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Evaluation of the Du Pont Pro-Tek® Formaldehyde Badge and the 3M Formaldehyde Monitor*

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The 3M Formaldehyde Monitor and the DuPont Pro-Tek® Formaldehyde Badge were evaluated for performance and reliability. This evaluation revealed that the 3M monitor results were variable and lower than reference concentrations determined independently. When the monitors were humidified before use and then exposed in humid (ca. 80% RH) formaldehyde-containing atmosphere, the monitors did give accurate results. Results of additional experiments led to the conclusion that quantitative reaction between formaldehyde generated in our chamber and the absorbent pad in the 3M monitor required the presence of a minimum level of absorbed water. The DuPont badges gave good agreement with the reference concentrations determined independently under the following conditions: a) sampling period of 1 to 12 hr with a minimum integrated sample loading of 4 ppm-hr; b) at least 3 m/min (10 ft/min) face velocity; c) correction for blank badges; and d) correction for loss of reagent from the samples. The evaluation indicated that the DuPont badge was not well suited to short term sampling and was subject to evaporation of liquid from the absorbing liquid blister. Blank values also were found to be variable, necessitating the analysis of several blanks to be used for blank correction with each set of samples. This blank variability also contributed to high variability found when short term measurements were made. The badge also had a negative interference from phenol at high phenol-to-formaldehyde ratios. Some of the major problems observed with both passive monitors were found only after devices which had been aged under storage conditions were analyzed and these results interpreted. If all testing had been done with fresh sampling devices, many of the problems would not have been noticed. Based on the results of this study, this factor of diffusive monitor aging needs to be addressed in any further work on passive monitor evaluation.

Introduction

Growing concern over the adverse health effects associated with formaldehyde has generated renewed interest in sampling and analytical methods for this compound. With the development of passive monitors for formaldehyde sampling, a new, less cumbersome sampling technique is potentially available. Because of the simplicity of these devices, NIOSH industrial hygienists desire to use them in occupational health surveys. Before using these devices in the field, a laboratory evaluation is requested to ensure that the monitors will perform as advertised. Since no independent evaluation of the formaldehyde monitors had been performed and past experience with other passive monitors for other compounds had indicated problems,(1) we undertook a full evaluation of the formaldehyde monitors in our laboratory.

At the time of this evaluation, only two commercial passive monitors for formaldehyde were available: the 3M Model 3750/3751 Formaldehyde Monitor and the DuPont Pro-Tek Badge. The 3M monitor consisted of a diffusion zone of defined geometry and a proprietary reagent-coated pad at the bottom of the diffusion zone. Formaldehyde diffused into the monitor and then reacted with the reagent-coated pad. The difference between the two model designations of this badge was that the Model 3750 had the cost of analysis by 3M included in the purchase price of the monitor. The Model 3751 monitors did not include analysis by 3M and were analyzed in our laboratory. The DuPont Pro-Tek badge consisted of an absorbing solution blister pack, incorporating a proprietary diffuser element and absorbing solution. The pack contained a second blister, which was sealed from the air and was used as a reagent blank during analysis. This entire sampling pack was housed in a white outer cover which had a lapel clip for attaching the sampling device to a worker or a stationary stand.

The purpose of this report is to present our findings on the evaluation of the Model 3750/3751 3M Formaldehyde Monitor and the DuPont Pro-Tek Formaldehyde Badge using experiments designed to demonstrate the usefulness of the badges in potential sampling situations.

Experimental

Exposure Chamber

The exposure chamber used was a semi-closed loop system with a volume of approximately 677 L, designed for use with reactive compounds (Figure 1). The chamber was constructed of 0.64 cm (0.25 in) acrylic sheet and lined with adhesive backed Teflon® (1 mil, Cole-Parmer Instrument Co., Chicago, Ill.). Removable access plates held in place with screws were either taped with vinyl-backed tape or sealed with silicone caulk to prevent leakage of the atmosphere in the chamber. Even with these precautions against leakage, the chamber had an integral leak (ca. 5-10%, depending on face velocity). Because of this leak and the air

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*Mention of any manufacturer or product name does not constitute endorsement by the National Institute for Occupational Safety and Health.

removed by the active sampling devices used (2 to 4 L of contaminated air removed per min), make-up air was metered into the chamber through a tubing connection on the panel mount by a mass flow controller (Nav-Tec, Inc., Hauppauge, N.Y.). For high humidity exposures, prior to entering the chamber the make-up air was passed through a 500-mL impinger containing deionized water. The centrifugal blower (27-cm wheel diameter, Grainger Inc., Cincinnati, Ohio) used to circulate the test atmosphere was also Teflon-coated. All of the internal chamber components (except four 14 × 14-cm glass viewing ports, the hygrometer and the neoprene gloves) were either constructed of or coated with Teflon. Two doors connected in series by an antechamber (so that samples could be added or removed during exposures) provided access into the chamber. A 30-m coil of Teflon tubing (6-mm o.d.) was connected to a constant temperature bath (Forma Scientific Model 2095) to maintain exposure temperatures between 22-25° C and provide temperature control during the high (38° C) and low (17° C) temperature exposures.

A pressure-drop plate (0.5-mm Teflon sheet with 5-mm diameter holes spaced 2 cm apart) was used to provide uniform face velocities across the samplers. For the majority of experiments, the face velocity averaged 17.4 m/min (57 ft/min) with a relative standard deviation of 8.9%, based on a 36-point Pitot traverse at each point where a sampler could be placed. A Kurtz Model 441 Hot Wire Anemometer with a 61-cm (2-ft) probe was used to make the face velocity measurements. It should be noted that this type of device is not directionally sensitive and readings can be influenced by local vortexes. The lowest measurable limit with this anemometer was 1.5 m/min (5 ft/min). Measurements which were taken that caused a meter deflection but were below 1.5 m/min were reported as <1.5 m/min. Because of the design of the exposure chamber, low face velocities were not uniform across the chamber and varied between 1.5 and 6.1 m/min (5 and 20 fpm), depending on location. By mapping areas of lower and higher face velocities across the chamber, monitor exposures at two different face velocities were completed during one run.

Humidity was monitored periodically during the exposures with a hygrometer (Taylor Instruments, Arden, N.C.). Humidity was increased by manual injection of water (0.5-5.0 mL) into the air stream exiting the blower with a syringe through septa in the panel mount. Since the chamber was flushed with clean, dry air (<1% relative humidity) after each exposure run, it was not necessary to lower the humidity during any of this experimentation. A CEA Instruments TGM 555 Air Monitor (Westwood, N.J.) or a Lion Formaldemeter (MDA Scientific, Glenview, Ill.) was used as a continuous formaldehyde monitor to alert us to any concentration upsets, but not as an independent method. A syringe pump (Sage Instruments, Model 355) equipped with a 20-mL syringe was used to inject an aqueous standard solu-

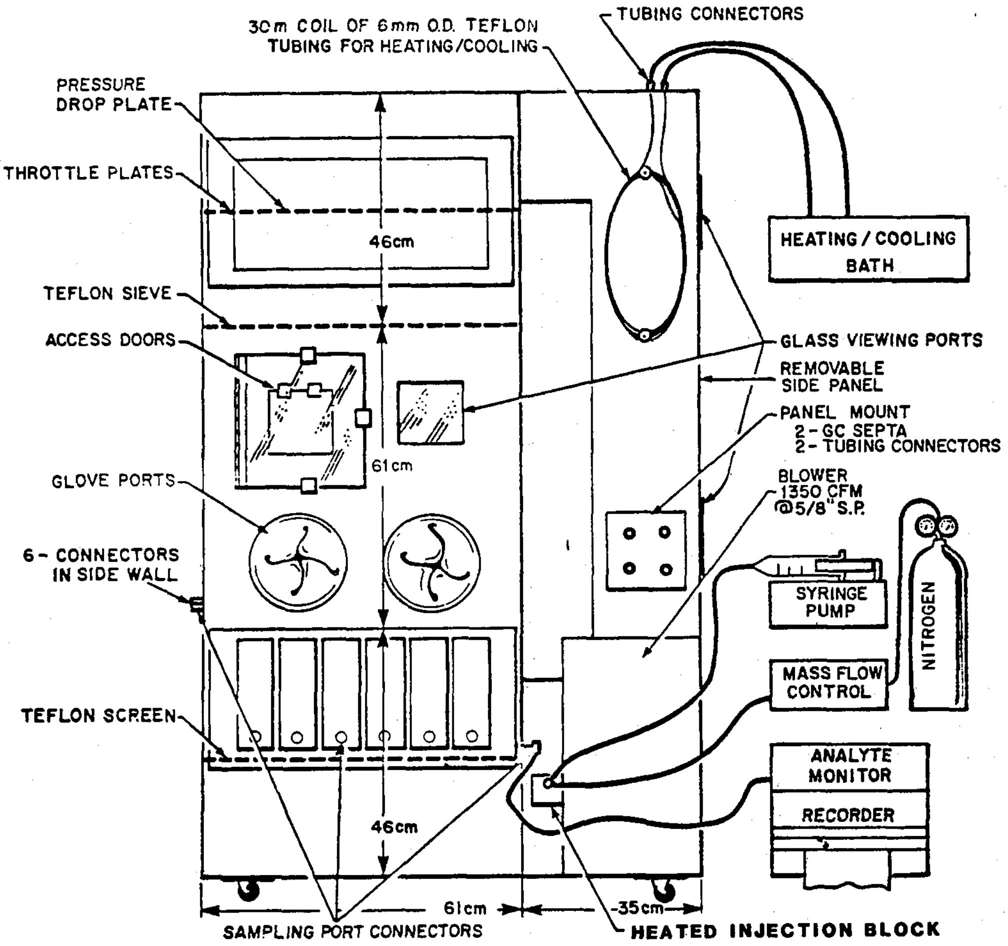

Figure 1 — Schematic diagram of diffusive monitor exposure chamber.

TABLE I
Summary of Data for Evaluation of the 3M Formaldehyde Monitors

Experiment No.	Temp. (°C)	Rel. Hum. (%)	Storage Time (days)	Period of Exposure (hr)	Reference Conc.[A] (ppm)	Measured Conc.[A] (ppm)	Monitor Precision (RSD %)	No. of Samp.
2	23	56	6	0.125-12	(See Figure 2)[B]		--	30
3	21	28	1	4	4.2±0.2	0.59±0.04	9.9	10
	21	--	1	8[C]	2.1±0.1	0.27±0.02	11.6	10
Auxiliary Experiments								
A	27	53	8		2.0±0.2[B]	1.1±0.1	11.6	12
B	25	30	2	4	1.7±0.1	0.4±0.03	11.8	12
	25	30	7	4	1.7±0.1	0.4±0.1[D]	20.2	6
C	26	43	1	4	1.9±0.1	0.6±0.06	9.9	6
	26	43	6	4	1.9±0.1	1.4±0.3[D,E]	23.7	6
	26	43	1	4	1.9±0.1	1.8±0.2[F]	9.3	6
	26	43	1	4	1.9±0.1	1.8±0.04[E]	2.1	6

[A] Concentrations are reported with their 95% confidence limits.

[B] P&CAM 354 analyses were out of control and not used for reference concentration determination.

[C] 4.2 ppm for 4 hr, then 0 ppm for 4 hr.

[D] Analyzed by 3M.

[E] Equilibrated at 92% RH before exposure.

[F] Equilibrated in inner plastic bag at 92% RH.

tion of paraformaldehyde [prepared from α-polyoxymethylene (Fisher Chemical) and distilled water] into an injection block (Hamilton Co., Reno, Nev.) heated to 170°C. The generated formaldehyde vapor was swept into the exposure chamber with nitrogen flowing at 250 cm^3/min. Different concentrations in the chamber were achieved by adjusting

TABLE II
Summary of Data for Evaluation of the DuPont Formaldehyde Badges

Experiment No.	Temp. (°C)	Rel. Hum. (%)	Storage Time (days)	Period of Exposure (hr)	Reference Conc.[A] (ppm)	Measured Conc.[A] (ppm)	Monitor Precision (RSD %)	No. of Samp.
2	24	44	1	0.125-12	(See Figure 3)		--	30
3	22	46	1	4	1.0±0.1	1.1±0.1	12.4	10
	22	--	1	8[B]	0.5±0.05	0.55±0.04	10.9	10
	23	80	4	3.5	5.4±0.2	5.4±0.5	11.6	10
	23	--	4	7[C]	2.7±0.1	2.5±0.2	8.1	10
4	23	80	1	6	2.4±0.2	2.3±0.1	7.1[H]	12
	23	80	14	6	2.4±0.2	2.5±0.2	10.4	10
	23	80	14[D]	6	2.4±0.2	2.7±0.1	9.4	10
6	17	61	1	4	2.3±0.1[E]	2.3±0.7	4.6	10
	27	53	6	4	2.0±0.2	2.0±0.1	10.3[H]	12
	38	34	1	4	8.4±0.3[E]	7.7±0.2	2.7	10
7	23	80	1	4	0.29±0.05	0.35±0.07[F]	32.7	12
	23	77	1	7	0.30±0.03	0.35±0.17	74.5	12
	23	87	3	7	0.30±0.04	0.33±0.03[G]	12.9	20
	22	46	1	4	1.0±0.1	1.1±0.1	12.1	20
	25	30	2	4	1.7±0.1	1.7±0.1	5.1	12
	27	53	6	4	2.0±0.2	2.0±0.1	10.3	12
	23	80	1	6	2.4±0.2	2.3±0.1	7.1	12
	23	80	4	4	5.4±0.2	5.2±0.3	4.9	20

[A] Concentrations are reported with their 95% confidence limits.

[B] 1.0 ppm for 4 hr, then 0 ppm for 4 hr.

[C] 5.4 ppm for 3.5 hr, then 0 ppm for 3.5 hr.

[D] Stored at 5 °C.

[E] P&CAM 354 analyses were out of control and not used for reference concentration determination.

[F] Badge loadings were less than 2 ppm-hr.

[G] Badges corrected for residual volume.

[H] Included with the data from Experiment 7 in the pooled relative standard deviation.

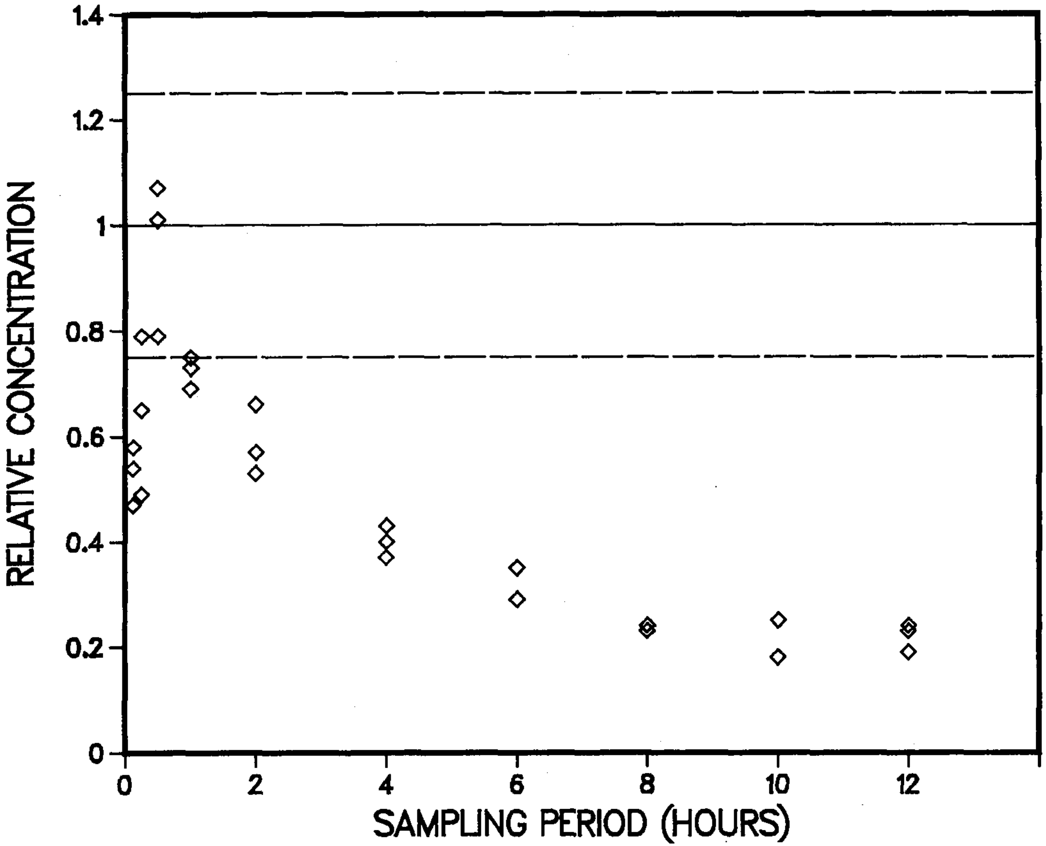

Figure 2 — Sampling rate and capacity study of 3M Formaldehyde Monitors. Theoretical uptake in relative concentration versus time plotted as a solid line. Dashed lines represent ± 25% of the theoretical uptake. Actual sampler performance plotted as diamonds. In some instances points are plotted on top of one another, giving appearance of only one or two points being present.

the injection speed of the syringe pump (4.0-17.0 μL/min) and the concentration of the paraformaldehyde solution (36-93 mg/mL). When phenol was required as an interference, phenol vapor was generated by placing several grams of phenol in a U-tube, passing make-up air over the phenol and directing it into the chamber. Phenol concentrations generated in this fashion ranged from 2 to 6 ppm.

Even though a concentration profile at the 36 different sampling locations in the chamber was measured with the CEA TGM 555 Air Monitor and showed that concentration gradients did not exist, samplers were placed in the chamber in random order, except for the very low face velocity exposures previously noted.

Independent Methods

Formaldehyde concentration in the exposure chamber was monitored using three independent methods: NIOSH method P&CAM 125;(2) NIOSH method P&CAM 354;(3) and a method using 2,4-dinitrophenylhydrazine.(4,5) The sampling devices were attached to the chamber by short lengths of glass or Teflon tubing and Teflon fittings. Critical orifice assemblies (Langer Jewel Bearing Plant, Rolla, N.D.) were used in conjunction with the laboratory vacuum system (328 mm Hg) for independent sample collection. Flow rates of critical orifice assemblies (nominally 60 cm^3/min for P&CAM 354 and 140-180 cm^3/min for P&CAM 125 and the 2,4-dinitrophenylhydrazine methods) were determined both before and after each exposure.

P&CAM 125 involved formaldehyde collection in an impinger containing 1% aqueous sodium bisulfite solution and sample treatment with chromotropic acid and sulfuric acid prior to spectrophotometric analysis. Formaldehyde was collected for P&CAM 354 by reaction with N-benzylethanolamine (coated on Amberlite XAD-2® in sorbent tubes). The resulting 3-benzyloxazolidine was desorbed and analyzed by capillary-column gas chromatography with flame ionization detection. The 2,4-dinitrophenylhydrazine-coated silica gel tube (2,4-DNP) method(4) collected formaldehyde by forming the 2,4-dinitrophenylhydrazone of formaldehyde. This derivative was quantitated by high performance liquid chromatography. A method using 2,4-DNP in acetonitrile in an impinger and the same analysis technique was used for most of the later runs to allow easier sampling device preparation and sample workup.(5) Coated silica gel-tubes were used for Experiments Nos. 2 and 3 conducted with the 3M monitors, and the impinger method was used for all other experiments.

Results of the three methods for each run were pooled to determine average chamber concentration. In cases where a method was found out of control, the results from it were not used.

TABLE III
Parameter Values for the Fractional Factorial Experiment

Face Vel. (m/min)	Phenol Conc. (ppm)	Relative Humidity	Time (min)	Orientation To Flow	Ref. Conc. (ppm)	Relative Conc.^A DuPont	3M
<1.5	0	30%	150	parallel	0.89	0.61	0.03
<1.5	0	80%	420	perpendicular	0.75	0.80	0.75
<1.5	0	33%	150	perpendicular	4.2	0.84	0.10
<1.5	0	80%	420	parallel	4.5	0.89	0.83
<1.5	6.6	30%	420	parallel	0.66	0.12	0.01
<1.5	6.2	90%	150	perpendicular	0.63	0.37	0.57
<1.5	5.2	30%	420	perpendicular	4.1	0.46	0.02
<1.5	3.9	90%	150	parallel	4.2	0.60	0.63
76	0	50%	420	perpendicular	0.13	1.08	1.15
76	0	80%	150	parallel	0.24	1.13	0.71
76	0	50%	420	parallel	4.9	1.06	0.55
76	0	80%	150	perpendicular	4.4	1.03	1.02
76	1.9	51%	151	perpendicular	0.41	0.73	0.88
76	2.0	80%	420	parallel	0.37	0.92	1.08
76	1.6	51%	150	parallel	5.3	1.02	0.80
76	1.6	90%	420	perpendicular	4.0^B	0.93	1.04

^A Relative concentration = monitor concentration ÷ reference concentration.

^B P&CAM 354 analyses were out of control and not used for reference concentration determination.

When phenol was present in the chamber, P&CAM 125 was not used to measure formaldehyde concentration, because phenol was an interference. NIOSH method S330[(6)] was used to measure phenol concentration. This method involved collection of phenol in an impinger containing 0.1 N aqueous sodium hydroxide solution. The solution was acidified with concentrated sulfuric acid prior to analysis by gas chromatography.

Passive Monitor Analysis

The 3M Formaldehyde Monitors (Models 3750, Lot No. 2060 04; and 3751, Lot Nos. 2102 004 and 2098 004) were

TABLE IV
Summary of Effect Factors from the Fractional Factorial Exposure Experiment (Experiment 5)

	DuPont Factor Values	Significance Level^A 0.1	0.05	0.01	3M Factor Values	Significance Level^A 0.1	0.05	0.01
Main Effects:								
Concentration (C)	0.069	X			-0.019			
Rel. Humid. (RH)	0.047				0.199	X	X	X
Interference (I)	-0.143	X	X	X	-0.013			
Time (T)	-0.003				0.050			
Face Vel. (FV)	0.201	X	X	X	0.262	X	X	X
Orientation (O)	-0.007				0.061			
3-Way Interactions:								
C*RH*I	-0.011				-0.047			
C*RH*T	0.009				0.010			
Combined 2-Way Interactions:								
C*RH + FV*O	-0.037				0.070			
C*I + T*O	0.041				0.00			
C*FV + RH*O	-0.045				-0.045			
C*O + I*T	-0.032				-0.129	X		
RH*I + T*FV	0.013				0.015			
RH*T + I*FV	0.056				0.048			

^A If factor value exceeds critical value for a given significance level, then the factor is significant at that level. The critical values for the Du Pont monitors are 0.06, 0.075 and 0.107 for the 0.1, 0.05 and 0.01 levels. For the 3M monitors, the critical values are 0.107, 0.132 and 0.190 for the 0.1, 0.05 and 0.01 levels.

TABLE V
Effect of Face Velocity and Phenol on DuPont Formaldehyde Badge Performance

Reference Concentration^A		DuPont Concentration (ppm)^A	
		Face Velocity	
Formaldehyde (ppm)^B	Phenol (ppm)	10 ft/min	20 ft/min
5.1±0.2	0	4.6±0.2	4.7±0.1
4.1±1.6	2.9±0.2	4.1±0.1	4.1±0.1

^{A}Reference concentrations are reported with their 95% confidence limits.

^{B}P&CAM 354 analyses were out of control and not used to determine reference concentration.

purchased from Netherland Rubber Co. (Cincinnati, Ohio). The procedure used for analysis of the 3M monitors included desorbing the monitor reagent-coated pad with 3 mL of distilled, deionized water. Two mL of this solution were placed in a 25-mL flask and one mL of 1% chromotropic acid added. In instances where it was necessary to dilute the eluate before analysis so as to stay in the linear range of the calibration curve, dilutions of the 3-mL badge eluate solutions were made using 1% aqueous sodium bisulfite solution. The color was developed by addition of 5 mL of concentrated sulfuric acid and heating in a 90 °C water bath for 15 min. The heating during color development was not specified in the manufacturer's analysis instructions,(7) but was included to ensure complete color development and consistency among all the methods, since the other colorimetric methods (P&CAM) 125 and the DuPont badge) were heated. A color development time of 2 hr from the addition of the chromotropic acid to the spectrophotometric analysis was used for all 3M monitor analyses. Formaldehyde content of the samples was determined spectrophotometrically at 580 nm.

Standards were prepared by the addition of aliquots of a standardized formalin solution to 3-mL portions of a 1% aqueous sodium bisulfite solution. These solutions then were worked up as outlined above.

DuPont Formaldehyde Badges, Series II, Type C-60 (Lot Nos. C-60A-4, 601, 602, 605 and an unnumbered lot), were purchased from the Applied Technology Division of E.I. DuPont de Nemours & Co. Sampling and analysis procedures were followed as outlined in the manufacturer's recommendations,(8) incorporating the following two modifications: 1) All badge absorbance data were blank corrected. The reagent blister on the badge was used to prepare the reference blank for the spectrophotometer. Unexposed badges from the same lot as the exposed badges were processed according to the analysis procedure and used for blank correction. 2) In Experiment 6, a correction factor was applied to the absorbance of the badge solution for the residual volume of solution in the badge after the 2-mL sample aliquot was removed. The residual volume was measured by removal of the remaining solution in the badge with a volumetric syringe and the volume recorded. This residual volume was used to correct the absorbance measured, using the following equation:

$$\text{corrected absorbance} = \frac{[2\ \text{mL} + \text{residual volume (mL)}]}{2.4\ \text{mL (theoretical badge volume)}} \times \text{measured absorbance}$$

Blank absorbances also were corrected in this manner for Experiment 6.

Quality Control

A quality control program was maintained during the course of experimentation. Blind quality control samples (formaldehyde loadings were not known by the analyst) were submitted and analyzed with each sample set. Blind quality control samples for P&CAM 125 and 3M monitor analysis were aliquots of standard formalin solutions. These solutions were analyzed in the same manner as the bisulfite impinger solutions for P&CAM 125 and the monitor eluate for 3M samples. P&CAM 354 and the 2,4-DNP quality control samples were prepared by spiking an aliquot of a standard formalin solution onto the sorbent tubes or into the 2,4-DNP impinger solution. These samples also were analyzed in the same manner as the samples from the chamber. Results were charted using standard control charting techniques.(9) Blank samples were analyzed along with each sample set and corrections for the contributions of the appropriate blanks were made to the measurements from the independent method, monitor and quality control samples.

Concentration results throughout this paper are presented with their 95% confidence limits.

Experimental Evaluation Protocol and Results

The individual experiments used to evaluate the passive monitors are described in detail below with the results. Tables I and II provide a summary of experimental conditions and results. Face velocity for all runs unless otherwise indicated was 15-18 m/min (50-60 ft/min).

Experiment 1.: For the 3M monitors, which required desorption prior to analysis, six monitors were spiked with aliquots of a standard formalin solution at each of four concentration levels (approximately 0.1, 1.5, 3.0 and 6.0 ppm, assuming a sampling time of 4 hr and a sampling rate of 65.9 cm^3/min) to determine recovery efficiency. These levels were 2.2, 27.8, 55.5 and 111 μg formaldehyde per sampler. The monitors were allowed to stand overnight before analysis. Recoveries at these levels were 115.8 ± 44.2%, 106.6 ± 10.5%, 102.9 ± 12.2% and 103.8 ± 6.0%, respectively.

Because of the design of the DuPont Pro-Tek® Formaldehyde Badge and the fact that desorption was not a part of the analysis of this badge, spiking to determine analytical recovery was not conducted.

Experiment 2.: The sampling rate and capacity of the monitors were investigated by exposing 30 monitors from each manufacturer to 4 - 6 ppm of formaldehyde and 56% RH for times ranging from 1/8 to 12 hr (1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 and 12 hr). Three monitors were exposed and analyzed for each time interval.

This experiment was designed to define the sampling rate and determine the range over which this rate is constant or at least predictable.

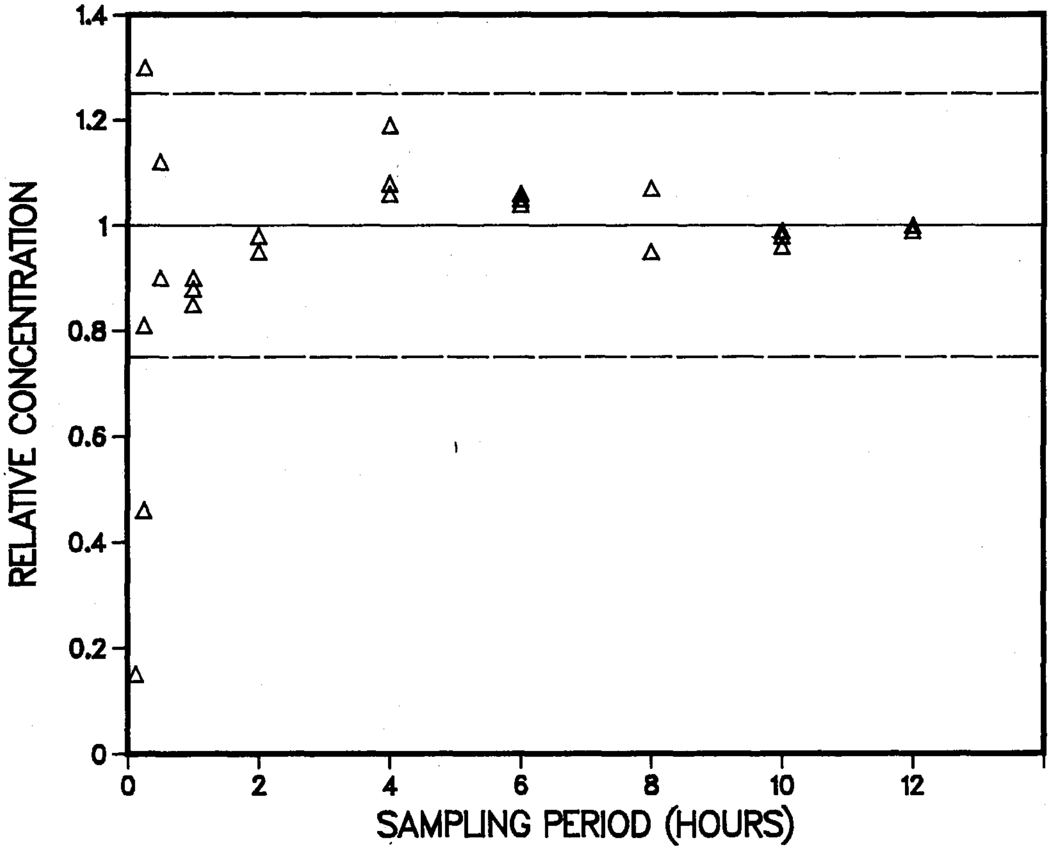

Figure 3 — Sampling rate and capacity study of DuPont Formaldehyde Badges. Theoretical uptake in relative concentration vs. time plotted as a solid line. Dashed lines represent ± 25% of the theoretical uptake. Actual sampler performance plotted as triangles. In some instances points are plotted on top of one another giving appearance of only one or two points being present.

Based on the independent determination of concentration of the exposure chamber over three contiguous 4-hr sampling periods, the concentration decreased from a high of 7.7 ± 0.8 ppm to 4.4 ± 0.4 ppm during the 3M monitor exposures. The average concentration over the 12 hr exposure period was 6.3 ± 0.7 ppm. By design, the beginning of the exposure periods for all the monitors did not coincide. For example, the 1/8- and 1/4-hr exposures were not conducted during the initial 1/4-hr period of the 12-hr exposure and were completed during the last 4-hr sampling period in the run. In instances where the monitors' exposures overlapped 4-hr sampling periods, a weighted average concentration was used, based on the number of hours that the monitors were exposed during each of the 4-hr sampling periods. If a monitor had been exposed for 1 hr during one 4-hr sampling period and 3 hr during the next 4-hr sampling period, the monitor dose was calculated by 1/4 of the first 4-hr sampling period concentration plus 3/4 of the second 4-hr sampling period concentration.

Figure 2 shows the discrepancy between the concentration of formaldehyde measured with the 3M formaldehyde monitors and the expected concentration (solid line) determined by the independent methods. The data have been normalized to correct for the concentration variation during the exposure.

For the 12-hr exposure of the DuPont badges, independent method samplers were changed at 6-hr intervals during the 12-hr period to prevent sample overloading. The results of the independent methods for the two 6-hr sampling periods indicated that there was no change in concentration during the entire 12-hr exposure period. The average concentration for the 12-hr exposure was 4.2 ± 0.2 ppm. Again, the beginning of the exposure periods for all the badges did not coincide. Figure 3 shows the results of the badges in terms of relative concentration *vs.* time.

Experiment 3.: To determine sample stability during the course of an exposure, 20 badges from each manufacturer were exposed to 6 ppm formaldehyde and 28-80% RH for 4 hr. Ten of these badges were then exposed to 0 ppm formaldehyde for an additional 4 hr.

Results from this exposure are listed as Experiment No. 3 in Table I for the 3M monitors and in Table II for the DuPont badges. Due to a mechanical problem with the generation system, the first attempt at this experiment with the DuPont badges was conducted with a concentration of 1.0 ± 0.1 ppm. The experiment was repeated at 5.4 ± 0.2 ppm for the DuPont badges.

The 3M monitors were exposed to 4.2 ± 0.2 ppm. The concentrations calculated for all the badges exposed were based on their actual exposure (either 4 hr or 8 hr). At this point in our evaluation, the 3M monitors were giving results which were grossly different from the reference concentrations determined independently and were dropped from further evaluation with the testing experiments except for Experiment No. 5.

Experiment 4.: To determine sample stability between exposure and analysis, 32 monitors from DuPont were exposed to 2.4 ± 0.2 ppm at 80% RH, for 6 hr. Twelve badges were analyzed on the day after exposure (Day 1), and ten badges stored at room temperature and ten badges stored at 5 °C were analyzed 14 days later. Results for these exposure/storage treatments are shown in Table II under Experiment No. 4.

Experiment 5.: A fractional factorial exposure experiment(10,11) was used to study the effects of six factors—formaldehyde concentration; exposure time; face velocity; relative humidity; chemical interference; and monitor orientation—on badge performance. In addition to determining if any of these individual factors affect sampler performance, the factorial experiment also determined if two-way and some three-way interactions occurred among the factors, significantly affecting the results obtained. The ranges investigated for the different factors are outlined in Table III. Five DuPont badges and three 3M monitors were used in each of the sixteen runs in the fractional factorial experiment. Phenol was selected as the interference since it is a compound often used in conjunction with formaldehyde. Calculation of the effects of the factors from the set of sixteen experimental runs was accomplished using a Visicalc® calculation template for a 16-run fractional factorial design.(12,13) Any factor that caused a statistically significant difference in the recovery of the monitors at the 95% confidence level was evaluated further.

During the fractional factorial low face velocity exposures, a partial mechanical failure in the chamber blower drive system caused face velocities to drop below 1.5 m/min (5 ft/min) instead of the planned 3 - 6 m/min (10-20 ft/min).

For the 3M monitor, significant factors were face velocity and relative humidity (Tables III and IV) at the 90, 95 and 99% confidence levels. At the 90% confidence level, the interaction of concentration*orientation plus interference*time was significant. Because of a lack of additional monitors, these factors were not evaluated further.

The factors which were found to be significant at the 99% and 95% confidence levels for the DuPont badge were face velocity and interference (see Table IV). At the 90% confidence level, concentration was a significant factor.

To evaluate the significant effects of face velocity and presence of interference on the DuPont badge, a series of exposures was made in which the exposure conditions included high (6.1 m/min, 20 ft/min) and low (3 m/min, 10 ft/min) face velocity and presence and absence of interference (phenol). The low face velocity used was higher than that used for the low face velocity runs in the factorial experiment (3 m/min *vs.* <1.5 m/min; 10 ft/min *vs.* <5 ft/min). The data from this series of four experiments are summarized in Table V.

Experiment 6.: Ten DuPont badges were exposed to formaldehyde at each of three different temperatures (17, 27

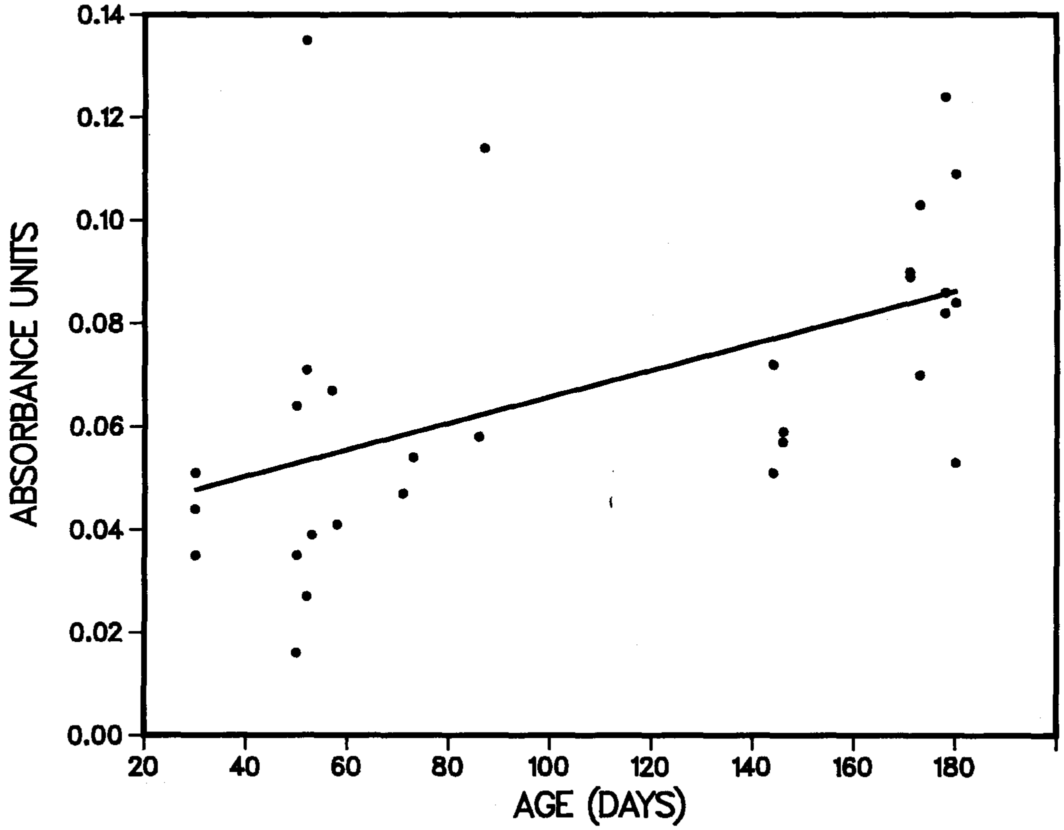

Figure 4 — Increase of blank absorbance vs. time for DuPont Pro-Tek® Lot 601. The effective shelf life of the DuPont badges has been assumed to be 180 days. The least squares regression fit of the absorbance-versus-time data is represented by the solid line.

and 38 °C) to determine if changes in temperature affected monitor performance. Reference concentrations for the exposures were 2.3 ± 0.1, 2.4 ± 0.2 and 8.4 ± 0.3 ppm, respectively. Results for the badges at the respective temperatures were 2.3 ± 0.1 ppm, 2.0 ± 0.1 ppm and 7.7 ± 0.2 ppm. Although the target concentration for the high temperature exposure was 2.4 ppm, offgassing of formaldehyde from the Teflon lining of the chamber walls during the high temperature exposure raised the concentration to 8.4 ppm.

Experiment 7.: Precision of the DuPont badges was determined from the results of exposures at 0.30, 1.0, 1.7, 2.0, 2.4 and 5.4 ppm. Data from Experiments Nos. 3-6 (Table II) were also used in these calculations. In order to meet previously-defined precision criteria,(14) only sample sets with relative standard deviations (RSD) less than 10.5% were used for calculation of the method precision. These sets covered the range from 1.7 to 5.2 ppm. Homogeniety of the RSDs of these sets was tested, and precision was determined by pooling the homogeneous RSDs.(14) The data are reported in Table II under Experiment No. 7.

Discussion

3M Formaldehyde Monitor

Manufacturer's recommendations stated that the standard and monitor eluate solutions could be analyzed spectrophotometrically at 580 nm after a 30-min color development time. Preliminary experimentation prior to Experiment No. 1 showed that the recommended 30-min color development time was insufficient for precise analysis. This was true not only for the monitor solutions but also for the standard solutions. When this time was increased to 2 hr, precision decreased from greater than 30% to less than 10% relative standard deviation, both with samples and standards.

By following this modified analysis procedure, the average recoveries of formaldehyde from each of the four sets of the 3M monitors in Experiment No. 1 were not significantly different from each other at the 95% level of significance.(15) The badges did exhibit variable precision over the range of recoveries. It was noted that the blank values were also highly imprecise with an average of 0.56 μg/sample with a relative standard deviation of 46.1%. The badges spiked at the lowest level were spiked with 2 μL of standard formalin solution. The transfer of this small volume may account for some of the variability in the low level recoveries. There was no obvious reason for the imprecision noted with these higher level samples.

Results from the 3M 12-hr exposure indicated that the monitor was not performing as expected and indicated that either the sampling rate was changing with time or the sampler was being overloaded (Figure 2).

In exposure results from Experiment No. 3 (Table I), there was no formaldehyde loss from the second set of badges (those exposed to clean air for the last 4 hr) when compared to the first set, but all of the 3M monitors gave results (0.56 ± 0.03 ppm) significantly lower than the independent methods (4.2 ± 0.2 ppm). The low recoveries for the 3M monitor in this experiment and the results observed in Experiment No. 2 (Figure 2) indicated the working range of the monitors might be below the exposure levels used for monitors in an "as delivered" condition.

In auxiliary experiments to define the range over which the passive samplers would agree with the independent methods, monitors were exposed to concentrations below 2 ppm for 4-hr periods. Results from all these experiments are shown in Table I. In Experiment A, 3M monitor values (1.1 ± 0.1 ppm) were again lower than the independent methods (2.0 ± 0.2 ppm) as in Experiment No. 2 (Figure 2 and Table I).

Both Experiment No. 2 and Auxiliary Experiment A were run between 53 and 56% relative humidity. In order to verify that the differences in recovery were not due to analytical problems, Auxiliary Experiment B (Table I) was conducted. In this experiment, 18 monitors were exposed to formaldehyde for 4 hr. Six of the monitors plus one blank were returned to 3M for analysis, and the remainder were analyzed by NIOSH. All the monitors gave low results when compared to the reference concentrations (Table I), but there was good agreement between the monitor analyses performed by NIOSH and 3M. This exposure was conducted at a relative humidity of approximately 30%. Experiment No. 3 (Table I) was conducted at 28% relative humidity and gave results for the 3M monitors similar in recovery to Auxiliary Experiment B (Table I). Results for both of these exposures were considerably lower in relation to the reference concentrations than Experiment No. 2 and Auxiliary Experiment A (Table I). This variation suggested that humidity might be responsible for the apparent change in the sampling rate.

The hypothesis was made that a loss of water from the sorbent pad during storage was the cause of these low results with the 3M monitor. If this hypothesis were correct, pretreatment with a humid atmosphere would reactivate the monitors, yielding results similar to those from the independent methods. Untreated monitors should continue to read low when compared to either the independent methods or the pretreated monitors.

This hypothesis was tested with 21 pretreated monitors. Pretreatment consisted of placing the monitors in a constant humidity atmosphere, maintained in a closed glass container at 93% relative humidity by a saturated sodium sulfate solution.(16) Fourteen monitors were removed from their protective packaging and allowed to equilibrate in the high humidity for approximately 20 hr. Two of these fourteen monitors were used as blanks. The remaining seven monitors from the set of twenty-one were stored for 24 hr in the high humidity while still sealed in their inner plastic bags. One of these seven was used as a blank.

The results from this experiment are shown in Table I as Auxiliary Experiment C. Results of the blank monitors which were equilibrated to high humidity were in the same range as the blank monitors which had no pretreatment, thus ruling out the possibility that the monitors could have been exposed to formaldehyde during the high humidity equilibration. These data show a dramatic effect on monitor performance when the monitors are humidified as a pretreatment when compared with the nonequilibrated monitors. Apparently the inner plastic bags in which the monitors are sealed are permeable to water vapor since there was no difference in the results between the methods of equilibrating the monitors to high humidity. These results supported the hypothesis that a loss of water from the sorbent pad was responsible for the low results obtained with the monitors.

To further substantiate this effect of relative humidity on 3M monitor performance, this monitor was included with the DuPont badge in the fractional factorial study, Experiment No. 5. The results for the 3M monitor are summarized in Table IV. Significant effects were observed for relative humidity and face velocity at the 90, 95 and 99% confidence levels. These were exactly the results expected with this monitor since previous experiments (Auxiliary Experiments A-C, Table I) had outlined the humidity effect and the 3M product literature(7) had indicated a face velocity limitation of 4.5 to 6 m/min (15 to 20 ft/min).

DuPont Pro-Tek Formaldehyde Badges

Since the DuPont badge uses a liquid sorbent, desorption was not required for analysis. Consequently, the determination of analytical recovery by spiking was not done. Before beginning work with these badges, however, DuPont did supply NIOSH with badges which had been dynamically spiked in their laboratory. The NIOSH results on these blind spikes (19.3 ± 2.0 ppm-hr) compared well with those of DuPont's Haskell Laboratories (19.7 ± 1.0 ppm-hr) and their Applied Technology Division (20.5 ± 0.6 ppm-hr).

The findings of Experiment No. 2 (12-hr exposure, Figure 3) indicated that the DuPont badge results agreed with the independent method concentration determinations over the period from 1 hr to 12 hr and were within the ± 25% limits on the expected concentrations except at exposure times of less than 1 hr. The precision of the badges decreased at exposure times of 1 hr or less.

As can be seen in Figure 3, there was an initial period of time during which the badges had high variability. The ppm-hr loading found on the badges as a result of these short exposure periods was less than the manufacturer's recommendation for the limit of quantitation (LOQ, 2 ppm-hr).(8) Based on these results, the potential user of these devices would be well advised to sample for periods at least as long as 1 hr.

In an attempt to explain this variation at short exposure times, the sample blank data collected during our DuPont badge evaluation work was reviewed. Blank values were found to vary with lot number and had variable precision within each lot. The average blank values in absorbance units and their associated 95% confidence limits for the different sets of badges used in this work are 0.055 ± 0.022, 0.054 ± 0.011, 0.068 ± 0.011 and 0.063 ± 0.014 AU. The relative standard deviation of these values ranges from 26 to 70%. Enough data were collected with one particular lot of badges to plot blank age *vs.* absorbance (Figure 4). Badge age was calculated based on the manufacturer's statement that the usable lifetime of the badges was 180 days (*i.e.,* badges must be used prior to the expiration date on each lot of badges). The date of the use of each particular blank was then calculated as to which day of the 180 day period it was and reported as the badge age. As can be seen in this plot, blank values increased with the age of the badges.

In Experiment No. 3, there was no formaldehyde loss from the second set of badges (those exposed to clean air for the last 4 hr) when compared to the first set (Table II). These badges also have good agreement with the reference concentration (Table II). In Experiment No. 4 (Table II), statistical analysis of the results of the badges stored at room temperature and analyzed on days 1 (2.3 ± 0.1 ppm) and 14 (2.5 ± 0.2 ppm) indicated no significant difference at the 95% significance level (Table II). These data indicated that the badges could be stored for up to 2 weeks at room temperature after sampling and analyzed with no significant sample loss, consistent with the manufacturer's recommendations.

The results for Experiment No. 5 indicated that the factors of interference and face velocity were significant to the performance of the DuPont badge at the 99% level of significance. These results differed from the product literature supplied with the badges.(8) The phenol concentrations and face velocities used in this study, however, covered a broader range.

A possible face velocity-interference interaction was indicated at the 90% significance level. At low face velocities (<3 m/min; <10 ft/min), the negative effect of interference on the badge results was more pronounced than at higher face velocities. Upon further inspection of the data from the runs where interference was present, the badge seemed to be influenced negatively by high phenol-to-formaldehyde concentration ratios (*e.g.,* 10:1). If these badges were to be used in environments of high phenol concentration relative to formaldehyde concentration, then further study of this effect would be warranted.

The significant factors for the DuPont badges were evaluated further by exposing the badges to 4.1 - 5.1 ppm of formaldehyde at face velocities of 3 and 6 m/min (10 and 20 ft/min). Exposures were made without and with phenol present at the 2.9 ppm level. The results shown in Table V indicated that the badges will give results consistent with the reference concentrations at face velocities of 3 m/min (10 ft/min) and above with a phenol-to-formaldehyde ratio 0.7 to 1.

The basis for Experiment No. 6 was that diffusion theory predicted that a difference should be observed between exposures made at different temperatures. The diffusion constant and consequently the badge concentration determinations should be directly proportional to the ratio of the square roots of the two temperatures in degrees Kelvin.(17,18,19) The equation used for calculating these ratios is shown below. Data were normalized prior to these calculations.

$$\frac{C_{17^\circ C}}{C_{27^\circ C}} = \frac{(273 + 17)^{1/2}\ ^\circ K}{(273 + 27)^{1/2}\ ^\circ K} = 0.98$$

In our study the observed ratio was 1.0 for the exposures made at 17 and 27 °C, although the predicted ratio based on temperature calculations was 0.98. Although theory predicted a difference, it might not have been observable because of experimental error. When the exposures made at 17 and 38 °C were compared, a ratio of 1.1 was observed based on concentration and a ratio of 0.97 was predicted from temperature calculations. The finding of no temperature dependence on badge performance at the two lower temperatures was consistent with the DuPont literature.(8) Results at the higher temperature were not easily explained. One explanation for the negative bias of the DuPont badges during this exposure was the possible presence of oligomeric formaldehyde in the chamber. Formaldehyde offgassed from the chamber walls during the high temperature exposure and resulted in chamber concentrations higher than previously observed. This high concentration of formaldehyde may have given rise to the formation of oligomeric formaldehyde, which would diffuse into the badge at a slower rate than monomeric formaldehyde. This could have caused a negative bias in results when compared to the independent methods.

In Experiment No. 7 (Table II), there was good agreement between the reference concentrations and the badge results throughout the range of concentrations studied; however, the variability was quite large at lower concentrations. The relative standard deviations (RSDs) of the sample sets were homogeneous(14) over the range of 1.7 to 5.4 ppm, and a pooled relative standard deviation of 6.9% was calculated. The poor precision at lower levels was cause for concern since DuPont indicated in its literature that precision was better than 10% for levels down to 2 ppm-hr. In our work, precision did not drop below 10% until the dose was above 4 ppm-hr. A possible explanation for the variability observed was in the badges used for blank corrections. As indicated in Figure 4 and discussed above, blank variability increased with age and would contribute to badge result variability, especially at the lower levels where exposed badge absorbances and blank absorbances were of similar magnitude.

This lack of precision at low and intermediate concentration levels (ca. 1 ppm) prompted the study of residual levels of solution left in the sorbent blisters after the 2 mL of solution had been removed for analysis. After several badges were checked, the residual volume in the badge was found to vary significantly from the expected 0.4 mL. In one instance there was insufficient liquid in the badge before analysis to obtain even the 2 mL required for analysis. As the badges approached their expiration date, the amount of liquid in the badges was found to be less than 2.4 mL and moisture was found outside the badges in their foil pouches. Moisture apparently diffuses from the badge during storage even at reduced temperatures (5 °C). The moisture apparently was due to the badge eluent and not water, since considerable corrosion was observed on the rivet that attached the lapel clip to the badge. If the liquid level in the badge was less than 2.4 mL when it was used for sampling and the concentration determined by the badge calculated, then results were positively biased. Conversely, when the volume was greater than 2.4 mL, the results of the badge were negatively biased. Also, since the absorbent volume in the badge was found to be inconsistent, the variability of results with the badges was high. Several sets of samples help illustrate this point. For Experiment No. 7, 12 badges were exposed to 0.3 ± 0.04 ppm of formaldehyde. Badge results with and without volume correction were 0.3 ppm (RSD=12.9%) and 0.3 ppm (RSD=15.1%), respectively. By correcting for this volume difference, the precision was increased by over 2%. In exposures during the fractional factorial experiment (Experiment No. 5), results of one of the runs were 4.05 ppm (RSD=7.4%) without volume correction and 4.20 ppm (RSD=1.0%) with volume correction.

Conclusions

This work revealed a problem of variable sampling rate with the 3M Formaldehyde Monitor when used as received from the manufacturer. Our findings also indicated that the recommended color development time for analysis was not long enough to allow full color development.

Results of additional experiments led to the conclusion that quantitative reaction between formaldehyde generated in our chamber and the absorbent pad in the 3M monitor required the presence of a minimum level of absorbed water. This level of absorbed water appeared to be affected by at least the conditions of storage of the monitors prior to use and the relative humidity of the atmosphere being sampled. Data from the humidity equilibration experiment indicated that, if the conditions of storage could be controlled (*e.g.*, storage at >90% relative humidity), then the humidity of the atmosphere being sampled might have a much reduced effect on monitor performance. More work in this area will be required to determine if this is true. Until the accuracy of the monitors has been shown to be largely independent of the factors likely to be encountered when monitoring workplace environments for formaldehyde, however, their use in industrial hygiene studies is limited.

Results of the DuPont badge evaluation indicated that the badge did perform according to the manufacturer's advertised claims with certain limitations. The DuPont Pro-Tek Formaldehyde Badge showed effects of interference and face velocity on its performance and the limitation for short sampling times. Recent work by Hakes, *et al.* may have some application here in reducing the effect of phenol as an interference in the badge analysis.(20) The evaluation did define a lower limit above which the significant factors of face velocity and interference would not affect performance for this badge. Further work did indicate that, contrary to DuPont's specifications, a blank correction was required. The value of the blank was quite variable and could cause bias when measuring low levels of formaldehyde. The loss of absorbing solution from the badge was also another area of the badge which requires additional study.

The limitations of the DuPont badge do not preclude its use for industrial hygiene sampling. If the badge is not used at face velocities of less than 3 m/min, high phenol-to-formaldehyde ratios and sampling times of less than 1 hr, then results should be equivalent to more conventional active sampling methods. This statement assumes that the users of the badges follow the manufacturer's instructions for use and storage of the devices and the laboratories analyzing the badges make blank and volume corrections.

Some of the major problems observed with both passive monitors were found only after devices which had been aged under storage conditions were analyzed and these results interpreted. If all of this testing had been done with fresh sampling devices, many of the problems would not have been noticed. Based on the results of this study, this factor of diffusive monitor aging needs to be addressed in any further work on passive monitor evaluation.

The basic concept of passive monitoring is very attractive but has some limitations which often are not recognized. The series of experiments described in this paper has helped define the operational limitations of two passive monitors for formaldehyde. This and similar passive monitor evaluations(17) have helped to refine the basic experimental evaluation protocol used in these studies to a point approaching general applicability to the field of passive monitoring.

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