



NRL/MR/6180--12-9454

Formaldehyde Five-Day Passive Chemical Dosimeter Badge Validation Study

KEVIN J. JOHNSON

*Navy Technology Center for Safety and Survivability
Chemistry Division*

JANET M. HUGHES

*Nova Research, Inc.
Alexandria, Virginia*

November 30, 2012

Approved for public release; distribution is unlimited.

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 this 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 Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 30-11-2012		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Formaldehyde Five-Day Passive Chemical Dosimeter Badge Validation Study				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Kevin J. Johnson and Janet M. Hughes*				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 61-9496-E-2-9	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6180--12-9454	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Commanding Officer Naval Submarine Research Laboratory PO Box 900 Groton, CT 06349-5900				10. SPONSOR / MONITOR'S ACRONYM(S) NSMRL	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *Nova Research, Inc., 1900 Elkin Street, Suite 230, Alexandria, VA 22308					
14. ABSTRACT The utility of commercially available chemical dosimeter badges to adequately sample low-concentration formaldehyde vapor aboard Navy submarines was evaluated. In this work, badges were exposed to formaldehyde vapor at two approximate concentrations: 6 ppb and 2.5 ppb (13% and 6% of the Navy 90-day exposure limit, respectively) and for durations of 30, 60, 90, and 120 hours. Certified permeation tubes were used to generate formaldehyde vapor, which was then validated by a reference method (NIOSH 2016) based on active sampling with sorbent tubes. Badges and cartridges spiked with known concentrations of formaldehyde demonstrated extraction efficiencies of 59.26% and 69.75%, respectively. In these tests, the chemical dosimeter badges exhibited a consistent uptake rate with respect to exposure (expressed in units of parts-per-billion hours) as would be predicted theoretically by Fick's law of diffusion, indicating that they are effective at monitoring low-level concentrations of formaldehyde for extended sampling durations. The uptake rate was observed to be 0.002 micrograms of formaldehyde adsorbed per ppb hour.					
15. SUBJECT TERMS Submarine atmosphere Trace Vapor Chemical dosimeter Formaldehyde					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unclassified Unlimited	18. NUMBER OF PAGES 25	19a. NAME OF RESPONSIBLE PERSON Kevin J. Johnson
a. REPORT Unclassified Unlimited	b. ABSTRACT Unclassified Unlimited	c. THIS PAGE Unclassified Unlimited			19b. TELEPHONE NUMBER (include area code) (202) 404-5407

CONTENTS

Executive Summary	E-1
Introduction.....	1
Experimental.....	1
Materials	1
Test Chambers.....	2
Experimental Procedure for Badges.....	5
Experimental Procedure for Cartridges	7
Instrumental Method.....	8
Results	9
Extraction Efficiency	9
Badge Exposure Test	10
Conclusions.....	15
Appendix A - System Validation	A-1
Vapor Evaluation.....	A-1
Chamber Evaluation	A-1

FIGURES

Figure 1	Reaction of formaldehyde with DNPH.....	2
Figure 2	Diagram of new test chamber.	3
Figure 3	Cross section of the badges, (A-F) in the test chamber.	3
Figure 4	Schematic of testing system.	4
Figure 5	Schedule of badge removal/replacement.	5
Figure 6	Schedule of badge removal/replacement for Blank Chamber.....	6
Figure 7	Example of commercially available DNPH-cartridges.	7
Figure 8	Example of commercially available packed granular potassium iodide (KI) ozone scrubber.	8
Figure 9	Example of configuration of a single-port carbonyl sampler using DNPH- coated cartridges.	8
Figure 10	Extraction Efficiency of Cartridges and Badges	10
Figure 11	Badge results of both the low and high formaldehyde samples. Samples from Oven #1 are represented by diamonds at 30 and 90 hours and those from Oven #3 are at 60 and 120 hours. Samples from Oven #2 are represented as triangles at 30 and 90 hours while those from Oven #4 are at 60 and 120 hours.	12
Figure 12	Mass of sample recovered from the “high” and “low” concentration badges versus exposure in ppb*hrs.....	13
Figure 13	Linear fit of all data from Figure 12	14

TABLES

Table 1	Results obtained from “Low” Formaldehyde Chambers	11
Table 2	Results obtained from “High” Formaldehyde Chambers	11

Executive Summary

The purpose of this study was to evaluate the utility of commercially available passive chemical dosimeter badges to adequately sample low concentration formaldehyde vapor aboard Navy submarines for sampling durations up to 120 hours. The proposed Navy 90-day exposure limit for formaldehyde is 100 ppb. Previous studies have measured formaldehyde concentrations on Navy submarines that vary between 14 and 24 ppb. In this work, badges were exposed to formaldehyde vapor at two approximate concentrations: 6 ppb (25% of the highest observed level) and 2.5 ppb (10% of the highest observed level) and for durations of 30, 60, 90, and 120 hours. Certified permeation tubes were used to generate formaldehyde vapor, which was then validated by a reference method based on active sampling with sorbent tubes (NIOSH 2016.) Badges and cartridges spiked with known concentrations of formaldehyde demonstrated extraction efficiencies of 59.26% and 69.75%, respectively.

The chemical dosimeter badges demonstrated an approximately linear uptake rate of formaldehyde with respect to sample duration for each of the vapor concentrations tested, indicating that they are effective at monitoring low-level concentrations of formaldehyde for extended sampling durations. Further, the badges exhibited a consistent uptake rate with respect to exposure as would be predicted theoretically by Fick's law of diffusion. This rate was estimated to be 0.002 micrograms per ppb hour. (Indicating, for example, an exposure to 10 ppb for 100 hours would result in approximately 2 micrograms of formaldehyde on a badge.)

Introduction

The submarine is a unique working and living environment, as submariners are contained in this environment 24 hours a day for the duration of deployment. It is important to know and monitor the safety of the atmosphere to which they are exposed. Current methods of air monitoring onboard U.S. Navy (USN) nuclear submarines include the Central Atmosphere Monitoring System (CAMS) and active, colorimetric sampling tubes (Draeger). The CAMS provides continuous, real-time air analysis for only a few critical compounds. Draeger tubes provide real-time results for other species of interest, but sampling is not continuous, and subject to the uncertainties of colorimetric tubes. Additionally, the Draeger tube methods are labor intensive and have poor reproducibility because of the use of a manually operated hand pump, multiple interpretations of the manually read tube results, and lack of training in proper sampling technique. Implementing passive badges would greatly reduce sources of error, as they are professionally analyzed and require very little human manipulation. They may supplement or even replace certain sampling procedures while providing continuous air sampling, thereby relieving the sailors to perform other important duties onboard the boat. Additionally, numerous analytes can be tested at the same time using one or multiple badges.

The Navy currently wishes to examine passive badge deployment to provide continuous air monitoring for up to five consecutive days onboard submarines. Before the badges can be used in this application, they must be validated for long-term use, as they are currently only validated commercially for a normal eight-hour working day. To assess their long-term responses, for exposures up to five days, the badges were compared to reference analyses utilizing active air sampling on sorbent tubes. The badges and tubes were tested using exposure chambers designed to provide a homogenous test vapor to all sampling devices. The analyte of interest for this study was formaldehyde. The current 90-day limit for formaldehyde is 500 ppb according to the Submarine Atmosphere Control Manual¹ although approval of a more stringent 90-day limit of 100ppb is imminent.²

Experimental

Materials

Aldehyde badges (#571) were obtained from Assay Technology, Inc., Livermore, CA. This badge collects aldehydes on a glass fiber filter treated with acidified 2,4-dinitrophenylhydrazine (DNPH.) Standard field-sampling protocol for the Navy's Submarine Atmospheric Health Assessment Program (SAHAP) will be to send exposed badges to Assay Technology for analysis. In this work, the analytical procedure used by Assay Technology was obtained and replicated at NRL.

¹ Nuclear Powered Submarine Atmosphere Control Manual, S9510-AB-ATM-010, Revision 5.

² Personal communication with Submarine Atmosphere Health Assessment Program (SAHAP.)

This method is based on the reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH-coated silica gel badges/cartridges in the presence of a strong acid, as a catalyst, to form a stable colored hydrazone derivative according to the following reaction:

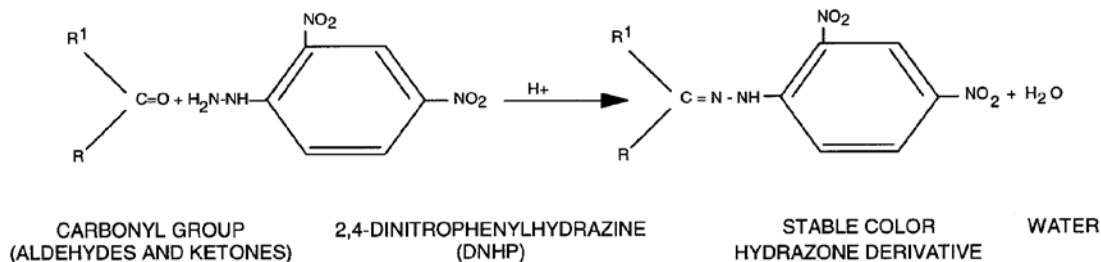


Figure 1 Reaction of formaldehyde with DNPH

Trace sources of formaldehyde vapor were delivered to the badge test chambers via certified permeation tubes obtained from KIN-TEK Laboratories, Inc., La Marque, TX. Standard active-sampling sorbent tubes (Sep-Pak® DNPH-Silica cartridges, Waters Corporation, Milford, MA) were used to validate the formaldehyde vapor stream. Formaldehyde-DNPH at 500 µg/mL (as aldehyde) in acetonitrile was purchased from Cerilliant Corporation, Round Rock, TX. Potassium acetate, o-phosphoric acid, acetonitrile, isopropanol, formaldehyde ampules and HPLC grade water were purchased from Fisher Scientific Company, LLC, Pittsburgh, PA. 2, 4-dinitrophenylhydrazine, HPLC grade was purchased from Sigma-Aldrich, St. Louis, MO.

Test Chambers

Test chambers were used to deliver a reproducible, homogenous test vapor. Five (5) test chambers were constructed for this work from stainless steel passivated with Restek Sulfinert™ coating (Figure 2). The main body of the badge exposure chamber is 10.11 cm in diameter (OD) and 18.67 cm long. A removable column in the center of the chamber allows adjustment of the total internal volume of the chamber, allowing for adjustment of linear face velocity at the badge surface at a given volumetric flow rate through the chamber. As configured, the inside, horizontal cross-sectional area of each exposure chamber is 25.28 cm². The chamber accommodates six badges and six active sampling tubes, each being exposed to a uniform airstream at a specific face velocity. Figure 3 shows the arrangement of the badges in the chamber. The manufacturer specifies a minimum face velocity of 15 cm/sec, thus the badge exposure chamber was configured to provide a linear face velocity of 17 cm/sec. The corresponding required volumetric flow rate was calculated to be 25.8 L/min, according to Equation 1.

$$25.28 \text{ cm}^2 \times \frac{17.0 \text{ cm}}{\text{sec}} \times \frac{60 \text{ sec}}{\text{min}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 25.8 \text{ L/min} \quad \text{Equation 1}$$

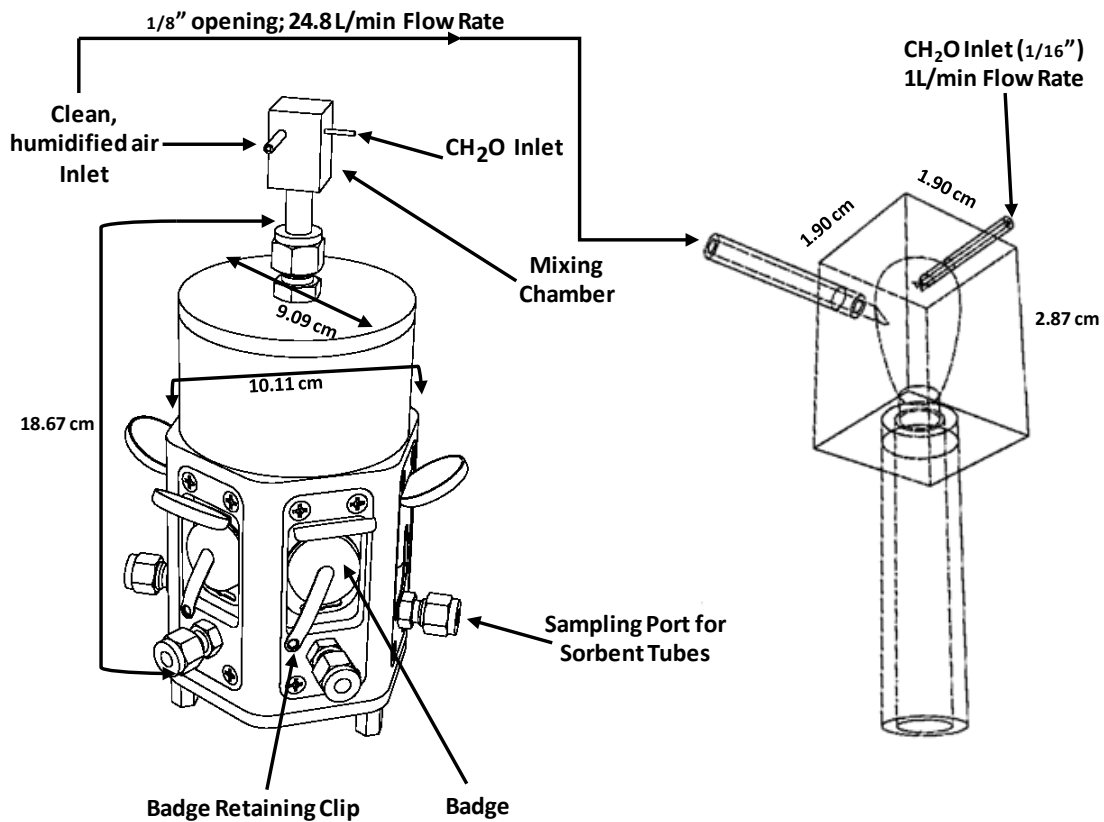


Figure 2 Diagram of passive chemical dosimeter badge test chamber.

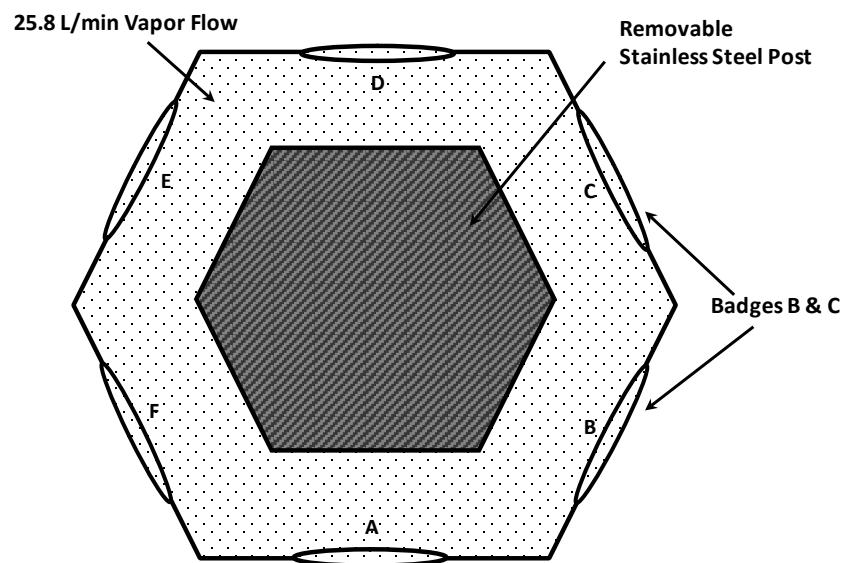
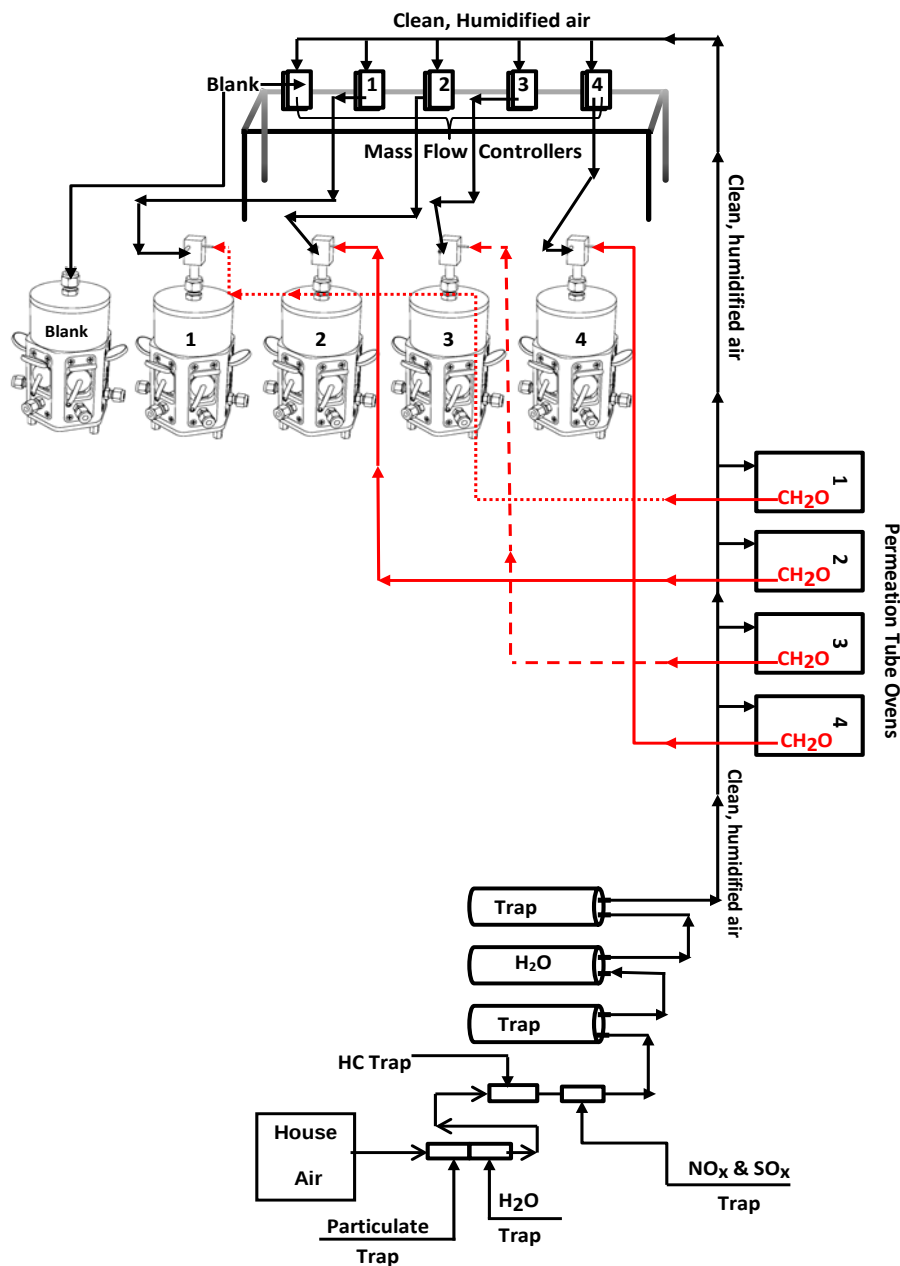


Figure 3 Horizontal cross section of the test chamber, showing badge positions A-F and removable stainless steel post.

Vapor Generation

Four test chambers and one control chamber were used for this study (Figure 4). Each chamber was supplied with 24.8 L/min of clean, humidified diluent air through Sierra mass flow controllers. Clean, humidified air was obtained by passing compressed house-air through a compressed air dryer outfitted with a particulate trap and a coalescer (PureGas model PHF112M##B), followed by two hydrocarbon traps and finally a Purafil® Chemisorbant media trap for removal of NO_x and SO_x gases. This clean air was



then passed through a

Figure 4 Schematic of testing system.

pressurized distilled water tank at ambient temperature for re-humidification, resulting a nominal relative humidity of 25-30%. Clean, humidified air, only, was delivered to the control chamber at all times. Each test chamber was also supplied with formaldehyde vapor from one of four Kin-Tek permeation tube ovens. The flow rate of air through the permeation ovens was set to 1.0 L/min, leading to a total flow in each test chamber of 25.8 L/min which provided the required linear face velocity of 17 cm/s. The ovens were equipped with formaldehyde permeation tubes certified to emission rates of 71, 103, 183, and 190 ng/min. With a total flow of 25.8 L/min at each chamber, this provided nominal concentrations of 2.2, 3.2, 5.8, and 6.0 ppb in the four test chambers.

Experimental Procedure for Badges

Test chambers #1 and #3 contained the lower concentration formaldehyde vapor streams (3.2 ppb and 2.2 ppb, respectively) while chambers #2 and #4 contained the higher formaldehyde concentrations (6.0 ppb and 5.8 ppb, respectively). The badges were press fit into the badge holder and held in place with a metal clip with the badge face oriented towards the inside the chamber (see Figures 2 and 3). The experiment ran for five days with a scheduled number of badges systematically removed at regular intervals during the test to provide badge subsets with varying exposure durations. All exposed badges were analyzed to assess their behavior and reference method sorbent tube samples were acquired as per EPA method TO-11A³ during the experiment and analyzed to verify the vapor concentration. There were a total of 42 badges exposed, with 6 badges receiving 120 hours of exposure and 12 badges each for exposures of 90, 60, and 30 hours. After each 30-hour interval, three badges each were removed from two of the chambers and replaced with unexposed badges. The badge replacement schedule is graphically depicted in Figure 5.

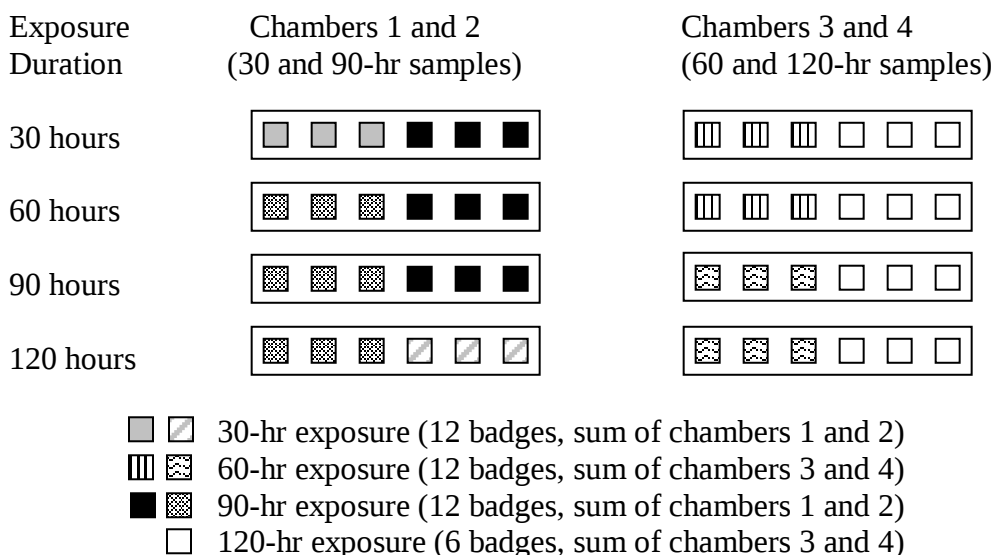


Figure 5 Schedule of badge removal/replacement.

³ "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition" EPA/625/R-96/010b, 1999.

Following chamber 1 as an example, the experiment begins with a fresh badge in each of the six positions. After 30 hours, three badges are removed and replaced with new, unexposed badges. The removed badges thus received an exposure of 30 hours (solid gray boxes in Figure 5.) After 90 hours, the remaining three badges that had been originally placed in the chamber are removed and replaced with new, unexposed badges. The removed badges have thus received an exposure of 90 hours (solid black boxes in Figure 5.) After 120 hours, the experiment is ended and the six badges currently in chamber 1 are removed. The three badges that were placed in chamber one after the first 30 hour interval (check pattern filled boxes in Figure 5) have received a 90 hour exposure while the three badges placed in chamber 1 after the 90 hour interval (diagonal line filled boxes in Figure 5) have received a 30 hour exposure. Thus, of the 12 badges that passed through chamber 1 during the 120 hour experiment, half received a 30 hour exposure and half received a 90 hour exposure. Chamber 2 was operated in parallel in an identical manner to chamber 1. Chambers 3 and 4 were operated in a different, but similar fashion to yield 12 badges receiving 60 hour exposures and 6 badges receiving 120 hour exposures. This was accomplished by removing half of the badges at the end of the 60 hour interval and replacing them with new, unexposed badges. The removed badges (vertical line filled boxes in Figure 5) and replacement badges (wavy line filled boxes in Figure 5) thus both received 60 hour exposures while the badges that remained in chambers 3 and 4 for the duration of the experiment (solid white boxes in Figure 5) received 120 hour exposures.

For the control samples placed in the blank chamber, the removal/replacement of badges followed the schedule listed below in Figure 6.

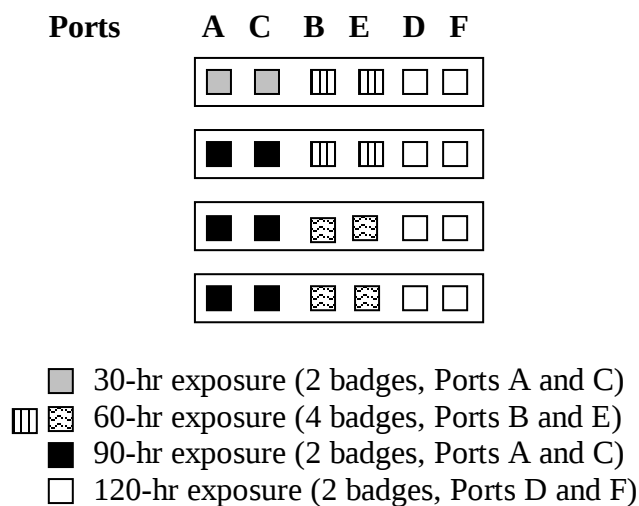


Figure 6 Schedule of badge removal/replacement for Blank Chamber.

All the badges were analyzed using a modified version of the analytical method used by Assay Technology, Inc. This method employs high-pressure liquid chromatography

(HPLC) with UV detection and is a modified version of NIOSH 2016.⁴ In brief, after exposure the DNPH-silica badge was removed from the badge housing, placed in a 0.45 µm Whatman UNIPREP™ syringeless filter device and 1.00 mL of acetonitrile was added. The contents were mixed on an auto-mixer for approximately 1 hour, after which 1.00 mL of 0.05 M potassium acetate buffer solution was added. The plunger with the filtering media was pressed down and the clear extract was transferred to a small labeled vial. Samples were stored in a refrigerator until analyzed by HPLC.

Experimental Procedure for Cartridges

The formaldehyde vapor stream concentration was validated by active sampling onto sorbent cartridges and subsequent quantitative analysis according to EPA method TO-11A. As per this method, Waters Sep-Pak® DNPH-Silica Cartridges (Figure 7), were connected to Waters Sep-Pak® Ozone Scrubbers (Figure 8). Each ozone scrubber was connected to the test chamber and then to the DNPH-Silica cartridge which was connected to an adjustable, low-flow, SKC Pocket Pump® 210-1002 (Figure 9). Cartridges were sampled for 65 hours at 125 mL/min. After exposure, the cartridges were extracted and these reference exposures were compared to those obtained from passive badges.

The extraction of the cartridges was similar to the badges with some minor modifications. Each cartridges was extracted with acetonitrile and the extract was directly transferred to a 5.00 mL volumetric flask. One milliliter of this extract was transferred to a small vial and 1.00 mL of HPLC grade water was added.

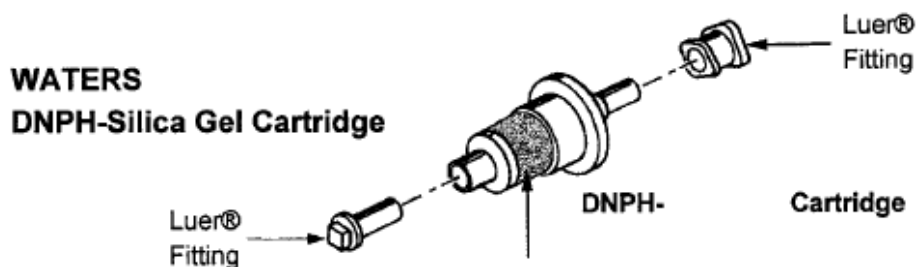


Figure 7 Example of commercially available DNPH-cartridges.

⁴ NIOSH Manual of Analytical Methods, 4th Edition, Schlect, P.C. and O'Connon, P.F., Eds. DHHS (NIOSH)

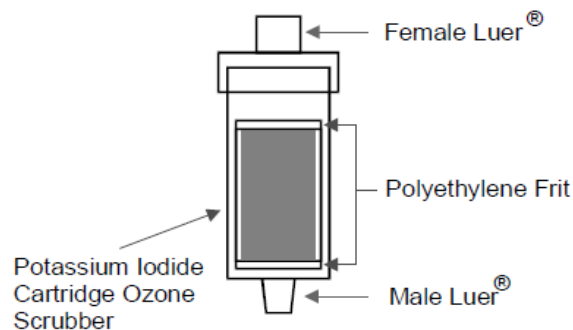


Figure 8 Example of commercially available packed granular potassium iodide (KI) ozone scrubber.

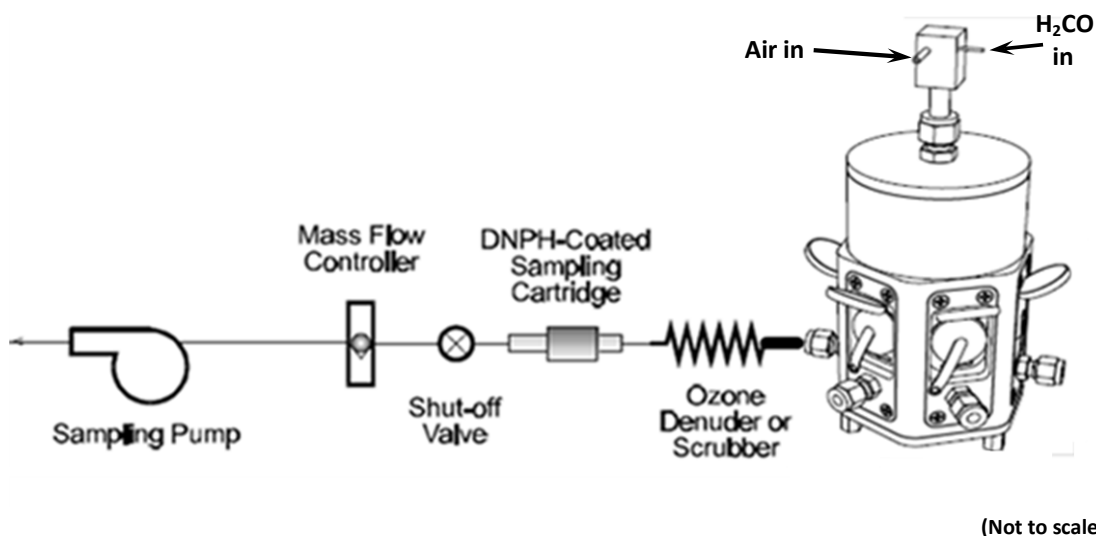


Figure 9 Example of configuration of a single-port carbonyl sampler using DNPH-coated cartridges.

Instrumental Method

All samples were analyzed on a Hewlett Packard Series 1100 HPLC instrument with a UV detector. Data Analysis was carried out using Agilent Open LAB CDS Chem Station Software, Version A.01.02. The mobile phase was 60% methanol with 40% water. A 150 x 3.2 mm Pinnacle II® C18 reversed-phased column with a 5µm particle size from Restek Corporation was used for separation. Flow rate through the column was set at 0.455 mL/min. The column temperature was maintained at 40.0°C. The injection volume was 10.0 µL. The UV detector was set at 355 nm with a band width of 4 nm against a reference wavelength of 680 nm with a reference band width of 50 nm. The run time varied from a minimum of 6.00 min to a maximum of 8.50 minutes.

Results

Extraction Efficiency

In order to accurately quantify the amount of formaldehyde adsorbed on both dosimeter badges and reference method cartridges, a determination was made of the extraction efficiencies of the respective extraction methods employed in each analysis method. Standard solutions of formaldehyde-DNPH were formulated through serial dilution of the purchased stock solution to concentrations that ranged from 0.24 to 480 mM. These standards were analyzed by HPLC with UV detection. The resulting chromatographic peaks were integrated and a linear calibration model related peak area to formaldehyde-DNPH concentration was constructed with an R^2 of 0.996. Subsequent studies focused on concentrations less than or equal to 100 ppb, as shown in the calibration curve in Figure 10 ($R^2 = 0.9911$.) Concentrations of the formaldehyde-DNPH derivative were converted to $\mu\text{mol/mL}$ (mM) providing an equivalence for the molar concentration of formaldehyde present in the extract solution.

To determine extraction efficiency, 1 mL ampules of 16% (w/v) formaldehyde standard solution were purchased from Fisher Scientific, Inc. A 40.0 mM formaldehyde solution was prepared and quantities ranging from 3.1 μL to 200 μL were spiked onto the sorbent tubes followed by a five drops of acetonitrile. The sorbent tubes were then re-capped and allowed to stand for approximately 20-30 minutes. The cartridges were extracted according to the procedure mentioned earlier. The theoretical concentrations of the extracted formaldehyde solutions ranged from 0.025 mM to 1.6 mM, if one assumes 100% extraction. The curve representing the active sampling tubes (cartridges) can be found in Figure 10. The extraction efficiency of the active sampling tubes was determined to be 69.7%. In a similar fashion, the badges were spiked with formaldehyde and extracted. These data are also depicted in Figure 10. The extraction efficiency of the badges was determined to be 59.3%.

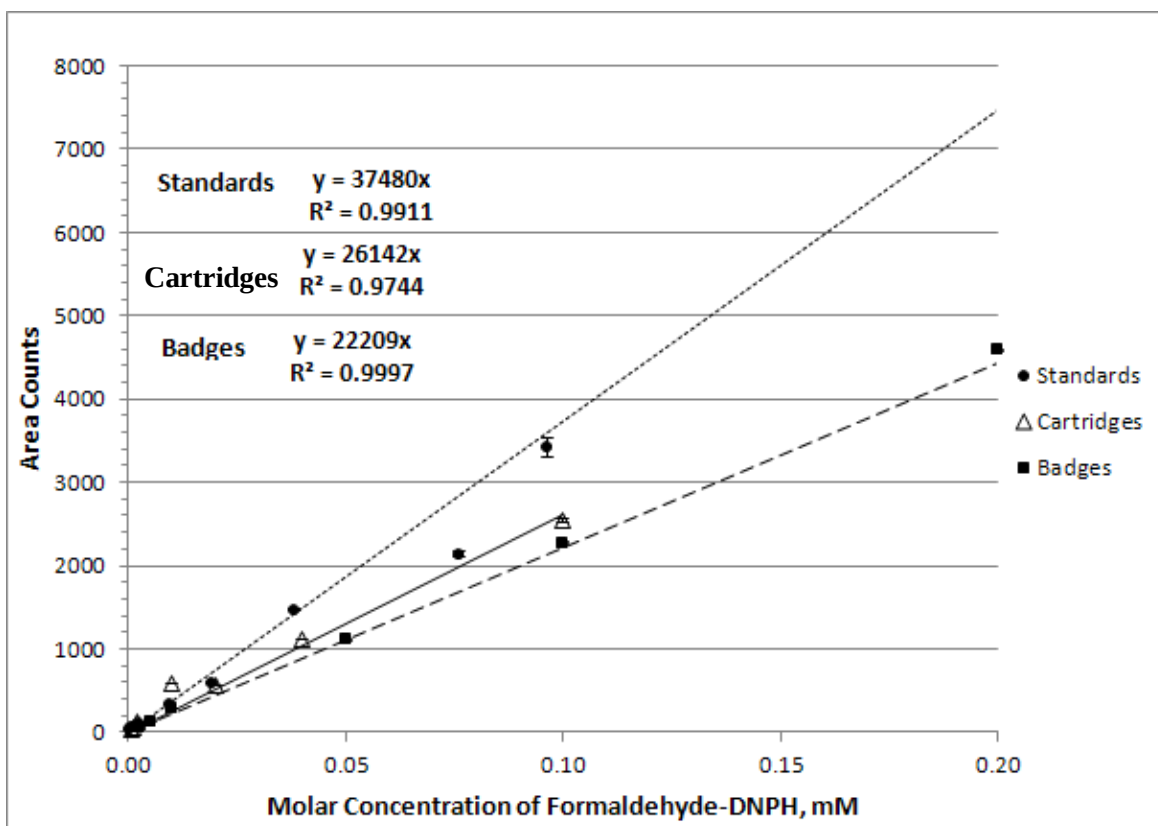


Figure 10 Extraction Efficiency of Cartridges and Badges

Badge Exposure Test

The amount of formaldehyde extracted from the badges was determined as milli-molar concentration (mM) utilizing the standard calibration curve and the estimated badge extraction efficiency. The amount of formaldehyde as nano-moles of analyte per moles of air, ppb, was determined by the calculation below:

$$\text{ppb of } H_2CO = \frac{\text{mass of } H_2CO, \mu\text{g}}{\text{volume of air, L}} \times \frac{24.4 \text{ L}}{1 \text{ mole of air}} \times \frac{1 \mu\text{mole of } H_2CO}{30.03 \mu\text{g of } H_2CO} \times \frac{1000 \text{ nmole}}{1 \mu\text{mole}} \quad \text{Equation 2}$$

The results of the badge trials appear in Tables 1 and 2 below. The molar volume of air is 24.4 L/mol at 23°C, the average temperature of the testing location. The last column of each table refers to the percent relative standard deviation of the mass of formaldehyde determined across the replicate samples.

Table 1 Results obtained from “Low” Formaldehyde Chambers

Chamber Number	Vapor Conc. ppb	Time, hrs	Average Area Counts	Concentration, mM	Mass of H₂CO, µg	Rel. Std. Dev., %
1	2.2	30	24	0.00108	0.32	22
3	3.2	60	74	0.00333	1.00	26
1	2.2	90	61	0.00274	0.82	27
3	3.2	120	136	0.00611	1.84	18

Table 2 Results obtained from “High” Formaldehyde Chambers

Chamber Number	Vapor Conc. ppb	Time, hrs	Average Area Counts	Concentration, mM	Mass of H₂CO, µg	Rel. Std. Dev., %
2	5.8	30	106	0.00477	1.43	17
4	6.0	60	217	0.00979	2.94	20
2	5.8	90	307	0.0138	4.15	10
4	6.0	120	415	0.0187	5.61	3

A graph summarizing the results is shown in Figure 11. It should be noted that the low concentration samples were very close to the quantitation limit. As might be expected, the linearity of formaldehyde exposure as a function of sampling duration for the higher concentration vapor was somewhat better than that of the lower concentration vapor.

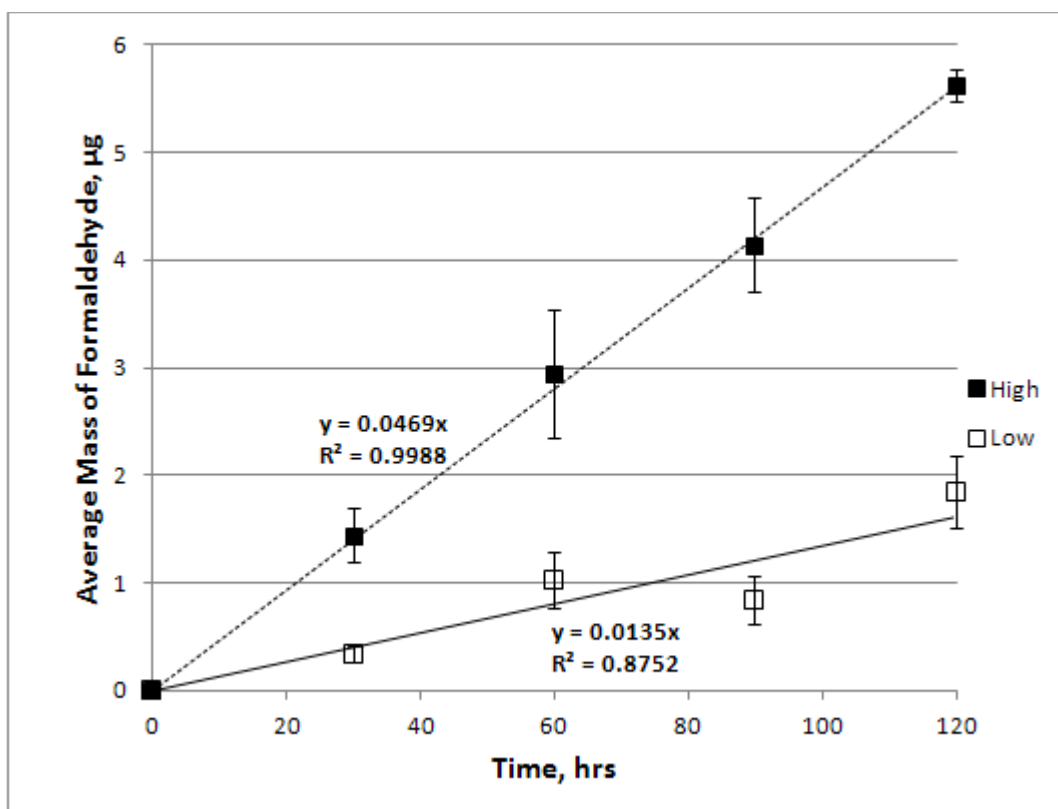


Figure 11 Badge results of both the low and high formaldehyde samples. Samples from Oven #1 are the low amounts at 30 and 90 hours and those from Oven #3 are at 60 and 120 hours. Samples from Oven #2 are the high levels of formaldehyde at 30 and 90 hours while those from Oven #4 are at 60 and 120 hours.

Using the average validated concentration of formaldehyde in each chamber (detailed in Appendix A) the mass of sample collected on the badges were plotted against exposure expressed in units of ppb hours, Figure 12.

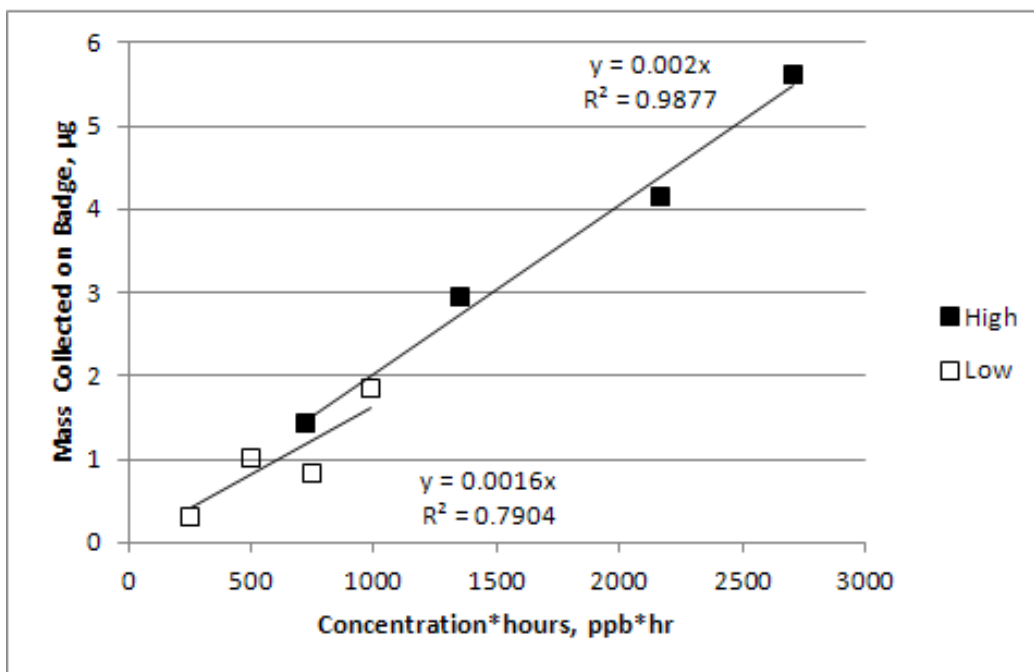


Figure 12 Mass of sample recovered from the “high” and “low” concentration badges versus exposure in ppb*hrs.

A linear fit of all data points (Figure 13) yields an R^2 value of 0.97. This linear relationship suggests that the uptake rate of formaldehyde on these badges was constant in the concentration range investigated. According to Fick’s law of diffusion, the mass of analyte per unit time is related to the concentration of the analyte according to the formula:

$$\frac{m}{t} = D \frac{A}{L} (C_{ma} - C_{ms}) \quad \text{Equation 3}$$

Where m is the mass of sample recovered from the badge, t is the time, D is the diffusion coefficient of the analyte, A is the surface area of the membrane, L is the membrane’s thickness, C_{ma} is the concentration of the analyte on the surface of the membrane exposed to air, and C_{ms} is the concentration of the analyte at the membrane-sorbent surface. If a sorbent is functioning properly, the concentration of analyte at the membrane-sorbent interface is zero because the sorbent (in this case, the phenylhydrazine) reacts with the analyte (formaldehyde) essentially removing it from the interface. Therefore C_{ms} is generally taken to be equal to zero^{5,6}. The concentration of the analyte on the surface of

⁵ Seethapathy, Suresh, “Development, Validation, Uptake Rate Modeling and Field Applications of a New Permeation Passive Sampler,” Dissertation from the University of Waterloo, Ontario, Canada, 2009.

⁶ Bohlin, Pernilla, “Passive Sampling of PAHs and Some Trace Organic Compounds in Occupational and Residential Air – needs, evaluation and limits,” Dissertation from the Institute of Medicine at Sahlgrenska Academy, University of Gothenburg, 2010.

the membrane exposed to air, C_{ma} , is related to the ambient concentration of the analyte in air, C_0 , and the partition coefficient, K , accordingly:

$$C_{ma} = KC_0 \quad \text{Equation 4}$$

At constant temperature, for a particular analyte and passive badge, D , A , L , and K are constant, therefore, the concentration of the analyte in ambient air can be determined from the mass of the analyte collected on the badge in a given time by:

$$C_0 = \frac{km}{t} \quad \text{Equation 5}$$

Where k is a constant. Thus, the mass of the analyte collected on a badge over a given duration is directly related to its concentration in air. Rearranging Equation 5 yields:

$$m = \frac{1}{k} * tC_0 \quad \text{Equation 6}$$

This linear relationship is illustrated in Figure 13, with the slope as $1/k$. This condition is valid as long as one remains in the linear phase of the accumulation, before the badge becomes saturated with analyte.

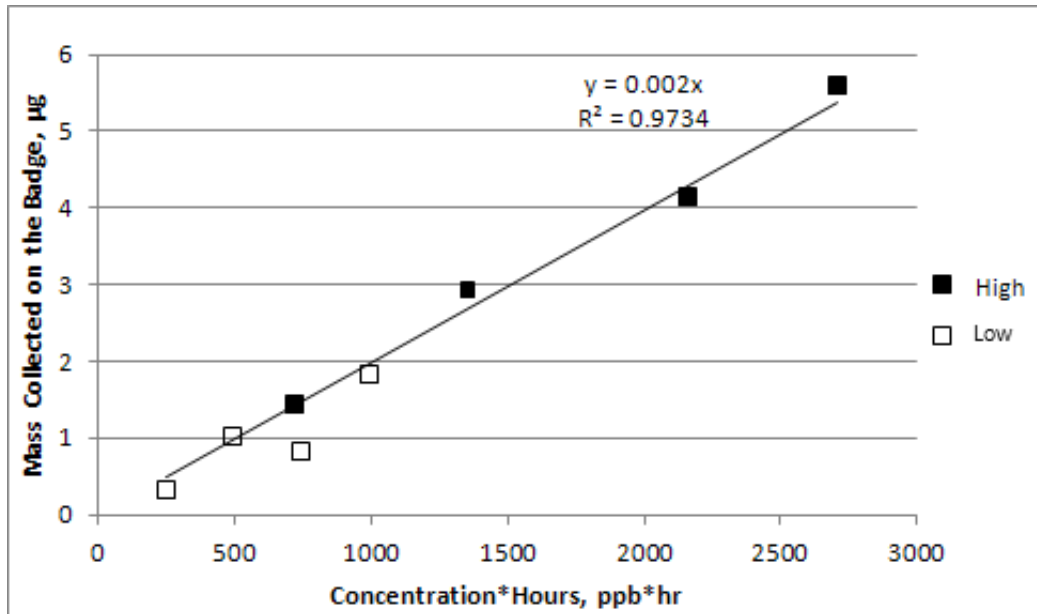


Figure 13 Linear fit of all data from Figure 12

Conclusions

The purpose of this study was to evaluate the utility of commercially available chemical dosimeter badges to adequately sample low concentration formaldehyde vapor aboard Navy submarines for up to 120 hour sampling durations. The proposed USN 90-day exposure limit for formaldehyde is 100 ppb. Callahan, et al. measured average formaldehyde concentration on board Navy submarines at 24 ppb⁷, while later studies monitored levels of 23, 20, 11, 21 and 17 ppb in the forward compartments and 14, 18, 15, 24 and 16 in the aft compartments, respectively^{8,9,10,11,12}. In this work, badges were exposed to formaldehyde vapor at two approximate concentrations: 6 ppb (25% of the highest observed level) and 2.5 ppb (10% of the highest observed level) and for durations of 30, 60, 90, and 120 hours. Certified permeation tubes were used to generate formaldehyde vapor, which was then validated by a reference method based on active sampling with sorbent tubes (NIOSH 2016.) Badges and cartridges spiked with known concentrations of formaldehyde demonstrated extraction efficiencies of 59.26% and 69.75%, respectively.

For each vapor concentration, the chemical dosimeter badges demonstrated an approximately linear uptake rate of formaldehyde with respect to sample duration, indicating that they are effective at monitoring low-level concentrations of formaldehyde for extended sampling durations. Further, the badges exhibited a consistent uptake rate with respect to exposure (expressed in units of parts-per-billion hours) as would be predicted by Fick's law of diffusion. This rate was estimated to be 0.002 micrograms per ppb hour, indicating that, for example, a 10 ppb exposure over 100 hours would result in an accumulation of 2 micrograms on a badge.

⁷ Callahan, J.H., DiNardi, S. R., Manning, C.R., Woolrich, R.C., Burnside, D.M., and Slavin, D., "Diffusive Sampling of US Navy Submarine Atmospheres," SAE Technical Paper 2002-01-2297, 2002, doi:10.4271/2002-01-2297.

⁸ Johnson, K.J., Rose-Pehrsson, S.L., DiGiulio, C., Burnside, D., USS *Toledo* Atmospheric Sea Trials: Analytical Results, NRL Memorandum Report, NRL/MR/6112-05-8889, July 18, 2005.

⁹ Johnson, K.J., Rose-Pehrsson, S.L., DiGiulio, C., Burnside, D., USS *Virginia* Atmospheric Sea Trials: Analytical Results, NRL Memorandum Report, NRL/MR/6180-06-8940, March 6, 2006.

¹⁰ Johnson, K.J., Rose-Pehrsson, S.L., Burnside, D., USS *Texas* Atmospheric Sea Trials: Analytical Results, NRL Memorandum Report, NRL/MR/6180-07-9046, May 4, 2007.

¹¹ Johnson, K.J., Rose-Pehrsson, S.L., Burnside, D., USS *New Hampshire* Atmospheric Sea Trials: Analytical Results, NRL Memorandum Report, NRL/MR/6180-09-9224, November 18, 2009.

¹² Johnson, K.J., Rose-Pehrsson, S.L., Burnside, D., USS *North Carolina* Atmospheric Sea Trials: Analytical Results, NRL Memorandum Report, NRL/MR/6180-09-9225, November 18, 2009

Appendix A - System Validation

Vapor Evaluation

Two different sets of experiments were performed in order to evaluate the test chambers and the output at the permeation ovens. Even though the permeation tubes were calibrated and certified and the extraction efficiency of the cartridges was determined; it seemed prudent to check the permeation tube output through a cartridge against the extract obtained. To this end, cartridges were attached directly to the output of the permeation tube oven and formaldehyde sample was drawn through the cartridge for a set time. The flow through the cartridge was monitored during collection using a flow meter and the average flow was calculated. The duration of collection was also monitored and varied between 128-150 minutes depending on the cartridge. Assuming that the permeation tube delivered a given amount of formaldehyde per minute and knowing the time and flow through the cartridge, a theoretical concentration of formaldehyde was determined. The cartridges were then extracted and the samples were run using HPLC. A minimum of three repeated samples were analyzed for each cartridge. Using the average area counts, the concentration of formaldehyde was determined. It was observed that for Chamber 1, which contained the permeation tube delivering 103 ng/min of formaldehyde, the concentration extracted agreed within 4% of the theoretical formaldehyde concentration delivered from the permeation tube. For Chamber 2, delivering 190 ng/min of formaldehyde the agreement was within 0.3%. This agreement supports both the certified calibration of the permeation tubes and the extraction efficiency of the cartridges.

Chamber Evaluation

A second assumption made was that the mixing of the formaldehyde and air and its subsequent flow through the test chamber was uniform, such that, sampling from any one port would yield similar results as sampling from any other port in the chamber. To test this assumption, cartridges were attached to Port A of each chamber and were actively sampled at 125 mL/min for 65 hours. After this time, each cartridge was extracted and analyzed by HPLC. A total of seven cartridges were collected in this manner and the data for each chamber appear in figures A-1 through A-4 (◇). The average concentrations extracted from Port A for each chamber can be found in Table A-1. The “low” concentration chambers are 1 and 3 and the “high” concentration ones were 2 and 4. From these data it is evident that the “low” concentration chambers emitted the same average concentration of vapor and the Chambers 2 and 4, the “high” concentration chambers, emitted the same average concentration of vapor.

Another 65 hour test was carried out where cartridges were attached to each port in a chamber and collected. The results of these tests are also found in the same figures (●). The average concentration extracted from each chamber can be found in Table A-1. When compared to the Port A only data, it shows that the collection of sample is independent of the port where the sample was acquired. Also these data show that the average extracted concentration of the “low” chambers were similar. The same was true for the extracted concentrations of the “high” concentration chambers. From these data it appears that the collection of formaldehyde by active sampling is independent of the port sampled; which also indicates that the formaldehyde delivered in the chamber is homogeneously mixed.

Table A-1 Average Concentrations Extracted from Each Chamber

Chamber	Average of Port A, mM	%RSD	Average of All Ports, mM	%RSD
1	0.0055 ± 0.0003	4.2	0.0052 ± 0.0003	4.7
3	0.0055 ± 0.0004	5.4	0.0055 ± 0.0003	5.2
2	0.016 ± 0.002	10.6	0.0151 ± 0.0005	3.6
4	0.0156 ± 0.0007	4.4	0.0147 ± 0.0006	4.2

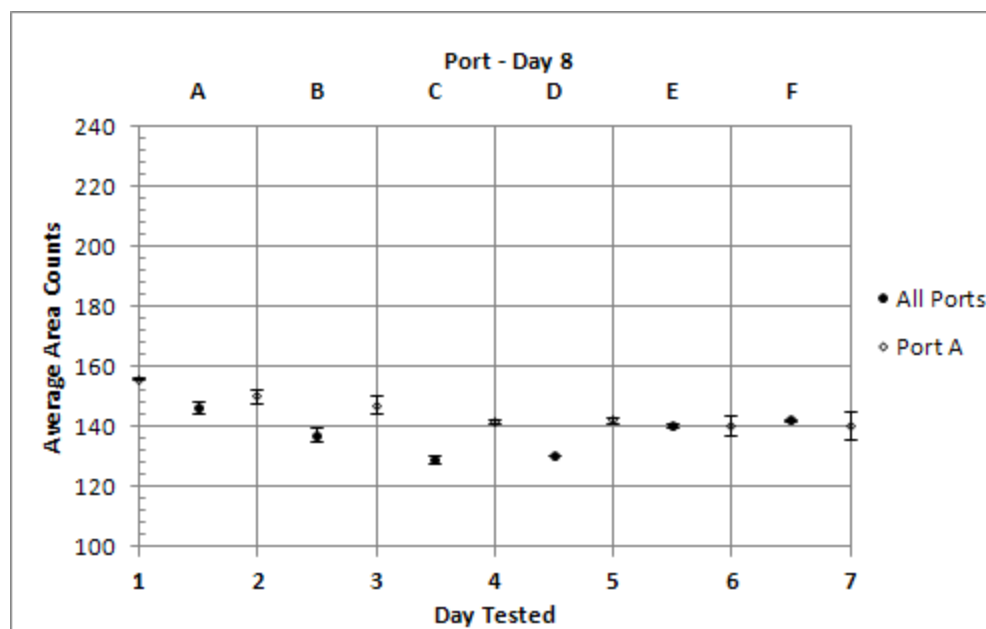


Figure A-1. Data from Chamber 1 (103 ng/min)

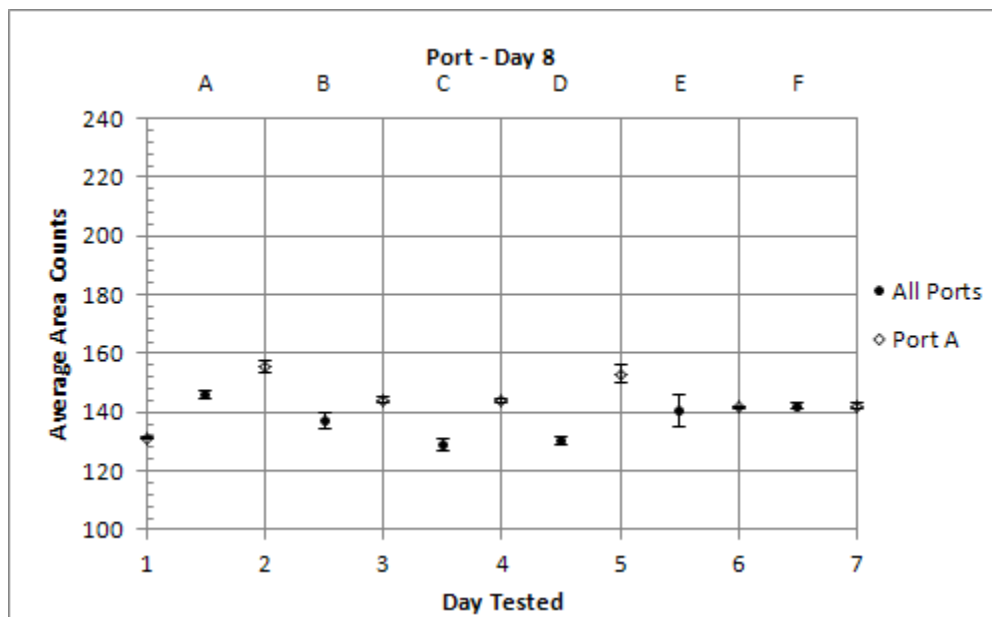


Figure A-2. Data from Chamber 3 (71 ng/min)

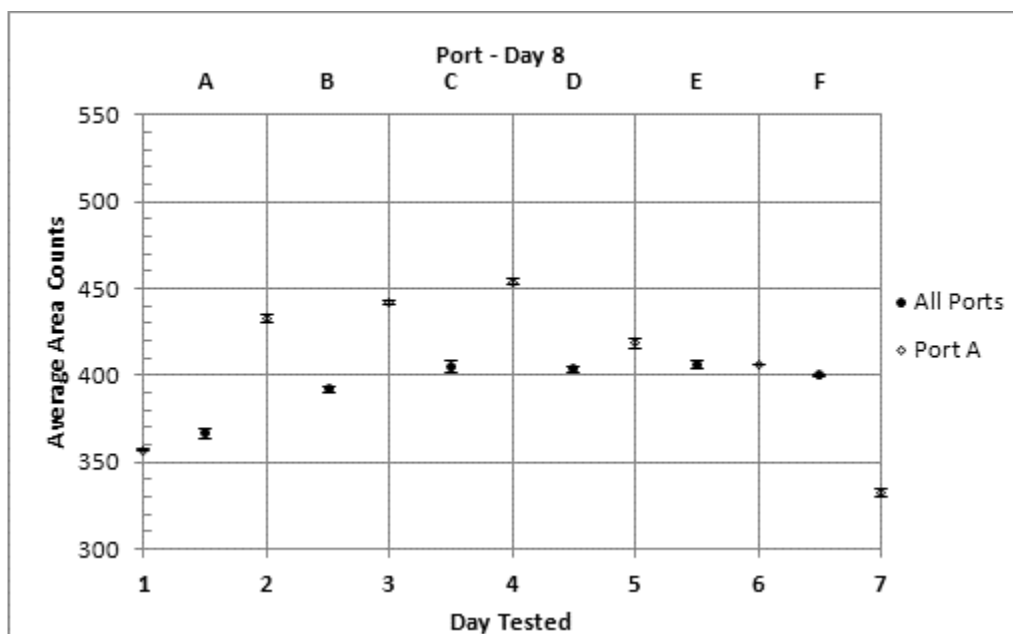


Figure A-3. Data from Chamber 2 (190 ng/min)

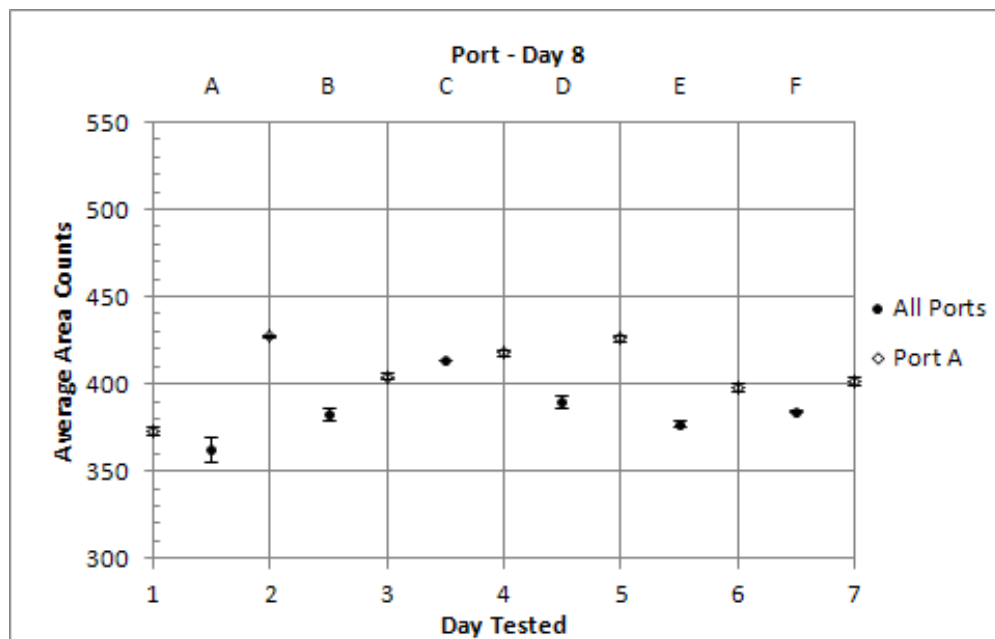


Figure A-4. Data from Chamber 4 (183 ng/min)