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

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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 acrolein detection were tested. 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. The badges and tubes were exposed to acrolein vapor at concentrations of 0.2 and 0.1 ppm, resulting in a time-weighted-average of exposure at 100% and 50% of the USN 90-day submarine-specific limit (0.01 ppm). The badges and tubes continued to accumulate the analyte for 21 days, with recovery of the analyte onto badges consistently about 30% lower than recovery onto tubes. The badges and tubes seemed to reach full capacity before the full 28 days of the validation expired. Volatility of the derivatizing agent may have resulted in premature saturation of the sampling substrate. Badge results appear to be stable for continuous, qualitative air monitoring for up to seven days and possibly for up to 14 days.					
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PASSIVE BADGE ASSESSMENT FOR LONG-TERM, LOW-LEVEL AIR MONITORING ON SUBMARINES: ACROLEIN 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 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. Additionally, the Draeger tube methods are labor intensive and have poor reproducibility because of the use of a manually operated hand pump and multiple interpretations of the manually read tube results. 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 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, for exposures up to 28 days, the badges were compared to commonly-used active sampling tubes. The badges and tubes were simultaneously tested using exposure chambers that were designed to provide a homogenous test vapor to all sampling apparatuses (1).

Acrolein is found on submarines as an off-gassed compound of high-temperature paints and as a byproduct of tobacco smoke and deep fat fryers. It is considered to have high acute toxicity and an OSHA recommended exposure limit of 0.1 parts-per-million (ppm). Exposure to acrolein may result in respiratory congestion and dermal burns. However, because of the unique environment onboard submarines, the USN 90-day limit for acrolein was set at 0.01 ppm at the time of our testing. Passive badge monitoring for acrolein was evaluated for long-term exposures at 50% and 100% of the USN 90-day limit (0.005 ppm and 0.01 ppm respectively). Levels below the 90-day limit were employed to assure that this level could be accurately measured.

2.0 Experimental

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. The clear Plexiglas® chambers are comprised of multiple sections:

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 Plexiglas® plate within the chamber was designed 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 acrolein badge, as specified by the manufacturer, was 8.56 mL/min. To maintain this sampling rate, a minimal linear face velocity of ≥ 17 cm/sec, or 13 L/min, was sustained (2). The plate directed a total volume of 30 L/min of test vapor through the six 1.2 cm $\times$ 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 Plexiglas® baffles at the front of the chamber, with several randomly patterned holes, aided in mixing the vapor stream.

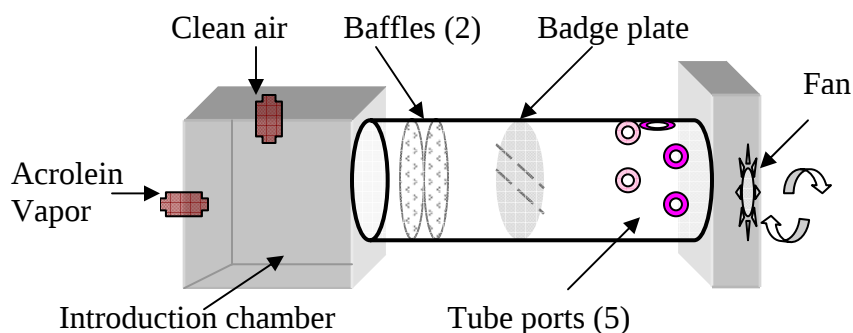


Figure 1. Diagram of a validation chamber.

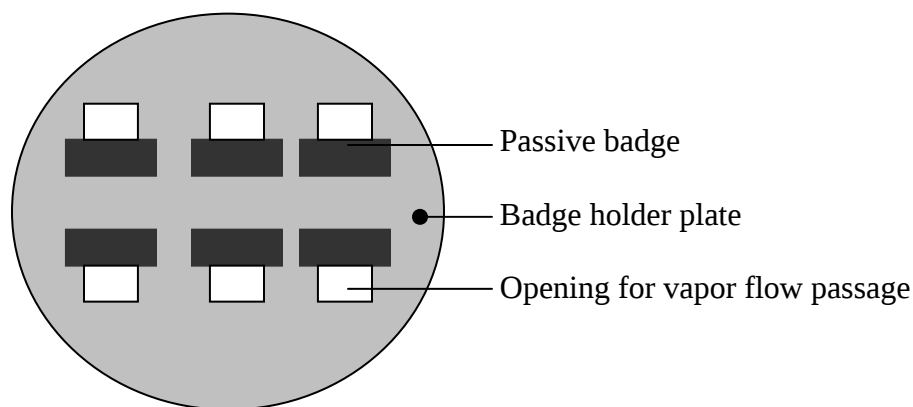


Figure 2. The badge plate, with 6-badge capacity.

2.2 Vapor Generation

The test vapor was generated using a diffusion-tube method. One milliliter (mL) of neat acrolein was transferred into an open-topped ampoule vial. A medium sized, glass capillary tube (length, 4 cm; OD, 0.6 cm; ID, 0.1 cm) was inserted into the top of the ampoule, making a snug fit with the use of a Teflon compression fitting, Figure 3. The

ampoule/capillary setup was contained in an impinger apparatus, which was kept in a water bath to maintain a temperature of 26°C. The acrolein vapor diffused from the vial, through the capillary, at a rate dependent on the vapor pressure and temperature of the compound; the vapor pressure of acrolein, at 20°C, is 209.4 mmHg. Nitrogen gas was delivered into the impinger at 300 mL/min, controlled by a Sierra mass flow controller, to carry the acrolein vapor from the diffusion tube and out to the test chambers, Figure 4. An adjustable, 4-port, manifold split the acrolein vapor flow among the four test chambers, providing 100 mL/min of vapor to each of the two 100% level test chambers and 50 mL/min of vapor to each of the two 50% level test chambers. Each chamber diluted the acrolein vapor into 30 L/min of clean, humidified air using Sierra mass flow controllers. Clean, humidified air was obtained by passing compressed house-air through dual-tower molecular sieves, removing moisture and CO₂, then through pressurized distilled water tanks for controlled rehumidification. Clean, humidified air, only, was delivered to the control chamber at all times. The flow rates of all controlled airstreams were measured using a Dry-Cal flow meter.

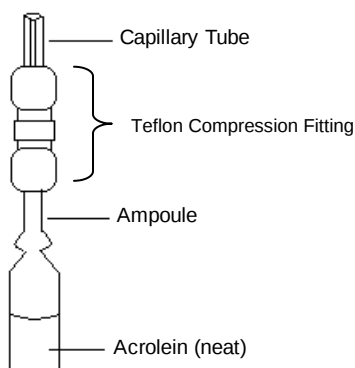


Figure 3. The ampoule vial with capillary diffusion tube.

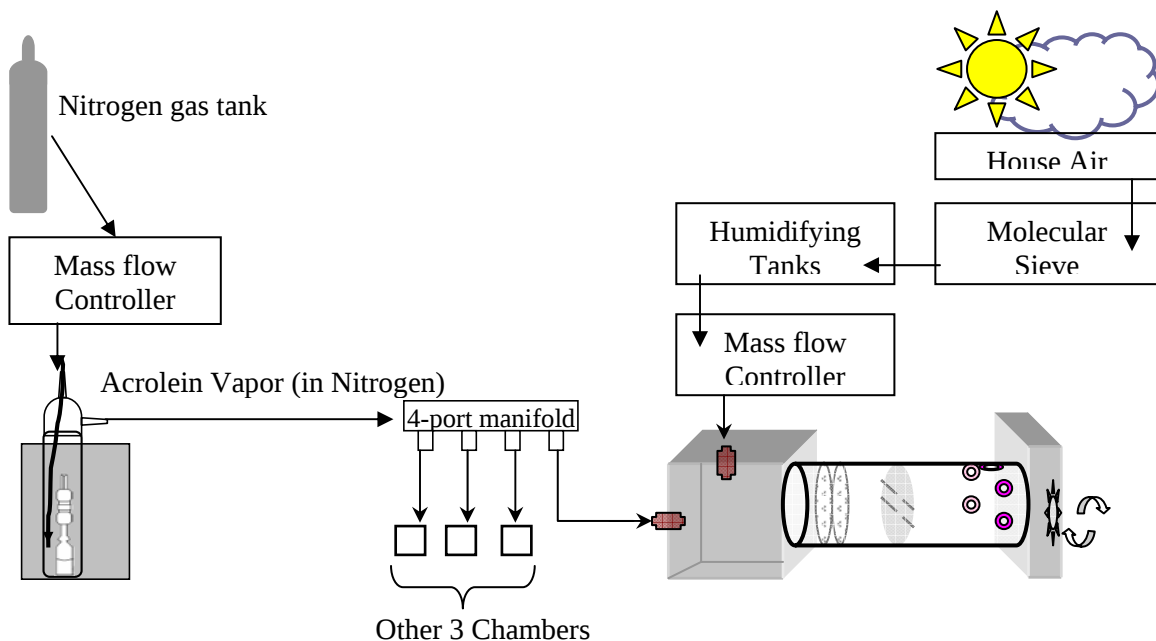


Figure 4. Schematic of the vapor-generation as it was delivered to the test chamber. “House air” is outside air that is compressed then redistributed throughout the laboratory.

The analyte exposures were conducted using the “pulse” method. Instead of exposing the samples to the analyte vapor continuously, the exposures were delivered only three times per week. The concentrations of the pulsed vapor were 0.2 ppm and 0.1 ppm for the 100% and 50% levels, respectively. Each pulsed exposure lasted approximately 168 minutes. The cumulative, time-weighted-average (TWA) exposure per week was equivalent to a continuous exposure at the 50% and 100% levels, refer to Equation 1. 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 spike of exposure to a hazardous compound.

$$\frac{0.01 \text{ ppm}}{\text{minute}} \times \frac{60 \text{ minutes}}{\text{hour}} \times \frac{24 \text{ hours}}{\text{day}} \times \frac{28 \text{ days}}{\text{validation}} = \frac{403.2 \text{ Total ppm}}{\text{validation period}}$$

$$\frac{403.2 \text{ Total ppm}}{4 \text{ weeks}} \times \frac{\text{week}}{3 \text{ days}} \times \frac{\text{day}}{168 \text{ minutes}} = \frac{0.2 \text{ ppm pulsed}}{\text{minute}}$$

Equation 1. Determines the vapor concentration to be delivered to the test chambers for the 100% level of the USN 90-day limit.

2.3 Sampling Methods

The analyte was collected onto passive badges (Assay Technology, Inc. #592) coated with 2-hydroxymethylpiperidine (HMP), a derivatizing and stabilization reagent. The same chemistry was used by the active sampling tubes (SKC 226-117), which had HMP coated onto XAD-2 resin. 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. Results obtained from all samples were compared against a standard curve covering the range of 0.5-60 µg, corresponding to the total analyte accumulated per sampler over time.

2.4 Independent Method

An independent method of acrolein detection was used to verify the concentration within the chambers for each pulse. Acrolein vapor was collected onto silica gel tubes (SKC #226-120) coated with dinitrophenylhydrazine (DNPH) for the duration of the pulsed exposure using SKC pocket pumps (210-1002), set at a sampling rate of 50 mL/min. After each pulse, the exposed tubes were removed from the chamber and analyzed, while new silica gel tubes were inserted into the chamber. Each tube monitored a single pulse and the clean air period prior to the pulse. Individual pulse samples were added together and compared to a respective sampling period of the badges.

2.5 Experimental Procedure

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, four-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 collect 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 through the tubes. Therefore, 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 experiment ran for 4 weeks (28 days). Chambers "A" and "B" tested the 100% level, and Chambers "C" and "D" tested the 50% 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 5. Each week three badges were

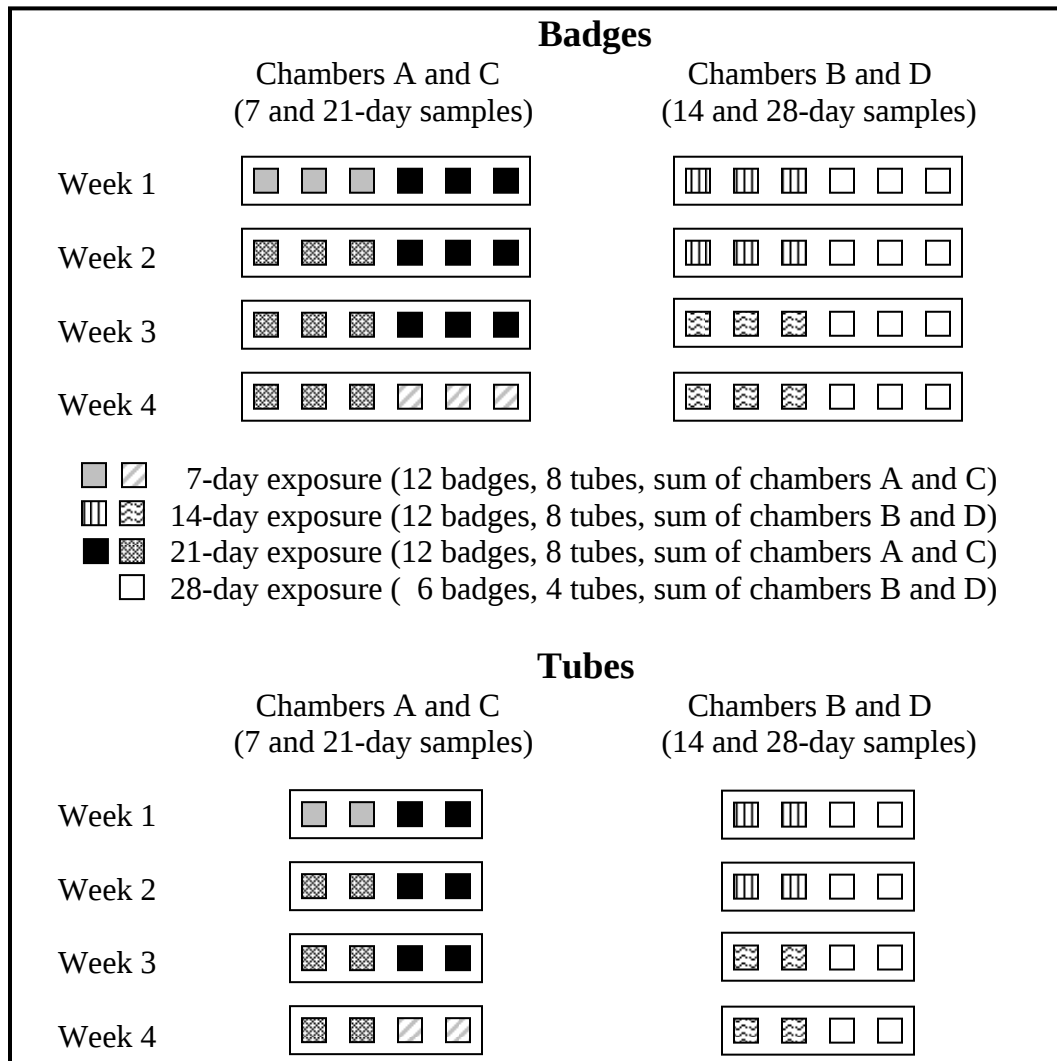


Figure 5. Schedule of badge and tube removal/replacement.

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. This pattern was repeated for the duration of the validation. 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. Clean air was moving through the chambers as the change-outs occurred. 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 7, 14, and 21 days. The total numbers of data points were as follows:

7 days	20 data points	} Total = 70 data points
14 days	20 data points	
21 days	20 data points	
28 days	10 data points	

2.6 Analysis

Each week, following removal from the test chamber, the tubes and badges were extracted for acrolein analysis. Analysis was similar to NIOSH 2539 analytical method (3). The faces of the badges were removed to acquire the sample disc. The disc was transferred to a clean sample vial filled with 2 mL of toluene solvent (anhydrous, 99.8%). The glass sample tubes were scored then broken open to empty the contents into a clean sample vial filled with 2 mL of toluene solvent. The tube and badge samples were sonicated for 60 minutes, then small aliquots of sample were transferred to autosampler vials to be analyzed by GC/MS (Agilent 5890/HP 5972, respectively). Figure 6 illustrates the chemistry of the derivatization reaction. Specifications of the GC/MS included: an Rtx-5 30 m, 0.25 id, 0.25 μ m column, with auto-sampler injection. The instrument temperature program was as follows: 60°C (hold 2 min) to 140°C @10°C/min, to 300°C @30°C/min (hold 2 min). The method runtime was 17.33 minutes with the retention time of the acrolein derivative at approximately 8.5 minutes and the excess HMP at 7.4 minutes. Sample data obtained from the GC/MS were compared against the calibration curve. The curve was generated by spiking tube and badge sampling substrates with increasing amounts of acrolein and desorbing the samples in 2 mL of toluene.

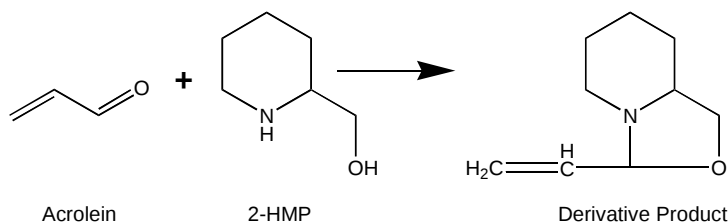


Figure 6. Chemistry of the derivatization reaction.

The independent method tube samples were analyzed by similarly following NIOSH analytical method 2016 (4). The media was extracted into 2 mL of acetonitrile and

sonicated for 30-60 minutes. The samples were analyzed by HPLC, at 365 nm, and compared against a standard calibration curve.

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.

Table 1. Raw data for the active sampling tubes.

100% Level, 10 ppb					50% Level, 5 ppb				
Days of Exposure	Total µg sampled	Sampling rate, L/min	Conc in chamber, ppb	%RSD	Days of Exposure	Total µg sampled	Sampling rate, L/min	Conc in chamber, ppb	%RSD
7	13.76	0.0505	11.79	8.14	7	7.17	0.0485	6.40	0.46
	14.83	0.0485	13.23			7.20	0.0490	6.36	
14	25.19	0.0495	11.01	9.73	14	16.79	0.0490	7.41	7.09
	27.45	0.0470	12.64			19.13	0.0505	8.20	
21	36.13	0.0475	10.97	5.90	21	20.38	0.0475	6.19	5.51
	38.04	0.0460	11.93			21.34	0.0460	6.69	
28	20.06	0.0455	4.77	4.42	28	14.99	0.0515	3.15	5.45
	23.23	0.0495	5.08			14.62	0.0465	3.40	
21	21.60	0.0485	6.42	4.68	21	5.85	0.0525	1.61	23.24
	23.07	0.0485	6.86			7.84	0.0505	2.24	
14	10.25	0.0460	4.82	13.11	14	7.86	0.0505	3.37	0.38
	12.75	0.0475	5.81			7.59	0.0485	3.39	
7	8.93	0.0450	8.59	9.54	7	3.52	0.0440	3.46	1.53
	7.89	0.0455	7.51			3.60	0.0460	3.39	
average ppb				8.68	average ppb				4.66
average %RSD				7.93	average %RSD				6.24

Table 2. Raw data for the passive badges.

100% Level, 10 ppb				50% Level, 5 ppb			
Days of Exposure	Total µg sampled	Conc in chamber, ppb	%RSD	Days of Exposure	Total µg sampled	Conc in chamber, ppb	%RSD
7	2.07	10.45	2.59	7	0.93	4.72	3.74
	1.96	9.92			1.00	5.04	
	2.02	10.20			1.00	5.04	
14	3.82	9.65	3.33	14	1.93	4.87	3.65
	3.65	9.24			1.89	4.79	
	3.58	9.05			2.03	5.13	
21	4.64	7.81	5.14	21	2.11	3.56	1.47
	4.40	7.41			2.09	3.52	
	4.18	7.05			2.05	3.46	
28	1.92	2.42	20.39	28	0.59	0.74	25.43
	1.69	2.14			0.71	0.90	
	1.27	1.60			0.42	0.53	
21	3.63	6.12	2.17	21	0.50	0.84	3.31
	3.75	6.31			0.53	0.89	
	3.79	6.39			0.53	0.89	
14	1.87	4.73	11.22	14	0.49	1.25	8.22
	1.53	3.88			0.42	1.06	
	1.56	3.95			0.45	1.14	
7	1.94	9.81	7.96	7	0.27	1.35	9.95
	1.78	9.02			0.31	1.55	
	2.09	10.58			0.32	1.64	
average ppb			7.04	average ppb			2.52
average %RSD			7.54	average %RSD			7.97

Calculations were based on weekly measurements of the gas analyte, airstreams, and sampling rates, refer to Equation 2. The sampling rate of the badges was expected to be

constant for each badge, 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 acrolein contamination, indicating that there were no interferences causing false-positive results.

$$\text{Total } \mu\text{g collected on sampler} \times \frac{\text{Tube / badge}}{\text{sampling rate, LPM}} \times \frac{\text{exposure period, minutes}^*}{24.46 \text{ L mole Air}} \times \frac{\text{mole Acrolein}}{56.06 \text{ g}} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} \times \frac{10^6}{1} = \text{Acrolein ppm}$$

Equation 2. Determines the observed concentration of acrolein vapor within the test chamber, per sample. *Exposure periods are in increments of 7 days (10080, 20160, 30240, or 40320 minutes) as this is a TWA value.

Accumulation of the analyte onto badges was consistently lower than accumulation onto tubes. The relative standard deviation (%RSD) of tubes per week ranged from 0.38 – 23.24%, with an average of 7.08%. The %RSD of badges per week ranged from 1.47 – 25.43%, with an average of 7.76%. When comparing the results of badges and tubes of the same exposure period, the %RSDs ranged from 14.5-80.5%, with an average of 44.3% at the low concentration level (50%), and ranged from 4.3-50.1%, with an average of 19.4% at the high concentration level (100%). Results collected weekly for tubes and badges were relatively consistent, as indicated by acceptable RSD values, <10%. However, the increased RSD levels, when comparing badges to tubes, verify that the badge results were different than the tube results, Table 3. On average, the badges had 30% lower recovery of the analyte than the tubes when compared against the theoretical values, 10 ppb and 5 ppb.

Although the badges did not provide the same level of response as the tubes, the badges did have similar behavioral patterns as the tubes, Figure 7. Unfortunately, the independent method did not work and the patterns were not verifiable by comparison to the independent method. During this research, an instrument broke that was critical to the analysis of the independent method samples. Because the samples could not be analyzed immediately, the samples began to degrade and form new compounds on the sample substrate. This process is a known phenomenon (Tejada 1986) and the reason that many analysts have chosen to use the HMP derivation method of acrolein capture and analysis. The low response of the badges may be attributed to the volatility of the derivatizing agent on the sampling substrate. The HMP seemed to disappear much faster than the acrolein was being accumulated. The acrolein and HMP react in a 1:1 mole ratio to form one mole of the derivative product, thereby finding an even exchange rate of the two compounds. If the HMP diffused from the substrate surface, the badges would approach full capacity much sooner. A demonstration of this behavior may be inferred in Figure 7 where the badges continued to accumulate acrolein for the first three weeks of the validation, however each week the rate of accumulation decreased as saturation was reached. It may also be possible that, in addition to HMP volatility, that the acrolein-HMP derivative is also more volatile than expected and diffused from the sampling

substrate prior to analysis. This may be interpreted from the response of the badges and tubes after four weeks of testing. The week 4 results were lower than those of week 3, indicating no further accumulation of acrolein and a loss of previously accumulated acrolein.

Table 3. Weekly comparison of tubes and badges.

100% Level							
Chamber A				Chamber B			
	Tube Conc †	Badge Conc †	%RSD		Tube Conc †	Badge Conc †	%RSD
7 days	1	11.79	10.45	14 days	1	11.01	9.65
	2	13.23	9.92		2	12.64	9.24
	3	NA	10.20		3	NA	9.05
21 days	4	10.97	7.81	28 days	4	4.77	2.42
	5	11.93	7.41		5	5.08	2.14
	6	NA	7.05		6	NA	1.60
21 days	1b	6.42	6.12	14 days	1b	4.82	4.73
	2b	6.86	6.31		2b	5.81	3.88
	3b	NA	6.39		3b	NA	3.95
7 days	4b	8.59	9.81	average %RSD			
	5b	7.51	9.02				
	6b	NA	10.58				
12.9							
19.4							
50% Level							
Chamber C				Chamber D			
	Tube Conc †	Badge Conc †	%RSD		Tube Conc †	Badge Conc †	%RSD
7 days	1	6.40	4.72	14 days	1	7.41	4.87
	2	6.36	5.04		2	8.20	4.79
	3	NA	5.04		3	NA	5.13
21 days	4	6.19	3.56	28 days	4	3.15	0.74
	5	6.69	3.52		5	3.40	0.90
	6	NA	3.46		6	NA	0.53
21 days	1b	1.61	0.84	14 days	1b	3.37	1.25
	2b	2.24	0.89		2b	3.39	1.06
	3b	NA	0.89		3b	NA	1.14
7 days	4b	3.46	1.35	average %RSD			
	5b	3.39	1.55				
	6b	NA	1.64				
46.3				44.3			

† Concentrations are expressed in ppb, referring to the exposure concentration.

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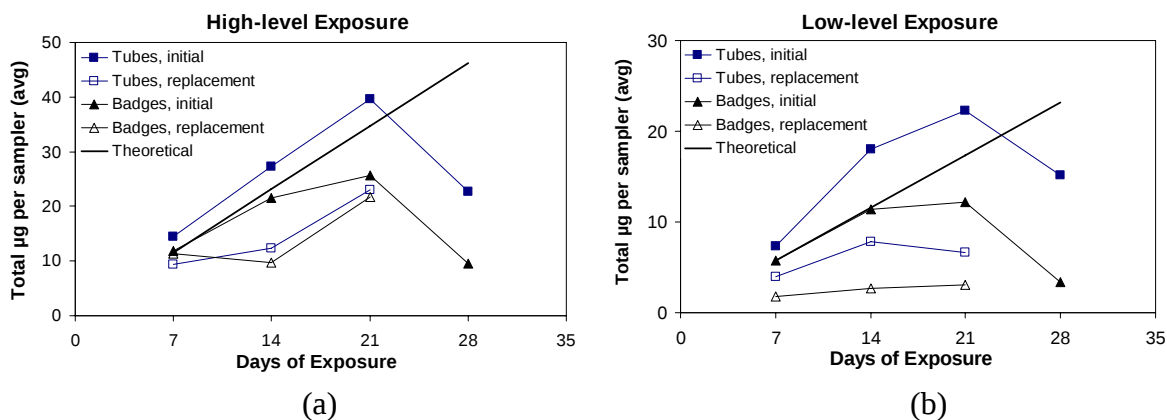


Figure 7. Accumulation of acrolein onto tubes and badges for 28 days at (a) 100% and (b) 50% of the 90-day limit.

Formaldehyde and acetaldehyde contamination were also observed, eluting in the mass spectra at approximately 7.0 minutes and 7.1 minutes, respectively. These compounds also react readily with the HMP derivative, presenting competition for the derivatizing agent. This may have resulted in an initial decrease of available HMP on the sampling substrate, however the level of contamination did not significantly increase over time. Lower levels of contamination were observed in blank badge samples and samples containing only the HMP derivative. It is likely that contamination may have occurred during the manufacturing process of the HMP and again during the manufacturing process of the badges when HMP is applied to them. Other sources of contamination may include other manufacturing processes, storage, laboratory handling, etc., resulting in a cumulative level of contamination.

4.0 Conclusions

The results provided by the four sampling chambers were compared to establish response patterns of the passive badges, relative to active tubes, for acrolein over a 28-day exposure period. The badges and tubes continued to accumulate the analyte for 21 days, with recovery of the analyte by badges consistently about 30% lower than recovery by tubes. The badges and tubes seemed to reach full capacity before the full 28 days of the validation expired. Badge results appeared to be stable for continuous, qualitative air monitoring for up to seven days and possibly for up to 14 days. A correction factor may need to be applied to obtain more accurate, quantitative results. Additional research should be done to more fully understand the long-term behavior and stability of the acrolein-HMP product before using the badges for exposures greater than 14 days.

5.0 References

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