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FINAL REPORT - NRL Tasks

**NOVEL
CHEMICAL AND OPTICAL
DIAGNOSTIC TECHNIQUES**

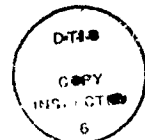
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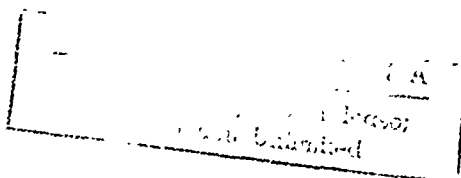
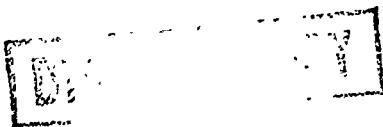
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INTRODUCTION

In this final report, the results obtained by GEO-CENTERS, INC. for the tasks performed in support of Naval Research Laboratory (NRL) Chemical Diagnostics Branch (Code 6110) Contract Number N00014-86-C-2266 during the period, September 1986 through January 1991 are summarized.

The tasks performed at NRL in support of Research of Novel Chemical and Optical Diagnostic Techniques are reported in this volume. Research conducted at other locations related to ordnance detection will be reported separately when that portion of the contract period of performance has ended.

GEO-CENTERS support at NRL addressed existing problems in the areas listed below:

1. Citric Acid Hydrazines Sampler
2. Photoionization
3. Materials Compatibility
4. Electrochemistry
5. Color Chemistry for the Detection of Hydrazines
6. Paper Tape Instrument Evaluation
7. Color Chemistry for the Detection of Nitrogen Dioxide (NO₂)
8. Nitrogen Dioxide Instrument Evaluation
9. Coulometric Titration Method Optimization
10. Color Chemistry for Detection of HCl
11. Additional Studies

Results from work performed in the areas listed above have been published either in refereed journals or reported as NRL Memorandum Reports or GEO-CENTERS reports. Additionally, results were presented in various meetings, including the American Chemical Society. Consequently, in this final report, only a summary is reported along with a list of

the publications/presentations. Copies of the papers and abstracts of the reports are given for each area in the Appendices. Following is a chronological summary of accomplishments in each pertinent area listed above.

RESULTS

1.0 Citric Acid Hydrazines Sampler

1986:

An evaluation commenced for a passive hydrazines sampler utilizing diffusion methods. The sampler used a collection medium of citric acid in methanol coated onto a polyester substrate. In October, citric acid samplers were characterized for collection of unsymmetrical dimethylhydrazine (UDMH). Various dosimeter badge designs for MMH collection were designed and evaluated in November. Extensive laboratory evaluation was conducted to determine the best candidate material and design for the badges. Linearity, precision, accuracy, and relative humidity and face velocity effects were examined for the dosimeters.

1987:

A badge design and material were selected by June. NASA/Kennedy Space Center (NASA/KSC), the sponsor, was notified of our findings and a company was located to manufacture the dosimeters. By July, the polyethylene badges were received and the test plan for characterization of the badges was implemented. The following parameters were examined: linearity, sampling rate, and humidity effects. Storage stability tests were carried out, leading to a study of the citric acid collection medium. In September, a paper on the badges was presented at the Third Conference on the Environmental Chemistry of Hydrazine Fuels. A kick-off meeting was held at KSC in Florida to initiate a field test of the dosimeters. During the field test, the badge substrate was found to be the culprit of the storage stability problems. New substrate materials were evaluated.

1988:

The polyester substrate was replaced by a filter paper substrate. In May, NASA/White Sands Testing Facility (WSTF) agreed to a small scale field test of the badges. By October, the field test at KSC had continued for approximately one year. A problem had been encountered with the coulometric analysis of citric acid badges. It was traced to sunlight exposure. In an attempt to alleviate the problem, the badges were molded from



black polyethylene. A patent on the citric acid dosimeter was granted in October. It was assigned patent number 4,780,200. Appendix A contains a copy of the patent.

1989:

A paper was written on the development of the badge and presented at the Joint Army Navy NASA Air Force (JANNAF) meeting in April. By October, the field test at KSC was completed.

1990:

In April, Naval Research Laboratory (NRL) Memorandum Report 6613 was completed. It details the two-year field evaluation of the passive sampling device. A copy of the paper is located in Appendix B. Due to the impending lowering of the threshold level values (TLV) for MMH, UDMH, and hydrazine to 10 ppb, the citrate sampler was evaluated at low levels. A paper on the findings of the field test was presented at the JANNAF in June. A paper to be submitted to the American Industrial Hygiene Association Journal is being written on the development and applications of the sampler.

2.0 Photoionization

1986:

The Photovac Tip, a photoionization instrument manufactured by Photovac was evaluated for detection of UDMH, monomethylhydrazine (MMH), and hydrazine. It displayed inconsistent behavior which could not be rectified at NRL. It was consequently returned to Photovac for repair.

1987:

In June, a new off-the-shelf model of the Photovac Tip was purchased. Testing was delayed as well on this Tip since the batteries failed, and attempts to run the instrument off the battery charger or to charge the batteries failed. A third instrument sent to NRL from KSC was not in working order either. Both instruments were sent to Photovac for repair. In November, one of the Tips was returned to NRL from the manufacturer. It still did not function properly.

1988:

A fixed-point photoionization instrument was purchased for testing. Replacement lamps were ordered. The project was placed on hold.

3.0 Materials Compatibility

1986:

A study of the transport efficiency of various tubing materials with MMH and hydrazine was sponsored by NASA. The evaluation was accomplished using a chemiluminescence-based breadboard instrument developed by Thermo Electron Corp.

1987:

The evaluation was completed and NRL Memorandum Report 6291 (Appendix B) was written and distributed.

1989:

The Air Force Space Systems Division sponsored a material compatibility study similar to the NASA-sponsored study. This evaluation involved the use of UDMH. A commercially available chemiluminescence-based instrument developed by Thermedics, Inc. (formerly Thermo Electron Corp.) was initially used in the evaluation; however, the instrument experienced a multitude of operational problems. A paper tape colorimetry-based instrument, the MDA 7100, manufactured by MDA Scientific replaced the Thermedics instrument for the duration of the test.

1990:

By February, the evaluation was completed. NRL Memorandum Report 6679 was written and released in July. Appendix B contains a copy of the report.

4.0 Electrochemistry

1987:

Ecolyzer 7660 instruments, which incorporate electrochemical cells, are routinely used as hypergolic propellant leak detectors on the launch pad of the Space Shuttle. After unsatisfactory performance of replacement cells, KSC tasked NRL to evaluate cells developed by several companies. The test plan required daily and weekly linearity, stability, precision, accuracy, and noise tests on the cells. A meeting with our sponsors was held in August to discuss the findings. Cells developed by National Draeger, Inc., incorporating a gelled electrolyte performed best.



1988:

It was decided to concentrate the investigation on the gel cells. The task was split between Wiltech at KSC and NRL. A paper on the initial work was presented at JANNAF in May. Testing of the gel sensors began with a revised test plan. Testing was terminated in August. NRL Letter Reports 6110-192a:KPC and 6110-416a:KPC detail the work on all sensors tested. Both reports are included in Appendix B.

5.0 Color Chemistry for the Detection of Hydrazines

1987:

Research was begun on a color dosimeter based on the condensation reaction of hydrazine and an aldehyde. Testing included evaluating various aldehydes and substrate materials. A disclosure of invention was submitted to the patent office in June. Using the aldehyde vanillin to react with the hydrazines, initial tests began. A second disclosure of invention was submitted in July. In September, a color wheel or dose estimator was designed to match the color development of the vanillin coated substrate. A small scale field test of the coated substrates was set-up at Kennedy Space Center (NASA/KSC) and White Sands Test Facility (NASA/WSTF).

1988:

In March, GMD Systems, Inc. was chosen to manufacture the color dosimeters for the field and laboratory evaluation. The badges incorporated vanillin and a chemistry formulated by GMD. The GMD badges were incorporated into the field test involving the citric acid badges. A presentation of the vanillin work was made at the JANNAF meeting in May. A licensing agreement between GEO-CENTERS and National Draeger regarding the vanillin dosimeters was discussed. In October, two companies, Sensidyne and MDA, were approached as potential commercial manufacturers of the vanillin dosimeters because an agreement was not reached with Draeger.

1989:

In January, an extensive laboratory evaluation of the GMD-produced dosimeters began at NRL and Wiltech at KSC. The field test continued through October 1989. A licensing agreement was not reached with any of the parties involved. Navy representatives contacted NRL to discuss using passive and active vanillin samplers. Badges were exposed to low (<10 ppb) concentrations of hydrazine for the Navy. Badges were also sent to the Navy representatives for field use onboard submarines.

In FY 1989, there was a collaborative effort between the Boston and Washington offices of GEO-CENTERS to compete for a Phase I effort of a Small Business Innovation Research Project (SBIR). The effort was to design and test an optical sensor capable of detecting hydrazine, MMH, and UDMH using the vanillin chemistry. The Phase I effort was granted to GEO-CENTERS. The majority of the ensuing tests were conducted at the GEO-CENTERS office in Boston. However, many of the hydrazine exposures were performed at NRL.

1990:

The laboratory evaluation of the GMD-produced badges was completed. Two NRL Memorandum Reports, 6613 and 6668, were prepared and issued in April and June, respectively. Appendix B contains copies of these papers. In anticipation of lower TLVs for the hydrazines, the remaining GMD badges were tested at NRL with low levels of MMH. A paper on the vanillin chemistry and its development as a dosimeter badge is being written for submission to *Analytical Chemistry*.

NRL was tasked by Air Force Space Systems Division to research possible chemistries that would produce colored products upon reaction with UDMH. By August, two promising chemistries were discovered and NRL Letter Report 6110-391a:KPC was issued. Appendix B contains this report. Funding was granted for a Task 1 effort on the UDMH chemistries. A patent on the chemistries is being pursued. Task 2 was underway and NRL Letter Report 6110-18:KPC:1 was written. This report is also included in Appendix B.

Commercially available MMH color badges manufactured by Perfect View, Inc. were evaluated alongside the GMD Systems badges. NRL Letter Report 6110-513a:SLR (see Appendix B) details this work.

6.0 Paper Tape Instrument Evaluation

1987:

A study of the performance capabilities of a commercially available paper tape instrument manufactured by MDA Scientific, Inc. was accomplished. The detector is a colorimetry-based instrument which contains chemically impregnated tape. A visible color development occurs on the tape upon reaction with hydrazines; the optical reflectivity of the color is measured and translated to concentration. The purpose of the test was to determine the performance capabilities of the instrument under high flow conditions.



In late 1987, NASA/KSC tasked NRL to evaluate several commercially available paper tape colorimetry-based instruments under normal working conditions. The evaluation was titled Sniff-Off II since it was similar to an earlier evaluation of instruments entitled Sniff-Off I. Instruments tested were developed by MDA Scientific, Inc. and GMD Systems, Inc.

1988:

The evaluation of the MDA Scientific instrument under high flow conditions was completed and NRL Letter Report 6110-16a:KPC (Appendix B) was issued to NASA sponsors. The evaluation results were presented at the JANNAF meeting in May.

Testing of the paper tape instruments for Sniff-Off II was temporarily delayed due to functional problems with the GMD instruments. Testing began again in September. The test plan included instrument functionality, instrument/operator interface, linearity, precision, accuracy, and relative humidity and interferent effects.

1989:

Sniff-Off II was completed and NRL Letter Report 6110-181:KPC was issued in March. This report is included in Appendix B. The Air Force Space Systems Division tasked NRL to test the MDA Scientific paper tape instruments for response to UDMH. One of the instruments required slight modification for testing with UDMH. The evaluation was completed in approximately four months. NRL Letter Report 6110-611:KPC was issued in November. See Appendix B for the report.

1990:

A small scale evaluation of paper tapes was carried out using an instrument from MDA. Paper tapes coated with various chemistries, including the vanillin chemistry invented at NRL, were examined at low levels of MMH and hydrazine. After initial testing, the program was put on hold due to project priorities.

7.0 Color Chemistry for the Detection of Nitrogen Dioxide (NO₂)

1990:

Due to the interest of NASA/KSC in NO₂, various chemistries were investigated to form colored products upon reaction with NO₂. One chemistry, o-tolidine (3,3-dimethylbenzidine), was selected for further study in passive dosimetry badge systems. The initial laboratory evaluation of the chemistry was promising. In July, the o-tolidine badges

were evaluated alongside commercially available NO₂ badges manufactured by Perfect View, Inc. NRL Letter Report 6110-464a:SR:bmd was issued in September. It is included in Appendix B.

Task 1 efforts were completed. In September, a review with NASA sponsors was held at KSC to discuss current and future work on the project.

8.0 Nitrogen Dioxide Instrument Evaluation

1990:

With funding from NASA to study commercially available NO₂ detectors, various instruments were ordered. A test plan for the evaluation slated to require six months was drawn up and approved.

9.0 Coulometric Titration Method Optimization

1990:

Various efforts have been made to optimize the coulometric procedure. The method parameters were evaluated in mid-1990 to improve the analysis method for low levels of hydrazines. The studies were coordinated between NASA/KSC and NRL. NASA had requested that NRL take the steps necessary to obtain NIOSH approval of the coulometric titration method for the measurement of hydrazines. All coulometry work to date has been compiled for a comprehensive paper on the method. This will be submitted to the American Industrial Hygiene Association Journal.

10.0 Color Chemistry for Detection of HCl

1988:

In June, a passive, colorimetric dosimeter for the determination of HCl vapors was invented and evaluated for future use. A small scale field test was launched at KSC in August during the launch of the Space Shuttle Atlantis.

1989:

The field test data was presented at the JANNAF HCl workshop in Los Angeles. A laboratory demonstration and field test of the badges were performed at Fort Detrick in

Maryland. The badges were exposed during the test firing of a double BATES motor at Edwards Air Force Base. All data to date were presented at the JANNAF meeting in April. Appendix B contains a copy of the JANNAF paper. The Army indicated an interest in further research on the dosimeters.

In August, sample HCl badges were prepared for Captain Warren Schultz, for the detection of HCl vapors resulting from the combustion of PVC materials. A request was made for information for a similar use by Bellcore Labs. A patent was pursued for the dosimeters.

11.0 Additional Studies

In 1986, a project was initiated to test hydrogen chemfet sensors for Standard Oil. The project was dropped by Standard Oil two months later. NASA/KSC tried to locate a supply of sensors for testing.

In October 1987, a hydrazine emission test was carried out at Hill Air Force Base in Utah. The emission tests involved sampling for hydrazine from the F-16 Emergency Power Test Unit Exhaust Incinerator. The purpose was to insure compliance with acceptable levels approved by the Environmental Protection Agency.

In 1990, research was begun on active samplers for the detection of nicotine on submarines. Due to project priority, further method development was put on hold.



APPENDIX A

**Citric Acid Dosimeter Patent
Number 4,780,282**



GEO-CENTERS, INC.

APPENDIX A

Patents



GEO-CENTERS, INC.

[54] DOSIMETER FOR MEASURING EXPOSURE
TO HYDRAZINE AND HAZARDOUS
HYDRAZINE DERIVATIVES

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Chester M. Hawkins, Trappe, Md.

[73] Assignees: Geo-Centers, Inc., Newton Centre,
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Washington, D.C.

[21] Appl. No.: 905,683

[22] Filed: Sep. 9, 1986

[51] Int. Cl.⁴ G01N 31/22; G01N 33/22

[52] U.S. Cl. 422/56; 422/58;
422/88; 436/106; 436/902

[58] Field of Search 422/88, 94; 436/106,
436/902; 422/56, 58

[56] References Cited

U.S. PATENT DOCUMENTS

3,455,656 7/1969 Roberts et al. 436/106 X
3,985,017 10/1976 Goldsmith 422/83 X
4,256,694 3/1981 McAllister et al. 422/86 X

FOREIGN PATENT DOCUMENTS

859919 8/1981 U.S.S.R. 436/106
864074 9/1981 U.S.S.R. 436/106

OTHER PUBLICATIONS

Leichnitz, *Detector Tube Handbook*, Dräger, Lübeck,
Germany (1979) 4th Ed., p. 84.

Primary Examiner—Barry S. Richman

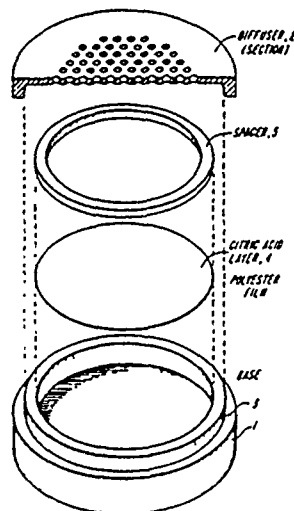
Assistant Examiner—Jill Johnston

Attorney, Agent, or Firm—Wolf, Greenfield & Sacks

[57] ABSTRACT

A dosimeter for collecting vapors and gases of hydrazine and of hazardous derivatives of hydrazine such as monomethylhydrazine and 1,1-dimethylhydrazine, employs a housing with a perforated cover. Situated inside the housing is a removable disk on which is coated a solution of citric acid in methanol. The solution initially contains 20% to 30% of citric acid monohydrate dissolved in methanol and the solution is permitted to age for seven or eight days before being coated on to the disk.

3 Claims, 1 Drawing Sheet



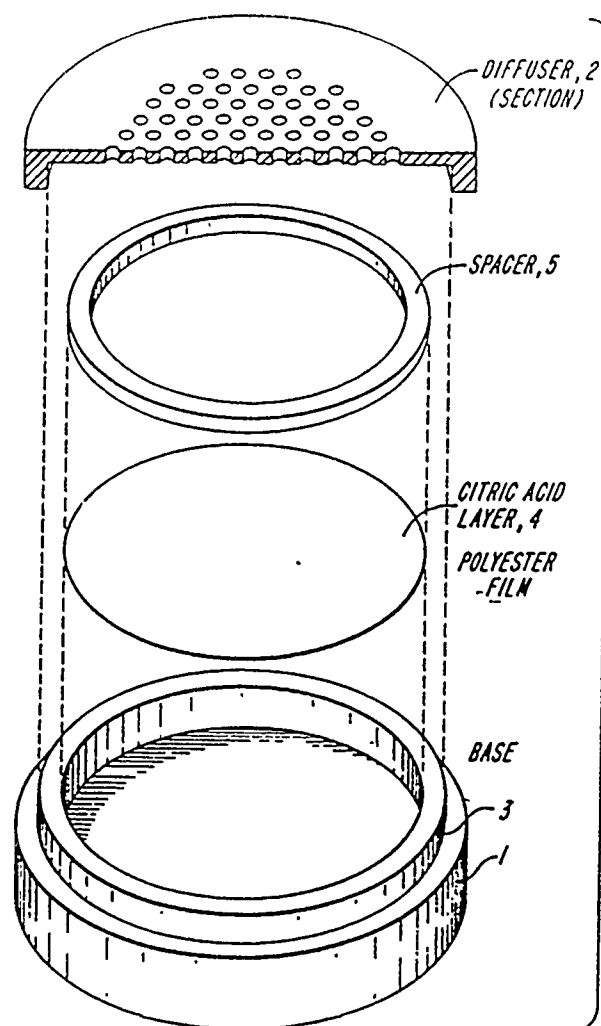


FIG. 1

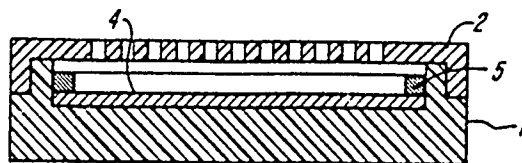


FIG. 2

DOSIMETER FOR MEASURING EXPOSURE TO HYDRAZINE AND HAZARDOUS HYDRAZINE DERIVATIVES

U.S. GOVERNMENT RIGHTS IN THE INVENTION

This invention was made jointly by employees of the Naval Research Laboratory and an employee of Geo-Centers, Inc., who was in the performance of work under Naval Research Laboratory contract N00014-84-C-2011. The United States of America has certain rights in the invention arising out of that contract, including a nonexclusive, nontransferable irrevocable, paid-up license to practice the invention or have it practiced for or on behalf of the United States throughout the world.

FIELD OF THE INVENTION

This invention relates in general to safety devices for detecting gases and vapors of hazardous materials. More particularly, the invention pertains to a passive device for monitoring the exposure of a person to vapors of hydrazine and hazardous derivatives of hydrazine, such as monomethylhydrazine and 1,1-dimethylhydrazine.

BACKGROUND OF THE INVENTION

Hydrazine is a colorless liquid, H_2NNH_2 , with a fish-like odor and a boiling point of $114^\circ C$. Major uses of hydrazine include its employment for rocket fuels, as a corrosion inhibitor in boilers, and for the synthesis of biologically active materials such as plant-growth regulators. Exposure to vapors of hydrazine or vapors of a hydrazine derivative such as monomethylhydrazine is harmful to the human body. Even small concentrations of liquid hydrazine or certain hazardous derivatives of hydrazine can be harmful because of the ability of those substances to enter the body through the skin and attack internal organs. Vapors of those substances, even in low concentrations, are suspected of being carcinogenic. Consequently, in an environment where some persons may be exposed to the harmful vapors for different periods of time and to different vapor concentrations, there is a need for an inexpensive device for measuring each person's exposure to such vapors.

Few acceptable techniques are known for measuring a person's exposure to hydrazine or to hazardous derivatives of hydrazine. Of the few techniques that are now available, those that rely upon substances which change color when exposed to hydrazine lack the necessary sensitivity to low concentrations of hydrazine or its hazardous derivatives and most of the other techniques are either too cumbersome for use in personal monitoring or are not sufficiently reliable to enable a dependable evaluation of exposure to be made.

OBJECT OF THE INVENTION

Hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine are volatile compounds that tend to decompose when exposed to the atmosphere. It is an object of the invention to provide a portable dosimeter for collecting hydrazine and those hydrazine derivatives and keeping those collected substances in their stable states until the collections can be analyzed to ascertain the amounts collected.

THE INVENTION

The invention arises out of the observation that a weak acid inhibits the decomposition of hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine when those substances are exposed to the atmosphere. It has been determined that hydrazine and monomethylhydrazine remain stable for periods of at least 8 days after vapors of those substances are deposited upon a substrate coated with a solution of citric acid in methanol. The invention resides in a badge having an arrangement for collecting vapors and gases of hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine on a removable disk coated with a solution of citric acid in methanol.

THE DRAWINGS

FIG. 1 is an exploded perspective view showing the preferred embodiment of the invention.

FIG. 2 is a cross-sectional view in elevation of the preferred embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the exploded view of the invention depicted in FIG. 1 and to the cross-sectional view in FIG. 2, the preferred embodiment of the invention is in the form of a badge to be worn on the outer clothing of the person to be monitored for exposure to the vapors of hydrazine and derivatives of hydrazine. The badge has a housing formed by a hollow cylindrical base 1 and a perforated cover 2. The base and cover are molded of a chemically inert material such as Teflon, that is minimally affected by hydrazine or by monomethylhydrazine, or by 1,1-dimethylhydrazine. The cylindrical base 1 has a shallow chamber that is, for example, about $3/32$ " deep with an internal diameter of about $1\frac{1}{4}$ ". The cover 2 preferably provides an air tight closure around the base and because of that tight fit, the cover cannot be easily separated from the base. To aid in the formation of an air tight seal, the cover rests on a ledge 3 on the base. Where desired, the cover can be secured to the base by a bayonet mount, by screw threads, or by other attachment means and the ledge can be eliminated.

Disposed within the housing is a disk 4 of Mylar drafting film (or of a polyester film having similar characteristics) which was dipped in a solution of citric acid in methanol. Preferably the citric acid-methanol solution was permitted to age for at least seven or eight days before being used. It has been found from experience that the citric acid is less apt to crystallize on the disk when the solution has been aged. The solution is prepared by mixing 20% to 30% of citric acid monohydrate with methanol. It is believed that a percentage of those constituents react to form methyl citrate although an experiment made to test that belief proved to be inconclusive. However, the improvement obtained with aging of the solution and the tendency of the solution when aged too long to rapidly dry out when deposited on the Mylar film, lends support to the belief that a slow reaction has occurred. It is likely that an unknown but certain percentage of methyl citrate must be formed in the solution to obtain optimal performance of the badge. If such a reaction is a necessary condition, then it is probable that a solution of methyl citrate can be applied to the Mylar disk in place of the citric acid-methanol solution.

Citric acid is commercially available in anhydrous form, in monohydrate form, and in other hydrated forms. No reason is apparent why those forms of citric acid cannot be used interchangeably with equal or similar results. Commercial polyester drafting films, such as that sold under the Mylar trademark, have a matte surface on one side with the opposite side usually being glossy. When that kind of drafting film is used, the glossy side of the disk is washed to remove the citric acid-methanol coating and the coating on the matte surface is allowed to dry for five or ten minutes before the disk is placed in the housing. The coated surface remains tacky—that is, remains somewhat sticky to the touch. The disk, with the tacky surface uppermost, is placed on the floor of the base and is held in place by a retaining ring 5 which is pressed into the shallow chamber of the base. In lieu of using a press fit, other retaining means, such as screw threads may be provided.

After the coated film and retaining ring have been inserted into the base, the housing is closed by seating the cover 2 on the ledge 3 of the base. There is then a space of about 3/32" between the cover and the coated disk. The cover 2, for example, has 140 holes of 1 mm. diameter in it which are evenly distributed within a 1" diameter circle. The holes are for diffusion control and aid in reducing air velocity effects where the hydrazine vapors or monomethylhydrazine vapors are air borne with air velocities in the range normally encountered in workplace environments. To promote diffusion control, it is desirable to minimize seepage around the cover.

The hydrazine deposited on the disk tends to be stabilized by the citric acid-methanol coating—that is, decomposition of the hydrazine is inhibited by the film of citric acid-methanol solution on the disk. Monomethylhydrazine and 1,1-dimethylhydrazine which are somewhat less stable than hydrazine are also stabilized by the coating.

It has been determined that badges can be stored for up to 8 days after exposure with no discernable loss of collected hydrazine or monomethylhydrazine. Badges have been exposed for periods of time up to 4 days and the results have remained linear except where the vapor concentration and/or exposure time has approached zero. Ammonia, freons, and isopropyl alcohol interfere minimally with sampling by the badge. There are virtually no humidity effects associated with the citric acid coating itself. However, the badge itself does have some small humidity effects, especially at low dosages. The humidity effects are minimized by molding the Teflon casing rather than machining it.

To determine the amount of hydrazine and hydrazine derivatives that have been collected, the badge is disassembled to remove the coated disk. The citric acid coat with its collected hydrazine and hydrazine derivatives is removed from the Mylar disk. The citric acid coat can, for example, be washed off the disk with dilute sulfuric acid. A strong acid, such as concentrated mineral acids, should not be used as it tends to destabilize the collected hydrazine and hydrazine derivatives. Wet chemical or other methods can then be used to ascertain the hydrazine and the hydrazine derivative content. Monomethylhydrazine can be analyzed, for example, using phosphomolybdic acid in NIOSH approved method #S149. Alternatively, monomethylhydrazine can be analyzed by coulometric titration with bromide and amperometric detection of the endpoint. The methods of analysis form no part of this invention and any suitable analytic method may be employed to ascertain the amount of collected hydrazine or the amount of collected hydrazine derivatives.

Although the invention has been described in the preferred embodiment of a badge to monitor the exposure of the bearer to hydrazine and its hazardous derivatives, the invention can be embodied in forms other than as a badge. For example the invention can be placed at fixed sites to monitor the presence of hydrazine vapors or vapors of its hazardous derivatives at locations where spillage of the material or release of the vapors is likely to occur. In circumstances where the invention is to be employed at fixed sites, the coated film can be held in an immovable casing of suitable configuration.

We claim:

1. In a dosimeter for collecting vapors and gases of hydrazine and hazardous hydrazine derivatives, where the dosimeter comprises

a case with a shallow cavity therein, the case having a perforate cover in which there are a plurality of holes providing entry for the vapors and gases into the shallow cavity,

the improvement comprising

a removable substrate disposed in the shallow cavity in a manner providing a space in the cavity between the cover and a surface of the substrate, and a coating of a solution of citric acid in methanol disposed on said surface of the substrate.

2. The improvement according to claim 1, wherein the substrate is a polyester sheet.

3. The improvement according to claim 1, wherein the coating initially contains citric acid or a hydrate thereof dissolved in methanol.

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United States Patent [19]

Taffe et al.

[11] Patent Number: 4,900,681

[45] Date of Patent: Feb. 13, 1990

[54] HYDRAZINE DETECTION

[76] Inventors: Patricia A. Taffe, 8083 Steeple Chase Ct., Springfield, Va. 22153; Susan L. Rose-Pehrsson, 3808 Stonebridge Rd., Alexandria, Va. 22306

[21] Appl. No.: 201,767

[22] Filed: Jun. 2, 1988

[51] Int. Cl.⁴ G01N 21/78

[52] U.S. Cl. 436/106; 436/112;
436/164; 436/169; 436/902

[58] Field of Search 436/106, 112, 128, 131,
436/164, 169, 902

[56] References Cited

U.S. PATENT DOCUMENTS

2,162,978 6/1939 Seaton 422/56 X
2,206,282 7/1940 Jacobius 422/56 X
3,455,656 7/1969 Roberts et al. 436/106 X
4,271,121 6/1981 Diller et al. 436/902 X
4,775,633 10/1988 Rounbehler 436/106
4,780,282 10/1988 Holtzclaw et al. 436/106 X

FOREIGN PATENT DOCUMENTS

1254362 8/1986 U.S.S.R. 46/169

OTHER PUBLICATIONS

Grdinic et al., *Pharmazie*, vol. 41, pp. 715-716, 1986.

Franc et al., *Chemical Abstracts*, vol. 106, Abstract No. 106:12065v, 1/12/87.

Blaxart et al., *Chemical Abstracts*, vol. 95, Abstract No. 95:231460c, 1981.

Maslii et al., *Chemical Abstracts*, vol. 98, Abstract No. 98:118876s, 1983.

Rychkova et al., *Chemical Abstracts*, vol. 101, Abstract No. 101:59864s, 1984.

Chernaya et al., *Chemical Abstracts*, vol. 103, Abstract No. 103:42284w, 1985.

The Merck Index, Tenth Edition, Edited by Windholz et al., Published by Merck & Co., Inc., Rahway, N.J., 1983, pp. 97 & 1419.

Shouquan, *Chemical Abstracts*, vol. 107, Abstract No. 107:12524q, 7/13/87.

Somova, *Chemical Abstracts*, vol. 85, Abstract No. 85:103332u, 1976.

Bakal et al., *Chemical Abstracts*, vol. 89, Abstract No. 89:16104k, 1978.

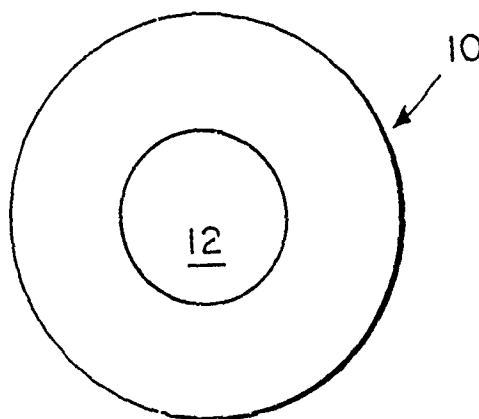
Primary Examiner—Robert J. Hill

Attorney, Agent, or Firm—Herbert L. Bello

[57] ABSTRACT

A solution of various benzaldehyde derivatives dissolved in suitable solvents are used in impinger sampling or as a coating on substrates to provide passive, real-time visual colorimetric indication of the presence of hydrazine and its derivatives.

15 Claims, 1 Drawing Sheet



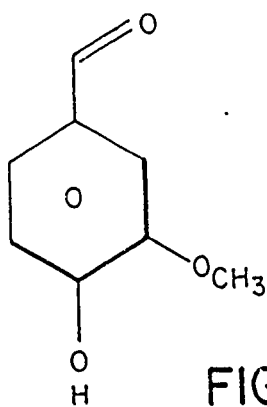


FIG. 1

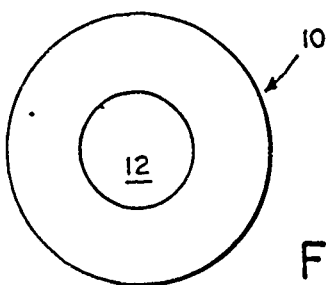


FIG. 2

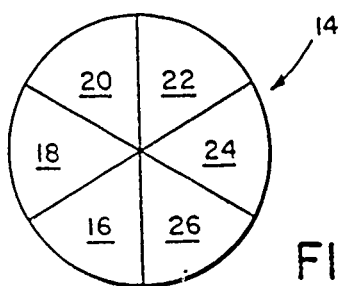


FIG. 3

HYDRAZINE DETECTION

This invention was made with Government support under NRL Contract No. N00014-86-C-2266. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION 1. Field of the Invention:

The present invention relates to the detection of hydrazine compounds and, more particularly, is directed toward real-time, passive detection of hydrazine compounds using benzaldehyde and its derivatives.

2. Description of the Prior Art:

Hydrazine is an extremely toxic chemical which is used in industry as a blowing agent for blow molded plastic products, for the synthesis of agricultural products, as a oxygen scavenger agent for water treatment to inhibit corrosion, pharmaceutical applications and as a rocket propellant. Due to the high toxicity of hydrazine, employers must meet specified standards for monitoring exposure levels of hydrazine for all employees who might be exposed. Currently, hydrazine monitoring is accomplished by use of expensive instrumentation which is transported to various facilities for non-continuous monitoring of air and water. Such instrumentation requires calibration regularly and is not particularly adapted for individual monitoring. A citric acid dosimeter collects analyte data, but not in real-time. The use of para-N, N-dimethylaminobenzaldehyde is a known wet chemical method, but it is not used as a dosimeter.

U.S. Pat. No. 3,455,656 discloses colorimetric detection of hydrazine compounds by means of a solid carrier that is impregnated with solutions containing a silicic acid and a molybdic acid. These methods have not been demonstrated for real-time, passive detection.

There are few commercial real-time detectors or acceptable techniques available for detection of hydrazine exposure at threshold limiting values (100-500 parts-per-billion, depending upon the specific hydrazine to be detected). Passive electrochemical techniques have not proven reliable; liquid sorbent badges lack the required precision and accuracy; strong acids on supports are not applicable to monomethylhydrazine; and collection on citric acid coated disks does not provide real-time analysis.

A need exists for a simple, inexpensive and reliable method and device which provides a passive, real-time visual indication of hydrazine exposure as well as individual personnel monitoring of exposure to hydrazine.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a simple, inexpensive and reliable method and device for passive detection of hydrazine and its derivatives.

It is another object of the present invention to provide a method and device to provide a real-time colorimetric indication of exposure to hydrazine and its derivatives.

It is yet another object of the invention to provide a colorimetric dosimeter for real-time detection of threshold limiting values of hydrazine and monomethylhydrazine in air. The invention involves the condensation of an aromatic aldehyde with a hydrazine to form a colored hydrazone. The aldehyde indicators are characterized by a para substituent which activates the chromophore.

It is a further object of the present invention to provide a method and device which provides a real-time colorimetric indication of the presence of threshold limiting values of hydrazine and its derivatives. The invention is characterized by the use of various benzaldehyde derivatives that are dissolved in suitable solvents, typically methanol or isopropanol, to provide a solution which is used as a collection media in impinger sampling of low levels of hydrazine in air and as a coating on substrates to provide an indication of exposure to hydrazine and its derivatives. In a second application, solvents such as diethylether or acetone may be used. In one example, vanillin turned yellow upon exposure to a threshold limiting level of monomethylhydrazine in five to ten minutes.

These and other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the methods and devices, together with their steps, parts, elements and interrelationships that are exemplified in the following disclosure, the scope of which will be indicated in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

A fuller understanding of the nature and objects of the present invention will become apparent upon consideration of the following detailed description taken in connection with the accompanying drawings, wherein:

FIG. 1 is a structural formula of vanillin which is used for the detection of hydrazine according to the present invention;

FIG. 2 is a plan view of a passive colorimetric badge embodying the invention; and

FIG. 3 is a plan view of a color wheel which is used for interpolation of badge color.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention described herein provides a method and apparatus for real-time colorimetric detection of hydrazine and its derivatives by use of benzaldehydes or aromatic conjugated aldehydes with activation in the para position by a substituent —, OH, —NR₂, or —OR group. Also, cinnamaldehyde and its substituted derivatives have been found to be effective in the detection of hydrazine and its derivatives.

Various benzaldehyde derivatives are dissolved in suitable solvents, such as diethyl ether, acetone, alcohol or isopropanol to form a solution which when coated on a substrate can be used for the passive, real-time detection of hydrazine and its derivatives. If the coated substrate is used for detecting hydrazine, the pH must be approximately 5 or less and for unsymmetrical dimethylhydrazine, the pH must be adjusted to approximately 2. The solution can be used as a collection media in impinger sampling of low levels of hydrazine in air. Such solutions have detected the presence of hydrazine and its derivatives when used as a coating on substrates such as silica gel. Other substrates, for example, filter paper, silica gel thin layer chromatography plates, silica gel packing and a solid support resin such as sold under the trademark Amberlite IRC-50 (H) resin and microporous membranes have been used as substrates.

One purpose of the invention is to provide an aldehyde-hydrazine condensation reaction which results in a highly colored product that is not pH dependent to a great extent. The aldehyde selected contains a chromophore in order to obtain a visible reaction product.

In one example, vanillin, 3-methoxy 4-hydroxyl benzaldehyde, FIG. 1, a non-toxic chemical, was used as a coating on a silica gel substrate that reacted with a monomethylhydrazine (MMH) contaminated gas stream. The coating reacted with the contaminated gas stream and yielded a product that absorbed in the visible region. At threshold limiting value (TLV) exposure, 200 parts-per-billion, the first distinct indication of color came after five to ten minutes when a yellow cast was observed. The yellow color continued to intensify and, after approximately two hours of exposure, it was a very bright lemon yellow. The color development has shown to be linear to approximately 3.8 parts-per-million Hrs which is equivalent to 19 hrs of TVL MMH exposure.

Other benzaldehyde derivatives have been tested and found to provide passive, real-time colorimetric indication of exposure to hydrazine and its derivatives. The most successful candidates are characterized by para-substituents of $-\text{OH}$, $-\text{OR}$, or $-\text{NR}_2$. Vanillin has a para-hydroxyl substituent. In the compounds discussed, R has been a methyl group. However, the reaction mechanism should not limit the potential candidates to this substitution. Each of these substituents are known as ortho, para activating groups of benzene. It is believed that other benzaldehyde derivatives which have substituents activating the aldehyde position would also work.

In addition to vanillin, four other compounds have been successfully tested. P-anisaldehyde reacts with hydrazine to form a bright greenish yellow and p-dimethylamino benzaldehyde reacts with hydrazine to form a bright orange. 2,4 - Dimethoxybenzaldehyde and 2,4 - Dihydroxybenzaldehyde provide a yellow indication upon reaction. Typically, the concentration of vanillin, P-anisaldehyde and P-dimethylamino benzaldehyde is in the range of 0.004 grams per milliliter to 0.04 grams per milliliter, preferably 0.007 grams per milliliter. These compounds have been used as coatings on silica gel thin layer chromatography plates. The compounds with a hydroxy group react to MMH without addition of an acid. For reaction with hydrazine and unsymmetrical dimethylhydrazine, the addition of a stronger acid is necessary.

This benzaldehyde class of chemical compounds provides a variety of possibilities in the detection of hydrazines. Analysis of the color change may be determined qualitatively, and in real-time by visualization. Quantitative analysis in real-time is possible by spectroscopic methods. The benzaldehyde compounds may be used in solution, or as coatings on selected sorbents, which opens applications in passive dosimetry, paper tape instruments, detector tubes, liquid impinger sampling, wet chemical analysis, or optical waveguide detection.

FIG. 2 shows a passive colorimetric badge 10, having a substrate 12, that is coated with a benzaldehyde derivative to provide a visual indication of exposure to hydrazine and its derivatives. FIG. 3 shows a color wheel 14 having a plurality of color zones 16, 18, 20, 22, 24 and 26. In the illustrated embodiment, by way of example, color zone 16 has a color which is the equivalent to 0.07 ppm-hours of MMH exposure; color zone 18 has a color which is the equivalent to 0.14 ppm-hours of MMH exposure; color zone 20 has a color which is the equivalent to 0.48 ppm-hours of MMH exposure; color zone 22 has a color which is the equivalent to 1.1 ppm-hours of MMH exposure; color zone 24 has a color which is the equivalent to 3.8 ppm-hours of MMH exposure; and

color zone 26 is a standard color of saturation. The badge 10 exposure, i.e., the color of stratum 12, is interpolated from a comparison of badge color with the colors of the zones 16, 18, 20, 22, 24 and 26.

In one example, tests were performed on dilute hydrazone solutions resulting from the reaction of vanillin with MMH. A stock standard of MMH in isopropanol was used to prepare working standards. The vanillin indicator was dissolved in isopropanol and acidified with concentrated hydrochloric acid (HCL). Known amounts of the working standards were added to volumetric flasks containing the vanillin solution. A yellow color developed immediately, indicating formation of the hydrazone.

Vanillin (3-methoxy-4-hydroxybenzaldehyde) has been shown to be an excellent derivatization agent for hydrazine and MMH, through less effective for unsymmetrical dimethylhydrazine UDMH. Due to the chemistry of the reaction, few, if any, interferences are expected. The formation of the hydrazone is a quick and clean reaction. This has been shown in the initial spectrophotometric investigations on dilute MMH standard solutions. Vanillin has not shown extreme pH sensitivity in reacting with MMH, however it is more sensitive to pH in hydrazine and UDMH reactions. This characteristic allows a wider pH range than with other aldehydes, such as with para-N, N-dimethylaminobenzaldehyde (PDAB) when monitoring MMH.

The vanillin must be in an acidified state to form a visual product upon reaction with hydrazine and UDMH. Results from initial tests, performed using HCl for the acidification, exhibited detection limits of <0.1 and 0.06 ppm hours for hydrazine and UDMH, respectively. The volatility of HCl is a source of potential problems, therefore the use of citric, phosphoric and sulphuric acids have been investigated and found to perform successfully for hydrazine.

Vanillin has been investigated as a coating on various substrates with design applications as detector tubes and passive dosimeters. The coating solution can be prepared by dissolving vanillin in acetone and alcohols, it is not water soluble.

For use as a substrate in a passive system, the silica gel glass TLC plates exhibited many desirable qualities. The samples made using TLC plates were affected the least by the relative humidity and in general the color that formed was brighter than with other substrates.

Since certain changes may be made in the foregoing disclosure without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description and depicted in the accompanying drawings be construed in an illustrative and not in a limiting sense.

What is claimed is:

1. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the step of exposing vanillin to hydrazine, said vanillin providing a colorimetric indication of the presence of hydrazine and its derivatives.
2. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the step of exposing p-anisaldehyde to hydrazine, said p-anisaldehyde providing a colorimetric indicating of the presence of hydrazine and its derivatives.
3. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the step of exposing 2,4-dimethoxybenzaldehyde to hydrazine, said 2,4-dimethoxybenzaldehyde providing a colorimetric

indication of the presence of hydrazine and its derivatives.

4. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the step of exposing 2,4-dihydroxybenzaldehyde to hydrazine, said 2,4-dihydroxybenzaldehyde providing a colorimetric indication of the presence of hydrazine and its derivatives.

5. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the steps of:

- (a) providing a substrate coated with vanillin; and
- (b) exposing said coated substrate to hydrazine, said vanillin coating providing a colorimetric indication of the presence of hydrazine and its derivatives.

6. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the steps of:

- (a) providing a substrate coated with P-anisaldehyde; and
- (b) exposing said coated substrate to hydrazine, said P-anisaldehyde coating providing a colorimetric indication of the presence of hydrazine and its derivatives.

7. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the steps of:

- (a) providing a substrate coated with 2,4-dimethoxybenzaldehyde; and
- (b) exposing said coated substrate to hydrazine, said 2,4-dimethoxybenzaldehyde coating providing a colorimetric indication of the presence of hydrazine and its derivatives.

8. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the steps of:

- (a) providing a substrate coated with 2,4-dihydroxybenzaldehyde; and
- (b) exposing said coated substrate to hydrazine, said 2,4-dihydroxybenzaldehyde coating providing a colorimetric indication of the presence of hydrazine and its derivatives.

9. A method for real-time colorimetric detection of hydrazine and its derivatives comprising the steps of:

- (a) providing a substrate coated with a solution containing vanillin at a concentration in the range of 0.004 grams per milliliter to 0.04 grams per milliliter; and
- (b) exposing the coated substrate to hydrazine, the vanillin providing a colorimetric indication of the presence of hydrazine and its derivatives.

10. The method as claimed in claim 9 wherein said substrate is a silica gel substrate.

11. The method as claimed in claim 9 wherein said substrate is paper.

12. The method as claimed in claim 9 wherein said substrate is a microporous membrane.

13. The method as claimed in claim 9 including the step of providing a plurality of color zones adjacent the coated substrate.

14. The method as claimed in claim 13 wherein said color zones have different colors which correspond to different hydrazine exposure levels.

15. The method as claimed in claim 9 including the step of providing a plurality of color zones.

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APPENDIX B

Publications and Reports



GEO-CENTERS, INC.

REMOTE ANALYSIS OF MONOMETHYLHYDRAZINE USING HIGH FLOW SAMPLING

INTRODUCTION

Hydrazine (Hz), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) are widely used as high energy propellants. Space shuttle operations require large quantities of Hz and MMH. As the use of the propellants has increased, the toxicological properties of the propellants have caused a great amount of concern. In order to provide the best protection for personnel against the adverse toxicological effects of hydrazines, NASA continually supports test and evaluation of new and/or improved hydrazine instrumentation.

Many studies have shown that hydrazines cause teratogenic as well as mutagenic activity. Investigations also indicate adverse blood and liver effects that may be the result of exposure to these chemicals. The fuels are believed to affect behavior by significantly altering the performance capabilities; the maximum tolerated toxic level has been reported to be five parts per million (ppm). Moreover, hydrazine fuels have also been shown to adversely affect nonmammalian life forms and are, therefore, a danger to the environment. Because it is highly suspected that hydrazines cause carcinogenic activity in man and because of other toxic properties attributed to hydrazines, the American Conference of Governmental Industrial Hygienist (ACGIH) has recommended that threshold limit values (TLV) of 100, 200, and 500 parts per billion (ppb) be set for Hz, MMH, UDMH respectively [1]. The National Institute of Occupational Safety and Health (NIOSH) has recommended values of 30, 40, and 60 ppb for the same compounds [2].

The toxicity of the hydrazine fuels and the large quantities of the fuels that both NASA and the Department of Defense use, make it necessary that special precautions be taken to ensure the safety of personnel. Part of the safety program involves routine air monitoring whenever the hydrazines are being handled. Kennedy Space Center (KSC) requires that the hydrazine levels not exceed the ACGIH recommended TLV. To support this requirement, KSC requested that NRL test the MDA Scientific Incorporated model 7100 Hydrazines Detector as a fixed point monitor with sampling lines of various lengths.

The purpose of this test was to determine the performance capabilities of the MDA 7100 paper tape instrument when sampling contaminated air through tubing of differing lengths. Based on a tubing study conducted previously at NRL, the response time of an instrument is drastically reduced by long sample lines due to the adsorption of hydrazine on the tubing walls. This test was designed to determine the response times with an auxiliary pump to deliver the contaminated air to the instrument at a faster rate.

EXPERIMENTAL

The MDA 7100 sampled known concentrations (near TLV) of monomethylhydrazine (MMH) through several different lengths of 3/8" outer diameter (od), 1/4" internal diameter (id) Bev-a-line IV tubing at room temperature with a relative humidity between 30-50%. Employing 100, 50, and 10 foot lengths of tubing, in addition to the three foot teflon sample probe, the MDA 7100 was tested for response time to TLV concentrations

with the assistance of an auxiliary pump. This was accomplished by using a Little Giant Jr. pressure/vacuum pump from Gelman Instrument Company pulling approximately 22 l/min of room air through the tubing. A gas stream flowing at one l/min and containing approximately 6 ppm of MMH was teed onto the inlet of the sample line, providing a final concentration near the TLV. The MDA 7100 sampled a portion of the air at 800 mls/min from the other end of the tubing. Figure 1 diagrams the test set-up as explained here. The MMH vapor concentrations were verified by impinger collection at the inlet tee and analyzed by coulometric generation of bromine with amperometric endpoint detection [3]. Tests were also performed using only the sample probe, a 3 foot piece of teflon tubing, and simply attaching a teflon flow restrictor in line to achieve the same flow restriction and dilution rate of approximately 22 l/min. The sampling rate of the MDA 7100 was set to 800 mls/min, compensating for the vacuum of the pump and each different length of tubing tested. The set-up for flow adjustment is illustrated in Figure 2. The MDA 7100 sampling rate was adjusted using a flowmeter at the sample inlet, thereby taking into account the pressure drop due to the length of tubing attached. In one test, to determine the accuracy of the instrument when the back pressure was ignored, the MDA 7100 was adjusted to 800 mls/min using the flowmeter on the face of the instrument.

The MDA 7100 detector contains a phosphomolybdic acid impregnated paper tape that is exposed to a known volume of gas. Hydrazines in the gas sample reduce the substance on the paper tape forming a blue stain. The intensity is proportional to the concentration of hydrazine present. The MDA 7100 optically measures the color intensity of the stain and reports the concentration of the gas in ppb. A fresh chemcassette was inserted in the MDA 7100 prior to the onset of these tests and the instrument was calibrated using the calibration card provided by the manufacturer.

The MDA 7100 printed the MMH measurements at two minute intervals despite attempts to enable the instrument to printout data at one minute intervals. The digital display on the face of the instrument continuously updates the data. These updates were timed with a stopwatch in order to determine the first indication of MMH through the tubing.

RESULTS

During the preliminary set-up of this experiment, we noticed that with the auxiliary pump pulling air at a rate of 24 l/min through 100 feet of 3/8" od tubing, the MDA 7100 was not capable of sampling 800 mls/min. When the flow rate was reduced to 12 l/min by placing a valve in line to the auxiliary pump, the MDA 7100 was only capable of sampling approximately 230 mls/min rather than 800 mls/min. This inability of the MDA 7100 to sample at 800 mls/min implied a possible leak in or around the pumping mechanism in the MDA 7100 or in the connecting tubing. After a careful check of the teflon tubing which goes into the sample port and the exhaust port of the instrument, it was decided to remove the sharp metal ferrule at the fitting on the sample port. Although no visible hole could be seen in the teflon tubing, it was very abraded where the metal ferrule gripped the tubing. When the ferrule was removed and the tubing fed directly through the sample port and into the detection head of the MDA 7100, the instrument was able to sample at 800 mls/min with the auxiliary pump pulling approximately 21 l/min.

For the first test, the MDA 7100 sampled MMH contaminated air at a concentration of 232 ppb without the auxiliary pump. The sampling rate was set at 800 mls/min. The MDA 7100 was tested with the three feet of 1/4" od teflon that is normally attached to

the instrument as well as with 100 feet of the Bev-a-line tubing. The results of these tests in Table I indicate a response time eleven times greater for the 100 foot length than for the three foot teflon to both 50% and 90% actual response.

TABLE I. INSTRUMENT WITHOUT AUXILIARY PUMP

TUBING LENGTH(FT)	FLOW RATE (L/MIN)	EXPECTED RESPONSE(PPB)	ACTUAL RESPONSE(PPB)	RESPONSE TIME (MIN) 50%	RESPONSE TIME (MIN) 90%
NONE	.8	232	293	.5	2
100	.8	232	246	5.5	22

For the second test, the MDA 7100 was tested without additional tubing and with tubing lengths of 10, 50, and 100 feet Bev-a-line. The auxiliary pump pulled between 21 to 23.6 l/min dilution air depending upon the tubing length. For these tests, the MDA 7100 sample rate was adjusted to 800 mls/min using a flowmeter placed at the sample inlet. Table II shows the response times to 50% and 90% for Bev-a-line lengths of 0, 10, 50, and 100 feet. There appears to be no significant difference in the response times between the different lengths of tubing.

TABLE II.

INSTRUMENT WITH AUXILIARY PUMP; SAMPLE SET TO 0.8 L/MIN USING FLOWMETER AT SAMPLE INLET

TUBING LENGTH(FT)	FLOW RATE (L/MIN)	EXPECTED RESPONSE(PPB)	ACTUAL RESPONSE(PPB)	RESPONSE TIME (MIN) 50%	RESPONSE TIME (MIN) 90%
NONE	21	288	255	1.5	3.5
NONE	21	288	255	4	7
NONE	21	288	258	1.5	4
10	23.6	246	222	2	6
10	23.6	250	219	1.5	9
10	23.6	250	209	1	2.5
50	23	226	236	.5	6.5
50	23	246	240	1	6.5
100	21	288	302	3	8
100	21	288	302	1.5	7
100	21	246	252	2	9
100	21	246	263	1.5	7

The above mentioned tests took into account the effect of partial vacuum due to the various tubing lengths. However, further tests with 100 feet of Bev-a-line were performed by adjusting the MDA 7100 sampling rate with the flowmeter on the front of the instrument and ignoring the effect of the vacuum due to the 100 feet of tubing and auxiliary pump. These results were compared with data from a similar test with the three foot teflon instrument probe. Table III gives the results of these tests. There is no significant difference in the response times between the tests done without Bev-a-line

and those done with the 100 feet of tubing, although the accuracy of the measurement is reduced.

TABLE III.

INSTRUMENT WITH AUXILIARY PUMP; SAMPLE SET TO 0.8 L/MIN USING FLOWMETER ON FACE OF MDA

TUBING LENGTH(FT)	FLOW RATE (L/MIN)	EXPECTED RESPONSE(PPB)	ACTUAL RESPONSE(PPB)	RESPONSE TIME (MIN) 50%	RESPONSE TIME (MIN) 90%
NONE	21	288	211	2.5	10
NONE	21	288	211	1.5	6
NONE	21	288	192	.75	8
100	21	288	224	2.5	6
100	21	288	194	3	12.5

Tests measuring the pressure drop due to the various lengths of tubing were performed in order to find the longest length of 3/8" od Bev-a-line tubing that the MDA 7100 can sample at 800 mls/min with an auxiliary pump pulling at 21 l/min. Beyond this length, the MDA cannot be adjusted for the increased partial vacuum at its inlet. Tubing of the following lengths were connected between the MDA and the auxiliary pump: 10, 50, 90, 100, 135, and 190 feet. The vacuum was measured in inches of mercury for each of these lengths. The results are illustrated in Figure 3. At 4.75 inches of mercury, the MDA 7100 could no longer be adjusted to sample at 800 mls/min. From the data, the length of tubing corresponding to this pressure drop was calculated to be 115 feet of 1/4" id Bev-a-line tubing.

CONCLUSION

The MDA 7100 demonstrates excellent response time when an auxiliary pump is used to deliver the hydrazines to the sample probe. Leaks can be a major problem with the instrument because the color change is very dependent on the volume of gas sampled. The metal ferrules on both sides of the sample inlet connector have cut the teflon tubing resulting in leaks. Apparently, due to internal leaks or leakage around the paper tape, the sample rate should be set using a rotameter to monitor the flow rate at the inlet rather than using the rotameter that follows the paper tape internal to the instrument. The instrument pump can sample at 800 mls/min as long as the vacuum is less than 4.75 inches of mercury. Calibration with the card provided by the manufacturer appears to be sufficient in the TLV range when these precautions are taken.

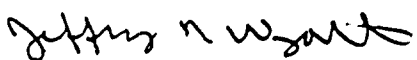
Several cautions are in order:

- 1) Considering the large volume of air sampled, contamination of the 100 foot sampling line may pose a problem. A filter placed at the tubing inlet could reduce the air contaminants drawn through the tubing, but might reduce the amount of hydrazine transported.
- 2) An indicating flow sensor compatible with MMH should be placed at the inlet of the MDA 7100 to ensure that the instrument is drawing sample from the inlet of the auxiliary pump. This is shown with dashed lines in Figure 1.

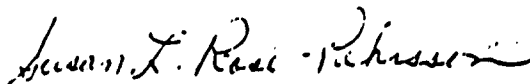
- 3) Since it is drawing from sub-ambient pressure, a leak in the sampling line between the MDA 7100 and the main sampling line could result in a failure to detect MMH.
- 4) Any flow restriction of the 100 foot line would increase the partial vacuum and possibly produce a failure. This could be brought about by a clogged filter at the tubing inlet. Monitoring the vacuum should be performed to prevent this scenario.

REFERENCES

1. J.A.E. Hannum, Recent Developments in the Toxicology of Propellant Hydrazines, Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. I.F. Sevin, Criteria for a Recommended Standard Occupational Exposure to Hydrazines, Div. of Criteria Documentation and Standards Development, U.S. Department of Health, Education and Welfare, NIOSH Pub. No. 78-172, June 1978, pp 280.
3. S.L. Rose and J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Report 8848, March 19, 1985.



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TEST SET-UP

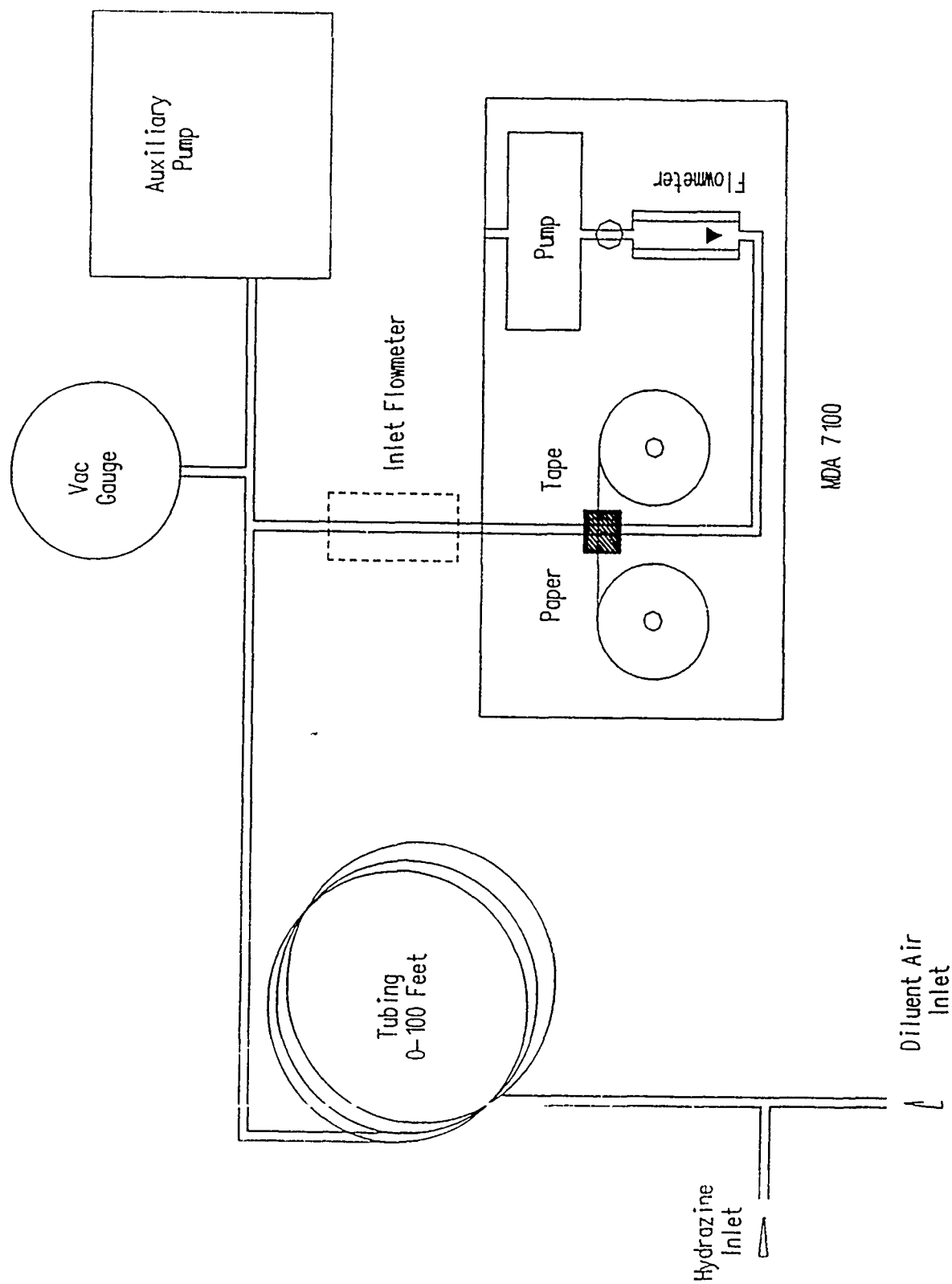


Figure 1.

SET-UP FOR FLOW ADJUSTMENT

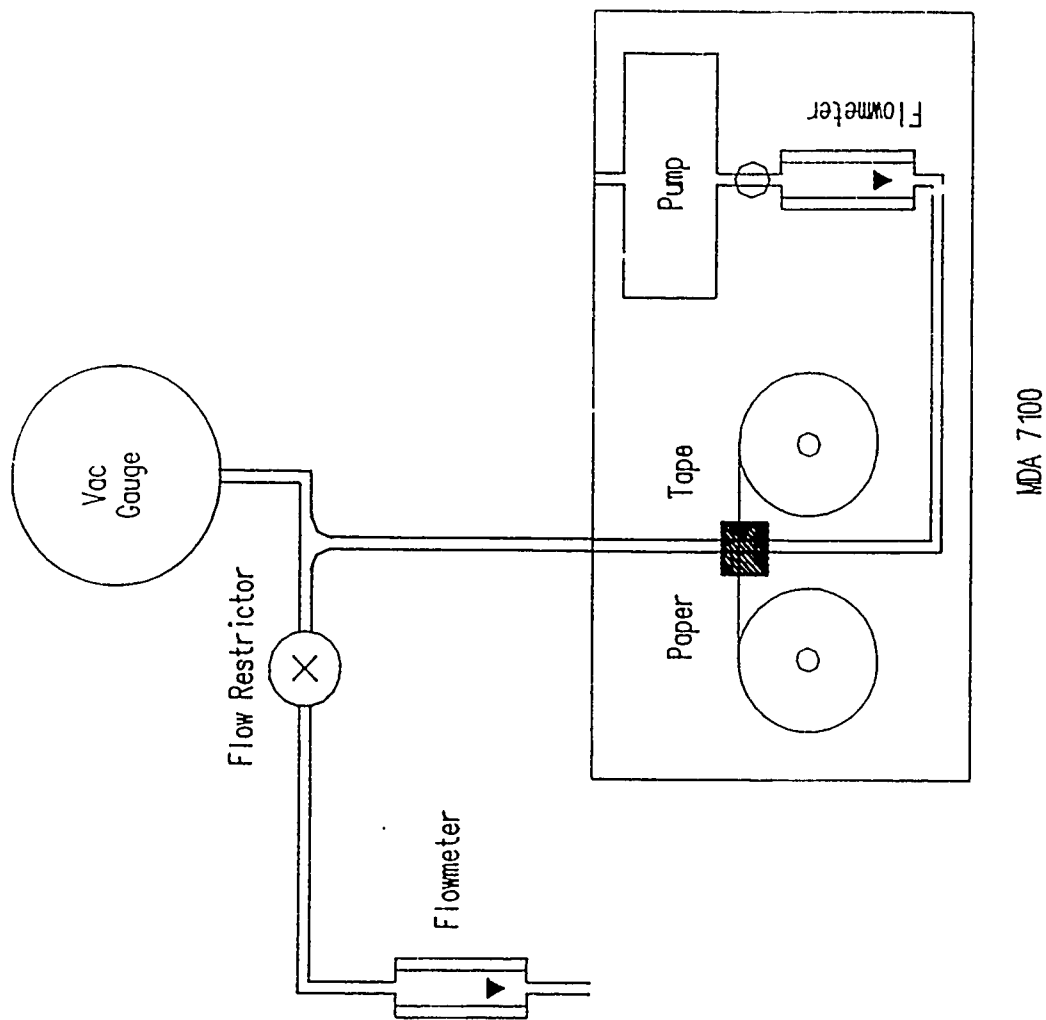
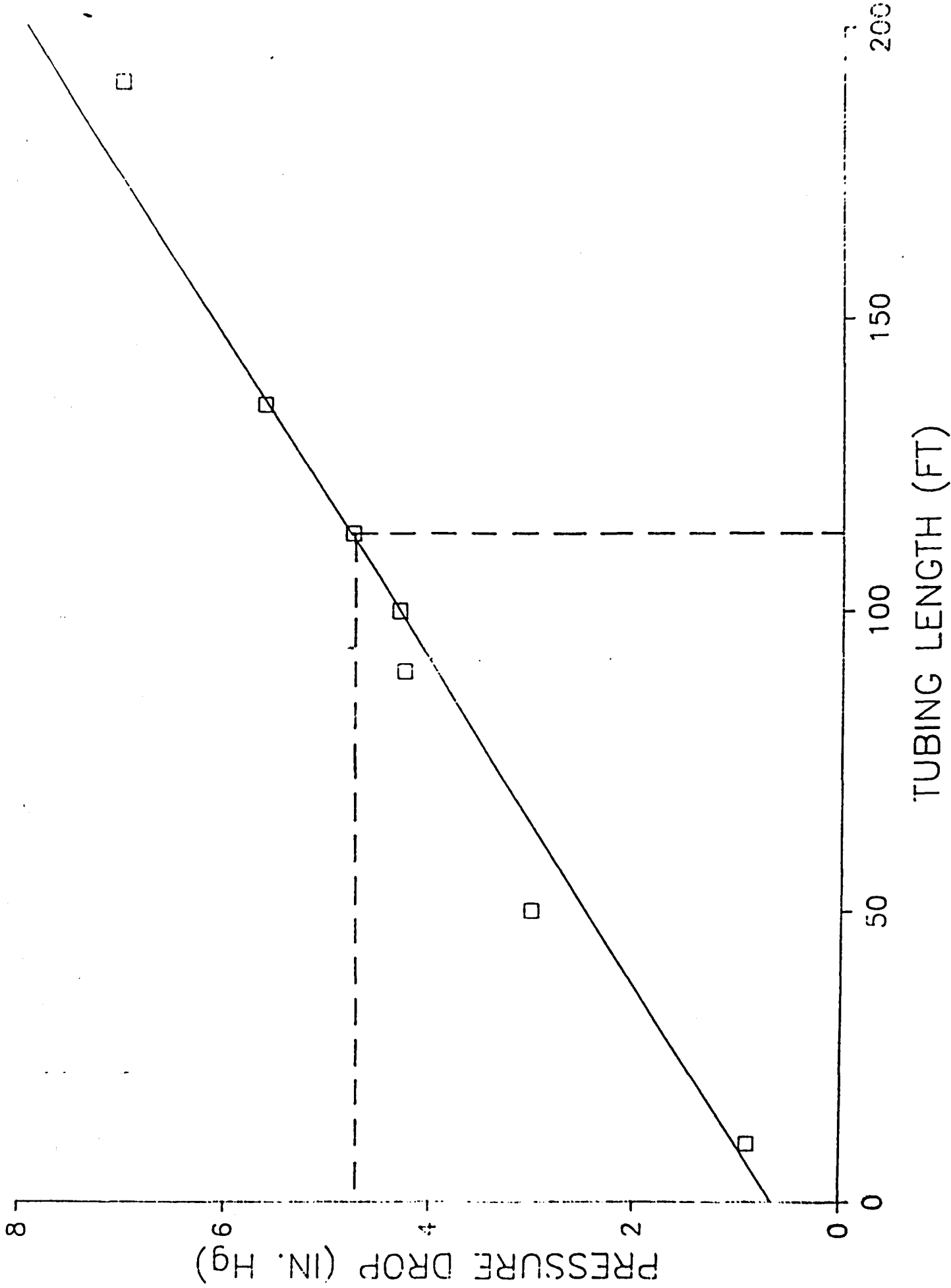


Figure 2.

PRESSURE DROP DUE TO TUBING



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27 April 1988

EVALUATION OF ECOLYZER 7660 HYPERGOLIC FUEL VAPOR DETECTION CELLS

INTRODUCTION

Hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) are widely used as high energy propellants. Space shuttle operations require large quantities of hydrazine and MMH. In order to provide the best protection for the space shuttle, NASA continually supports test and evaluation of new and/or improved hydrazine instrumentation. The use of monitors to detect leaks of the hydrazines on the launch pad is necessary due to the explosive nature of the propellant and its toxicity.

Ecolyzer 7660 Hypergolic Fuel Vapor Detectors are the alarm devices utilized to alert personnel to levels of propellant which may be hazardous to the space shuttle and attending employees. These instruments detect hydrazine vapor by electrochemically reducing the hydrazine at a fixed potential. The instrument uses electrochemical cells that require replacement after about three months. After several years of satisfactory performance, the replacement electrochemical cells performed poorly during evaluation at Kennedy Space Center (KSC). The cells evaluated at KSC arrived with cracked cell casings, corroded electrodes, and electrolyte leakage problems. Many of the cells did not respond to calibration gas or could not be calibrated. Energetic Sciences, the original manufacturers of the Ecolyzer instruments and cells, (ESI cells) was sold to National Draeger, Inc. Just prior to and after the sale of the company, the quality of the cells manufactured suffered. Concerned about the reliability of the measurements, NASA scientists met with National Draeger and Transducer Research, Inc. (TRI) to discuss the problems and possible solutions. It was decided that a more reliable cell was needed to replace the ESI cells. New cells were designed by TRI and National Draeger. The Naval Research Laboratory (NRL) was asked to evaluate all the new cells alongside the original ESI cells. The ensuing study was designed to test critical performance of the various cells.

EXPERIMENTAL

Four Ecolyzer 7600 instruments were obtained from KSC. Four different types of cells were evaluated over a period of several months. Each analyzer houses two cells which operate independently from one another. Whenever possible, one or two of each type of sensor were tested simultaneously. As sensors leaked or failed to respond, they were replaced with new cells of the same type, if possible.

The original sensors made by TRI for testing at NRL performed poorly and exhibited electrolyte weepage through and around the membrane. TRI modified its cell design to alleviate the weepage problem. The new cells were constructed with different backing materials and o-ring sizes. These modified cells were evaluated in this study. NRL purchased eighteen of the sensors from TRI. KSC provided nine sensors of the old ESI

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design manufactured by National Draeger. National Draeger provided NRL with four cells of a new design filled with 23% KOH and heat-sealed. It became apparent that movement of the KOH cells while being exposed to MMH vapor caused increased noise in the output signal. Therefore, Draeger also supplied four heat-sealed cells that contained a gel.

Three of the TRI sensors were filled with 25% CsOH solution and the remainder of the sensors were filled with a 23% KOH solution. The TRI cells required 10 milliliters (mls) of solution. After filling the sensors, a threaded plug was inserted into the filling port and tightened gently. The cells were then allowed to sit for a one hour period of equilibration and then were voltage biased for one hour. At this time, the sensors could be calibrated. The ESI sensors were filled with approximately 25 mls. of 23% KOH solution just prior to use. Although it was not stipulated, the ESI cells received the same pre-calibration treatment as the TRI sensors. The TRI cells and the ESI cells were filled with electrolyte solution as they were needed; they were stored empty until used. The Draeger cells were shipped to NRL filled with electrolyte and sealed. They were used as received.

The test plan required a set of cells to be exposed to MMH every day and another set to be tested once a week. Three Ecolyzers were used for the daily tests while one Ecolyzer was dedicated to the weekly exposures. The cells exposed once weekly were usually TRI cells since there was a greater availability of them. A couple of ESI cells were also used in this capacity. The instruments were exposed to 4-5 parts-per-million (ppm) of MMH or clean air, both humidified to 40-50% RH for the majority of the tests. The sensors which were exposed to the MMH vapor on a daily basis, continuously sampled 1.0 scf/h of clean air at approximately 40-50% RH between MMH exposures. Between test periods, sensors exposed weekly were not attached to a clean air source but instead they continuously pulled 1.0 scf/h of air from the hood at 30-35% RH.

The instruments containing the various sensors were evaluated using MMH. The system used to generate known concentrations of MMH is described in detail (1). This system consists of sources of MMH and zero-grade air. Clean air, which was humidified to the desired level, flowed through one of two pyrex gas manifolds. Similarly humidified air mixed with MMH flowed through the other manifold. The two manifolds were connected by several solenoid valves. To control the concentration of the test gas, the source was placed in a constant temperature water bath and the dilution air was controlled. Mass flow controllers controlled the gas flows and the relative humidity (RH) was determined with a HygroDynamics hygrometer. The MMH gas concentration was verified by impinger collection in 0.1 M H₂SO₄ and analyzed by coulometric generation of bromine with amperometric endpoint detection (2).

The data for the cells was collected in the following manner. The recorder input from each Ecolyzer was interfaced to an analog-to-digital (A/D) converter. The output of the A/D converter was then sampled with a Hewlett Packard Model 85 computer. The data collection program collects a maximum of 240 points from each instrument during each of three stages of a standard test. Twenty-five data points are collected first. From this, the average, minimum and maximum zero values and the standard deviation is determined. Then the gas collection process begins. The cells sample zero gas and the computer collects approximately one minute of baseline data. The solenoid valves are switched so that the cells may sample contaminated gas. The computer continuously monitors the sensors output for ten minutes, then pauses. The final stage is started and

after one minute, the solenoid valves are deactivated so that the sensors will again sample zero gas.

Data analysis programs interpret the data collected. One program plots the response curves for each cell while another program displays the average, minimum and maximum zero and span values as well as the corresponding standard deviation. The response and recovery times to 50, 75, and 90% of full scale are also determined. The response times are evaluated from the time the solenoid valves were activated through the next five minutes. The full scale values are calculated from the next five minutes of data. The recovery times are evaluated for five minutes following the deactivation of the solenoid valves. The final zero values are determined from the last five minutes of data. A complete exposure lasts twenty minutes.

The following test plan was used. The sensors tested prior to the inception of the test plan were calibrated once every one to two weeks. After the test plan was initiated, the sensitivity of the sensors was measured and they were recalibrated after a five week period of testing was finished. The cells were also recalibrated if they were moved to a different Ecolyzer. One instrument containing two cells was the exception to this course of action. It was set aside after it was initialized and calibrated. The cells in this instrument were exposed to test vapors once a week. They were not recalibrated for the duration of their useful lifetime. The purpose of this procedure was to provide data on long term stability.

INITIALIZATION AND CALIBRATION

Stabilization Time

The signal drift of each cell is determined after placing the cell on bias for one hour (stabilization time). This is done prior to calibration of the cell as stated previously.

Calibration

1. The cell samples zero gas for ten minutes after which the zero pot is adjusted to produce a zero reading on the Ecolyzer meter.
2. The cell then samples MMH standard vapor at five ppm for ten minutes and the span pot is adjusted to produce a five ppm reading on the meter.
3. Steps one and two are repeated until the zero and span readings are stable and within 5% (± 0.25 ppm) of the span and zero gas values.

Sensitivity

The maximum span value of each cell is measured and recorded while sampling five ppm MMH standard gas by adjusting the span pot fully clockwise until the meter reading is stable. The critical maximum span value is determined at the end of the five week period.

TEST PLAN

Response Time

Response time is measured with cells at exposure intervals of no less than 12 hours. Response times to 50, 75, and 90% of the full scale (the final MMH reading at the end of a ten minute exposure) were determined for MMH concentrations varying from 0.5 ppm to 15.0 ppm. In the majority of the tests, the cells reached equilibrium at the end of the ten minute exposure.

Linearity and Accuracy

Vapor exposures were made at MMH concentrations ranging from 0 to 18 ppm. The data points were collected by the process described previously in the test plan. The test gas concentration (ppm) versus cell output (ppm) on the x10 range was plotted for each instrument.

Zero Drift

After exposing the sensors to zero gas for ten minutes, the cell output is monitored for a one hour period while the cells are sampling zero gas. The change in response is determined.

Span Drift

After exposing the sensors to span gas at five ppm for ten minutes, the cell output is monitored for a one hour period while the cells are sampling 5 ppm of MMH vapor. The change in response is determined.

Noise

The noise on the output signal is measured during periods of constant input of span gas or zero gas. It is determined from the maximum and minimum values and the full scale value on the x10 range.

POST TEST EVALUATION

Post Test Cell Check

The critical maximum span value of each cell is determined while sampling 5 ppm of MMH vapor. This is done after the five week test period. Together with the sensitivity measurement made during initialization and calibration of the cell, this provides information on the degradation in cell performance during the lifetime of the cell.

Cell Life

Cell life is defined as the number of days after initial calibration of the cell until the cell leaks or cannot be recalibrated. The cell life of each cell is determined with the following stipulation: the cell must hold the original calibration for 30 days with a deviation from the calibration value not to exceed $\pm 25\%$.

RESULTS

TRI

Most of the KOH sensors demonstrated a steadily decreasing response to the MMH gas until the cells leaked or were removed from the instrument for low response. The cells were expected to perform for five weeks. However, most TRI cells failed in less than five weeks. Two of the CsOH sensors could not be calibrated following the standard set-up procedure. These were removed from the instrument and were not tested. The remaining CsOH cell was tested weekly for a period of 11 weeks at which time it leaked into the surrounding tubing.

All of the TRI cells that were checked for stabilization time exhibited signal drifts ranging from 0.01 to 0.07 ppm for the first hour of operation and therefore passed this portion of the acceptance test which specified a signal drift no greater than 1.0 ppm for the first hour. The cell response and response time of the CSOH and the KOH cells were comparable. The KOH cells averaged 4.9 minutes to 90% of full scale and the CSOH cells averaged 4.5 minutes to 90% of full scale. Typical response curves of the KOH cells and the CSOH cell after five weeks of testing are shown in Figures 1A and 1B respectively.

The accuracy of the cell response for both the KOH and CSOH cells did not meet the acceptance test requirements. The accuracy of the KOH cells was very erratic from test to test for individual cells, and also from cell to cell. The percent error in the response of the TRI cells was generally between +5% to -45% and one sensor exhibited a point of +90% error from the actual concentration. The error range of the CSOH cell tested was +10% to -100%.

Linearity tests were performed at concentrations ranging from 0.0 ppm to 18 ppm MMH. The TRI sensors perform poorly at high concentrations of MMH. They averaged 40% lower than expected. Figure 2 illustrates a typical linearity plot for a TRI KOH cell.

The KOH cells passed the zero drift requirement of no greater than 0.25 ppm drift over a one hour period, with an average drift of 0.04 ppm for a one hour test. The majority of the cells failed the span drift requirement. The average drift for the KOH cells was 0.42 ppm. The noise of the KOH cells averaged 2.4% of full scale at the x10 range and 0.4% of full scale on the x100 range. The CSOH cell displayed noise of 2.2% of full scale on the x10 range. All TRI cells failed the post test sensitivity check; some of the cells leaked and the others displayed a maximum span value less than was required to pass the acceptance test. Testing of the TRI sensors was halted due to their poor performance.

DRAEGER

National Draeger has supplied NRL with four KOH cells as well as four gel cells. The gel was added to reduce noise in the sensors. The KOH cells demonstrated good response to the MMH initially, but they gradually decreased in response to the gas until they leaked or were removed for low response. This decrease in cell response occurred after the initial five weeks of testing.

Of the four gel cells tested, one performed poorly, one was outstanding, and two were average. The first performed for only two weeks at which time it was removed due

to low sensitivity. The second gel cell to be placed in an ecolyzer performed very well from the initial calibration on 9/30/87, until testing was terminated six months later. The response to MMH was consistent and accurate until the last week of January when the cell was exposed to MMH vapor diluted with dry air (10% RH). The cell did not respond to the MMH vapor. It was recalibrated with wet air (65% RH) and tested for a couple of days with dry air. The sensor gave a 50% low response initially, then gave no response to a 4 ppm MMH gas stream. When subjected to vapor of 45% to 55% RH, the cell gradually revived. Apparently, the moisture contained in the gel evaporated causing the gel to contract and draw away from the electrical contacts within the sensor body. With humidified air, the cell receives enough moisture for the gel to expand and make contact with the connections in the cell housing. It is not known when this evaporation begins to affect the performance of the sensor as no previous tests with dry air were performed. A third cell was initially calibrated on 10/14/87 and performed well until 11/27/87 when it stopped responding to the MMH vapor altogether. It was removed the following week. The last gel cell was calibrated on 12/4/87 and performed well until 1/7/88 when it began exhibiting very irregular responses. It was tested for another week but the response curve observed during an exposure continued to degrade.

Only two of the Draeger cells were tested for initial stabilization time. The cells checked were gel cells and both passed the test. One cell demonstrated a 0.00 ppm signal drift for the first hour of operation and the other cell had a 0.02 ppm signal drift.

Linearity tests indicated good linear responses, although occasionally at high concentrations, the gel cells deviated by 20% for the gel cells and the KOH cells deviated by 15%. Typical linearity graphs of a Draeger KOH cell and a gel cell are shown in Figures 3 and 4 respectively. The accuracy of the Draeger cells is better than that of the TRI cells. The KOH cells remain within 25% error for the first 30 days of testing and the gel cells average within 30% error for the first 30 days after initial calibration.

Both types of Draeger cells performed well on the zero drift portion of the acceptance test and averaged 0.02 ppm for a one hour period. They also passed the one hour span drift test. The gel cells averaged a drift of 0.07 ppm for a one hour period and the KOH cells averaged 0.05 ppm. The average response time to 90% of full scale for the gel cells is 1.9 minutes. This is the same for the KOH cells. They both fail this portion of the acceptance test, however, which requires a response time of no longer than one minute to 90% full scale. For the longest working gel cell, the response time to 90% of full scale improved with time from approximately two minutes to 0.6 minutes. Typical response curves of the KOH cells and the gel cells after five weeks of testing are shown in Figures 1C and 1D respectively.

On the x10 range, the noise of the gel cells average 1.0% of full scale while the KOH cells average 0.9% of full scale. On the x100 range, the KOH cells average 0.2% of full scale. The gel cells showed the greatest sensitivity in the post test cell check after five weeks. The KOH cells, however, failed this test. Half of the cells leaked before the maximum span value could be ascertained, and the rest gave a lower value than needed to pass the test.

ESI

The poor cell performance that prompted this test has not been demonstrated by the cells received from KSC, and recently manufactured by National Draeger. However, the performance of the ESI cells needs improvement in some areas. The ESI cells passed

the initial stabilization time test with an average signal drift of 0.32 ppm. They have shown good response to the MMH stream. The accuracy range of the cells averages at +2% to -50% error with the exception of two stray points at +50% and -120% error. The response time to 90% of full scale averages 2.4 minutes and in several of the cells, the response time increases with time. Figure 1E displays a typical response curve of an ESI cell at five weeks of testing.

The linearity tests on the ESI cells give much the same results as the Draeger gel cells, although at less than one ppm of MMH, one ESI cell gave a response that was 50% higher than the actual concentration. Another cell has given a response of 50% lower than expected. A graph of linearity is displayed in Figure 5.

The cells passed both the zero and the span drift test with averages of 0.01 ppm and 0.16 ppm respectively for a one hour period. The noise of the ESI cells average 1.2% of full scale on the x10 range and 0.3% on the x100 range. Only two cells were checked for the post test cell check since the acceptance test was not written at the time that several of the cells were removed from testing. Both cells failed this test.

A comparison of premature failure percentages (cell life of one week or less) for the TRI, Draeger, and ESI cells is shown in Table I. Table II contains a chart of average response time and cell life of the various sensors.

CONCLUSION

The Draeger gel cells have performed the best and are the most consistent. In future tests, the problem of moisture evaporation from the gel cells will be addressed. We will have to determine when the gel loses enough moisture to affect the cell's response to MMH vapor. The TRI KOH cells and the TRI CsOH cells perform the poorest and the performance of the Draeger KOH cells and the ESI cells fall in between the two categories.

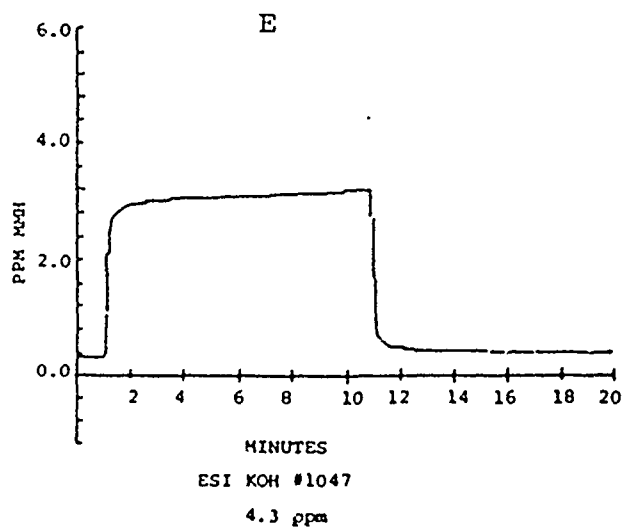
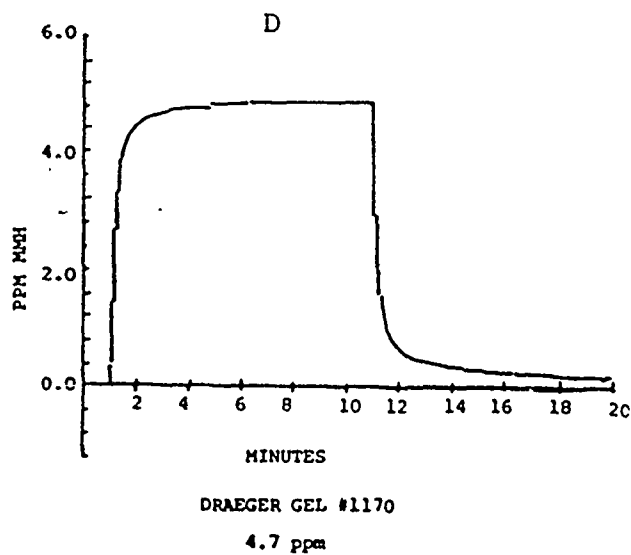
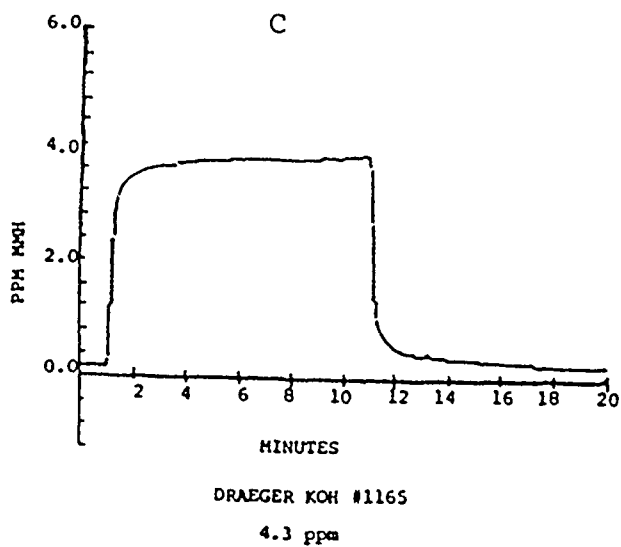
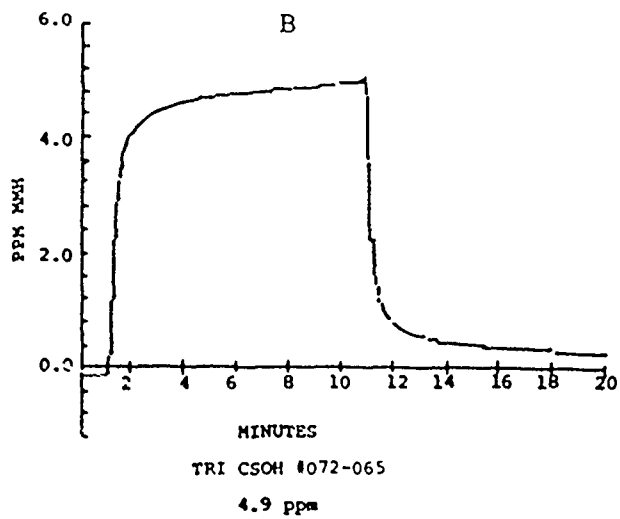
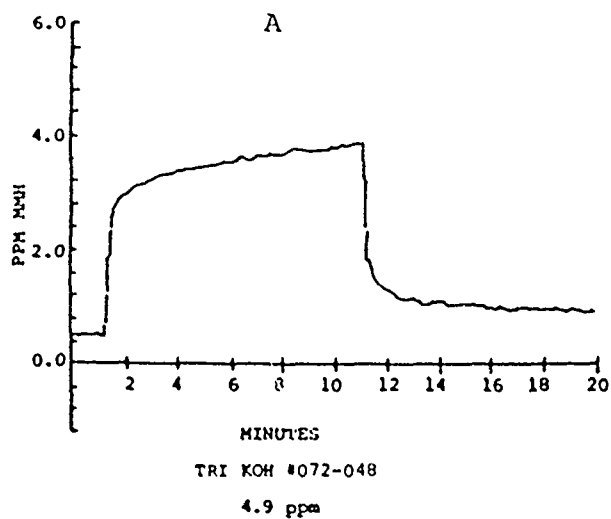


Figure. 1

SENSOR LINEARITY

TRI

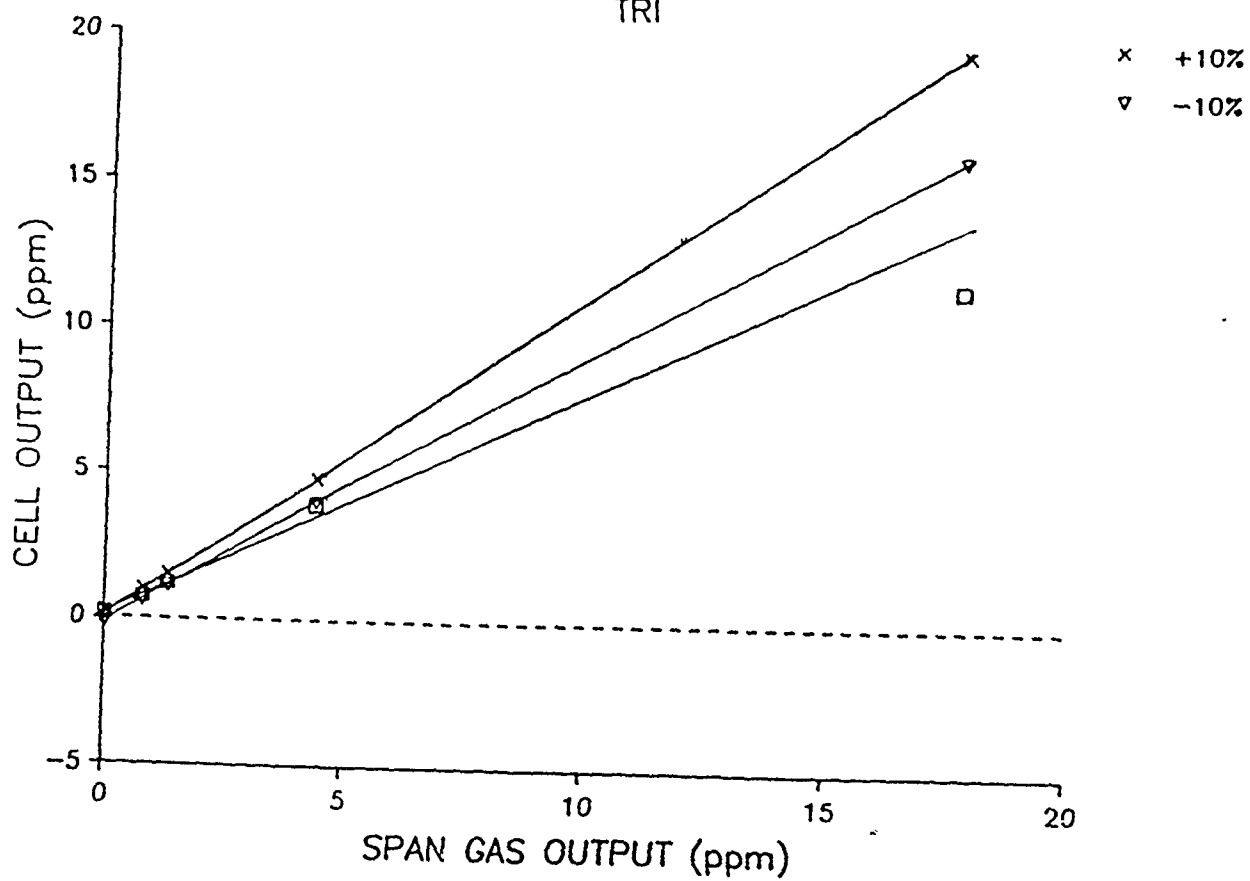


Figure. 2

SENSOR LINEARITY

DRAEGER KOH

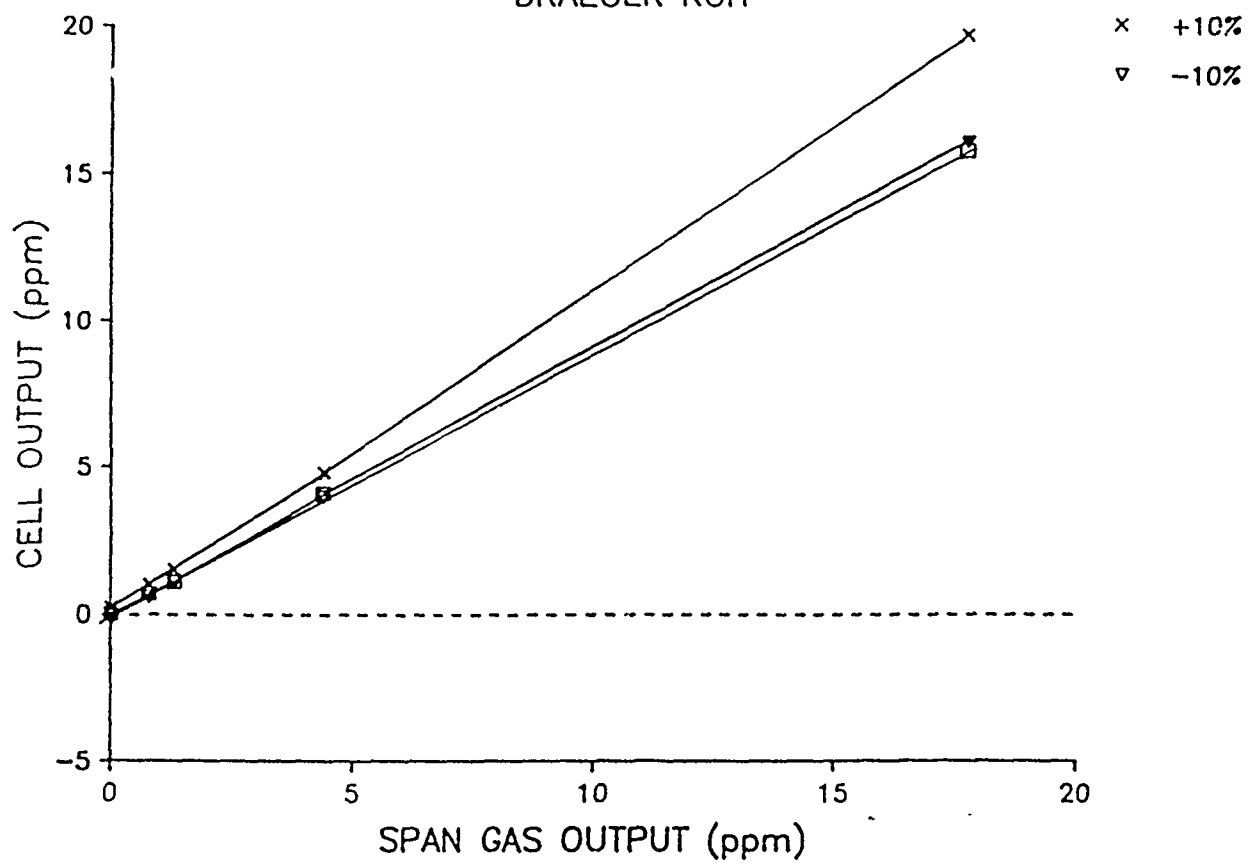


Figure. 3

SENSOR LINEARITY

DRAEGER GEL

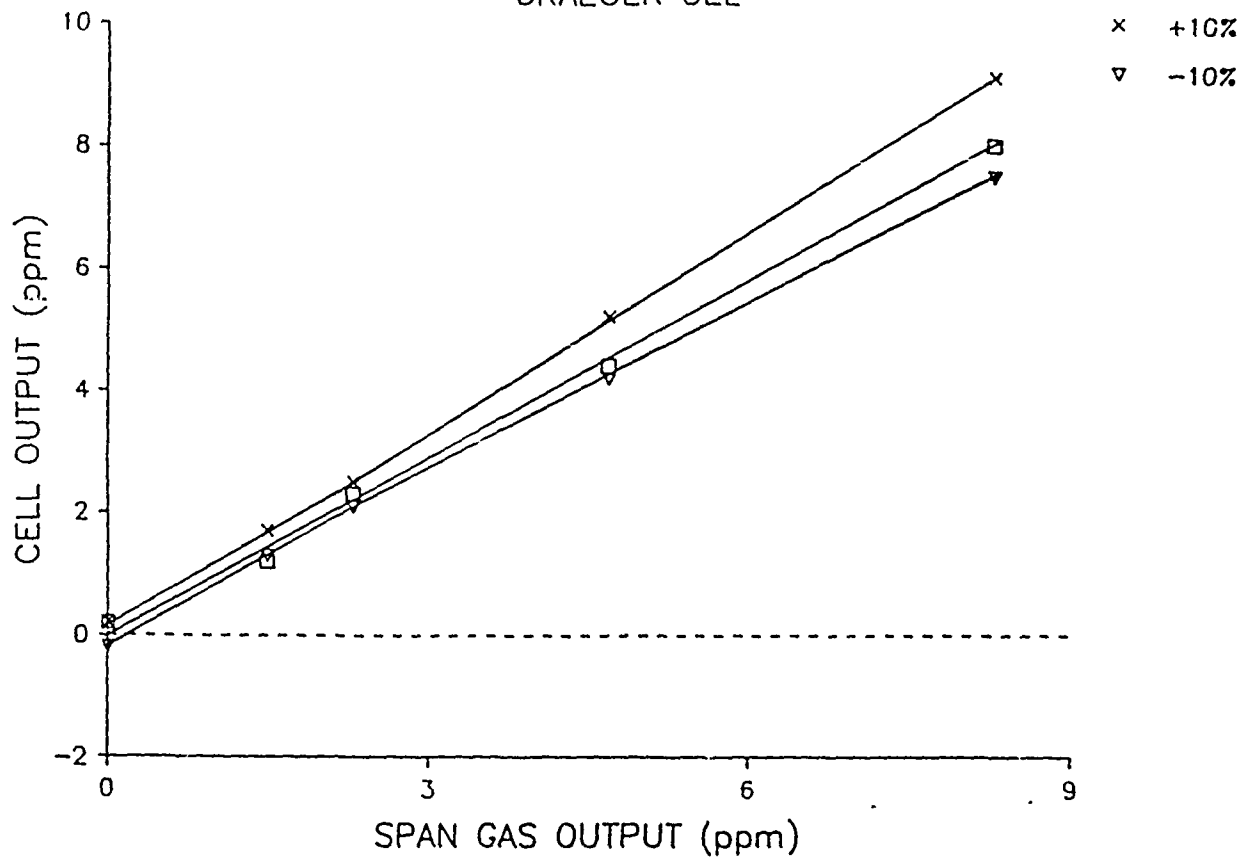


Figure. 4

SENSOR LINEARITY

ESI

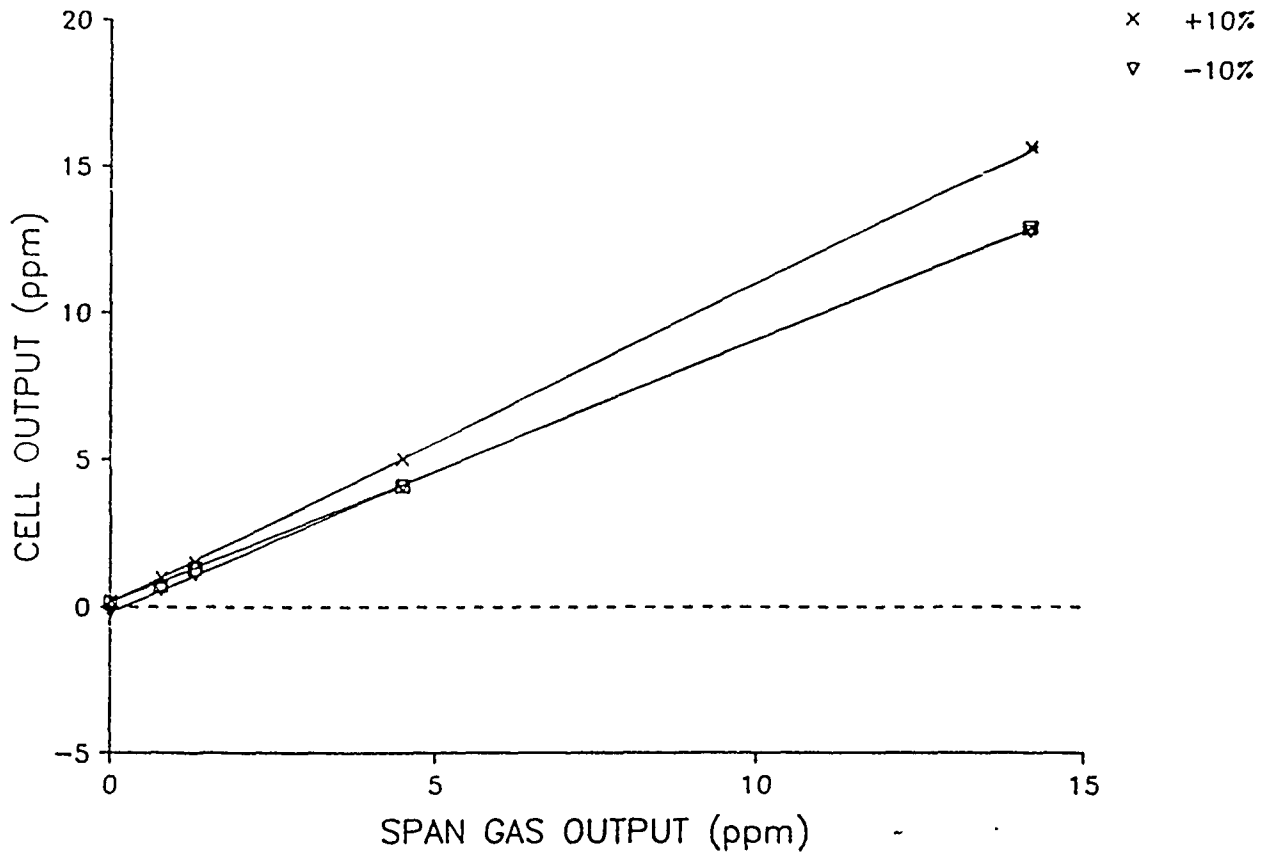


Figure. 5

Table I. PREMATURE FAILURE RATE

	TOTAL # OF CELLS	FAILURE RATE (%)
TRI KOH	14	46
TRI CSOH	3	67
ESI	8	43
DRAEGER KOH	4	0
DRAEGER GEL	4	25

Table II. RESPONSE TIME AND CELL LIFE

	AVERAGE RESPONSE TIME TO 90% (min)	AVERAGE CELL LIFE (days)
TRI KOH	4.9 $\pm$ 2.1	29 $\pm$ 18
TRI CSOH*	4.5	57
ESI	2.4 $\pm$ 0.39	41 $\pm$ 20
DRAEGER KOH	1.8 $\pm$ 0.42	43 $\pm$ 10
DRAEGER GEL	1.9 $\pm$ 0.67	59 $\pm$ 26

Premature failures were not averaged into cell life values

* Values based on one cell

REFERENCES

1. S.L. Rose and J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Report 8848, (1985).
2. Olson, E.C., Analytical Chemistry, 1960, 32, 1545.

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EVALUATION OF ECOLYZER 7660 HYPERGOLIC FUEL VAPOR DETECTION GEL CELLS

INTRODUCTION

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After the promising initial performance of gel cells, NASA requested that NRL perform additional tests on a number of newly manufactured gel cells. The first study was conducted using air with 45% relative humidity while this study was primarily designed to examine the effects of humidity on the cells. The results of tests at different relative humidities are presented in this report.

EXPERIMENTAL

Using Ecolyzer 7660 instruments previously obtained from KSC, gel cells were evaluated over a period of several months. Each analyzer houses two cells which operate independently. Eight cells were operating at one time. As the cells failed, they were replaced with new cells.

Draeger provided NRL with 17 gel cells. This type of electrolyte was used to reduce noise in the sensors due to motion. Effects from motion of the cells was evident in the liquid KOH cells examined prior to this series of tests. The cells were shipped to NRL filled with electrolyte and sealed with a threaded plug which could be removed for the addition of water during the test period. The cells were voltage biased for one hour prior to calibration.

During the previous testing of Draeger gel cells, the gel experienced water evaporation to the point that it affected the cell's performance. The gel in the cell contracts and draws away from the electrical connections within the sensor body. When tested with air at 45% relative humidity (RH), the evaporation effect was less noticeable than when the cells were tested with dry air.

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With humidified air, the cell receives enough moisture for the gel to expand and make contact with the connections in the cell housing. To determine the cells' reaction to various humidities, the following procedure was used. The sensors were exposed to 4-6 parts-per-million (ppm) of monomethyl hydrazine (MMH) or clean air, both humidified to identical relative humidities (RH) for the majority of the tests. The sensors continuously sampled 1.0 scf/h of clean air or laboratory air between MMH exposures.

Four cells were used as controls and continuously sampled air at approximately 45% RH. Another set of two cells sampled dry air (10% RH or less) continuously. A third set was tested under various relative humidities from 10% to 90%. Table I details the daily testing sequence for the various sets of sensors.

Table I DAILY TESTING SEQUENCE

CELL CONDITIONS	RH	MON	TUES	WED	THURS	FRI
DRY	<10%	X	X			
CONTROL	45%			X	X	
VARIABLE	<10-96%	X	X	X	X	X

Out of twelve cells tested, four were recalibrated within 6 weeks. These were respanned at week 9 or 10 after water was added to combat the moisture evaporation problem. Four others could not be spanned at 6 weeks and were removed. The cells which replaced these were calibrated and received water 2 to 3 weeks later. Most of the cells that received water required more than one recalibration within a few days after the water was added as they were not stable.

The system used to generate known concentrations of MMH has been described in detail (2). This system consists of sources of MMH and zero-grade air. Clean air, which was humidified to the desired level, flowed through one of two manifolds. Similarly humidified air mixed with MMH flowed through the other manifold. The instruments were connected to the manifolds with two feet of 1/4 inch O.D. teflon tubing and a solenoid valve. To control the concentration of the test gas, a MMH diffusion source was placed in a constant temperature water bath and the dilution air was controlled. Mass flow controllers controlled the gas flows and the relative humidity (RH) was determined with a HygroDynamics hygrometer. The MMH gas concentration was verified by impinger collection in 0.1 M H_2SO_4 and analyzed by coulometric generation of bromine with amperometric endpoint detection (3).

The data for the cells was collected in the following manner. The recorder input from each Ecolyzer was interfaced to an analog-to-digital (A/D) converter. The output of the A/D converter was then sampled with a Hewlett Packard Model 85 computer. The data collection program collects a maximum of 240 points from each instrument during each of three stages of a standard test. Twenty-five data points are collected first. From this, the average, minimum, maximum and the standard deviation of the zero value is determined. The cells sample zero gas and the computer collects approximately one minute of baseline data. The solenoid valves are switched so that the cells sample contaminated gas. The computer continuously monitors the sensors output for ten minutes, then pauses. The final collection stage is started and after one minute, the solenoid valves are deactivated so that the sensors will again sample zero gas.

Data analysis programs interpret the data collected. One program plots the response curves for each cell while another program displays the average, minimum, maximum, and the standard deviation of the zero and span values. The response and recovery times to 50, 75, and 90% of full scale are determined. The response times are evaluated from the time the solenoid valves were

activated through the next five minutes. The full scale values are calculated from the next five minutes of data. The recovery times are evaluated for five minutes following the deactivation of the solenoid valves. The final zero values are determined from the last five minutes of data. A complete exposure lasts twenty minutes.

The sensitivity of the sensors was measured after the cells were calibrated initially. Most cells were recalibrated after a six week period of testing. Several of the cells were also filled with water to their pre-test weight and then recalibrated. The following test plan was used.

INITIALIZATION AND CALIBRATION

Stabilization Time

The signal drift of each cell was determined after placing the cell on bias for one hour (stabilization time). This was done prior to calibration of the cell.

Calibration

1. The cell samples zero gas for ten minutes after which the zero pot is adjusted to produce a zero reading on the Ecolyzer meter.
2. The cell then samples MMH standard vapor at five ppm for ten minutes and the span pot is adjusted to produce a five ppm reading on the meter.
3. Steps one and two are repeated until the zero and span readings are stable and within 5% (± 0.25 ppm) of the span and zero gas values.

Sensitivity

The maximum span value of each cell is measured and recorded while sampling approximately five ppm MMH standard gas by adjusting the span pot fully clockwise until the meter reading is stable. The critical maximum span value is determined at the end of the five week period.

PERFORMANCE EVALUATION

Relative Humidity

Following set-up of sensors mentioned previously, the sensors were subjected to various relative humidities from 0-96% RH.

Response Time

Response time is measured on cells that have not been exposed to MMH for intervals of greater than 12 hours. Response times to 50, 75, and 90% of the full scale (the final MMH reading at the end of a ten minute exposure) were determined for MMH concentrations varying from 0.5 ppm to 15.0 ppm.

Linearity and Accuracy

Vapor exposures were made at MMH concentrations ranging from 0 to 18 ppm. The data points were collected by the process described previously in the test plan. The test gas concentration (ppm) versus cell output (ppm) on the x10 range was plotted for each instrument.

Zero Drift

After exposing the sensors to zero gas for ten minutes, the cell output is monitored for a one hour period while the cells are sampling zero gas. The change in response is determined.

Span Drift

After exposing the sensors to span gas at five ppm for ten minutes, the cell output is monitored for a one hour period while the cells are sampling 5 ppm of MMH vapor. The change in response is determined.

Noise

The noise of the output signal is measured during periods of constant input of span gas or zero gas. It is determined from the maximum and minimum deviations in the full scale value on the x10 range.

POST TEST EVALUATION

Post Test Cell Check

The critical maximum span value of each cell is determined while sampling 5 ppm of MMH vapor. This is done after the five week test period. Together with the sensitivity measurement made during initialization and calibration of the cell, this provides information on the degradation in cell performance during the lifetime of the cell.

Cell Life

The cell life is the number of days that the sensors perform within the $\pm 25\%$ performance specifications following the initial calibration. The cell life of each sensor is determined using with the following criteria: the cell must hold the original calibration for 30 days with a deviation from the calibration value not to exceed $\pm 25\%$.

RESULTS

DRY CONDITIONS

All the cells were tested for initial stabilization time. Cells 008 and 005, which were continuously exposed to dry air (<10% RH) demonstrated a 0.85 ppm and a 1.6 ppm signal drift respectively for the first hour of operation while sampling clean air. Cell 005 displayed an initial signal drift higher than the allowable drift of 1 ppm.

Table II lists the initial sensitivities of all the cells as well as the sensitivities measured at six weeks. The initial sensitivity of the dry cells is very good. However, at six weeks into the testing period, the sensitivities of the dry cells have declined considerably and the sensors do not pass this requirement of the performance evaluation.

The "dry" cells showed a decreased response to MMH vapor within a few days after calibration. Within the first five weeks of testing, cell 008 responded with an average of 75% error while cell 005 averaged 90% error at approximately 5 ppm MMH. The response curves show a gradual climb to 90% of full scale. Both sensors exhibited response times of >10 minutes to 90% of full scale. The acceptance evaluation of the cells requires a response time of no more than 1 minute to 90% of full scale. Within a couple of days after calibration, both cells were subjected to a zero drift test and a span drift test. Both performed well on the tests. A zero drift of 0.02 ppm and a span drift of about 0.05 ppm were observed for both sensors. Figure 1 gives a graph of sensor accuracy for cell 008. Table III details the percentage of error of all the cells at several stages in the testing.

A linearity test was run after 2 weeks. The cells were exposed to MMH vapor concentrations of 0.73, 1.1, 5.1, and 11.6 ppm. The cells responded poorly to the various concentrations of MMH. Cell 008 gave responses of <50% of impinger value to all concentrations except 1.1 ppm. The cell response at this concentration was 136% of the impinger value. Although the accuracy of the sensors' responses was poor, they appear to be fairly linear. Figures 2 and 3 illustrate the linearity curves.

Noise was calculated only if a sensor exhibited a noisy response curve. The "dry" cells did not exhibit noise >1% of the signal on span or zero gas.

CONTROL CONDITIONS

Seven cells (controls) were subjected to approximately 45% RH during MMH exposures as well as clean and hood air humidified to 45%. Four cells occupied spaces in the Ecolyzers at any one time. Two of these cells were tested twice weekly, the other two were tested on an average of once every 9 days. All of the control cells displayed signal drifts of less than 0.2 ppm for the first hour of operation while sampling zero gas. They passed this section of the performance evaluation which requires a signal drift of no more than 1 ppm for the first hour of operation. The sensitivities of the cells can be found in Table II. The control cells performed very well in initial sensitivity evaluation. By six weeks, three of the cells were no longer functioning. Of the four cells still working, only the two cells exposed to MMH gas twice weekly, displayed the required sensitivity.

The accuracy of the control cells varied greatly. The error in the responses of these sensors ranged from 4% to 383% after the initial calibration. The greatest error was observed during the linearity test. One cell was removed at its sixth week of testing because it could not be spanned down from 17.5 ppm while sampling 6.1 ppm MMH. Table III shows the error in the accuracy of the cells.

One example of the strange behavior was demonstrated by cell 002. The responses fluctuated between +300 to -20% error within the first 14 days after calibration. After the addition of water at day 20, to bring the sensor to its pre-test weight, a second recalibration on day 23, and a third on day 35, the cell signal remained stable at an average error of 37%. This lasted for the next twenty

days when testing ceased. The cell had to be recalibrated three times from day 20 to day 35 as the instrument display was not stable after the addition of water to the cell. The needle in the output display swung from negative to greater than 20 ppm on the x10 range.

The most stable performance was demonstrated by cell 006. For the first 16 days of testing, its response remained within $\pm 30\%$. The error continued to increase as can be seen in Table III. Two recalibrations in the sixth week did not improve the accuracy of the cell. In the ninth week, water was added to the sensor and it was recalibrated. The response recovered to within $\pm 30\%$ error for the next 40 days when testing was ceased. The accuracy graph for cell 006 is displayed in Figure 4.

The response times to 90% of full scale averaged to 2.7 minutes for the three cells exposed to MMH twice weekly. Those control cells exposed to MMH less frequently exhibited response times of 2.4 minutes to 90% of full scale. The requirement for response times to 90% of full scale is 60 seconds or less. The control cells did not pass this requirement.

At two weeks, cells 013 and 006 were subjected to a linearity test. The cells were exposed to MMH concentrations of 0.64, 1.2, 5.0, and 19.4 ppm. As can be seen from Figures 5 and 6, the sensors responded very differently from one another. Again, the accuracy is poor for cell 013, but the responses are linear. Sensor 006 is the only cell whose responses fall within $\pm 10\%$ error.

The control cells tested at 45% RH once weekly, 010, 014, and 016, behave somewhat similarly to one another. By the fifth week of testing, the accuracy of the cell responses has continuously dropped despite recalibration attempts. The one exception was cell 007 which, after an initial dip in accuracy, showed a brief improvement. The response then continued to decrease until the sensor was removed from testing in its sixth week because it could not be spanned to the calibration gas concentration. Figure 7 shows sensor accuracy vs. time of one of the weekly control cells.

The only control cell that exhibited noise problems was cell 002. This was an infrequent occurrence, however. One week after the initial calibration, an exposure at 4.7 ppm MMH led to noise of 13% of full scale. One week later, at 4.7 ppm MMH, the cell gave noise of 35% of full scale. Two weeks after the initial calibration, the noise problem disappeared.

VARIABLE CONDITIONS

Two of the cells subjected to various humidities were tested for signal stability. For the first hour, cell 018 gave a signal drift of 0.07 ppm and cell 003 gave a signal drift of 0.01 ppm. During the course of testing, the cells were tested for span and zero drift. Cell 018 displays an average span drift of 0.06 ppm for a one hour exposure to 5 ppm MMH. The zero drift for a one hour clean air exposure was 0.20 ppm for cell 018. Cell 003 displayed a zero drift of 0.03 ppm to clean air, and an average span drift of 0.04 ppm. The cells passed the zero and span drift section of the evaluation with less than 0.25 ppm signal drift over a one hour period of exposure to zero air or MMH gas. The relative humidity of the dilution air does not seem to affect the span drift.

Table II gives the sensitivities of the calibrated cells. The initial sensitivity measurements are very good. The sensitivities of the same cells at six weeks of testing are varied. One of the cells was not still functioning at this time, one cell gave a sensitivity far lower than the acceptable limit, and the final cell displayed an adequate measure of sensitivity at this time.

These cells, from which the greatest amount of data was collected since they were exposed daily to MMH gas, gave varied responses. They responded poorly to exposures with <10% RH. The cells would generally display an increase in response at approximately 45% RH. Finally, the sensors experienced an even greater recovery when subjected to relative humidities between 75% and 96% RH.

The accuracy of cell 003 fluctuates between -90% and +40% error within the first five weeks of testing. Several calibrations were required in the cell's sixth week as the sensor responded with a large positive error to the first recalibration at this time and in a subsequent test gave no response. Replenishing the cell with water and recalibrating it at the ninth week of testing did not solve the problem of the large fluctuations in response. After the hydration of the cell, it had to be recalibrated several times as the needle on the output display showed a constant drift upwards.

Cell 018 also responded to the MMH gas with large fluctuations ranging from +20% to -90% error for the first two weeks when the cell stopped responding to the gas. This was at relative humidities of <10% and 45% RH. After a recovery to 100% of the impinger value at 95% RH, the cell stopped responding to MMH vapor at any relative humidity. It was removed from testing.

The final variable cell gave similar fluctuations in responses. By the time cell 001 had been replenished with water and recalibrated on the nineteenth day of testing, the accuracy of its response had shown fluctuations between +5 and -85% error. Until the termination of testing, the cell displayed further fluctuations of +70 to -230% error. Figure 8 is a graph of the accuracy of sensor 003.

The average response time to 90% of full scale is 2.5 minutes for the three cells tested. This falls outside the acceptable limit of 1 minute or less to 90% of full scale.

A linearity test was run on sensors 018 and 003 after two weeks of testing. Sensor 018 was not responding to the MMH gas at this time. This was the week prior to its removal. Two linearity tests were run on sensor 003. One test was run at 8% RH while the other was at 45% RH. At <10% RH, the accuracy of cell 003 is poor, but the cell responds in a linear fashion. At 45% RH, cell 003 is more accurate although it does not fall within $\pm 10\%$ error. The linearity curves are shown in Figures 9 and 10.

Noise did not pose a real problem with two of these cells. Cell 003 only displayed two instances of 2-3% signal noise. Cell 001 had several instances of signal noise. Within the first two weeks, there were three occurrences of noise at approximately 3% of the signal. The RH was at 45% for two of the exposures. There were only three other occurrences of greater than 1% noise on the output signal while testing cell 001. They all appeared at 45% RH exposures and ranged from 8-17%.

CONCLUSION

During this series of experiments, the gel cells did not perform as well as they had in the previous study. The relative humidities that the cells were subjected to had an immense effect on their accuracy. The cells constantly exposed to <10% RH begin to lose accuracy immediately after calibration. The addition of water to the dehydrated gel does not appear to improve the accuracy of the "dry" cells. However, these cells exhibit a negligible amount of noise and appear linear.

The responses of the control cells at 45% RH were inconsistent as well. Only one cell, cell 006, displayed a marked improvement from the addition of water prior to recalibration. This cell is also the only cell to give linear data points within $\pm 10\%$ error during a linearity test. The control cells demonstrated periodic noise problems. It is not clear as to why these cells performed so differently than the gel cells tested during the previous experiments at the same RH.

The variable humidity cells showed clearly how the range of relative humidities affected the performance of the cells. As stated previously, the cells responded poorly to <10% RH. After sampling a gas stream with 45% RH, the cells appeared to recover slowly. By the end of the week when the cells were exposed to humidities of 75% to 96%, they had generally recovered very well. The cells gave linear responses during a linearity test and posed no extreme noise problem.

The response times to 90% of full scale for the dry cells were >10 minutes. The response times for the other cells to 90% of full scale averaged 2.5 minutes.

The humidity effects have to be resolved before the gel cells are used in a variety of climates. The addition of water as part of the recalibration process, in most cases, did not resolve the problem of gel dehydration. We would only recommend using these cells instead of liquid KOH cells if immunity to noise caused by vibration is essential.

Table II. CELL SENSITIVITY

CELL	RH	MMH CONC (ppm)	INITIAL SENSITIVITY (ppm)	MMH CONC (ppm)	SENSITIVITY AT 6 WEEKS (ppm)
005	<10%	3.7	20	5.3	9.25
008	<10%	3.7	22.5	5.3	7.5
002	45%	6	34	ND	ND
006	45%	3.7	22.5	6.1	20
013	45%	3.7	17.75	6.1	17.5
007	45%	3.7	22.5	6.1	4.5
010	45%	4.7	14.25	ND	ND
014	45%	3.7	18.6	6.1	.5
016	45%	6	35	ND	ND
001	<10-96%	6	40	ND	ND
003	<10-96%	3.7	24	6.1	15.7
018	<10-96%	3.7	22.5	6.1	1.5

Table III. PERCENT ERROR OF ACCURACY

WEEKS AFTER INITIAL CALIBRATION								
CELL	RH	1	3	5	7	9	11	14
008^	<10%	-80	-77	-75	-121	H2O	-173	-185
005	<10%	-90	-90	-90	-159	H2O	-206	-212
006	45%	6#	-53	-45	-102	H2O	(+30-----)	
013^^	45%	8#	97	175				
002	45%	19+	H2O	(-37-----)				
007	45%	-74	-102	-100				
010	45%	-57	H2O	-85	-109			
014	45%	-75	-100	-95				
016	45%	-100	H2O	-85	-148			
003*	<10-96%	-89	-80	-60	-262	H2O	-334	-347
018*	<10-96%	-87	-100					
001*	<10-96%	-55	H2O	71	-8			

^ Spike in response to +36% error in second week

Disregard response at 75% RH

^^Spikes in response to +300-+400% error in second week

+ Off-scale positive signal prior to 1 week mark

* Large fluctuations between calibrations

SENSOR ACCURACY #008

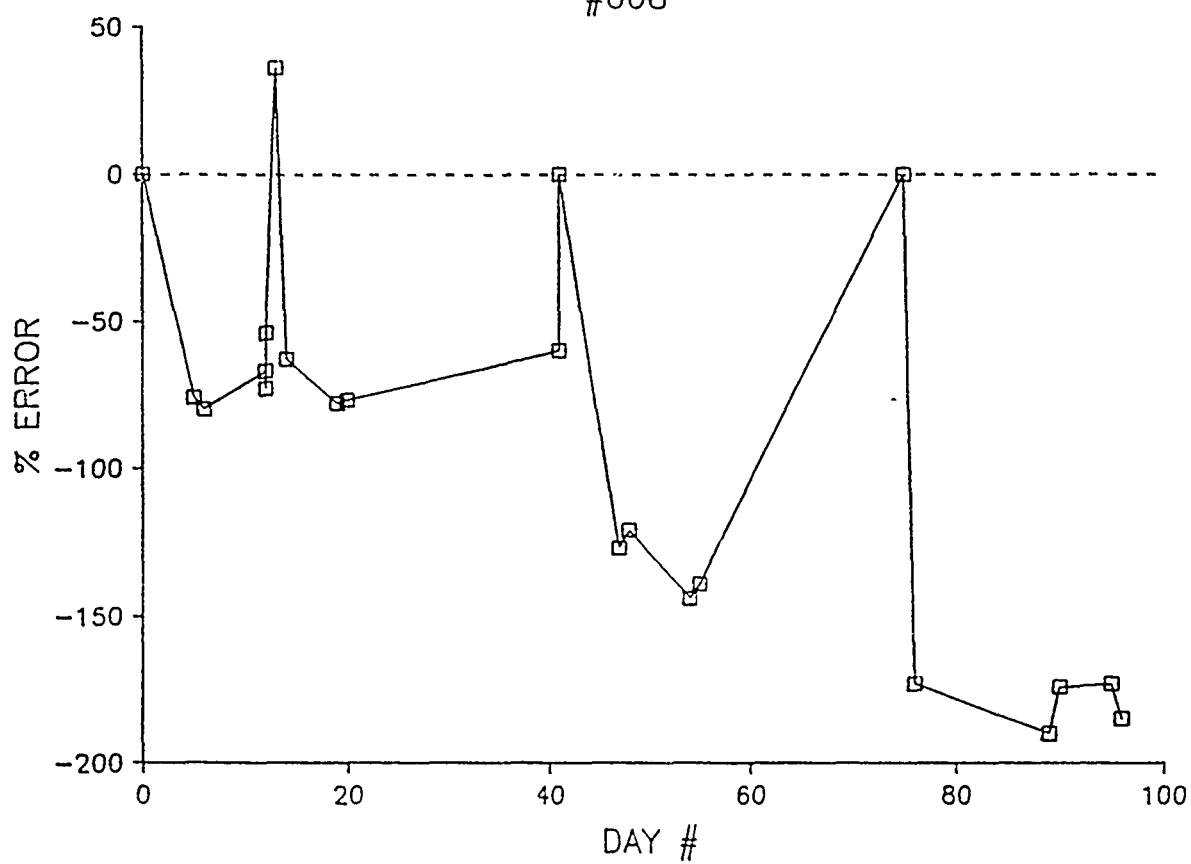


Figure 1.

CELL LINEARITY
#005

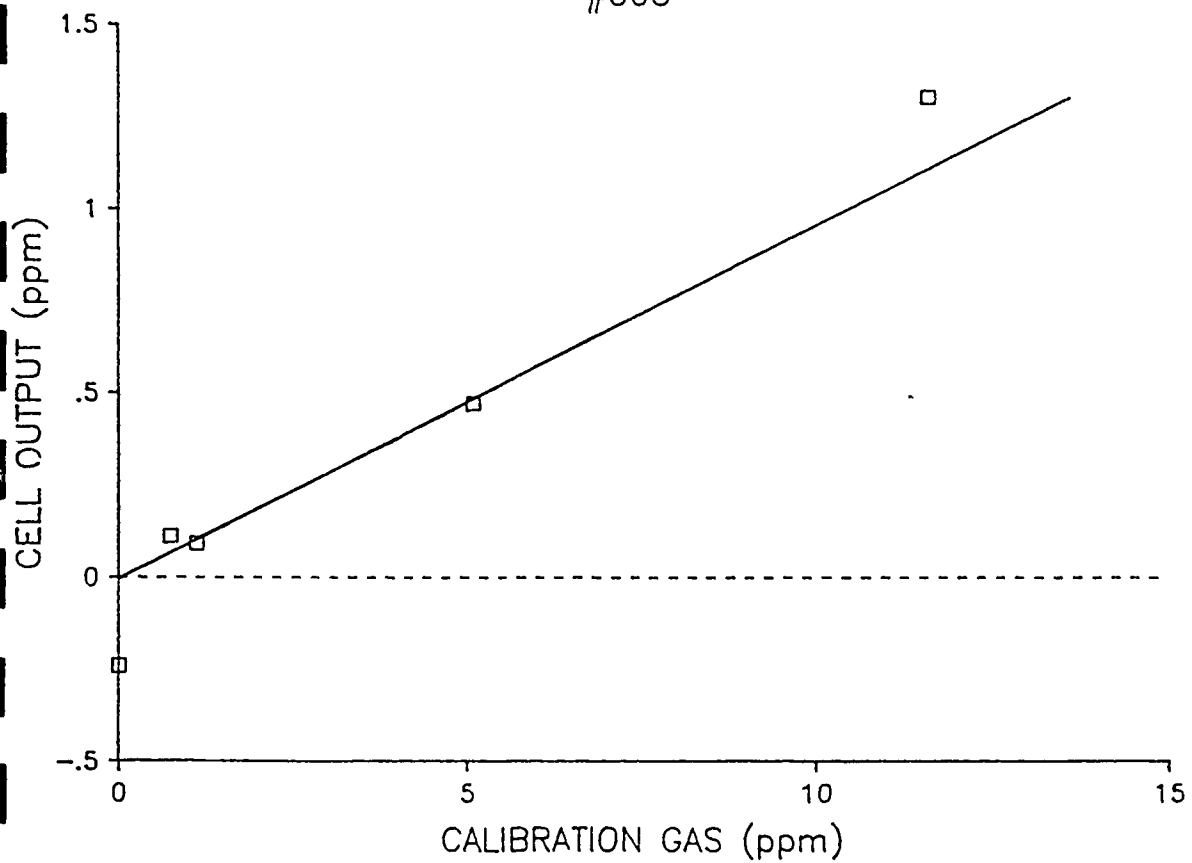


Figure 2.

CELL LINEARITY #008

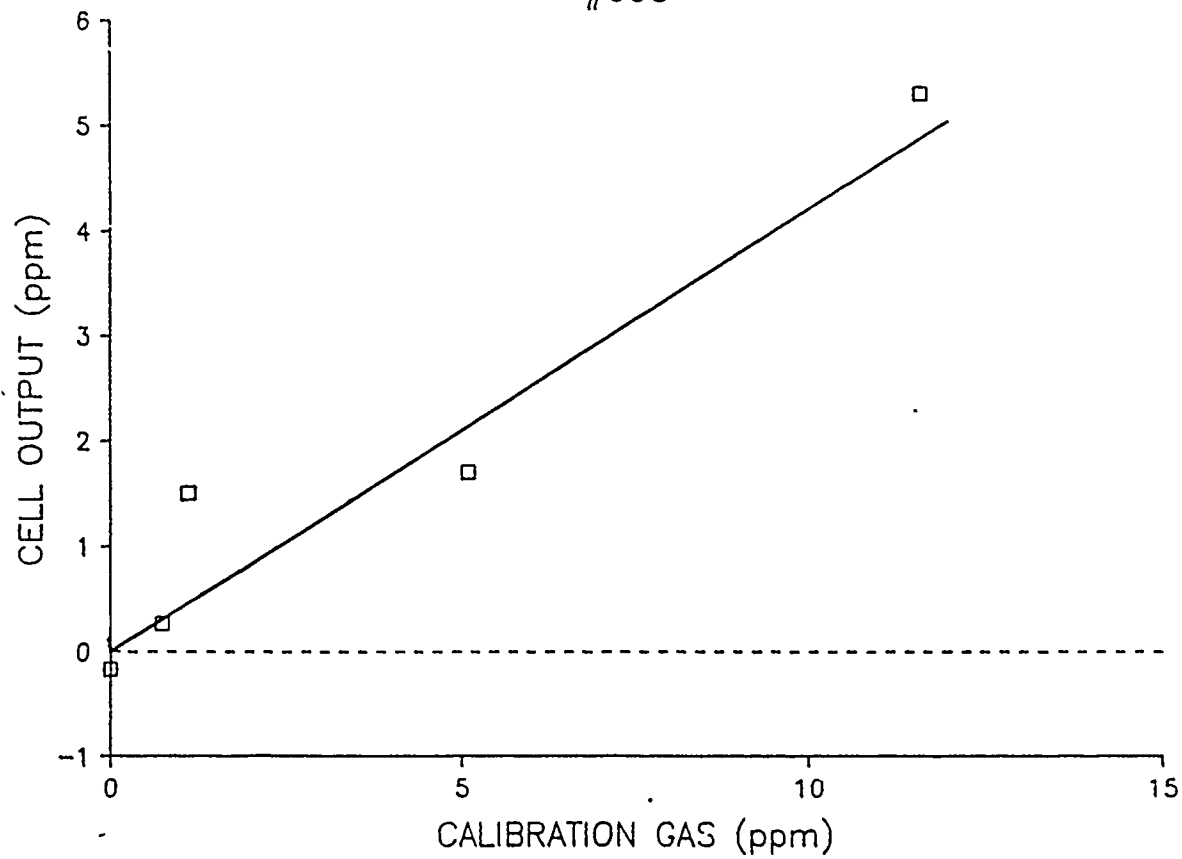


Figure 3.

SENSOR ACCURACY #006

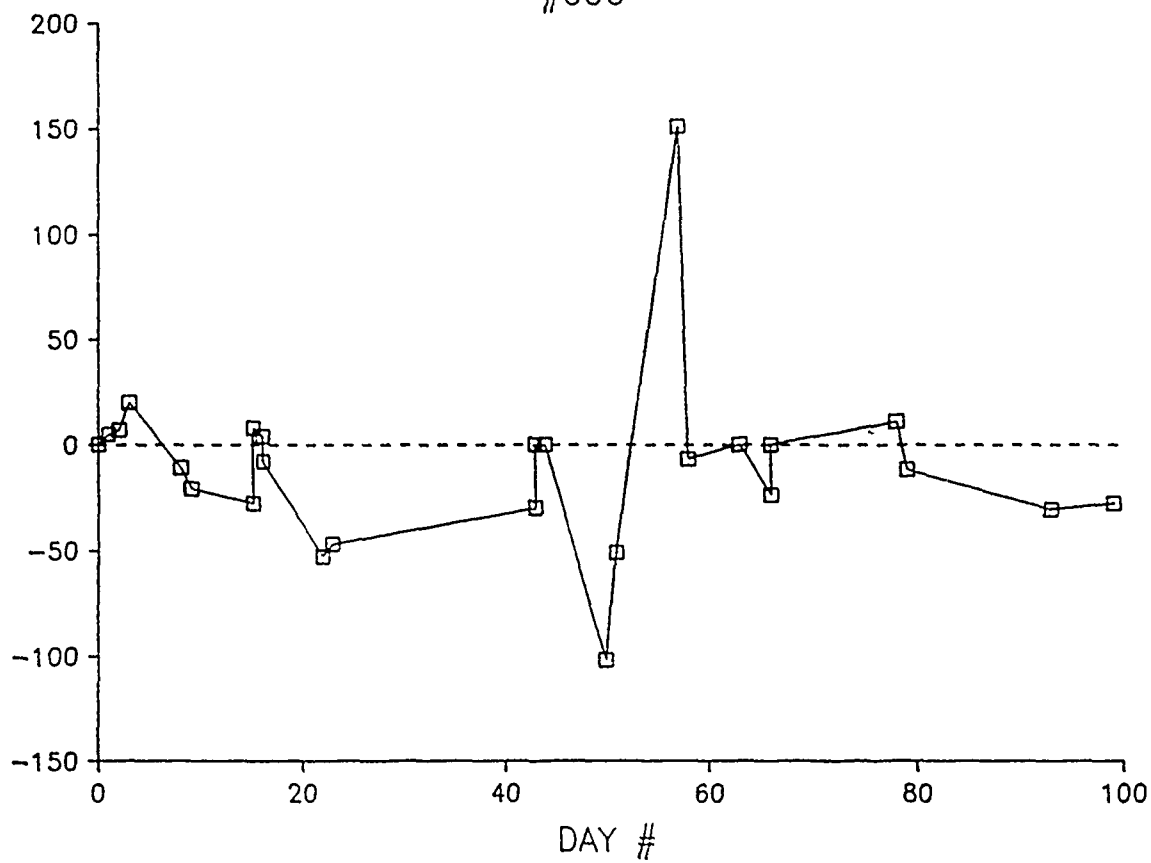


Figure 4.

CELL LINEARITY #013

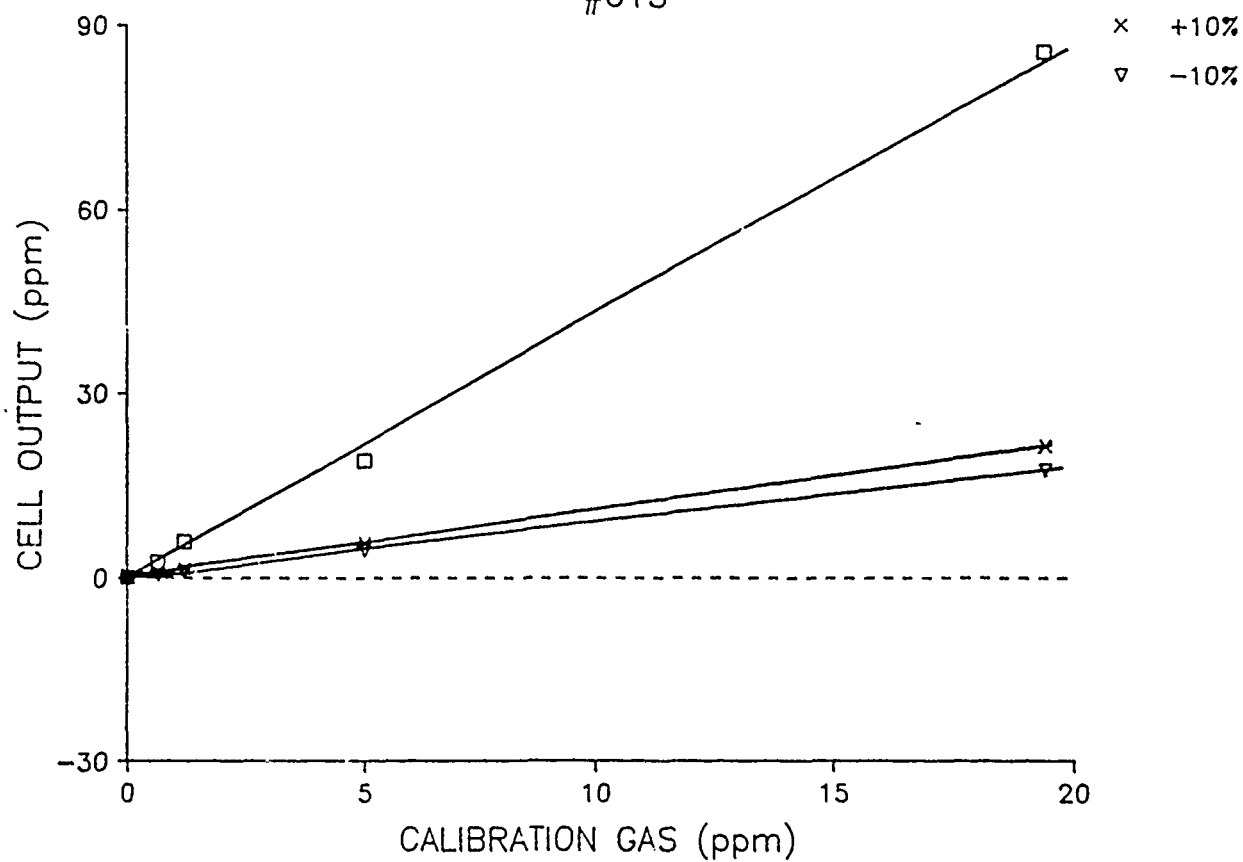


Figure 5.

CELL LINEARITY #006

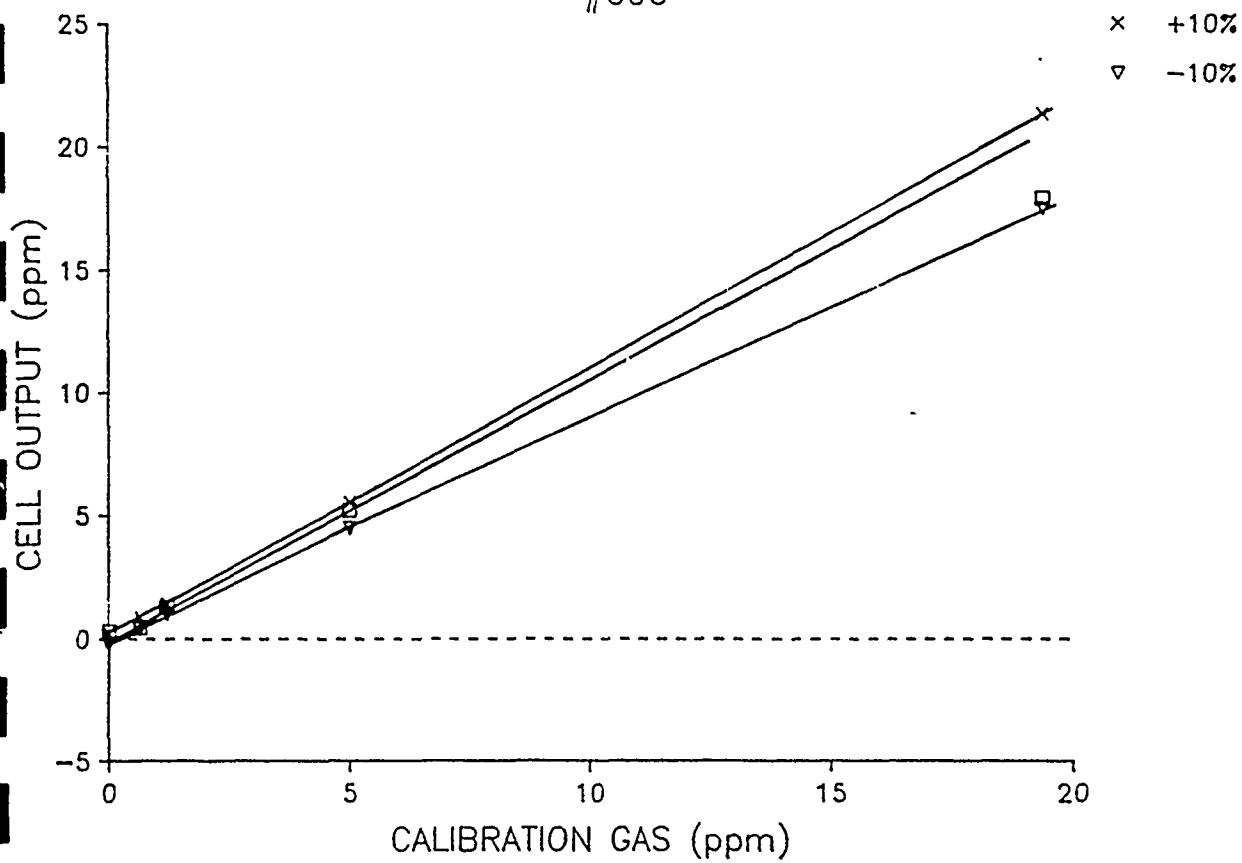


Figure 6.

SENSOR ACCURACY #007

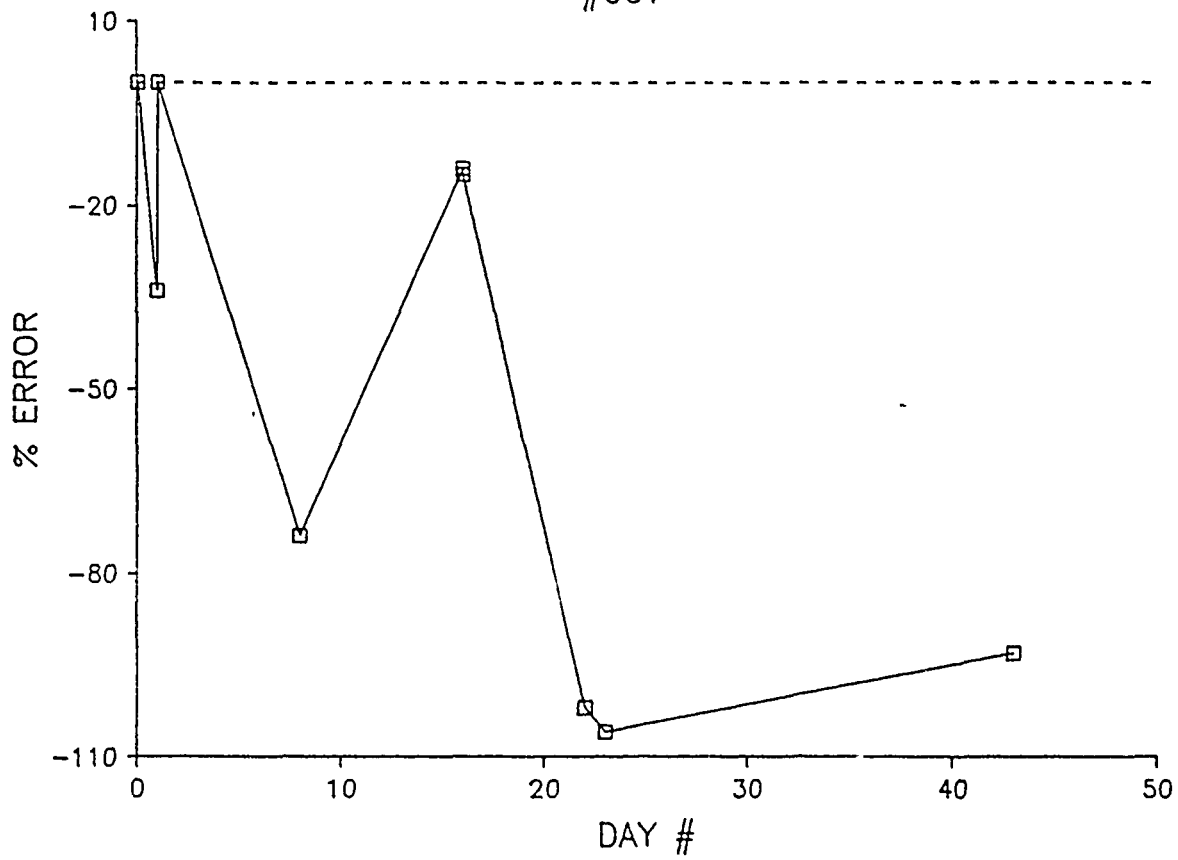


Figure 7.

SENSOR ACCURACY

#003

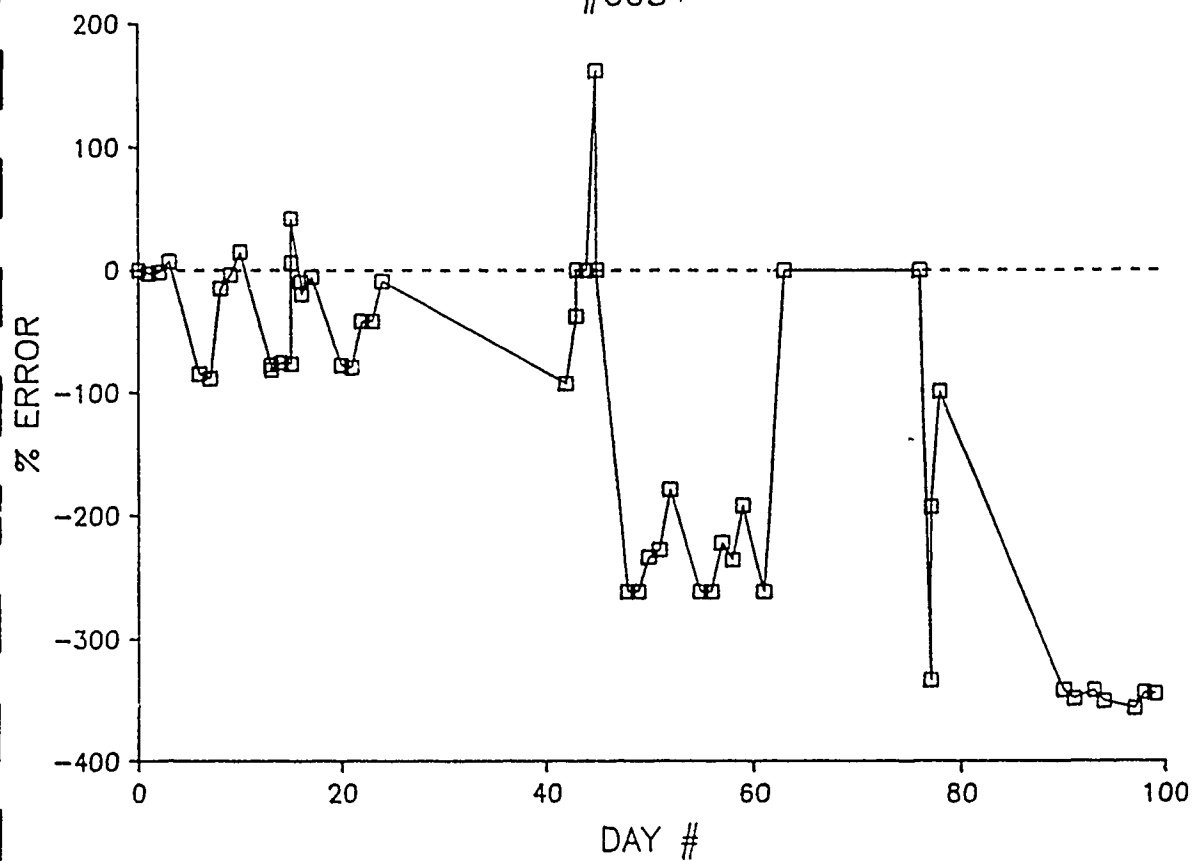


Figure 8.

CELL LINEARITY
#003 AT 8% RH

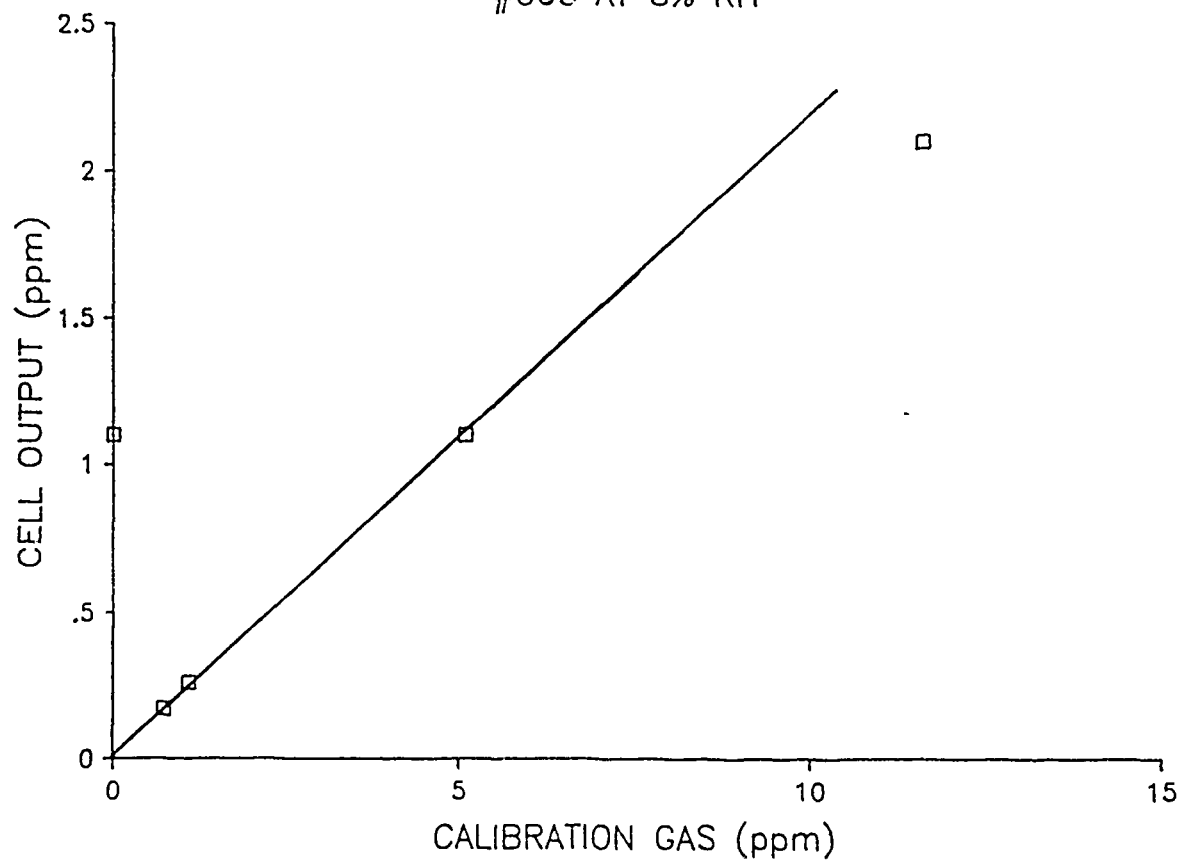


Figure 9.

CELL LINEARITY #003 AT 45% RH

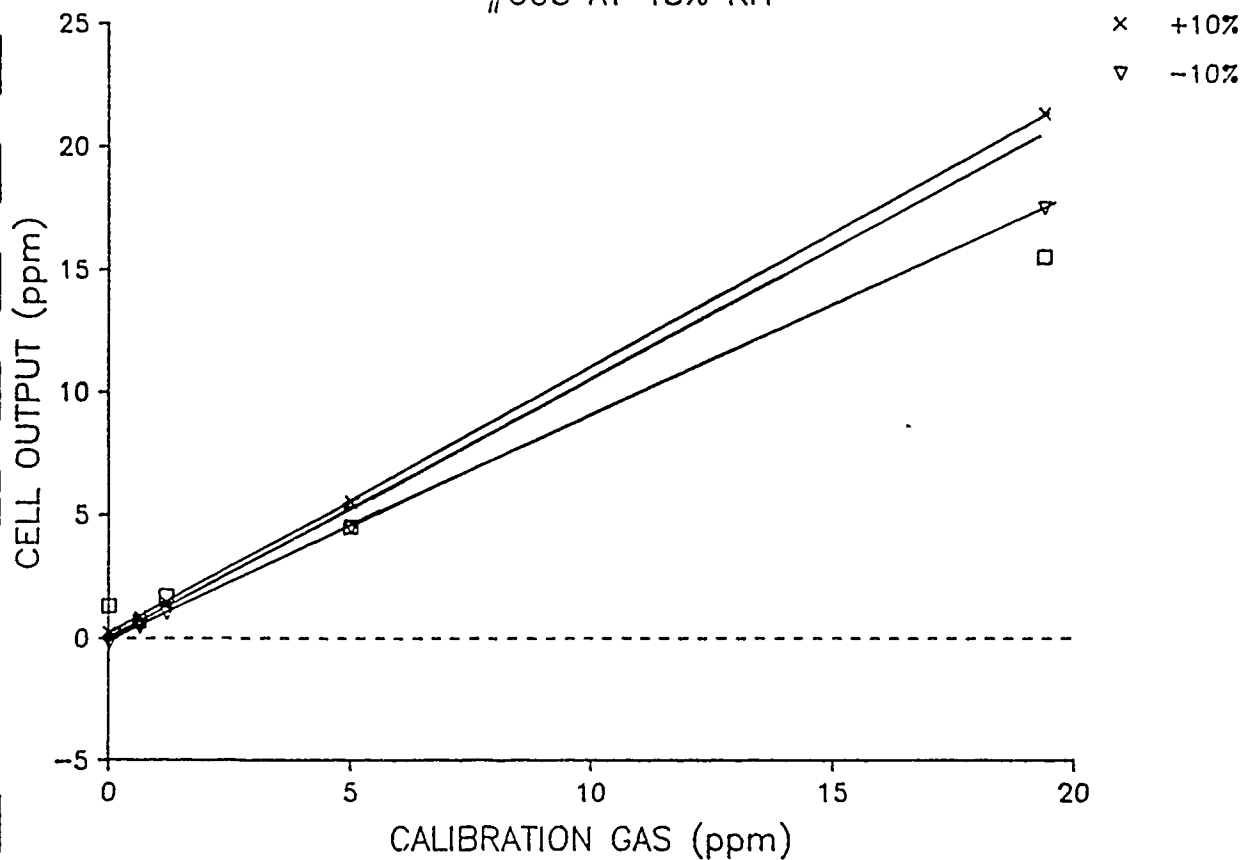


Figure 10.

REFERENCES

1. K.P. Crossman, S.L. Rose-Pehrsson, and J.R. Wyatt, Evaluation of Ecolyzer 7660 Hypergolic Fuel Vapor Detection Cells, Naval Research Laboratory, Washington, D.C., NRL Letter Report 6110-192a:KPC, (1987).
2. S.L. Rose and J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Report 8848, (1985).
3. E.C. Olson, Analytical Chemistry, 1960, 32, 1545.

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Materials were evaluated for potential use as ambient air sample lines for hydrazines. Fluorinated polymers performed the best, metals the worst. Various sample lengths were investigated; increasing the length enhanced the differences between samples, although the ranking of performance remained essentially unchanged. The effects of internal diameter (id) upon transport ability was evaluated by testing samples with ids of 3/16, 1/4, and 3/8 inch. The 3/8 inch id tubing consistently transported a larger percentage of the contaminant. Additional areas examined for their effects on performance were: temperature, humidity, joining of segments, pushing the pulling of the gas stream, and conditioning of the sample tube. The only variable found to have a significant effect on the results was conditioning; indicating that all new tubing should be thoroughly rinsed prior to use as well as periodically between sampling to remove ambient contaminants.					
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MATERIAL COMPATIBILITY WITH THRESHOLD LIMIT VALUE LEVELS OF MONOMETHYL HYDRAZINE

INTRODUCTION

The use of hydrazine (Hz), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH), especially as high energy propellants, has increased dramatically in recent years. The space shuttle program requires large amounts of both Hz and MMH. In addition, substantial quantities of hydrazines are used as propellants in Titan ballistic-missiles, satellites, and aircraft auxiliary-power units. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Studies indicate that exposure to hydrazines may cause damage to the liver, kidneys, and other internal organs and may produce blood abnormalities. Hydrazines not only cause physical damage but also alter the behavior of personnel by significantly decreasing performance capabilities.¹ A recent study cites irreversible damage to the nervous system as a possible consequence of hydrazines exposure.² Effects in man can be teratogenic as well as mutagenic. The adverse effects extend to nonmammalian life forms, thereby potentially endangering the environment.

Since the hydrazines are suspected carcinogens, a maximum tolerated toxic level has been set at five parts-per-million (ppm). The American Conference of Governmental Industrial Hygienist (ACGIH) has recommended the threshold limit values (TLV) of Hz, MMH, and UDMH to be 100, 200, and 500 parts-per-billion (ppb), respectively.¹ To protect personnel from overexposure, NASA, the Air Force, and the Department of Defense, require air monitoring for hydrazines in areas where they are handled and/or stored.

For several reasons, it is desirable to monitor a number of these potential exposure sites with one fixed-point analyzer which samples through a network of tubing in which sections may be 200 feet or more in length. With many ambient air contaminants this

method of sampling would pose no addition problems, but due to the reactive nature of hydrazines and their known interaction and decomposition on surfaces, the transport tubing could significantly effect the concentration of MMH to reach the analyzer.

This report describes the results of a materials compatibility study comparing the ability of several commercially available tubings to transport TLV levels of MMH under various conditions. The object of this study was to determine which tubing type(s) optimumly transport hydrazine contaminated air. Table 1 lists the types of tubings tested during the screening test. Variables studied for their effects on performance include: temperature, humidity, length of tubing, internal diameter of tubing, jointing segments verses one continuous piece, pushing and pulling of the gas stream, new tubing with no conditioning or washing, methanol washing of tubing, and the performance of tubing conditioned with ambient air. This study was approached as a survey rather than a statistical analysis due to the time allotted and the number of variables to be investigated.

EXPERIMENTAL

Figure 1 is a schematic of the test apparatus which was constructed of FEP teflon. The air supply was house-compressed air conditioned by passing through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular-sieve scrubber, and finally through a canister containing potassium permanganate coated alumina (PURAFIL) and charcoal. The clean air was rehumidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of relative humidity was achieved by varying both the gas washer head pressure and the ratio of rehumidified to dry air. A mass flow controller passed 4.9 liters per minute of zero grade, humidified air through a chamber where the humidity was measured by a hygrometer. Finally, the air flow was controlled by a solenoid valve system attached to the coil of

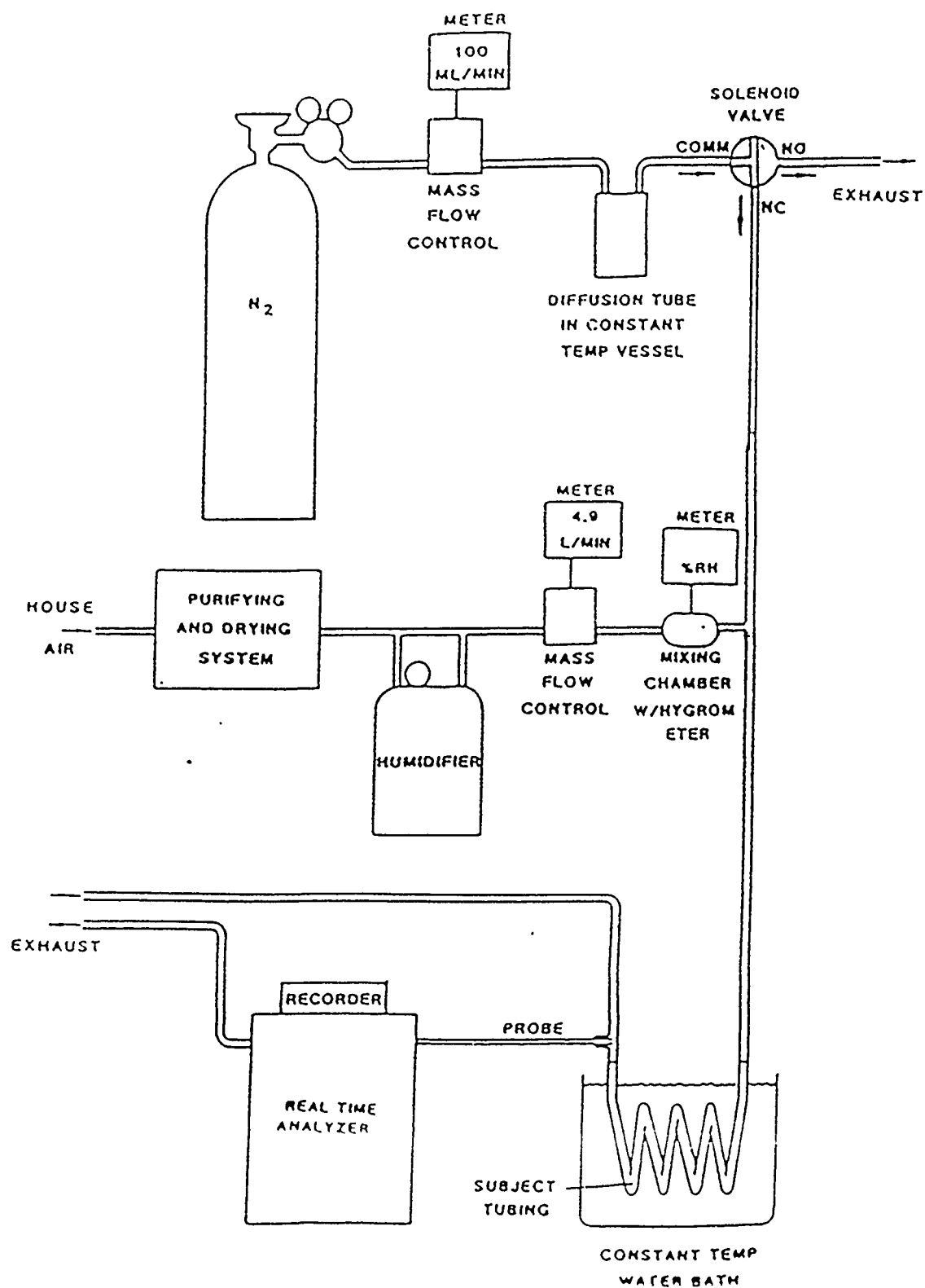


Figure 1. Apparatus for testing of material compatibility.

tubing to be tested. Control of the sample tubing temperature was achieved by placing the tubing into a water bath, where the water was circulated from an exterior constant temperature bath.

Monomethylhydrazine vapor was generated from a diffusion tube held at 32°C. The MMH was swept from the diffusion tube with 100 ml/min dry nitrogen to the above mentioned teflon solenoid valve system which normally vents the MMH. When activated, the solenoid valve controls mixing of MMH with the clean air at a point just ahead of the sample tubing inlet. This is the technique used to deliver the TLV level, 200ppb, of MMH. Impinger samples were collected at this location to verify the MMH concentration. They were analyzed by a coulometric titration with bromide and amperometric endpoint detection. The coulometric method is the NRL/White Sands modification of reference 3, in which we miniaturized the system to improve sensitivity. This concentration measurement was performed before and after each tubing challenge test.

Real-time monitoring of ppb levels of MMH was accomplished using one of two instruments. The majority of tests utilized the TECO analyzer, which is a chemiluminescence-based breadboard instrument developed by Thermo Electron Corporation (now Thermedics, Inc.). The response time of this instrument is a few seconds which is considered to be real-time for our purpose. The results used for comparison were normalized to the full scale deflection (FSD) of the instrument, which was established during the concentration verification procedure, before and after each test. During phase 7 numerous problems were encountered with the TECO instrument and it was replaced with an MDA Scientific Inc., Model 7100 instrument, for real-time monitoring. The MDA 7100 is a commercially available paper tape instrument which measures the color change that develops upon exposure to MMH. The intensity of the color is proportional to the concentration. The color is measured and the concentration is printed every 2 minutes. This technique has few interferences and worked well in these studies.

A typical tubing MMH challenge experiment consisted of three steps. First, the contaminated air stream was monitored with the TECO analyzer through a two inch FEP teflon tube and the FSD was established and recorded. Simultaneously the MMH concentration was verified by coulometric analysis. These values were later used to calculate the amount of MMH transported by a coil of sample tubing in comparison to the amount detected without the coil. Next, the solenoid valve controlling the MMH contaminant was deactivated and the MMH was exhausted to the hood. When the concentration of MMH dropped below detectable limits (about 10 ppb) the subject tubing was connected to the test system and placed in the controlled-temperature water bath. The tubing was allowed to equilibrate by flowing humidified clean air through it for approximately 20 minutes while the TECO analyzer sampled gas from the outlet end of the subject tubing to establish a baseline. Finally, the solenoid valve was activated, providing TLV challenge level of MMH at the subject tube inlet. The outlet of the tubing was monitored.

An example of the data is shown in Figure 2. This data was used to determine the times required to reach 50, 75, 90, and 100 percent of the challenge MMH concentration. The first indication and the time to 50 percent were comparable. When 100 percent transport was not achieved, the maximum percentage of MMH reached and the time required to reach that value was recorded.

At the end of a test, the tubing was rinsed with methanol and dried with compressed breathing air. Cleaning the tubing material between tests had virtually no effect on the results of subsequent tests. Initial washing of new tubing was found to improve the transport performance of some tubings. We postulate that the methanol removes plasticizers or other formulation ingredients of the tubing which may impede transport. Solvents which are ketones, such as acetone, were not used as they react

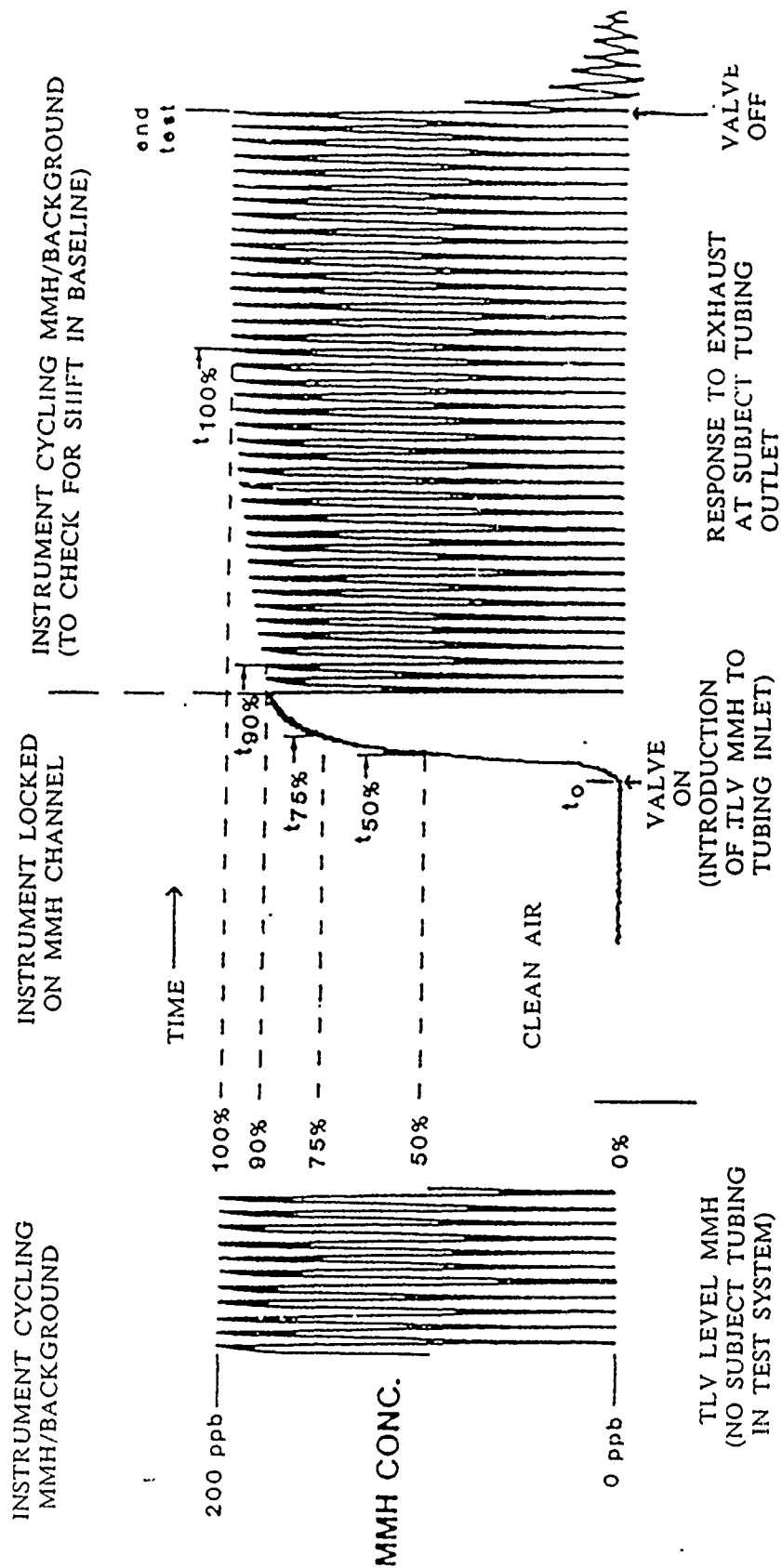


Figure 2. An example of the instrument response to MMH through a coil of tubing.

with hydrazines. Variations and additions to the experimental set-up and design are discussed where applicable in the next section.

EXPERIMENTAL SET-UP AND RESULTS

Phase 1 - Preliminary Screening

A preliminary screening procedure was used in an effort to eliminate the candidates with poor performance. Eight foot lengths of the tubings listed in Table 1 were tested at 21 degrees Celsius and 45 percent relative humidity for a period of 20 minutes. The results are presented in Table 2, and graphically compared in Figure 3. While all metal tubing performed poorly, nearly all other polymeric tubing performed equally in the screening tests. Figure 4 compares all of the metal tubes tested and Figure 5 compares several of the plastic tubes tested. The metals reduced the final equilibrium transport concentration of MMH to 50% or less of the challenge concentration. Tygon and teflon PFA were unable to transport 100% of the MMH. Based upon the results of this preliminary screen, the metals were eliminated from further testing. Materials which did not possess the desired flexibility, such as acrylic and tenite, were also dropped from the evaluation.

Phase 2 - Temperature and Humidity Effects

The selection of candidate tubings for additional testing at lengths of up to 75 feet was based on (1) known or assumed compatibility with hydrazines, (2) cost, (3) flexibility, and (4) resistance to heat. For the second phase of testing, temperatures of 8, 21, and 40 degrees Celsius and relative humidities of 20, 45, and 65 were selected to mimic, as closely as possible, the extremes of expected field conditions. All combinations of temperature and humidity were achieved except 40 C and 65% relative humidity, which was beyond the capability of the humidifying system. Tubing in 75 foot lengths was tested for 40 minutes, lesser lengths for 30 minutes. In some cases, tubings of the same

Table 1. Tubings Evaluated in the Screening Test

Tubing Material	Reference	Supplier	Manufacturer (when available)
Acrylic	ACRY	Read	Thermoplastic Processes, Inc.
Aluminum	ALUM	NRL	
Bev-A-Line IV	BEV	Read	Thermoplastic Scientifics
Brass	BRASS	NRL	
Copper	COPPER	NRL	
Nylon	NYLON	Read	Polymer Corporation
Polycarbonate	PCAR	Read	Thermoplastic Processes, Inc.
Polyethylene	POLYETH	NRL	
Polyethylene, High Density	HDPE	NRL	
	"	Read	Hudson Extrusions, Inc.
Polyethylene, Low Density	LDPE	Read	"
Polypropylene	POLYP	Read	"
Rubber	RUBBER	NRL	
Steel	STEEL	NRL	
Teflon FEP	FEP	Read	Atlantic Tubing Company
	"	Norton	Norton
	"	Cole	Zeus
Teflon PFA	PFA	Norton	Norton
Teflon TFE	TFE	Read	Atlantic Tubing Company
	"	Norton	Norton
Tenite	TENITE	Read	Thermoplastic Processes, Inc.
Tygon	TYGON	NRL	

Cole: Cole-Parmer Scientific
 NRL: Naval Research Laboratory Supply Store
 Norton: Norton Company
 Read: Read Plastics

Table 2. Results from Preliminary Screen.

TUBING	LENGTH (FEET)	SOURCE	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENTS
FEP	8	COLE	.75	1.5	2.5	6	100	6	
FEP	8	NORTON	1.25	2.5	9		97	11	
FEP	8	READ	1.5	2	3.5	9	100	9	
PFA	8	NORTON	2.5	3	5		94	9	
TFE	8	NORTON	.75	1	2	6	100	6	
BEV	8	READ	.75	1	2	4	100	4	
TYGON	8	NRL	1	1.5	5		92	6.5	bath cut off during test
FEP	8	COLE	1	2	6		95	12	
FEP	8	COLE	.75	1	2.5	10	100	10	
PFA	8	NORTON	1.25	2	10		94	9	
TFE	8	NORTON	1	1.5	2.5	14	100	14	
TFE	8	READ	1	2	4	11	100	11	
TYGON	8	NRL	1	2	4		95	10	
TYGON	8	NRL	.75	3	4.5		92	8	
POLYETH	8	NRL	1	1.25	2	13	100	13	1/4" internal diameter
POLYETH	8	NRL	1.5	2	4		95	6	1/8" internal diameter
HDPE	8	READ	1.25	2	5	12	100	12	
LDPE	8	READ	1	1.5	3.75	12	100	12	
POLYP	8	READ	1	1.5	2.75	13	100	13	
PCAR	8	READ	2	2.5	4	13	100	13	
POLYETH	8	NRL	1	1.5	2	16	100	16	1/4" internal diameter
POLYETH	8	NRL	1	1.75	3.75		95	13	1/4" internal diameter
POLYETH	8	NRL	1	1.5	4		95	6	1/8" internal diameter
COPPER	8	NRL					7.5	6	
COPPER	8	NRL					7.5	6	
COPPER	8	NRL					5.3	5	
STEEL	8	NRL	17				50	17	
STEEL	8	NRL					45	26	
STEEL	8	NRL					42	18	
STEEL	8	NRL					47	20	
ALUM	8	NRL					15.8	5	
ALUM	4	NRL	13				53	13	
BRASS	8	NRL					6.3	6	
RUBBER	7	NRL	1.25	3.5	9		90	9	
NYLON	8	READ	1.25	2	3.5	8	100	8	
ACRY	6	READ	1.5	2.25	5	12	100	12	
TENITE	6	READ	9	20			75	20	small crack in tubing
BEV	8	READ	.75	1.5	3	8	100	8	
POLYP	8	READ	1	1.75	4.25				

Conditions: 20 C, 45% RH, pushing 200 ppb MMH air stream at 5 l/min. All tubing tested for 20 minutes.
Internal diameter of tubing was 3/16" unless otherwise noted.

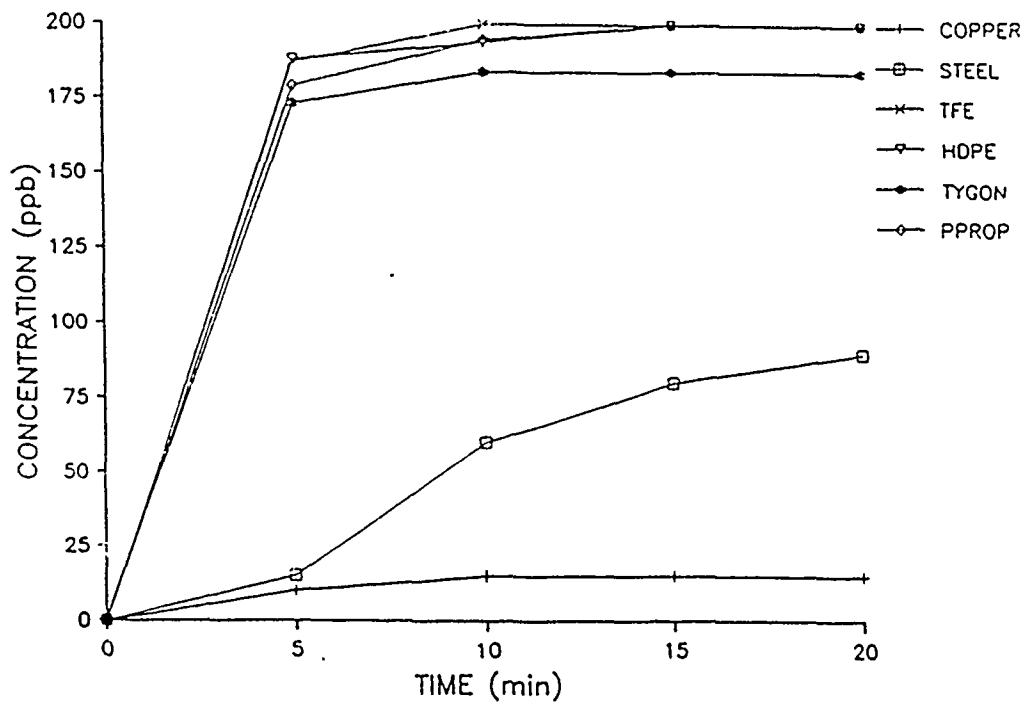


Figure 3. The amount of 200 ppb monomethylhydrazine transport^a down 8 feet of several different tubes under moderate conditions (21°C and 45% RH).

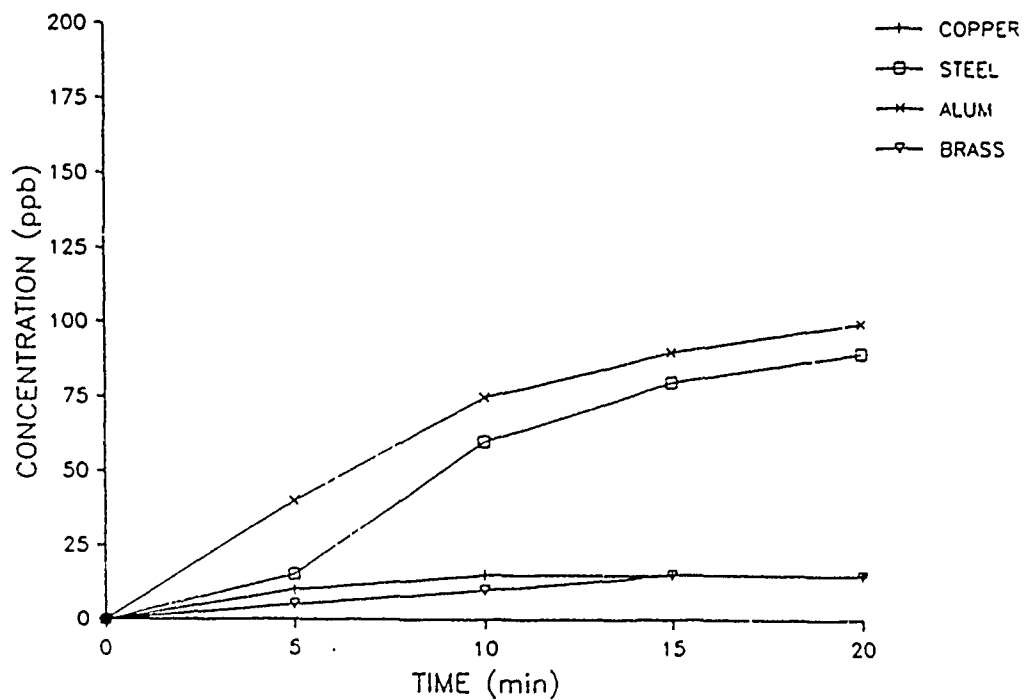


Figure 4. The ability of 8 feet of metal tubing to transport 200 ppb of monomethylhydrazine under moderate conditions (21°C and 45% RH).

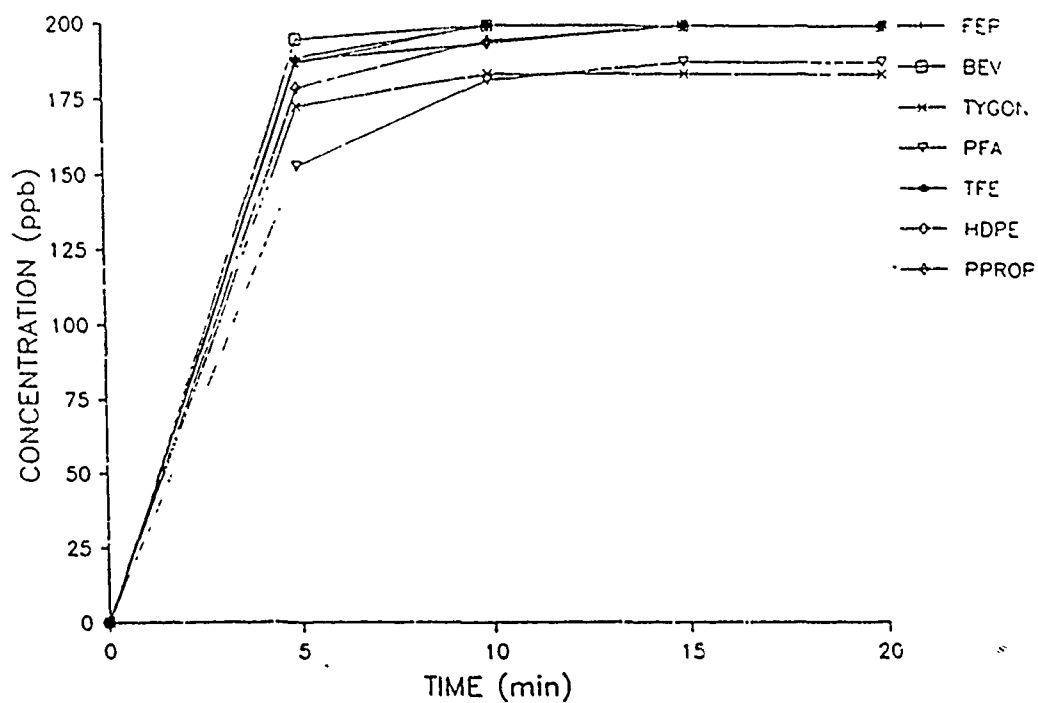


Figure 5. The amount of 200 ppb monomethylhydrazine transported by 8 feet of several different plastic tubes under moderate conditions (21°C 45% RH).

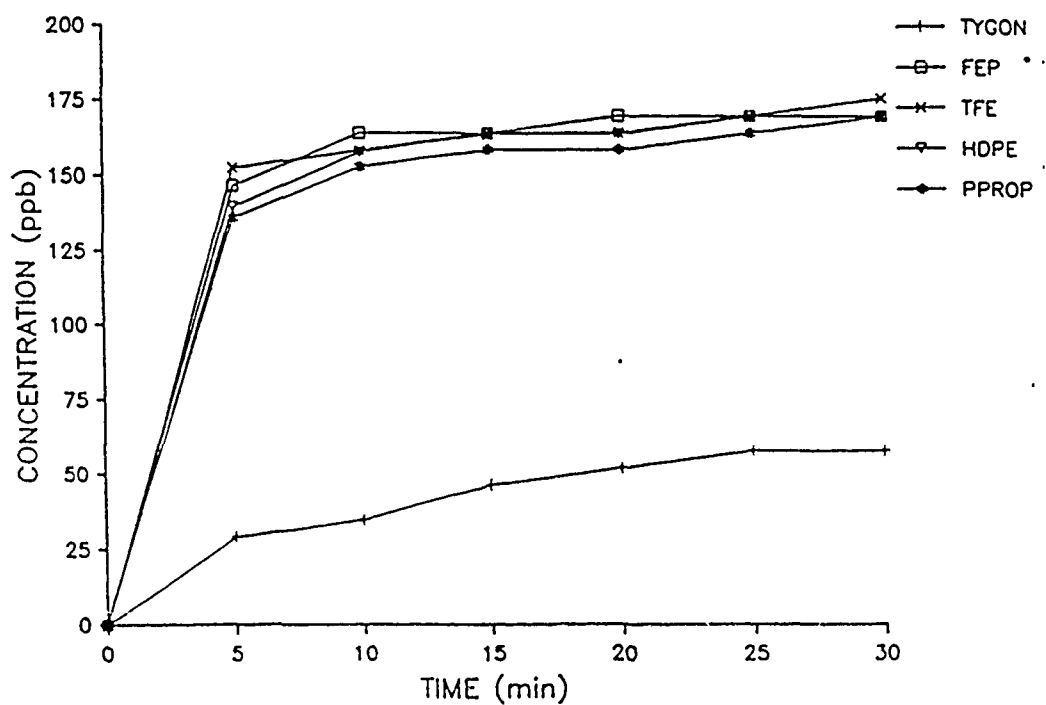


Figure 6. The amount of 200 ppb monomethylhydrazine transported by 75 feet of several tubes under moderate conditions (21°C and 45% RH).

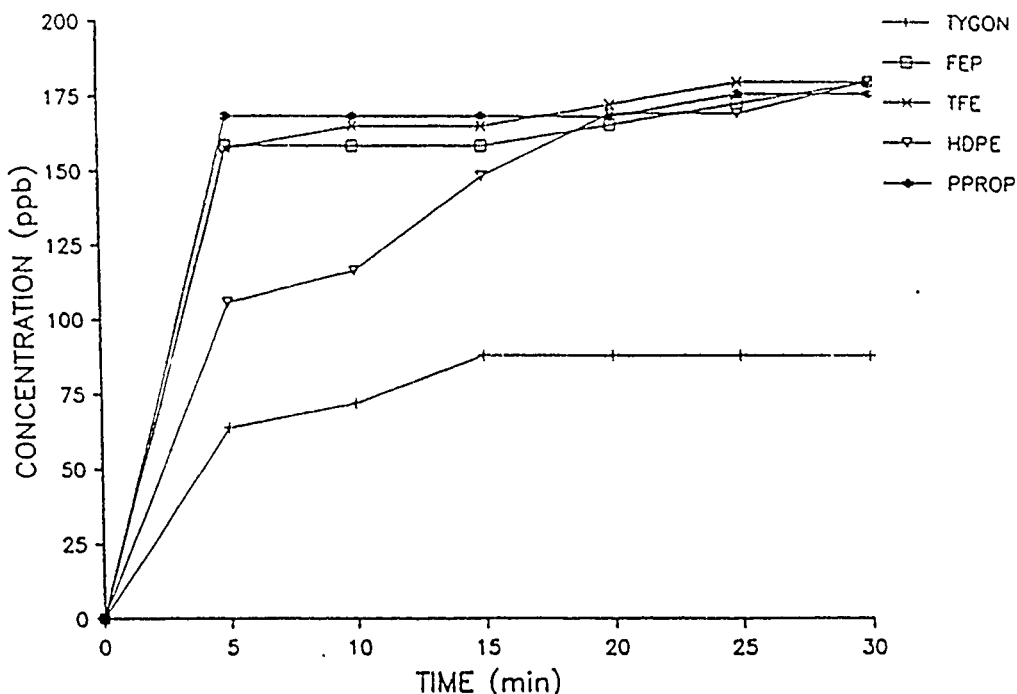


Figure 7. An example of some of the results for transporting 200 ppb monomethylhydrazine at low temperature and high humidity (8°C and 65% RH) through 75 feet of tubing.

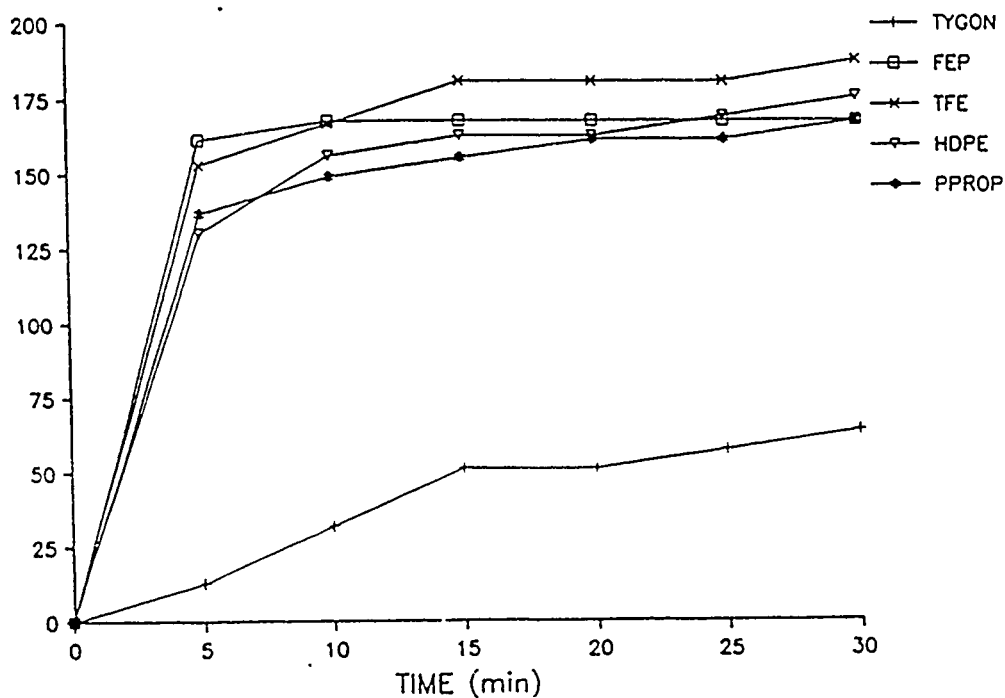


Figure 8. An example of some of the results for transporting 200 ppb monomethylhydrazine at high temperature and low humidity (40°C and 20% RH) through 75 feet of tubing.

type, but from different manufacturers or suppliers, were tested and compared. This was done as a result of data obtained from other test programs at Thermoelectron Corporation and Aerospace Corporation indicating possible wide performance variations based solely upon the source of the tubing. Figures 6, 7 and 8 compare 75 foot lengths of tygon, teflon FEP and TFE, high density polyethylene (HDPE), and polypropylene tubing for three of the conditions tested. Consistently Tygon gave the poorest performance while the other materials were comparable. None of the materials achieved 100% transport of the MMH over 75 feet in a 40 minute challenge. Varying the temperature and relative humidity had little effect on ability of the tubing samples to transport MMH. The relative time required and the magnitude of MMH transported was consistent for all tests. The data are presented in Table 3.

Phase 3 - Effects of Internal Diameter of the Tubing

For selected materials the effect of tubing internal diameter (id) upon transport efficiency of MMH was investigated. Id's of 3/16", 1/4", and 3/8" were evaluated when available. The materials tested and data collected are presented in Table 4. Like materials were purchased from the same supplier in an effort to control potential variables. Maintaining a constant wall thickness between tubing samples was not possible. The assumption was made that this factor would not interfere with the tubing's ability to transport the challenge gas, it did however influence the ease of handling. Note the dead volume of 100 feet of 3/16", 1/4", and 3/8" id tubing is 0.53, 0.95, and 2.14 liters respectively. These dead volumes would account for hold ups in transport times of 6, 11, and 26 seconds respectively. Since the results obtained in phase 2 revealed little or no effect from variations in the temperature and relative humidity (RH), one set of nominal conditions was chosen for this series of experiments, 21 C and 20% RH.

Table 3 (a). Tests Involving a 20% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENT
21 C AND 20% RH										
TYGON	75	NRL	40 MIN					44	29	1/8" ID
FEP	75	READ	"	1.5	3	20		91	22	
FEP	75	COLE	"	1	2.5	10		94	24	
TFE	75	READ	"	2	4	16		97	24	
NYLON	75	READ	"	1	2.5	6		97	20	
POLYETH	75	NRL	"	1	2	10	14	100	14	1/4" ID
LDPE	75	READ	"	1.5	5			88	21	
HDPE	75	READ	"	1.75	4			88	17	
POLYP	75	READ	"	1.5	4.5			86	18	
FEP	17	NORTON	30 MIN	1	2.5	6		97	14	
TFE	16	NORTON	"	1	2	5	14	100	14	
PFA	16.5	NORTON	"	1.25	2.25	7		97	15	
BEV	47	READ	"	1	2	4		97	23	1/8" ID
8 C AND 20% RH										
TYGON	75	NRL	40 MIN					39	26	1/8" ID
FEPO	75	READ	"	1.25	3	8		94	14	
FEP	75	COLE	"	.75	1.25	7		94	10	
TFE	75	READ	"	1.5	3	18		90	18	
NYLON	75	READ	"	1	2	10		97	23	
POLYETH	75	NRL	"	1	2	9		94	27	1/4" ID
LDPE	75	READ	"	1.25	3.5			88	21	
HDPE	75	READ	"	1	2.75	19		90	19	
POLYP	75	READ	"	1.5	3	17		91	20	
FEP	17	NORTON	30 MIN	1	2	8		94	12	
TFE	16	NORTON	"	.75	1.5	3	17	100	17	
PFA	16.5	NORTON	"	1	2	9		94	16	
BEV	47	READ	"	.75	1.75	3.5		94	12	1/8" ID
40 C AND 20% RH										
TYGON	75	NRL	40 MIN					32	28	1/8" ID
FEP	75	READ	"	2	3.75			84	5	
FEP	75	COLE	"	1.5	2.5	11		90	11	
TFE	75	READ	"	2	3.5	16		94	24	
NYLON	75	READ	"	2	2.5	25		90	25	
POLYETH	75	NRL	"	2	4.5	21		90	21	1/4" ID
LDPE	75	READ	"	2	4			81	17	
HDPE	75	READ	"	2	5			88	15	
POLYP	75	READ	"	2.75	7			84	20	
FEP	17	NORTON	30 MIN	1.5	2.5	6		94	19	
TFE	16	NORTON	"	1.25	2.25	4		94	12	
PFA	16.5	NORTON	"	1.5	2.75	11		91	17	
BEV	47	READ	"	1.5	2.5	4.5		94	12	1/8" ID

Internal diameter of 3/16" was used unless otherwise noted.

Table 3 (b). Tests Involving a 45% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN % MAX.	TO	COMMENT
21 C AND 45% RH											
TYGON	75	NRL	40 MIN					29	20		1/8" ID
FEP	75	READ	"	2.5	4			85	9		
FEP	75	COLE	"	2	4.5			35	15		
TFE	75	READ	"	2	3.5			88	17		
NYLON	75	READ	"	2.25	4			79	10		
POLYETH	75	NRL	"	2	3.5			88	14		1/4" ID
LDPE	75	READ	"	2.5	6			85	14		
HDPE	75	READ	"	2	6			85	13		
POLYP	75	READ	"	1.25	2.5			85	12		
FEP	17	NORTON	30 MIN	1.5	2.5	7		97	18		
TFE	16	NORTON	"	1	1.25	2	14	100	14		
PFA	16.5	NORTON	"	4	5			88	18		
BEV	47	READ	"	1.25	2	3	11	100	11		1/8" ID
8 C AND 45% RH											
TYGON	75	NRL	40 MIN					39	26		1/8" ID
FEP	75	READ	"	1.5	2.5	18		94	16		
FEP	75	COLE	"	1.75	4.5			84	12		
TFE	75	READ	"	2.25	5	20		90	20		
NYLON	75	READ	"	2.75	9			84	15		
POLYETH	75	NRL	"	1.25	3	11		94	16		1/4" ID
LDPE	75	READ	"	1.5	2			88	14		
HDPE	75	READ	"	.75	1.5			84	9		
POLYP	75	READ	"	2	9			81	15		
FEP	17	NORTON	30 MIN	1	2	5	21	100	21		
TFE	16	NORTON	"	1	2	4	11	100	11		
PFA	16.5	NORTON	"	1.75	3	12		97	22		
BEV	47	READ	"	1	2.5	7		54	16		1/8" ID
40 C AND 45% RH											
TYGON	75	NRL	40 MIN					26	18		1/8" ID
FEP	75	READ	"	2.5	4	11		94	18		
FEP	75	COLE	"	2	3.5	10		97	24		
TFE	75	READ	"	2.5	5	17		90	17		
NYLON	75	READ	"	2	4	18		90	18		
POLYETH	75	NRL	"	1.25	2.25	15		94	24		1/4" ID
LDPE	75	READ	"	2	7			84	21		
HDPE	75	READ	"	2.5	7			84	18		
POLYP	75	READ	"	2.5	9			84	15		
FEP	17	NORTON	30 MIN	2	3	5	13	100	13		
TFE	16	NORTON	"	1.5	2.5	4.5	16	100	16		
PFA	16.5	NORTON	"	1.75	2.25	3		94	15		
BEV	47	READ	"	1.5	2.5	7		91	12		1/8" ID

Internal diameter of 3/16" used unless otherwise noted.

Table 3 (c). Tests Involving a 65% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENT
21 C AND 65% RH										
TYGON	75	READ	40 MIN					43	27	1/8" ID
FEP	75	READ	"	1.75	3	10		93	14	
FEP	75	COLE	"	2.5	4.5	17		93	25	
TFE	75	READ	"	2.75	4	17		93	22	
NYLON	75	READ	"	8				70	21	
POLYETH	75	NRL	"	2	3.5	13		90	13	1/4" ID
LDPE	75	READ	"	4.75	23			75	23	
HDPE	75	READ	"	1.75	5			83	10	
POLYP	75	READ	"	2	5			83	15	
FEP	17	NORTON	30 MIN	1.75	3	5	16	100	16	
TFE	16	NORTON	"	1.5	2.5	4	13	100	13	
PFA	16.5	NORTON	"	2	3	7	16	100	16	
BEV	47	READ	"	1.5	2.25	4	20	100	20	1/8" ID
8 C AND 65% RH										
TYGON	75	NRL	40 MIN					44	19	1/8" ID
FEP	75	READ	"	2	4	24		90	24	
FEP	75	COLE	"	1.5	2.5	6		90	6	
TFE	75	READ	"	1.5	2.75	17		90	17	
NYLON	75	READ	"	10				65	25	
POLYETH	75	NRL	"	1	1.75	7		96	22	1/4" ID
LDPE	75	READ	"	1.25	2.5	13		90	13	
HDPE	75	READ	"	1	2	17		90	17	
POLYP	75	READ	"	1.5	2			88	22	
FEP	75	NORTON	"	.75	1.25	1.75	9	100	9	
TFE	16	NORTON	30 MIN	1	1.5	2	12	100	12	
PFA	16.5	NORTON	"	1	1.5	2		96	9	
BEV	47	READ	"	1.25	1.75	2.5		96	15	1/8" ID

At 40 C the maximum relative humidity attainable with our set-up was 45%.

Internal diameter of 3/16" used unless otherwise noted.

Table 4. Phase 3: Effects of Internal Diameter on Transport

Tubing Material	Length (Feet)	Internal Diameter	50% (Min)	75% (Min)	90% (Min)	Max Percent	Min to Max %
BEV-A-LINE	75	3/16"	1	1.75	14	91.9	17
BEV-A-LINE	75	3/8"	1	2	3	100	32
FEP	75	1/4"	3	5.5	--	89	16
FEP	75	3/8"	1	3	12	93.5	18
HDPE	75	3/16"	1	2	--	84	18
HDPE	75	1/4"	1	2	7.5	90	7.5
HDPE	75	3/8"	1	2	6	96.8	50
PFA	75	3/16"	2.5	6	--	79	9
PFA	75	1/4"	3	7	36	90	36
PFA	75	3/8"	2.5	12	--	81.4	34
POLYPROP	75	3/16"	1	1.5	--	88	5
POLYPROP	75	1/4"	1	2	5	93.2	34.5
POLYPROP	75	3/8"	1	2	5.5	96.7	25
TFE	75	3/16"	1.25	2.5	12	90	12
TFE	75	1/4"	2.25	5	82	90	82
TFE	75	3/8"	3.5	8	21	95	48

Conditions: 21 C, 20% RH, pushing 200 ppb MMH air stream at 5 l/min

The data indicates interactions more complex than the expected direct relationship to surface area. The changes in the id did not measurably affect the time required to transport 50% of the MMH for Bev-a-line IV, HDPE, PFA, or polypropylene. For 75% of the MMH to be transported, the 3/8" id PFA took twice the transport time as the 3/16" id and the 1/4" id of the same material, the FEP gave the opposite results where the 3/8" id took approximately one half the time. The transport time of MMH through TFE increased with diameter. By the 90% transport point only, the HDPE (1/4" and 3/8" ids) and polypropylene (1/4" and 3/8" ids) showed no significant differences between the ids. The 3/8" id Bev-a-line IV reached 90% transport in nearly one fifth the time required for 3/16" id. The FEP tubing with 3/8" id reached 90% transport in twelve minutes, the 1/4" id never transported 90%.

Generally the 3/8" id tubings transported closer to 100% of the MMH. The basic ranking of material efficiency was not altered by varying the id. For the remaining experiments, 1/4 inch id tubing was selected because it was easier to work with and obtain. The 3/8 inch id tubings had two major problems; the thin walled samples had a tendency to crimp, and the thicker walls did not exhibit the desired flexibility.

Phase 4 - Effects of Teflon Jointing of Tubing Segments

To achieve the desired lengths of tubing for testing, it was sometimes necessary to connect multiple segments. This was done with molded teflon Swagelok fittings. To investigate the effects these fittings would have on results, a test was conducted in which a 75 foot continuous piece of high density polyethylene (HDPE) was tested, cut into segments, connected with fittings, and re-evaluated. The results showed no significant effects that can be attributed to the jointing. The tubing was rinsed with methanol between each test to eliminate the potential conditioning which may have occurred from the previous exposure. The data from this experiment is given in Table 5 and depicted in Figure 9.

Table 5. Effects from Teflon Jointing of HDPE Tubing Segment

Length (Feet)	ID (Inch)	Segment Length	50% (Min)	75% (Min)	90% (Min)	Max %	Min to Max
75	1/4	75'	1	2	7.5	90	7.5
75	1/4	75'	1	2	7	90	7
75	1/4	25'+50'	1	1.75	5	94	18
75	1/4	25'+25'+25'	1.25	2.5	21	90	21

Conditions: 21 C, 20% RH, pushing 200 ppb MMH air stream at 5 l/min

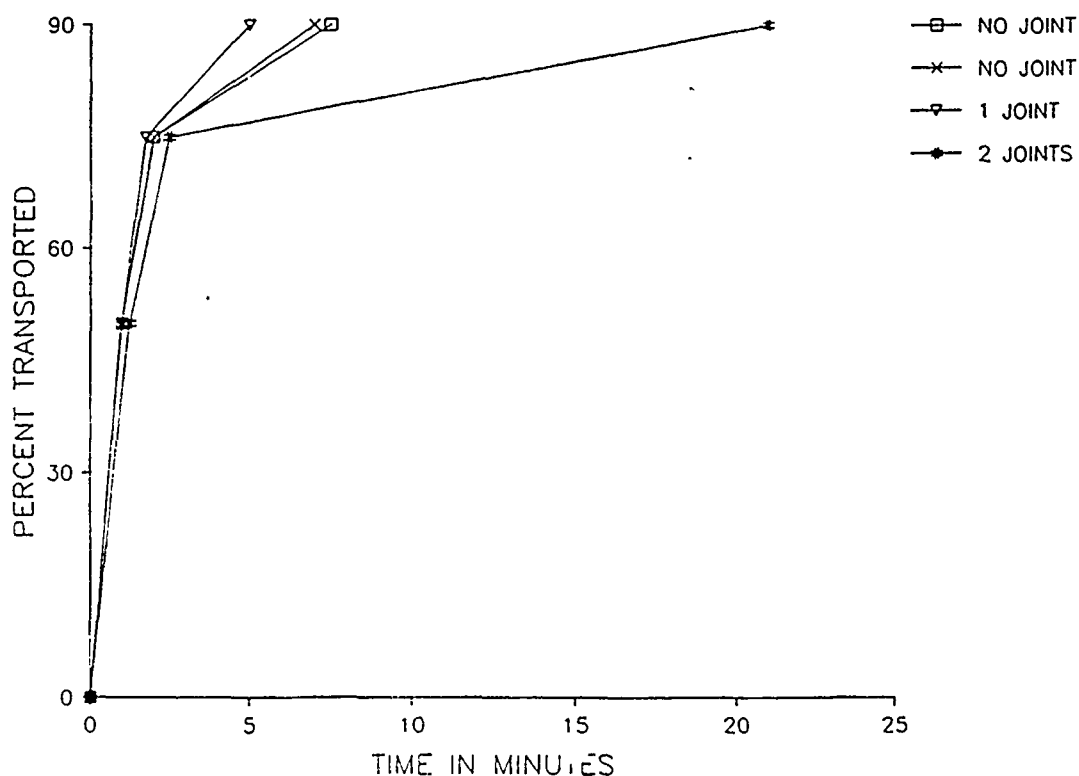


Figure 9. The ability of the same 75 feet of HDPE to transport 200 ppb MMH when used as one continuous piece or as jointed segments.

Phase 5 -Effects of Tubing Length on Transport Efficiency

A larger than expected increase in transport time was observed for lengths of 200 feet. The relationship of length to efficiency was investigated using a 200 foot sample of polyethylene. It was tested at full length and following a series of 20 foot reductions. The data collected is presented in Table 6 and Figures 10 and 11.

A higher percentage of MMH was transported through short tubing samples. Figure 11 graphically represents the time required to transport 75% of the MMH verses length of tubing. At the same time, lengths between 75 and 180 feet require comparable time to reach 50% transport. In addition, for the material tested, lengths under 120 feet were the only samples to achieve 90% or greater transport of the MMH assault gas.

Phase 6 - Introduction of MMH Stream, Pushing vs Pulling

Most air monitoring instruments pull the air through the tubing, therefore the effect of pulling the stream rather than pushing was examined. The set-up used for previous tests involved the pushing of the contaminated air stream through the tubing using the equipment as described earlier, (fig. 1). Slight modifications of the design were made for this phase of testing. During pulling experiments an additional tee was placed between the air source outlet and the tubing inlet. A personnel sampling pump, pulling two liters per minute, was attached to one port on a tee at the exit end of the sample tubing. An impinger containing 0.1 M sulfuric acid was placed in line just prior to the pump to remove the MMH. The third port of this tee was used to connect the TECO analyzer, which pulled an additional 1 liter per minute. These accounted for a total flow through the tubing of 3 liters per minute. The set-up is depicted in figure 12

In our experiment, we found no significant difference in the final measured concentration based on the method the gas is transported. The data collected is located in Table 7. The flow rates through the tubing were slower for pulling verses pushing

Table 6. Effects of Tubing Length upon Transport
Using 1/4" Polyethylene

Length (Feet)	50% (Min)	75% (Min)	90% (Min)	Maximum Percent	Minutes to Max
* 200	27	262	--	81	528
* 200	36	162	--	82	684
200	10	54	--	86	474
180	3	11	--	88	84
160	3.5	28.5	--	89	300
140	3	9	--	89	60
120	4	12	136	90	136
100	3	11	36	94	261
75	2.5	10	37	90	37
8	1	1.25	2	100	13

Conditions: 19 C, 45% Relative Humidity, Pushing 200 PPB MMH

* Tested prior to rinsing with methanol

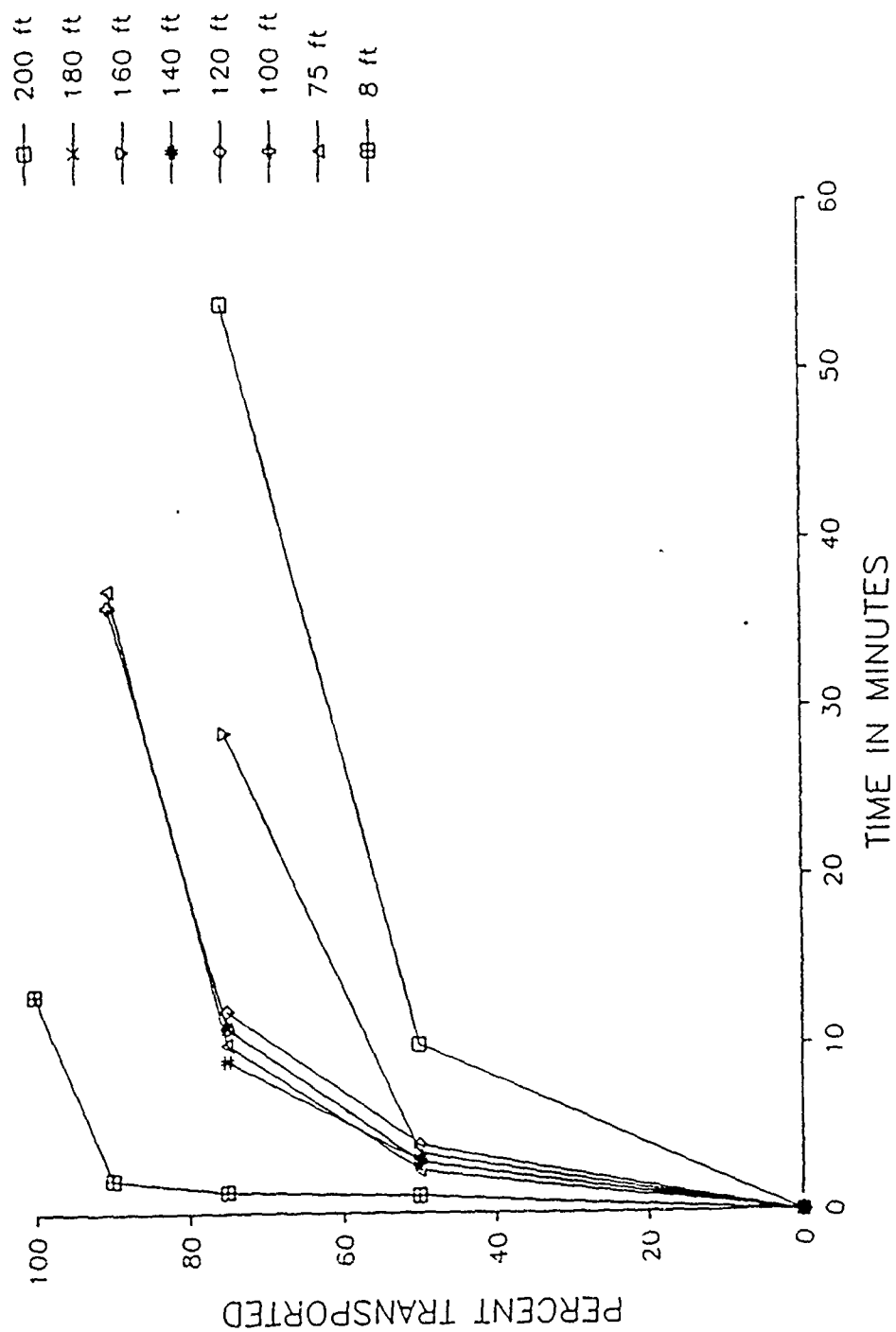


Figure 10. The effect of sample line length upon transport efficiency.

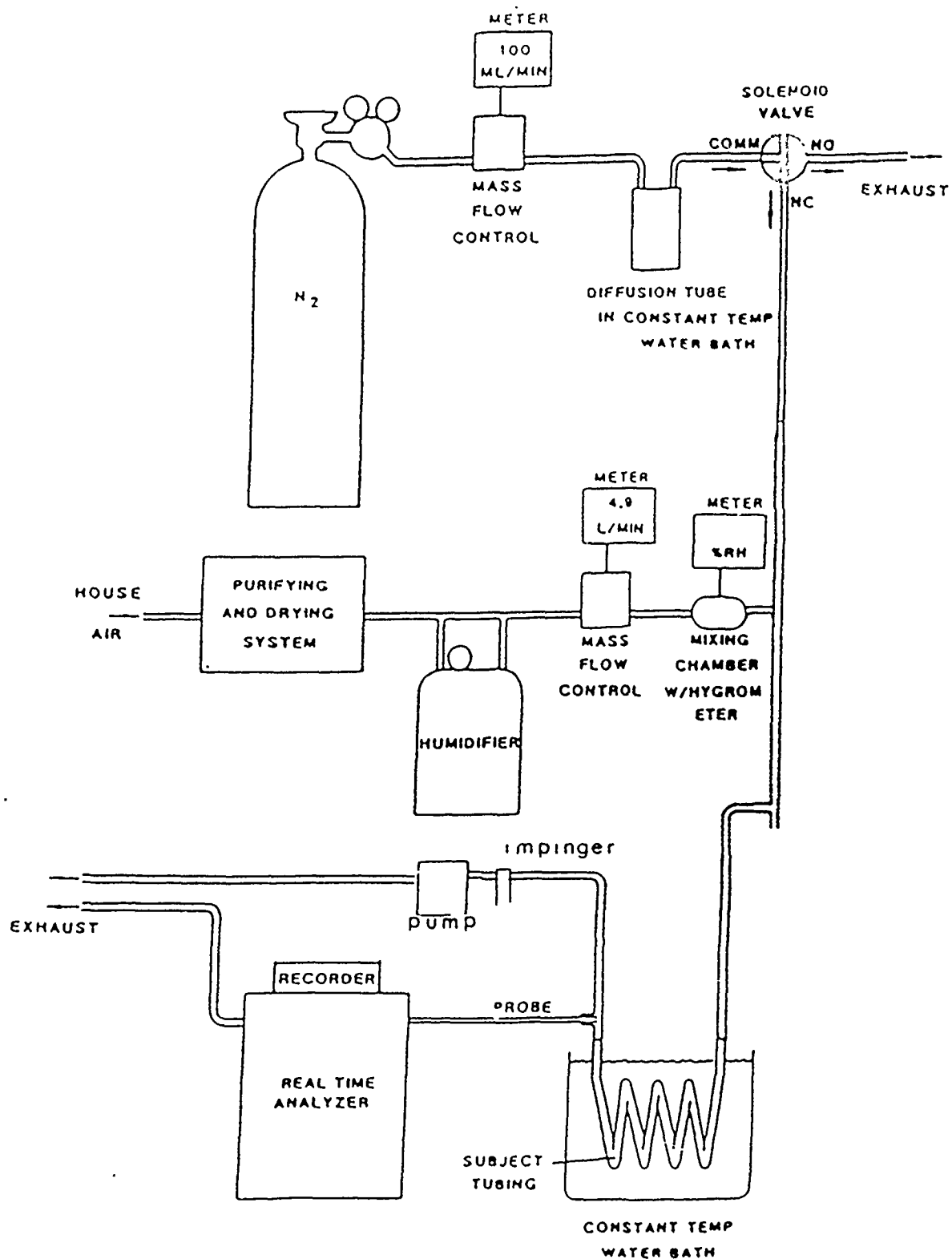


Figure 12. The modified apparatus for testing of material compatibility during experiments requiring "pulling" of the challenge gas.

Table 7. Effects of Pushing -vs- Pulling the 200 PPB MMH Air Stream Through 75 Feet of 1/4 Inch ID Tubing

Tubing Material	Flow Direction	Rate (L/Min)	50% (Min)	75% (Min)	90% (Min)	Max %	Min to Max
FEP	PUSH	5	1.25	3.25	12	97	35
FEP	PULL	3	2.5	7.5	--	88	33
HDPE	PUSH	5	2	4	13	94	29
HDPE	PULL	3	3	6	22	92	29
PFA	PUSH	5	4.5	10	30	94	66
PFA	PULL	3	6	12	--	87	31
POLYPROP	PUSH	5	1	2	9	97	36
POLYPROP	PULL	3	3	6.5	26	92	40
TFE	PUSH	5	2.5	6	22	96	45
TFE	PULL	3	4	18	77	90	77

Conditions: 20 C, 45% relative humidity.

which may explain the longer transport times observed. However the ranking of materials remained constant. Polypropylene and FEP yielded the best times and highest maximum percentages of MMH transported with HDPE a close third.

Phase 7 - Preconditioning of Tubing by Ambient Exposure

Two hundred foot samples of the most promising tubing materials were conditioned with ambient air. This procedure was accomplished by sampling 2.5 liters per minute of ambient air from the roof of the chemistry building at NRL. The sample coil and pump were sheltered, with the inlet of the tubing located in the open approximately 3 feet above the roof surface. Exposures were typically carried out for a period of one month. Following the conditioning, the tubings were evaluated for transport efficiency. The data collected is presented in Table 8. A direct comparison between tubings is not feasible since they did not all undergo the same conditioning. The polyethylene (polyeth) and the FEP were conditioned in the fall when high temperature and humidity prevailed. The Bev-a-line IV was not available until winter, therefore the ambient conditioning environments were different.

After extended conditioning with ambient air, samples showed a retardation in their ability to transport MMH. Polyethylene was affected to the greatest extent, so much so that the tubing essentially allowed no MMH through until it had been rinsed with methanol. The Bev-a-line IV was the only material to transport 100% after ambient exposure. Less than 50% was transported for the first 31 minutes, then a break-through seemed to occur, and 100% was reached in 34 minutes.

The results of the FEP pre- and post conditioning tests looked equivalent at the 50% and maximum percent transport times. The post exposure test took twice as long to reach 75% transport as the pre-exposure.

Table 8: The Effects Of Preconditioning Tubing With Ambient Air

Tubing Material	Length (feet)	Internal Diameter	50% (min)	75% (min)	90% (min)	MAX %	Min to Max %
polyeth	200	1/4"	--	--	--	--	--
polyeth	200	1/4"	215	--	--	64	948
*polyeth	200	1/4"	10	54	--	86	474
FEP	193	1/4"	11	44	--	81	120
*FEP	193	1/4"	8.5	23	--	85	132
Bev	200	1/4"	31	31	31	100	34
*Bev	200	1/4"	5	7	21	100	51

*Data collected prior to ambient conditioning.

^Sample was washed with methanol following th ambient conditioning.

Conditions: 21 C and 45% RH. Pushing 200ppb MMH gas stream at 5 l/min.

CONCLUSIONS AND DISCUSSION

From the results obtained in the preliminary screening, metal tubings are not recommended. Many of the teflons and polymers proved to be acceptable candidates, including: Bev-a-line IV, FEP, HDPE, PFA, polyethylene, polypropylene, and TFE.

The clean Bev-a-line IV had the best transport properties. It was the only material tested to transport 100% at the increased lengths. Many of the above mentioned candidates had transport times and percentages which would be adequate for some applications. In addition the Bev-a-line IV exhibited the desired flexibility. Many of the other tubings showed a tendency to crimp.

The decision of which material to use must be made on an individual use basis. For shorter lengths some of the less expensive polymers will provide satisfactory performance. Some basic considerations to be made when selecting a tubing material are: length and flexibility needed, desired flow rate, cost, and whether location will allow access (for purposes of washing with methanol if needed). We have shown that the temperature and relative humidity of the environment to be sampled have essentially no effect on the selection. The environment of the areas the tubing will transverse must be taken into account and a material selected that can withstand the conditions.

The fate of the MMH which is not transported to the outlet of the tubing line has not been determined. The exhaust was monitored by the TECO analyzer which would not differentiate between MMH and NH_3 , which is a known break-down product. An alternate instrument, the MDA 7100, which is not sensitive to NH_3 , NO, or NO_2 , was also used and gave a comparable MMH response. This suggests that break-down is not the reason for the loss.

In addition, the sampling line was checked for residual MMH by collecting and concentrating an acetone wash, and analyzing it by gas chromatography. No MMH was detected.

REFERENCES

1. J.A.E. Hannum, Recent Developments in the Toxicology of Propellant Hydrazines. Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. Committee on Toxicology, "Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants", Vol. 5, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council, National Academy Press, Washington, DC 1985.
3. Edward C. Olson, Analytical Chemistry, 1960, 32(12), 1545.
4. J.R. Holtzclaw, S.L. Rose, and J.R. Wyatt, Analytical Chemistry, 1984, 56(14), 2952.

A COMPARISON OF COMMERCIALY AVAILABLE PAPER TAPE HYDRAZINE DETECTORS

INTRODUCTION

Hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) are widely used as high energy propellants. Space shuttle operations require large quantities of hydrazine and MMH. Because of the toxicological properties of the hydrazines, monitoring them at trace levels is necessary for personnel protection.

In order to provide the best protection for personnel who may handle hydrazines, NASA supports test and evaluation of new and/or improved hydrazine instrumentation. Routine air monitoring wherever hydrazines are handled is part of the program to insure the safety of personnel. Kennedy Space Center (KSC) requires that hydrazine levels not exceed the limits specified by the American Conference of Governmental and Industrial Hygienists (ACGIH). The threshold limit values (TLV) recommended by ACGIH are 100, 200, and 500 parts per billion (ppb) for hydrazine, MMH, and UDMH respectively [1].

In 1983, KSC sponsored an extensive side-by-side comparison of commercially available hydrazine, MMH, and UDMH detectors to determine the performance characteristics of the instruments under identical test conditions [2]. At NASA's request, a similar comparison has been conducted on newly developed instrumentation. This report reflects the effort of the Naval Research Laboratory in support of NASA's requirement for reliable monitoring instrumentation.

TEST APPARATUS AND DATA COLLECTION PROCEDURES

The instruments were evaluated using hydrazine, MMH, and UDMH. Most tests were performed at 35-45% relative humidity (RH). The system used to generate known concentrations of the hydrazines has been described in detail [2]. This system uses sources of hydrazines and zero-grade air. Clean air, humidified to the desired level, flowed through one of two pyrex gas manifolds. Similarly humidified air mixed with the hydrazine flowed through the other manifold. Instruments were connected to the two manifolds by solenoid valves. To control the concentration of the test gas, the source was placed in a constant temperature water bath and the dilution air was controlled.

Mass flow controllers regulated the gas flows and the relative humidity (RH) was determined with a HygroDynamics hygrometer. The hydrazine concentration was verified by impinger collection in 0.1 M H_2SO_4 and analyzed by coulometric generation of bromine with amperometric endpoint detection [3]. The hydrazine concentrations were measured in parts-per-million (ppm) by volume.

Data was collected in the following manner. The recorder output from each instrument was digitized and sampled with a Hewlett Packard Model 85 computer. The data collection program collected a maximum of 240 points from each instrument during each of three stages of a standard test. The first twenty-five data points were used to calculate the average, minimum, maximum and the standard deviation of the zero value. Then the gas collection process began. The cells sampled zero gas and the computer collected approximately one minute of baseline data. The solenoid valves

were activated so that the instruments sampled contaminated gas. The computer continuously monitored the detectors' output for 20 minutes, then paused. The final stage was started and after one minute, the solenoid valves were deactivated to again sample zero gas.

The response curves for each detector were plotted and the average, minimum, maximum, zero, and span values as well as the corresponding standard deviation were displayed. The response and recovery times to 50, 75, and 90% of full scale were also determined. The response times were evaluated from the time the solenoid valves were activated through the next 10 minutes. The full scale values were calculated from the next 10 minutes of data. The recovery times were evaluated for the 10 minutes following the deactivation of the solenoid valves. The final zero values were determined from the last 10 minutes of data. A complete exposure test cycle required 40 minutes.

TEST AND EVALUATION PROTOCOL

Functional Test

Evaluation of functionality and operator/instrument interface.

Warm-Up Time

Elapsed time required for the instrument, after being off for 15 hours, to performance specified by manufacturer.

Zero Stability Test

Maximum absolute change in output response to zero input concentration over an 8 hour period of unadjusted operation is measured. We report mean, standard deviation, and maximum absolute deviations.

Span Stability Test

Eight-hour continuous exposure to TLV concentration and convenient higher concentrations are monitored. We report mean, standard deviation, and maximum absolute deviations.

Linearity

Using MMH, hydrazine, and UDMH, the instruments are tested using concentrations of the hydrazines from 0.0-2.0 ppm.

Response and Recovery Time

At several hydrazine concentrations, the following tests are run: rise time (to 50, 75, and 90% of final value); recovery time (to 50, 75, and 90% of final zero).

Precision

Comparisons are made of several identical measurements during an eight hour period. The instruments are tested at TLV and convenient higher concentrations.

Accuracy

Compare instrument response with an approved method [3] to assess error from zero to full scale, including the TLV. We report mean and standard deviation of absolute errors at representative points, including the TLV.

Sensitivity - Lower/Upper Limits of Detection

A sample of the analyte is successively diluted until a measurable response can no longer be discerned. Instrument response exceeding 2 ppm is also determined.

Relative Humidity Effects

Instrument responses are compared using several known concentrations of each hydrazine while varying the relative humidity.

Interference Test

Sensitivity to chemical interferents is determined in the following sequence of tests: expose to known concentration of hydrazine; expose to interference compound; then expose to the same concentration of hydrazine plus the test interference compound. The following chemicals are evaluated:

- freons
- sulfur dioxide
- nitrogen dioxide
- hydrogen
- methanol
- ammonia
- carbon dioxide
- carbon monoxide
- acetone
- ethanol
- nitric oxide

Tubing Test

The capability of the instrument to sample air through differing lengths of tubing is determined. An auxiliary pump is used to draw a large volume of air through the tubing and create a vacuum. The maximum length of tubing is determined that can be used in conjunction with the instruments without generating too great a vacuum on the instruments' input which prevents them from performing.

TEST INSTRUMENTS

Four instruments from two different companies were evaluated. Two of the instruments were from MDA Scientific, Inc., the Model 7100 and the Model TLD-1. The other two instruments from GMD Systems, Inc. were identical. They were Remote Intelligent Sensor Area Monitors (RIS), Model 720-020. The GMD instruments are referred to as GMD 1 and GMD 2.

The MDA 7100 and TLD-1 detectors use cassette detector tapes which contain a chemically impregnated paper that is exposed to a known volume of gas. Hydrazines in the gas sample reduce the substance on the paper tape and a blue stain is formed. The intensity of the stain is related to the amount of hydrazine present. The optical reflectivity of the stain is measured and the concentration of the hydrazine is calculated and displayed on a meter which reads in ppb. The MDA 7100 has factory set ranges of 0 to 1000, 2000, and 5000 ppb for hydrazine, MMH, and UDMH.

respectively. The MDA TLD-1 has ranges of 0 to 300, 600, and 1500 ppb for hydrazine, MMH, and UDMH respectively. Although the TLD-1 instrument we tested was specifically set for hydrazine monitoring, it can be adjusted for MMH and UDMH by the company. For this report, the range was 0-300 ppb for all the hydrazines. The digital display on the instrument reads from 0 to 299 ppb; the first non-zero output is 10 ppb.

The GMD instruments also use chemically impregnated paper tape and work similarly to the MDA instruments. The GMD detectors use two tracks on the tapes to sample gas. Each track is independently monitored by a photocell. When a stain forms on track one, the sample flow is directed to track two and the tape is exposed. The detectors have a range of 0.01 to 2.00 ppm for hydrazine, MMH, and UDMH and use the same internal calibration curve for all three gases. Routine maintenance requires replacing the chemcassettes and verifying the flow rate and the light levels on tracks one and two at four week intervals.

All instruments were operated from line voltage. The MDA 7100 was the only model tested which did not have an internal battery pack. The instruments were switched off overnight. The instruments operated for an eight hour period each day.

TEST AND EVALUATION

Functional Test

The following is an evaluation of the instruments functionality and the operator/instrument interface. We also report the effort required to maintain the instruments in operating condition. The chemcassettes in both instruments were replaced every two weeks while in use and the air sampling rate was checked periodically. Each time the chemcassettes were replaced, the MDA 7100 was calibrated with the calibration card provided by the manufacturer. The system response of the MDA TLD-1 was also verified with its accompanying test card.

Being a fixed point monitor, the MDA 7100 is large and heavy. This did not cause a problem as it is easy to open up and make adjustments. The 7100 was relatively easy to maintain. Replacing the chemcassette or calibrating the instrument consisted of setting the appropriate function, using the escape and set buttons on the face of the instrument, lifting the top of the instrument and completing the task. Calibration of the instrument can be carried out in several ways; the easiest being card calibration with the card provided. Replacing the paper tape cassette is more complicated. First the instrument is set in the cassette replacement mode to allow the user to remove the paper tape from the detector head. The used cassette has to be unwound from the take-up spool and the new tape threaded. This is the most time-consuming task in the maintenance of this instrument. Prior to this evaluation, it was discovered that the sample inlet port was fitted with a sharp metal ferrule that abraded and punctured the teflon tubing used as the sample probe. The ferrule was removed and the tubing fed directly into the detection head. The outside area surrounding the inlet was covered with black tape to keep out stray light.

The audio and visual alarms can be adjusted to alarm at any concentration within the instrument's parameters. The audio alarm can also be disabled. The MDA 7100 features a flowmeter on the face of the instrument. It was discovered to read low by approximately 50 ml/min. Using a rotameter at the sample inlet, the flow was adjusted to the correct sampling rate.

The 7100 model is equipped with a hardcopy printout device in addition to the digital display. An update of the detector's response to the gas concentration was printed every two minutes below the programmed alarm levels. Above these levels, the concentration is printed out every minute.

The MDA TLD-1 is a compact and lightweight portable monitor. It required little maintenance. It was easy to replace the chemcassette, verify the system response, turn the instrument on, and access the alarm buttons. Replacing a cassette required threading the paper tape through the instrument and onto the take-up reel. The cover of the reel was then snapped on. The only problem associated with this design was that the take-up reel cover had a tendency to work loose. If this occurred while the instrument was on, the audio and visual alarms activated.

The instrument is supplied with a test card which was used to verify the system response. This card was simple to use and the system response was verified each time the chemcassette was replaced. The alarms on the instrument are factory preset and cannot be changed by the user. However, since the audio alarm was set at the upper limit of the detector, this did not cause a problem during testing. There is no flowmeter on the instrument. We measured the flow rate to be approximately 750 ml/min. The detector does not have a hardcopy printout; however, the instrument has an analog output which can be connected to a strip chart recorder or other device. The digital display is very legible.

The GMD instruments are also compact and lightweight. They are designed to be fixed-point detectors and to be mounted on a wall. This design restricts the user's options for mounting the instrument for easy access. If not mounted upright, the digital display cannot be viewed with ease. It was necessary to open the instrument to turn the power on as well as to activate the test mode. To open the instrument, the lid of the detector had to be unscrewed with a special key made by GMD.

It was easier to replace the paper tape cassettes in these instruments as they did not have to be threaded into the detector. The chemcassettes are self-contained and are simply pressed into place while the instrument is in the test mode. In the test mode, the display scrolls through a series of system checks of the instrument's parameters, all of which can be corrected (except for the calibration curve) by the user. There was an audio alarm but the instrument has the capacity for one. The visual alarm is a flashing bell moving across the face of the detector. The alarm level can be set by the user. When the instrument is turned off, the alarm resets to zero and must be reset when the detector is turned on. There is also no flowmeter on the instrument. The sampling rate (200 ml/min) has to be checked and adjusted by the user. It did not drift more than ± 35 ml/min during the testing.

Adjusting the light levels of the two tracks in the optics block is difficult. The light levels must be within the range of 200-255. They were set to approximately 227 by the company. This can be checked while the instrument is in the test mode. If the levels drift outside this range, they can be corrected using pots on the inside the chassis. However, the pots are located underneath the chemcassette. To access them, the cassette must be removed and a section of paper tape has to be rethreaded through the detector head leaving the cassette out of its normal position. The light levels are then adjusted, the cassette replaced, and the levels checked in the test mode. If the levels have not been correctly adjusted, the procedure must be repeated. The light levels never drifted outside the range of 200-255.

The GMD instruments displayed several problems when they were first tested. The decimal point on the digital display faded in and out during an exposure. This software problem was corrected by the company. The instruments had a tendency to "miss" a sample. The response would drop to zero for an entire sampling period of four minutes. This happened infrequently and did not hinder the evaluation.

Warm-Up Time

The MDA 7100 achieves a stable zero response as soon as the instrument is turned on. It takes two minutes for the first reading to print out. When calibrating the instrument, there is an initial warm-up period of approximately three minutes when the card calibration mode is first entered. To begin displaying a stable zero reading on zero gas, the MDA TLD-1 requires 1.5 minutes

after the instrument is turned on. The display reads "Battery OK" for this entire period. The GMD instruments do not require a warm-up period prior to giving a stable zero reading.

Zero Stability

An eight hour zero stability test was conducted on all instruments using clean air at 45% RH. The instruments displayed no overall drift for the duration of the test.

Span Stability

An eight hour span stability test was conducted using 564 ppb of UDMH at 45% RH. The changes in output response during the eight hour period are as follows: for the MDA 7100, +54 ppb, for GMD 1, -43 ppb, and for GMD 2, +46 ppb. The MDA TLD-1 was not tested here since the concentration of the gas was greater than the instrument's upper limit.

Linearity

Linearity tests were performed on all instruments for MMH, hydrazine, and UDMH with the exception of the MDA TLD-1. The TLD-1 was exposed to MMH and hydrazine only for these tests. Figures 1a through 4c represent linear, unweighted least square fits of the data obtained from each instrument.

As shown in figure 1a, the MDA 7100 responded in a linear fashion to MMH. For hydrazine, the responses of the MDA 7100 are almost always outside $\pm 25\%$ error, but are linear. Figure 1b contains this data. In the case of UDMH, the detector shows reasonable linearity, but the response was outside $\pm 25\%$ error. Figure 1c shows the linearity curve for UDMH.

The MDA TLD-1 gave reasonably linear responses throughout the limited range of MMH tested. Its responses were at times outside $\pm 25\%$ error range. When exposed to various concentrations of hydrazine, the TLD-1 responded with very good linearity and within 25% error. The linearity plots for these exposures are shown in figures 2a and b.

Although most data points are outside $\pm 25\%$ error, the GMD instruments show good linearity for MMH. Figure 3a gives the linearity data for GMD 1 and figure 4a gives linearity data for GMD 2. For hydrazine, there is very good linearity. The responses are within 25% error up to one ppm. Figures 3b and 4b are graphs of hydrazine linearity data. For UDMH, the GMD instruments are reasonably linear. The accuracy is outside 25% error. This is shown in figures 3c and 4c.

Response and Recovery Times

The response times of the instruments to the various hydrazines was dependent upon the concentration. In general, a substantial increase in concentrations causes a decrease in response times. For example, at 171 ppb hydrazine, the response time to 90% of full scale is approximately 9.1 minutes for GMD 1, 7.0 minutes for GMD 2, and 7.6 minutes for MDA 7100. At an increased concentration of 1.04 ppm, the respective response times to 90% of full scale are 3.7, 3.9, and 4.9 min. The same trend occurs for MMH. With UDMH, there was a slight decrease in response times with an increase in gas concentration for the GMD instruments. The MDA 7100 did not display this trend. The concentration range of the TLD-1 for MMH and UDMH was too narrow to make a comparison for this instrument, although for hydrazine it performed in the same manner as the other instruments. Tables 1a, b, and c detail the response times to 50%, 75%, and 90% of full scale for hydrazine, MMH, and UDMH.

The recovery times for the GMD detectors were not dependent upon the initial concentration of the hydrazine. The MDA 7100 displayed decreased recovery times with an increase in concentration for hydrazine and MMH. The MDA TLD-1 also followed this trend for hydrazine. Due to the limited range of the instrument, a similar comparison could not be made for MMH or UDMH. There was no definite trend for the effects of relative humidity on response and recovery times. The recovery times for hydrazine, MMH, and UDMH are shown in tables 2a, b, and c.

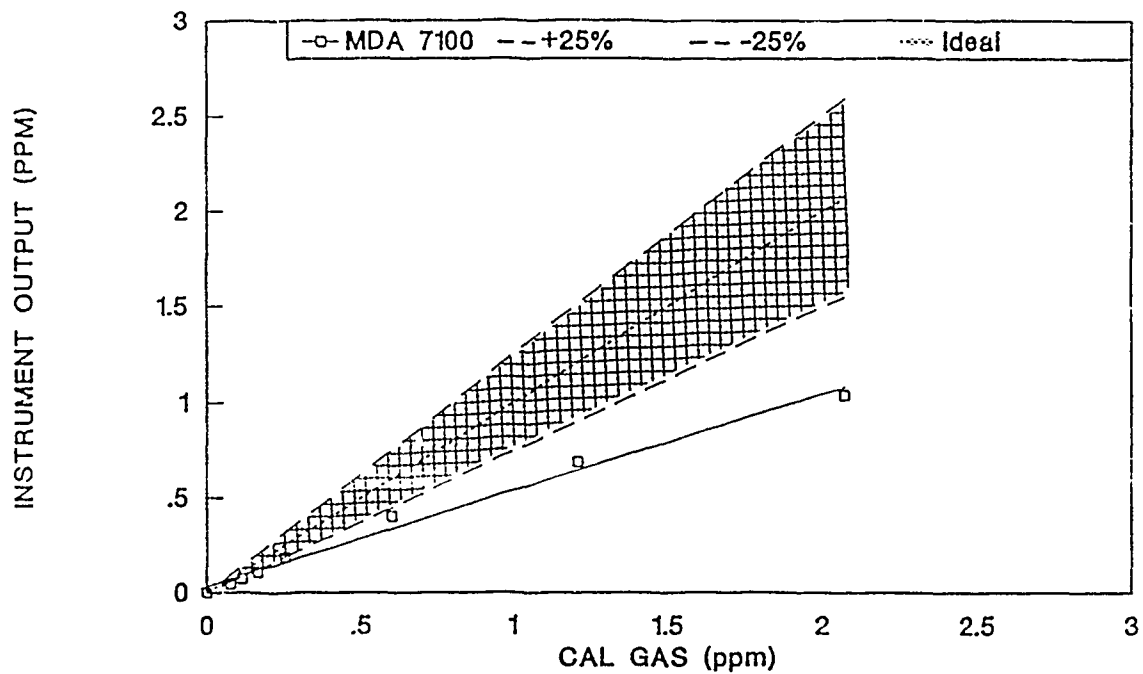


Fig. 1a. Linearity plot of MDA 7100 for MMH

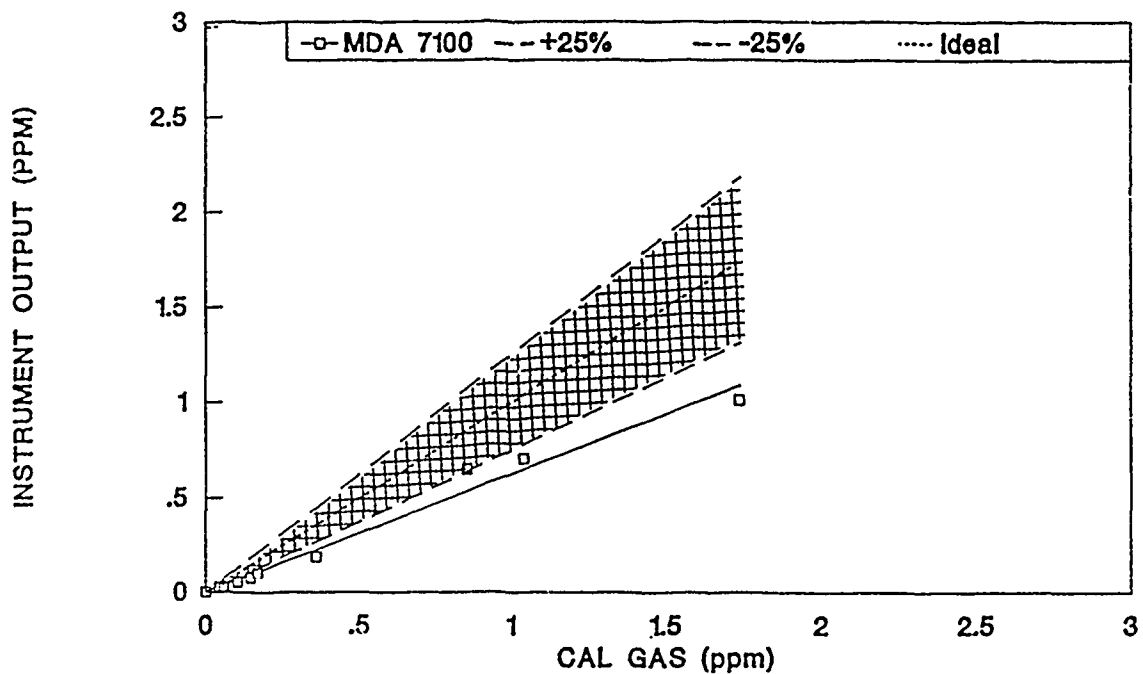


Fig. 1b. Linearity plot of MDA 7100 for hydrazine

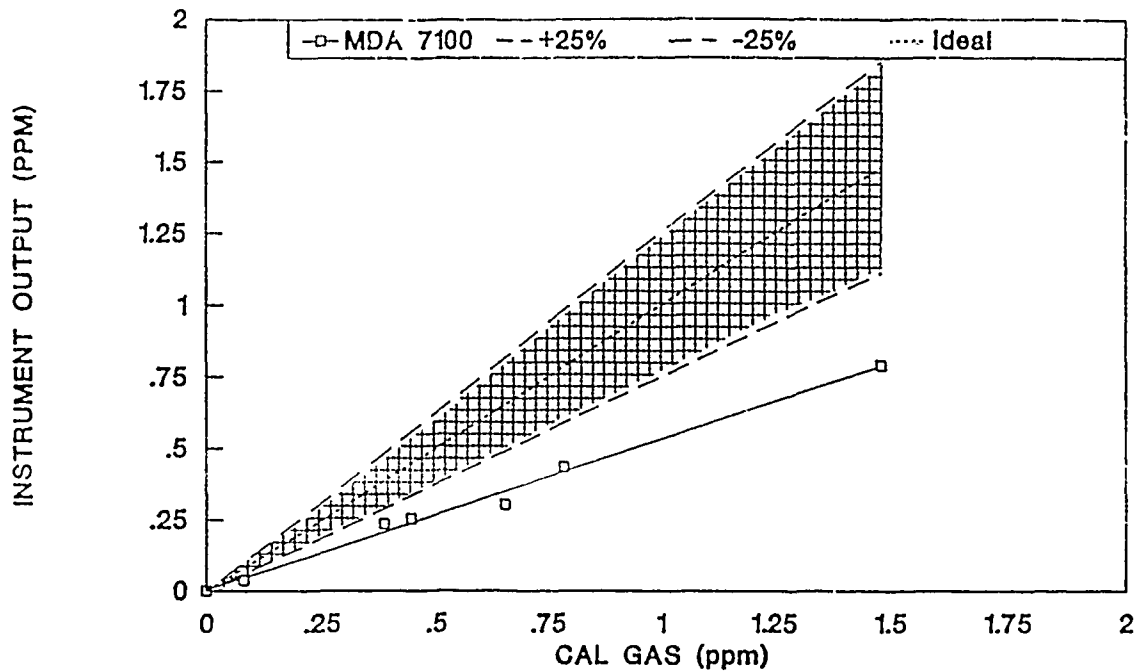


Fig. 1c. Linearity plot of MDA 7100 for UDMH

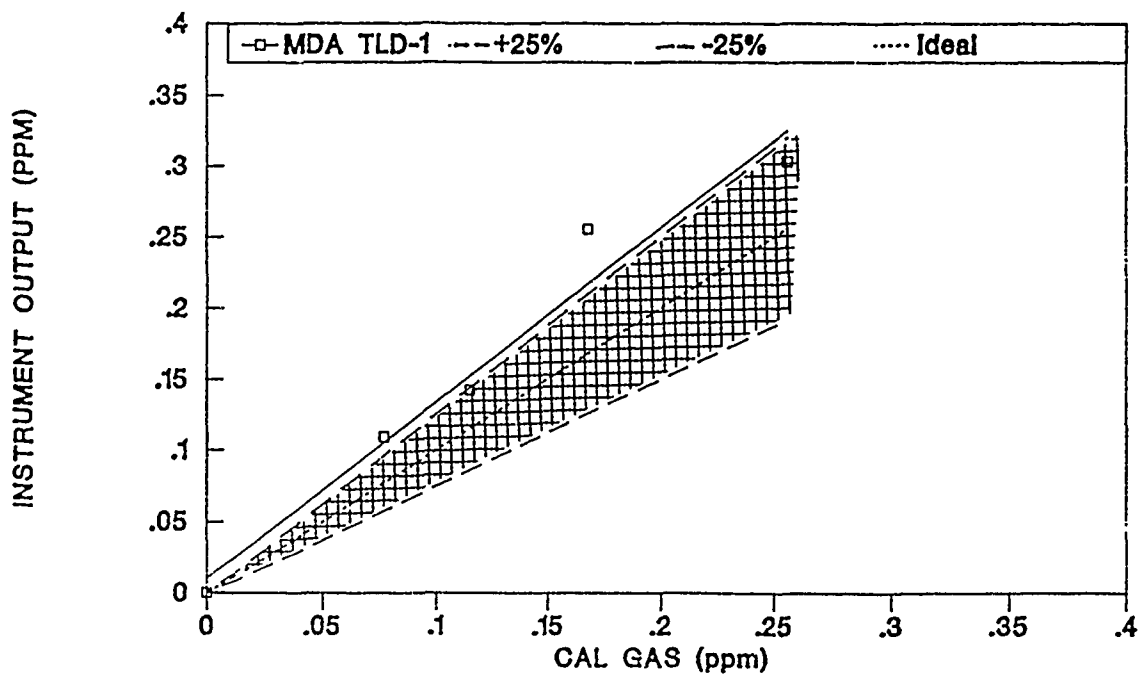


Fig. 2a. Linearity plot of MDA TLD-1 for MMH

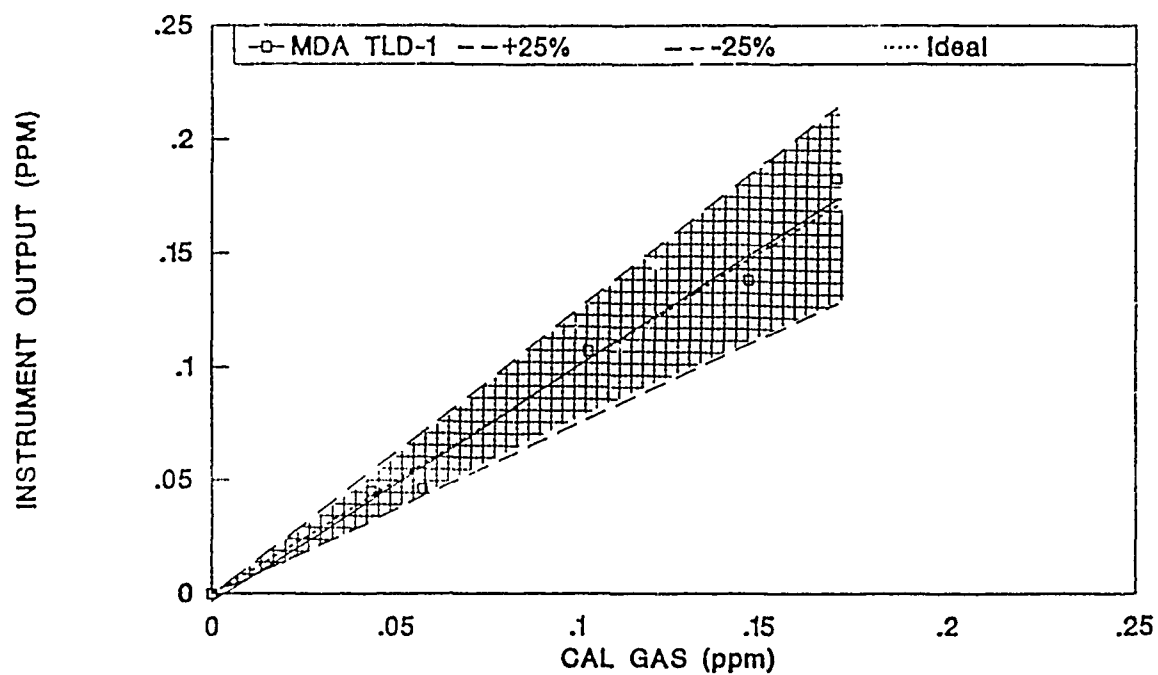


Fig. 2b. Linearity plot of MDA TLD-1 for hydrazine

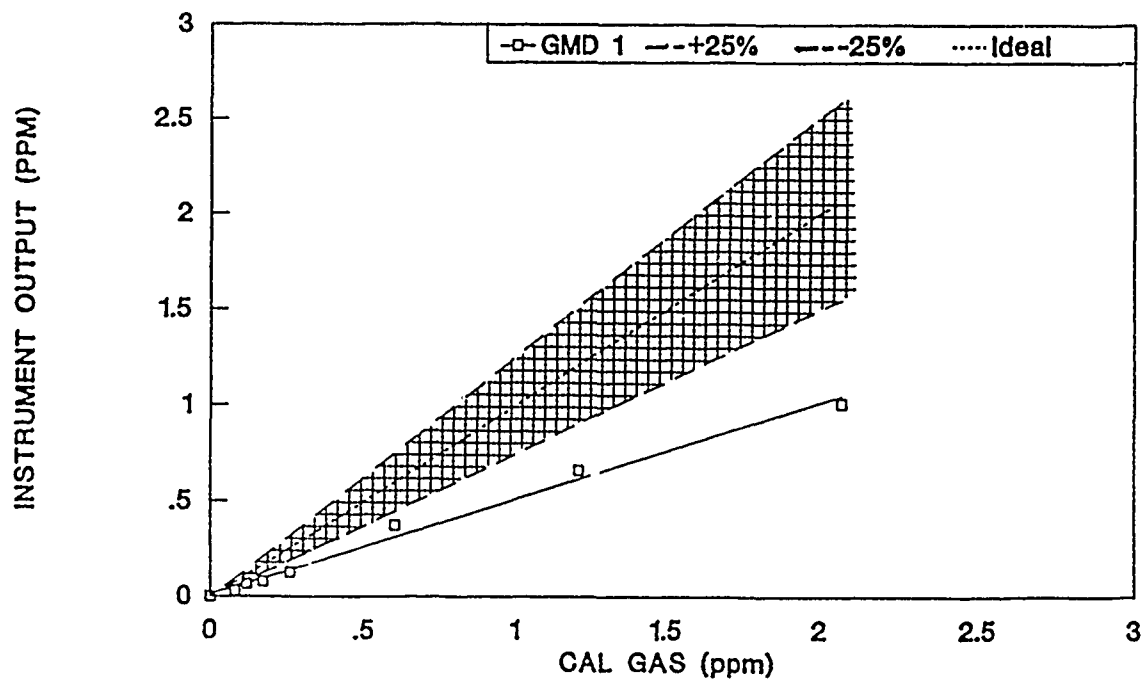


Fig. 3a. Linearity plot of GMD 1 for MMH

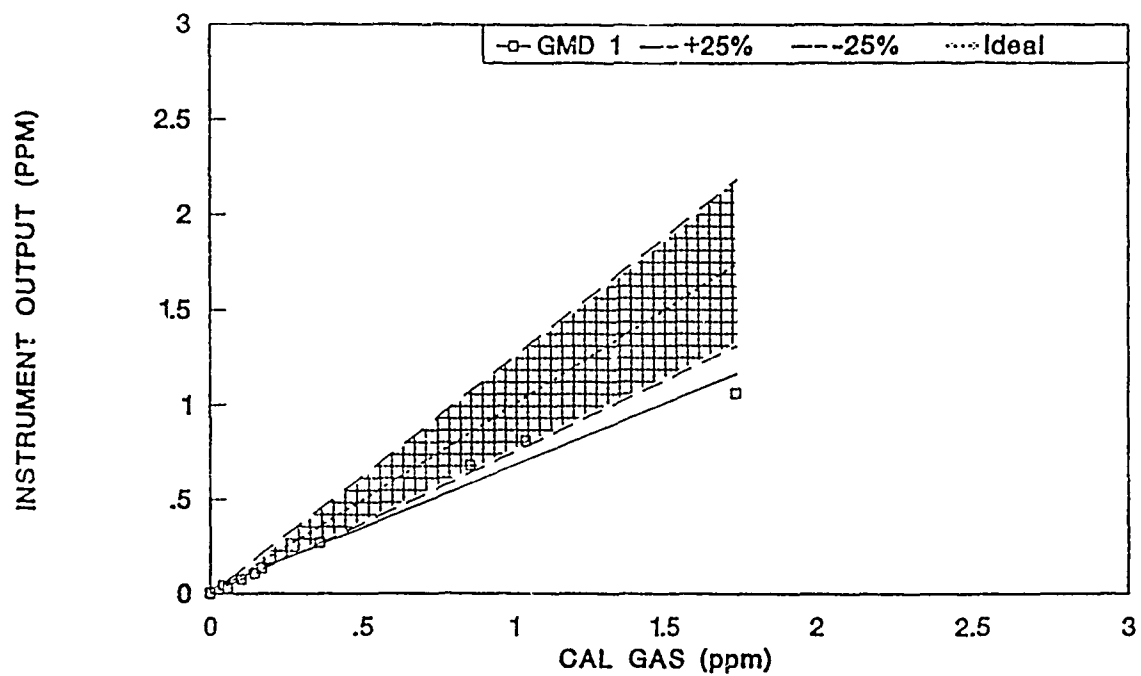


Fig. 3b. Linearity plot of GMD 1 for hydrazine

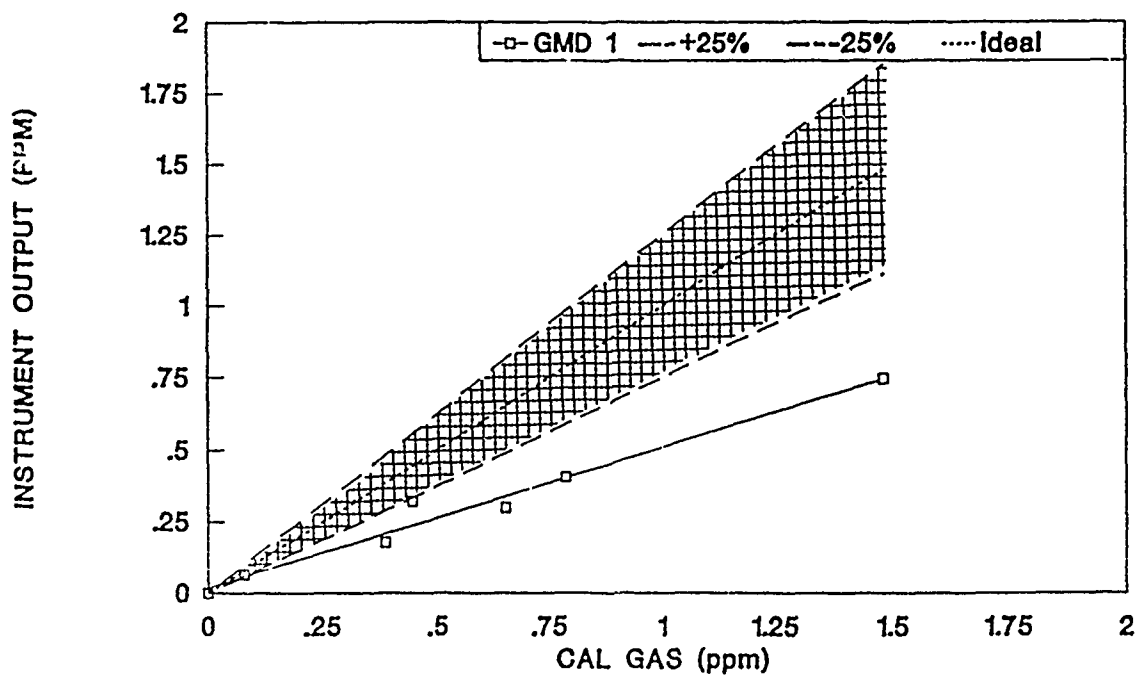


Fig. 3c. Linearity plot of GMD 1 for UDMH

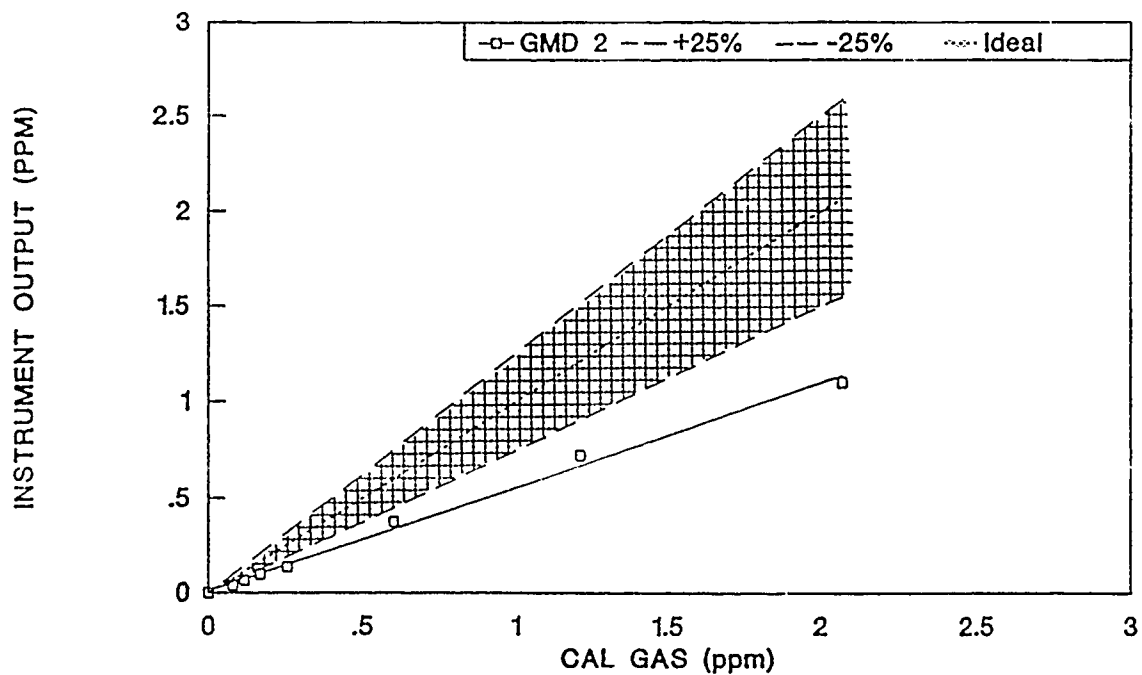


Fig. 4a. Linearity plot of GMD 2 for MMH

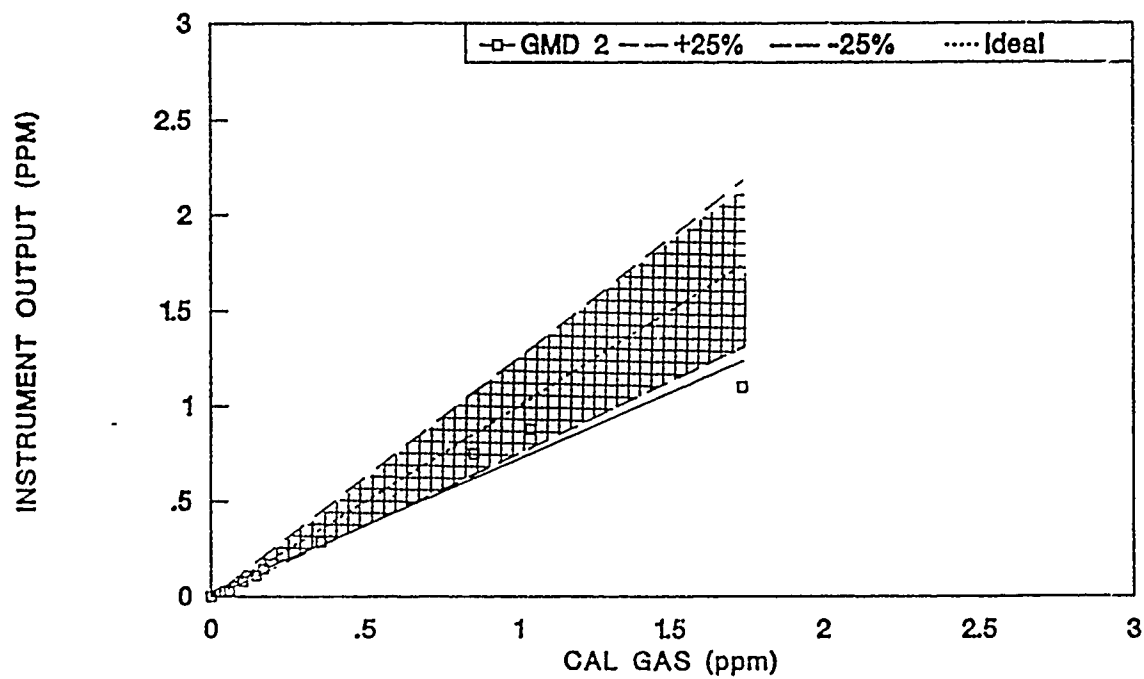


Fig. 4b. Linearity plot of GMD 2 for hydrazine

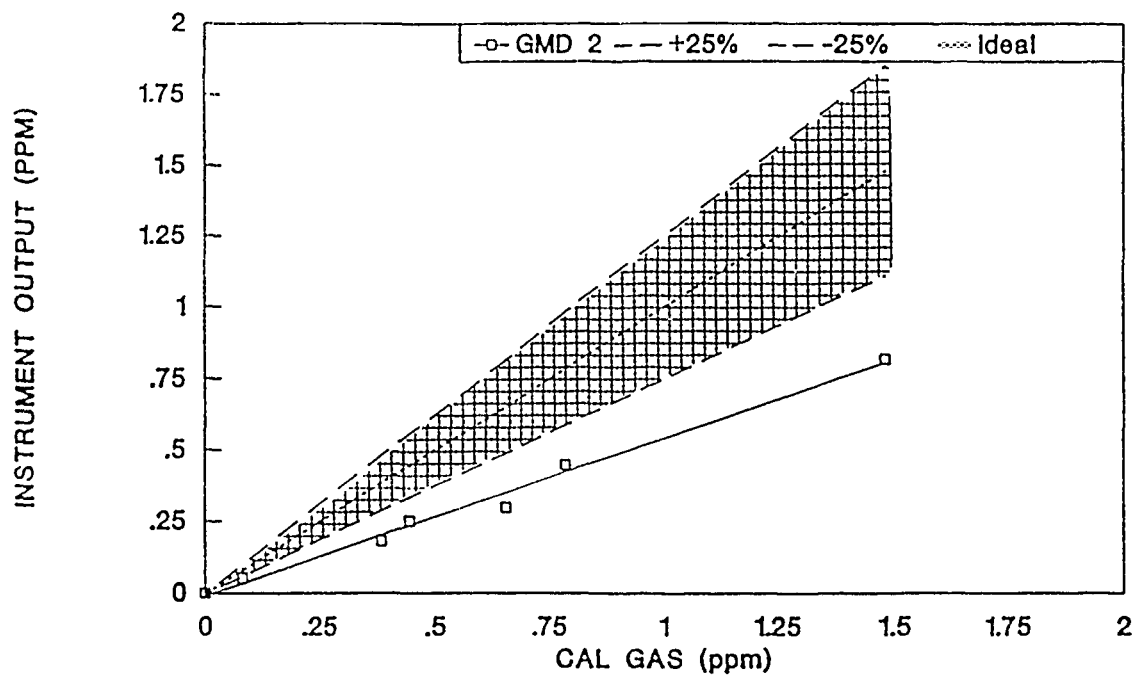


Fig. 4c. Linearity plot of GMD 2 for UDMH

Table 2a Recovery Time For Hydrazine in Minutes (Std. Dev.)

Gas Conc.	GMD 1			GMD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.5 TLV	5.5(2.3)	7.1(2.2)	7.9(2.0)	4.2(1.6)	5.9(1.1)	6.2(1.2)	5.1(2.5)	6.5(2.2)	7.8(1.0)	2.8(0.39)	3.5(1.4)	4.1(1.6)
1 TLV	5.5(2.0)	6.3(1.8)	7.5(1.7)	5.5(1.7)	6.1(1.4)	6.9(1.5)	5.0(1.3)	6.8(2.5)	8.3(1.6)	2.6(0.61)	3.4(0.49)	3.8(0.56)
2 TLV	6.0(0.83)	6.3(0.97)	7.9(1.7)	4.4(0.84)	5.5(0.87)	5.7(0.87)	3.2(0.66)	4.8(0.25)	8.1(1.3)	2.3(0.46)	3.0(0.57)	3.6(0.46)
4 TLV	4.6(0.14)	5.7(2.0)	7.2(2.5)	5.4(0.95)	5.6(0.92)	6.7(0.69)	3.8(0.53)	3.9(0.51)	6.6(1.5)			
8 TLV	4.6(1.1)	5.8(1.0)	8.2(1.3)	2.5(1.5)	3.6(2.4)	5.7(3.1)	2.8(0.72)	4.0(0.38)	5.1(0.64)			
10 TLV				3.5(1.2)	4.74(0.53)	6.8(1.6)	3.0(0.62)	3.3(0.56)	4.8(0.43)			
20 TLV	4.2(0.25)	5.2(1.4)	7.9(0.58)	4.5(0.29)	4.7(0.29)	5.7(1.3)	2.5(0.23)	3.2(0.92)	5.4(0.96)			

Table 2b Recovery Time For MMH in Minutes (Std. Dev.)

Gas Conc.	GMD 1			GMD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.5 TLV	4.3(1.1)	5.4(1.7)	6.3(2.1)	4.4(0.71)	6.0(0.98)	6.1(0.99)	3.6(0.71)	5.9(2.4)	6.4(2.7)	2.7(0.53)	2.84(0.49)	5.6(2.5)
1 TLV	5.5(1.1)	5.9(0.74)	6.8(1.3)	4.9(1.1)	5.7(1.1)	7.1(1.5)	3.0(0.71)	3.8(0.65)	5.1(1.4)	2.5(0.59)	3.1(0.26)	3.3(0.25)
3 TLV	4.3(1.5)	6.1(0.91)	6.9(0.71)	3.0(0.69)	6.5(1.0)	6.7(1.0)	2.7(0.34)	2.9(0.34)	4.18(0.66)			
8.5 TLV	4.2(0.85)	5.2(1.0)	6.3(1.4)	4.1(0.22)	4.3(0.21)	6.1(1.6)	2.6(0.77)	3.8(0.80)	3.9(0.82)			

Table 2c Recovery Time For UDMH in Minutes (Std. Dev.)

Gas Conc.	GMD 1			GMD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.15 TLV	3.4(1.3)	3.7(1.2)	5.1(1.7)	4.4(1.0)	4.5(1.0)	4.8(1.0)	1.8(0.40)	3.3(2.0)	4.1(1.6)	3.3(1.7)	3.9(1.5)	5.1(2.2)
0.7 TLV	5.2(1.2)	6.5(0.75)	6.6(0.71)	4.8(1.7)	6.6(1.0)	6.8(1.0)	1.4(0.21)	1.5(0.20)	2.0(0.25)			
1 TLV	3.9(1.0)	6.0(1.3)	6.6(1.0)	4.4(1.6)	6.5(1.1)	6.7(0.93)	1.8(0.21)	2.0(0.21)	2.9(0.64)			
1.5 TLV	4.7(1.3)	6.4(1.2)	6.5(1.2)	3.9(1.8)	5.2(2.2)	6.0(2.1)	1.3(0.40)	2.0(0.28)	2.5(0.66)			
3 TLV	3.8(0.84)	4.8(1.3)	5.7(1.7)	3.8(0.72)	5.1(1.9)	6.5(1.7)	1.5(0.74)	1.9(0.72)	2.9(1.7)			

Table 1a Response Time For Hydrazine in Minutes (Std. Dev.)

Gas Conc.	GHD 1 -			GHD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.5 TLV	7.9(1.2)	8.7(1.2)	8.9(1.0)	6.4(0.91)	7.2(1.0)	8.7(1.2)	5.5(2.1)	6.6(1.6)	7.7(1.5)	3.0(0.97)	4.3(1.5)	6.3(1.8)
1 TLV	6.4(1.5)	7.0(1.4)	7.9(1.7)	6.3(1.5)	6.9(1.2)	7.2(1.5)	5.2(1.0)	7.7(2.0)	9.4(0.62)	2.8(0.73)	3.9(1.4)	4.6(1.7)
2 TLV	5.3(0.90)	7.8(1.0)	9.1(1.3)	5.7(1.3)	5.9(1.3)	7.0(2.1)	4.5(0.21)	6.1(1.1)	7.6(1.2)	3.1(0.41)	3.3(0.44)	4.9(1.5)
4 TLV	5.3(1.2)	7.3(0.98)	9.4(0.65)	6.7(0.21)	6.8(0.20)	7.1(0.17)	4.0(0.59)	4.7(0.37)	7.0(1.3)			
8 TLV	3.6(0.73)	5.6(1.6)	7.7(1.9)	3.0(0.33)	3.7(0.83)	4.6(0.94)	3.0(1.3)	4.6(0.47)	6.3(1.3)			
10 TLV	2.8(0.25)	3.0(0.21)	3.7(0.58)	3.0(0.62)	3.5(0.23)	3.9(0.67)	3.2(0.53)	3.4(0.55)	4.9(0.68)			
20 TLV	2.3(0.64)	2.8(0.78)	3.4(1.0)	1.7(0.41)	1.9(0.38)	2.1(0.36)	1.6(0.43)	1.8(0.38)	3.2(0.82)			

Table 1b Response Time For MMH in Minutes (Std. Dev.)

Gas Conc.	GHD 1			GHD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.5 TLV	9.0(1.5)	9.8(0.45)	9.8(0.42)	7.3(2.1)	8.4(1.7)	9.5(0.81)	4.6(1.2)	7.4(1.6)	9.1(1.8)	3.4(0.72)	3.9(0.97)	6.0(0.96)
1 TLV	6.6(1.4)	7.9(1.2)	8.7(0.81)	6.1(1.3)	7.0(1.0)	8.1(1.3)	3.9(0.69)	5.0(0.72)	6.4(1.2)	3.6(0.59)	3.8(0.55)	5.9(1.5)
3 TLV	4.8(0.90)	5.5(0.81)	7.3(1.4)	5.3(0.96)	5.5(0.96)	6.2(0.36)	2.0(0.23)	3.3(0.93)	5.1(0.96)			
8.5 TLV	3.1(0.81)	3.5(0.79)	3.8(0.86)	2.6(0.62)	2.8(0.63)	3.0(0.64)	1.9(0.43)	2.6(0.55)	3.5(0.85)			

Table 1c Response Time For UDMH in Minutes (Std. Dev.)

Gas Conc.	GHD 1			GHD 2			MDA 7100			MDA TLD-1		
	50%	90%	75%	50%	75%	90%	50%	75%	90%	50%	75%	90%
0.15 TLV	4.3(0.56)	6.1(1.5)	8.1(1.3)	4.1(1.5)	6.5(1.1)	6.9(1.2)	1.8(0.20)	2.0(0.20)	2.6(0.62)	2.3(1.0)	2.9(1.0)	3.0(1.0)
0.7 TLV	3.9(1.1)	4.9(0.92)	5.8(1.1)	4.7(1.0)	5.5(1.1)	6.4(1.4)	1.7(0.29)	2.0(0.24)	3.3(1.2)			
1 TLV	4.5(0.81)	5.8(0.64)	6.9(0.98)	4.6(1.2)	6.7(0.82)	7.0(0.75)	1.8(0.42)	2.2(0.11)	3.7(1.1)			
1.5 TLV	4.0(1.1)	4.6(1.1)	5.4(1.2)	3.9(1.2)	4.5(1.4)	5.9(1.3)	1.6(0.36)	1.9(0.28)	3.3(1.4)			
5 TLV	3.0(1.0)	3.6(1.3)	4.0(1.4)	3.1(0.62)	3.6(0.52)	4.0(0.70)	1.5(0.32)	1.8(0.17)	2.1(0.56)			

Precision

The precision of each instrument was evaluated by exposing them several times in an eight hour period to a particular concentration of hydrazine, MMH, or UDMH. This was done for several different concentrations of each gas. Tables 3a, b, and c show the precision data for the instruments.

For hydrazine, the precision of the MDA 7100 decreases as the gas concentration increases. It is very good through 0.171 ppm with a standard deviation of 0.008 ppm, but at 1 ppm the standard deviation has increased to 0.040 ppm. The repeatability of the MDA 7100 was very good for TLV MMH with a standard deviation of 0.005 ppm. It declines slightly as the MMH concentrations increase. At 1.75 ppm of MMH, the standard deviation is 0.042 ppm. For UDMH, the instrument is very precise. The standard deviation only varies from 0.002 ppm at 0.08 ppm UDMH to 0.010 at 1.48 ppm UDMH.

The TLD-1 shows very good precision at TLV hydrazine with a standard deviation of 0.003 ppm. The responses to TLV hydrazine were very accurate. At 80 ppb UDMH, the instrument displayed excellent precision but very poor accuracy. It was not tested at any other UDMH concentrations.

The precision of the GMD instruments showed the same trend as the other detectors. The precision of the responses decreased with increasing concentrations of the hydrazines.

Accuracy

Each time the instruments were exposed to a hydrazine gas, the signal output was taken as a measure of accuracy. The responses of the instruments were compared to the results from the wet chemical method of quantitation referenced earlier [3]. From this, the accuracy was determined. Accuracy data, in the form of percentage of error, was plotted for each instrument for the entire test period.

Table 4 is a chart of the average accuracy and standard deviation for the instruments' exposures to each hydrazine. Figures 5a, b, c, and d detail the error in accuracy for each instrument as the evaluation progressed. The responses of the MDA TLD-1 are shown in Figure 5a. Figure 5b shows the low responses of the MDA 7100 and the increasing scatter in response as the evaluation progressed. The instrument demonstrated good accuracy for all the vapors except UDMH. Figure 5c covers GMD 1 and Figure 5d shows the decrease in response of the GMD 2 as the evaluation continued. The detectors were exposed to MMH from day 1 through day 19 and again from day 57 to day 83 of the test period. Hydrazine was tested from day 20 to day 40 and from day 85 through day 107. UDMH was used on days 41 through 55 and day 97.

The MDA 7100 responded outside 25% accuracy during most of the evaluation period. For UDMH, the instrument's accuracy was outside 25% error for all exposures to the gas. However, the error of the detector was the most consistent for UDMH and did not demonstrate the scatter it showed with MMH and hydrazine. During the later exposures to MMH between days 57 and 83, the 7100 responded within 25% error for the majority of the exposures.

The MDA TLD-1 was not exposed to UDMH for more than three tests due to its limited range and very high response to UDMH. For the few exposures to UDMH, the instrument responded almost 100% high. For MMH, the TLD-1 displayed a wide range in accuracy, but responded within 25% error for half of the exposures. It was not exposed during tests when the concentration of the MMH was higher than the range of the instrument, but even at concentrations within the range, the instrument often read so high that it alarmed and had to be turned off. For hydrazine, the accuracy of the detector was very good and within 25% error for the majority of the exposures.

Table 3a Precision Test For Hydrazine

IMPINGER CONC. (ppm)	CHD 1	CHD 2	MDA 7100	MDA TLD-1
0.103	0.076 0.090 0.083	0.083 0.087 0.084	0.055 0.057 0.056	0.107 0.114 0.109
MEAN	0.083	0.085	0.056	0.110
STD DEV	0.006	0.002	0.001	0.003
REL STD DEV	0.007	0.002	0.001	0.004
ACCURACY (% ERROR)	19	18	46	7
0.171	0.121 0.128 0.128 0.133	NA 0.131 0.150 0.145	0.082 0.087 0.094 0.104	0.142 0.162 0.182 0.183
MEAN	0.128	0.142	0.092	0.167
STD DEV	0.004	0.008	0.008	0.017
REL STD DEV	0.005	0.010	0.010	0.019
ACCURACY (% ERROR)	25	17	46	1
0.358	0.272 0.236 0.214 0.275	0.287 0.297 0.300 0.315	0.189 0.184 0.197 0.217	NA
MEAN	0.249	0.300	0.197	
STD DEV	0.025	0.010	0.013	
REL STD DEV	0.029	0.012	0.015	
ACCURACY (% ERROR)	30	16	45	
1.04	0.800 0.750 NA 0.809	1.03 1.05 0.895 0.878	0.731 0.810 0.726 0.705	NA
MEAN	0.786	0.963	0.743	
STD DEV	0.026	0.077	0.040	
REL STD DEV	0.032	0.089	0.046	
ACCURACY (% ERROR)	24	7	29	

Table 3b Precision Test For MMH

IMPINGER CONC. (ppm)	CHD 1	CHD 2	MDA 7100	MDA TLD-1
0.200	0.096 0.099 0.105 0.107	0.114 0.111 0.105 0.109	0.136 0.143 0.146 0.148	NA
MEAN	0.102	0.110	0.143	
STD DEV	0.004	0.003	0.005	
REL STD DEV	0.005	0.004	0.005	
ACCURACY (% ERROR)	49	45	28	
0.627	0.344 0.355 0.346 0.334	0.176 0.178 0.177 0.196	0.240 0.241 0.253 0.225	NA
MEAN	0.345	0.379	0.402	
STD DEV	0.007	0.006	0.027	
REL STD DEV	0.009	0.007	0.031	
ACCURACY (% ERROR)	45	39	36	
1.75	1.03 1.05 1.04	1.09 1.08 0.984	1.07 1.16 1.16	NA
MEAN	1.04	1.05	1.13	
STD DEV	0.008	0.048	0.042	
REL STD DEV	0.010	0.059	0.052	
ACCURACY (% ERROR)	41	40	35	

Table 3c Precision Test For UDMH

IMPINGER CONC. (ppm)	CHD 1	CHD 2	MDA 7100	MDA TLD-1
0.080	0.081 0.068 0.06 0.06	0.063 0.049 0.050 0.049	0.038 0.039 0.038 0.035	0.152 NA 0.155 0.151
MEAN	0.067	0.053	0.038	0.153
STD DEV	0.009	0.006	0.002	0.002
REL STD DEV	0.010	0.007	0.002	0.002
ACCURACY (% ERROR)	16	34	53	91
0.385	0.181 0.175 0.182 0.169	0.176 0.178 0.177 0.196	0.240 0.241 0.233 0.225	NA
MEAN	0.177	0.182	0.235	
STD DEV	0.005	0.008	0.006	
REL STD DEV	0.006	0.010	0.007	
ACCURACY (% ERROR)	54	53	39	
0.445	0.340 0.325 0.310 0.310	0.214 0.297 0.232 0.260	0.249 0.260 0.252 0.249	NA
MEAN	0.321	0.251	0.253	
STD DEV	0.012	0.031	0.005	
REL STD DEV	0.014	0.036	0.005	
ACCURACY (% ERROR)	28	44	43	
0.786	0.373 0.443 0.391 0.418	0.466 0.470 0.422 0.439	0.434 0.436 0.402 0.436	NA
MEAN	0.406	0.449	0.427	
STD DEV	0.027	0.020	0.014	
REL STD DEV	0.031	0.023	0.017	
ACCURACY (% ERROR)	48	43	46	
1.48	0.683 0.701 0.704 0.890	0.808 0.803 0.831 0.834	0.779 0.782 0.802 0.797	
MEAN	0.745	0.819	0.790	
STD DEV	0.084	0.014	0.010	
REL STD DEV	0.097	0.016	0.011	
ACCURACY (% ERROR)	50	45	47	

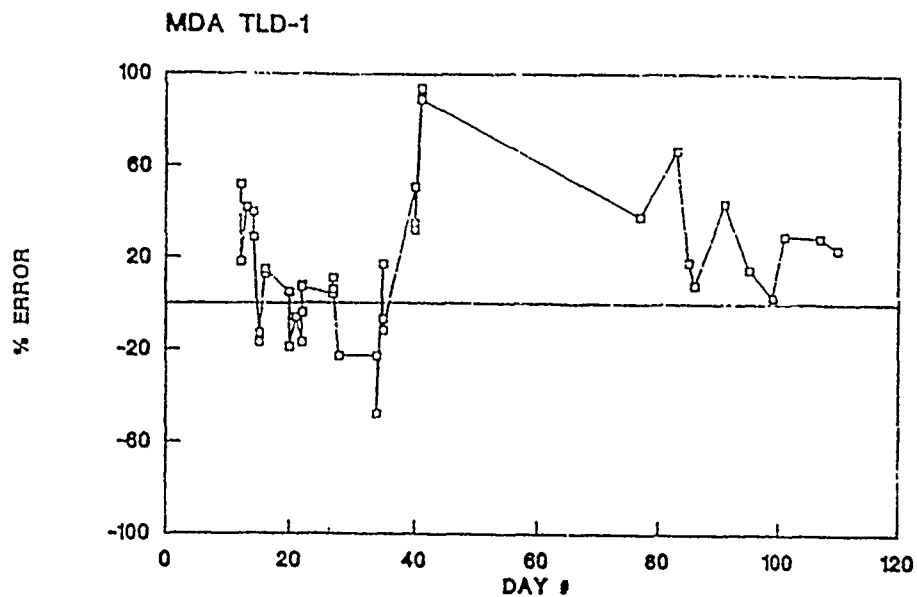


Fig. 5a. Percent error in response to changing gas challenge as a function of time

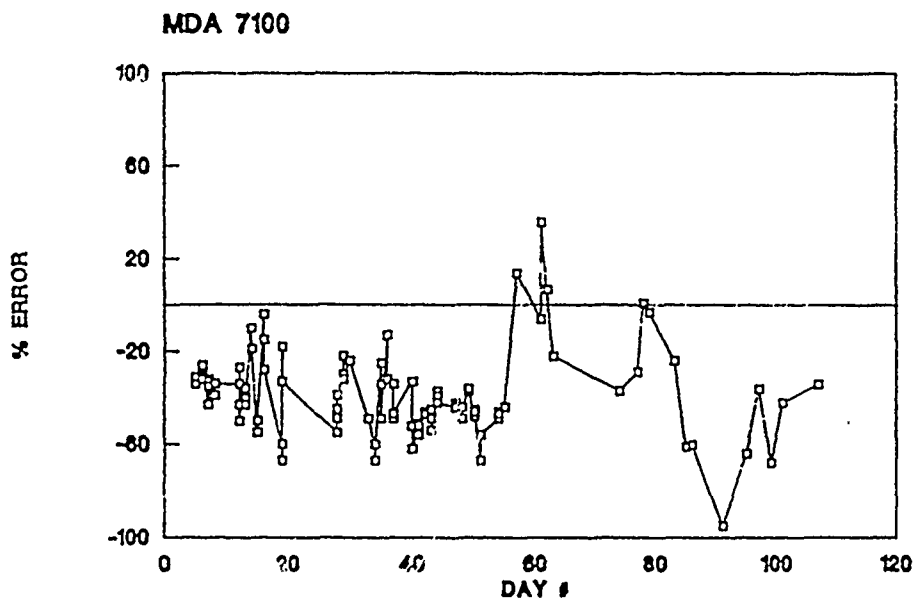


Fig. 5b. Percent error in response to changing gas challenge as a function of time

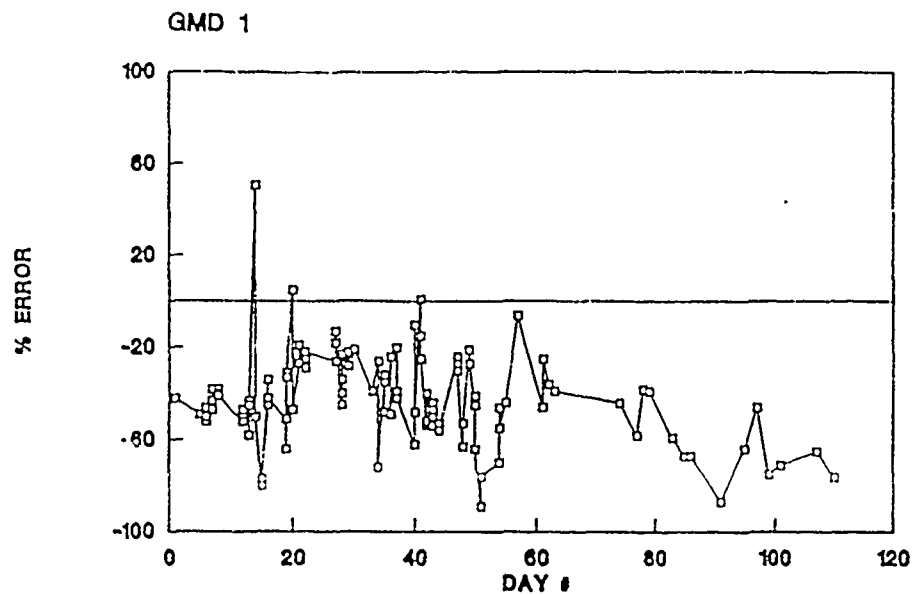


Fig. 5c. Percent error in response to changing gas challenge as a function of time

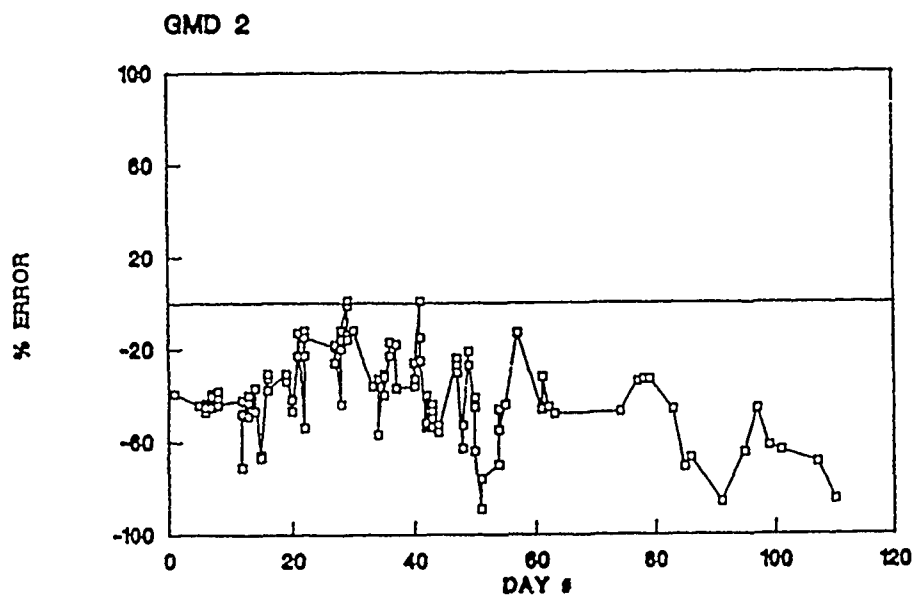


Fig. 5d. Percent error in response to changing gas challenge as a function of time

Table 5 Lower Limit of Detection

Instrument Response in ppb (% Error in Accuracy)

Actual Gas Conc (ppb)	MDA 7100	MDA TLD-1	GMD 1	GMD 2
Hydrazine				
36	15(58%)	NA	NR	NR
44	6(86%)	NA	4(91%)	NR
43*	28(28%)	45(5%)	45(5%)	25(42%)
55	10(82%)	NA	7(87%)	3(95%)
57*	27(53%)	45(21%)	30(47%)	30(47%)
MMH				
44	18(59%)	NA	NR	NR
66	49(26%)	NA	28(58%)	15(77%)
77*	38(51%)	109(42%)	32(58%)	39(49%)
UDMH				
80*	38(53%)	NA	67(16%)	53(34%)

* Exposure at first month of testing

NA- The TLD-1 was not exposed for these tests

NR- No Response

Table 6a Upper Limit of Detection Near 25% Error

Instrument Response in ppm (% Error in Accuracy)

Gas (ppm)	MDA 7100	MDA TLD-1	GMD 1	GMD 2
MMH				
0.256		0.303(18%)		
1.6*	1.31(18%)		1.10(31%)	1.06(34%)
Hydrazine				
0.261		0.201(-23%)		
1.04	0.738(29%)		0.957(8%)	0.796(24%)
* 22% RH				

Table 6b Instrument Response at Range Maximum

Instrument Response in ppm (% Error in Accuracy)

Conc (ppm)	MDA 7100	MDA TLD-1	GMD 1	GMD 2
MMH				
0.256		0.303(18%)		
2.07	1.04(50%)		1.01(51%)	1.10(47%)
hydrazine				
0.261		0.201(-23%)		
1.74	0.795(32%)		1.06(39%)	1.10(37%)
UDMH				
1.48	0.790(47%)	NA	0.745(50%)	0.814(45%)

The GMD detectors showed poor accuracy for the first 19 days of testing with MMH. When they were subsequently exposed to hydrazine, their accuracy initially improved. Through the next three weeks of testing with hydrazine and a few exposures to UDMH, their accuracy was within 25% error for 50% of the tests. Their accuracy then started to decline slowly throughout the remainder of the evaluation until the completion of the evaluation when their error was approximately -80%.

Table 4 Accuracy

Percent Error of Response (Std. Dev.)

Gas	MDA 7100	MDA TLD-1	GMD 1	GMD 2
MMH	-27 (19)	26 (23)	-45 (13)	-42 (10)
Hydrazine	-45 (16)	7 (22)	-40 (22)	-36 (23)
UDMH	-46 (6)	91 (2)	-41 (16)	-50 (11)

TLD-1 data on UDMH based on 3 exposures.

Sensitivity-Lower/Upper Limits of Detection

The signal noise for the instruments is as follows. The GMD instruments both show noise of approximately ± 6 ppb, the MDA 7100 shows noise of ± 2 ppb, and the MDA TLD-1 shows noise of ± 1 ppb. With a signal to noise ratio of 3:1 being the lowest acceptable, the estimated limits of reliable detection for the instruments are: 36, 12, and 6 ppb for the GMD detectors, the MDA 7100, and the MDA TLD-1 respectively. Table 5 shows the instrument responses to low gas concentrations as well as the accuracy of those responses. The data in the table were obtained four months into the testing period with the exception of the exposures marked with an asterisk.

The upper limits of detection, within approximately 25% accuracy, for the instruments are shown in Table 6a. Table 6b shows the instruments' responses near their range maximum.

Relative Humidity Effects

Each instrument was subjected to various concentrations of hydrazine, MMH, and UDMH at relative humidities from 0 - 66%. The only significant effect of humidity on instrument response was in the performance of the GMD instruments when exposed to UDMH. The responses of GMD 1 to approximately 425 ppb of UDMH increased steadily from 36% of the verified concentration at 0% RH to 79% of the concentration at 60% RH. At 650 ppb UDMH, the responses of GMD 1 increased from 24% of the concentration at 0% RH to 45% at 60% RH. The instrument responses to 1.4 ppm UDMH increased steadily from 11% of the concentration at 0% RH to 59% of the concentration at 58% RH. A similar trend occurred with the GMD 2. Table 7 shows the instrument responses for varying humidity and hydrazine concentration.

Table 7a Relative Humidity Effects

PERCENT OF IMPINGER						
GAS	GAS CONC (ppm)	%RH	GMD 1	GMD 2	MDA 7100	MDA TLD-1
Hydrazine						
	0.069	0	38	64	67	151
	0.069	24	90	74	48	135
	0.057	33	53	53	47	81
	0.069	63	52	67	38	132
	0.138	0	65	69	75	117
	0.138	24	68	68	66	93
	0.147	35	73	77	54	94
	0.138	63	52	60	51	88
	0.713	0	51	77	87	N/A
	0.713	25	76	83	68	
	0.853	33	79	88	76	
	0.713	60	80	82	66	
	1.75	0	58	65	53	N/A
	1.75	21	61	63	53	
	1.75	36	61	64	51	
	1.75	60	61	63	51	
MMH						
	0.078	4	49	53	90	140
	0.078	22	50	67	81	129
	0.077	45	42	51	60	142
	0.092	66	23	34	45	83
	0.197	0	55	67	96	113
	0.197	23	66	69	85	115
	0.168	45	48	58	66	152
	0.197	60	58	62	72	115
	1.6	0	49	69	40	N/A
	1.6	22	66	69	82	
	1.2	45	55	60	57	
	1.6	60	67	69	67	
UDMH						
	0.412	0	36	36	51	N/A
	0.412	25	47	39	56	
	0.437	47	73	56	64	
	0.437	60	79	67	63	
	0.628	0	24	23	46	N/A
	0.659	21	30	27	51	
	0.659	45	54	47	54	
	0.659	60	45	53	53	
	1.56	0	11	12	33	N/A
	1.31	21	36	33	54	
	1.31	45	55	47	54	
	1.31	58	59	48	54	

Interference Effects

A number of compounds were evaluated both individually and in the presence of MMH or hydrazine to determine their effect on the response of the instruments. Tables 8a and 8b show the rejection ratios calculated for the various compounds. A rejection ratio is a measure of the amount of compound required to produce a response similar to 1 ppm of a hydrazine. The MDA TLD-1 was not exposed to the interferences with MMH.

With hydrazine, there was an inconsistent response to the interferent nitric oxide (NO). All instruments showed a measurable response to NO with hydrazine, however the two MDA instruments reacted quite differently to the mixture. The responses to NO individually were also unique for each instrument. The chemcassettes were switched between the two instruments to determine if they were at fault. The results for the mixture of hydrazine and NO were much the same, negative for TLD-1 and positive for 7100. When exposed to NO, the TLD-1 instrument gave the same results as previously. The response of the 7100 model to NO was negligible.

The response of the MDA instruments to hydrazine and a mixture of gaseous freons was similar to the responses to NO and hydrazine. The MDA 7100 gave a positive rejection ratio while the TLD-1 gave a negative rejection ratio. The chemcassettes were not switched between the instruments to determine if they were at fault. The GMD detectors gave positive rejection ratios. A mixture of hydrazine and sulfur dioxide produced a decrease in instrument response with respect to that produced by hydrazine alone. With the exception of the MDA TLD-1, SO₂ by itself did not prove to be an interferent.

Freons and nitrogen dioxide, when mixed with MMH, produced a response less than that of MMH alone; thereby giving negative rejection ratios. With the exception of the MDA TLD-1 which did respond to the freons, the two interferents did not produce significant responses by themselves. Ammonia produced a positive response in the instruments if they had been exposed to hydrazine or MMH previously.

Tubing Test

Only the GMD instruments were subjected to this test. The manufacturer of the MDA TLD-1 said that the instrument was not designed to be used with an auxiliary pump. They recommended that the instrument not undergo this test. The MDA 7100 was tested and reported on earlier [4]. Due to the poor overall performance of the GMD instruments, a complete tubing/auxiliary pump test was not carried out. The instruments were briefly spot checked, however. A coil of 100 feet of Beva-line 3/8 inch od, 1/4 inch id tubing was connected to the two foot piece of 1/4 inch teflon sample probe normally attached to GMD 1. The instrument was exposed to a concentration of hydrazine slightly higher than TLV through this coil. The instrument did not respond to the gas during the twenty minute exposure.

The sampling rate of the GMD was adjusted to its maximum and measured. It sampled at approximately 265 ml/min. With the instrument sampling at this rate, the flow was restricted external to the detector to the normal rate of 200 ml/min. The pressure drop that the GMD could withstand while continuing to sample at 200 ml/min was 0.5 inches of mercury. When the vacuum was increased to 1.5 inches of mercury, the sample rate of the GMD was reduced to less than half its normal rate.

An auxiliary pump pulling 26 l/min of room air was then added to the test set-up. Different lengths of tubing were attached to the GMD to determine the length of tubing which would cause a pressure drop of 1.3 inches of mercury, sufficient to reduce the sample rate by half. It was determined that a tubing length approximately 6 feet corresponds to this pressure drop. Table 9 shows the drop in pressure as a function of tubing length for the GMD instruments.

Table 8a Rejection Ratio from Interference Tests

COMPOUNDS	INTERFERENT CONC. (ppm)	ACTUAL MMH CONC. (ppm)	MDA 7100	MDA TLD-1	GMD 1	GMD 2
MMH + CO	833	0.252	119000:1	NA	*	*
CO	833	0.011	*	NA	*	*
MMH	0	0.235				
MMH + CO ₂	5040	0.237	194000:1	NA	458000:1	560000:1
CO ₂	5040	0.011	*	NA	*	*
MMH	0	0.222				
MMH + NH ₃	50	0.292	250:1	NA	100:1	80:1
NH ₃	50	0.176	625:1	600:1	300:1	400:1
NH ₃	50	0.176	1350:1	3125:1	500:1	800:1
MMH	0	0.253				
MMH + FREONS	21	0.197	-780:1	NA	-750:1	-1000:1
FREONS	21	0.019	*	1400:1	*	*
MMH	0	0.220				
MMH + MEOH	817	0.231	11000:1	NA	102000:1	-51000:1
MEOH	817	0.031	*	*	*	*
MMH	0	0.238				
MMH + NO ₂	1	0.115	-7:1	NA	-14:1	-14:1
NO ₂	1	0.017	*	*	*	*
MMH	0	0.234				
MMH + ACETONE	500	0.221	-125000:1	NA	83000:1	*
ACETONE	500	0.129	*	28000:1	*	*
MMH	0	0.211				
MMH + H ₂	0.119	0.291	1:1	NA	3:1	2.5:1
H ₂	0.119	0.119	1.5:1	NA	NA	NA
MMH	0	0.181				

* Response negligible

NA No data available

Table 8b

Rejection Ratios from Interference Tests

COMPOUNDS	INTERFERENT CONC. (ppm)	ACTUAL HZ CONC. (ppm)	MDA 7100	MDA TLD-1	GMD 1	GMD 2
HZ + FREON 113	56	0.103	14000:1	9300:1	14000:1	4300:1
Freon 113	56	0.024	*	4300:1	*	*
HZ	0	0.113				
HZ + H2	1000	0.103	-350000:1	100000:1	*	*
H2	1000	0.024	*	143000:1	*	*
HZ	0	0.115				
NH3**	50	0.087	700:1	900:1	350:1	250:1
NH3**	50	0.041	2950:1	25000:1	2800:1	950:1
NH3**	50	0.020	*	3850:1	50000:1	1850:1
HZ + NH3	50	0.129	595:1	945:1	275:1	155:1
NH3	50	0.058	520:1	440:1	300:1	285:1
HZ	0	0.121				
HZ + NO	5	0.106	145:1	-715:1	170:1	170:1
NO	5	0.021	-80:1	315:1	*	*
HZ	0	0.094				
HZ + NO	5	0.102	835:1	-355:1	455:1	455:1
NO	5	0.026	*	315:1	*	*
HZ	0	0.121				
HZ + SO2	5	0.241	-1250:1	-280:1	-335:1	-500:1
SO2	5	0.185	*	355:1	*	*
HZ	0	0.107				
HZ + UDMH	0.658	0.464	0.85:1	NA	1.7:1	2.5:1
UDMH + HZ	0.126	0.126^	2.1:1	NA	42:1	4.8:1
UDMH	0.658	0.329	0.89:1	NA	NA	NA
HZ	0	0.126				
HZ + MMH	0.181	0.291	0.68:1	NA	1.7:1	1.6:1
MMH	0.181	0.181	0.88:1	NA	NA	NA
HZ	0	0.119				
HZ + FREONS	21	0.115	4200:1	-1100:1	*	2625:1
FREONS	21	0.016	*	1400:1	*	*
HZ	0	0.130				
HZ + ETHANOL	567	0.116	*	47000:1	*	*
ETHANOL	567	0.012	*	113000:1	*	*
HZ	0	0.130				

* Response negligible

** NH3 passed through clean air manifold

^ Calculated for UDMH; hydrazine in the interferent

NA No data available

Table 9

Tubing Pressure Drop for a Flow Rate of 26 l/min

Tubing Length (ft)	Pressure Drop (in Hg)
0	0
1.7	0.5
3	0.75
4.7	1.0
45	3.25
100	5.0

CONCLUSION

The MDA 7100 was relatively easy to maintain and did not exhibit any major operating problems during the course of the evaluation. The instrument's zero and span exposures were very stable. Overall, linearity was good for all the hydrazines although the accuracy was generally outside $\pm 25\%$ error. The response times of the instrument are comparable to those of the GMD detectors for hydrazine and MMH, but are lower for UDMH than the GMD instruments. The precision of the detector decreases with increasing concentration for hydrazine and MMH.

The accuracy of the MDA 7100 is poor for the hydrazines, although slightly better for MMH than hydrazine or UDMH. It was erratic for MMH and hydrazine but relatively stable for UDMH. For the majority of the exposures to all gases, the error was greater than $\pm 25\%$. The responses of the MDA 7100 were not significantly affected by humidity for the hydrazines.

During interferent testing, the only interferents in conjunction with hydrazine or MMH that produce a significant change in response are ammonia (if the sample lines have been previously exposed to a hydrazine), NO_2 , NO, and SO_2 . If sampling for a specific hydrazine, the other hydrazines, if present, will be detected with a different relative sensitivity.

Ammonia, when mixed with MMH elicited a response in all instruments tested. By itself, ammonia appeared at first to be an interferent to a lesser extent. It was tested several times by itself and each exposure to ammonia produced a smaller response than the previous exposure. During hydrazine interference tests, ammonia was passed through the clean air manifold. The instruments were exposed to it several times with the same trend occurring, a sharp response tapering off as the exposure continued. It appears that the ammonia was displacing the contaminated gas manifold of residual MMH in the first case. When passed through the clean air manifold, the ammonia must have stripped any residual hydrazine from the tubing used to sample gas from the manifold.

The overall performance of the MDA 7100 is worse than previously reported, but we are not sure why [2]. The instrument diagnostics do not indicate a problem, the paper tape is fresh, and the flow rate is accurate.

The MDA TLD-1 did not exhibit many operational problems during the course of the evaluation. The problem with slippage of the chemcassette take-up reel cover caused the instrument to alarm during a few exposures. The fact that the instrument was keyed for hydrazine and the range was so limited did not allow for many UDMH exposures and caused the instrument to read high for MMH and UDMH. At the TLV of MMH, the instrument often alarmed even though the actual gas concentration was within the instrument's range and below the alarm level.

The linearity of the TLD-1 was good for MMH and hydrazine and its responses were within 25% error for most of the linearity test exposures. The accuracy of the TLD-1 was very good for hydrazine. For the concentrations of MMH that were low enough for the range of the TLD-1, it responded within 25% error for about half of the exposures. The instrument proved to be very precise for TLV levels of hydrazine and for 80 ppb UDMH. Its accuracy for these tests was very good for hydrazine but poor for UDMH.

The response times for hydrazine and MMH were better than those of the MDA 7100 and the GMD detectors. The recovery times for hydrazine were lower than those of the other instruments tested. For MMH, the recovery times were comparable to the 7100. The TLD-1 is not significantly affected by changes in the relative humidity.

During interference testing, the instrument was not exposed to mixtures of MMH plus the interferent as the MMH was at TLV and the TLD-1 had a tendency to alarm. Ammonia, freons, NO, and SO₂ produce a change in response with MMH or hydrazine. NO and SO₂ produce a measurable response on their own. As explained previously, the ammonia effect appeared to be due to the gas stripping residual hydrazine from the tubing and mixing-chamber walls.

The GMD instruments were maintained easily during the evaluation. Other than the tendency of the instruments to miss a sampling period occasionally, there were no operational problems. The detectors were stable during eight hour zero and span gas exposures. The instruments show good linearity to the hydrazines. The responses were within 25% error for the hydrazine linearity curve up to 1 ppm.

The accuracy of the GMD instruments was poor initially when exposed to MMH. For hydrazine, it improved and was within 25% error for 50% of the exposures. The accuracy of both instruments began to decline for the remainder of the evaluation.

The GMD detectors had longer response and recovery times for UDMH than the MDA 7100. The response times were also longer for MMH and slightly longer for hydrazine. Unlike the MDA 7100 and the MDA TLD-1, the GMD detectors showed no significant effect on recovery times with a change in hydrazine concentration. For MMH and hydrazine, there is no apparent RH effect on response except for a very low response at 69 ppb hydrazine at 0% RH. The signal was very noisy at this concentration. For UDMH, the instruments' responses increase with increasing RH.

When exposed to the various interferents, the GMD detectors responded similarly to the MDA instruments. A mixture of MMH and freons produced a lesser response than that from MMH alone, giving a negative rejection ratio for the GMD detectors. The same response occurred with NO₂. With hydrazine, NO and freon produce measurable positive changes in response when mixed with hydrazine. SO₂ and hydrazine gave a negative change in instrument response. The effects of ammonia on the GMD instruments were similar to the MDA detectors.

The results of the tubing test on the GMD instruments indicate that the auxiliary pump is of limited use due to the small pressure drop tolerated by the instruments.

A qualitative summary is presented in table 10. Each instrument is ranked for each performance test as it compared with the other instruments. In areas where the instruments performed comparably, they were given the same score. The lowest final value reflects the instrument with the best overall performance. This approach places equal weight on each test. The user will have to determine the importance of the instrument's performance in each area based on his specific needs.

Table 10 Qualitative Summary of Instruments' Performance

Performance Tests	MDA 7100	TLD-1	GMD 1	GMD 2
Functionality	1	2	3	3
Warm-up Time	2	2	1	1
Zero Stability	1	1	1	1
Span Stability	1	N/A	1	1
Linearity	1	1	1	1
Response Time				
To 50%	2	1	3	3
To 90%	2	1	3	3
Recovery Time				
To 50%	2	1	4	3
To 90%	2	1	4	3
Precision	1	1	1	1
Accuracy	3	2	3	3
Sensitivity				
Lower Limit	3	1	2	3
Higher Limit	1	1	1	2
At Range Maximum	3	1	3	3
RH Effects	1	1	2	2
Interferents	1	1	1	1
Total	27	17	34	34

REFERENCES

1. J.A.E. Hannum, Recent Developments in the Toxicology of Propellant Hydrazines, Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. S.L. Rose and J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Report 8848, (1985).
3. Olson, E.C., Analytical Chemistry, 1960, 32, 1545.
4. J.R. Wyatt, S.L. Rose-Pehrsson, and K.P. Crossman, Remote Analysis of Monomethylhydrazine Using High Flow Sampling, Naval Research Laboratory, Washington, D.C., NRL Letter Report 6110-16a:KPC, (1988).



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UNSYMMETRICAL DIMETHYLHYDRAZINE DETECTION USING COMMERCIALY AVAILABLE PAPER TAPE INSTRUMENTS

INTRODUCTION

Hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) are widely used as high energy propellants. Because of the toxicological properties of the hydrazines, monitoring them at trace levels is necessary for personnel protection.

In 1983, Kennedy Space Center (KSC) sponsored an extensive side-by-side comparison of commercially available hydrazine, MMH, and UDMH detectors to determine the performance characteristics of the instruments under identical test conditions [1]. At NASA's request, a similar comparison was conducted on newly developed instrumentation [2]. KSC is concerned primarily with hydrazine and MMH. Therefore, most tests have concentrated on these vapors.

In order to provide the best protection for personnel who handle UDMH, the Air Force Space Division asked the Naval Research Laboratory to test and evaluate new and existing hydrazine monitoring instrumentation; emphasizing instrument performance in the presence of UDMH. This report reflects the effort of the Naval Research Laboratory in support of the Air Force Space Division's requirement for reliable monitoring instrumentation.

TEST APPARATUS AND DATA COLLECTION PROCEDURES

The instruments were evaluated using UDMH. The system used to generate known concentrations of the hydrazines has been described in detail [1]. This system uses sources of hydrazines and zero-grade air. Clean air, humidified to the desired level, flowed through one of two pyrex gas manifolds. Similarly humidified air mixed with the test vapor flowed through the other manifold. Instruments were connected to the two manifolds by solenoid valves. To control the concentration of the test gas, a UDMH diffusion source was placed in a constant temperature water bath and the quantity of dilution air was controlled. Mass flow controllers regulated the gas flows and the relative humidity (RH) was determined with a HygroDynamics hygrometer. The UDMH concentration was verified by impinger collection in 0.1 M H_2SO_4 that was analyzed by coulometric generation of bromine with amperometric endpoint detection [3]. The test vapor concentrations were measured in parts-per-million (ppm) by volume.

Data was collected in the following manner. The recorder output from each instrument was digitized and sampled with a Hewlett Packard Model 85 computer. The data collection program collected a maximum of 240 points from each instrument during a standard test. The first twenty-five data points were used to calculate the average, minimum, maximum and the standard deviation of the zero value. Then the gas collection process began. The cells sampled zero gas and the computer collected approximately one minute of baseline data. The solenoid valves were activated so that the instruments sampled contaminated gas. The computer continuously monitored the detectors' output for 20 minutes, then paused. The final stage was started and after one minute, the solenoid valves were deactivated to again sample zero gas.

The response curves for each detector were plotted and the average, minimum, maximum, zero, and span values as well as the corresponding standard deviation were displayed. The response and recovery times to 50, 75, and 90% of full scale were also determined. The response times were

evaluated from the time the solenoid valves were activated through the next 10 minutes. The full scale values were calculated from the next 10 minutes of data. The recovery times were evaluated for the 10 minutes following the deactivation of the solenoid valves. The final zero values were determined from the last 10 minutes of data. A complete exposure test cycle required 40 minutes.

TEST AND EVALUATION PROTOCOL

Functional Test

Evaluation of functionality and operator/instrument interface.

Warm-Up Time

Elapsed time required for the instrument, after being off for 15 hours, to perform as specified by manufacturer.

Zero Stability Test

Maximum absolute change in output response to zero input concentration over an 8 hour period of unadjusted operation is measured. We report mean, standard deviation, and maximum absolute deviations.

Span Stability Test

Eight-hour continuous exposure to TLV concentration and convenient higher concentrations are monitored. We report mean, standard deviation, and maximum absolute deviations.

Linearity

The instruments are tested using concentrations of UDMH from 0.0-1.5 ppm.

Response and Recovery Time

At several UDMH concentrations, the following tests are run: rise time to 50, 75, and 90% of final value; and recovery time to 50, 75, and 90% of final zero.

Precision

Comparisons are made of several identical measurements during an eight hour period. The instruments are tested at TLV and other convenient concentrations.

Sensitivity - Lower/Upper Limits of Detection

A sample of the analyte is successively diluted until a measurable response can no longer be discerned. Instrument response at 1.5 ppm is also determined.

Accuracy

Compare instrument response with an approved method [3] to assess error from zero to full scale, including the TLV. We report mean and standard deviation of absolute errors at representative points, including the TLV.

Relative Humidity Effects

Instrument responses are compared using several known concentrations of UDMH while varying the relative humidity.

Interference Test

Sensitivity to chemical interferents is determined in the following sequence of tests: expose to known concentration of UDMH; expose to interference compound; then expose to the same concentration of UDMH plus the test interference compound. The following chemicals are evaluated:

- freons
- sulfur dioxide
- nitrogen dioxide
- ammonia
- nitric oxide
- acetone

TEST INSTRUMENTS

Two MDA Scientific, Inc. instruments were evaluated, the MDA 7100 and the MDA TLD-1. The MDA 7100 is a fixed point monitor while the TLD-1 is a portable instrument. The MDA 7100 and TLD-1 detectors use cassette detector tapes which contain a chemically impregnated paper that is exposed to a known volume of gas. Hydrazines in the gas sample reduce the substance on the paper tape and a blue stain is formed. The intensity of the stain is related to the amount of hydrazine present. The optical reflectivity of the stain is measured and the concentration of the hydrazine is calculated and displayed on a meter which reads in ppb. The MDA 7100 and the MDA TLD-1 have factory set ranges of 0 to 5000 ppb and 0 to 1500 ppb respectively, for UDMH. Although the TLD-1 instrument we tested was specifically set for UDMH monitoring, it can be adjusted by the company to measure levels of MMH and hydrazine. The digital display on the instrument reads from 0 to 1499 ppb, with the first non-zero output being 50 ppb.

Both instruments were operated from line voltage. The MDA TLD-1 has an internal battery pack which was not used during the evaluation. The instruments were switched off overnight and operated for an eight hour period each day.

TEST AND EVALUATION

Functional Test

The following is an evaluation of the instruments' functionality and the operator/instrument interface. We also report the effort required to maintain the instruments in operating condition. The chemcassettes in both instruments were replaced every two weeks while in use and the air sampling rate was checked periodically. Each time the chemcassettes were replaced, the MDA 7100 was calibrated with the calibration card provided by the manufacturer. The system response of the MDA TLD-1 was also verified with its accompanying test card.

Being a fixed point monitor, the MDA 7100 is large and heavy. This did not cause a problem as it is easy to open up and make adjustments. The 7100 was relatively easy to maintain. Replacing the chemcassette or calibrating the instrument consisted of setting the appropriate function using the escape and set buttons on the face of the instrument, then lifting the top of the instrument to complete the task. Calibration of the instrument can be carried out in several ways; the easiest being card calibration with the card provided. Replacing the paper tape cassette is more complicated. First

the instrument is set in the cassette replacement mode to allow the user to remove the paper tape from the detector head. The used cassette has to be unwound from the take-up spool and the new tape threaded. This is the most time-consuming task in the maintenance of this instrument. During an earlier evaluation of this instrument, it was discovered that the sample inlet port was fitted with a sharp metal ferrule that abraded and punctured the teflon tubing used as the sample probe. The ferrule was removed and the tubing fed directly into the detection head. The outside area surrounding the inlet was covered with black tape to keep out stray light.

The audio and visual alarms can be adjusted to alarm at any concentration within the instrument's parameters. The audio alarm can also be disabled. The MDA 7100 features a flowmeter on the face of the instrument. Due to error in the instrument's flowmeter, the instrument's flow rate was verified with a rotameter placed in the sample line. During the testing period, the flow rate of the MDA 7100 remained within approximately 10% of the set flow rate of 800 ml/min. The sampling rate was adjusted to 800 ml/min when it drifted. The 7100 model is equipped with a hardcopy printout device in addition to the digital display. An update of the detector's response to the gas concentration was printed every minute below the programmed alarm levels. Above these levels, the concentration is printed out every minute.

The MDA TLD-1 is a compact and lightweight portable monitor. It required little maintenance. It was easy to replace the chemcassette, verify the system response, turn the instrument on, and access the alarm buttons. Replacing a cassette required threading the paper tape through the instrument and onto the take-up reel. The cover of the reel was then snapped on.

The instrument is supplied with a test card which was used to verify the system response. This card was simple to use and the system response was verified each time the chemcassette was replaced. The alarms on the instrument are factory preset and cannot be changed by the user. For UDMH, the audio alarm was originally set at 500 ppb. This was a problem during high concentration exposures, therefore, the instrument was returned to the manufacturer where the alarm was disabled. The visual alarms were still functioning. There is no flowmeter on the instrument. We initially measured the flow rate to be approximately 800 ml/min. During the testing period, the sampling rate varied within 10% of the initial reading. The detector does not have a hardcopy printout; however, the instrument has an analog output which can be connected to a strip chart recorder or other device.

Warm-Up Time

The MDA 7100 achieves a stable zero response as soon as the instrument is turned on. It takes two minutes for the first reading to print out. When calibrating the instrument, there is an initial warm-up period of approximately three minutes when the card calibration mode is first entered. To begin displaying a stable zero reading on zero gas, the MDA TLD-1 requires 1.5 minutes after the instrument is turned on. The display reads "Battery OK" for this entire period.

Zero Stability

Two eight hour zero stability tests were conducted on the instruments using clean air. The first test was conducted after three weeks of testing. The humidity was set at 45%. The TLD-1 displayed little overall drift for the duration of the test. The 7100 model showed no overall drift, however, approximately halfway through the test, the instrument output dipped dramatically for a very short period of time. The eight hour time weighted average generated by the instrument shows a drift of 0 ppb. Eleven weeks into the testing period, a second zero stability test was conducted with low humidity. The instruments showed no significant drift for the testing period. Table 1 lists the mean, standard deviation, and maximum absolute deviation of the zero test for each instrument.

Span Stability

Two eight hour span stability tests were conducted during the same weeks that the zero stability tests were conducted. The instruments were exposed to 740 ppb of UDMH at 45% RH for

Table 1. Zero Stability Test for Clean Air

	TEST RUN	MEAN (ppm)	STD DEV (ppm)	MAX ABSOLUTE DEV (ppm)
MDA 7100	1	0.001	0.028	0.169
	2	0.002	0.003	0.005
MDA TLD-1	1	0.001	0.001	0.002
	2	0.001	0.001	0.002

Table 2. Span Stability Test for UDMH

	TEST RUN	MEAN (ppm)	STD DEV (ppm)	MAX ABSOLUTE DEV (ppm)
MDA 7100	1	0.477	0.015	0.062
	2	0.235	0.013	0.056
MDA TLD-1	1	1.34	0.088	0.400
	2	0.562	0.019	0.074

the first test. The drifts in output response during the test were 62 ppb for the MDA 7100, and 400 ppb for the MDA TLD-1. The signal for the MDA TLD-1 was very noisy. The reason for the high drift of the MDA TLD-1 signal is not clear. In the second test, the UDMH concentration was 551 ppb at 50% RH. The instruments showed drifts of 56 ppb for the MDA 7100 and 74 ppb for the MDA TLD-1. Table 2 gives the mean, standard deviation, and maximum absolute deviation of the span test for each instrument.

Linearity

Two linearity tests were performed on the instruments for UDMH. One was performed early in the testing period, the other during the last week of the testing period. Figures 1a through 2b represent linear, unweighted least square fits of the data obtained from each instrument.

As shown in Figure 1a, the MDA 7100 responded in a linear fashion to the gas early in the testing period. The instrument's responses to >1 ppm UDMH are outside $\pm 25\%$ error. The data point at 1.27 ppm in this linearity plot was obtained from a gas stream with 78% RH. The remainder of the exposures were performed at 45% RH. Figure 1b shows the linearity of the MDA TLD-1 in the first few weeks of testing the instruments. The detector showed good linearity, but the responses were outside $\pm 25\%$ error. Figure 2a shows the linearity curve for the MDA 7100 during the final week of testing. The detector exhibited linear responses throughout the range of UDMH tested, however, its responses were outside $\pm 25\%$ error. The overall linearity during the final week of testing of the TLD-1 was not as good as seen previously, although the detector's responses through TLV were quite linear. The data points all fell within $\pm 25\%$ error. The linearity plot for this exposure is shown in Figure 2b.

Response and Recovery Times

The response time of the MDA 7100 to UDMH was dependent upon the concentration of the UDMH and the relative humidity (RH) of the tests atmosphere. Generally, the instrument response time increased with increasing humidity. An increase in UDMH concentration caused a decrease in response time. The response time of the MDA TLD-1 was not dependent on these variables. Tables 3a and b show the response times of the MDA 7100 and the TLD-1 models respectively. The tables are broken down into concentration of the UDMH and relative humidity. The response times of the two instruments were comparable at 0% RH. At high relative humidities, the TLD-1 displayed much shorter response times than the 7100.

A similar trend occurred for the recovery times of the instruments. The MDA 7100 showed a slight dependence on relative humidity; however, the concentration of the UDMH had little effect on the recovery times of the MDA 7100. The MDA TLD-1 was not affected in any consistent manner by varying the humidity or the concentration of the UDMH. The data for the recovery times is included in Tables 4a and b. These tables are also broken down according to concentration and RH.

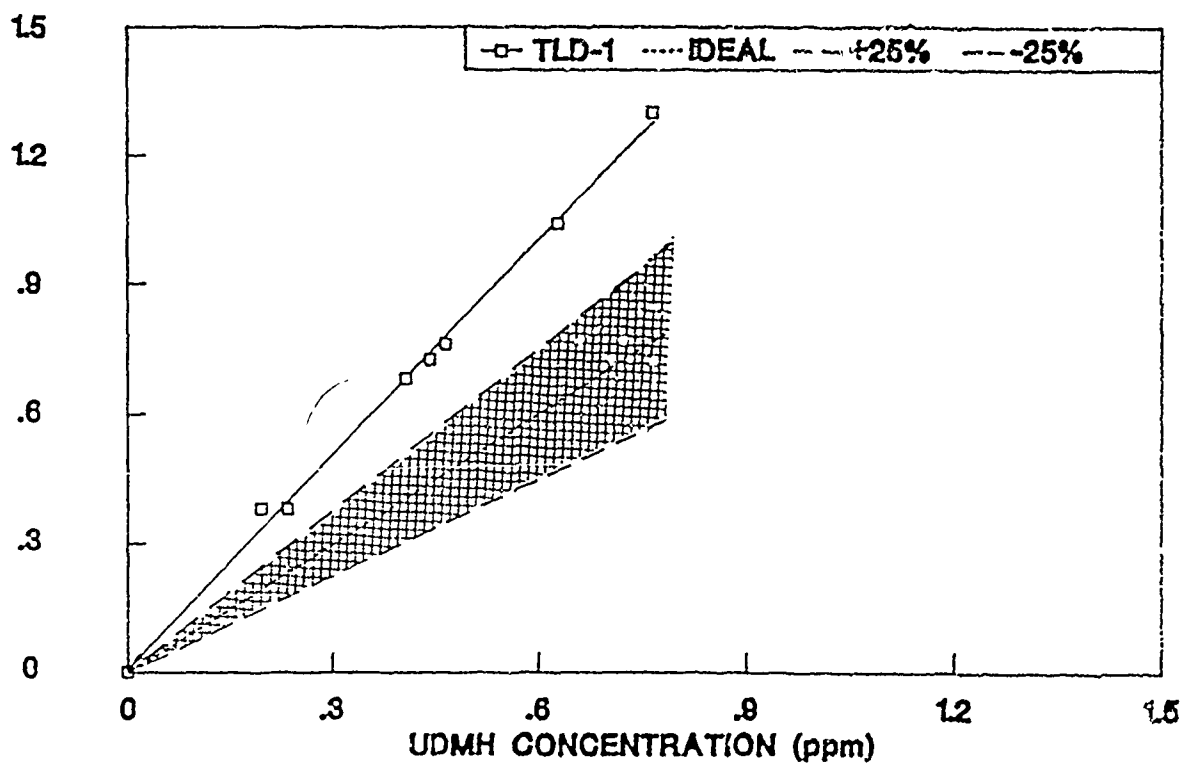
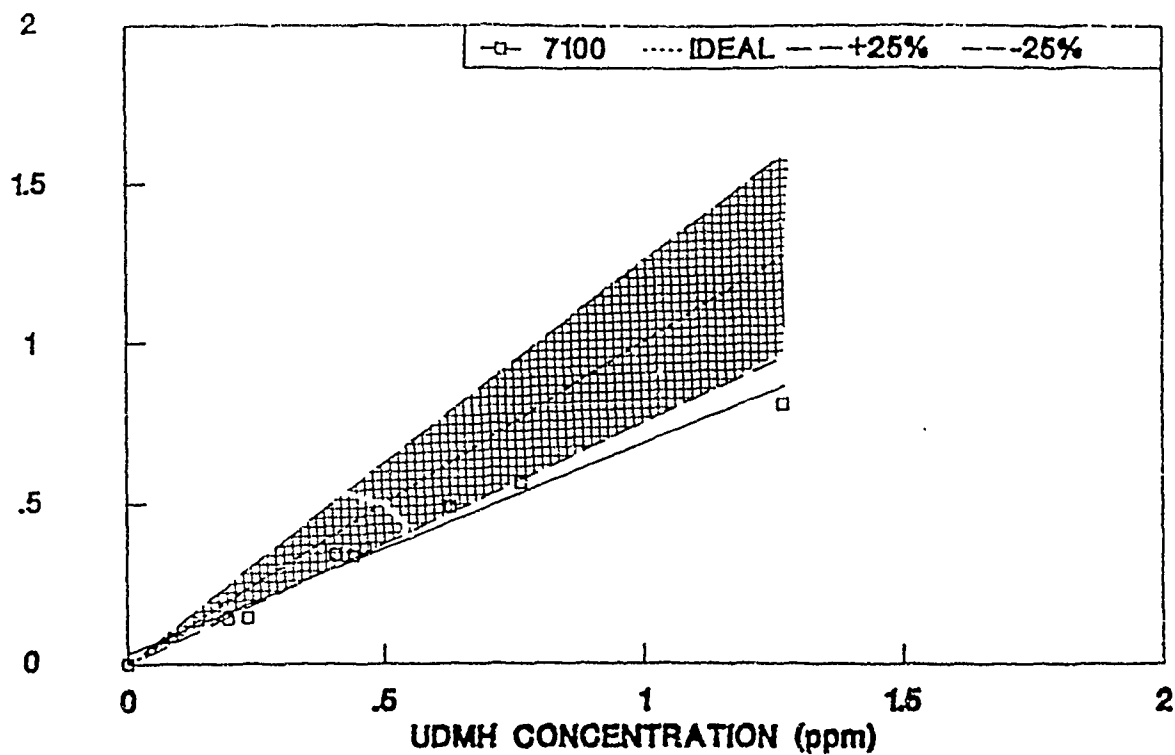
Precision

The precision of each instrument was evaluated by exposing them several times in an eight hour period to a particular concentration of UDMH. This was done for several different concentrations of UDMH. Table 5 shows the precision data for the instruments.

Both instruments displayed very good reproducibility through 0.8 ppm of UDMH. At 1.3 ppm, the MDA 7100 showed fair precision though the instrument's responses were not as reproducible as for lower concentrations. At 1.3 ppm, the MDA TLD-1 became saturated. The accuracy of the instruments during these tests is also included in Table 5. The 7100 model shows error ranging from -24% to -49% , while the TLD-1 model displays error of $+52\%$ to $+86\%$.

Sensitivity- Lower/Upper Limits of Detection

A theoretical lower detection limit was calculated as follows. The MDA 7100 shows noise of



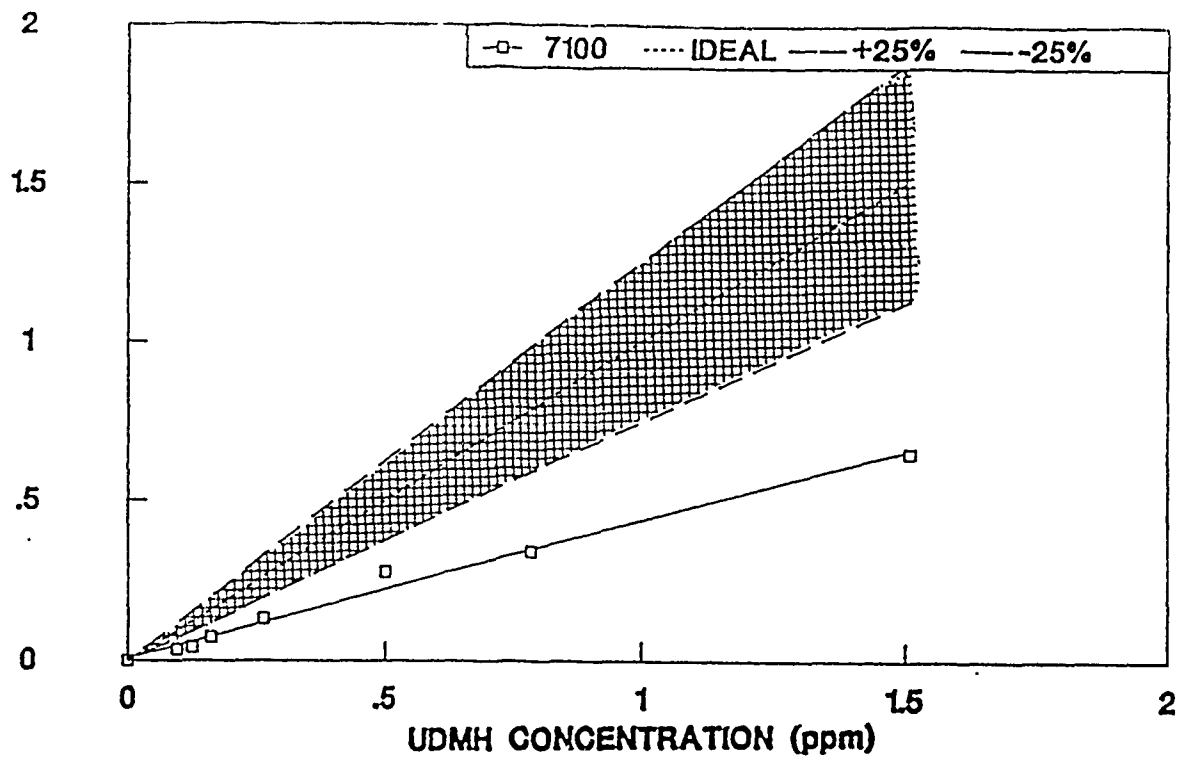


Fig. 2a. Linearity plot of MDA 7100 for UDMH at end of test period

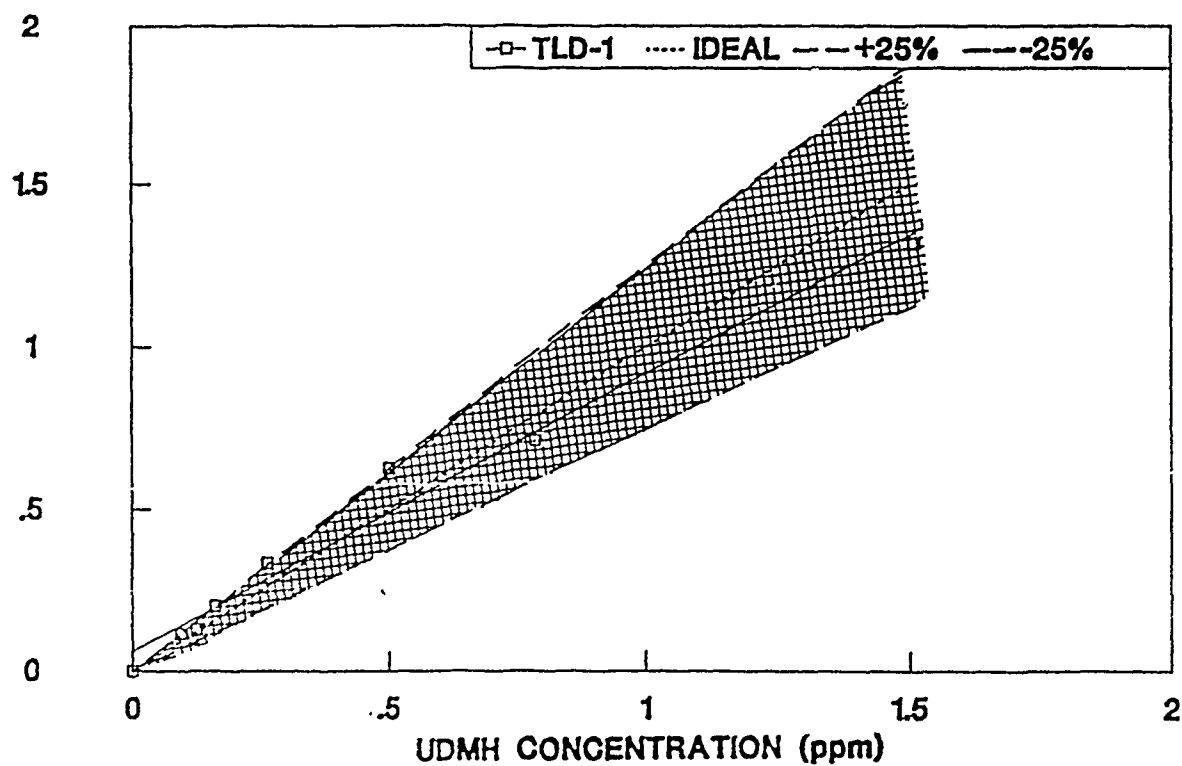


Fig. 2b. Linearity plot of TLD-1 for UDMH at end of test period

Table 3a. Response Time of MDA 7100 to UDMH

UDMH CONC. (ppb)	% RH	Response Times in Minutes (Std Dev)		
		50%	75%	90%
80	46	3.9 (1.1)	4.5 (0.53)	4.7 (0.56)
105	0	1.7 (0.35)	1.9 (0.35)	2.0 (0.3)
	22	3.2 (0.65)	3.4 (0.65)	3.5 (0.7)
	41	2.5 (0.45)	6.1 (1.9)	6.3 (1.8)
	73	8.6 (1.4)	9.1 (0.90)	10.0 (0.0)
180	28	1.5	3.7	7.2
	47	2.6 (0.23)	4.3 (0.43)	8.5 (1.5)
240	0	1.9 (0.10)	2.1 (0.10)	2.5 (0.30)
	37	2.0 (0.24)	3.6 (0.82)	6.6 (1.1)
	54	3.6 (1.5)	6.2 (2.8)	8.6 (2.0)
490	0	1.6 (0.25)	1.8 (0.25)	2.0 (0.25)
	26	1.7 (0.51)	2.4 (0.13)	4.7 (0.87)
	50	2.0 (0.38)	2.9 (0.37)	4.7 (0.87)
	77	3.6 (0.28)	4.6 (0.49)	7.3 (1.4)
750	0	1.4 (0.22)	1.6 (0.31)	3.1 (2.1)
	23	1.6 (0.22)	2.0 (0.21)	3.1 (0.86)
	47	2.0 (0.36)	2.6 (0.42)	4.3 (0.65)
	75	3.4 (0.35)	4.9 (0.15)	5.9 (0.15)
1000-1500	49	1.5 (0.14)	2.1 (0.33)	2.9 (0.40)
	78	2.4 (0.35)	3.8 (0.45)	6.0 (1.3)

Table 3b. Response Time of MDA TLD-1 to UDMH

UDMH CONC. (ppb)	% RH	Response Times in Minutes (Std Dev)		
		50%	75%	90%
80	46	1.5 (0.38)	2.1 (0.18)	2.4 (0.21)
105	0	1.6 (0.10)	1.8 (0.05)	2.3 (0.25)
	22	1.9 (0.10)	2.1 (0.10)	2.6 (0.25)
	41	1.6 (0.37)	2.3 (0.36)	2.6 (0.51)
	73	1.4 (0.40)	2.1 (0.10)	3.0 (0.25)
180	28	1.7	1.8	2
	47	1.5 (0.33)	2.1 (0.23)	2.5 (0.17)
240	0	1.4 (0.49)	1.9 (0.29)	2.3 (0.12)
	37	1.0 (0.0)	2.1 (0.10)	2.3 (0.05)
	54	1.6 (0.33)	1.8 (0.37)	2.4 (0.19)
490	0	1.3 (0.45)	1.9 (0.10)	2.1 (0.10)
	26	1.4 (0.27)	1.9 (0.25)	2.4 (0.81)
	50	1.5 (0.31)	1.9 (0.28)	2.3 (0.82)
	77	1.7 (0.36)	2.1 (0.59)	3.0 (0.82)
750	0	1.2 (0.22)	1.6 (0.29)	2.1 (0.21)
	23	1.4 (0.27)	1.8 (0.37)	2.2 (0.37)
	47	1.7 (0.35)	2.1 (0.24)	2.3 (0.19)
	75	1.9 (0.10)	2.1 (0.10)	2.3 (0.05)
1000-1500	49	1.5 (0.40)	1.8 (0.33)	2.0 (0.35)
	78	1.5 (0.20)	1.7 (0.15)	1.9 (0.15)

Table 4a. Recovery Time of MDA 7100 to UDMH

UDMH CONC. (ppb)	% RH	Recovery Times in Minutes (Std Dev)		
		50%	75%	90%
80	46	2.0 (0.38)	4.9 (1.2)	5.1 (1.1)
105	0	1.2 (0.15)	1.8 (0.25)	2.0 (0.25)
	22	1.8 (0.05)	2.4 (0.15)	2.5 (0.20)
	41	1.8 (1.0)	3.2 (1.5)	3.3 (1.3)
	73	4.2 (2.4)	8.4 (1.7)	10.0 (0.0)
180	28	1.7	1.8	2
	47	2.2 (0.21)	4.2 (1.4)	5.1 (0.92)
240	0	1.5 (0.25)	1.6 (0.25)	2.2 (0.15)
	37	2.0 (0.41)	2.5 (0.24)	3.5 (0.36)
	54	1.8 (0.12)	2.7 (0.50)	6.3 (0.14)
490	0	1.3 (0.0)	1.5 (0.0)	1.7 (0.0)
	26	1.4 (0.44)	2.0 (0.23)	2.4 (0.29)
	50	1.7 (0.37)	2.2 (0.23)	3.3 (0.66)
	77	2.2 (0.25)	3.3 (0.26)	6.0 (1.6)
750	0	1.5 (0.41)	1.8 (0.39)	2.2 (0.21)
	23	1.5 (0.39)	1.9 (0.32)	2.4 (0.12)
	47	1.6 (0.28)	2.1 (0.29)	3.0 (0.41)
	75	2.1 (0.25)	3.3 (0.25)	5.0 (0.70)
1000-1500	49	1.6 (0.23)	2.2 (0.34)	2.7 (0.12)
	78	1.5 (0.0)	2.7 (0.0)	3.8 (0.0)

Table 4b. Recovery Time of MDA TLD-1 to UDMH

UDMH CONC. (ppb)	% RH	Recovery Times in Minutes (Std Dev)		
		50%	75%	90%
80	46	1.8 (0.12)	1.9 (0.16)	2.1 (0.13)
105	0	1.6 (0.40)	1.8 (0.45)	1.9 (0.40)
	22	1.9 (0.15)	2.0 (0.20)	2.2 (0.15)
	41	1.3 (0.11)	1.5 (0.14)	1.7 (0.11)
	73	1.4 (0.10)	1.6 (0.10)	1.75 (0.05)
180	28	2	2.2	2.3
	47	1.5 (0.30)	1.9 (0.35)	2.0 (0.21)
240	0	1.0 (0.0)	1.6 (0.40)	1.8 (0.45)
	37	1.7 (0.29)	1.8 (0.29)	2.0 (0.20)
	54	1.4 (0.49)	1.9 (0.22)	2.0 (0.21)
490	0	1.6 (0.10)	1.8 (0.05)	1.9 (0.10)
	26	1.4 (0.32)	1.7 (0.28)	1.9 (0.10)
	50	1.4 (0.21)	1.6 (0.20)	2.1 (0.27)
	77	1.4 (0.34)	1.8 (0.29)	2.1 (0.18)
750	0	1.3 (0.15)	1.9 (0.34)	2.1 (0.33)
	23	1.2 (0.24)	1.7 (0.40)	2.1 (0.22)
	47	1.5 (0.33)	1.7 (0.29)	2.1 (0.16)
	75	1.9 (0.15)	2.0 (0.20)	2.2 (0.15)
1000-1500	49	1.7 (0.29)	2.1 (0.19)	2.3 (0.18)
	78	1.5 (0.50)	2.1 (0.10)	2.3 (0.05)

Table 5. Precision Test for UDMH

IMPINGER CONC. (ppb)	MDA 7100 (ppb)	MDA TLD-1 (ppb)
78	43	150
	40	146
	38	136
MEAN	40	147
STD DEV	2	6
ACCURACY (% ERROR)	-49	85
235	142	373
	149	397
	142	375
MEAN	144	382
STD DEV	3	11
ACCURACY (% ERROR)	-39	63
442	320	737
	330	707
	350	716
	348	738
MEAN	337	725
STD DEV	13	13
ACCURACY (% ERROR)	-24	64
724	452	1260
	472	1410
	467	1390
MEAN	434	1350
STD DEV	8	66
ACCURACY (% ERROR)	-40	86
804	607	1270
	607	1220
	604	1190
MEAN	606	1230
STD DEV	1	33
ACCURACY (% ERROR)	-25	53
1270	806	*
	855	*
	997	*
MEAN	886	
STD DEV	81	
ACCURACY (% ERROR)	-32	

* Instrument became saturated

Table 6a. Lower Limit of Detection of Instruments to UDMH

UDMH CONC. (ppb)	Instrument Response (% Error)	
	MDA 7100 (ppb)	MDA TLD-1 (ppb)
26*	14 (-46)	0
44*	15 (-66)	0
77*	20 (-74)	60 (-22)
78	41 (-48)	144 (+84)
86	43 (-50)	136 (+58)
89*	24 (-73)	73 (-18)

* UDMH and water solution used to generate gas in the final week of the test.

Table 6b. Upper Limit of Detection of Instruments to UDMH

UDMH CONC. (ppm)	Instrument Response (% Error)	
	MDA 7100 (ppm)	MDA TLD-1 (ppm)
0.804	0.603 (-25)	1.22 (+52)
1.51	0.660 (-56)	1.32 (-12)

± 5 ppb, and the MDA TLD-1 shows noise of ± 2 ppb. With a signal to noise ratio of 3:1 being the lowest acceptable, the estimated limits of reliable detection for the instruments are: 30 ppb for the MDA 7100 and 12 ppb for the MDA TLD-1. Table 6a shows the instrument responses to low gas concentrations as well as the accuracy of those responses. At a concentration of 26 ppb, the MDA 7100 responded while the MDA TLD-1 did not. A lower concentration of 20 ppb had been attained; however, neither instrument showed a response to the gas stream at this concentration. The first response of the TLD-1 occurred at 77 ppb UDMH. In order to generate the lower UDMH concentrations, the UDMH in the diffusion tube of the gas generation system was diluted with water. Exposures to the gas stream generated by this method are marked with an asterisk. There are dramatic differences in instrument response between those obtained from a UDMH gas stream generated from a mixture of water and UDMH, and those from neat UDMH. The two gas streams were generated at different times in the test program. The exposures to the UDMH gas stream generated as stated in the Test Apparatus section of this report, were made 4.5 weeks into the test period. The final exposures to the gas stream generated by dilution of UDMH with water were made in the last week of testing. As observed in Figure 3, the overall sensitivity of the MDA TLD-1 and the MDA 7100 instruments dropped by 40% and 20% respectively between these tests.

The upper limits of detection for the instruments were not measured. Table 6b lists instrument responses at approximately 1.5 ppm UDMH. When the TLD-1 was exposed to 1.3 ppm of UDMH 17 days into the testing period, its response became saturated at 1.6 ppm. At 64 days, the TLD-1 was subjected to 1.5 ppm of UDMH. This time the response was within the instrument's range.

Accuracy

Each time the instruments were exposed to UDMH, the signal output was taken as a measure of accuracy. The responses of the instruments were compared to the results from the wet chemical method of quantitation referenced earlier [3]. From this, the accuracy was determined. Accuracy data, in the form of percentage of error, was plotted for each instrument for the entire test period.

Figure 3 details the error in accuracy for each instrument. The graph of the TLD-1 indicates substantial scatter and high responses. The MDA 7100 shows slightly better accuracy and the instrument's responses from exposure to exposure are more consistent than those of the TLD-1. For the testing period from day 1 through day 65, the average of the instruments' accuracy reported in percent error is -38% with a standard deviation of $\pm 13\%$ for the 7100 and +54% with a standard deviation of $\pm 30\%$ for the TLD-1. Data points taken between day 100 to day 109 were obtained when generating low UDMH concentrations for the detection limit test. When these data points are averaged in, the overall accuracy in percent error of the MDA 7100 is -40% with a $\pm 15\%$ standard deviation. The error of the TLD-1 is +51% with a standard deviation of $\pm 33\%$.

Relative Humidity Effects

Both instruments were subjected to various concentrations of UDMH at relative humidities from 0 - 79%. Table 7 shows the instrument responses with varying humidity and UDMH concentration. There did not appear to be any variations in accuracy of response due to changes in humidity. As mentioned previously, the response and recovery times of the MDA 7100 were affected by changes in the relative humidity.

Interference Effects

A number of compounds were evaluated both individually and jointly with UDMH to determine their effect on the response of the instruments. A more extensive interference test was previously carried out with hydrazine and MMH [2]. Therefore, only those compounds which had been shown to interfere with hydrazine and/or MMH were tested with UDMH. Table 8 shows the rejection ratios calculated for the various compounds. A rejection ratio is a measure of the amount of compound required to produce a response similar to 1 ppm of a hydrazine.

All interferents tested, with the exception of NH_3 , when mixed with UDMH, produced a response less than that produced by UDMH alone; thereby giving negative rejection ratios. When the

instruments were exposed to each interferent alone, they did not give significant responses. Ammonia produced a positive response in the instruments when UDMH was not present. When mixed with UDMH, ammonia also caused an increase in the response of both instruments as compared to the responses of the instruments exposed to UDMH alone.

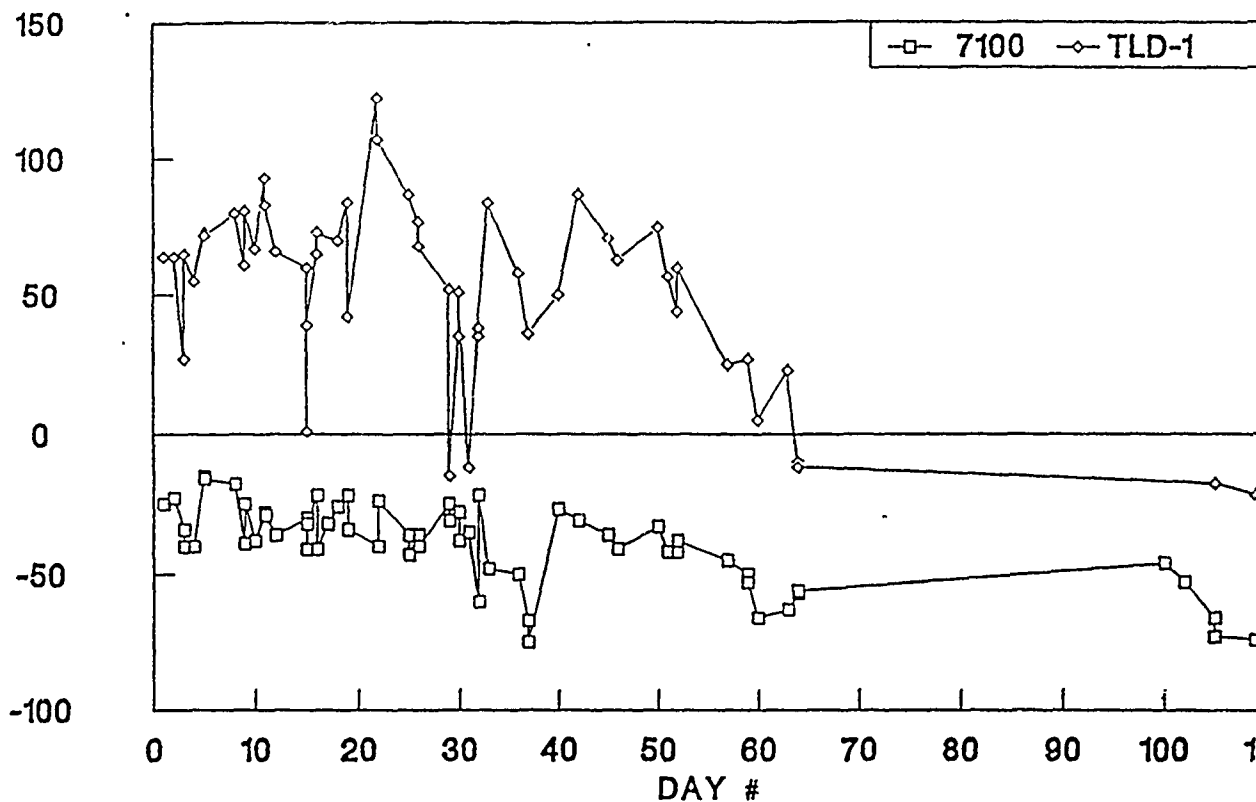


Fig. 3. Percent error in response to changing gas challenge as a function of time

Table 7. Relative Humidity Effects with UDMH

UDMH CONC. (ppb)	% RH	Percent Error of Impinger	
		MDA 7100	MDA TLD-1
94	0	-60	35
94	22	-22	38
86	47	-50	56
104	64	-67	36
104	75	-75	36
238	0	-30	60
238	28	-36	66
197	28	-29	83
235	37	-39	61
197	47	-28	93
226	59	-38	67
462	0	-34	27
403	23	-15	73
465	30	-23	64
411	45	-16	72
462	54	-25	65
472	74	-40	55
664	0	-41	1
664	23	-32	39
628	47	-22	65
628	79	-41	73
647	0	-34	42
647	23	-22	84
626	44	-24	7
600	76	-40	22
802	0	-34	87
791	23	-28	35
804	46	-25	52
791	75	-38	51

Table 8. Rejection Ratios From Interference Tests

Compounds	Interferent Conc. (ppm)	Coulometric Conc. (ppm)	MDA 7100 (ppm)	MDA TLD-1 (ppm)
UDMH + Freons	20	0.40	-370:1	-145:1
Freons	20	0.02	*	*
UDMH	0	0.46		
UDMH + NO	5	0.42	-420:1	-96:1
NO	5	0.01	*	*
UDMH	0	0.50		
UDMH + NH3	50	0.45	94:1	83:1
NH3	50	0.02	1920:1	5000:1
UDMH	0	0.43		
UDMH + NO2	1	0.42	-83:1	-63:1
NO2	1	0.03	*	*
UDMH	0	0.43		
UDMH + SO2	5	0.90	-67:1	-35:1
SO2	5	0.42	*	*
UDMH	0	0.52		
UDMH + Acetone	1665	0.47	-189000:1	-79000:1
Acetone	1665	0.04	*	*
UDMH	0	0.47		

* Response negligible

CONCLUSION

The MDA 7100 was relatively easy to maintain and did not exhibit any major operating problems during the course of the evaluation. The instrument's overall eight hour zero and span exposures were stable. Linearity was good although the accuracy during the second linearity test was outside $\pm 25\%$ error. Cassette tapes tested at Kennedy Space Center have shown variations in sensitivity to MMH up to 25%. If this variation occurs with UDMH, it could explain the differences between the linearity tests. A different cassette tape was exposed to UDMH for the first test than that used for the second linearity test. The response times of the instrument are dependent on the UDMH concentration and the relative humidity of the test atmosphere. The recovery times show a slight dependence on the relative humidity of the test vapor. The detector showed very good reproducibility through 0.8 ppm of UDMH. It dropped off slightly at 1.3 ppm. The accuracy of the MDA 7100, though poor for UDMH, was relatively stable and slightly better than that of the TLD-1. The accuracy of the instrument was not significantly affected by varying the humidity of the test atmosphere. The 7100 responds to a test UDMH atmosphere of as low as 26 ppb. At 0.8 ppm, the instrument responds to within $\pm 25\%$ error. When exposed to 1.5 ppm, the accuracy drops off to $\pm 56\%$ error.

Except for ammonia, the interferents tested with UDMH gave negative rejection ratios. Ammonia, when mixed with UDMH elicited a response in both instruments. By itself, ammonia appeared at first to be an interferent to a lesser extent. This behavior was noted previously with MMH and hydrazine [2]. The conclusion reached during the earlier testing with ammonia was that the ammonia had stripped any residual hydrazine from the tubing used to sample gas from the manifold. Therefore, the instruments gave positive responses.

The overall performance of the MDA 7100 is comparable to that previously reported [2].

The MDA TLD-1 did not exhibit many operational problems during the course of the evaluation. The audio alarm, originally set at 500 ppb, caused some problems as the TLD-1 gave high responses to the test gas. The alarm was disconnected by the manufacturer and testing was resumed.

The detector showed very stable zero gas stability over an eight hour period. At 740 ppb, the TLD-1 gave a very high overall response and the deviation in response was rather high at 400 ppb. During the second eight hour span gas exposure at TLV, the instrument displayed good signal stability with a low deviation in response during the test period. The linearity of the TLD-1 was good during the first test, however, the responses were outside $\pm 25\%$ error. For the subsequent linearity test, the instrument displayed linear responses through TLV. The response are within $\pm 25\%$ error for the range tested. As mentioned previously, the variations in sensitivity of different cassettes noted at KSC could explain the differences between the two linearity tests for the TLD-1.

The response and recovery times were better than those of the MDA 7100. The TLD-1 is not significantly affected by changes in the UDMH concentration or relative humidity. The lower limit of detection for the instrument is near 77 ppb UDMH. When exposed to 1.3 ppm early in the testing, the instrument response was outside of its range. However, at a later date, the detector was exposed to 1.5 ppm of UDMH and it gave a response of 1.3 ppm. The accuracy of the TLD-1 was poor for UDMH and showed significant scatter during the 110 days of testing.

The TLD-1 gave responses to the interferents tested comparable to those of the MDA 7100. Ammonia also caused an increase in response for the instrument. As explained previously, the ammonia effect appeared to be due to the gas stripping residual hydrazine from the tubing and mixing-chamber walls.

A qualitative summary is presented in Table 9. The instruments are ranked for each performance test as compared with each other. In areas where the instruments performed comparably, they were given the same score. The lowest final value reflects the instrument with the best overall performance. This approach places equal weight on each test. The user will have to determine the importance of the instrument's performance in each area based on his specific needs. Although precision and linearity are acceptable for both instruments, their accuracy could be improved by adjusting the internal calibration curves of the detectors.

Table 9. Qualitative Summary of Instrument Performance

Performance Tests	MDA 7100	MDA TLD-1
Functionality	1	1
Warm-up Time	1	1
Zero Stability	2	1
Span Stability	1	2
Linearity	1	2
Response Time		
To 50%	2	1
To 90%	2	1
Recovery Time		
To 50%	2	1
To 90%	2	1
Precision	1	1
Accuracy	1	2
Sensitivity		
Lower Limit	1	2
Higher Limit	2	1
RH Effects	2	1
Interferents	1	1
Total	22	19

REFERENCES

1. S.L. Rose and J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Report 8848, (1985).
2. K.P. Crossman, S.L. Rose-Perhsson, and J.R. Wyatt, A Comparison of Commercially Available Paper Tape Hydrazine Detectors, Naval Research Laboratory, Washington, D.C., NRL Letter Report 6110-181:KPC, (1989).
3. Olson, E.C., Analytical Chemistry, 1960, 32, 1545.

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13. ABSTRACT (Maximum 200 words) A passive sampler-dosimeter has been developed for evaluating part-per billion (ppb) levels of hydrazine and monomethyl hydrazine (MMH) in ambient air. It is designed for quantitative documentation of personnel exposures as well as ambient atmosphere concentrations. It has undergone extensive laboratory and field evaluations. The laboratory tests are reviewed in this report. Tests were conducted in controlled atmospheres to evaluate the following performance parameters: collection rate, face velocity, relative humidity effects, sample stability, reproducibility, linearity, and interference effects of selected chemical vapors. Field tests were conducted to evaluate performance under typical anticipated conditions. The test locations were selected to provide information on the probable interferents. A double-bind protocol was used which involved three groups: industrial hygienists; analytical chemists; and auditors. The data obtained from the field evaluation disclosed a performance problem not encountered in the laboratory. The cause was identified and the prototype system was modified and re-tested. The results from the modified sampler indicate that it is suitable for work place monitoring applications with two minor interferents: tobacco smoke and intense direct sunlight.				
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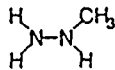
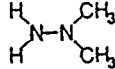
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FIELD VALUATION OF A PASSIVE SAMPLING DEVICE FOR HYDRAZINES IN AMBIENT AIR

INTRODUCTION

The potential carcinogenicity of hydrazine (Hz), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) has caused concern for the health and safety of the workers who may be exposed to them. For brevity the term "hydrazines" in this report is used to mean any of these three hydrazines. The chemical structures of these compounds and their ACGIH [1], NIOSH [2], and proposed [3] recommended exposure limits are listed in Table 1.

Table 1. Recommended Exposure Levels for Hydrazine Propellants

<u>Compound</u>	<u>Structure</u>	<u>ACGIH</u>	<u>NIOSH</u>	<u>Proposed</u>
Hydrazine		0.1 ppm	0.03 ppm	0.01 ppm
Monomethyl Hydrazine		0.2 ppm	0.04 ppm	0.01 ppm
Unsymmetrical Dimethylhydrazine		0.5 ppm	0.06 ppm	0.01 ppm

Monitoring of personnel exposure and the work place environment is necessary to insure that exposure remains below the defined limit and to comply with regulations issued in the Occupational Safety and Health Act of 1970. Two approaches to accomplish this monitoring have been developed by our group--passive sampling and real-time colorimetric dosimetry. Each procedure has advantages and disadvantages. The passive sampler traps and stabilizes the hydrazine for later quantitative analysis; however, it cannot warn the personnel of exposure in real-time. The colorimetric dosimeter provides real-time measurements and can warn personnel of a hazardous condition.

Because the colorimetric dosimeter is directly exposed to the atmosphere its sampling rate depends upon the motion of the air in front of it. A color indicator could be placed behind a diffusion barrier but this would reduce its sensitivity by an order of magnitude making it difficult to read. Thus it is not possible to correlate the exposure of the indicator to the actual concentration in the atmosphere with any certainty. Ideally the colorimetric and the passive systems could be combined onto one badge that could provide an immediate warning and a quantitative record for documentation. Before that can be done each system must be developed independently. This report deals with development of a passive sampler. The real-time dosimeter will be discussed in a separate report.

The reactivity of the hydrazines and their tendency to undergo oxidative decomposition poses a problem to the development of detection systems. A collection scheme is required with the ability to stabilize the hydrazines without interfering with accepted analytical procedures [4].

Current methods of sampling involve detector tubes or midge impingers with an acidic collection solution. These are "active" sampling methods, meaning they involve the use of a sampling pump to draw the atmosphere through the collection medium. The pumps are bulky and expensive, increasing the size, weight, and cost of the system, placing undesirable constraints upon performance. In addition, a power source is required to operate the pump which places a limit on the sampling period.

Using passive diffusion technology, we have developed a lightweight, inexpensive, sampler that can be used to quantitate ppb exposures to hydrazine and MMH. The following section gives a general description of the sampler and the laboratory tests to characterize its performance. More detailed descriptions are available [5, 6, 7 and 8]. The prototype was evaluated in the laboratory for collection rate, sample stability, reproducibility, linearity, and effects of selected interferents and relative humidity. Following the laboratory characterization, the system was tested at Kennedy Space Center (KSC) in field locations and conditions where it may find future use.

APPROACH

The prototype sampler consists of a coated polyester collection disk and four plastic pieces which included a base, spacer, diffuser, and cap, US Patent 4,780,282. Of these four pieces, the diffuser is the most critical. It controls the collection rate and avoids dependence upon the ambient face velocity. Several design criteria were special for a system design to sample hydrazines. Because of the low exposure limits of hydrazines compared to most other chemicals, it is necessary that the badge sample at a higher rate to obtain sufficient sample for analysis. Hydrazines are polar and reactive precluding the use of metals and most plastics as materials for badge construction. It has been our experience that machined teflon surfaces are unsuitable for sampling low levels of hydrazines.

The most desirable form of a personal sampling device utilizes a passive collection scheme. For an ideal badge design the sampling rate (M) of the passive collector depends only upon the diffusion coefficient (D) of the analyte as described by Fick's first law of diffusion, equation 1.

$$M = D (A/L) (C_1 - C_2) \quad (1)$$

Where: A = The area of the diffusion channel;
L = The length of the diffusion channel;
C₁ = The external (ambient) concentration of the analyte; and
C₂ = The gas-phase concentration of the analyte at the surface of the collector.

Theoretical modeling was employed during the design of a diffuser. Our design is based upon the fact that viscous flow is proportional to A²/L; whereas diffusion is proportional to A/L, see

equation 1. Thus increasing the number of holes on the badge, while keeping the total area of the holes constant, decreases the viscous conductance without affecting the diffusion rate. Viscous flow into the badge is due to small pressure differences across the diffuser because of air movement. Additionally, less turbulence is caused at the badge face by many small holes. The disadvantage of increasing the number of holes is the increased surface area of the walls of the holes and greater difficulty in manufacturing the badge face.

Several styles of badge were fabricated and tested. The number and size of holes was varied while maintaining a constant sampling area. Face velocity experiments were performed on the machined badges to select the optimum design. A design having a 2.5 cm diameter pattern of 144 1.0 mm diameter holes was selected for its ability to minimize face velocity effects without severely increasing the detection limit. Designs with fewer, larger diameter holes, exhibited pronounced face velocity effects.

Tests were conducted with badges machined from polyethylene, polypropylene, and teflon. No significant material-dependent differences were found. We were concerned with the potentially detrimental effect of the rough surfaces produced during the drilling of the holes. To minimize this effect, and to aid in the quality control and mass production of the sampler, it was necessary to have the badges molded. Moldsavers, Inc. of Miami, Florida was selected as the manufacturer. Low density polyethylene was the only tested material which could be molded successfully into the desired badge face having the desired hole pattern. The badge was designed to snap together, allowing the cap to be snapped on the back of the base during badge exposure and snapped over the diffuser for storage. The diffuser was designed to snap on the base and to accommodate the cap or a second diffuser. The design of the badge is shown in Figure 1.

The current badge design has 144 one mm diameter holes with a length of 2 mm. Between the diffuser and the substrate there is a 2 mm deep gap 25 mm in diameter. Based upon equation 1 the conductance of the badge is 4.65 cm. This results in a *theoretical* sampling rate of 42, 34, and 29 ml/min for Hz, MMH and UDMH respectively, based upon diffusion constants of 0.154, 0.122, and 0.104 cm²/sec. The measured sampling rate for MMH is 25 ml/min. The theoretical rate may be in error due the assumption that the value of C_2 in equation 1 is zero. By stacking diffusion barriers on top of each other the sampling rate can be decreased. Colorless polyethylene badges were used for initial field tests (K01-K10). Later, black low-density polyethylene badges were used to reduce effects of exposure to strong sunlight, (tests K10A-K18).

The substrate used for the original prototype sampler was a matted polyester drafting film. Initial tests using this material were promising, later it was found to cause the captured MMH on the citric acid to slowly disappear. It is believed that the hydrazine slowly reacts with the substrate. After this discovery, the substrate was changed to Whatman #42 filter paper, which is the substrate currently in use. In laboratory tests, the filter paper substrate did not affect the storage stability of the analyte [7]. Citric acid monohydrate was selected as the coating agent. It has desirable properties as an acid and an antioxidant, additionally it is non-toxic. Using the polyester substrate it was found that the preparation of the citric acid solution was critical to obtaining good results. The solution was made by dissolving citric acid monohydrate in methanol to form a 30% solution. The solution was aged for one week at room temperature and was discarded after two weeks. If retained for longer

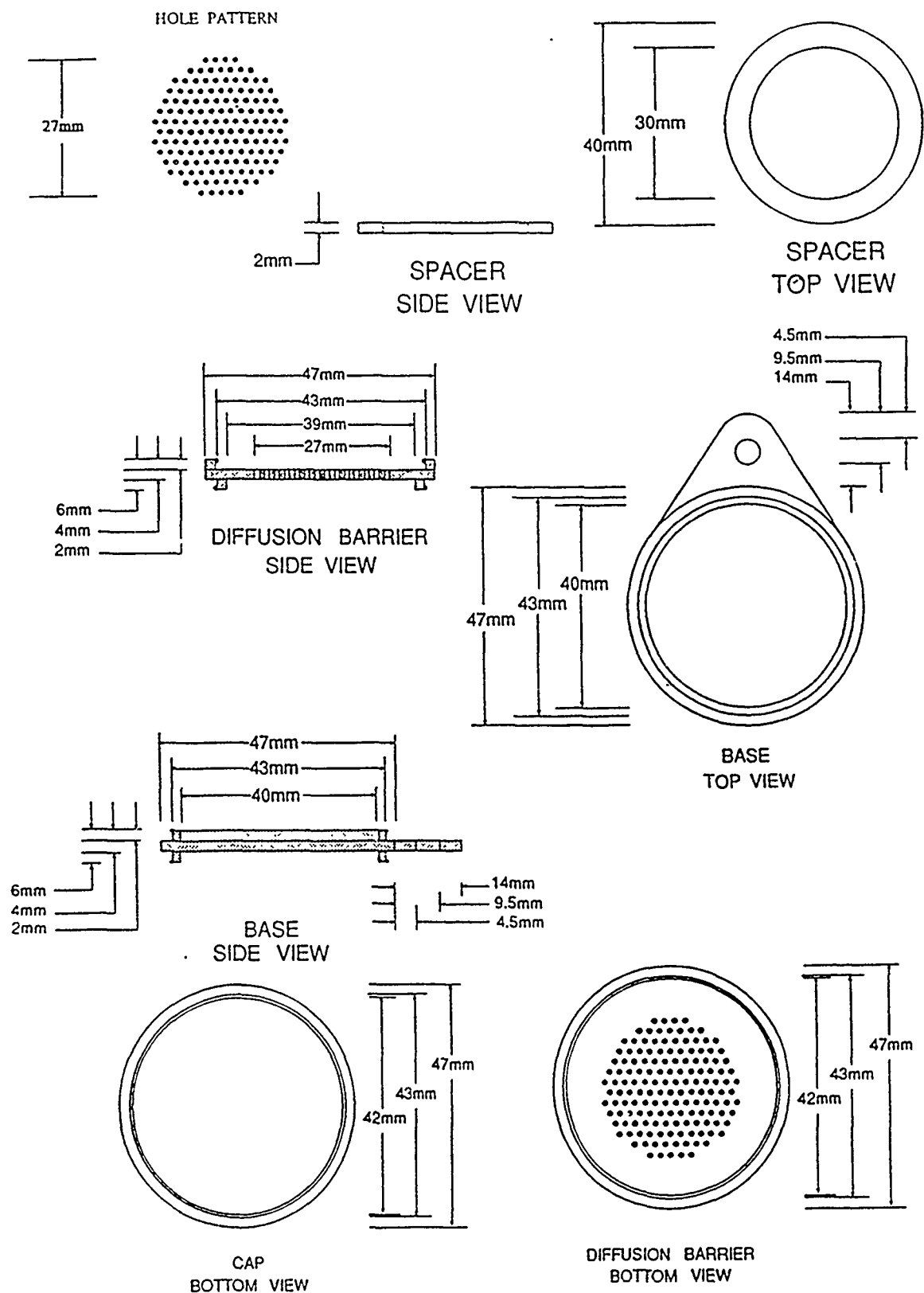


Figure 1. Drawing of the molded polyethylene sampler.

periods, the formation of methyl esters causes significant variations in the coating consistency [5]. Using filler paper substrates, the citric acid solution could be used immediately and stored indefinitely.

The filter paper disks are coated by immersion in the citric acid solution. Teflon-coated tweezers are used to remove the disks. Contact with metals is avoided in order to prevent metal ion catalyzed decomposition of the hydrazines. Large quantities of the coated disks may be prepared and stored in a refrigerator (approximately 3°C) for later use. Prepared samplers have been stored for periods of one month prior to laboratory testing with no effect on performance. Appendix A describes in detail the techniques used for badge preparation.

LABORATORY TESTING

Test Atmosphere: Generation and Verification. The reactivity of the hydrazines makes it necessary to generate dynamically the low ppb levels required for testing. The gas generation system, depicted in Figure 2, can generate hydrazine concentrations from approximately 0.1 to 10 times the TLV (Table 1, ACGIH values) for each compound. Diffusion tubes housed in a constant temperature bath, and continually purged with 100 ml/min of dry nitrogen generate hydrazines. The desired concentration is obtained by adjusting the temperature of the bath, size of the diffusion capillary, and/or the volume of diluent gas.

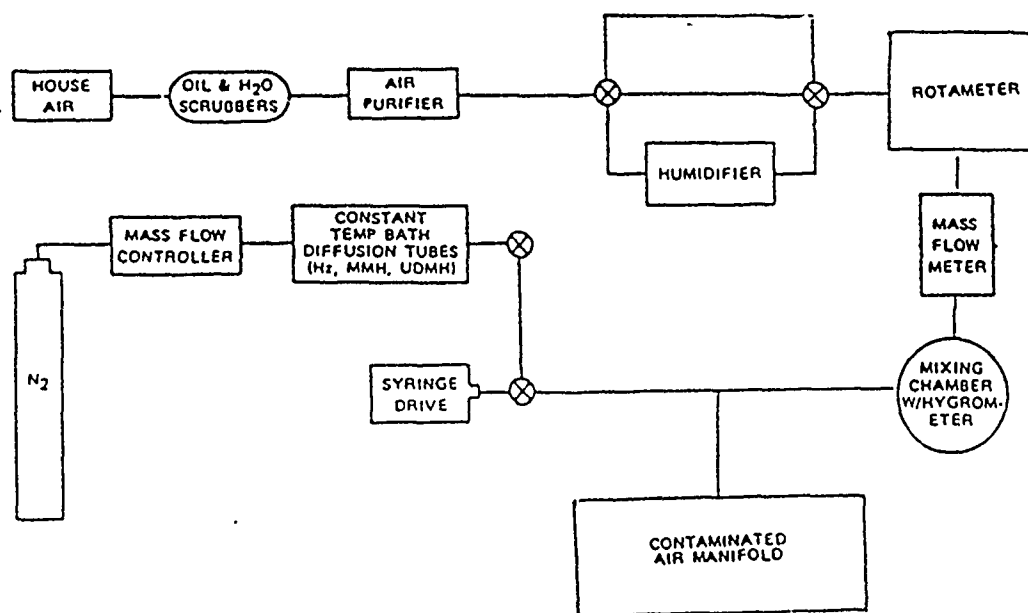


Figure 2. Test gas generator schematic.

Conditioned house-compressed air is used as the diluent. The conditioning procedure consists of passing the house air through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular sieve scrubber, and finally through a canister containing potassium permanganate coated alumina (Purafil) and charcoal. The cleaned air is humidified using a stainless steel

gas washer (bubbler) containing distilled, deionized water. Control of the relative humidity is achieved by varying both the gas washer head pressure and the ratio of the humidified to dry air. The moisture content of the air is measured by a hygrometer. Dilution is selected and monitored using calibrated 0 to 10 l/min mass flow controllers.

The exposure experiments were conducted in three similar glass exposure chambers, one of which is depicted in Figure 3. They are cylindrical with conical ends. The exhaust end was removable to allow insertion of the samplers. Teflon baffles were placed at each end to induce laminar flow. The internal diameter of each chamber was different in order to permit the study of a variety of face velocities while holding other gas stream conditions constant. Further variation in face velocity could be attained by varying the flow rate of dilution air in combination with substituting chambers. Table 2 lists the chambers and the conditions available for testing.

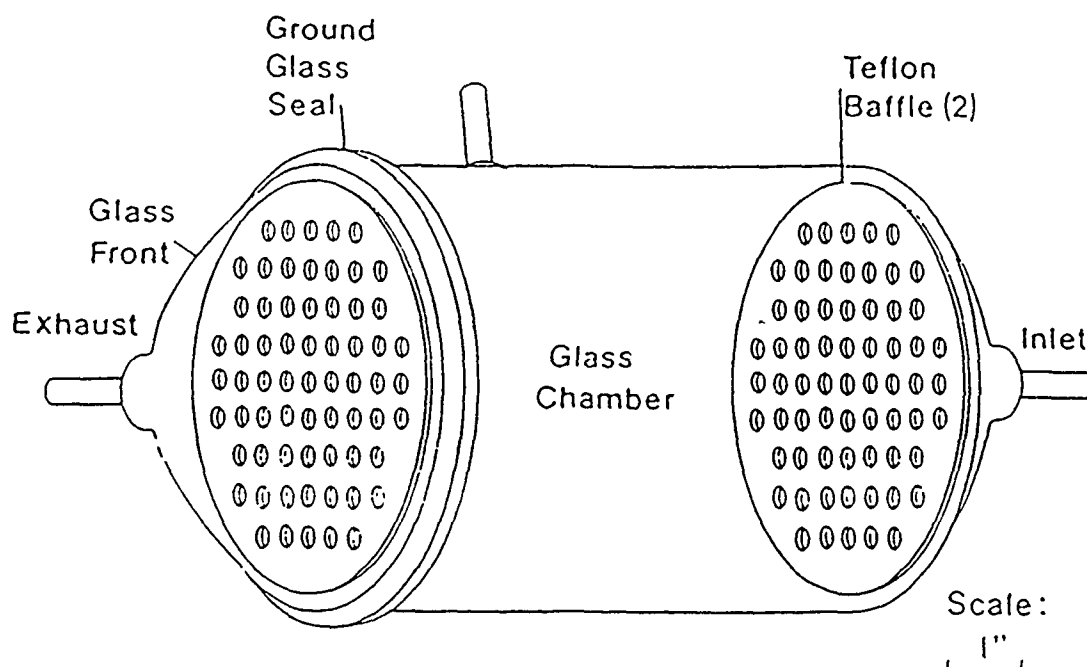


Figure 3. Glass exposure chamber used for laboratory badge testing.

Performance Evaluations. The samplers were prepared as described (Appendix A) and exposed to controlled atmospheres. Typically, four samplers were tested simultaneously. They were placed in the chamber in a 2x2 pattern (each badge in a pair was at the same axial position in the chamber but facing outward). Occasionally six samplers were exposed at one time (2x3 pattern). The badges were mounted on a glass rod suspended between the end baffles of the chamber. This could be done when the concentration and face velocity of the test atmosphere were adequate to prevent depletion of the analyte in the gas stream by the samplers. At low flow rates and concentrations we found that the forward pair of badges captured more hydrazine.

Table 2. Size of the gas exposure chambers and typical conditions.

Diameter	Area	Flow	Face velocity
5.5 cm	23.8 cm ²	5 l/min	335 cm/min* (11 ft/min)
9.0 cm	63.6 cm ²	5 l/min	79 cm/min (2.6 ft/min)
14 cm	154 cm ²	5 l/min	34 cm/min (1.1 ft/min)

* For the small chamber the badge consumed a relatively large portion of the test volume. The face velocity calculations were estimated using the adjusted chamber area.

A variety of equivalent combinations of time and concentration were used to provide conditions for testing the linearity and reproducibility of the sampler. For example, 1 hour at 600 ppb = 3 hours at 200 ppb = 0.6 ppm hours. Exposure times ranged from 0.25 to 65 hours. The concentration of the test atmosphere was verified before and after each exposure experiment by liquid impinger samples that were collected and analyzed using coulometric titration or colorimetric procedures described in Appendix B. In addition, a Thermedics Model 141-1 chemiluminescence instrument and a MDA 7100 paper-tape instrument were occasionally used to monitor the gas stream.

Analysis of the samplers was performed using the coulometric titration procedure described in the analytical portion of the experimental section and detailed in Appendix B. It is not as selective as the colorimetric method, but it is much more sensitive [4]. In laboratory experiments, where no interferents are expected, it is the method of choice.

The effect of face velocity upon the collection rate of the machined prototype diffusers was tested in a MMH gas stream with face velocities of approximately 60, 120, 240, 335, and 670 cm/min (2, 4, 8, 11, and 22 ft/min). The test atmosphere was dry air with 200 ppb MMH. The badges were exposed for five hours. The selected prototype diffuser was tested under the same conditions. The average measured collection rate was 38 ml/min with a minimum of 31 ml/min and a maximum of 45 ml/min [5]. These results are shown in Figure 4.

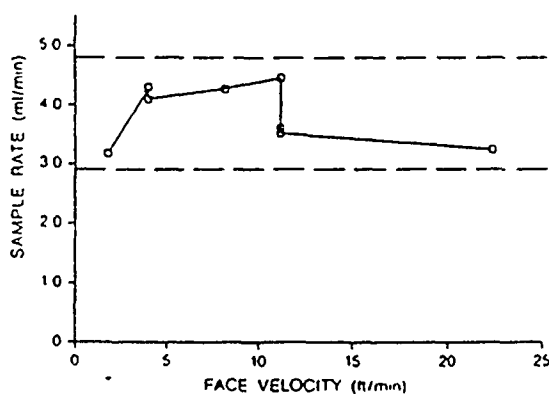


Figure 4. The Effect of Face Velocity on the Sampling Rate of the Machined Prototype Diffuser. The outer lines represent 30% error limits.

The sampling rate of the molded diffuser is approximately 25 ml/min, which is less than that of the drilled prototype. It was calculated from a series of exposures to MMH ranging from 0.25 to 65 hours, Figure 5. Concentrations of MMH between 170 and 500 ppb were used. Each data point represents a test consisting of 4 to 6 individual samples. This and additional data were used to verify the linearity of the sample collection process [5]. The larger sampling rate of the prototype badge is due to the holes being slightly larger than the one millimeter diameter holes in the molded badge.

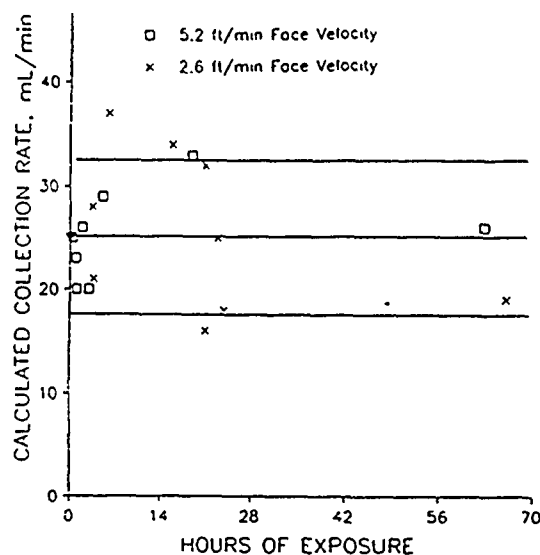


Figure 5. Sampling Rate of the Molded Badge. The center line is the rate, the outer lines are 30% error limits.

The effects of ammonia, freons, and isopropyl alcohol vapors were investigated and no interferences were found [6]. In addition, the collection rate of the dosimeter was found to be independent of the relative humidity of the exposure atmosphere [5].

The stability of the trapped hydrazines was examined by capping and storing exposed prototype badges for periods up to 62 hours. The storage experiments were performed on samples collected from 200 ppb gas streams of MMH at various relative humidities and exposure times. Storage tests were conducted by storing the exposed badges at room temperature and in a refrigerator at 3°C. In addition, the storage of the extracted solution was investigated. Room temperature storage resulted in a significant loss of analyte [5]. A loss of 30% to 75% of the original value was observed after storage for 24 hours. The refrigerated storage or the extraction of the analyte extended the storage stability [8]. This would not allow the badge to be used for long term, low level sampling. For this use it is necessary that the analyte be stable at room temperature.

Initial investigations of the storage instability focused on the citric acid coating. Its composition was investigated by mass spectroscopy and HPLC during the two week aging process [5]. The performance of the solution as a hydrazine trap was also monitored during the same period. Results were inconclusive.

Variations in the substrate material were investigated. Initially, polyester drafting film was used as the substrate. This material wetted well with the citric acid solution, forming a smooth, tacky film. Glass and filter paper materials were tested with the polyester and their performance was compared. The percentage of analyte retained during room temperature storage was greater for glass and filter paper than for polyester. We speculated that the hydrazine reacted with the ester to form a hydrazone which is not easily removed for analysis. Surface microscopy performed by R. Young at NASA KSC indicated that the exposed surface of the polyester was mostly silica and not the ester. The mechanism of analyte loss was not investigated further.

Based on the storage stability data from the substrate study, it was decided to replace the polyester substrate with 4.25 cm diameter disks of Whatman #42 filter paper which is readily available from various chemical supply houses. The disks fit the molded badges, requiring no alterations.

The exposure linearity of the badge was tested by exposure to 200 ppb of MMH for times between 0.25 and 65 hours. The test atmosphere was 45% relative humidity (RH) and a velocity of 79 cm/min (2.2 ft/min). In addition, tests were conducted in which the time was held constant and the concentration was varied between 0.1 and 2 ppm. All of the data except a one hour exposure and a 0.25 hour exposure, fell within the acceptable region, as shown in Figure 6. Fluctuations of the

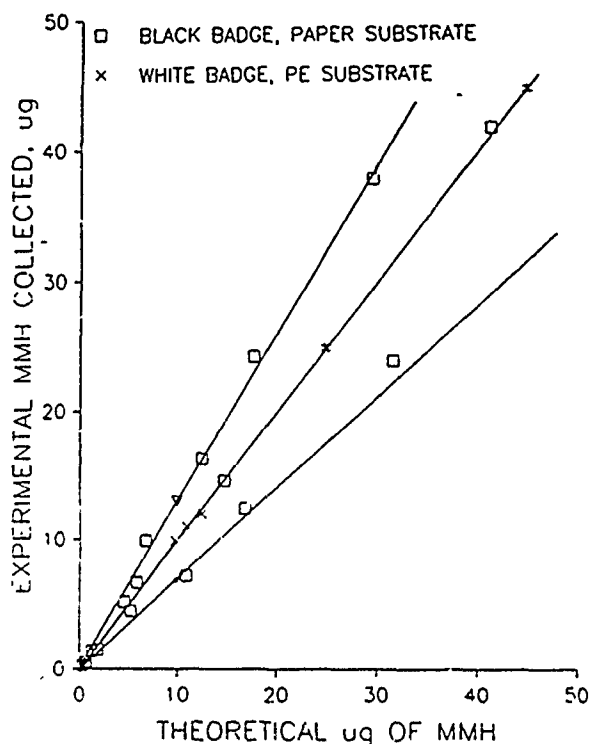


Figure 6. Linearity of the Results Obtained Using the Molded Badge, assuming a collection rate of 25 ml/min. The center line is ideal assuming a 25 ml/min sampling rate, the outer line 30% error limits.

shorter exposures may be due to disruption of the test atmosphere when the badges were placed in the chamber. Adsorption on the badge housing could also be a factor.

FIELD TESTING

Test Locations. Test areas at the Kennedy Space Center were divided into three major categories based on their potential for hydrazine or MMH exposure: unlikely to be exposed, potential exposure, and expected exposure. The locations were selected to encompass the potential field interferences and the effects they may have upon performance. Locations are listed in Table 3.

Sampling. The samplers were prepared by Wiltech Analytical Laboratory at KSC following the procedure described in Appendix A. A group of badges was retained by the analytical laboratory to be used as blanks in their analytical procedures. The blanks were stored in a refrigerator. Samplers for field testing were distributed to the industrial hygienist on the work day preceding the test period.

At each test location, two areas were selected for sampling. A sampling board, holding 12 citrate badges, was placed at each area by EG&G Environmental Health personnel on Monday mornings. The badges were uncapped every morning and recapped at the end of an 8 hour work day. At the end of the sampling period on Monday, Wednesday, and Friday a set of badges was collected for analysis. A set consisted of four badges from each board. Two badges were coded for coulometric analysis (A) and two for verification analysis (B). The exposed badges were submitted to the analytical lab where they were stored in a refrigerator until analysis. In addition, the industrial hygienist submitted a few unexposed badges designated as field blanks. The coulometric analysis was typically performed the first work day following the submission of the sample.

Table 3. Locations Selected for the KSC Field Testing of the Citrate Sampler

<u>Category</u>	<u>Location</u>	<u>Test Number</u>
Unlikely to be Exposed	Hanger S Life Support	K04
	M&O paint shop	K03, K16
	EG&G	K14
	Beach	K10
	Vehicle Assembly Building (VAB) Lounge	K11
Potential Exposure	Hazardous Maintenance Facility (HMF) 96	K02, K18
	Wiltech Labs	K01
	Rotating Service Structure (RSS)	K09, K10A, K15
	Orbiter Processing Facility (OPF)	K13
Expected Exposure	Fuel Storage #1	K06
	Aft Skirt Testing Facility (ASTF)	K07, K08, K12, K17

In addition to the area samples, the citrate badges were also tested as personnel dosimeters. Typically, two workers were monitored; each wearing two citrate badges, an "A" and a "B". These badges were distributed and collected for analysis on a daily basis. Impinger samples (D) were collected daily at the locations of the sample boards in order to verify the exposure the samples received using a validated procedure. Air was drawn through a midjet glass impinger containing 15 ml of 0.1 M H_2SO_4 . Prior to and after sampling, the collection rate of the impinger system was verified to be 200 ml/min using a bubble flow meter. The impingers were submitted to the analytical laboratory where they were stored in the refrigerator until analysis.

In addition to the citrate badge, a colorimetric dosimeter badge was tested. A description of the testing of this indicating system is available [5 and 9]. During the field test, three color badges were placed on each area sampling board on Monday mornings. The dose estimation was evaluated and recorded daily. The disks were collected at the end of the week, stored in zip-lock plastic bags, and sent to NRL for evaluation. On occasion, selected personnel were also monitored with color badges. They were issued a new color badge daily. The used badge was collected, sealed in a zip lock bag and sent with the area samples to NRL for evaluation. Further information on the prototype colorimetric dosimeter will be presented in a future report.

Firebrick samples were scheduled to be used, in place of impingers, in the field tests conducted at White Sands Testing Facility (WSTF). Tabulated results from these tests are available in a report issued by WSTF [9].

The field samples were coded by EG&G using the following label: W - XX - YYY - Z. The key to the label is: W = location, XX = lot #, YYY = sample #, and Z = type of sample. The key for Z is: A = citrate, coulometric analysis; B = citrate, verification analysis (PMA colorimetric or coulometric spike); C = vanillin, D = impinger; and E = firebrick. The analytical laboratory only received the coded samples. The data pertaining to the collection of the samples were recorded by EG&G personnel. The analysis data were recorded by Wiltech. Each group independently sent their data sheets weekly to NRL for compilation. If the analytical laboratory found a quantifiable amount of analyte they would immediately inform the hygienist and the auditor. This was done to allow additional information to be collected by the hygienist while the exposure conditions could be easily recalled.

Citrate Badge Analysis. The coated substrate is removed from the housing assembly with teflon coated tweezers and placed in a glass container. The analyte is desorbed from the disk with a solvent designated by the selected technique. Two accepted wet chemical methods are applicable to this procedure: (1) Coulometric titration miniaturized to achieve the desired sensitivity [11]; and (2) Colorimetric method, phosphomolybdic acid, NIOSH approved method #S149. These methods are detailed in Appendix B, parts 13.3 and 13.2, respectively. The badges were analyzed for MMH exposure unless otherwise specified.

The coulometric titration was used for the laboratory characterization of the badge performance. The schematic of this procedure is shown in Figure 7. It involves the electrochemical generation of bromine from potassium bromide. As the molecular bromine is formed, it instantly reacts with the hydrazine in the solution. When there is no more hydrazine present bromine will accumulate,

forming a redox couple with the bromide. When a redox generated current is measured by the sensing electrode the titration has reached the endpoint. The formula used to calculate the hydrazine in the sample is given in Appendix B. The coulometric procedure is quick, easy and sensitive for analysis of hydrazines, but it is not extremely selective. For the analysis of field samples, the PMA spectrophotometric method was also used. This method is less sensitive, but more selective.

All the "A" badges were analyzed using the coulometric procedure. If a detectable amount of analyte was found, the duplicate "B" badge was analyzed using one of two procedures. The PMA colorimetric analysis was used if the amount detected was greater than the PMA detection limit. If the "A" result was less than the PMA detection limit the coulometric spike procedure was used. In addition, all the Friday "B" badges were analyzed by the PMA method. The unused "B" samples were stored in the refrigerator.

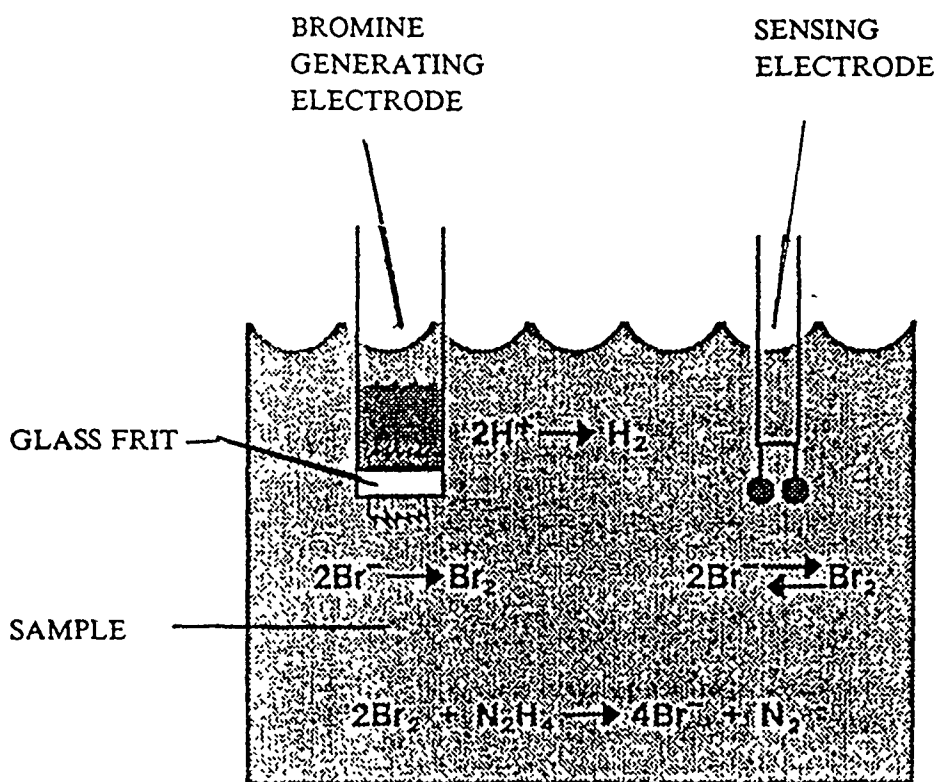


Figure 7. Schematic of coulometric titration.

Liquid Impinger Analysis. The liquid impinger samples, collected to verify the test atmosphere, were analyzed by the ASTM para-dimethylamino benzaldehyde (PDAB) colorimetric method. A copy of the procedure is given in Appendix B (part 8.1 for MMH analysis and 8.2 for Hz analysis). It is based on the condensation reaction of hydrazines with an aldehyde, Figure 8. In the case of unsubstituted hydrazine, two moles of aldehyde can react with one mole of hydrazine to form the azine. The mechanism involves the nucleophilic addition of the nitrogen base, followed by the

elimination of water. This reaction is frequently acid catalyzed by protonation of the carbonyl. The resulting hydrazone absorbs visible light. The ASTM method requires measuring the absorbance spectrophotometrically at 458 nm. These measurements have been shown to conform to Beer's Law, where the amount of absorbed light is proportional to the concentration of the hydrazone in the sample [12].

Vanillin Color Dosimeter Analysis. The same basic chemistry is used with the real-time color badge system. In this case vanillin, 3-methoxy 4-hydroxy benzaldehyde, reacts with the hydrazine. The vanillin is coated on Whatman #42 filter paper and placed in a badge housing that has been modified by cutting away the diffuser section. Hydrazine and MMH present in the ambient environment are trapped on the coated paper where they react with the vanillin indicator; UDMH does not react with the badge to produce a color. The reaction product is detected by the development of a yellow stain on the paper substrate. The intensity of the color is related to the exposure. A color wheel was developed for dose estimation. The dosimeter exposure can be interpolated from a comparison of the badge color with the wheel containing colors equivalent to 0.07, 0.14, 0.48, 1.1, 3.8 ppm-hours of MMH exposure.

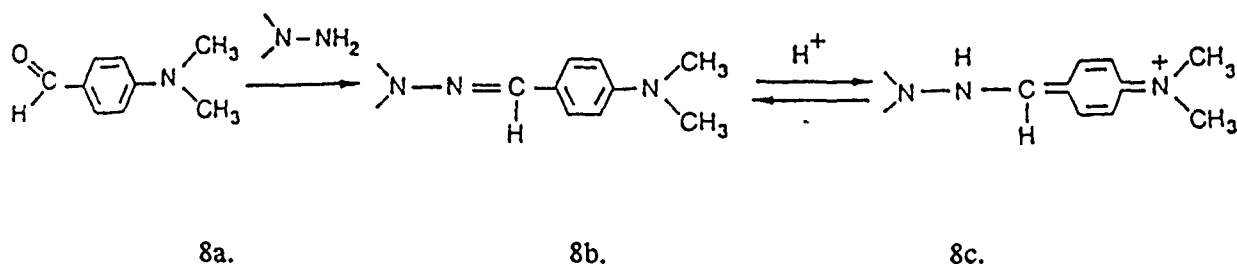


Figure 8. The reaction of PDAB, 8a, with a hydrazine to form the hydrazone, 8b, that becomes yellow on protonation, 8c.

This wheel was used by the industrial hygienists to obtain a dose reading on the field samples (as stated in the sampling procedure). The badges were then sent to NRL. At NRL, the color badges were visually inspected, exposed to MMH and their performance was compared to a control. The control was a sample coated at the same time, but never used in the field.

RESULTS

Field Testing. Eighteen tests were conducted in the field at KSC. Data from test five (K05) was excluded from this report because the samples were left out during a rain storm and were not analyzed. Retesting of the location was performed in test K06. The white badge housing was used for the first tests, K01 through K10. Test K10A was the first field test to use black badges. The black badges were used exclusively for test K10A through K13. In test K14 through K18 white and black badges were tested side-by-side.

A review of the individual tests conducted at KSC is given in Appendix C. The analysis data for each test was tabulated and grouped by the sample type described previously in the report. The industrial hygienists description of the test area is included in Appendix D. The following paragraphs organized by sample type, summarize the results from each test. The data from the field blanks are included in the summaries. The results from the laboratory and EG&G blanks are not in the summaries, but are included in the Appendix C tables.

TEST K01

Location: Wiltech Laboratory

Date: November 1987

Category: Potential Exposure

- A) Two of the twenty-two citrate samples, analyzed by coulometry, indicated analyte present at greater than the detection limit of 0.12 μg . These were not verified by any other method.
- B) The data obtained by the PMA analysis of the citric acid samples are suspected of contamination.
- C) The vanillin colorimetric samples gave no indication of exposure to hypergols.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K02

Location: Hypergol Maintenance Facility M7-961

Date: November 1987

Category: Potential Exposure

- A) Five of the twenty-two citrate samples and one blank, analyzed by coulometric titration, indicated analyte present at greater than the detection limit of 0.12 μg . Two samples were exposed at levels greater than the quantitation limit. All five were personnel samples.
- B) As in test K01, the PMA results for the citrate badges are suspect. The analysis was attempted with and without citric acid added to the standards. The results were still questionable.
- C) No change was noticed on the vanillin color badges.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K03

Location: Maintenance and Operations (M&O) Paint Shop

Date: December 1987

Category: Unlikely to be Exposure

- A) Six of the twenty-two citrate samples analyzed by coulometric titration indicated analyte present at greater than the detection limit of 0.12 μ g. Four of these were personnel samples, the other two were five day area samples.

Two of the personnel samples indicated hypergol exposure above the quantitation limit of the coulometric procedure.

- B) The duplicate badges were analyzed by spiked coulometric analysis. The analysis data did not match the "A" data.
- C) No color badges were available for this test.
- D) The daily impingers, analyzed by PDAB, gave no indication of detectable exposure to hypergols.

TEST K04

Location: Hanger S Life Support South Annex

Date: January 1988

Category: Unlikely to be Exposure

- A) One of twenty-two citrate samples analyzed by coulometry indicated a detectable amount of analyte. It was a personnel sample.
- B) None of the duplicate samples was analyzed.
- C) No change was noted on any of the vanillin color badges.
- D) The daily impingers, analyzed by PDAB, gave no indication of detectable exposure to hypergols.

TEST K06

Location: Fuel Storage Area #1

Date: February 1988

Category: Expected Exposure

- A) Eight of the twenty-two citric acid samples analyzed by coulometry indicated a greater than detectable amount of analyte; one was quantifiable.

Area I results were slightly higher than Area II results.

- B) The duplicate samples were analyzed by the coulometric spike procedure. In general the results correlated well with the "A" badge data.
- C) No change was noted on any of the vanillin color badges.
- D) The daily impingers, analyzed by PDAB, gave no indication of detectable exposure to hypergols.

TEST K07

Location: Aft Skirt Test Facility

Date: May 1988

Category: Expected Exposure

- A) All twenty samples analyzed by coulometric titration indicated levels of analyte greater than the quantitation limit of the method, 0.4 μg . Area I samples had significantly greater exposure than Area II samples and appear to increase by $\sim 4 \mu\text{g/day}$. A SCAPE operation was performed on day 3 during the test period, four samples were expected to indicate hypergol exposure.
- B) Five of the twelve samples analyzed by PMA had a detectable amount of analyte. The results did not mimic the coulometric results of "A". The badges were originally analyzed for MMH and the data later corrected for Hz.
- C) Three of the vanillin badges indicated exposure to hypergol. The color was initially noted on only 2 of the 3. Following acidification by HCl vapor the color of the 2 intensified and the third developed color.
- D) The sample collected in Area II on day 3 indicated the presence of hypergol. Again, the analytical lab was not informed that the analyte was Hz so the samples were analyzed as MMH.

TEST K08

Location: Aft Skirt Testing Facility

Date: May 1988

Category: Expected Exposure

- A) All of the citrate samples analyzed by coulometry indicated exposure to hypergols. All but 2 results were greater than the quantitation limit of 0.4 μg . Results from Area I were significantly greater than Area II.
- B) The duplicate citrate samples, analyzed by PMA, did not verify any exposure information.
- C) No change was noted on any of the vanillin color badges.

- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K09

Location: Rotating Service Structure

Date: June 1988

Category: Potential Exposure

- A) All of the citrate samples analyzed by coulometry indicated exposure to hypergols. All the results were greater than the quantitation limit of 0.4 μg . Results from Area I were greater than Area II. Blind blanks also indicated exposures.
- B) The spectrophotometer was broken. The "B" samples were analyzed by coulometric spike procedure. The spiked results correlate well with the corresponding "A" samples.
- C) Four samples indicated a slight exposure to hypergols. All these samples were in Area I with the dose increasing daily.
- D) The samples from day 1 of each area indicate a slight exposure to hypergol.

TEST K10

Location: Beach Location

Date: July 1988

Category: Unlikely to be Exposed

- A) Area samples indicated a high exposure. No hypergols were in this area. The indication must be due to an interferant. The capped blank samples also indicated interference in the coulometric method.
- B) The PMA samples did not verify any MMH exposure. The results were all below detection limit.
- C) One sample had a slight coloration.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K10A

Location: Rotating Service Structure

Date: January 1989

Category: Potential Exposure

- A) This was the first field test conducted using the black badges. Four of the eighteen citrate samples analyzed by coulometric titration gave a response greater than the detection limit. None of the results were equal to or greater than the quantitation limit.

- B) Two of the citrate badges had detectable amounts of analyte by the PMA method. Each of these were 5 day exposure samples from Area II. One was a sample the other was a blank.
- C) No color badges were available for sampling.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K11

Location: Vehicle Assembly Building Break Room

Date: February 1989

Category: Unlikely to be Exposed

- A) Twelve of the eighteen citrate samples analyzed by coulometric titration gave responses greater than the detection limit. Five of the samples indicated quantifiable amounts. First indication of interference due to tobacco smoke.
- B) The samples analyzed by coulometric spike procedure correlated well with the "A" samples. The samples analyzed by PMA did not detect any analyte.
- C) No color badges were available for sampling.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K12

Location: Aft Skirt Testing Facility

Date: February 1989

Category: Expected Exposure

- A) Three of the eighteen citrate badges analyzed by coulometric titration gave results greater than the detection limit. Two samples had quantifiable amounts, these were six day exposures in Area II.
- B) No exposure was verified by PMA analysis of the duplicate citrate badges.
- C) No color badges were available for sampling.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K13

Location: Orbiter Processing Facility

Date: March 1989

Category: Potential Exposure

- A) One sample from the eighteen placed in Areas I and II had a detectable amount of analyte.
- B) The duplicate samples from area I and II did not detect any analyte.
- C) No color badges were available for sampling.
- D) The liquid impinger samples from the second day detected slight exposure.

TEST K13A

Location: EG&G Roof, Horizontal Placement

Date: March 1989

Category: Unlikely to be Exposed

- A) Six of the nine samples had quantifiable amounts of analyte. The samples that did not indicate exposure were 3 capped blanks.
- B) None of the samples were analyzed by an alternate method. The five samples analyzed by the coulometric spike procedure gave similar results to the corresponding "A" samples.
- C) No color badges were available for sampling.
- D) No impinger samples were collected from the area.

TEST K14

Location: EG&G Environmental Health Roof and Remote Antenna Site

Date: May 1989

Category: Unlikely to be Exposed

- A) The citrate samples in black badges indicated quantifiable amounts when placed in both the vertical and horizontal positions. The results from the samples in a horizontal position were much greater than the vertical. The vertical black badges in area 1 and 2 had equivalent results. The black badge blanks did not detect any analyte.

The white badges were only placed in the horizontal position. All the samples gave extremely high results, including the blanks.
- B) The only samples to indicate analyte were the white badge samples placed in a horizontal position.

- C) No color badges were available for sampling.
- D) No impingers collected. No hypergols were anywhere in the vicinity so no verification was needed.

TEST K15

Location: Rotating Service Structure, 39B

Date: August 1989

Category: Potential Exposure

- A) All twelve of the white badges indicated detectable amounts of analyte, nine of the results were above the quantitation limit.

One of the eighteen black badge samples indicated a detectable amount of analyte.
- B) None of the samples analyzed by PMA detected any analyte. The samples analyzed by the coulometric spike procedure gave similar results to corresponding "A" samples.
- C) GMD prototype badges were used for the color dosimeters. They contained two exposure windows, each with a different indicator. The upper window used PDAB and the lower window used Vanillin. The vanillin section did not indicate exposure. The PDAB section developed a slight yellow color; the reaction product formed by exposure to hydrazine is an orange-red.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K16

Location: M&O Paint Shop

Date: August 1989

Category: Unlikely to be Exposed

- A) The white badges consistently gave high results for the coulometric analysis. Four of the six black badges indicated slight exposure with one result greater than the quantitation limit.
- B) Three of the white badge samples analyzed by PMA indicated exposure.
- C) The color badges were not used during this test.
- D) No liquid impinger samples were taken during this test.

TEST K17

Location: Aft Skirt Testing Facility

Date: August 1989

Category: Expected Exposure

- A) The white badges consistently gave high results for the coulometric analysis. Nothing was detected by the black badge samples.
- B) None of the sample analyzed by PMA detected any analyte. The samples analyzed by the coulometric spike procedure gave similar results to corresponding "A" samples.
- C) GMD prototype badges were used for the color dosimeters. They contained two exposure windows, each with a different indicator. The upper window used PDAB and the lower window used Vanillin. The vanillin section did not indicate exposure. The PDAB section developed a slight yellow color; the reaction product formed by exposure to hydrazine is an orange-red.
- D) The daily impingers analyzed by PDAB gave no indication of detectable exposure to hypergols.

TEST K18

Location: Hypergol Maintenance Facility M7-961

Date: August 1989

Category: Potential Exposure

- A) The white badges consistently gave high results for the coulometric analysis with the exception of day one in Area 1. The black badges did not detect any analyte.
- B) None of the sample analyzed by PMA detected any analyte. The samples analyzed by the coulometric spike procedure gave similar results to corresponding "A" samples.
- C) GMD prototype badges were used for the color dosimeters. They contained two exposure windows, each with a different indicator. The upper window used PDAB and the lower window used Vanillin. The vanillin section did not indicate exposure. The PDAB section, of the badges issued for day two, developed a slight yellow color; the reaction product formed by exposure to hydrazine is an orange-red.
- D) No liquid impinger samples were taken during this test.

Details of the results of tests performed at NASA, WSTF are given in separate report [10]. In general, high results were obtained on colorless badge samples exposed to sunlight that were analyzed by coulometry but not with a WSTF ion chromatography method. WTSF found that the black badge provided adequate protection from sunlight exposure. A slight decrease in the concentration of a spiked sample was observed.

Quality Assurance and Quality Control (QA/QC). To verify the proficiency of the analytical laboratory, a set of spiked samples were incorporated into the field test. These badges were prepared at NRL. They were then given to the industrial hygienist for random, blind incorporation. Table 4 details the exposure of the spiked samples. The theoretical loading of the badges was calculated and kept as proprietary information by the auditors.

Table 4. Spiked Citrate Samples for QA/QC

Sample Number	Spiked with	Conc. (ppb)	Duration (hrs)	Volume** (l)	μg Spiked	μg Found	Analytical Method
874	MMH	*	4.6	6.9	1.7	1.7	Coul
875	MMH	*	4.6	6.9	2.9	2.5	PMA
880	MMH	*	90.6	136	28	26	Coul
881		*	90.6	136	37	24	PMA
898	MMH	*	16	24	5.6	5.4	Coul
899	MMH	*	16	24	7.4	5.2	PMA
902	MMH	0	0	0	0	0	Coul
903	MMH	0	0	0	0	nd	PMA
1001	MMH	500	67.5	101	95	>87	Coul
1002	MMH	500	67.6	101	95	>27	Coul
1007	MMH	214	16	24	9.7	6.2	PMA
1008	MMH	214	16	24	9.7	11.4	PMA
1009	MMH	214	16	24	9.7	9.0	Coul
1010	MMH	214	16	24	9.7	11.1	Coul
1014	MMH	235	5.5	8.3	3.7	2.3	Coul
1015	MMH	235	5.5	8.3	3.7	4.3	Coul
1016	MMH	235	5.5	8.3	3.7	6.4	PMA
1017	MMH	235	5.5	8.3	3.7	3.9	Coul
1021	Hz	65	5.5	8.3	1.0	1.1	Coul
1022	Hz	65	5.5	8.3	1.0	3.9	PMA
1023	Hz	65	5.5	8.3	1.0	3.9	Coul
1024	Hz	65	5.5	8.3	1.0	1.9	Coul

* Conc. unknown. Amount spiked was determined by analysis of duplicates at NRL.

** Assuming collection rate of 25 ml/min.

The results from the analysis of the spiked samples are listed in Table 4. The analytical methods used were the coulometric titration procedure (Coul) and the PMA colorimetric procedure. The industrial hygienist did not inform the analytical laboratory that some of the samples were to be analyzed for Hz instead of MMH. Because of this, the analytical laboratory analyzed all the samples for MMH exposure. This would not effect the coulometric titration results, but the colorimetric

results could be off for the hydrazine samples. Therefore, the PMA results are of questionable value for sample 1022.

DISCUSSION AND CONCLUSIONS

Laboratory Test. The molded polyethylene badge provides an excellent housing for the collection disk. The diffuser minimizes face velocity effects and establishes a collection rate of 25 ml/minute for MMH. At this sampling rate, detection of MMH at a concentration of 200 ppb MMH requires a ten minute exposure when analyzed by the coulometric titration procedure. An upper detection limit, or saturation limit of the badge, has not been defined. Quantifiable data was obtained from exposures to 200 ppb MMH for 65 hours. Since the badge is simply the collection media, the detection limits of the sampler are dependant upon the analytical method selected. The coulometric procedure is much more sensitive, but less selective than the available colorimetric methods. If better analytical methods were available, then the detection limit could be decreased.

The badge is a simple plastic design and its current production cost is less than \$0.25. Assembly of the badge is simplified by its ability to be securely snapped together. The resulting badge is durable and lightweight. These are desirable qualities for a disposable personal dosimeter. The laboratory performance of the original white badge housing and the black badge modification was acceptable.

The room-temperature instability of the analyte on the original prototype badge was improved by replacing the substrate material used for the collection disk. The original polyester substrate experienced a loss of analyte, decreasing by 30% to 75% in a period of twenty-four hours [5]. The new filter paper substrate has exhibited no significant loss of the analyte for periods of 7 days at room temperature [8]. Long term storage is possible with either system, polyester or paper, if the sample is stored in the refrigerator or extracted and stored as a solution.

The effects of ammonia, freons, and isopropyl alcohol vapors were investigated and no interference effects were found. In addition, the collection rate of the dosimeter was found to be independent of the relative humidity of the exposure atmosphere.

Field Test. The performance of the white badge housing using the filter paper substrate was acceptable for sampling in locations with no sunlight exposure. The sunlight interference was noticed in both coulometric and colorimetric analysis. The effect is much greater when the coulometric analysis is used. Both field tests conducted at KSC and WSTF indicated the sunlight interference effect.

To avoid this interference the badge was modified. The same mold was used to manufacture the sampler, but black polyethylene was used. By substituting the black housing for the white housing it is possible to use the badge in bright sunlight if care is taken not to point the badge directly at the sun for any length of time. The black badge has been field tested and has performed successfully. Field tests, conducted in the intense summer sun at KSC, indicated minimal interference when used in vertical positions, test K14. When used in a horizontal position the sun can penetrate directly through the diffusion holes and interact with the citrate surface, interfering

significantly with the coulometric and colorimetric analysis. As previously mentioned, the effect is greatest with the coulometric procedure. Based on this, we recommend samples that are known to have been exposed to sunlight be analyzed by the colorimetric procedure. Testing has been conducted with the black badge at WSTF. A report containing the results will be issued in the near future. WSTF has informed us that the black badge significantly reduced the sunlight interference effect they had observed with the original white badge.

There was one other interference effect noted during the field testing. Badges placed in the break rooms (lounges), where personnel smoked, exhibited elevated coulometric results, Field Test K11. The tobacco smoke did not interfere with the PMA analysis of the duplicate badges or the PDAB analysis of impingers. We recommend colorimetric analysis for samples that have significant exposure to tobacco smoke.

Personnel found the badge easy to use. Its design allowed it to be worn without interfering with ones duties. The analytical chemists found it simple to prepare and analyze. Application of the badge could be simplified further by use of an identification/data sticker. It would have an assigned sample number and contain spaces for exposure information. Included should be the desired analyte (MMH or Hz) and the preferred analytical technique, if any, based on known exposure to an interferant. When the badge is available for routine use, we feel it will be an asset to the industrial hygienist in documenting Hz and MMH exposures. However, one must remember that passive systems have inherent inaccuracy and results must not be expected to have accuracy greater than 30% of the actual exposure.

REFERENCES

1. DHEW (NIOSH) Publication No 78-210.
2. DHEW (NIOSH) Publication No 78-172.
3. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.
4. Miller, E.L. "Interim Report: Evaluation of Analytical Methods for Determining Propellant Hydrazines in Aqueous Solutions," NASA WSTF Document No. TR-569-001, 12 Dec 1988.
5. Taffe, P.A., J.H. Callahan, K.P. Crossman, S.L. Rose-Pehrsson, "Hydrazine Dosimetry," Proceedings of the Third Conference on the Environmental Chemistry of Hydrazine Fuels, (Panama City, FL, 15-17 Sept 1987) sponsored by: Air Force Engineering and Services Center, Electronics Division.
6. Hawkins, C.M., S.L. Rose, J.R. Wyatt, "A Passive Dosimetry Method for Determining Hydrazine in Air," CPIA 436, Proceedings of the 1985 JANNAF Safety and Environmental Protection Subcommittee Meeting, (Monterey, CA, 4-8 Nov 1985) Naval Postgraduate School, Nov 1985.
7. Taffe, P.A., J.C. Travis, S.L. Rose-Pehrsson, "Field Evaluation of the Passive Hydrazine Dosimeters", Proceedings of the 1989 JANNAF Safety and Environmental Protection Subcommittee Meeting, (San Antonio, TX, April 1989). To be published by CPIA.
8. Taffe, P.A., S.L. Rose-Pehrsson, J.R. Wyatt, "Laboratory Development of a Passive Sampling Device for Hydrazines in Ambient Air." To be published as a NRL Memorandum Report.
9. Taffe, P.A., S.L. Rose-Pehrsson, "Real-Time Passive Dosimeter Hydrazines", CPIA 485, Proceedings of the 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, (Monterey, CA May 1988) Naval Postgraduate School, May 1988. Patent Application Allowed, Serial Number 201767, Issuing Fee Paid.
10. Smith, I.D. Evaluation of the KSC Dosimeter Badges, Part II - Field Tests. TP-WSTF-549, NASA White Sands Tests Facility, Las Cruces, NM, Feb 1987.
11. Olson, E.C. "The Coulometric Determination of Hydrazine and Substituted Hydrazine," Analytical Chemistry, Vol. 32, No. 12, November 1960, pp. 1545-1547.
12. Snow, A., S. Rose, Review of Specific Chemical Interactions for Hydrazine Analysis and Proposed Adaptation for Microsensor Chemical Detection, NRL Memorandum Report 5461, Naval Research Laboratory, Washington, DC, 30 November 1984.

APPENDIX A

Reference 4-0-111 Page 1 of 2 Appendix 13.1

The badge preparation method used by Wiltech Analytical Laboratory are compiled in the following Appendix. The method retains its internal Wiltech reference number under the Appendix title.

13.1 MMH/N₂H₄ DOSIMETER BADGE PREPARATION

13.1.1 Apparatus

- 13.1.1.1 Balance, top load.
- .2 Volumetric flasks, 100 ml.
- .3 Whatman No. 42 filter paper, 4.25 cm
- .4 Forceps, plastic.
- .5 Kimwipes.
- .6 Polypropylene bags, 4 x 4 inches.
- .7 Labels.
- .8 Bag sealer.

13.1.2 Reagents

- 13.1.2.1 Citric acid, monohydrate, HO₂C(OH)C(CH₂CO₂H)₂·H₂O, reagent grade.
- .2 Methanol, CH₃OH, reagent grade.
- .3 D.I. water.

13.1.3 Safety - Refer to Section IV of 4-0-111 for safety requirements and specific hazards, precautions, and emergency procedures concerning fire (Paragraph 4.4.1) and solvents (Paragraph 4.4.3).

13.1.4 Preparation of Coating Solution

- 13.1.4.1 Transfer 30 g of citric acid into a 100 ml volumetric flask.
- .2 Add approximately 80 ml methanol to dissolve all crystals. Add methanol again to mark. Mix.
- .3 Allow the solution to age for at least one full week before using. Solution should be discarded if crystals start to develop in the solution or if the coating applied to the film dries out or crystallizes.

This step is not necessary for badges using paper substrates, see text of this report.

APPENDIX A

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13.1.5 Assembly of Dosimeters

- 13.1.5.1 Wash dosimeter parts with warm soapy water by agitation (do not use brush); rinse with D.I. water; pat dry. Blow the diffuser with GN_2 to ensure no water is lodged in the holes.
- .2 Pour some of the coating solution into a 250 ml beaker and place the filter discs in the solution and allow to soak for 5 minutes.
 - .3 Load the disc in the dosimeter holder, ensuring the disc is free of wrinkles or scratches. Press the spacer on top of the disc with forceps.
 - .4 Let the coating cure at room temperature with disc uncovered for 3 to 4 minutes.

NOTE

Cured coating should be sticky and shiny, not dried out with crystals.

This step is not necessary for badges using paper substrates, see text of this report.

- .5 Place the diffuser and then the cover on the dosimeter holder.
- .6 Properly label the dosimeter with lab number and data assembled.
- .7 Place the dosimeters in a polypropylene bag and store in a refrigerator.

APPENDIX B

The badge analysis method used by Wiltech Analytical Laboratory are compiled in the following Appendix. The method retains its internal Wiltech reference number under the Appendix title.

APPENDIX B

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8.1 DETERMINATION OF MONOMETHYL HYDRAZINE VAPOR CONCENTRATION IN NITROGEN OR AIR

8.1.1 Apparatus

- 8.1.1.1 Spectrophotometer, UV-VIS, Varian Series 634, or equal.
- .2 Cells, Silica, UV-VIS, 1 cm rectangular.
- .3 Balance, analytical.
- .4 Gas meter, wet test, precision, ASTM D1071, calibrated, or equal.
- .5 Air sampling pump.
- .6 Glass midget impinger, fritted, 170-220 μ maximum pore diameter.
- .7 Pipets, serological, 10 ml.
- .8 Pipets, volumetric, 0.5 ml, 1 ml, 2 ml, 4 ml, 10 ml, 15 ml, and 25 ml.
- .9 Flasks, volumetric, 100 ml, 200 ml, and 500 ml.
- .10 Glass vials with screw caps, 20 ml.
- .11 Graduated cylinder, 250 ml.
- .12 Amber reagent bottle, 250 ml.
- .13 Glass wool.
- .14 Stopcock grease.
- .15 Flow control valve.
- .16 Tubing, Teflon and Tygon, assorted sizes and lengths.

8.1.2 Chemicals

- 8.1.2.1 Sulfuric acid H_2SO_4 , concentrated, reagent grade.
- .2 p-Dimethylaminobenzaldehyde, p-DAB, reagent grade.
- .3 Monomethyl hydrazine sulfate salt, $MMH \cdot H_2SO_4$, reagent grade.
- .4 Methanol, CH_3OH , absolute, reagent grade.

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8.1.3 Safety

- 8.1.3.1 General - Refer to Section IV of Toxic Vapor Detector Calibration Manual 4-0-111 for safety requirements and specific hazards, precautions and emergency procedures concerning fire (Paragraph 4.4.1) and hypergols (Paragraph 4.4.4.)
- 8.1.3.2 Safety Equipment (Personal)
 - 8.1.3.2.1 Face shield.
 - .2 Laboratory coat or rubber apron.
 - .3 Gloves, chemical-resistant.
- 8.1.3.3 Safety Equipment (Laboratory)
 - 8.1.3.3.1 Fume hood.
 - .2 Safety shower and eyewash fountain.
 - .3 MMH concentration monitoring device.
 - .4 Fire extinguisher.

WARNING

Monomethyl hydrazine is a suspected carcinogenic chemical. Handle hydrazine only in a fume hood. Avoid all oxidizing agents. Wear personal safety equipment. Note location of the closest fire extinguisher, safety shower, and eyewash fountain. Ensure test area conforms to good housekeeping standards. Monitor working area MMH concentration with a calibrated monitoring device.

8.1.4 Preparation of Reagents

- 8.1.4.1 Sulfuric acid absorbing solution, 0.1 N (nominal)-
Pipet 3 ml of concentrated sulfuric acid into 1 liter volumetric flask containing approximately 500 ml D.I. water, mix, and bring volume to mark with D.I. water.
- .2 p-DAB Solution - Mix 1.6 g p-DAB, 5 ml concentrated H_2SO_4 , and 200 ml methanol in an amber reagent bottle. Store in dark place. Shelf life of the solution is two weeks.

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- 8.1.4.3 Monomethyl hydrazine stock solution - 100 ppm -
Transfer 0.157 g of MMH·H₂SO₄ salt, weighed to the nearest 0.01 mg, to a 500 ml volumetric flask containing about 100 ml of 0.1 N H₂SO₄. Mix. Fill to the mark with 0.1 N H₂SO₄.
- .4 MMH working standard solutions - Pipet 0.5, 1.0, and 2.0 ml of monomethyl hydrazine stock solution respectively into 100 ml volumetric flasks and bring to volume with 0.1 N H₂SO₄. The concentrations of the working standard solutions are 0.5, 1.0, and 2.0 ppm.
- 8.1.5 Sampling of Monomethyl Hydrazine Vapor
- 8.1.5.1 Set up the sampling apparatus as in Figure 1.
- .1 Pipet 25 ml of 0.1 N H₂SO₄ into the impinger, grease the stopper lightly, and close.
- .3 Turn on the air pump and adjust the flow rate control valve to pass 0.5 liter per minute flow.
- .4 Attach the inlet of midget impinger to hydrazine vapor source with a short piece of Teflon tubing.
- .5 As a guide, sample 6 liters for 1.5 ppm monomethyl hydrazine vapor and 3 liters for 5 ppm monomethyl hydrazine vapor.
- 8.1.6 Analysis of Sample
- 8.1.6.1 Pipet 10 ml of 0.1 N H₂SO₄, 0.5 ppm, 1.0 ppm, and 2 ppm working standard solutions and sample solutions respectively into labeled glass vials. The 10 ml of 0.1 N H₂SO₄ solution is used as reagent blank.
- .2 Pipet 4 ml of p-DAB solution into each vial; cap, and mix thoroughly.
- .3 After 30 minutes, zero the spectrophotometer with reagent blank at 457 nm and slit 2.
- .4 Read the absorbances of the standard and sample solutions against reagent blank.

NOTE

Refer to spectrophotometer instruction manual as required.

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- 8.1.6.5 Plot absorbance readings vs. concentrations of the standard solutions.
- .6 Determine from the standard curve the concentrations of MMH present in each sample solution.

8.1.7 Calculation

$$\text{ppm MMH in nitrogen (or air)} = \frac{13.3 A}{V}$$

A = ppm of MMH in sample solution

V = liters of MMH vapor sampled

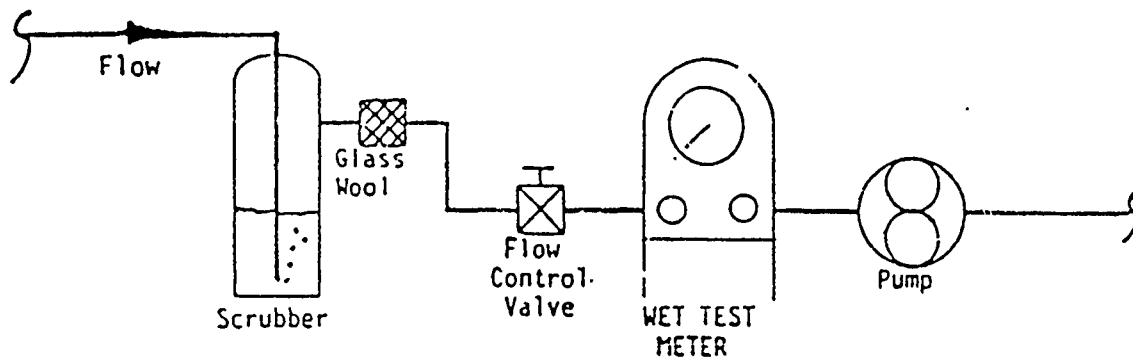


FIGURE 1 - HYPERGOLIC FUEL VAPOR SAMPLING APPARATUS

APPENDIX B

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8.2 DETERMINATION OF HYDRAZINE VAPOR CONCENTRATION IN NITROGEN OR AIR

8.2.1 Apparatus

- 8.2.1.1 Spectrophotometer, UV-VIS, Varian Series 634, or equal.
- .2 Cells, Silica, UV-VIS, 1 cm rectangular.
- .3 Balance, analytical.
- .4 Gas meter, wet test, precision, ASTM D1071, calibrated, or equal.
- .5 Air sampling pump.
- .6 Glass midget impinger, fritted, 170-220 μ maximum pore diameter.
- .7 Pipets, serological, 10 ml.
- .8 Pipets, volumetric, 0.5 ml, 1 ml, 2 ml, 10 ml, 15 ml, and 20 ml.
- .9 Flasks, volumetric; 100 ml, 200 ml, and 500 ml.
- .10 Glass vials with screw caps, 20 ml.
- .11 Graduated cylinder, 200 ml.
- .12 Amber reagent bottle, 250 ml.
- .13 Glass wool.
- .14 Stopcock grease.
- .15 Flow control valve.
- .16 Tubing, Teflon and Tygon, assorted sizes and lengths.

8.2.2 Chemicals

- 8.2.2.1 Sulfuric acid, H_2SO_4 , concentrated, reagent grade.
- .2 p-Dimethylaminobenzaldehyde, p-DAB, reagent grade.
- .3 Hydrazine sulfate, $(N_2H_4) \cdot H_2SO_4$, reagent grade.
- .4 Methanol, CH_3OH , absolute, reagent grade.

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8.2.2.5 D. I. water.

8.2.3 Safety

8.2.3.1 General - Refer to Section IV of Toxic Vapor Detector Calibration Manual 4-0-111 for safety requirements and specific hazards, precautions and emergency procedures concerning fire (Paragraph 4.4.1) and hypergols (Paragraph 4.4.4.).

8.2.3.2 Safety Equipment (Personal)

8.2.3.2.1 Face shield.

.2 Laboratory coat or rubber apron.

.3 Gloves, chemical-resistant.

8.2.3.3 Safety Equipment (Laboratory)

8.2.3.3.1 Fume hood.

.2 Safety shower and eyewash fountain.

.3 N₂H₄ concentration monitoring device.

.4 Fire extinguisher.

WARNING

Hydrazine is a suspected carcinogenic chemical. Handle hydrazine only in a fume hood. Avoid all oxidizing agents. Wear personal safety equipment. Note location of the closest fire extinguisher, safety shower, and eyewash fountain. Ensure test area conforms to good housekeeping standards. Monitor working area hydrazine concentration with a calibrated monitoring device.

8.2.4 Preparation of Reagents

8.2.4.1 Sulfuric acid absorbing solution, 0.1 N (nominal)-
Pipet 3 ml of concentrated sulfuric acid into 1 liter volumetric flask containing approximately 500 ml D.I. water, mix, and bring volume to mark with D.I. water.

.2 p-DAB Solution - Mix 1.6 g p-DAB, 5 ml concentrated H₂SO₄, and 200 ml methanol in an amber reagent bottle. Store in dark place. Shelf life of the

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8.2.4.3 Hydrazine stock solution - 100 ppm - Transfer 0.204 g of $(\text{N}_2\text{H}_4)\cdot\text{H}_2\text{SO}_4$ salt, weighed to the nearest 0.01 mg, to a 500 ml volumetric flask containing about 100 ml of 0.1 N H_2SO_4 . Mix. Fill to the mark with 0.1 N H_2SO_4 .

.4 Hydrazine working standard solutions - Pipet 0.5, 1.0, and 2.0 ml of hydrazine stock solution respectively into 100 ml volumetric flasks and bring to volume with 0.1 N H_2SO_4 . The concentrations of the working standard solutions are 0.5, 1.0, and 2.0 ppm.

8.2.5 Sampling of Hydrazine Vapor

8.2.5.1 Set up the sampling apparatus as in Figure 1.

.2 Pipet 25 ml of 0.1 N H_2SO_4 into the impinger, grease the stopper lightly, and close.

.3 Turn on the air pump and adjust the flow rate control valve to pass 0.5 liter per minute flow.

.4 Attach the inlet of midjet impinger to hydrazine vapor source with a short piece of Teflon tubing.

.5 As a guide, sample 6 liters for 1.5 ppm hydrazine vapor and 3 liters for 5 ppm hydrazine vapor.

8.2.6 Analysis of Sample

8.2.6.1 Pipet 10 ml of 0.1 N H_2SO_4 , 0.5 ppm, 1.0 ppm, and 2 ppm working standard solutions and sample solutions respectively into labeled glass vials. The 10 ml of 0.1 N H_2SO_4 solution is used as reagent blank.

.2 Pipet 0.5 ml of p-DAB solution into each vial; cap, and mix thoroughly.

.3 After 30 minutes, zero the spectrophotometer with reagent blank at 457 nm and slit 2.

.4 Read the absorbances of the standard and sample solutions against reagent blank.

NOTE

Refer to spectrophotometer instruction manual as required.

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- 8.2.6.5 Plot absorbance readings v . concentrations of the standard solutions.
- .6 Determine from the standard curve the concentrations of hydrazine present in each sample solution.

8.2.7 Calculation

$$\text{ppm N}_2\text{H}_4 \text{ in nitrogen (or air)} = \frac{19.1 A}{V}$$

A = ppm of hydrazine in sample solution

V = liters of hydrazine vapor sampled

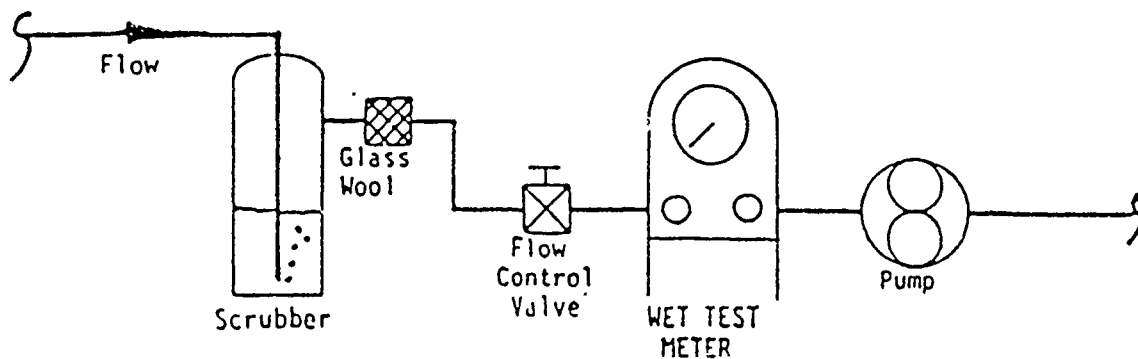


FIGURE 1 - HYPERGOLIC FUEL VAPOR SAMPLING APPARATUS

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13.2 DETERMINATION OF MMH AND N_2H_4 CONCENTRATION COLLECTED ON DOSIMETERS USING PHOSPHOMOLYBDIC ACID (PMA) METHOD

13.2.1 Apparatus

- 13.2.1.1 Balance, top load.
- .2 Dark bottle, 500 ml.
- .3 Spectrophotometer, Spectronic 21 or equal.
- .4 Sample tube for spectrophotometer.
- .5 Temperature-controlled environment.
- .6 Volumetric flasks, 25 ml, 100 ml, 2 liter.
- .7 Beakers, 500 ml.
- .8 Graduated cylinder, 500 ml.
- .9 Magnetic stirrer and stirring bar.
- .10 Syringe, 50 μ l.
- .11 Whatman No. 41 filter paper.
- .12 Unexposed dosimeter badges, as prepared in Appendix 13.1.
- .13 Micropipets, 10, 20, 50, and 100 μ l sizes, with disposable tips.

13.2.2 Reagents

- 13.2.2.1 Phosphomolybdic acid, $20MoO_3 \cdot 2H_3PO_4 \cdot 48H_2O$, reagent grade.
- .2 Hydrochloric acid, HCl, reagent grade.
- .3 Hydrazine, N_2H_4 , reagent grade.
- .4 Monomethyl hydrazine, MMH, reagent grade.
- .5 D.I. water.
- .6 Ice.

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13.2.3 Safety - Refer to Section IV of 4-0-111 for safety requirements and specific hazards, precautions, and emergency procedures concerning fire (Paragraph 4.4.1), hypergols (Paragraph 4.4.4), and acids (Paragraph 4.4.6).

13.2.3.1 Safety Equipment (Personal)

13.2.3.1.1 Face shield.

.2 Laboratory coat or rubber apron.

.3 Gloves, chemical-resistant.

WARNING

Concentrated sulfuric acid is very corrosive. Wear gloves while handling this chemical.

13.2.3.2 Safety Equipment (Laboratory)

13.2.3.2.1 Fume hood.

.2 Safety shower and eyewash fountain.

.3 MMH and N_2H_4 vapor concentration monitoring devices.

.4 Fire extinguisher.

WARNING

Monomethyl hydrazine and hydrazine are suspected carcinogenic chemicals. Handle MMH and N_2H_4 in a fume hood. Avoid all oxidizing agents. Wear personal safety equipment. Note location of the closest fire extinguisher, safety shower, and eyewash fountain. Ensure test area conforms to good housekeeping standards. Monitor working area MMH and N_2H_4 concentrations with a calibrated monitoring device.

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13.2.4 Preparation of Reagents

- 13.2.4.1 Phosphomolybdic acid color develop solution: Stir 9 grams of PMA in 300 ml of D.I. water in a beaker overnight. Filter into a dark bottle and store in a dark place. Do not allow the solid or liquid reagent to contact metal.
- .2 Hydrochloric acid, 0.1N: Add 8.6 ml of HCl to a 2-liter volumetric flask containing approximately 1 liter D.I. water. Add D.I. water to mark and mix.
- .3 Stock hydrazine solution, 320 $\mu\text{g/ml}$: Fill a 100 ml volumetric flask to mark with 0.1N HCl solution. Add, below the surface, 31.7 μl N_2H_4 to the solution. Mix well.
- .4 Stock MMH solution, 320 $\mu\text{g/ml}$: Fill a 100 ml volumetric flask to mark with 0.1N HCl solution. Add, below the surface, 36.6 μl MMH to the solution. Mix well.
- .5 Determine the actual concentration of the stock N_2H_4 or MMH solution by coulometric analysis as outlined in Appendix 8.11 of 4-0-111 using 10 μl of the stock solution for the analysis.
- .6 Reagent blank and working standards: Extract one previously prepared, unexposed dosimeter badge for the reagent blank and each standard to be used. Extract by placing the paper badge in 8 ml of 0.1N HCl and place on a magnetic stirrer for approximately 1 minute. Transfer the solution to a labeled 25 ml volumetric flask. Rinse off badge with 5 ml of 0.1N HCl and add this portion to the contents of the volumetric flask. Add the amount of N_2H_4 or MMH stock solution listed in the table below to each standard flask to yield the desired concentration.

Number of μl	Concentrations	
	N_2H_4	MMH
0 (blank)	0	0
10	3.17	3.20
20	6.34	6.40
50	15.85	16.00
100	31.70	32.00

13.2.5 Analysis of Dosimeter Samples

- 13.2.5.1 Extract the sample badges in the same manner that the unexposed badges were extracted in Paragraph 13.2.4.6.
- .2 Add 7.5 ml of PMA to each of the 25 ml flasks containing blank standards and samples. Fill to mark with 0.1N HCl. Mix.

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- 13.2.5.3 Digest each of the 25 ml flasks at 87°C for 50 minutes.
- .4 Cool in ice bath to stop reaction.
- .5 Allow solution to come to room temperature.
- .6 Obtain absorbance readings at 730nm within 30 minutes. Zero instrument with D. I. water. Read reagent blank, standards, and samples against D. I. water.

NOTE

Refer to instrument manual as required.

13.2.6 Calculation

- 13.2.6.1 Plot absorbance vs. concentration of the standards.
- .2 Read the result of the samples directly in μg from the graph.

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- 13.3 DETERMINATION OF MMH AND N_2H_4 COLLECTED ON DOSIMETERS USING COULOMETRIC METHOD
- 13.3.1 Apparatus
- 13.3.1.1 Coulometer, 0.1ma, 30mv, with platinum wire electrodes.
- .2 150 ml beaker with 40 ml mark, used as reaction vessel.
- .3 Stirring bar and magnetic stirrer.
- .4 Recorder, Soltec Model 1241, or equal.
- .5 Volumetric flask, 2 liter.
- .6 Forcep, plastic.
- .7 Pipet, graduated, 10 ml.
- .8 Scoop, two scoops yield approximately 0.4 g KBr.
- 13.3.2 Reagents
- 13.3.2.1 Potassium bromide, KBr, reagent grade.
- .2 Sulfuric acid, H_2SO_4 , concentrated, reagent grade.
- .3 D.I. water.
- .4 Hydrazine, N_2H_4 , reagent grade.
- .5 Monomethylhydrazine, reagent grade.
- 13.3.3 Safety
- 13.3.3.1 Refer to Section IV of 4-0-111 for safety requirements and specific hazards, precautions, and emergency procedures concerning fire (Paragraph 4.4.1), hypergols (Paragraph 4.4.4), and acids (Paragraph 4.4.6).
- 13.3.3.2 Safety Equipment (Personal)
- 13.3.3.2.1 Face shield.
- .2 Laboratory coat or rubber apron.
- .3 Gloves, chemical-resistant.

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WARNING

Concentrated sulfuric acid is very corrosive. Wear gloves while handling this chemical.

13.3.3.3 Safety Equipment (Laboratory)

13.3.3.3.1 Fume hood.

- .2 Safety shower and eyewash fountain.
- .3 MMH and N_2H_4 vapor concentration monitoring devices.
- .4 Fire extinguisher.

WARNING

Monomethyl hydrazine and hydrazine are suspected carcinogenic chemicals. Handle MMH and N_2H_4 in a fume hood. Avoid all oxidizing agents. Wear personal safety equipment. Note location of the closest fire extinguisher, safety shower, and eyewash fountain. Ensure test area conforms to good housekeeping standards. Monitor working area MMH and N_2H_4 concentrations with a calibrated monitoring device.

13.3.4 Preparation of Reagents

13.3.4.1 Sulfuric acid, 0.1M: Pipet 5.6 ml of H_2SO_4 concentration into a 1000 ml volumetric flask containing approximately 700 ml of D.I. water. Add D.I. water to the mark. Mix well.

- .2 Hydrazine stock solution, 100 ppm: Fill a 100 ml volumetric flask to the mark with 0.1M H_2SO_4 solution. Add, below the surface, 10 μ l of N_2H_4 into the solution. Mix well. Solution is stable for one week.
- .3 MMH stock solution, 100 ppm: Fill a 100 ml volumetric flask to the mark with 0.1M H_2SO_4 solution. Add, below the surface, 11.4 μ l of MMH into the solution. Mix well. Solution is stable for one week.

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13.3.5 Instrument Preparation

13.3.5.1 Set recorder parameters as follows:

Range - 500 mv
Speed - 60 cm per hour

- .2 Turn coulometer power on.
- .3 Fill the glass vessel containing a stirring bar to the mark with 0.1M H₂SO₄.
- .4 Place the glass vessel on the magnetic stirrer. Stir at medium speed.
- .5 Add 1.5 scoops of KBr to the solution. Stir until KBr is dissolved.
- .6 Place the electrodes in the solution. Ensure the electrolyte (0.1M H₂SO₄) in the bromine generating electrode is approximately 1 inch above the solution in the vessel.
- .7 Turn on the recorder and lower the pen to start recording. When the line on the chart paper is level, simultaneously activate the coulometer CELL switch and the recorder marker.
- .8 When the recording line deflects upward approximately 1-1/2 inches, deactivate the cell switch, lift up the recorder pen, and promptly place the electrode in clean D.I. water.
- .9 Discard the solution in the vessel; rinse the vessel with D.I. water, then with 0.1M H₂SO₄.
- .10 Measure the reaction time in terms of distance in cm.
- .11 Repeat Paragraphs 13.3.6.3 and 13.3.6.10 until three consecutive runs indicate the same distance. This is the blank value.
- .12 To ensure that the instrument is functioning properly, repeat Paragraphs 13.3.6.3 to 13.3.6.10 with 30μl of N₂H₄ stock solution added to 0.1M H₂SO₄ in the vessel. The measured distance should be 6.0 cm +/-0.2 cm. If this distance cannot be achieved, notify the shift chemist.

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13.3.6 Analysis of Dosimeter Samples

- 13.3.6.1 Place dosimeter spacer and disc into the reaction vessel containing approximately 35 ml 0.1M H₂SO₄ and stir for approximately 30 seconds.
- .2 While taking them out, rinse the spacer and disc with approximately 10 ml 0.1M H₂SO₄. Ensure the volume of solution in the reaction vessel is 40 ml.
- .3 Repeat Paragraphs 13.3.6.4 through 13.3.6.10.

13.3.7 Calculation

moles MMH (or N₂H₄) =

$$\frac{(\text{cm specimen} - \text{cm blank}) \times 60 \frac{\text{sec}}{\text{min}} \times (.1 \times 10^{-3} \text{ amp})}{\text{chart speed} \frac{\text{cm}}{\text{min}} \times 96486 \times 4e^{-} \frac{(\text{amp-sec})}{\text{mole}}}$$

$$\mu\text{g MMH} = \text{moles MMH} \times 4.6 \times 10^7$$

$$\mu\text{g MMH} = \text{net cm for analysis titration} \times 0.715$$

$$\mu\text{g N}_2\text{H}_4 = \text{moles N}_2\text{H}_4 \times 3.2 \times 10^7$$

$$\mu\text{g N}_2\text{H}_4 = \text{net cm for analysis titration} \times 0.497$$

$$\text{PPM MMH in Air} = \frac{(\mu\text{g MMH}) (24.45 \text{ l/mole})}{(46.07 \text{ g/mole}) (\text{l sampled})}$$

$$\text{PPM N}_2\text{H}_4 \text{ in Air} = \frac{(\mu\text{g N}_2\text{H}_4) (24.45 \text{ l/mole})}{(32.05 \text{ g/mole}) (\text{l sampled})}$$

APPENDIX C

Data tables for the KSC Field Testing of the Citrate Sampler.

The data for each individual test is presented in one table.

The first column indicates the type of sample and distinguishes area and personnel samples.

The second column is used to designate the sampling site. At each test location two sites were selected.

The column titled "Day" indicates the day(s) the sample was exposed. For samples that were placed on a Monday and collected on Friday a "to 5" would appear.

The results of the analysis are in the remaining columns labeled A, B, C, and D.

The "A" column contains the coulometric titration results.

The "B" column contains the PMA results unless indicated by an * which indicates the coulometric spike procedure was used.

The "C" column is used for color badge results. NC is used to indicate No color.

The "D" column is used for the PDAB results obtained from the liquid impinger samples.

DATA FROM FIELD TEST K01

TYPE	AREA	DAY	MICROGRAMS		PPM	
			A	B	HRS C	PPM D
CITRATE PERSONNEL	1	1	0			
	2	1	0.11			
	1	2	0.07			
	2	2	0.07			
	1	3	0.11			
	2	3	0.07			
	1	4	0.14			
	2	4	0.07			
	1	5	0.07	3.5		
	2	5	0.07	2.92		
CITRATE AREA	1	TO 1	0.04			
	1	TO 1	0.07			
	2	TO 1		*0.07		
	2	TO 1	0.04			
	1	TO 3	0.07			
	1	TO 3	0.11			
	2	TO 3	0.07			
	2	TO 3	0.18			
	1	TO 5	0.07	3.11		
	1	TO 5	0.07	2.92		
	2	TO 5	0.07	1.96		
	2	TO 5	0.04	2.53		
CITRATE LAB BLANK	WT		0.04			
	WT		<0.04			
	WT		0.04			
	WT		0.07			
COLOR AREA	1	TO 5			NC	
	2	TO 5			NC	
IMPINGER AREA	1	1				<0.05
	2	1				0.06
	1	2				<0.05
	2	2				<0.05
	1	3				<0.05
	2	3				<0.05
	1	4				<0.05
	2	4				<0.05
	1	5				<0.05
	2	5				<0.05

* Analyzed by coulometric spike procedure.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K02

TYPE	AREA	DAY	MICROGRAMS		PPM HRS C	PPM D
			A	B		
CITRATE PERSONNEL	BOTH	1	0.07	3.7		
		1	0.04			
		2	0.21	4.2		
		2	0.79	3.8		
		3	0.32	3.1		
		3	0.25	2.8		
		4	0.07	*0.34		
		4	0.47	*0.18		
		5	0.04	3.6		
		5	0.11	2.5		
CITRATE AREA	1	TO 1	0.04			
	1	TO 1	0.07			
	2	TO 1	0.11			
	2	TO 1	0.07			
	1	TO 3	0.04			
	1	TO 3	0.04			
	2	TO 3	0.04			
	2	TO 3	0.04			
	1	TO 5	0.04	2.1		
	1	TO 5	<0.04	2.1		
CITRATE FIELD BLANK			0.07			
			0.11			
CITRATE LAB BLANK	WT		0.07			
	WT		<0.04			
	WT		<0.04			
COLOR AREA	(1)	TO 5			NC	
	(2)	TO 5			NC	
IMPINGER AREA	1	1				<0.05
	2	1				<0.05
	1	2				<0.05
	2	2				<0.05
	1	3				<0.05
	2	3				<0.05
	1	4				<0.05
	2	4				<0.05
	1	5				<0.05
	2	5				<0.05

* Analyzed by the coulometric spike procedure.

Detection Limit = 0.12 ug (coul)
Quant Limit = 0.4 ug (coul)

DATA FROM FIELD TEST K03

TYPE	AREA	DAY	MICROGRAMS		PPH	
			A	B	HRS C	PPH D
CITRATE PERSONNEL	1	1	1.36	*0.14		
	2	1	0.07			
	1	2	0.04			
	2	2	0.07			
	1	3	0.11			
	2	3	2.6	*0.86		
	1	4	0.07			
	2	4	0.14			
	1	5	0.11			
	2	5	0.18			
CITRATE AREA	1	TO 1	<0.04			
	1	TO 1	<0.04			
	2	TO 1	0.04			
	2	TO 1	0.04			
	1	TO 3	0.07			
	1	TO 3	0.07			
	2	TO 3	0.07			
	2	TO 3	0.07			
	1	TO 5	0.07			
	1	TO 5	0.25			
	2	TO 5	0.11			
	2	TO 5	0.14			
CITRATE FIELD BLANK			0.07			
			0.11			
			0.04			
CITRATE LAB BLANK WT			0.07			
			<0.04			
			0.04			
CITRATE BLANK			0.1			
COLOR					N/A	
IMPINGER AREA	1					<0.05
	2					<0.05
	1					<0.05
	2					<0.05
	1					<0.05
	2					<0.05
	1					<0.05
	2					<0.05
	1					<0.05
	2					<0.05

* Analyzed by coulometric spike procedure.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K04

TYPE	AREA	DAY	MICROGRAMS		PPM	PPM
			A	B	HRS	D
CITRATE PERSONNEL	BOTH	1	0.14			
	BOTH	1	0.04			
	BOTH	2	0.07			
	BOTH	2	0.04			
	BOTH	3	0.04			
	BOTH	3	0.11			
	BOTH	4	0.04			
	BOTH	4	0.04			
	BOTH	5	0.04			
	BOTH	5	0.04			
CITRATE AREA	1	TO	1	0.04		
	1	TO	1	0.04		
	2	TO	1	0.04		
	2	TO	1	0.04		
	1	TO	3	0.07		
	1	TO	3	0.04		
	2	TO	3	0.04		
	2	TO	3	0.04		
	1	TO	5	<0.04		
	1	TO	5	0.04		
	2	TO	5	<0.04		
	2	TO	5	<0.04		
CITRATE FIELD BLANK	1			<0.04		
	2			<0.04		
	EG&G			0.04		
	EG&G			0.0		
CITRATE LAB BLANK	WT			0.04		
	WT			0.04		
	WT			0.04		
	WT			0.04		
CITRATE BLANK				0.07		
COLOR AREA	1	TO	5		NC	
	2	TO	5		NC	
COLOR PERSONNEL	BOTH	TO	5		NC	
	BOTH	TO	5		NC	
	BOTH	TO	5		NC	
	BOTH	TO	5		NC	
IMPINGER AREA	1		1			<0.05
	2		1			<0.05
	1		2			<0.05
	2		2			<0.05
	1		3			<0.05
	2		3			<0.05
	1		4			<0.05
	2		4			<0.05
	1		5			<0.05
	2		5			<0.05

* Analyzed by coulometric spike procedure.
Detection Limit = 0.12 ug (coul)
Quant Limit = 0.4 ug (coul)

DATA FROM FIELD TEST K06

TYPE	AREA	DAY	MICROGRAMS		PPM	
			A	B	HRS C	PPM D
CITRATE PERSONNEL		2	0.04			
		2	0.21	*0.57		
		4	0.04			
		4	0.04			
CITRATE AREA	1	TO 1	0.32	*0.21		
	1	TO 1	0.36	*0.32		
	2	TO 1	0.07			
	2	TO 1	0.11			
	1	TO 3	0.32			
	1	TO 3	0.18	*0.38		
	2	TO 3	0.07	*0.31		
	2	TO 3	0.18			
	1	TO 4	0.07			
	1	TO 4		*0.21		
CITRATE BLANK	EG&G	2	0.02			
	EG&G	2	0.04	*4		
	EG&G	4	0.79	*1		
	EG&G	4	0.07			
CITRATE FIELD BLANK	1	TO 2	0.07	*0.45		
	2	TO 2	0.61	*0.04		
	1	TO 3	0.04			
	2	TO 4	0.04	*0.04		
	WT		0.04			
	WT		0.04			
CITRATE LAB BLANK	WT		0.01			
	WT		0.04			
	WT		0.01			
COLOR AREA	1	TO 1			NC	
	2	TO 1			NC	
	1	TO 2			NC	
	2	TO 2			NC	
	1	TO 3			NC	
	2	TO 3			NC	
	1	TO 4			NC	
	1	TO 4	**0.11		NC	** Suspected of misnumbering
	2	TO 4			NC	
	2	TO 4			NC	
IMPINGER AREA	1	1				<0.05
	2	1				<0.05
	1	2				<0.05
	2	2				<0.05
	1	3				<0.05
	2	3				<0.05
	1	4				<0.05
	2	4				<0.05

*Analyzed by coulometric spike procedure. Detection Limit = 0.12 ug (coul) Quant Limit = 0.4 ug (coul)

DATA FROM FIELD TEST K07

TYPE	AREA	DAY	MMH MICROGRAMS		HRS C	PPM D	COMMENT
			A	B			
CITRATE	AREA	1	TO	1	3.18	<0.5	
		1	TO	1	4.58	0.9	
		2	TO	1	1.57	<0.5	
		2	TO	1	0.57	0.7	
		1	TO	3	8.65	0.2	
		1	TO	3	18.66	1.1	
		2	TO	3	3.75	<0.5	
		2	TO	3	1.86	<0.5	
		1	TO	5	13.59	0.7	
		1	TO	5	23.67	<0.5	
		2	TO	5	2.71	<0.5	
		2	TO	5	2.57	<0.5	
CITRATE	PERSONNEL	4			5.58	3.25	THE "A" BADGE WAS WET
		4			5.11	4.29	
		5			8.79	<0.5	
		5			11.26	2.6	
CITRATE	BLANK	1			8.4		
		1			12.1		
		2			1.75		
		2			1.43		
COLOR	AREA	1	TO	1		NC	
		1	TO	2		NC	
		1	TO	3		NC	
		1	TO	4		NC	
		1	TO	5		NC	
		2	TO	1		NC	
		2	TO	2		NC	
		2	TO	3		NC	COLOR AFTER AFTER HCl EXPOSURE
		2	TO	4	<0.07	"	
		2	TO	5	<0.07	"	
IMPINGER	AREA	1		1		<0.05	
		2		1		<0.05	
		1		2		<0.05	
		2		2		<0.05	
		1		3		<0.05	
		2		3		0.28	
		1		4		<0.05	
		2		4		<0.05	
		1		5		<0.05	
		2		5		<0.05	

Detection Limit = 0.12 ug (coul)
Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K08

TYPE	AREA	DAY	HYDRAZINE MICROGRAMS		PPM		COMMENT
			A	B	HRS C	PPM D	
CITRATE AREA	1	TO 1	5.29	<1.5			
	1	TO 1	6.21	<1.5			
	1	TO 3	4.85	<1.5			
	1	TO 3	5.96	<1.5			
	1	TO 5	9.02	<1.5			
	1	TO 5	9.99	<1.5			
	2	TO 1	1.42	<1.5			
	2	TO 1	0.97				
	2	TO 3	1.12	<1.5			
	2	TO 3	0.75	<1.5			
	2	TO 5	0.37	<1.5			
	2	TO 5	0.12	<1.5			
	CITRATE BLANKS	1	TO 1	3.85			
1		TO 2	3.16				BLIND BLANKS
1		TO 3	3.21				"
1		TO 4	5.09				"
1		TO 5	4.35				"
2		TO 1	2.24				"
2		TO 2	0.55				"
2		TO 3	1.09				"
2		TO 4	1.64				"
2		TO 5	0.87				"
CITRATE BLANK	OFFICE		<0.03				
	OFFICE		0.22	<1.5			
COLOR AREA	1	TO 1			NC		
	1	TO 2			NC		
	1	TO 3			NC		
	1	TO 4			NC		
	1	TO 5			NC		
	2	TO 1			NC		
	2	TO 2			NC		
	2	TO 3			NC		
	2	TO 4			NC		
	2	TO 5			NC		
IMPINGER AREA	1	1				<0.02	
	2	1				<0.02	
	1	2				<0.02	
	2	2				<0.02	
	1	3				<0.02	
	2	3				<0.02	
	1	4				<0.02	
	2	4				<0.02	
	1	5				<0.02	
	2	5				<0.02	

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K09

TYPE	AREA	DAY	MICROGRAMS		PPM		COMMENTS
			A	B	HRS C	PPM D	
CITRATE AREA	1	TO 1	5.08	--			
	1	TO 1	5.61	N/A			
	1	TO 3	6.36	--			
	1	TO 3	8.58	--			
	1	TO 3	7.61	--			
	1	TO 3	8.08	* 7.6			
	2	TO 1	3.00	*2.99			
	2	TO 1	2.54	*2.56			
	2	TO 3	5.68	--			
	2	TO 3	2.72	N/A			
	2	TO 3	3.54	*3.52			
	2	TO 3	3.25	N/A			
CITRATE BLANK	1	TO 1	3.47				
	1	TO 2	2.93				
	1	TO 3	4.25				
	1	TO 3	2.90				
	1	TO 3	3.18				
	2	TO 1	2.11				
	2	TO 2	1.93				
	2	TO 3	2.25				
	2	TO 3	1.75				
	2	TO 3	>43.8				SUSPECT DATA
COLOR AREA	1	TO 1				<0.07	
	1	TO 2				0.07	
	1	TO 3				0.14	
	1	TO 3				0.14	
	1	TO 3				0.14	
	2	TO 1				<0.07	
	2	TO 2				<0.07	
	2	TO 3				<0.07	
	2	TO 3				<0.07	
IMPINGER AREA	1	1				0.05	
	2	1				0.1	
	1	2				<0.1	
	2	2				<0.1	
	1	3				<0.1	
	2	3				<0.1	

* Analyzed by coulometric spike procedure.

-- SPEC 20 broken, samples lost.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K10

TYPE	AREA	DAY	MICROGRAMS	PPH		PPH	COMMENTS
				A	B		
CITRATE	AREA	1	TO 1	12.58	<1.5		
		1	TO 1	13.01	<1.5		
		1	TO 3	27.78	<1.5		
		1	TO 3	20.20	<1.5		
		1	TO 5	--	<1.5		WET
		1	TO 5	--	<1.5		"
* CITRATE	AREA	1	TO 1	0.04			
		1	TO 1	0.07			
		1	TO 3	2.07			
		1	TO 3	1.5			
		1	TO 5	--			
		1	TO 5	--			
CITRATE	BLANK	2	3	2.82			
		2	4	1.32			
		2	5	1.72			
CITRATE	BLANK	1	TO 1	6.44	<1.5		
		1	TO 2	12.19	<1.5		
		1	TO 3	6.47	<1.5		
		1	TO 4	8.72	<1.5		MAY HAVE BEEN WET, DRY AT ANALYSIS TIME
		1	TO 5	13.94	<1.5		WET
COLOR	AREA	1	TO 1			NC	
		1	TO 2			NC	
		1	TO 3			<0.07	
		1	TO 4			--	WET
		1	TO 5			--	CONTAMINATED WITH SAND
IMPINGER	AREA	1	1			<0.05	
		1	1			<0.05	
		1	2			<0.05	
		1	2			<0.05	
		1	3			<0.05	
		1	3			<0.05	
		1	4			<0.05	
		1	4			<0.05	
		1	5			<0.05	

BLANKS AND STANDARDS

	7/12/88	7/13/88	7/14/88	7/15/88	7/18/88
100 PPM STD	96.5	104	106	106	105
WT BLK 1	0.11	0.11	0.18	.57	.18
WT BLK 2	0.18	0.11	0.18	1.07, .43	1.07
MYLAR BLK	0.07		0.07	<.04	.14

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

* A Mylar substrate was used for these samples.

Detection Limit = 0.12 ug (cou)

DATA FROM FIELD TEST K10A

TYPE	AREA	DAY	MICROGRAMS		PPM		COMMENTS
			A	B	HRS C	PPM D	
CITRATE AREA	1	TO 1	--	<1.0			
	1	TO 1	<0.04	<1.0			
	1	TO 3	<0.04	--			
	1	TO 3	<0.04	<1.0			
	1	TO 5	<0.04	--			
	1	TO 5	0.09	<1.0			
	2	TO 1	0.04	<1.0			
	2	TO 1	0.21	<1.0			
	2	TO 3	0.09	<1.0			
	2	TO 3	0.27	<1.0			
	2	TO 5	0.13	<1.0			
	2	TO 5	0.09	1.0			
CITRATE BLANK	1	TO 1	<0.04	<1.0			
	1	TO 3	<0.04	<1.0			
	1	TO 5	0.13	<1.0			
	2	TO 1	<0.04	<1.0			
	2	TO 3	<0.04	<1.0			
	2	TO 5	0.09	1.2			
IMPINGER AREA	1	1				<0.05	
	2	1				<0.05	
	1	2				<0.05	
	2	2				<0.05	
	1	3				<0.05	
	2	3				<0.05	
	1	4				<0.05	
	2	4				<0.05	
	1	5				<0.05	
2	5				<0.05		

BLANKS AND STANDARDS

	1/17/89	1/19/81/23/89
100 PPM STD	102	109 104
WT BLK 1	0.18	0.18 0.04
WT BLK 2	--	0.29 0

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

-- Samples lost

Detection Limit = 0.12 ug (coul)
Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K11

TYPE	AREA	DAY	MICROGRAMS		PPM	
			A	B	HRS C	PPM D
CITRATE AREA	1	TO 1	--	<1.0		
	1	TO 1	0.29	<1.0		
	1	TO 3	0.45	<1.0		
	1	TO 3	0.45	<1.0		
	1	TO 5	0.5	* 0.7		
	1	TO 5	0.3	* 0.5		
	2	TO 1	0.07	<1.0		
	2	TO 1	0.14	<1.0		
	2	TO 3	0.23	<1.0		
	2	TO 3	0.45	<1.0		
	2	TO 5	0.21	* 0.21		
	2	TO 5	0.14	* 0.14		
CITRATE BLANK	1	TO 1	0.07	<1.0		
	1	TO 3	0.3	<1.0		
	1	TO 5	<0.04	* <0.04		
	2	TO 1	0.07	<1.0		
	2	TO 3	0.5	<1.0		
	2	TO 5	<0.04	* <0.04		
IMPINGER AREA	1	1				<0.05
	2	1				<0.05
	1	2				<0.05
	2	2				<0.05
	1	3				<0.05
	2	3				<0.05
	1	4				<0.05
	2	4				<0.05
	1	5				<0.05
	2	5				<0.05

BLANKS AND STANDARDS

	2/14/89	2/16/89	2/20/89
100 PPM STD	100	104	103
WT BLK 1	0.04	0.07	0.04
WT BLK 2	0.00	0.09	0.04

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

* Analyzed by the coulometric spike procedure.

Detection Limit = 0.12 ug (coul)

Quant Limit = 0.4 ug (coul)

DATA FROM FIELD TEST K12

TYPE	AREA	DAY	MICROGRAMS		PPH	PPH	COMMENTS
			A	3	HRS C	D	
CITRATE AREA	1	TO 1	<0.03	<1.0			
	1	TO 1	<0.03	<1.0			
	1	TO 3	<0.03	---			
	1	TO 3	<0.03	<1.0			
	1	TO* 7	<0.03	<1.0			
	1	TO* 7	0.25	<1.0			
	2	TO 1	<0.03	---			
	2	TO 1	0.1	<1.0			
	2	TO 3	<0.03	---			
	2	TO 3	0.03	<1.0			
	2	TO* 7	0.6	<1.0			
	2	TO* 7	0.5	<1.0			
CITRATE BLANK	1	TO 1	0.05	<1.0			
	1	TO 3	0.1	---			
	1	TO* 7	<0.03	<1.0			
	2	TO 1	<0.03	<1.0			
	2	TO 3	<0.03	<1.0			
	2	TO* 7	<0.03	<1.0			
IMPINGER AREA	1	1				<0.02	
	2	1				<0.02	
	1	2				<0.02	
	2	2				<0.02	
	1	3				<0.02	
	2	3				<0.02	
	1	4				<0.02	
	2	4				<0.02	
	1	7				<0.02	
	2	7				<0.02	

BLANKS AND STANDARDS

	2/22/89	2/24/89	2/28/89
100 PPM STD	99.6	98.5	96.7
WT BLK 1	0.07	0.0	0.0
WT BLK 2	0.14	0.0	0.0

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

--- Suspended matter, no PMA data.

* Samples sealed over weekend, total exposure only 5 days.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K13

TYPE	AREA	DAY	MICROGRAMS		PPH	PPH	COMMENTS
			A	B	HRS		
CITRATE AREA		1	TO	1			
		1	TO	1	0.07	<1.0	
		1	TO	1	<0.04	<1.0	
		1	TO	3	<0.04	<1.0	
		1	TO	3	<0.04	<1.0	
		1	TO	5	<0.04	<1.0	
		1	TO	5	<0.04	<1.0	
		2	TO	1	0.14	<1.0	
		2	TO	1	<0.04	<1.0	
		2	TO	3	<0.04	<1.0	
		2	TO	3	<0.04	<1.0	
		2	TO	5	<0.04	<1.0	
		2	TO	5	0.04	<1.0	
CITRATE BLANK		1	TO	1	<0.04	<1.0	
		1	TO	1	<0.04	1.6	
		1	TO	3	0.04	<1.0	
		2	TO	3	0.07	<1.0	
		2	TO	5	<0.04	<1.0	
		2	TO	5	0.04	<1.0	
IMPINGER AREA		1		1		<0.05	
		2		1		<0.05	
		1		2		0.09	
		2		2		0.09	
		1		3		<0.05	
		2		3		<0.05	
		1		4		0.06	
		2		4		<0.05	
		1		5		<0.05	
		2		5		<0.05	

BLANKS AND STANDARDS

	3/28/89	3/30/89	4/3/89
100 PPM STD	107	104	107
WT BLK 1	0.00	0.00	0.21
WT BLK 2	0.00	0.14	0.21

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

* Samples analyzed by coulometry.

**Samples were damp.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K13A

TYPE	AREA	DAY	MICROGRAMS		PPH	
			A	B	HRS C	PPH D
CITRATE AREA	1	TO 1	21.77	*26.62		
	1	TO 1	16.52	* 17.55		
	1	TO 3	15.61	* 23.19		
	1	TO 3	23.54	* 22.65		
	1	TO 5	**>28	**,*>28		
	1	TO 5	**24.5			
CITRATE BLANK	1	TO 1	<0.04			
	1	TO 3	<0.04			
	1	TO 5	**<0.04			

BLANKS AND STANDARDS

	3/28/89	3/30/89	4/3/89
100 PPM STD	107	104	107
WT BLK 1	0.00	0.00	0.21
WT BLK 2	0.00	0.14	0.21

AVERAGE OF WT BLK 1 AND 2 USED TO CORRECT DATA

* Samples analyzed by coulometry.

**Samples were damp.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K14

TYPE	AREA	DAY	MICROGRAMS		BADGE HOUSING		
			A	B	BB = BLACK	WB = WHITE	
CITRATE AREA	1	TO 1	>14.2	<1	BB	ROOF, HORIZ	
	1	TO 3	>15.9	<1	BB	"	
	1	TO 5	>14.6	<1	BB	"	
	2	TO 1	2.4	<1	BB	ROOF, VERT., SOUTH	
	2	TO 3	3.5	<1	BB	"	
	2	TO 5	9.0	<1	BB	"	
	3	TO 1	13.5	7.4	WB	ANTENNA, HORIZ	
	3	TO 3	>15.3	>10.0	WB	"	
	3	TO 5	>14.9	>10.0	WB	"	
	4	TO 1	2.9	<1.0	BB	ANTENNA, VERT., SOUTH	
	4	TO 3	5.0	<1.0	BB	"	
	4	TO 5	>14.4	<1.0	BB	"	
	CITRATE BLANK	1	TO 1	<0.04		BB	BLANKS
		2	TO 1		<1.0	BB	
		1	TO 3	<0.04		BB	
		2	TO 3		<1.0	BB	
		1	TO 5	*<0.04		BB	
		2	TO 5		--	BB	
3		TO 1	14.3		WB		
4		TO 1		<1.0	WB		
3		TO 3	>17.7		WB		
4		TO 3		<1.0	WB		
3		TO 5	*>25.5		WB		
4		TO 5		<1.0	WB		
BLANK		OFFICE TO 5	<0.04	<1.0	BB		
		OFFICE TO 5	4.2	<1.0	WB		

*Problem with coulometric instrument, data may be suspect.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K15

TYPE	AREA	DAY	MICROGRAMS		PPM		COMMENTS
			A	B	HRS C	PPM D	
CITRATE AREA	1	TO 1	2.7	<1			W
	1	TO 1	<0.04				B
	1	TO 1	0.05				B
	1	TO 3	0.79	*0.09			W
	1	TO 3	<0.04				B
	1	TO 3	<0.04	<1			B
	1	TO 5	0.29	*0.63			W
	1	TO 5	0.07	<1			B
	1	TO 5	<0.04	<1			B
	1	TO 5	<0.04	<1			B
CITRATE AREA	2	TO 1	1.93	<1			W
	2	TO 1	<0.04				B
	2	TO 1	0.05				B
	2	TO 3	0.36	*0.2			W
	2	TO 3	<0.04				B
	2	TO 3	<0.04				B
	2	TO 5	0.57	*0.84			W
	2	TO 5	0.07	<1			B
	2	TO 5	<0.04	<1			B
CITRATE BLANKS	1	TO 1	2.36	<1			W
	1	TO 1	<.04				B
	1	TO 3	.5				W
	1	TO 3	<.04				B
	1	TO 5	.41	*0.52			W
	1	TO 5	.14	*<0.04			B
CITRATE BLANKS	2	TO 1	.93	<1			W
	2	TO 1	<.04				B
	2	TO 3	.36	*0.17			W
	2	TO 3	<.04				B
	2	TO 5	.79	*0.7			W
	2	TO 5	<.04	<1			B
COLOR AREA	1	1					NC
	2	1					NC
	1	2					NC
	2	2					NC
	1	3					NC
	2	3					NC
	1	4					NC
	2	4					NC
	1	5					NC
	2	5					NC
IMPINGER AREA	1	1					<0.1
	2	1					<0.1
	1	2					<0.1
	2	2					<0.1
	1	3					<0.1
	2	3					<0.1
	1	4					<0.1
	2	4					<0.1
	1	5					LOST
	2	5					LOST

* Analyzed by the coulometric spike procedure.

Detection Limit = 0.12 ug (coul) Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K16

TYPE	AREA	DAY	MICROGRAMS		BADGE HOUSING
			A	B	
CITRATE PERSONNEL	1	1	13.66	<1.0	W
	1	1	<0.04	<1.0	B
	2	1	>16.8	1.0	W
	2	1	1.0	<1.0	B
	1	2	4.65	1.7	W
	1	2	0.14	*<0.04	B
	2	2	>14.3	<1.0	W
	2	2	<0.04	<1.0	B
	2	3	>14.3	2.7	W
	2	3	0.21	*0.07	B
	1	3	5.36	<1.0	W
	1	3	0.14	*<0.04	B

* Analyzed by the coulometric spike procedure.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K17

TYPE	AREA	DAY	MICROGRAMS		PPM		BADGE HOUSING	
			A	B	HRS	PPM		
CITRATE AREA	1	TO 1	1.79	<1.0			W	
	1	TO 1	<0.04				B	
	1	TO 1	<0.04	* <0.04			B	
	1	TO 3	4.6	<1.0			W	
	1	TO 3	0.07				B	
	1	TO 3	<0.04	<1.0			B	
	1	TO 5	2.86	<1.0			W	
	1	TO 5	<0.04				B	
	1	TO 5	<0.04				B	
	2	TO 1	1.39	<1.0			W	
	2	TO 1	<0.04				B	
	2	TO 1	<0.04				B	
	2	TO 3	0.57	<1.0			W	
	2	TO 3	<0.04	* <0.04			B	
	2	TO 3	<0.04	* <0.04			B	
	2	TO 5	<0.04	<1.0			W	
	2	TO 5	<0.04				B	
	2	TO 5	<0.04				B	
	CITRATE BLANKS	1	TO 1	1.79	<1.0			W
		1	TO 1	<0.04				B
1		TO 3	3.79	<1.0			W	
1		TO 3	<0.04				B	
1		TO 5	2.79	<1.0			W	
1		TO 5	<0.04				B	
2		TO 1	1.43	<1.0			W	
2		TO 1	<0.04	* <0.04			B	
2		TO 3	0.14	<1.0			W	
2		TO 3	<0.04				B	
2		TO 5	0.18	<1.0			W	
2		TO 5	<0.04				B	
CITRATE PERSONNEL		1	2.15	<1.0			W	
		1	<0.04				B	
		1	1.43	<1.0			W	
		1	<0.04				B	
		3	<0.04				B	
		3		<1.0			W	
		3	2.36				W	
		5	<0.04	<1.0			B	
	5	<0.04	<1.0			W		
COLOR AREA	1	1		** NC/VAN			SLIGHT YELLOW/POAB	
	1	1		"			"	
	2	1		"			"	
	2	1		"			"	
	1	2		"			"	
	1	2		"			"	
	2	2		"			"	
	2	2		"			"	
	1	3		"			"	
	1	3		"			"	
	2	3		"			"	
	2	3		"			"	

DATA FROM FIELD TEST K17

TYPE	AREA	DAY	MICROGRAMS		PPM		BADGE HOUSING
			A	S	HRS C	PPM D	
IMPINGER AREA	1	1				<0.1	
	2	1				<0.1	
	1	2				<0.1	
	2	2				<0.1	
	1	3				<0.1	
	2	3				<0.1	
	1	4				<0.1	
	2	4				<0.1	
	1	5			--	LOST	
	2	5			--	LOST	

Badge housing: W = white, B = Black

* Samples analyzed by the coulometric spike procedure.

** GMD Dosimeter used as the color badge.

It contained two indicator sections:

Vanillin and P-Dimethylaminobenzaldehyde.

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

DATA FROM FIELD TEST K18

TYPE	AREA	DAY	MICROGRAMS		PPH		BADGE HOUSING
			A	B	HRS C	PPH D	
CITRATE	AREA	1	1	<0.04			W
		1	1	<0.04			B
		1	2	<0.04			B
		1	2	0.64			W
		1	3	0.68			W
		1	3	<0.04			B
CITRATE	PERSONNEL	2	1	1.5			W
		2	1	<0.04			B
		2	2	3.9			W
		2	2	<0.04			B
		2	3	2.5			W
		2	3	<0.04			B
CITRATE	BLANK	1	1	0.5			W
		1	1	<0.04			B
		1	2	0.5			W
		1	2	<0.04			B
		1	3	0.82			W
		1	3	<0.04			B
COLOR	AREA	1	1				** NC/VAN, PDAB
		1	1				** NC/VAN, PDAB
		1	2				** NC/VAN, SLIGHT YELLOW/PDAB
		1	2				** NC/VAN, SLIGHT YELLOW/PDAB
		1	3				** NC/VAN, SLIGHT YELLOW/PDAB
		1	3				** NC/VAN, SLIGHT YELLOW/PDAB
COLOR	PL JHNEL	2	1				** NC/VAN, PDAB
		2	1				** NC/VAN, PDAB
		2	2				** NC/VAN, SLIGHT YELLOW/PDAB
		2	2				** NC/VAN, SLIGHT YELLOW/PDAB
		2	3				** NC/VAN, SLIGHT YELLOW/PDAB
		2	3				** NC/VAN, SLIGHT YELLOW/PDAB

Detection Limit = 0.12 ug (coul)

Quant limit = 0.4 ug (coul)

* Analyzed by coulometric spike procedure

** GMD Dosimeter used as the color badge.

It contained two indicator sections:

Vanillin and P-Dimethylaminobenzaldehyde

APPENDIX D

Facility data sheets from the field testing of the citric acid sampler. The information was collected by the industrial hygienist at the initiation of a test. It describes the area, operations, and chemicals in the test location.

FACILITY DATA SHEET

FACILITY NAME: WILTECH K7-516FACILITY POINT OF CONTACT: ARDELL THURLOWDATE: 11/16/87

DESCRIPTION OF FACILITY/AREA: WILTECH Building K7-516 is a chemical analysis laboratory. This facility is located within the Propellants storage and service area of Kennedy Space Center. To the east of the facility is a deionized water plant and gaseous nitrogen loading station. To the west is a hazardous waste facility and meter station. K7-516 is a 32,000 sq ft. facility housing several different laboratories. The facility includes a chemical analysis lab, vapor detection lab, fuel and oxidizer labs, a component calibration shop, a recharger maintenance shop and a vacuum pump/systems repair shop. Mobile tankers and gas trailers are also present in the area parking lot.

DESCRIPTION OF OPERATIONS:

This facility is an industrial laboratory utilized by Kennedy Space Center to analyze any operations needed. This may include fuel and oxidizer purity level tests, precision cleaning of launch equipment, calibration of propellant detectors, analysis of potential hazardous waste and inspection of launch equipment.

CHEMICAL SUBSTANCES USED/STORED:

The facility is known to house at least 411 different chemical substances or reagents. Fuel and oxidizer are present in the building. All of these chemicals are used under a hood/ventilation system and the utmost care is taken when handling them. Technicians commonly use demineralized water, CCl₄, Isopropyl Alcohol, Methanol, weak acids, Freon 21, and numerous solvents.

FACILITY DATA SHEET

FACILITY NAME: HMF, M7-961FACILITY POINT OF CONTACT: E J JandaDATE: 11/30/87 - 12/4/87

DESCRIPTION OF FACILITY/AREA: The Hyperogol Maintenance Facility M7-961 is isolated in the southeast corner of the Industrial Complex at Kennedy Space Center. The area is surrounded by woods on all but the south side. Approximately one half mile to the south is M7-1061 which is utilized as offices and a control room. Within M7-961 there are two identical cells containing both fuel and oxidizer lines. These cells or rooms can be opened to the outside by large pull-up doors. A Mechanical Shop, Equipment Shop, and Office areas are also located within the building.

DESCRIPTION OF OPERATIONS:

The HMF M7-961 is the main facility to check out, service, and repair flight hardware on the OMS Pods and forward RCS before being sent to the OPF to be installed on an orbiter. The fuel and oxidizer found within the facility is flight residual and not stored or maintained in the building.

CHEMICAL SUBSTANCES USED/STORED:

The HMF M7-961 has both fuel and oxidizer lines in the east and west cells. This is flight residual and not stored or maintained in the building. Technicians may utilize Freon, methyl Ethyl Ketone, Isopropyl Alcohol, and 1,1,1 Trichloroethane to clean and maintain the flight hardware. Gaseous Nitrogen and Helium are also found within the facility.

FACILITY DATA SHEET

FACILITY NAME: M+O Paint Shop M6-486FACILITY POINT OF CONTACT: A. FranciscoDATE: 12/14/87 - 12/18/87

DESCRIPTION OF FACILITY/AREA:

The M+O Facility M6-486 is located in the Industrial Complex of Kennedy Space Center. The Industrial paint shop is located in the east corner of the M+O Facility. In addition to the paint shop the facility contains a carpentry shop, AC shop, electrical shop, tool crib, moving and roofing crew, machine shop, sheet metal and weld shop. No interior walls separate the individual shops. Vehicular traffic occurs adjacent to this facility and heavy mobile equipment is stored directly to the south.

DESCRIPTION OF OPERATIONS:

The M+O paint shop M6-486 is utilized by Kennedy Space Center for spray paint and sandblast operations. Silkscreens and stencils are also prepared in the shop. In addition paint equipment repair and maintenance also occurs in the facility.

CHEMICAL SUBSTANCES USED/STORED:

Technicians in the paint shop most often utilize methyl ethyl Ketone, lacquer thinner, xylene, mineral spirits, polyurethane thinner, epoxy thinner, zinc thinner, enamels, zinc primer, polyurethane varnish, coal tar epoxy paint, epoxy, lacquers and wash primers. A paint crib is also located in the shop to store the various paints and chemicals, and when technicians use the paints they wear MSA Full face respirators.

FACILITY DATA SHEET

FACILITY NAME: Hangar S, Life Support South AnnexFACILITY POINT OF CONTACT: B. MartinDATE: 11/19/88-1/15/88

DESCRIPTION OF FACILITY/AREA: Hangar S South Annex - EG & G Life Support Building 1726 is located in the Cape Canaveral Air Force Station Industrial Area. The 52,000 sq.ft. facility is utilized for portable breathing air maintenance and Automated Payload Assembly and checkout. Behind the hangar is a hazardous waste staging facility, to the south is Hangar AF or SRO recovery Bldg. and to the northeast is building AE or missile assembly building. The south annex or building to the left of the facility's main hangar is utilized as a life support building. This is the facility we utilized for the study.

DESCRIPTION OF OPERATIONS:

Hangar S South Annex is utilized for checkout, maintenance, and repair of portable breathing units, SCAPE suits, helmets, gloves and boots. They also provide life support for individuals during hazardous operations; and are responsible for the upkeep of tube bank breathing lines and emergency egress breathing units or ELSA's for all Kennedy Space Center and Cape Canaveral Air Force Station.

CHEMICAL SUBSTANCES USED/STORED:

Technicians at the facility commonly use a Toluene/Freon mix, Freon 113, Isopropyl Alcohol, Seal Grip, and O-ring lubrication. These chemicals are utilized to clean, repair, and maintain the scape suits, gloves and boots.

K016

FACILITY DATA SHEET

FACILITY NAME: Fuel Storage Area #1FACILITY POINT OF CONTACT: Jerry NormanDATE: 2/9/88 - 2/12/88

DESCRIPTION OF FACILITY/AREA: Fuel Storage Area #1 is located at the Cape Canaveral Air Force Station. This Area is utilized for liquid propellant and fuel storage. There is a fuel, oxidizer, sodium hydroxide, and incinerator area, as well as a storage area for A-50, JP-5 and RP-1. To the north of the facility is the solid fuel storage area #2, and a non-destruct test laboratory. To the west of the area is the banana river and to the south is a new fuel storage area under construction at this time.

DESCRIPTION OF OPERATIONS:

Liquid Fuel Storage Area #1 is used to store and maintain various hazardous liquid fuels and propellants. These may include hydrazine, MMH, N_2O_4 , NaOH, A-50, JP-5, and RP-1. These propellants and oxidizers are utilized for various launch programs and must be kept stable while they wait for future use.

CHEMICAL SUBSTANCES USED/STORED:

Liquid Fuel Storage Area #1 stores liquid propellants, fuels and oxidizers to include N_2H_4 , MMH, N_2O_4 , NaOH, A-50, JP-5, and RP-1, various gaseous tanks and trailers of GN_2 and Helium are also present in the area.

K07

FACILITY DATA SHEET

FACILITY NAME: Aft Skirt Test Facility (ASTF)FACILITY POINT OF CONTACT: John Roberts III or Craig MastersDATE: 5/2 - 5/6/88

DESCRIPTION OF FACILITY / AREA: The Aft Skirt Test Facility is located southeast of the Booster Assembly Refurbishment Facility. It consists of two levels, a fuel farm to the north, 2 test cells located to the east and west, a technical work shop, service and control room, and a scope suit-up area. To the south and east of the facility is swamp and to the north of the facility is the Lockheed Logistics equipment.

DESCRIPTION OF OPERATIONS: The area is utilized for acceptance testing and checkout of the SRB aftskirt's thrust vector control system (TVC system). Hydrazine testing, fuel system testing, and loading and checking of the fuel system with nitrogen is performed at this facility. The nitrogen system is piped underground which is used for purging the fuel load.

CHEMICAL SUBSTANCES USED/STORED: The fuel storage area maintains hydrazine along with temporary drums of hydraulic fluid. Also, isopropyl alcohol is utilized for flushing G.D's in the fuel storage area.

FACILITY DATA SHEET

608

FACILITY NAME: Aft Skirt Test Facility (ASTF)

FACILITY POINT OF CONTACT: John Roberts III or Craig Masters

DATE: 5/16-5/20/88

DESCRIPTION OF FACILITY / AREA: The Aft Skirt Test facility is located southeast of the Booster Assembly Refurbishment Facility. It consists of two levels, a fuel farm to the north, 2 test cells located to the east and west, a technical work shop, service and control room, and... a scape suit-up area. To the south and east of the facility is swamp and to the north of the facility is the Lockheed Logistics equipment.

DESCRIPTION OF OPERATIONS: The area is utilized for acceptance testing and checkout of the SRB aftskirt's thrust vector control system (trc system). Hydrazine testing, fuel system testing, and loading and checking of the fuel system with nitrogen is performed at this facility. The nitrogen system is piped underground which is used for purging the fuel load.

CHEMICAL SUBSTANCES USED/STORED: The fuel storage area maintains hydrazine along with temporary drums of hydraulic fluid. Also, isopropyl alcohol is utilized for flushing QO's in the fuel storage area.

FACILITY DATA SHEET

1609

FACILITY NAME Rotating Service Structure Launch Complex 39B

FACILITY POINT OF CONTACT _____

DATE. 6/15- 6/17

DESCRIPTION OF FACILITY: AREA: The Rotating Service Structure (RSS) is located in Launch Complex 39B. The RSS supports the payload change out room, the FRCS room and propellant loading platforms. The badges were placed on the 107 foot level next to the MMH propellant loading lines.

DESCRIPTION OF OPERATIONS:

No operations were performed at the time of this test. During propellant loading operations, MMH is piped into the OMS pod thru the propellant lines located on the 107 foot level.

CHEMICAL SUBSTANCES USED/STORED.

None

FACILITY DATA SHEET

K10

FACILITY NAME KSC Beach house

FACILITY POINT OF CONTACT _____

DATE 7/11 - 7/15/88

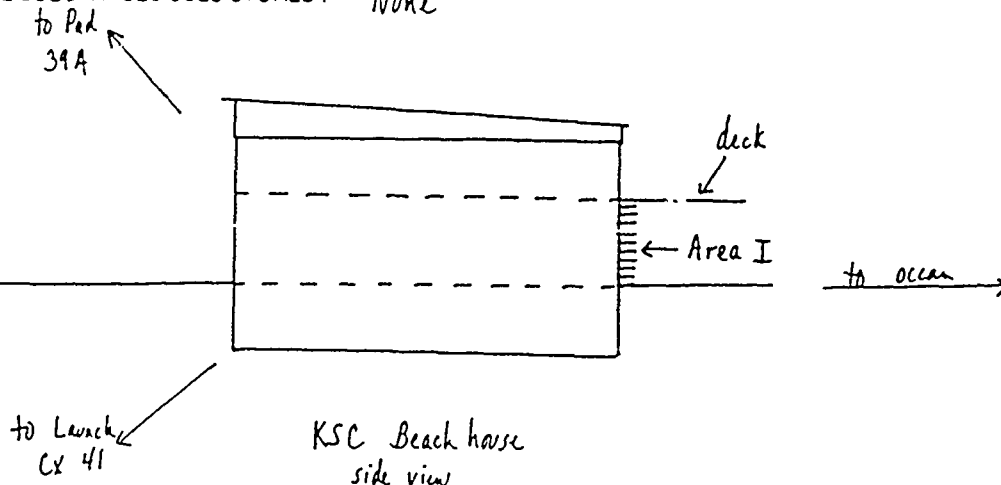
DESCRIPTION OF FACILITY AREA

The KSC Beachhouse is located southeast of Pad 39A, northeast of Launch Complex 41, and approximately 70 yards from the ocean. It consists of 3 levels including a basement. There are ~~to~~ no facilities to the immediate north, south, or west of the beachhouse.

DESCRIPTION OF OPERATIONS:

A roofing operation continued throughout the week which included the removal of a tar/rock material and the preliminary work for the installation of a new roof. There were contaminants (i.e. dust, roofing debris, windblown sand) in the area throughout the week.

CHEMICAL SUBSTANCES USED/STORED: None



FACILITY DATA SHEET

K10A

FACILITY NAME: Rotating Service Structure Launch Cx 39B

FACILITY POINT OF CONTACT: _____

DATE: 1/16/89 - 1/20/89

DESCRIPTION OF FACILITY / AREA :

The Rotating Service Structure (RSS) is located in Launch Complex 39B. The RSS supports the payload changeout room, the FRCS room and propellant loading platforms. The badges were placed on the 107 foot level next to the MMH propellant loading lines.

DESCRIPTION OF OPERATIONS :

No operations were performed at the time of this test.

During propellant loading operations, MMH is piped into the Orin pod through the propellant lines located on the 107 foot level.

CHEMICAL SUBSTANCES USED/STORED :

None

FACILITY DATA SHEET

K11

FACILITY NAME: VAB breakrooms 6B10 + 10B6

FACILITY POINT OF CONTACT: _____

DATE: 2/13-2/17/89

DESCRIPTION OF FACILITY / AREA :

Rooms 6B10 (Area I) and 10B6 (Area II) are the only designated smoking areas in Tower 'B'. Room 6B10 is located on the sixth floor with an area of 182 sq. ft. Room 10B6 is located on the tenth floor, level 115'-9", with an area of 217 sq. ft. Normal occupancy during an 8 hr. workday is approximately 3 people for both rooms. Various offices are located adjacent to both rooms and across the hallway from the rooms.

DESCRIPTION OF OPERATIONS :

The operations would include usual breakroom activities, such as smoking, eating, drinking, etc.

CHEMICAL SUBSTANCES USED/STORED :

None

VEHICLE ASSEMBLY BUILDING
Ground Floor Space Access & Usage

02-02-89

02-02-89

C-2

FACILITY DATA SHEET

K12

FACILITY NAME: Aft Skirt Test FacilityFACILITY POINT OF CONTACT: Craig MartensDATE: 2/21-2/27/89

DESCRIPTION OF FACILITY / AREA:

The Aft Skirt Test Facility is located southeast of the SRB Assembly Refurbishment Facility. It consists of two levels, a fuel farm to the north (Area I for this testing period), 2 test cells located to the east and west (test cell 1 which is located to the west is Area II for this testing period), a technical work shop, service and control room, and a scape suit-up area. To the south and east of the facility is swamp and to the north of the facility is Lockheed Logistic equipment.

DESCRIPTION OF OPERATIONS:

The area is utilized for acceptance testing and checkout of the SRB aftskirt's thrust vector control system (tvc system). Hydrazine testing, fuel system testing, and loading and checking of the fuel system with nitrogen is performed at this facility. The nitrogen system is piped underground which is used for purging the fuel load.

CHEMICAL SUBSTANCES USED/STORED:

The fuel storage area maintains hydrazine along with temporary drums of hydraulic fluid. Also, isopropyl alcohol is utilized for flushing OD's in the fuel storage area.

FACILITY DATA SHEET

K13

FACILITY NAME: Orbiter Processing Facility HB 1

FACILITY POINT OF CONTACT: _____

DATE: 3/27-3/31/89

DESCRIPTION OF FACILITY / AREA:

The OPF is situated west of the VAB. It consists of two high bays and a low bay all in one large building, a 10,000 sq. ft. office and training annex, fuel and oxidizer deservicing pads, and GO_2 and GH_2 storage pads. The latter are well separated and placed well away from the main building. The hangar accommodates the Orbiter and the access platforms, which effectively surround the Orbiter for ease of access and maintenance. Area I was located on the 2nd level access platform to the right of the Orbiter nose cap without the FRES installed. Area II was located on work level 10, panel 43 to the right of the GSE without the PHHS pad. Both areas were surrounded with various ground servicing and ground support equipment. (See attached for locations of areas)

DESCRIPTION OF OPERATIONS:

The OPF is used for processing returned Orbiters in preparation for reuse. Among the activities carried out in the OPF are Orbiter satting and deservicing, thermal protection subsystem refurbishment, payload removal and installation, and Orbiter active systems checkout.

CHEMICAL SUBSTANCES USED/STORED:

Chemical substances include ammonia, oxidizer, mono methyl hydrazine, tps chemicals and hydraulics.

K13

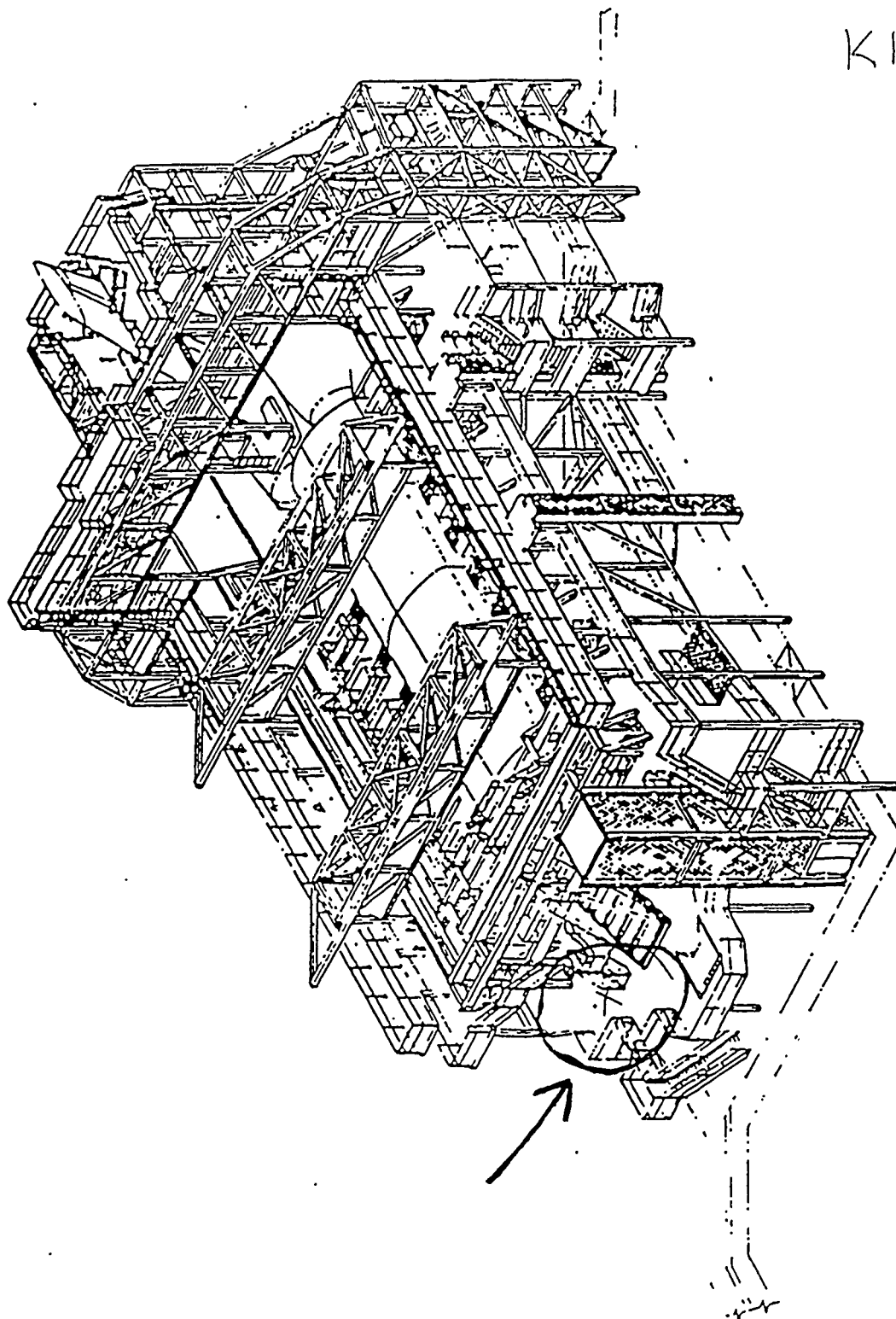


Figure 27-3. OPF Access Platforms
AREA I

FACILITY DATA SHEET

K13A

FACILITY NAME: Environmental Health Facility

FACILITY POINT OF CONTACT: _____

DATE: 3/27 - 3/31/89

DESCRIPTION OF FACILITY / AREA:

The Environmental Health Facility is located southeast of the ARF and northwest of Headquarters. It houses a health physics lab and an environmental sanitation and pollution control lab, in addition to a PLM lab located immediately behind the facility.

DESCRIPTION OF OPERATIONS:

This facility provides office space for approximately 50 Environmental Health employees and equipment for Industrial Hygiene, Environmental Sanitation and Pollution Control, and Health Physics. There was only one area for E and F badges which included the remaining badges after areas I and II at the OPF were set up. These badges were placed next to an antenna superstructure on the roof of this facility. The badges were facing directly toward the sun. No operations were performed on the roof during this week.

CHEMICAL SUBSTANCES USED/STORED:

None

FACILITY DATA SHEET

K14

FACILITY NAME: L7-1557 (Environmental Health Facility) Root Top and L7-1557 East Antenna SiteFACILITY POINT OF CONTACT: S.W. BrownDATE: 5/7-5/12/89

DESCRIPTION OF FACILITY / AREA:

The Environmental Health Facility Root Top is located southeast of the ARF and northwest of Headquarters. EHF houses a health physics lab and an environmental sanitation and pollution control lab. In addition, a PLM lab is located immediately behind this facility. The L7-1557 East Antenna Site was used as a remote monitoring site. It is approximately .3 mile east of the Environmental Health Facility and is surrounded by woods.

DESCRIPTION OF OPERATIONS:

During this testing period, there were no operations in either of these areas. L7-1557 Root Top was Areas I and II. Area I badges were placed flat and facing up. Area II badges were placed in a vertical position and were facing south. L7-1557 East Antenna Site was Areas III and II. Area III badges were placed flat and facing up. Area II badges were placed in a vertical position and were facing south. The badges in Area III were all white while the badges in the other areas were black.

CHEMICAL SUBSTANCES USED/STORED:

None

K14

KSC WEATHER CONDITIONS FOR 5/8-5/12/89

DAY	TEMPERATURE degrees F high,low	CLOUD COVERAGE OR VISIBILITY
Mon. 5/8	79,54	sunny
Tues. 5/9	82,61	sunny
Wed. 5/10	88,69	partly cloudy, heavy rains during the night
Thurs. 5/11	78,67	mostly sunny
Fri. 5/12	81,54	mostly sunny

TOTAL TIME EXPOSED BY DAY (MINUTES)

	Areas I and II	Areas III and IV
Mon. 5/8	328	333
Tues. 5/9	427	423
Wed. 5/10	377	356
Thurs. 5/11	464	469
Fri. 5/12	340	335

K15 & K16

Available Weather Conditions at KSC for 7/31-8/4/89

DAY	Temperature, degrees F high, low	cloud coverage/visibility
Mon. 7/31	data being used for a report, July unavailable	
Tues. 8/1	95, 74	mostly cloudy, 10 miles
Wed. 8/2	92, 74	mostly cloudy, 10
Thurs. 8/3	91, 73	mostly cloudy, 9
Fri. 8/4	91, 76	partly cloudy, 6

Test #16

FACILITY DATA SHEET

FACILITY NAME: m+o Paint Shop M6-486

FACILITY POINT OF CONTACT: A. Francisco

DATE: 8-2-89, 8-3-89, 8-4-89

DESCRIPTION OF FACILITY/AREA:

The m+o Facility M6-486 is located in the Industrial Complex of Kennedy Space Center. The Industrial paint shop is located in the east corner of the m+o Facility. In addition to the paint shop the facility contains a carpentry shop, AC shop, electrical shop, tool crib, moving and roofing crew, machine shop, sheet metal and weld shop. No interior walls separate the individual shops. Vehicular traffic occurs adjacent to this facility and heavy mobile equipment is stored directly to the south.

DESCRIPTION OF OPERATIONS:

The m+o paint shop m6-486. is utilized by Kennedy Space Center for spray paint and sandblast operations. Silkscreens and stencils are also prepared in the shop. In addition paint equipment repair and maintenance also occurs in the facility.

CHEMICAL SUBSTANCES USED/STORED:

Technicians in the paint shop most often utilize methyl ethyl Ketone, lacquer thinner, xylene, mineral spirits, polyurethane thinner, epoxy thinner, zinc thinner, enamels, zinc primer, polyurethane varnish, coal tar epoxy paint, epoxy, lacquers and wash primers. A paint crib is also located in the shop to store the various paints and chemicals, and when technicians use the paints they wear Full face respirators.

Test #18

FACILITY DATA SHEET

FACILITY NAME: HMF m7-961

FACILITY POINT OF CONTACT: E.J. Janda

DATE: 8-9-89, 8-10-89, 8-11-89

DESCRIPTION OF FACILITY/AREA: The Hyperogol maintenance Facility m7-961 is isolated in the southeast corner of the Industrial Complex at Kennedy Space Center. The area is surrounded by woods on all but the south side. Approximately one half mile to the south is m7-1061 which is utilized as offices and a control room. Within m7-961 there are two identical cells containing both fuel and oxidizer lines. These cells or rooms can be opened to the outside by large pull-up doors. A Mechanical Shop, Equipment Shop, and Office areas are also located within the building.

DESCRIPTION OF OPERATIONS:

The HMF m7-961 is the main facility to check out, service, and repair flight hardware on the OMS Pods and forward RCS before being sent to the OPF to be installed on an orbiter. The fuel and oxidizer found within the facility is flight residual and not stored or maintained in the building.

CHEMICAL SUBSTANCES USED/STORED:

The HMF m7-961 has both fuel and oxidizer lines in the east and west cells. This is flight residual and not stored or maintained in the building. Technicians may utilize Freon, methyl Ethyl Ketone, Isopropyl Alcohol, and 1,1,1 Trichloroethane to clean and maintain the flight hardware. Gaseous Nitrogen and Helium are also found within the facility.

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1990 May 30	3. REPORT TYPE AND DATES COVERED Final		
4. TITLE AND SUBTITLE Laboratory Development of a Passive Sampling Device for Hydrazines in Ambient Air		5. FUNDING NUMBERS		
6. AUTHOR(S) Taffe,* P. A., Crossman,* K. P., Wyatt, J. R., and Rose-Pehrsson, S. L.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5000		8. PERFORMING ORGANIZATION REPORT NUMBER NRL Memorandum Report 6660		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Kennedy Space Center, FL 32899		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
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12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) A passive sampling method applicable to personnel and area monitoring has been developed for the quantitation of hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) in ambient air at the part-per-billion (ppb) level. The method uses a black molded low density polyethylene badge consisting of a diffusion barrier and a citric acid collection medium. It collects samples that can be analyzed by the NIOSH colorimetric method or a coulometric titration procedure. The two millimeter thick diffusion barrier contains 144 one millimeter diameter holes and produces a collection rate for MMH of approximately 27 ml/min. The accuracy of data collected with this badge is within 30% of actual values. The dosimeter has demonstrated accuracy for sampling periods of 15 minutes to 66 hours, when sampling MMH at the threshold limit value (TLV) concentration of 200 ppb. The limits of detection are dictated by the specific analytical method. Coulometric titration will detect exposures of 30 ppb-hours. An evaluation of the effects of face velocity, relative humidity, and potential interferences was conducted.				
14. SUBJECT TERMS Threshold limit value (TLV) Monomethyl hydrazine Hydrazine			15. NUMBER OF PAGES 24	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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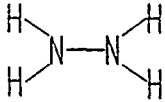
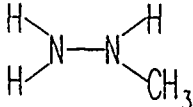
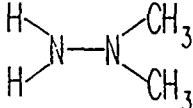
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LABORATORY DEVELOPMENT OF A PASSIVE SAMPLING DEVICE FOR HYDRAZINES IN AMBIENT AIR

INTRODUCTION

The potential carcinogenicity of hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) has caused concern for the health and safety of the workers that may come in contact with them. The monitoring of employee exposure and work place contamination is necessary to insure exposure remains below the defined limits and complies with the law. The chemical structures of these compounds, their ACGIH [1] and NIOSH [2] recommended exposure limits, and their diffusion constants are shown in Table 1. Potentially the exposure limits may be lowered to 10 ppb for all three hydrazines [3].

Table 1. Recommended Exposure Levels and Diffusivities for Hydrazine Propellants

Compound	Structure	ACGIH	NIOSH	D (cm ² /s)
Hydrazine		0.1 ppm	0.03 ppm	0.154
Monomethyl Hydrazine		0.2 ppm	0.04 ppm	0.122
Unsymmetrical Dimethylhydrazine		0.5 ppm	0.06 ppm	0.104

The reactivity of the hydrazines and their tendency to undergo oxidative decomposition has hindered the development of detection systems. For convenience, the term "hydrazines", when used in this report, refers to all three of the hydrazines in Table 1. Hydrazines are particularly prone to decompose catalytically on metal surfaces [4]. In order to sample hydrazines, a collection scheme is required with the ability to stabilize hydrazine and its derivatives without interfering with accepted analytical procedures. In addition a personnel dosimeter should be simple, cheap, not sensitive to typical work place interferences and not impede with worker performance.

Current methods of sampling hydrazines involve detector tubes or midget impingers with an acidic collection solution [5]. These are "active" sampling methods, meaning they involve the use of an air pump to draw the atmosphere through the collection medium. The pumps are bulky, expensive and require a power source for long-term operation, hence they are not ideal for personnel monitoring. Because of these constraints active methods are unsuitable to monitor large areas where many sampling points are required such as the servicing area for the Space Shuttle. It is desirable to monitor this area continuously so that if some hydrazine is accidentally released, the amount and area

affected can be determined. Maintaining a large number of active samplers in this area is not practical. It was the goal of this project to develop a passive dosimeter for hydrazine and MMH in the form of a badge that could be used either as an area monitor or personal sampler.

The first form of a quantitative personal sampling device utilizing passive collection was reported by Palmes and Gunnison in 1973 [6]. In its simplest form it consists of a tube with a collecting substance at the bottom. This type of sampler is often referred to as a "Palmes' tube" and has been found to behave ideally when the area to length ratio of the tube (A/L) is less than 0.1 cm [7]. Another passive sampler design in the form of a badge is shown in Figure 1. Ideally the diffusion barrier/draft shield is constructed so that the sampling rate only depends upon diffusion and is independent of the flow rate of the ambient air. Some designs incorporate a screen that can hold a loose collection medium such as activated charcoal in place [8,9]. The screen can also serve as the diffusion barrier. These types of devices are available commercially [10]. Such a system is not suitable for hydrazine collection [11].

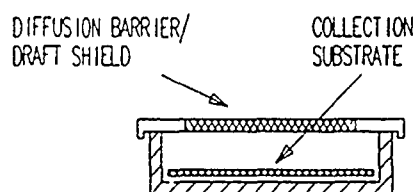


Figure 1. Schematic of a passive badge.

Due to the reactivity of hydrazine the choice materials for the badge design is limited. For instance it is not possible to use metal screens as a diffusion barrier/draft shield. Porous perfluoro polymers, such as *GoreTex*, cannot be used due to their large surface area. The behavior of low concentrations hydrazine with various materials has been previously studied at this Laboratory [12]. The only suitable materials of construction for a diffusion barrier are perfluoro polymers, polyethylene, and polypropylene. In addition to inertness, the diffusion barrier must sample at a rate high enough to collect sufficient material for measurement in a reasonable time. This is a stringent requirement as the TLV values for hydrazines are so low.

THEORY

Before discussing our particular badge design, it is worthwhile to review the theory of passive sampling. For an ideal badge design the mass sampling rate (M) of the passive collector depends only upon the diffusion coefficient (D) of the analyte as described by Fick's first law of diffusion integrated for a tube [13].

$$M = D (A/L) (C_1 - C_2) \quad (1)$$

Where: A = The area of the diffusion channel;
 L = The length of the diffusion channel;
 C_1 = The external (ambient) concentration of the analyte; and
 C_2 = The gas-phase concentration of the analyte at the surface of the collector

Hence the diffusive conductance (C_d) is merely:

$$C_d = D (A/L) \quad (\text{cm}^3/\text{s}) \quad (2)$$

Typically D is in cgs units. For our final badge design, that has a diffusion barrier consisting of 144 one mm diameter by two mm long holes, the C_d is $0.85 \text{ cm}^3/\text{s}$ based on a diffusion constant of $0.15 \text{ cm}^2/\text{s}$. Including the conductance of the air gap of the badge, the net sampling rate is $0.79 \text{ cm}^3/\text{s}$. The total conductance is the inverse of the sum of the inverses of the individual conductances when calculating conductances in series. These and subsequent calculations are based upon a diffusion constant of $0.15 \text{ cm}^2/\text{sec}$, one atmosphere pressure and 25°C . Additionally it is assumed that the concentration at surface of the collection medium is zero. Note the amount of material collected does not depend upon the ambient pressure and only depends upon the square root of temperature; thus these parameters can be neglected when performing diffusive sampling.

In contrast to equation 1, where diffusion is proportional to the area of the hole, the viscous flow conductance (C_v) is proportional to the area squared. In similar terms to equation 2, the Poiseuille equation can be reduced to equation 3 for flow at an average pressure of one atmosphere [13].

$$C_v = 2.2 \times 10^8 (A^2/L) \quad (\text{cm}^3/\text{s}/\text{atm}) \quad (3)$$

The mass flow is obtained by multiplying C_v by the gas concentration and the pressure difference. The advantage of using many small holes is based upon the fact that viscous flow is proportional to A^2/L ; whereas diffusive flow is proportional to A/L , see equation 1. Thus increasing the number of holes of the diffusion barrier of the badge, while keeping the total area of the holes constant, decreases the viscous conductance in proportion to the number of holes without affecting the diffusion rate. The principal assumption made using equations 1 and 3 is that these holes can be treated as tubes. This situation has been treated theoretically [14] and would reduce the viscous conductance by about factor of two.

Because of the magnitude of the constant in equation 3, it is understandable that viscous flow could have a large effect on the collection rate. For example, assume that there is a pressure imbalance across the badge face. Based on equation 3 a pressure difference on the order of 10^{-5} atmospheres would be sufficient to cause a flow of $1 \text{ cm}^3/\text{s}$ through ten of the holes. Although this pressure may seem extraordinary low, it should be compared to the pressure necessary to produce the flow in the one of the chambers used to measure the badge performance. The chamber is 10 cm diameter by 30 cm long and had a flow rate of 5 l/min. Based on equation 3, a pressure gradient of 10^{-9} atm would be sufficient to produce this flow. Thus in a normal environment there would be a negligible pressure difference across the badge face due to laminar flow across it. There might be some turbulence at the surface of the badge due to the holes that could result in slight pressure differences sufficient to induce flow through the holes. Thus reducing the C_v of the badge is important and having the badge face smooth would lessen this effect. Both are achieved by having a large number of small holes.

In order for the sampling rate of the badge to be independent of face velocity, the rate at which the sample can be transferred from the atmosphere to the badge should be much greater than the badge sampling rate. It is important to calculate this rate at low flows. At low flows the total conductance to the badge, C_t , is determined by two mechanisms: a pure diffusive term, C_d , that is independent of flow; and a convective term, C_c , that depends on the face velocity.

$$C_t = C_d + C_c \quad (4)$$

The diffusive term can be calculated from equation 2, assuming a face diameter of 2.5 cm and a length of 2.0 cm. This results in a flow rate of about 0.5 cm³/s for the diffusive term. Thus at the lowest face velocities the net sampling rate of the badge would be 0.3 cm/sec due to the C_d terms from equations 2 and 4.

Calculation of the convective term follows the method given by Bennett and Myers [15].

$$C_c = 0.66 D (A/x) (Re_L)^{0.5} (Sc)^{0.33} \quad (5)$$

Where: x = diameter of the badge face
 Re_L = the Reynold's number for flow along a surface
 Sc = the Schmidt number

This equation is for a wide plate and ignores edge effects; neither assumption is valid for our badge which is disk shaped. A disk would have a higher sampling rate; hence equation 5 provides a lower bound for the convective sampling rate. The Schmidt number, which is the ratio of viscosity to the product of the diffusion constant and the density, is about one. The Reynold's number is product of x , gas velocity, and density divided by gas viscosity. For our case the Reynold's number is about 1.5 times the gas velocity (v) in cm/s. Hence equation 5 can be simplified to:

$$C_c = 0.88 D (A/x) v^{0.5} \quad (6)$$

Substituting the dimensions of our badge:

$$C_c = 2.6 v^{0.5} \quad (7)$$

Thus the sampling rate of the badge will be dominated by the convective term until the gas velocity is less than 1 cm/s (2 ft/min). Since typical work place air velocities are 25-40 cm/s [11], the convective term will dominate equation 4 and the sampling rate of the badge is only dependent upon the conductance of the diffusion barrier.

EXPERIMENTAL

Experimental Set-Up. The reactivity of the hydrazines makes it difficult to generate and maintain the low ppb levels required for testing. A dynamic system, Figure 3, was assembled which supplies concentrations from approximately 0.1 to 10 times the TLV for each compound. Diffusion tubes

housed in a constant temperature bath, and continually purged with 100 ml/min of dry nitrogen provide the hydrazine vapors [16]. The desired concentration is obtained by adjusting the temperature of the bath, the size of the diffusion capillary, and/or the amount of dilution air.

Conditioned house-compressed air is used as the diluent. The conditioning procedure consists of passing the house air through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular sieve scrubber, and finally through a canister containing potassium permanganate coated alumina (Purafil) and charcoal. The cleaned air is humidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of the relative humidity is achieved by varying both the gas washer head pressure and the ratio of the humidified to dry air. The moisture content of the air is measured by a hygrometer. The dilution air is selected and monitored using calibrated mass flow controllers capable of providing 0 to 10 l/min. This apparatus is similar to one constructed previously at this laboratory [17].

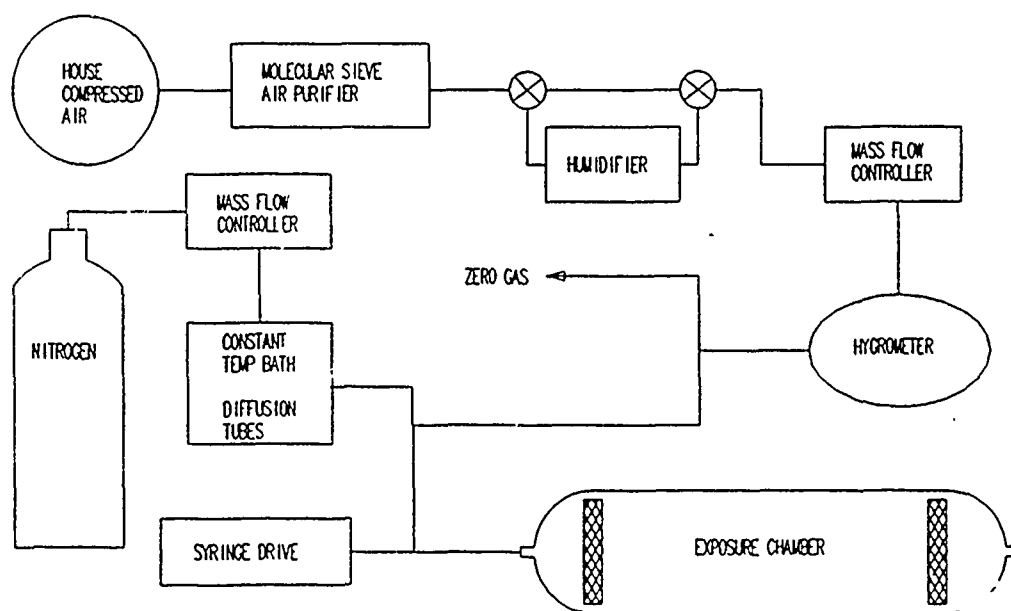


Figure 3. Test gas generator schematic.

The concentration of the test atmosphere was verified before and after each exposure by standard wet chemical techniques. Liquid impinger samples were collected and analyzed by coulometric titration [18] or colorimetric procedures [5]. In addition, a chemiluminescence instrument, Thermedics Model 141, and a paper-tape instrument MDA Model 7100 were occasionally used to monitor the gas stream.

The experiments were conducted in three glass exposure chambers, one of which is depicted in Figure 4. They were cylindrical with hemispherical ends. The exhaust end was removable to allow insertion of the samplers. Teflon baffles placed at each end were used to induce laminar flow. The internal diameter of each chamber was different in order to allow us to study a variety of the face velocities while holding other gas stream conditions constant. Further variation in face velocity

could be attained by varying the volume of dilution air in combination with substituting chambers. Table 2 lists the statistics of the chambers available for testing.

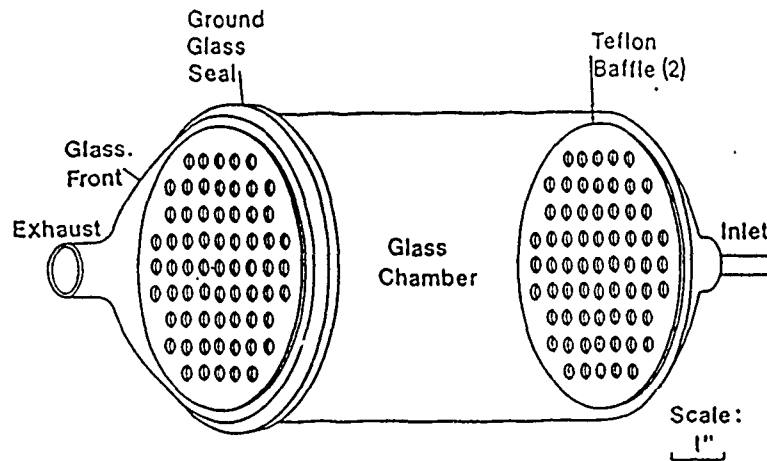


Figure 4. Glass exposure chamber used for laboratory badge testing.

Table 2. Size of the Gas Exposure Chambers and Typical Conditions.

Diameter	Area	Flow	Face velocity*
5.5 cm	23.8 cm ²	5 l/min	275 cm/min (9.0 ft/min)
9.0 cm	63.6 cm ²	5 l/min	86 cm/min (2.8 ft/min)
14 cm	154 cm ²	10 l/min	67 cm/min (2.2 ft/min)

*The badge area of 5.6 cm² (viewed from the side) reduces the effective cross sectional area of the chambers. The face velocity calculations were carried out using the adjusted chamber area. Note these are average velocities, since the gas velocity profile will be a maximum at the center of the chamber [19].

Fabrication of the Passive Sampler. The prototype sampler was made by placing a collection disk into a housing similar to Figure 1. The badge housing consisted of three parts: base, spacer, and machined diffuser. As discussed in the introduction, the diffuser is the most critical portion of the housing. It controls the collection rate and minimizes dependence upon the ambient face velocity. Various designs for diffusers were tried. The number and size of holes was varied while maintaining a constant total hole area. Tests were conducted on a series of badges machined with hole sizes of 1.0, 1.5, and 2.0 mm in diameter. The number of holes on each diffuser was 140, 76, and 35 respectively. Several styles were machined and tested. The machined samples were prepared from chlorofluoro polymers (Kel-F) [20], polypropylene, and teflon in order to examine material dependencies.

Based upon the results obtained with the prototype badge, a new badge was designed suitable for molding and mass production. A drawing of the design is shown in Figure 5. The badge was

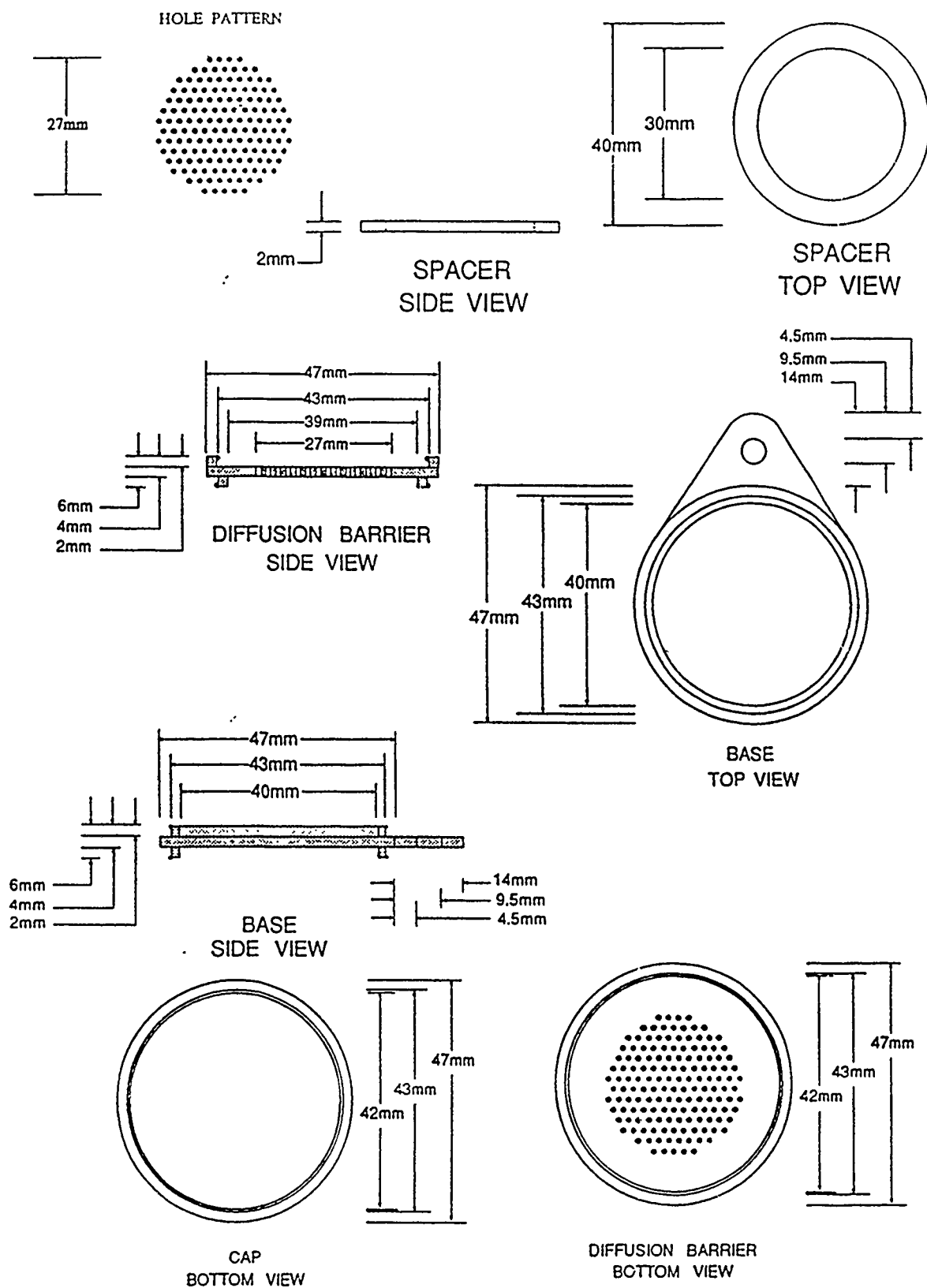


Figure 5. Design and dimensions of the complete badge.

produced by Moldsavers, Inc of Miami, Florida and made of low density polyethylene. The first lot was colorless which worked well in the laboratory; after field testing revealed a sunlight problem, a second lot was molded from black low density polyethylene. Moldsavers was unable to cast the badge in polypropylene or Kel-F due to these plastics sticking to the diffuser mold.

The molded badge housing consists of four pieces: the base, spacer, diffuser, and cap. The cap may be snapped on the back of the base during badge exposure and snapped over the diffuser for storage. The spacer holds the collection substrate against the bottom of the base. The diffusers were designed so that two or more could be snapped on top of each other to reduce the sampling rate if desired. A slight modification was made to the diffuser for production purposes. Three of the holes were moved from the center of the disk to the edge of the hole pattern. The solid areas that replaced the holes were needed for injection of the plastic and removal from the mold.

Collection disk. The collection disk is placed in the base of the badge housing and held in place with the spacer. Initially, we tried etched-glass disks coated with concentrated sulfuric acid solutions as a collection medium. These are messy and did not stabilize MMH well. We found that plastic disks coated with citric acid were a much better collection medium. Eventually we discovered that filter paper was superior to plastic as a substrate for citric acid. Citric acid was selected as the coating agent for its properties as an acid and an antioxidant.

The disk is coated by dipping it into a citric acid monohydrate (CA) solution. Citric acid is dissolved in methanol to form a 30% (gm/cm³) solution. This solution has been tested for its coating abilities and performance during an aging period. The aging period is defined as the time interval between the preparation of the solution and its use as a coating. Preliminary results indicated that the formation of methyl esters of the citric acid caused the coating properties to change. At an age of one to two weeks the solution was found to have the best performance when coated on the polyester substrate [21]. If the solution was used at any other time, the citric acid tended to crystallize on the surface of the substrate. The properly aged solution will be referred to as the standard or control coating. Most testing was conducted with the standard coating. An experiment was conducted on the ability to preserve the standard coating by refrigeration to retard the formation of esters.

It is desirable to have a solution that does not require aging. To facilitate this, variations of the standard coating recipe were tested. Solutions were prepared where a percentage of the methanol (MeOH) solvent was replaced with water, Table 3. The percent water was calculated using a total volume of 25 ml of solution (solvent and solute). The citric acid and water were combined and the solutions were adjusted to the 25 ml mark with methanol. The 7.5 grams of citric acid displaced approximately 2.5 ml of solution, therefore the solution referred to as 90% water contained no methanol.

Table 3. Solutions Prepared with Water

% Water*	(ml)	Citric Acid (g)
1	0.25	7.5
5	1.25	7.5
10	2.5	7.5
25	6.25	7.5
50	12.5	7.5
75	18.75	7.5
90	22.75	7.5

* Percentage water based on 25 ml total volume.

In addition, tests were conducted on solutions prepared with isopropanol (IPOH), with and without stoichiometric amounts of methanol. The methanol was added to allow formation of the methyl esters. By this technique, the ratio of methyl ester to acid could be controlled and solutions prepared to simulate the standard solution at various stages of aging. In some cases, an acid was added to catalyze the ester formation. We hoped to synthesize the ideally aged standard coating which could be used immediately. Table 4 outlines the coating solution variations examined.

Table 4. Coating Solutions Used in Aging Study.

	MeOH	CA (H ₂ O)IPOH		Additive
g/mol	32	210		
g/ml	0.79			
MeOH : CA	ml	gm	ml	
1:1	0.61	5.04	15	
1:1	0.61	5.04	15	H ₂ SO ₄ (one drop)
1:1	0.61	5.04	15	H ₂ O 0.5 ml
1:4	0.15	5.04	15	
Control 3:1	15	5.04	0	

Glass, polyester, and paper have been investigated as collection disk substrate. The glass was obtained in etched disks with a diameter of 4 cm. The polyester disks were cut from sheets of matted drafting film [22]. The paper was Whatman #42 filter paper purchased as 4.25 cm diameter disks [23]. The substrate disks were coated by immersion in the citric acid solution. Teflon-coated tweezers are used to remove the disks. As a precaution, to avoid the potential for metal-catalyzed

decomposition of the hydrazines, no metals are allowed to come in contact with the solution. Large quantities of the coated paper disks were prepared in the citric acid solution, placed on a clean surface, and allowed to dry. They could be used immediately or stored in plastic badges for future use. As discussed later, they should be stored in the dark and as a precaution in a refrigerator.

The use of paper as a substrate inhibited the crystallization of the citric acid coating. With this feature we thought it may be possible to use coating solution that was not aged for the seven days. Tests were conducted to monitor the effects the aging process had upon the performance of the citric acid solution coated on the paper substrate.

Experimental Conditions. Standard exposure conditions that were: 200 ppb MMH, 35% to 45% RH, and at a face velocity of 86 cm/min (2.8 ft/min). These conditions were used for the evaluation of the badge unless otherwise noted. Most of this work was with MMH because it is the hydrazine used in greatest quantity by NASA and is the most prone to decomposition on surfaces or in solution [24]. The sampling rates of the diffusors were calculated from a series of experiments. Standard exposure conditions were used for exposure periods of 0.25 to 66 hours.

The effects of face velocity upon the collection rate of the badges was tested with a MMH gas stream at face velocities between 86 and 670 cm/min. The test atmosphere was dry air contaminated with approximately 200 ppb MMH. The badges were exposed for five hours. Bare collection disks (no diffusors) were tested along with a variety of diffuser styles. The final black badge design was spot checked at 86 and 170 cm/min face velocities only.

The linearity and reproducibility of the molded prototype sampler was examined by exposure to a variety of equivalent combinations of time and concentration. For example, 1 hour at 600 ppb MMH = 3 hours at 200 ppb = 0.6 ppm hours. Exposure times ranged from 0.25 to 65 hours and standard face velocity and RH were used.

Interference effects from isopropanol, ammonia, and Freon (mixture of Freon 11, 12, and 114) were investigated using the Kel-F badge and polyester substrate. The ammonia (50 ppm) and Freon mix (50 ppm each) containing gas streams were generated by dilution of mixtures from analyzed gas cylinders. The isopropanol containing gas stream (500 ppm) was obtained by volatilization of the liquid injected into the clean air flow by an automated syringe.

Analytical Procedure. The methods used for quantitation of the hydrazines have been described in detail [25]. The coated substrate is removed from the housing assembly with teflon-coated tweezers and placed in a glass container. The analyte is desorbed from the disk for approximately 20 minutes. The desorption time required for the paper substrate was examined by analyzing aliquots of a sample during the desorption period. The solution obtained after desorption is treated as a liquid sample and analyzed using any of the accepted analytical methods may be used [5]. The solvent system and the amount used for desorption is dictated by the analytical method selected. Initially, three methods were examined, phosphomolybdic acid (PMA) and para-N,N-dimethylaminobenzaldehyde (PDAB) colorimetric procedures and the coulometric titration procedure.

RESULTS AND DISCUSSION

In order to determine the maximum rate that the badge could sample bare coated substrate disks were placed in the chamber. Duplicate samples were collected at two flow rates, two humidities and three times. The gas contained 100 ppb of hydrazine. The results are shown in Figure 6. The data shows no dependence upon humidity. Based upon equation 7 and a flow of 5 cm/sec (10 ft/min), the minimum collection rate for one side of the disk should be 5.8 ml/s. Since both sides of the disk would collect the sample, the rate would be twice this or 11.6 ml/s or 700 ml/min. At a flow rate of 1.2 cm/sec (2.5 ft/min) the calculated collection rate is 350 ml/min. The measured rates of 318 ± 30 ml/min and 927 ± 95 ml/min compare quite well with these calculated rates. It is interesting that the measured velocity dependence has a 0.8 power dependence which is what would be expected in a turbulent environment [26].

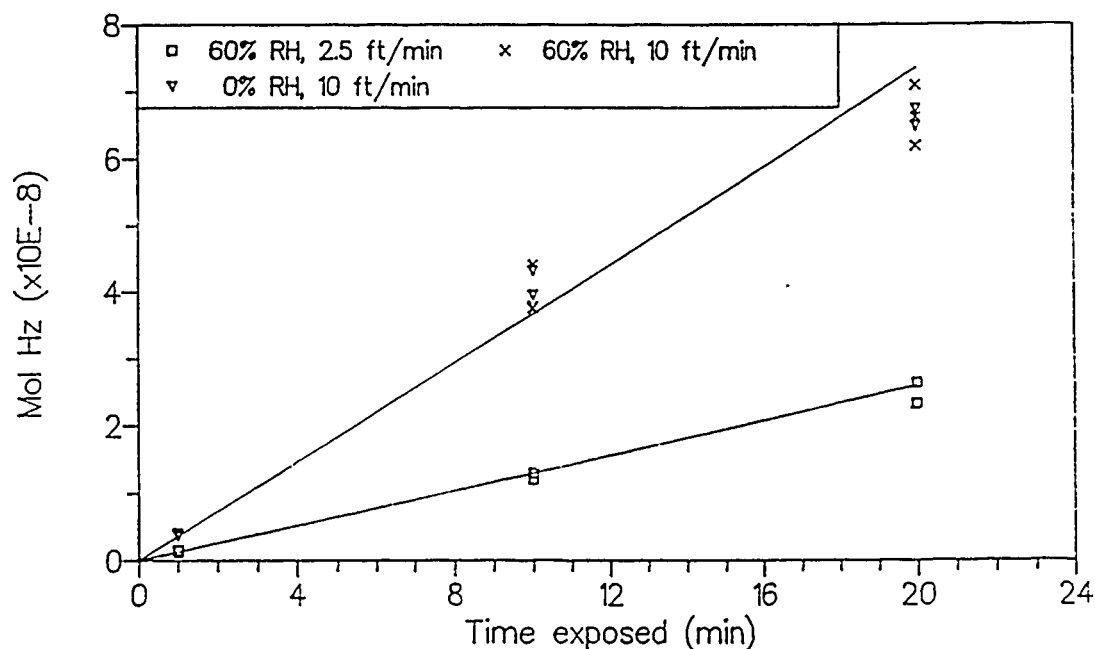


Figure 6. Collection rate of a bare disk.

The main result of this experiment is that the transport rate to the face of the badge is much greater than the sampling rate of the badge in accord with theory. Thus for all real environments the sampling rate of the badge will only be determined by diffusion through the badge face. This experiment also shows there is no dependence on the collection rate of the disk with humidity and that rate is rapid implying that the sticking probability of hydrazine on the disk is close to one.

Based on a collection rate of 1000 ml/min and a detection limit of $0.1 \mu\text{g}$ of MMH by coulometry, an exposure dose of one ppb-hr could be detected using a bare disk. Thus bare disks could be used as a very sensitive method to determine hydrazine exposure and could be useful in setting an upper limit to the concentration in an environment. The user must be aware, however, of the strong dependence of sampling rate on ambient air velocity. Additionally it should be possible to use coated

disks as quantitative collectors by pulling a known volume of air through them. Based upon other work at this Laboratory, a rate of 5 l/min is feasible. The detection limit would be about one ppb of MMH for a 10 min sample.

Badges were produced with diffusion barriers with hole sizes of 2, 1.5 and 1 mm diameter. Within experimental error no significant differences in the sampling rate or face velocity dependence were observed. Since the use of small holes can reduce the effect of viscous flow, a prototype design was selected having a 2.5 cm diameter pattern of 144 one millimeter diameter holes. This was the smallest size which we believed practicable to machine and is practicable to mold as we later discovered.

The material dependency was examined by testing badges produced from polypropylene, Teflon and Kel-F. The badges made from polypropylene and Teflon were machined from solid rods of the respective material. Some of the data obtained with these systems is shown in Figure 7. The calculated average collection rate is plotted against the exposure time. The machined badge housings deviated from linearity especially at low concentrations and higher humidities. Adsorption of the hydrazines into the sintered teflon stock and the tool marks from machining were thought to be responsible. Performance improved with the use of a molded Kel-F badge housing with drilled holes. This data is summarized in Table 5.

Table 5. Time in Hours to Reach Fraction of Maximum Collection Rate.

Material	Time to reach 50%		Time to reach 80%	
	Dry	45% RH	Dry	45% RH
Kel-F	0.2	0.5	1	2
Polyprop.	1	3	4	8
Teflon	3	8	6	>16

The reason for the lower collection rate at shorter times is assumed to be that the badge material depletes the hydrazine concentration by absorbing the hydrazine on the surfaces of the badge including the walls of the holes. A simple model can be constructed assuming that the absorption on the walls follows an standard Langmuir equation [27]. Based on this assumption, the instantaneous sampling rate (R) of the badge as a function of time is given by the following equation:

$$R = R_M(1 - e^{-At}) \quad (8)$$

Where: R_M = The maximum rate reached after equilibration; and
 A = the time constant of the absorption on the walls

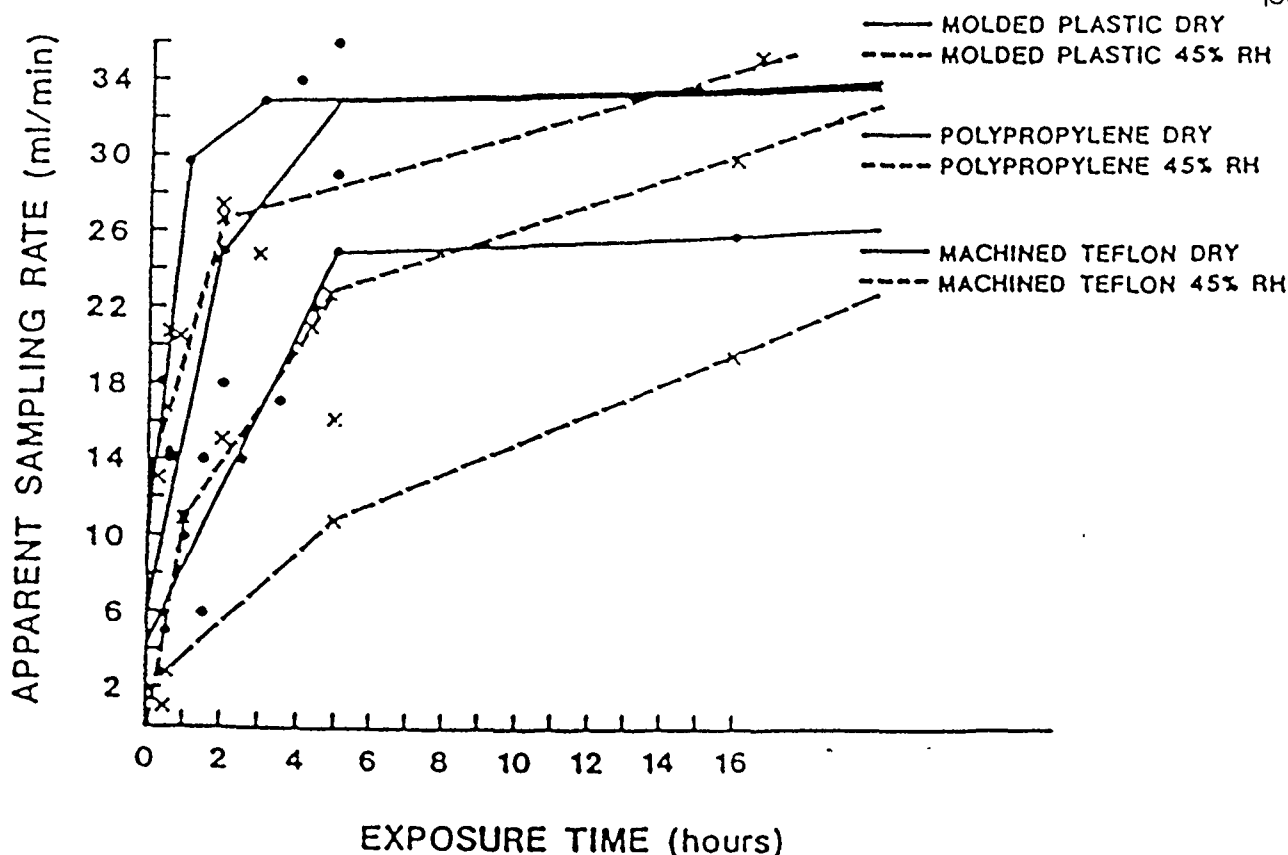


Figure 7. Average collection rate as a function of time.

If equation 8 integrated from time 0 to time T, then the average rate (R_A), which is the rate measured in the experiment, is given by:

$$R_A = R_M(1+(e^{-AT}-1)/(AT)) \quad (9)$$

As an example using data for Kel-F in Table 5, it takes about 0.5 hr to reach an average rate of 50% of the maximum for 45% RH. Thus R_A/R_M equals 0.5 and T equals 0.5 hr in equation 9. Since this is a transcendental equation, it must be solved numerically for A, which in this case is 3.2/hr. Substituting this value into equation 8, the instantaneous rate at 0.5 hr is 0.8 of the final rate. The Kel-F badge was tested at different face velocity conditions; this data is presented in Table 6. There is no apparent face velocity affect using this badge design.

Table 6. Face Velocity Test Data.

Exposure Time (hrs)	Relative Humidity (%RH)	Face Velocity (cm/s)	MMH (ppb) concentration	Sample Rate (ml/min)
3	65	2.5	180	29
3	65	10	179	30
64	25	1	189	27
64	25	2.5	173	26

The Kel-F badge was used for interference testing. The interfering compounds are ones that could be present in operations at the Kennedy Space Center. The data obtained is presented in Table 7. It should be noted that the scatter in the data falls within the precision expected for this sampling technique.

Table 7. Interference Testing.

MMH * (ppb)	Interfering Compound (ppm)	Measured Sampling Rate ml/min (% change)
174	IPOH, 500	30
188	Ammonia, 50	25
176	Freons, 15	29

*Two hour exposure with 65% RH at 5.2 ft/min.

The molded badge was tested to determine the sampling rate at the TLV level of MMH and 40% RH. The data is summarized in Table 8. The average rate of 27 ml/min is lower than the theoretical rate of 38 ml/min. The most plausible reason for the difference would be that the concentration of the MMH at the surface of the substrate is not zero but about 29% of the sample concentration, that is C_2 is 29% of C_1 in equation 1. The lower rate at 0.25 hours is due to both equilibration of the badge surface and the chamber surfaces after the chamber was opened to insert the badges. The badge certainly has reached 80% of the maximum rate within 15 min. Based on equations 8 and 9 the time for the instantaneous sampling rate to be 50% of the maximum is less than 2 minutes. The drop off in sampling rate for the 65 hr sample is due to storage problem of the substrate, see below. The total dose collected corresponds to a range of 3.2 to 880 nmol of MMH. This data also shows there is no dependence of the collection rate upon dose collected in this range. Based on a detection limit of MMH of 0.1 μg , the minimum detectable dose is 30 ppb-hr.

Table 8. Badge Sampling Rate.

MMH Conc. (ppb)	Time (hrs)	Measured Rate (ml/min)
215	0.25	24
215	0.25	20
215	0.25	29
212	0.67	28
212	0.67	31
192	4.0	22
192	4.0	26
192	4.0	30
187	5.0	27
187	5.0	27
187	5.0	29
225	18	29
225	18	26
237	65	23
237	65	23
Average*		27.5
Std. Dev.*		2.4

*The data for 0.25 hrs and 65 hrs was not used (see text).

The fall off in sampling rate at longer sampling times was traced to storage problems of the MMH on the citric acid coated polyester substrate. We had used the polyester drafting paper as the citric acid solution wet it uniformly since its surface texture was designed for inking. We did not realize that would cause long term storage problems. The original storage tests were performed using a glass substrate, and did not indicate any problem with storage stability. This data is shown in Table 9 which shows the results from the original tests. In each test four badges were exposed to MMH, two of the badges were analyzed immediately and two were stored in the dark until analysis. No storage problem was found in either test. Glass disks are not a desirable substrate since they are fragile and have an uncertain availability. We used disks in from our stockroom which had been ordered many years ago. We do not know the source and could not find any listed in several different catalogs.

Table 9. Storage Tests.

MMH Conc. (ppb)	Days Stored	Sample Rate (ml/min)

Test 1 - Exposure time 18 hrs

242	0	26	12.8
242	0	24	11.8
242	3	28	13.8
242	3	24	11.8

Test 2 - Exposure time 5 hrs

268	0	26
268	0	24
268	5	31
268	7	27

Investigations were conducted to find an alternate substrate for the polyester due the poor stability of the trapped MMH. Many materials were investigated, including filter paper, fiber glass, and porous membranes made of a variety of materials. The filter paper was the most promising. It was investigated and compared to polyester. The collection performance of the two substrates was similar. The room temperature storage stability of the paper was much greater than that of the polyester. This data is shown in Table 10.

Table 10. Paper Storage

Days Stored	Pcr Cent of Theoretical
6	89
8	74
8	74
10	85
10	86
10	86
12	103

MMH = 194 ppb, RH = 65%

In comparison, the polyester substrate retains between 10 to 50% of the amount of MMH sampled after one week of storage. We hypothesize that the MMH was reacting with the carbon oxygen double bond of the ester linkage of the polymer. Since the citric acid coated paper worked so well, uncoated paper was tried as a substrate. This test was unsuccessful as the paper only retained 30% of the MMH after one day of storage. The citric acid coated substrate was tested with all three analytical methods. No difference or interference problem was found. Exposed badges were stored

in an oven at 38°C (100 °F) for 24 hrs., no decrease in the stored hydrazine was detected. In addition to badge storage, the storage of the extracted solution was investigated. The collection disk was placed in a glass vial with 15 ml of 0.1 M H₂SO₄, capped and stored in the dark or on the bench top until analysis. Storage tests of the extracted solution have been conducted for periods approaching three months. Again no significant change was observed.

The performance of the citric acid solution coated on the paper substrate was monitored during the aging process. A solution was prepared but not set aside for aging. On days 0 (day of preparation) through 4, 7, 8, and 14 the coating solution was used to prepare 6 badges. The molded polyethylene housing was used. The badges were exposed to the standard MMH testing conditions. Three were analyzed immediately following exposure, the others were held for storage stability testing. No significant difference was detected. Thus the age of the citric acid solution is not important for paper substrate. Currently we know of no reason why paper cannot be used exclusively for the badge substrate. We have discussed the aging process of the citric acid solution in the event that a different badge substrate is used in the future which may require aged solution. Potentially a different substrate might be needed to be compatible with a future analytical method.

The prototype system has demonstrated a detection limit of 15 minutes of TLV exposure when analyzed with the coulometric titration method. We were unable to define a lower limit experimentally due to the time required to equilibrate the test atmosphere.

At the end of this development these badges were field tested at the Kennedy Space Center. The field test is reported in detail in a separate report [25]. The principal discovery was an interference to analysis using coulometry. The interference was determined to be caused by sunlight irradiating the badge. This effect had not been observed in tests on the roof of the Chemistry building at NRL. These tests were conducted in the fall and winter when there is negligible amount of UV radiation transmitted by the atmosphere [28]. In order to decrease this effect, a new set of badges was molded from black polyethylene. Using these badges the effect of sunlight was marginal [25]. Laboratory tests of the black badges showed them to perform comparable to white badges. In one test exposed badges were stored for 6 weeks at room temperature. No loss of MMH was detected.

CONCLUSIONS

A passive dosimeter has been developed for hydrazines. The dosimeter overcomes problems caused by the reactivity of the hydrazines by molding a dosimeter from polyethylene and a collection disk made from filter paper coated with a citric acid solution. This coating has shown an ability to trap and stabilize the hydrazines without interfering with colorimetric or coulometric quantitation procedures. TLV levels of MMH can be detected for exposures as short as 15 minutes.

The paper substrate system has additional advantages. It has demonstrated room temperature stability of the trapped analyte for periods greater than one week, and high temperature stability for 24 hours. This was not possible with the polyester substrate. Storage of the polyester system must take place in the freezer, or the analyte must be desorbed and stored as an extracted solution. This would not allow the badge to be used to measure a time-weighted-average (TWA) exposures for

periods any greater than one work day. With the use of a paper substrate, the period of use can be extended to one week if needed. A badge could be placed in an area, or dispensed to an employee at the beginning of a work shift on a Monday, and collected for analysis at the end of the work day on Friday.

The molded low density polyethylene badge provides an excellent housing for the collection disk. A molded housing has many advantages over the machined badge. The resulting product is cost effective at \$0.10 per unit. The molding process reduces the available surface area, which decreases the amount of analyte lost by adsorption into the badge housing. In addition, the badge-to-badge reproducibility is better because of identical diffusion barriers. The diffuser minimizes face velocity effects while retaining a detection limit of 15 minutes for 200 ppb MMH contaminated air. The assembly of the badge is simplified by its ability to be securely snapped together. Once snapped in place, the cap protects the badge from exposure to analyte. The resulting badge has the desirable qualities of a disposable personal dosimeter. It is durable, inexpensive, and lightweight.

The sampler must be returned to a laboratory for analysis where NIOSH recommended procedures may be used to quantitate the extract. The data obtained from the paper substrate system is acceptable for TWA exposure documentation. We envision a final design of the hydrazine dosimeter as being a combination of the badge described and a colorimetric real-time indicator. The indicator would serve as a warning system for the user and as a dose estimator for the analytical laboratory.

REFERENCES

1. DHEW (NIOSH) Publication No 78-210.
2. DHEW (NIOSH) Publication No 78-172.
3. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.
4. E. W. Schmidt, *Hydrazine and its Derivatives*, (John Wiley, New York, 1984), Chap. 5.
5. *NIOSH Manual of Analytical Methods*, 2nd ed., DHEW(NIOSH), Cincinnati, OH. 1977, Vol 3, Publication 77-157c.
6. E. D. Palmes and A. F. Gunnison, *Amer. Ind. Hyg. Ass. J.* 34, 78-81 (1973).
7. E. D. Palmes and A. F. Gunnison, *Amer. Ind. Hyg. Ass. J.* 37, 570-577 (1976).
8. W. J. Lautenberger, E. V. Kring, and J. A. Morello, *Ann. Am. Conf. Gov. Ind. Hyg.* 1, 91-99 (1981).
9. V. E. Rose and J. L. Perkins *Amer. Ind. Hyg. Ass. J.* 43, 605- 621 (1982).
10. Pro-Tek Systems, Inc., 3M and Dupont all manufacture these devices which are described in reference 9.
11. R. Ellersick, *Research on Personnel Dosimeters to Measure Hydrazine Fuels in Air*, Air Force Report SAM-TR-79-22 (1979).
12. P. A. Taffe, S. L. Rose-Pehrsson, and J. R. Wyatt, *Material Compatibility with Threshold Limit Values of Monomethyl Hydrazine*, NRL Memorandum Report 6291 (1988).
13. S. Dushman and J. M. Lafferty, Ed., *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, New York, 1962), p 82-86.
14. G. Lewin, *Fundamentals of Vacuum Science and Technology* (McGraw-Hill, Inc., New York, 1965), p 16-18.
15. C. O. Bennett and J. E. Myers, *Momentum, Heat, and Mass Transfer*, 3rd Ed, (McGraw-Hill, Inc., New York, 1982), Chap. 32.
16. A. P. Altshuller and I. R. Cohen, *Anal. Chem.* 32, 802-810 (1960).
17. S. L. Rose and J.R. Holtzclaw, *A Critical comparison of Commercially Available Hydrazine Detectors*, NRL Report 8848, Naval Research Laboratory, Washington, DC, March 19, 1985.

18. E. C. Olson, *Anal. Chem.* 32, 1545-1547 (1960), this procedure has been miniaturized by both NASA, WSTF and NRL personnel and will be the subject of a future report.
19. Reference 15, p121.
20. The badges were made by drilling holes in the top of Fluoroware (Fluoroware, Inc., Chaska, Minn.) cassettes designed for holding silicon wafers. These cassettes were molded from Kel-F (3-M trademark for chlorotrifluoroethylene polymer).
21. C. M. Hawkins, S.L. Rose, and J.R. Wyatt, "A Passive Dosimetry Method for Determining Hydrazine in Air," CP1A 436, *Proceedings of the 1985 JANNAF Safety and Environmental Protection Subcommittee Meeting*, (Monterey, CA, 4-8 November 1985) Naval Postgraduate School, November 1985.
22. Maryland Blue Print Company of Columbia, Maryland (stock # D-F3).
23. This material is available from a variety of scientific supply companies.
24. J. R. Holtzclaw, S. L. Rose, J. R. Wyatt, D. P. Rounbehler, and D. H. Fine, *Anal. Chem.* 56, 2952-2956 (1984).
25. P. A. Taffe, S. W. Brown, A. R. Thurow, J. C. Travis, S. L. Rose-Pehrsson, and J. R. Wyatt, *Field Evaluation of a Passive Sampling Device for Hydrazines in Ambient Air*, NRL Memorandum Report 6613 (1990).
26. Reference 15, p564.
27. D. F. Eggers, N. W. Gregory, G. D. Halsey, and B. S. Rabinovitch, *Physical Chemistry*, (John Wiley and Sons, Inc., New York, 1964), Chap. 18.
28. B. E. Shaefer, "The Astrophysics of Suntanning", *Sky and Telescope*, 75, 595-596 (1988).

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13. ABSTRACT (Maximum 200 words) A passive, colorimetric dosimeter badge was manufactured for NASA by GMD Systems. The badge consisted of two indicators: para-dimethylaminobenzaldehyde (PDAB) and vanillin. When exposed to hydrazine or monomethylhydrazine (MMH), the PDAB turns orange and the vanillin turns yellow. The intensity of the color is proportional to the concentration in the environment. A color wheel was also manufactured to evaluate the color and estimate the dose of hydrazine for each indicator. The laboratory investigations and the preliminary results of the field test indicate that the badge is qualitatively accurate with few interferences. The badges were exposed for sample times between 0.25 and 16 hours at different concentrations of hydrazine and MMH. The badges were evaluated for linearity, relative humidity effects, and interferences. The evaluation was conducted at the Naval Research Laboratory and Wiltech at the Kennedy Space Center. The badges responded with a measurable color change in each test. At low dose and short sample times, there was much scatter in the dose measured. The badges saturated, exceeding the darkest color on the color wheel after 8 TLV-hours. Relative humidity has little effect on the badge responses. Sunlight was an interferent for PDAB, turning it yellow. Tobacco smoke was an interferent for vanillin, turning it pink-purple.				
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LABORATORY EVALUATION OF A COLORIMETRIC HYDRAZINE DOSIMETER

INTRODUCTION

The three hydrazines currently being used by the Department of Defense as hypergolic fuels are hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The space shuttle program uses large quantities of hydrazine and MMH. In addition, substantial amounts of hydrazine are used by Titan missiles, satellites, and aircraft auxiliary-power units. While useful as propellents, the hydrazines impose health hazards to personnel who may come in contact with them. Hydrazine, MMH, and UDMH are considered potential carcinogens and threshold limit values (TLV) for exposure to their vapors have been established at 100, 200, and 500 ppb respectively by the American Conference of Governmental Industrial Hygienist (ACGIH) [1]. At higher concentrations there is added danger due to the explosive nature of the hydrazines. To minimize risk, monitoring of the employees and their work environment should be conducted to insure the presence of hydrazines remains below the defined levels. While instruments to monitor areas are commercially available, a small, reliable, real-time, passive device that can be worn by personnel is not.

Geo-Centers and Naval Research Laboratory (NRL) scientists invented a passive sampler for the determination of personnel exposure to MMH and hydrazine [2]. The sampler required laboratory evaluation. For real-time qualitative detection, a badge which incorporates vanillin as an indicator showed potential in laboratory evaluations at NRL. When exposed to a hydrazine, the coated substrate develops a yellow color. A patent for the vanillin indicator was issued in February 1990 [3].

GMD Systems, Inc. investigated several colorimetric systems for incorporation into a passive dosimeter through a Small Business Initiative Research Contract with NASA/Kennedy Space Center (KSC). One chemistry was identified by GMD Systems. This indicator, para-N,N-dimethylaminobenzaldehyde (PDAB), can also be used for real-time qualitative hydrazine detection. The PDAB coated dosimeter develops an orange-red color upon exposure to the hydrazines. NASA requested that the vanillin developed by Geo-Centers and NRL personnel be incorporated into the GMD prototype dosimeter badges. Geo-Centers and NRL personnel agreed to collaborate with GMD. An extensive laboratory test was designed to investigate the prototype badges. The color dosimeters were evaluated as dose indicators for MMH and hydrazine by NRL and by Wiltech at KSC.

The evaluation of the color badges was a joint effort between Wiltech and Boeing Aerospace Operations at the Kennedy Space Center, and NRL and Geo-Centers, 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, resulting in a product known as a hydrazone. The formation of a hydrazone is depicted in Figure 1. In the case of unsubstituted hydrazine (N_2H_4), two moles of aldehyde can react with one mole of hydrazine to form the azine. The mechanism involves the nucleophilic addition of the nitrogen base, followed by the elimination of water. This reaction is frequently acid catalyzed by protonation of the carbonyl. The ASTM method condenses the hydrazine with para-N,N-dimethylaminobenzaldehyde (PDAB), Figure 2. In an acidic solution, the absorbance of the protonated p-quinone structure is measured spectrophotometrically at 458 nm [4].



Figure 1. The condensation reaction of a carbonyl group with a hydrazine to form a hydrazone

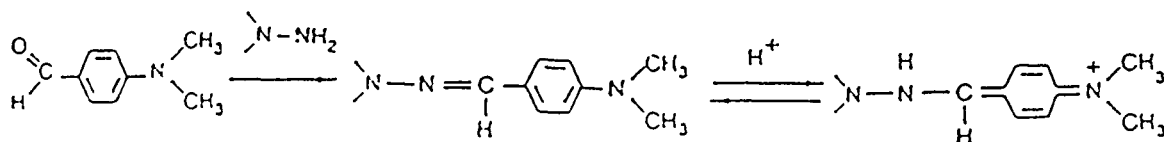


Figure 2. Condensation reaction of PDAB with a hydrazine to form the protonated p-quinone structure

Vanillin (3-methoxy-4-hydroxybenzaldehyde) is also an excellent derivatization agent for hydrazine and MMH. Figure 3 shows the reaction of hydrazine and vanillin. The formation of the hydrazone is rapid. Vanillin does not need to be acidified to react with MMH, however, it does require acidification to form a colored species upon reaction with hydrazine. Reaction with UDMH does not form a colored species. This characteristic allows a wider pH range than with other aldehydes (such as the PDAB previously mentioned) when monitoring MMH. This has proven beneficial when investigating interferences, such as ammonia, that can alter the pH.

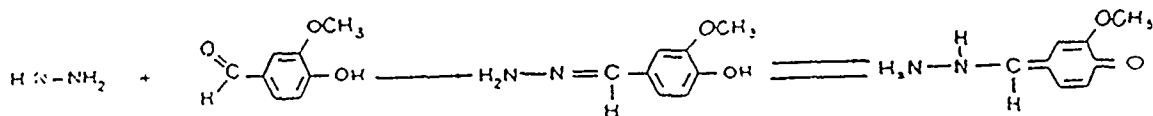


Figure 3. Condensation reaction of vanillin and hydrazine

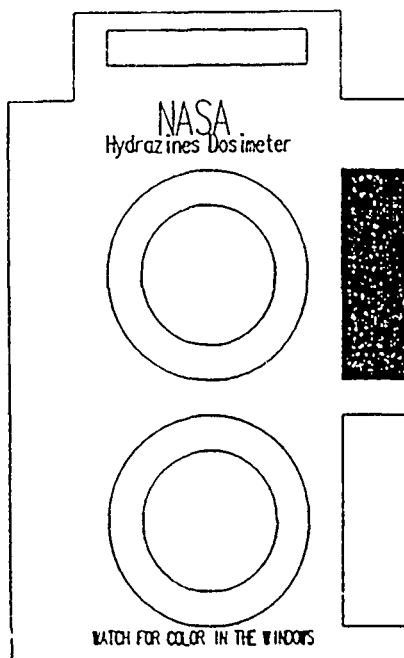
The vanillin must be acidified to form a visual product upon reaction with hydrazine. Hydrochloric acid (HCl) was tested in this capacity, however, HCl was too volatile. Therefore, the use of citric, phosphoric and sulfuric acids were investigated. Phosphoric acid was the most suitable. We believe that non-acidified vanillin reacts with hydrazine to form the hydrazone. Upon acidification, the hydrazone turns yellow. This effect was used to make a badge sensitive to acid vapors [5].

EXPERIMENTAL

BADGE SYSTEM

Approximately 350 color badge systems were evaluated at NRL and 275 by Wiltech at the Kennedy Space Center. The badge designs incorporated vanillin and PDAB and were designed as dual spot units. Each unit was given a serial number and foil wrapped by the manufacturer. As a randomization procedure, all badges were scrambled by KSC personnel prior to distribution. The dosimeters were composed of two strips of filter paper coated with either indicator. These strips were sandwiched in a thin cardboard housing 7.3 cm by 4.4 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 the protective cover over the indicator spots immediately prior to use. Figure 4 shows the badge. Badges with different color chemistries were designated as D12, D14, D13+D12, and D13. Later in the testing period, composite badges of D12+D14 were produced. Table 1 lists the indicators coated on each badge type. All badges with the exception of the D13+D12 badges and the later composite badges had a diffusion membrane over the indicator spot at the top of the badge. The membrane had little effect on color development. After three months of testing, the diffusion membrane was removed from all badges used in subsequent exposures at NRL. The membrane was not removed from the badges tested at Wiltech.

Front View of Badge



Back View of Badge

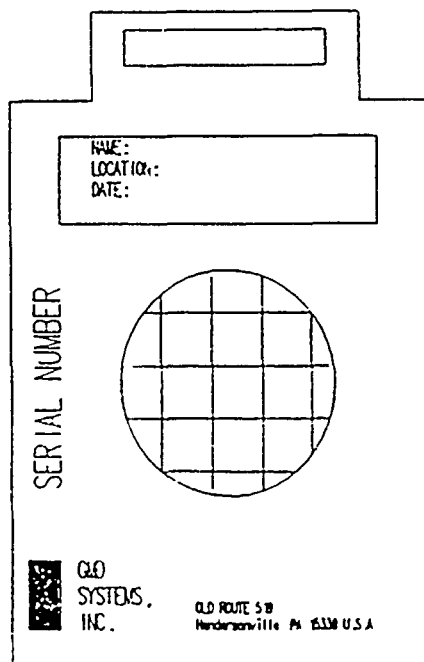


Figure 4. GMD Systems, Inc. Hydrazine Color Dosimeter

Table 1. Badge Types Evaluated

Badge Designation	Indicator	Testing Facility
D12	PDAB	NRL/Wiltech
D13	Vanillin/Citric acid	NRL
D14	Vanillin/Phosphoric acid	NRL/Wiltech
D13+D12	Vanillin/CA + PDAB	NRL/Wiltech
D12+D14	PDAB + Vanillin/Phos. Acid	NRL/Wiltech

GMD provided color wheels (badges dose indicators) with which to match the color development on the exposed dosimeters. During the course of testing, three different color wheels were used. The first consisted of nine shades of increasing intensity of yellow for vanillin (D13, D14) or red-orange for PDAB (D12). It was noted that some of the colors on the wheel were so close in shade there was difficulty in distinguishing between them. Another problem was that the low-dosage shades on the PDAB color wheel were much more pink than the badges exposed to MMH. The color mismatch made it difficult to read the badges well. New color wheels were produced with color intensities ranging from 1 to 5. The five colors on the new vanillin wheel were intended to be the same as the odd numbered colors on the original wheel. However, the number 4 color on the new wheel matched the number 8 color on the old wheel and the color of the number 5 dot on the new wheel was slightly more intense than the 9 color on the old wheel. The colors on the PDAB color wheel were altered slightly for more orange shades. This is more evident in the lower numbered color dots on the old new wheel. The intensities of the color dots on the new PDAB wheel were similar to the color intensities of the odd numbered colors on the old wheel. However, the number 4 color dot on the new wheel more closely matches 7.5 color on the old wheel. The number 5 color dot on the new PDAB wheel is slightly darker than the number 9 color on the old wheel. The new color wheel was used to evaluate the newer PDAB/vanillin (D12+D14) badges.

The shade of orange produced when PDAB reacts with hydrazine is different than that produced with MMH. Therefore, a different PDAB color wheel was designed for hydrazine exposures. The color spots on this wheel were orange.

TEST PLAN

The following tables outline the test plan for the dosimeter evaluation for MMH. Table 2a gives linearity test parameters, Table 2b, humidity parameters, and Table 2c lists interferences to be tested. Additional badges were sent to NRL for evaluation as hydrazine dosimeters under similar conditions. Each exposure was replicated. Some required doses were duplicated between NRL and Wiltech to insure no laboratory bias. The following tolerances applied to all controlled test parameters: MMH concentration (ppm), $\pm 20\%$; exposure time (hrs), $\pm 5\%$; relative humidity (%), $\pm 5\%$; and temperature (C), ± 2 .

To achieve the desired doses of MMH or hydrazine, the badges were exposed to various concentrations of the contaminant gas for different periods of time. Figure 5 shows the glass chamber in which the badges were exposed to MMH and hydrazine. The chamber was cylindrical with conical ends. The exhaust end was removable to allow insertion of the dosimeters. Teflon baffles placed at each end were used to induce laminar flow. The badges were hung vertically and back-to-back on a glass rod which was secured to the front and rear teflon baffles in the chamber. A flow of $5.0 \pm 10\%$ SLPM was specified for the evaluation. This corresponds to a velocity of 79 cm/min (2.6 ft/min).

The system used to generate MMH and hydrazine supplies concentrations from approximately 0.5 to 10 times the TLV for each compound. This system has been previously described in detail [6]. Diffusion tubes, housed in a constant temperature bath and continually purged with 100 ml/min of dry nitrogen, provide the hydrazine vapors. The desired concentration is obtained by adjusting the temperature of the bath, the size of the diffusion capillary, and/or the amount of dilution air. The concentration in the test chamber was independently verified using impinger collection and coulometric titration before and after each test. The coulometric titration procedure used to verify the concentrations of the dynamic test environment is described in detail in earlier reports [7].

The same type of glass chamber was used to expose the badges to the gaseous interferences that were tested at NRL. Badges were subjected to heat, cold, UV light and sunlight at Wiltech. Those badges exposed to heat and cold were placed in a convection oven (40°C) and freezer, respectively. To assess interference by UV light, badges were exposed to a UV lamp.

Immediately after each exposure ($T=0$), the color development on the dosimeters was judged by three people using the appropriate color wheel. Three people also judged the color on the badges one hour after exposure ($T=1$). Whenever possible, the same people who evaluated the badges at $T=0$ read them again at $T=1$. Although the colors on the color wheels were whole numbers (x), judges could choose a shade in between two colors (x.5), if necessary. The badges exposed to the interferences were evaluated both after exposure to MMH and to the interference. The serial numbers, exposure conditions, and data obtained from each badge were recorded on log sheets (Appendices A and B).

Table 2a. Linearity Response

MMH Conc (ppm)	Exposure Time (hours)	Dose (TLV-hrs)	RH %	Facility	Priority
Control	4.0	0.0	40	WT/NRL	I
0.1	0.25	0.13	40	WT/NRL	II
0.1	0.5	0.25	40	WT	III
0.1	1.0	0.5	40	WT	III
0.1	2.0	1.0	40	WT/NRL	II
0.1	4.0	2.0	40	NRL	III
0.1	8.0	4.0	40	NRL	III
0.1	16.0	8.0	40	WT/NRL	II
0.2	0.25	0.25	40	WT/NRL	II
0.2	0.5	0.5	40	WT	III
0.2	1.0	1.0	40	WT	III
0.2	2.0	2.0	40	WT/NRL	II
0.2	4.0	4.0	40	NRL	III
0.2	8.0	8.0	40	NRL	III
0.2	16.0	16.0	40	WT/NRL	II
0.4	0.25	0.5	40	WT/NRL	II
0.4	0.5	1.0	40	WT	III
0.4	1.0	2.0	40	WT	III
0.4	2.0	4.0	40	WT/NRL	II
0.4	4.0	8.0	40	NRL	III
0.4	8.0	16.0	40	NRL	III
0.4	16.0	32.0	40	WT/NRL	II
1.0	0.25	1.25	40	WT/NRL	II
1.0	1.0	5.0	40	WT/NRL	II
1.0	3.0	15.0	40	WT/NRL	II
4.0	0.5	10.0	40	WT/NRL	II
6.0	0.25	7.5	40	WT/NRL	II

Table 2b. Humidity Response

MMH Conc (ppm)	Exposure Time (hours)	Dose (TLV-hrs)	RH (%)	Facility	Priority
Control	4.0	0.0	10	WT	IV
Control	4.0	0.0	80	NRL	IV
0.1	0.25	0.13	10	WT	IV
0.1	2.0	1.0	10	WT	IV
0.1	0.25	0.13	80	NRL	IV
0.1	2.0	1.0	80	NRL	IV
0.2	0.25	0.25	10	WT	IV
0.2	2.0	2.0	10	WT	IV
0.2	0.25	0.25	80	NRL	IV
0.2	2.0	2.0	80	NRL	IV
0.4	0.25	0.5	10	WT	IV
0.4	2.0	4.0	10	WT	IV
0.4	0.25	0.5	80	NRL	IV
0.4	2.0	4.0	80	NRL	IV
1.0	0.25	1.25	10	WT	V
1.0	2.0	10.0	10	WT	V
1.0	0.25	1.25	80	NRL	V
1.0	2.0	10.0	80	NRL	V

Table 2c. MMH/Interferent Interaction Response

MMH Conc (ppm)	Dose (ppm-hours)	Interferent	Int. Conc. (ppm)	Exposure Time (hrs)	Facility
0.2	2	Sunlight	NA	4.0	WT
0.2	2	UV Light*	NA	0.5	WT
0.2	2	Heat 40 C	NA	4.0	WT
0.2	2	Cold 0 C	NA	4.0	WT
0.2	1	NO2	5	1.0	NRL
0.2	1	NH3	20	1.0	NRL
0.2	1	Freons	30	1.0	NRL

* 254 and 350 nm

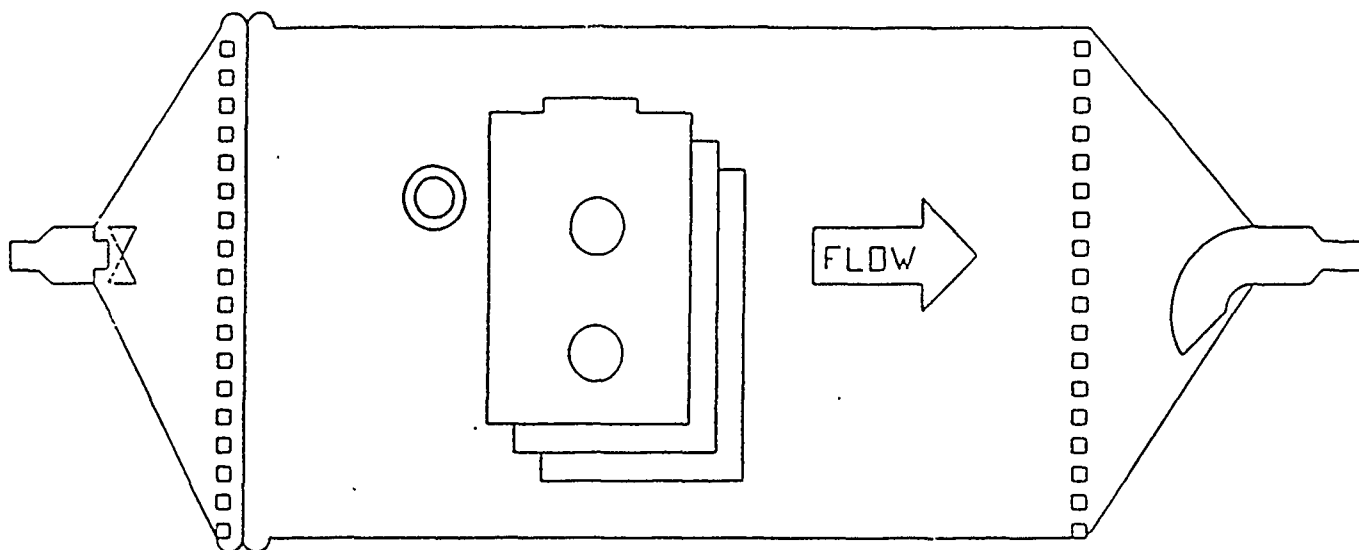


Figure 5. Dosimeter Exposure Chamber

FIELD TEST

The badges were field tested at Kennedy Space Center to investigate their performance in the field and to identify potential interferences. The badges were tested as area monitors and personal dosimeters. Individuals who wore the dosimeters were interviewed to determine their activities during the day. Eleven tests were conducted at different locations over a two month period. Three different location types were identified for testing: Expected Exposure, Unlikely Exposure, and Potential Exposure. Badges in the expected exposure area had a high probability of being exposed because hydrazine or MMH was being used or stored in that area. The unlikely exposure areas were used to test unusual interferences only, no hydrazine or MMH was ever used in those areas. The potential exposure areas included areas where hydrazines were used or stored at some time, but were clean during the test. These areas were selected to examine likely interferences. All of the tests and locations are given in Table 3.

Citric acid badges were used in conjunction with the colorimetric badges as a reference to independently monitor exposures. The performance of the citric acid badges was described in detail in an NRL Memorandum Report entitled "Field Evaluation of a Passive Sampling Device For Hydrazines in Ambient Air" [7]. Two badges were provided at each location. One badge was analyzed using coulometric titration [8]. The second badge was analyzed by a colorimetric method, phosphomolybdic acid, NIOSH approved method #S149 [9], or the badge was spiked and analyzed with the coulometric method. All of the badges were distributed and collected for analysis on a daily basis. For some tests, liquid impingers were also collected and analyzed by the .STM para-dimethylaminobenzaldehyde colorimetric method.

RESULTS

DOSE RESPONSE RESULTS FOR MMH

All of the badges showed a large range in color development at doses less than 2.5 TLV-hours regardless of MMH concentration. At low sample times, some of the scatter is due to the experimental procedure. When the chamber is opened to insert the badges, the MMH atmosphere is disturbed. Thus, when the dosimeters are exposed to the gas for a short time, the atmosphere in the chamber may not stabilize during the time the badges are present.

Figures 6a and 6b are dose response graphs of PDAB (D12) badges without the diffusion membrane at T=0 and T=1, respectively. These badges show an increase in color development from T=0 to T=1. Although the time dependence is independent of dosage, the outlying data points at ≤ 5 TLV-hours show the greatest increase in color from T=0 to T=1. Because of this, the scatter in the outlying data points evident at T=0 is diminished by T=1 as the colors become more intense and approach saturation color. At 10 TLV-hours, the badges reached a saturation color of 9.5. Figures 6c and 6d are dose response graphs of the top color dot on PDAB (D12) badges that had the membrane. The outlying data points at < 5 TLV-hours noted on the badges without the membrane are not present here. Color saturation occurs by 16 TLV-hours at T=0. Due to the increase in color

Table 3. Field Tests Conducted at Kennedy Space Center.

Locations	Area	Chemical Agent
Expected Exposure:		
Wiltech Lab	I Personnel	Hydrazine MMH
Orbiter Processing Facility (OPF)	I	MMH
	II	MMH
Aft Skirt Testing Facility (ASTF)	I	Hydrazine
	II	Hydrazine
	Personnel	Hydrazine
Unlikely Exposure:		
M & O Paint Shop	Personnel	Solvents
VAB Break room (Lounge)	I	Cigarette Smoke
Astronaut Beach House	I	Sea Breeze
Potential Exposure:		
Rotating Service Structure (RSS)	I	Hydrazine
	II	MMH
Hypergol Maintenance Facility (HMF)	Personnel	MMH
Fuel Storage Area (FSA)	Personnel	Hydrazine

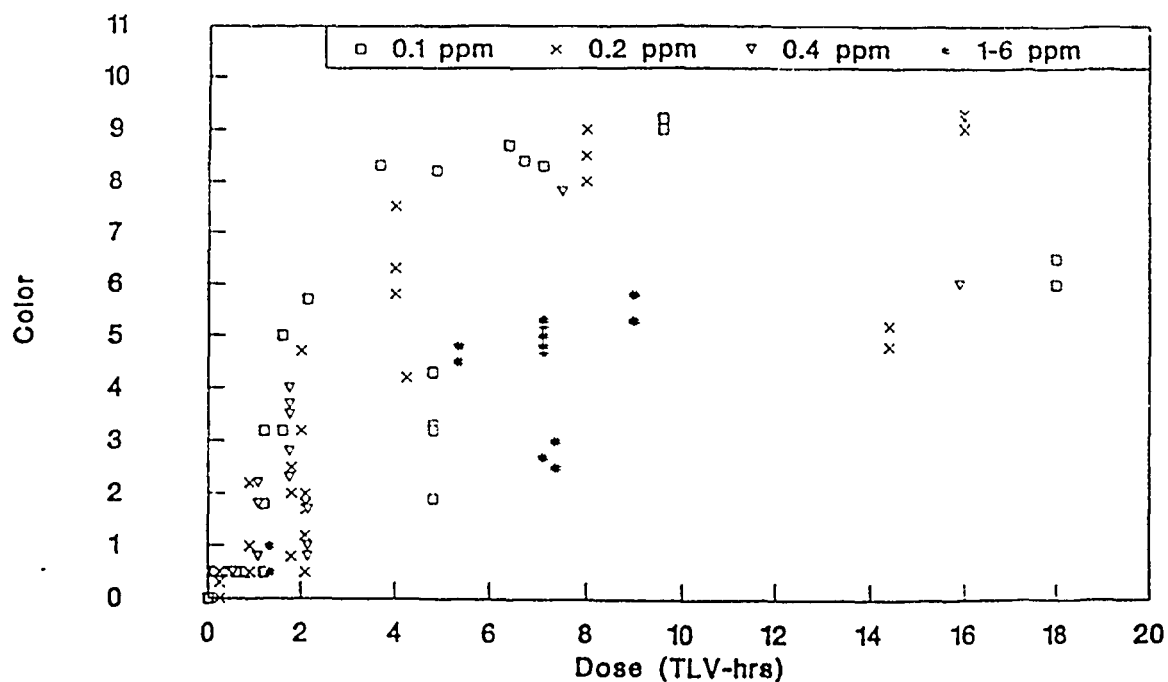


Fig. 6a. MMH Dose Response Curve at T=0 for PDAB (D12) without Diffusion Membrane

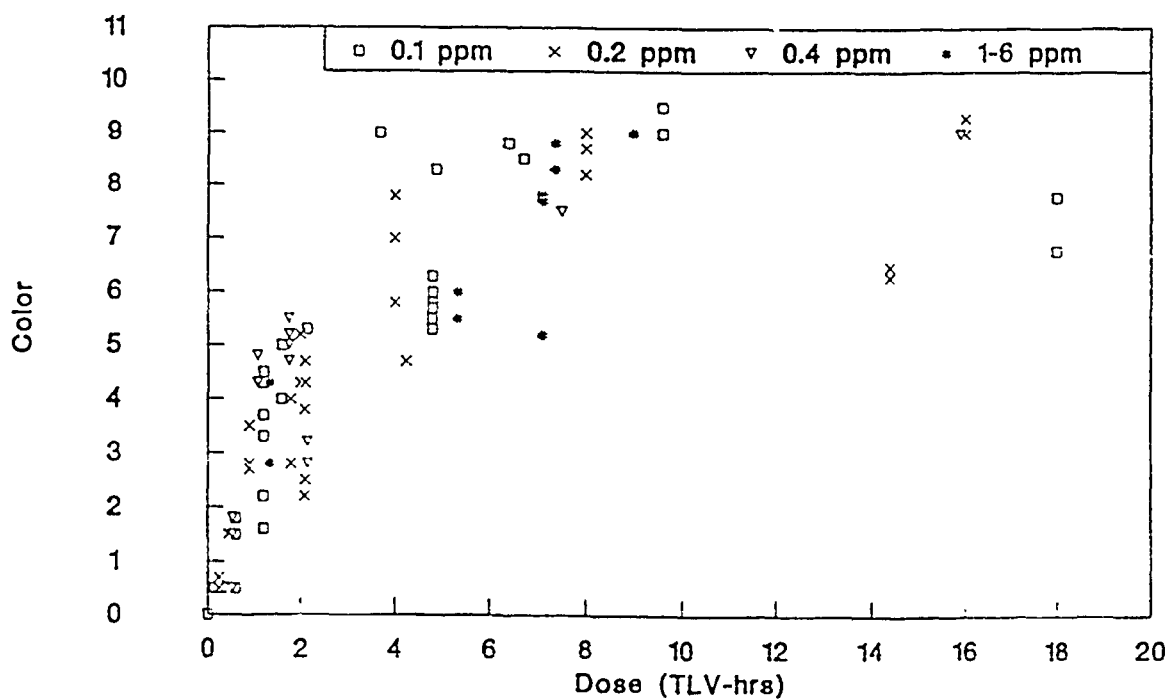


Fig. 6b. MMH Dose Response Curve at T=1 for PDAB (D12) without Diffusion Membrane

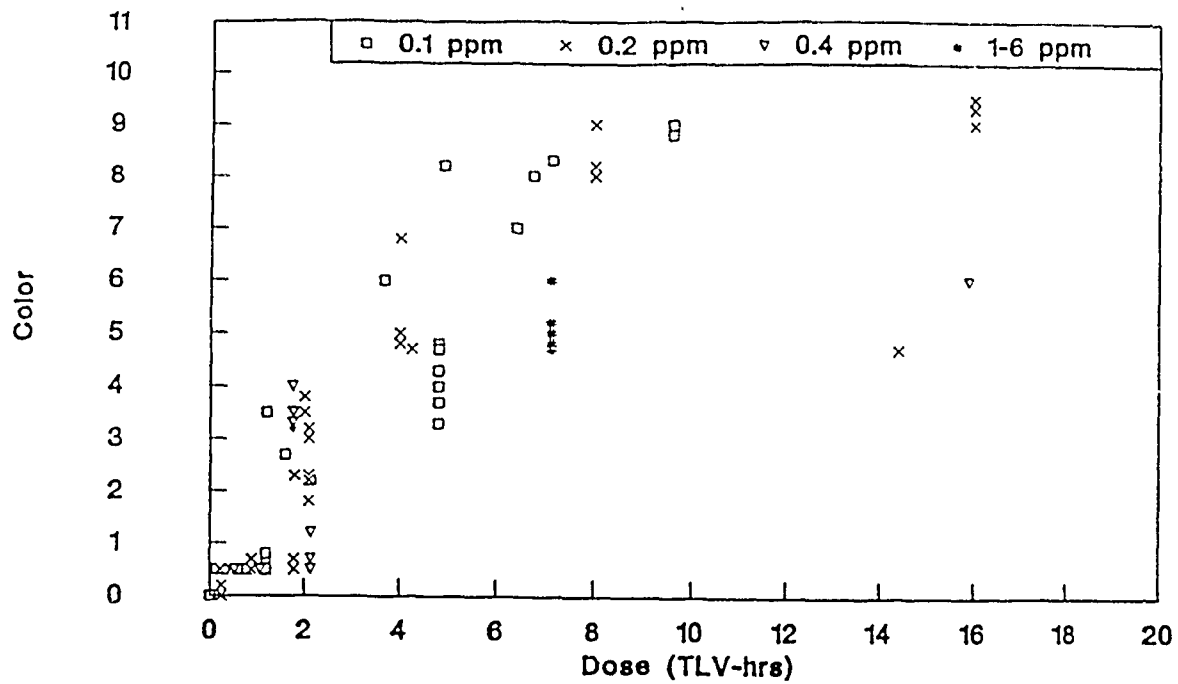


Fig. 6c. MMH Dose Response Curve at T=0 for PDAB (D12) with Diffusion Membrane

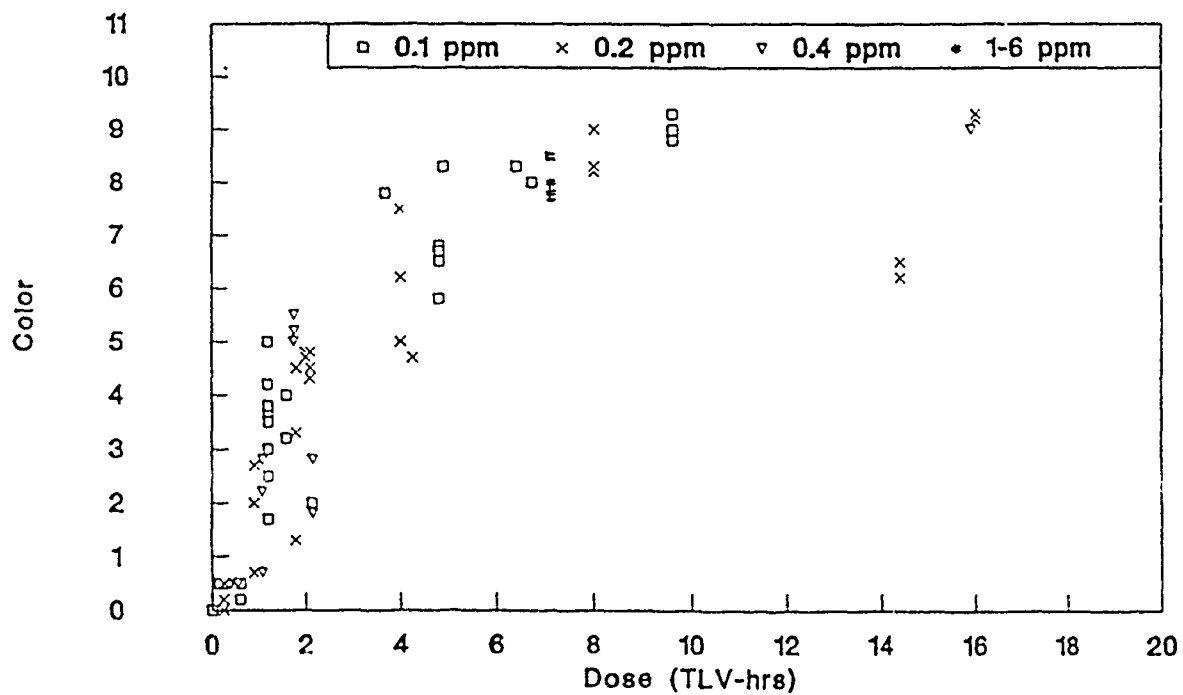


Fig. 6d. MMH Dose Response Curve at T=1 for PDAB (D12) with Diffusion Membrane

development at T=1, badges exposed to 10 TLV-hours appear to reach saturation. At T=0, there is less scatter in the data taken from badges with a diffusion membrane than data from badges without a membrane. However, at T=1, the scatter for both types of badges is comparable.

Time dependence is evident for the vanillin/citric acid (D13) badges without the diffusion membrane. Figures 7a and 7b show the graphs for T=0 and T=1. At T=0, there is scatter at every dose. This is especially true for those exposures obtained at higher concentrations (1-6 ppm) and lower exposure times. These points increase in color significantly by T=1. They are no longer outlying points and have moved onto the response curve. The badges with the diffusion membranes over the top color dot Figures 7c and 7d give a smoother, more linear plot at T=0 than at T=1. There was a slight increase in color saturation between T=0 and T=1. The D13 badges that included the membrane in their design were only exposed to 0.1 and 0.2 ppm MMH. Those badges without the membrane were exposed to the entire range of concentrations stipulated in the test plan. If the data taken from concentrations of 0.4 and 1-6 ppm is disregarded for a direct comparison between the two types of badges, the scatter in both is comparable. The membrane has little effect on the color produced at any particular dose.

The vanillin/phosphoric acid (D14) badges without the diffusion membrane exhibit a slight color development time dependence. The outlying data points present at T=0 show the greatest increase in color by T=1. The curve looks smoother an hour after exposure. Several of the outlying points represent exposures to high MMH concentrations. Saturation occurs at 16 TLV-hours. Dose response plots of this data are found in Figures 8a and 8b. The badges with the membrane show little increase in color from T=0 to T=1. As shown in Figures 8c and 8d, there is much scatter at <2.5 TLV-hours as noted previously. Saturation occurs between 6 to 8 TLV-hours with a color of 9.5. The use of a diffusion membrane does not have an effect on the development of color. Both badges, with and without the membrane, develop comparable intensities of color.

In addition to each of the individual chemistry badges, a composite badge incorporating the vanillin and the PDAB (D13+D12) was designed. The same badge design was used incorporating one chemistry in each position. The diffusion membrane was not used. Dose response data for vanillin on the composite badges is shown in Figures 9a and 9b. The color development for vanillin increases from T=0 to T=1. With the exception of a few outlying data points, there is the same amount of scatter at both readings of the badge. Those points obtained at higher concentrations of the MMH show the greatest increase in color. Color saturation occurs at 10 TLV-hours. The vanillin color dot on the composite badges is slightly more sensitive to MMH than the noncomposite D13 badges.

Except for a few outlying points, the response curve is very smooth at T=0 and T=1 for the composite PDAB (Figures 9c and 9d). Almost all of the outliers have moved up into the linearity curve with increased color by T=1. Saturation occurs at 9 TLV-hours with a color of 9.5. The PDAB color dot on the composite badges is much more stable than the PDAB color dot on the noncomposite badges. The sensitivity to MMH is comparable for both badges. Incorporating the two chemistries on the same badge may permit each to influence the performance of the other.

The composite badges D12+D14, which were produced late in the test program, are PDAB and vanillin/phosphoric acid. PDAB was coated on the top of the dosimeter, while the

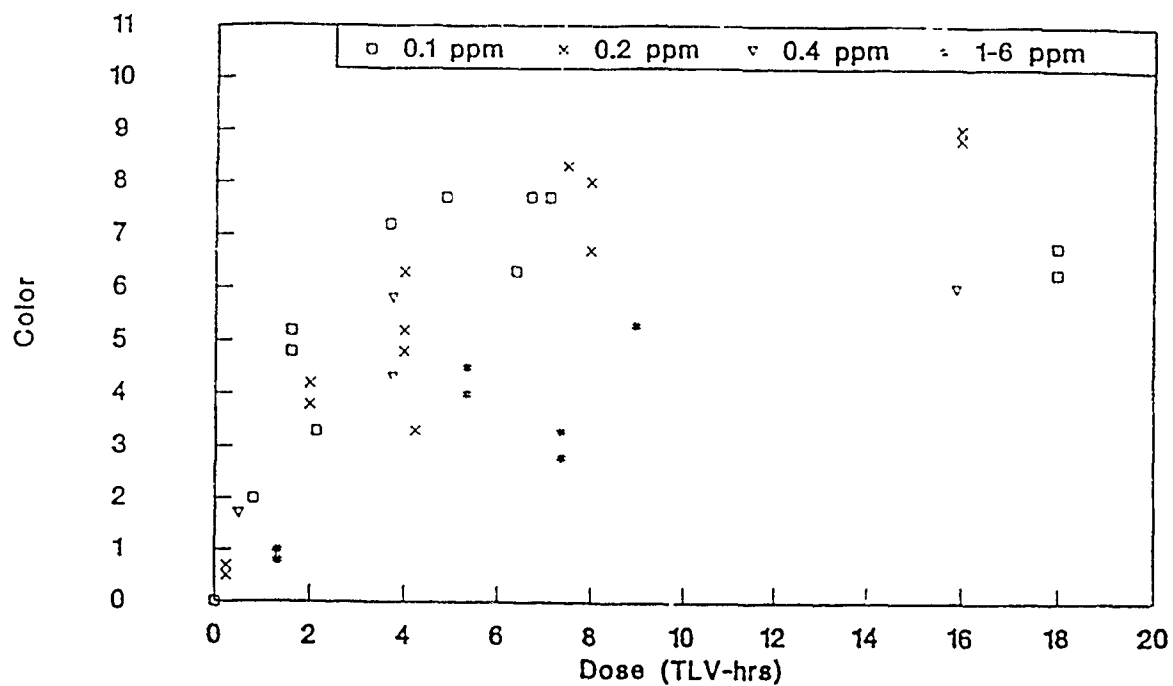


Fig. 7a. MMH Dose Response Curve at T=0 for Vanillin (D13) without Diffusion Membrane

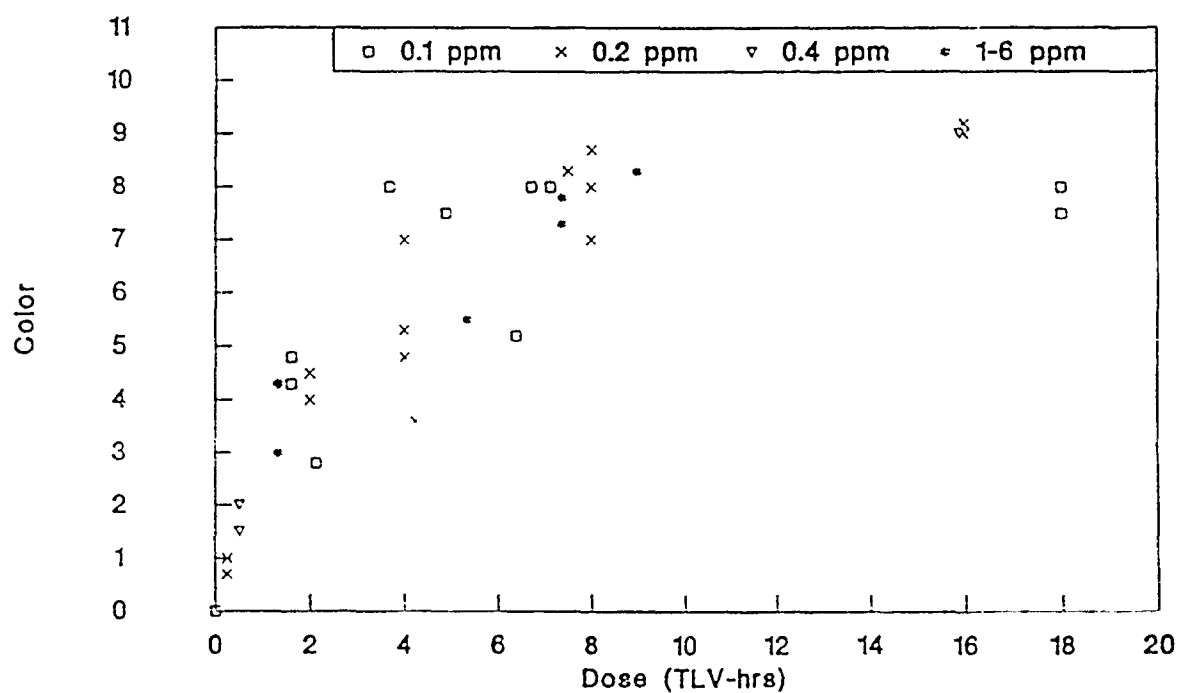


Fig. 7b. MMH Dose Response Curve at T=1 for Vanillin (D13) without Diffusion Membrane

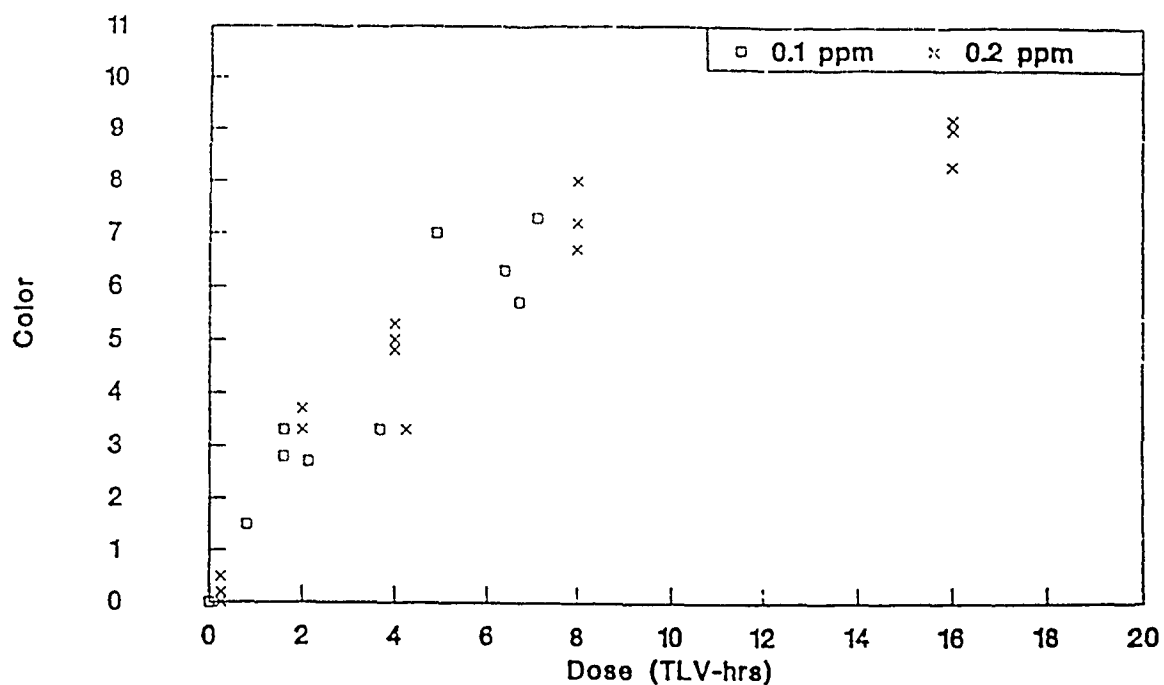


Fig. 7c. MMH Dose Response Curve at T=0 for Vanillin (D13) with Diffusion Membrane

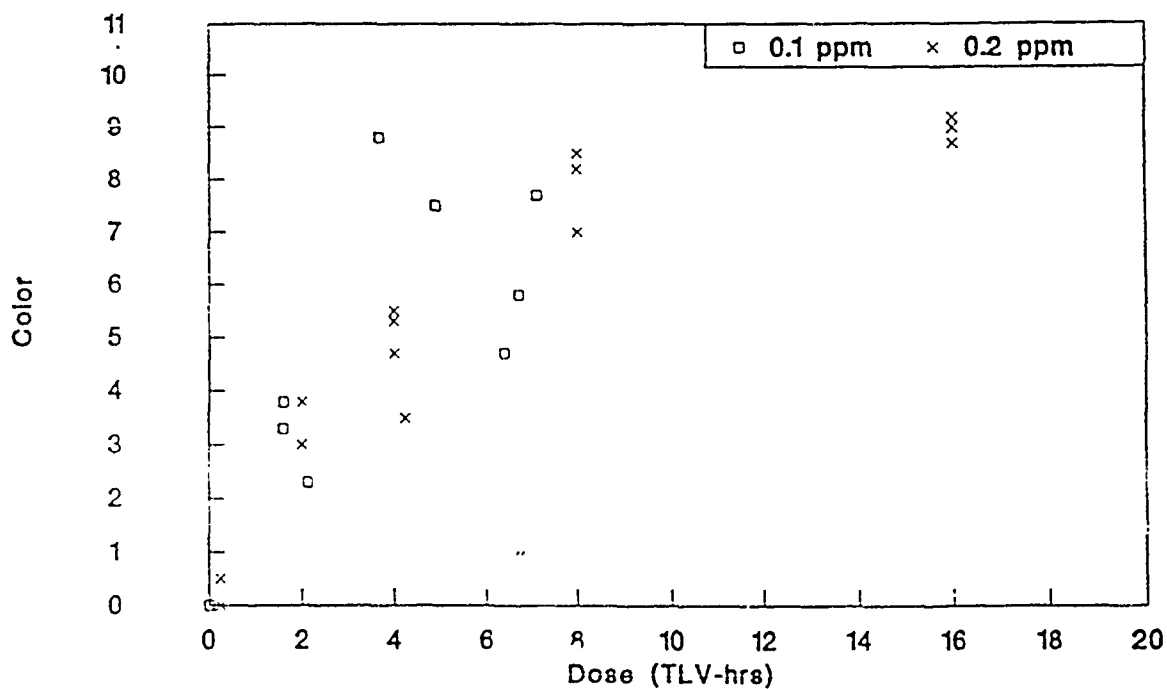


Fig. 7d. MMH Dose Response Curve at T=1 for Vanillin (D13) with Diffusion Membrane

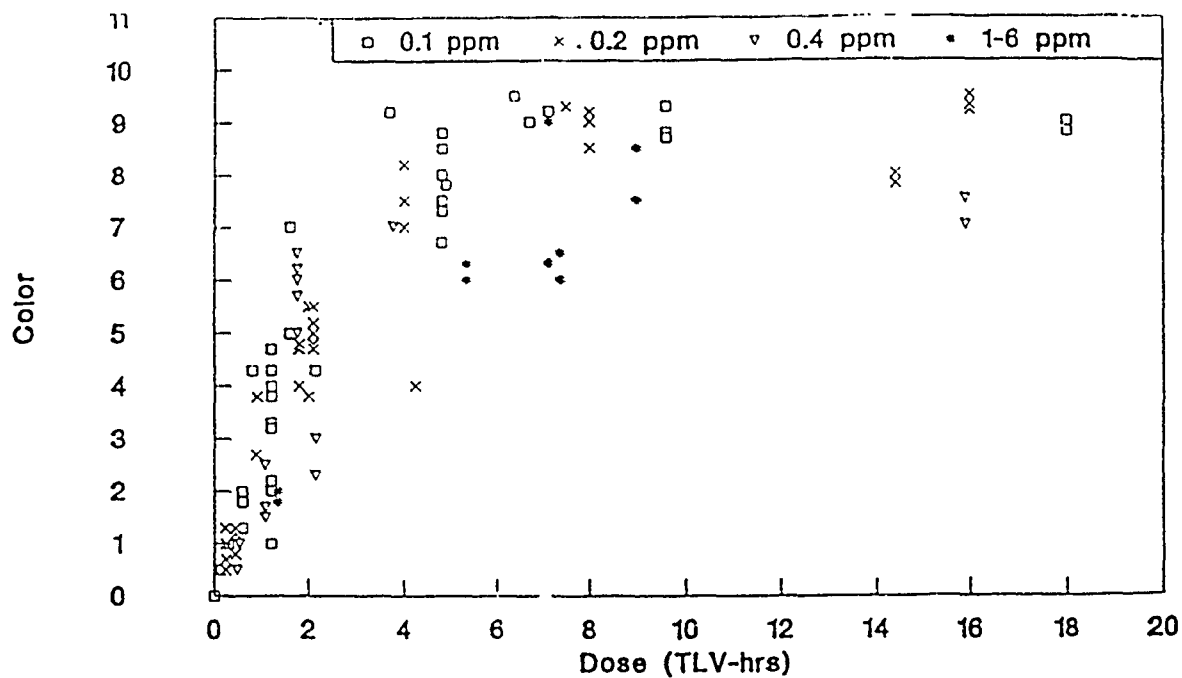


Fig. 8a. MMH Dose Response Curve at T=0 for Vanillin (D14) without Diffusion Membrane

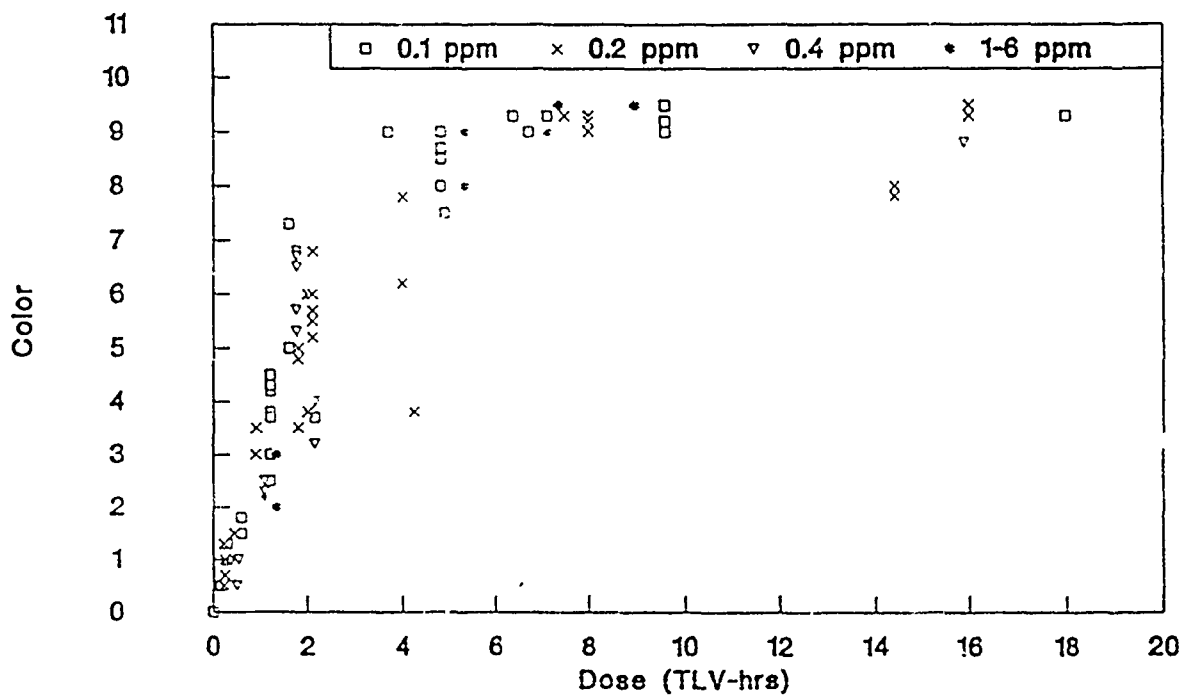


Fig. 8b. MMH Dose Response Curve at T=1 for Vanillin (D14) without Diffusion Membrane

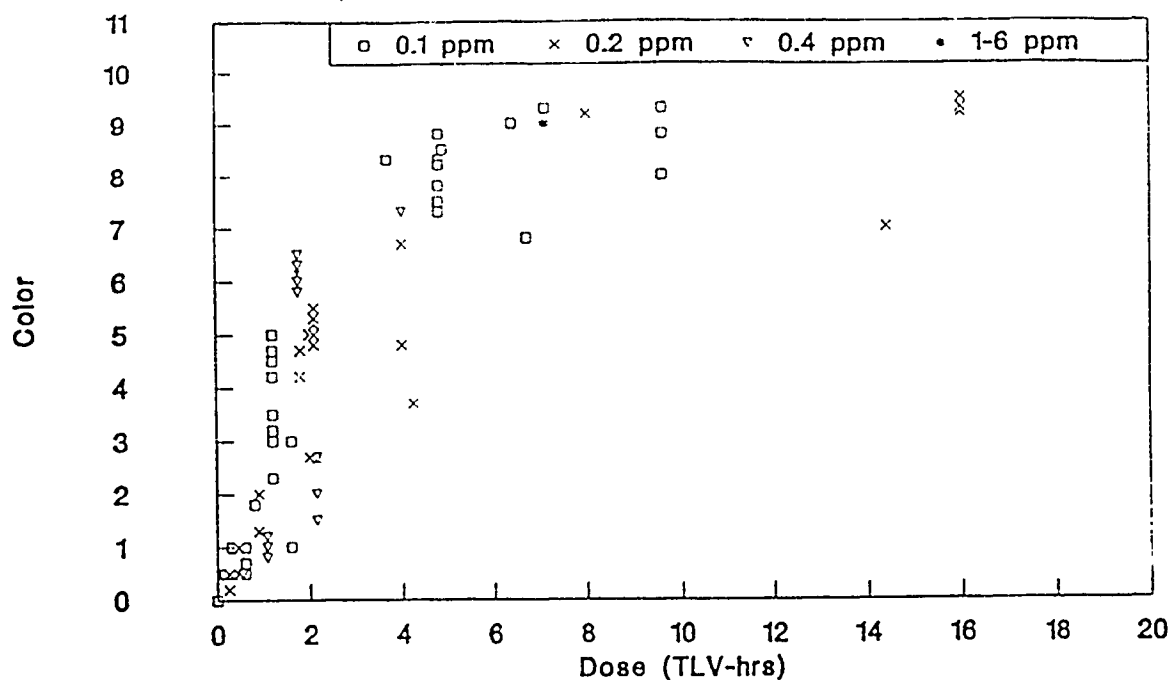


Fig. 8c. MMH Dose Response Curve at T=0 for Vanillin (D14) with Diffusion Membrane

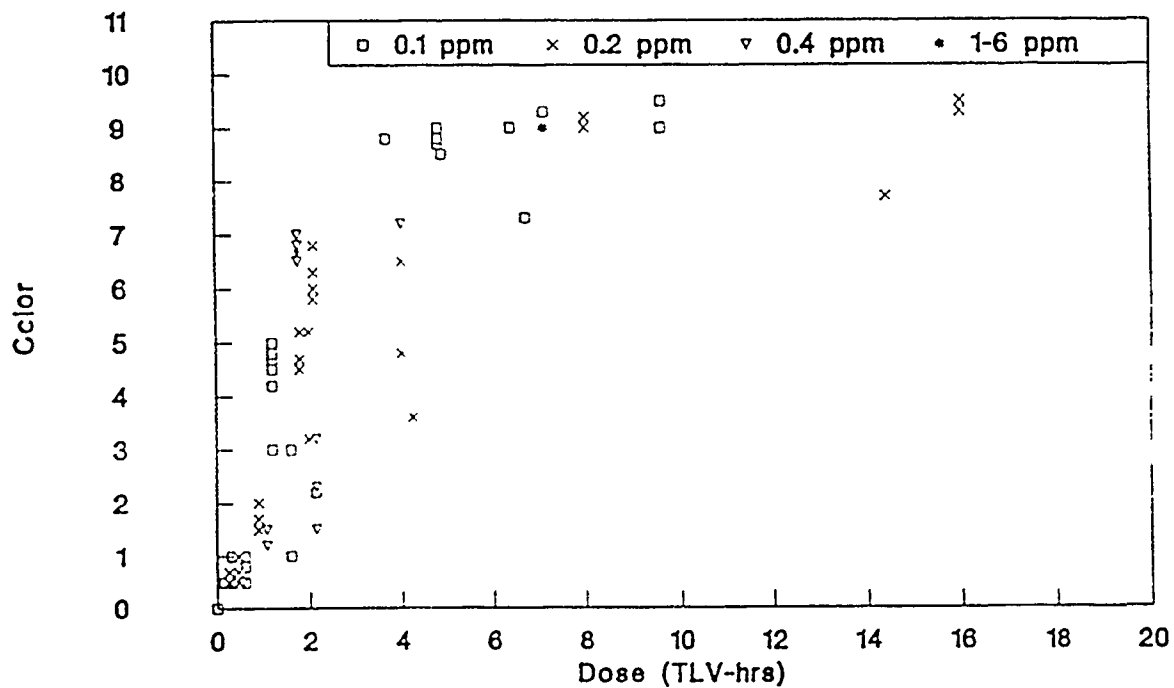


Fig. 8d. MMH Dose Response Curve at T=1 for Vanillin (D14) with Diffusion Membrane

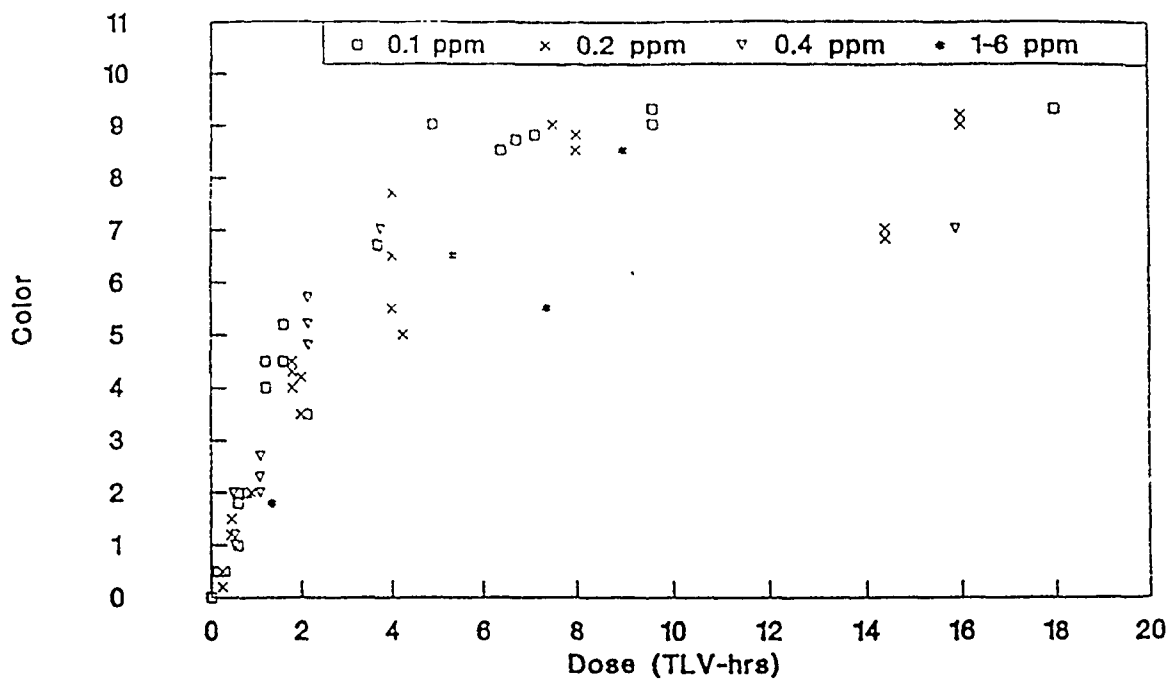


Fig. 9a. MMH Dose Response Curve at T=0 for Vanillin (D13, D13+D12)

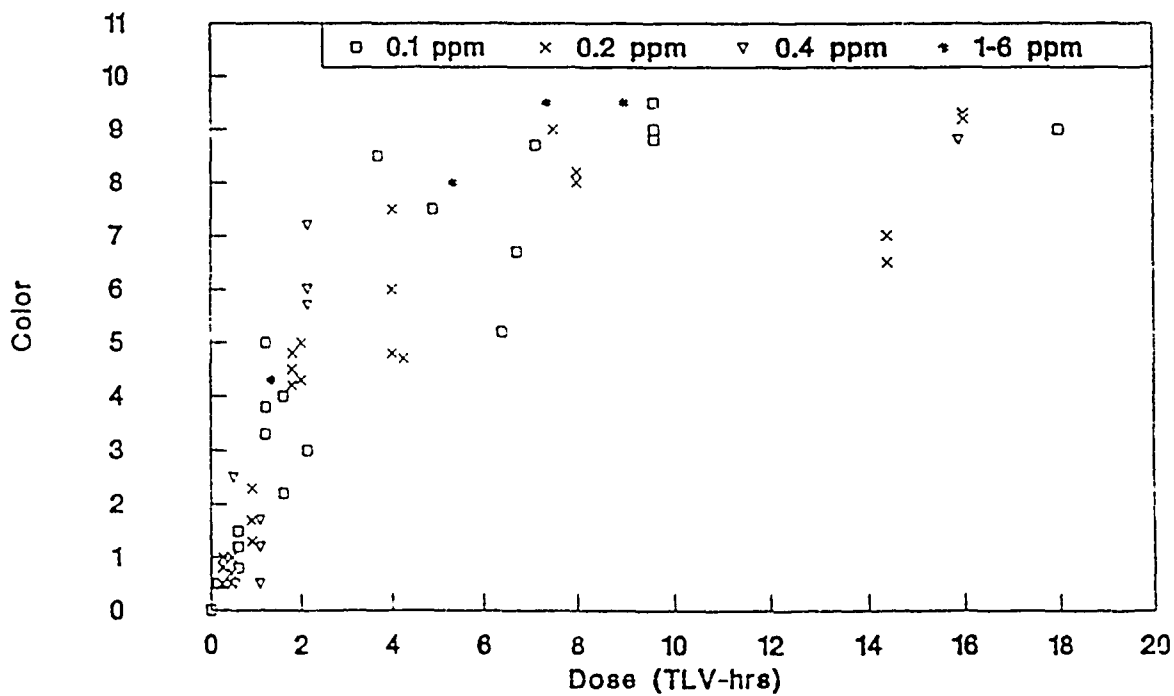


Fig. 9b. MMH Dose Response Curve at T=1 for Vanillin (D13, D13+D12)

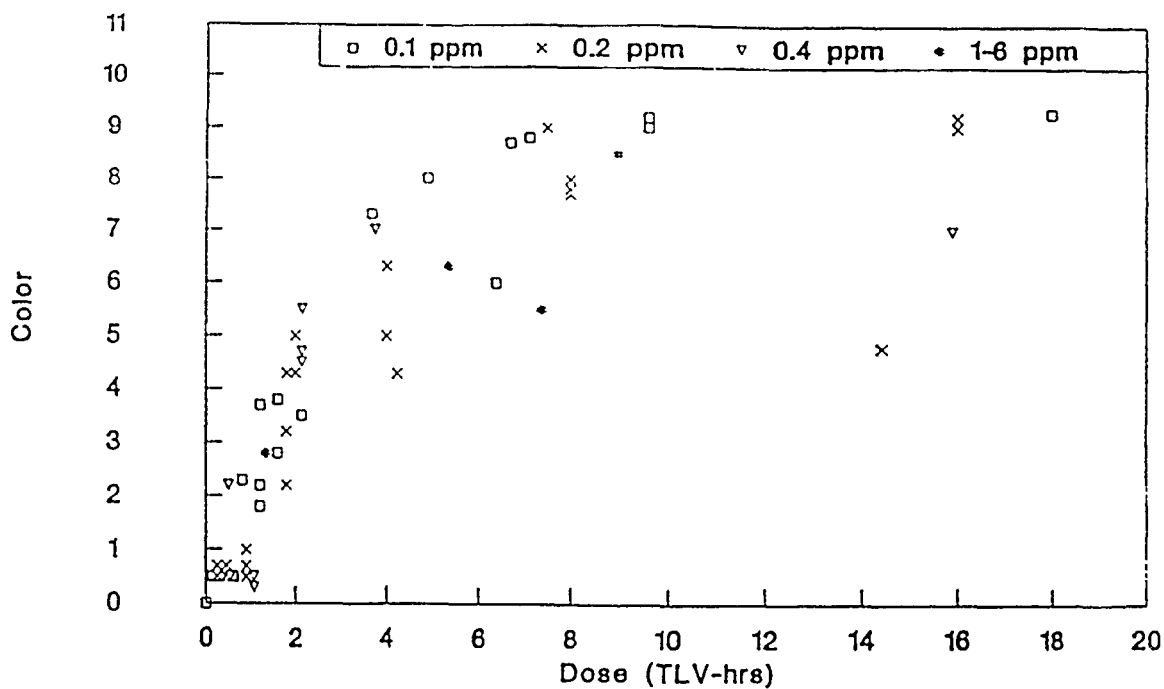


Fig. 9c. MMH Dose Response Curve at T=0 for PDAB (D12, D13+D12)

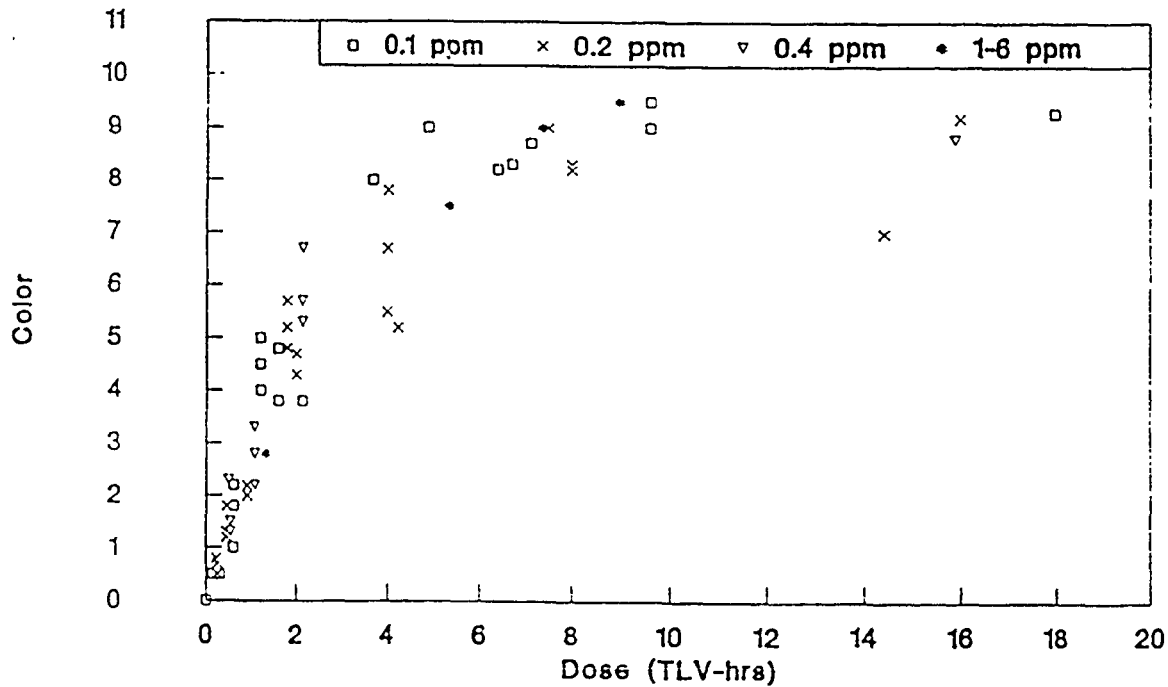


Fig. 9d. MMH Dose Response Curve at T=1 for PDAB (D12, D13+D12)

vanillin/phosphoric acid was coated on the bottom. These badges were tested at doses up to 15 TLV-hours with concentrations of MMH ranging from 0.15 ppm to 1.0 ppm. They were evaluated with the color wheel consisting of colors 1-5. There is an increase in color from T=0 to T=1 for both PDAB and vanillin. However, this time dependence is much pronounced in the PDAB badges. The scatter evident at T=0 is less so at T=1. Vanillin reached saturation by 15 TLV-hours with a color of 5.5. There are no data points between 2 and 15 TLV-hours; therefore, the exact saturation dose was not determined. The PDAB badges reach an average color of 5 by 15 TLV-hours. This data is plotted in Figures 10a-10d.

To compare the two color wheels designed for MMH, several of the composite badges D12+D14 were exposed to MMH and their color development was evaluated with both color wheels. Figures 11a and 11b represent dose response graphs of the PDAB spots on the badges. There was excellent correlation between the color wheels. The vanillin spots were evaluated as well. Figures 11c and 11d show the plots for vanillin. There is very good correlation between the two color wheels for vanillin. There appears to be the same amount of scatter for both vanillin and PDAB regardless of which color wheel is used for evaluation of the badges.

DOSE RESPONSE RESULTS FOR HYDRAZINE

Dose response tests with hydrazine were carried out at the TLV level (0.1 ppm) of hydrazine. Figures 12a-12d give the response data for the badges. PDAB (D12) shows a time dependence at doses less than 16 TLV-hours. Vanillin (D13) also shows a time dependence at the lower doses. Vanillin (D14) indicates a slight time dependence, while the composite badge (D13+D12) does not show this trend. The color change shows a good correlation with dose; however, there is not enough data to make conclusions on the precision or the saturation point.

Most of the data collected for exposure to hydrazine were obtained from the composite PDAB and vanillin/phosphoric acid (D12+D14) badges produced for use with the new color wheel. This data provides a more complete picture of the dose response of the badges for hydrazine. The data is represented in Figures 13a-13d. The saturation point at T=0 is between 3 to 3.5 TLV-hours for the PDAB. More data is needed to determine the saturation dosage for vanillin. Saturation color for the PDAB is 3.5. There is a slight time dependence in the PDAB data and a fair amount of scatter below one TLV-hour. The curve for PDAB shows slightly greater sensitivity for hydrazine than MMH at T=0. Vanillin, however, is more sensitive to MMH than hydrazine.

RELATIVE HUMIDITY RESULTS

When exposed to MMH at different relative humidities, badges D12, D13, and D14 were not affected in any consistent way. At <1.0 TLV-hours, the composite badge D13+D12 shows a slightly higher response at 70% RH for both D13 and D12. Limited testing was done with hydrazine at different humidities. When exposed to hydrazine at 70% RH and 40% RH, the composite badge D13+D12 and D14 displayed no effect in color development between the two humidities. At 2 TLV-hours, the D13 and D12 badges showed more intense color development with hydrazine humidified

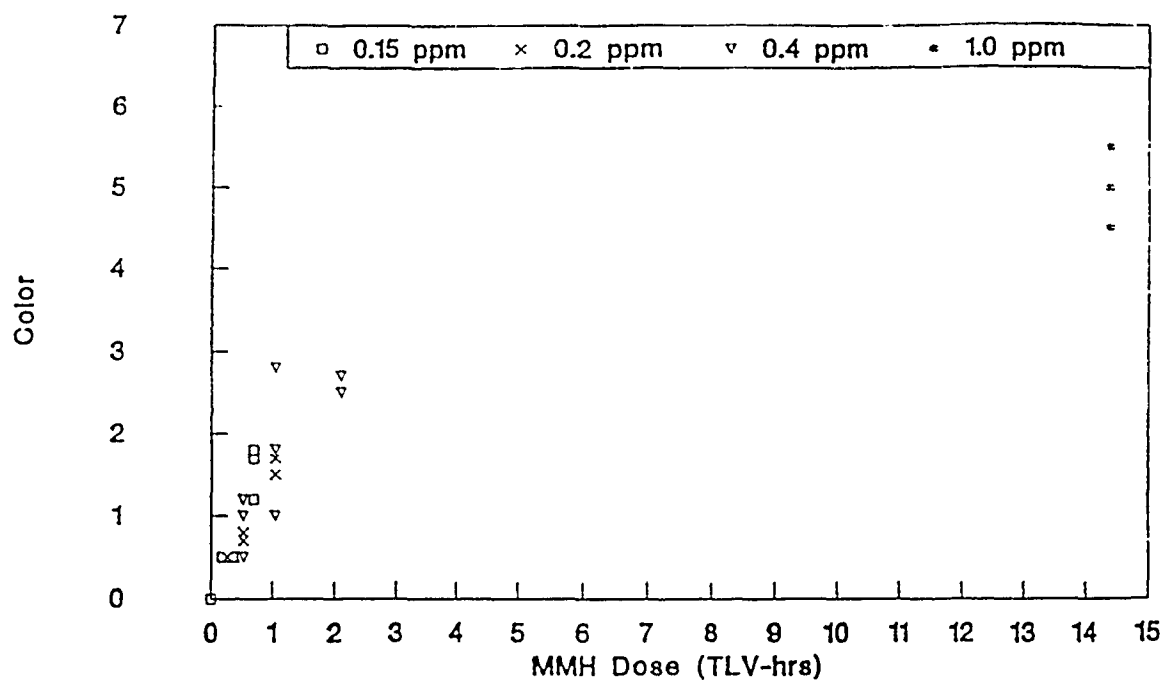


Fig. 10a. MMH Dose Response Curve at T=0 for PDAB (D12, D12+D14)

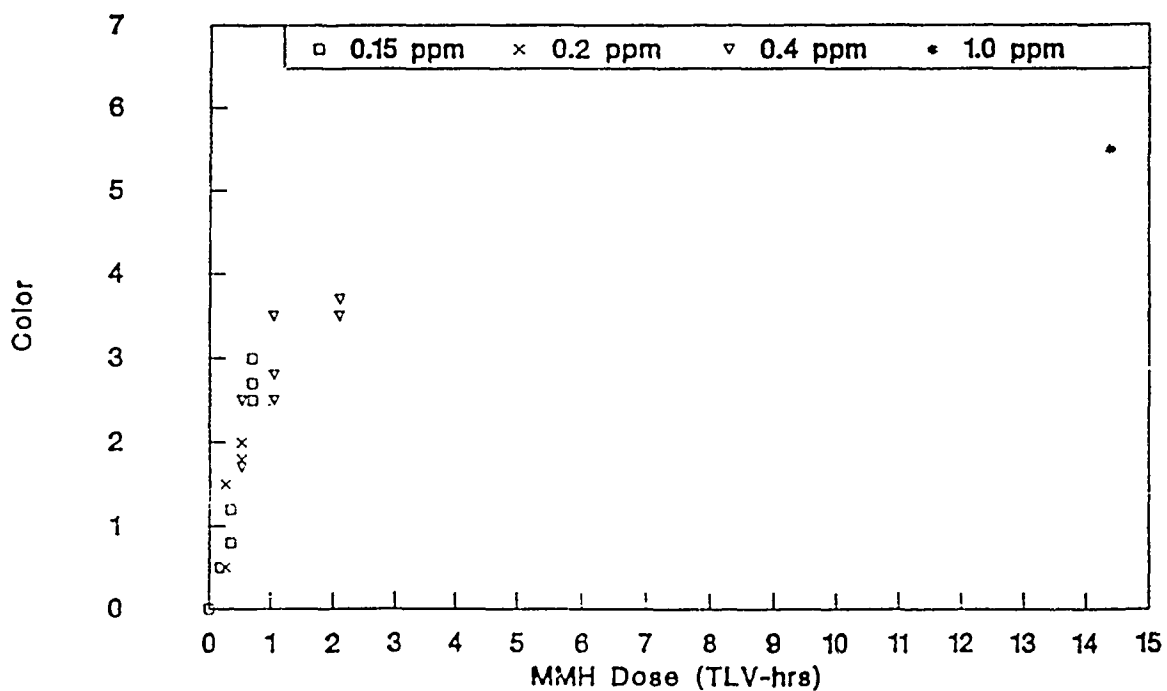


Fig. 10b. MMH Dose Response Curve at T=1 for PDAB (D12, D12+D14)

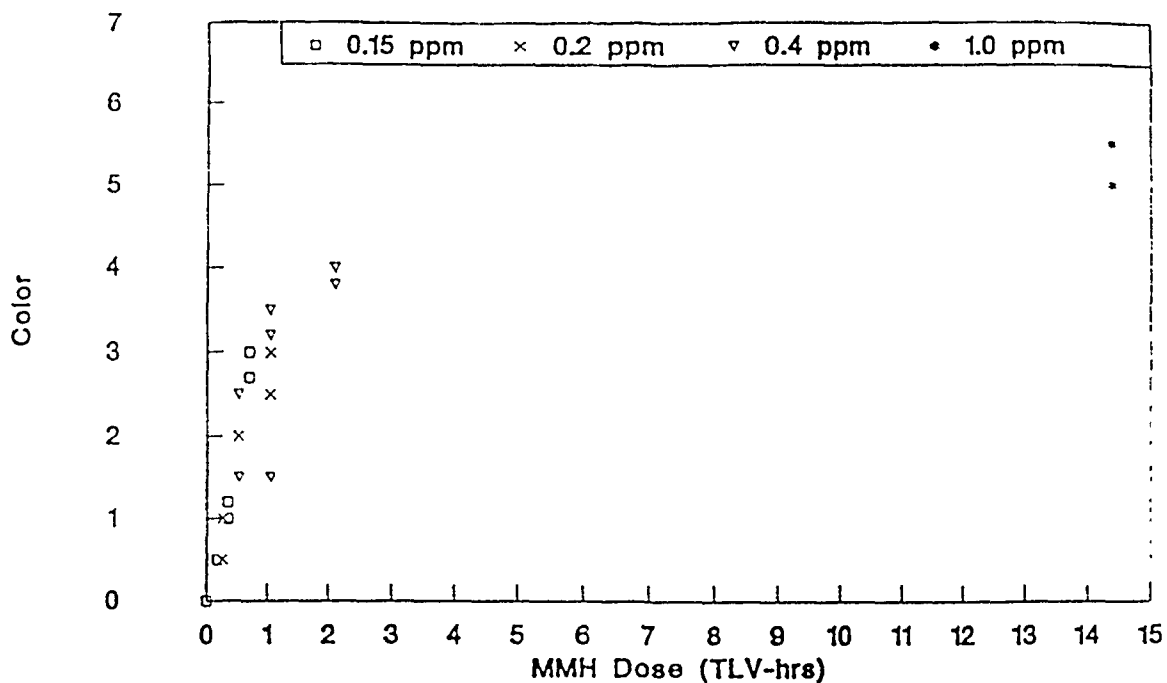


Fig. 10c. MMH Dose Response Curve at T=0 for Vanillin (D14, D12+D14)

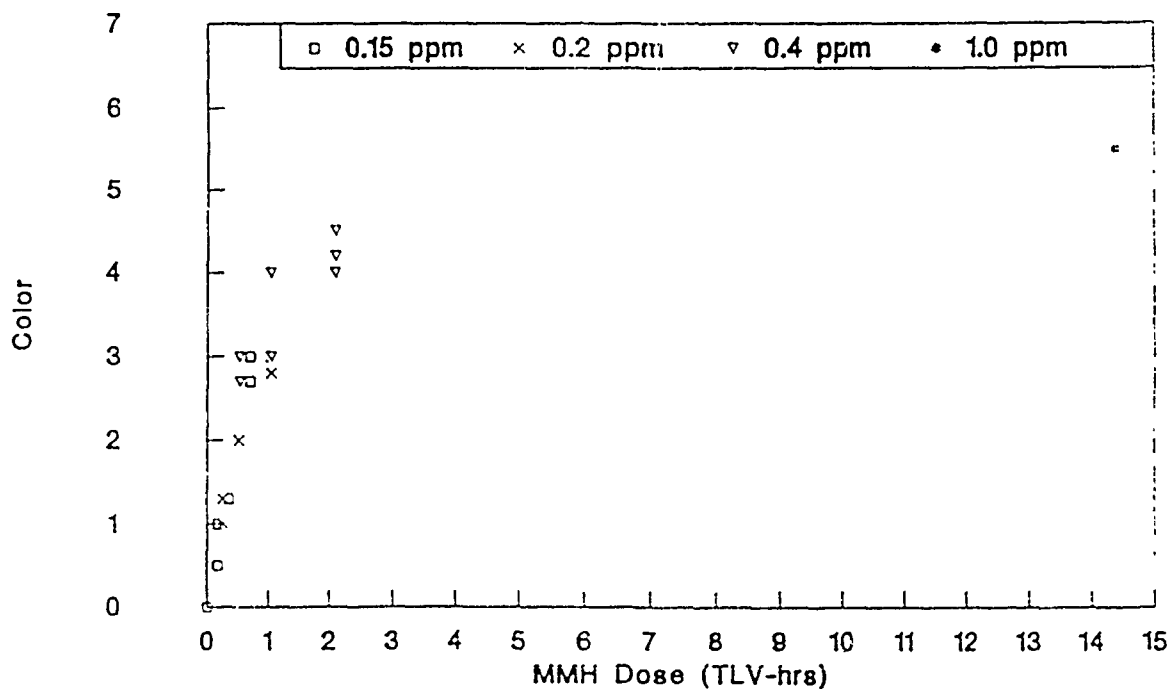


Fig. 10d. MMH Dose Response Curve at T=1 for Vanillin (D14, D12+D14)

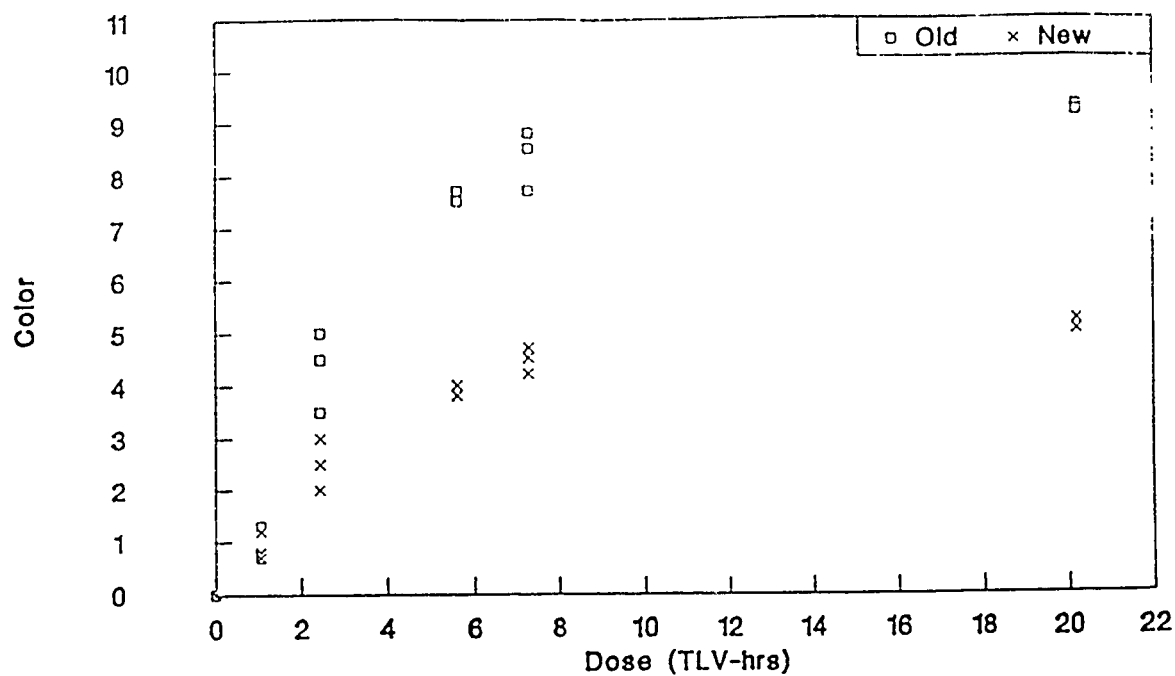


Fig. 11a. Dose Response Comparison Between Old and New PDAB (D12) Color Wheels Using D12+D14 Badge at T=0

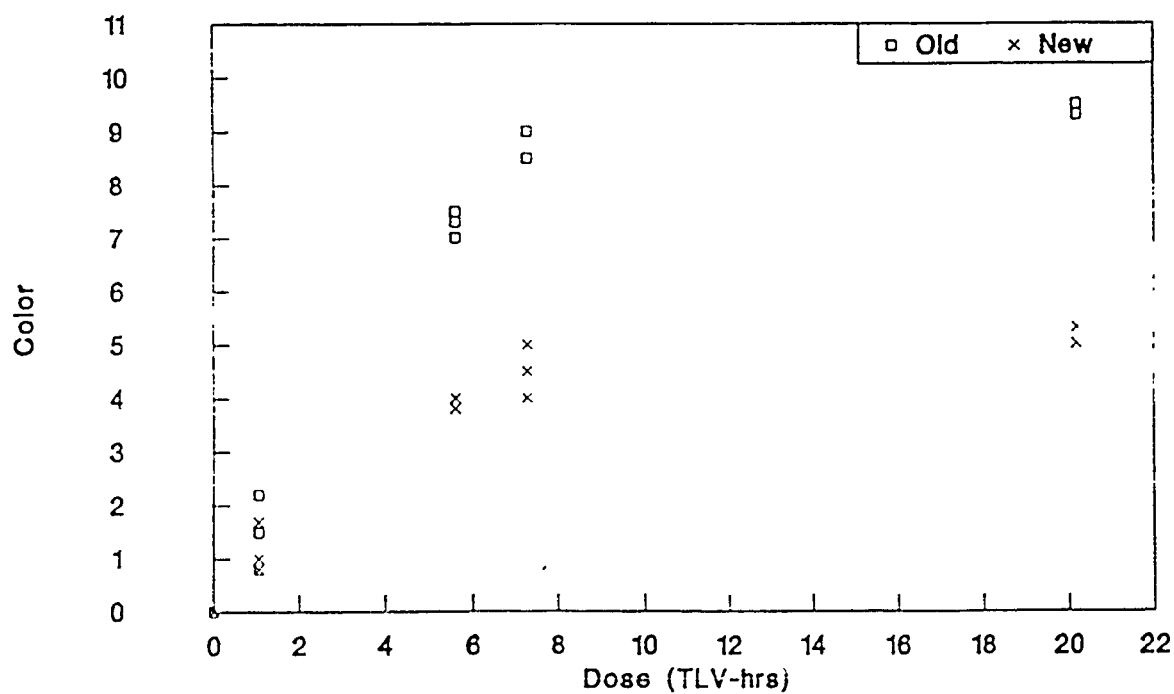


Fig. 11b. Dose Response Comparison Between Old and New PDAB (D12) Color Wheels Using D12+D14 Badge at T=1

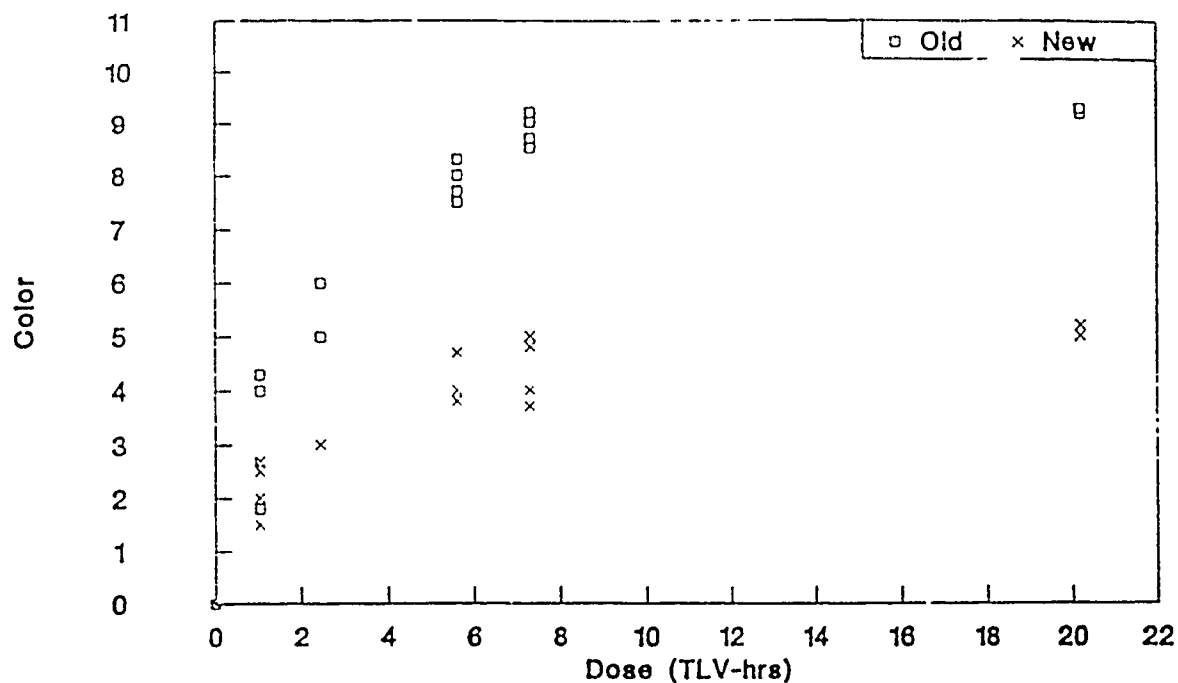


Fig. 11c. Dose Response Comparison Between Old and New Vanillin (D14) Color Wheels Using D12+D14 Badge at T=0

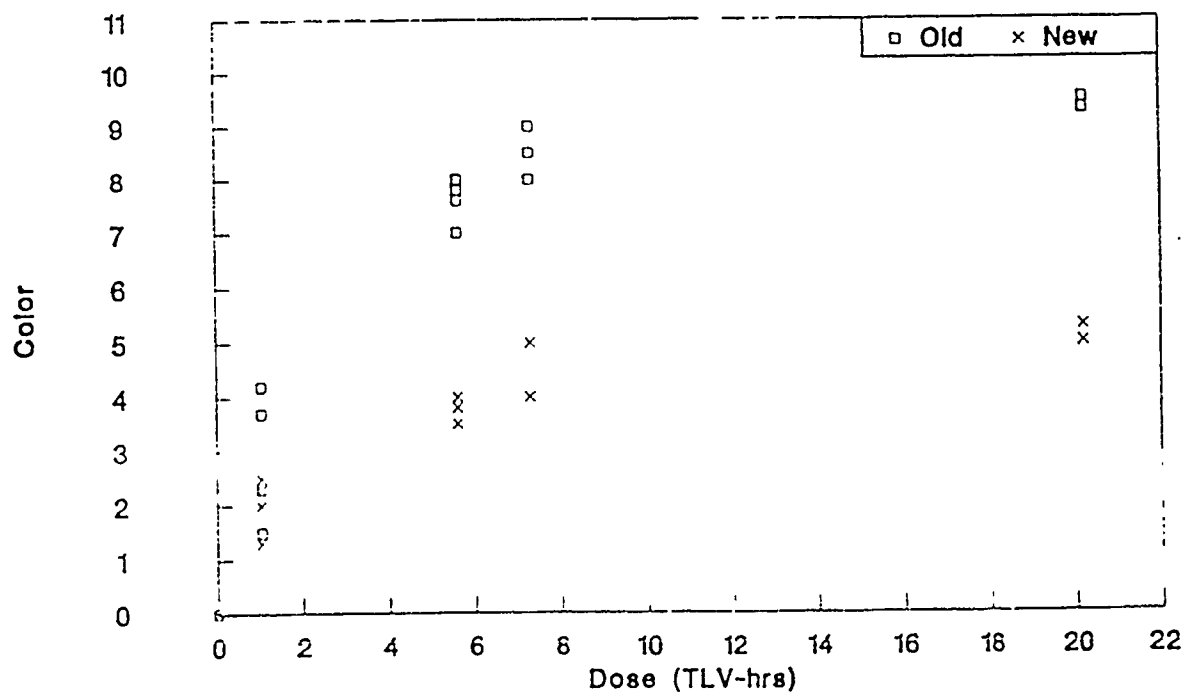


Fig. 11d. Dose Response Comparison Between Old and New Vanillin (D14) Color Wheels Using D12+D14 Badge at T=1

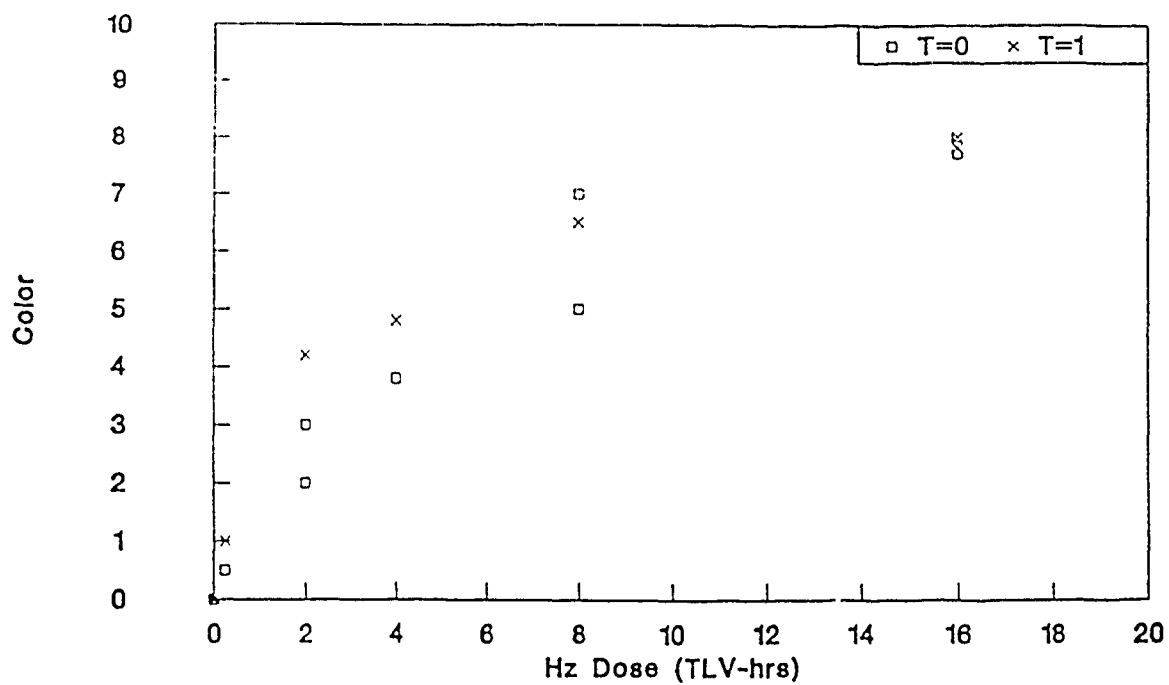


Fig. 12a. Hydrazine Dose Response Curve for PDAB (D12)

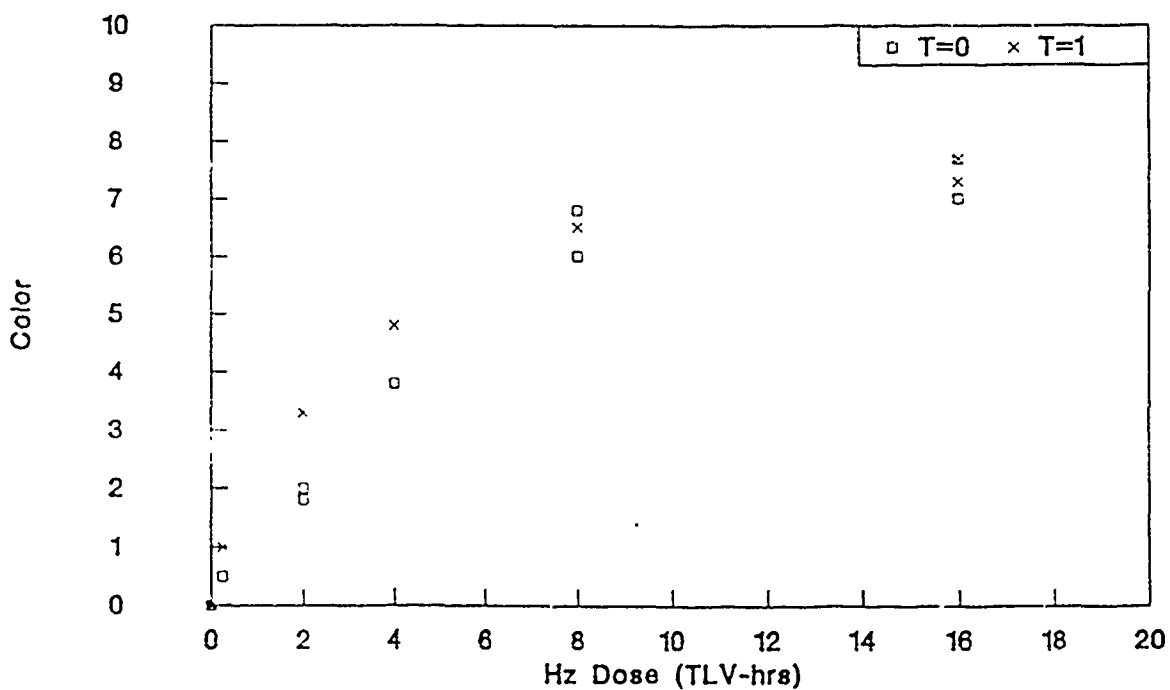


Fig. 12b. Hydrazine Dose Response Curve for Vanillin (D13)

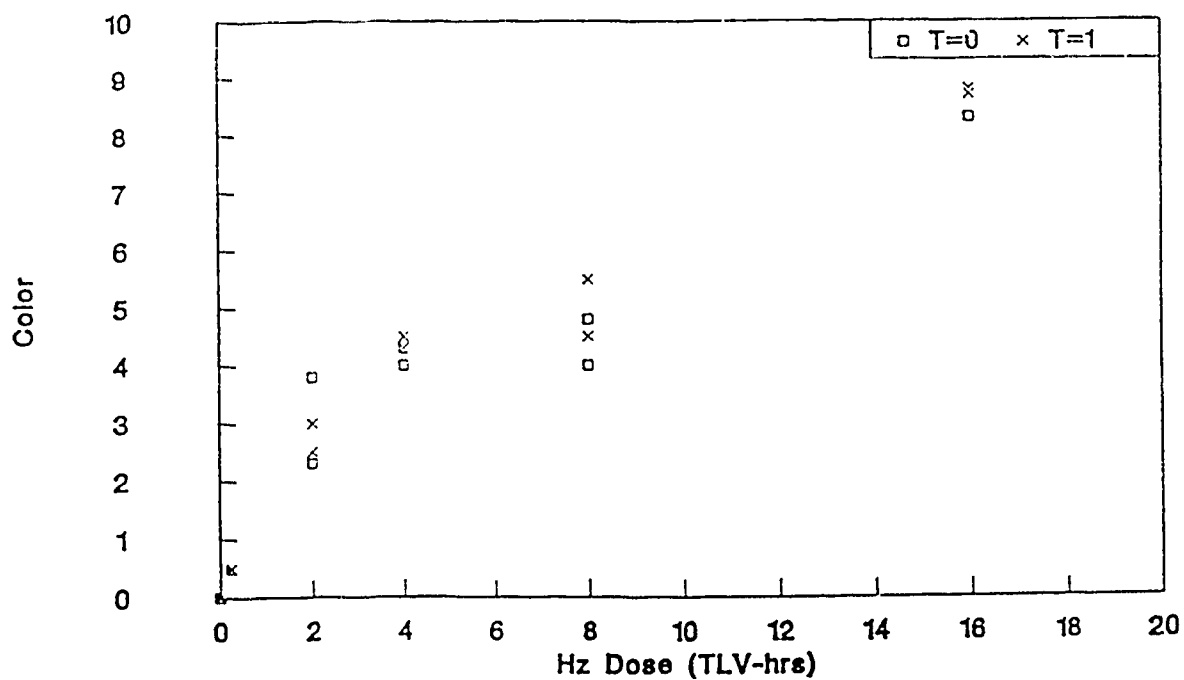


Fig. 12c. Hydrazine Dose Response Curve for Vanillin (D14)

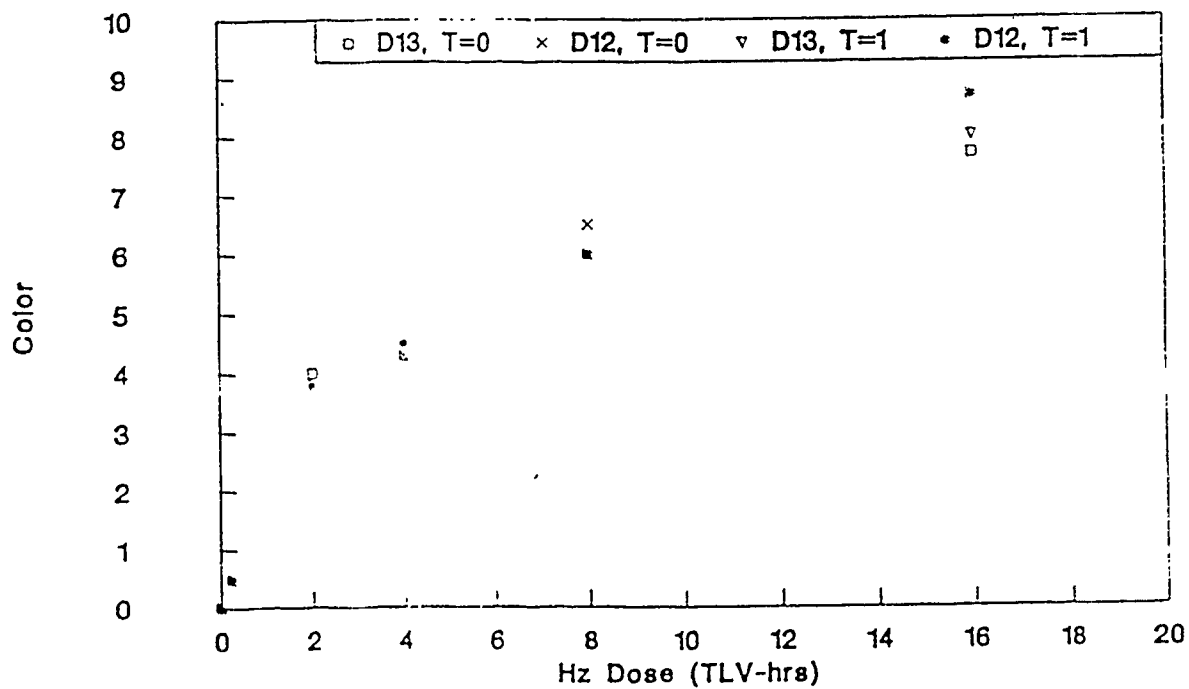


Fig. 12d. Hydrazine Dose Response Curve for Vanillin (D13) and PDAB (D12) Using D13+D12 Badge

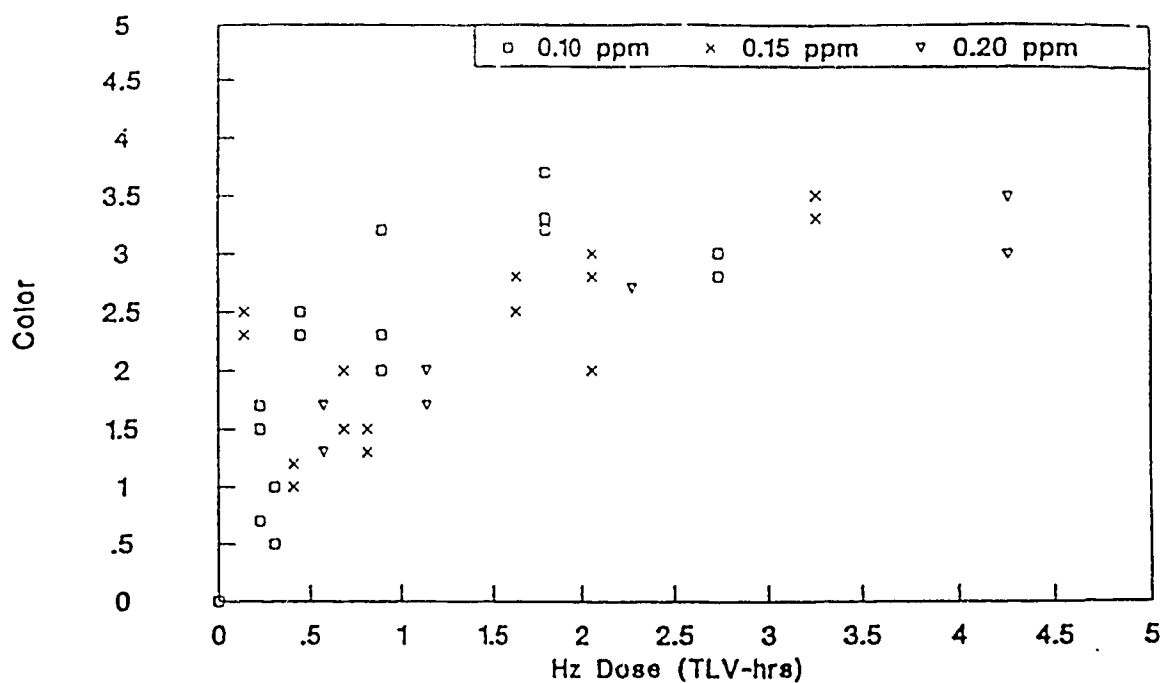


Fig. 13a. Hydrazine Dose Response Curve at T=0 for PDAB (D12, D12+D14)

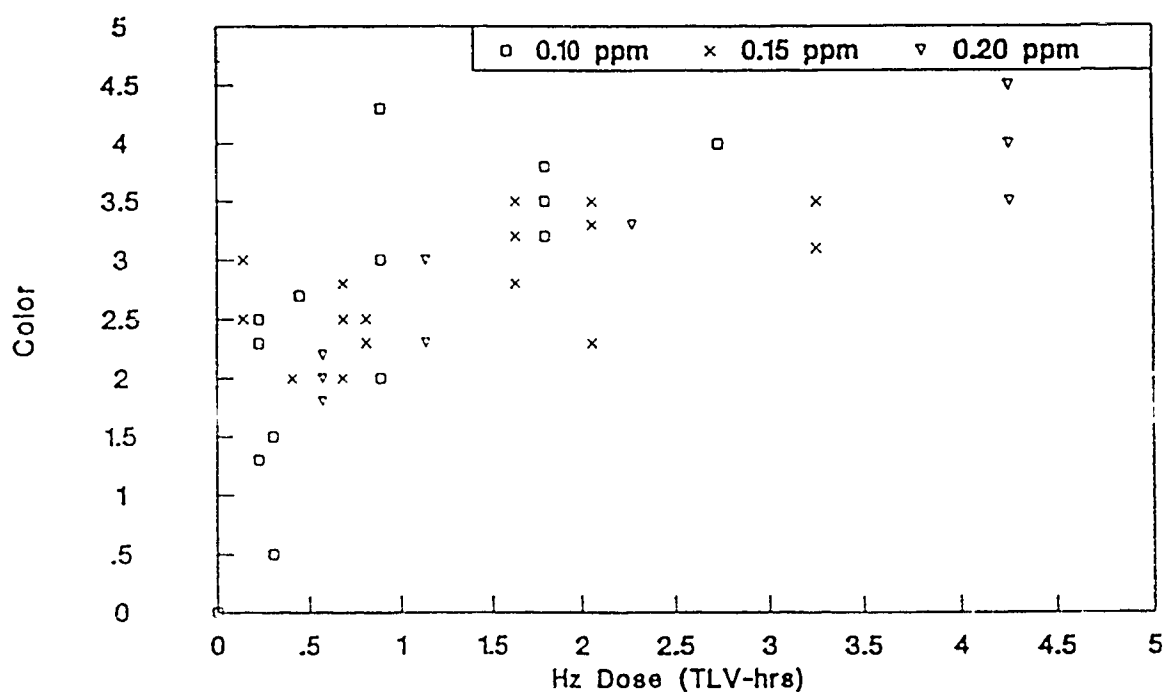


Fig. 13b. Hydrazine Dose Response Curve at T=1 for PDAB (D12, D12+D14)

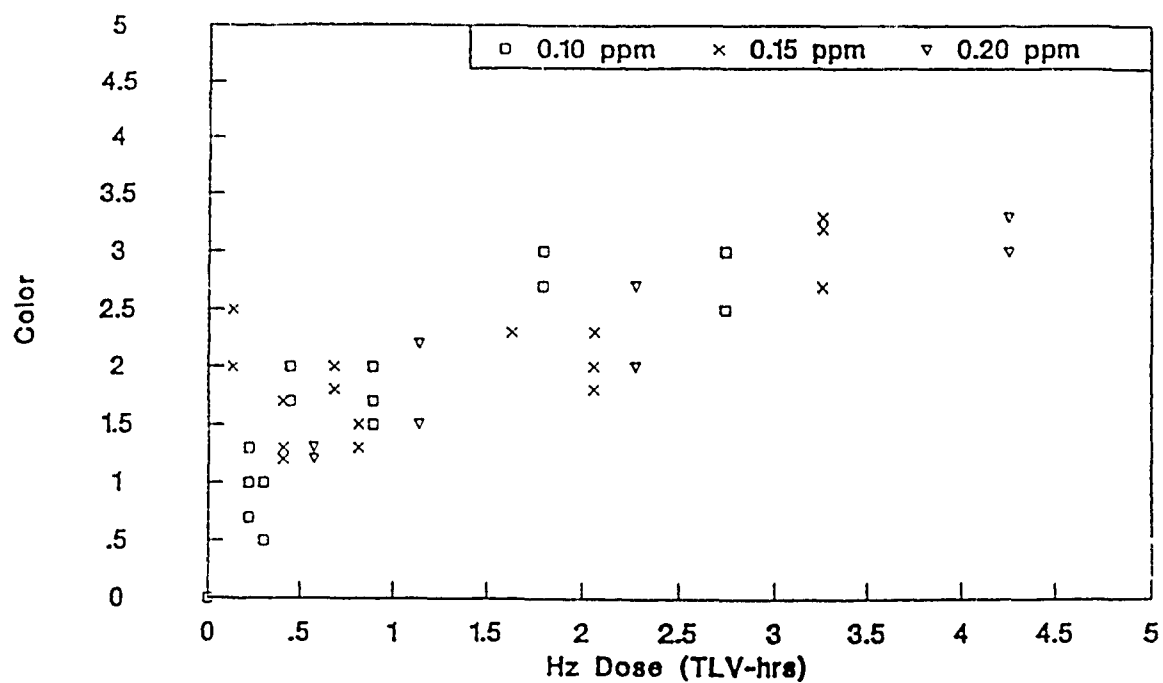


Fig. 13c. Hydrazine Dose Response Curve at T=0 for Vanillin (D14, D12+D14)

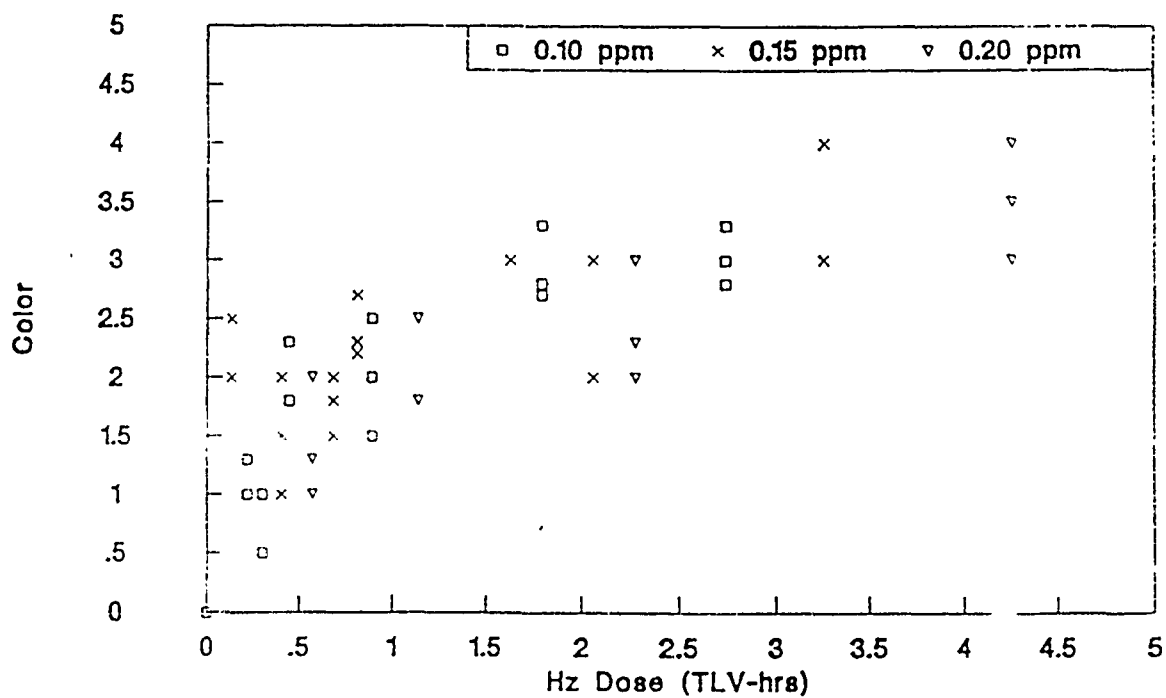


Fig. 13d. Hydrazine Dose Response Curve at T=1 for Vanillin (D14, D12+D14)

to 70% RH than at 40%. However, more data points would be needed for statistical certainty. The data for RH effects on MMH is compiled in Tables 4a-4d. The responses are given by dose and humidity as well as the location of the spot on the badge (top or bottom).

For dosimeters D12, D13, D14, and the composite D13+D12, there is limited data on humidity effects for hydrazine. Table 5 gives the color intensity averages for the two humidities tested. There is not a consistent trend due to humidity for any of the badge types.

Composite badges D12+D14 were exposed to hydrazine at several humidities. Figures 14a-14d detail the relative humidity trends for the PDAB and vanillin sections of these badges. Vanillin is not affected by differing humidities. PDAB data shows lower color intensity for badges exposed to <10% RH at T=0. However, at T=1, the badges at <10% RH have increased in color intensity and no longer give lower results than the other humidities.

INTERFERENT RESPONSES

All interference tests involving heat, cold, UV light, and sunlight were carried out at Wiltech. Heating the badges was accomplished by placing them in a convection oven at 40°C. Badges exposed to cold temperatures were placed in a freezer. When a UV light source was used, badges were exposed to 254 nm or 350 nm wavelengths of light. Exposure to heat and cold lasted for 4 hours, UV light for 0.5 hour. The composite PDAB and vanillin/phosphoric acid (D12+D14) badges were used and evaluated with the 1-5 color wheel. The badges were exposed to heat, cold, and UV light both before and after exposure to MMH. The badges were exposed to sunlight prior to MMH exposure. Table 6 gives the color development of the badges exposed to MMH prior to these interferents. Table 7 shows color development for badges exposed to the interferents first, MMH second. The PDAB badges exposed to sunlight or a UV lamp were evaluated on the vanillin color wheel after interferent exposure as the color development was yellow.

Table 6 shows the interferent data in which the badges were exposed to MMH before the interferents. The colors of the badges were less intense than normal after exposure to MMH and prior to heat exposure. After subsequent exposure to heat, the increase in color brought the badges closer to the normal color intensity. Both PDAB and vanillin were affected by the addition of heat.

When the badges were exposed to heat for 2 hours before exposure to MMH, (Table 7) they showed a minimal color development. The average colors achieved after exposure to both heat and MMH, are less intense than the normal color development for 2.1 TLV-hours of MMH. The colors of both chemistries were less intense than the final colors achieved from exposure to MMH and then heat.

Exposure to cold temperatures after MMH exposure caused no significant changes in the color intensity of either badge. When the badges were exposed to MMH after 2 hours of cold temperatures, they behaved similarly to the heat interference. There was a minimal color development to the cold (0.5) and the badges achieved similar color intensities with the subsequent exposure to MMH. The final average colors were less intense than the colors normally achieved after

Table 4a. Humidity Response of PDAB Badge (D12)

Dose (TLV-hrs)	Color at 70% RH				Color at 40% RH			
	T=0	T=0	T=1	T=1	T=0	T=0	T=1	T=1
	Top	Bot	Top	Bot	Top	Bot	Top	Bot
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.13	0.0	0.4	0.1	0.6	0.25	0.25	0.25	0.5
0.25	0.1	0.4	0.1	0.6	0.1	0.3	0.2	0.6
0.47	0.5	0.5	2.0	1.0	0.5	0.5	0.5	0.5
0.79	0.7	2.0	1.0	2.2	0.5	0.5		
1.13	1.5	2.7	0.9	2.4	0.8	1.4	3.1	3.6
1.36	0.8	1.0	2.0	3.3	1.0	0.5	4.3	2.8
2.0	2.0	4.3	2.3	3.4	3.2	4.5	3.8	4.9
3.5	5.3	5.5	5.5	6.0	6.0	8.3	7.8	9.0
11.7	9.5	9.5	9.5	9.5				

Table 4b. Humidity Response of Vanillin Badge (D13)

Dose (TLV-hrs)	Color at 70% RH				Color at 40% RH			
	T=0	T=0	T=1	T=1	T=0	T=0	T=1	T=1
	Top	Bot	Top	Bot	Top	Bot	Top	Bot
0.0					0.0	0.0	0.0	0.0
0.12	0.1	0.7	0.0	0.5	0.5	0.5	0.5	0.5
0.25	0.5	0.8	0.2	1.1	0.2	0.6	0.3	0.9
0.47	0.5	0.5	0.9	0.8	1.7	1.7	2.0	1.5
0.79	2.0	3.7	2.0	3.3	1.5	2.0		
1.02	1.9	3.6	1.9	3.3	1.2	1.0	3.0	1.8
1.36	0.5	0.5	1.8	1.8	0.8	1.0	3.0	4.3
2.00	3.0	3.9	3.1	4.3	3.2	3.8	3.0	3.8
3.50	5.5	6.0	6.0	6.3	6.0	7.7	7.2	8.0
11.7	9.5	9.5	9.5	9.5				

Table 4c. Humidity Response of Vanillin Badge (D14)

Dose (TLV-hrs)	Color at 70% RH				Color at 40% RH			
	T=0	T=0	T=1	T=1	T=0	T=0	T=1	T=1
	Top	Bot	Top	Bot	Top	Bot	Top	Bot
0.00					0.0	0.0	0.0	0.0
0.13	0.2	0.6	0.2	0.6	0.25	0.5	0.25	0.5
0.25	0.6	1.0	0.5	0.9	0.4	0.7	0.6	0.8
0.47	0.8	2.7	1.3	3.0	0.5	0.5	0.5	0.5
0.79	0.8	2.7	1.3	3.0	1.8	4.3		
1.13	1.7	3.5	1.8	3.5	3.2	2.8	3.8	3.4
1.36	4.5	4.8	4.8	4.8	2.0	1.8	3.0	2.0
2.00	3.9	5.0	3.9	5.2	3.5	4.5	3.5	4.5
3.50	5.8	6.0	5.3	6.0	8.3	9.2	8.8	9.0
11.7	8.5	9.0	9.0	9.5				

Table 4d. Humidity Response of Vanillin/PDAB Badge (D13+D12)

Dose (TLV-hrs)	Color at 70% RH				Color at 35% RH			
	T=0	T=0	T=1	T=1	T=0	T=0	T=1	T=1
	Top	Bot	Top	Bot	Top	Bot	Top	Bot
0.00					0.0	0.0	0.0	0.0
0.13	0.5	0.3	0.6	0.5	0.5	0.5	0.5	0.5
0.25	0.7	0.6	0.6	0.6	0.6	0.4	0.8	0.6
0.47	0.9	1.7	1.3	1.8	2.2	2.0	2.5	2.3
0.79	3.0	2.2	3.0	2.7	2.3	2.0		
1.13	5.0	3.4	4.9	3.9	1.8	3.2	2.8	3.7
1.36	4.3	4.0	4.0	4.0	2.8	1.8	4.3	2.8
2.00	4.4	4.3	4.3	4.0	4.3	3.7	4.1	4.3
3.50	7.5	8.5	7.3	7.8	7.3	6.7	8.5	8.0
11.7	9.5	9.5	9.5	9.5				

Table 5. Humidity Response of Badges for Hydrazine

Badge	Dose (TLV-hrs)	Color at 70% RH		Color at 40% RH	
		T=0	T=1	T=0	T=1
D12	0.24	0.5	0.8	0.5	1.0
	2.00	4.0	4.5	2.5	4.3
D13	0.24	0.5	0.5	0.5	1.0
	2.00	3.4	4.5	1.9	3.3
D14	0.24	0.5	0.5	0.5	0.5
	2.00	2.9	4.3	3.1	2.8
D13+D12 D13	0.24	0.5	0.5	0.5	0.5
	2.00	4.0	4.5	4.0	3.8
D12	0.24	0.5	0.5	0.5	0.5
	2.00	2.3	5.0	3.8	3.8

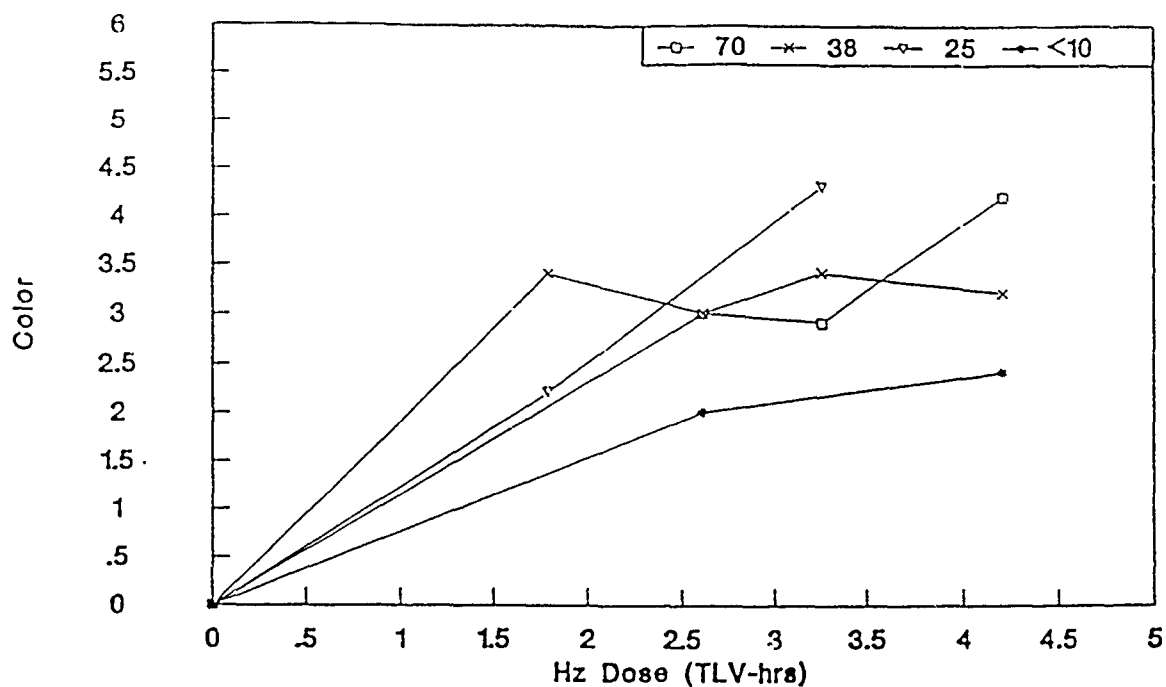


Fig. 14a. Hydrazine Humidity Response at T=0 for PDAB (D12, D12+D14)

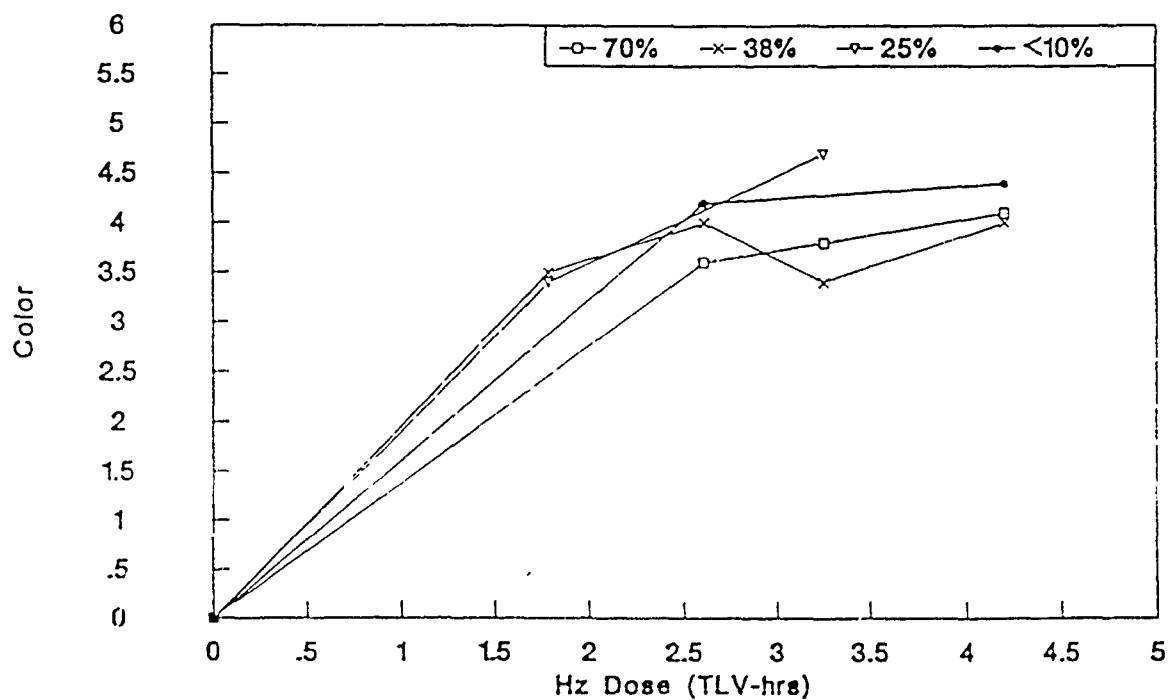


Fig. 14b. Hydrazine Humidity Response at T=1 for PDAB (D12, D12+D14)

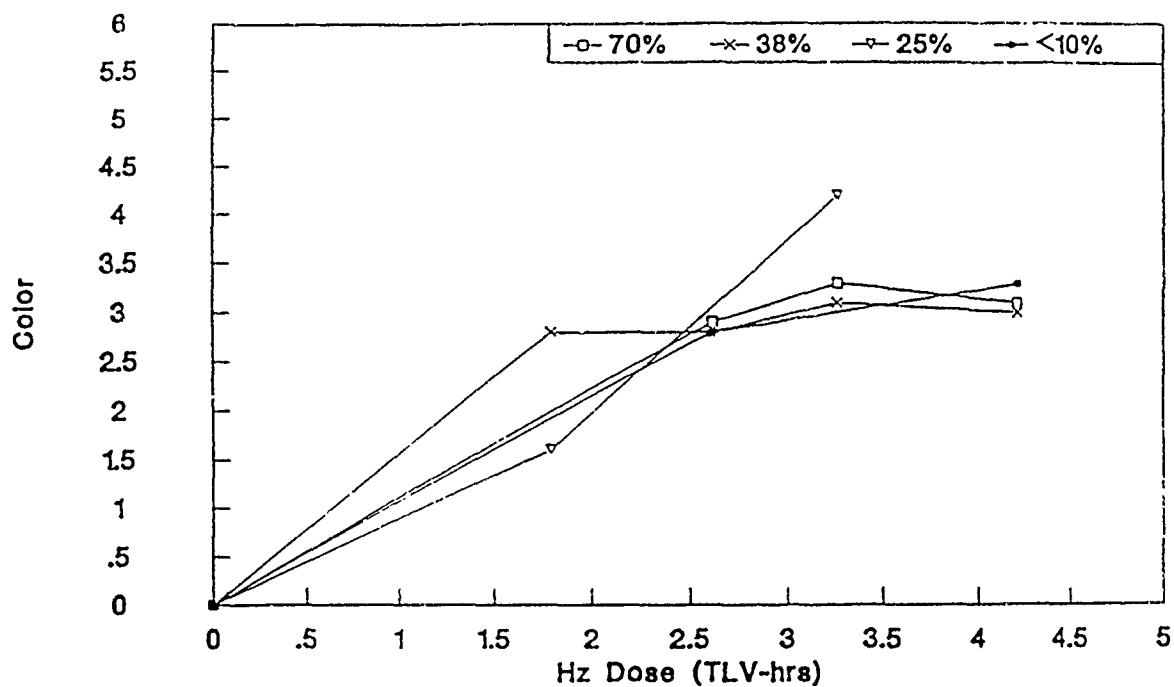


Fig. 14c. Hydrazine Humidity Response at T=0 for Vanillin (D14, D12+D14)

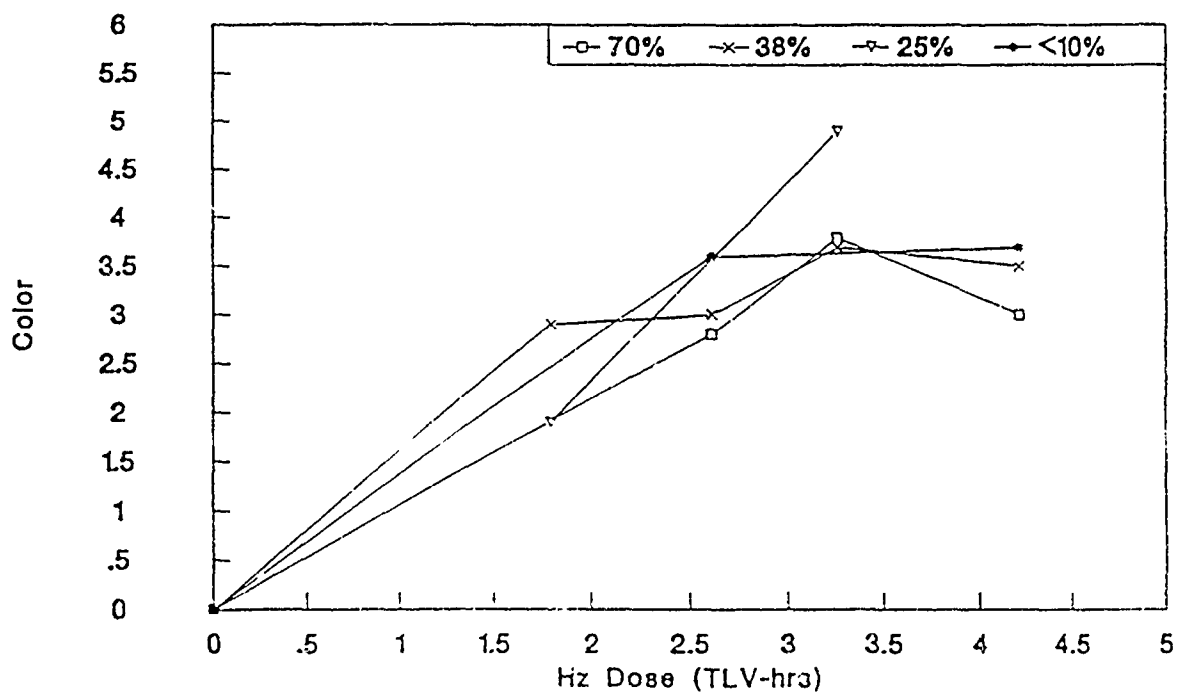


Fig. 14d. Hydrazine Humidity Response at T=1 for Vanillin (D14, D12+D14)

Table 6. Interferent Response of Badges

Badge Type	Interferent	MMH Dose (TLV-hrs)	Color	
			Post MMH	Post Interferent
PDAB	Heat	2.1	2.8	4.0
VAN	Heat		3.2	4.0
PDAB	Heat		1.7	3.0
VAN	Heat		2.4	2.7
PDAB	Heat		2.0	2.8
VAN	Heat		2.0	2.8
PDAB	Cold		3.0	3.2
VAN	Cold		2.3	3.2
PDAB	Cold		2.2	2.8
VAN	Cold		3.0	3.0
PDAB	Cold		2.0	2.5
VAN	Cold		2.0	2.0
PDAB	Sun		3.0	3.7
VAN	Sun		3.0	3.5
PDAB	Sun		2.5	2.7
VAN	Sun		3.2	3.5
PDAB	Sun		3.2	3.5
VAN	Sun		2.5	2.8
PDAB	UV-254		2.3	2.8
VAN	UV-254		2.3	2.3
PDAB	UV-254		2.8	3.3
VAN	UV-254		3.0	3.0
PDAB	UV-350		1.8	2.0
VAN	UV-350		2.0	2.0

Table 7. Interferent Response for Badges

Badge Type	Interferent	MMH Dose (TLV-hrs)	Color	
			Post Interferent	Post MMH
PDAB	Heat	2.1	0.5	2.3
VAN	Heat		0.5	2.8
PDAB	Heat		0.5	2.2
VAN	Heat		0.5	2.3
PDAB	Heat		0.5	2.3
VAN	Heat		0.5	2.0
PDAB	Cold		0.5	2.0
VAN	Cold		0.5	2.0
PDAB	Cold		0.5	3.0
VAN	Cold		0.5	3.8
PDAB	Cold		0.5	2.2
VAN	Cold		0.5	3.0
PDAB	UV-254		0.5	3.3
VAN	UV-254		0.5	3.1
PDAB	UV-350		0.5	3.3
VAN	UV-350		0.5	3.3
PDAB	UV-350		0.5	3.0
VAN	UV-350		0.5	3.2

exposure to 2.1 TLV-hours of MMH for both PDAB and vanillin.

There was no significant change in color intensity from exposure to sunlight after MMH exposure. The average color for the PDAB badges after exposure to MMH was similar to the normal color intensity for 2.1 TLV-hours. The color of the vanillin was less intense than normal.

Exposure to a UV lamp source caused no significant change in color for either badge chemistries. When exposed to UV light initially, the badges developed a minimal color as they had with the heat and cold interferents. Exposure to UV light did not hinder subsequent color development in the presence of MMH. After exposure to MMH, both the PDAB and vanillin developed color of 3.2 intensity. This was normal color intensity for PDAB; slightly lower than normal for vanillin.

Several badges were exposed to sunlight alone during late summer (Table 8). They were tested in both horizontal and vertical positions for periods ranging from 0.25 to 2 hours. The vanillin badges showed no color development in either position. The PBAB badges developed 0.5 color within 0.25 hours and 1-2 color by 2 hours. These badges were evaluated on the vanillin color wheel as they developed a yellow color on exposure to sunlight.

Table 8. Sunlight Interferent Response

Badge Type	Badge Position	Exposure Time (hrs)				
		0.25	0.5	0.75	1.0	2.0
PDAB	Horiz	0.5	1.0	1.5	1.5	1.5
Van		0.0	0.0	0.0	0.0	0.0
PDAB	Vert	0.5	1.5	1.5	1.5	2.0
Van		0.0	0.0	0.0	0.0	0.0
PDAB	Horiz	0.5	0.5	0.5	0.5	1.0
Van		0.0	0.0	0.0	0.0	0.0
PDAB	Vert	0.5	0.5	0.5	0.5	1.0
Van		0.0	0.0	0.0	0.0	0.0

Interferent tests with NO_2 , NH_3 , and freons were accomplished at NRL. The dosimeters were exposed to the interferents both before and after MMH. Exposure times for both the MMH and the interferents were one hour. Table 9a shows the data for NO_2 exposure after MMH exposure. NO_2 did not affect the badges after exposure to MMH. When exposed to NO_2 prior to MMH, the badges developed minimal color (0.5) after first exposure to the interferent as shown in Table 9b. NO_2 did not retard color development for subsequent exposure to MMH.

The PDAB badges were affected by exposure to NH_3 after MMH (Tables 10a and 10b). The color intensity of the badges increased after they were exposed to the interferent. The vanillin badges did not show a significant color change due to the interferent. As shown in Table 10b, both PDAB and vanillin showed a minimal increase in color of 0.5 when first exposed to NH_3 . Table 11a and 11b give freon exposure information. The PDAB showed a slight increase in color when exposed to MMH and then freons. The vanillin was not affected by exposure to freons before or after exposure to MMH.

A color change was observed on a few of the field tested badges. In most cases the color was very pale and in some cases the color was different than expected. Only one exposure was independently measured using the citric acid badge. This exposure occurred in the Wiltech Lab. Three citric acid badges showed a small hydrazine exposure. The vanillin portion of the badge turned yellow on four of ten badges. Three of the badges corresponded to the positive exposures on the citric acid badges. The PDAB portion of the badge showed an orange response in nine of the ten badges. These unverified responses have not been explained.

The PDAB portion of the badges that were field tested outside showed color development; this could indicate a sunlight interference. The PDAB spot turned yellow in several of the tests. In a few of the tests, badges outside did not develop color and badges inside turned pale yellow. The vanillin badge did not change color in the sun. The inconsistencies cannot be explained.

All of the vanillin badges in the break room (lounge) turned pale pink. The air in the break room contained much cigarette smoke. To evaluate cigarette smoke as an interferent, a badge was exposed to cigarette smoke in a jar. It also turned pink.

CONCLUSIONS

The dosimeters show a large amount of scatter in color development at low doses. Some of this scatter can be attributed to experimental procedure. The PDAB badges (D12) show the greatest amount of scatter. The use of a membrane does not significantly affect the performance of the badges. Color development shows a time dependence for all badge types tested. Therefore, the immediate color development of the badges should be viewed as a warning sign, while the later development of the color on the badges after removal from a contaminated area may be more accurate.

Table 9a. Post-MMH NO₂ Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post MMH	Post Interferent
PDAB	5.0	0.89	2.0	2.0
VAN			2.3	2.3
PDAB	5.0	0.89	1.0	1.0
VAN			2.0	2.0
PDAB	5.0	0.89	1.5	2.0
VAN			3.0	3.0
Control	0.0	0.89	1.0	1.5
			2.0	2.0

Table 9b. Pre-MMH NO₂ Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post Interferent	Post MMH
PDAB	5.0	0.89	0.5	1.3
VAN			0.5	2.5
PDAB	5.0	0.89	0.5	1.3
VAN			0.5	2.3
PDAB	5.0	0.89	0.5	1.3
VAN			0.5	2.5
Control	5.0	0.00	0.5	0.5
			0.5	0.5

Table 10a. Post-MMH NH₃ Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post MMH	Post Interferent
PDAB	20.4	0.82	1.5	3.0
VAN			3.0	3.3
PDAB	20.4	0.82	1.3	2.0
VAN			2.0	2.0
PDAB	20.4	0.82	2.0	3.0
VAN			2.5	3.3
Control	0.0	0.82	1.5	2.0
			2.0	2.0

Table 10b. Pre-MMH NH₃ Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post Interferent	Post MMH
PDAB	20.4	0.82	0.5	3.0
VAN			0.5	3.0
PDAB	20.4	0.82	0.5	2.8
VAN			0.5	2.8
PDAB	20.4	0.82	0.5	2.8
VAN			0.5	2.5
Control	20.4	0.00	0.5	0.8
			0.5	0.5

Table 11a. Post-MMH Freon Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post MMH	Post Interferent
PDAB VAN	29.4	0.99	1.0	1.8
			2.0	2.0
PDAB VAN	29.4	0.99	1.8	2.3
			3.0	3.0
PDAB VAN	29.4	0.99	1.8	2.3
			2.8	3.0
Control	0.0	0.99	1.5	2.0
			2.0	2.0

Table 11b. Pre-MMH Freon Interferent Response

Badge Type	Interferent Conc. (ppm)	MMH Dose (TLV-hrs)	Color	
			Post Interferent	Post MMH
PDAB VAN	29.4	0.99	0.0	2.0
			0.0	2.5
PDAB VAN	29.4	0.99	0.0	1.8
			0.0	2.0
PDAB VAN	29.4	0.99	0.0	1.8
			0.0	2.0
Control	29.4	0.00	0.0	0.0
			0.0	0.0

The composite badges (D13+D12) show an increased sensitivity and stability when compared to badges where the chemistries are used individually (D13, D12). The incorporation of two different chemistries on one badge may allow each to influence the performance of the other due to sublimation of the materials. Doses required to produce mid-range colors; that is, a color of 5 on the old wheel and a color of 3 on the new wheel, have been summarized in Table 12.

Relative humidity does not significantly affect the color development on any badge chemistry. The interferent tests indicate that heat is an interferent when badges are exposed to MMH first. Sunlight affects color development in the PDAB badges. The badges developed a yellow color that had to be evaluated with the vanillin color wheel. The PDAB badges were also affected by exposure to NH_3 after exposure to MMH. The vanillin badges were not significantly affected by the interferents tested. It was noted that vanillin is affected by tobacco smoke. A pink-purple color develops.

The yellow color development of the PDAB and the pink color response of the vanillin was observed in the field tests. The yellow responses of PDAB were not always consistent with the sunlight exposure. The expected color responses of orange for PDAB and yellow for vanillin were only observed in one location of the field test. The vanillin produced four positive results and all but one were independently verified. The PDAB badges produced six apparently false positive responses.

Table 12. Summary of Doses Required for Mid-Range Color

Badge Type	Gas	Diffusion Membrane	Dose (TLV-hrs)	
			T=0	T=1
PDAB (D12)	MMH	no	4.5	3.0
		yes	5.0	3.0
	Hz	no	6.0	4.0
Vanillin (D13)	MMH	no	4.0	2.5
		yes	4.0	4.0
	Hz	no	6.0	4.0
Vanillin (D14)	MMH	no	2.0	2.0
		yes	2.0	2.0
	Hz	no	7.0	5.0
Vanillin (D13) (D13+D12)	MMH	no	2.5	2.0
	Hz	no	4.0	4.0
PDAB (D12) (D13+D12)	MMH	no	2.0	2.0
	Hz	no	4.0	4.0
PDAB (D12) (D12+D14)	MMH	no	2.0	1.0
	Hz	no	1.25	1.0
Vanillin (D14) (D12+D14)	MMH	no	1.0	0.9
	Hz	no	2.0	1.5

REFERENCES

1. Hannum, J.A.E., "Recent Developments in the Toxicology of Propellant Hydrazines", Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. Hawkins, C.M., S.L. Rose, J.R. Wyatt, "A Passive Dosimetry Method for Determining Hydrazines in Air", CPFA 436, Proceedings of the 1985 JANNAF Safety and environmental Protection Subcommittee Meeting, (Monterey, CA, 4-8 November 1985) Naval Postgraduate School, November 1985.
3. Taffe, P.A., S.L. Rose, "Hydrazine Detection", U.S. Patent #4,900,681, issued 13 February 1990
4. Snow, A., S. Rose, Review of Specific Chemical Interactions for Hydrazine Analysis and Proposed Adaptation for Microsensor Chemical Detection, NRL Memorandum Report 546 1, Naval Research Laboratory, Washington, DC, 30 November 1984.
5. Taffe, P.A., J.R. Wyatt, "Real-Time Passive Dosimeter for HCL Vapor", Proceedings of the 1989 JANNAF Safety and Environmental protection Subcommittee Meeting, (Brooks Air Force Base, San Antonio, TX, 3-6 April, 1989).
6. Rose, S.L., J.R. Holtzclaw, A Critical Comparison of Commercially Available Hydrazine Detectors, NRL Report 8848, Naval Research Laboratory, Washington, D.C., March 19, 1985.
7. Taffe, P.A., Brown, S.W., Thurow, A.R., Travis, J.C., Rose-Pehrsson, S.L., and Wyatt, J.R., "Field Evaluation of a Passive Sampling Device for Hydrazines in Ambient Air", NRL Memorandum Report 6613 (1990).
8. Olson, E.C., "The Coulometric Determination of Hydrazine and Substituted Hydrazine", Analytical Chemistry, 32 (12), 1960, pp.1545-1547.
9. NIOSH Manual of Analytical Methods, 2nd ed., DHEW (NIOSH), Cincinnati, OH, 1977, Vol 3, Publication 77-157c.

APPENDIX A
NRL Data Sheets

GMD COLOR BADGE LOG SHEET

TEST 1

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83477	D12	1/24	.107	none	4	2.14	40	25	2.0	2.0	2.5	2.2	2.0	2.0	2.0	2.0
	D12								5	5	7	5.7	4.5	5.5	6	5.3
84753	D13								2	3	3	2.7	2	2	3	2.3
	D13								3	4	3	3.3	3	3	2.5	2.8
83449	D13								3	4	3.5	3.5	3	3	3	3.0
	D12								3	4	3.5	3.5	3.5	4	4	3.8
59397	D14								2	3	3	2.7	2	2.5	2	2.2
	D14								4	4	5	4.3	4	4	3	3.7

GMD COLOR BADGE LOG SHEET

TEST 2

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84304	D12	1/24	.084	none	16	6.72	40	25	8	8	8	8.0	7.5	8.5	8.0	8.0
	D12								8.5	9	9	8.8	8	8.5	9	8.5
82962	D13								6	6	5	5.7	6.5	5	6	5.8
	D13								8	7	8	7.7	8	8	8	8.0
85557	D13								8	9	9	8.7	7	6	7	6.7
	D12								8	9	9	8.7	8	9	8	8.3
59549	D14								7	6.5	7	6.8	7	8	7	7.3
	D14								9	9	9	9.0	9	9	9	9.0

GMD COLOR BADGE LOG SHEET

TEST 3

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82408	D12	1/24	.06	none	.25	.075	40	25	0	0	0	.0	.0	.0	.0	.0
	D12								0	0	0	.0	.5	.5	.5	.5
84778	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5
83486	D13								0	0	0	.0	.5	.5	.5	.5
	D12								0	0	0	.0	.5	.5	.5	.5
59630	D14								0	0	0	.0	0	0	0	.0
	D14								.5	.5	0	.3	.5	1	.5	.7

GMD COLOR BADGE LOG SHEET

TEST 4

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83467	D12	1/24	.06	none	.42	.126	99	25	0	0	0	.0	.0	.0	.0	.0
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83919	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81192	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59632	D14								.5	.5	.5	.5	.5	0	.5	.3
	D14								1	1	1	1.0	1	1	1	1.0

GMD COLOR BADGE LOG SHEET

TEST 5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84232	D12	1/24	.06	none	1	.3	40	25	.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84779	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D13								1	1	1	1.0	1	1	1	1.0
81209	D13								1	1	1	1.0	1	1	1	1.0
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59520	D14								0	0	0	.0	0	.5	.5	.3
	D14								1	1	1	1.0	1	1	1	1.0

GMD COLOR BADGE LOG SHEET

TEST 6

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84321	D12	1/25	.06	none	.42	.126	40	25	0	0	0	.0	.0	.0	.0	.0
	D12								0	0	0	.0	.5	.5	.5	.5
83909	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5
85528	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59629	D14								0	0	0	.0	0	0	0	.0
	D14								.5	.5	.5	.5	.5	.5	.5	.5

GMD COLOR BADGE LOG SHEET

TEST 7

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83522	D12	1/24	.089	none	16	7.12	40	25	8	8.5	8.5	8.3	8.5	8.5	8.5	8.5
	D12								8	8.5	8.5	8.3	7.5	8.5	7.5	7.8
84774	D13								8	8	6	7.3	8	8	7	7.7
	D13								8	8	7	7.7	8	8	8	8.0
	D13								9	9	8.5	8.8	8.5	9	8.5	8.7
	D12								9	9	8.5	8.8	8.5	9	8.5	8.7
59371	D14								9.5	9.5	9	9.3	9.5	9.5	9	9.3
	D14								9.5	9.5	8.5	9.2	9.5	9.5	9	9.3

GMD COLOR BADGE LOG SHEET

TEST 8

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84322	D12	1/24	.08	none	4	1.6	40	25	2.5	2.5	3	2.7	2.5	2.5	4.5	3.2
	D12								4.5	5.5	5	5.0	4.5	5.5	5	5.0
84745	D13								3	3	4	3.3	3	3	4	3.3
	D13								4.5	4.5	5.5	4.8	5	4.5	5	4.8
85543	D13								3.5	4	4	3.8	4	4	4	4.0
	D12								4	4.5	5	4.5	4.5	5.5	4.5	4.8
59542	D14								3	3	3	3.0	3	3	3	3.0
	D14								5	5	5	5.0	5	5	5	5.0

GMD COLOR BADGE LOG SHEET

TEST 9

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83532	D12	1/24	.08	none	2	.8	40	25	.5	.5		.5				
	D12								.5	.5		.5				
84831	D13								1.5	1.5		1.5				
	D13								2	2		2.0				
81272	D13								2	2.5		2.3				
	D12								1.5	2.5		2.0				
59384	D14								2	1.5		1.8				
	D14								4	4.5		4.3				

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TEST 10

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84287	D12	1/24	.08	none	16	6.4	40	25	7.5	7.5	6	7.0	7.5	8.5	9.0	8.3
	D12								9	9	8	8.7	8.5	9	9	8.8
84766	D13								5	5	9	6.3	5	5	4	4.7
	D13								5	5	9	6.3	5	5.5	5	5.2
8351 ^e	D13								6	6	6	6.0	5.5	5	5	5.2
	D12								8	8.5	9	8.5	8	8.5	8	8.2
59362	D14								9	9	9	9.0	9	9	9	9.0
	D14								9.5	9.5	9.5	9.5	9.5	9.5	9	9.3

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TEST 11

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
80000	D12	1/24	.08	none	4	1.6	40	25	2.5	3.5	2	2.7	3.5	4.0	4.5	4.0
	D12								2	3.5	4	3.2	3.5	4	4.5	4.0
83839	D13								3.5	4	1	2.8	3.5	4	4	3.8
	D13								4	4.5	7	5.2	4	4.5	4.5	4.3
81260	D13								2.5	3	3	2.8	2.5	2	2	2.2
	D12								2.5	4	9	5.2	3	4	4.5	3.8
											9					
59581	D14								1	8	1	3.3	1	1	1	1.0
	D14								6	8	7	7.0	7	7	8	7.3

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TEST 12

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83479	D12	1/24	.097	none	2.25	1.09125	70	25	.5	.5	5.5	2.2	.5	1.0	1.5	1.0
	D12								2.5	3.5	4	3.3	2.5	3.5	1.5	2.5
83927	D13								1	1	2	1.3	1	1	1	1.0
	D13								2	2	3.5	2.5	2	2	2.5	2.2
85507	D13								4.5	5	5.5	5.0	5	5	5.5	5.2
	D12								3.5	3.5	4	3.7	3.5	4.5	4.5	4.2
59372	D14								1.5	1.5	2	1.7	2	1.5	2	1.8
	D14								2.5	3	3.5	3.0	3	3	3	3.0

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TEST 13

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83481	D12	1/24	.096	none	.25	.12	70	25	0	0	0	.0	.0	.0	.0	.0
	D12								.5	.5	0	.3	.5	.5	1	.7
83921	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81253	D13								.5	.5	.5	.5	1	1	1	1.0
	D12								0	0	0	.0	.5	.5	.5	.5
59577	D14								0	0	0	.0	0	0	0	.0
	D14								.5	.5	.5	.5	.5	.5	1	.7

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TEST 14

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83449	D12	1/24	.096	none	.25	.12	70	25	0	0	0	.0	.0	.5	.0	.2
	D12								.5	.5	0	.3	.5	.5	.5	.5
84883	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81208	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	0	.3	.5	.5	.5	.5
59459	D14								0	0	0	.0	.5	.5	0	.3
	D14								.5	.5	.5	.5	.5	.5	1	.7

TEST 15

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
	D12	1/24	.096	none	.25	.12	70	25	0	0	0	.0	.0	.0	.5	.2
	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								0	.5	0	.2	.5	.5	0	.3
	D13								.5	.5	3	1.3	.5	.5	.5	.5
	D13								.5	.5	0	.3	.5	.5	.5	.5
	D12								0	.5	0	.2	.5	.5	.5	.5
	D14								.5	0	0	.2	0	0	0	.0
	D14								.5	.5	1	.7	.5	.5	.5	.5

TEST 16

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83500	D12	1/24	.075	none	2.66	1.00	70	25	.5	.5	1	.7	.5	.5	1.0	.7
	D12								1.5	1.5	3	2.0	2	2	3	2.3
84818	D13								2.5	2	3	2.5	3	2.5	3	2.8
	D13								4.5	4.5	5	4.7	4.5	4.5	4	4.3
85524	D13								4.5	4.5	6	5.0	4	4.5	5	4.5
	D12								2	3	4	3.0	2.5	4	4	3.5
59480	D14								1.5	1.5	2	1.7	2	1.5	1.5	1.7
	D14								4	4	4	4.0	4	4	4	4.0

TEST 17

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83487	D12	1/24	.077	none	2	.77	70	25	.5	.5	1	.7	1.0	1.0	1.0	1.0
	D12								1.5	2	2.5	2.0	2	2	2.5	2.2
84833	D13								2	2	2	2.0	2	2	2	2.0
	D13								3	4	4	3.7	3	3	4	3.3
83487	D13								3	3	3	3.0	3	3	3	3.0
	D12								1.5	2	3	2.2	3	3	2	2.7
59608	D14								1	.5	1	.8	1	2	1	1.3
	D14								2.5	2	3.5	2.7	3	3	3	3.0

TEST 18

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82379	D12	2/1	.092	none	8	3.68	40	25	6	6	6	6.0	8.0	7.5		7.8
	D12								8	9	8	8.3	9	9		9.0
83906	D13								8	8	7	7.7	9	8.5		8.8
	D13								7	7	7.5	7.2	8	8		8.0
85559	D13								7	8	7	7.3	9	8		8.5
	D12								6	7	7	6.7	8	8		8.0
59369	D14								8	9	8	8.3	9	8.5		8.8
	D14								9	9.5	9	9.2	9	9		9.0

TEST 19																
I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84283	D12	2/1	.122	none	8	4.88	40	25	8	8	8.5	8.2	8.0	8.5		8.3
	D12								8	8	8.5	8.2	8	8.5		8.3
82981	D13								7	8	6	7.0	8	7		7.5
	D13								8	8	7	7.7	8	7		7.5
81201	D13								8	8	8	8.0	8	7		7.5
	D12								9	9	9	9.0	9	9		9.0
59555	D14								8.5	9	8	8.5	9	8		8.5
	D14								7.5	8	8	7.8	8	7		7.5

TEST 20																
I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83517	D12	2/9	.13	none	6.2	4.03	40	25	6	6.5	7	6.5	6.0	5.5	7.0	6.2
	D12								5.5	6.5	7	6.3	6	5.5	7.5	6.3
84747	D13								5.5	5.5	5	5.3	5.5	5	5	5.2
	D13								6	6	6	6.0	6	6	6	6.0
85584	D13								5	5	6	5.3	5	5	5	5.0
	D12								5	5.5	6	5.5	5.5	5	7	5.8
59546	D14								5	5.5	7	5.8	6	5	5	5.3
	D14								8	8	8	8.0	7.5	8	8	7.8

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I.D.	BADGE	DATE	MMH	INTER-	TIME	DOSE	RH	TEMP	T=0				T=1				
#	TYPE		(ppm)	FERANT	(hrs)	TLV-hrs	(%)	(C)	1	2	3	Aver	1	2	3	Aver	
84251	D12	2/13	.212	none	4	4.24	40	25	4.5	4.5	4.0	4.3	4.5	4.5	5.0	4.7	
	D12								4.5	4	4	4.2	4.5	4.5	5	4.7	
84804	D13								4	4	2	3.3	4	3.5	3	3.5	
	D13								4	4	2	3.3	4	4	3	3.6	
81264	D13								4.5	4.5	4	4.3	4.5	4.5	5	4.7	
	D12								4.5	5.5	5	5.0	5	5.5	5	5.2	
59444	D14								4	4	3	3.7	4	4	3	3.6	
	D14								4.5	4.5	3	4.0	4	4.5	3	3.8	

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TEST 22

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82330	D12	2/13	.2	none	.25	.25	40	25	0	0	0	.0	.5	.5	.5	.5
	D12								0	0	0	.0	.5	.5	.5	.5
84777	D13								.5	0	0	.2	.5	.5	.5	.5
	D13								.5	.5	.5	.5	1	1	1	1.0
85567	D13								.5	.5	.5	.5	1	.5	1	.8
	D12								0	.5	0	.2	.5	.5	1	.7
59481	D14								.5	0	0	.2	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	1	.7

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TEST 23

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82423	D12	2/13	.2	none	.25	.25	40	25	0	0	0	.0	.0	.0	.0	.0
	D12								.5	.5	0	.3	.5	.5	.5	.5
82914	D13								0	0	0	.0	0	0	0	.0
	D13								.5	.5	1	.7	.5	.5	1	.7
83513	D13								.5	.5	1	.7	1	1	1	1.0
	D12								.5	.5	.5	.5	.5	.5	1	.7
59571	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	1	.7	.5	.5	1	.7

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TEST 24

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82395	D12	2/13	.2	none	16	16	40	25	9	9	9	9.0	9.0	9.5	9.0	9.2
	D12								9	9	9	9.0	9	9	9	9.0
82971	D13								9	9	9	9.0	9	9.5	9	9.2
	D13								9	9	9	9.0	9	9.5	9	9.2
83469	D13								9	9	9	9.0	9.5	9.5	9	9.3
	D12								9	9.5	9	9.2	9.5	9	9	9.2
59621	D14								9.5	9	9	9.2	9.5	9.5	9.5	9.5
	D14								9.5	9	9	9.2	9.5	9.5	9.5	9.5

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TEST 22

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82330	D12	2/13	.2	none	.25	.25	40	25	0	0	0	.0	.5	.5	.5	.5
	D12								0	0	0	.0	.5	.5	.5	.5
84777	D13								.5	0	0	.2	.5	.5	.5	.5
	D13								.5	.5	.5	.5	1	1	1	1.0
85567	D13								.5	.5	.5	.5	1	.5	1	.8
	D12								0	.5	0	.2	.5	.5	1	.7
59481	D14								.5	0	0	.2	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	1	.7

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TEST 23

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82423	D12	2/13	.2	none	.25	.25	40	25	0	0	0	.0	.0	.0	.0	.0
	D12								.5	.5	0	.3	.5	.5	.5	.5
82914	D13								0	.0	0	.0	0	0	0	.0
	D13								.5	.5	1	.7	.5	.5	1	.7
83513	D13								.5	.5	1	.7	1	1	1	1.0
	D12								.5	.5	.5	.5	.5	.5	1	.7
59571	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	1	.7	.5	.5	1	.7

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TEST 24

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82395	D12	2/13	.2	none	16	16	40	25	9	9	9	9.0	9.0	9.5	9.0	9.2
	D12								9	9	9	9.0	9	9	9	9.0
82971	D13								9	9	9	9.0	9	9.5	9	9.2
	D13								9	9	9	9.0	9	9.5	9	9.2
83469	D13								9	9	9	9.0	9.5	9.5	9	9.3
	D12								9	9.5	9	9.2	9.5	9	9	9.2
59621	D14								9.5	9	9	9.2	9.5	9.5	9.5	9.5
	D14								9.5	9	9	9.2	9.5	9.5	9.5	9.5

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TEST 25

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84281	D12	2/14	.2	none	.25	.25	40	25	0	0	.5	.2	.0	.0	.5	.2
	D12								.5	.5	.5	.5	.5	.5	1	.7
82964	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	1	.7	1	1	1	1.0
81207	D13								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59400	D14								.5	.5	.5	.5	.5	.5	1	.7
	D14								1	1	1	1.0	1	1	1	1.0

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TEST 26

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82336	D12	2/14	.2	none	4	4	40	25	6	7.5	7	6.8	7.5	7.5	7.5	7.5
	D12								7	8	7.5	7.5	8	7.5	8	7.8
84809	D13								4.5	5	5	4.8	5	5.5	5.5	5.3
	D13								4.5	5	5	4.8	5	5.5	5.5	5.3
83493	D13								6	6	7	6.3	7.5	7	8	7.5
	D12								7	8	8	7.7	7.5	7.5	8.5	7.8
59591	D14								7	8	7	7.3	8	7	6.5	7.2
	D14								8	8.5	8	8.2	8.5	8	7	7.8

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TEST 27

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82342	D12	2/14	.2	none	16	16	40	25	9.5	9.5	9	9.3	9.5	9.5	9.0	9.3
	D12								9.5	9.5	9	9.3	9.5	9.5	9	9.3
82986	D13								8	9	8	8.3	8.5	9	8.5	8.7
	D13								9	9	8.5	8.8	9	9	9	9.0
85590	D13								9	9.5	9	9.2	9.5	9	9	9.2
	D12								9	9.5	9	9.2	9.5	9	9	9.2
59389	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5

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TEST 28

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82357	D12	.133	.2	none	2	2	40	25	2	3.5	5	3.5	4.5	5.0	5.0	4.8
	D12								4.5	4.5	5	4.7	5	5.5	5	5.2
83881	D13								3.5	4.5	3	3.7	4	4.5	3	3.8
	D13								3.5	4	4	3.8	4	4	4	4.0
85598	D13								5	5	5	5.0	5	5	5	5.0
	D12								3	4.5	5	4.2	4.5	4.5	5	4.7
59449	D14								3	3	2	2.7	3.5	3	3	3.2
	D14								4	4.5	3	3.8	4	4.5	3	3.8

GMD COLOR BADGE LOG SHEET

TEST 29

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84309	D12	2/15	.2	none	2	2	40	25	3.5	4	4	3.8	4.5	5.0	4.5	4.7
	D12								3	3.5	3	3.2	4	4.5	4.5	4.3
83884	D13								3	3	4	3.3	3	3	3	3.0
	D13								4.5	4	4	4.2	4.5	4.5	4.5	4.5
81210	D13								4.5	4.5	4	4.3	4.5	4.5	4	4.3
	D12								3	3.5	4	3.5	4	4.5	4.5	4.3
59456	D14								5	5	5	5.0	5	5.5	5	5.2
	D14								5.5	6	5	5.5	6	6	6	6.0

GMD COLOR BADGE LOG SHEET

TEST 30

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82392	D12	2/15	.2	none	16	16	40	25	9.5	9.5	9.5	9.5	9.5	9.5	9.0	9.3
	D12								9	9	9.5	9.2	9	9	9	9.0
82906	D13								9	9.5	9	9.2	9	9	9	9.0
	D13								9	9	9	9.0	9	9	9	9.0
85562	D13								9	9	9	9.0	9	9.5	9	9.2
	D12								9	9	9	9.0	9	9.5	9	9.2
59356	D14								9.5	9.5	9	9.3	9.5	9.5	9	9.3
	D14								9.5	9.5	9	9.3	9.5	9.5	9	9.3

GMD COLOR BADGE LOG SHEET

TEST 31

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84244	D12	2/16	.2	none	4	4	40	25	5	5		5.0	5.5	6.0	7.0	6.2
	D12								6	6.5		6.3	6	7	8	7.0
83871	D13								5	5.5		5.3	5	5.5	6	5.5
	D13								6.5	6		6.3	7	7	7	7.0
83506	D13								6.5	6		6.3	6	6	6	6.0
	D12								6.5	6.5		6.5	6.5	6.5	7	6.7
59649	D14								5	4.5		4.8	5	5.5	4	4.8
	D14								7	7		7.0	7	7.5	4	6.2

GMD COLOR BADGE LOG SHEET

TEST 32

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84277	D12	2/16	.2	none	.25	.25	70	25	0	0	0	.0	.0	.0	.0	.0
	D12								.5	.5	0	.3	.5	.5	1	.7
82912	D13								0	0	.5	.2	0	0	0	.0
	D13								1	.5	1	.8	1	1	1	1.0
81266	D13								.5	.5	1	.7	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	1	.7
59531	D14								.5	.5	1	.7	.5	.5	0	.3
	D14								1	1	1	1.0	1	1	1	1.0

GMD COLOR BADGE LOG SHEET

TEST 33

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83438	D12	2/16	.2	none	.25	.25	70	25	0	.5	0	.2	.5	.0	.0	.2
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84815	D13								.5	.5	.5	.5	.5	.5	0	.3
	D13								1	1	1	1.0	1.5	1.5	1.5	1.5
81247	D13								.5	1	.5	.7	.5	.5	.5	.5
	D12								.5	1	.5	.7	.5	.5	.5	.5
59626	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1	1	1	1.0	1	1	1	1.0

GMD COLOR BADGE LOG SHEET

TEST 34

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83352	D12	2/16	.2	none	.25	.25	70	25	0	0	0	.0	.5	.0	.0	.2
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83845	D13								.5	0	.5	.3	0	0	.5	.2
	D13								.5	1	.5	.7	1	.5	1	.8
81218	D13								.5	1	.5	.7	1	.5	.5	.7
	D12								.5	1	.5	.7	.5	.5	.5	.5
59411	D14								.5	.5	.5	.5	1	.5	.5	.7
	D14								1	1	1	1.0	.5	1	1	.8

GMD COLOR BADGE LOG SHEET

TEST 35

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84286	D12	2/17	.2	none	8	8	40	25	7.5	8.5	8.5	8.2	8.0	8.5	8.0	8.2
	D12								7.5	8	8.5	8.0	8	8.5	8	8.2
83004	D13								7	7	6	6.7	7	7	7	7.0
	D13								7	7	6	6.7	7	7	7	7.0
85603	D13								8	8	7	7.7	8	8	8	8.0
	D12								8	8.5	9	8.5	8.5	8.5	8	8.3
59539	D14								8	9.5	8	8.5	9	9	9	9.0
	D14								9	9.5	9	9.2	9	9.5	9.5	9.3

GMD COLOR BADGE LOG SHEET

TEST 36

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84234	D12	2/22	.2	none	8	8	40	25	9	9	9	9.0	9.0	9.0	9.0	9.0
	D12								9	9	9	9.0	9	9	9	9.0
83923	D13								7	7.5	7	7.2	8	8.5	8	8.2
	D13								8	8	8	8.0	8	8	8	8.0
85595	D13								7	8	8.5	7.8	8	8	8.5	8.2
	D12								8.5	8.5	8.5	8.5	8	8.5	8.5	8.3
59401	D14								9	9.5	9	9.2	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0

GMD COLOR BADGE LOG SHEET

TEST 37

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82409	D12	2/23	.2	none	8	8	40	25	8	8	8	8.0	8.0	8.5	8.5	8.3
	D12								8	8.5	9	8.5	8.5	9	8.5	8.7
83848	D13								8	8	8	8.0	9	8	8.5	8.5
	D13								8	8	8	8.0	8.5	9	8.5	8.7
83457	D13								8	8	8	8.0	8	8	8.5	8.2
	D12								9	8.5	9	8.8	8	8	8.5	8.2
59651	D14								9	9.5	9	9.2	9.5	9	9	9.2
	D14								9	9.5	9	9.2	9.5	9	9	9.2

GMD COLOR BADGE LOG SHEET

TEST 38

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84788	D12	2/24	.2	none	4	4	40	25	4.5	4.5	5.5	4.8	5.0	4.5	5.5	5.0
	D12								5.5	6	6	5.8	5.5	6	6	5.8
82413	D13								5	5	5	5.0	4.5	4.5	5	4.7
	D13								5.5	5	5	5.2	5	4.5	5	4.8
83463	D13								5	5	5	5.0	5	4.5	5	4.8
	D12								5	6	5.5	5.5	5.5	5.5	5.5	5.5
59595	D14								6	7	7	6.7	6.5	6	7	6.5
	D14								7	8	7.5	7.5	8	8	7.5	7.8

GMD COLOR BADGE LOG SHEET

TEST 39

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84299	D12	2/28	.2	none	2	2	70	25	1	1	1	1.0	1.0	2.0	1.0	1.3
	D12								4	4	4	4.0	3.5	4	4	3.8
84800	D13								2	2.5	3	2.5	2	2	3	2.3
	D13								3.5	4.5	4	4.0	4	4	4	4.0
85510	D13								4	4.5	4	4.2	4	4	4	4.0
	D12								2.5	3.5	3	3.0	2	3.5	3	2.8
59614	D14								4	4	3.5	3.8	4	4	3.5	3.8
	D14								4.5	4.5	4	4.3	4.5	4.4	4.5	4.5

GMD COLOR BADGE LOG SHEET

TEST 40

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	
83434	D12	3/1	.2	none	2	2	70	25	1	1	.5	.8	.5	1.0	.5	.7
	D12								3	3.5	4	3.5	3	4	4	3.7
84800	D13								2	2.5	2.5	2.3	3	3	2	2.7
	D13								3	4.5	5	4.2	5	5	5	5.0
85510	D13								5	3	5	4.3	4.5	4.5	5	4.7
	D12								3	4.5	4	3.8	2.5	4	3	3.2
59614	D14								2	2	2	2.0	2	2	2	2.0
	D14								3	4.5	4	3.8	4.5	4.5	5	4.7

GMD COLOR BADGE LOG SHEET

TEST 41

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82410	D12	3/2	.2	none	2	2	70	25	1.0	1.0	1.0	1.0	1.0	1.5	1.0	1.2
	D12								4	4	4	4.0	4	4.5	4	1.2
83006	D13								4	4	3	3.7	3.5	3	4	3.5
	D13								4.5	4.5	3	4.0	4	4.5	4	4.2
81200	D13								4.5	4.5	4	4.3	4	4	4	4.0
	D12								4.5	4.5	5	4.7	4.5	4.5	5	4.7
59434	D14								4	4.5	4	4.2	4	4.5	4	4.2
	D14								6	6	5.5	5.8	5.5	6	5.5	5.7

GMD COLOR BADGE LOG SHEET

TEST 42

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver

Test invalid

GMD COLOR BADGE LOG SHEET

TEST 43

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83457	D12	4/19	.4	none	.25	.5	40	25	.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59501	D13								2	2	1	1.7	2	2	2	2.0
	D13								1.5	1.5	2	1.7	1.5	1.5	1.5	1.5
59536	D13								2	2.5	2	2.2	2	2.5	3	2.5
	D12								2	2	2	2.0	2	2	3	2.3
83530	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	.5	.5

GMD COLOR BADGE LOG SHEET

TEST 44

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84323	D12	4/20	.375	none	4	7.5	40	25	8	7.5		7.8	7.5	7.5		7.5
	D12								8	7.5		7.8	7.5	7.5		7.5
84311	D13								8	8.5		8.3	8	8.5		8.3
	D13								8	8.5		8.3	8	8.5		8.3
59646	D13								9	9		9.0	9	9		9.0
	D12								9	9		9.0	9	9		9.0
59448	D14								9.5	9		9.3	9	9.5		9.3
	D14								9.5	9		9.3	9	9.5		9.3

GMD COLOR BADGE LOG SHEET

TEST 45

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82407	D12	4/20	.375	none	2	3.75	40	25	5	5		5.0				
	D12								5	4.5		4.8				
83461	D13								4	4.5		4.3				
	D13								5.5	6		5.8				
59584	D13								7	7		7.0				
	D12								7	7		7.0				
59562	D14								7	7		7.0				
	D14								7	7		7.0				

GMD COLOR BADGE LOG SHEET

TEST 46

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83439	D12	4/20	.375	none	16	30	40	25	9.5	9.5		9.5	9.5	9.5		9.5
	D12								9.5	9.5		9.5	9.5	9.5		9.5
82331	D13								9.5	9.5		9.5	9.5	9.5		9.5
	D13								9.5	9.5		9.5	9.5	9.5		9.5
59468	D13								9.5	9.5		9.5	9.5	9.5		9.5
	D12								9.5	9.5		9.5	9.5	9.5		9.5
59387	D14								9.5	9.5		9.5	9.5	9.5		9.5
	D14								9.5	9.5		9.5	9.5	9.5		9.5

GMD COLOR BADGE LOG SHEET

TEST 47

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82400	D12	4/21	.34	none	2	3.4	75	25	5	5.5		5.3	5.5	5.5		5.5
	D12								5	6		5.5	6	6		6.0
83448	D13								5.5	5.5		5.5	6	6		6.0
	D13								6	6		6.0	6	6.5		6.3
59484	D13								8	7		7.5	7	7.5		7.3
	D12								9	8		8.5	7.5	8		7.8
59385	D14								5.5	6		5.8	5	5.5		5.3
	D14								6	6		6.0	6	6		6.0

GMD COLOR BADGE LOG SHEET

TEST 48

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84241	D12	4/21	.34	none	.25	.425	75	25	.5	.5		.5	.5	.5		.5
	D12								.5	.5		.5	.5	.5		.5
84308	D13								.5	.5		.5	.5	.5		.5
	D13								.5	.5		.5	.5	.5		.5
59569	D13								1	1		1.0	1	1		1.0
	D12								1.5	1.5		1.5	1.5	1.5		1.5
59557	D14								1.5	1.5		1.5	1.5	1.5		1.5
	D14								1.5	1.5		1.5	1.5	1.5		1.5

GMD COLOR BADGE LOG SHEET

TEST 49

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82363	D12	4/25	.419	none	7.6	15.922	40	25	6			6.0	9.0	9.0	9.0	9.0
	D12								6			6.0	9	9	9	9.0
84246	D13								6			6.0	9	9	9	9.0
	D13								6			6.0	9	9	9	9.0
59421	D13								7			7.0	9	9	8.5	8.8
	D12								7			7.0	9	9	8.5	8.8
59478	D14								7.5			7.5	9	9	8.5	8.8
	D14								7			7.0	9	9	8.5	8.8

GMD COLOR BADGE LOG SHEET

TEST 50

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82376	D12	4/26	.38	none	.25	.75	70	25	.5	.5		.5	2.0	2.0		2.0
	D12								.5	.5		.5	1	1		1.0
83459	D13								.5	.5		.5	1	1.5		1.3
	D13								.5	.5		.5	1	1		1.0
59593	D13								.5	1		.8	1.5	1.5		1.5
	D12								1.5	2		1.8	2	2		2.0
59497	D14								1.5	3		2.3	4	4		4.0
	D14								1	2		1.5	2	2		2.0

GMD COLOR BADGE LOG SHEET

TEST 51

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83470	D12	4/26	.4	none	1	2	70	25	5	5		5.0	6.0	6.0		6.0
	D12								4	7.5		5.8	5	4.5		4.8
82332	D13								3	3.5		3.3	4	4		4.0
	D13								3	3.5		3.3	4	4		4.0
59491	D13								4.5	5		4.8	4.5	4.5		4.5
	D12								5	6		5.5	5.5	5		5.3
59519	D14								5.5	5.5		5.5	5.5	5.5		5.5
	D14								6	6		6.0	6	6		6.0

GMD COLOR BADGE LOG SHEET

TEST 52

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82380	D12	4/27	3.6	none	.5	9	40	25	5.5	6		5.8	9.0	9.0		9.0
	D12								5	5.5		5.3	9	9		9.0
82347	D13								5	5.5		5.3	8	8.5		8.3
	D13								5	5.5		5.3	8	8.5		8.3
59607	D13								8	9		8.5		9.5		9.5
	D12								8	9		8.5		9.5		9.5
59399	D14								7	8		7.5		9.5		9.5
	D14								8	9		8.5		9.5		9.5

GMD COLOR BADGE LOG SHEET

TEST 53

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83460	D12	4/28	1.2	none	3	18	40	25		7	6	6.5		7.5	8.0	7.8
	D12									6	6	6.0		5.5	8	6.8
84297	D13									7	6.5	6.8		8	8	8.0
	D13									6	6.5	6.3		7.5	7.5	7.5
59551	D13								9.5	9	9.3		9	9	9.0	
	D12								9.5	9	9.3		9.5	9	9.3	
59513	D14								9.5	8.5	9.0		9.5	9	9.3	
	D14								9	8.5	8.8		9.5	9	9.3	

GMD COLOR BADGE LOG SHEET

TEST 54

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83516	D12	4/28	1.07	none	.25	1.34	40	25	1	1		1.0		4.0	4.5	4.3
	D12								.5	.5		.5		2	3.5	2.8
82370	D13								.5	1		.8		2	4	3.0
	D13								1	1		1.0		4	4.5	4.3
59457	D13								2.5	3		2.8		4.5	4	4.3
	D12								1.5	2		1.8		2.5	3	2.8
59450	D14								2	2		2.0		3	3	3.0
	D14								1.5	2		1.8		2	2	2.0

GMD COLOR BADGE LOG SHEET

TEST 55

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82345	D12	4/28	1.07	none	1	5.35	40	25	4.5	5	4.8		6.0	6.0	6.0	
	D12								4.5	4.5	4.5		5	6	5.5	
83518	D13								4.5	4.5	4.5		5	6	5.5	
	D13								4	4	4.0		4.5	6.5	5.5	
59461	D13								6	6.5	6.3		9	7	8.0	
	D12								6	7	6.5		8	7	7.5	
59458	D14								6	6	6.0		9	9	9.0	
	D14								5.5	7	6.3		8	8	8.0	

GMD COLOR BADGE LOG SHEET

TEST 56

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83471	D12	5/2	1.1	none	.25	1.375	70	25	1	.5		.8	2.0	2.0	2.0	
	D12								1	1		1.0	3.5	3	3.3	
84227	D13								.5	.5		.5	1.5	2	1.8	
	D13								.5	.5		.5	1.5	2	1.8	
59414	D13								4	4.5		4.3	4	4	4.0	
	D12								4	4		4.0	4	4	4.0	
59390	D14								4.5	4.5		4.5	4.5	5	4.8	
	D14								4.5	5		4.8	4.5	5	4.8	

GMD COLOR BADGE LOG SHEET

TEST 57

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82352	D12	5/3	1.17	none	2	11.7	70	25	9	9		9.0	9.5			9.5
	D12								9	9		9.0	9.5			9.5
84239	D13								9	9		9.0	9.5			9.5
	D13								9	9		9.0	9.5			9.5
59522	D13								9.5	9.5		9.5	9.5			9.5
	D12								9.5	9.5		9.5	9.5			9.5
59487	D14								9	8		8.5	9			9.0
	D14								9	9		9.0	9.5			9.5

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TEST 58

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83496	D12	5/4	.15	none	1.3	.975	40	25	1.5	1.5	1.5	1.5	3.0	4.0		3.5
	D12								1.5	1.5	1.5	1.5	4	4		4.0
84316	D13								1	1	1.5	1.2	3	3		3.0
	D13								1	1	1	1.0	1.5	2		1.8
59439	D13								3.5	4	2.5	3.3	4	4.5		4.3
	D12								3	3	2	2.7	4	4		4.0
59416	D14								3	3	3	3.0	4	4.5		4.3
	D14								3.5	4	3	3.5	4	4.5		4.3

GMD COLOR BADGE LOG SHEET

TEST 59

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83443	D12	5/5	5.9	none	.25	7.38	40	25	2	4		3.0	8.5	9.0		8.8
	D12								2	3		2.5	8	8.5		8.3
84288	D13								2.5	4		3.3	7.5	8		7.8
	D13								2.5	3		2.8	7	7.5		7.3
59423	D13								5	6		5.5	9.5	9.5		9.5
	D12								5	6		5.5	9	9		9.0
59395	D14								6	6		6.0	9.5	9.5		9.5
	D14								6	7		6.5	9.5	9.5		9.5

GMD COLOR BADGE LOG SHEET

TEST 60

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83482	D12	5/5	.095	none	.25	.24	40	25	.5	.5		.5	1.0	1.0		1.0
	D12								.5	.5		.5	1	1		1.0
83442	D13								.5	.5		.5	1	1		1.0
	D13								.5	.5		.5	1	1		1.0
59594	D13								.5	.5		.5	.5	.5		.5
	D12								.5	.5		.5	.5	.5		.5
59451	D14								.5	.5		.5	.5	.5		.5
	D14								.5	.5		.5	.5	.5		.5

GMD COLOR BADGE LOG SHEET

TEST 61

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83433	D12	5/5	.095	none	.25	.24	70	25	.5	.5		.5	.5	.5		.5
	D12								.5	.5		.5	1	1		1.0
83529	D13								.5	.5		.5	.5	.5		.5
	D13								.5	.5		.5	.5	.5		.5
59412	D13								.5	.5		.5	.5	.5		.5
	D12								.5	.5		.5	.5	.5		.5
59514	D14								.5	.5		.5	.5	.5		.5
	D14								.5	.5		.5	1	1		1.0

GMD COLOR BADGE LOG SHEET

TEST 62

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84252	D12	5/8	.1	none	4	4	40	25	3.5	4		3.8	4.5	5.0		4.8
	D12								3.5	4		3.8	4.5	5		4.8
84262	D13								3.5	4		3.8	4.5	5		4.8
	D13								3.5	4		3.8	4.5	5		4.8
59418	D13								4.5	4		4.3	4.5	4.5		4.5
	D12								4.5	4		4.3	4.5	4.5		4.5
59656	D14								4.5	4		4.3	4.5	4.5		4.5
	D14								4	4		4.0	4	4.5		4.3

GMD COLOR BADGE LOG SHEET

TEST 63

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82385	D12	5/9	.1	none	2	2	40	25	2	2		2.0	5.0	4.0	4.0	4.3
	D12								3	3		3.0	5	4.5	3	4.2
82334	D13								1.5	2		1.8	4	2	4	3.3
	D13								2	2		2.0	4	3	3	3.3
59440	D13								3.5	4.5		4.0	4	4.5	3	3.8
	D12								3.5	4		3.8	4	4.5	3	3.8
59436	D14								3.5	4		3.8	3	4	2	3.0
	D14								2.5	2		2.3	3	2.5	2	2.5

GMD COLOR BADGE LOG SHEET

TEST 64

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84258	D12	5/9	.1	none	2	2	70	25	4	5		4.5	4.5			4.5
	D12								2.5	4.5		3.5	4.5			4.5
84294	D13								2	4.5		3.3	4.5			4.5
	D13								3	4		3.5	4.5			4.5
59546	D13								3.5	4.5		4.0	4.5			4.5
	D12								2.5	2		2.3	5			5.0
59564	D14								3	3		3.0	4			4.0
	D14								2.5	3		2.8	4.5			4.5

GMD COLOR BADGE LOG SHEET

TEST 65

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83505	D12		.1	none	16	16	40	25	7	9	7	7.7	8.0	8.0	8.0	8.0
	D12								8	9	7	8.0	7.5	8	8	7.8
82383	D13								6	8	7	7.0	7	7	8	7.3
	D13								8	8	7	7.7	7	8	8	7.7
59359	D13								7	8	8	7.7	8	8	8	8.0
	D12								9	9	8	8.7	9	9	8	8.7
59625	D14								8	9	8	8.3	9.5	9	8	8.8
	D14								8	9	8	8.3	9	9	8	8.7

GMD COLOR BADGE LOG SHEET

TEST 66

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82335	D12	5/10	.1	none	8	8	40	25	7	7		7.0	7.0	6.0		6.5
	D12								5	5		5.0	6	7		6.5
82403	D13								6.5	7		6.8	7	6		6.5
	D13								6	6		6.0	7	6		6.5
59548	D13								6	6		6.0	5	7		6.0
	D12								6	7		6.5	6	6		6.0
59443	D14								5	4.5		4.8	5	6		5.5
	D14								4	4		4.0	4	5		4.5

GMD COLOR BADGE LOG SHEET

TEST 67

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0			T=1		
									1	2	3 Aver	1	2	3 Aver
38647		8/18	.122	none	.25	.305	35	25	1 1	1 1	1.0 1.0	1.5 1	1.5 1	1.5 1.0
38867									.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5
38844									1 1	1 1	1.0 1.0	1.5 1	1.5 1	1.5 1.0

GMD COLOR BADGE LOG SHEET

TEST 68

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0			T=1		
									1	2	3 Aver	1	2	3 Aver
38905		8/21	.137	none	2	2.74	35	25	3 3	3 3	3.0 3.0	4.0 3.5	4.0 3	4.0 3.3
38975									3 2.5	2.5 2.5	2.8 2.5	4 2.5	4 3	4.0 2.8
38971									3 3	3 3	3.0 3.0	4 3	4 3	4.0 3.0

GMD COLOR BADGE LOG SHEET

TEST 69

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0			T=1		
									1	2	3 Aver	1	2	3 Aver
38873		8/21	.137	none	1.5	2.055	35	25	3 2	3 2	3.0 2.0	3.5 2	3.5 2	3.5 2.0
38963									3 2	2.5 2.5	2.8 2.3	3 3	3.5 3	3.3 3.0
38876									2 2	2 1.5	2.0 1.8	2 2	2.5 2	2.3 2.0

GMD COLOR BADGE LOG SHEET

TEST 70

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
39003		8/21	.137	none	.1	.137	35	25	2	2.5		2.3	2.5	2.5		2.5
									2	2		2.0	2	2		2.0
38682									2.5	2.5		2.5	3	3		3.0
									2.5	2.5		2.5	2.5	2.5		2.5
38845									2.5	2.5		2.5	3	3		3.0
									2	2		2.0	2	2		2.0

GMD COLOR BADGE LOG SHEET

TEST 71

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38996		8/21	.137	none	.5	.685	35	25	2	2		2.0	2.5	2.5		2.5
									2	1.5		1.8	2	1.5		1.8
38974									2	2		2.0	2	2		2.0
									2	2		2.0	2	2		2.0
39004									1	2		1.5	2.5	3		2.8
									2	1.5		1.8	1.5	1.5		1.5

GMD COLOR BADGE LOG SHEET

TEST 72

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38960		8/22	.121	none	2	2.41	65	25	3	3		3.0	3.0	3.0		3.0
									3	3		3.0	3	3		3.0
38943									3	3		3.0	4	3.5		3.8
									2.5	2		2.3	2	2.5		2.3
38747									4	2		3.0	4	4		4.0
									3	3.5		3.3	3	3		3.0

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TEST 73

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38998		8/22	.134	none	2	2.68	<10	25	2	1.5	2	1.8	4.0	4.0	4.0	
									3	2	3.5	2.8	3.5	4	3.8	
38864									2	2.5	2	2.2	4.5	4.5	4.5	
									2	2.5	3	2.5	3	3	3.0	
38748									2	2	2	2.0	4	4	4.0	
									3	3	3.5	3.2	4	4	4.0	

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TEST 74

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38874		8/23	.211	none	2	4.22	<10	25	2.5	3	2	2.5	4.5	5.0	5.0	4.8
									3.5	3	4	3.5	4	4	4	4.0
38866									2	2.5	2	2.2	4	4	4	4.0
									3.5	3	4	3.5	4	4	4	4.0
38865									2.5	2.5	2.5	2.5	4.5	5	4	4.5
									3	3	2.5	2.8	3	3.5	3	3.2

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TEST 75

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38928		8/23	.23	none	.25	.58	35	25	1	1.5	1.5	1.3	1.5	2.0	2.0	1.8
									1	1.5	1.5	1.3	2	2	2	2.0
38834									1	2	2	1.7	2	2	2.5	2.2
									1	1	1.5	1.2	1	1	1	1.0
38838									1	1.5	1.5	1.3	2	2	2	2.0
									1	1	1.5	1.2	1.5	1.5	1	1.3

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TEST 76

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38881		8/23	.228	none	1	2.28	35	25	2.5	2.5	3	2.7	2.5		4.0	3.3
									2	2	2	2.0	2.5		2	2.3
38751									2.5	2.5	3	2.7	3		3.5	3.3
									2.5	2.5	3	2.7	3		3	3.0
38955									2.5	2.5	3	2.7	2.5		4	3.3
									2	2	2	2.0	2		2	2.0

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TEST 77

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38710		8/23	.228	none	.5	1.14	35	25	1.5	2	1.5	1.7		2.5	2.0	2.3
									2	2	2.5	2.2		2.5	2.5	2.5
38737									2	2	2	2.0		3	3	3.0
									1.5	1.5	1.5	1.5		2	1.5	1.8
38752									1.5	2	1.5	1.7		2.5	2	2.3
									1.5	1.5	1.5	1.5		2	1.5	1.8

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TEST 78

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38957		8/24	.213	none	2	4.26	35	25	3	3		3.0	3.5	3.5		3.5
									3.5	3		3.3	4	4		4.0
38664									3.5	3.5		3.5	4.5	4.5		4.5
									2.5	3		2.8	3	3		3.0
38672									3	3		3.0	4	4		4.0
									3	3		3.0	3.5	3.5		3.5

GMD COLOR BADGE LOG SHEET

TEST 79

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38956		8/24	.21	none	2	4.2	64	25	4 2.5	4 2.5		4.0 2.5	4.0 2.5	4.0 2.5		4.0 2.5
38826									4 4	4 3.5		4.0 3.8	4 3.5	4 3.5		4.0 3.5
38858									4.5 3	4.5 3		4.5 3.0	4.5 3	4 3		4.3 3.0

GMD COLOR BADGE LOG SHEET

TEST 80

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST MMH				POST INTERFERANT			
									1	2	3	Aver	1	2	3	Aver
38735		9/14	.178	NO2 5 ppm	1	.89	45	25	2.0 2	2.0 2.5		2.0 2.3	2 2	2 2.5		2.0 2.3
38856			.178	5					1 2	1 2		1.0 2.0	1 2	1 2		1.0 2.0
38966			.178	5					1.5 3	1.5 3		1.5 3.0	2 3	2 3		2.0 3.0
38832	CON		.178	0					1 2	1 2		1.0 2.0	1.5 2	1.5 2		1.5 2.0

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TEST 81

I.D. #	BADGE TYPE	DATE	INTER-FERANT	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST INTERFERANT				POST MMH			
									1	2	3	Aver	1	2	3	Aver
38944		9/14	NO2 5 ppm	.178	1	.89	45	25	.5 .5	.5 .5		.5 .5	1.0 2.5	1.5 2.5		1.3 2.5
38712			5	.178					.5 .5	.5 .5		.5 .5	1 2	1.5 2.5		1.3 2.3
38979			5	.178					.5 .5	.5 .5		.5 .5	1 2.5	1.5 2.5		1.3 2.5
38839	CON		5	0					.5 .5	.5 .5		.5 .5	.5 .5			.5 .5

GMD COLOR BADGE LOG SHEET

TEST 82

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38734		9/14	.178	none	1	.89	45	25	1	1.5		1.3	2.0	2.5		2.3
									3	2.5		2.8	3	3		3.0
38912									1	1		1.0	1.5	1.5		1.5
									2	2		2.0	2	2		2.0
38652									2	2		2.0	3	3		3.0
									2.5	3		2.8	3	3		3.0
38678									1.5	1.5		1.5	2.5	3		2.8
									2.5	2		2.3	2.5	3		2.8

GMD COLOR BADGE LOG SHEET

TEST 83

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST MMH				POST INTERFERANT			
									1	2	3	Aver	1	2	3	Aver
38717		9/15	.164	NH3 20.4 ppm	1	.82	45	25	1.5	1.5		1.5	3	3		3.0
									3	3		3.0	3	3.5		3.3
38868			.164	20.4					1	1.5		1.3	2	2		2.0
									2	2		2.0	2	2		2.0
38910			.164	20.4					2	2		2.0	3	3		3.0
									2.5	2.5		2.5	3	3.5		3.3
38959	CON		.164	0					1.5	1.5		1.5	2	2		2.0
									2	2		2.0	2	2		2.0

GMD COLOR BADGE LOG SHEET

TEST 84

I.D. #	BADGE TYPE	DATE	INTER-FERANT	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST INTERFERANT				POST MMH			
									1	2	3	Aver	1	2	3	Aver
38711		9/15	NH3 20.4 ppm	.164	1	.82	45	25	.5			.5		3.0		3.0
									.5			.5	3	3		3.0
38825			20.4	.164					.5			.5	3	2.5		2.8
									.5			.5	3	2.5		2.8
38827			20.4	.164					.5			.5	3	2.5		2.8
									.5			.5	3	2		2.5
38833	CON		20.4	0					.5			.5	1	.5		.8
									.5			.5	.5	.5		.5

GMD COLOR BADGE LOG SHEET

TEST 85

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST MMH				POST INTERFERAN			
									1	2	3	Aver	1	2	3	Aver
38925		9/19	.198	FREONS	1	.99	45	25	1	1		1.0	1.5	2		1.8
				29.4 ppm					2	2		2.0	2	2		2.0
38753			.198	29.4					1.5	2		1.8	2	2.5		2.3
									3	3		3.0	3	3		3.0
38990			.198	29.4					1.5	2		1.8	2	2.5		2.3
									2.5	3		2.8	3	3		3.0
38749	CON		.198	0					1	2		1.5	2	2		2.0
									2	2			2	2		

Freon 11, 12, 114: 8.6, 10.6, 10.2 ppm

GMD COLOR BADGE LOG SHEET

TEST 86

I.D. #	BADGE TYPE	DATE	INTER-FERANT	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	POST INTERFERANT				POST MMH			
									1	2	3	Aver	1	2	3	Aver
38903		9/19	FREONS	.198	1	.99	45	25	0	0		.0	2.0	2.0		2.0
			29.4 ppm						0	0		.0	2.5	2.5		2.5
38842			29.4	.198					0	0		.0	1.5	2		1.8
									0	0		.0	2	2		2.0
39005			29.4	.198					0	0		.0	1.5	2		1.8
									0	0		.0	2	2		2.0
38671	CON		29.4	0					0	0		.0	0	0		.0
									0	0		.0	0	0		.0

CON- Control badges were not exposed to the second vapor

GMD COLOR BADGE LOG SHEET

TEST 87

I.D. #	BADGE TYPE	DATE	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	WHEEL DESIGN	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
39006	VAN	12/22	.28	.75	1.05	43	25	OLD	4.5	4.5	4	4.3	4.0	4.5	4.0	4.2
								NEW	2.5	2.5	3	2.7	2.5	2.5	2.5	2.5
	PDAB							OLD	.5	1	1	.8	.5	1	3	1.5
								NEW	.5	1	1	.8	1	1	1	1.0
38687	VAN							OLD	3	2	3	2.7	3	2	2	2.3
								NEW	2	2	2	2.0	2	2	2	2.0
	PDAB							OLD	1	1.5	1.5	1.3	1.5	2.0	3.0	2.2
								NEW	1	1	1.5	1.2	1.5	1.5	2	1.7
38713	VAN							OLD	4	4	4	4.0	4.0	3.0	4	3.7
								NEW	2.5	2.5	2.5	2.5	2.5	2.5	2	2.3
	PDAB							OLD	1	1	2	1.3	1.5	2	3	2.2
								NEW	1	1	1.5	1.2	1.5	1.5	2	1.7
39008	VAN							OLD	2	1.5	2	1.8	2	1	1.5	1.5
								NEW	1.5	1.5	1.5	1.5	1.5	1.5	1	1.3
	PDAB							OLD	.5	.5	1	.7	.5	1	1	.8
								NEW	.5	.5	1	.7	.5	1	1	.8

GMD COLOR BADGE LOG SHEET

TEST 88

I.D. #	BADGE TYPE	DATE	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	WHEEL DESIGN	T=0				T=1									
									1	2	3	Aver	1	2	3	Aver						
38663	VAN	12/22	.28	4	5.6	43	25	OLD	7	8	8	7.7	7.8	7.5		7.6						
								NEW	4	4	3.5	3.8	3.5	3.5		3.5						
	PDAB							OLD	7	8	8	7.7	7	8		7.5						
								NEW	3.5	4	4	3.8	4	4		4.0						
38649	VAN							OLD	8	9	8	8.3	8	7.5		7.8						
								NEW	4	5	5	4.7	4	4		4.0						
	PDAB							OLD	7	7.5	8	7.5	7.0	8.0		7.5						
								NEW	4	4	4	4.0	4	4		4.0						
38650	VAN							OLD	8	8	8	8.0	8.0	8.0		8.0						
								NEW	4	4	4	4.0	4	4		4.0						
	PDAB							OLD	7.5	7.5	8	7.7	7	7.5		7.3						
								NEW	4	3.5	4	3.8	3.5	4		3.8						
38743	VAN							OLD	8	7	7.5	7.5	7	7		7.0						
								NEW	4	3.5	4	3.8	3.5	4		3.8						
	PDAB							OLD	7.5	7.5	8	7.7	7	7		7.0						
								NEW	3.5	4	4	3.8	3.5	4		3.8						

GMD COLOR BADGE LOG SHEET

TEST 89

I.D. #	BADGE TYPE	DATE	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	WHEEL DESIGN	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38898	VAN	12/22	.28	1.75	2.45	43	25	OLD	6			6.0				
								NEW	3			3.0				
	PDAB							OLD	3.5			3.5				
								NEW	2			2.0				
38754	VAN							OLD	5			5.0				
								NEW	3			3.0				
	PDAB							OLD	5			5.0				
								NEW	3			3.0				
38741	VAN							OLD	5			5.0				
								NEW	3			3.0				
	PDAB							OLD	4.5			4.5				
								NEW	2.5			2.5				
38715	VAN							OLD	5			5.0				
								NEW	3			3.0				
	PDAB							OLD	4.5			4.5				
								NEW	2			2.0				

GMD COLOR BADGE LOG SHEET

TEST 90

I.D. #	BADGE TYPE	DATE	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	WHEEL DESIGN	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
39001	VAN	1/9/90	.234	17.25	20.1825	35	25	OLD	9.5	9	9	9.2	9.5	9.0		9.3
								NEW	5.5	5	4.5	5.0	5	5		5.0
	PDAB							OLD	9.5	9	9	9.2	9.5	9		9.3
								NEW	5	5	5	5.0	5	5		5.0
38993	VAN							OLD	9.5	9	9.5	9.3	9.5	9.5		9.5
								NEW	5.5	5	5	5.2	5.5	5		5.3
	PDAB							OLD	9.5	9	9.5	9.3	9.5	9.5		9.5
								NEW	5.5	5	5	5.2	5.5	5		5.3
38980	VAN							OLD	9.5	9	9.5	9.3	9.5	9.5		9.5
								NEW	5	5	5	5.0	5	5.5		5.3
	PDAB							OLD	9.5	9	9	9.2	9.5	9		9.3
								NEW	5.5	5	5	5.2	5.5	5		5.3
38985	VAN							OLD	9.5	9	9.5	9.3	9.5	9		9.3
								NEW	5	5	5	5.0	5	5		5.0
	PDAB							OLD	9.5	9	9	9.2	9.5	9.5		9.5
								NEW	5	5	5	5.0	5	5		5.0

GMD COLOR BADGE LOG SHEET

TEST 91

I.D. #	BADGE TYPE	DATE	MMH (ppm)	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	WHEEL DESIGN	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38995	VAN	1\10\90	.195	7.5	7.3125	45	25	OLD	9.5	9	9	9.2	9.0			9.0
								NEW	5	5	5	5.0	5			5.0
	PDAB							OLD	9	9	8.5	8.8	8.5			8.5
								NEW	4.5	4.5	4.5	4.5	4.5			4.5
39013	VAN							OLD	8	9	9	8.7	8			8.0
								NEW	4	3.5	3.5	3.7	4			4.0
	PDAB							OLD	7.5	7	8.5	7.7	8.5			8.5
								NEW	4	4	4.5	4.2	4			4.0
38982	VAN							OLD	9	9	9	9.0	9.0			9.0
								NEW	5	4.5	5	4.8	5			5.0
	PDAB							OLD	9	9	8.5	8.8	9			9.0
								NEW	5	4.5	4.5	4.7	5			5.0
39000	VAN							OLD	9	8	8.5	8.5	8.5			8.5
								NEW	4	4	4	4.0	4			4.0
	PDAB							OLD	9	8	8.5	8.5	8.5			8.5
								NEW	4.5	4.5	4.5	4.5	4.5			4.5

APPENDIX B
Wiltech Data Sheets

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84256	D12	2/27	.12	none	.25	.15	31		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84285	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83515	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59588	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	.5	.5
59561	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	.5	.5
59394	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								.5	.5	.5	.5	.5	.5	.5	.5
81203	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81187	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
83451	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83495	D12	2/27	.12	none	.5	.3	31		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83416	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83519	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59618	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1	1	1	1.0	1	1	1	1.0
59589	D14								1	1	1	1.0	1	1	1	1.0
	D14								1	1	1	1.0	1.5	1	1.5	1.3
59498	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1	1	1	1.0	1	1	1	1.0
81231	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
85552	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
83519	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
84231	D12	2/27	.12	none	16	9.6	31		9	9	8.5	8.8	9	9	8.5	8.8
	D12								9	9	9	9.0	9	9	9	9.0
59404	D14								9	9	8.5	8.8	9	9	9	9.0
	D14								9	9	8.5	8.8	9	9	9.5	9.2
83452	D12								9	9	9	9.0	9	9	9	9.0
	D13								9	9	9	9.0	9	9	8.5	8.8

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82369	D12	3/2	.12	none	1	.6	30		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	1.5	1	2	1.5
84274	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59420	D14								1	1	1	1.0	1	1	1	1.0
	D14								2	2	2	2.0	2	1.5	2	1.8
59517	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								2	1.5	2	1.8	2	1.5	2	1.8
85583	D12								2	1.5	2	1.8	2	1.5	2	1.8
	D13								.5	.5	.5	.5	1.5	1.5	1.5	1.5
85511	D12								1	1	1	1.0	1	1	1	1.0
	D13								.5	.5	.5	.5	.5	.5	1.5	.8
83524	D12	3/2	.12	none	16	9.6	30		9	9	9	9.0	9.5	9.5	9	9.3
	D12								9	9.5	9	9.2	9.5	9.5	9.5	9.5
59639	D14								9	9.5	9.5	9.3	9.5	9.5	9.5	9.5
	D14								9	9.5	9.5	9.3	9.5	9.5	9.5	9.5
81179	D12								9	9.5	9.5	9.3	9.5	9.5	9.5	9.5
	D13								9	9.5	9	9.2	9.5	9.5	9.5	9.5

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I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83473	D12	3/3	.12	none	2	1.2	30		1	.5	.5	.7	4.0	1.5	2.0	2.5
	D12								4	3	2.5	3.2	5	4.5	4	4.5
84282	D12								1	.5	1	.8	2	1.2	2	1.7
	D12								2	1.5	2	1.8	4	3.5	3.5	3.7
84280	D12								4	3.5	3	3.5	5	5	5	5.0
	D12								3.5	2.5	3.5	3.2	4.5	4.5	4	4.3
59567	D14								4	4.5	4	4.2	5	5	4	4.7
	D14								5	4	4	4.3	4	4	3.5	3.8
59483	D14								5	5	5	5.0	5	5	5	5.0
	D14								5	4.5	4.5	4.7	5	4.5	4	4.5
59636	D14								3	3	3	3.0	3	3	3	3.0
	D14								4	2.5	3.5	3.3	4	4	4.5	4.2
83464	D12								4	4	4	4.0	5	4.5	4	4.5
	D13								2	2	2.5	2.2	4	4	3.5	3.8
83497	D12								4	4	4	4.0	4	4	4	4.0
	D13								2	1.5	2	1.8	4	3.5	2.5	3.3
85545	D12								4	4.5	5	4.5	5	5	5	5.0
	D13								4	3.5	3.5	3.7	5	5	5	5.0
82372	D12	3/3	.12		1	.6	30		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	2	1.5	2	1.8
59547	D14								.5	.5	1	.7	.5	1	1	.8
	D14								1	1.5	1.5	1.3	1.5	1.5	1.5	1.5
81196	D12								2	2	2	2.0	2	2	2.5	2.2
	D13								.5	.5	.5	.5	1.5	.5	1.5	1.2

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84230	D12	3/6	.18	none	.25	.225	33		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
83507	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84245	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
59521	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1	1	1	1.0	.5	.5	.5	.5
59512	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1.5	1.5	1	1.3	1.5	1.5	1	1.3
59597	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1.5	1.5	1	1.3	1.5	1.5	1	1.3
81252	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81191	D12								.5	.5	.5	.5	1	.5	1	.8
	D13								.5	.5	.5	.5	.5	.5	.5	.5
81181	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D13								.5	.5	.5	.5	.5	.5	.5	.5
84273	D12	3/6	.18	none	.5	.225	33		.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84300	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	.5	.5	.5	.5
84265	D12								.5	.5	.5	.5	.5	.5	.5	.5
	D12								.5	.5	.5	.5	1.5	1.5	1.5	1.5
59492	D14								.5	.5	.5	.5	1	.5	.5	.7
	D14								1	1.5	1	1.2	2	1.5	1	1.5
59645	D14								1	1	1	1.0	1	1	1	1.0
	D14								1.5	1.5	1	1.3	2	1.5	1	1.5
59538	D14								.5	.5	.5	.5	.5	.5	.5	.5
	D14								1	.5	1	.8	1	1	1	1.0
81273	D12								1.5	1.5	1.5	1.5	1.5	1.5	1	1.3
	D13								.5	.5	1	.7	.5	.5	1	.7
83496	D12								1	1.5	1	1.2	2	1.5	2	1.8
	D13								.5	.5	.5	.5	1.5	.5	1	1.0
83510	D12								1	1.5	1	1.2	1	1	1	1.0
	D13								.5	.5	.5	.5	.5	.5	.5	.5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82349	D12	3/6	.18	none	1	.9	33		.5	.5	.5	.5	2.5	2.5	3	2.7
	D12								.5	1.5	1	1.0	2.5	3	3	2.8
82368	D12								.5	.5	1	.7	1.5	2.5	2	2.0
	D12								.5	.5	.5	.5	2.5	2.5	3	2.7
82390	D12								.5	.5	.5	.5	.5	1	.5	.7
	D12								2	2.5	2	2.2	3.5	3.5	3.5	3.5
59422	D14								1.5	1.5	1	1.3	2	1.5	1	1.5
	D14								3	2.5	2.5	2.7	3	3	3	3.0
59413	D14								2	2	2	2.0	2	2	1	1.7
	D14								4	3.5	4	3.8	4	3.5	3	3.5
59410	D14								2	2	2	2.0	2	2	2	2.0
	D14								4	3.5	4	3.8	3.5	3.5	3.5	3.5
81182	D12								2	2	2	2.0	2.5	2	2	2.2
	D13								.5	.5	.5	.5	1.5	1.5	2	1.7
83477	D12								2	2	2	2.0	2	2	2	2.0
	D13								.5	1.5	1	1.0	2.5	2.5	2	2.3
85549	D12								2	2	2	2.0	2	2	2	2.0
	D13								.5	1	.5	.7	1.5	1	1.5	1.3
84269	D12	3/6	.12	none	16	9.6	33		9	9	9	9.0	9	9	9	9.0
	D12								9	9	9	9.0	9	9	9	9.0
59511	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	8	9	8.7	9	9	9	9.0
85594	D12								9	9	9	9.0	9	9	9	9.0
	D13								9	9	9	9.0	9	9	9	9.0

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83502	D12 D12	3/7	.43	none	.25	.5375	33		.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5
82350	D12 D12								.5 .5	.5 .5	.5 .5	.5 .5	.5 1.5	.5 2.5	.5 1.5	.5 1.8
83472	D12 D12								.5 .5	.5 .5	.5 .5	.5 .5	.5 1.5	.5 1.5	.5 1.5	.5 1.5
59460	D14 D14								.5 1	.5 1	.5 1	.5 1.0	.5 1	.5 1	.5 1	.5 1.0
59364	D14 D14								.5 1	.5 1	.5 1	.5 1.0	.5 1	.5 1	.5 1	.5 1.0
59643	D14 D14								.5 1	.5 1	.5 1	.5 1.0	.5 1	.5 1	.5 1	.5 1.0
83526	D12 D13								1 .5	1 .5	1 .5	1.0 .5	1.5 .5	1 .5	1.5 .5	1.3 .5
85600	D12 D13								1 .5	1 .5	1 .5	1.0 .5	1.5 .5	1.5 .5	1.5 .5	1.5 .5
85579	D12 D13								1 .5	1.5 .5	1 .5	1.2 .5	1.5 .5	1.5 .5	1.5 .5	1.5 .5
84292	D12 D12	3/7	.43	none	.5	1.075	33		.5 1	.5 1	.5 .5	.5 .8	.5 4.5	1 5	.5 3.5	.7 4.3
83508	D12 D12								.5 2	.5 2	.5 1.5	.5 1.8	2.5 5	2.5 5	3.5 4.5	2.8 4.8
82343	D12 D12								.5 2.5	.5 2.5	.5 1.5	.5 2.2	2.5 4.5	2.5 5	1.5 5	2.2 4.8
59504	D14 D14								1 1.5	1 2	1 1.5	1.0 1.7	1 2	1.5 2.5	1 2	1.2 2.2
59535	D14 D14								1 1.5	1 1.5	.5 1.5	.8 1.5	1.5 2.5	1.5 2.5	1.5 2	1.5 2.3
59489	D14 D14								1 2	1.5 2	1 1.5	1.2 1.8	1.5 2.5	2 3	1 2	1.5 2.5
85606	D12 D13								2.5 .5	2.5 .5	2 .5	2.3 .5	3 1.5	2.5 1.5	3 .5	2.8 1.2
81176	D12 D13								2 .5	2 .5	2 .5	2.0 .5	2.5 .5	2 .5	2 .5	2.2 .5
85572	D12 D13								3 1	3 .5	2 1	2.7 .8	3 1	4 2.5	3 1.5	3.3 1.7

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83463	D12	3/7	.43	none	1	2.15	33		.5	.5	1	.7	3	3.5	2	2.8
	D12								1	1	1	1.0	3.5	4	2	3.2
82339	D12								1	1	1.5	1.2	2	2	1.5	1.8
	D12								2	1.5	1.5	1.7	2.5	3.5	2.5	2.8
82415	D12								.5	.5	.5	.5	3	3	2.5	2.8
	D12								1	1	.5	.8	3.5	3.5	2.5	3.2
59490	D14								2	2	2	2.0	3	2	2	2.3
	D14								2.5	2.5	2	2.3	3.5	3	3	3.2
59485	D14								2.5	2.5	3	2.7	3	4	2.5	3.2
	D14								3	3	3	3.0	4	4	4	4.0
59612	D14								1.5	2	1	1.5	1.5	1.5	1.5	1.5
	D14								3	3	3	3.0	4	4	4	4.0
83520	D12								5	5.5	5	5.2	6	7	7	6.7
	D13								4.5	5	4.5	4.7	6.5	7.5	7.5	7.2
83484	D12								6	6	5	5.7	6	6	5	5.7
	D13								5	5	6.5	5.5	5.5	6	5.5	5.7
85571	D12								5	5	4.5	4.8	5.5	5.5	5	5.3
	D13								4.5	4.5	4.5	4.5	6	5.5	6.5	6.0
82367	D12	3/7	.43	none	16	34.4	33		9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D12								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
59590	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
85569	D12								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D13								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
83512	D12								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D13								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
84278	D12	3/8	.43	none	16	34.4	33		9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D12								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
59585	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	D14								9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
83476	D12 D12	4/5	.18	none	2	1.8	33		2 2.5	2.5 2.5	2.5 2.5	2.3 2.5	4.5 4.5	4.5 4	4.5 3.5	4.5 4.0
83527	D12 D12								.5 1	.5 1	.5 .5	.5 .8	3.5 4.5	4 4	2.5 3.5	3.3 4.0
82381	D12 D12								.5 2	1 2.5	.5 1.5	.7 2.0	1 2.5	1.5 3	1.5 3	1.3 2.8
59432	D14 D14								4.5 4	4 4	4 4	4.2 4.0	5.5 4.5	5 5	4.5 4.5	5.0 4.7
59378	D14 D14								4 5	4 4.5	4.5 4.5	4.2 4.7	4.5 5	4.5 5	4.5 4.5	4.5 4.8
59475	D14 D14								4.5 5	5 5	4.5 4.5	4.7 4.8	5 5.5	5.5 5.5	5 5	5.2 5.3
85576	D12 D13								4.5 4.5	4.5 4.5	4 4	4.3 4.3	5 5	5 5	4.5 4.5	4.8 4.8
85591	D12 D13								3.5 1.5	4 3.5	4.5 1.5	4.0 2.2	5.5 4.5	5.5 4.5	4.5 4.5	5.2 4.5
81220	D12 D13								4.5 3	4.5 4	4.5 2.5	4.5 3.2	5.5 4.5	6 4.5	5.5 3.5	5.7 4.2
82396	D12 D12	4/5	.18	none	16	14.4	33		4.5 5	5 5	4.5 5.5	4.7 5.2	6 7	6 6	7.5 6.5	6.5 6.5
84254	D12 D12								4.5 5	5 5	4.5 4.5	4.7 4.8	6 6.5	6 6	6.5 6.5	6.2 6.3
59644	D14 D14								6 7.5	8 8	7 8	7.0 7.8	7 8	8 8	8 8	7.7 8.0
59438	D14 D14								7 8	8 8	8 8	7.7 8.0	7 7.5	8 8	8 8	7.7 7.8
83443	D12 D13								7 5	8 5	6 4.5	7.0 4.8	6 6.5	8 7	7 7.5	7.0 7.0
85508	D12 D13								5.5 5	8 5	7 4.5	6.8 4.8	7 6	8 6	6 7.5	7.0 6.5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
84310	D12	5/1	.21	none	2	2.1	33		2	2	1.5	1.8	5	5	4.5	4.8
	D12								2	2	1.5	1.8	4.5	5	4.5	4.7
83501	D12								3	3.5	2.5	3.0	5	5	4.5	4.8
	D12								2	1.5	1.5	1.7	4	5	2.5	3.8
82406	D12								3.5	3.5	2.5	3.2	5	5	4.5	4.8
	D12								.5	.5	.5	.5	2.5	3.5	1.5	2.5
84270	D12								2.5	2	2.5	2.3	4.5	4	4.5	4.3
	D12								2	2	2	2.0	4.5	4	4.5	4.3
84317	D12								2	2	2.5	2.2	4.5	4	4.5	4.3
	D12								.5	.5	.5	.5	2.5	2.5	1.5	2.2
82393	D12								2	2	2.5	2.2	5	4	4.5	4.5
	D12								1	1.5	1	1.2	4	4	3.5	3.8
59615	D14								5	5	5.6	5.2	6.5	7	7	6.8
	D14								5	5	5.6	5.2	6.5	7	7	6.8
59446	D14								5	5	4.5	4.8	6	7	5	6.0
	D14								5	5	4.5	4.8	6	6	4.5	5.5
59473	D14								5	5	5	5.0	5.5	7	5	5.8
	D14								5	5	5	5.0	5.5	7	4.5	5.7
59622	D14								5	5	4.5	4.8	5.5	7	5	5.8
	D14								5	5	4.5	4.8	5	6	4.5	5.2
59402	D14								5.5	6	5	5.5	6.5	7	5.5	6.3
	D14								5	6	4.5	5.2	6	7	5	6.0
59370	D14								5.5	6	4.5	5.3	6	7	5	6.0
	D14								5	5	4	4.7	6	6	4.5	5.5
59631	D14								5.5	6	5	5.5	5.5	7	5.5	6.0
	D14								6	6	4.5	5.5	6	7	5	6.0

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82344	D12 D12	5/2	.42	none	.84	1.764	33		3 3	3.5 3.5	4 4	3.5 3.5	5.5 5.5	4.5 4.5	5 5	5.0 5.0
83456	D12 D12								3.5 1.5	2.5 1.5	4 4	3.3 2.3	6 4.5	4.5 4.5	5 5	5.2 4.7
83441	D12 D12								3 3	2.5 3.5	4 4	3.2 3.5	5.5 5.5	4.5 4.5	5 5	5.0 5.0
82371	D12 D12								2.5 2.5	2.5 3.5	5 5	3.3 3.7	5.5 5.5	6 5	5 5	5.5 5.2
82397	D12 D12								3 2	3.5 2.5	4 4	3.5 2.8	5.5 5.5	5 5	5 5	5.2 5.2
84225	D12 D12								3.5 3.5	3.5 3.5	5 5	4.0 4.0	5.5 5.5	5 5	5 6	5.2 5.5
59624	D14 D14								6 5	6.5 5	6 5	6.2 5.0	8.5 6	7 5	5 5	6.8 5.3
59604	D14 D14								6.5 5	7 6	6 6	6.5 5.7	8.5 8.5	6.5 6	6 6	7.0 6.8
59398	D14 D14								6.5 5	6 5	5 5	5.8 5.0	8.5 6.5	6 5.5	5 5	6.5 5.7
59426	D14 D14								7 6	6.5 7.5	6 6	6.5 6.5	7 7	7.5 7.5	6 5	6.8 6.5
59574	D14 D14								6 6	6 6	6 6	6.0 6.0	7 7	7 7	6 6	6.7 6.7
59606	D14 D14								7 7	6 6.5	6 5	6.3 6.2	7 7	7.5 7	6 6	6.8 6.7

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82346	D12	5/5	.96	none	.25	1.2	33		.5	.5	.5	.5	3.5	3.5	4.5	3.8
	D12								.5	.5	.5	.5	3.5	3	4.5	3.7
84275	D12								.5	.5	.5	.5	4.5	3.5	4.5	4.2
	D12								.5	.5	.5	.5	3.5	3	3.5	3.3
84289	D12								.5	.5	.5	.5	3.5	3	4.5	3.7
	D12								.5	.5	.5	.5	3.5	3	4.5	3.7
82538	D12								.5	.5	.5	.5	4.5	3.5	4.5	3.0
	D12								.5	.5	.5	.5	2.5	2.5	1.5	2.2
82405	D12								.5	.5	.5	.5	4	4	3.5	3.8
	D12								.5	.5	.5	.5	2.5	2.5	1.5	2.2
84255	D12								.5	.5	.5	.5	3.5	3.5	3.5	3.5
	D12								.5	.5	.5	.5	1.2	1.2	2.5	1.6
59465	D14								2	2	3	2.3	4	4	4.5	4.2
	D14								1	1	1	1.0	2.5	3	2	2.5
59486	D14								3	3	4.5	3.5	4.5	5	5	4.8
	D14								2	2	2	2.0	3.5	3.5	2	3.0
59610	D14								2	3	4.5	3.2	4	4	4.5	4.2
	D14								1.5	2	3	2.2	2.5	3.5	3	3.0
59382	D14								4.5	5	5.6	5.0	4.5	5	5	4.8
	D14								4	4	4	4.0	4	5	4	4.3
59405	D14								4	5	4.5	4.5	4.5	5	4	4.5
	D14								2	3	4.5	3.2	3	5	3	3.7
59550	D14								4.5	5	4.5	4.7	5	5	5	5.0
	D14								3.5	4	4	3.8	4	4	5	4.3

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82382	D12	5/5	.96	none	1	4.8	33		4.5	4	4.5	4.3	5.5	6	6	5.8
	D12								4.5	4	4.5	4.3	5.5	6	6	5.8
83462	D12								5	5	4.5	4.8	6.7	6.7	7	6.8
	D12								4.5	4	4.5	4.3	5.5	5	6	5.5
84263	D12								4.5	5	4.5	4.7	6.5	6	7	6.5
	D12								4.5	4	4.5	4.3	5.5	5.5	6	5.7
82373	D12								4	3.5	4.5	4.0	6.5	7	6.5	6.7
	D12								3	2.5	4.5	3.3	7	6.5	5.5	6.3
84238	D12								3	2.3	4.5	3.3	6.5	7	6.5	6.7
	D12								1.2	1	3.4	1.9	5.5	5	5.5	5.3
82426	D12								3.5	3	4.5	3.7	6.5	6.5	6.5	6.5
	D12								2.5	2.5	4.5	3.2	6.5	6	5.5	6.0
59559	D14								7	9	9	8.3	8.5	9	8.5	8.7
	D14								7	9	8	8.0	8	9	9	8.7
59406	D14								6.5	9	8	7.8	9	9	9	9.0
	D14								6.5	9	7	7.5	8.5	9	8.5	8.7
59431	D14								7.5	9	6	7.5	9	9	9	9.0
	D14								7	8	7	7.3	8	9	8.5	8.5
59642	D14								8.5	7	6.5	7.3	9	9	9	9.0
	D14								7	6.5	6.5	6.7	8	8	8	8.0
59455	D14								8	9	7.5	8.2	8.5	9	9	8.8
	D14								8	9	8.5	8.5	9	9	9	9.0
59518	D14								9	9	8.5	8.8	9	9	9	9.0
	D14								9	9	8.5	8.8	9	9	9	9.0

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
82411	D12	5/5	5.7	none	.25	7.125	33		4.5	4.5	5.5	4.8	8	7.5	7.5	7.7
	D12								5	5	5.5	5.2	8	7.5	8	7.8
84247	D12								6	5.6	6.5	6.0	9	8.5	8	8.5
	D12								5.5	5	5.5	5.3	8	7.5	7.5	7.7
84268	D12								4.5	5	5.5	5.0	8	7.5	7.5	7.7
	D12								1.5	2	4.5	2.7	5	5	5.5	5.2
84295	D12								4.5	5	4.5	4.7	8	8	7.5	7.8
	D12								4.5	5	4.5	4.7	8	7.5	7.5	7.7
84279	D12								5	5	5.5	5.2	8	7.5	8	7.8
	D12								5	5	4.5	4.8	8	7.5	7.5	7.7
83533	D12								5	5	4.5	4.8	8	7.5	8.5	8.0
	D12								4.5	5	5.5	5.0	8	7.5	7.5	7.7
59427	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0
59428	D14								9	9	9	9.0	9	9	9	9.0
	D14								7	7	5	6.3	9	9	9	9.0
59445	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0
59357	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0
59396	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0
59556	D14								9	9	9	9.0	9	9	9	9.0
	D14								9	9	9	9.0	9	9	9	9.0

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	Post MMH				Post Interfer.			
									1	2	3	Aver	1	2	3	Aver
37997	PDAB VAN	8/10	.21	HEAT HEAT	2	2.1	33	40 40	2.5 3	3.0 3	3.0 3.5	2.8 3.2	4.0 4	4.0 4	4.0 4	4.0 4.0
37990	PDAB VAN			SUN SUN					3 3	3 3	3 3	3.0 3.0	3.5 3.5	4 3.5	3.5 3.5	3.7 3.5
37970	PDAB VAN			HEAT HEAT				40 40	1.2 2.3	2 2.5	2 2.5	1.7 2.4	3 2	3 3	3 3	3.0 2.7
37963	PDAB VAN			HEAT HEAT				40 40	2 2	2 2	2 2	2.0 2.0	3 3	3 3	2.5 2.5	2.8 2.8
37985	PDAB VAN			SUN SUN					2.5 3	2.5 3	2.5 3.5	2.5 3.2	3.0 3	2.5 3	2.5 4.5	2.7 3.5
37958	PDAB VAN			SUN SUN					2.5 2.5	3.5 2.5	3.5 2.5	3.2 2.5	3 3	4 2.5	3.5 3	3.5 2.8
37968	PDAB VAN			COLD COLD				0 0	3 2	3 2.5	3 2.5	3.0 2.3	3 3	3 3	3.5 3.5	3.2 3.2
37961	PDAB VAN			UV-254 UV-254					2 2	2.5 2.5	2.5 2.5	2.3 2.3	3 2	3 2.5	2.5 2.5	2.8 2.3
37969	PDAB VAN			COLD COLD				0 0	2 3	2 3	2.5 3	2.2 3.0	3.0 3	3.0 3	2.5 3	2.8 3.0
37962	PDAB VAN			UV-350 UV-350					2 2	2 2	1.5 2	1.8 2.0	2 2	2 2	2 2	2.0 2.0
37984	PDAB VAN			COLD COLD				0 0	2 2	2 2	2 2	2.0 2.0	2.5 2	2.5 2	2.5 2	2.5 2.0
37977	PDAB VAN			UV-254 UV-254					2.5 3	3 3	3 3	2.8 3.0	3.5 3	3 3	3.5 3	3.3 3.0

Badges were exposed to MMH first, interferent second

PDAB color dots read on vanillin scale

Badges exposed to heat and cold for 4 hours, to UV for 0.5 hours

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	Post Interfer.				Post MMH			
									1	2	3	Aver	1	2	3	Aver
38173	P	8/17	.21	HEAT	2	2.1	33	40	.5	.5	.5	.5	2.5	2.5	2.0	2.3
	V			HEAT				40	.5	.5	.5	.5	2.5	3	3	2.8
38180	P			HEAT				40	.5	.5	.5	.5	2	2	2.5	2.2
	V			HEAT				40	.5	.5	.5	.5	2.5	2.5	2	2.3
37904	P			HEAT				40	.5	.5	.5	.5	2.5	2.5	2	2.3
	V			HEAT				40	.5	.5	.5	.5	2	2	2	2.0
37878	P			COLD				0	.5	.5	.5	.5	2	2	2	2.0
	V			COLD				0	.5	.5	.5	.5	2	2	2	2.0
37887	P			COLD				0	.5	.5	.5	.5	3.0	3.0	3.0	3.0
	V			COLD				0	.5	.5	.5	.5	4	4	3.5	3.8
37896	P			COLD				0	.5	.5	.5	.5	2	2	2.5	2.2
	V			COLD				0	.5	.5	.5	.5	3	3	3	3.0
3793	P			UV-254					.5	.5	.5	.5	3	3.5	3.5	3.3
	V			UV-254					.5	.5	.5	.5	3	3	3.4	3.1
37960	P			UV-350					.5	.5	.5	.5	3	3.5	3.5	3.3
	V			UV-350					.5	.5	.5	.5	3	4	3	3.3
37980	P			UV-350					.5	.5	.5	.5	3	3	3	3.0
	V			UV-350					.5	.5	.5	.5	3	3	3.5	3.2

Badges were exposed to interferent first, MMH second

Badges were exposed to heat and cold for 2 hours, to UV for 0.5 hours

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38184	P V	8/18	.96	none	3	14.4	33		5 5	5 5	5 5	5.0 5.0	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38177	P V								5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38170	P V								5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38172	P V								5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38206	P V								4.5 5	4.5 5	4.5 5	4.5 5.0	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38236	P V								5.5 5.5	4.5 4.5	5 5	5.0 5.0	5.5 5.5	5.5 5.5	5.5 5.5	5.5 5.5
38169	P V	8/21	.14	none	.25	.175	33		.5 .5	.5 .5	.5 .5	.5 .5	.5 1	.5 1	.5 1	.5 1.0
37909	P V								.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5
38147	P V								.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5	.5 .5
38161	P V		.14	none	.5	.35			.5 1	.5 1	.5 1.5	.5 1.2	1.5 1.5	.5 1	.5 1.5	.8 1.3
38226	P V								.5 1	.5 1	.5 1	.5 1.2	1.5 1.5	1 1	1 1.5	1.2 1.3
38154	P V								.5 1	.5 1	.5 1.5	.5 1.0	1 1	.5 1	.5 1.5	1.2 1.3
38163	P V		.14	none	1	.7			1 2.5	1.5 3	1 2.5	1.2 2.7	2.5 3	2.5 3	2.5 3	2.5 3.0
38156	P V								2 3	1.5 3	1.5 3	1.7 3.0	3 3	3 3	3 3	3.0 3.0
37848	P V								2 3	1.5 3	2 3	1.8 3.0	2.5 2	2.5 3	3 3	2.7 2.7

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38144	P V	8/21	.21	none	.25	.2625	33		.5 .5	.5 .5	.5 .5	.5 .5	.5 1	.5 1	.5 1	.5 1.0
38143	P V								.5 1	.5 1	.5 1	.5 1.0	1.5 1.5	1.5 1	1.5 1.5	1.5 1.3
38142	P V								.5 1	.5 1	.5 1	.5 1.0	1.5 1.5	1.5 1	1.5 1.5	1.5 1.3
37828	P V		.21	none	.5	.525			1 2	1 2	.5 2	.8 2.0	2 2	2 2	2 2	2.0 2.0
38212	P V								1 2	.5 2	.5 2	.7 2.0	2 2	2 2	1.5 2	1.8 2.0
38162	P V								.5 2	.5 2	.5 2	.5 2.0	1.5 2	2 2	1.5 2	1.7 2.0
37967	P V		.21	none	1	1.05			2 2.5	1.5 2.5	1.5 2.5	1.7 2.5	2.5 3	2.5 3	2.5 2.5	2.5 2.8
38155	P V								1.5 3	1.5 3	1.5 3	1.5 3.0	2.5 3	2.5 3	2.5 3	2.5 3.0
38148	P V								2 3	2 3	1.5 3	1.8 3.0	2.5 3.5	3 3.5	2.5 3.5	2.7 3.5

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
37974	P V	8/21	.42	none	1	2.1	33		3 4	2.5 4	2.5 4	2.7 4.0	3.5 4.5	4.0 4	3.5 4	3.7 4.2
37981	P V								2.5 4	2.5 4	2.5 3.5	2.5 3.8	3.5 4	3.5 4	3.5 4	3.5 4.0
37964	P V								2.5 4	2.5 4	2.5 4	2.5 4.0	3.5 4.5	3.5 5	3.5 4	3.5 4.5
37816	P V		.42	none	.25	.525			1 3	1 3	1 3	1.0 3.0	2.5 3	2.5 3	2.5 3	2.5 3.0
37971	P V								1.5 2.5	1 2.5	1 2.5	1.2 2.5	2.5 3	2.5 3	2.5 3	2.5 3.0
37778	P V								.5 2.5	.5 2.5	.5 2.5	.5 2.5	1.5 3	2 2.5	1.5 2.5	1.7 2.7
37831	P V		.42	none	.5	1.05			1 1.5	1.5 1.5	.5 1.5	1.0 1.5	2.5 3	2.5 3	2.5 3	2.5 3.0
37848	P V								1.5 3.5	2.5 3.5	1.5 3.5	1.8 3.5	3 4	3 4	2.5 4	2.8 4.0
37815	P V								3 3	2.5 3	3 3.5	2.8 3.2	3.5 4	3.5 4	3.5 4	3.5 4.0

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	MMH (ppm)	INTER- FERANT	CONDITIONS	RH (%)	TEMP (C)	HOURS OF EXPOSURE				
								.25	.5	.75	1	2
37839	P V	8/29		SUN	DIRECT	HORIZ		.5 0	1 0	1.5 0	1.5 0	1.5 0
37830	P V					VERT		.5 0	1.5 0	1.5 0	1.5 0	2 0
37849	P V				DIFFUSE	HORIZ		.5 0	.5 0	.5 0	.5 0	1 0
37879	P V					VERT		.5 0	.5 0	.5 0	.5 0	1 0

PDAB color dots were read on vanillin scale

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38229	P V	9/13	.0896	none	.25	.224	40		.5 .5	.5 .5	1 1	.7 .7	1 1	1.5 1	1.5 1	1.5 1.0
38222	P V								1.5 1.5	1.5 1.5	2 1	1.7 1.3	2.5 1.5	2.5 1.5	2.5 1	2.5 1.3
38228	P V								1.5 1	1.5 1	1.5 1	1.5 1.0	2.5 1	2.5 1	2 1	2.3 1.0
38201	P V		.0896	none	.5	.448			2.5 2	2 1.5	2.5 1.5	2.3 1.7	2.5 2	2.5 1.5	3 2	2.7 1.8
38193	P V								2.5 2	2.5 2	2.5 2	2.5 2.0	2.5 2.5	2.5 2.5	3 2	2.7 2.3
38234	P V								2.5 2	2.5 2	2.5 2	2.5 2.0	2.5 2	2.5 2.5	3 2.5	2.7 2.3
38125	P V		.0896	none	1	.896			3.5 2	3.5 2	2.5 1	3.2 1.7	4 2.5	4.5 2.5	4.5 2.5	4.3 2.5
38199	P V								2.5 2	2 2	2.5 2	2.3 2.0	3 2	3 2	3 2	3.0 2.0
38125	P V								2 1.5	2.5 1.5	1.5 1.5	2.0 1.5	2 1.5	2 1.5	2 1.5	2.0 1.5
38062	P V		.0896	none	2	1.792			3.5 2.5	3 2.5	3.5 3	3.3 2.7	3.5 3	3.5 2.5	3.5 2.5	3.5 2.7
38063	P V								3 2.5	3 2.5	3.5 3	3.2 2.7	3 3	3.5 2.5	3 3	3.2 2.8
38046	P V								3.5 3	3.5 3	4 3	3.7 3.0	4 3.5	3.5 3	4 3.5	3.8 3.3
38061	P V		.163	none	.25	.4075	40		1 2	1 1	1 2	1.0 1.7	2 2	2 2	2 2	2.0 2.0
38069	P V								1 1	1.5 2	1 1	1.2 1.3	2 1	2 1	2 1	2.0 1.0
38070	P V								1 1	1 1	1 1.5	1.0 1.2	2 1.5	2 1.5	2 1.5	2.0 1.5
38059	P V		.163	none	.5	.815			1.5 1.5	1.5 1.5	1 1	1.3 1.3	2.5 2.5	2.5 2.5	2 1.5	2.3 2.2
38060	P V								1.5 1.5	1.5 1.5	1 1	1.3 1.3	2.5 2.5	2.5 2.5	2 3	2.3 2.7
38045	P V								1.5 1.5	1.5 1.5	1.5 1.5	1.5 1.5	2.5 2.5	2.5 2.5	2.5 2	2.5 2.3

GMD COLOR BADGE LOG SHEET

I.D. #	BADGE TYPE	DATE	Hz (ppm)	INTER-FERANT	TIME (hrs)	DOSE TLV-hrs	RH (%)	TEMP (C)	T=0				T=1			
									1	2	3	Aver	1	2	3	Aver
38080	P V	9/15	.163	none	1	1.63	40		2.5 2.5	2.5 2.5	2.5 2	2.5 2.3	3 3.5	2.5 2.5	3 3	2.8 3.0
38081	P V								2.5 0	2.5 0	2.5 0	2.5 .0	3.5 0	3 0	3 0	3.2 .0
38082	P V								3.5 2.5	2.5 2.5	2.5 2	2.8 2.3	3.5 3	3.5 3	3.5 3	3.5 3.0
38064	P V		.163	none	2	3.26	40		3.5 3	3.5 3	3.5 3.5	3.5 3.2	3.5 4	3.5 4	3.5 4	3.5 4.0
38077	P V								3.5 2.5	3 2.5	3.5 3	3.3 2.7	3.4 3	3 3	3 3	3.1 3.0
38093	P V								3.5 3.5	3.5 3.5	3.5 3	3.5 3.3	3.5 4	3.5 4	3.5 4	3.5 4.0
38072	P V		.163	none	2	3.26	80		3 3	3 3	3 3	3.0 3.0	4.5 3.5	4 3.5	4 4	4.2 3.7
38078	P V								2.5 3.5	3 3.5	3 3.5	2.8 3.5	3.5 4	4 4	3.5 4	3.7 4.0
38079	P V								2.5 3.5	3 3.5	3 3.5	2.8 3.5	3.5 4	3.5 3.5	3.5 4	3.5 3.8
38076	P V	9/19	.163	none	2	3.26	25		4.5 4	4 4.5	4 4	4.2 4.2	4.5 5	4.5 5	4.5 5	4.5 5.0
38083	P V								4.5 4	4.5 4	4.5 4	4.5 4.0	5 5	4.5 5	4.5 5	4.7 5.0
38065	P V								4.5 4	4 4.5	4.5 4.5	4.3 4.3	5 4.5	5 5	5 5	5.0 4.8
38075	P V		.0896	none	2	1.792	25		1.5 1	1.5 1	1.5 1	1.5 1.0	2.5 1.5	2.5 1.5	2.5 1	2.5 1.3
38073	P V								2.5 2	2.5 2	2.5 1.5	2.5 1.8	4 2.5	4.5 2	4.5 2	4.3 2.2
38074	P V								2.5 2	2.5 2	2.5 2	2.5 2.0	3.5 2.5	3.5 2.5	3.5 2	3.5 2.3

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13. ABSTRACT (Maximum 200 words) Materials were evaluated for potential use as ambient air sample lines for unsymmetrical dimethylhydrazine (UDMH) and hydrazine. FEP (a fluorinated polymer) and high density polyethylene tubing materials reached the maximum response levels for TLV and lower concentrations of UDMH. Sample lengths of 23m and 61m were investigated for their effect on performance. Other areas examined were humidity, conditioning the sample tubing, and cleaning agents. High density polyethylene performed the best after ambient air conditioning of the tubing.				
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MATERIAL CAPABILITY FOR TRANSPORT OF UNSYMMETRICAL DIMETHYLHYDRAZINE

INTRODUCTION

The use of hydrazine (Hz), monomethyl hydrazine (MMH), and unsymmetrical dimethyl hydrazine (UDMH), especially as high energy propellants, has increased dramatically in recent years. Substantial quantities of hydrazines are used as propellants in Titan ballistic-missiles, satellites, and aircraft auxiliary-power units. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Studies indicate that exposure to hydrazines may cause damage to the liver, kidneys, and other internal organs and may produce blood abnormalities. Hydrazines not only cause physical damage but also alter the behavior of personnel by significantly decreasing performance capabilities [1]. A recent study cites irreversible damage to the nervous system as a possible consequence of hydrazines exposure [2]. Effects in man can be teratogenic as well as mutagenic. The adverse effects extend to nonmammalian life forms, thereby potentially endangering the environment.

Since the hydrazines are suspected carcinogens, a maximum tolerated toxic level has been set at five parts-per-million (ppm). The American Conference of Governmental and Industrial Hygienists (ACGIH) has recommended the threshold limit values (TLV) of Hz, MMH, and UDMH to be 100, 200, and 500 parts-per-billion (ppb), respectively [1]. Potentially this level may be lowered to 10 ppb for all three hydrazines [3]. To protect personnel from overexposure, NASA, the Air Force, and the Department of Defense, require air monitoring for hydrazines in areas where they are handled and/or stored.

For several reasons, it is desirable to monitor a number of these potential exposure sites with one fixed-point analyzer. The analyzer would sample through a network of tubing in which sections may be 61 m (200 ft) or more in length. For many ambient air contaminants this method of sampling would pose no addition problems, but due to the reactive nature of hydrazines and their known interaction and decomposition on surfaces, the transport tubing could significantly affect the concentration of hydrazines reaching the analyzer. This is particularly a concern when measuring the sub-ppm levels necessary with hydrazines.

This report describes the results of a materials compatibility study comparing the ability of several commercially available tubings to transport levels of UDMH at TLV and lower concentrations under various conditions. In addition, several of the tubings were spot checked with hydrazine. Most of the studies in this report used UDMH as the work was funded by the Air Force Space Division. The liquid fuel used in the Titan missile is Aerozene-50, which is a 50:50 mix of UDMH

and hydrazine. The vapor pressure of UDMH is 10 times greater than that of hydrazine. Therefore, a spill of the liquid will initially result in a 10 times greater vapor concentration of UDMH than hydrazine.

The objective of this study was to determine which tubing type(s) optimally transport UDMH contaminated air. Variables studied for their effects on tubing performance include: relative humidity (RH), length of tubing, conditioning with ambient air, and various wash solutions. An extensive tubing survey was conducted in 1985-1986 for MMH. A memorandum report describing the results was published [4]. The current project was designed to investigate many of the same parameters for UDMH and to spot check with hydrazine. This study was approached as a survey rather than a statistical analysis due to the time allotted and the number of variables to be investigated. This report supplements our previous report by including tests with the other hydrazine fuels.

TEST AND EVALUATION PROTOCOL

The wall adsorption characteristics of several tubing materials were examined using 0.5 ppm UDMH in air at room temperature humidified to approximately 40-60% RH. Table 1a lists the tubings tested during the evaluation. Table 1b details the chemical composition of those tubings [5]. The tubing characteristics were determined by comparing the response of the analyzer to a known concentration gas stream with and without a coil of test tubing in place between the instrument and the gas generation system. All of the initial tests were conducted using 23 m, 0.63 cm (75 ft, 1/4 in) internal diameter tubing of the following types: Teflons (PFA, FEP, TFE), Polyethylene, High Density Polyethylene, Polypropylene, and Bev-A-Line [6]. Bev-A-Line tubing with an internal diameter of 0.95 cm (3/8 in) was also examined.

In addition, the better materials were tested in lengths up to 61 m (200 ft). The effect of relative humidity on these materials was examined with a known UDMH concentration. Response time for hydrazine at 0.1 ppm was also investigated. The effect of aging and deterioration was investigated by exposing these materials to ambient air for one month prior to UDMH exposure. Alternative cleaning methods, including both gases and liquids, were investigated for materials exposed to prolonged ambient conditions.

All tests were conducted using air generated by the NRL gas generation system which is described in detail in the Experimental section. The response times to first indication, 50%, 75%, 90%, and maximum response were recorded. The 23 m lengths were tested for a maximum of 60 minutes. The longer tubing was examined for a longer period of time if needed. The tubing exposures to UDMH continued for up to eight hours following the prolonged ambient air exposure if needed. Tubing was cleaned by flushing with methanol and purged with clean air between each test.

Table 1a. Tubings Evaluated

Tubing Type	Reference	OD (in)	ID (in)	Supplier	Manufacturer
Bev-A-Line IV	BAL	3/8	1/4	Read	Thermoplastic Scientific
Bev-A-Line IV	BAL 1/2	1/2	3/8	Read	Thermoplastic Scientific
TFE Teflon	TFE	3/8	1/4	Read	Atlantic Tubing Company
PFA Teflon	PFA	3/8	1/4	Read	Atlantic Tubing Company
FEP Teflon	FEP	3/8	1/4	Read	Atlantic Tubing Company
High Density Polyethylene	HDPE	3/8	1/4	Read	Hudson Extrusions Inc.
Polypropylene	PP	3/8	1/4	Read	Atlantic Tubing Company
Polyethylene	PE	3/8	1/4	NRL	unknown

Read: Read Plastics, Rockville MD

NRL: Naval Research Laboratory

Table 1b. Chemical Composition of Tubing Materials

Tubing Type	Reference	Chemical Composition
Bev-A-Line IV	BAL	polyethylene liner, ethyl vinyl acetate shel.
Bev-A-Line IV	BAL 1/2	polyethylene liner, ethyl vinyl acetate shell
TFE Teflon	TFE	tetrafluoroethylene
PFA Teflon	PFA	tetrafluoroethylene - perfluoropropyl vinyl ether
FEP Teflon	FEP	tetrafluoroethylene - hexafluoropropylene
High Density Polyethylene	HDPE	high density polyethylene
Polypropylene	PP	polypropylene
Polyethylene	PE	polyethylene

EXPERIMENTAL

A schematic of the test apparatus is shown in Figure 1. The air supply was house compressed air conditioned by passing it through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular-sieve scrubber, and finally through a canister containing potassium permanganate coated alumina (PURAFIL) and charcoal. The clean air was rehumidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of relative humidity was achieved by varying both the gas washer head pressure and the ratio of rehumidified to dry air. A mass flow controller passed zero grade, humidified air through a chamber where the humidity was measured by a hygrometer. The amount of diluent air varied from 5.9 l/min to 7.9 l/min depending on the desired concentration of UDMH or hydrazine. The UDMH or hydrazine gas stream flowed into one of two pyrex glass manifolds. Similarly humidified zero grade air was passed into the other manifold. The analyzer and the coil of tubing to be tested were connected to the manifold system by a two-way Teflon valve and a Teflon tee. The valve controlled the flow of clean air or contaminated gas from the manifold system. An auxiliary pump was used in conjunction with the analyzer to pull a total of 3 l/min through the coil of tubing to be tested.

Unsymmetrical dimethylhydrazine and hydrazine vapors were generated from diffusion tubes held at a constant temperature in a water bath. The UDMH or hydrazine was swept from the diffusion tube with 100 ml/min dry nitrogen to the above mentioned manifold system. Impinger samples were collected at the contaminated gas manifold to verify the concentration and were analyzed by coulometric titration with bromine using amperometric endpoint detection. The coulometric method is the NRL/NASA-White Sands modification of reference 7, in which we miniaturized the system to improve sensitivity. This concentration measurement was performed before and after each tubing challenge test.

Real-time monitoring of ppb levels of UDMH and hydrazine was accomplished using one of two instruments. The majority of tests utilized the Thermedics Model 141-1 hydrazine analyzer (TECO), which is a chemiluminescence-based instrument. The Thermedics analyzer sampled a 1.5 l/min portion of the air flowing through the tubing. The response time of this instrument is a few seconds which is considered to be real-time for our purposes. The results used for comparison were normalized to the full scale deflection (FSD) of the instrument, which was established during the concentration verification procedure, before and after each test. During the evaluation procedure, numerous problems were encountered with the instrument and it was replaced with an MDA Scientific Inc., Model 7100 instrument. The MDA 7100 is a commercially available paper tape instrument which measures the color change that develops upon exposure to a hydrazine. The intensity of the color is proportional to the concentration. The color is measured and the concentration is printed every minute. This technique has few interferences and worked well in these studies.

A typical tubing UDMH or hydrazine challenge experiment consisted of three steps. First, the contaminated air stream was sampled through a 1.8 meter long, 0.32 cm I.D. teflon tube and the maximum reading was established and recorded. Simultaneously the UDMH or hydrazine concentration was measured by coulometric analysis. These values were later used to calculate the

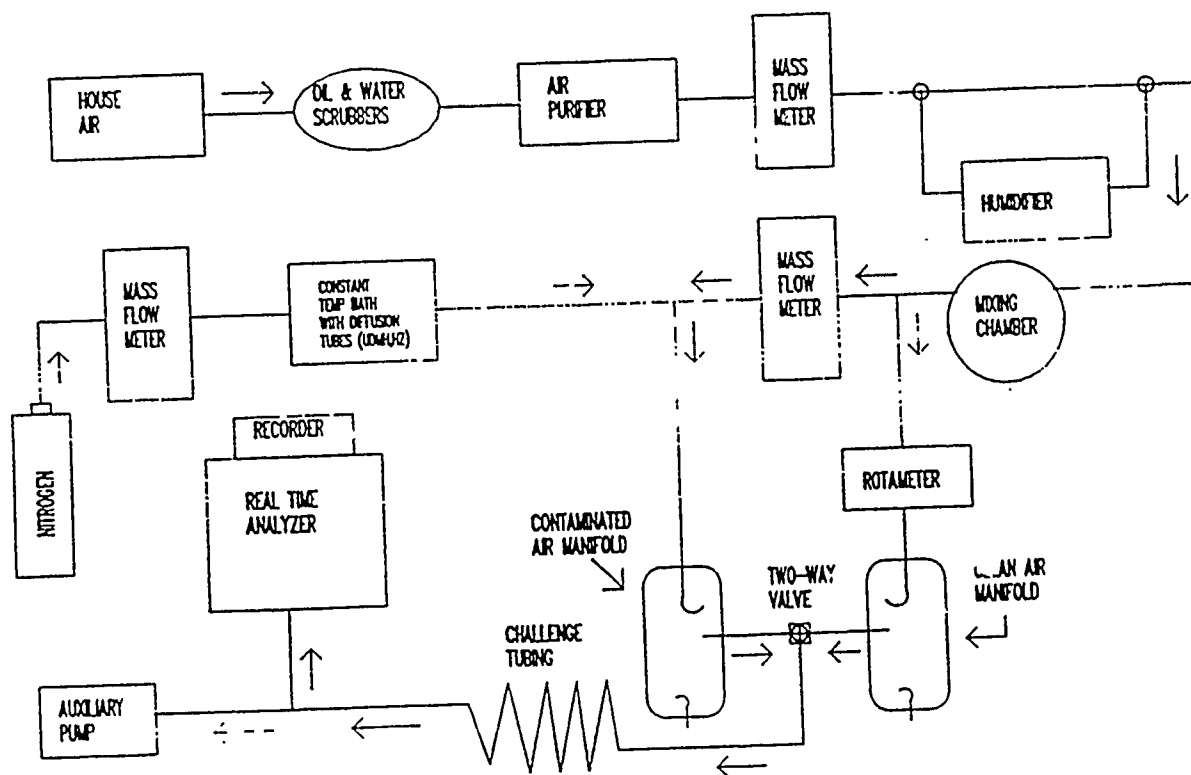


Figure 1. Apparatus for Evaluation of Tubing Materials

amount of UDMH or hydrazine transported by a coil of sample tubing in comparison to the amount detected without the coil. Next, the two-way valve shown in Figure 1 was switched to sample clean air. When the concentration of the hydrazine dropped below detectable limits (about 10 ppb) the subject tubing was inserted between the two-way valve and the 1.8 m tubing. A throttle valve on the auxiliary pump was adjusted so the total flow through the tubing was 3 l/min. The tubing was allowed to equilibrate by flowing humidified clean air through it for approximately 10 to 20 minutes. The two-way valve was switched to contaminated air, allowing the instrument to sample UDMH or hydrazine gas from the manifold.

When the instrument response to UDMH or hydrazine stabilized, the two-way valve was switched to clean air. The instrument response was allowed to return to baseline level and the challenge tubing was removed from the test system. The contaminated air stream was again sampled through the 1.8 meter tubing to monitor the maximum reading.

An example of the data is shown in Figure 2. This data was used to determine the times required to reach first indication, 50, 75, 90, and 100 percent of the challenge gas concentration without the tubing coil in place. The first indication and the time to 50 percent were comparable in many cases. When 100 percent transport was not achieved, the maximum percentage of UDMH or hydrazine transported and the time required to reach that value was recorded.

At the end of a test, the tubing was rinsed with methanol and dried with compressed breathing air or filtered compressed house air. Solvents such as acetone were not used as they react with hydrazines [8].

Table 2 lists the combinations of tubing length, UDMH or hydrazine concentration, and relative humidity (RH) which were examined. Relative humidities from 0 to 86% were selected to mimic, as closely as possible, the extremes of expected field conditions. Tubing in 23 m lengths were exposed to contaminated air for a maximum of 60 minutes. Sixty-one meter lengths were exposed until the readings were stable. With few exceptions, each test was run at least three times. The initial testing of 23 m lengths at TLV UDMH were repeated up to eight times. All of the figures in the Results Section reflect the average of all the exposure results for a given series of tests. Variations and additions to the experimental set-up and design are discussed where applicable in the next section. The appendix includes tables of all data obtained.

RESULTS AND DISCUSSION

Initial UDMH Screening Exposures

The results were very erratic in many of the tests. The fluctuations occurred for each tubing under different conditions. The selection of candidate tubings for testing at 23 m lengths was based on known or assumed compatibility with hydrazines. A 23 m length of 0.635 cm (0.25 in) ID tubing has a volume of 0.73 l, hence the minimum response time is 0.24 min. For a 61 m length of tubing with the same ID, the volume is 1.9 l and the minimum response time is 0.64 min. The first series

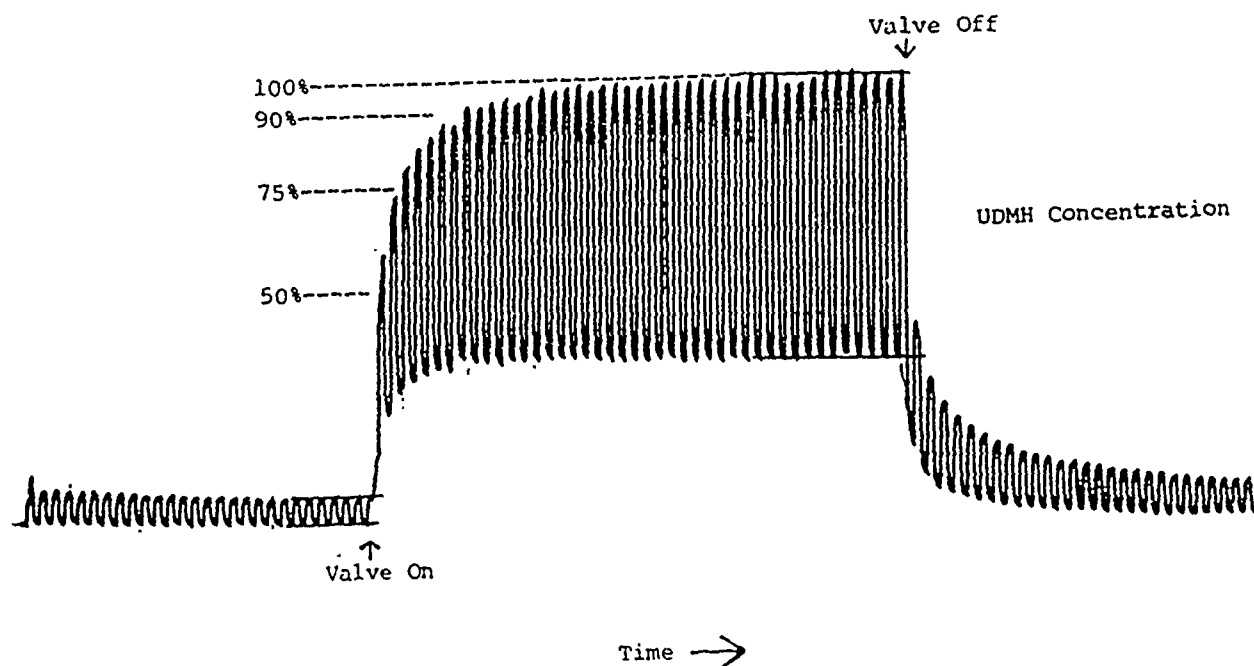


Figure 2. Instrument response to UDMH through subject tubing. This is a chart recorder trace from the TECO which cycles between sample and background channels. Unlike MMH and hydrazine, UDMH produces a response in the background channel.

Table 2. Parameters for Tubing Evaluation

Gas	Gas Conc. (ppb)	Tubing Length (m)	Tubing Length: (ft)	RH (%)
UDMH	300	23	75	0
UDMH	300	23	75	37
UDMH	500	23	75	0
UDMH	500	23	75	37
UDMH	500	61	200	0
UDMH	500	61	200	37
UDMH	500	61	200	85
UDMH	250	61	200	0
UDMH	250	61	200	37
UDMH	250	61	200	85
Hydrazine	100	61	200	37
Hydrazine	150	61	200	37
Hydrazine	200	61	200	37

of tests involved TLV levels of UDMH at 35% RH. Figure 3 shows the response times to 50, 75, and 90% of UDMH transported down the various tubing types. Polypropylene (PP), TFE, and polyethylene (PE) displayed the shortest response times, while PFA consistently gave the longest response time to 90% at 12 minutes. High density polyethylene (HDPE) and Bev-A-Line (BAL) gave the widest range in response times to 90%. HDPE achieved 90% in 3.0 to 24.3 minutes, while BAL required from 1.4 to 18.0 minutes to reach 90% of transport. Of the tubings tested, FEP gave the most repeatable response times to 90%. It reached 50% in 1.2 to 6.3 minutes. At these conditions, all of the tubings transported 100% of the UDMH; however, polyethylene and TFE reached 100% in 4 out of 7 exposures.

All 23 m lengths of tubing with the exception of FEP and PFA were exposed to TLV UDMH at 0% RH. Figure 4 shows the pertinent data in a bar graph. The results were very inconsistent from test to test for high density polyethylene and TFE. High density polyethylene responds to 90% from 0.9 to 24.9 minutes, while the range in response times to 90% for TFE is 1.8 to 26.9 minutes. Although the response time to the 90% level for polyethylene appears short, the tubing reached 90% in only 2 out of 3 tests. Therefore, it also gives inconsistent response times.

Figure 5 shows the response times of 23 m lengths of several types of tubings at 300 ppb of UDMH and 35% RH. All tubings achieved the 50% level with comparable response times. With the exception of the 6.0 minute response time to 75% of full scale for polypropylene, the tubings attained 75% with comparable response times. The average response times to 90% vary between tubing types. However, the greatest variations were in replicate exposures of each tubing. The response times for polypropylene at 90% were the most nonrepeatable. In one test the response time to 90% was 7 minutes, while in another test the tubing never reached 90% during the 60 minute exposure. Polyethylene and Bev-A-Line also gave very erratic response times from test to test.

At this point in the evaluation period, four of the tubings tested at 23 m were chosen to complete the test plan. These were Bev-A-Line, polyethylene, FEP teflon, and high density polyethylene. None of the tubings out-performed the others; therefore, they were chosen on the basis of cost, possibility of crimping, and flexibility.

Relative Humidity Effects

Sixty-one meter lengths of tubing were used in the next series of tests. The effects of relative humidity (% RH) and varying concentrations of UDMH and hydrazine were investigated. The tubings were exposed to TLV UDMH at 0% RH. Response times to first indication and 50% of transport were comparable between the four tubings. With the exception of the 4.7 minute response time to 75% for Bev-A-Line, the tubings performed similarly to 75% of full scale. The response times to 90% varied as shown in Figure 6. FEP showed the shortest response time to 90%, while Bev-A-Line never reached 90% during the exposures. Polyethylene and high density polyethylene reached 90% in 3 out of 4 tests.

At TLV UDMH and 35% RH, the response times to first indication and 50% were comparable for all four tubings. At 90%, the polyethylene, high density polyethylene, and Bev-A-Line tubings

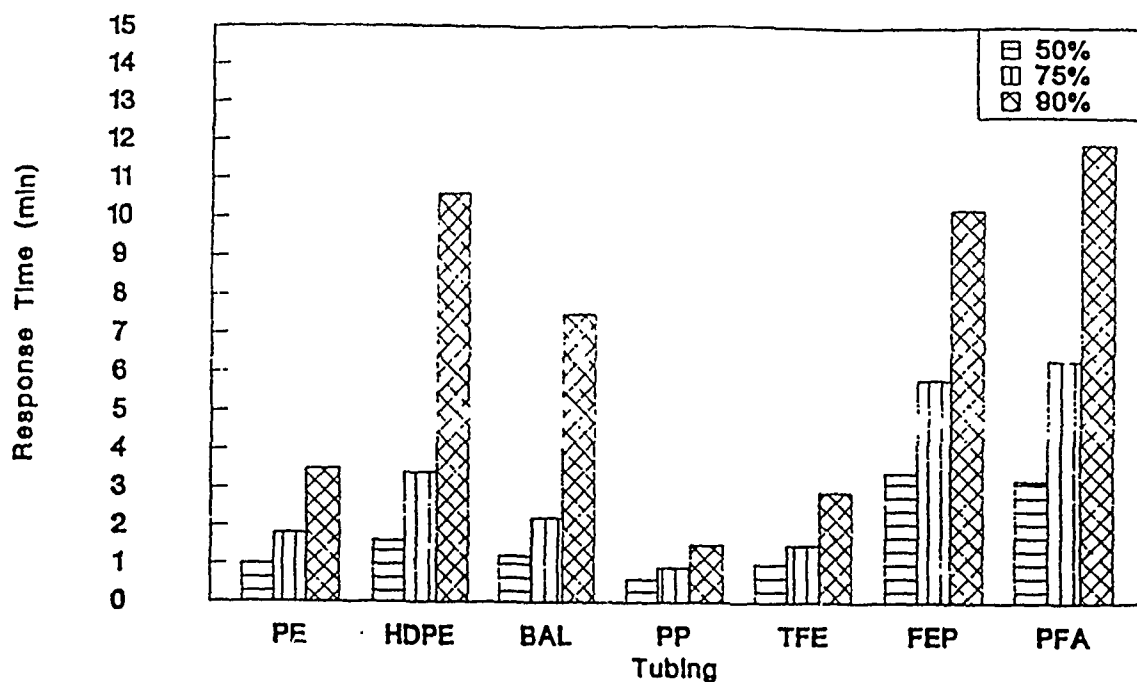


Figure 3. Response times of 23 m (75 ft) of tubing to TLV UDMH at 35% RH

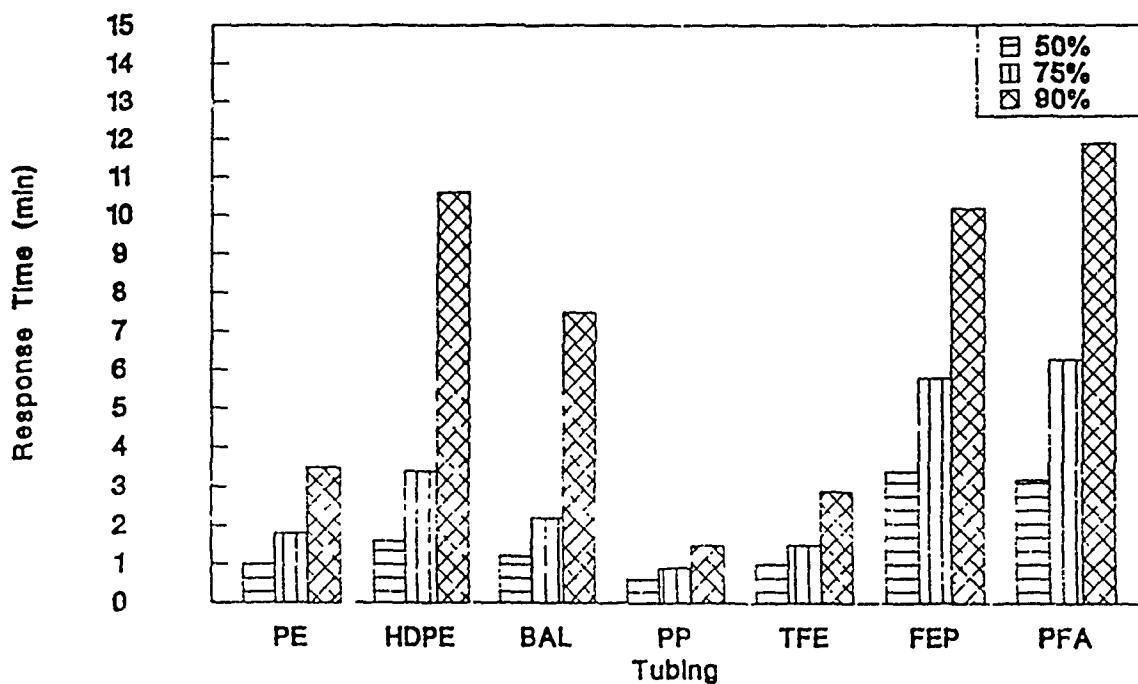


Figure 4. Response times of 23 m (75 ft) of tubing to TLV UDMH at 0% RH

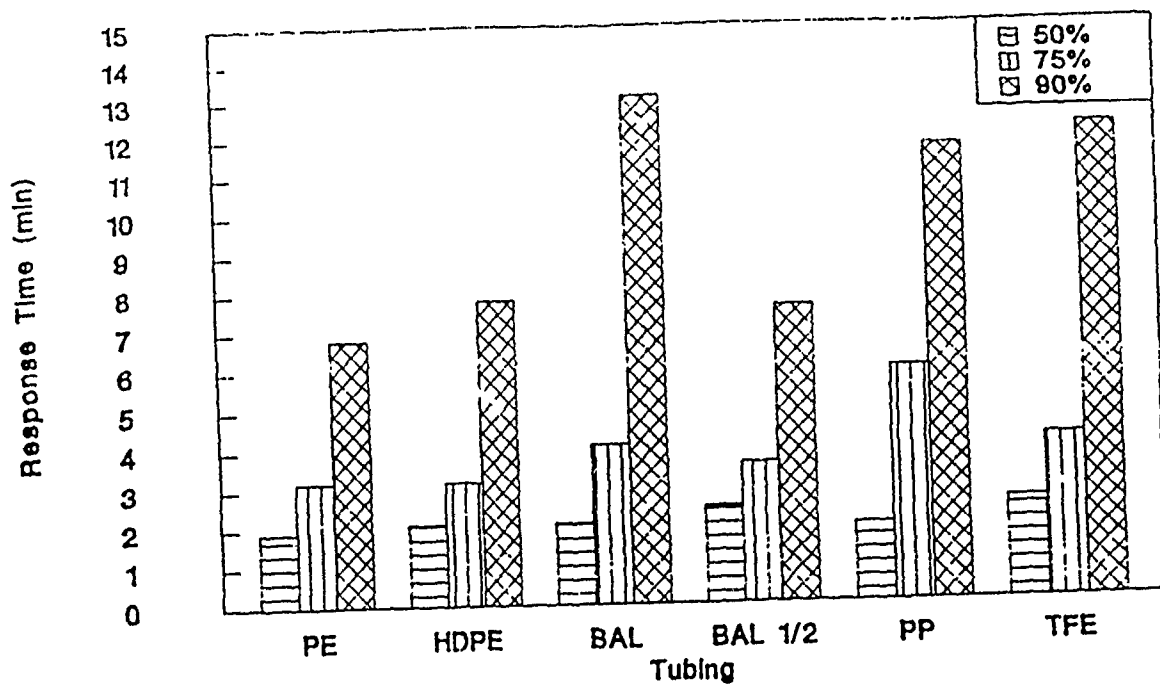


Figure 5. Response times of 23 m (75 ft) of tubing to 300 ppb of UDMH at 35% RH

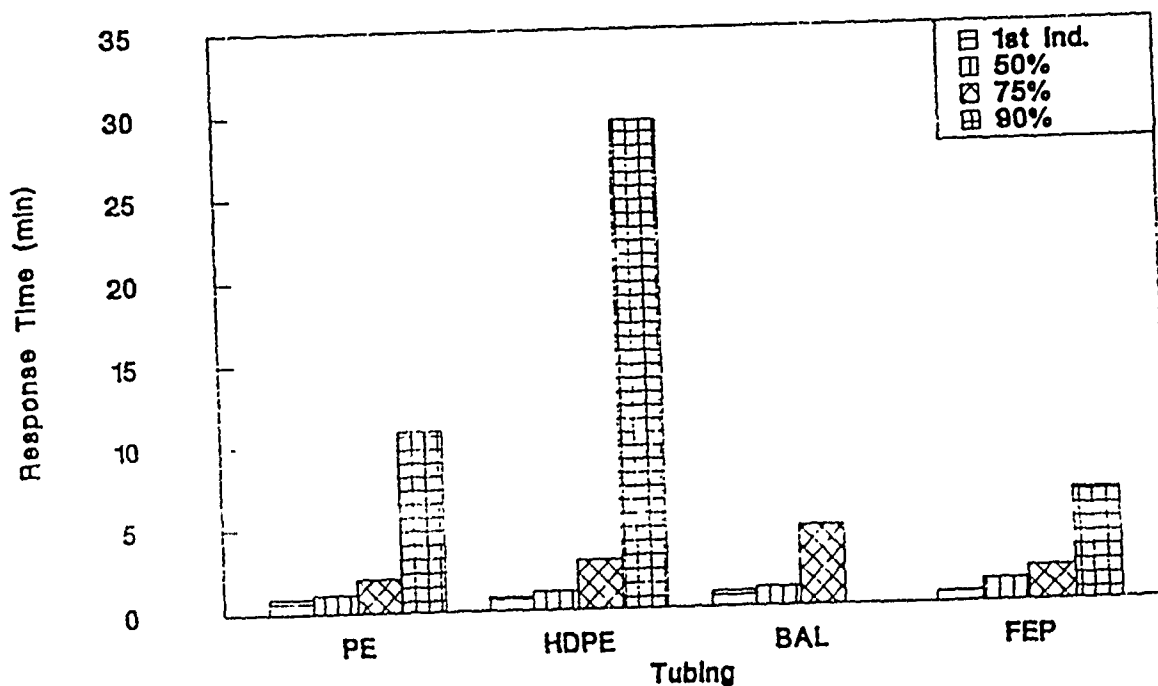


Figure 6. Response times of 61 m (200 ft) of tubing to TLV UDMH at 0% RH

responded similarly. The FEP gave much shorter response times to 75% and 90%. Figure 7 shows the various response times at these conditions.

The MDA 7100 was used for the polyethylene and HDPE tubing samples for exposure to TLV UDMH at 80% RH. These two tubings were exposed to these conditions later in the testing period after the Thermedics instrument had ceased to function properly. As shown in Figure 8, the shortest response times to 50%, 75%, and 90% were attained by high density polyethylene, while FEP had the shortest time to first indication. High density polyethylene reached 90% by 20 minutes. It took the polyethylene almost 50 min to attain 90% of full scale. The response times to 90% of Bev-A-Line and FEP fall within those of high density polyethylene and polyethylene.

The aforementioned tubings were also exposed to approximately 250 ppb (half the TLV) of UDMH at 0, 45, and 85% RH. Figures 9, 10, and 11 show the data for these exposures. At 0% and 45% RH, the response times to first indication are comparable for all tubings. At 85%, the response times to first indication are twice as long as those at 0% and 45% RH. At all three humidities, the response times to 50%, 75%, and 90% for polyethylene tubing were longer than the other tubings. At 0% RH, polyethylene did not reach 90% for any of the exposures to UDMH. High density polyethylene and Bev-A-Line reached 90% in 2 out of 3 exposures. FEP performed the best, reaching 90% in 15 minutes. At 45% RH, FEP appeared to perform the best, however, it only reached 90% in 1 out of 3 tests. Polyethylene achieved 90% full scale in 2 out of 3 tests. At 85% RH, polyethylene achieved 90% in only 1 out of 3 tests.

Comparisons can be made between exposures of 61 m of tubing to TLV UDMH and the same length of tubing at 250 ppb. Most of the tests showed a faster response at higher concentrations. Bev-A-Line and polyethylene responded more quickly to TLV levels of UDMH than to half that concentration at all the humidities tested. High density polyethylene responded faster to TLV UDMH at 0% and 85% RH. At mid range RH, the tubing gave shorter response times when exposed to one-half TLV. The FEP tubing responded to TLV UDMH at 0% RH fairly quickly. At 45%, the tubing reached 90% of full scale at one-half TLV quickly, however, it only attained 90% in 1 out of 3 exposures. At low and mid range RH, FEP gave quicker response times when exposed to TLV levels of UDMH. At high humidity, FEP attains 50, 75, and 90% of full scale faster at 250 ppb.

Relative humidity effects on the tubings are varied. Figures 12-15 show relative humidity effects on 61 m lengths of polyethylene, high density polyethylene, Bev-A-Line, and FEP at TLV UDMH. In most cases, increases in humidity had little effect on the response times to first indication or 50%. The 75% and 90% response times increased with increasing humidity for polyethylene and FEP. More erratic results were observed for high density polyethylene and Bev-A-Line. Bev-A-Line shows slightly longer response times with higher humidities to first indication and 50% of full scale. At 75% and 90%, there is an increase in response time from 0% RH to 40% RH, however, the average response times to 75 and 90% of full scale drop off at 85% RH. For Bev-A-Line, the response time to first indication remains stable throughout the humidity range tested. There is an increase in response times with increasing humidity to 50% and 75% of full scale. Bev-A-Line never attained 90% of full scale at 0% RH. There is a decrease in response time to 90% between 40% and 70% RH.

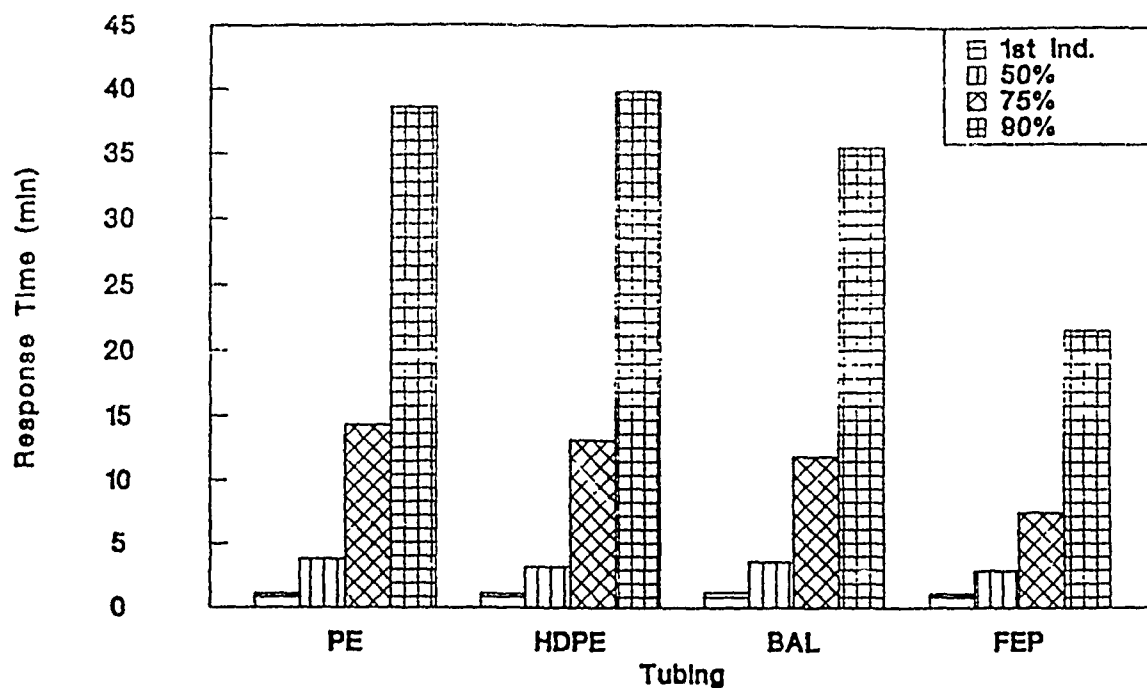


Figure 7. Response times of 61 m (200 ft) of tubing to TLV UDMH at 35% RH

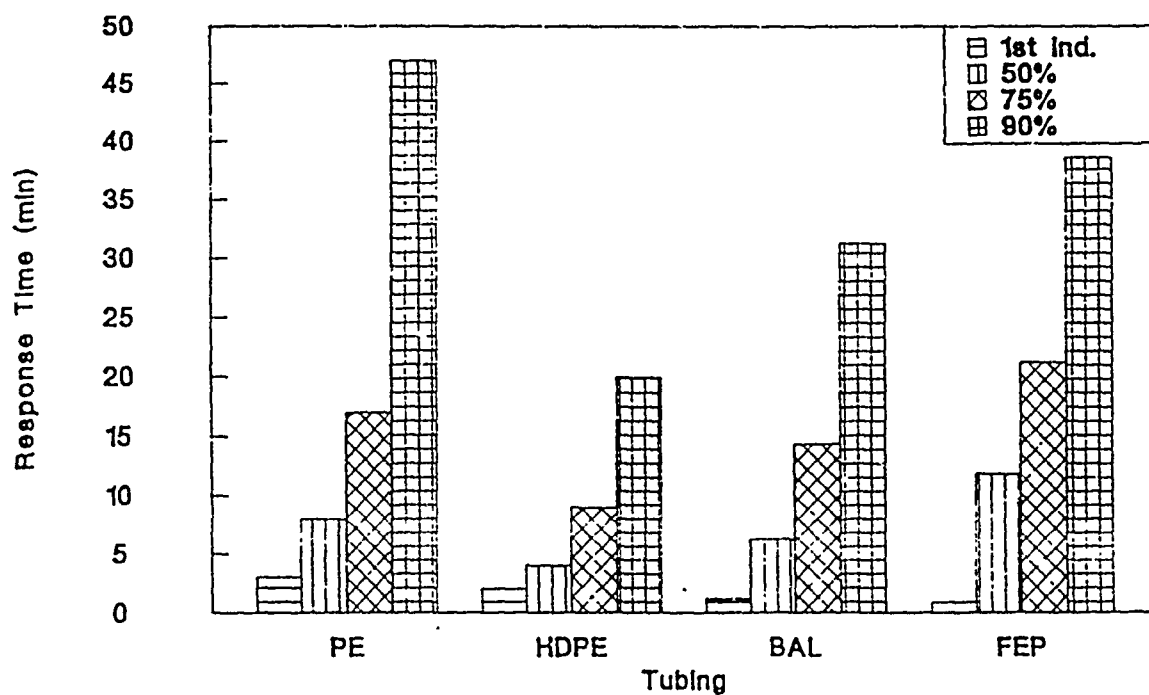


Figure 8. Response times of 61 m (200 ft) of tubing to TLV UDMH at 80% RH

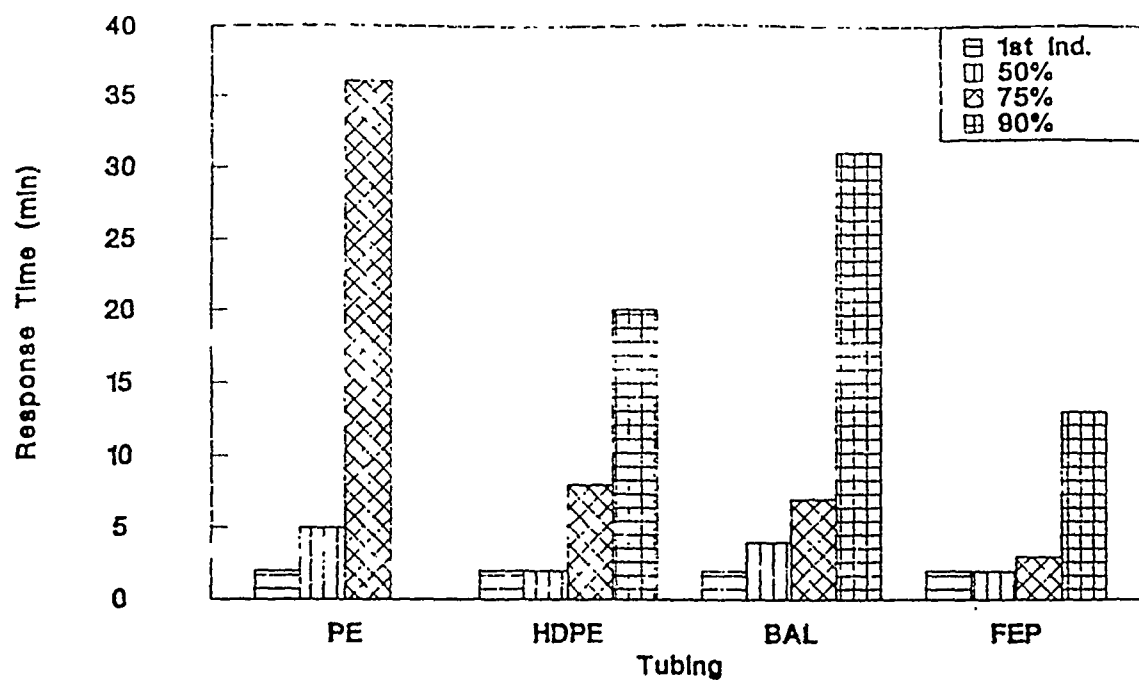


Figure 9. Response times of 61 m (200 ft) of tubing to 250 ppb UDMH at 0% RH

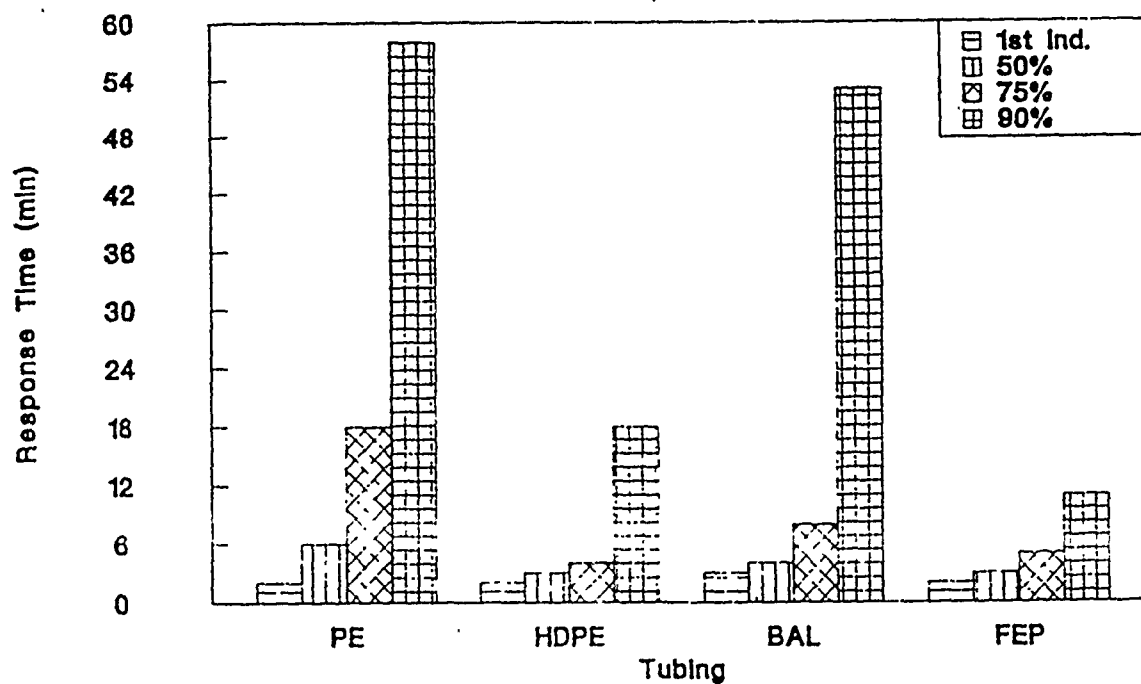


Figure 10. Response times of 61 m (200 ft) of tubing to 250 ppb UDMH at 45% RH

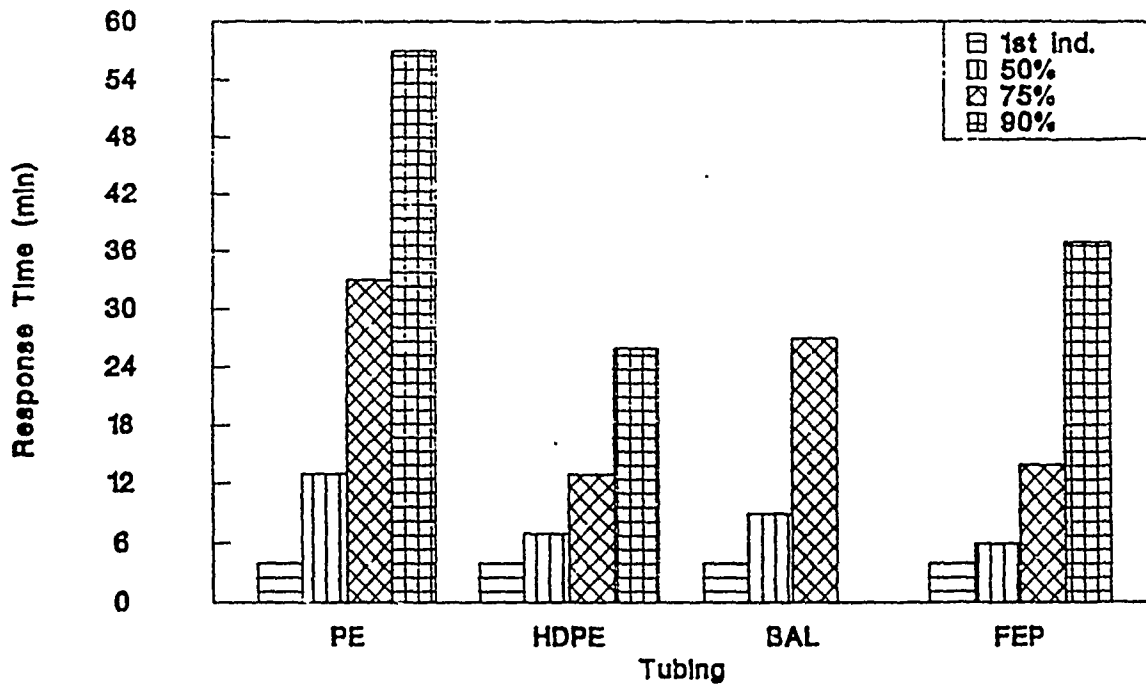


Figure 11. Response times of 61 m (200 ft) of tubing to 250 ppb UDMH at 85% RH

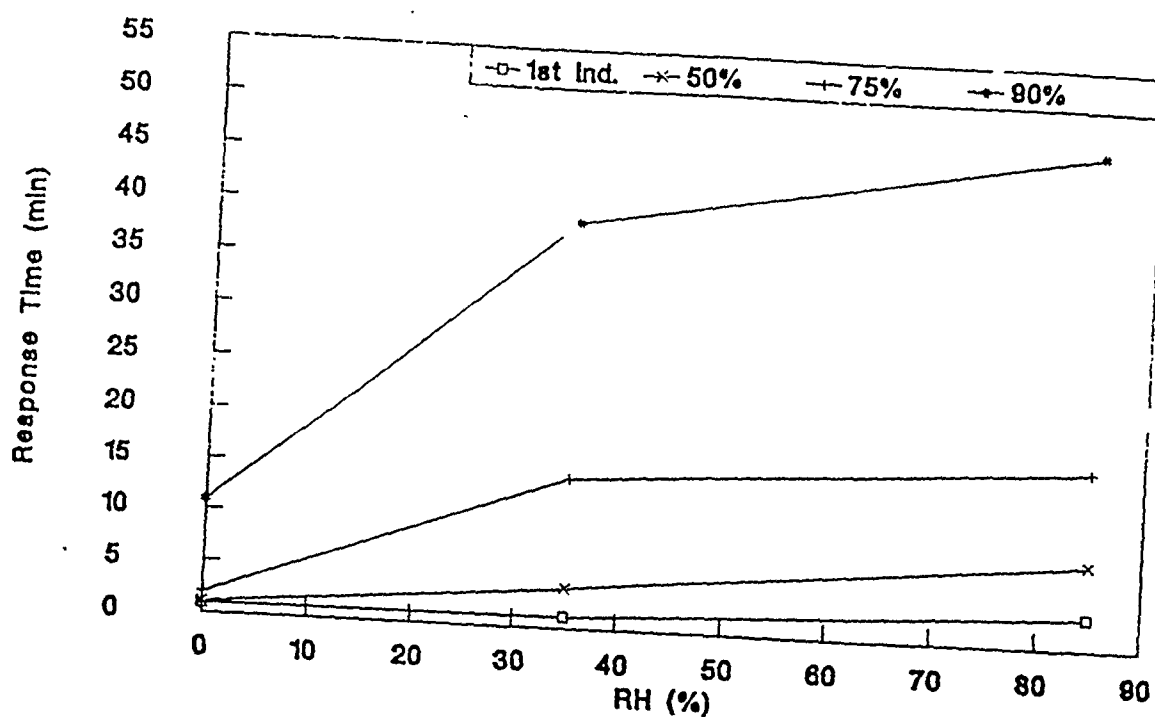


Figure 12. Relative humidity effect on 61 m (200 ft) of polyethylene exposed to TLV UDMH

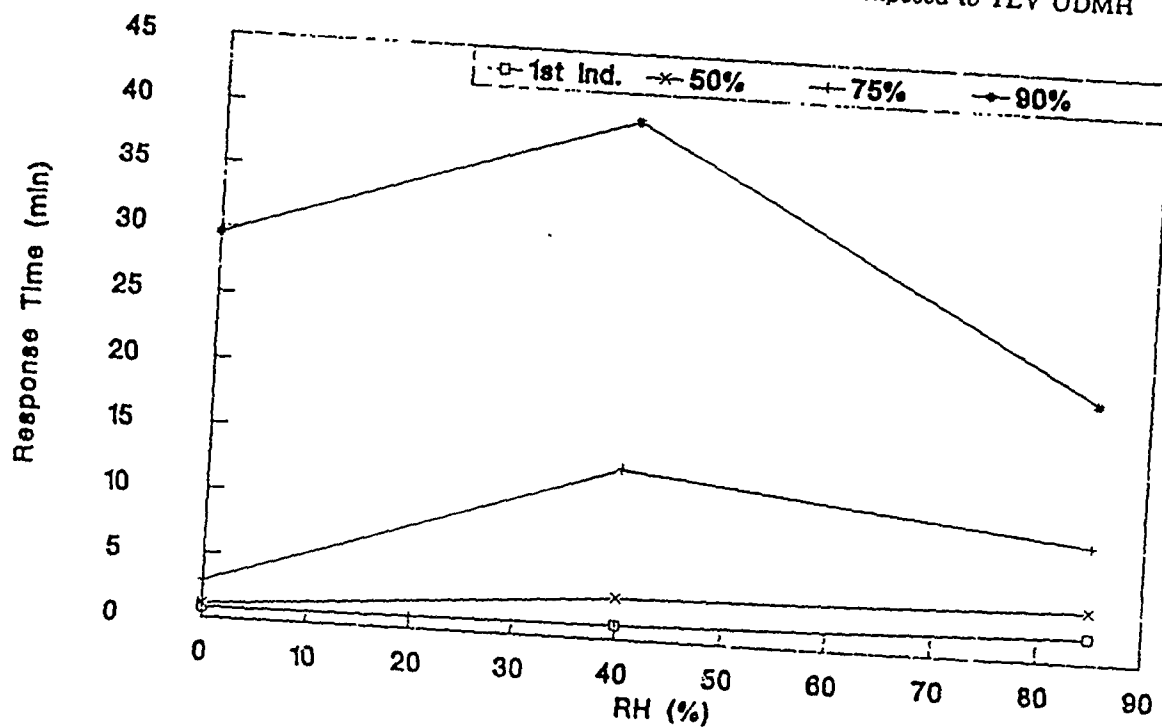


Figure 13. Relative humidity effects on 61 m (200 ft) of high density polyethylene exposed to TLV UDMH

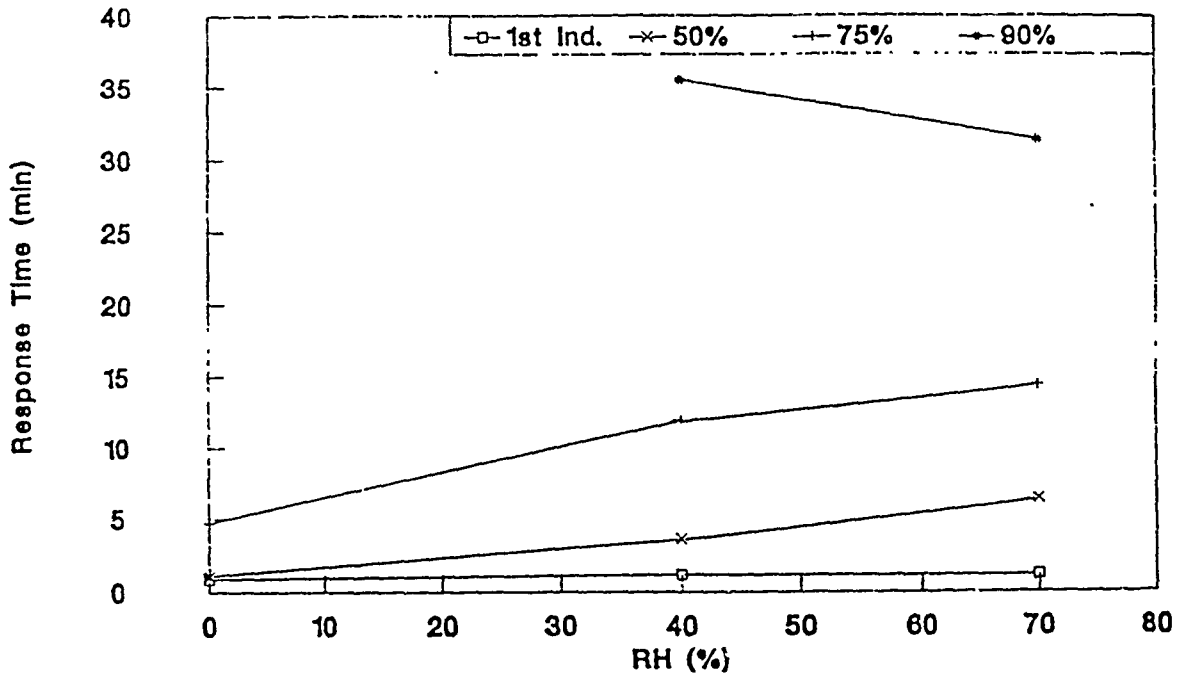


Figure 14. Relative humidity effects on 61 m (200 ft) of Bev-A-Line exposed to TLV UDMH

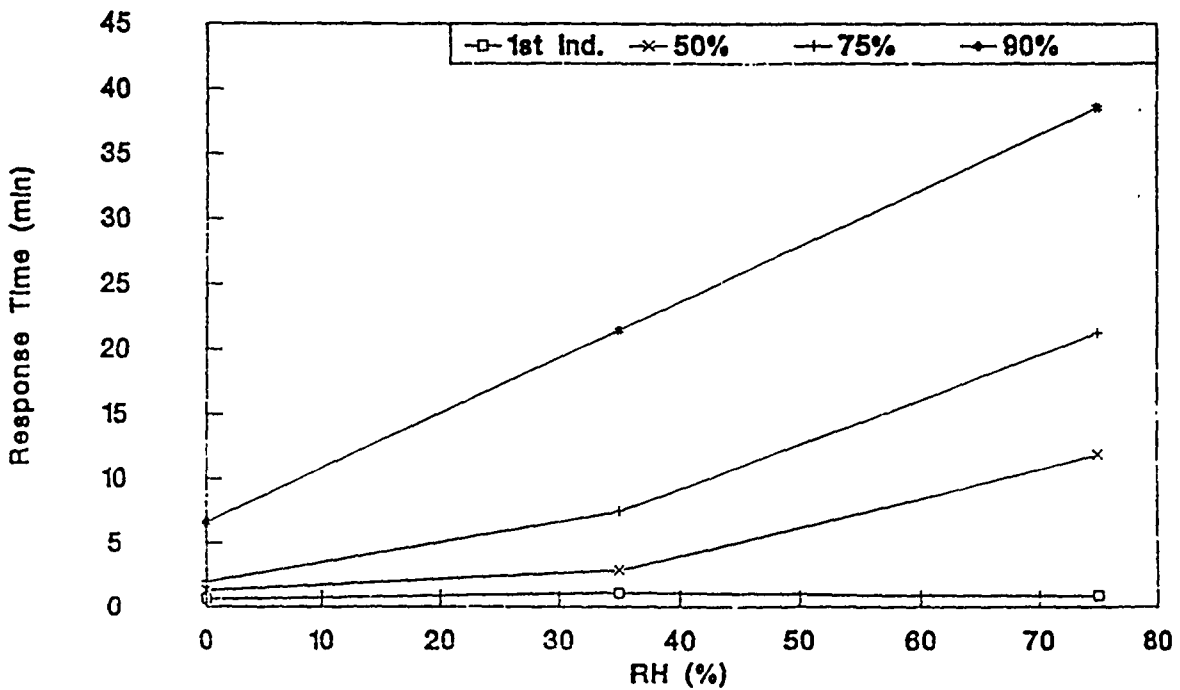


Figure 15. Relative humidity effects on 61 m (200 ft) of FEP exposed to TLV UDMH

Figures 16-19 show the humidity effect on tubing when exposed to 250 ppb of UDMH. In comparison with the responses to TLV levels of UDMH, the response times at high RH are increased from first indication to 90% of full scale for all tubings except FEP. As before, polyethylene shows a positive correlation between response time and RH at first indication and 50% of full scale. At 75% of full scale, however, polyethylene responds erratically to the various humidities tested. The tubing did not reach 90% of full scale at 0% RH. The response times remained stable between 45% and 85% RH. To first indication and 50% of full scale, high density polyethylene showed an increase in response times with an increase in RH as it had with TLV UDMH. For responses to 75% and 90% of full scale, high density polyethylene responded oppositely to its previous behavior at TLV UDMH. Bev-A-Line behaved similarly to its responses to TLV UDMH at first indication, 50%, and 75% of full scale. While Bev-A-Line never attained 90% of full scale at 0% RH with TLV UDMH, at 250 ppb it did not reach 90% of full scale at 87% RH. FEP demonstrates a positive correlation between response time and humidity to all but 90% of full scale. At 90% of full scale, the response times between 0% and 45% RH remained relatively stable, while they increased dramatically between 45% and 85% RH.

Hydrazine Exposures

Polyethylene, high density polyethylene, Bev-A-Line, and FEP were also tested with hydrazine. They were all exposed to approximately 100 ppb and 150 ppb of hydrazine. The results are shown in Figures 20 and 21. In Figure 20, all tubings except for polyethylene were exposed to hydrazine at 35% RH and analyzed with the Thermedics 141 (TECO) and the MDA 7100. The polyethylene was analyzed with the Thermedics analyzer. There is a significant difference between the response times of the HDPE taken with the TECO and the MDA 7100. With the TECO, the response times to first indication and 50% of FSD are very quick. The HDPE does not attain 75% or 90%. The response times of the Bev-A-Line are varied between the two analyzers. The Bev-A-Line did not achieve 90% when examined with the MDA 7100 as it did with the Thermedics analyzer. The FEP tubing performed similarly with both analyzers. In addition, FEP and high density polyethylene were exposed to 43 ppb and 185 ppb of hydrazine, respectively. Figures 22 and 23 detail the effect of hydrazine concentration on response time of FEP and high density polyethylene through all levels tested.

Comparisons can be made between tubing responses to TLV UDMH and TLV hydrazine at 35% RH. Polyethylene, Bev-A-Line, and FEP respond faster at first indication 50%, 75%, and 90% of FSD when exposed to UDMH. High density polyethylene attains first indication and 50% faster when exposed to hydrazine, however, it did not reach 75% or 90%. When exposed to UDMH, high density polyethylene achieved both 75% and 90%. When comparing the response times to hydrazine of the high density polyethylene taken with the MDA 7100, and those taken with the TECO, the tubing gave quicker response times to UDMH at all levels.

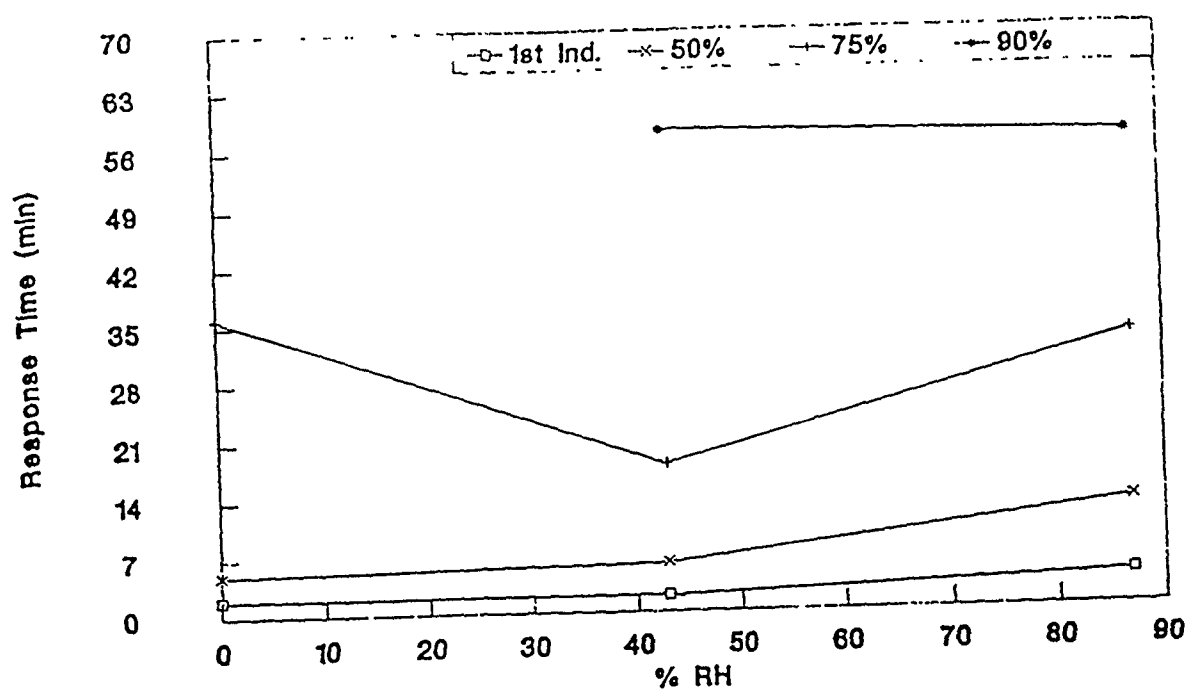


Figure 16. Relative humidity effects on 61 m (200 ft) of polyethylene exposed to 250 ppb UDMH

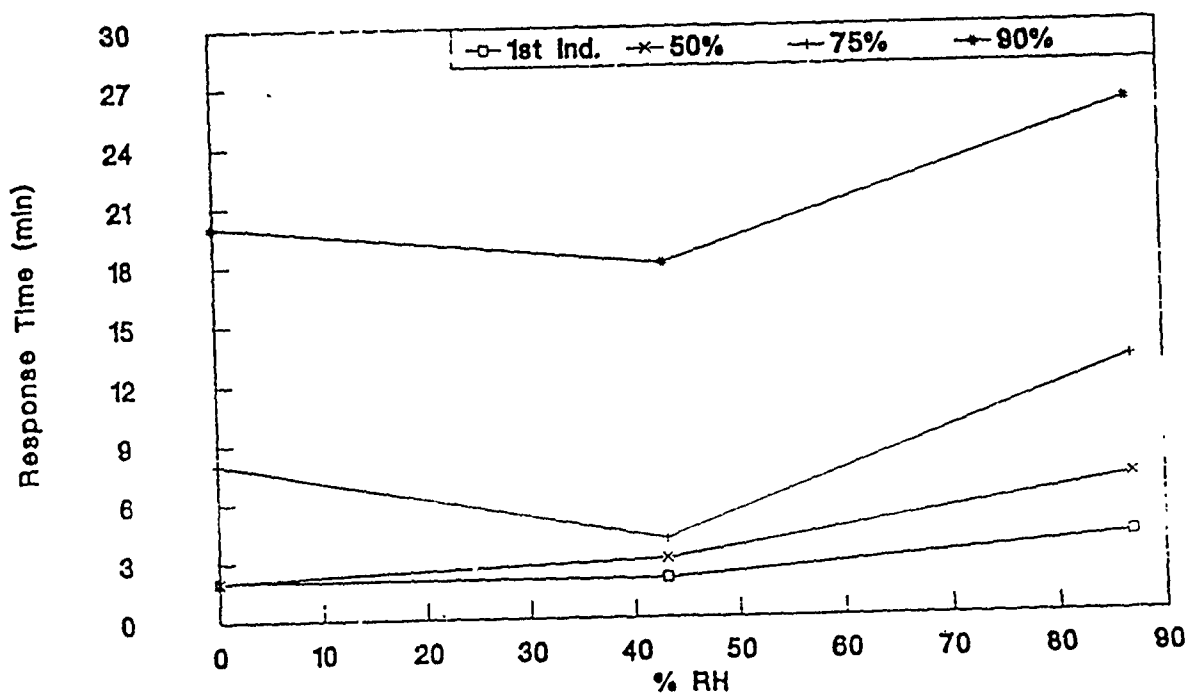


Figure 17. Relative humidity effects on 61 m (200 ft) of high density polyethylene exposed to 250 ppb UDMH

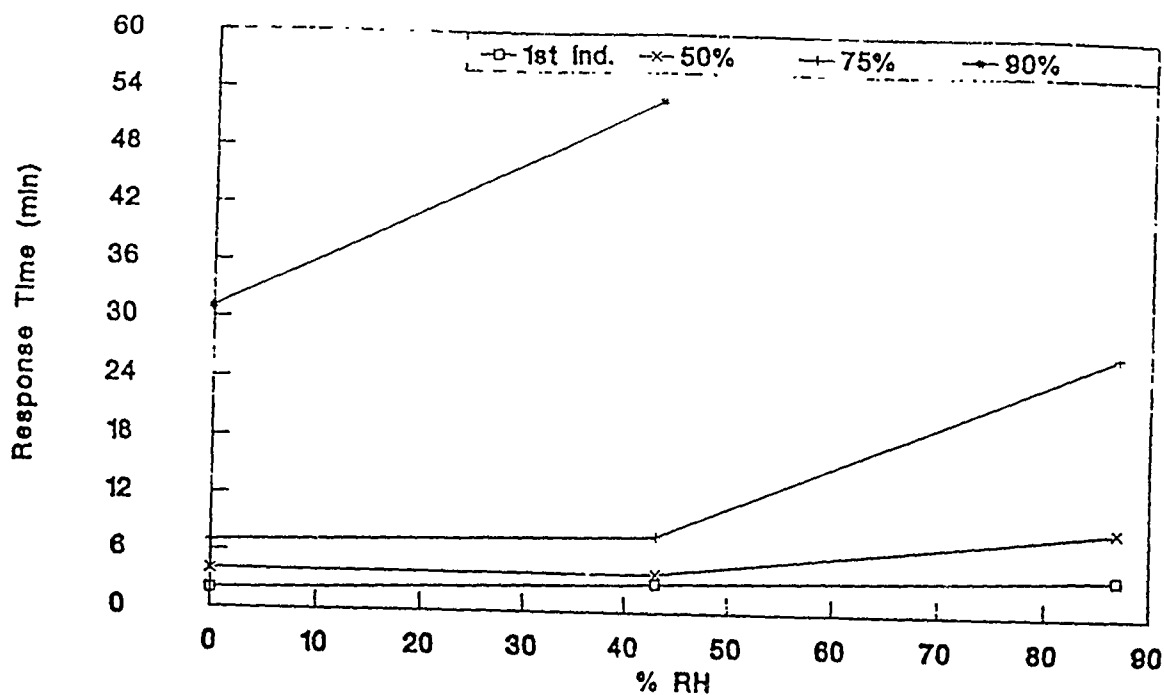


Figure 18. Relative humidity effects on 61 m (200 ft) of Bev-A-Line exposed to 250 ppb UDMH

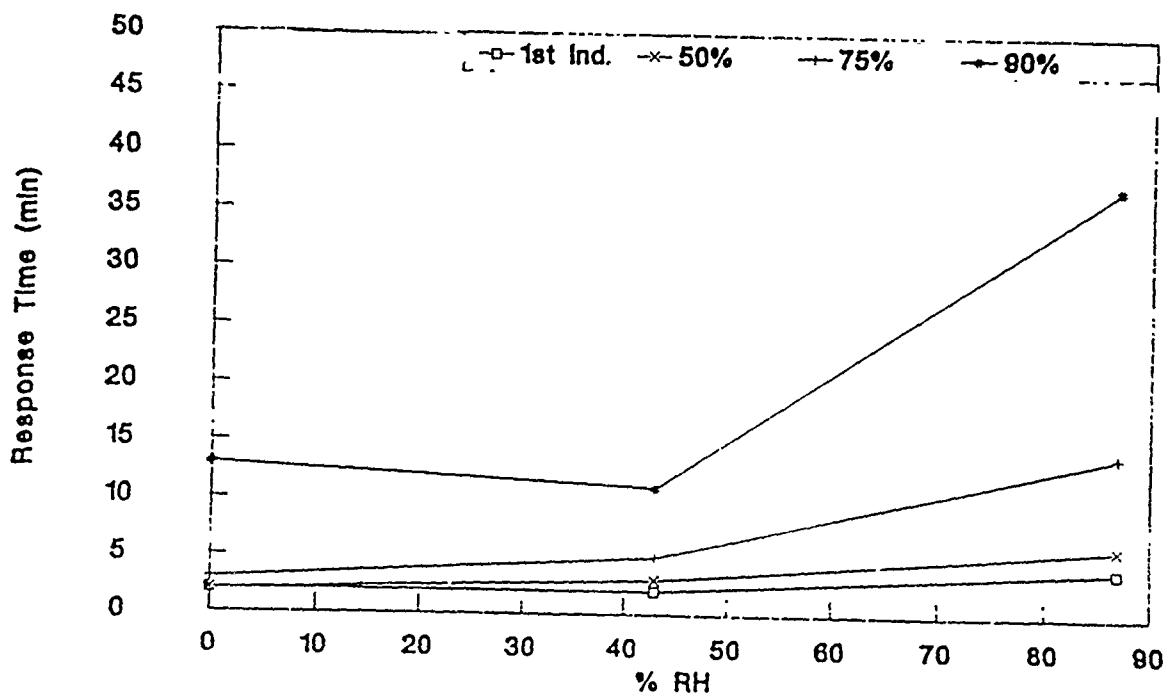


Figure 19. Relative humidity effects on 61 m (200 ft) of FEP exposed to 250 ppb UDMH

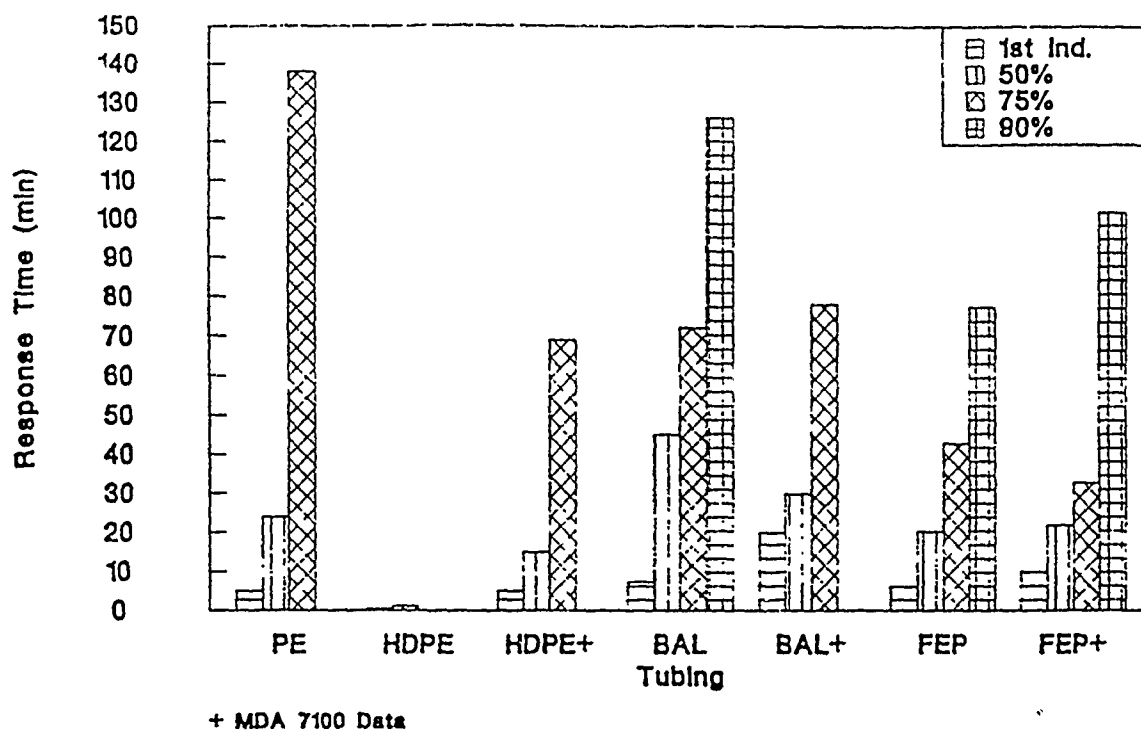


Figure 20. Response times of 61 m (200 ft) of tubing to 100 ppb hydrazine

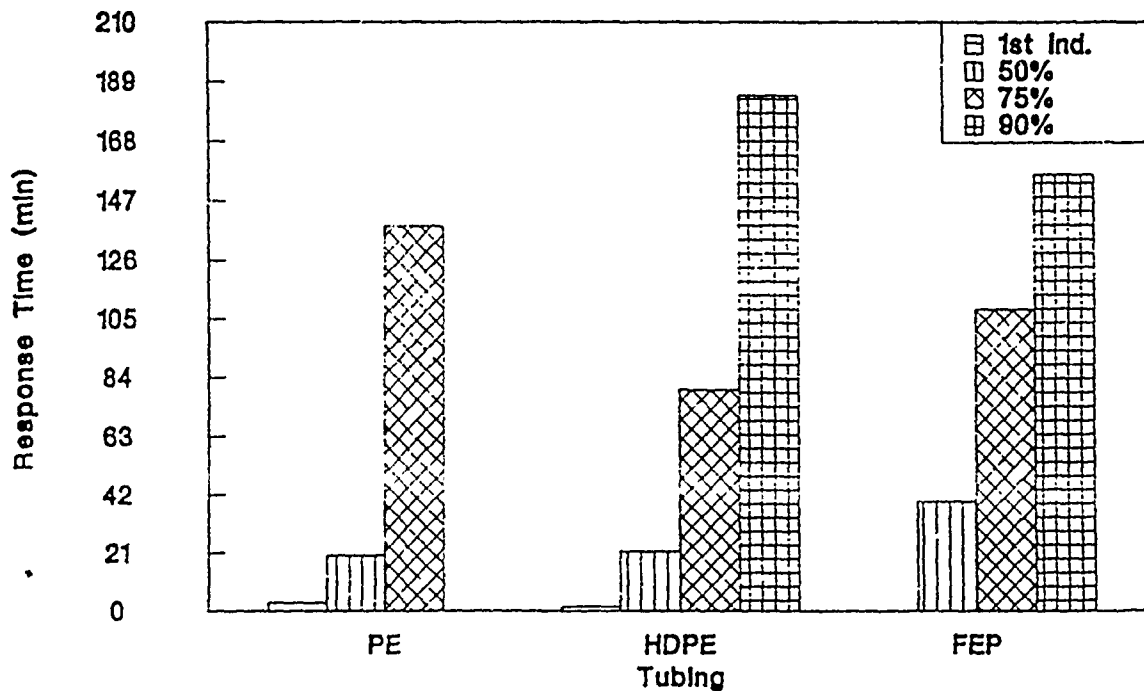


Figure 21. Response times of 61 m (200 ft) of tubing to 150 ppb hydrazine

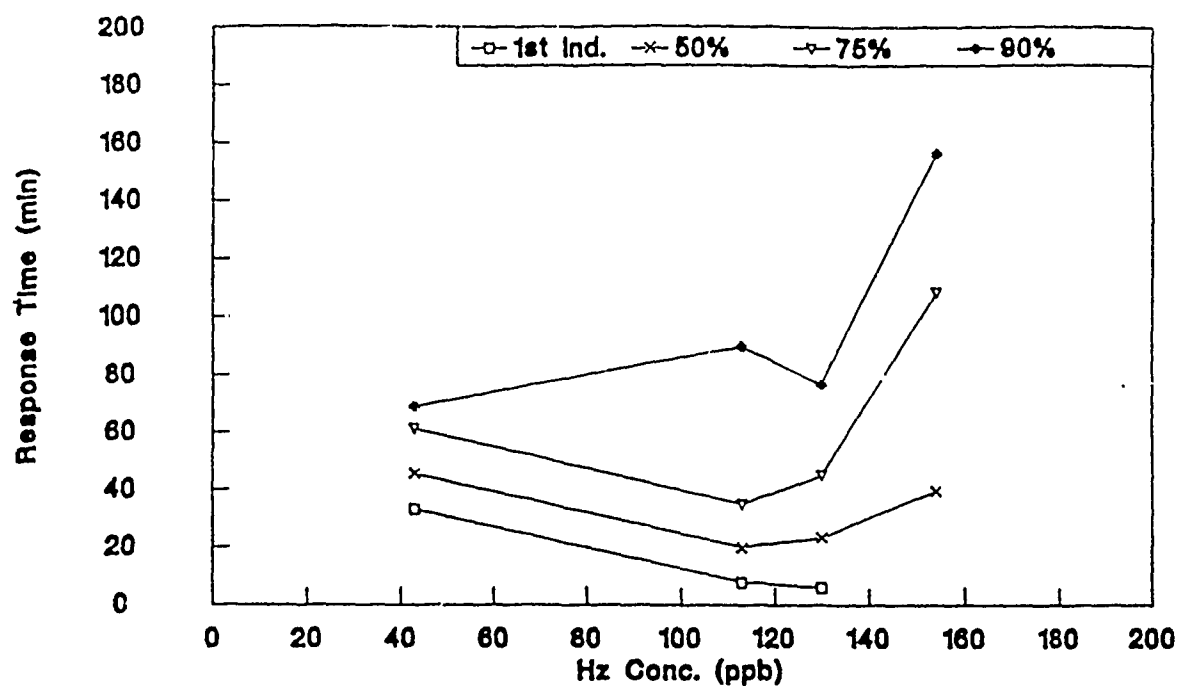


Figure 22. Effect of hydrazine concentration on 61 m (200 ft) of FEP tubing response time

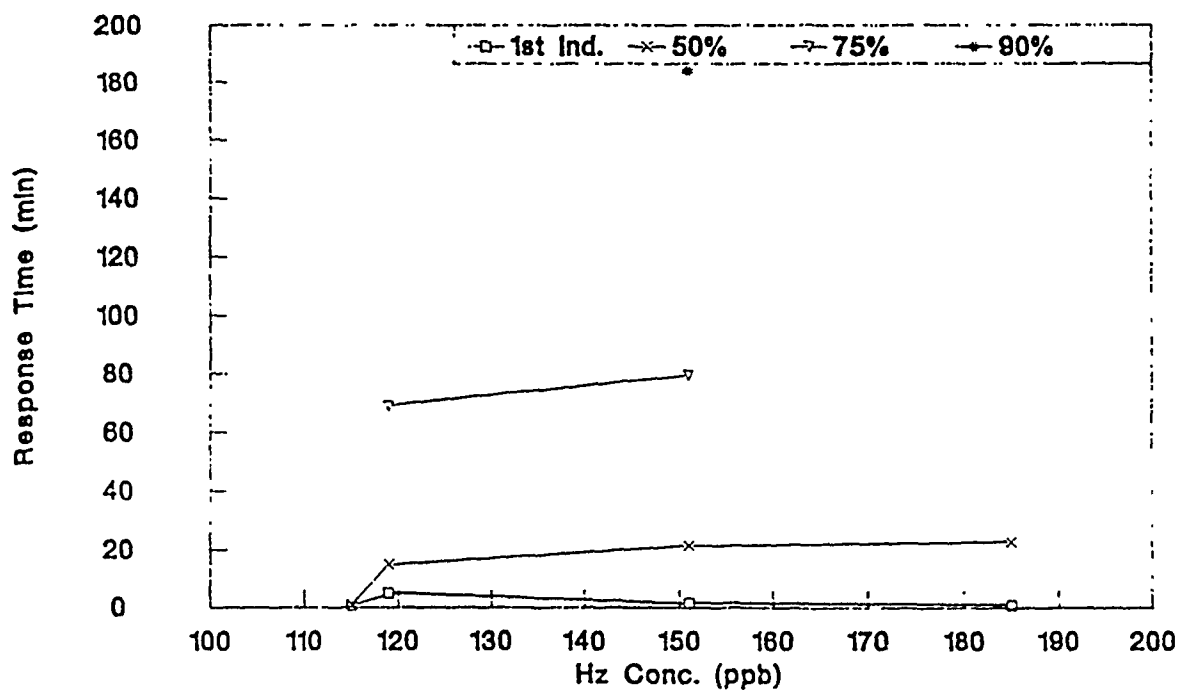


Figure 23. Effect of hydrazine concentration on 61 m (200 ft) of high density polyethylene tubing response time

Preconditioning of Tubing by Ambient Exposure

Sixty-one meter samples of the polyethylene, high density polyethylene, Bev-A-Line, and FEP tubing materials were conditioned with ambient air. This was accomplished by sampling outside air from a window on the fourth floor of the chemistry building at the Naval Research Laboratory. The sample coil and pump were sheltered, with the inlet of the tubing located in the stream of incoming ambient air. The tubings were continuously exposed for a period of one month during late summer. For two weeks, two tubings sampled air at a flow rate of 1 l/min, while the sampling rate of the other two tubings was 2 l/min. At the end of two weeks, the coils of tubing were switched. The tubings which were originally sampling air at a rate of 1 l/min were now sampling air at 2 l/min and vice versa. At the end of the month, the tubings had all sampled the same volume of air. Following the conditioning, the tubings were evaluated for transport efficiency. The tubings were exposed to TLV levels of UDMH at 35% RH and monitored. After extended conditioning with ambient air, samples showed a retardation in their ability to transport UDMH, as shown in Figure 24. FEP was affected to the greatest extent as compared with the average response times at TLV UDMH and 35% RH, requiring up to 13 times more time to reach first indication after preconditioning. The FEP did not attain 90% of full scale at all. Polyethylene required twice as much time to reach 75% and 90% of full scale, six times as long to the first indication, and three times as long to 50% of full scale. Other than the response times to first indication and 90% of full scale, high density polyethylene responded comparably to the average response time prior to preconditioning. After sampling ambient air for one month, the high density polyethylene tubing did not attain 90%. The Bev-A-Line was also affected by the preconditioning. The response times to first indication and 50% showed the greatest increase. After preconditioning, the Bev-A-Line required 4 times more time to reach the first indication, and 1.5 times as much time to attain both the 50% and 90% levels. There was no significant change in time required to reach 75%.

Effects of Cleaning Agents

Cleaning techniques were examined on the tubing exposed to ambient air for one month. After preconditioning of the tubing was complete and the tubings were exposed to UDMH, they were washed with methanol and reexposed to UDMH. In comparison with the response times to UDMH prior to ambient air exposure, FEP and Bev-A-Line responded slower to TLV levels of UDMH after ambient air exposure and subsequent UDMH exposure and methanol wash. High density polyethylene performed comparably after the ambient air exposure and methanol wash except to 90% of full scale, where twice as much time was required. Polyethylene gave quicker response times after ambient air conditioning and a methanol wash than prior to this. Exposure to UDMH and a methanol wash was repeated. The tubings were then exposed to UDMH and cleaned with 25 ppm of ammonia vapor in air. To obtain this gas concentration, a Matheson certified cylinder containing 509 ppm ammonia was diluted with clean air. The ammonia was blown through the contaminated tubing for one hour after exposure to UDMH. Exposure to UDMH and flushing with ammonia was repeated. Figures 25 and 26 show the comparisons between the ammonia and methanol wash. The polyethylene showed a greater decrease in response times after cleaning with ammonia as compared to methanol. The greatest improvements were at the 75% and 90% of full scale levels. The tubing achieved 90% of full scale in two out of three exposures.

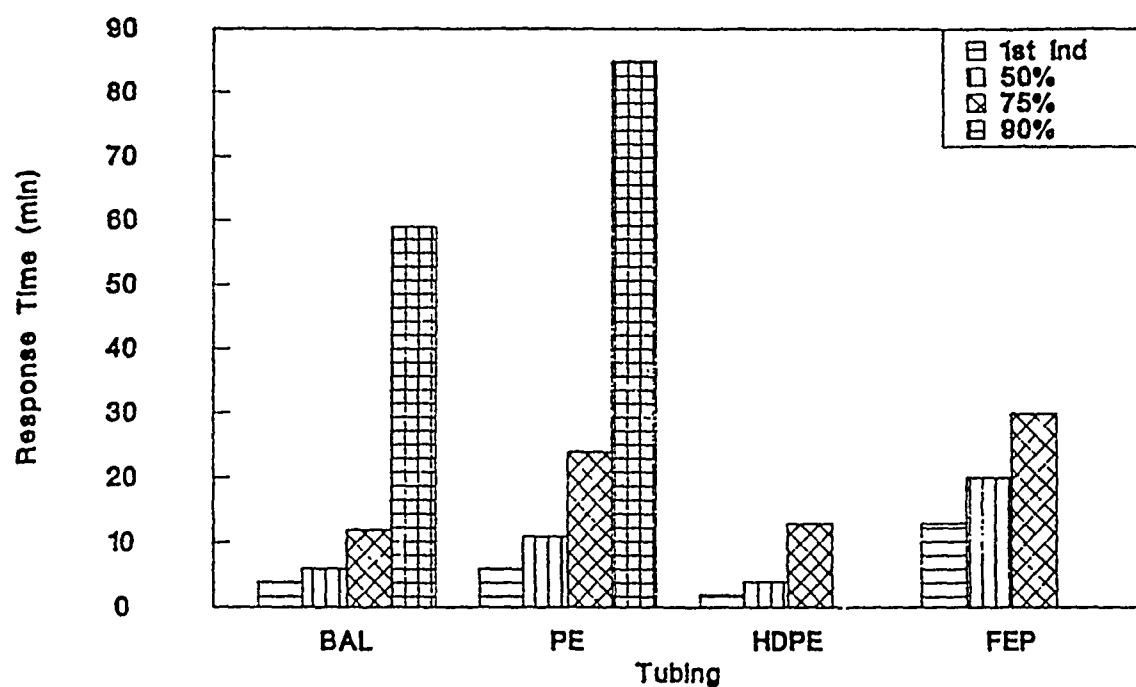


Figure 24. Response times to TLV UDMH of preconditioned tubings

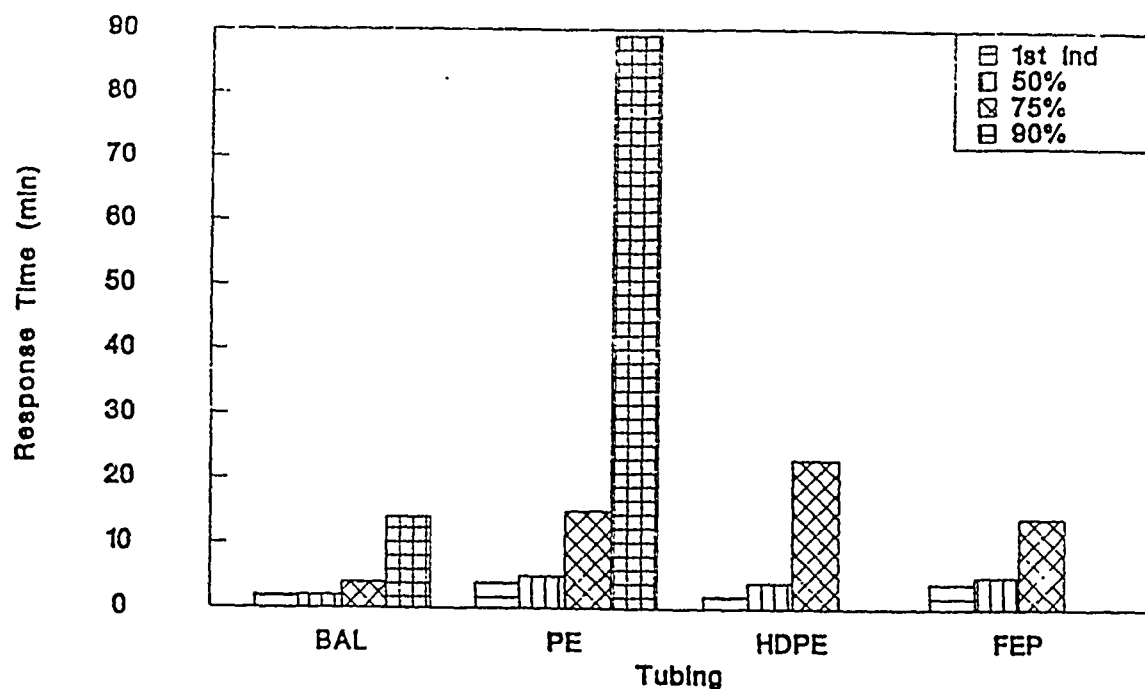


Figure 25. Response times to TLV UDMH of tubing cleaned with methanol

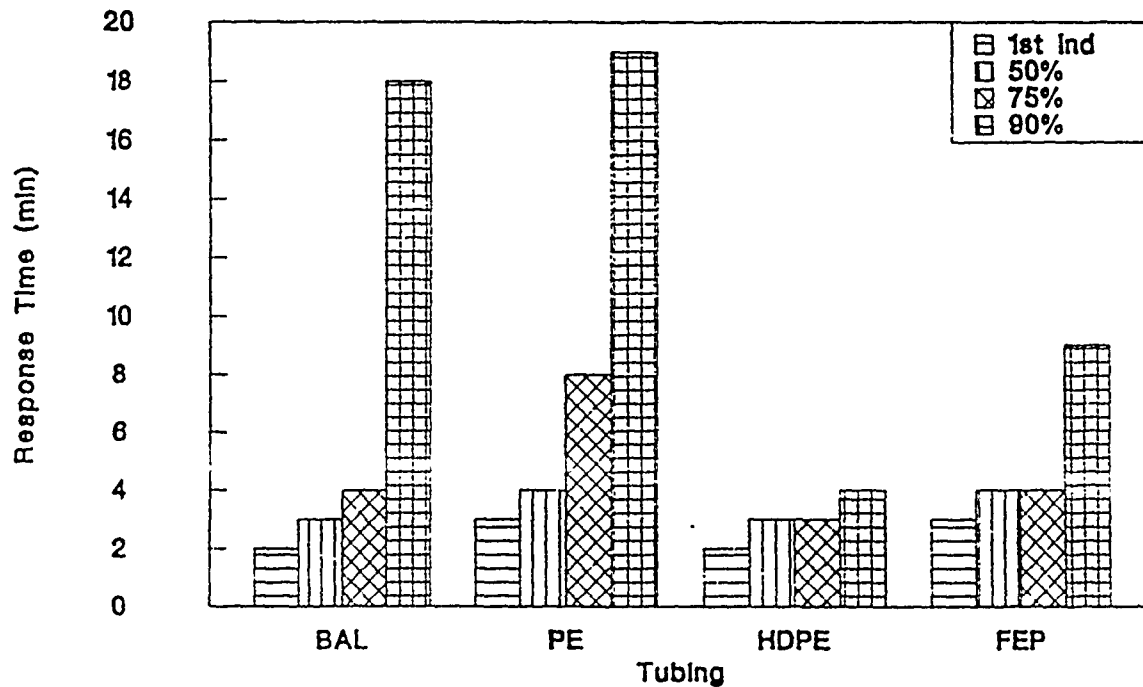


Figure 26. Response times to TLV UDMH of tubing cleaned with ammonia

In the one test where it did not reach 90%, the tubing had been purged with ammonia the day before the actual exposure to UDMH. The tubing was flushed with ammonia immediately prior to UDMH exposure for the other two tests. High density polyethylene responded quickly to the UDMH after flushing with ammonia vapor. After washing with methanol, the tubing did not reach 90% of full scale, however, it attained 90% within four minutes after cleaning with ammonia. Cleaning the Bev-A-Line tubing with ammonia or methanol did not make a significant difference in its subsequent performance. The FEP tubing performed significantly better after the ammonia cleaning procedure than it did after the methanol cleaning procedure at the 75% and 90% levels. The FEP attained 75% of full scale 3.5 times faster than after the methanol wash. It also reached 90% of full scale within 9 minutes, while it did not reach 90% at all after cleaning with methanol. There was not a significant increase in performance at the first indication and 50% levels.

CONCLUSIONS

The results of the vapor exposures are erratic. In some cases, the performance was good and consistent for all exposure replicates while in other cases, the response times varied between exposures. The variations observed cannot be correlated to any one parameter. The scatter in the results was probably due to a combination of the instruments used to analyze the vapor, the auxiliary pump, and the reactivity of the hydrazines. It is unclear why tubings which nominally have the same interior material, such as low and high density polyethylene, would behave differently. The results are erratic, but the high density polyethylene and FEP reach the maximum response level at both 500 ppb and 250 ppb for all the humidities tested. After preconditioning, all tubings showed retardation in their ability to transport UDMH. High density polyethylene was affected by the preconditioning the least. Only the tubing's response to the 90% level was hindered after exposure to ambient air.

Some basic considerations to be made when selecting a tubing material are: performance, length, flexibility, desired flow rate, cost, and whether location will allow access (for purposes of washing if needed). Many of the above mentioned candidates had transport times and percent vapor transported, which would be adequate for some applications.

Since most of the tests for the previous evaluation of tubing material with MMH were performed under different conditions than the exposures of tubing to UDMH and hydrazine, direct comparisons cannot be made. However, transport times of UDMH and MMH can be compared for the 23 m (75 ft) lengths of tubings tested, as the tests were run under identical conditions. In general, TLV levels of UDMH were transported down the tubings faster than MMH. For MMH, Bev-A-Line appeared to be the best overall tubing [3]. While Bev-A-Line is the most flexible, FEP and high density polyethylene generally performed better than the other tubings at longer lengths with UDMH. Increasing humidity had a similar effect on the tubing materials for both MMH and UDMH.

Use of cleaning agents must also be considered when choosing a tubing material. With the exception of Bev-A-Line, the tubings flushed with ammonia vapor gave better response times than

when cleaned with methanol. The polyethylene and high density polyethylene showed the greatest improvement. Bev-A-Line did not show a difference in performance depending on the cleaning agent used. The decrease in response times that occur after flushing the tubing with ammonia, may be due to the inability of the ammonia to thoroughly clean the tubing. The tubing may be preconditioned by the UDMH vapor to which it was previously exposed, allowing for quicker transport of UDMH vapor in subsequent exposures. The ammonia vapor may not be adequate to remove particulates that accumulate in tubing over time. Additional tests would be necessary to determine this, but a liquid wash seems a more reliable method. The choice of cleaning methods would also depend upon the actual installation and the ability to verify the tubing was dry after washing.

The Bev-A-Line exhibited the desired flexibility. High density polyethylene was the most difficult to work with in terms of flexibility. The decision of which material to use must be made on an individual use basis. The environment of the areas the tubing will transverse must be taken into account. A material that can withstand the conditions, for example, heating due to rocket exhaust, should be chosen.

REFERENCES

1. J.A.E. Hannum, Recent Developments in the Toxicology of Propellant Hydrazines, Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. Committee on Toxicology, "Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants", Vol. 5, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council, National Academy Press, Washington, DC 1985.
3. ACGIH Report on Proposed and Current Changes to TLV and BEI Lists, 21 May 1989.
4. P.A. Taffe, S.L. Rose-Pehrsson, and J.R. Wyatt, Material Compatibility with Threshold Limit Values of Monomethyl Hydrazine, Naval Research Laboratory, Washington, D.C., NRL Memorandum Report 6291, October, 1988.
5. F.J. Waller, Fluoropolymers, Journal of Chemical Education, 1989, 66(6), 487.
6. Teflon is a trademark of E.I. du Pont de Nemours and Company.
7. E. C. Olson, Analytical Chemistry, 1960, 32(12), 1545.
8. J.R. Holtzclaw, S.L. Rose, and J.R. Wyatt, Analytical Chemistry, 1984, 56(14), 2952.

APPENDIX
Tubing Exposure Data

High Density Polyethylene Tubing Exposures

UDMH Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
75	595	37		1.8	4.2	13.2	40.1	102	60
75	595	37		2.1	5.7	24.3	43.4	103	60
75	569	37		2.1	3.6	8.7	43.4	101	60
75	612	34		0.6	1.2	3.6	9.0	103	60
75	644	36		1.2	2.1	3.0	4.5	108	9.1
75	322	37		2.1	3.0	6.0	14.4	100	60
75	322	37		1.8	3.0	7.2	NA	96	60
75	307	38		2.4	3.6	10.2	NA	96	60
75	343	0		1.5	1.5	1.8	2.4	103	60
75	343	0		1.5	1.8	3.0	NA	85	60
75	337	0		0.9	1.2	1.2	2.1	85	60
75	523	0		<0.3	0.3	0.9	2.7	98	60
75	559	0		0.3	0.3	1.2	1.5	91	60
75	442	0		0.9	1.2	24.9	NA	92	60
200	516	0	0.9	1.5	5.4	48.2	NA	86	60
200	565	0	<0.6	0.6	1.5	NA	NA	79	60
200	591	0	0.6	1.2	1.8	10.8	23.4	105	60
200	547	38	1.2	3.3	12.3	37.7	114	100	114
200	563	37	0.9	3.0	13.8	41.9	102	105	102
*200	247	0	<2	2	4	29	NA	94	29
*200	212	0	2	3	15	NA	NA	97	83
*200	238	0	<2	2	4	11	NA	97	65
*200	238	47	2	3	4	18	95	100	95
*200	254	44	2	3	5	25	NA	95	28
*200	248	31	<2	2	4	10	81	100	81
*200	242	88	4	7	12	25	NA	97	120
*200	267	88	3	7	13	26	NA	99	95
*200	557	86	2	4	9	27	NA	96	81
*200	520	86	2	4	8	16	46	101	46
*200	497	86	2	5	9	18	NA	94	63

High Density Polyethylene Tubing Exposures

Hydrazine Exposures

Tubing Length (feet)	Hz Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
200	185	40	0.9	22.8	NA	NA	NA	71	78
200	164	37	1.2	24.3	87	206	NA	90	206
200	137	37	1.8	18.6	72	162	NA	89	186
200	115	38	0.6	1.2	NA	NA	NA	59	108
*200	119	37	5	14	NA	NA	NA	70	84
*200	119	37	5	16	69	NA	NA	75	69

* MDA 7100 used.

Tubing Preconditioned with Ambient Air

Tubing Length (feet)	Cleaning Agent	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
				1st Ind	50%	75%	90%	100%		
200	NONE	530	37	2	4	13	NA	NA	87	85
200	MEOH	476	38	2	4	36	NA	NA	76	36
200	MEOH	509	34	2	3	10	NA	NA	88	102
200	NH3(1)	462	32	2	3	3	6	16	106	30
200	NH3(1)	439	35	1	2	3	3	3	111	17
200	NH3(1)	452	38	2	3	3	4	28	102	28

The MDA 7100 was used for all post ambient air exposures.

NH3(1): Tubing cleaned with ammonia immediately prior to UDMH exposure.

FEP Tubing Exposures

UDMH Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
75	605	37		6.3	8.7	10.8	14.1	131	60
75	635	34		5.1	6.9	10.2	13.5	127	60
75	560	37		3.0	6.0	10.5	15.0	121	60
75	546	31	0.9	1.3	3.3	9.9	26.9	108	60
75	546	31	0.9	1.2	4.2	9.8	25.7	109	60
*75	530	0	1	2	2	2	NA	99	38
200	535	0		1.5	2.7	16.8	NA	92	60
200	535	0		1.2	1.8	4.5	NA	90	60
200	547	0	0.6	1.2	2.4	3.9	17.4	129	108
200	547	0	0.6	1.2	1.8	3.6	6.3	123	60
200	591	0	0.6	1.2	1.5	4.2	NA	99	60
200	584	36	0.9	2.7	7.2	19.8	46.7	106	90
200	549	38	1.2	3.0	7.8	23.1	53.0	106	108
200	460	73	0.9	12.9	22.2	36.5	72	105	108
200	463	72	0.9	10.8	20.4	40.7	84	106	84
*200	272	0	<2	2	3	19	40	102	40
*200	247	0	<3	3	4	9	44	102	66
*200	212	0	<2	2	3	12	NA	97	27
*200	238	47	2	4	6	NA	NA	88	19
*200	254	44	<2	2	4	13	NA	96	61
*200	238	31	2	3	4	9	64	104	70
*200	252	87	4	5	12	22	NA	99	140
*200	246	88	5	7	15	50	NA	96	100
*200	243	86	3	6	16	39	93	102	93

*MDA 7100 used.

FEP Tubing Exposures

Hydrazine Exposures

Tubing Length (feet)	Hz Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
200	43	47	33.0	45.5	61.1	68.9	198	278	480
200	154	37	NA	39.5	108	156	162	100	162
200	130	37	6.0	23.3	44.9	76.8	106.2	105	138
200	110	38	6.3	17.1	40.7	78	NA	91	144
*200	119	37	8	18	35	NA	NA	80	50
*200	111	37	11	26	30	102	NA	91	84

* MDA 7100 used.

Tubing Preconditioned with Ambient Air

Tubing Length (feet)	Cleaning Agent	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max (min)
				1st Ind	50%	75%	90%	100%		
200	NONE	416	41	13	20	30	NA	NA	81	49
200	MEOH	572	35	4	5	22	NA	NA	85	108
200	MEOH	427	35	3	4	5	8	NA	78	97
200	NH3	475	36	4	4	5	10	59	103	59
200	NH3(I)	475	36	2	3	3	8	42	103	65

The MDA 7100 was used for all post ambient air exposures.

NH3: Tubing cleaned with ammonia day prior to UDMH exposure.

NH3(I): Tubing cleaned with ammonia immediately prior to exposure.

Bev-A-Line Tubing Exposures

UDMH Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
75	563	34		1.5	3.9	9.3	31.1	101	60
75	572	35		1.2	2.1	10.8	45.2	102	60
75	550	35		0.6	2.4	18	60.0	100	60
75	620	36		1.5	1.8	2.4	4.8	101	9.3
75	638	34		0.9	1.2	1.8	3.9	103	19
75	638	34		1.2	1.5	2.4	3.6	102	4.5
75	333	38		2.1	6.0	19.8	NA	97	60
75	333	38		2.4	3.9	14.7	NA	98	60
75	324	37		1.8	2.4	4.7	9.6	96	60
75	517	0		0.9	1.2	1.8	6.6	101	13.6
75	517	0		1.2	1.8	NA	NA	83	6
75	549	0		1.2	1.2	1.2	2.1	114	4.8
75	581	0		0.6	1.2	3.3	6.9	101	7.8
75	581	0		0.6	2.1	6.6	NA	93	60
75	531	0		0.6	.3	3.0	8.4	100	8.4
200	522	0	1.8	2.4	6.0	NA	NA	81	60
200	581	0	0.6	0.6	2.4	NA	NA	89	60
200	569	0	0.2	0.2	5.7	NA	NA	86	60
200	561	40	1.2	3.6	12.6	38.9	NA	99	120
200	544	38	1.2	3.6	11.1	32.0	95.8	103	114
200	493	72	1.2	5.4	16.8	36.2	120	100	120
200	449	72	1.2	7.2	12.0	26.3	72	110	96
*200	238	0	3	4	6	27	NA	90	27
*200	260	0	2	3	6	35	NA	100	43
*200	236	0	2	4	10	NA	NA	88	52
*200	276	44	2	4	7	40	NA	96	55
*200	233	44	3	4	8	66	NA	92	66
*200	212	86	4	8	32	NA	NA	87	70
*200	227	86	4	9	21	NA	NA	86	63

* MDA 7100 used.

Bev-A-Line Tubing Exposures

Hydrazine Exposures

Tubing Length (feet)	Hz Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
200	116	37	9.0	47.9	72	126	NA	94	144
200	118	36	5.7	42.2	72	NA	NA	71	72
*200	120	37	24	33	198	NA	NA	75	96
*200	108	38	16	23	60	NA	NA	78	108
*200	126	38	20	33	NA	NA	NA	69	105

* MDA 7100 used.

Tubing Preconditioned with Ambient Air

Tubing Length (feet)	Cleaning Agent	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
				1st Ind	50%	75%	90%	100%		
200	NONE	530	37	4	6	12	59	106	105	108
200	MEOH	462	32	2	2	5	20	NA	98	62
200	MEOH	509	34	2	2	3	8	51	100	42
200	NH3(I)	452	38	2	3	3	30	102	94	51
200	NH3(I)	544	36	3	4	5	12	42	104	57
200	NH3	439	35	2	3	4	12	NA	103	114

The MDA 7100 was used for all post ambient air exposures.

NH3(I): Tubing cleaned with ammonia immediately prior to UDMH exposure.

NH3: Tubing cleaned with ammonia day prior to UDMH exposure.

Polyethylene Tubing Exposures

UDMH Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
75	560	34		1.2	2.4	4.5	37.1	104	58
75	612	34		1.2	2.1	4.2	15.9	100	60
75	616	35		1.2	1.5	3.6	NA	94	60
75	616	35		0.9	2.1	4.2	NA	95	60
75	625	35		0.9	1.5	3.0	NA	97	6.3
75	625	35		1.2	1.8	2.7	8.4	100	8.4
75	621	34		0.6	1.5	2.1	7.5	101	9.9
75	339	39		1.5	2.4	3.9	34.4	101	60
75	339	39		1.5	2.4	2.4	2.7	128	60
75	334	36		2.1	3.3	6.9	NA	98	60
75	341	39		2.4	4.8	14.1	NA	95	60
75	496	0		0.6	2.1	6.6	NA	89	60
75	538	0		<0.9	0.9	1.8	4.5	100	60
75	538	0		0.6	0.9	2.1	NA	90	60
200	618	0	<0.6	0.6	0.9	1.5	1.8	121	60
200	598	0	0.6	1.2	3.0	21.0	NA	93	60
200	598	0	1.2	1.5	1.8	10.2	NA	95	60
200	524	0	<1.2	1.2	2.4	NA	NA	83	105
200	638	37	1.2	4.5	16.5	38.9	NA	94	60
200	710	36	0.9	3.0	12.0	38.3	NA	100	150

TECO experiencing major problems; MDA 7100 to be used for remainder of testing.

200	236	0	2	4	16	NA	NA	85	47
200	280	0	2	7	70	NA	NA	78	70
200	218	0	2	5	22	NA	NA	84	116
200	276	44	3	7	23	NA	NA	89	78
200	239	42	2	4	13	58	NA	96	76
200	233	44	2	6	18	NA	NA	87	113
200	280	88	4	9	28	57	NA	90	57
200	262	86	5	15	38	NA	NA	89	108
200	238	86	3	14	34	NA	NA	88	102
200	540	86	2	7	19	48	NA	96	133
200	550	86	3	8	15	45	NA	96	132

Polyethylene Tubing Exposures

Hydrazine Exposures

Tubing Length (feet)	Hz Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
			1st Ind	50%	75%	90%	100%		
200	124	35	7.5	22.5	NA	NA	NA	55	59
200	109	37	5.7	31.6	NA	NA	NA	63	63
200	172	37	3.3	20.3	288	NA	NA	79	147
200	124	37	5	16	138	NA	NA	52	129

Tubing Preconditioned with Ambient Air

Tubing Length (feet)	Cleaning Agent	UDMH Conc (ppb)	RH (%)	Response Time (min)					Maximum Response (%)	Time to Reach Max % (min)
				1st Ind	50%	75%	90%	100%		
200	NONE	544	36	6	11	24	85	NA	92	85
200	MEOH	416	41	5	7	21	111	NA	95	126
200	MEOH	427	35	2	4	8	66	NA	96	66
200	NH3	529	36	3	5	14	NA	NA	86	37
200	NH3(1)	451	36	3	4	6	19			

NH3: Tubing cleaned with ammonia day prior to UDMH exposure.

NH3(1): Tubing cleaned with ammonia immediately prior to UDMH exposure.

PFA Tubing Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)				Maximum Response (%)	Time to Reach Max % (min)
			50%	75%	90%	100%		
75	608	34	3.3	6.6	12.6	33.5	105	60
75	595	36	6.0	10.2	15.3	22.5	120	60
75	595	36	2.1	5.4	12.3	22.5	117	60
75	550	34	1.2	3.0	7.2	*	108	60

* TECO experiencing problems.

TFE Tubing Exposures

Tubing Length (feet)	UDMH Conc (ppb)	RH (%)	Response Time (min)				Maximum Response (%)	Time to Reach Max % (min)
			50%	75%	90%	100%		
74	644	36	0.9	2.1	3.3	NA	90	6.0
74	595	37	<0.6	0.6	1.2	1.8	109	3.0
74	595	37	1.2	1.8	6.9	NA	76	3.9
74	628	36	0.9	1.5	1.8	3.0	103	5.4
74	621	34	1.2	1.5	2.4	3.6	103	7.4
74	639	37	0.9	1.8	3.0	NA	98	60
74	639	34	0.9	1.2	1.8	3.3	104	6.9
74	324	36	2.4	4.2	12.0	NA	99	60
74	324	36	2.7	3.9	8.4	23.7	104	60
74	329	39	2.7	4.5	16.2	NA	97	60
74	506	0	0.6	1.2	26.9	NA	99	60
74	506	0	0.6	0.6	1.8	NA	87	60
74	500	0	0.3	0.9	6.6	NA	91	60

Polypropylene Tubing Exposures

Tubing Length (feet)	UDMH Conc. (ppb)	RH (%)	Response Time (min)				Maximum Response (%)	Time to Reach Max % (min)
			50%	75%	90%	100%		
75	958	37	<0.9	0.9	1.5	3.3	101	60
75	958	37	0.6	1.2	1.5	NA	92	60
75	620	36	0.6	0.9	1.5	4.8	102	6.9
75	326	39	1.8	9.0	NA	NA	84	60
75	326	38	1.8	3.0	7.2	17.7	104	60
75	358	38	1.8	6.0	16.2	50.9	100	60
75	506	0	<0.3	0.3	2.4	NA	81	60
75	522	0	<0.3	<0.3	0.3	0.6	97	60
75	535	0	0.6	0.9	3.0	NA	94	60
75	535	0	0.9	2.7	NA	NA	88	18.9
75	524	24	0.9	1.5	3.0	NA	99	60
100	569	35	0.6	0.9	2.4	NA	99	60
100	569	22	0.3	0.9	2.1	NA	94	46

Bev-A-Line 1/2

Tubing Length (feet)	UDMH Conc. (ppb)	RH (%)	Response Time (min)				Maximum Response (%)	Time to Reach Max % (min)
			50%	75%	90%	100%		
75	329	39	2.4	3.3	6.0	NA	92	60
75	329	39	3.0	4.2	10.8	NA	93	60
75	312	42	2.1	3.3	6.0	NA	97	60
75	528	0	0.9	1.2	1.2	1.5	107	9.6
75	528	0	0.9	1.2	1.8	7.5	98	7.5
75	535	0	<0.9	<0.9	<0.9	0.9	105	60
75	506	0	<0.3	<0.3	0.3	1.2	106	60
75	518	0	0.6	0.9	2.1	18	97	60
75	518	0	1.2	1.5	4.2	NA	104	60
75	442	0	0.3	0.6	1.8	NA	89	60

A Real-Time Colorimetric Dosimeter for Unsymmetrical Dimethylhydrazine

INTRODUCTION

The three hydrazines currently being used by the Department of Defense as hypergolic fuels are hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The use of these hydrazines, especially as high energy propellants, has increased dramatically in recent years. Substantial quantities of hydrazines are used as propellants in Titan ballistic missiles, satellites, and aircraft auxiliary power units. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Since the hydrazines are suspected carcinogens, the American Conference of Governmental and Industrial Hygienists (ACGIH) has recommended the threshold limit values (TLV) of hydrazine, MMH, and UDMH to be 100, 200, and 500 parts-per-billion (ppb), respectively [1]. Potentially this level will be lowered to 10 ppb for all three hydrazines in May 1991 [2]. To minimize the risk of exposure, monitoring of employees who come into contact with hydrazines and the associated work environments should be conducted to insure that the presence of hydrazines remains below the defined levels. The Department of Defense and NASA require air monitoring for hydrazines in areas where they are handled and/or stored.

Vanillin (3-methoxy-4-hydroxybenzaldehyde) has been found to be an excellent derivatization agent for hydrazine and monomethylhydrazine. The hydrazone formed in the reaction between vanillin and hydrazine or MMH is yellow. The intensity of the color is proportional to the dose. Vanillin has been evaluated in the laboratory and field. An NRL Memorandum Report entitled "Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter" details the testing of the vanillin dosimeter [3]. Although highly reactive with hydrazine and MMH, vanillin must be strongly acidified to develop a colored compound with UDMH. This is not feasible with the substrate chosen.

Due to the interest of the Air Force in UDMH, a need has arisen for a reliable, real-time detection method for this hydrazine derivative. A number of compounds were examined for reactivity with UDMH to form colored products in both active and passive systems. Salicylaldehyde looked promising initially, however, the reaction was not stable. The color that developed upon reaction with the hydrazine faded rapidly. Two naphthoquinone compounds were examined. 1,4-naphthoquinone gave interesting results. When coated on filter paper and exposed to concentrated hydrazine, MMH, and UDMH, the naphthoquinone reacted with each hydrazine to form different colored products. However, the coated disks did not perform satisfactorily in a 10 ppb UDMH atmosphere, making it unsuitable for low level sampling. A well-known paper tape component, phosphomolybdic acid, forms a colored reaction product with the hydrazines in an active system. Therefore, it was investigated as a coating for a passive dosimeter. When coated on filter paper, it responded well to concentrated UDMH and turned a deep cornflower blue. However, after 24 hours in a 20 ppb UDMH environment, it developed only a pale green color.

Four nitrobenzaldehyde compounds were also evaluated. After initial testing, 4-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde showed potential in laboratory investigations. Further testing was concentrated on these two chemistries, and in particular 2,4-dinitrobenzaldehyde. When coated on a substrate and exposed to UDMH, hydrazine, or MMH, a yellow to yellow gold color develops, depending on the nitrobenzaldehyde. This report describes the development and laboratory evaluation of 4-nitrobenzaldehyde and 2,4 dinitrobenzaldehyde as colorimetric dosimeters.

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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. One method is based on the condensation of a hydrazine and an aldehyde, resulting in a product known as a hydrazone. The formation of a hydrazone is depicted in Figure 1. In the case of unsubstituted hydrazine (N_2H_4) two moles of aldehyde can react with one mole of hydrazine to form the azine. The mechanism involves the nucleophilic addition of the nitrogen base, followed by the elimination of water. This reaction is frequently acid catalyzed by protonation of the carbonyl. A well-known ASTM method uses this chemistry to condense the hydrazine with para-N,N-dimethylaminobenzaldehyde (PDAB), which is a good derivatization agent for hydrazine and MMH, though not for UDMH.



Figure 1. The condensation reaction of a carbonyl group with a hydrazine to form a hydrazone

2,4-dinitrobenzaldehyde is an excellent derivatization agent for UDMH and shows promise with hydrazine and MMH as well. Figure 2 shows the reaction of UDMH with 2,4-dinitrobenzaldehyde. The formation of the hydrazone is rapid. Because the nitro groups on the compound are strongly electron withdrawing, they disperse the negative charge of the benzaldehyde, and therefore increases the acidity of the carbonyl. Thus the basic hydrazine readily reacts with the benzaldehyde. 2,4-dinitrobenzaldehyde needs to be acidified to form a colored species upon reaction with the hydrazines. Phosphoric acid is used in the vanillin formulation with no adverse effects, and has been used satisfactorily with both 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde in this study.

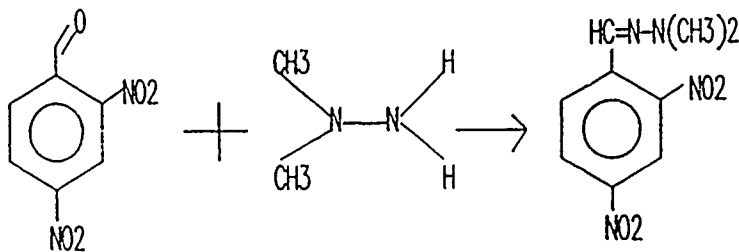


Figure 2. Condensation reaction of 2,4 dinitrobenzaldehyde

EXPERIMENTAL

Dosimeters were prepared by coating filter paper disks with a solution of 2,4-dinitrobenzaldehyde or 4-nitrobenzaldehyde dissolved in acetone and acidified with phosphoric acid. The coated disks were tested as both active and passive dosimeters. Passive disks consisted of the coated filter paper, while active disks consisted of a coated disk in a small filter cassette. The active disks were used for spot rapid spot tests.

The coated filter paper disks were exposed to low levels of UDMH in a cylindrical glass chamber with conical ends. Teflon baffles placed at each end of the chamber induced laminar flow. The exhaust end was removable to allow insertion of the dosimeters. When sampling actively, coated disks were placed in a filter cassette which was inserted into the chamber. The test vapor was drawn through the badge at approximately 1 L/min using a personal pump. When sampling passively, coated filter paper was placed on the bottom of the chamber for exposure. Both the sample times and the vapor concentration were varied for this investigation.

The system used to generate UDMH has been previously described in detail [4]. A diffusion tube, housed in a constant temperature bath and continually purged with 100 ml/min of dry nitrogen, provided the UDMH vapors. 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. The concentration in the test chamber was independently verified using impinger collection and coulometric titration before and after each test. The coulometric titration procedure used to verify the concentrations of the dynamic test environment has been described in detail in earlier reports [5].

Concentrations of UDMH ranging from 9 to 66 ppb were generated for badge exposures. Low and mid-range relative humidities were examined. Badges were exposed both actively and passively. The color development of the badges was evaluated on a color wheel prepared by GMD Systems, Inc. for the passive, vanillin colorimetric dosimeters [3]. The color development on the exposed dosimeters was matched as closely as possible to the yellow color wheel previously used for vanillin coated badges. There are 5 shades of yellow of increasing intensity on the color wheel. The nitrobenzaldehyde badges develop a more golden color than that of the color wheel. This was most noticeable at a color index of 3 or above. For this study, the color intensity rather than the actual shade was used to evaluate the exposed badges.

RESULTS

Figure 3 shows the dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde when used as active samplers. The dose response curve for 2,4-dinitrobenzaldehyde gives promising results. The curve is smooth with little scatter in the data points. The first indication of color is at 130 ppb-L. This means that a vapor concentration of 10 ppb could be detected in as little as 13 minutes when sampled at 1 L/min. If the sampling rate were increased, the response time would decrease. A color index greater than 5 is reached at 7000 ppb-L. The initial results on 4-nitrobenzaldehyde are good, however, the compound is less sensitive than the 2,4-dinitrobenzaldehyde. A dose of 500 ppb-L is needed to produce the first indication of color and almost 74000 ppb-L is required to give a color index of 3.5. There is not sufficient data to make conclusions on scatter.

Used as a passive dosimeter, 2,4-dinitrobenzaldehyde performs well. Figure 4 shows the dose response curve for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde. There is a first indication of color within 14 ppb-hours with 2,4-dinitrobenzaldehyde. There is good correlation between color and dose. More data is needed to make conclusions on scatter and saturation point. 4-nitrobenzaldehyde performs less satisfactorily. A color index of <1 is reached within 77 ppb-hours, however, an exact determination of the limit of detection has not been made. The color intensity of

the badge increases slowly from first indication to a color index of 3.5 within 1250 ppb-hours.

Relative humidity at low and mid-range levels does not have a significant effect on color development for either chemistry. An active sampler coated with 2,4-dinitrobenzaldehyde and exposed to 10 ppb of UDMH at <10% RH showed slightly sluggish color development. These results are preliminary and more work needs to be done to make conclusions on the effects of humidity.

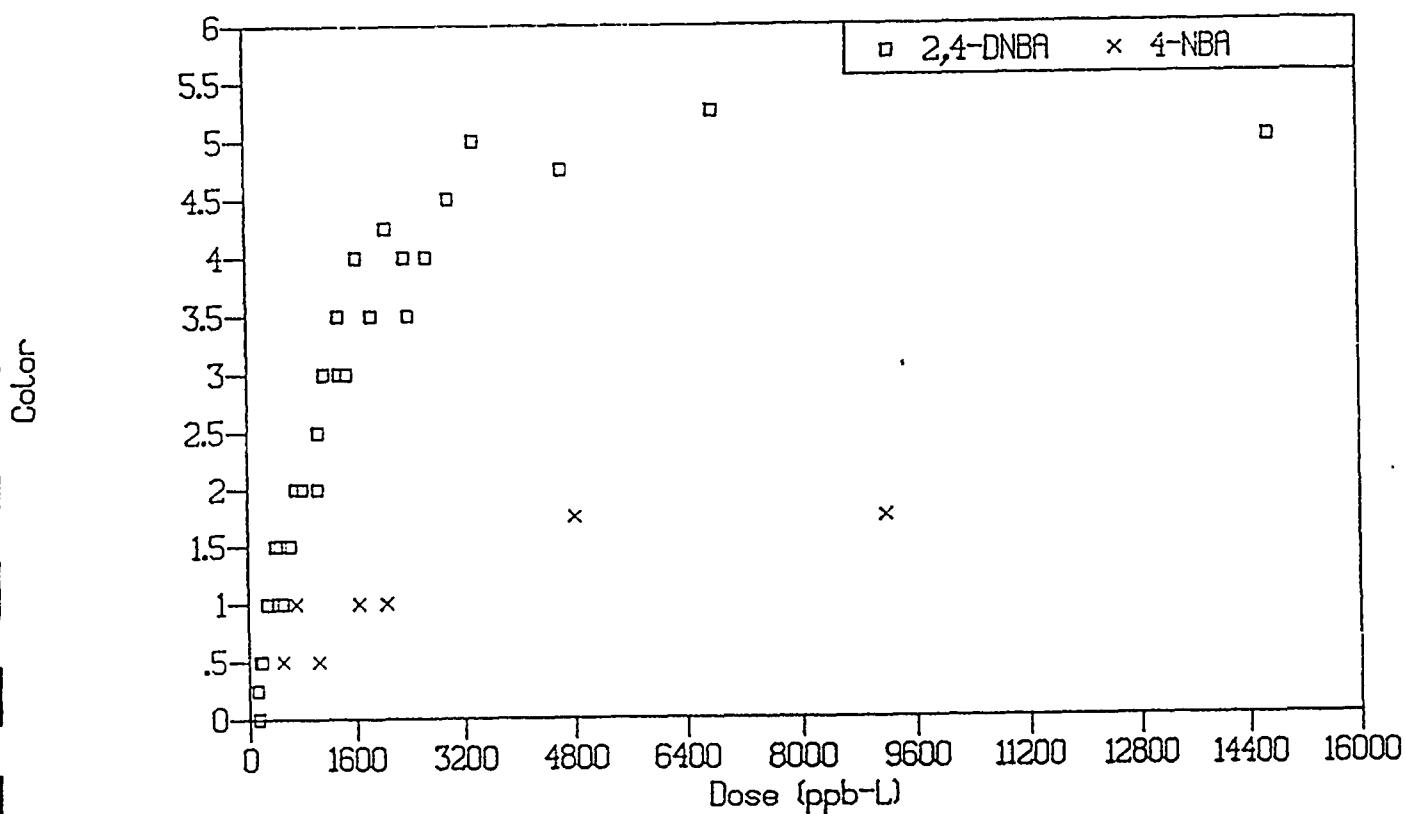


Figure 3. Dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde as active dosimeters

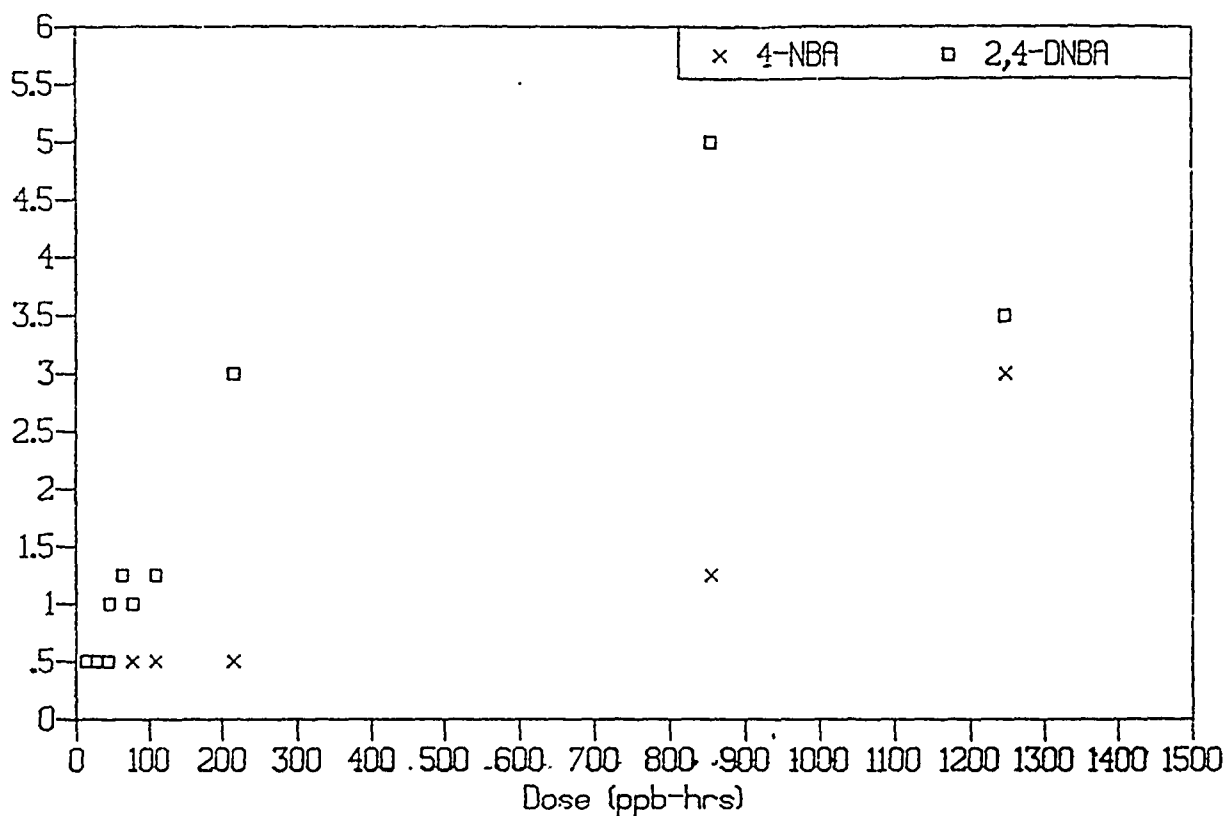


Figure 4. Dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde as passive dosimeters

CONCLUSIONS

These preliminary results look promising. The 2,4-dinitrobenzaldehyde appears to be the better chemistry for further investigation. In an active system, the precision in the color development is very good at each dose tested. The initial results indicate that it can meet the proposed TLV levels when used both actively and passively. In an active system, the lower limit of detection is 130 ppb-L for 2,4-dinitrobenzaldehyde and 500 ppb-L for 4-nitrobenzaldehyde. As a passive dosimeter, the 2,4-dinitrobenzaldehyde shows a detection limit of 14 ppb-hours, while 4-nitrobenzaldehyde gives a visual color within 77 ppb-hours. Further work is highly recommended upon indication of interest from the Air Force. If funds are available to complete the future work statement outlined below, we believe we could develop a viable device for active and passive sampling of UDMH.

FUTURE WORK STATEMENT

The following tasks need to be addressed to fully develop and evaluate a working active and passive dosimeter for UDMH.

1. Develop a standard method for the preparation of the dosimeters.
2. Conduct preliminary laboratory testing of badges at NRL.
3. Determine the shelf-life of the dosimeters.
4. Design and develop a dosimeter and dose estimator (color wheel) for use in an extensive evaluation.
5. Plan and execute an extensive laboratory evaluation to test the dosimeters under a variety of conditions. This would include investigating dose response, linearity, and relative humidity and interference effects.
6. Design and conduct a field test.

REFERENCES

1. Hannum, J.A.E., "Recent Developments in the Toxicology of Propellant Hydrazines", Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.
3. Crossman, K.P., P.T. Carver, J.R. Wyatt, S.L. Rose-Pehrsson, and A. Thurow, "Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter", NRL Memorandum Report 6668 (1990).
4. Rose, S.L., and J.R. Holtzclaw, "A Critical Comparison of Commercially Available Hydrazine Detectors", NRL Memorandum Report 8848 (1985).
5. Olson, E.C., "The Coulometric Determination of Hydrazine and Substituted Hydrazine", Analytical Chemistry, 32 (12), 1960, pp. 1545-1547.



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EVALUATION AND COMPARISON OF TWO COMMERCIALY AVAILABLE PASSIVE COLORIMETRIC MONOMETHYLHYDRAZINE DOSIMETERS

INTRODUCTION

The three hydrazines currently used by the Department of Defense as hypergolic fuels are hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The use of these hydrazines, especially as high energy propellants, has increased dramatically in recent years. Substantial quantities of hydrazines are used as propellants in Titan ballistic-missiles, satellites, aircraft auxiliary-power units and the space shuttle. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Since the hydrazines are suspected carcinogens, a maximum tolerated toxic level has been set at five parts-per-million (ppm). The American Conference of Governmental and Industrial Hygienists (ACGIH) has recommended the threshold limit values (TLV) of hydrazine, MMH, and UDMH to be 100, 200, and 500 parts-per-billion (ppb), respectively [1]. In addition, the ACGIH has recommended that the TLVs be lowered to 10 ppb for all the hydrazines in 1991 [2]. Monitoring of personnel and their workplace is necessary to insure that exposure remains below the defined levels. The Department of Defense and NASA require air monitoring for hydrazines in areas where they are handled and/or stored.

The National Aeronautics and Space Administration (NASA) asked the Naval Research Laboratory (NRL) to conduct a small evaluation to survey the general characteristics of the HydrazinoSenseTM, a commercially available passive dosimeter for MMH manufactured by Perfect View, Inc. A limited number of badges were to be investigated in a side-by-side test with the presently used dosimeter, manufactured by GMD Systems, Inc. for hydrazine and MMH. The test was designed to investigate the parameters that NASA considers the most important for a colorimetric detector to be used at Kennedy Space Center (KSC). Perfect View manufactures dosimeters for hydrazine, MMH, and UDMH. NASA primarily uses MMH and therefore requested we evaluate the MMH dosimeter.

EXPERIMENTAL

An experimental test plan was designed to evaluate the dosimeters for sensitivity, linearity, and effects due to vapor concentration, humidity, and chemical and sunlight interferences. The chemical interferences included hydrazine, UDMH, ammonia, and nitrogen dioxide. The dosimeters were exposed to concentrations of the hydrazines near the proposed TLV values. The TLV or the level of ammonia that workers can be exposed for 8 hours is currently 25 ppm. NASA has routinely used the TLV as the interference limit for all instrumentation used at KSC. No instrument or detector scheme is to respond to 25 ppm or less for an 8 hour exposure. The short-term exposure limit (STEL) for nitrogen dioxide has been recently dropped to 1 ppm for 15 minutes. The interference concentrations used in the test program were selected with the TLV and STEL levels in mind.

Table 1 outlines the test plan. Tests 1 and 2 are low level MMH sensitivity and linearity response tests. Tests 3 and 4 are relative humidity effect tests. Test 5 evaluates MMH concentration effects. Tests 6-15 are interference exposure tests, of which Test 6 and 15 evaluate sensitivity to other hydrazines. Interference vapors are tested prior to and following MMH exposures. Each experiment incorporated one perfect View badge that had been stored under refrigeration, one unrefrigerated Perfect View badge, and two GMD dosimeters.

Table 1. MMH Dosimeter Test Plan

Test	Badge Number	MMH Conc. (ppb)	Time (hr)	Dose (ppb-hr)	% RH	Interference
1	1	10	1	10	45	None
2	1	10	2	20	45	None
3	1	10	2	20	85	None
4	1	10	2	20	<1	None
5	1	80	0.25	20	45	None
6	1	0	4	40	45	HZ 10 ppb
7	1	0	4	2000	45	NO ₂ 0.5 ppm
8	1	0	4	100000	45	NH ₃ 25 ppm
9	1	0	4	30		Sunlight
10	1 of Test 2	0	4	2000	45	NO ₂ 0.5 ppm
11	1 of Test 3	0	4	100000	45	NH ₃ 25 ppm
12	1 of Test 7	10	2	20	45	None
13	1 of Test 8	10	2	20	45	None
14	1 of Test 9	10	2	20	45	None
15	1	0	4	40	45	UDMH 10 ppb

BADGE SYSTEM

Two sets of ten dosimeters were received from Perfect View, Inc. One set, "refrigerated", was shipped overnight and therefore unrefrigerated for only one day. The second set, "unrefrigerated" was 7 days in transit. Therefore, this set was unrefrigerated for 7 days. Both sets were refrigerated upon arrival and for the duration of this evaluation. Badges to be tested were removed from refrigeration just before exposure. The supply of GMD dosimeters used in this evaluation were manufactured 12 months ago and have been refrigerated since original receipt of the shipment.

The Perfect View dosimeters are individually sealed in plastic coated foil envelopes. The dosimeter has two windows on the face of the badge. One window is the reference region and the second is the sample region. The reference and sample regions contain paper coated with an indicator. On the front of the dosimeter, there is a gas permeable membrane which covers the inlet to the sample region. The membrane provides diffusion control. Vapors enter the dosimeter through the membrane and color changes can be observed by viewing the sample window on the back of the dosimeter. Upon exposure to MMH, the Perfect View dosimeter changes from a reference color of gold-tan to brown-red.

The responses of the Perfect View dosimeter can be obtained by visual inspection or through the use of an electronic optical reader, model PVI-5, manufactured by Perfect View, Inc. The manufacturer strongly recommends the use of the optical reader because it removes subjectivity. The electronic reading, in millivolts (mV), requires mathematical manipulation for conversion to MMH dose (ppb-hr). The data in this report are presented two ways, the millivolt readings read directly from the optical reader and the doses in ppb-hrs obtained by mathematical conversion of the millivolts using a calibration curve provided by the manufacturer. The calibration equations for MMH provided by Perfect View are as follows:

$$D(\text{ppb-hr}) = -40.689 + 5.15281 * R$$

for $8 < R < 27$, where R is the PVI-5 reading in mV.

$$D(\text{ppb-hr}) = -390.7047 + 18.1342282 * R$$

for $27 < R < 70$, where R is the PVI-5 reading in mV.

In addition to the millivolt responses, the visual color was used to characterize the dosimeter response. A color wheel relating color development to dose is not available at this time, therefore all color indications are general.

The GMD dosimeter is a dual spot, dual chemistry color dosimeter utilizing para-dimethylaminobenzaldehyde (PDAB) in one reaction site and vanillin in the other. The exposed dosimeter is evaluated by comparing color development to a color wheel consisting of five colors. The colors increase in intensity from 1 to 5 and correlate with specific doses. The PDAB indicator on the dosimeter changes from white to orange-red, while the vanillin indicator changes from white to yellow upon MMH exposure. The GMD badges do not have a diffusion barrier. Details of the GMD dosimeter design and laboratory evaluation have been previously reported [3].

TEST SYSTEM

The system used to generate controlled MMH concentration test environments has been previously reported in detail [4]. Diffusion tubes, housed in a constant temperature bath and continually purged with 100 ml/minute of dry nitrogen, provide the MMH vapors. The MMH in nitrogen combined with diluent air provides a known test vapor concentration. Final concentrations are controlled by the water bath temperature, size of the diffusion capillary, and/or the amount of

zero grade dilution air. The dilution air was adjusted to deliver a total of 5.0 liter/minute through the chamber. This corresponds to a face velocity of 79 cm/min (2.6 ft/min). The generation of the desired relative humidity (RH) in the gas stream is described earlier [4]. A hygrometer manufactured by HygroDynamics was used to verify the humidity. The concentrations are independently verified using a liquid impinger sampling method and coulometric titration analysis. These procedures have been previously described in detail [5]. The hydrazine and unsymmetrical dimethylhydrazine (UDMH) evaluated as interferences, were generated and verified using the same techniques as for MMH described above.

The nitrogen dioxide (NO_2) and ammonia (NH_3) interference test environments were generated using calibrated gas standards and zero grade dilution air. The NO_2 test chamber concentration was verified using the Thermedics Chemiluminescence detector. The detector was calibrated with 22 and 100 ppm nitric oxide (NO) calibrated gas standards. After calibration with NO, the detector response to NO_2 was tested using 116 and 1074 ppm NO_2 calibrated gas standards. All NO_2 gas standards and resulting test chamber environments were within 10% of expected values. The ammonia (NH_3) interference test vapor was similarly prepared.

The chamber used to expose the dosimeters to the vapor of interest is illustrated in Figure 1. The chamber is cylindrical with conical ends. Ten baffles installed at both ends of the chamber induce laminar flow. The badges were hung on a glass rod suspended between the baffles. The two Perfect View dosimeters, one refrigerated and one unrefrigerated, were hung face to face from the glass rod. The GMD dosimeters were hung from the same glass rod. The Perfect View dosimeter was positioned before the GMD dosimeter in reference to the gas inlet of the test chamber. Due to limited time in completing the test plan, the test procedure was modified for Tests 12-14. The Perfect View dosimeters from Tests 7-9 were exposed simultaneously to MMH and the GMD badges were not tested. GMD badge results for similar tests can be obtained from reference 3.

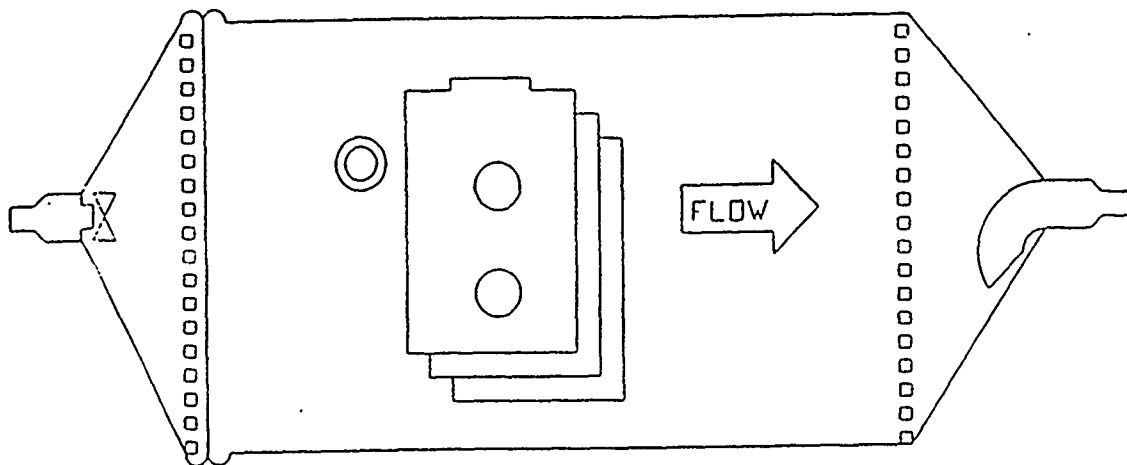


Figure 1. Dosimeter Exposure Chamber

An initial reading was taken with the optical reader for each Perfect View dosimeter prior to exposure. Post exposure readings of all of the badges were taken immediately after exposure (T=0), one hour after exposure (T=1), and 24 hours after exposure (T=24). Visual color changes were also ascertained during the exposures by observing the color change through the glass chamber.

RESULTS

All results are general due to the limited number of dosimeters evaluated and lack of replicates to provide statistical confidence.

PERFECT VIEW BADGE

Table 2 shows the millivolt responses for the tests characterizing the different dose responses, stability, concentration effects, humidity effects, and interference vapor effects of the refrigerated Perfect View dosimeter. Table 3 gives data for the same tests using unrefrigerated badges. The results are given as the net change, final reading minus initial reading. Little or no response in tests 6-11 and test 15 would indicate no interference effect. A comparison of the results in Tables 2 and 3 indicate no significant differences in badge performance due to storage under refrigeration or at room temperature for the Perfect View dosimeters.

Tables 4 and 5 show the dose responses that were calculated from the millivolt readings. A comparison of Tables 4 and 5 show similar trends for both the refrigerated and unrefrigerated badges, but the magnitudes of the responses are significantly different. Once converted to dose as per the manufacturer's instructions, the responses appear less accurate than the millivolt responses. There may be some problems with the mathematical conversion at the levels that were tested here.

Initial color development was visually observed after 40 minutes at 14.6 ppb MMH. This correlates to a test vapor dose of 9.7 ppb-hr. The dose response continues to develop for a period of approximately one hour after exposure in all the tests except that at 85% RH. After one hour, further development is minor for the millivolt readings shown in Tables 2 and 3, but the dose responses given in Tables 4 and 5 indicate significant increases at each measurement. The dosimeter response increases with increasing dose. The concentration effect cannot be accurately determined because of the limited data.

Relative humidity does not affect millivolt responses significantly (Tables 2 and 3). The initial readings are very low in very low humidity, but are comparable to those obtained at the higher relative humidities after one hour. The dose responses observed in Tables 4 and 5 increase with increasing relative humidity. The magnitude of the calculated dose responses are also much greater than the actual doses tested.

The dosimeter responds to hydrazine vapor (Test 6), although with less sensitivity. The dosimeter does not respond to UDMH (Test 15) at a dose of 41.2 ppb-hr. Exposure to 2 ppm-hr of NO₂ vapor causes a slight positive response (Test 7). Similarly, exposure to 100 ppm-hr of ammonia causes a positive response (Test 8). Upon subsequent exposure to MMH, normal color development is observed in both cases (Tests 12,13). Exposure to sunlight for 4.0 hours causes a positive response (Test 9). Sunlight interference hinders badge response to subsequent exposure to MMH (Test 14).

Exposure to NO₂ after MMH exposure does not change the badge response and is shown in the tables as a net change of zero (Test 10). Exposure to ammonia after MMH exposure causes a severe change in the response of the badges to MMH (Test 11). The responses shown in each of the Tables is 100% greater than the initial reading indicating that ammonia enhances the color change of the MMH. The sample color changed from a uniform brown color to a nonuniform mix of lime green and orange-brown.

Table 2. Results of Perfect View Refrigerated Dosimeters

Test Description	Test Vapor	Vapor Conc. (ppb)	Exposure Time (hr)	Dose (ppb-hr)	RH (%)	Net mV T=0	Net mV T=1	Net mV T=24
1 Low Level	MMH	14.6	2.00	29.2	45	12	19	22
2 Dose	MMH	14.6	4.00	58.4	45	24	32	33
3 Max RH	MMH	14.6	4.00	58.4	85	28	27	
4 Min RH	MMH	14.6	4.00	58.4	<1	15	34	35
5 Conc Resp	MMH	82.0	0.25	20.5	45	5	17	15
6 HZ Inter	HZ	8.0	4.00	32.0	45	5	6	6
7 NO ₂ Inter	NO ₂	500.0	4.00	2,000.0	45	4	5	5
8 NH ₃ Inter	NH ₃	25,000.0	4.00	100,000.0	45	7	7	14
9 Sunlight			4.00		30	7	7	11
10 Post MMH	NO ₂	500.0	4.00	2,000.0	45	0	0	0
11 Post MMH	NH ₃	25,000.0	4.00	100,000.0	40	38	38	44
12 Post NO ₂	MMH	15.0	4.00	60.0	47	20	29	28
13 Post NH ₃	MMH	5.0	4.00	60.0	47	17	23	24
14 Post Sun	MMH	5.0	4.00	60.0	47	7	8	8
15 UDMH Inter	UDMH	10.3	4.00	41.2	35	-1	0	1

Table 3. Results of Perfect View Unrefrigerated Dosimeters

Test Description	Test Vapor	Vapor Conc. (ppb)	Exposure Time (hr)	Dose (ppb-hr)	RH (%)	Net mV T=0	Net mV T=1	Net mV T=24
1 Low Level	MMH	14.6	2.00	29.2	45	12	12	19
2 Dose	MMH	14.6	4.00	58.4	45	13	24	26
3 Max RH	MMH	14.6	4.00	58.4	85	25	23	
4 Min RH	MMH	14.6	4.00	58.4	<1	18	32	33
5 Conc Resp	MMH	82.0	0.25	20.5	45	3	13	12
6 HZ Inter	HZ	8.0	4.00	32.0	45	6	7	8
7 NO ₂ Inter	NO ₂	500.0	4.00	2,000.0	45	3	6	8
8 NH ₃ Inter	NH ₃	25,000.0	4.00	100,000.0	45	7	4	16
9 Sunlight			4.00		30	3	3	9
10 Post MMH	NO ₂	500.0	4.00	2,000.0	45	1	1	1
11 Post MMH	NH ₃	25,000.0	4.00	100,000.0	40	31	32	39
12 Post NO ₂	MMH	15.0	4.00	60.0	47	16	23	23
13 Post NH ₃	MMH	15.0	4.00	60.0	47	24	30	31
14 Post Sun	MMH	15.0	4.00	60.0	47	10	11	11
15 UDMH Inter	UDMH	10.3	4.00	41.2	35	-1	0	1

Table 4. Results of Perfect View Refrigerated Dosimeters

Test Description	Test Vapor	Vapor Conc. (ppb)	Exposure Time (hr)	Dose (ppb-hr)	RH (%)	Dose (ppb-hr)		T=24
						T=0	T=1	
1 Low Level	MMH	14.6	2.00	29.2	45	21	57	73
2 Dose	MMH	14.6	4.00	58.4	45	83	190	207
3 Max RH	MMH	14.6	4.00	58.4	85	104	98	
4 Min RH	MMH	14.6	4.00	58.4	<1	37	226	245
5 Conc Resp	MMH	82.0	0.25	20.5	45	<0.5	45	37
6 HZ Inter	HZ	8.0	4.00	32.0	45	<0.5	<0.5	<0.5
7 NO ₂ Inter	NO ₂	500.0	4.00	2,000.0	45	<0.5	<0.5	<0.5
8 NH ₃ Inter	NH ₃	25,000.0	4.00	100,000.0	45	<0.5	<0.5	31
9 Sunlight			4.00		30	<0.5	<0.5	16
10 Post MMH	NO ₂	500.0	4.00	2,000.0	45	0	0	0
11 Post MMH	NH ₃	25,000.0	4.00	100,000.0	40	298	298	407
12 Post NO ₂	MMH	15.0	4.00	60.0	47	63	109	104
13 Post NH ₃	MMH	15.0	4.00	60.0	47	45	78	83
14 Post Sun	MMH	15.0	4.00	60.0	47	<0.5	<0.5	<0.5
15 UDMH Inter	UDMH	10.3	4.00	41.2	35	0	0	<0.5

Table 5. Results of Perfect View Unrefrigerated Dosimeters

Test Description	Test Vapor	Vapor Conc. (ppb)	Exposure Time (hr)	Dose (ppb-hr)	RH (%)	Dose (ppb-hr)		
						T=0	T=1	T=24
1 Low Level	MMH	14.6	2.00	29.2	45	21	21	57
2 Dose	MMH	14.6	4.00	58.4	45	26	83	93
3 Max RH	MMH	14.6	4.00	58.4	85	88	78	
4 Min RH	MMH	14.6	4.00	58.4	<1	52	190	208
5 Conc Resp	MMH	82.0	0.25	20.5	45	<0.5	26	21
6 HZ Inter	HZ	8.0	4.00	32.0	45	<0.5	<0.5	<0.5
7 NO ₂ Inter	NO ₂	500.0	4.00	2,000.0	45	<0.5	<0.5	<0.5
8 NH ₃ Inter	NH ₃	25,000.0	4.00	100,000.0	45	<0.5	<0.5	42
9 Sunlight			4.00		30	<0.5	<0.5	6
10 Post MMH	NO ₂	500.0	4.00	2,000.0	45	<0.5	<0.5	<0.5
11 Post MMH	NH ₃	25,000.0	4.00	100,000.0	40	171	190	317
12 Post NO ₂	MMH	15.0	4.00	60.0	47	42	153	78
13 Post NH ₃	MMH	15.0	4.00	60.0	47	83	153	171
14 Post Sun	MMH	15.0	4.00	60.0	47	11	16	16
15 UDMH Inter	UDMH	10.3	4.00	41.2	35	0	0	<0.5

GMD SYSTEMS BADGES

Table 6 shows the color indices from the five position color wheel for the tests characterizing the dose response, stability, concentration effect, humidity effect, and interference vapor effect of the GMD dosimeter tested with MMH. The results in the table are an average of the two badges that were exposed for each test. Initial color development was visually observed after 40 minutes at 14.6 ppb MMH. This correlates to a test vapor dose of 9.7 ppb-hr. The dose response appears to continue to develop for a period of approximately one hour after exposure when low MMH concentrations and short exposure times are tested. Badges exposed at low relative humidity also show continued color development up to one hour following exposure to MMH. After one hour, no further dose response development is observed. In all other cases, the badge color does not continue to develop after the initial evaluation at $T=0$.

Using the color wheel, the GMD dosimeter does not discriminate between doses of 20 and 29 ppb-hrs, but an increase is observed when the test vapor dose was increased to 58 ppb-hr. The concentration effect can not be accurately determined because of the limited data. As seen with the Perfect View badges, humidity does not appear to effect development except at humidities of less than 1% RH. In cases of very low humidity, further development does result when subsequently introduced to a more humid environment.

The GMD dosimeter displays sensitivity to hydrazine vapor similar to that with MMH (Test 6). The dosimeter does not respond to UDMH at a dose of 41.2 ppb-hr (Test 15). A response was not observed upon exposure to NO_2 (Test 7). A slight ammonia response was observed with the PDAB indicator, while the vanillin indicator was not affected (Test 8). The PDAB indicator developed a buff discoloration with a color index of <0.5 . Exposure to NO_2 or NH_3 after MMH exposure does not cause further color development or affect the color already present (Tests 10,11). Reference 3 may be consulted for data on GMD badge responses to MMH after exposure to NO_2 and NH_3 . A sunlight response was observed with the PDAB indicator while no response was observed with the vanillin indicator (Test 9). The PDAB indicator developed a yellow color upon exposure to sunlight, similar to vanillin color development, rather than the normal orange-red color development of the PDAB indicator when exposed to MMH. The results from the exposures of the GMD dosimeters support the findings previously documented [3].

CONCLUSIONS

The Perfect View dosimeters incorporate a diffusion barrier to reduce face velocity effects on the dose measurement; the GMD badges do not. Therefore, the Perfect View dosimeters should provide more quantitatively accurate results than the GMD badges over a wider range of face velocities. Due to the limited size of this test, face velocity effects were not examined.

Storage of the Perfect View dosimeters for one week under refrigeration temperatures or at room temperature did not significantly affect the performance as indicated by the millivolt readings. However, the responses in ppb-hours calculated from the equations supplied by Perfect View were significantly different. The mathematical conversion from millivolts to dose may be flawed for the low test vapor concentrations used in this test program.

The Perfect View and GMD MMH dosimeters respond similarly to MMH. Both badges show a response to a minimum MMH dose of approximately 9 ppb-hr. Therefore, they can be used to detect the lower TLVs of the hydrazines which will be in effect in 1991.

Table 6. Results of GMD Dosimeters

Test Description	Test Vapor	Vapor Conc. (ppb)	Exposure Time (hr)	Dose (ppb-hr)	RH (%)	PDAB T=0	Vanillin T=0	PDAB T=1	Vanillin T=1	PDAB T=24	Vanillin T=24
1 Low Level	MMH	14.6	2.00	29.2	45	0.5	0.5	1.0		1.0	1.0
2 Dose	MMH	14.6	4.00	58.4	45	1.25	1.25	1.5		1.25	
3 Max RH	MMH	14.6	4.00	58.4	85	1.5	1.5	1.5		N/T	N/T
4 Min RH	MMH	14.6	4.00	58.4	<1	0.5	1.25	1.5		N/T	N/T
5 Conc Resp	MMH	82.0	0.25	20.5	45	<0.5	0.5	1.0		1.5	
6 HZ Inter	HZ	8.0	4.00	32.0	45	0.5	0.5	1.0		N/T	N/T
7 NO ₂ Inter	NO ₂	500.0	4.00	2,000.0	45	0.0	0.0	0.0		0.0	
8 NH ₃ Inter	NH ₃	25,000.0	4.00	100,000.0	45	<0.5	0.0	<0.5		<0.5	
9 Sunlight			4.00		30	2.0	0.0	2.0		1.5	
10 Post MMH	NO ₂	500.0	4.00	2,000.0	45	0.0	0.0	0.0	0.0	N/T	N/T
11 Post MMH	NH ₃	25,000.0	4.00	100,000.0	40	0.0	0.0	0.0	0.0	0.0	0.5
12 Post NO ₂	MMH	15.0	4.00	60.0	47	N/T	N/T	N/T	N/T	N/T	N/T
13 Post NH ₃	MMH	15.0	4.00	60.0	47	N/T	N/T	N/T	N/T	N/T	N/T
14 Post Sun	MMH	15.0				N/T	N/T	N/T	N/T	N/T	N/T
15 UDMH Inter	UDMH	10.3	4.00	41.2	35	0.0	0.0	<0.5		<0.5	0.0

PDAB badges exposed to sun were evaluated on the vanillin color wheel.
N/T: Not tested.

Because the Perfect View dosimeter response continues to develop color within 1 hour after exposure, the initial color (T=0) should be viewed as a warning sign, while the later color development at T=1 would be more accurate. The GMD dosimeter response appears to be complete upon termination of the exposure, except for exposures in low humidity or to low MMH concentrations at short exposure times. In these cases, complete response is obtained within 1 hour after exposure. Neither dosimeter is affected by humidity changes except at very low humidity. This should not be a significant factor under normal environmental conditions.

Ammonia vapor and sunlight are the only significant interferences for the Perfect View dosimeters. GMD dosimeters previously exposed to MMH vapor do not respond significantly to ammonia vapor. The PDAB section of the GMD badges indicate a significant sunlight effect, although the color that develops is different than that produced by reaction with MMH. The response due to subsequent exposure of the GMD badges to MMH is not affected, whereas sunlight hinders subsequent color development of the Perfect View badges.

There are potential disadvantages associated with the Perfect View MMH dosimeter. The current cost is \$20 each. A color wheel to estimate dose is not currently available. The conversion procedure to calculate dose from the electronic optical reader output, millivolt raw data, appears incomplete at this time. The color change is visible on the back of the badge, which would be facing the user's clothing. Therefore, any color change is not immediately apparent, requiring that the user periodically inspect the badge.

Potential drawbacks of the GMD MMH dosimeter are listed below. The color wheel is not printed on the dosimeter, but instead is a separate unit. Therefore, the dosimeter dose cannot be immediately estimated by a simple visual evaluation of the badge. An optical reader is not available; the color wheel provides less discrimination between doses than an electronic optical reader. The badges do not have a diffusion barrier, therefore the results are semi-quantitative.

REFERENCES

1. "TLVs-Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1981"; American Conference of Governmental and Industrial Hygienists: Cincinnati, OH, 1981.
2. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.
3. Crossman, K.P., Carver, P.T., Wyatt, J.R., Rose-Pehrsson, S.L., and Thurow, A., "Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter", NRL Memorandum Report 6668, Naval Research Laboratory, Washington, D.C., 1990.
4. Rose, S.L., and J.R. Holtzclaw, "A Critical Comparison of Commercially Available Hydrazine Detectors", NRL Memorandum Report 8848, Naval Research Laboratory, Washington, D.C., 1984.
5. Taffe, P.A., Brown, S.W., Thurow, A.R., Travis, J.C., Rose-Pehrsson, S.L., and Wyatt, J.R., "Field Evaluation of a Passive Sampling Device for Hydrazines in Ambient Air", NRL Memorandum Report 6613, Naval Research Laboratory, Washington, D.C., 1990.

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Evaluation of A Real-Time Colorimetric Dosimeter for Unsymmetrical Dimethylhydrazine

ABSTRACT

A method for real-time, colorimetric detection of low levels of unsymmetrical dimethylhydrazine (UDMH) in air has been developed. The mechanism involves the condensation of an aromatic aldehyde with a hydrazine to form a colored hydrazone. 2,4-Dinitrobenzaldehyde has been found to be an excellent derivatization agent for UDMH, though less effective for hydrazine and monomethylhydrazine (MMH). The hydrazone formed in the reaction between 2,4-dinitrobenzaldehyde and UDMH is yellow to golden yellow. 2,4-Dinitrobenzaldehyde has been investigated for use in passive and active dosimetry systems. The intensity of the color is proportional to the dose. The compound has been evaluated at various doses of UDMH, relative humidities, interferences, and in accelerated shelf life tests.

INTRODUCTION

The three hydrazines currently used by the Department of Defense as hypergolic fuels are hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The use of these hydrazines, especially as high energy propellants, has increased dramatically in recent years. Hydrazines are used as propellants in space launch vehicles, satellites, and aircraft auxiliary power units. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Because the hydrazines are suspected carcinogens, the American Conference of Governmental Industrial Hygienists (ACGIH) has established threshold limit values (TLV) of hydrazine, MMH, and UDMH of 100, 200, and 500 parts-per-billion (ppb), respectively [1]. Potentially this level will be lowered to 10 ppb for all three hydrazines in May 1991 [2]. To safeguard employees who may come into contact with hydrazines, monitoring of employees and their work environments should be conducted. The Department of Defense and NASA require air monitoring for hydrazines in areas where they are handled and/or stored.

Vanillin (3-methoxy-4-hydroxybenzaldehyde) has been found to be an excellent derivatization agent for hydrazine and monomethylhydrazine. The hydrazone formed in the reaction between vanillin and hydrazine or MMH is yellow. The intensity of the color is proportional to the dose. Vanillin has been evaluated in the laboratory and field. An NRL Memorandum Report entitled "Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter" details the testing of the vanillin dosimeter [2]. Although highly reactive with hydrazine and MMH, vanillin must be acidified with a strong acid to develop a colored compound with UDMH. Hydrochloric acid was evaluated, however, it evaporates too quickly. Sulfuric acid reacts with the vanillin. In addition, both acids cause disintegration of the paper substrate. Therefore, this is not feasible with substrate chosen.

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Due to the interest of the Air Force in UDMH, a need has arisen for a reliable, real-time detection method for this hydrazine derivative. A number of compounds were examined for reactivity with UDMH to form colored products in both active and passive systems. After initial testing, where 4-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde showed potential, further investigations were concentrated on these chemistries. When coated on a substrate and exposed to UDMH, a yellow to yellow gold color develops, depending on the dose. Both benzaldehydes are also sensitive to hydrazine and MMH, though to a lesser extent. The Air Force tasked the Naval Research Laboratory to develop a colorimetric dosimeter for UDMH. This report describes the Task 1 development and laboratory evaluation of a colorimetric dosimeter for UDMH.

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. One method is based on the condensation of a hydrazine and an aldehyde, resulting in a product known as a hydrazone. The formation of a hydrazone is depicted in Figure 1. In the case of unsubstituted hydrazine (N_2H_4), two moles of aldehyde can react with one mole of hydrazine to form the azine. The mechanism involves the nucleophilic addition of the nitrogen base, followed by the elimination of water. This reaction is frequently acid catalyzed by protonation of the carbonyl. A well-known ASTM method uses this chemistry to condense the hydrazine with para-N,N-dimethylaminobenzaldehyde (PDAB), which is a good derivatization agent for hydrazine and MMH, though not for UDMH.

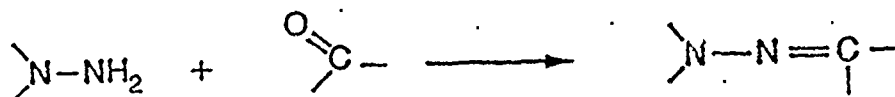


Figure 1. The condensation reaction of a carbonyl group with a hydrazine to form a hydrazone.

2,4-Dinitrobenzaldehyde is an excellent derivatization agent for UDMH and shows promise with hydrazine and MMH as well. Figure 2 shows the reaction of UDMH with 2,4-dinitrobenzaldehyde. The formation of the hydrazone is rapid. Because the nitro groups on the compound are strongly electron withdrawing, the acidity of the carbon in the carbonyl group is increased, making it more susceptible to nucleophilic attack. Thus, the basic hydrazine readily reacts with the benzaldehyde. 2,4-Dinitrobenzaldehyde and 4-nitrobenzaldehyde need to be acidified to form a colored species upon reaction with the hydrazines. Phosphoric acid is used in the vanillin formulation with no adverse effects, and has been used satisfactorily with both benzaldehydes in this study.

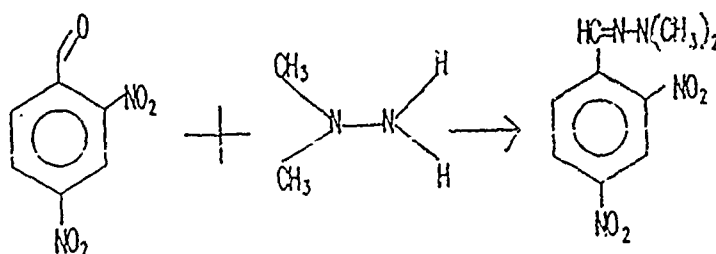


Figure 2. Condensation reaction between UDMH and 2,4-dinitrobenzaldehyde.

EXPERIMENTAL

A number of compounds were investigated for reactivity with UDMH to form colored products in active and passive systems. Whatman filter paper disks were coated with the compounds in solution and exposed to UDMH vapor. Table I details the various chemistries examined. Unless indicated in the table, the coated disks were exposed to concentrated UDMH vapors from an open bottle. The color development of the badges was evaluated on a color wheel prepared by GMD Systems, Inc. for use with the passive colorimetric dosimeters for the detection of hydrazines [3]. The portion of the wheel that corresponds to the vanillin coated section of the GMD dosimeters contains 5 shades of yellow of increasing intensity. On the portion of the wheel corresponding with the PDAB coated section of the GMD badges, there are 5 shades of orange.

After these initial tests, it was decided to concentrate further efforts on the 4-nitrobenzaldehyde and the 2,4-dinitrobenzaldehyde. Filter paper disks were coated with a solution of 2,4-dinitrobenzaldehyde or 4-nitrobenzaldehyde dissolved in acetone and acidified with phosphoric acid. The coated disks were tested as both active and passive dosimeters. Passive disks consisted of the coated filter paper, while active disks consisted of a coated disk in a small filter cassette. The active disks were used for rapid spot tests.

The exposures were conducted in a glass exposure chamber. The chamber is cylindrical with hemispherical ends. The exhaust end was removable to allow insertion of the samplers. Teflon baffles placed at each end induced laminar flow for uniform exposure of the disks. Figure 3 shows the exposure chamber and the orientation of the passive badges placed inside for exposure. When sampling actively, coated disks were placed in a filter cassette which was inserted into the chamber. The test vapor was drawn through the badge at approximately 1 L/min using a personnel sampling pump. When sampling passively, coated filter paper was suspended from a glass rod running the length of the chamber and secured in the baffles. The badges were hung parallel to the incoming gas flow. A few initial dose exposures were made by placing the coated disks on the bottom of the chamber.

The system used to generate UDMH has been previously described in detail [4]. A diffusion tube, housed in a constant temperature bath and continually purged with 100 ml/min of dry nitrogen, provided the UDMH vapors. 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. The concentration in the test 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 described in detail in earlier reports [5].

Concentrations of UDMH ranging from 9 to 66 ppb were generated for initial badge exposures. The majority of the Task 1 exposures were evaluated at 10 ppb of UDMH. Relative humidities ranging from 0 to 83 % were examined. Badges were exposed both actively and passively. As mentioned previously, the color development of the badges was evaluated on a color wheel prepared by GMD Systems, Inc. for the passive, hydrazine colorimetric dosimeters [3]. The nitrobenzaldehyde badges develop a more golden color than the color represented on the vanillin portion of the wheel. This was most noticeable at a color index of 3 or above. For this study, the color intensity rather than the actual shade was used to evaluate the exposed badges. The responses were observed immediately after exposure ($T=0$), one hour after exposure ($T=1$), and 24 hours after exposure ($T=24$). Badges were placed on the benchtop after exposure. Therefore, they were exposed to light during work hours.

In addition to dose tests, accelerated shelf life tests were performed on the coated disks. Disks were placed in a capped flask in a dark oven with a temperature of 40°C for approximately one week. They were exposed to the air trapped in the flask. After the badges were "aged" at the increased temperature, they were exposed to 10 ppb of UDMH alongside coated disks stored in a dark desiccator at room temperature.

Table I. Compounds Examined for Reactivity with UDMH				
Compound	Solution Conc. (%)	Acidification	Color Development with UDMH	Comments
salicylaldehyde in 2-propanol	0.5	phosphoric acid	pale yellow	All color development began to fade within minutes after exposure to UDMH. In some cases, color faded completely. Exposed and faded disks developed color after a second exposure to UDMH.
	1.0	HCl	none	
		none	medium yellow	
	6.0	phosphoric acid	none	
		none	yellow	
	12.0	none	bright yellow	
1,4-naphthoquinone in acetone	0.4	phosphoric acid	light wine with tan	Unexposed disks stored in plastic bag discolored to brown purple within one week.
			none	10 ppb UDMH for approx. 15 hrs. Dose=approx. 150 ppb-hrs.
		none	light orange tan	

Compound	Solution Conc. (%)	Acidification	Color Development with UDMH	Comments
2-hydroxy-1,4-naphthoquinone in acetone	0.3	none	orange	Coated, unexposed disks turned yellow upon drying on the benchtop. Color index 2.5 on vanillin wheel.
	0.075	none	orange yellow	At 20 ppb UDMH, disks developed color of medium intensity in 3 days. Unexposed disks discolored yellow (2) over 2 weeks. Vanillin color wheel used to determine color index of unexposed disks.
		phosphoric acid	orange color index 1.0	Color judged on the PDAB hydrazine wheel.
phosphomolybdic acid in methanol		none	deep cornflower blue	
			pale green	20 ppb UDMH for 24 hours. Dose = 480 ppb-hrs.

Compound	Solution Conc. (%)	Acidification	Color Development with UDMH	Comments
2-nitro-benzaldehyde in acetone	0.5	none	golden yellow color index 2.0	
		phosphoric acid	golden yellow color index >5.0	Disks showed light sensitivity.
			golden yellow color index 1.0	Dose=approx. 2880 ppb-hrs
3-nitro-benzaldehyde in acetone	0.5	phosphoric acid	yellow 2.5 yellow 2.0 yellow 2.5	pH=0 pH=2 pH=3
		none	yellow 2.0	pH=4, color development not immediate
		acetic acid	yellow 2.0	pH=3
2,4-dinitro-benzaldehyde in acetone	0.5	phosphoric acid	orange yellow	pH=2
			warm yellow color index 4.0	17 ppb UDMH for 17.5 hrs. Dose=297.5 ppb-hrs. RH=32%
	slightly higher than 0.5		warm yellow color index 0.5 color index 1.0 color index 3.5	Dose= 25.5 ppt-hrs 102 ppb-hrs 408 ppb-hrs
	0.5		yellow color index 0.5 golden yellow color index 4.0	Substrate: absorbant, woven material Substrate: woven material from GMD Systems, Inc. Dose=approx. 1200 ppb-hrs.

Compound	Solution Conc. (%)	Acidification	Color Development with UDMH	Comments
4-nitro-bezaldehyde in acetone	1.0	none	yellow color index 2.0	
	0.5	phosphoric acid	yellow color index 0.5	20 ppb UDMH for 17.5 hours. Dose=350 ppb-hrs.
			color index 3.0	Dose=approx. 2880 ppb-hrs.
			yellow color index >5.0	
			warm yellow color index 4.0	Egg-yolk shaped color- yellow in center, white around edges.

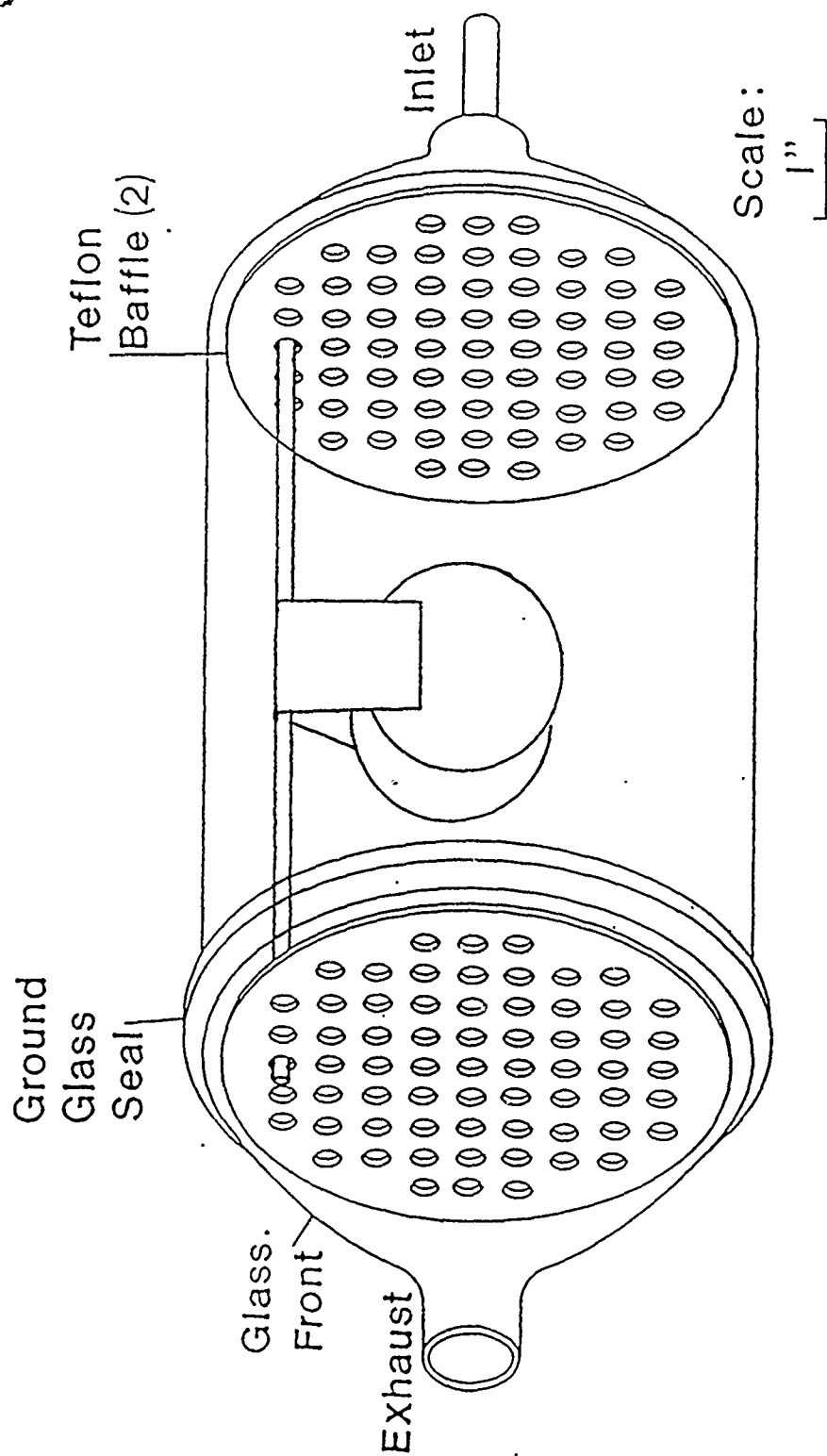


Figure 3. Glass chamber used for exposure of badges.

Physical and chemical interferences were evaluated. Badges were exposed to sunlight, tobacco smoke, nitrogen dioxide (NO_2), and ammonia (NH_3) before and after UDMH exposure. The GMD vanillin color wheel was used to evaluate color development in most instances. However, the GMD PDAB color wheel for hydrazine was used when color development was more orange.

Ultraviolet absorbers and antioxidants/inhibitors were investigated to eliminate an interference effect caused by exposure to sunlight. Absorbers and antioxidants examined during initial testing include 2-hydroxy-4-methoxybenzophenone (oxybenzone), p-aminobenzoic acid (PABA), naphthoquinone, 2-hydroxy-1,4-naphthoquinone (HNQ), hydroquinone, 2,6-di-tert-butyl-4-methylphenol (BHT), alpha-tocopherol (vitamin E), nordihydroguaric acid (NDHG acid), and propyl gallate.

Ciba-Geigy Corp. was contacted in reference to UV absorbers or inhibitors used in paint formulations. Two patented formulations, Tinuvin 1130 (a UV absorber) and Tinuvin 292 (an inhibitor) were sent to the Naval Research Laboratory (NRL) for examination with the 2,4-dinitrobenzaldehyde. Tinuvin 1130 is a substituted hydroxyphenyl benzotriazole containing two active compounds. Tinuvin 292 is a sterically hindered tertiary amine UV light stabilizer (HALS). Literature from Ciba Geigy suggests that they be mixed to enhance their properties as an inhibitor and an absorber. Figures 4 and 5 show the chemical structures of the active components in Tinuvin 1130 and 292.

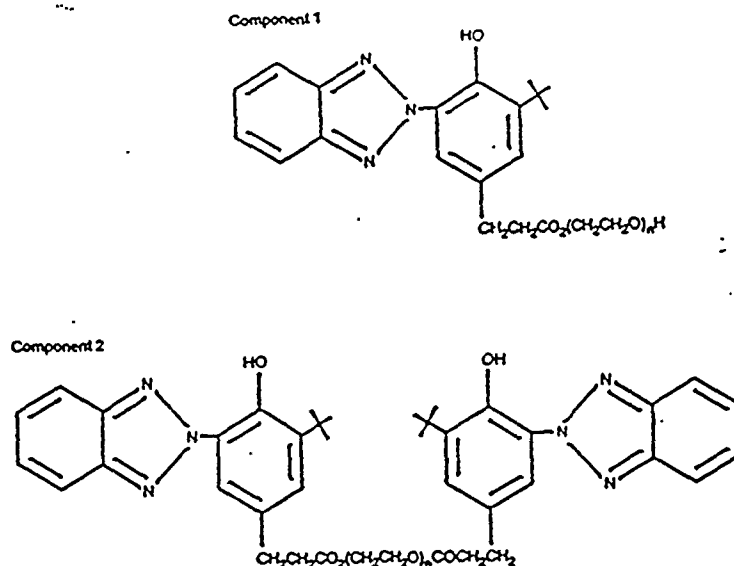


Figure 4. Active Components in Tinuvin 1130.

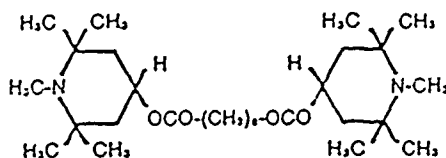


Figure 5. Active Component in Tinuvin 292.

LLumar, a transparent polyester sheet impregnated with UV absorbers was obtained from Read Plastics. It is tinted a pale dull yellow. LLumar effectively blocks UV interference, however, it is not UDMH gas permeable. Three badge designs which incorporate LLumar and allow for diffusion of UDMH vapor were examined. Figure 6 is a schematic of the badge designs.

Badge 1, machined out of nylon, allows for diffusion of UDMH vapor through holes where the cap snaps onto the base. The badge has an inside diameter of 2 inches and accomodates a Whatman filter paper disk with the same diameter. A small viewing window in the cap is covered with LLumar. Badge 2 was machined from polyethylene. The design includes a small well in the base where a 0.5 inch diameter coated substrate sits. A viewing window allows the user to view the entire substrate. The window is located in the center of the cap and is covered with LLumar. There are diffusion holes in the lid and around the badge where the cap snaps onto the base. Any sunlight that enters the badge through the diffusion holes in the lid, cannot directly reach the substrate in the well. Badge 3 was also machined out of polyethylene. It is rectangular in shape. The lid has viewing window which is covered with LLumar. There are troughs cut through the base in the shape of a cross where gas can enter the badge. The lid and base are attached by 4 nylon screws in the corners. It must be pointed out that because the badges were machined, they contain many rough surfaces where the UDMH can adsorb. Therefore, machined badges are not suitable for hydrazines detection. Molded badges provide less surface area for UDMH to adsorb. The badges could easily be molded from low density polyethylene. For our purposes, to test the suitability of LLumar, the machined badges were adequate.

RESULTS

Figure 7 shows the dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde when used as active samplers. The relative humidities used ranged from approximately 10 to 40% RH. The dose response curve for 2,4-dinitrobenzaldehyde gives promising results. The curve is smooth with little scatter in the data points. The first indication of color is at 130 ppb-L. This means that a vapor concentration of 10 ppb could be detected in as little as 13 minutes when sampled at 1 L/min. If the sampling rate was increased, the response time would decrease. A color index greater than 5 is reached at 7000 ppb-L. The initial results on 4-nitrobenzaldehyde are good, however, the compound is less sensitive than the 2,4-dinitrobenzaldehyde. A dose of 500 ppb-L is needed to produce the first indication of color and almost 74000 ppb-L is required to give a color index of 3.5. There is not sufficient data to make conclusions on scatter.

Used as a passive dosimeter, 2,4-dinitrobenzaldehyde performs well. Figure 8 shows the dose response curve for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde. All of the exposures for 2,4-dinitrobenzaldehyde were made at approximately 10 ppb of UDMH. The five data points for 4-nitrobenzaldehyde were made at either 9 or 55 ppb UDMH. Most of the data points are exposures made at 35-40% RH. However, a couple of exposures were made in lower humidity. The points collected at low humidities conform to the dose curve obtained from exposures at mid-range humidities. There is a first indication of color within 14 ppb-hours with 2,4-dinitrobenzaldehyde. There is good correlation between color and dose. The average scatter in the data points at a given dose is limited to approximately ± 0.30 on the color index scale. Saturation occurs at 1600 ppb-hours. The responses observed one hour later are similar. A 10 to 20% reduction was observed for larger doses when evaluated 24 hours after exposure. Larger reductions were observed after 24 hours at low doses. 4-Nitrobenzaldehyde performs less satisfactorily. A color index of < 1 is reached within 77 ppb-hours, however, an exact determination of the limit of detection has not been made. The color intensity of the badge increases slowly from first indication to a color index of 3.5 within 1250 ppb-hours. At this point in the investigation, it was decided to concentrate further efforts on 2,4-dinitrobenzaldehyde.

Disks coated with 2,4-dinitrobenzaldehyde were exposed to 10 ppb of UDMH at different humidities. Variations in relative humidity did not have a significant effect on color development. No definite trend was observed. Variations are within the scatter observed on the dose response curve. However, passive badges exposed

BADGE DESIGN 1

BADGE DESIGN 2

BADGE DESIGN 3

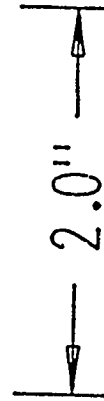
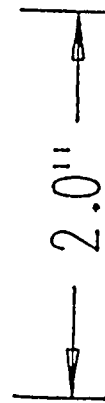
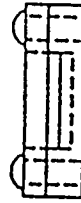
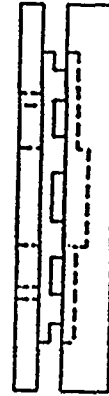
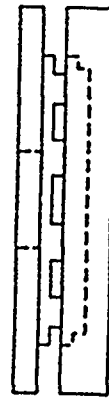
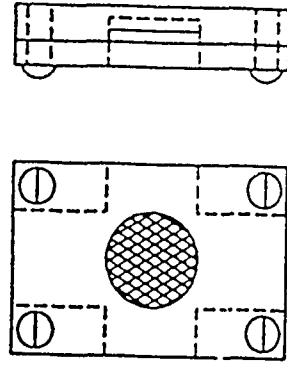
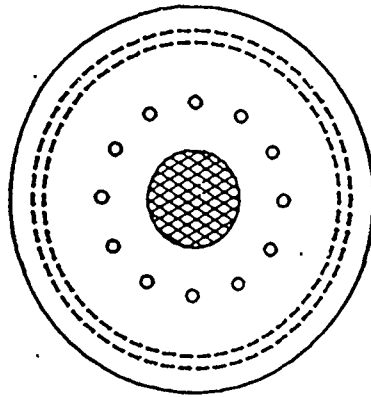
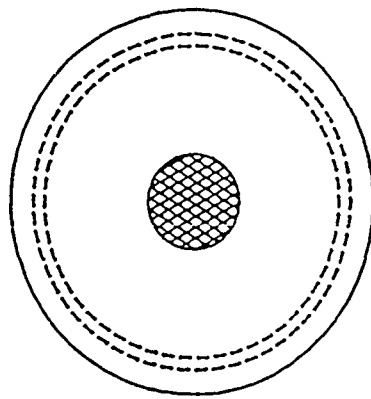


Figure 6. Schematic of machine gun designs. Crosshatched area represents LLumar sun shield.

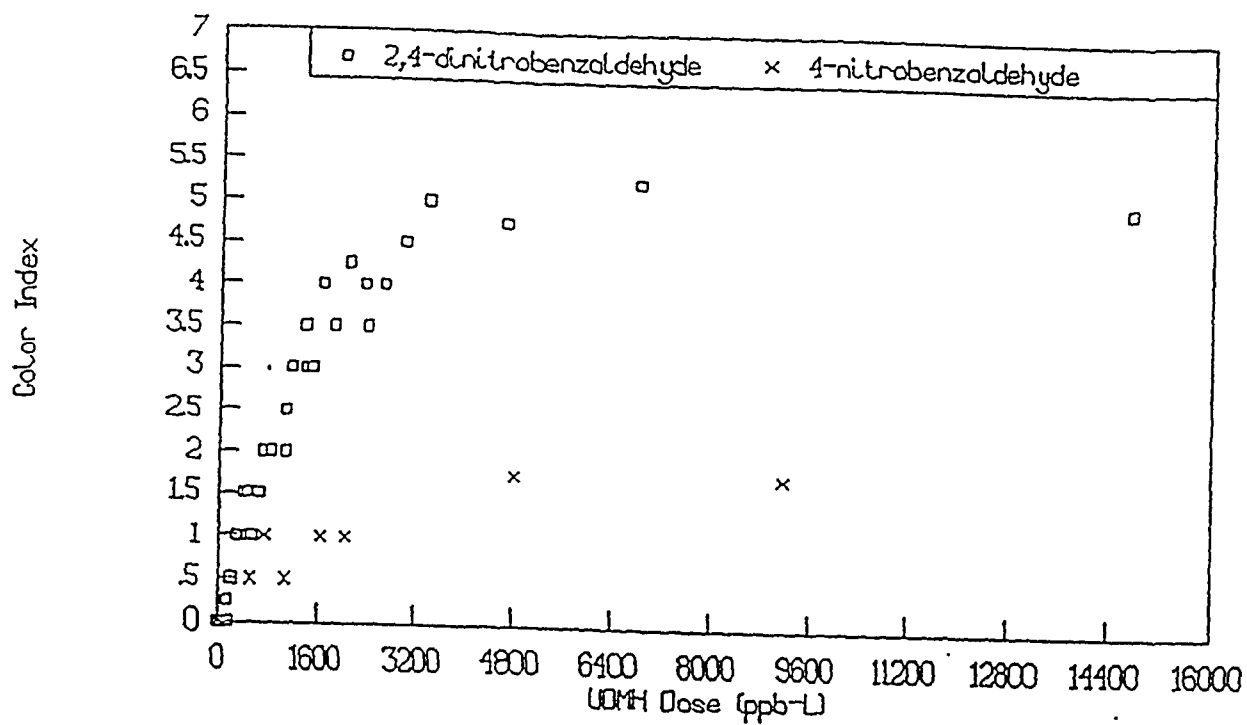


Figure 7. Dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde as active dosimeters.

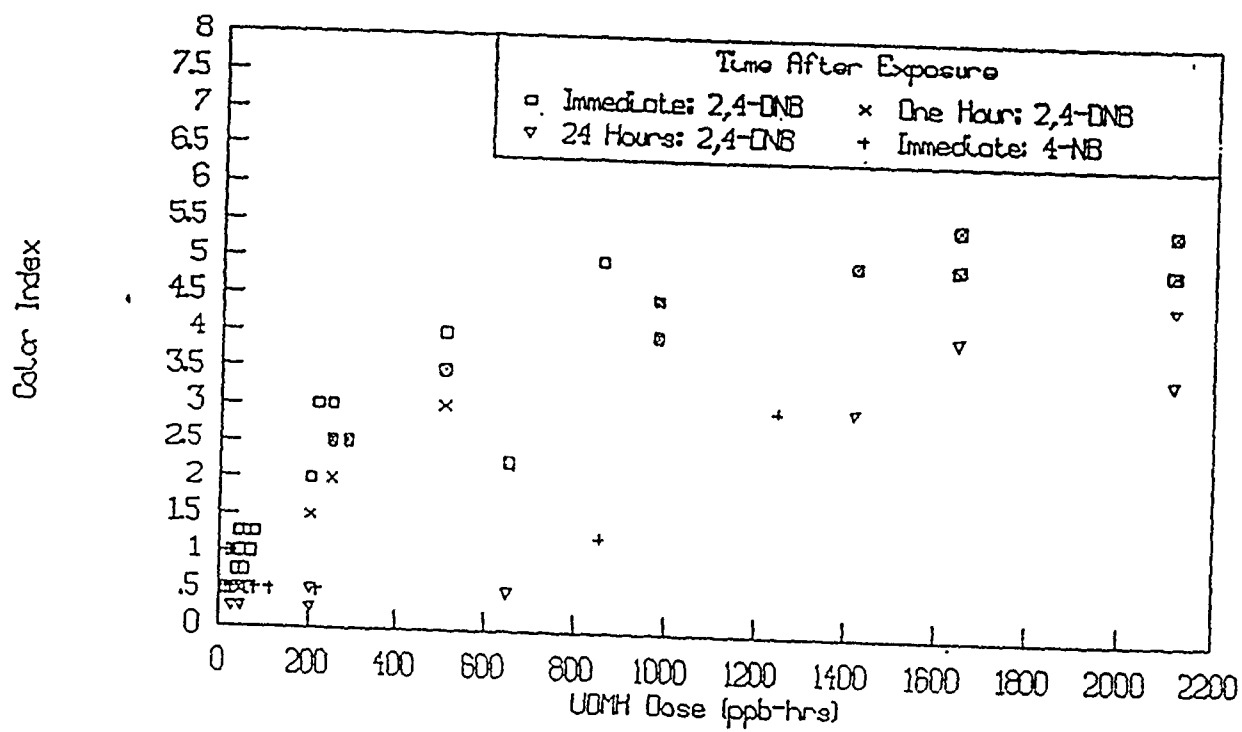


Figure 8. Dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde as passive dosimeters.

to UDMH humidified to 83% RH give a response 64% higher than the average responses at the other humidities tested. An active sampler coated with 2,4-dinitrobenzaldehyde and exposed to 10 ppb of UDMH at <10% RH showed slightly sluggish color development. Table II details the humidity data for the badges exposed passively.

Badges that were "aged" in air in a dark oven at 40°C for one week did not discolor. Figure 9 shows the dose response of the badges to UDMH after accelerated shelf life exposures. The badges stored at room temperature and the "aged" disks performed comparably. Scatter at low doses was similar to that of the "non-aged" badges. Although saturation cannot be determined from the limited data, the aged badges reached a color index of 5 within approximately 1000 ppb-hours.

Interference tests were performed on the coated disks. Badges exposed to NO₂ after UDMH exposure indicate a slight bleaching of the color. Tables IIIa and b give the color indices for badges exposed to NO₂. Exposure to NO₂ prior to UDMH exposure does not cause color development on the badges. When subsequently exposed to UDMH, normal color development is observed. NH₃ is not an interferent to the 2,4-dinitrobenzaldehyde chemistry. Tables IVa and b give the data for NH₃ exposure. The badges are not affected by exposure to NH₃ either before or after UDMH exposure.

Badges were exposed both passively and actively to an environment with a high concentration of tobacco smoke. Table Va shows the data for passive sampling of a tobacco environment and subsequent UDMH exposure. Table Vb shows the data for active sampling of the tobacco interferent and subsequent UDMH exposure. When exposed initially to the smoke, there was no effect noted either passively or actively. When subsequently exposed to various doses of UDMH, the passive samplers showed normal color development, while the active samplers showed a slightly higher color development than previously observed.

Sunlight proved to cause interference effects with the coated disks. A coated disk was exposed to sunlight in late August. Within 30 minutes, it developed a yellow color with an index of 0.5-1 on the vanillin color wheel.

Disks were coated with mixtures of the various absorbers or inhibitors and 2,4-dinitrobenzaldehyde and exposed to sunlight. Table VI shows the effects of sunlight on the coated badges. None of the substances tested effectively eliminated the sunlight interference. Alpha-tocopherol (vitamin E), nordihydroguaiaretic acid (NDHG acid), and propyl gallate were obtained for testing. The literature suggested using citric acid (CA) in conjunction with the inhibitors. The citric acid enhances the effectiveness of the inhibitors. Disks coated with various inhibitors and 2,4-dinitrobenzaldehyde were exposed to sunlight or to a UV lamp with a spectral bandwidth of 254 nm. The sunlight exposures occurred on days with bright sunlight in September and October. The parameters of the UV lamp are 115 V, 60 Hz, and 0.16 Amps. Table VII details the results from sunlight and subsequent UDMH exposures of these coated disks. Exposure to UDMH was accomplished by holding the disk over an open bottle of concentrated UDMH. Color development of the badges in the presence of UDMH is hindered when exposed to sunlight first. Exposure to UDMH after sunlight exposure caused the badges to develop a more orange shade than the normal golden tone.

The Tinuvin compounds obtained from Ciba-Geigy were evaluated. Filter paper disks were coated with 2,4-dinitrobenzaldehyde allowed to dry, then coated with a 3% Tinuvin 1130, 2% Tinuvin 292 solution. The 3% 1130 to 2% 292 ratio was suggested in the literature received with the samples. Exposure of the disks for 1.5 hours under the 254 nm UV lamp caused a yellow color index of 2 to develop. With subsequent exposure to UDMH, the color deepened to an intensity of 3.5. Badges coated with the Tinuvin compounds and 2,4-dinitrobenzaldehyde and exposed to UDMH developed an orange yellow color of 4.5. This is comparable to the color index reached on badges without the Tinuvin compounds in the coating solution.

Finally, LLumar was examined. LLumar effectively blocks UV interference on coated disks. Coated disks covered with LLumar and exposed for up to 3.5 hours of sunlight in October showed no color development. Minor color (<1) was observed on badges where sunlight was allowed to directly reach the edges of the substrate.

Table II. Relative Humidity Effects on Passive Badges				
RH (%)	UDMH Dose (ppb-hrs)	Color Development After Exposure		
		Immediate	One Hour	24 Hours
0	22.8	0.25		0.25
0	22.8	0.5		0.25
14	21.0	0.25		
14	21.0	0.25		
32	26.7	0.5		
32	26.7	1.0		
0	38.3	0.5	0.5	0.5
0	38.3	1.0	0.75	0.25
14	41.8	0.5	0.5	0.25
14	41.8	0.5	0.5	0.25
30	39.0	1.0		
30	39.0	0.75		
34	46.0	1.0		
50	45.9	1.0		
50	45.9	1.0	0.5	0.25
83	46.4	1.25	1.25	
83	46.4	1.25	1.25	
At low concentrations of UDMH, the slight variations in dose are normal. The doses from 38.3 to 46.4 ppb-hrs are essentially equal.				

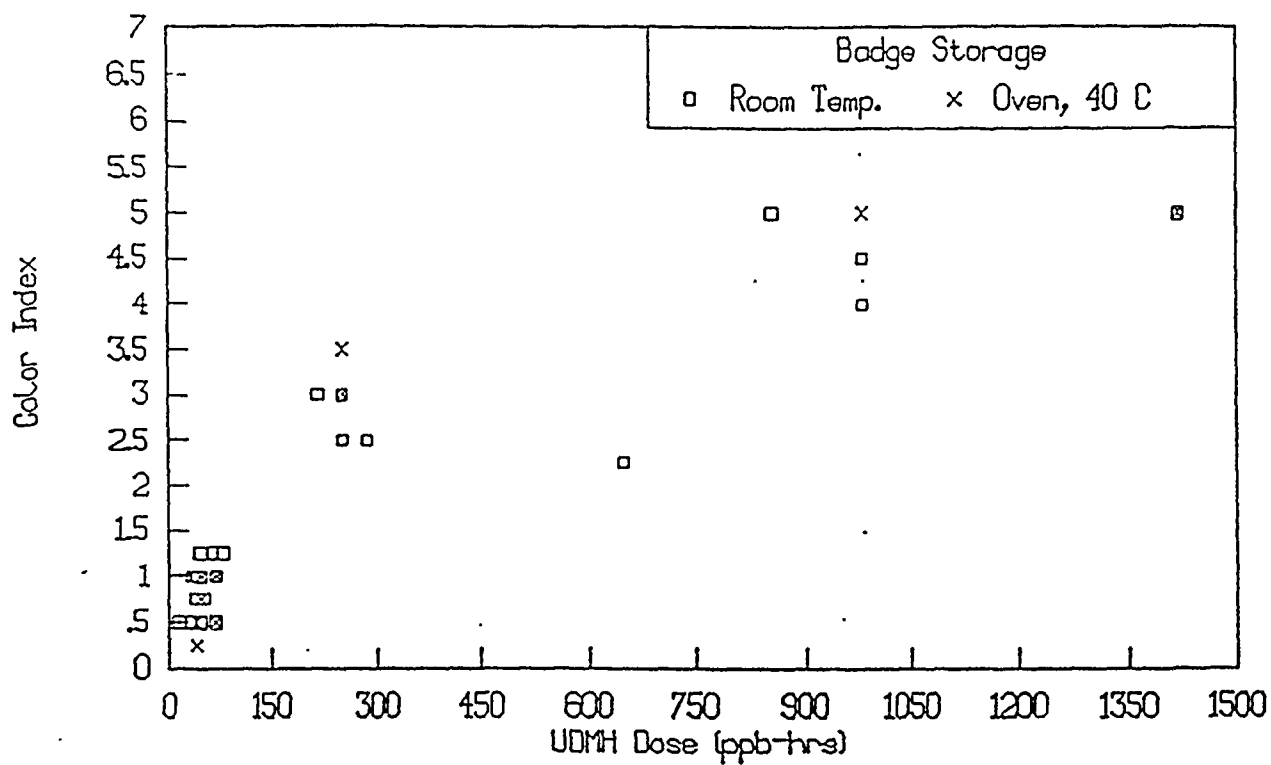


Figure 9. Dose response of badges that were stored at room temperature or at 40°C prior to UDMH exposure.

Table IIIa. NO ₂ Interferent Effects After UDMH Exposure			
UDMH Dose (ppb-hrs)	Post UDMH Color	NO ₂ Dose (ppm-hrs)	Post NO ₂ Color
36.4	0.75	4.24	0.5
36.4	1.0	4.24	0.5

Table IIIb. NO ₂ Interferent Effects Before UDMH Exposure			
NO ₂ Dose (ppm-hrs)	Post NO ₂ Color	UDMH Dose (ppb-hrs)	Post UDMH Color
4.24	0.0	36.4	0.75
4.24	0.0	36.4	0.75

Table IVa. NH ₃ Interferent Effects After UDMH Exposure			
UDMH Dose (ppb-hrs)	Post UDMH Color	NH ₃ Dose (ppm-hrs)	Post NH ₃ Color
32.8	0.5	100.0	0.5
32.8	1.0	100.0	1.0

Table IVb. NH ₃ Interferent Effects Before UDMH Exposure			
NH ₃ Dose (ppm-hrs)	Post NH ₃ Color	UDMH Dose (ppb-hrs)	Post UDMH Color
100.0	0.0	32.8	0.5
100.0	0.0	32.8	1.0

Table Va. Tobacco Interferent Effects Before UDMH Exposure on Passive Badges

Tobacco Exposure Time (hrs)	Post Tobacco Color	UDMH Dose (ppb-hrs)	Post UDMH Color
1.0	0.0	0	N/A
2.0	0.0	0	N/A
4.0	0.0	123	2.0
8.0	0.0	123	2.0

Table Vb. Tobacco Interferent Effects Before UDMH Exposure on Active Badges

Tobacco Exposure Time (hrs)	Post Tobacco Color	UDMH Dose (ppb-L)	Post UDMH Color
2.0	0.0	183.3	1.0
2.0	0.0	382.7	2.0
4.0	0.0	220.2	1.25

Table VI. Sunlight Exposures of Badges Coated with 2,4-Dinitrobenzaldehyde and Additives

Additive	Pre-UV Color	Sunlight Exposure Time (hrs)	Post UV Color
oxybenzone	white	1.3	yellow 1
PABA	yellow 2	1	yellow 2.5-3
hydroquinone	white	1	gold-yellow 2.5-3
BHT	white	1	tan-yellow
naphthoquinone	white	1	yellow 2.5-3
INQ	yellow 1.5	1	gold-yellow 2-2.5

Table VII. UV Lamp and Sunlight Exposures of Badges Coated with 2,4-Dinitrobenzaldehyde and Additives

Additive	Post UDMH Color	Pre-UV Color	UV Exposure Time (hrs)	Post UV Color	Color After UV and UDMH Exposure
tocopherol + CA		white	1	yellow 2.5-3	
tocopherol + CA*		white	1	yellow 2.5	
hydroquinone	gold-yellow	beige	1	tan-orange	
BHT	gold-yellow	white	1	yellow 2.5-3	
BHT*	gold-yellow 5	white	1	yellow 1.5	gold-yellow 3-5
NDGH acid + CA	orange yellow >5 **	beige-yellow 1.5	3	tan-yellow 3.5	tan-orange 3 **
propyl gallate + CA	yellow 1	orange yellow 4 **	18	gold-yellow 3	tan-orange 3 **

* UV lamp exposure at 254 nm.

** Evaluated on PDAB hydrazine wheel.

Figure 10 shows the UV-vis spectra in percent transmittance of the 2,4-dinitrobenzaldehyde solution and also that of the LLumar. The spectra indicate that LLumar transmits in the same region as the 2,4-dinitrobenzaldehyde. Conversely, the LLumar absorbs UV light in the same region that the 2,4-dinitrobenzaldehyde absorbs, therefore, the LLumar would effectively protect the badges from any UV effects.

LLumar was then incorporated into the three machined badges discussed in the Experimental section. All three badges were exposed to UV light from a lamp placed approximately 5 inches above the face of the badge. Badge 1 was exposed to the UV lamp at 254 nm for 3.5 hours with no discoloration. Badges 2 and 3 were placed at different angles to the lamp. They were exposed to UV light set at 366 nm for 4.0 to 8.0 hours. The parameters of this lamp were as follows: 115 V, 60 Hz, and 0.16 Amps. Table VIII gives the data from these UV exposures. Data marked with an asterisk on Table VIII represent color development on the side of the substrate shielded by LLumar. Data not marked represent color development on the side of the substrate facing the badge base. In most cases, there was no color development on the front of the substrate. Color development was observed on the back of the substrate facing the base of the badge. This is probably due to the badges being semi-transparent, thus allowing UV light to penetrate. The LLumar adequately shields the substrate from the effects of UV light with only minor discoloration for exposures times of 6.5 hours and longer.

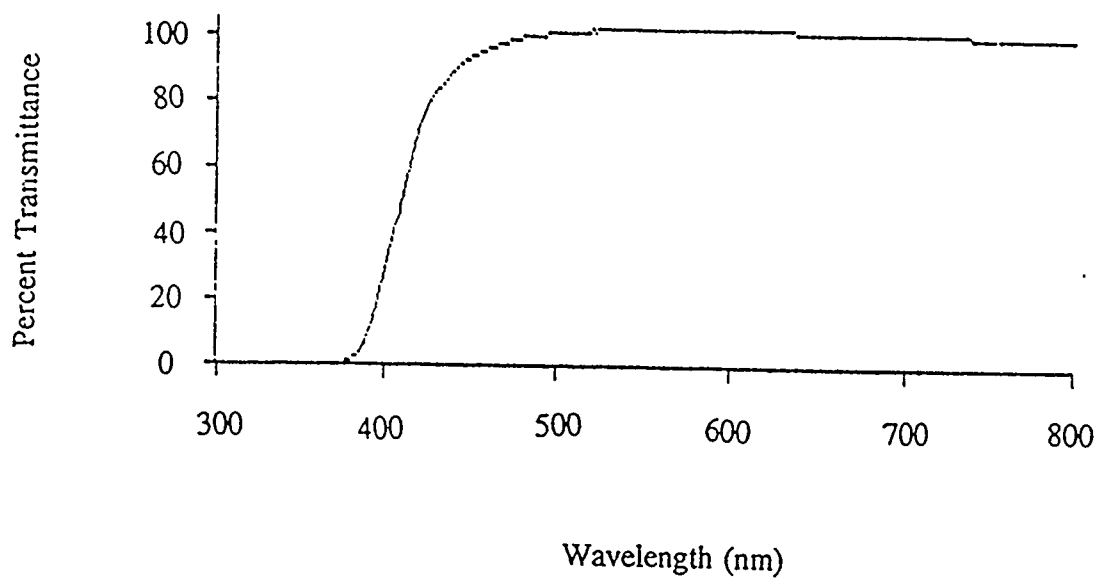
All three of the badges were exposed to concentrations of UDMH of 40 and 300 ppb. Table IX details the exposure results of the badges. Badge 1 did not perform adequately. The cap design does not allow the user to see the entire substrate through the LLumar. Only the center portion of the substrate can be seen. Since UDMH reacts with the 2,4-dinitrobenzaldehyde immediately upon contact with the coated substrate, the color change occurs at the edges where the gas is diffusing into the badge and does not reach the center of the substrate in a reasonable time.

The designs of badges 2 and 3 allowed for better diffusion of the UDMH. Color was visible within 94 ppb-hours for badge 2. Badge 3 performed better than badge 2, giving a color index of 0.5 within 48 ppb-hours.

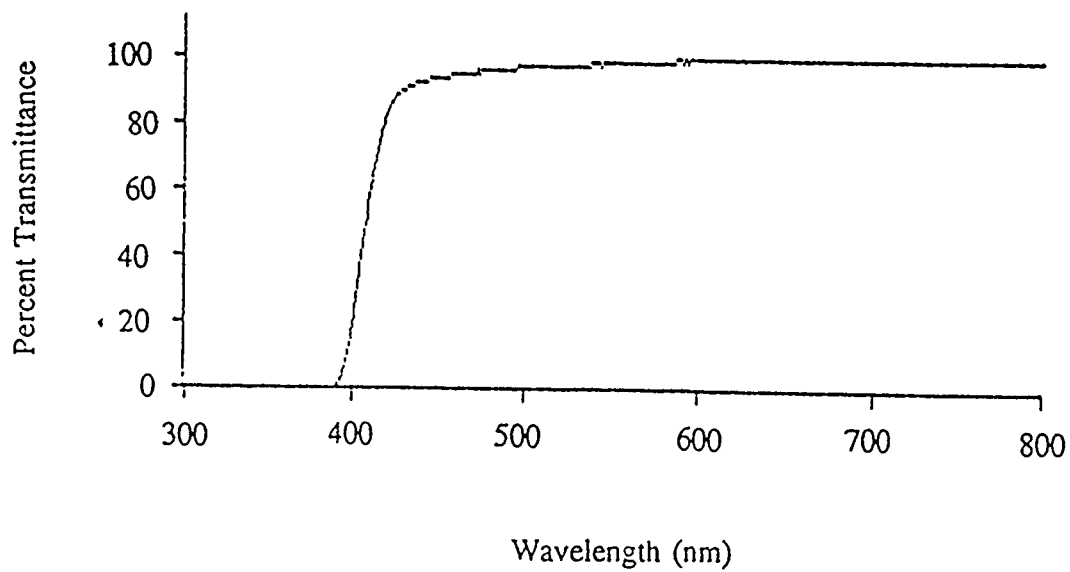
CONCLUSIONS

These results look promising. In an active 2,4-dinitrobenzaldehyde system, the precision in the color development is very good at each dose tested. The lower limit of detection is 130 ppb-L. The initial results indicate that the dosimeter can meet the proposed TLV levels when used both actively and passively. As a passive dosimeter, the 2,4-dinitrobenzaldehyde shows a detection limit of 14 ppb-hours. The badge is not significantly affected by exposure to UDMH at various humidities other than a sluggish color development noted with the active system at <10% RH and an enhanced color in the passive system at 83% RH. The badges are not discolored by accelerated aging tests, and in the presence of UDMH they perform comparably to the badges stored at room temperature.

The only interferent problems encountered are a slight bleaching effect on badges exposed to UDMH and then NO_2 , and a sunlight interference. The sunlight effect can be eliminated with the use of LLumar incorporated into a badge design, as well as molding the badges from black polyethylene.



(a)



(b)

Figure 10. Percent transmittance spectra in the UV-visible range for a) 2,4-dinitrobenzaldehyde and b) LLumar.

Table VIII. UV Interference Effects with Machined Badges

Angle UV Light to Face of Badge	Exposure Time (hrs)	Color on Badge 2	Color on Badge 3
0	4.0	0.5	0.5
0	6.5	1.0	1.5
0*	6.5	0.25	0.25
45	4.0	0.5	0.0
90	4.0	0.5	0.5
90	8.0	1.25	0.5
90*	8.0	0.5	0.25

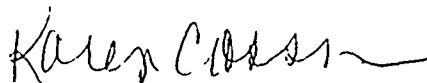
* Color on side of substrate shielded with LLumar

Table IX. UDMH Exposure of Machined Badges with LLumar

Badge Number	UDMH Conc. (ppb)	UDMH Dose (ppb-hrs)	Color Index
1	37	752	0.25 (3 edges)
2	40	94	0.25
2	300	900	2.0
3	40	48	0.5
3	40	94	0.75
3	40	176	1.0

REFERENCES

1. Hannum, J.A.E., "Recent Developments in the Toxicology of Propellant Hydrazines", Chemical Propulsion Information Agency, CPTR 82-15, June 1982.
2. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.
3. Crossman, K.P., P.T. Carver, J.R. Wyatt, S.L. Rose-Pehrsson, and A. Thurow, "Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter", NRL Memorandum Report 6668 (1990).
4. Rose, S.L., and J.R. Holtzclaw, "A Critical Comparison of Commercially Available Hydrazine Detectors", NRL Memorandum Report 8848 (1985).
5. Olson, E.C., "The Coulometric Determination of Hydrazine and Substituted Hydrazine", Analytical Chemistry, **32 (12)**, 1960, pp. 1545-1547.



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A REAL-TIME PASSIVE DOSIMETER FOR HCL VAPOR

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ABSTRACT

A real-time dosimeter has been invented for the colorimetric detection of hydrochloric acid in ambient air. The technique involves the coating of a substrate with a hydrazone or azine that is colorless in neutral conditions and develops an intense color upon acidification. Laboratory investigations have been performed using controlled atmospheres provided by the US Army Biomedical Research and Development (USABRD) facility (Ft. Detrick, MD), and the Aerospace Corporation Laboratory (Los Angeles, CA). The system has also undergone field evaluation at Kennedy Space Center during the launch of the space shuttle Atlantis, and at Edwards Air Force Base during test firing of a double BATES motor. The results of these tests are described in this paper.

INTRODUCTION

Hydrochloric acid is regarded as a hazardous chemical and exposure may cause adverse health effects as serious as chemical pneumonia. The Occupational Safety and Health Administration has established an atmospheric exposure ceiling limit of 5 ppm. Monitoring of employees and their work environment is suggested to insure that the exposure remains below the defined limit. In the propulsion industry an area of concern is the use of perchlorate-based rocket fuels in which HCl is formed as a combustion product.

Interest has been shown by branches of the DOD for the development of a small, inexpensive, passive system for the detection of HCl. In response to this need we have developed a dosimeter that can be used for personnel and area monitoring. The dosimeter uses a color chemistry that involves the hydrazone or azine produced from the reaction of vanillin and hydrazine. This product is colorless in neutral conditions and develops an intense yellow color upon acidification.

This report describes the results of laboratory investigations conducted at NRL, USABRD, and Aerospace. The results of the preliminary field investigations performed at Kennedy Space Center (KSC) and Edwards Air Force Base (EAFB) are also addressed.

EXPERIMENTAL

Dosimeter. The dosimeter consists of three basic parts: the coating, the substrate, and the badge housing. The coating material is the hydrazone or azine product formed from the condensation reaction of hydrazine and vanillin, Figure 1. The preparation of the coating has been done as a one or two step process. In each technique a solution was prepared by dissolving 1 gram of vanillin into 50 milliliters of solvent. Typically acetone or isopropanol were used as the solvents. From here the hydrazine can be introduced by two methods. The substrate can be coated with the vanillin and exposed to hydrazine vapor, or liquid hydrazine (typically 15 μ L) can be injected directly into the vanillin solution and which is then coated on the substrate. The effect of the hydrazone concentration has been examined by testing coating solutions containing 5, 10, 15, 20, 30, and 60 microliters of liquid hydrazine.

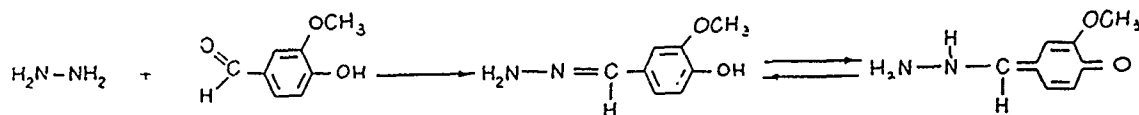
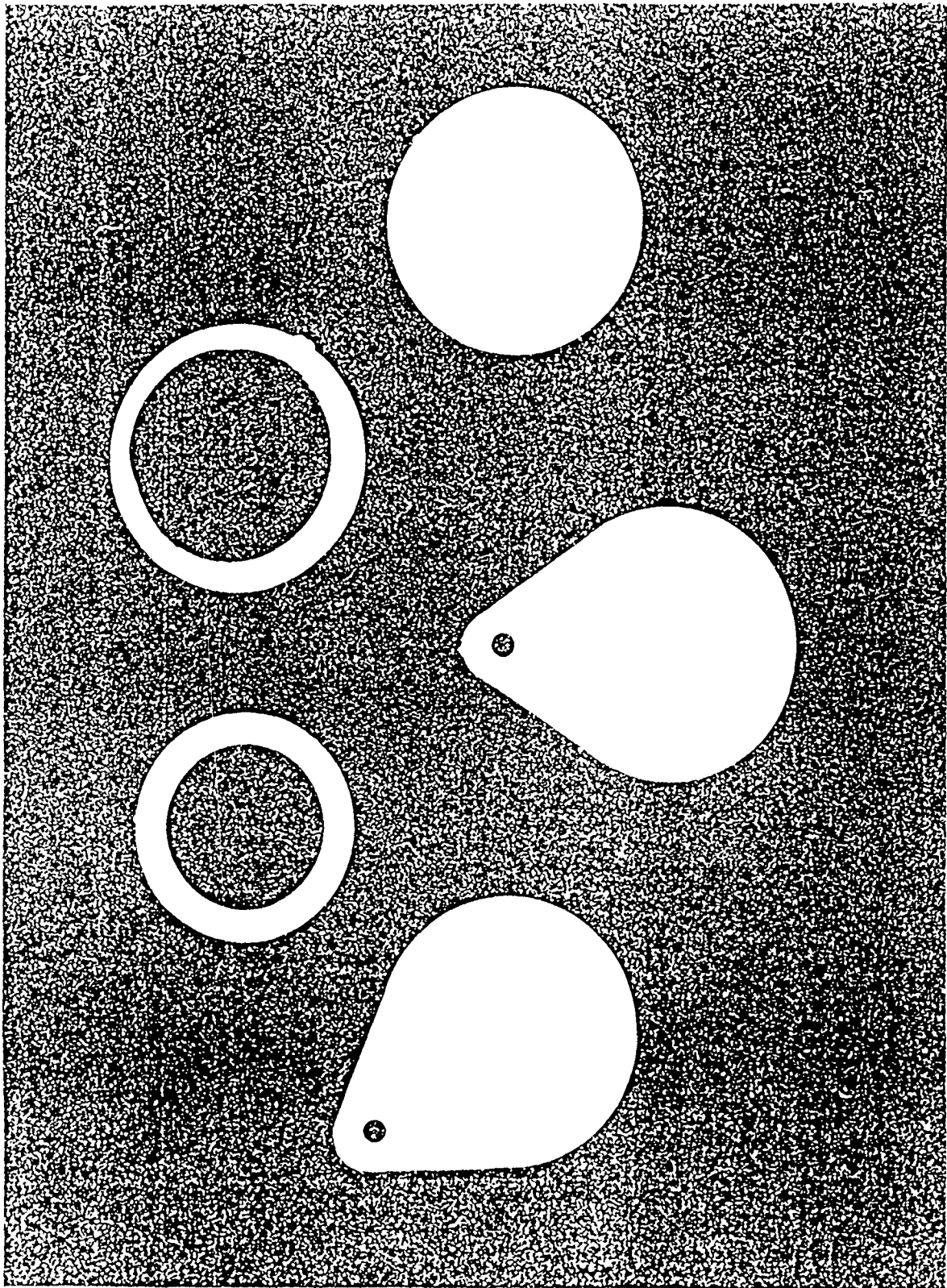


Figure 1. The condensation reaction of vanillin (A) and hydrazine (B).

The substrate can be any material that will accept the coating. We have used Whatman number 42 and 40 paper purchased as 4 25 cm diameter disks. This size fits into the badge housing available without requiring alterations. We also have investigated the use of silica gel as a substrate. Silica gel thin layer chromatographic (tlc) plates with plastic backing were cut into disks with diameters of 38 millimeters.

The badge housing is shown in Figure 2. It is molded from polyethylene. The badge was designed to be used in a passive sampling system for hydrazines¹. The base, diffusion barrier and cap were designed to snap together. It may be used with or without the diffusion barrier. The function of the diffusion barrier is to control the collection rate and prevent effects from the face velocity of the atmosphere. It does however reduce the visibility of the indicating surface.



HCl Exposure Environments. The experiments discussed will be divided into two categories: laboratory exposures and field exposures.

Laboratory Exposures. Experiments were performed at three different locations. Table 1 outlines information pertaining to the exposure environment for each of the laboratory locations.

Table 1. Laboratory Evaluation Information

<u>LOCATION</u>	<u>ENVIRONMENT</u>
NRL	Head space gases of a concentrated HCl acid bottle.
USABRDL	A standard gas cylinder diluted with ambient air and fed into a wind tunnel.
Aerospace	A standard gas cylinder diluted with nitrogen and fed through a glass midget impinger.

The exposure experiments conducted at NRL were performed by holding the coated substrate over an open vial of concentrated hydrochloric acid. These tests were purely qualitative since there was no control on any of the variables.

The next series of experiments were performed with Dr. Hoke et.al. upon his invitation to USABRDL at Ft. Detrick, MD., in order to use a controlled atmosphere to test the dosimeter. A wind tunnel that supplied <50 to 800 ft/min. face velocities was used as the exposure chamber. The test atmospheres of 4.6 to 27 mg HCl/m³ were generated by dilution of a standardized gas. The concentrations were verified by continuous monitoring with a prototype USABRDL HCl instrument.²

The Aerospace laboratory generated controlled test atmospheres of 0.7, 2.0, 25, 50, and 100 ppm HCl gas by dilution of a HCl mixture from a gas cylinder. The concentrations were monitored by prototype IR instruments. Relative humidities of <10 and 40% were tested. For dry test environments the dilution gas was nitrogen, and for humid condition a nitrogen and air mixture was used. A midget glass impinger with a tapered inlet tip was used as the exposure chamber, Figure 3. The chamber held one coated disk per test.

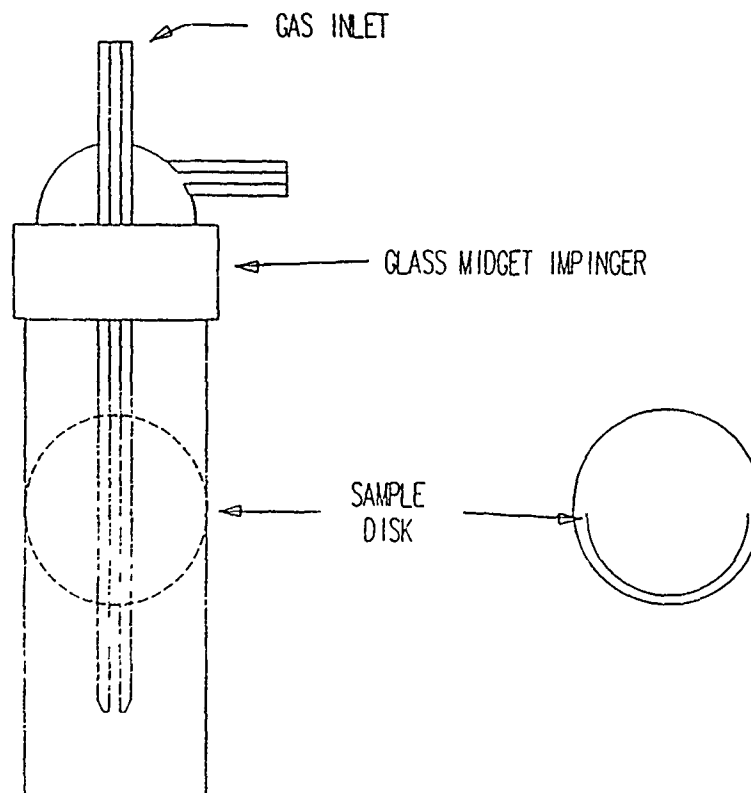


Figure 3. Exposure apparatus used at Aerospace Lab in Los Angeles

Initial tests were performed on the effluent gas from the Spectral Sciences, Inc. IR instrument. It was later discovered that the concentration exiting the instrument was affected by the presence of metal and other non-compatible materials. Subsequent tests were conducted directly sampling the gas stream.

Field Exposure Field exposure experiments were performed at KSC and at EAFB. Table 2 outlines information pertaining to the exposure environment for each of the field tests.

Table 2. Field Evaluation Information

<u>LOCATION</u>	<u>SOURCE</u>
KSC	Two solid rocket boosters of the space shuttle.
EAFB	Test firing of a double BATES motor. 140 pounds of propellant.

Field evaluation of the dosimeter was performed at KSC during the December 2, 1988 launch of the space shuttle Atlantis, STS-27. Sampling sites are shown on the map in Figure 4. For this experiment it was necessary to have the dosimeters in position two days prior to launch. The samples at locations 1 through 8 were nailed to telephone-type poles, Figure 5. Four samples were placed on each pole. Each sample was designated with its position number and a letter, A,B,C, or D. The meaning of each letter is listed in Table 3 below.

Table 3. Description of Sample Types

<u>LETTER</u>	<u>MEANING</u>
A	Whatman # 42 substrate, white badge, no diffuser
B	Whatman # 40 substrate, white badge, no diffuser
C	Whatman # 42 substrate, black badge, no diffuser
D	Whatman # 42 substrate, Black badge, with diffuser

An initial set of samples was placed on the perimeter fence during a site tour on November 29, 1988. This was done to ensure sample placement in the event of restricted area access on the following days. This was not the case and the samples were replaced the following day. The collected samples were qualitatively tested along side fresh disks.

Samples at locations 9-20 consisted of only type A and B samples. These samples were placed in standard outlet electrical junction boxes to protect them from the environment (intense sunlight, rain, etc.), Figure 6. The use of the junction box could not be approved for samples located inside the perimeter fence, (samples 1-8). This was because the box was designated a potential projectile.

The meteorological conditions at the time of the launch of STS-27 are listed in Table 4.

Table 4. Meteorological Conditions

Wind Direction	From 330°
Wind Speed	18 knots, gusting to 20 knots
Temperature	57°F - 59°F
Dew Point	35°F
Bar. Pressure	30.35 inches Hg

The field testing of the dosimeters at EAFB was conducted on January 12, 1988. Badges were deployed approximately one hour prior to exposure. Table 5 contains information on the samples. The samples were placed in badges when possible, and taped to various surfaces. They were placed facing the source and perpendicular to the ground. The placement of the samples is depicted in Figure 7. The approximate path of the HCl cloud, as determined visually, is indicated by the dotted area in the figure.

Table 5 EAFB Field Samples

<u>Type</u>	<u>Substrate</u>	<u>Housing</u>	<u>Locations Sampled</u>
A	Paper, Old*	Naked	1 through 11
B	Silica Gel	Naked	1 through 4, 6, and 9 (Diffuser on 1, 2, and 3)
C	Paper, New*	Diffuser	1 through 11 (No diffuser on 7, 8, 10, and 11)

* Old and New refer to the coating date. The old paper was coated 11/22/88 and the new paper was coated 1/5/89.

Interferant Testing. The effects of sunlight and ammonia were tested at NRL on unexposed dosimeters. Coated disks were cut in two. One half of the disk was exposed to the interferant and the other half retained as a control in a zip-lock plastic bag. Following the interferant exposure the halves were recombined and qualitatively tested with HCl vapor. Comparisons of the response time and color intensity were made. Table 6 lists the interferant exposure conditions.

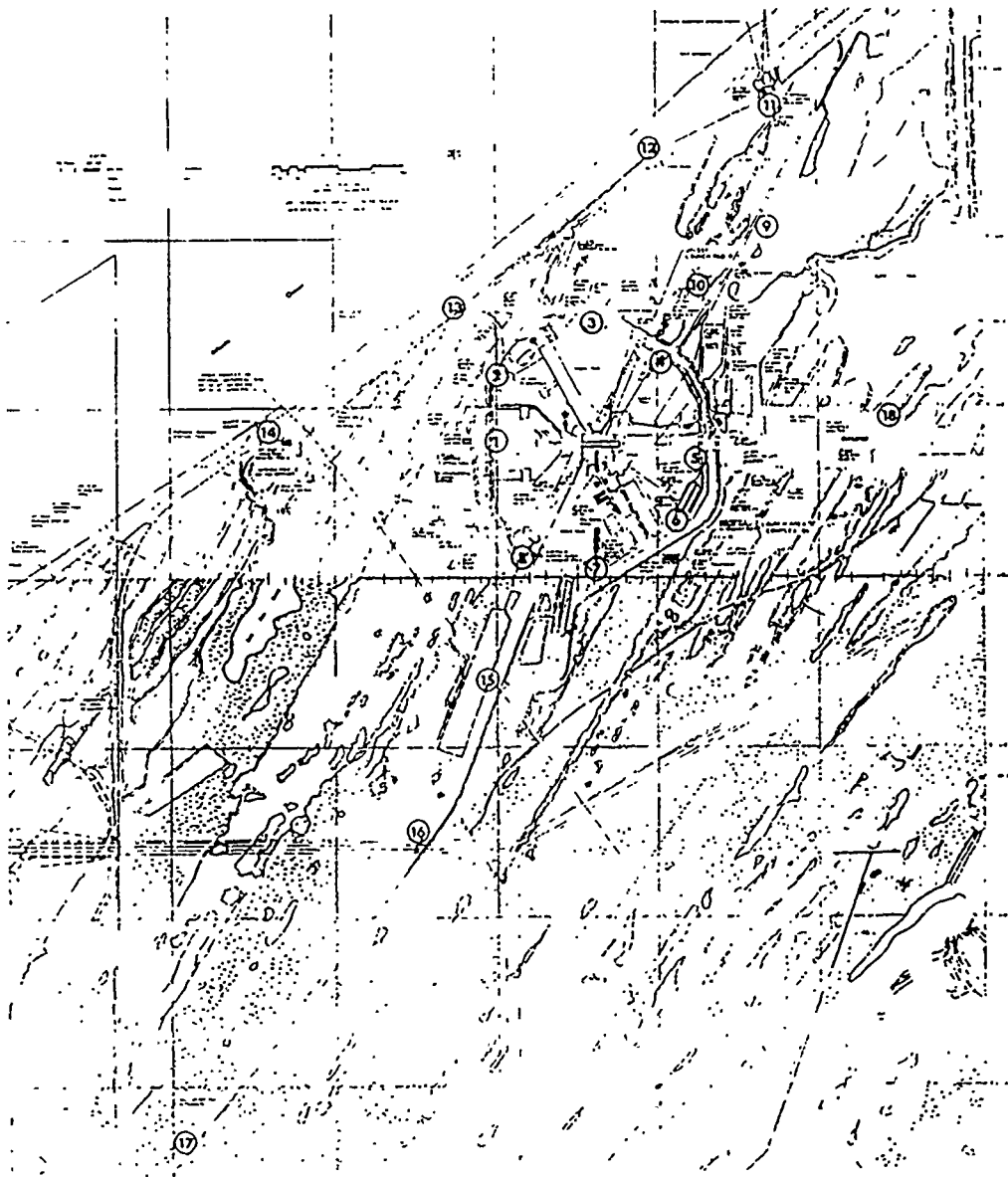


Figure 4 Composite of NASA Maps F1 and F2 indicating the sites sampled during the field test.

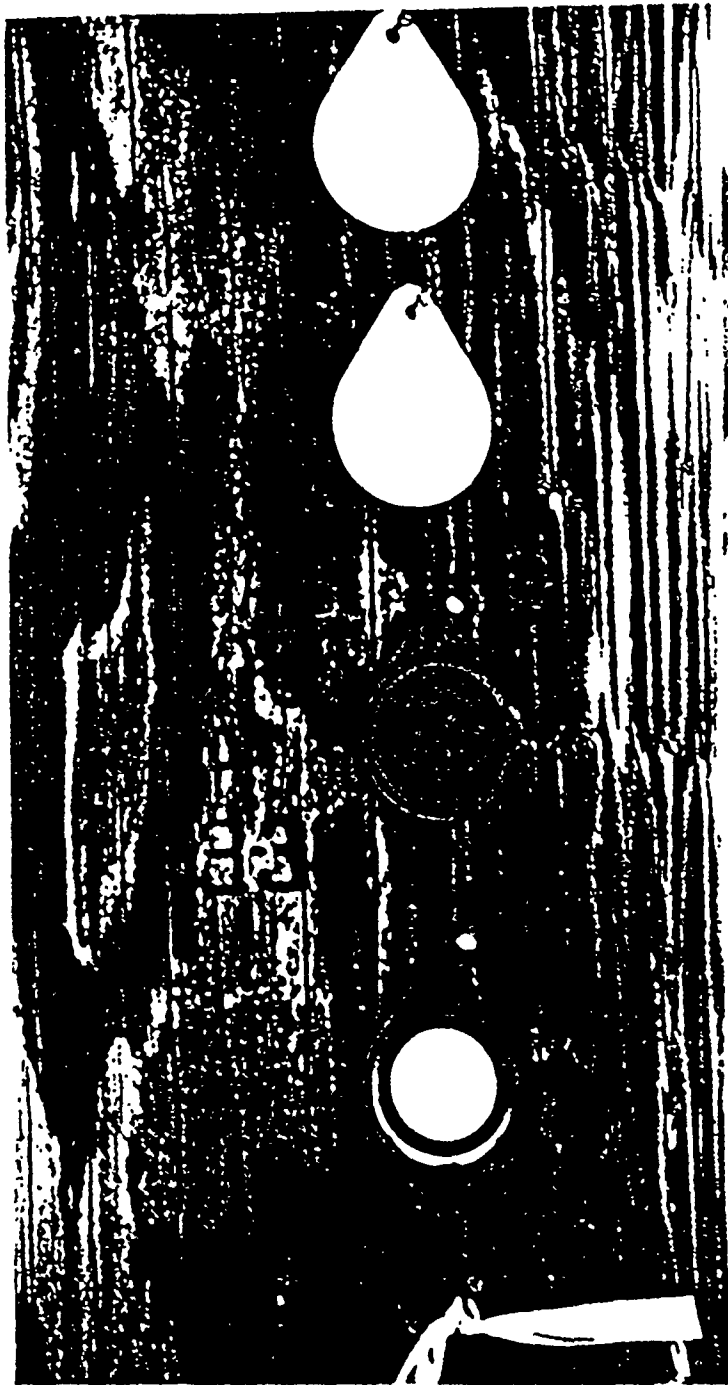


Figure 5. Example of sampling set-up used for samples 1 through 8, and 19.
The samples are designated A, B, C, and D from top to bottom.

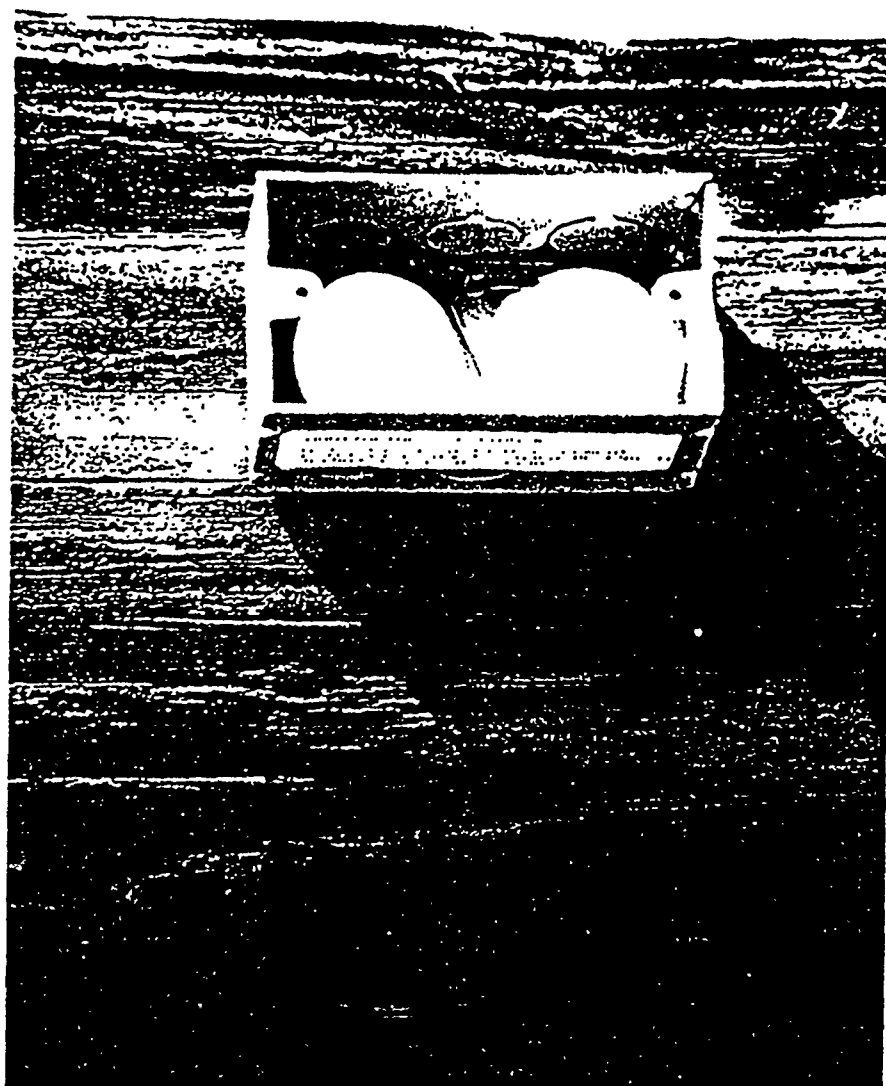


Figure 6. Example of sampling set-up used for samples 9 through 18, and 20. The samples are designed A and B from top to bottom. The label on the side contained information on: the site designation, the type of sampler, and the point of contact.

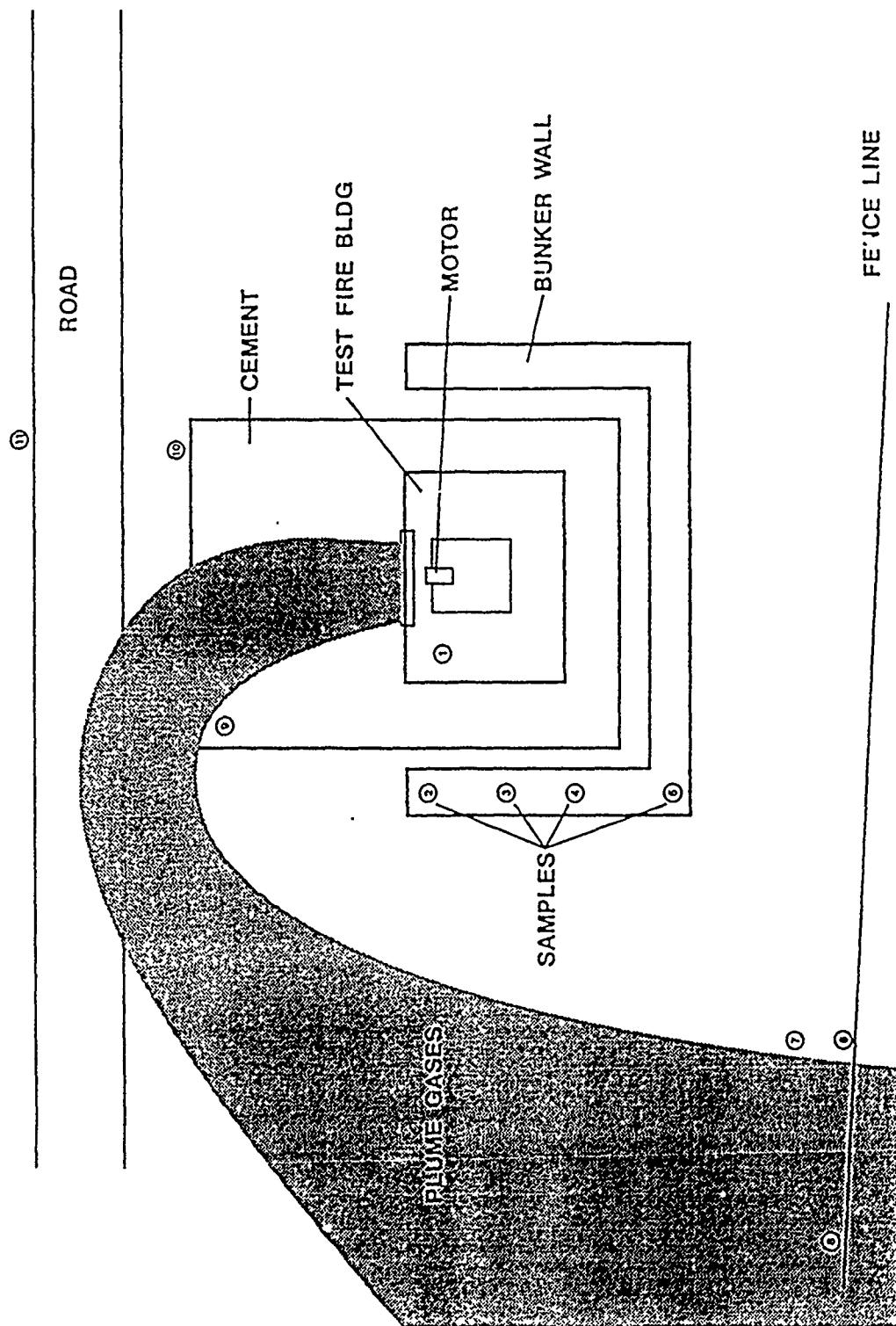


Figure 7. Map depicting the field sampling sites at Edwards Air Force Base.

Table 6. Interferant Exposure Conditions

<u>Interferant</u>	<u>Exposure Time</u>	<u>Exposure Comments</u>	<u>Results</u>
Sunlight	6 hours	50-55°F, Low RH	No effect
Ammonia	1 hour	10 ppm, 55% RH	No effect
Ammonia	21 hours	20 ppm, 35% RH	No effect

RESULTS

Dosimeter. Upon acidification the coated substrate will develop a bright yellow color. The response is dose related. However, the intensity of the saturation color appears to be directly dependant upon the amount of hydrazine used to prepare the coating. When 20, 30, and 60 microliters of Hydrazine were used in the coating solution, the coated substrate developed a yellow discoloration. Two substrate materials, paper and silica gel, were coated for testing. The results of their performance will be discussed under the HCl Exposure section.

HCl Exposure The results are divided into two categories: laboratory exposures and field exposures.

Laboratory Exposure. The colorimetric system appears to be extremely sensitive. At the laboratory tests performed at USABRDL and Aerospace we were unable to determine the lower limit of detection because we could not obtain low enough concentrations. All tests performed saturated the dosimeters. Some of the variations in the concentration of the test atmosphere were achieved by holding the HCl constant and increasing the dilution air. In these situations the flow rate and the amount of dilution gas did not effect the color development. The color development appeared to be dependant the mg/min of HCl.

As mentioned earlier, two substrate materials, paper and silica gel, had been coated for testing. The silica gel substrate appeared to perform better than the paper in dry testing. First indication of color was noted within the first two minutes of exposure for all tests except the paper in dry conditions.

Exposure to the interferent ammonia did not appear to affect the performance of the paper system. The silica system was not tested. The tests were conducted with 10 and 420 ppm hours ammonia doses. The response of the ammonia exposed indicator was identical to that of a control.

Field Exposure. The launch of STS-27 provided an excellent opportunity for evaluating the field performance of the HCl detection system. The initial samples placed two days prior to the launch were removed after 24 hours. Their performance was qualitatively tested along side control samples. No effect was noted from the 24 hours of ambient exposure. The responses obtained from the badges that were in place during the launch are outlined in Table 7. Refer to Figure 4 for information on the sample sites. Samples located at sites 13 through 17 and 20 gave little to no indication of exposure.

Table 7. Samples with Positive HCl Indication
(Listed in order of intensity.)

<u>Inside Perimeter</u>	<u>Outside Perimeter</u>
1 Residue (Most Intense Color)	10 similar to 2D (Most intense color)
2 -	9
3 -	11
4 -	12 similar to 4
5	18
6	
7	
8	

"C" samples 1, 2, 3, 4, and 6 were lost. A residual dust from the SRB (solid rocket booster) combustion was present on samples in positions 1 through 4. The dust was a dirty yellow color. The diffusion cap protected the "D" samples to some extent from the contamination.

EAFB Field Test. A map containing information on the location of the samples is found in Figure 7. The samples at site 9 were a bright yellow saturated color. The silica gel system developed a much more intense color than the paper system. The samples at positions 2 through 5 were very similar in color development. Again the silica gel was more intense. At sample sites where two paper systems were deployed, one with and one without a diffusor, a direct comparison could be made. The sample with the diffusor did not develop the color intensity observed in the naked system.

Sites 6, 7, and 8 gave greater than moderate indication. The color intensity of the silica gel samples was greater than that of the paper samples. Sites 10 and 11 had moderate indications of exposure. Due to a shortage of silica gel samples, only the paper systems were deployed at these locations.

The color stability of the silica gel substrate system is greater than that of the paper system. Upon return to NRL the samples were inspected. The paper systems had lost the majority of their color. The silica gel samples retained color. There are no means to quantitate the color at this point; therefore the color stability comments are only qualitative.

CONCLUSIONS AND DISCUSSION

The performance of the passive indication system has been successfully demonstrated in the laboratory and in the field. The colorimetric system appears to be extremely sensitive and fast. In the laboratory tests we have been unable to define the lower limit of detection. We estimate that it is less than 1 ppm-min. All of the tests saturated the dosimeters. The color development begins immediately upon exposure to the TLV, with a clearly visible color developing in a few minutes. The system also appears to be unaffected by exposure to ammonia, 10 and 42 ppm hours, prior to HCl exposure.

Field tests have indicated that ambient deployment of the sample for up to 48 hours prior to HCl exposure does not affect performance. For testing in dry environments the use of silica gel as the substrate has been found to improve performance. In addition, the stain stability of the silica gel samples appears to be superior to that of the paper substrate.

We have been encouraged by our results from our initial laboratory and field investigations that have shown the ability of this system to detect low-levels of HCl vapor. Future work needs to be done with this real-time colorimetric technique in order to determine the detection limit and ability to provide quantitative information.

REFERENCES

1. Hawkins, C.M., S.L. Rose, J.R. Wyatt, "A Passive Dosimetry Method for Determining Hydrazine in Air," CIPA 436, Proceedings of the 1985 JANNAF Safety and Environmental Protection Subcommittee Meeting, (Monterey, CA, 4-8 Nov 1985) Naval Postgraduate School, Nov 1985.
2. Hoke, S.H., V.R. Rivera, "A Near Real-Time HCl Monitor," CIPA 485, Proceedings of the 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, (Monterey, CA, 23-26 May 1988) Naval Postgraduate School, May 1988.