Second Generation Electronic Nose

Real-Time Air Quality Monitoring in Human Habitat

Advanced Environmental Monitoring & Control Project

Advanced Life Support Program

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SUMMARY

Objective: *further develop the JPL Electronic Nose as a miniature, automated event monitor which will detect, identify and quantify spacecraft air contaminants at or below the 24-hour SMAC*

Problems addressed:

- Increase sensitivity and capability of device
  - Decrease sensor noise and increase sensitivity of response
  - Optimize sensing array
  - Model polymer-analyte interaction and sensor response for array selection and unknown classification
- Miniaturize device, expand acquisition capability
- Analyze in real-time; extend capability to deconvolute mixtures

Measure for success: *Size and mass reduced to <50%, expand analyte set, analyze in real time, deconvolute mixtures of 3-4 analytes, identify and quantify analytes at 24 hour SMAC; demonstrate in extensive ground testing*

AIR QUALITY MONITORING REQUIREMENTS

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

- **Trace contaminants - less frequent monitoring required**

  ~ 40 organic compounds

- **Event Monitoring - rapid response time**
  - **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

AIR QUALITY MONITORING

JPL ELECTRONIC NOSE

FUNCTIONS

- Incident monitor for targeted contaminants exceeding Spacecraft Max Allowable Concentration (SMAC). Identify and quantify target compounds at SMAC level.
- Monitor for presence of compounds associated with fires or overheating electronics
- Monitor clean-up process

CHARACTERISTICS

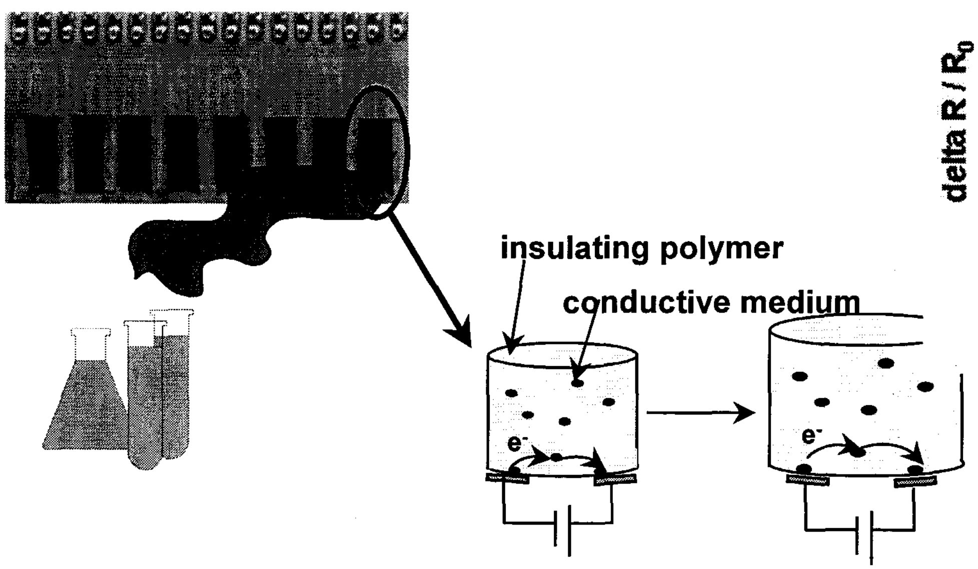
- Low mass, low power device
  First Generation *1.5 kg; ~ 2 L; 1.5 W avg, 3 W peak*
  Second Generation *< 1 kg; < 1 L; 1.5 W avg, 3 W peak*
- Requires little crew time for maintenance and calibration

WHAT IS AN ELECTRONIC NOSE?

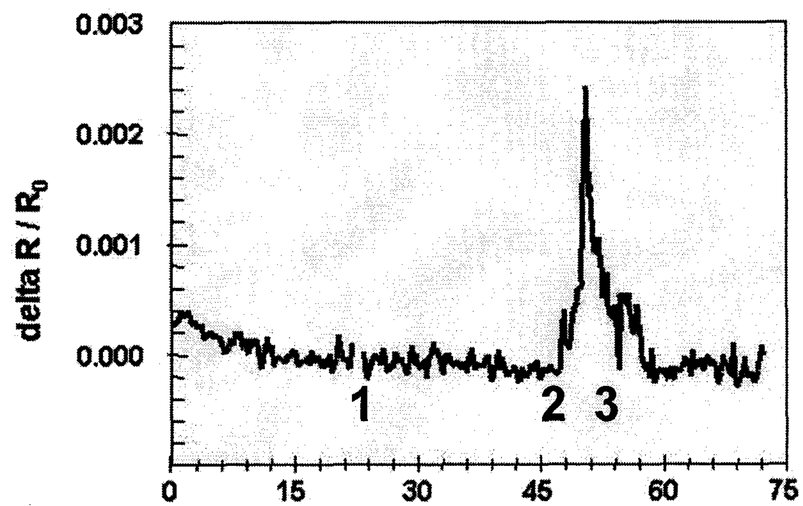
An array of non-specific chemical sensors, controlled and analyzed electronically, which have overlapping responses to compounds. Compounds are identified and quantified by recognition of patterns of response.

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

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

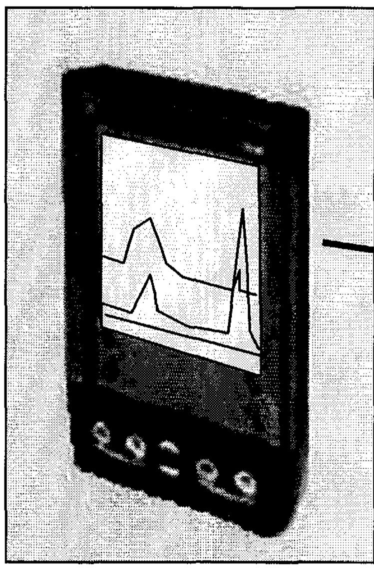


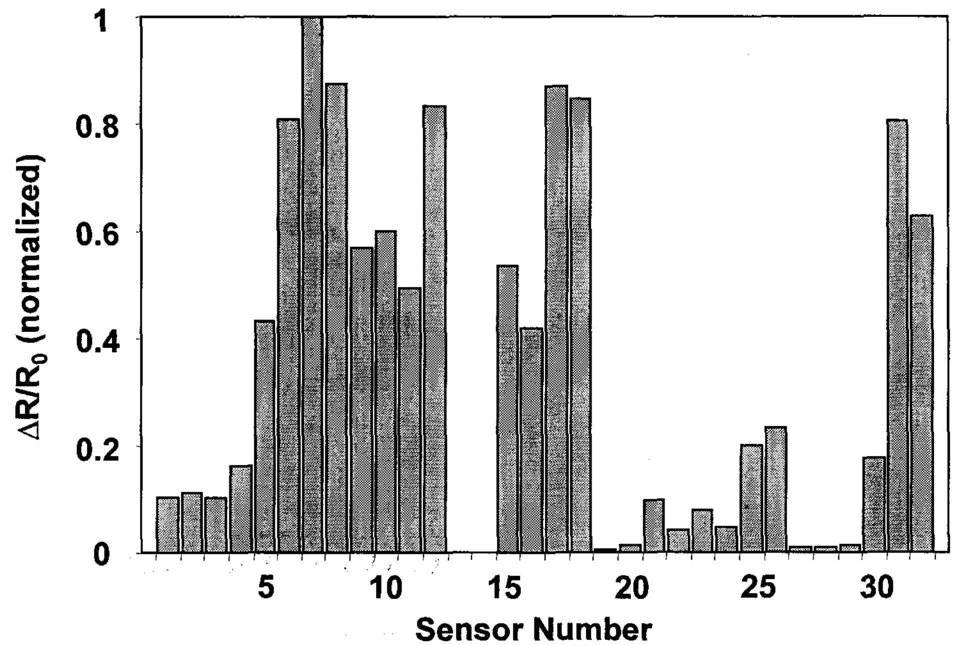
3. The sensors, polymer films loaded with a conductive medium such as carbon black, change resistance by swelling or shrinking as air composition changes.



WHAT IS AN ELECTRONIC NOSE?

4. Resistance is recorded, the change in resistance is computed, and the distributed response pattern ("fingerprint") of the sensor array is used to identify gases and mixtures of gases. The magnitude of response is used to quantify the identified compound.





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

n-propanol, 30 ppm

FOCUS OF WORK IN FY02

SENSOR AND ARRAY OPTIMIZATION

- *Sensor Formulations and Processing*
- *Conductive Medium*
- *Sensitivity*
- *Reproducibility of Sensors and Repeatability of Response of Sensors and Array*
- *Analytes*
- *Model of Polymer-Analyte Interaction*
- *Polymer Selection and Computation of Array Optimization*
- *Humidity, Temperature and Pressure Effects*

ELECTRONICS

- *Device control and data acquisition system*
- *Eight sensor circuit*
- *Control software*

DATA ANALYSIS

- *On-screen analysis for laboratory*
- *Deconvolution of Humidity*
- *Classification by Functional Group*
- *Real Time Analysis*

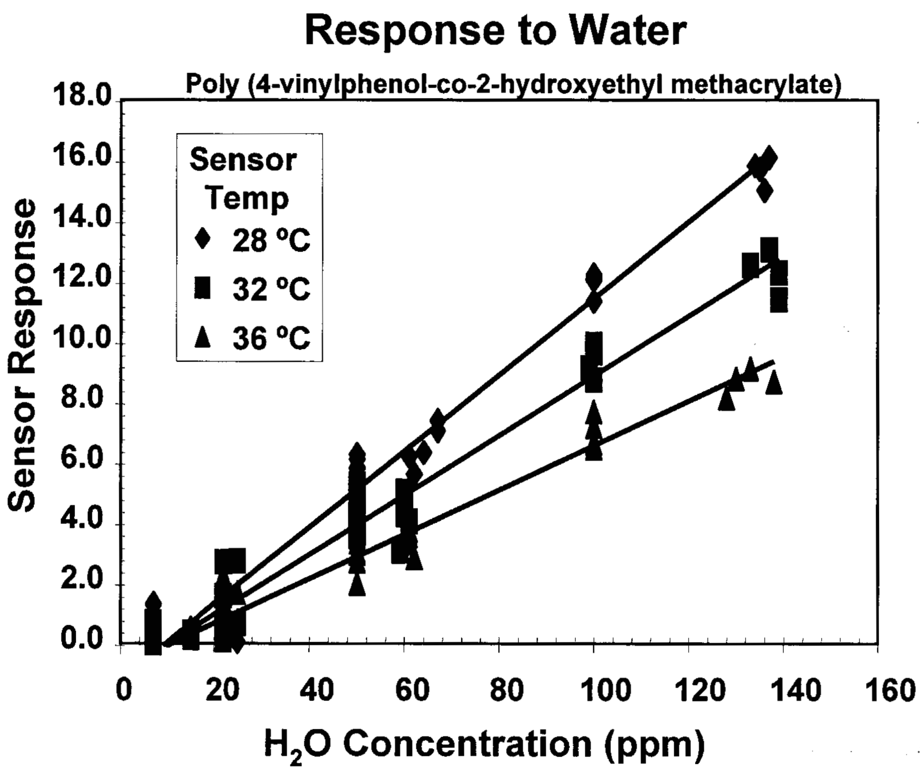
HARDWARE AND SYSTEM INTEGRATION

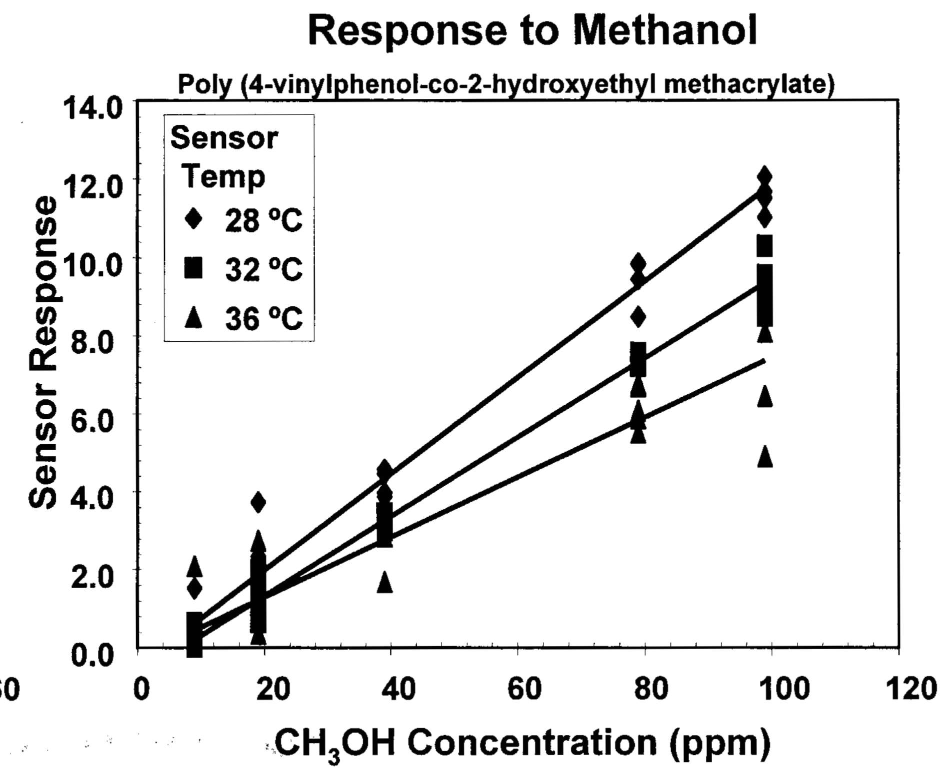
- *Hardware design - integrated plumbing, hard anodized aluminum*

DEVICE TESTING

- *Test array*
- *Test Chamber*

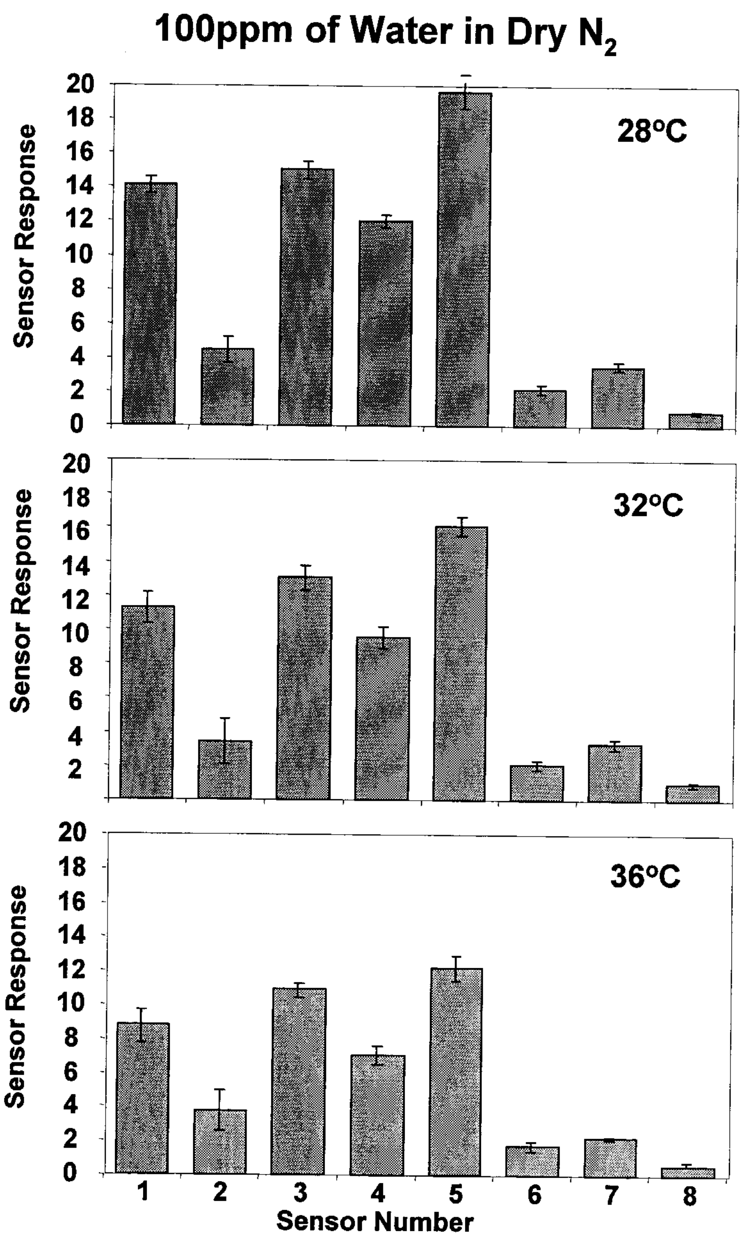
TEMPERATURE RESPONSE OF SENSORS



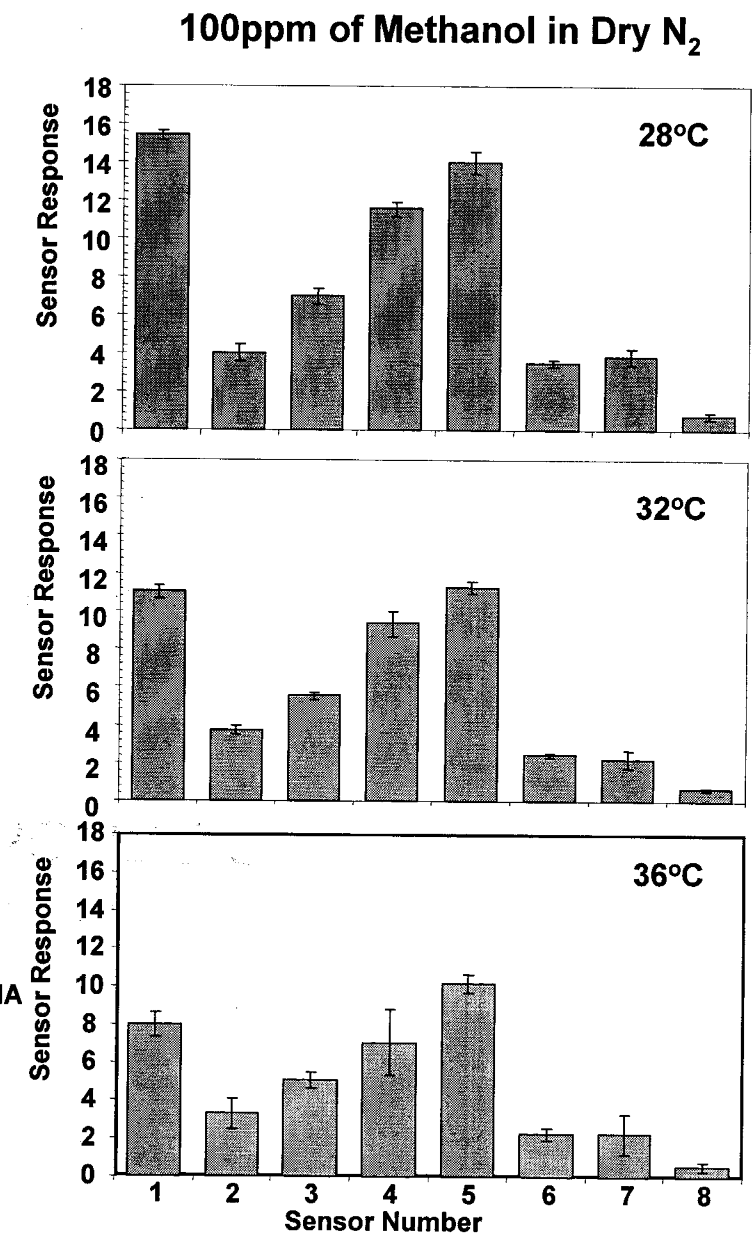


Sensor response changes with temperature; The overall pattern of response is similar, but ratios of response change. Temperature dependence can be used as a dimension of data to aid in identifying compounds, in classifying unknown compounds and in deconvoluting mixtures.

TEMPERATURE RESPONSE OF SENSORS



Polymers:
1-PVPyr-A
2-P2VPy-A
3-PMVe-MA2
4-P4VPhcHEMA
5-PVPyr-B
6-P2VPy-B
7-EC
8-N



REPRODUCIBILITY AND REPEATABILITY

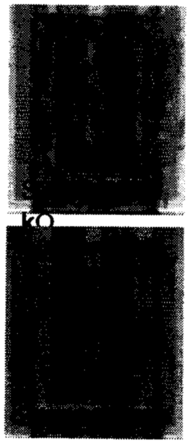
Sensor optimization studies included determining the reproducibility of sensors (similarity of sensors made from different solutions, by different people) and repeatability of sensor response.

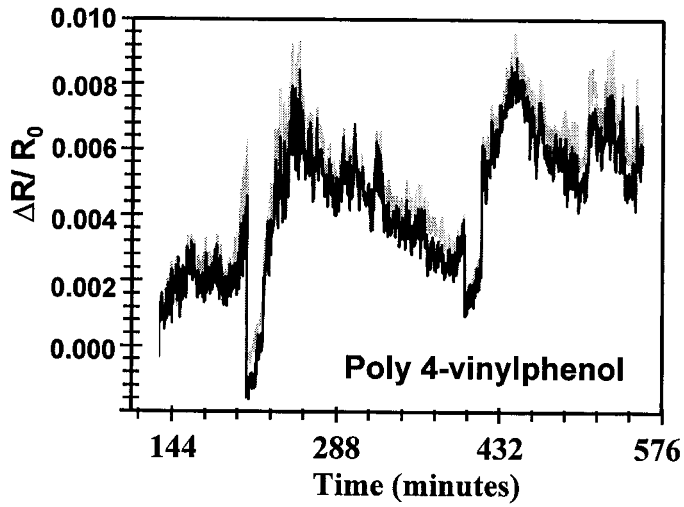
Reproducicility should be sufficient that each new array requires only testing and calibration, not full training

Major results:

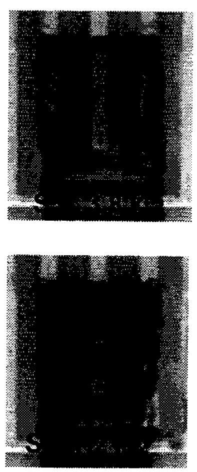
- Although sensing films made from the same polymer may have baseline resistances differing by an order of magnitude, the response $(R-R_0)/R_0$ of the films is the same
- Two sensors made from the same solution and deposited by different people at different times have the same response to analytes. Baseline resistances may differ.
- Sensor response response to analytes is repeatable over several exposures to the analyte

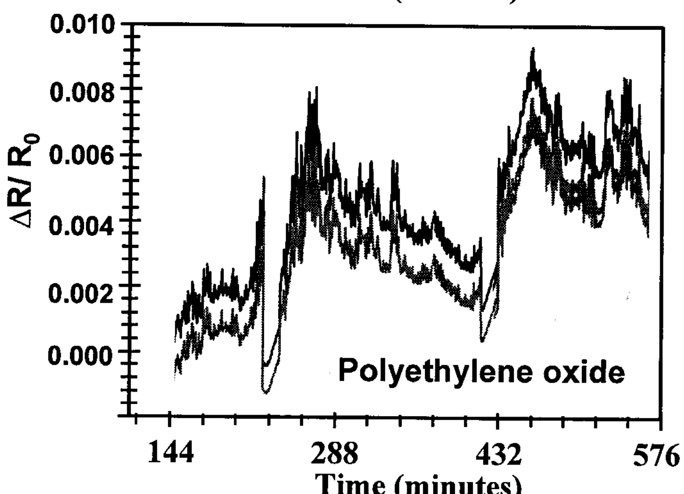
REPRODUCIBILITY AND REPEATABILITY





Two films of Poly4-vinylphenol have baseline resistances of 11.5 and 138 kΩ, and their responses overlie each other.



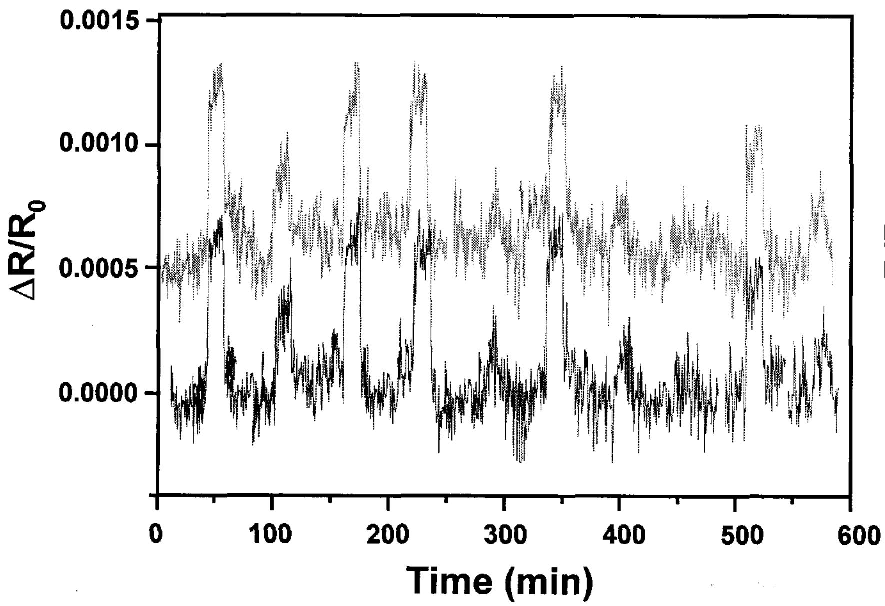


Two films of Polyethylene oxide have baseline resistances of 3.8 and 1.2kΩ, and their responses overlie each other.

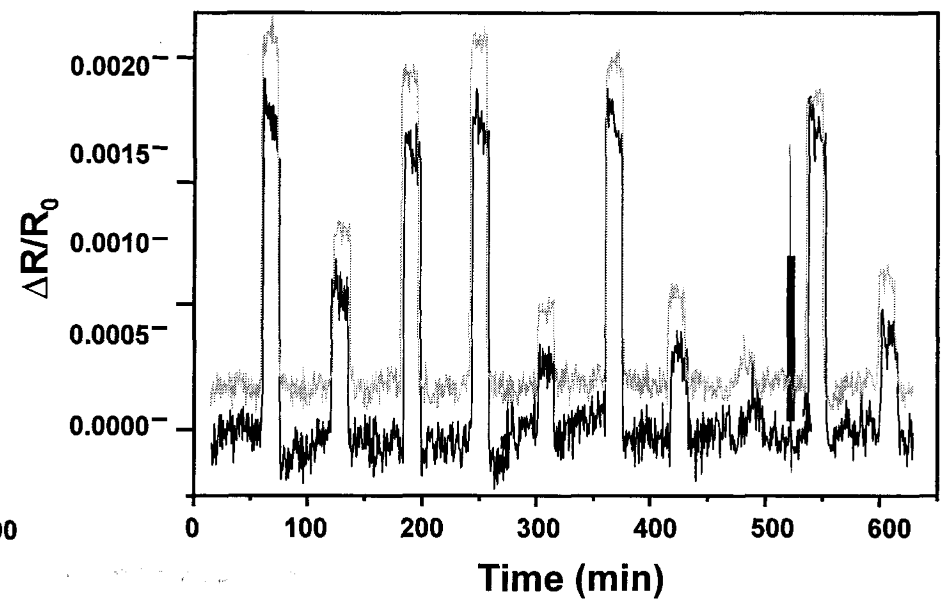
Although sensing films made from the same polymer may have baseline resistances differing by an order of magnitude, the response $(R-R_0)/R_0$ of the films is the same.

REPRODUCIBILITY AND REPEATABILITY

Poly 4-Vinylpyridine
Response to Hexane, 50 -1100 ppm



Polyepichlorhydrin
Response to Hexane, 50 -1100 ppm

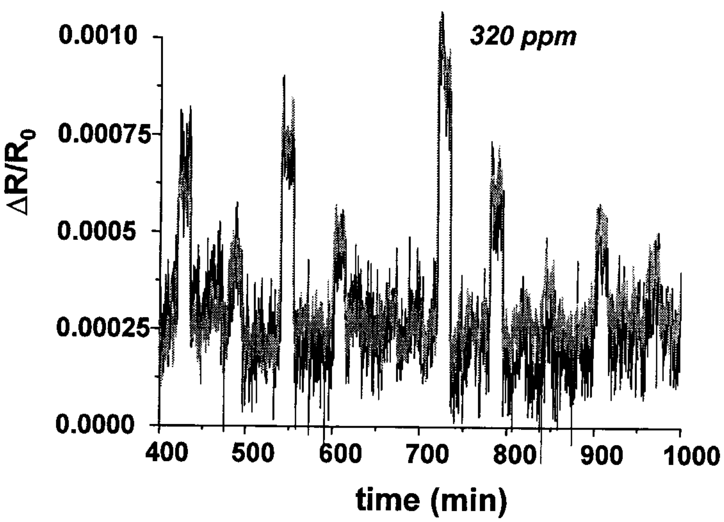


Two sensors made from the same solution and deposited by different people at different times have identical response to hexane (traces are offset to show event peaks)

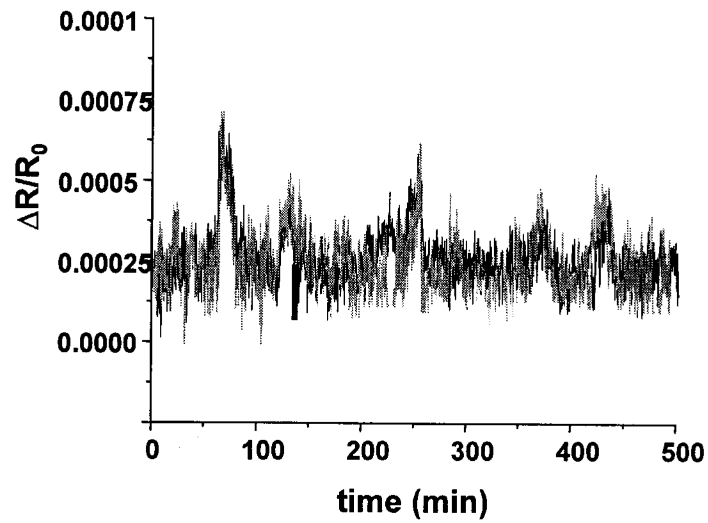
REPRODUCIBILITY AND REPEATABILITY

Polyepichlorhydrin		Ethylene-propylene-diene terpolymer

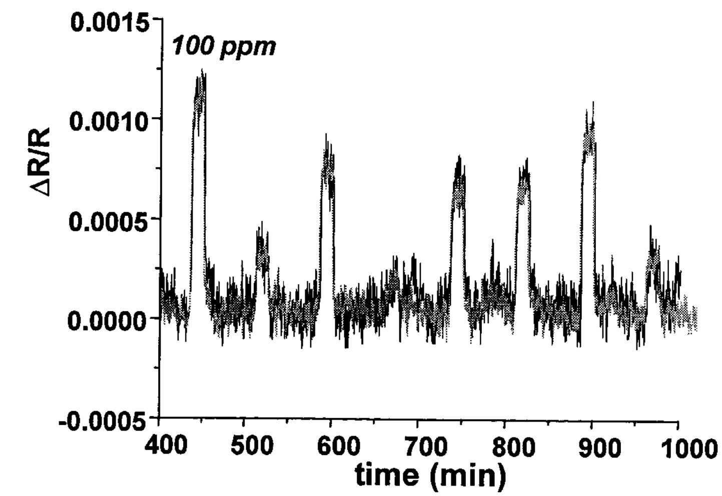
Polyepichlorhydrin

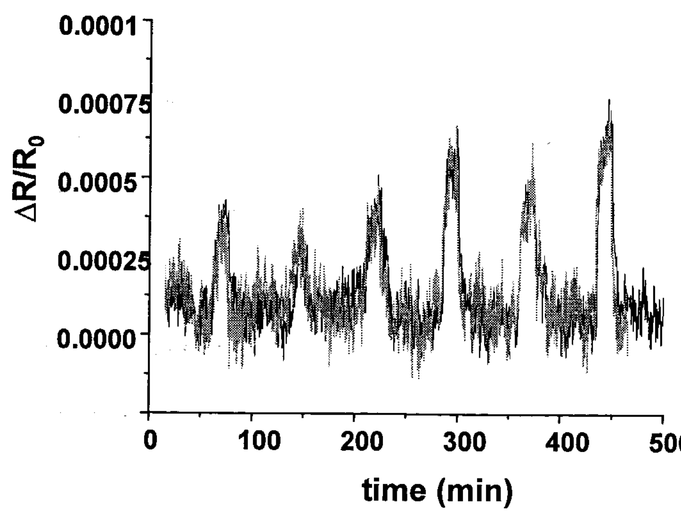


Ethylene-propylene-diene terpolymer



1-Propanol 30-320 ppm



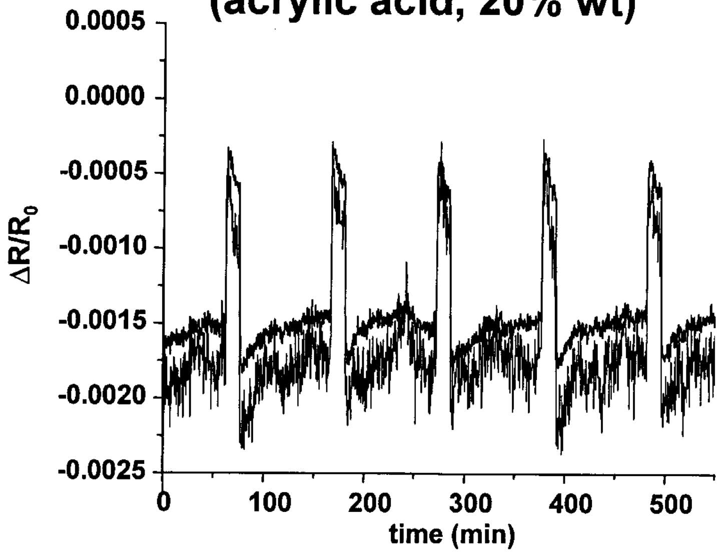


1-Butanol 10-100 ppm

REPRODUCIBILITY AND REPEATABILITY

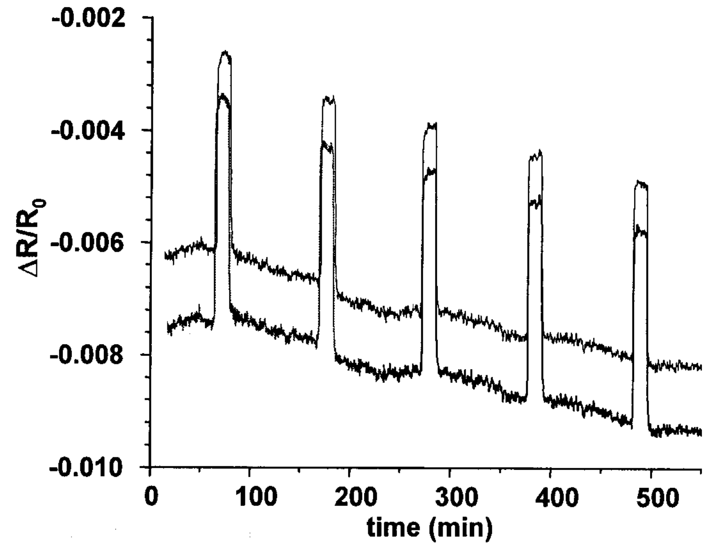
Repeated Response to 650 ppm Ethanol

Poly (ethylene-co-acrylic acid) (acrylic acid, 20% wt)



PEcAA20	avg response	std deviation
sensor 1	9.7	1.1
sensor 2	9.7	0.4

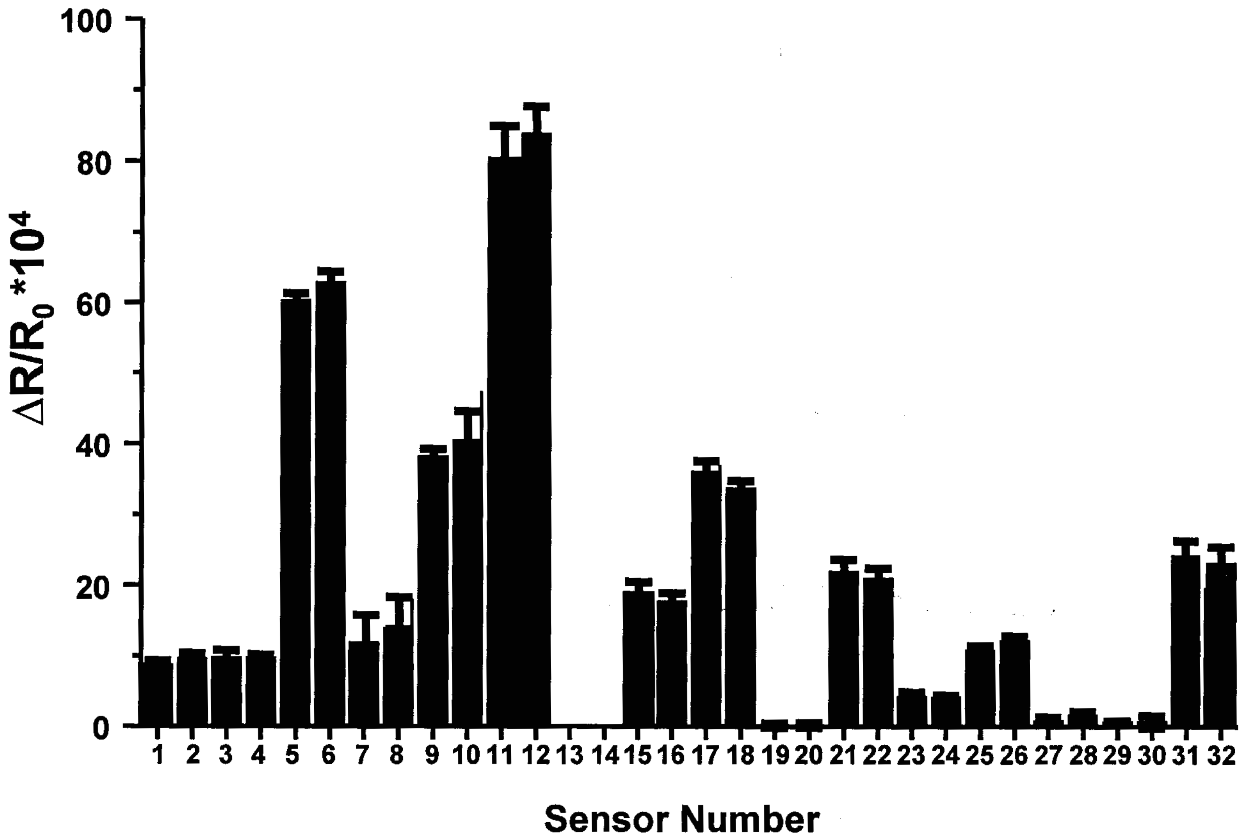
Ethylcellulose



EC	avg response	std deviation
sensor 1	33	1.1
sensor 2	36	1.6

REPRODUCIBILITY AND REPEATABILITY

Array Response to 10 events - 650 ppm Ethanol



DATA PROCESSING AND ANALYSIS

Data Analysis Algorithm

Analysis by Levenberg-Marquart Non-Linear Least Squares (LM-NLS) fitting

- **array response to an analyte does not change linearly with concentration**
- **fractional resistance change, $(R-R_0)/R_0$, is used as the response,**
- **all sensors used in all analysis. Sensors may be weighted in the array response**
- **identification and quantification are not separate steps -- no normalization using a weighted sum of resistance change from all or a subset of sensors.**

Deconvolution of Mixtures

Identify and quantify the constituents of mixtures of 3-4 compounds if the mixture is made up of target compounds

- **LM-NLS based algorithm for data analysis (identification and quantification)**
- **Sensor response to mixtures is linearly additive**
- **Incidents which involve leaks or spills of more than three compounds are unlikely. There are no guidelines yet available.**
- **device can be trained to identify and quantify target materials which exist as standard mixtures (i.e. mixed xylenes, oils) without need to deconvolute**

SENSORS AND SENSOR ARRAY

Sensor Array

The sensing array is made up of 32 sensors. Sensors are made with 16 carbon-polymer composites with overlapping response; sensor response is read as change in resistance in the film

- usual array sizes are 12 - 20 sensors
- ability of array to distinguish similar compound depends on number of sensors and identity of sensors; more than 40-50 sensors will slow computation
- sensing films which do not add significantly to array performance are eliminated; sensing films which have low response but add somewhat to performance are weighted less than others
- a much larger number of sensors can be used if they are divided into subsets, but computation will be significantly slowed

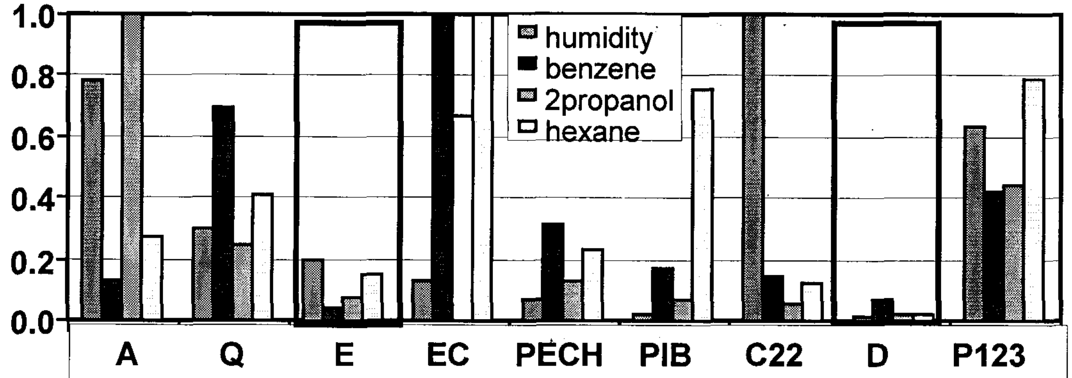
Sensor Recovery and Lifetime

Sensors recover from analyte stimulus in seconds to minutes. Corrosive compounds such as hydrazine have not attacked sensors. Array lifetime is 12-18 months.

SENSOR ARRAY OPTIMIZATION

Polymers for Sensors Selected by Distance Calculation
Sensors Weighted According to Contribution

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



9 polymers

	humidity	benzene	2-propanol	hexane
humidity	0.00	1.49	1.14	1.55
benzene	1.49	0.00	1.06	0.77
2-propanol	1.14	1.06	0.00	1.13
hexane	1.55	0.77	1.13	0.00

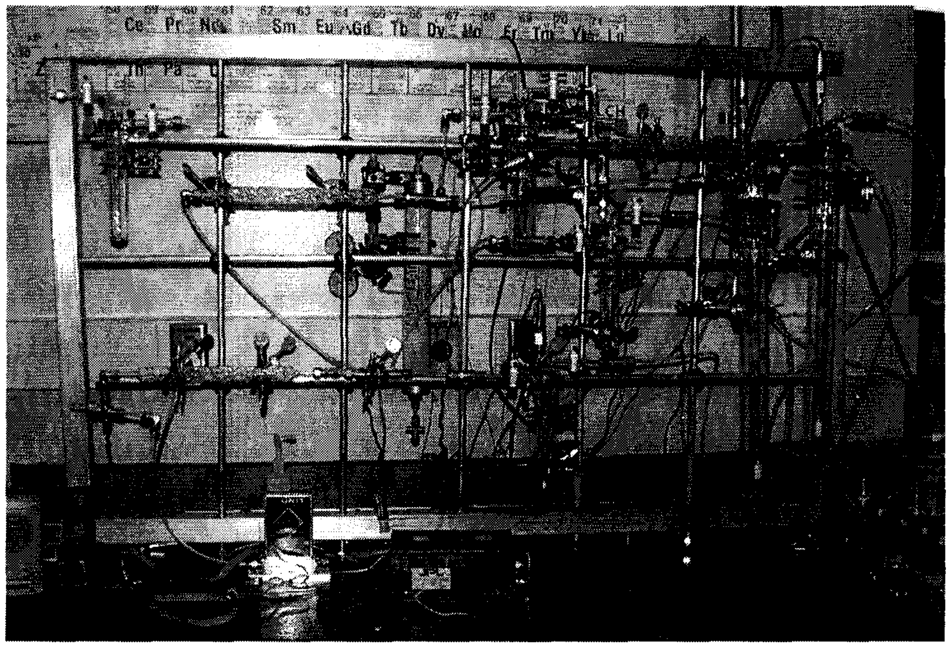
7 polymers

	humidity	benzene	2-propanol	hexane
humidity	0.00	1.48	1.13	1.55
benzene	1.48	0.00	1.06	0.76
2-propanol	1.13	1.06	0.00	1.12
hexane	1.55	0.76	1.12	0.00

Calculate sensor-analyte distances with 9 polymers. Polymers D & E have similar, small responses; recalculate with 7 polymers. The distances between the patterns for these 4 analytes change very little if polymers D and E are excluded.

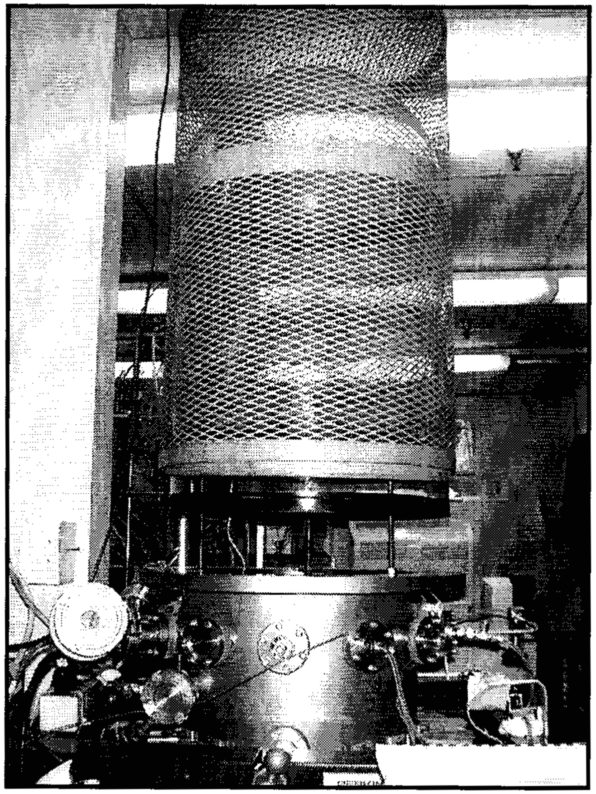
AIR / ANALYTE DELIVERY SYSTEM

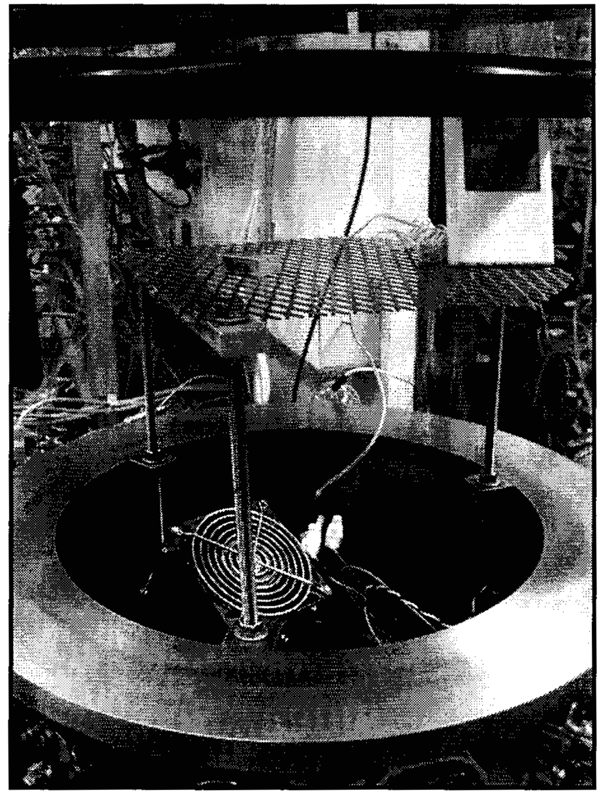
A computer-controlled gas delivery system bubbles air through solvents and mixes them with humidified air. Temperature is controlled in the gas delivery system using heaters.



- concentrations are verified using a Rosemont Hydrocarbon Analyzer calibrated to standard gases (methanol, methane, toluene, acetone). Humidity is verified using calibrated sensors.
- Background gases can be cleaned air or bottled gas. Humidity is added by bubbling through water and mixing humidified air with dry air.

100 LITER TEST CHAMBER





Temperature and Pressure Controlled 100 L Test Chamber

- Liquid test analytes are delivered using a syringe or a syringe pump
- Solid analytes are delivered by placing a measured quantity in a feedthrough; gaseous analytes are delivered through a tube.
- Chamber air can be circulated within the chamber or directed through a filter to simulate the Air Revitalization System.

SENSOR ARRAY OPTIMIZATION

POLYMER SELECTION

Select polymers from five categories of chemical functionality:
Show structures

- Hydrogen-bond acidic - 16 considered; 10 tested; 3 selected
- Hydrogen-bond basic - 8 / 4 / 3
- Dipolar and hydrogen-bond basic - 12 / 6 / 4
- Moderate dipolarity and moderately weak H-bond basicity/acidity - 19 /12 / 3
- Weakly dipolar, weak or no hydrogen-bond properties - 12 / 10 / 3

Consider molecular weight - has an effect on percolation threshhold

POLYMER SELECTION

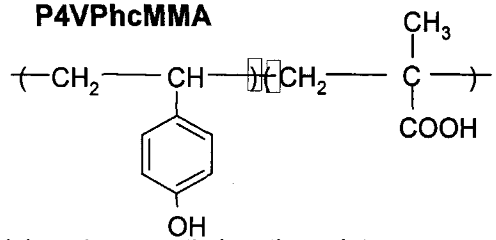
Polymer Selection

Sixteen polymers are chosen from five types of chemical structure to make an array with broad chemical functionality, to respond to a wide suite of analytes.

- ❖ Hydrogen Bond Acidic
- ❖ Hydrogen Bond Basic
- ❖ Dipolar And H-Bond Basic
- ❖ Moderate Dipolarity, Weak Hydrogen Bonding
- ❖ Weakly Dipolar, Weak or No Hydrogen-Bonding

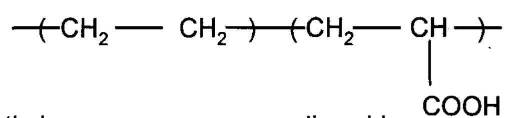
HYDROGEN BOND ACIDIC

Poly (4-vinylphenol-co-methyl methacrylate)
P4VPhcMMA



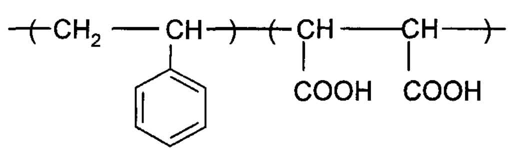
4-vinylphenol methyl methacrylate

Poly (ethylene-co-acrylic acid) (80/20)
PEcAA20



ethylene acrylic acid

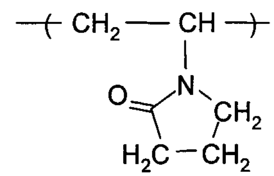
Poly (styrene-co-maleic acid)
PScMA-me



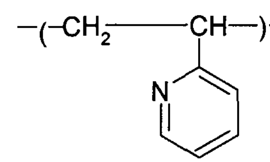
styrene maleic acid

HYDROGEN BOND BASIC

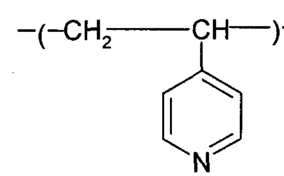
Poly N-vinylpyrrolidone (F)



Poly (2-vinyl pyridine)
P2VPy



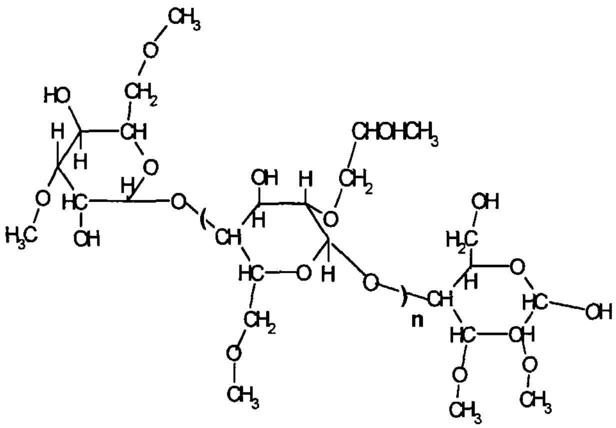
Poly (4-vinylpyridine)
P4VPy



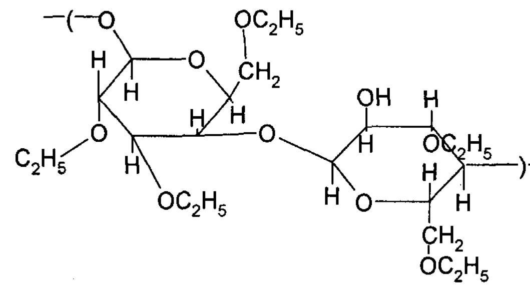
POLYMER SELECTION

DIPOLAR AND HYDROGEN BOND BASIC

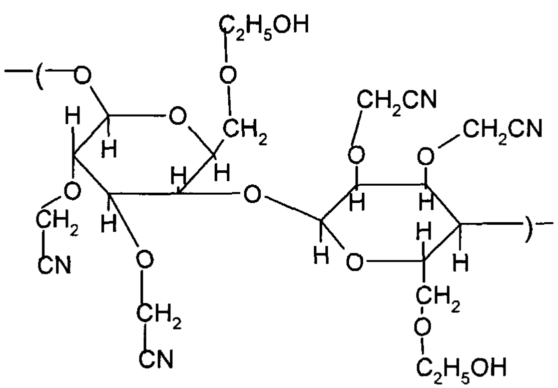
Hydroxypropyl methyl cellulose (C20)



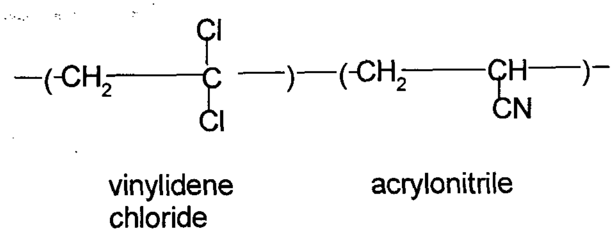
Ethyl Cellulose (EC)



Cyanoethyl hydroxyethyl cellulose (CR-EH)



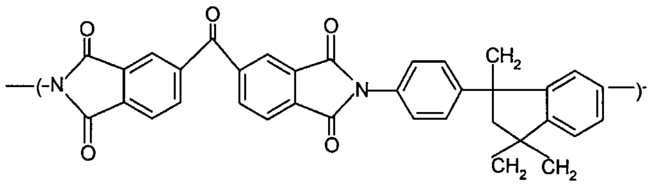
Polyvinylidene chloride-acrylonitrile (N)



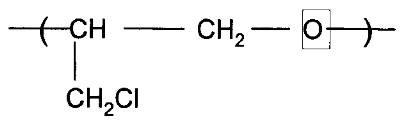
POLYMER SELECTION

MODERATE DIPOLARITY WEAK HYDROGEN BONDING

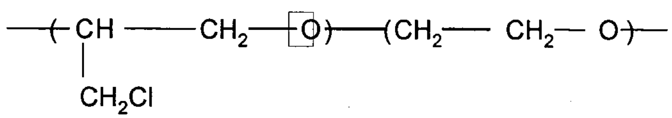
Soluble polyimide (Mat5218)



Polyepichlorohydrin (PECH)



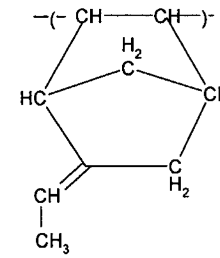
Poly (epichlorohydrin-co-ethylene oxide) (PECHcEO)



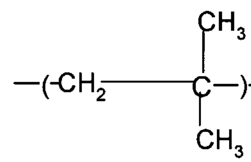
epichlorohydrin ethylene oxide

WEAKLY DIPOLAR, WEAK OR NO HYDROGEN-BONDING

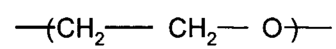
Ethylene-propylene diene terpolymer (EPDT)



Polyisobutylene (PIB_{400})

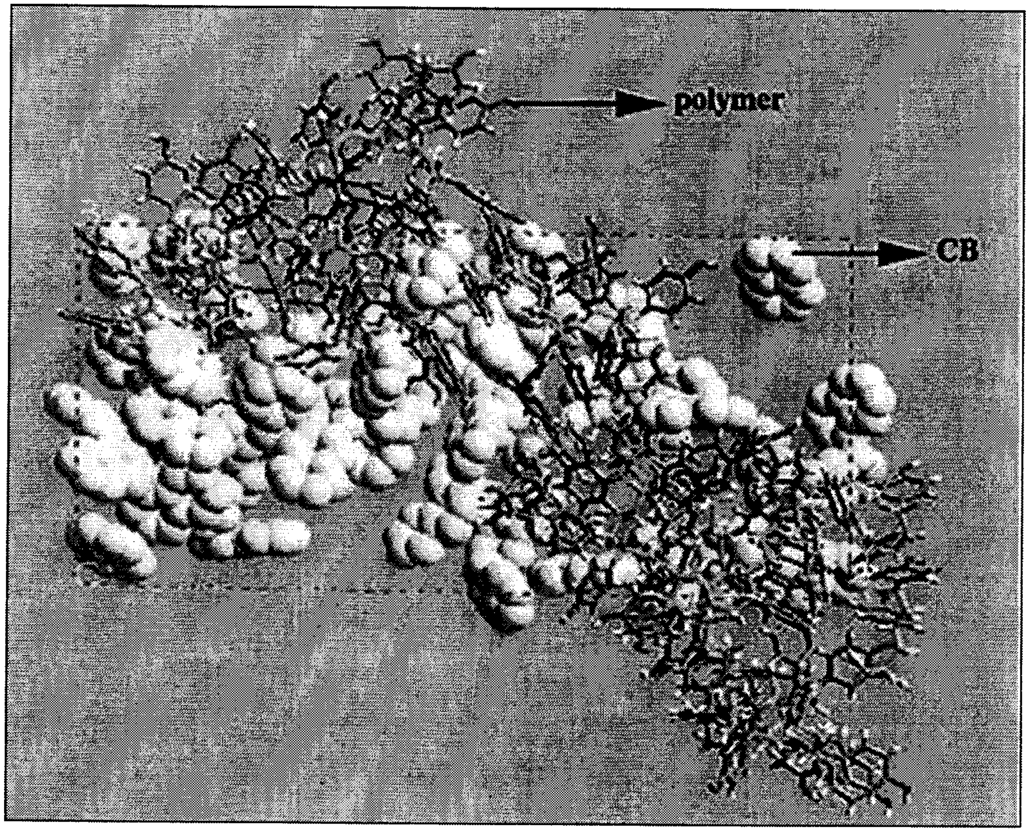


Polyethylene oxide (PEO_{600})



SENSOR ARRAY OPTIMIZATION

Model of Sensor and Array Response

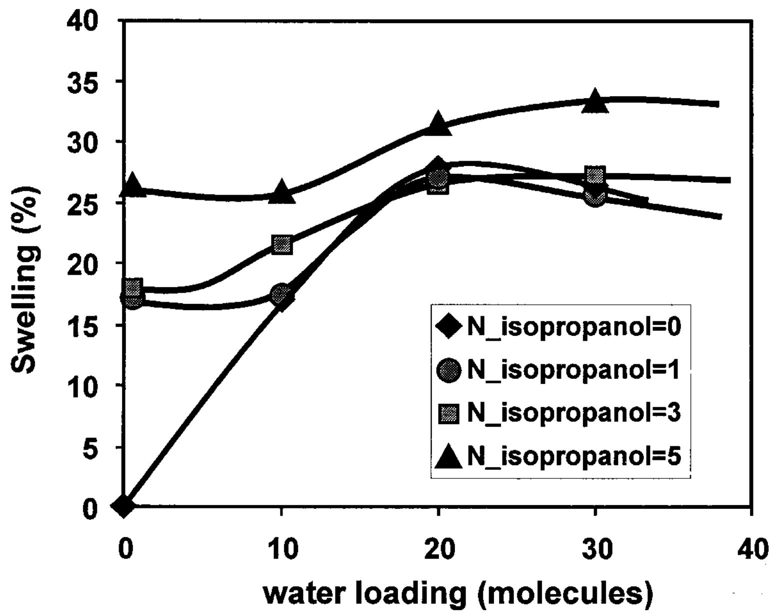


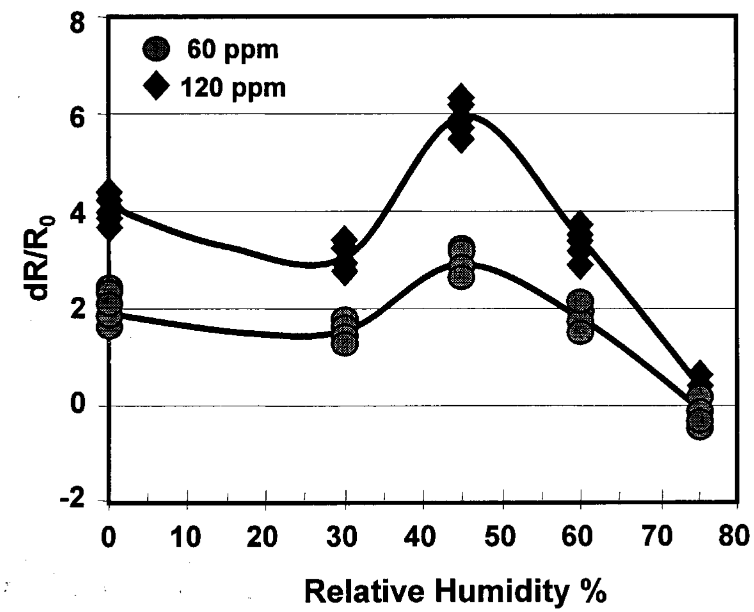
Structure of poly(4-vinylphenol)-CB composite film; structure equilibrated using molecular dynamics. Van der Waals, electrostatic and H-bonding energy terms will be analyzed in this structure in the presence of analyte molecules.

SENSOR ARRAY OPTIMIZATION

Model of Sensor and Array Response

PEO-water-isopropanol

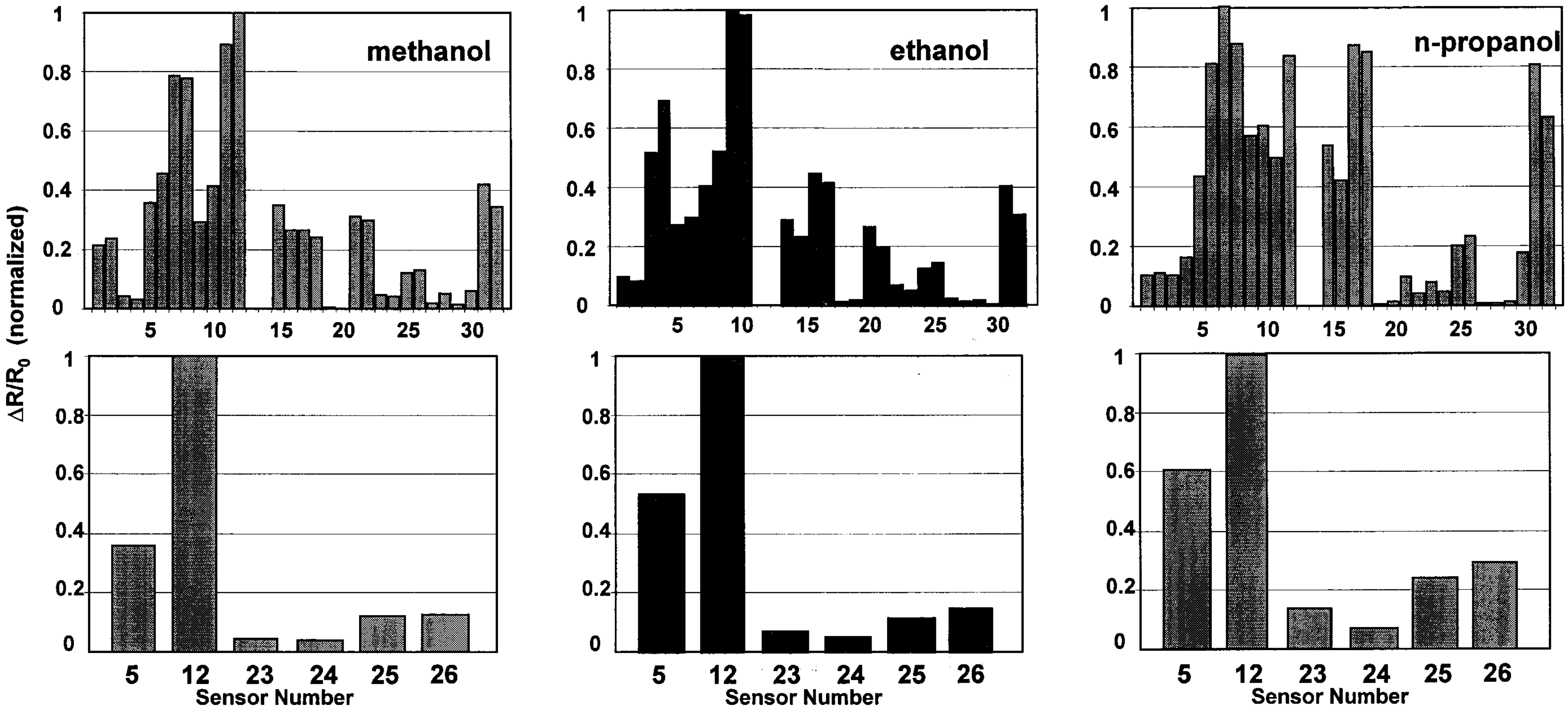




Modeled response (left) and measured response (right) show similar behavior.

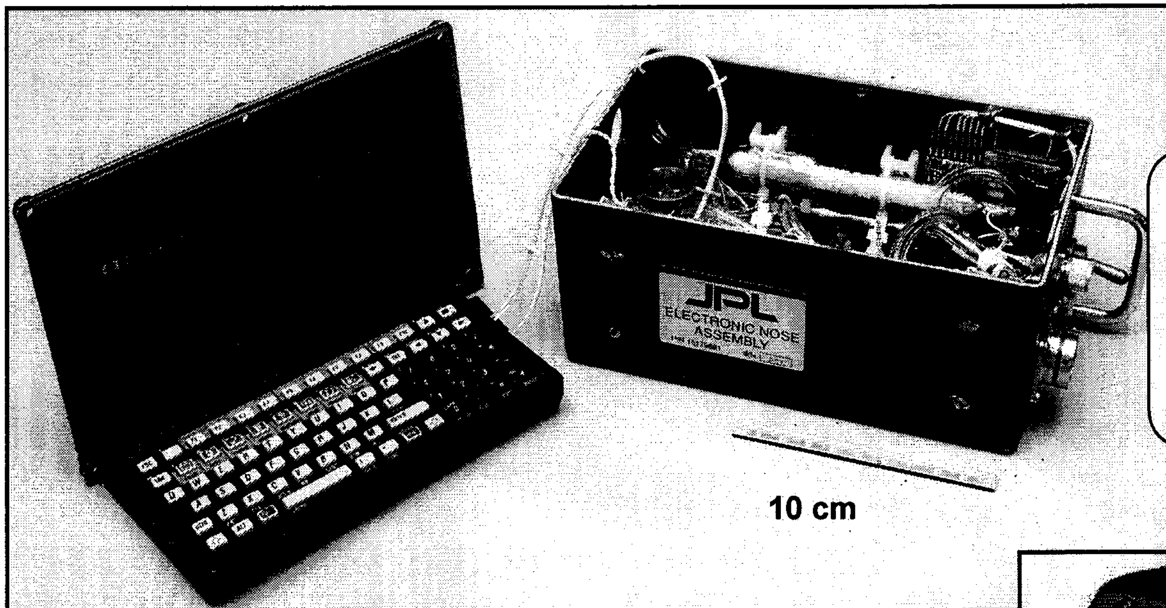
DATA ANALYSIS

Functional Group Classification



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.

HARDWARE AND DATA ACQUISITION SYSTEM



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

ISSUES/CHALLENGES REMAINING

- *Complete catalogue of temperature and humidity effects on sensors; incorporate into analysis software*
- *Complete model for sensor-analyte interaction; integrate with distance calculations to select array components; validate*
- *Include functional group classification in analysis software*
- *Fabricate and test new hardware and electronics*
- *Determine whether model can be used to classify unknown contaminants*
- *Train new sensor set to new analyte set*
- *Initiate Ground Testing & Blind Testing of device and software*

ACKNOWLEDGEMENTS

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