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Performance Evaluation of a Colorimetric Hydrazine Dosimeter

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13. ABSTRACT <i>(Maximum 200 words)</i> A dosimeter for real-time, colorimetric detection of hydrazine in air has been developed. The passive badge consists of a dosimeter card containing a vanillin solution coated on a thin paper substrate. The active patch consists of a thick cellulose substrate coated with a vanillin solution. When placed in a plastic sample holder attached to a personnel pump, up to 5 L/min can be drawn through the active badge substrate. Through a condensation reaction, vanillin reacts with hydrazine to form a colored product that absorbs in the visible region. The hydrazone formed in the reaction is yellow; its intensity is proportional to the dose. When exposed passively to hydrazine, the experimental detection limit is < 20 ppb-hrs. Extrapolated results indicate a detection limit of < 5 ppb-hrs for long sampling periods. Actively sampling of hydrazine vapors gives an experimental detection limit of < 100 ppb-L at a sample rate of 5 L/min. Relative humidity effects on badge response were minor. High humidity enhanced the color development on the vanillin badge; while low humidity had no effect on badge response. Interference testing of the dosimeters revealed a tobacco smoke interference. Preliminary shelf life tests indicated no decrease in sensitivity to hydrazine when stored at room temperature for 6 months. <div style="text-align: right;">DTIC QUALITY INSPECTED 3</div>			
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CONTENTS

INTRODUCTION	1
THEORY	2
EXPERIMENTAL	3
Exposure Apparatus	3
Badge System Apparatus	4
Laboratory Evaluation	6
RESULTS AND DISCUSSION	7
CONCLUSIONS	14
REFERENCES	15
APPENDIX A	17
APPENDIX B	19
APPENDIX C	21

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PERFORMANCE EVALUATION OF A COLORIMETRIC HYDRAZINE DOSIMETER

INTRODUCTION

Unsubstituted hydrazine (N_2H_4) has found widespread use, most notably as a propellant in aerospace applications, an oxygen scavenger in boiler water and in commercial production of textiles and pesticides. While useful in its many applications, hydrazine poses a health hazard to personnel who come in contact with the compound. The threshold limit values (TLV) for exposure to hydrazine vapors have been established at 100 parts-per-billion (ppb) by the American Conference of Governmental Industrial Hygienists (ACGIH) which lists hydrazine as a suspected human carcinogen.⁽¹⁾ The National Institute for Occupational Safety and Health (NIOSH) has recommended that exposure to hydrazine not exceed 30 ppb.⁽²⁾ The ACGIH plans to lower the exposure limit of hydrazine.⁽¹⁾ To safeguard employees who may come into contact with hydrazine, employees and their work environments should be monitored.

A real-time colorimetric dosimeter for the determination of personnel exposure to hydrazine and its methylated derivative monomethylhydrazine (MMH) was developed at the Naval Research Laboratory (NRL) and was issued a patent.^(3,4,5) The dosimeter relies on the rapid reaction between vanillin (3-methoxy-4-hydroxybenzaldehyde) and hydrazine or MMH. The chemistry can be used in a passive or active sampling system. Previously the passive dosimeter was evaluated in the laboratory and field for NASA applications; the primary concern was response to MMH.⁽³⁾ The Navy has an interest in a real-time detection method for hydrazine in submarine environments. Not only does this present a unique sampling environment, but due to the prolonged exposure of submarine personnel, lower TLVs must be met. In 1989, NAVMEDCOM lowered the desired detection limit of hydrazine exposure for Navy personnel to 0.1 ppb.

The Navy first requested an action plan and cost estimate in 1989. NRL was tasked by the Navy to develop passive and active badges that would meet their detection needs. The

vanillin patches used in the past by the Navy sponsors were prepared by hand at NRL. Recently, the badges were accepted by the Navy for routine use. To meet the new demand for a larger quantity of badges, a commercial manufacturer was needed and a request to qualify a vendor was made. Because GMD Systems, Inc. is licensed to manufacture vanillin badges, the company was contracted to machine coat and assemble badges for the Navy. GMD has previous experience with the preparation of the dosimeters and supplied similar dosimeters for the laboratory evaluation of the passive vanillin dosimeter with MMH vapor, mentioned previously.⁽³⁾ The Navy then tasked NRL to evaluate the performance of both the active and passive dosimeters manufactured by GMD systems, Inc. for response to hydrazine. This paper is the culmination of the joint research effort between NRL, Geo-Centers, Inc. and GMD Systems, Inc.

THEORY

The extreme reactivity of the hydrazines is responsible for a variety of technical problems encountered in performing ambient air monitoring. One approach that utilizes this reactivity is derivatization of the hydrazine to a species that is easier to analyze. There currently exists an ASTM analytical method that is based on the condensation of a hydrazine and an aldehyde, to form a hydrazone. In the case of unsubstituted hydrazine, two moles of aldehyde can react with one mole of hydrazine to form the azine. The mechanism involves nucleophilic addition to the nitrogen base, followed by the elimination of water. This reaction is acid catalyzed by protonation of the carbonyl group. The ASTM method condenses the hydrazine with para-N,N-dimethylaminobenzaldehyde (PDAB).⁽⁶⁾ In an acidic solution, the absorbance of the protonated p-quinone structure is measured spectrophotometrically at 458 nm.⁽⁶⁾ A similar condensation reaction occurs between vanillin and hydrazine or MMH. Figure 1 shows the reaction between hydrazine and vanillin.

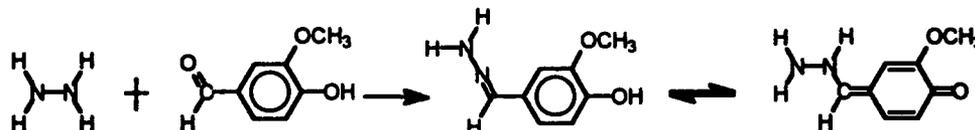


Figure 1. The condensation reaction between unsubstituted hydrazine and vanillin.

Similarly to the ASTM reaction of PDAB and hydrazine, an acidified vanillin solution is required to form a colored product upon reaction with hydrazine. We believe that non-acidified vanillin reacts with hydrazine to form a colorless hydrazone. Upon acidification, the hydrazone is protonated, shifting the absorbance to the visible range and turning the product yellow. The colored hydrazone yields a peak absorbance at 420 nm.

EXPERIMENTAL

Exposure Apparatus

The reactivity of hydrazine makes it difficult to generate and maintain the low ppb levels required for testing. A dynamic system was assembled which supplied the hydrazine vapor. A diffusion tube containing propellant grade liquid hydrazine (Olin Chemicals) was housed in a constant temperature bath, and continually purged with 100 mL/min of dry nitrogen to provide the hydrazine vapors.⁽⁷⁾ The desired concentration was obtained by adjusting the temperature of the bath, the size of the diffusion capillary and/or the amount of dilution air. To generate low concentrations in the range of 5 to 20 ppb, the hydrazine in the diffusion tubes was mixed with water.

Conditioned house-compressed air was used as the diluent. The conditioning procedure consisted of passing the house air through a series of demisters, an organic removal cartridge, a reciprocating dual-tower molecular sieve scrubber, and finally through a canister containing potassium permanganate coated alumina (Purafil) and charcoal. The cleaned air was humidified using a stainless steel gas washer (bubbler) containing distilled water. Control of the relative humidity was achieved by varying both the gas washer head pressure and the ratio of the humidified to dry air. The moisture content of the air was measured by a HygroDynamics hygrometer (Silver Spring, MD). The dilution air was monitored with calibrated mass flow controllers capable of providing up to 10 L/min (Matheson Gas Products, E. Rutherford, NJ).

A cylindrical glass chamber with conical ends was used as a test chamber to expose the coated substrate to the test vapor. The exhaust end was removable to allow insertion of

the dosimeters. Teflon baffles placed at each end induced uniform flow. A flow of $10.0 \pm 10\%$ SLPM was generally used corresponding to a face velocity of approximately 160 cm/min (5.2 ft/min). The concentration of the test vapor in the chamber was independently verified using impinger collection and coulometric titration. The coulometric titration procedure used to verify the concentrations of the dynamic test environment has been characterized at NRL.¹⁸⁾

Badge System Apparatus

Because the badge design of interest to the Navy was not yet available, the passive badges used in the evaluation were those designed for use by NASA. The passive badges contained two reaction sites; however, the second reaction site, coated with PDAB was not used in this evaluation. The site of interest to the Navy was coated with 2% (w/v) vanillin in isopropanol. The acid concentration was 2% (v/v). The PDAB site was not used because it discolors in less than 7 days of ambient exposure. The paper substrates used for both passive and active badges were machine coated by drawing them through an indicator solution after which they were air dried and cut to proper size. For the passive badges, the coated filter paper was separated into strips and sandwiched in a thin cardboard housing 7.3 cm X 4.4 cm X 0.1 cm in size. The housing face had two 1.25 cm diameter circles cut out for exposure of the coated paper. A tabbed section at the bottom of the badge provided a means of easily removing a protective cover over the indicator spots immediately prior to use. The active patches consisted of a thicker cellulose substrate coated with the vanillin solution. Figure 2 shows the passive badge and the active patch and sample holder. Although the passive badge used in the evaluation was imprinted with the NASA logo, the final badges available to the Navy will contain a suitable logo.

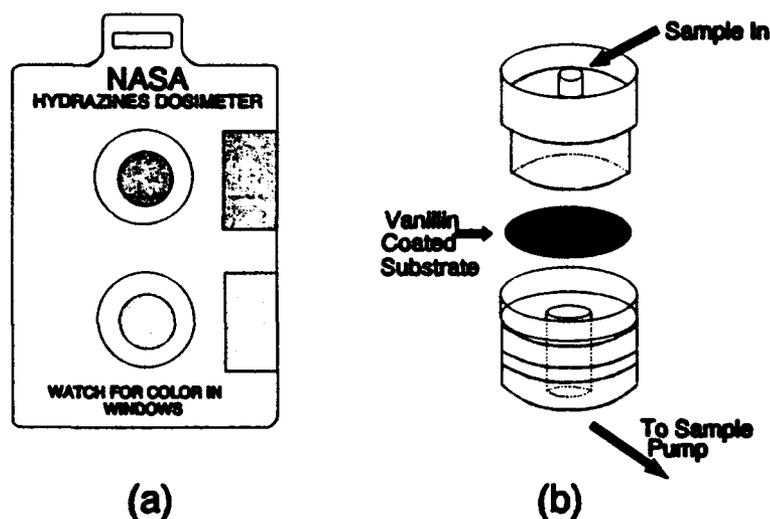


Figure 2. The vanillin dosimeters used in the laboratory evaluation were a) the passive badge and b) the active patch and sample holder.

In the test chamber, passive badges were hung vertically and back-to-back for exposure to the vapors. The active badges were placed in the plastic sample holder shown diagrammatically in Figure 2. The holder was connected to a personal sampling pump which pulled air through the coated substrate at approximately 5 L/min. The color development on the badges was measured with a color wheel or dose estimator which contains five color indices of increasing intensity in the yellow color group. Figure 3 shows a schematic of the color wheel. The color wheel was designed to accept the passive badge into the back of the wheel. Once in place, the color wheel can be easily manipulated to match the badge color development. The final Navy badge and color wheel designs will be included in a later report.

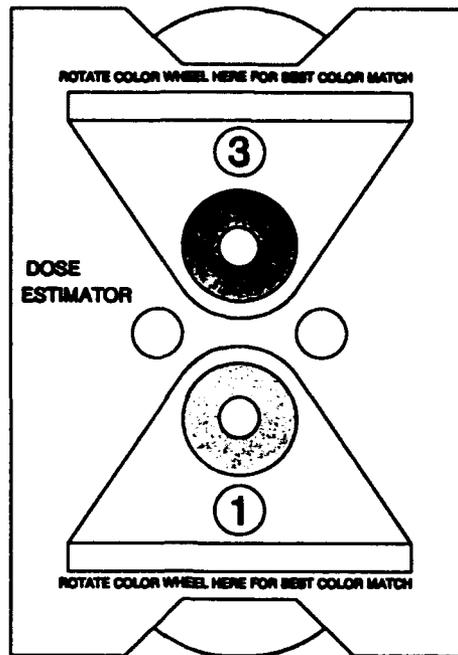


Figure 3. Color wheel (dose estimator) used for measuring amount of color developed on exposed badges.

Laboratory Evaluation

The active badges were evaluated for dose response, relative humidity and interference effects and reasonable shelf-life. The test plan for this evaluation can be found in Appendix A. Because the passive badges were previously evaluated for relative humidity effects, only the active badges were evaluated for humidity effects in the current study.⁽³⁾ To achieve the desired doses of hydrazine, the badges were exposed to concentrations of hydrazine ranging from 5 to 4500 ppb at different sample times. Relative humidity tests were comprised of exposures to 5, 20 and 200 ppb of hydrazine at humidities of <10% and 90%. Interference effects were studied by exposing the badges to substances typical to submarine environments including kerosene, turbine oil, paint vapors and cigarette smoke. Passive badges were exposed to the potential interferences prior to or after exposure to 100 ppb-hrs of hydrazine. Active badges were exposed to 900 ppb-L of hydrazine before or after exposure to the

interferences. Shelf life tests, in which passive and active badges were stored for one year at 40°C or 25°C and exposed to hydrazine each month, have not been completed to date. The preliminary results are presented in this report. Color development on the passive dosimeters was judged immediately after each exposure. For the active badges, color was judged within one minute after exposure. The standard relative humidity was 30 - 40% for all tests unless noted otherwise.

RESULTS AND DISCUSSION

Dose response tests for the passive badges were conducted at concentrations of hydrazine ranging from 5 to 4500 ppb and exposure times of 1 minute to 120 hours. Figure 4 shows the dose response plot for the passive badges as measured with the color wheel. The plot shows the median color wheel index and 95% error bars at a given dose. With the exception of the points at 50 and 6000 ppb-hrs which were comprised of 4 badges apiece, each point represents at least 36 badges. Although the exact saturation dose has not been determined, the badges reached a saturation color of 5.0 within a dose of 6000 ppb-hrs.

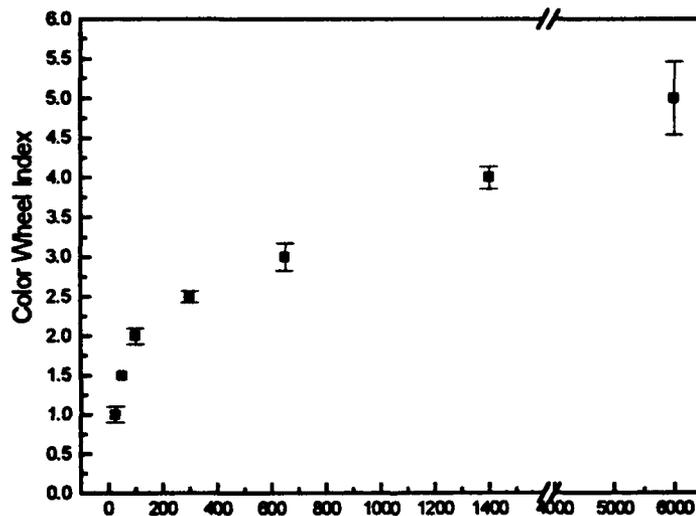


Figure 4. Dose response plot of passive badge exposed to hydrazine.

Appendix B presents the passive badge data in grid form. For a given exposure time and resultant color wheel index, the approximate hydrazine concentration can be determined.

Active badge exposures are graphically depicted in Figure 5. Using hydrazine concentrations of 5 to 1500 ppb and exposure times of 1 to 60 minutes, doses of 100 to 20,000 ppb-L were obtained. A median of approximately 14 badges and the resultant 95% error bars comprise each point shown on the graph. Although the precise saturation point is not apparent with the given data, saturation appears to occur within a dose of 20,000 ppb-L with a color wheel index of 5.0. Appendix C presents the active badge data in a table. As with the table in Appendix B for the passive badges, Appendix C allows the determination of the approximate hydrazine concentration for a given exposure time and color wheel index.

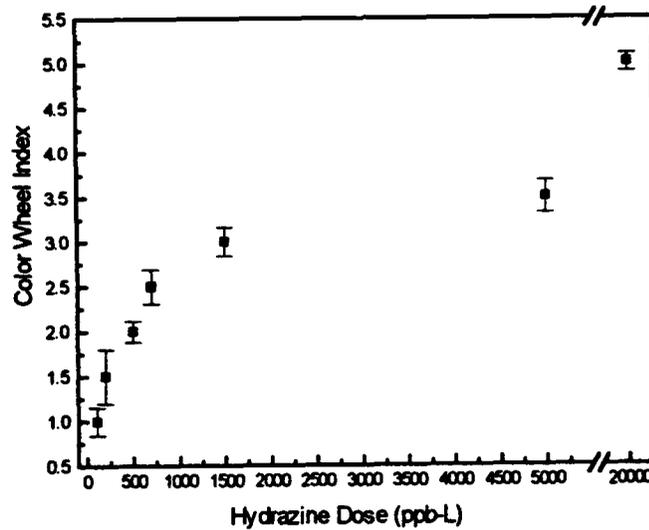


Figure 5. Dose response plot of active exposures to hydrazine.

Relative humidity effects were studied through a series of exposures to 5 to 200 ppb of hydrazine with the humidity controlled to < 10% and 90%. Only the active badges were exposed to these conditions. Figure 6 depicts the results of these exposures. Exposures at < 10% and 90% RH were compared with the "standard" condition of 40% RH. Each point

in the figure represents the median of approximately 8 badges. High humidity appeared to enhance the color development on the badges. With the exception of the exposure to 6500 ppb-L of hydrazine at 90% RH, all badge responses were within $\pm 30\%$ of the response at the standard of 40% RH.

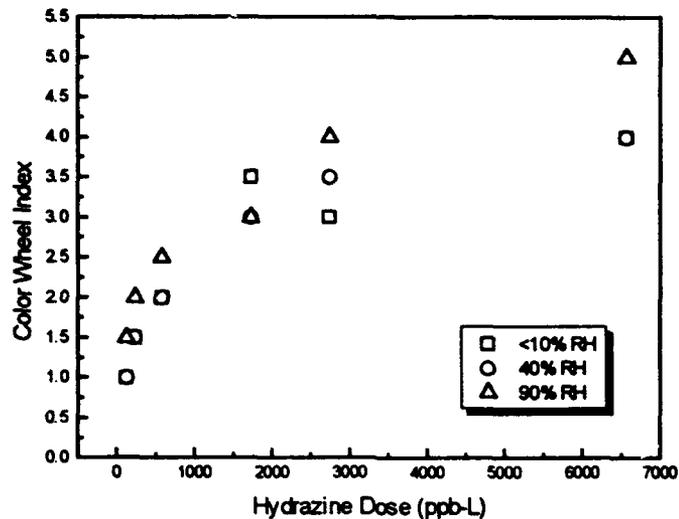


Figure 6. Relative humidity effects for active exposures to hydrazine

Interference testing was conducted with both passive and active badges. As discussed previously, potential interferences examined were paint, turbine oil, kerosene (diesel fuel) and cigarette smoke. The exposure apparatus consisted of placing the interferent in a beaker, or in the case of the cigarette smoke interference, on a watch glass. A 1 L beaker was inverted over the interferent with the badges inside. This formed an exposure chamber which would allow the badges to be exposed to the interference vapors. Passive badges were exposed for 3 hours to the potential interference before or after they were exposed to a 100 ppb-hr dose of hydrazine (3 hours at 30-40 ppb). The active badges were exposed to interferences before or after they were exposed to a 900 ppb-L dose of hydrazine (30-40 ppb). Active samples were taken for 5 min at a sampling rate of 5 L/min for both hydrazine and the interferences. Figure 7a shows the set up for the passive badges, while Figure 7b shows the set up for the

active badges exposed to the interferences.

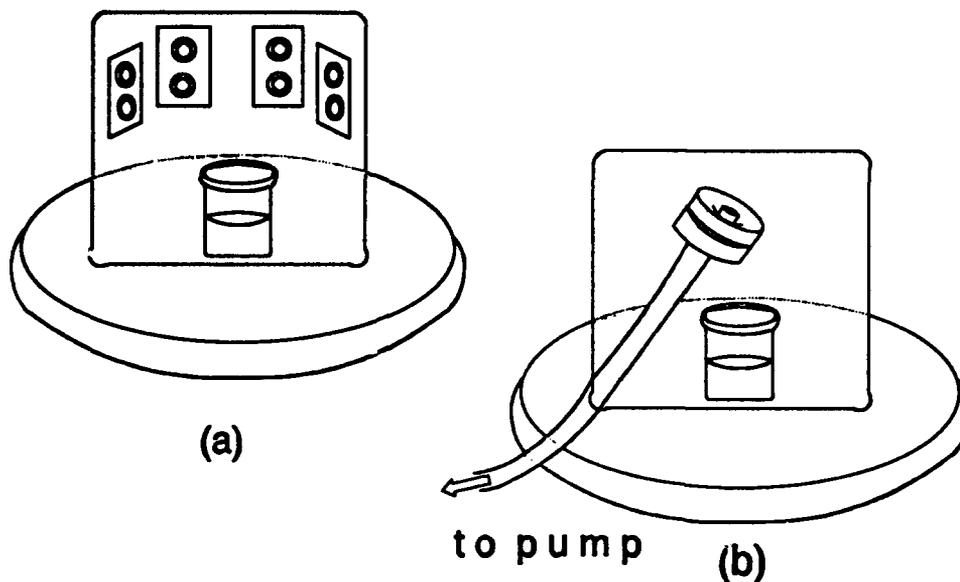


Figure 7. Chamber set up for interference testing with a) passive badges and b) active badges.

Table I shows the passive badge response to the interferences and hydrazine. Since a dose of 100 ppb-hrs of hydrazine was used in these exposures, the appropriate color wheel value must be determined from response data at this dose. The color wheel index for a 100 ppb-hr exposure to hydrazine is 2.0 ± 0.5 indices. Alternatively, using the Passive Exposure table in Appendix B, a color wheel value of 2.0 is found for a 3 hour exposure to 40 ppb of hydrazine. Therefore, 2.0 ± 0.5 color indices was considered the "ideal" color development to which the interferent-exposed badges were compared. To read the table, follow data across a row. For example, for the first test, the badges were exposed to hydrazine as test vapor 1 (see first column). The median color wheel index and standard deviation measured from the badges after exposure to hydrazine is listed in the second column. The same badges were then exposed to turbine oil (see third column). The color development after both

exposures is shown in the fourth column.

Table I. Passive Badge Response to Interferences

Test Vapor 1	Color Wheel Index After Vapor 1	Test Vapor 2	Color Wheel Index After Vapor 2
hydrazine	2.0 ± 0.0	turbine oil	2.5 ± 0.5
turbine oil	0.0 ± 0.0	hydrazine	2.0 ± 0.0
hydrazine	2.5 ± 0.5	paint	2.5 ± 0.5
paint	0.0 ± 0.0	hydrazine	2.0 ± 0.0
hydrazine	2.0 ± 0.0	kerosene	2.0 ± 0.0
kerosene	0.0 ± 0.0	hydrazine	2.0 ± 0.0
hydrazine	2.0 ± 0.0	cigarette smoke	1.0 ± 0.0
cigarette smoke	2.0 ± 0.0*	hydrazine	2.0 ± 0.0*

* These badges were yellow-peach with purple-pink edges under the viewing ring.

As indicated in the above table, only cigarette smoke caused an interference effect on the vanillin badges. Exposure to the cigarette smoke prior to hydrazine caused a yellow-peach color to develop. Although this color did not match the shades on the color wheel, the color intensity was ascertained to correlate with a color wheel index of 2. No further color development was noted upon subsequent exposure to hydrazine. Exposure to cigarette smoke after hydrazine caused a bleaching effect to occur on the badge, rendering the response invalid. In an earlier field test at Kennedy Space Center, badges were exposed to cigarette smoke in a personnel lounge. The badges developed a pale pink color. The current evaluation

subjected the vanillin badges to a higher concentration of cigarette smoke than the earlier field test. We conclude that cigarette smoke is an interferent to the vanillin badge and an accurate assessment of a exposure to hydrazine cannot be made in the presence of cigarette smoke.

Table II shows the active badge response to the interferences and hydrazine. A dose of 900 ppb-L of hydrazine was used in the active interference tests. Therefore, the dose response data at this dose is important for comparison purposes with these badges. The color wheel index for a 900 ppb-L exposure to hydrazine is 2.5 ± 0.0 indices. Therefore, 2.5 ± 0.0 color indices was considered the "ideal" color development to which the interferent-exposed badges were compared.

Table II. Active Badge Response to Interferences

Test Vapor 1	Color Wheel Index After Vapor 1	Test Vapor 2	Color Wheel Index After Vapor 2
hydrazine	2.0 ± 0.0	turbine oil	2.5 ± 0.0
turbine oil	0.5 ± 0.0	hydrazine	2.0 ± 0.5
hydrazine	2.0 ± 0.5	paint	2.0 ± 0.0
paint	0.5 ± 0.5	hydrazine	2.5 ± 0.5
hydrazine	2.0 ± 0.5	kerosene	2.5 ± 0.0
kerosene	0.0 ± 0.0	hydrazine	2.0 ± 0.0
hydrazine	2.5 ± 0.5	cigarette smoke	yellow-brown front, pink edges and back
cigarette smoke	yellow-brown front, pink edges and back	hydrazine	yellow-brown front, pink edges and back

It was concluded that neither oil, paint nor kerosene was an interference with the active badges. Cigarette smoke, however, was an interferent as shown in Table II. If badges are exposed to cigarette smoke prior to hydrazine exposure, any measurement of color development on the badge in the presence of hydrazine will be severely hindered. Any color development of the badge upon exposure to hydrazine before exposure to cigarette smoke can be measured; however, the color will soon be obscured if cigarette smoke is present.

Active control badges were exposed in several ways. Coated substrates were exposed to the same dose of hydrazine as the test badges (900 ppb-L) and then exposed to 25 L of room air. The badges responded similarly to the test badges for oil, paint and kerosene. In another control test, an uncoated substrate was exposed to cigarette smoke. The substrate turned a spotty brown color.

Shelf-life or storage stability tests are currently being conducted each month for a year after receipt of the badges from the manufacturer. Data for the first 6 months has been completed and is presented here. Badges were separated into two storage categories, oven (40°C) and room (25°C) temperature. Once a month, 2 oven-stored and 2 room-stored passive badges were exposed to hydrazine doses of approximately 90 and 360 ppb-hrs (15 ppb for 6 and 24 hours, respectively). The passive badges stored at room temperature showed no discoloration due to storage and when exposed to hydrazine vapors, showed no degradation in sensitivity over the 6 months of testing completed to date. The badges stored in the oven discolored to a color wheel value of 0.5 within 2.5 months of storage. Although the badges stored in the oven showed consistently decreasing sensitivity to hydrazine vapors over the preliminary test period, badge response for the room- and oven-stored badges remained within $\pm 30\%$ of the ideal value. The ideal value was selected from passive dose response tests at the two doses tested in the shelf life evaluation. In addition, 3 oven- and 3 room-stored active badges were exposed to hydrazine doses of approximately 375 and 2250 ppb-L (15 ppb for 5 and 30 minutes, respectively). The active badges stored at room temperature showed no degradation in sensitivity over the 6 months of testing. The oven-stored badges discolored to a taupe color within 2.5 months of storage. Upon exposure to hydrazine the badges showed a response to the vapors; however the sensitivity was significantly decreased. The badges were too discolored to be measured with the color

wheel.

CONCLUSIONS

Because the response of the dosimeters are dose dependent and not concentration dependent, they are useful at a wide range of hydrazine concentrations. This evaluation tested concentrations of 4 to 4600 ppb of hydrazines. The active badge data suggests that a reliable measurement of 4 ppb of hydrazine can be made at a quick-check sampling time of 5 minutes at a 5 L/min sampling rate. Using results from data extrapolation hydrazine concentration of less than 1 ppb could be measured in 30 minutes of active exposure. Passively, measurement of 20 ppb hydrazine is possible in as little as 1 hour. Extrapolated passive results show that less than 1 ppb of hydrazine can be detected in approximately 72 hours of exposure.

Relative humidity effects on badge response were minor. High humidity enhanced the color development on the vanillin badge. Low humidity had no effect on badge response. Interference testing of the dosimeters revealed a cigarette smoke interference. The active badges developed a yellow-brown color on the front of the badge and a pink color on the back and edges in the presence of cigarette smoke. Although the active badge turned slightly more yellow in the subsequent presence of hydrazine, indicating some remaining level of sensitivity to hydrazine, the color is extremely difficult to measure with the color wheel. The reaction site on the passive badges developed a yellow-peach color with purple-pink under the viewing ring. The passive badge did not retain sensitivity to hydrazine vapors after exposure to cigarette smoke. It is recommended that the badges not be used in areas of heavy cigarette smoke.

The specifications for the hydrazine dosimeter are included in the test plan in Appendix A. With the exception of the cigarette smoke interference, the dosimeter produced by GMD Systems, Inc. met the minimum specifications stipulated in the test plan.

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APPENDIX A

SPECIFICATIONS FOR A HYDRAZINE VAPOR DETECTION DOSIMETER

1. SCOPE

This document defines the requirements for the performance and design of a hydrazine vapor dosimeter for the detection of hydrazine concentrations at the Threshold Limit Value (TLV) in a submarine atmosphere.

2. REQUIREMENTS

2.1 SYSTEM REQUIREMENTS.

2.1.1 Operational Time: The passive dosimeter shall be capable of detection of hydrazine levels for up to one week of continued use. The active dosimeter shall be capable of 60 minutes of monitoring at 5 L/min.

2.1.2 Single Point Sensing: Each sample area shall be provided with an individual dosimeter. Multiple sample points sensed by one dosimeter are not acceptable.

2.2 TECHNICAL REQUIREMENTS.

2.2.1 Dimension: The maximum dimension of the passive dosimeter shall not exceed 4.5 x 7.0 x 0.1 cm. With the addition of a molded plastic holder, the total dimensions shall not exceed 5.0 x 9.0 x 1.0 cm. The active dosimeter may be similar to Sure-Spot (GMD Systems, Inc., Old Route 519, Hendersonville, PA 15339, (412) 746-3600) if a substrate suitable for sampling 5 L/min for 60 min can be identified. If this is feasible, a rectangular clear plexiglass sampler designed by NASA/Kennedy Space Center personnel will be used. The active card shall not exceed 4.5 x 6.5 x 0.1 cm. With the addition of the NASA sampler, the active dosimeter system shall not exceed 6.0 x 8.0 x 2.0 cm. In the event that locating a substrate suitable for the Sure-Spot design is not feasible, a thick cellulose support will be used as the substrate in the active dosimeter. The sample holder will then consist of a round clear plastic two piece sampler with dimensions not exceeding 3 cm length x 3 cm diameter.

2.2.2 Detection Range: The passive dosimeter shall detect hydrazine at concentrations of 0 to 16000 ppb. The active dosimeter shall detect hydrazine at concentrations of 0 to 1000 ppb.

2.2.3 Sensitivity: The passive dosimeter shall detect hydrazine at a concentration of 1 ppb over a 24-hour period with a signal to noise ratio of 3 to 1. The active dosimeter shall detect hydrazine at a concentration of 1 ppb in a 15 minute sample at a sampling rate of 5 L/min with a signal to noise ratio of 3 to 1.

2.2.4 Precision: The dosimeters shall yield repeatable test results such that the maximum

deviation from the average response (use 10 badges for average) is within 20% of the average response, while measuring a 10 ppb hydrazine vapor.

2.2.5 Accuracy: The maximum absolute deviation from an ideal output shall not exceed $\pm 30\%$. This will be evaluated for several doses at five concentrations and several sample times.

2.2.5 Response Time: Using 10 ppb of hydrazine vapor, the passive dosimeter shall give a first indication in 45 minutes. The active dosimeter shall give a first indication within 1 minute when a sampling rate of 5 L/min is used.

2.2.6 Interferences: The following interference vapors typical of the submarine atmosphere in which the dosimeters will be used shall be required for testing. The minimum vapors required for testing are kerosene, turbine oil, paint vapors and cigarette smoke. High concentrations of these interferences will not result in a reading on the dosimeter greater than the detection limit of the badge.

2.3 ENVIRONMENTAL REQUIREMENTS.

2.3.1 Operational Relative Humidity (RH) Range: The dosimeters shall operate normally within a range of $< 10\%$ to 95% RH. The RH error shall not exceed $\pm 30\%$.

2.3.2 Operational Temperature Range: The dosimeters shall operate normally within a temperature range of 65°F and 80°F . The temperature error shall not exceed $\pm 30\%$.

2.4 RELIABILITY AND MAINTAINABILITY REQUIREMENTS.

2.4.1 Shelf Life: Storage of dosimeters over a period of one year shall not affect the performance of the dosimeters. On batch of dosimeters will be stored at room temperature; another will be stored at elevated temperatures. Over the one year period, the dosimeters shall respond to within $\pm 30\%$ of the normal value.

APPENDIX B

Exposure Table for Passive Vanillin Badges

Hydrazine Concentration (ppb)

Exposure Time	Color Wheel Value									
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1 min	1500	1500	4500*	7000	15000	35000	45000	79000	84000	91000
5 min	315	345	780	1400	3000*	6600	9100	16000	17000	18000
10 min	150	160	390	700	1500*	4500*	4500	7900	8400	9100
20 min	80	85	165*	350	725	1700	2300	3900	4200	4500
30 min	60*	60	130	185*	485	1100	2100	2600	2800	3000
1 hour	20*	25	65	115	175*	555	755	1500*	1500	1500
3 hours	9	9*	20	40	80	180	180*	440	465	505
6 hours	4	5*	10	25*	50*	90	125	185*	230	250
24 hours	1	1	4	5*	9*	25*	30	55	60*	65
72 hours (3 days)	0.4	0.4	1	2	3	5*	15	20	20	20*
120 hours (5 days)	0.2	0.2	0.5	1	2	5	6*	10	10	15
168 hours (7 days)	0.2	0.2	0.4	0.9	1	3	6*	8	8	9

* Experimental data; all other data was calculated.

APPENDIX C

Exposure Table for Active Vanillin Badges

Hydrazine Concentration (ppb)											
Exposure Time	Color Wheel Value										
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0		
1 min	20	25*	75	105*	365	665	1300	1500*	4600*		
2 min	10*	15	25*	70	170*	330	670	755	1900		
5 min	4*	6	15	20*	105*	170*	250*	300	750		
10 min	2	4*	10*	15	35	65	105*	150	325*		
15 min	1	2	5*	10*	20*	45	90	100	250		
20 min	1	2	4	7	19	35	65	75	165*		
30 min	0.7	1	2	4*	9*	20*	45	50	125		
60 min	0.3	0.5	0.8	4*	6	9*	20*	25	65		

* Experimental data; all other data was calculated.