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EVALUATION TESTING OF A PORTABLE VAPOR DETECTOR FOR PART-PER-BILLION (PPB) LEVEL UDMH AND N_2H_4

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ABSTRACT

Trace level detection of hydrazine (N_2H_4), monomethyl hydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) has been receiving increased attention over the past several years. In May 1995 the American Conference of Government Industrial Hygienists (ACGIH) lowered their acceptable threshold limit value (TLV) from 100 parts-per-billion (ppb) to 10 ppb. Several types of ppb-level detectors are being developed by the United States Air Force (USAF) Space and Missile Systems Center (SMSC).

A breadboard version of a portable, lightweight hydrazine detection sensor was developed and produced by Giner Corp. for the USAF. This sensor was designed for ppb level UDMH and N_2H_4 vapor detection in near real-time. This instrument employs electrochemical sensing, utilizing a three electrode cell with an anion-exchange polymer electrolyte membrane as the only electrolyte in the system. The sensing, counter and reference electrodes are bonded to the membrane forming a single component. The only liquid required to maintain the sensor is de-ionized water which hydrates the membrane.

At the request of the USAF Space and Missile Systems Center (SMSC), independent testing and evaluation of this breadboard instrument was performed at NASA's Toxic Vapor Detection Laboratory (TVDL) for response to ppb-level N_2H_4 and UDMH and MMH. The TVDL, located at Kennedy Space Center (KSC) has the unique ability to generate calibrated sample vapor streams of N_2H_4, UDMH, and MMH over a range from less than 10 ppb to thousands of parts per million (ppm) with full environmental control of relative humidity (0-90%) and temperature [0-50 ° Celsius (°C)]. The TVDL routinely performs these types of tests. Referenced sensors were subjected to extensive testing, including precision, linearity, response/recovery times, zero and span drift, humidity and temperature effects as well as ammonia interference. Results of these tests and general operation characteristics are reported.

INTRODUCTION

This report presents the results of the initial laboratory testing of a conceptual portable fuel vapor detector developed by Giner Corporation under an SBIR contract for the USAF. Five breadboard instruments were delivered by Giner Corp., the units with serial numbers 3, 4, and 5 were subjected to evaluation testing in the TVDL at KSC. The purpose of these tests were to evaluate the performance characteristics of the Giner hydrazine detectors when exposed to low ppb vapor concentrations of UDMH and N_2H_4. Tests conducted included linearity, precision, response/recovery time, 4-hour zero and span drift, humidity effects [20-80% relative humidity (R/H)], temperature effects [5-45° Celsius (°C)], and interference response to ammonia vapor.

The Giner hydrazine detector is 170 millimeters (mm) [6.7 inches (in.)] high, 85 mm (3.3 in.) wide and 35 mm (1.4 in.) deep and weighs 430 grams (g) [15.2 ounces (oz.)]. A liquid crystal diode (LCD) display on the upper right side of the front panel displays a reading in 1 ppb increments. The display is updated every 5 seconds. A rechargeable battery powers the internal electronics in addition to the sample pump which flows at 200 cubic centimeters per minute (cm^3/min.). The unit is activated by loading the data collection program from a computer through an RS-232 port on the side of the instrument. This program begins data collection at a rate of one measurement per minute. The event mark button on the top of the unit annotates the log file at the time it is actuated. The data is stored as time of day versus sensor signal. Marked events are also display in the data file. A

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computer program was supplied to calibrate the instruments. In the calibration mode the display is updated once a second and no data is logged. An analog output is provided on the units and the full scale output was measured at approximately 2.2 volts. A threaded plug on the side of the unit allows for addition of de-ionized water which hydrates the anion exchange membrane.

APPARATUS

The TVDL test apparatus was designed to deliver known concentrations of UDMH and N_2H_4 at controlled conditions of temperature and relative humidity. The system consists of five components: two toxic vapor generators (2), two flow/temperature/relative humidity (F/T/RH) controllers (2), two sample vessels (hydrazine vessel and hydrazine free or zero vessel), two temperature and relative humidity monitors (2), and the three Giner instruments. The Kin Tek Span Pac (Model 361) is a precision standard toxic vapor generator that produces controlled concentrations. The vapors are further diluted by controlled mixing with humidified instrument grade air from the F/T/RH. Each vapor generator consists of three permeation devices in three individually temperature-controlled ovens. For UDMH, liquid filled stainless steel permeation devices were used, and for N_2H_4 sealed permeation tubes in glass permeation devices were used. Two vapor generators were used to provide from 10 to 200 ppb concentrations of UDMH and N_2H_4 vapors for these tests. Sample vapors were verified using impinger collection and coulometric titration. The analyzed vapor concentrations for the tests are listed in Table 1.

Table 1. Sample Vapor Concentrations

Component	Verified Concentration (ppb)				
UDMH	12	30	57	111	198
N2H4	10	25	45	99	–

The F/T/RH controller, Miller Nelson Model HCS-301, and a computer for Process Control and Data Acquisition System (PCDAS) were used to precisely control the flow, temperature, and R/H of the diluent air to provide desired vapor concentrations over a range of R/H conditions. Two F/T/RH controllers were used for the test, one for providing diluent air to the UDMH/N_2H_4 sample vessel and the second for providing hydrazine free "zero" air. A short distance upstream of the hydrazine vessel, a specially designed Teflon injection tee is used to inject the sample vapor from the vapor generator into the flowing stream where it is mixed with the conditioned diluent air from the F/T/RH controller. The injection tee was designed to optimize vapor delivery and mixing efficiency, while minimizing sample loss to tubing surface adsorption. A three-way Teflon body solenoid valve is employed between the sample vessel and the hydrazine free vessel to allow the automated introduction of hydrazine vapor and zero air to the detectors using the PCDAS computer. For all tests, except response/recovery time determination, a Teflon sampling manifold was attached to the three-way Teflon body solenoid valve. A small pump was used to pull sample or zero vapor at a rate of 2 liters per minute through the manifold from which the three instruments being tested were allowed to sample. Because of the low sample rate of the test instruments (200 cm^3/min.) the pressure influence at the manifold sample ports was verified to be less than 0.1 inches of water using a calibrated Omega PCL-200 pressure calibrator. A Vaisala temperature humidity sensor, (Model HMP 130Y Series) is used to monitor the temperature and humidity in each sample vessel. Automation of the system was achieved by computer control of the vapor generators, the F/T/RH controllers, and the three-way solenoid valve. The test setup is shown in Figure 1.

PROCEDURES

The sample vapors used for all tests except the temperature and humidity effect tests, were at 23°C and 50% relative humidity. Prior to each test described below, the instruments were calibrated at 30 ppb for UDMH and 25 ppb for N_2H_4. The units were allowed to stabilize while sampling UDMH calibration vapor for 20 minutes before the span potentiometer (pot) was adjusted. Due to these units' slower response to N_2H_4, 60 minutes of stabilization time was allowed before adjusting the span pot. The units were cycled from zero air to calibration vapor at the appropriate intervals until no span or zero adjustments were required. De-ionized water was added to the reservoirs on a daily basis. The majority of the tests were done using the PCDAS system that controlled and recorded sample generation system flow rates, temperature, relative humidity, sampling mode (zero or span), sensor response, etc... For all tests, the data log files from the PCDAS were used to evaluate sensor response. Strip charts were also used to record sensor response during all tests.

Linearity

The linearity of the instruments was tested at the concentrations listed in Table I. For UDMH, the units were allowed to sample zero air and test vapor at each of the concentrations at 30 minute intervals. While testing N_2H_4 linearity, 60 minute cycles were used. The sample was drawn from the Teflon manifold. The average of the last 5 minutes of sampling was recorded as the units final response for each vapor concentration. The testing started at the lowest concentration and finished at the highest with two sample cycles at each concentration.

Precision Test

The precision test was intended to test the ability of the instruments to measure a precise concentration accurately on a repeatable basis. The precision is calculated as the percent deviation of the maximum (worst case) value from the average value during the final 5 minutes of each cycle. After the instruments were calibrated, a series of readings were taken by alternating five 30 minute exposure cycles to zero air and UDMH vapor, 60 minutes cycles were used for N_2H_4. For UDMH a 12 ppb sample was used and a 25 ppb sample for N_2H_4. Again the sample was drawn from the Teflon manifold.

Response and Recovery Time

Response times were measured with units that had not been exposed to hydrazine vapors for at least 8 hours. Each unit sampled through a 6 inch length of Bev-a-Line tubing and was cycled from zero air to test vapor by manually shifting the sample tubing in order to eliminate the automated three way valve and manifold from the test setup to minimize delay caused by the surface adsorption of hydrazine. The response time was defined as the time required to reach 90% of the final response (20 minutes for UDMH and 60 minutes for N_2H_4), and recovery time was defined as the time required to return to a 10% of the maximum response. Responses were measured while sampling 12 ppb UDMH and 25 ppb N_2H_4.

Relative Humidity

This test characterized the effect of R/H on the performance of the instruments. After the instruments were calibrated with a known standard at 50% R/H and 23 °C; they were exposed to zero/span cycles at 20, 40, 60, and 80% R/H. At each humidity, the zero/span cycles were repeated three times at 30 minute cycles for UDMH and 60 minutes cycle for N_2H_4. The units sampled from the manifold setup and both the zero and the span vapor humidities were ramped through the same range during the test. For UDMH tests 30 ppb vapor was used, while 25 ppb vapor was used for the N_2H_4 humidity tests.

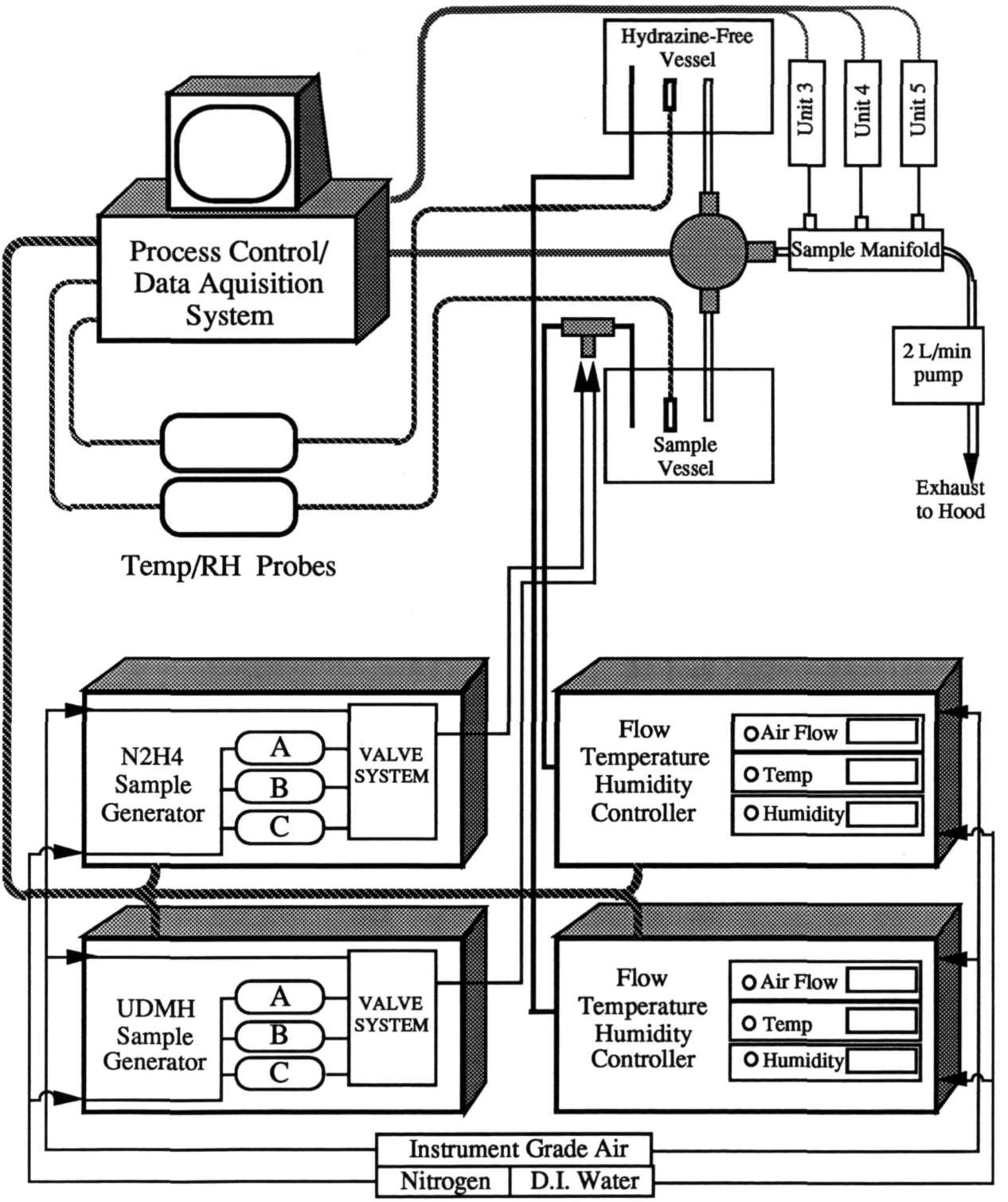
Four Hour Zero and Span Drift

This test was designed to measure the ability of the instruments to hold an accurate span or zero value for a period of 4 hours. The instruments sampled zero air from the manifold setup continuously for 4 hours. At that time, the input was switched to the span vapor and the units were allowed to sample for another 4 hours. The span portion of this test was done using 12 ppb vapor for UDMH and 25 ppb vapor for N_2H_4.

Temperature Tests

Temperature effects on sensor response were tested using a Hotpack model 417532 environmental control chamber. The vapor sample mixing Tee, zero and span vessels, the Teflon body three way solenoid valve, sample manifold, and the sensors were placed inside the environmental chamber. Using sample vapors of 30 and 57 ppb UDMH and 45 ppb N_2H_4, the units were allowed to sample test vapors at 5, 15, 25, 35, and 45 °C. Temperature effects on sensor response were recorded in four separate tests, two tests with UDMH and two with N_2H_4. The conditions for initial sampling cycles for all tests were 25 °C, and 50% R/H, the temperature was adjusted up during one test and down for the second test for each hydrazine species evaluated. Relative humidity was maintained at 50% for all temperatures. The sensors were allowed to equilibrate at the set temperature for approximately 30 minutes while sampling zero air. Then they were exposed to the span vapor and allowed to sample until a stable response was attained. Verification scrubs were done in parallel with the testing and, at all temperatures, concentrations tested within ±5% of scrubs done at room temperature.

Figure 1 TEST SET-UP



Interference Tests

An interference test was performed on the sensors after they were calibrated with 30 ppb UDMH. The units were exposed to 30 ppb UDMH for 20 minutes, then allowed to recover sampling zero air for 15 minutes. When a stable baseline was reestablished, the units were exposed to 50 ppm (twice the TLV) of ammonia vapor in air at 23 °C and 50% R/H for 15 minutes. The units were then exposed to zero air, and after stabilization they were again exposed to the 30 ppb UDMH vapor.

TEST RESULTS

Unit 5 could not be calibrated on N_2H_4. Maximum response was limited to 50% of the verified concentration, and so the only data for unit 5 included is the response/recovery time.

Linearity

Linearity testing on UDMH vapor, with vapor concentrations from 12 to 198 ppb, showed that the unit responded within a ±15% tolerance range from 12 ppb through 111 ppb. At the 198 ppb test point the units all responded below the -15% tolerance range. After this test it was discovered that the saturation level of the sensors (maximum readout) was 166 ppb. For hydrazine, units 3 and 4 performed well, responding within 15% of the verified test vapor concentration throughout the tested range of 10 to 99 ppb. Linearity results are shown in figures 2 and 3.

Precision Test.

The precision of each unit was determined by calculating maximum deviation above the average value during a span cycle for all three of the hydrazines. The five 30 minute cycle average response, to a verified UDMH concentration of 12 ppb, was 12.2, 12.0, and 12.2 for units 3, 4 and 5 respectively. Furthermore the maximum deviation was calculated to be 3.2%, 4.7%, 4.6% from the average for units 3, 4, and 5 respectively. When exposed to N_2H_4 at a verified concentration of 25 ppb, the average maximum response of five 60 minute cycles for sensors 3 and 4 was 26.3 and 28.1, respectively. The maximum deviation calculated to be 7.7% for unit 3 and 9.2% for unit 4. The results showed that the instruments' precision was well within a ±10% tolerance range. The precision data is shown in table 2.

Table 2. Precision Results

Vapor	Unit	Cycle 1 (ppb)	Cycle 2 (ppb)	Cycle 3 (ppb)	Cycle 4 (ppb)	Cycle 5 (ppb)	Average (ppb)	Maximum Deviation (%)
UDMH	3	11.9	12.5	12.3	12.1	12.5	12.2	3.2
UDMH	4	11.4	11.5	12.0	12.3	12.6	12.0	4.7
UDMH	5	11.8	12.0	12.4	12.8	12.2	12.2	4.6
Hz	3	24.3	26.0	26.7	27.1	27.5	26.3	7.7
Hz	4	25.5	27.4	28.8	29.3	29.4	28.1	9.2

Response and Recovery Time.

Response/recovery time tests for UDMH were done using 12 ppb vapor and sampling through a six inch section of Bev-a-line IV tubing. During the 20 minute test cycle, the time to attain 90% of maximum response were calculated to be 3.1, 3.5, and 2.8 minutes for units 3, 4 and 5 respectively. The times required to return to 10% of maximum response for the same units were 4.2, 4.4, and 2.3 minutes.

Significantly longer response/recovery times were recorded for N_2H_4 tests that for UDMH tests. During the 60 minutes sample period for N_2H_4, response times for units 3, 4 and 5 were 28, 33, and 31 minutes respectively. As noted above, the maximum calibration setting for unit 5 was approximately 50% of actual vapor concentration. Upon recovery, the time to return to 10% of full response for the three units was 14, 22 and 15 minutes. The response and recovery charts are shown in figures 4 and 5.

Figure 2: UDMH Linearity
Maximum response after 30 Minute exposure, Calibrated at 30 ppb

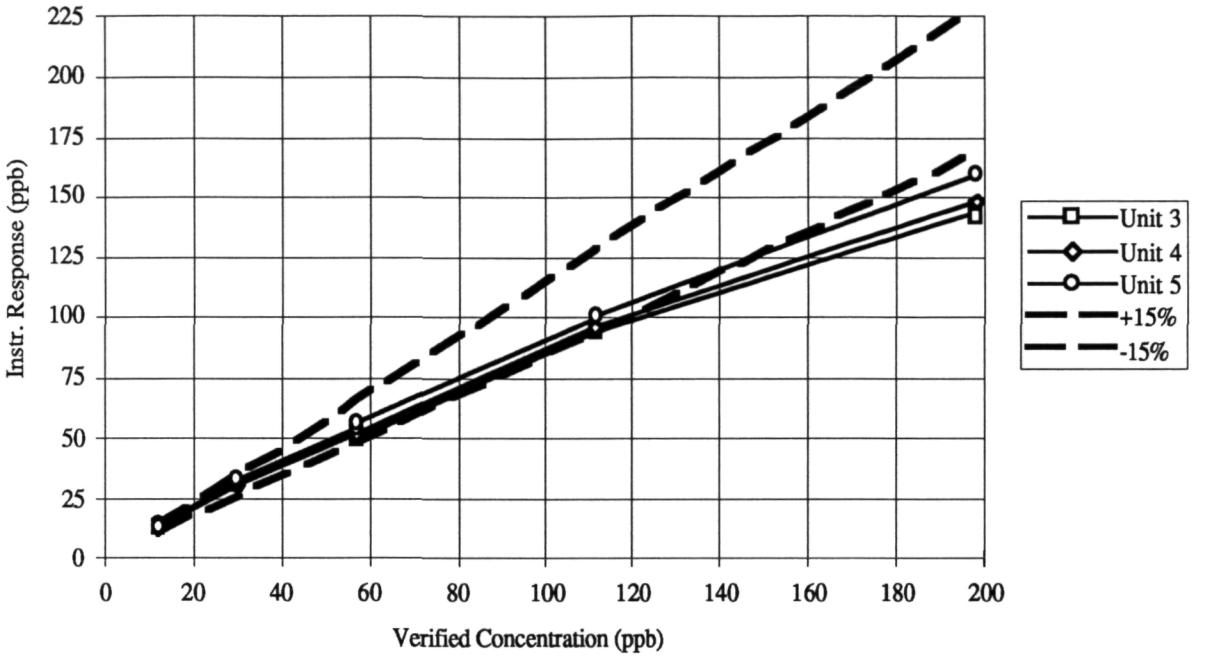


Figure 3: N_2H_4 Linearity
Maximum response after 60 minute exposure, Calibrated at 25 ppb

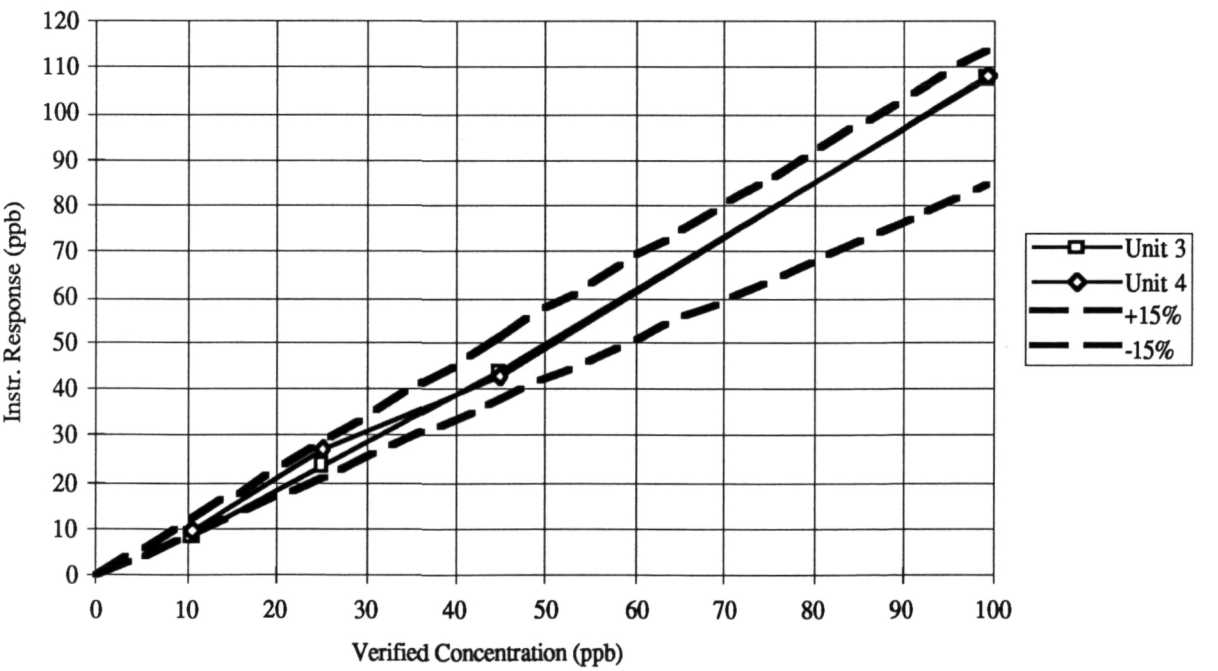


Figure 4: UDMH Response/Recovery
Sample Vapor: 12ppb

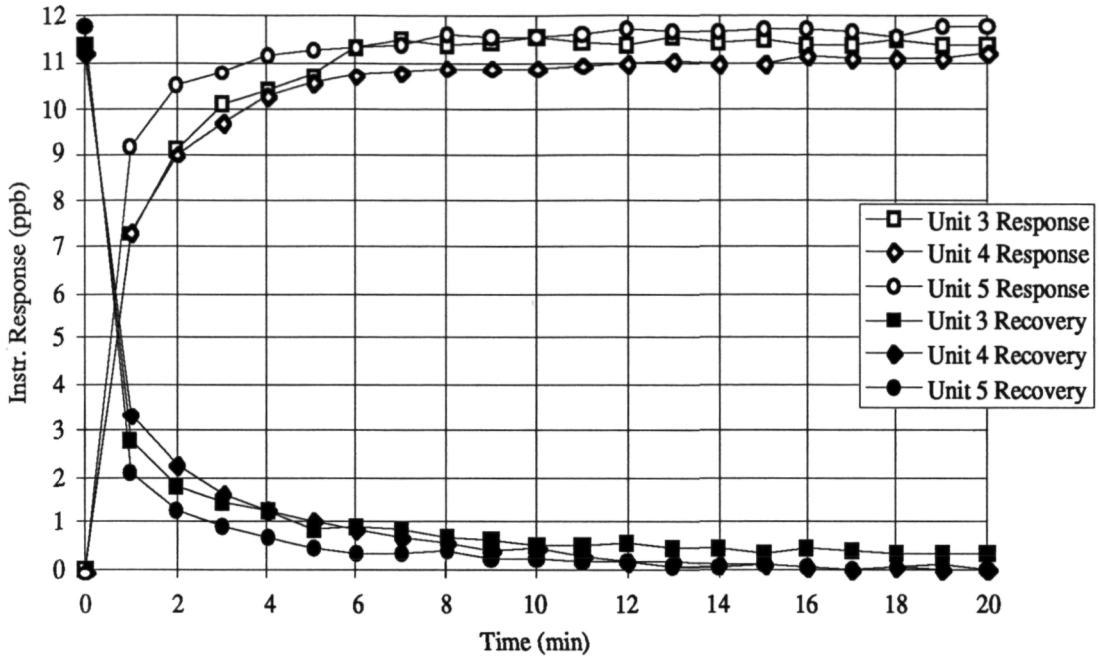


Figure 5: N_2H_4 Response/Recovery
Sample Vapor: 25 ppb

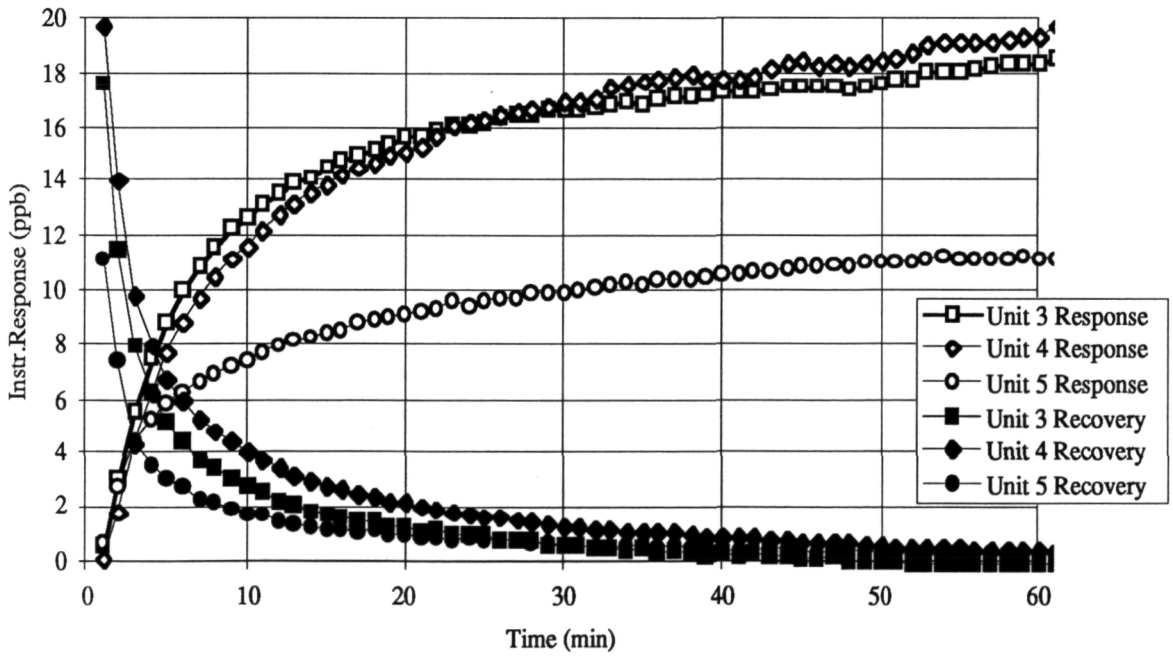


Figure 4: UDMH Response/Recovery
Sample Vapor: 12ppb

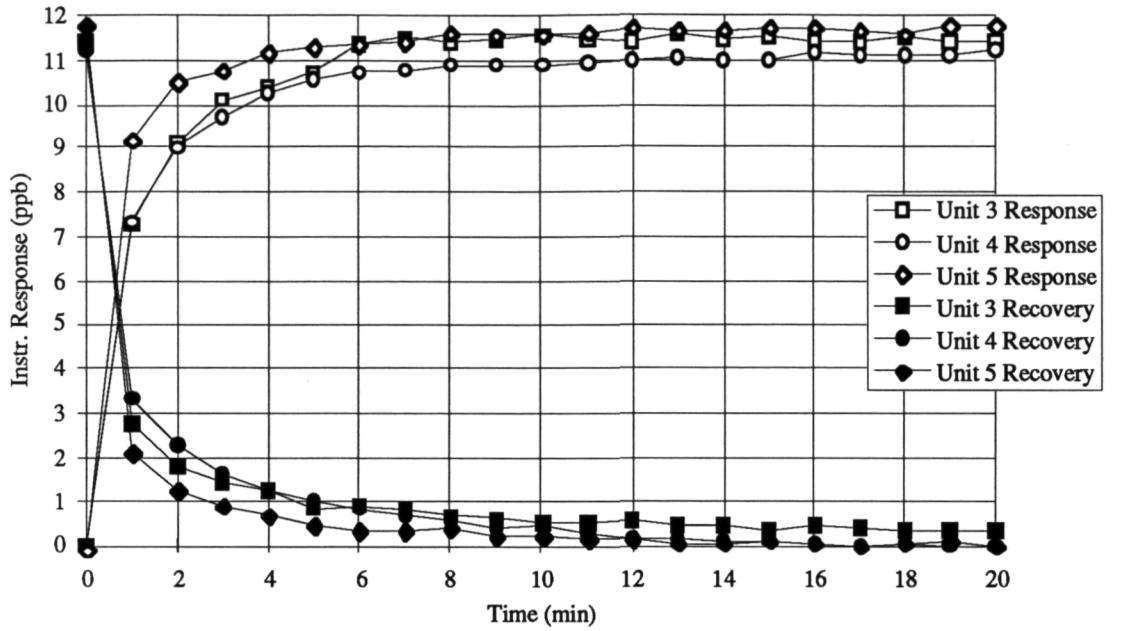
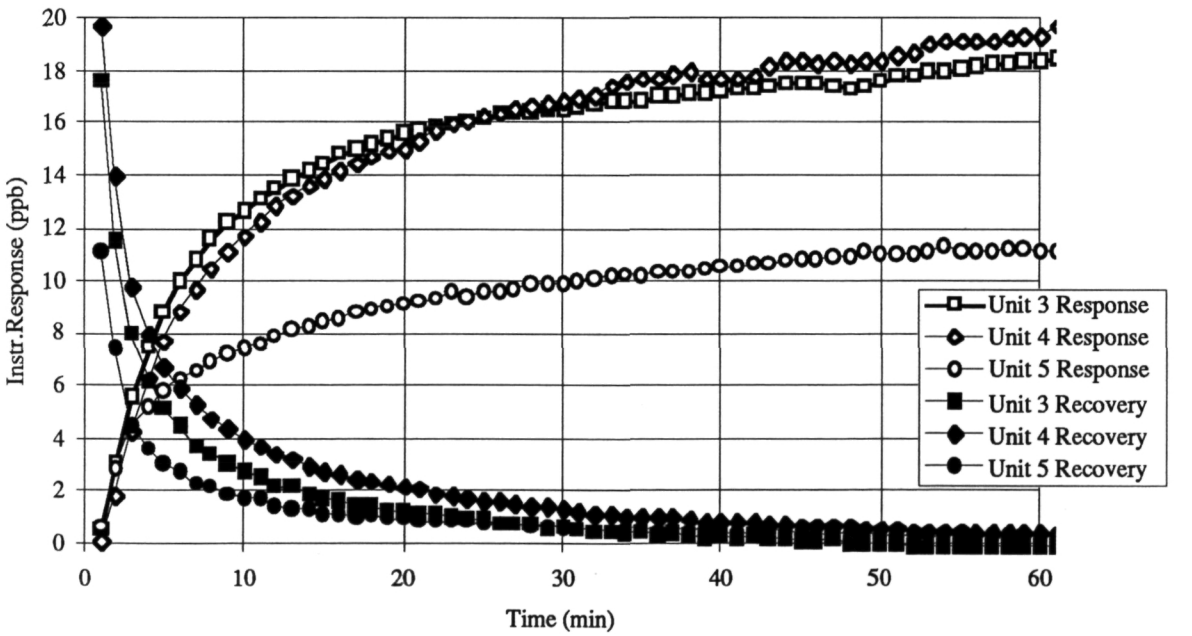


Figure 5: N_2H_4 Response/Recovery
Sample Vapor: 25 ppb



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Relative Humidity.

The instrument showed good stability when sampling 30 ppb UDMH at relative humidities of 20, 40, 60, and 80%. The responses for all three sensors were within 10% of the calibrated value at all R/H levels. Increasing the sample vapor R/H from 20 to 80% caused less than a 1 ppb drift in the baseline response when sampling zero air. The primary effect noticed during UDMH R/H testing was a slower response/recovery time at the 80% R/H. While response/recovery times of 3 to 4 minutes were recorded at 20, 40 and 60% R/H, at 80% R/H these times increased to around 10 minutes.

Humidity tests at 25 ppb N_2H_4 at 20, 40, 60 and 80% R/H showed a pronounced loss of response at higher humidities. Response decreased about 12 percent when RH was increased from 40 to 60%. An R/H increase from 40% to 80% resulted in a 30 percent decrease in response. As with UDMH at 80% R/H, the response to N_2H_4 was significantly slower than at lower R/H levels. Relative humidity results are shown in figures 6 and 7.

Four Hour Zero and Span Drift.

All three units showed very good stability during the 4 hour span drift cycle sampling UDMH, less than 0.5 ppb upward drift from the 30 minute point to the end of the test at a 12 ppb concentration. The baseline drift, during the four hour zero air sampling cycle, was also less than 0.5 ppb for all three units.

Baseline drift during the N_2H_4 zero/span drift test was similar to that observed in the UDMH test. When the units were exposed to 25 ppb N_2H_4 for four hours the reading increased approximately 25% over the last three hours of the sampling cycle. The zero/span drift results are shown in figures 8 and 9.

Temperature Tests

Temperature effects on sensor response were tested in four separate tests, two on UDMH and two on N_2H_4. The initial conditions for for all tests were 25 °C, and 50% R/H. The temperature was adjusted up during the first test and down for the second test for each specie. Relative humidity was maintained at 50% for all temperatures. Generally, sensor response showed a significant inverse reaction to changes in temperature. At 30 ppb UDMH, the sensor output increased approximately 20% for a temperature change from 25 °C to 15 °C. At 5 °C the sensors responded more than 60% higher than they did when sampling the same concentration at 25 °C. For the high temperature UDMH test 57 ppb vapor was used. Units 3 and 4 responded about 20% lower at 35 °C and about 35% lower at 45 °C. Data from unit 5 was not available.

The same trend in was observed in the N_2H_4 tests performed at 45 ppb. As the temperature was decreased from 25 °C to 15 °C the response increased nearly 50%. Responses increased 132% and 88% for the units at 5 °C. When temperatures were increased, response decreased by about 26 % at 35 °C, and about 40% at 45 °C.

For both UDMH and N_2H_4 response times generally decreased at temperatures lower than 25 °C and increased a slightly at temperatures higher than 25 °C. Results of temperature tests are shown in tables 3 and 4.

Table 3. UDMH Temperature Results

Sample Concentration: 30 ppb						
Temperature	Response (ppb)			Percent increased response		
(°C)	Unit 3	Unit 4	Unit 5	Unit 3	Unit 4	Unit 5
25	34	33	31			
15	42	42	37	23.5	27.3	19.4
5	57	56	50	67.6	69.7	61.3
Sample Concentration: 57 ppb						
Temperature	Response (ppb)			Percent decreased response		
(°C)	Unit 3	Unit 4	Unit 5	Unit 3	Unit 4	Unit 5
25	56	55	62			
35	43	45	N/A	-23.2	-18.2	N/A
45	35	37	N/A	-37.5	-32.7	N/A

Figure 6: UDMH Relative Humidity Response
Sample concentration: 30 ppb

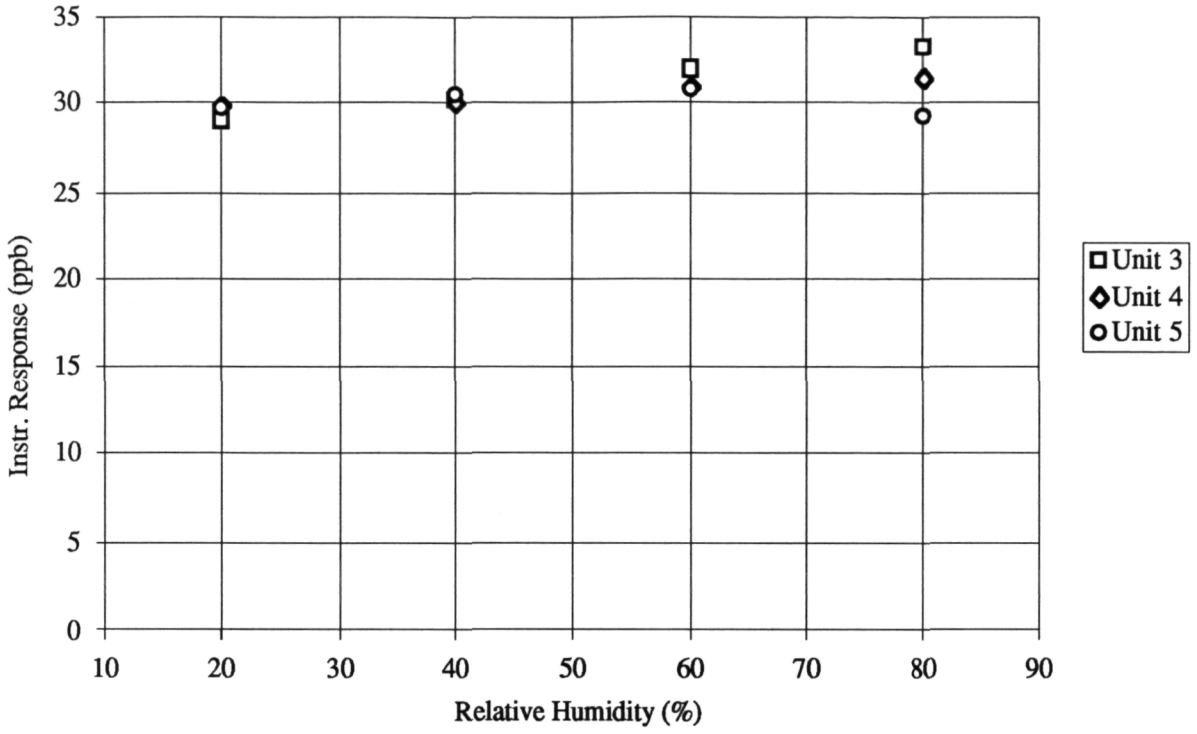


Figure 7: N_2H_4 Relative Humidity Response
Sample concentration: 25 ppb

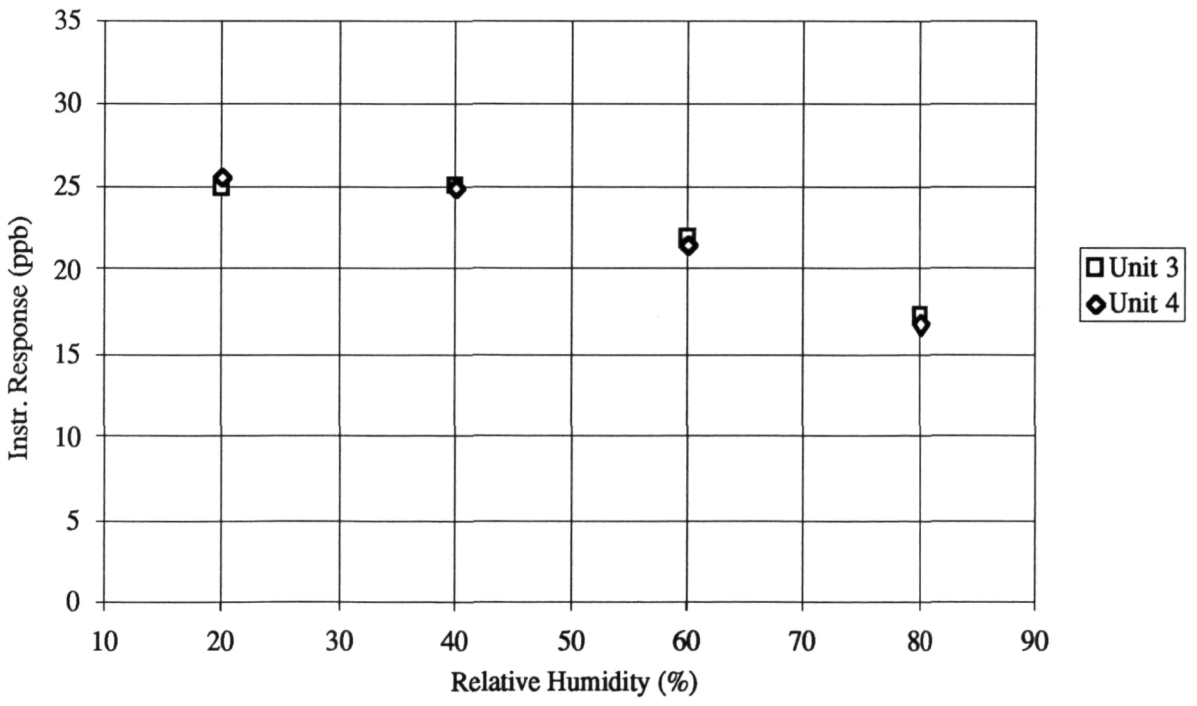


Figure 8: UDMH Zero/Span Drift
Sample Vapor: 12 ppb

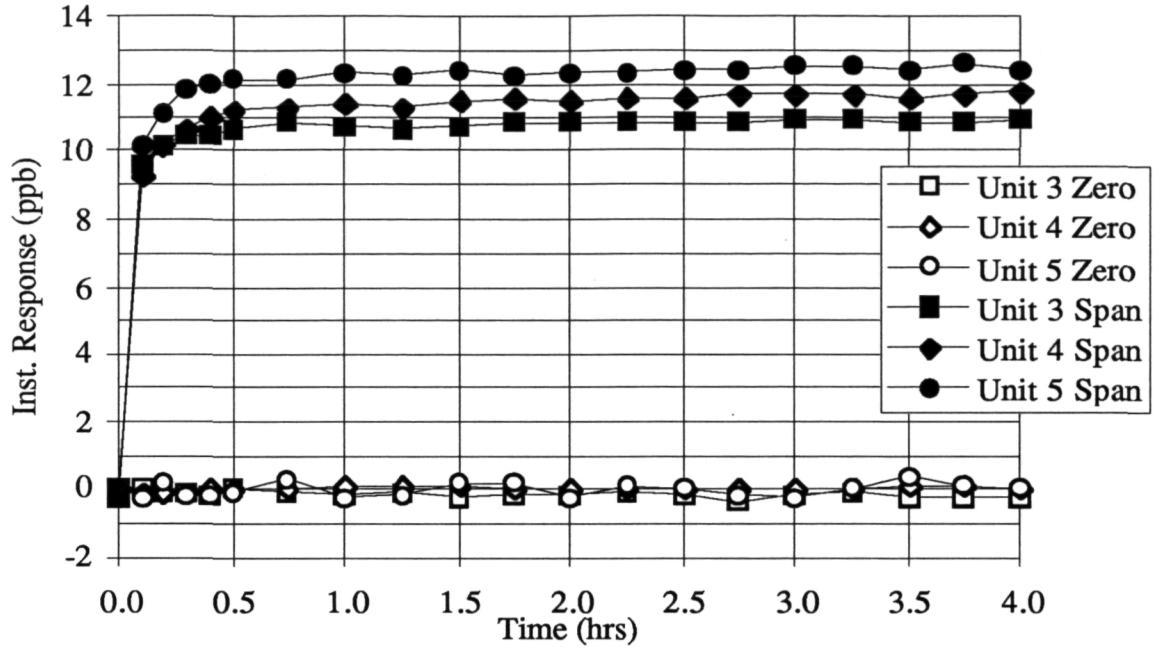


Figure 9: N_2H_4 Zero/Span Drift
Sample: 25 ppb

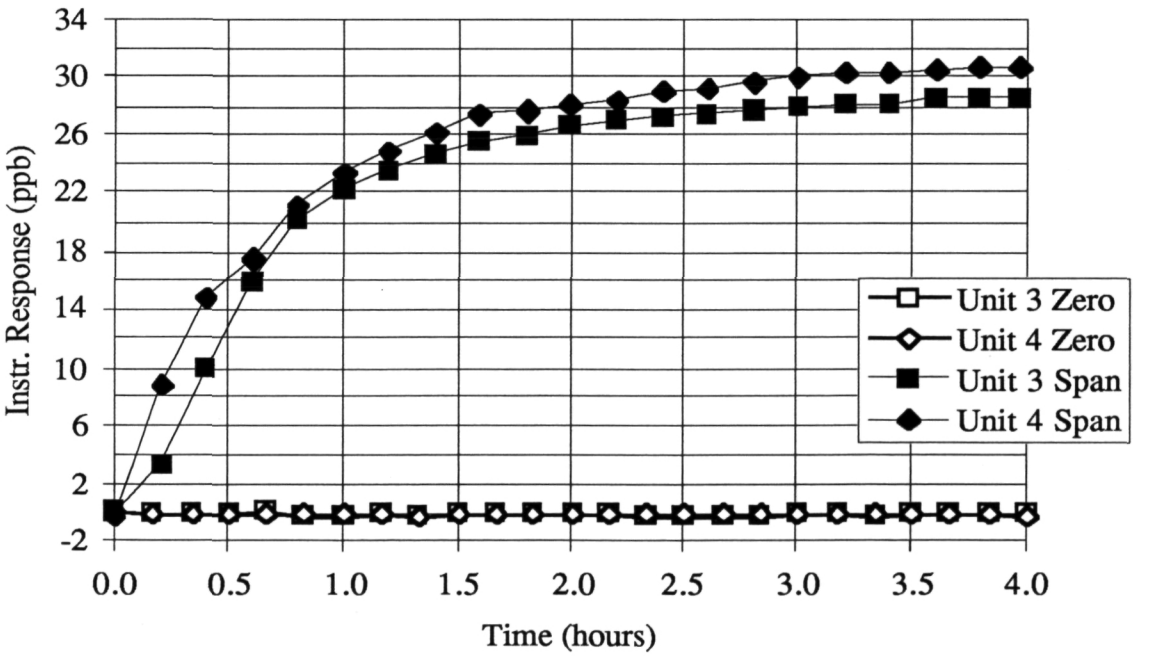


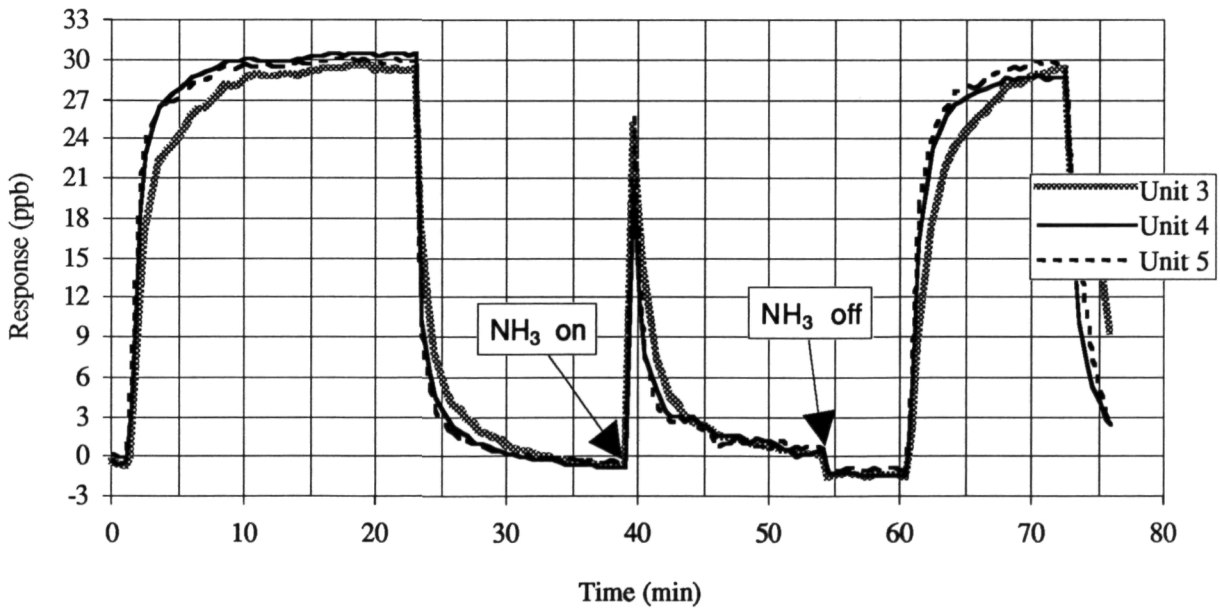
Table 4. N_2H_4 Temperature Results

Sample Concentration: 45 ppb				
Temperature (°C)	Response (ppb) Unit 3	Unit 4	Percent increased response Unit 3	Unit 4
25	43	44		
15	68	63	58.1	43.2
5	100	83	132.6	88.6
Sample Concentration: 45 ppb				
Temperature (°C)	Response (ppb) Unit 3	Unit 4	Percent decreased response Unit 3	Unit 4
25	46	46		
35	34	34	-26.1	-26.1
45	27	28	-41.3	-39.1

Interference Tests

Exposure to 50 ppm ammonia caused a rapid response which peaked at 25 ppb then immediately began to recovery towards baseline. While ammonia sampling continued, response decreased to 3 ppb after 5 minutes and returned to 0 ppb after 12 minutes. An exposure to 30 ppb UDMH vapor following about five minutes of sampling zero air showed no sensor poisoning and no serious effect one the units' ability to respond quickly to 30 ppb UDMH. Response to 50 ppm ammonia vapor is shown in figure 10.

Figure 10: 30 ppb UDMH Exposures and 50 ppm Ammonia (NH_3) Interference



General Observations

A test was done to determine battery life. The sensor batteries were fully charged and the sensors were turned on and set-up to sample intermittent UDMH samples, while logging data, without the charger plugged in. The sensors ran for just over 11 hours before the pump stopped. Water evaporation rates were monitored by weighing the sensors at various times during long term tests. While sampling sample vapors with 50% R/H, the average consumption rate was one gram of water every 18.5 hours. The capacity of the reservoir was not determined, but was estimated to be about 8 milliliters. A larger water reservoir may be desirable to reduce maintenance requirements. The data logging function and software was used and seemed to work well, although it was not used extensively. Direct analog output was the primary source used for analysis. The full capacity of the logging memory was not tested, but log files of 16 hours were collected while testing with the units attached to the battery chargers.

CONCLUSION

Results of UDMH testing show these Giner breadboard sensors will reliably and precisely detect concentrations of 10 ppb. The linear range of the sensors is from 10 ppb to at least 100 ppb. The sensors responded precisely to repeated samples at the same concentration. Response times to 90% were less than 4 minutes, and recovery times to 10% were less than 5 minutes. The sensors exhibited noise of less than 0.5 ppb, and while sampling zero air showed a four hour drift of less than 0.5 ppb. When sampling a stable ppb level UDMH sample for four hours, the units response drifted less than 0.5 ppb after the thirty minute equilibration period. At relative humidities from 20 to 80 % the sensors' response accuracy was not effected, however at 80 % R/H response time to 90% full response increased to about 10 minutes. The sensors showed a rejection ratio of more an 200:1 for 50 ppm ammonia vapor, responding with an instantaneous spike that quickly returned to baseline when ammonia sampling continued. Exposure to ammonia vapor did not inhibit the sensors from responding quickly and accurately to UDMH vapor. The only limitation of the sensors performance in the UDMH set of tests was the effect of temperature changes. An increase in temperature causes a decrease in sensor response. A change in temperature of 10 °C up or down caused a change of 20% or more in sensor output. This effect must be corrected if the units are to be used in an environment where temperature variations are likely.

The response to N_2H_4 was linear, within 15%, over the concentration range of 10 to 100 ppb and the sensors response to repeated exposures to the same concentration was acceptable. However the sensors response/recovery times were about ten times longer at 25 ppb than for UDMH. This much slower response time effected results during the R/H tests, showing a loss of response at higher humidities. During the 4 hour span drift test the sensor signal continued to increase monotonically over the entire sampling period. Temperature effects were similar to the results noted for sampling UDMH.