Real-Time Air Quality Monitoring in Human Habitat

The JPL Electronic Nose

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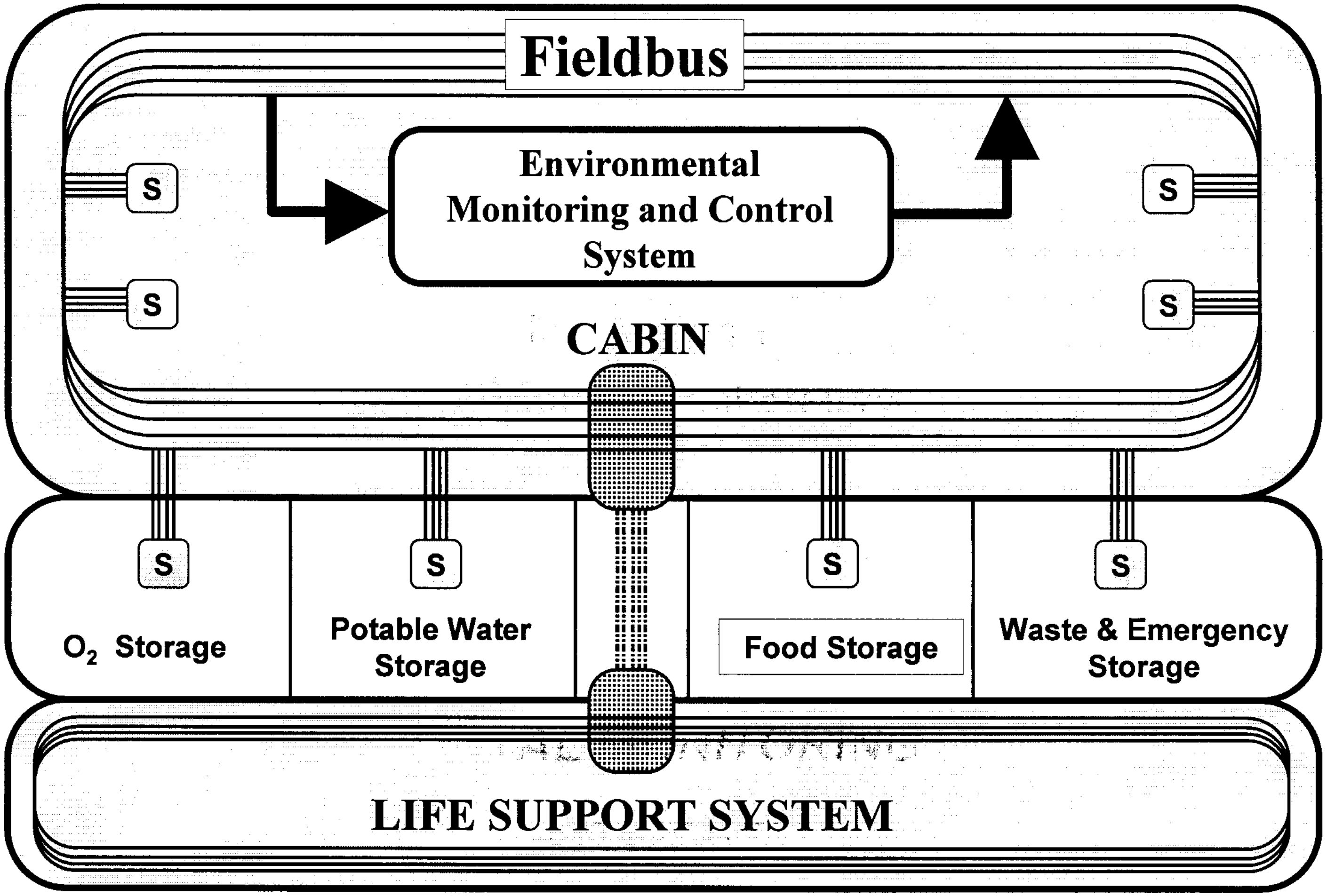

Figure 3 - Contextual Diagram. Fieldbus Sensors have local intelligence.

AEMC *Requirements for Technology Development*, 1998, Section 4

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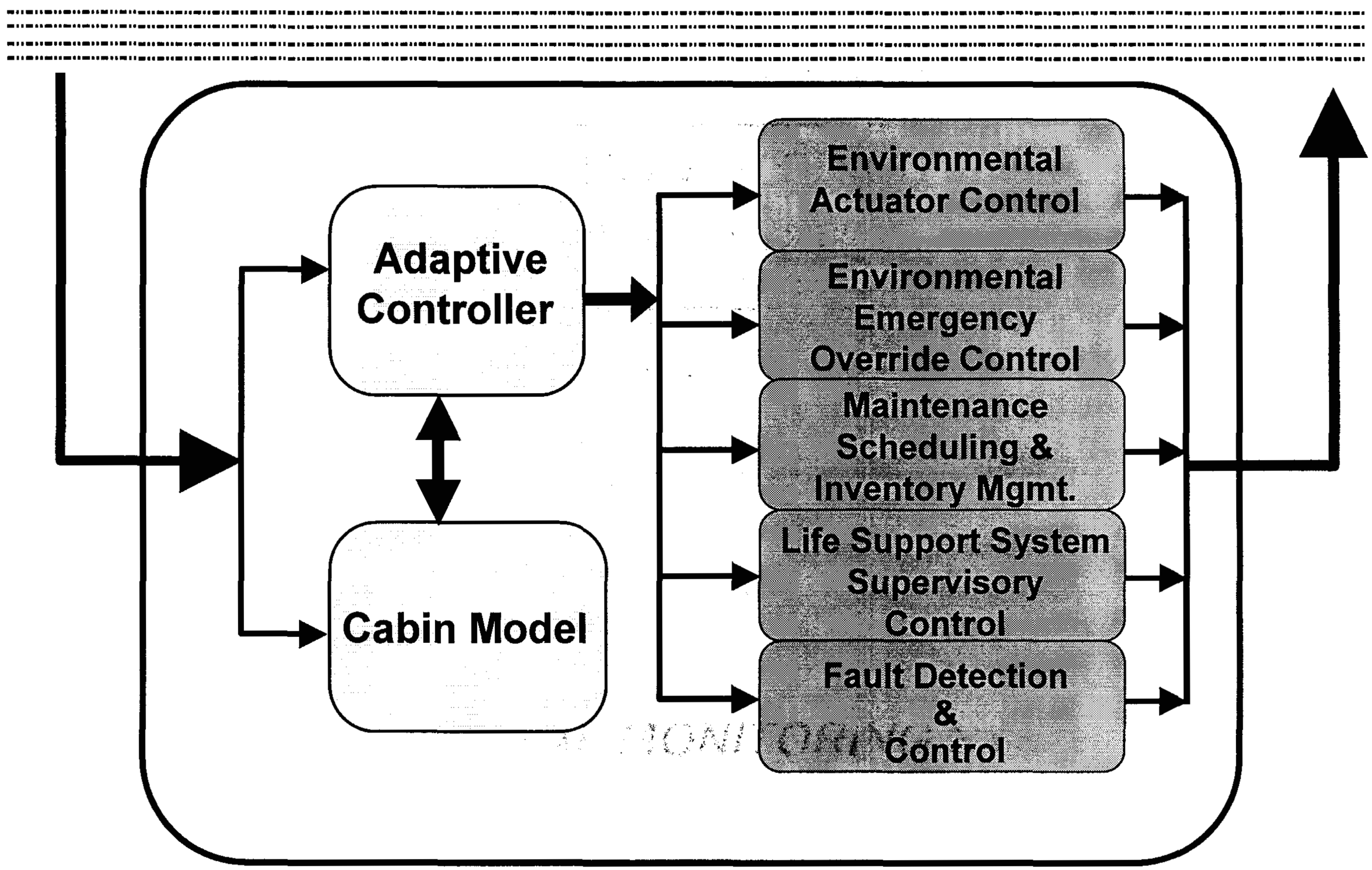

Figure 4 Environmental Monitoring and Control System.

AEMC *Requirements for Technology Development*, 1998, Section 4

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Air Quality Monitoring Requirements for Spacecraft - Chemicals

Monitor cabin environment with time stamped measurements and rates of change

- **Major constituents - "near-continuous" monitoring**
  - N_2 O_2 CO_2 H_2O
  - H_2 CH_4 CO CO_2
- **Trace contaminants - less frequent monitoring required**
  - ~ 40 organic compounds
- **Event Monitoring - rapid response time (~ 15 seconds)**
  - pyrolysis markers - CO HCN HCl
  - marker compounds for electronics overheating
  - monitoring for sudden release from fluid systems, experiments, EVA, waste
  - follow progress of decontamination after an event

based on AEMC *Requirements for Technology Development*, 1998, Section 5

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What Is Rapid Response or "Real-Time Monitoring"?

- air monitored often enough to find health hazards before they can injure crew member

  "near continuous" - every 5/10/15 seconds?

- analysis returned quickly enough to identify health hazards so action can be taken to protect crew health

  15 seconds - 2 minutes?

-

LONG-DURATION SPACE FLIGHT

- High level of crew productivity; little habitat maintenance
- Decouple environmental control from ground control
  - Distributed network of sensors and actuators
  - Sound an alarm and/or actuate remedial action
  - Early identification of areas requiring remediation

AIR QUALITY MONITORING

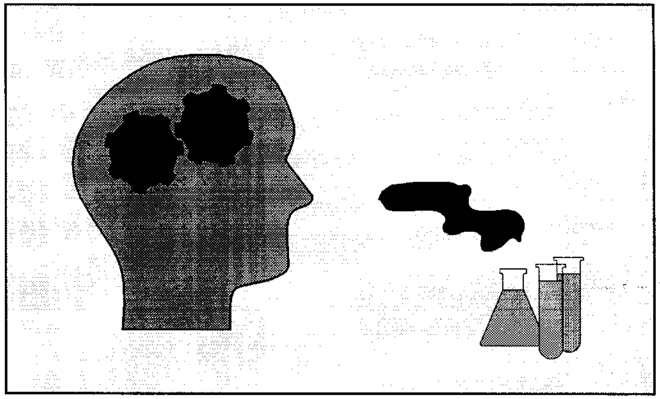
	Analysis Time (min)	Concentration of Constituents	Discrimination of Constituents
ENose	.5 - 15	0.01 - 10,000 ppm	good for target set
GC-MS	10 - 100	< 10 ppb	very good
VOC	1- 5	.1 - 2000 ppm	poor
FID	1 - 5	.1 - 50,000 ppm	poor
Smoke Alarm	.5 - 5	1 - 10 ppb	none

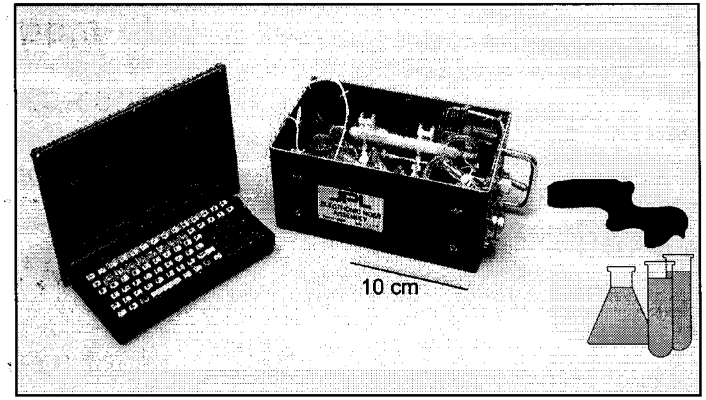
ELECTRONIC NOSE

- Incident monitor for contaminants exceeding Spacecraft Max Allowable Concentration (SMAC)
- Monitor clean-up process
- Identify and quantify target compounds at SMAC level
- Low mass, low power device
- Requires little crew time for maintenance and calibration

Electronic Nose

REAL TIME AIR QUALITY MONITORING





HUMAN NOSE

- array of thousands of sensors
- broad band capability
- trainable to new odors
- data acquisition in the brain
- analysis by true Neural Network processing; pattern recognition

LIMITS ON HUMAN NOSE

- fatigue
- becoming accustomed to an odor
- insensitivity to some compounds
- toxicity of some contaminants.

JPL/CALTECH ELECTRONIC NOSE

- array of a few tens of sensors
- thin film polymer based sensors
- broad band capability
- polymers selected to respond to particular compounds
- trainable to new analytes
- data acquisition by computer
- data analysis by computational methods and pattern recognition

LIMITS ON ENOSE

- insensitivity to compounds; can be overcome by sensor film selection

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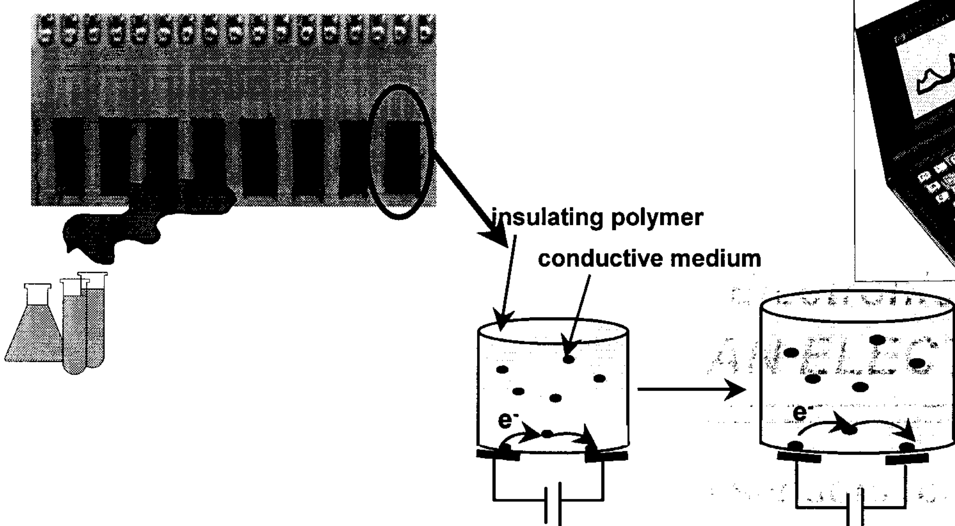
Electronic Nose
WHAT IS AN ELECTRONIC NOSE?

An array of non-specific chemical sensors, controlled and analyzed electronically, which have overlapping responses to compounds. Sensing mimics the action of the mammalian nose by recognizing patterns of response

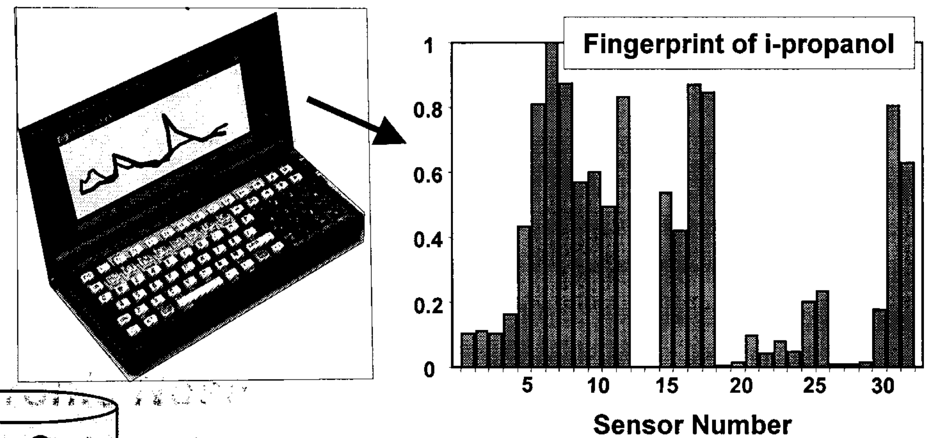
1. ENose measures background resistance in each sensor and establishes R_0.

2. Contaminant comes in contact with and sorbs into sensors .



3. The sensors, polymer films loaded with a conductive medium such as carbon black, change resistance by swelling or shrinking as air composition changes.

4. Resistance is recorded, the change in resistance is computed, and the distributed response pattern of the sensor array is used to identify gases and mixtures of gases



5. Responses of the sensor array are analyzed and quantified using software developed for the task.

n-propanol, 30 ppm

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HOW CAN AN ELECTRONIC NOSE BE USED?

Limited Suite of Compounds in a Well-Known Environment

- Limited (10 - 50) number of sensors,
- Train electronic nose to recognize and quantify a limited suite of compounds in a restricted odor space
- Deconvolute mixtures of a few compounds
- Identify unknowns by functional group
- Applications
  - *Event monitoring in Space Shuttle, Space Station, Human Habitat with fully recycled air*
  - *Industrial Process control*
  - *Change in contaminants against known background*

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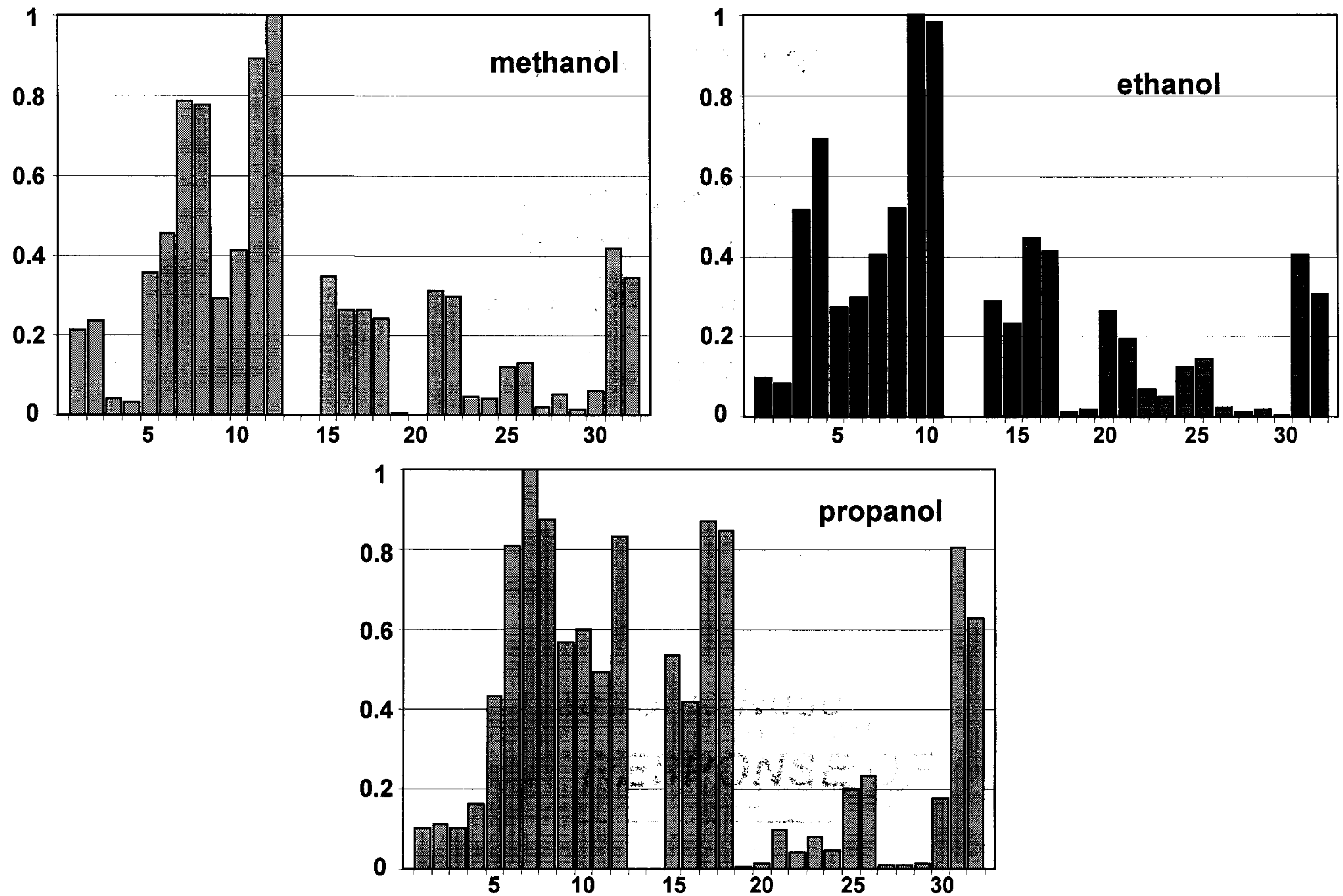
Electronic Nose
FINGERPRINT RESPONSE OF ARRAY

NASA



Similar compounds can be distinguished by their fingerprints. 3 primary alcohols (methanol, ethanol, 1-propanol) have similar but distinguishable response patterns.

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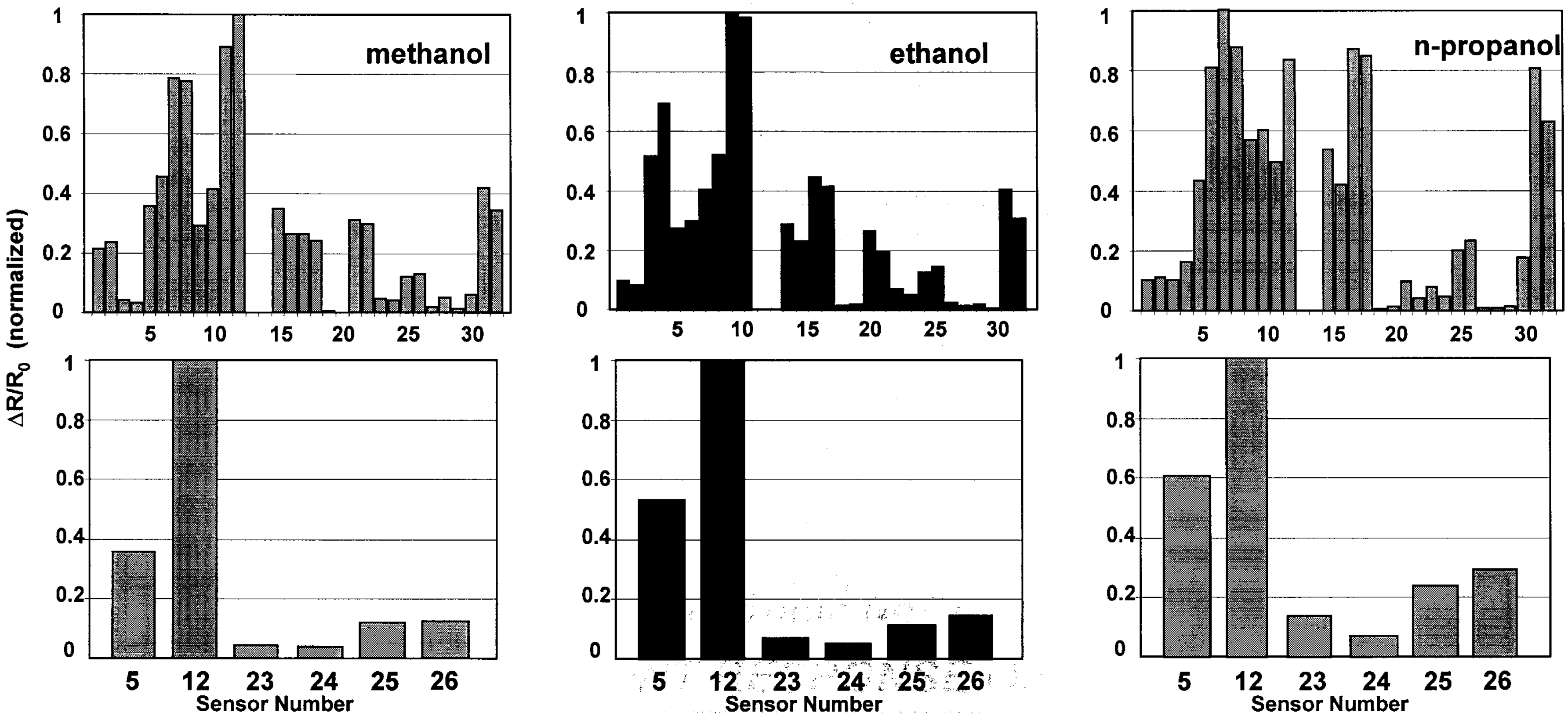
FINGERPRINT RESPONSE OF ARRAY

NASA

Identification by Functional Group



Three primary alcohols (methanol, ethanol, 1-propanol) can be distinguished by their response patterns. A sub-pattern made up of five sensors has been identified as being indicative of primary alcohols. This technique can be used to identify compounds by functional group.

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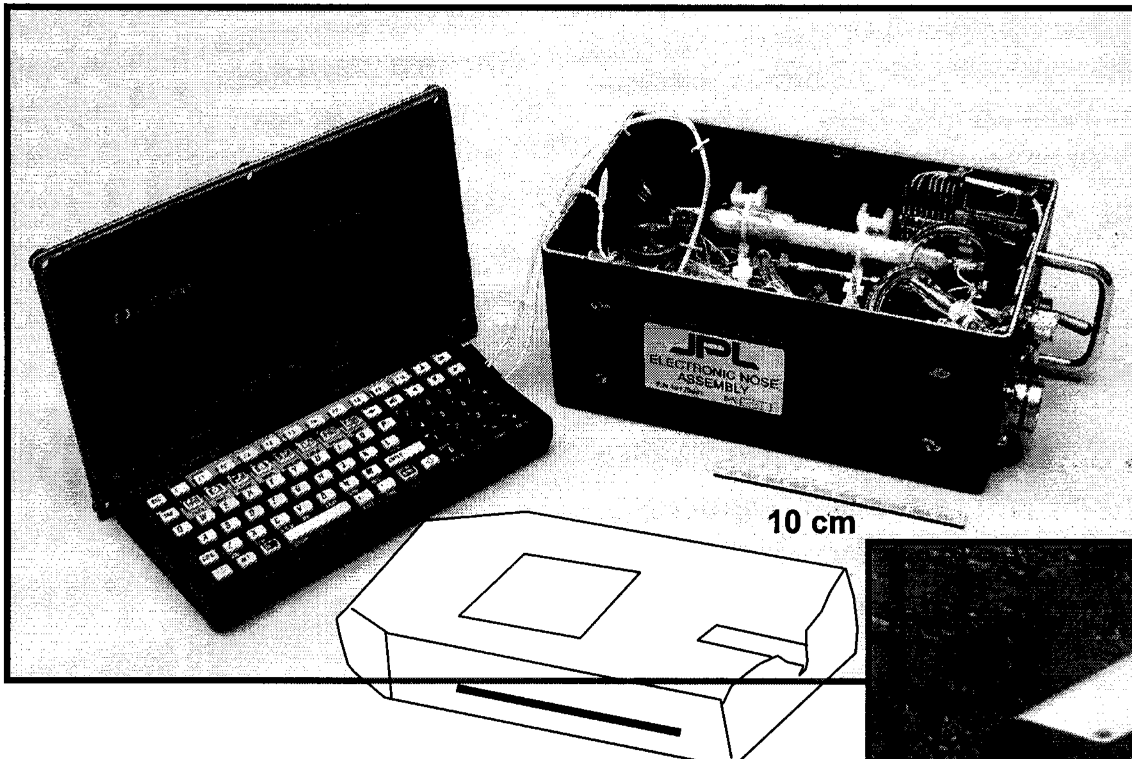
Electronic Nose
SECOND GENERATION DESIGN

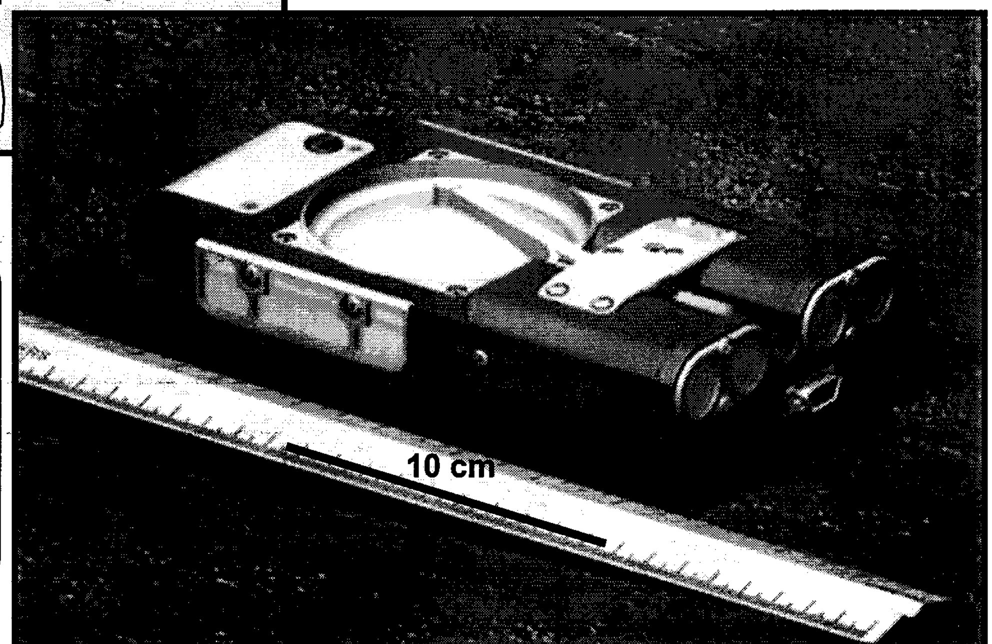


Flight Experiment

Volume: 2000 cm^3 including computer
Mass: 1.4 kg including computer
Power: 1.5 W ave., 3 W peak
Computer: HP 200LX
(Size and mass influenced by requirements for flight experiment)

Second Generation ENose

Optimized sensors, faster analysis, improved sensitivity
Volume: 760 cm^3 including computer
Mass: 800 g including computer
Power: 1.5 W avg., 3 W peak
Computer: PDA



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PHASE I TARGET COMPOUNDS

Compound	Detected on shuttle (ppm) [1]	SMAC 1hr (ppm	mg/m³) [2,3]	Detected at JPL (ppm	mg/m³)
alcohols					
methanol	< 1	30	40	5	7
ethanol	.5 - 5	2000	4000	50	25
2-propanol	.4 - 4	400	1000	50	6
methane	1 - 10	5300	3800	3000	2150
ammonia	0	30	20	20	13
benzene	< .1	10	35	10	35
formaldehyde	0	.4	.5	25	30
Freon 113	.1 - 1	50	400	20	160
indole	0	1	5	0.03	.15
toluene	.4 - 4	16	60	15	56

[1] J.T. James, *et al.*, *Aviation, Space Environ. Med.*, **65**, 851 (1994).
[2] *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).
[3] *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).

Electronic Nose

PHASE II TARGET COMPOUNDS

Compound	24 hr SMAC [1,2] (ppm)
acetaldehyde	6
acetone	270
acetonitrile	4
2-butanone	150
chlorobenzene	10
dichloromethane	35
furan	0.1
hexamethylcyclotrisiloxane	25
hydrazine	0.3
methyl hydrazine	0.002
tetrahydrofuran	40
1,1,1-trichloroethane	11
xylenes	100
compounds associated with incipient fires	

[1] *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).

[2] *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).

HOW CAN AN ELECTRONIC NOSE BE USED?

Broad-Band Sensing in an Enclosed Background

- Broader range of analytes will require larger number of sensors, possibly a variety of sensor types
- Mixtures of several constituents will require a larger number of sensors, additional dimension(s) of data and/or separation techniques
- Applications
  - *Monitoring contaminated sites for change in concentration of contaminants*

HOW CAN AN ELECTRONIC NOSE BE USED?

Broad-Band Sensing in an Open and/or Unknown Environment

- Broad range of analytes will require a variety of sensor types
- Mixtures of several constituents will require separation techniques or reaction of constituents
- Baseline on environment and probe for measure change after separation or reaction of compounds
- Analysis includes building up compounds from unknown signals using theoretical model of sensor/analyte interaction

SELECTION OF POLYMERS FOR ARRAY

Select polymers for analyte set or application

1. ***Select polymers from four types:***
   - **Hydrogen-bond acidic**
   - **Hydrogen-bond basic**
   - **Dipolar and hydrogen-bond basic**
   - **Weakly dipolar with weak or no hydrogen-bond properties**

2. ***Determine how well array will distinguish analytes:***
   - **Calculate distance (vector magnitude) for each analyte using all selected polymers:**

$$\Delta S_{mn} = \frac{1}{N}\sum_{i}^{N}\left|dR_m(i) - dR_n(i)\right|$$

$dR_m(i)$ is the ith sensor's (fractional) resistance change for the mth gas, sum over N sensors

   - **Select polymers with most distinct signatures from max distances**

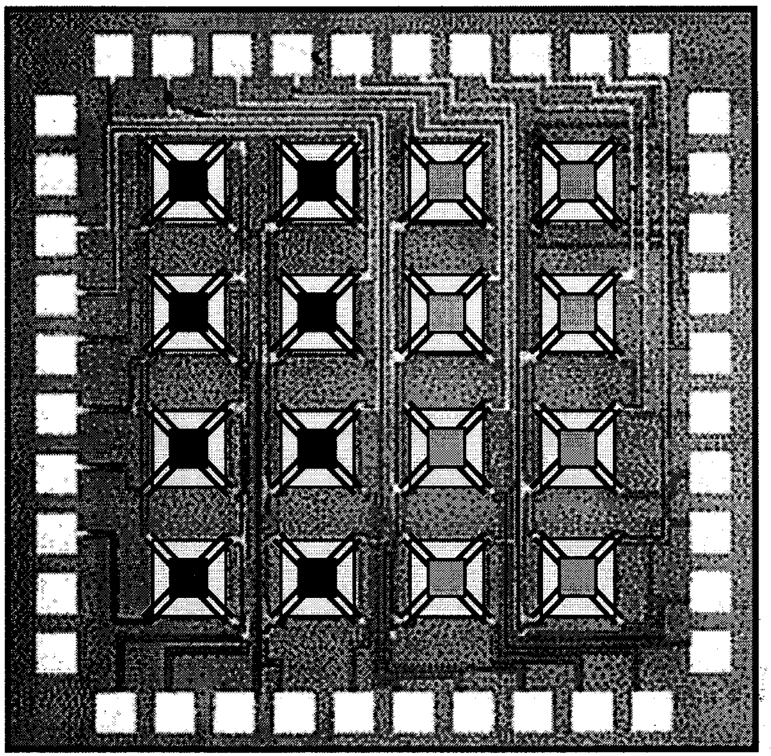
SELECTION OF POLYMERS FOR ARRAY

Select polymers for analyte set or application

3. *Determine whether distinctions can be improved by substitutions*
   - Remove or replace polymer(s) if response to every analyte is small
   - Recalculate distances to determine if there is improvement

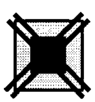
4. *Use model of polymer-analyte interaction to determine whether other polymers may substitute to increase distances*
   - Model based on binding interactions of polymer film composite with analyte
   - Magnitude of response is correlated with binding energy
   - Inclusion of concentration underway - needs partition information

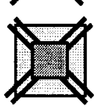
Hybrid Sensor Array: Metal Oxide & Polymer Films



A hybrid array allows detection of compounds which are accessible to one type of sensing film but not the other, *e.g.*

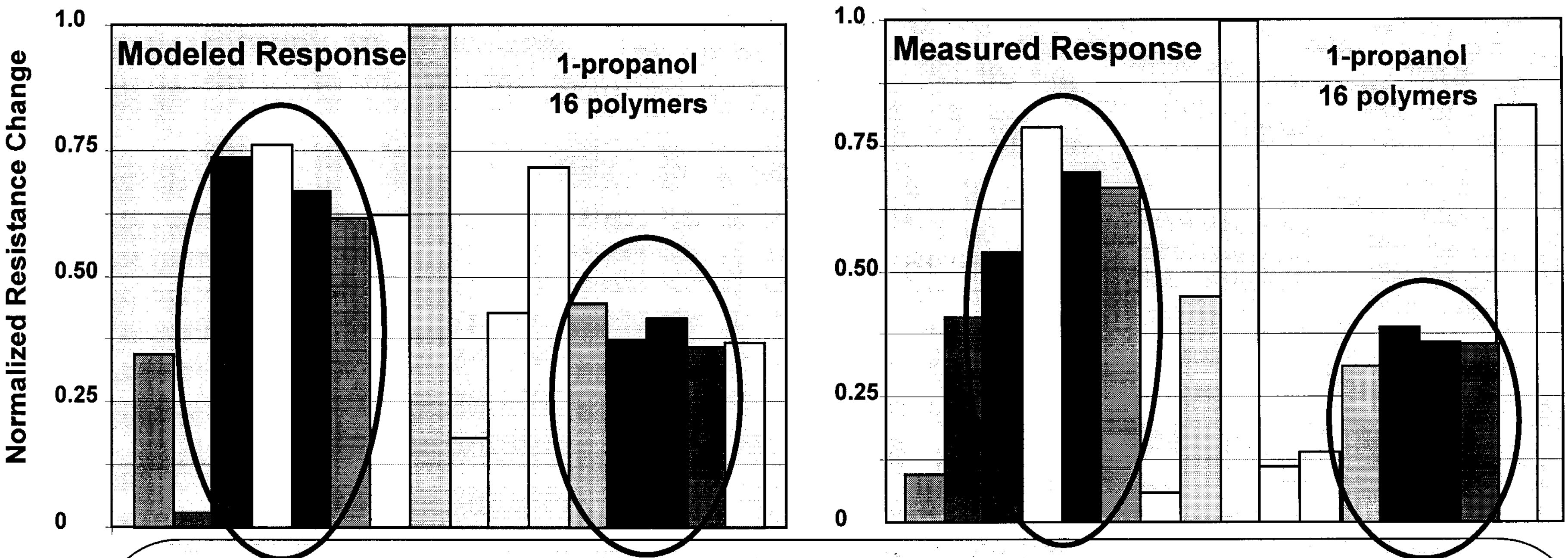
- MO_x films detect CO_2, H_2 and other inorganic compounds which polymers do not
- Polymer films can detect sulfur containing compounds, which poison MO_x films

 metal oxide sensor

 polymer sensor

This work is in collaboration with S. Semancik, NIST

Electronic Nose
MODEL OF SENSOR RESPONSE



Model of Sensor Response

- Response of each polymer to one analyte is estimated by calculating the polymer-analyte binding energy interactions (lower energy → larger response)
- Measured response is compared to modeled response (above)
  - For two sets of four polymers, the pattern of response to 1-propanol is similar in modeled and measured plots (above)
  - Polymers which do not predict response well need further calculations which will include solubility and partition of analyte in polymer
- Energies and responses have been calculated for 12 compounds

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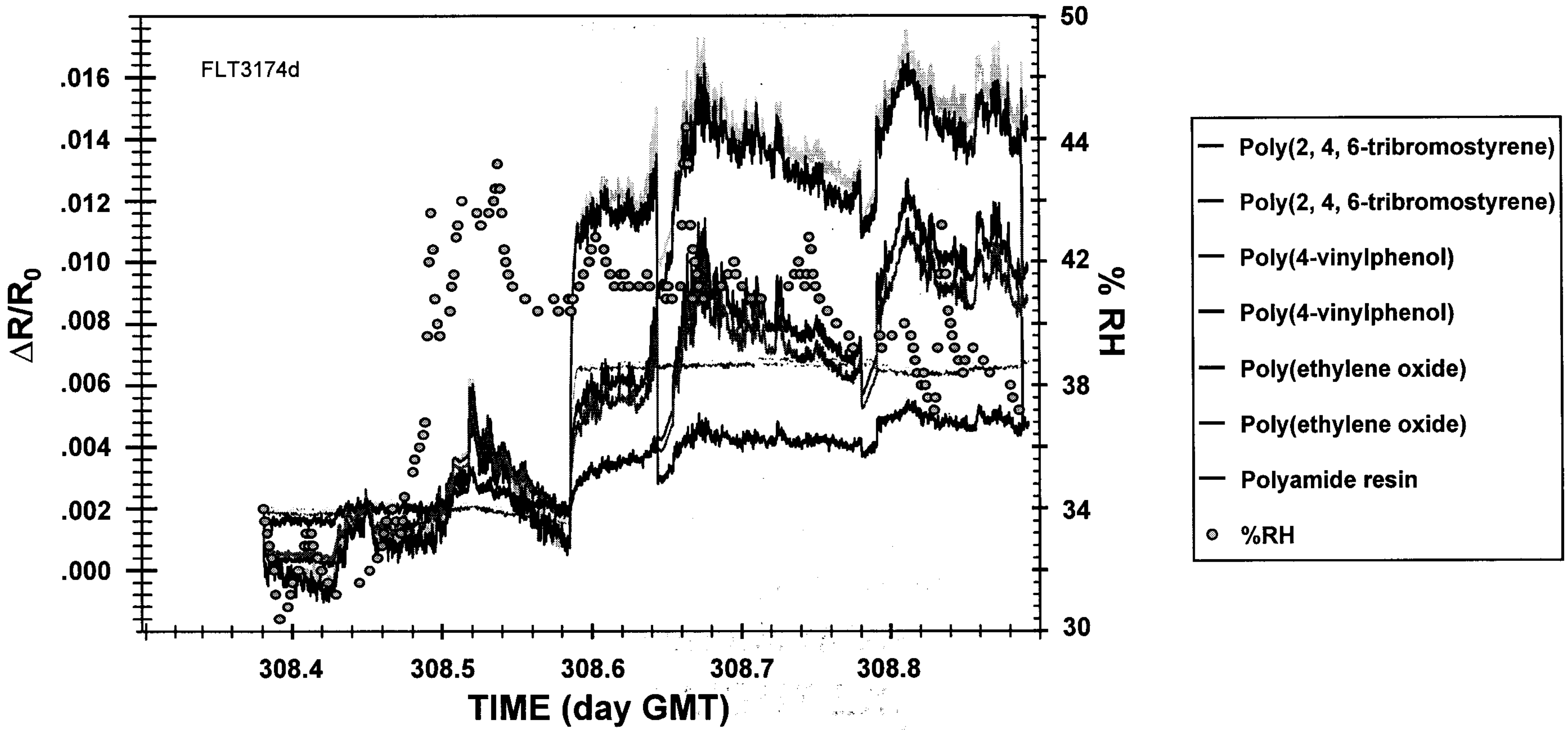
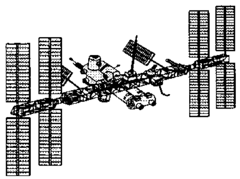
DATA FROM FLIGHT EXPERIMENT



Flight data show several event peaks, with dips which correspond to reference cycles. Large cabin humidity changes (circles) correlate with event peaks in ENose data. The step in ENose data at 308.58 is caused by a 4°C temperature step on the chips, to keep chip temperature above cabin temperature.

Electronic Nose
POSSIBLE APPLICATIONS

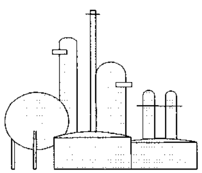


SPACE STATION ENVIRONMENTAL MONITORING

Event monitor for early warning of spills, leaks, fires; clean-up monitoring; automated environmental control.

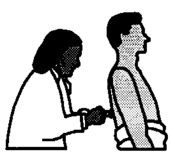
MILITARY APPLICATIONS

Air quality monitor for enclosed spaces.
Detection of explosives, chemical/biological warfare agents.



INDUSTRIAL MONITORING AND PROCESS CONTROL

Monitor food processing, identity and condition of raw materials, leaks and buildup of toxic compounds.



MEDICAL

Diagnosis of diseases with characteristic odors, monitor patients' rooms, monitor labs.

OTHER ENVIRONMENTAL MONITORING

Air quality in buildings, aircraft. Presence of toxic materials in designated spaces.

PLANETARY EXPLORATION

Study planetary atmosphere to determine constituents and fluctuations

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