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**SURFACE ACOUSTIC WAVE (SAW) MICROSENSORS
TO MONITOR MULTI-COMPONENT VAPOR CHALLENGES
TO ADSORBENTS AND ADSORBENT-BASED AIR FILTRATION SYSTEMS**

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N. Lynn Jarvis

MICROSENSOR SYSTEMS, INC.
Springfield, VA 22151

July 1994

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PREFACE

The work described in this report was authorized under Contract No. DAAA15-90-C-1028. This work was started in May 1990 and completed in May 1991.

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SURFACE ACOUSTIC WAVE (SAW) MICROSENSORS TO MONITOR MULTI-COMPONENT VAPOR CHALLENGES TO ADSORBENTS AND ADSORBENT-BASED AIR FILTRATION SYSTEMS

1. INTRODUCTION

Even though carbon-based filters have been used for many years to provide protection against CW agents and other toxic vapors, there is still relatively little reliable data on their performance against multicomponent vapor challenges. This lack of adsorption data is due in large part to the non-availability of analytical instruments that can monitor in-situ, in real time, and at very low concentrations, the individual vapor components that are distributed between the adsorbed and vapor phases, especially in dynamic flow systems. The newly emerging chemical microsensor technologies, are providing new classes of very small, sensitive, and readily automated chemical vapor detectors, that offer novel and exciting approaches to the monitoring of multicomponent vapor challenges to an adsorbent based air filtration system.

The present study was undertaken to determine whether presently available chemical microsensors, such as the Surface Acoustic Wave devices, can meet the sensitivity limits necessary for monitoring selected vapors of interest to the Air Purification Branch of the U. S. Army Chemical Research, Development and Engineering Center. The specific vapor constituents are water, Freon 113, hexanol and perfluorocyclobutane. Ideally the chemical microsensor system would be able to monitor each individual vapor alone or in a multi-component vapor challenge.

2. OBJECTIVE

The overall objective of the present study was to develop a new and novel microsensor based approach to the monitoring of the individual vapor constituents in a multi-component vapor challenge to an adsorbent bed. It encompassed the design, fabrication, and evaluation of a chemical microsensor based analytical instrument capable of the in-situ, real time, fully automated monitoring of multicomponent vapor challenges to adsorbent based filtration systems. The vapors included in the present study were water, Freon 113, hexanol and perfluorocyclobutane. The goal for the detection limit of each vapor was:

Water	≈ 35 ppm (-50°C dew point)
Freon 113	≈ 1 mg/m ³
Hexanol	≈ 1 mg/m ³
Perfluorocyclobutane	≈ 1 mg/m ³

3. TECHNICAL APPROACH

The overall approach pursued in this study was basically as described in the proposal and summarized in the following tasks:

Task 1. Evaluation of SAW Coating and Sensor Performance.

Determine whether the present coatings for SAW devices are sufficiently sensitive and selective for monitoring multi-component vapor challenges to an adsorbent based filter.

Task 2. Determine Most Effective Instrumental Approach

If the present SAW coatings are not sufficiently sensitive or selective to the vapors included in this study, review other microsensor and/or instrumental approaches (including MSI proprietary sensors) and determine most effective for this application.

Task 3. Design and Fabricate a Microsensor-Based Vapor Monitor

Task 4. Evaluate the Microsensor-Based Instrument for Sensitivity and Selectivity to the Vapors Included in This Study.

4. RESULTS

Task 1. Evaluation of SAW Coating and Sensor Performance

MSI felt it would be most efficient and effective to first test the SAW sensors and coatings individually rather than design and construct a complete Four SAW Array Vapor Monitor before determining whether the individual coated sensors performed adequately for this application. The coatings selected for evaluation included poly(ethyleneimine), ethyl cellulose, a fluorinated polyol (FPOL), and polyisobutylene (PIB). It was anticipated that poly(ethyleneimine) would show high sensitivity to water vapor, while the ethyl cellulose would respond strongly to hexanol. From prior experience it was expected that Freon 113 and perfluorocyclobutane would each give a significant response on the FPOL and PIB coated SAW sensors.

In the initial proposal it was also proposed to evaluate thin layers of very finely divided activated carbon bonded to the SAW device surfaces, as a new approach to achieving very high sensitivity to organic vapors. As in the preliminary investigation, carbon coated SAW devices exhibited very high sensitivity to organic vapors, on the order of 1 mg/m³ or less; however, it was discovered that the carbon coatings were very difficult to prepare reproducibly or to control. The problem is associated with difficulty of adhering small carbon particles to the device surfaces. None of the procedures suggested in the proposal gave entirely satisfactory results. Thus we were unable to incorporate carbon coatings into this program.

For the coating evaluation study, 158 MHz dual SAW devices were used. One of the two SAW delay lines of each device was coated with the material to be evaluated while the second delay line was used as a reference to compensate for temperature and pressure fluctuations. The coated SAW devices were mounted on a standard circular electronic package that could "plug" into a receptor on an electronic circuit board containing the necessary RF and other support electronics. The output of the electronic package was an RF

signal whose frequency difference, Δf , was proportional to the vapor concentration. Each SAW sensor package had small, 1/8" diameter, vapor inlet and outlet tubes attached to a close fitting lid. Known concentrations of each vapor were passed over the sensors and the respective changes in frequency were noted.

The individual SAW sensors were exposed to water, Freon 113 and hexanol vapors, however, no perfluorocyclobutane was available for study at the time of these measurements. Of the three vapors evaluated at this point, only water vapor could be detected at the required concentration level [by the poly(ethyleneimine) coated SAW sensor]. The detection limits for both Freon 113 and hexanol were approximately two orders of magnitude higher the desired level. It was projected that the detection limit for perfluorocyclobutane would likewise be considerably higher than that required.

Results of the evaluation clearly show that the individual SAW sensors with their selective coatings did not have sufficient sensitivity to the vapors of interest, other than water vapor. It is apparent that a Four SAW Sensor Array using these best available coatings would not provide the required sensitivity, or possibly the selectivity either. However, there are several approaches that could be used to improve both sensitivity and selectivity.

Task 2. Determine Most Effective Instrumental Approach

The sensitivity of a Four SAW Array Vapor Monitor could in principle be significantly improved by going to SAW devices of higher operating frequencies. The immediate disadvantage of this approach is the relatively large cost, as well as the amount of time required, to design a new, smaller device, have it fabricated and then evaluate it. The cost involved would have greatly exceeded the funds available in the contract.

An alternative approach to improving SAW sensitivity would be to use a sample concentrator ahead of the SAW sensors. Sample concentration involves compressing the vapors present in a large volume of air into a much smaller volume for injection into the sensor. This can be accomplished by sampling ambient air at a high collection rate (e.g., 500 sccm) and passing the sample through an adsorbent tube that preferentially traps all the vapors but the very

low boiling compounds. The adsorbent tube is then heated (e.g. 140°C) to vaporize the trapped vapors which are then injected into the sensors, using scrubbed air as the carrier gas, at a much lower rate of flow (e.g., 20 sccm). The enrichment factor of the sample concentration procedure can be adjusted by varying the time of sampling at the higher flow rate. The practical limits for sample concentration are a function of such parameters as the adsorbent used, the bed depth, the vapors to be concentrated, and desorption temperature. Sample concentration factors of 50X to 100 X can be obtained by this technique.

Thus in principle the sensitivity of a Four SAW Sensor Array could be increased sufficiently to meet the required detection limits, but only marginally so. However, with SAW sensors that are only marginally sensitivity it will be difficult to obtain effective vapor selectivity at low concentrations, as the algorithms used to identify specific vapors depend upon measuring the ratios of the specific SAW signals. When the signals are all small (e.g., the signal to noise ratios are small) the ratios between these signals cannot be determined with good precision.

An alternate procedure to the use of a Four SAW Sensor Array, with a data analysis algorithm for obtaining high selectivity, would be to use a simple gas chromatographic column ahead of the microsensor and select the various vapors to be analyzed based on their retention times on the column. Using this basic approach it should be possible to monitor a number of the compounds of interest simultaneously with a single instrument, by careful selection of GC column packing, carrier gas flow rate, column temperature, etc. It is also possible, using the GC approach, that a microsensor other than a SAW device could be used as the detector, one that would have better sensitivity for this application. Microsensor Systems, Inc. has several proprietary chemical microsensors that could be used.

Considering the limited sensitivity of SAW sensors for the compounds included in this study, as described above, the decision was made to pursue the GC analytical approach, using the most sensitive microsensors available as the detectors. The design and fabrication of the microsensor based instrument will be described in the following task.

Task 3. Design and Fabricate a Microsensor-Based GC Vapor Monitor

The basic concept of the design was to use a simple, temperature controlled gas chromatograph to separate the several vapors according to their retention times on the column and then measure them quantitatively with a sensitive, yet low maintenance, solid state microsensor. A microcomputer is used to operate the instrument and to analyze and store the sensor signals. A schematic of the instrument is shown in Figure 1.

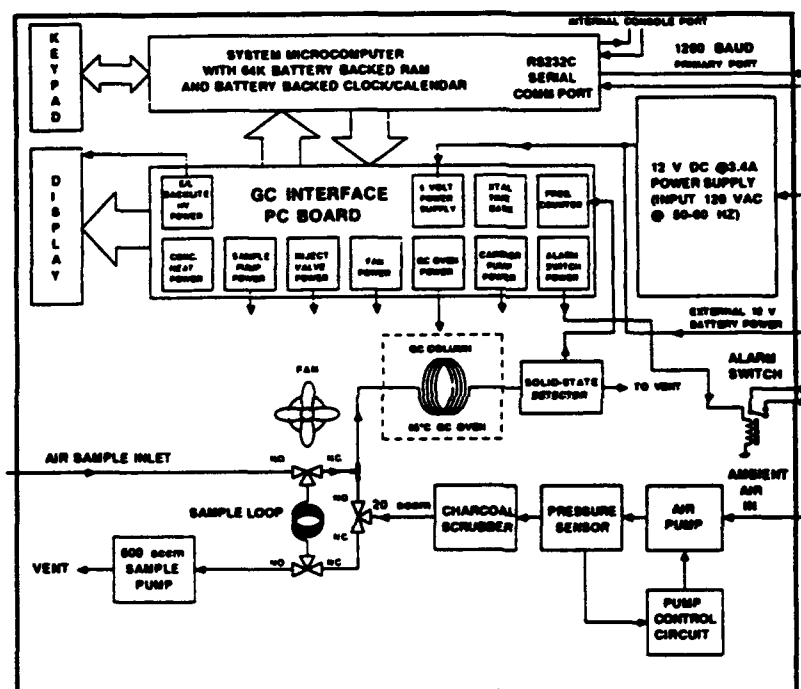


Figure 1. Schematic Diagram of Microsensor Based GC Vapor Monitor.

Vapor samples are automatically drawn into the a 2 cc sample loop by a small onboard air pump, although if desired the sample can also be injected by a syringe. The system valves are then reset and the vapor in the sample loop is injected into the chromatographic column using scrubbed air as the carrier gas. All pumps, valves, and system operations are controlled by the onboard microcomputer. Once the chromatogram is completed, the microcomputer determines the baseline corrected heights for all peaks with pre-selected

retention times corresponding to the vapors to be monitored. The peak heights can be converted to concentrations using calibration tables stored in memory. When initially turned on, the system requires 20 to 30 minutes for the oven to become stable at its operating temperature, before going into run mode. During warm-up the carrier pump and detector are automatically checked for proper operation. Also during warm-up the operator can modify system parameters and generate reports. A typical system automatic operating schedule is shown in Figure 2.

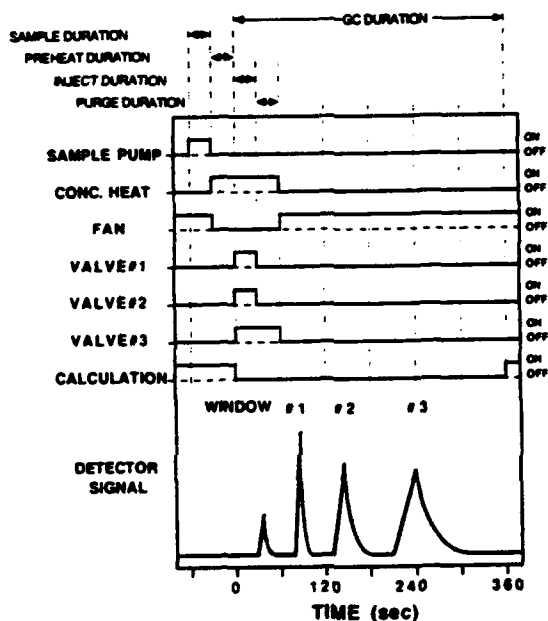


Figure 2. Typical System Operating Schedule.

The isothermal chromatographic column used in the instrument is a 3 foot, 1/8" diameter, packed column, using HAYESEP Q as the column packing. The column operates at 100°C. The carrier gas is generated from ambient air using a small pump and an activated carbon scrubber to remove impurities. The pressure in the scrubber tank is held constant by means of a silicon chip pressure sensor and a feedback control loop. The carrier gas pump adds air to the scrubber tank as required. The duty cycle of this pump is low, less than 20%.

The solid state detector use in the instrument is an MSI proprietary device that is very rugged and guaranteed for 5 years of operation. Vapors eluting from the GC column adsorb onto detector, with the

vapor/detector interaction resulting in a signal whose frequency is related to the vapor concentration. Because the detector has a non linear response, the system is designed for five point calibration and the software is written so that instructions appear on the front panel display to guide the user stepwise through the calibration process. The data is automatically fit to a second order polynomial which is used to convert frequency data to concentration values. The calibration table and algorithm are stored in memory. Subsequent re-calibrations only require a single point span check. If the re-measured concentration of a vapor standard differs from the known concentration, a system response factor, R, can be adjusted so that the measured concentration equals the known value. This can be done automatically by the microprocessor.

The weight of the final instrument is approximately 12 pounds and its dimensions are 3.5" x 14.5" x 13". The measurement cycle of the instrument is approximately 5 minutes, although this can be varied depending upon the measurements to be made. The system actually operates at 12 volts and has an onboard power supply that accepts 120VAC, 60 HZ power. The power required is 40 W maximum, and 10 W average. The microcomputer was programmed to store up to 8 hours of the most recent data, which can be reported in several formats. There is also an RS232C port to interface the system to a computer, a serial printer, or other electrical network as desired. The system can be completely controlled remotely by a computer terminal and the RS232C port.

Task 4. Evaluation of Microsensor-Based GC Vapor Monitor

The Microsensor based instrument designed and built in Task 3 was first evaluated for sensitivity, selectivity, and reproducibility of performance with water vapor and Freon 113. The goal was to detect water vapor at a dew point equivalent of -50°C (≈ 35 ppm) and Freon 113 at ≈ 1 mg/m³. Results of the evaluation for water and Freon 113 are discussed.

Water Vapor

Water vapor samples with concentrations in the range of 300 to 18,000 ppm were prepared by saturating clean, dry, zero air with water (bubbling it through a column of water at constant

temperature) and diluting it sequentially with additional zero air, using precision flow controllers. The individual water vapor samples were collected in standard gas sample bags which were then connected to the inlet of the instrument. The onboard pump automatically withdrew a water vapor sample from the sample bag at a rate of 25 sccm for 12 seconds, which purged and filled a 2 cc sample loop. A 36" long, 1/8" diameter, packed column was used in the Vapor Monitor. The column packing was HAYESEP Q and the column temperature was maintained at 100°C. The water vapor sample was injected into the GC column with scrubbed air carrier gas at a flow rate of 40 cc/min.

The vapor concentrations used (in parts per million) are shown in Table 1. Two to four runs were made at each concentration to assure reproducibility. Results of the individual runs, as well as the average values, are also given in Table 1 as Peak Heights in Hertz.

Table 1. Calibration Data for Monitor Response to Water Vapor

Water Vapor Concentration (ppm)	Peak Heights	
	Individual Measurements (Hz)	Average (Hz)
347	155, 135, 153, 141	146
869	181, 173, 173, 170	174
1738	234, 233	233
4347	477, 482, 494	484
5216	704, 687, 674	688
8693	882, 900, 873, 909	891
12171	997, 1008, 996	1000
17387	1155, 1181	1175

The Vapor Monitor was found to have an intrinsic noise level of 2 to 3 Hertz, thus a signal of 5 Hertz could be easily detected and measured. By extrapolation of the signal for water vapor at 347 ppm, a 35 ppm water vapor sample should give a signal of approximately 15 Hertz, which would be equivalent to a 5:1 signal to noise ratio and thus readily detected and quantified. Thus the Microsensor-Based Vapor Monitor does meet the goal of detecting water vapor at a dew point equivalent of -50°C ($\approx$ 35 ppm). If a sample concentrator were to be used in the instrument in place of the sample loop, the detection limit could be further reduced by 50X to 100X. The overall repeatability of the instrument for each concentration is seen to be on the order of 5%.

Typical chromatograms for each water vapor concentration are shown in Figures 3 (a) to 3 (h). A pronounced shift in the retention time, as well as in the shape of the chromatogram, was observed with increasing water vapor concentration. At concentrations above 2,000 ppm the retention time, as defined as the highest point of the GC peak, shifted from 24 seconds to 16 seconds and the peak became much narrower. As the onboard computer was programmed to use peak height rather than peak area to quantify vapor concentration, the observed changes in peak character with concentration would effect the shape of a calibration curve. Also, as mentioned above, the proprietary sensor itself is nonlinear.

The combined effect of sensor nonlinearity and change in GC peak character with concentration is shown in the calibration curve for the microsensor based Vapor Monitor (Figure 4). The curve shows that sensitivity does decrease at higher vapor concentrations. Even so, water vapor should be easily monitored over a wide range of concentrations, from below 35 to over 20,000 ppm. The shape of the curve also shows why the proposed multipoint calibration scheme would be essential in order to use the Vapor Monitor effectively.

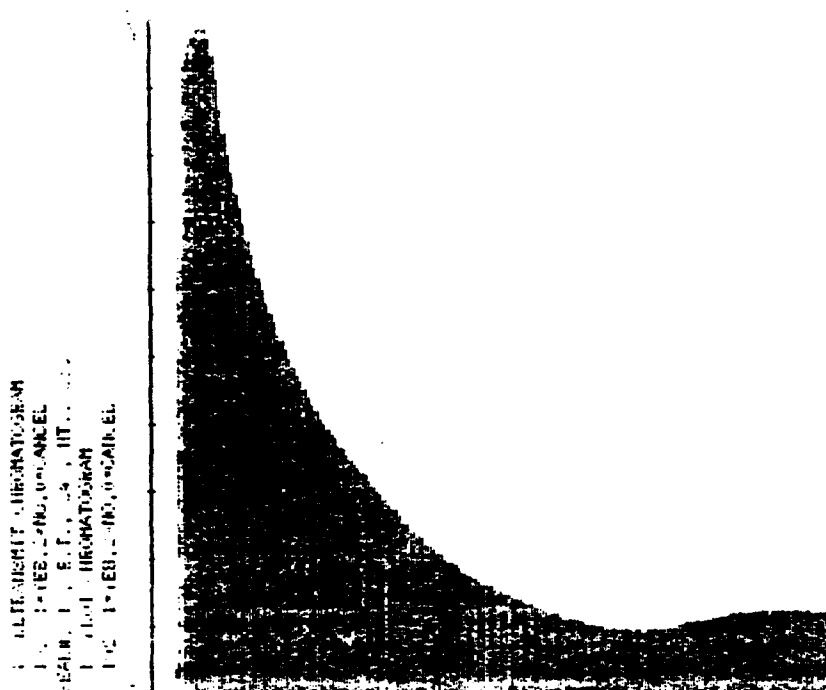


Figure 3. (c) Monitor Response to 1738 ppm Water Vapor
 (Retention Time 24 sec., Peak Height 233 Hz)

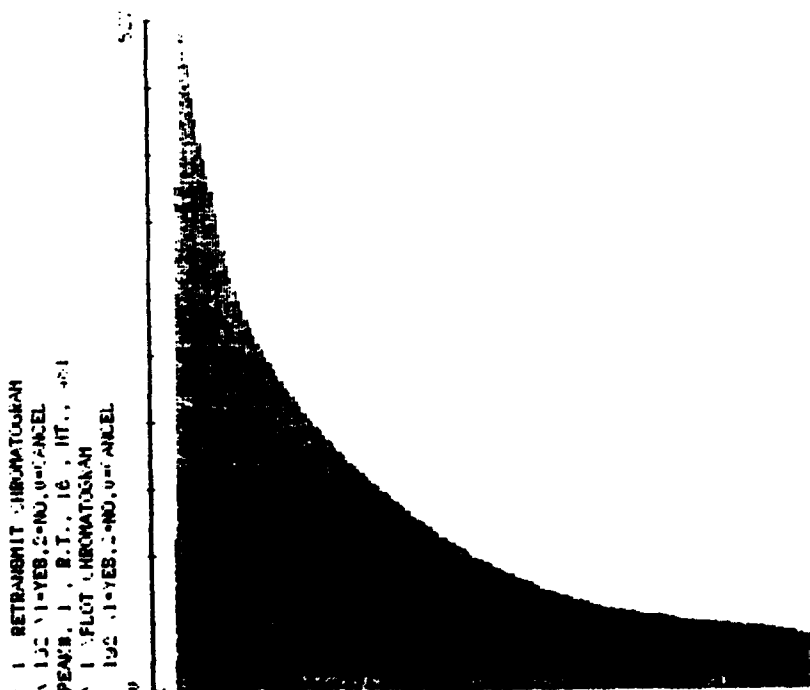
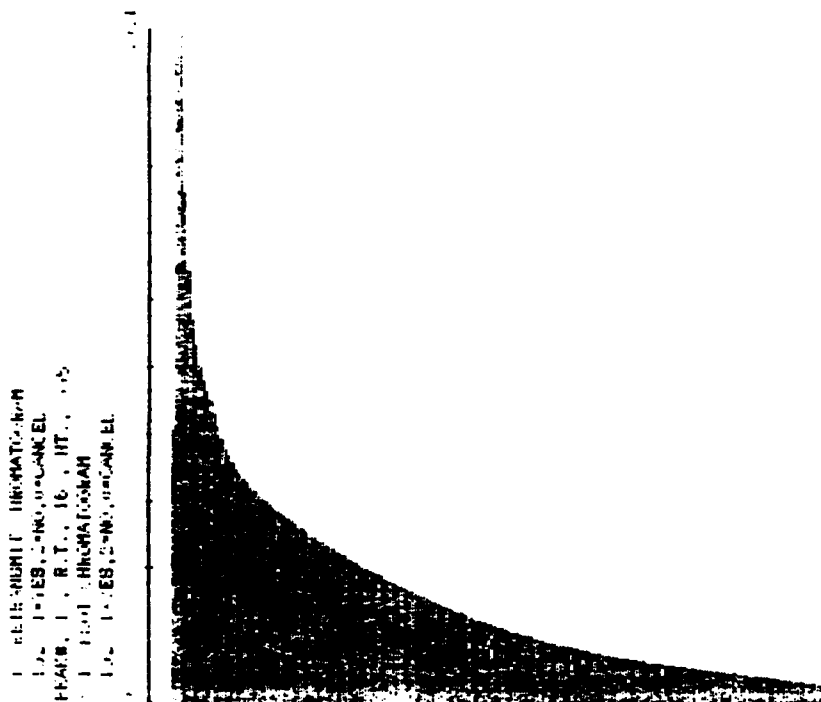
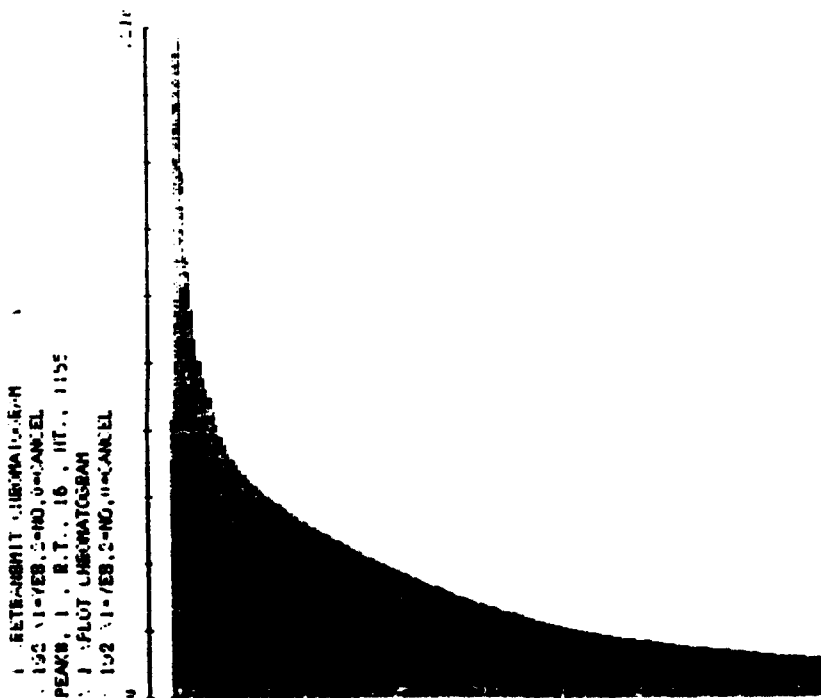


Figure 3. (d) Monitor Response to 4347 ppm Water Vapor
 (Retention Time 16 sec., Peak Height 482 Hz)



**Figure 3. (g) Monitor Response to 12171 ppm Water Vapor
 (Retention Time 16 sec., Peak Height 996 Hz)**



**Figure 3. (h) Monitor Response to 17387 ppm Water Vapor
 (Retention Time 16 sec., Peak Height 1155 Hz)**

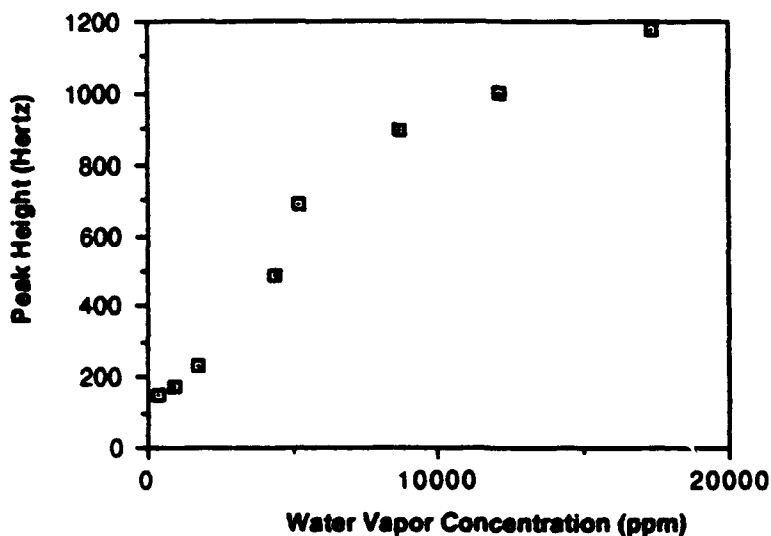


Figure 4. Calibration Curve for Water Vapor

Freon 113

Freon 113 samples in the concentration range of 10 to 10,000 ppm were prepared by dilution of a 10,000 ppm Freon 113 standard in zero air using precision flow controllers. The Freon vapor samples were injected into gas sample bags which were then connected to the gas inlet on the front panel of the Vapor Monitor, for injection into the 2 cc sample loop. As with water vapor, a 36" long, 1/8" diameter, packed column was used to separate the vapor components. The column packing was HAYESEP Q and the column temperature was maintained at 100°C. The Freon samples were injected into the GC column using scrubbed air carrier gas at a flow rate of 40 cc/min.

The Freon vapor concentrations are shown in Table 2 in parts per million. Results of the individual runs, as well as the average values, are given as Peak Heights (in Hertz). The intrinsic noise level of the Vapor Monitor remained 2 to 3 Hertz, thus the minimum signal that could be detected at a 3:1 noise level was approximately 6 Hertz.

Table 2. Calibration Data for Monitor Response to Freon 113 Vapor

Freon 113 Concentration (ppm)	Peak Heights	
	Individual Measurements (Hz)	Average (Hz)
10	5, 6, 5	5
20	22, 18	20
30	48, 44, 49	47
100	125, 113, 136	125
200	243	243
1,000	1700, 1820, 1721, 2074	1828
10,000	22559, 23160, 22166 23262	22786

From Table 2 it is apparent that the minimum detectable Freon 113 vapor concentration is about 10 ppm, using the Vapor Monitor in the sample loop configuration. The concentration of 10 ppm is equivalent to about 70 mg/m³. Thus the system, as configured, is 70X above the target of detection limit of 1 mg/m³; however, if a sample concentrator were used in place of the sample loop the 1 mg/m³ detection limit could be achieved. With a sample concentrator in place of the 2 cc sample loop, the detection limit of the Vapor Monitor for Freon 113 can be readily reduced by 50X to 100X.

Typical chromatograms for Freon 113 vapor at concentrations of 20, 30, 1000 and 10000 ppm are shown in Figures 5 (a) to 5 (d). The GC peaks for Freon 113 were well separated from the water peak, but were considerably broader. Their retention times also appeared to shift to lower values at the higher concentrations, but could be easily monitored within a given retention time window. The calibration curve for Freon 113 is shown in Figure 6, as a log-log plot to better show the data over the four-fold concentration range.

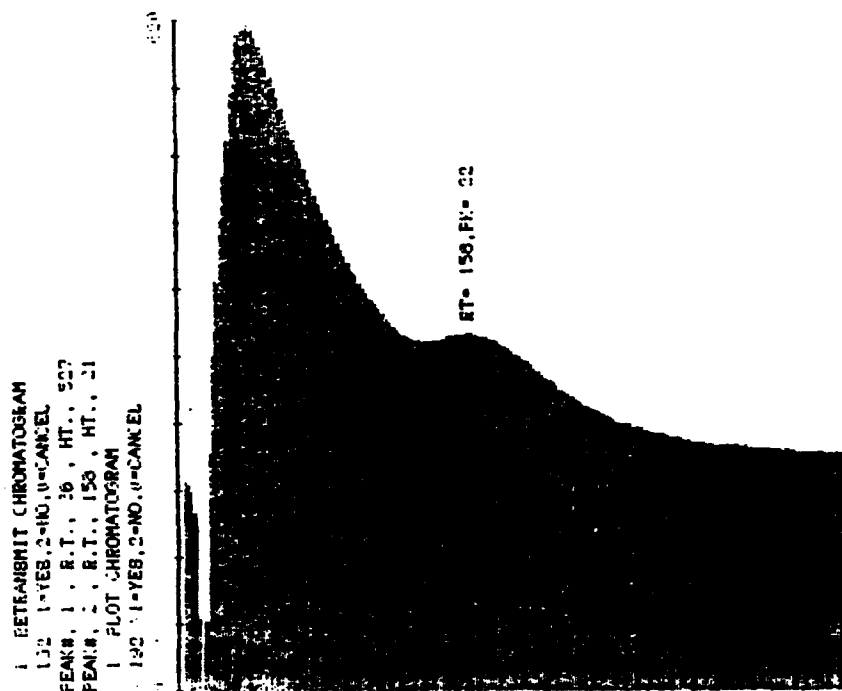


Figure 5. (a) Vapor Monitor Response to 20 ppm Freon 113
 (Retention Time 158 sec., Peak Height 21 Hz)

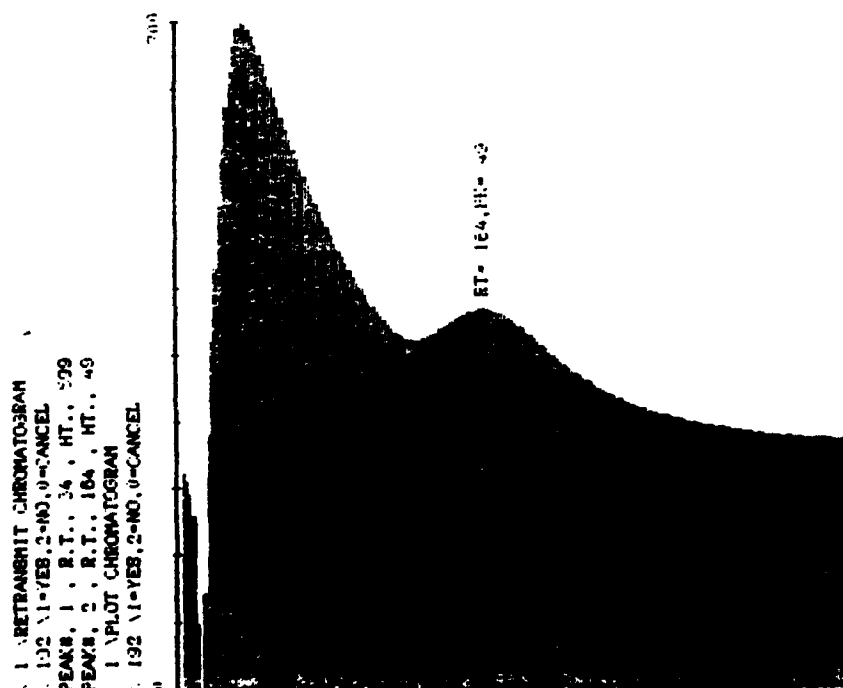


Figure 5. (b) Vapor Monitor Response to 30 ppm Freon 113
 (Retention Time 164 sec., Peak Height 49 Hz)

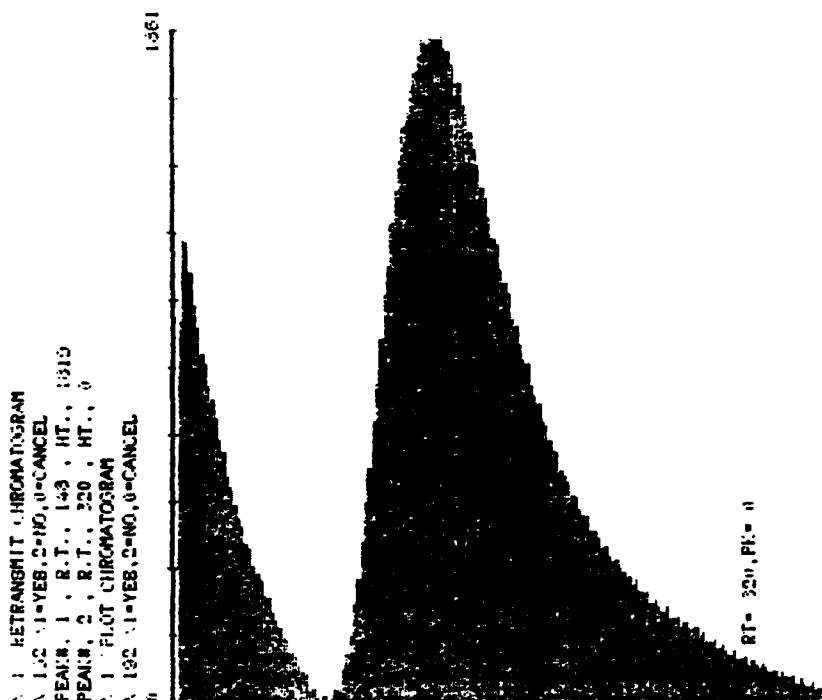


Figure 5. (c) Vapor Monitor Response to 1000 ppm Freon 113
 (Retention Time 148 sec., Peak Height 1819 Hz)

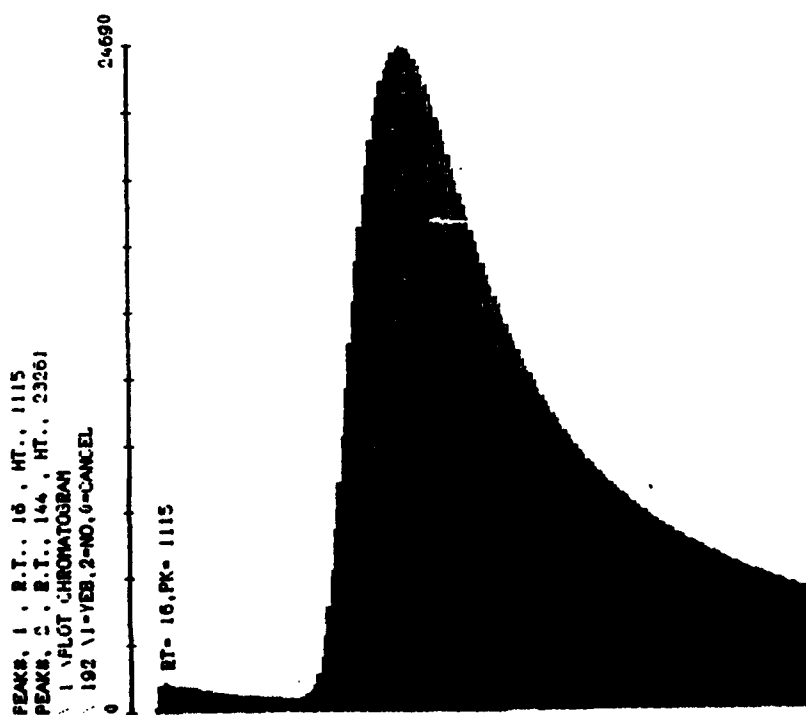


Figure 5. (d) Vapor Monitor Response to 10000 ppm Freon 113
 (Retention Time 144 sec., Peak Height 23261 Hz)

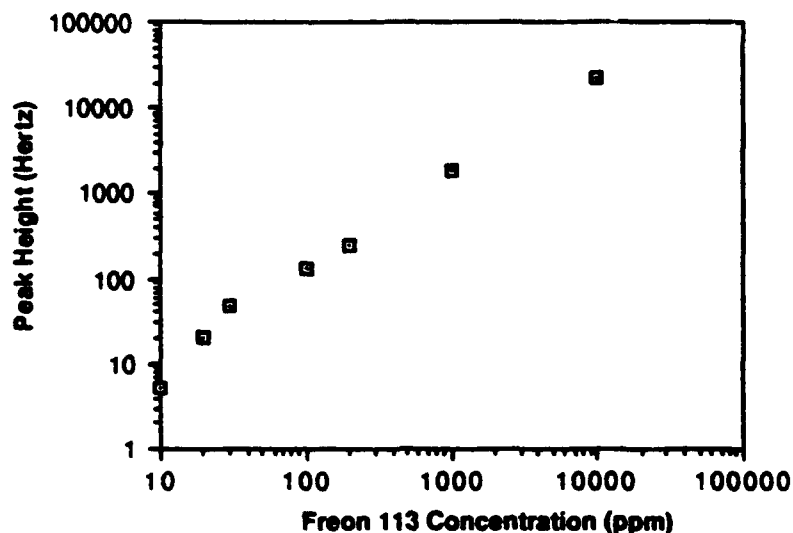


Figure 6. Calibration Curve for Water Vapor

Hexanol Vapor

To determine the detection limit for hexanol, samples of hexanol headspace vapor at room temperature were injected by syringe into the sample loop of the instrument. The vapor pressure of hexanol at room temperature (25°C) is 1 mm of Hg, thus the headspace concentration is approximately 1300 ppm (v) or 5300 mg/m³. A typical chromatogram for hexanol vapor is shown in Figure 7. The hexanol peak had a retention time of 268 on this column and the peak heights for repeat runs varied from 4300 to 4400 Hertz. The signal was therefore about 0.8 Hertz/mg/m³. With an intrinsic noise level for the Vapor Monitor of 2 to 3 Hertz, the minimum signal that can be detected at a 3:1 noise level is on the order of 6 Hertz. Thus the Vapor Monitor in the sample loop configuration will detect hexanol at about 10 mg/m³, somewhat above the required 1 mg/m³. However, if the sample loop were replaced by a sample concentrator, the detection limit will be on the order of 0.5 mg/m³. The retention time of 268 seconds for hexanol is well removed from the retention times for water and Freon 113, approx. 24 and 160 seconds, respectively. The the Vapor Monitor, using the 3 foot HAYESEP Q column, and the GC conditions described above, should therefore be able to detect and monitor these three gases simultaneously.

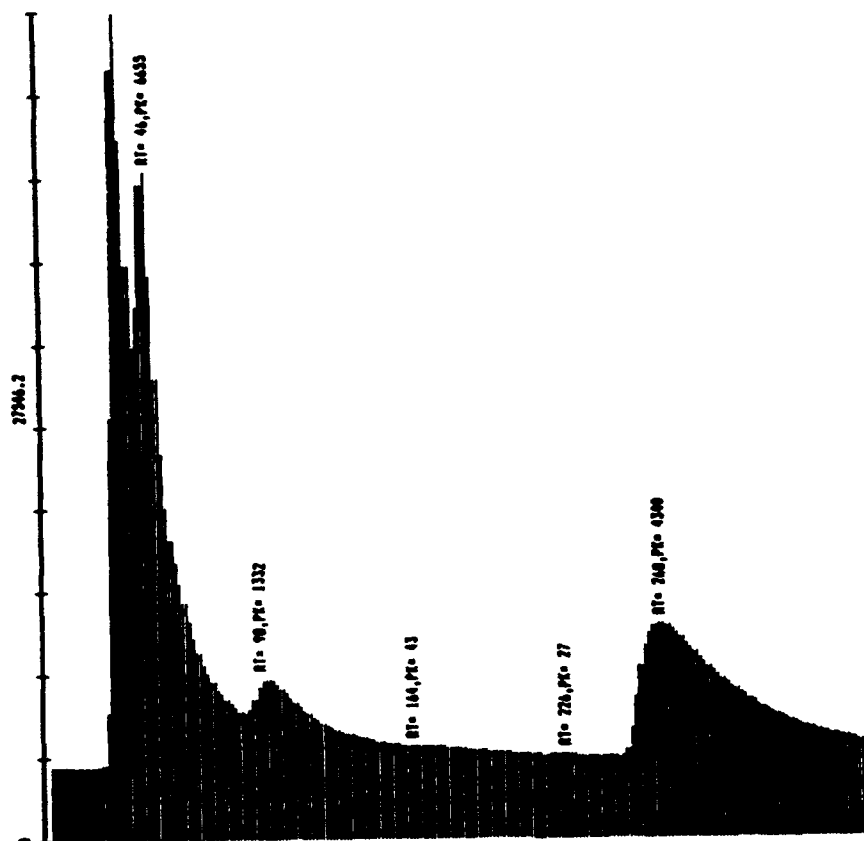


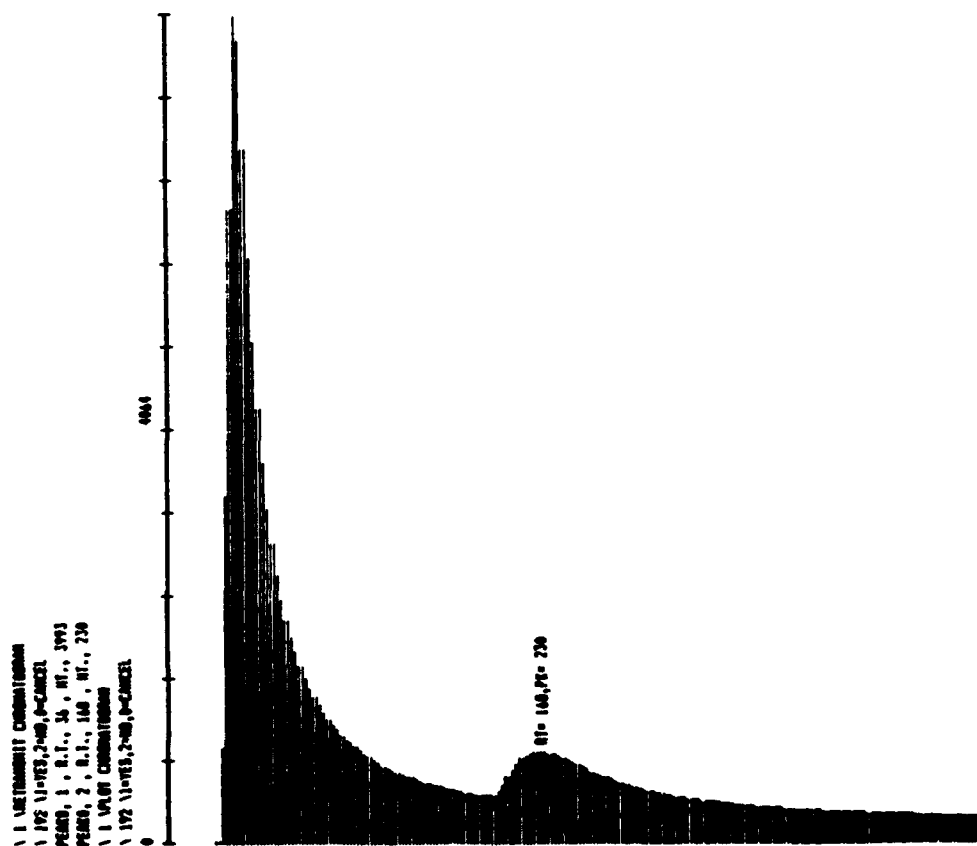
Figure 7. Vapor Monitor Response to approx. 5400 mg/m³ Hexanol Headspace Vapor (Retention Time 268 sec., Peak Height 4340 Hz)

Perfluorocyclobutane Vapor

To determine the detection limit of the microsensor-based Vapor Monitor for perfluorocyclobutane, the instrument was taken to the laboratories of the Air Purification Branch at CRDEC, where samples of the gas were available. A sample of perfluorocyclobutane was placed in a gas sample bag with a septum fitting. A small sample of the gas was withdrawn by syringe and then further diluted in the syringe before injection into the sample loop of the instrument. A typical chromatogram for perfluorocyclobutane is shown in Figure 8, for a 100:1 dilution (approximately 10,000 ppm). The retention time for perfluorocyclobutane was 36 seconds and the average peak height for repeat runs was about 4,000 Hertz.

The system response was therefore about 0.4 Hertz/ppm of perfluorocyclobutane, or about 0.04 Hertz/mg/m³, at a concentration

The retention time of 36 seconds for perfluorocyclobutane is very close to that for water vapor (Figure 3), thus it will not be possible to detect and monitor water and perfluorocyclobutane simultaneously.



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5. SUMMARY OF RESULTS

Results of the above study showed that the most effective microsensor-based instrument for monitoring multi-component vapor challenges to an adsorbent based air filtration system would be one in which an appropriate GC column is used ahead of the sensor to separate the individual components before injection into the sensor. Such an instrument was designed and built, using a 2 cc sample collection loop, a 3 foot, 1/8" diameter, packed column, using HAYESEP Q as the column packing. Scrubbed air was used as the carrier gas and a Microsensor Systems proprietary sensor was used as the GC detector. The column temperature was maintained at 100°C and the gas flow rates adjusted to optimize vapor separation. Water vapor, Freon 113, hexanol and perfluorocyclobutane were studied as the challenge vapors.

Results of the evaluation of the Vapor Monitor are given in the following table:

<u>Vapor</u>	<u>Required Detection Limit</u>	<u>Measured Detection Limit (Sample Loop)</u>	<u>Estimated Detection Limit (Concentrator)</u>
Water Vapor	35 ppm	25 ppm	0.5 ppm
Freon 113	1 mg/m ³	70 mg/m ³	1.0 mg/m ³
Hexanol	1 mg/m ³	10 mg/m ³	0.5 mg/m ³
Perfluorocyclobutane	1 mg/m ³	25 mg/m ³	1.0 mg/m ³

From the above data it is apparent that the Microsensor/GC Vapor Monitor, in the sample loop configuration will not detect or monitor Freon 113, Hexanol or Perfluorocyclobutane at the desired .1 mg/m³ level. However, previous studies have shown that many such vapors can be readily concentrated up to 50X or 100X, depending upon the adsorbent used in the concentrator, sample volume collected, desorption temperature used, etc. Thus based on the previous work it is estimated that each of the above compounds could actually be monitored at the required level, provided the Vapor Monitor were modified by replacing the sample loop with an appropriate sample concentrator.

It was further observed in the above studies that the GC retention times for water vapor, Freon 113 and Hexanol were well separated, thus they could be monitored simultaneously using the GC parameters described. Unfortunately the retention time for perfluorocyclobutane coincides with that of water on the HAYESEP Q column. In order to monitor water vapor and perfluorocyclobutane simultaneously other column packing materials will have to be investigate, or two instruments used for the measurements.