

ACTIVE HYDRAZINE VAPOR SAMPLER (AHVS)

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ABSTRACT

The Active Hydrazine Vapor Sampler (AHVS) was developed to detect vapors of hydrazine (HZ) and monomethylhydrazine (MMH) in air at parts-per-billion (ppb) concentration levels. The sampler consists of a commercial personal pump that draws ambient air through paper tape treated with vanillin (4-hydroxy-3-methoxybenzaldehyde). The paper tape is sandwiched in a thin cardboard housing inserted in one of the two specially designed holders to facilitate sampling. Contaminated air reacts with vanillin to develop a yellow color. The density of the color is proportional to the concentration of HZ or MMH. The AHVS can detect 10 ppb in less than 5 minutes. The sampler is easy to use, low cost, and intrinsically safe and contains no toxic material. It is most beneficial for use in locations with no laboratory capabilities for instrumentation calibration. This paper reviews the development, laboratory test, and field test of the device.

INTRODUCTION

Hydrazine and monomethylhydrazine are widely used in space programs as rocket propellants. HZ is used in the Emergency Power Unit of the United States Air Force F-16 fighter planes. Commercially, HZ is used in applications such as a polymerization catalyst, boiler feedwater oxygen scavenger, blowing agent, and photographic developer. Hydrogen compounds are highly toxic and suspected carcinogens. In 1989, the American Conference of Governmental Industrial Hygienists (ACGIH) [1] proposed to reduce the HZ and MMH Threshold Limit Value (TLV) from 100 ppb and 200 ppb respectively to 10 ppb to protect personnel working with these substances. This reduction will significantly impact personnel safety monitoring because a near realtime, easy-to-use, commercial detector for measuring such a low level was not available. In response to the ACGIH proposal, the NASA Instrumentation Section at the John F. Kennedy Space Center (KSC) initiated an effort to develop the needed instrument. Contracts were awarded to three vendors for the development of electrochemical, ion-mobility, and paper tape technologies for a portable vapor detector. At the same time, the NASA Toxic Vapor Detection Laboratory (TVDL) initiated an in-house development for an AHVS for interim use. This paper reviews the development effort and provides the laboratory and field test results.

BACKGROUND

In 1991, techniques and prototype samplers capable of detection of 10-ppb HZ and MMH in air were developed [2]. The samplers were based on the use of a commercially available, intrinsically safe personal pump drawing ambient air through paper treated with a mixture of vanillin and phosphoric acid. Special holders were designed to facilitate sampling through the paper tape. The detection and quantification of this low-ppb concentration are based on the development of yellow color on the paper upon exposure to the HZ/MMH vapors. After laboratory development testing, two designs of the prototype were field tested and evaluated by KSC Environmental Health and Safety personnel. While the users found the detection capability of the prototype generally acceptable, they requested modifications that would minimize possible contamination and degradation of the chemically treated paper, allow easier use and documentation of results, and provide improved viewing of the color development during sampling. To achieve these requirements, new sample holders were designed and tested both in the laboratory and in the field at KSC, White Sands Test Facility, and Hill Air Force Base.

SAMPLER DESIGN

The AHVS shown in figure 1 consists of three parts:

- (1) A commercial, intrinsically safe personal pump. Its flowrate is preset at 1 or 2 liters per minute.
- (2) A card holder. The TVDL designed two card holders. The open-face design is for monitoring general areas, whereas the closed-face design with a viewing window is for sampling through a small opening for leak detection.
- (3) An HZ/MMH card. The card is made of a strip of paper tape coated with vanillin that develops a yellow color upon contact with HZ or MMH. The chemistry is shown in figure 2. The intensity of the yellow color is proportional to the concentration of HZ or MMH. The paper tape is sandwiched in a thin cardboard housing with two 1.5-centimeter-diameter windows in the front and back. The windows are designed to align exactly with the air passage in the card holder. The card is enveloped in a special packet to ensure the integrity of vanillin chemistry until the card is ready for use. The NASA vanillin hydrazine card was obtained from GMD Systems Inc.

OPERATION

Three steps are followed to use the device: (1) attach the appropriate sample holder to the pump, (2) insert and clamp a card in the sample holder, and (3) turn on the pump to take the sample. For a 10-ppb concentration, the recommended sample time is 5 minutes at a 1-liter-per-minute sampling rate. Higher concentrations require less sample time. The color, as it is developing, shows on the front window of the card. After sampling, the card is removed from the holder, and the color is compared with a calibrated concentration estimator, which is a wheel consisting of five shades of yellow corresponding to five HZ/MMH concentrations. Using the color wheel, the approximate HZ/MMH concentration can be determined in the field. The color developed can also be measured in terms of a chroma reading using a Minolta Chroma Meter. Accurate concentration is determined by comparing the chroma reading to an HZ/MMH chroma calibration curve. The color wheel and chroma calibration chart are shown in figure 3. The color wheel was obtained from GMD Systems Inc.

LABORATORY TEST

Vapor Generation and Validation Equipment

The TVDL precision vapor generation system was designed to deliver known concentrations of HZ and MMH at controlled conditions of temperature (T) and relative humidity (RH) (figure 4). The system consists of four components: (1) a Kin-Tek Span Pac Model 361 precision vapor generator, (2) a Miller-Nelson Model HCS-301 flow/T/RH controller, (3) a sample vessel, and (4) a T/RH monitor.

The Kin-Tek vapor generator consists of three permeation devices housed in three temperature-controlled ovens. The permeation rate of the device is determined by the temperature of the oven, the length of the polymeric tube, and the polymeric material used. By first flowing small amounts of nitrogen through the permeation device and then diluting the hydrazine/nitrogen mixture with "conditioned" air from the Miller-Nelson unit, precise concentrations of HZ and MMH vapors are generated for use as standards. The TVDL uses a coulometric procedure for the validation of the standard vapor concentrations.

The coulometric procedure is simple and accurate. The hydrazine vapor is first collected in an impinger containing a 0.1-molar sulfuric acid absorbing solution. Following the vapor absorption, the amount of hydrazine in the solution is analyzed by constant-current coulometric titration. The procedure calls for dissolving a small amount of potassium bromide crystal in the absorbing solution. A direct electric current passing through a solution electrolyzes potassium bromide to form bromine, which rapidly reacts with hydrazine present in the solution. As long as hydrazine is present, the bromine concentration is undetected. At the moment all hydrazine has reacted, the

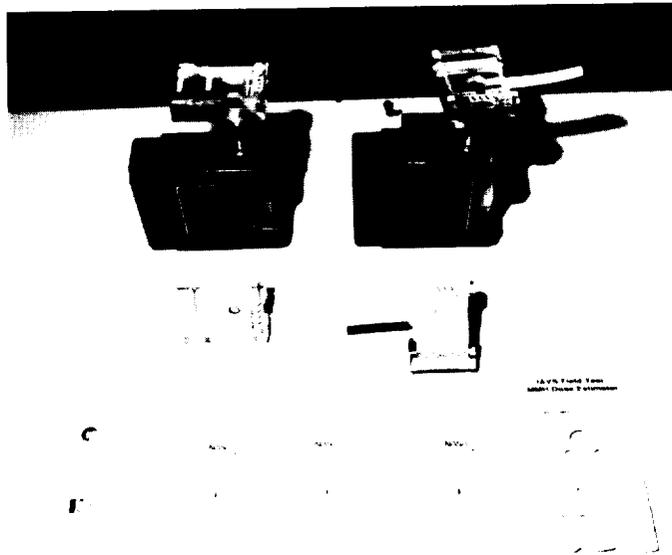


Figure 1. Active Hydrazine Vapor Sampler

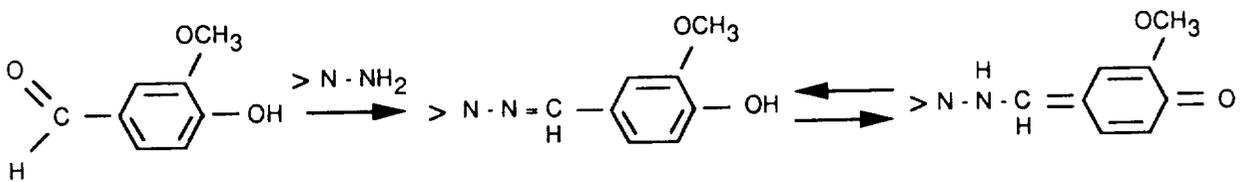


Figure 2. Reaction of Vanillin and Hydrazine

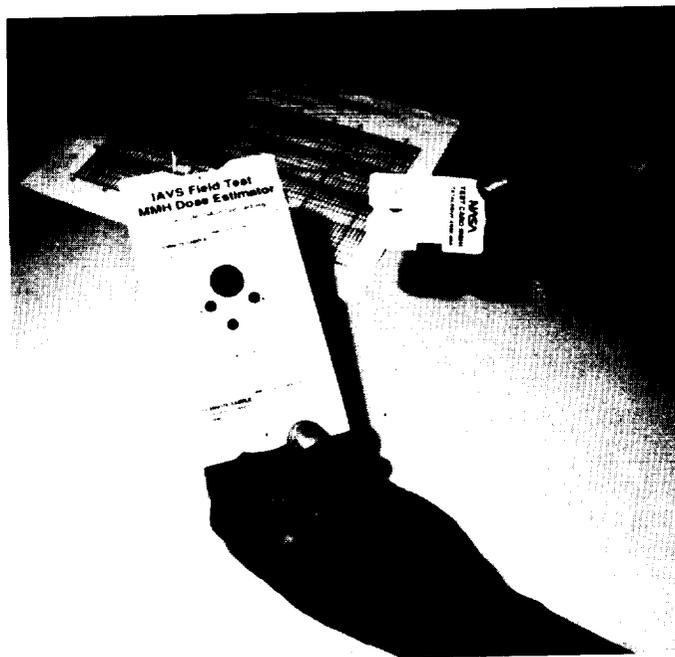


Figure 3. Color Wheel and Chroma Calibration Chart

bromine concentration increases to a detectable level, which signifies the end of titration. The length of titration time is determined by the amount of hydrazine. This titration result is used for subsequent calculation of hydrazine vapor concentration [3].

Color Measurement Equipment

For laboratory characterization of the hydrazine vapor sampler, a Minolta Chroma Meter Model CR-200 was used (figure 5). The Chroma Meter Luminosity Chroma Hue Angle (LCH°) color system uses cylindrical coordinates to measure color. For measuring the yellow color developed by the reaction of hydrazine and vanillin, the chroma variable was used because the luminosity and hue angle are fairly constant and the chroma readings are proportional to the vapor concentrations. In the lab, calibration curves are established using chroma readings and hydrazine vapor standards. Using the lab calibration curve and chroma readings corresponding to the five colors on the color wheel, concentration charts on the color wheel are established for field use.

Lab Test Parameters

The following test parameters and procedures were used:

- (1) **Precision and Linearity:** The samplers were exposed to MMH concentrations of 9.2, 38.6, 296, and 950 ppb for four iterations at a standard laboratory vapor condition of 25 degrees Celsius and 45 percent relative humidity.
- (2) **Comparison of Open-Face and Closed-Face Samplers:** Both sampler designs were subjected to the same precision and linearity tests and the results were compared.
- (3) **HZ Versus MMH Test:** With all other test conditions held constant, the sampler was tested with an HZ or MMH vapor of comparable concentrations.
- (4) **Temperature/Relative Humidity Effects and Response Time:** The sampler was exposed to a 10-ppb MMH vapor of a combination of temperature and RH conditions (0 to 84 percent RH and 5 to 40 degrees Celsius) for 3 minutes. Color measurements were taken every minute at 25 degrees Celsius and 45 percent RH until the readings were stable.
- (5) **Interference:** Sunlight, ammonia, nitrogen dioxide, Freon, methyl ethyl ketone (MEK), and isopropyl alcohol (IPA) were tested for positive or negative color development.
- (6) **Shelf Life:** Two batches of HZ/MMH cards were stored in the refrigerator and ambient laboratory storage area respectively for up to 42 days. During this period, cards were drawn from the batches and tested for integrity.

LABORATORY TEST RESULTS AND COMMENTS

The following laboratory test results were obtained:

- (1) **Precision and Linearity:** Two data sets were obtained. For the lower concentrations, a 5-minute sample time was used; whereas for the higher concentrations, the sample time was decreased to 1 minute. For both sets, the sample rate was 2 liters per minute, and chroma readings were taken 1 minute after exposure. Tables 1 and 2 show the chroma readings of the respective sets of data. Figure 6 shows the linearity plot.
- (2) **Comparison of Open-Face and Closed-Face Samplers:** Table 1 shows data for both sampler designs subjected to the same test conditions. The results showed no significant differences between the two designs.

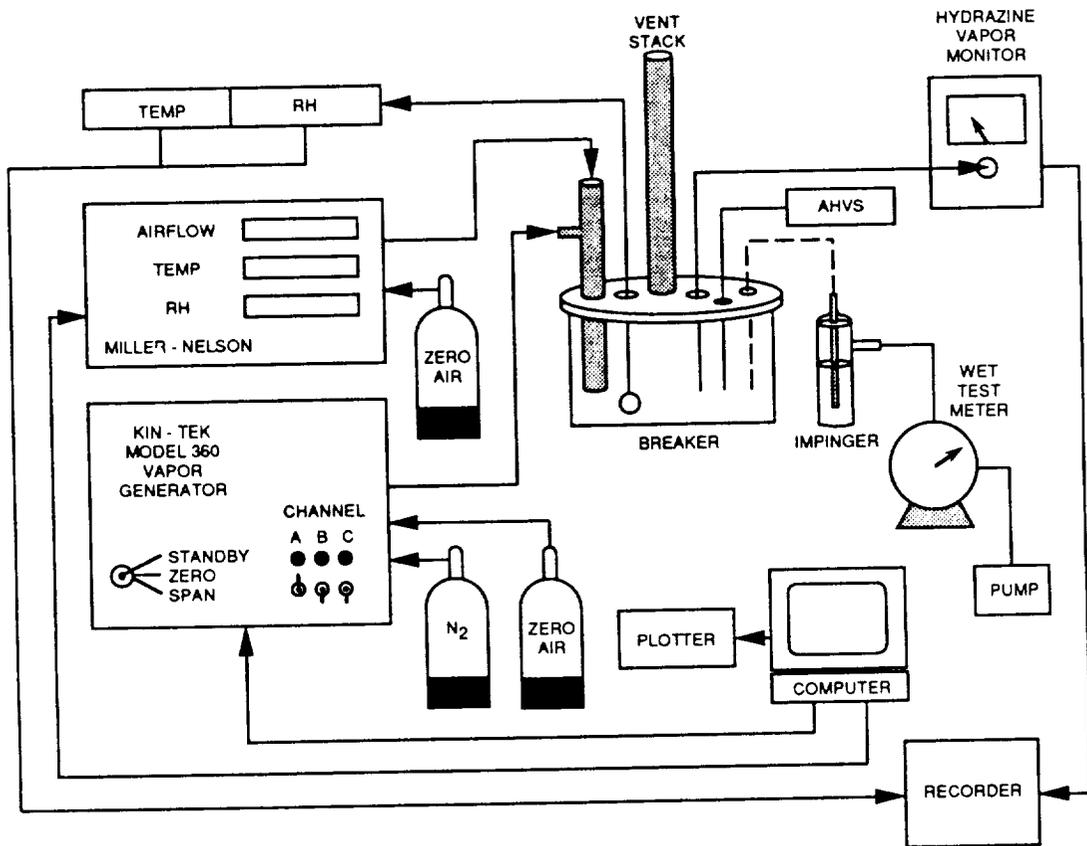


Figure 4. Hydrazine Vapor Generation System



Figure 5. Minolta Chroma Meter

Table 1. Precision and Linearity Test (Five-Minute Sample)

Run	Chroma for 9.2 ppb	Chroma for 38.6 ppb	Chroma for 296 ppb
Open Face			
1	22.60	43.52	69.03
2	23.90	42.96	69.12
3	22.23	42.60	68.16
4	22.01	42.91	68.49
Mean	22.69	43.00	68.70
Standard deviation	0.85	0.38	0.45
Closed Face			
1	22.63	42.23	67.44
2	23.02	43.82	67.82
3	23.95	42.49	67.51
4	23.10	43.84	67.67
Mean	23.18	43.10	67.61
Standard deviation	0.56	0.86	0.17

Table 2. Precision and Linearity Test (One-Minute Sample)

Run	Chroma for 38.9 ppb	Chroma for 95 ppb	Chroma for 296 ppb	Chroma for 950 ppb
1	20.14	33.70	47.40	68.84
2	20.20	32.72	48.13	67.52
3	20.46	33.07	49.79	70.10
4	20.69	33.55	48.45	70.32
Mean	20.37	33.26	48.44	69.20
Standard deviation	0.25	0.45	1.00	1.29

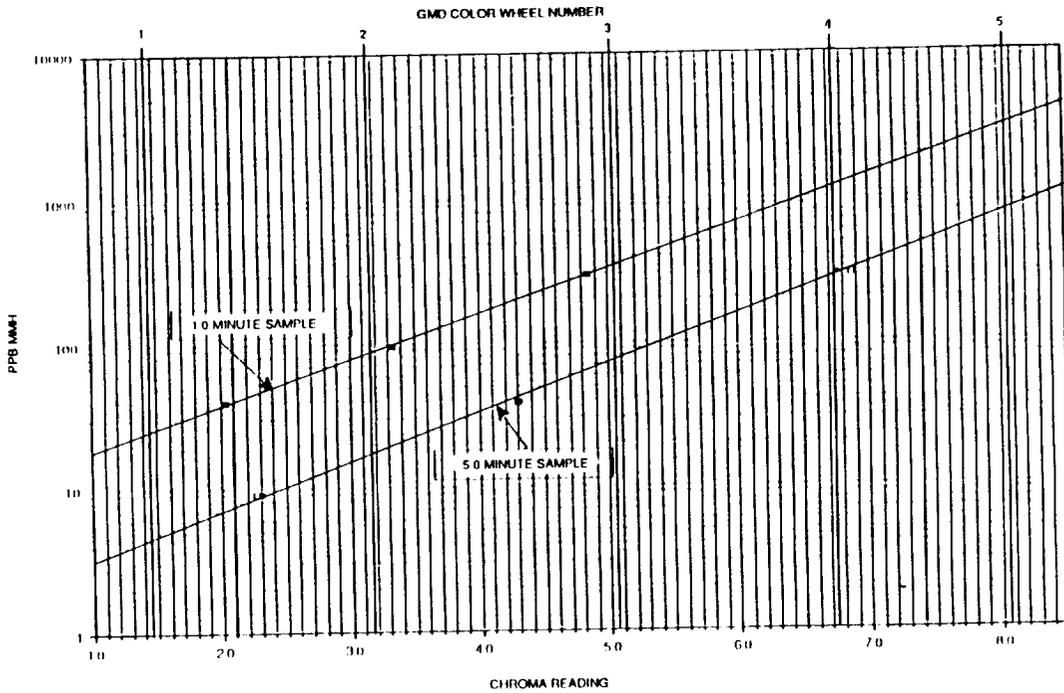


Figure 6. Linearity Plot

Table 3. HZ Versus MMH Test

MMH Run	Chroma for 9.2 ppb	Chroma for 38.6 ppb	Chroma for 296 ppb
1	15.55	33.93	66.82
2	16.09	34.65	65.36
3	15.67	33.63	68.23
4	16.06	33.78	64.91
5	14.81		66.52
Mean	15.64	34.00	66.37
Standard deviation	0.52	0.45	1.31
HZ Run	Chroma for 9.1 ppb	Chroma for 42.0 ppb	Chroma for 338 ppb
1	20.97	37.77	55.92
2	20.36	39.10	56.41
3	20.98	38.78	58.28
4	20.53	38.69	58.07
5	20.79	37.42	57.53
Mean	20.71	38.35	57.24
Standard deviation	0.31	0.72	1.04

- (3) **HZ Versus MMH Test:** With all other test conditions held constant, the sampler tested with HZ or MMH vapor of comparable concentrations indicated a difference in results. Data are shown in table 3 and plotted in figure 7.
- (4) **Temperature/Relative Humidity Effects and Response Time:** Chroma readings after exposure of each card to a T/RH condition were plotted (figure 8). The results indicated a minor temperature effect above freezing point and a minor RH effect. The color development was much slower at absolutely dry conditions. Color is developed as the vanillin-coated paper picks up moisture from the air [2]. At a 10-ppb level, a difference of two chroma units represents 1.5 ppb.
- (5) **Interference:** No color is developed due to sunlight, ammonia, nitrogen dioxide, and Freon [4]. Table 4 shows MEK and IPA interference test results. The sample time was 5 minutes and the sample rate was 1 liter/minute. These tests indicated MEK and IPA do not interfere with MMH and HZ color development significantly.
- (6) **Shelf Life:** Chroma readings obtained from the test are shown in table 5 and plotted in figure 9. There appears to be a small degradation of the chemical. Although slight degradation is detected by the Chroma Meter, the degradation probably will not be detected by the color wheel in the field. A study performed by the Naval Research Laboratory [5] indicated vanillin cards that passed the expiration date of November 1989 for approximately two years read an average of 20 percent lower compared with a fresh card.

FIELD TEST

The open-face and close-face AHVS was field tested by the industrial hygienists at KSC, White Sands Test Facility, and Hill Air Force Base. Although Hill Air Force Base has not completed the test, both KSC and White Sands users have reported the high sensitivity of the devices has greatly benefited them in the detection of extremely low levels of HZ/MMH vapors in near realtime. For example, the AHVS proved invaluable in the location and elimination of a serious, low-level source of contamination that had evaded detection using standard available monitors. The contamination source was identified as a pump used for the analysis of nonvolatile residue content in liquid hydrazine, which was moved from the fume hood to the lab's bench area in order to provide more space in the hood. As hydrazine vapor emitted from the pump due to hydrazine desorption, it contaminated the laboratory work area. KSC industrial hygienists used a conventional portable hydrazine instrument and a detection tube in an attempt to find the source. Both of these devices failed; however, AHVS quickly determined the pump as the culprit. Additionally, other devices failed to identify area contamination due to the cumulation of hydrazine vapor in a floor drain and a pin hold in a hydrazine storage drum. Both were identified by AHVS.

The field test has also verified that the AHVS is rather specific for HZ/MMH detection. Color development due to interferant was reported only in one instance that occurred when sampling a lunch room. In the lunch room, the AHVS developed a pink color. The pink color was later confirmed in the lab as interference due to cigarette smoke. White Sands has reported that chlorine gas does not interfere with the vanillin chemistry. This was found during a hydrazine spill cleanup where the decontamination process called for the use of Clorox.

Over all, the user's evaluations of AHVS are very positive. More units were requested by users from other NASA centers and Air Force organizations.

CONCLUSION

The Active Hydrazine Vapor Sampler is an important development because it is the only known device to date that can accurately measure 10-ppb HZ/MMH in less than 5 minutes. In addition, the device is lightweight, extremely easy to use, relatively inexpensive (less than \$1,000 per unit), and contains no hazardous materials. Since the device requires no chemical calibration, it would be specially useful for organizations that have no chemical laboratory to support instrument calibration. The device is also versatile; in addition to using it as an area monitor or a leak detector, it can be easily adapted for use as a breathing zone monitor. Furthermore, the device is not

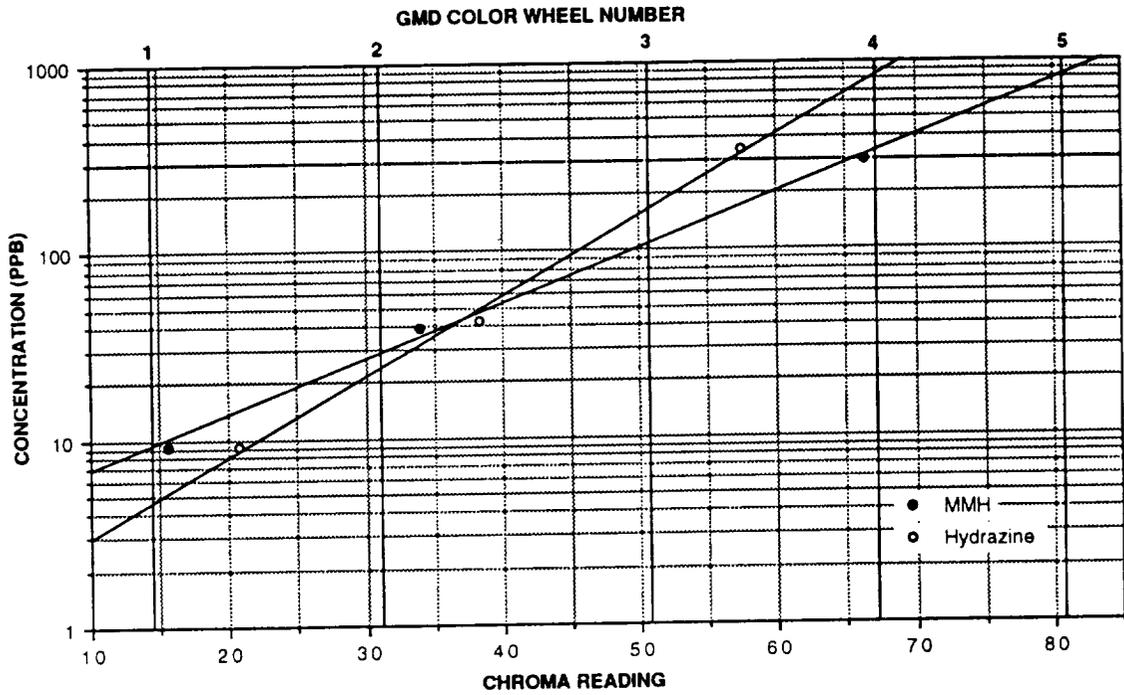


Figure 7. GMD Color Wheel Number

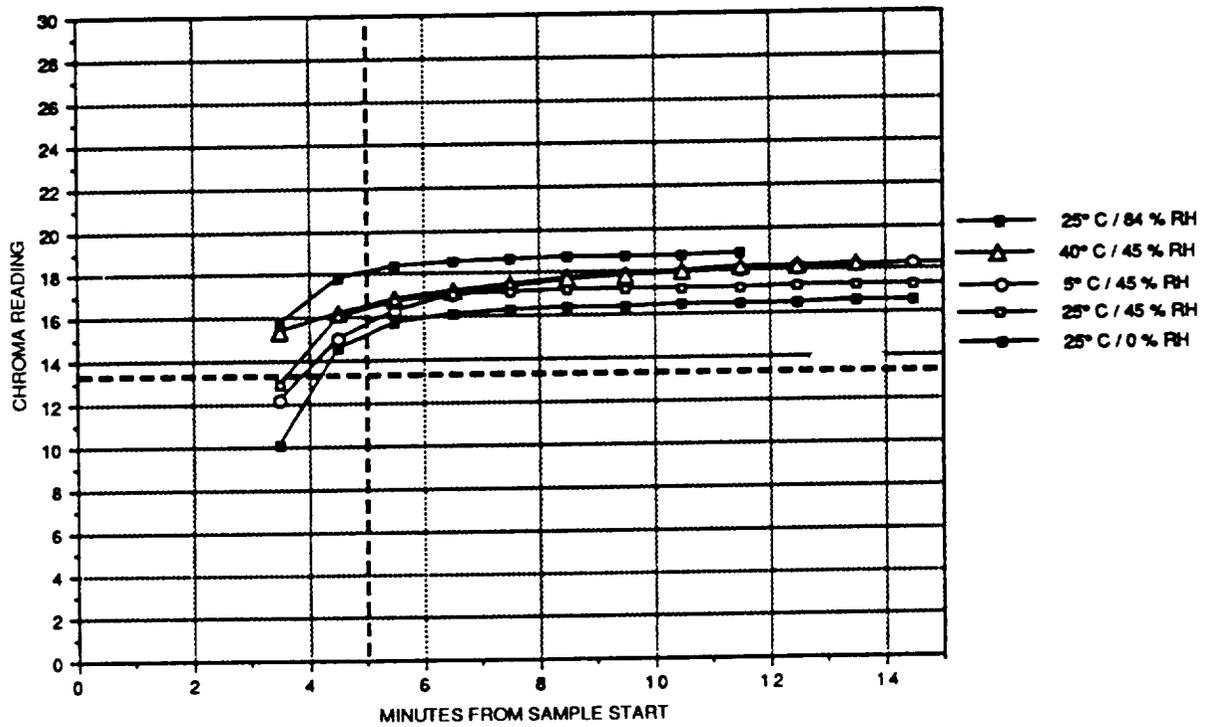


Figure 8. Response Time at Varying Temperature and Relative Humidity (10-ppb MMH, 3-Minute Sample Time, 2 Liters/Minute Sample Rate)

Table 4. Interference Test With Methyl Ethyl Ketone and Isopropyl Alcohol

Test Vapor	Concentration (ppb)	Interference Vapor	Concentration (ppm)	Chroma Reading
Hydrazine	24	-	-	16.49
Hydrazine	24	IPA	5,000	18.02
Hydrazine	15	MEK	4,000	13.35
Hydrazine	15	-	-	11.70
-	-	MEK	4,000	4.63
MMH	14	-	-	14.84
MMH	14	IPA	5,000	13.29
MMH	14	MEK	4,000	19.55

Table 5. Shelf Life With Cards Stored in Refrigerator and Ambient

Day	Refrigerator Chroma Reading	Ambient Chroma Reading
8	50.39	50.34
	50.64	51.19
	52.01	51.49
Mean	51.01	51.01
15	51.26	53.50
	52.04	51.89
	50.97	52.58
Mean	51.42	52.66
29	49.98	51.48
	49.73	49.98
	50.91	51.24
Mean	50.21	50.90
42	48.06	48.43
	48.36	49.00
	49.48	48.72
Mean	48.63	48.72
Standard deviation	1.27	1.57

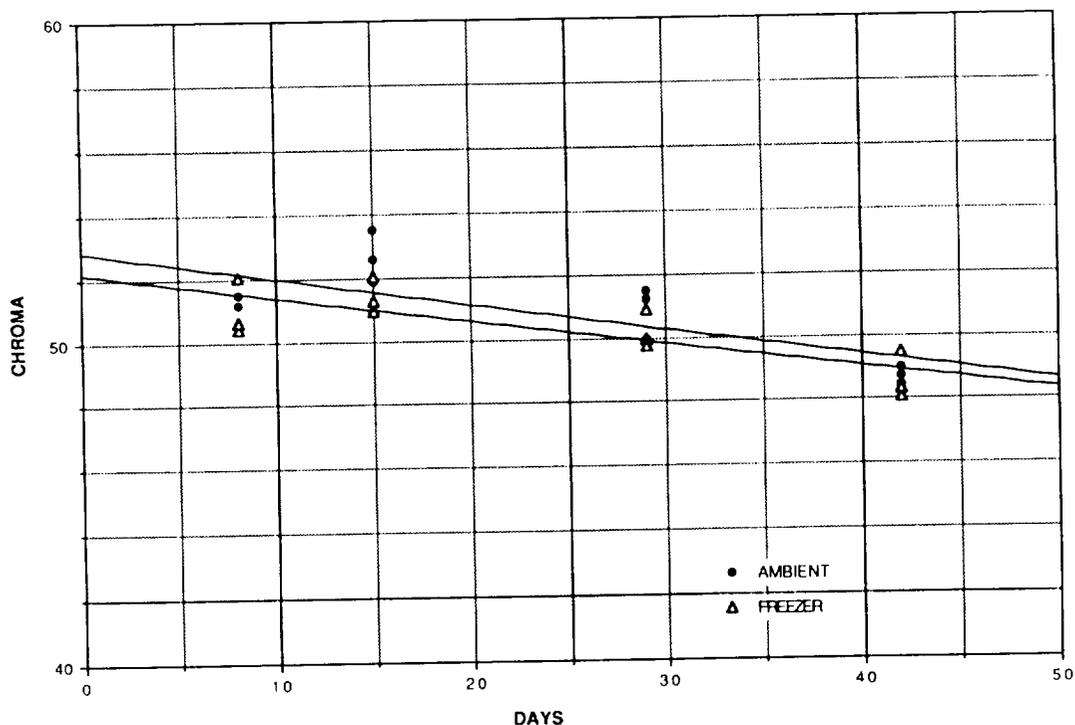


Figure 9. Shelf Life

limited to the measurement of HZ or MMH. Its application can be extended to measure numerous other toxic vapors by a simple change of the tape chemistry. The device has potential to significantly improve the response time for early detection of other toxic vapors and, thus, enhance protection of all personnel working with toxic substances.

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