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Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose

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ABSTRACT

A miniaturized electronic nose has been constructed at JPL in collaboration with Caltech. This array of conductometric sensors has been trained to detect and quantify the presence of vapors in the air; the compounds detected have been found as contaminants in shuttle air. This device has potential application as a miniature, distributed device for monitoring and controlling the constituents in air.

INTRODUCTION

The ability to monitor the constituents of the breathing air in a closed chamber in which air is recycled is important to NASA for use in closed environments such as the space shuttle and the space station. At present, air quality is determined after the fact by collecting samples and analyzing them on the ground in laboratory analytical instruments such as a gas chromatograph-mass spectrometer (GC-MS). The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at part-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. Such an instrument is the Electronic Nose now under development at JPL and Caltech [1-3].

An electronic nose is an array of non-specific chemical sensors, controlled and analyzed electronically, which mimics the action of the mammalian nose by recognizing patterns of response to vapors. The sensors used here are conductometric chemical sensors which change resistance when exposed to vapors. The sensors are not specific to any one vapor; it is in the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be identified by the pattern of response of the array. Electronic Noses have been discussed by several authors, and may be applied to environmental monitoring and quality control in such wide fields as food processing, and industrial environmental monitoring [4,5].

A baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors may be deconvoluted, and contaminants identified and quantified by using a software analysis program such as pattern recognition and/or neural network.

At present, the best real time, broad band air quality monitor available in space habitats is the human nose. It is limited by human factors such as fatigue and exposure to toxins. Most existing chemical sensors are designed to detect specific molecules. Array-based sensing uses non-specific sensors in which the pattern and magnitude of response are used to identify and quantify the presence of contaminants. Array-based sensors are based on a biological model of "sniffing", detecting changes in odor, and can be trained to detect new patterns.

The overall goal of the program at JPL/Caltech is the development of a miniature sensor which may be used to monitor the breathing air in the international space station, and which may be coordinated with the environmental control system to solve air quality problems without crew intervention. Progress toward that goal will depend on the success of this portion of the Electronic Nose program, which is the development of a prototype system which will be the subject of an experimental test during a space shuttle flight in 1998.

THE ELECTRONIC NOSE DEVELOPMENT MODEL

The conductometric sensors used in the Electronic Nose (ENose) built at JPL are polymer films deposited on gold contacts. The films are made from polymers in which a conductive medium, carbon black, has been dispersed [2].

Presence of a contaminant in air is measured as a change in resistance in the polymer films. Sensor response is expressed as a ratio of change in resistance at time t to resistance at time t=0, $(R_t-R_0)/R_0$. Data are acquired on a Hewlett Packard HP200 LX palm top

computer using a program written for this purpose in LabWindows.

DESIGN OF SENSOR HEAD

Substrate and Sensing Films The sensor head of the Electronic Nose used in this experiment consists of 32 sensor positions arranged on 4 substrates, each with 8 sensor positions. The substrates were made using hybrid microelectronic cofired ceramic (alumina) processes. Electrodes and contacts were deposited as thick films using screen printing. The substrate layout and fabrication has been discussed in detail elsewhere [9]. A guard ring is used around each sensor to minimize cross-talk and sensor interaction. A sketch of a sensor chip is shown in Figure 1.

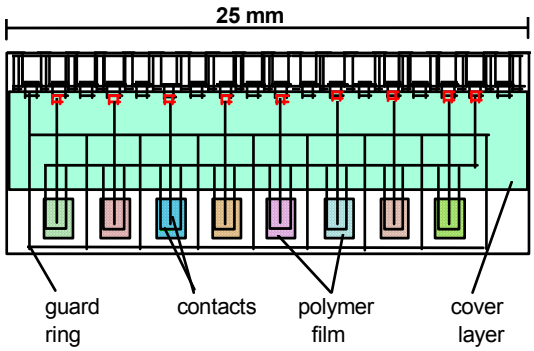

Figure 1: Sketch of the ceramic substrate chip containing eight sensors

The polymeric sensor films were made by depositing a solution of polymer mixed with carbon black to make a film 1 - 5 microns thick in contact with gold electrodes. 16 polymers were used in this experiment, four on each ceramic substrate. Each polymer was deposited in 2 positions on each chip, with the positions side-by-side to ensure that each sensor would see the same vapor environment. A thermistor is included on each chip and on the sensor head for temperature monitoring.

Temperature can be controlled from room temperature to 36°C using RuO_2 heaters deposited on the back of each chip in the ceramic fabrication process. The sensor resistance is sensitive to changes in temperature, so the ENose is operated with the sensors held at a constant temperature of 28°C.

The 16 polymers used are:

1. poly(2, 4, 6-tribromostyrene)
2. poly(4-vinylphenol)
3. poly (ethylene oxide)
4. polyamide resin
5. cellulose triacetate
6. poly (2-hydroxyethyl methacrylate)
7. poly (caprolactone)
8. vinyl alcohol/ vinyl butyral copolymer
9. poly (α -methylstyrene)
10. poly (vinyl chloride-co-vinylacetate)
11. poly (vinyl acetate)
12. poly (N -vinylpyrrolidone)
13. styrene/isoprene, block copolymer
14. poly (vinyl stearate)
15. methyl vinyl ether/ maleic acid
16. hydroxypropyl methyl cellulose

These polymers were selected by statistical analysis of the responses of 100 polymers to the set of contaminants listed in Table 1. Data for the statistical analysis were provided by Caltech [11]. The analysis selected the set of polymers which would result in the maximum difference in patterns of response.

Deposition of Films 160 mg of each polymer was dissolved in 15 mL of organic solvent. Solvents used were tetrahydrofuran (THF), acetone, dichloro methane, toluene or a mixture of solvents. 40 mg of carbon black was added to the solution, and dispersed by sonication. 1 - 3 μL of solution was pipetted onto the sensor area and allowed to dry in flowing, clean dry air while the sensor chip was held at 28°C. The resistance of the resulting films was in the range 1 -50 kΩ. Solution was added in increments of 1 μL until the desired resistance was reached. The use of polymer films as sensing media in an electronic nose has been discussed in detail by several authors, including the Caltech group working with JPL on this project [1-5].

ENOSE SYSTEM

A diagram of the ENose system used in this experiment is shown in Figure 2.

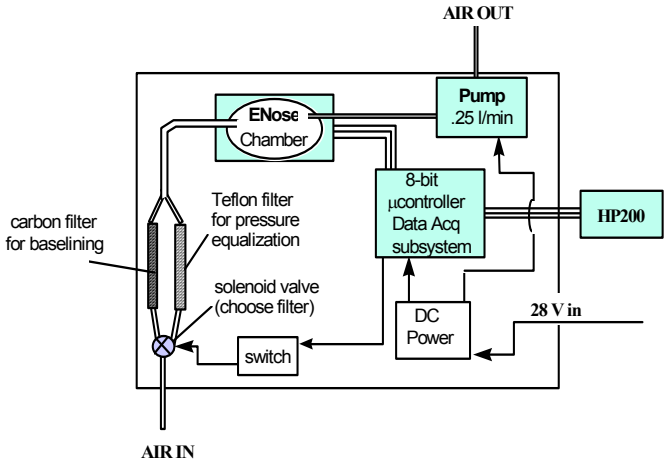

Figure 2: Diagram of ENose system.

Flowing air (.25 L/min) is pumped from the room into the sensor chamber of the ENose using a Thomas

model X-400 miniature diaphragm pump. The air is directed either through an activated charcoal filter, put in line to provide clean air baseline data, or though a dummy Teflon bead filter, put in line to provide a pressure drop similar to the charcoal filter. Solenoid valves are programmed to open the path to the charcoal filter and provide 30 minutes of clean air flow every four hours; otherwise, the air is directed through the Teflon bead filter. Air then enters the glass enclosed sensor head chamber where resistance is measured every 30 seconds, and then is returned to the room.

The experiment is controlled using a HP200 LX palm top computer and a circuit designed for the purpose [9,10]. The circuit is commanded by the HP 200 to operate the pump, to open and close the solenoid valve, and to acquire resistance data from the sensors by measuring the voltage at a current provided.

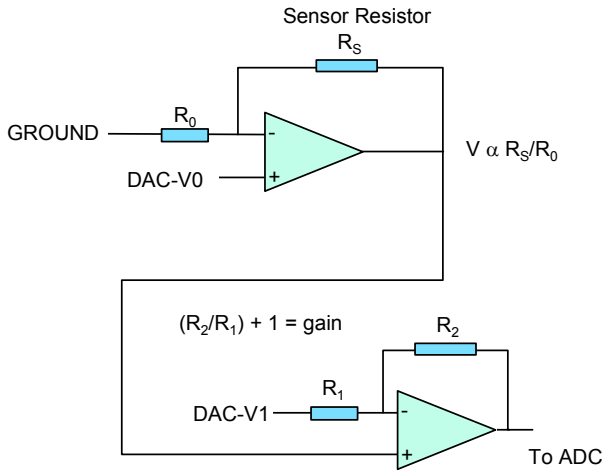

Figure 3: Diagram of ENose measuring circuit.

Data Acquisition and Control Data acquisition and device control are accomplished using a PIC 16C74A microcontroller. The Hewlett Packard HP 200 LX palm top computer is programmed to direct the microcontroller to open or close the solenoid valve which controls access to the charcoal or Teflon filter and to record sensor resistance. Typical resistance change for 10-50 ppm of contaminant is on the order of $2x10^{-4}$ (200 ppm resistance change), and may be as small as $x10^{-5}$. The data acquisition circuit is shown schematically in Figure 3. Small changes in resistance are measured using a 12 bit dual offset nulling amp, in which a known current is put through the sensor resistor R_S by DAC-V0 and fixed resistor R_0. The voltage across the sensor is measured with precision by subtracting DAC-V1, an experimentally determined voltage, from V_S, the voltage drop across the sensor resistor, R_S. The difference is then multiplied by a fixed gain, $(R_2/R_1) + 1$, where R_2 and R_1 are fixed resistors. For each measurement, the DAC and ADC are locked to the same voltage reference, where DAC is Digital to Analog Converter (12 Bit MAX538 and MAX539), and ADC is Analog to Digital Converter (12 Bit LTC1286).

Data are stored in flash memory in the HP 200, and are analyzed later using software designed for the task.

Data Analysis The goal of the ENose development is the construction of an air quality monitor capable of identifying the target compounds in Table 1 at less than SMAC levels. To accomplish this goal, we have developed data analysis software which recognizes the patterns of response of the target compounds. The data analysis software forms, from training data, a characteristic vector of sensor responses for each target compound. The characteristic vector for an unknown compound is expressed as a linear combination of the characteristic vectors of the target compounds via a least squares solution using pseudo inverses computed by the singular value decomposition algorithm. The result is a listing of what quantities of which target compounds compose the unknown compound. At present, unknown compounds are expressed as a combination of up to four contaminants. In the case of exposure to a single contaminant, additional verification of the analysis is obtained by a standard backpropagation-trained neural network and by linear discriminant functions.

Table 1 shows the minimum concentration detected for each of the target compounds using the software analysis program, and Figures 4 a-d show the linear region of concentration detection. The goal of this program was to quantify contaminants +/- 50% of delivered concentration; the shaded region in the plots describes the 50% error region. Humidity was controlled from 20 -60 % relative humidity during training. Water content of the air raises the resistance of the sensors, and can either be deconvoluted from the response as a separate vapor, or zeroed out of the measurement if humidity has not changed since the last baseline.

CONCLUSIONS

The miniaturized ENose designed and built at JPL has the capacity to detect a limited suite of contaminants at 1 hour SMAC levels with +/- 50% accuracy. Combinations of four or fewer vapors can also be detected and deconvoluted for identification and quantification. The ENose experiment will be performed on a shuttle flight in 1998 to verify its operation. The experiment will consist of several steps:

a. ENose response will be recorded over 5 - 8 days

b. Daily calibration of ENose to 2-propanol done by a crew member

c. Daily air samples ("grab samples") taken for post flight analysis at JSC

Compound	Detected on shuttle (ppm) [6]	SMAC (ppm) [7,8] 1hr	Detected at JPL (ppm)
alcohols			
methanol	< 1	30	25
ethanol	.5 - 5	2000	50
2-propanol	.4 - 4	400	50
methane	1 - 1	5300	3000
ammonia	0	30	20
benzene	< .1	10	10
formaldehyde	0	0.4	10
Freon 113	.1 - 1	50	50
indole	0	< 1	0.03
toluene	.4 - 4	16	15

Table I: Compounds detected by the ENose, Spacecraft Maximum Allowable Concentration of each compound , and minimum concentration detected by this model ENose.

d. Post flight analysis of data using software developed under this program

e. Post flight analysis of grab samples by gas chromatography/mass spectrometry

f. Post flight comparison of analyzed ENose response to ground analysis of grab samples.

At its present level of maturity, the ENose is not an analytical instrument, but can be used to monitor an environment against a baseline, which is determined at intervals using filtered air.

Long-duration space flight requires a high level of crew productivity in tasks other than habitat maintenance. Decentralization of habitat control and de-coupling of spacecraft from ground control requires a move to a distributed network of small sensors and actuators. The ENose can be programmed to monitor habitat air for the presence of contaminants which exceed the Spacecraft Maximum Allowable Concentration (SMAC) and to sound an alarm or actuate remedial action, a form of feedback control. ENose sensors lend themselves to distribution of several miniature arrays linked to a common computer for control and analysis. The presence of several arrays distributed about the habitat will allow early identification of areas requiring remediation

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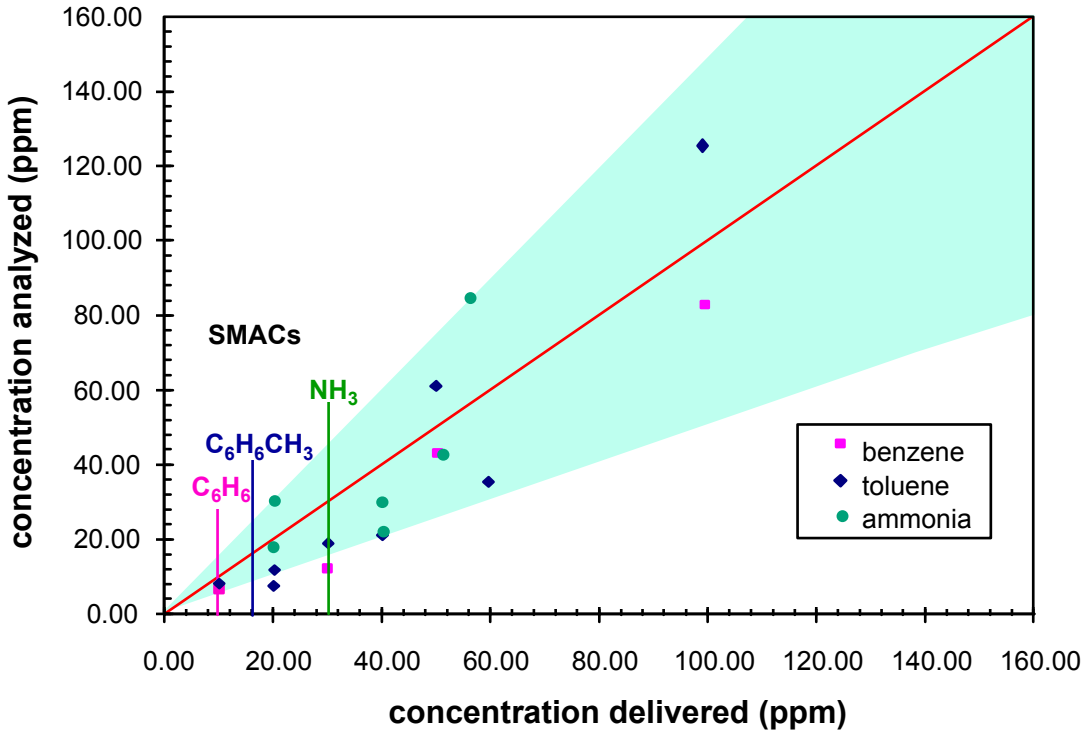

Figure 4a: Identification and Quantification of Benzene, Toluene and Ammonia. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.

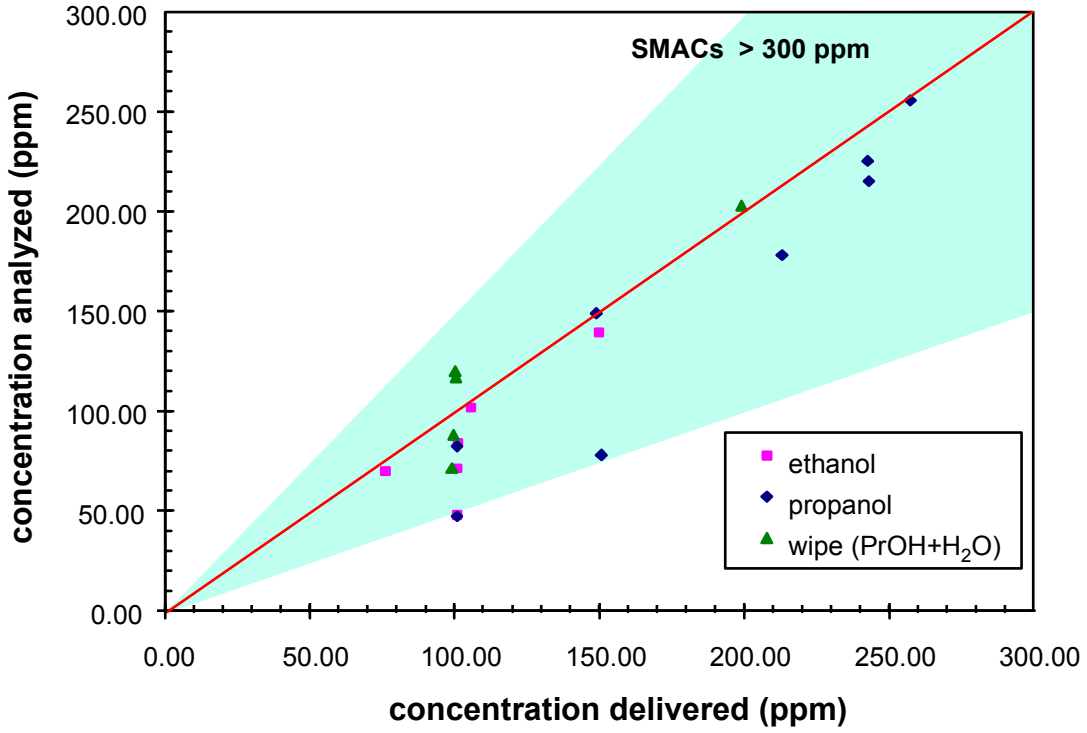

Figure 4b: Identification and Quantification of Ethanol, Propanol and the Propanol Wipe to be used as calibration. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.

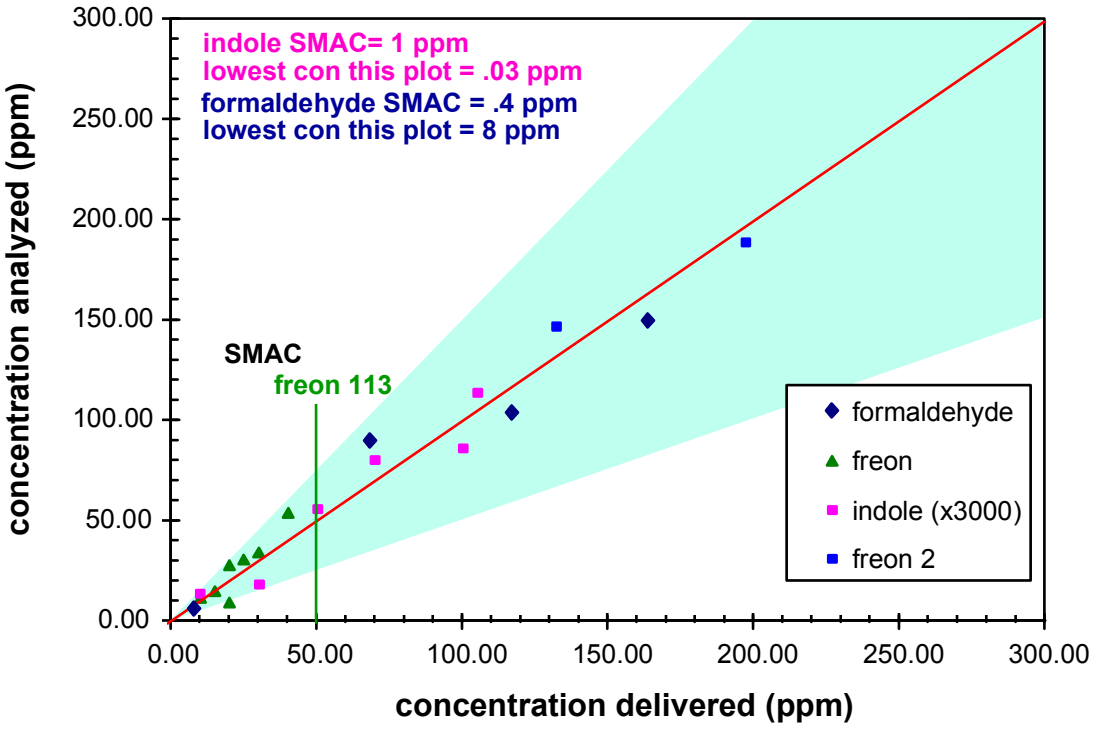

Figure 4c: Identification and Quantification of Indole, Freon 113 and Formaldehyde. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.

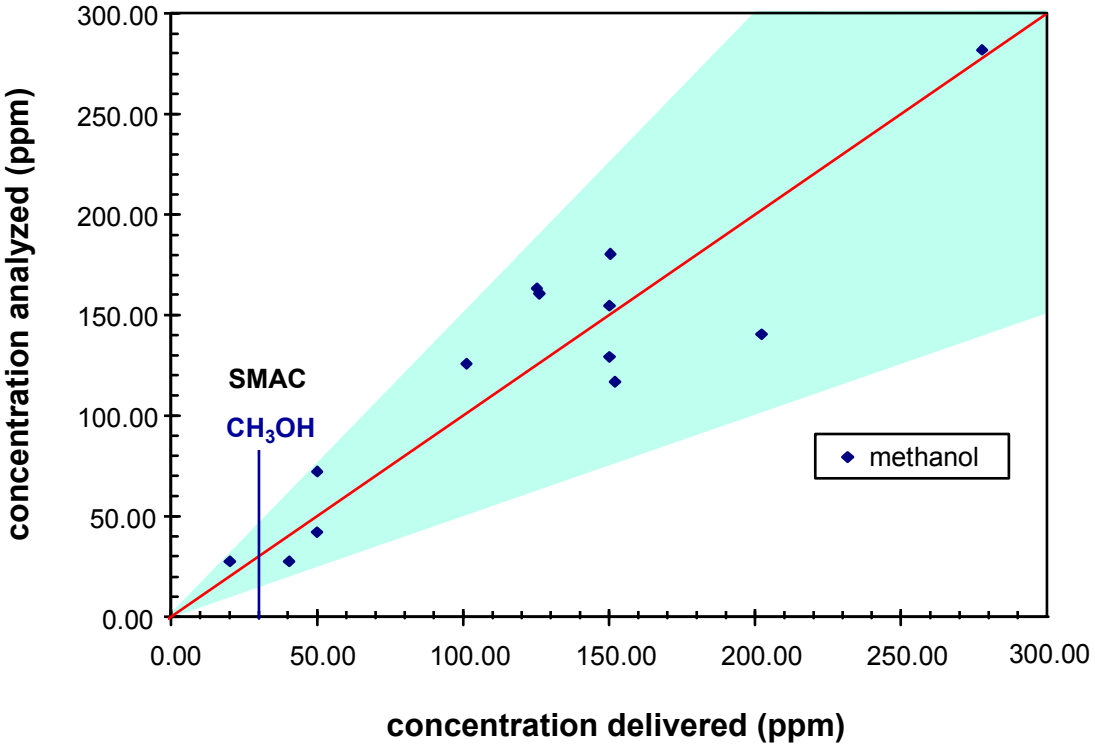

Figure 4d: Identification and Quantification of Methanol. The SMAC is marked on the plot. The shaded area is the +/- 50% target zone.