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Passive Badge Assessment for Long-term, Low-level Air Monitoring on Submarines: Nitrogen Dioxide Badge Validation

KIMBERLY P. WILLIAMS

Nova Research, Inc.
Alexandria, VA

SUSAN L. ROSE-PEHRSSON

Chemical Dynamics and Diagnostics Branch
Chemistry Division

DAVID A. KIDWELL

Surface Chemistry Branch
Chemistry Division

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14. ABSTRACT

Passive diffusion badges are being tested as a long-term, low-level method of analyte-specific air analysis onboard U.S. Navy (USN) nuclear submarines. Passive badge monitors for nitrogen dioxide detection were studied. Long-term sampling efficiency was evaluated for a 28-day period by comparing the response of the passive badge to an active tube sampling method. Simultaneous exposure of badges and tubes, at concentration levels 100% and 50% of the USN 90-day submarine-specific limits, was performed. High- and low-level concentrations were tested to examine the response range of the badge. Badge results were stable and reproducible but were typically 13% higher than tube results.

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Passive Badge Assessment for Long-term, Low-level Air Monitoring on Submarines: Nitrogen Dioxide Badge Validation

1.0 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 tube sampling (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. The Draeger tube methods are labor intensive and have poor reproducibility as the result of a manually operated hand pump, as well as multiple interpretations of the manually read tube results. This labor intensive method introduces the problem of human error and lack of reproducibility. 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, relieving the sailors to perform other important duties onboard the ship. Additionally, numerous analytes can be tested at the same time using one or multiple badges.

For use on submarines, passive badges should provide continuous air monitoring for up to 28 consecutive days. 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 8-hour working day. To assess their long-term responses, the badges were compared to commonly-used active sampling tubes for up to a 28-day exposure. An exposure chamber was designed to provide a homogeneous test vapor to both the tubes and the badges. Six of these chambers were manufactured to allow multiple concentration levels to be tested simultaneously (1).

Nitrogen dioxide (NO_2) is an important gas to monitor in closed space environments and can be toxic at levels as low as 5 parts-per-million (ppm). Possible sources of NO_2 include unvented gas stoves and heaters, burning flames, and tobacco smoke. Aboard submarines, a major source of NO_2 could be from the carbon monoxide/hydrogen burners used in the process of purifying the air. Exposure to NO_2 may result in upper respiratory irritation, pulmonary edema, and at severe levels, impaired breathing resulting in death by asphyxiation. Passive badge monitoring for NO_2 was evaluated for long-term exposure levels at 50% and 100% of the USN 90-day limit, 0.25 ppm and 0.50 ppm respectively. Lower levels were employed to assure that the 100% level could be measured accurately.

Manuscript approved September 30, 2005.

2.0 Experimental

Certified gas cylinders provided the nitrogen dioxide gas (Airgas 150 ppm and 500 ppm), which was diluted into a cleaned, humidified airstream to provide the desired test concentration. Nitrogen dioxide-specific badges were purchased from Assay Technology, Inc. as custom test devices. The NO_2 vapor diffused into the badge and was adsorbed onto molecular sieve beads, coated with triethanolamine (TEA). The same chemistry was used by the active sampling tubes (SKC 226-40-02). The active tube samples were collected using a sample pump, SKC Airchek 224-PCXR7, to pull approximately 50 mL/min of vapor across each tube's substrate. A real-time electrochemical sensor was used as an independent verification of the NO_2 concentration within the chamber (ENMET Omni 4000). For analysis, the NO_2-TEA coated sieve beads were desorbed into an absorbing solution (TEA diluted in deionized water), then color-reacted and analyzed by ultraviolet (UV) spectroscopy (Varian Cary 5E) following NIOSH 6014 analytical method (2). The samples were analyzed over a spectral range of 400-650 nm, with a maximum absorbance at approximately 540 nm. Results obtained from the UV spectrometer were compared against an 8-point calibration curve covering the range of 0.5-50 µg/mL. The calibration curve was prepared by making volumetric dilutions of a stock standard (100 µg/mL), prepared by diluting sodium nitrite ($NaNO_2$) in deionized water.

2.1 Test Chambers

The test chambers were designed for the purpose of delivering a reproducible, homogenous test vapor, while simultaneously accommodating six passive badges and five active tubes. During this research, the badge design was modified by Assay Technology, resulting in reconfiguration of the badges in the chamber allowing six badges to be sampled instead of five. The chambers are comprised of multiple parts: introduction chamber, mixing baffles, badge plate, tube ports, and a fan, as shown in Figure 1. The chamber's body is tubular, chosen over a traditional rectangular shape to reduce "dead" air space within corners of the chamber. The body is 10.8 cm in diameter (ID) and 30.5 cm long. A plate within the chamber was reconfigured to hold six badges, each being exposed to a uniform airstream at a specified face velocity, as shown in Figure 2. The sampling rate of the NO_2 badge, as specified by the manufacturer, was 12.7 mL/min. To maintain this sampling rate, a minimal linear face velocity of $\geq$17 cm/sec, or 13 L/min, was sustained (3). The plate directed a total volume of 30 L/min of test vapor through the six 1.2 cm × 2 cm openings, one in front of each of the six badges, providing the appropriate face velocity. The fan at the back of the chamber pulled the test vapor through the chamber as it was introduced, at approximately 29 L/min. A slight overpressure in the chamber prevented room air from leaking into the system. Two baffles at the front of the chamber aided in mixing the vapor stream.

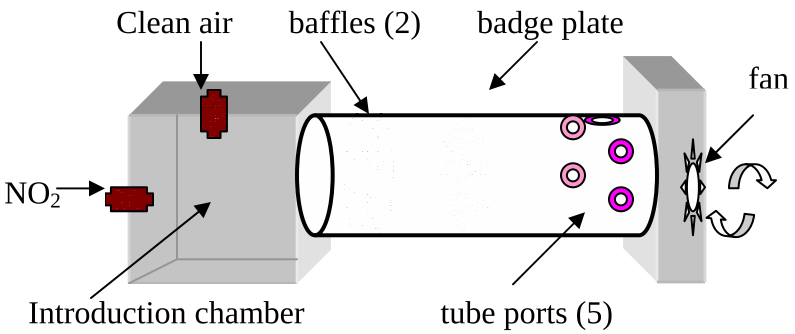

Figure 1. Diagram of a validation chamber.

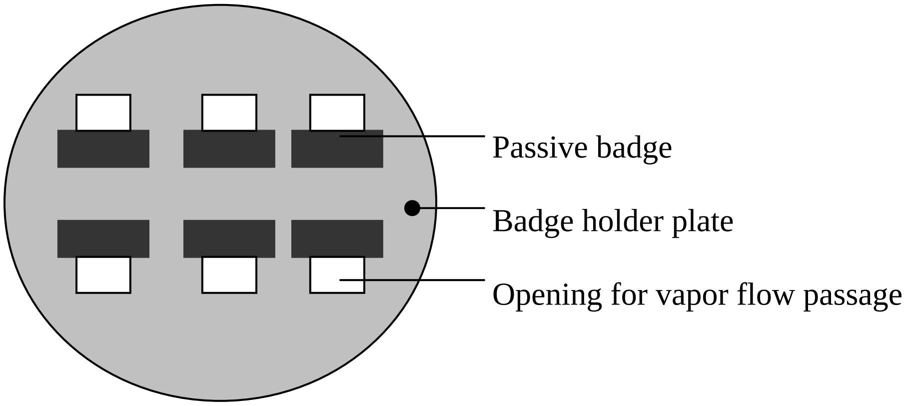

Figure 2. The badge plate, with 6-badge capacity.

2.2 Experimental Design

Zero grade air was obtained by passing compressed house-air through two independent molecular sieves, to remove moisture and CO_2. The clean air was humidified by passing it through a pressurized tank filled with deionized water, then it was distributed between five mass flow controllers, each set to deliver approximately 30 L/min of the clean, humidified air to its respective test chamber. The test gas, NO_2, was supplied by two certified gas cylinders, 150 ppm and 500 ppm. A single gas stream from each cylinder was distributed among 2 mass flow controllers, delivering 4 separate gas streams, one to each exposure chamber. One tank delivered the desired concentration for low level testing (50% USN limit) and the other tank for high level testing (100% USN limit). The control chamber received only clean, humidified air. The flow rates of all controlled airstreams and gas streams were measured using a Dry-Cal flow meter.

The badges were inserted into the badge plate, all badge faces facing the opening above it. The active sampling tubes were connected to adjustable, low-flow 4-tube manifolds, SKC 224-26-04. Each chamber's manifold allowed a single pump to sample for the four tubes attached. The pumps were set to pull 200 mL/min, to be distributed among the four sampling tubes, providing a nominal sampling rate of 50 mL/min per tube. Due to slight differences in the tubes as a result of manufacturing processes, the pressure drop across the tubes varied resulting in small variations of flow though the tube. The flow rate of each tube was measured independently using an in-line Sierra mass flow meter before being inserted into the chamber and again before its removal. The average flow rate, per tube, was used when analyzing the final data results.

The analyte exposures were administered using a “pulse” method. Instead of exposing the samples to the analyte continuously, the exposures were administered only three times per week. Each exposure lasted 360 minutes (6 hours). The exposure of the analyte was provided at a higher concentration than the 50% and 100% levels of the USN 90-day limit, however, the cumulative, time-weighted-average (TWA) exposure per week was equivalent to a continuous exposure at the 50% and 100% levels. Clean air was passed through the chambers continuously when the analyte was not being delivered. Running the pulse method was advantageous in monitoring system mechanics to ensure that all of the equipment was functioning properly. It may also be a more realistic demonstration of how the badge might respond to an instantaneous toxic level exposure to a hazardous compound.

The vapor concentration within the chamber was verified using a NO_2-specific electrochemical sensor in an ENMET Omni 4000 detector. The NO_2 sensor was factory calibrated for a detection range of 1.5-30 ppm, with an accuracy of +/- 25%, and provided real-time results. One chamber was measured at a time and for the duration of the pulsed vapor exposure. The instrument was switched to different chambers, between high and low levels, for consecutive pulses.

The experiment ran for 4 weeks (28 days). Chambers “A” and “B” tested the 50% level, and Chambers “C” and “D” tested the 100% level. To monitor the progress of the experiment, a scheduled number of badges and tubes were systematically removed per week. These badges and tubes were analyzed to guarantee that the system was functioning properly and to assess the behavior of the badges over time. The data was catalogued each week and used to compile a final data analysis at the end of the 28-day testing period. The schedule is illustrated in Figure 3. Each week, three badges were removed from a low-level testing chamber and three badges were removed from a high-level testing chamber. Badges the first week were removed from chambers A and C. The next week, badges were removed from chambers B and D. Simultaneously, two tubes were removed from each chamber following the same procedure as for badges. New badges and tubes were inserted in the chambers in place of the removed samples. This pattern was repeated for the duration of the validation. At the end of the 28 days all of the remaining tubes and badges were removed from the chambers. Collectively, the data were representative of the first 7, 14, 21, and 28 days and for the last 21, 14, and 7 days. The total numbers of data points were as follows:

7 days	20 data points
14 days	20 data points
21 days	20 data points
28 days	10 data points

Total = 70 data points

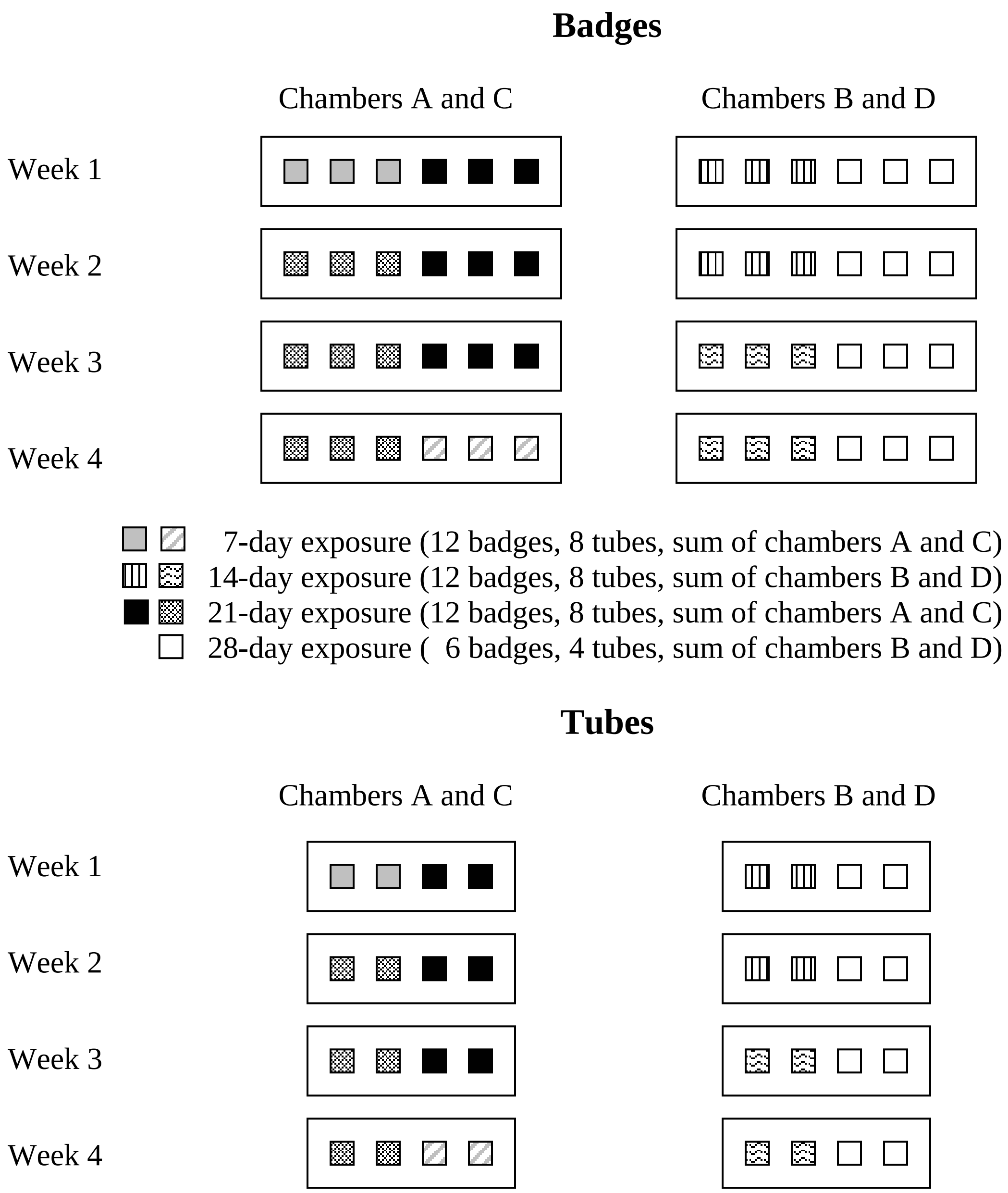

Figure 3. Schedule of badge and tube removal/replacement. Overlapping series helped average-out any errors in NO_2 concentration over the long exposure.

2.3 Chemistry of the Tubes and Badges

The tubes and badges used the same chemical technique to accumulate the analyte; the sampling substrate was coated with triethanolamine (TEA), which reacted with NO_2 from the test vapor. As a result of the extraction process, NO_2^- ions were formed, in the presence of nitrous acid (HNO_2), relative to the NO_2 concentration adsorbed by the sample substrate, see Figure 4. The NO_2^- concentration was determined using UV spectroscopy by comparing the maximum absorbance of the sample against a calibration curve. The concentration of NO_2 was determined by quantifying the amount of NO_2^- ions in the extract, then converting the result to the corresponding amount of NO_2. To do this a correction factor, 0.63, was applied. The correction factor represents the number of moles of nitrite ion produced by one mole of nitrogen dioxide gas, for gas concentrations less than 10 ppm (2).

$$2NO_2 \quad <=> \quad N_2O_4$$

$$N_2O_4 \ + \ (HOCH_2CH_2)_3N \quad --> \quad (HOCH_2CH_2)_3NNO^+NO_3^-$$

$$(HOCH_2CH_2)_3NNO^+NO_3^- \ + \ H_2O \quad --> \quad (HOCH_2CH_2)_3NH^+NO_3^- \ + \ HNO_2$$

$$HNO_2 \quad --> \quad H^+ \ + \ NO_2^-$$

Figure 4. The proposed conversion mechanism of NO_2 gas to nitrite ions.

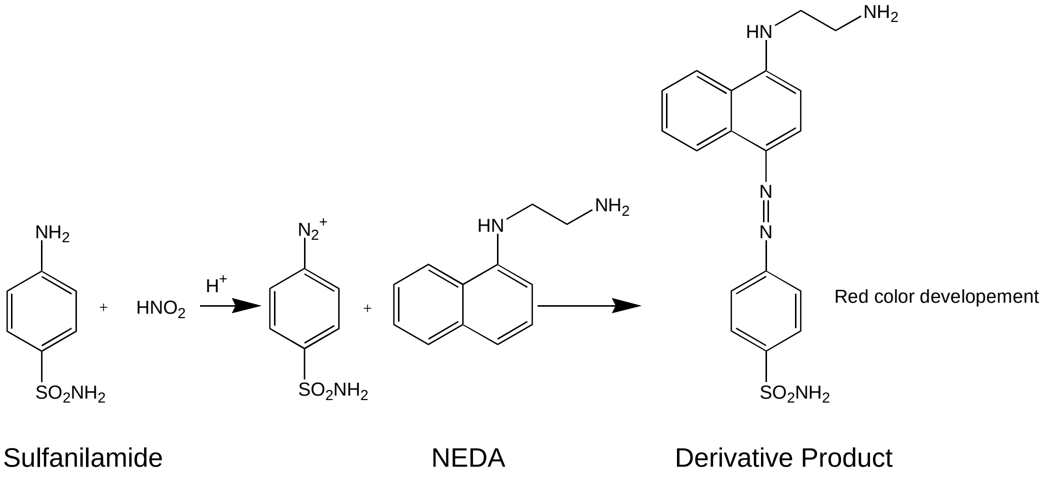

Figure 5. Chemistry of the color activation as reagents are added to the sample extract.

2.4 Analysis

Each week, following removal from the test chamber, the tubes and badges were extracted for NO_2 analysis following the NIOSH 6014 analytical method. The glass tubes were scored, then broken open to empty the molecular sieve beads into a 50 mL volumetric flask filled halfway with NO_2 absorbing solution. While rinsing the sides of the flask, the flask was filled to the 50 mL mark with NO_2 absorbing solution. The volumetric flask was capped and shaken vigorously for 30 seconds to extract the analyte from the sieve beads. Similarly, the badge was extracted by removing the protective films of material and transferring the sieve beads into a 50 mL volumetric flask, filled halfway with NO_2 absorbing solution. The remaining procedure was followed as described above.

Once the samples were extracted, they were color-reacted for analysis by UV spectroscopy, as described below. One milliliter of the 50 mL extracted sample was transferred to a clean 50 mL volumetric flask, partially filled with deionized water. One milliliter was used for all samples because of the high concentration levels being extracted, relative to the 6014 method. One milliliter of hydrogen peroxide solution, 10 mL sulfanilamide solution, and 1.4 mL N-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) solution were added, mixing thoroughly between each reagent addition. The flask was filled to the 50 mL mark with deionized water, capped, and mixed well. Ten minutes were allowed for full color development. The samples developed into graduated shades of pink, with the darker color indicating a higher concentration. The proposed chemistry of the reaction is shown in Figure 5. The range of the NO_2 curve was 0.5-50 µg/mL, see Figure 6. The reference was made by reacting 1 mL of absorbing solution at the same time as the rest of the samples.

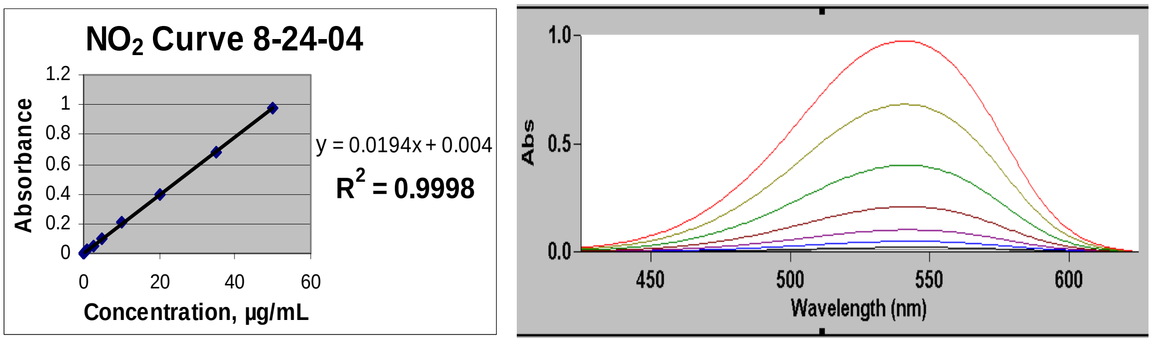

Figure 6. Standard curve for NO_2^- quantitation and the corresponding UV spectra.

3.0 Results and Discussion

Data were gathered and compiled on a weekly basis by removing a scheduled number of tubes and badges from each chamber. The raw data are given in Tables 1 and 2. Calculations were based on weekly measurements of the gas analyte, airstreams, and sampling rates. The expected sampling rate of the badges was constant, whereas, the sampling rate of each tube varied slightly. The flow rates of the tubes were measured upon introduction to the system and again prior to the tube's removal from the chamber. The average flow measurement, per tube, was used when calculating the concentration accumulated by each tube. All sample values, tubes and badges, were calculated to reflect the concentration within the chamber, respective to each sample. With all data presented in the same manner, direct comparisons could be made. Data from the control "clean" chamber showed no indication of NO_2 or other contamination in the spectral range of interest. This indicated that there were no interferences causing false-positive results. Accumulation of the analyte onto badges was consistently higher than accumulation onto tubes, with an average difference of approximately 13%. The percent relative standard deviation (%RSD) of tubes among all sample chambers ranged from 1.2 – 20.7%, with an average of 8.8%. The %RSD of badges among all sample chambers ranged from 0.46 – 7.28%, with an average of 3.1%. The low %RSD values indicate that the results among all chambers were consistent.

Table 1. Raw data for the active sampling tubes. Boxes 1, 2, 3, and 4 are the same as Chambers A, B, C, and D, respectively.

The correction factor (CF) is the number of moles of nitrite ions produced by one mole of nitrogen dioxide

50% Level, theoretical concentration 0.25 PPM

Box 1	Obs Conc, µg/mL NO_2	CF, 0.63 µg/mL NO_2	total µg sampled	sampling rate, L/min	Chamber conc, ppm	average ppm	%RSD
1	1.685	2.674	133.69	0.0515	0.137	0.136	1.4
2	1.572	2.495	124.73	0.0490	0.134		
4	11.036	17.517	875.84	0.0490	0.314	0.279	17.9
5	8.812	13.987	699.35	0.0505	0.243		
1b	10.680	16.953	847.65	0.0480	0.310	0.310	na
2b	lost sample			lost sample		na	
4b	2.454	3.895	194.77	0.0475	0.216	0.212	2.5
5b	2.542	4.035	201.77	0.0510	0.209		

Box 2	Obs Conc, µg/mL NO_2	CF, 0.63 µg/mL NO_2	total µg sampled	sampling rate, L/min	Chamber conc, ppm	average ppm	%RSD
1	8.013	12.719	635.94	0.0560	0.299	0.302	1.2
2	8.222	13.051	652.55	0.0565	0.305		
4	10.580	16.794	839.72	0.0500	0.221	0.234	7.9
5	11.353	18.020	901.00	0.0480	0.247		
1b	4.512	7.162	358.12	0.0520	0.182	0.180	1.4
2b	4.254	6.752	337.59	0.0500	0.178		

100% Level, theoretical concentration 0.50 PPM

Box 3	Obs Conc, µg/mL NO_2	CF, 0.63 µg/mL NO_2	total µg sampled	sampling rate, L/min	Chamber conc, ppm	average ppm	%RSD
1	11.855	18.818	940.89	0.0500	0.992	0.888	16.6
2	9.273	14.719	735.93	0.0495	0.784		
4	18.543	29.433	1471.65	0.0495	0.523	0.506	4.5
5	17.043	27.052	1352.60	0.0485	0.490		
1b	16.587	26.328	1316.40	0.0495	0.468	0.507	11.1
2b	19.402	30.796	1539.81	0.0495	0.547		
4b	6.388	10.140	507.00	0.0495	0.540	0.512	7.9
5b	5.715	9.071	453.57	0.0495	0.483		

Box 4	Obs Conc, µg/mL NO_2	CF, 0.63 µg/mL NO_2	total µg sampled	sampling rate, L/min	Chamber conc, ppm	average ppm	%RSD
1	13.714	21.769	1088.45	0.0480	0.598	0.578	4.9
2	13.058	20.727	1036.37	0.0490	0.558		
4	27.236	43.232	2161.59	0.0470	0.606	0.542	16.9
5	22.329	35.443	1772.13	0.0490	0.477		
1b	8.187	12.995	649.77	0.0445	0.385	0.336	20.7
2b	6.371	10.113	505.65	0.0465	0.287		

7 days = 10080 minutes

Average airflow rates, L/min, in the chambers	
Blk Box	31.35
Box 1	31.83
Box 2	32.36
Box 3	32.36
Box 4	33.39

	Low level,	High level,
average weekly concentration among the chambers, ppm =	0.236	0.553
average %RSD among the chambers =	5.4	11.8

Table 2. Raw data for the passive badges. Boxes 1, 2, 3, and 4 are the same as Chambers A, B, C, and D, respectively.

The correction factor (CF) is the number of moles of nitrite ions produced by one mole of nitrogen dioxide gas.

50% Level, theoretical concentration 0.25 PPM

Box 1	Obs Conc, µg/mL NO_2^-	CF, 0.63 µg/mL NO_2	total µg sampled	Chamber conc, ppm	average ppm	%RSD
1	lost sample		na	na	0.158	7.3
2	0.505	0.802	40.092	0.166		
3	0.456	0.723	36.164	0.150		
4	2.590	4.111	205.572	0.285	0.305	6.3
5	2.796	4.438	221.895	0.307		
6	2.936	4.660	233.022	0.323		
1b	3.134	4.975	248.732	0.344	0.344	0.5
2b	3.121	4.953	247.668	0.343		
3b	3.149	4.999	249.959	0.346		
4b	0.668	1.060	52.978	0.220	0.212	3.4
5b	0.630	1.001	50.033	0.208		
6b	0.628	0.997	49.869	0.207		

Box 2	Obs Conc, µg/mL NO_2^-	CF, 0.63 µg/mL NO_2	total µg sampled	Chamber conc, ppm	average ppm	%RSD
1	2.133	3.386	169.285	0.352	0.362	2.5
2	2.232	3.543	177.140	0.368		
3	2.221	3.525	176.240	0.366		
4	3.428	5.442	272.091	0.282	0.289	2.5
5	3.478	5.521	276.060	0.287		
6	3.599	5.713	285.673	0.297		
1b	1.185	1.881	94.052	0.195	0.198	1.7
2b	1.203	1.910	95.484	0.198		
3b	1.225	1.944	97.202	0.202		

100% Level, theoretical concentration 0.50 PPM

Box 3	Obs Conc, µg/mL NO_2^-	CF, 0.63 µg/mL NO_2	total µg sampled	Chamber conc, ppm	average ppm	%RSD
1	3.392	5.384	269.187	1.118	1.106	3.0
2	3.240	5.143	257.159	1.068		
3	3.432	5.448	272.378	1.131		
4	5.905	9.373	468.663	0.649	0.662	1.9
5	6.055	9.611	480.527	0.665		
6	6.125	9.723	486.132	0.673		
1b	4.755	7.548	377.393	0.522	0.515	1.2
2b	4.666	7.406	370.316	0.513		
3b	4.653	7.386	369.293	0.511		
4b	1.023	1.624	81.206	0.337	0.336	1.4
5b	1.031	1.636	81.820	0.340		
6b	1.004	1.594	79.692	0.331		

Box 4	Obs Conc, µg/mL NO_2^-	CF, 0.63 µg/mL NO_2	total µg sampled	Chamber conc, ppm	average ppm	%RSD
1	4.586	7.279	363.934	0.756	0.763	6.6
2	4.347	6.901	345.034	0.716		
3	4.955	7.865	393.225	0.816		
4	7.466	11.851	592.538	0.615	0.613	1.5
5	7.320	11.618	580.920	0.603		
6	7.532	11.956	597.815	0.621		
1b	2.301	3.652	182.622	0.379	0.397	3.9
2b	2.457	3.900	194.976	0.405		
3b	2.467	3.916	195.794	0.407		

7 days = 10080 minutes

Average airflow rates, LPM, in the chambers	
Blk Box	31.35
Box 1	31.83
Box 2	32.36
Box 3	32.36
Box 4	33.39

	Low level,	High level,
**** **average** weekly **concentration** among the chambers =	0.267	0.627
***** **average** weekly **stdev** among the chambers =	0.006	0.017

The observed concentration was determined by comparing the maximum absorbance of the UV spectrum peak against the standard curve. The corresponding concentration value, µg/mL, was multiplied by the correction factor, 0.63, to obtain the concentration of NO_2. The NO_2 value was used to calculate the representative concentration within the chamber. The theoretical concentration (µg/mL), assuming a sampling rate of 0.050 L/min, was determined by using the following equation:

$$C_s = \frac{C_g}{10^6} * \frac{M}{M_{air}} * \frac{f_g}{f_t} * t_{min} * \frac{0.050\ L}{min} * \frac{1}{50\ mL} * \frac{10^6\ \mu g}{1\ g} \qquad \text{where,}$$

C_g = Concentration of the gas cylinder, ppm
M = molar mass of NO_2, 46.01 g
M_{air} = molar volume of air, 24.46 L
f_g = flow rate of the NO_2 gas stream, L/min
f_t = total flow rate of NO_2 and air, L/min
t_{min} = sampling time, minutes
samples are extracted into 50 mL

The badges and tubes continued to accumulate the analyte for the entire 28 days of the validation, without the indication of saturation of the sampling media. Comparison of tubes and badges showed that the two sampling methods obtained similar results, see Table 3. The %RSDs, when comparing tubes and badges of the same exposure period, ranged from 2.7% - 24.2% with an average of 10.95%. Results appeared to be more stable and reproducible at the lower detection level, as indicated by the lower %RSDs. This trend can also be seen by plotting the accumulation trends of the validation period, as seen in Figure 7. The response of the badges was consistently greater than what was expected.

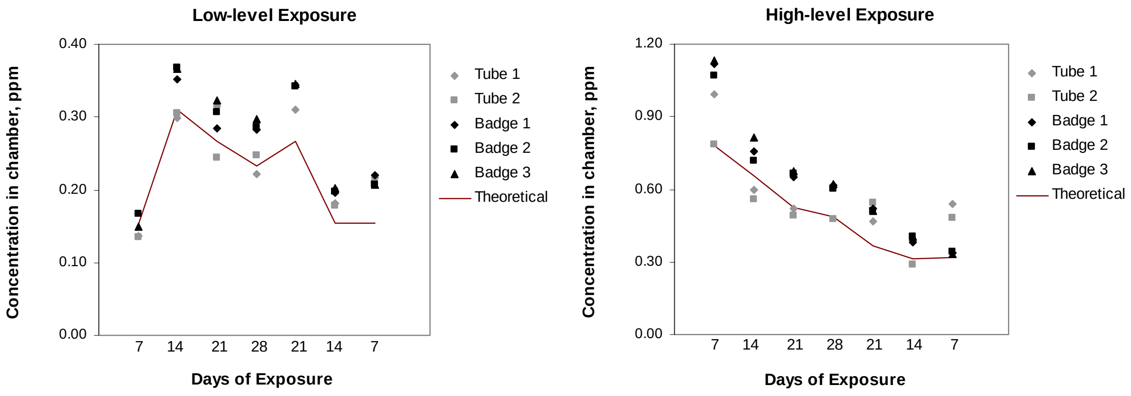

Figure 7. Trends of NO_2 in the chambers as observed by tube and badge results, ppm. Trends are not intended to be linear, as the result of pulses administered at different concentration levels.

Table 3. Weekly comparison of tubes and badges, ppm.

50% Level, 0.25 PPM

Box 1		Tube Conc	Badge Conc	%RSD	**Box 2**		Tube Conc	Badge Conc	%RSD
	1	0.137	na			1	0.299	0.352	
	2	0.134	0.166	**10.0**		2	0.305	0.368	**9.9**
7 days	3	NA	0.150		14 days	3	NA	0.366	
	4	0.314	0.285			4	0.221	0.282	
	5	0.243	0.307	**10.8**		5	0.247	0.287	**11.8**
21 days	6	NA	0.323		28 days	6	NA	0.297	
	1b	0.310	0.344			1b	0.182	0.195	
	2b	data lost	0.343	**5.1**		2b	0.178	0.198	**5.5**
21 days	3b	NA	0.346		14 days	3b	NA	0.202	
	4b	0.216	0.220						
	5b	0.209	0.208	**2.7**					
7 days	6b	NA	0.207						

100% Level, 0.50 PPM

Box 3		Tube Conc	Badge Conc	%RSD	**Box 4**		Tube Conc	Badge Conc	%RSD
	1	0.992	1.118			1	0.598	0.756	
	2	0.784	1.068	**13.9**		2	0.558	0.716	**15.7**
7 days	3	NA	1.131		14 days	3	NA	0.816	
	4	0.523	0.649			4	0.606	0.615	
	5	0.490	0.665	**14.4**		5	0.477	0.603	**10.4**
21 days	6	NA	0.673		28 days	6	NA	0.621	
	1b	0.468	0.522			1b	0.385	0.379	
	2b	0.547	0.513	**5.6**		2b	0.287	0.405	**13.3**
21 days	3b	NA	0.511		14 days	3b	NA	0.407	
	4b	0.540	0.337						
	5b	0.483	0.340	**24.2**					
7 days	6b	NA	0.331						

Table 4. Enmet Omni results in parts-per-million (ppm).

50% Level, ppm

	Date	Omni	Theoretical
Pulse 3	9/3/2004	1.798	1.346
Pulse 4	9/7/2004	1.763	1.271
Pulse 6	9/9/2004	7.362	5.399
Pulse 7	9/10/2004	7.019	4.947
Pulse 8	9/14/2004	1.613	1.296
Pulse 12	9/22/2004	1.857	1.480

100% Level, ppm

	Date	Omni	Theoretical
Pulse 5	9/8/2004	10.882	7.287
Pulse 9	9/15/2004	4.379	2.931
Pulse 10	9/16/2004	4.342	2.965
Pulse 13	9/23/2004	4.160	2.954

Data is unavailable for Pulses 1, 2, and 11.

The results provided by the Enmet Omni sensor were not used in the calculations of theoretical or observed values. The purpose of the instrument was to give a real-time, relative verification of the vapor exposure within the chambers, see Table 4. Having real-time verification allowed recognition of problems before they were escalated by time. This was a resource greatly appreciated in the early weeks of the experiment. It was discovered that the chambers were being exposed to a different concentration than expected. The NO_2 flow controllers, already set to provide the appropriate 50% and 100% test vapors, were mistakenly connected to their opposite 150 ppm and 500 ppm NO_2 gas tanks. This resulted in Boxes 1 and 2 having a pulsed exposure at 1.5 ppm and Boxes 3 and 4 at 7.6 ppm versus their appropriate exposures at 2.3 ppm and 4.67 ppm, respectively. Although the test vapor was monitored on a daily basis (per pulse), the problem was not apparent until the 5th pulse. Early readings from the Enmet sensor reported the lower level chambers at approximately 1.8 ppm, which was 78% of the theoretical concentration. While this was acknowledged, discrepancy within 25% was not alarming, as this was within the instrument parameters. Readings of the high level chambers, however, were 230% greater than expected, resulting in corrective action. One of the advantages of the pulse method is that the number, duration, and concentration of pulses may be changed as needed, as long as the total 28-day exposure is equivalent to a 28-day continuous exposure. With this in mind, the chambers were re-equilibrated to continue the experiment, see Figure 8. Because the NO_2 flow controllers were reversed, the high concentration chambers had been exposed to 67.8% of the 28-day exposure and the low concentration chambers were exposed to only 26.8% of the 28-day exposure. To equilibrate the chambers, the two high concentration chambers were kept idle while the two low concentration chambers were pulsed two additional times at a higher concentration, bringing them up to 33.9% of the 28-day exposure. The experiment then proceeded, exposing the low and high level chambers at 1.5 ppm and 3.0 ppm, respectively. The total 28-day accumulated exposure was equivalent to a continuous 28-day exposure.

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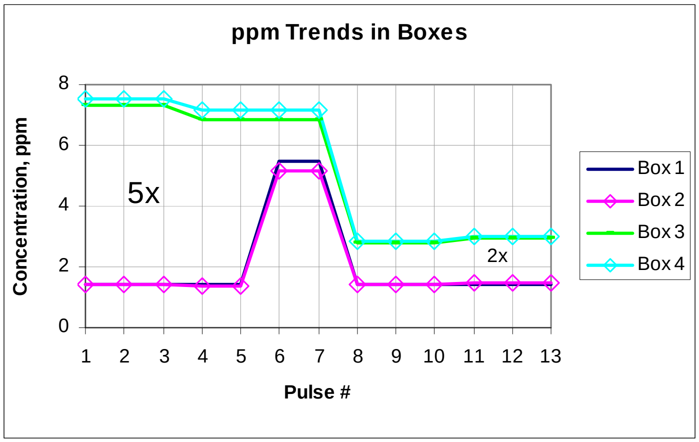

Boxes 3 and 4 did not receive an exposure for pulse numbers 6-7.

Figure 8. Theoretical concentration trends within the chambers.

4.0 Conclusions

The results provided by the four sampling chambers were compared to establish a response pattern of the passive badges, relative to active tubes, when exposed to NO_2 over a long-term period. Reproducibility among passive badges was demonstrated as well as among active sampling tubes. Average %RSDs less then 10% indicated that the results were a stable and reproducible representation of the response of the badges to the analyte over time. Accumulation of the analyte onto badges was consistently about 13% higher than accumulation onto tubes. While precision of the passive badge was demonstrated, the sampling rate may need to be investigated to verify that the badge response provides an accurate measurement of the vapor that it is sampling. The NO_2 badge demonstrates promising results for being used on submarines for long-term, low-level air monitoring.

5.0 References

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