	10	N/A
Hz	7.2	Hz	7	-2.7
Hz	7.2	MMH	9	N/A
Hz	7.2	MMH	8	N/A
Hz	95	Hz	95	0
Hz	95	Hz	101	6.3
Hz	95	Hz	98	3.2
Hz	95	Hz	102	7.4
Hz	95	Hz	102	7.4
Hz	95	Hz	103	8.4
Hz	250	Hz	249	-0.4
Hz	250	Hz	251	0.4
Hz	250	Hz	251	0.4
Hz	250	Hz	245	-2.0
Hz	250	Hz	246	-1.6
Hz	250	Hz	243	-2.8
Hz	524	Hz	532	1.5
Hz	524	Hz	528	0.8
Hz	524	Hz	510	-2.7
Hz	524	Hz	514	-1.9
Hz	524	Hz	488	-6.9
Hz	524	Hz	507	-3.2
MMH	11	MMH	9	-18
MMH	11	MMH	10	-9
MMH	11	MMH	8	-27
MMH	11	MMH	7	-36
MMH	11	Hz	4	N/A
MMH	11	MMH	8	-27
MMH	95	MMH	84	-12
MMH	95	MMH	84	-12
MMH	95	MMH	85	-10
MMH	95	MMH	87	-8.4
MMH	95	MMH	85	-10
MMH	95	MMH	88	-7.4
MMH	250	MMH	227	-9.2
MMH	250	MMH	228	-8.8
MMH	250	MMH	229	-8.4
MMH	250	MMH	225	-10
MMH	250	MMH	226	-9.6



MMH	250	MMH	230	-8
MMH	461	MMH	465	0.9
MMH	461	MMH	452	-1.9
MMH	461	MMH	466	1.1
MMH	461	MMH	472	2.4
MMH	461	MMH	456	-1.1
MMH	461	MMH	464	0.6

Table 2 – Validation data results

Table 3 shows the summary statistics for each concentration. The overall classification success rate is 92%, and the mean  $|\%error|$  is 7% (5% excluding MMH at 11 ppb). Note that errors of just a few ppb have large  $\%errors$  at 11 ppb; the average error in estimation at 11 ppb for MMH is only 2.6 ppb.

Vapor	Std. Conc. (ppb)	% correctly identified	Mean $ \%error $
Hz	7.2	50	5.5
Hz	95	100	5.5
Hz	250	100	1.3
Hz	524	100	2.8
MMH	11	83	23
MMH	95	100	10
MMH	250	100	9
MMH	461	100	1.3

Table 3 – Summary Statistics

## Summary

A prototype portable e-nose capable of detecting 10 ppm MMH and Hz has been developed at KSC NASA, capable of detecting, identifying, and quantifying vapors in only 90 seconds, with a 2 to 8 minute recovery time (depending on the concentration of the exposure). This unit classifies vapors with better than 90% accuracy, and quantifies the concentration with an average of about 5% error, except at 10 ppb levels, where the error is less than 3 ppb.

## References

- [1] H. Nagle, R. Gutierrez-Osuna, S. Schiffman, "The How and Why of Electronic Noses", IEEE Spectrum, September 1998, pp. 22-34.
- [2] J. Wyatt, S. Rose-Pehrsson, T. Cecil, K. Crossman, N. Mehta, R. Young, "Coulometric Method for the Quantification of Low-Level Concentrations of Hydrazine and Monomethylhydrazine", American Industrial Hygiene Association Journal, June 1993, pp. 285-292
- [3] "Determination of Concentrations of N<sub>2</sub>H<sub>4</sub> or MMH Vapor in Nitrogen or Air by the Columnetric Titration Method", Applied Chemistry Laboratory, Kennedy Space Center, internal document.
- [4] P. Taffe, S. Rose-Pehrsson, J. Wyatt, "Material Compatibility with Threshold Limit Value Levels of Monomethyl Hydrazine", NRL Memorandum Report 6291, October 1988.

[5] R.O. Duda and P.E. Hart, "Pattern Classification and Scene Analysis", John Wiley&Sons, New York, 1973.

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Presented by Barry Meneghelli

## Overview

- Background
- Experimental setup
- E-nose screening
- Algorithms
- Results
- Conclusions

## Need for Hypergol detection

- Hypergolic fuels hydrazine (Hz) and monomethyl hydrazine (MMH) are very toxic, and are suspected carcinogens
- Need to detect 10 ppb levels
- Current technology takes 10-20 minutes to respond to 10 ppb
- Current technology does not confirm that the detected vapor is MMH or Hz
- Need for fast response, specific identification & quantification at very low concentrations

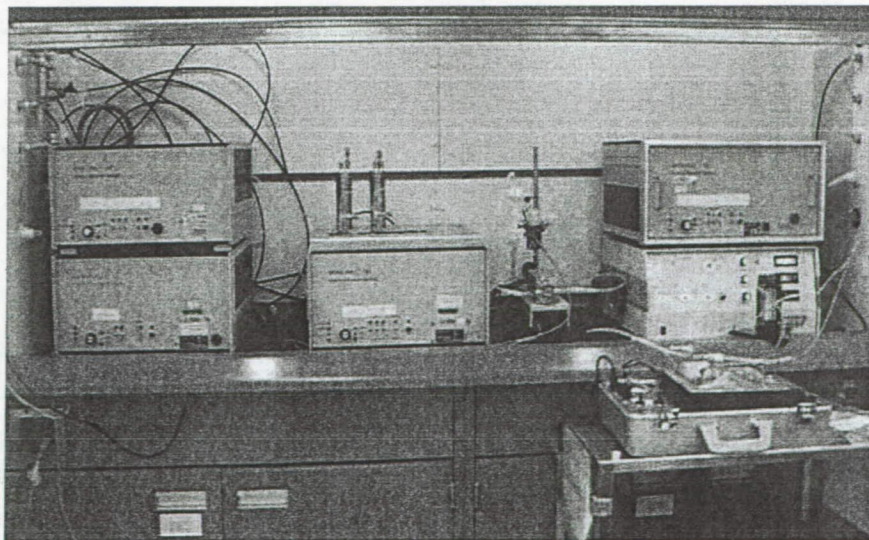
## Electronic nose

- Typically consists of 5-60 non-specific vapor sensors
- Pattern recognition software
- Most applications are qualitative (food quality, medical diagnosis, etc.)
- E-noses not normally used for quantitative analysis (concentration estimation)

## Experimental Setup I

- Kintek model 360 permeation devices provide test vapors
- Miller-Nelson model HCS-40 controller provides dilution air at known temperature, flow rate, and humidity

## Experimental Setup II



## E-noses tested

- Airsense i-Pen2 – 10 MOS sensors
  - SamDetect – 5 MOS sensors
  - Cyranose – 32 PC sensors
  - KAMINA – 38 MOS sensors
- 
- MOS = metal-oxide semiconductor
  - PC = polymer composite

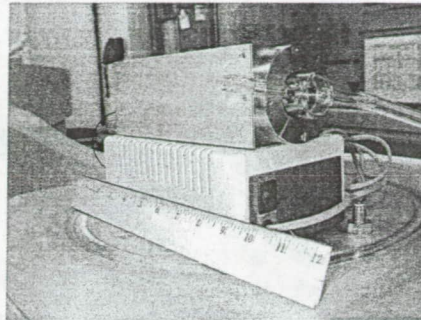
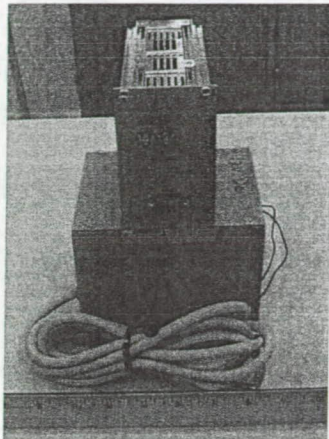
## Initial Screening

- Only Airsense and Kamina were able to detect vapors at 10 ppb with acceptable response times (90 seconds)
- Airsense selected for further development because of S/N ratio, sensor stability, and willingness of vendor to provide communications protocols to e-nose

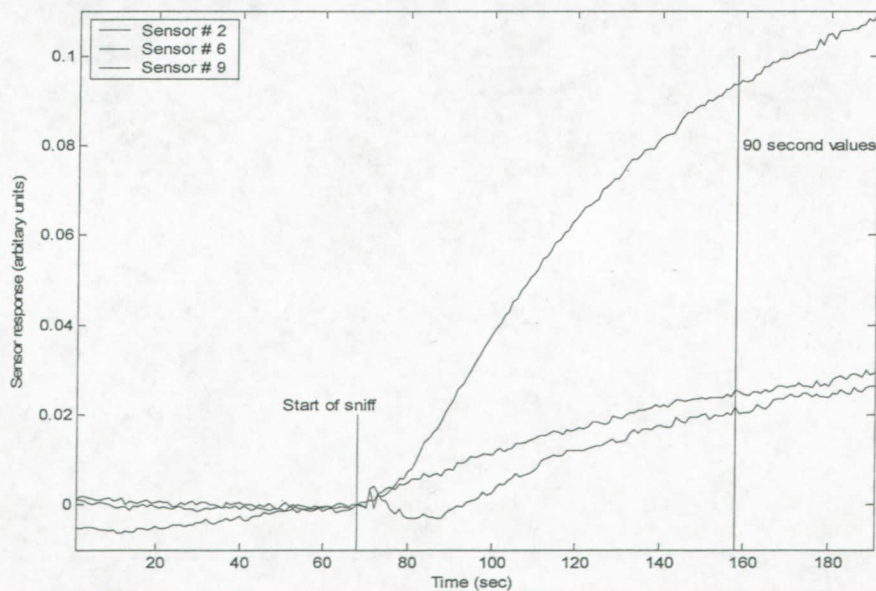
# E-noses tested

Airsense

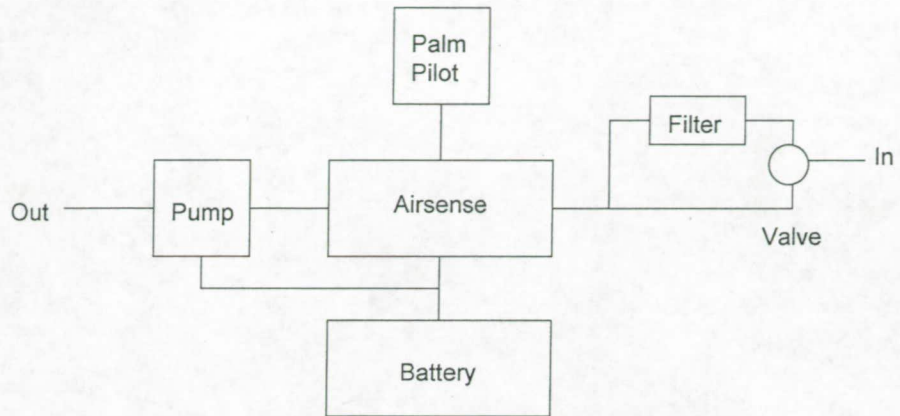
Kamina



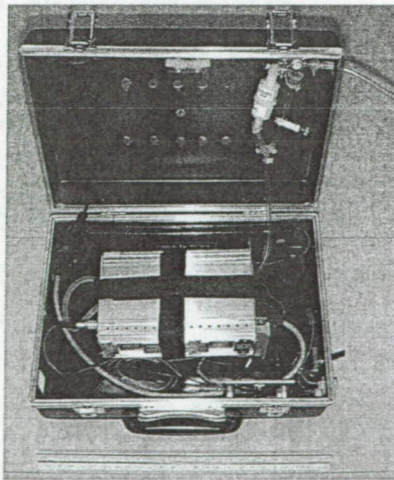
## Airsense 10 ppb Hz response



## Prototype Unit (schematic)



## Prototype Unit





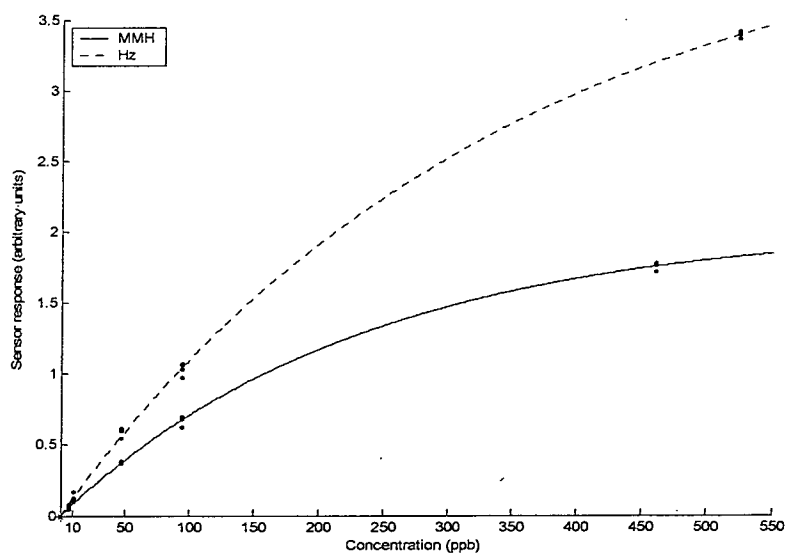
## Classification Algorithm

- Quadratic classifier : given class  $i$  with mean  $\mu_i$  and covariance matrix  $\Sigma_i$ , an unknown sample  $x$  is assigned to the class with the smallest value of

$$(x-\mu_i)^T \Sigma_i^{-1} (x-\mu_i) + \ln(|\Sigma_i|)$$

- Once classified, the example may be rejected as an unknown vapor if it is too far from the assumed class.

## Concentration Estimation I



## Concentration Estimation II

- Data fitted to  $A(1-e^{Bx})$
- Inverse formula converts each sensor response to a concentration estimation
- Combine 10 estimates into one : tried mean, mean weighted by quality of curve fit, multiple linear regression, etc.
- Best results came from using the estimate of one specific sensor

## Training and Validation

- Training data : 10, 50, 100, 500 ppb at 50%, 70%, and 85% relative humidity
- Data acquired by lab computer, processed in Matlab, downloaded to Palm Pilot
- Validation data : 10, 100, 250, 500 ppb at 70% RH
- Gathered by Palm Pilot

## Results

Vapor	Std. Conc. (ppb)	% correctly identified	Mean   %error
Hz	7.2	50	5.5
Hz	95	100	5.5
Hz	250	100	1.3
Hz	524	100	2.8
MMH	11	83	23
MMH	95	100	10
MMH	250	100	9
MMH	461	100	1.3

## Conclusions

- A portable e-nose has been developed at KSC NASA which can detect, identify, and quantify hypergolic fuels
- 10 ppb threshold
- 90 second sample time
- $\geq 90\%$  identification success
- $\leq 5\%$  quantification %error (for  $>10$  ppb)
- 2-8 minute recovery time