

ON-SITE REAL-TIME AIR SAMPLING METHOD VALIDATION OF A LONG-TERM DETECTOR TUBE FOR METHYLENE CHLORIDE PERSONAL EXPOSURES

Keith Garber, University of Utah
Duane Lee, OSHA Salt Lake Technical Center
Carl Elskamp, OSHA Salt Lake Technical Center
Dean Lillquist, University of Utah
George White, University of Utah
Stephen Alder, University of Utah

ABSTRACT

USDOL-OSHA validation procedures were performed to determine the sampling performance of long-term detector tubes for methylene chloride. A dynamic test atmosphere generation system was used to simultaneously expose six tubes. Known concentrations were generated at 0.5x, 1x, 2x, and 5x a target concentration (OSHA 8-hour PEL). Three conditions of relative humidity (<5%, 40%, and 80%) were evaluated. The linearity of response for this method was established as 1.5 to 167 ppm. The detection limit was determined from <0.25x the target concentration. Readings were linear over the concentration range studied and independent of relative humidity. Detector tube readings were stable for 48 hours (<10% variation) at the 1x target concentration and exhibited <20% variation from channeling affects over the 1x to 5x target concentration range. Methanol and/or toluene concentrations produced false negative readings. A pooled overall uncertainty result from all sample sets was determined to be 28.6%.

INTRODUCTION

Extensive research initiatives for strengthening the evaluation and control of occupational exposures to airborne methylene chloride (MC) have remained in focus since the U.S. DOL Occupational Safety and Health Administration's (OSHA) amendment to the MC standards' permissible exposure limits (PELs) in 1997. The current MC PELs are 25 parts MC per million parts (ppm) of air for an eight-hour time-weighted average (TWA), a short-term exposure limit of 125 ppm measured as a 15-minute TWA, and an action level of 12.5 ppm measured as an 8-hour TWA (OSHA, 1997). Due to the potential acute and chronic health effects of MC and its principal route of human exposure being inhalation (DHHS, 2000), a reliable direct reading method is essential for immediate compliance determination. A real-time on-site air (OSA) sampling method for the determination of 8-hour TWA MC exposures was subjected to the *Evaluation Guidelines, with Testing and Reporting Protocols, for OSHA On-site Air and Surface Sampling Methods* established by the OSHA Salt Lake Technical Center Applied Industrial Hygiene Chemistry Team (OHSA, 2002a). The result was an approved sampling method using Dräger Type 50/a-L long-term detector tubes (LTDT) (OHSA, 2002b). Since this method's validation, the Type 50/a-L long-term detector tube has been discontinued by Dräger Safety for

business reasons. OSHA evaluation guidelines and testing protocols for real-time air sampling methods as seen in this research provides a model for other independent researchers pursuing the validation of direct reading instruments.

EXPERIMENTAL MATERIALS AND METHODS

Test Atmosphere Generation System

Figure 1 schematically illustrates the dynamic controlled test atmosphere generator. MC was introduced into a heated glass manifold as a liquid using an Isco (Lincoln, NB) Model 100DM Syringe Pump. Purified air from a MNR Model HCS-401 (Miller-Nelson Research, Inc., Monterey, CA) Flow, Temperature, and Humidity Control System diluted and swept the vaporized MC through the generator system. The MC/air mixture sequentially entered a glass mixing chamber followed by a six-port glass sampling chamber. The sample introduction manifold, mixing chamber, and sampling chamber were connected using Teflon-coated rubber o-ring joints to minimize loss of analyte. Dilution airflow rates from the MNR HCS-401 controller were measured with a Singer DTM-115 Dry Test Meter. Purified deionized water was vaporized and metered to the dilution air according to the desired preset relative humidity (RH) of each generated test atmosphere. The relative humidity and temperature of each test atmosphere was measured with a calibrated Solomat MPM500e meter. MC concentrations were measured and continually monitored with a calibrated Brüel & Kjær (Marlborough, MA) Type 1302 photoacoustic infrared (PIR) analyzer. Sample chamber barometric air pressures were monitored and measured with an Omega PX212 Pressure Transducer interfaced to a DP41-S High Performance Strain Gage Indicator. The entire test atmosphere generation system was contained in a walk-in exhaust hood.

Dynamic Test Atmospheres

MC test atmospheres were generated at 0.5x, 1x, 2x, and 5x the target concentration (TC). At the onset of each OSA method study, OSHA deems the analyte's TC to be the most appropriate current eight-hour TWA occupational exposure limit (OSHA, 2002a). In this study, the OSHA PEL (25 ppm) was chosen as the most appropriate TC. All room temperature test atmospheres were generated at approximately 72 °F (22.2 °C). Each test atmosphere MC concentration was generated in conjunction with three different levels of relative humidity (RH) to determine potential interferences from water vapor concentrations. The three water vapor concentrations studied were <1 mg/L, 7.9 mg/L, and 15.8 mg/L. At 72 °F (22.2 °C), the water content of 5% RH, 40% RH, and 80% RH is approximately 1 mg/L, 7.9 mg/L, and 15.8 mg/L respectively. In this study, the generated room temperature test atmospheres containing water vapor at nominal concentrations of <1 mg/L, 7.9 mg/L, and 15.8 mg/L are referred to as dry, 40% RH_{eq}, and 80% RH_{eq} respectively, where "eq" is an abbreviation for equivalent.

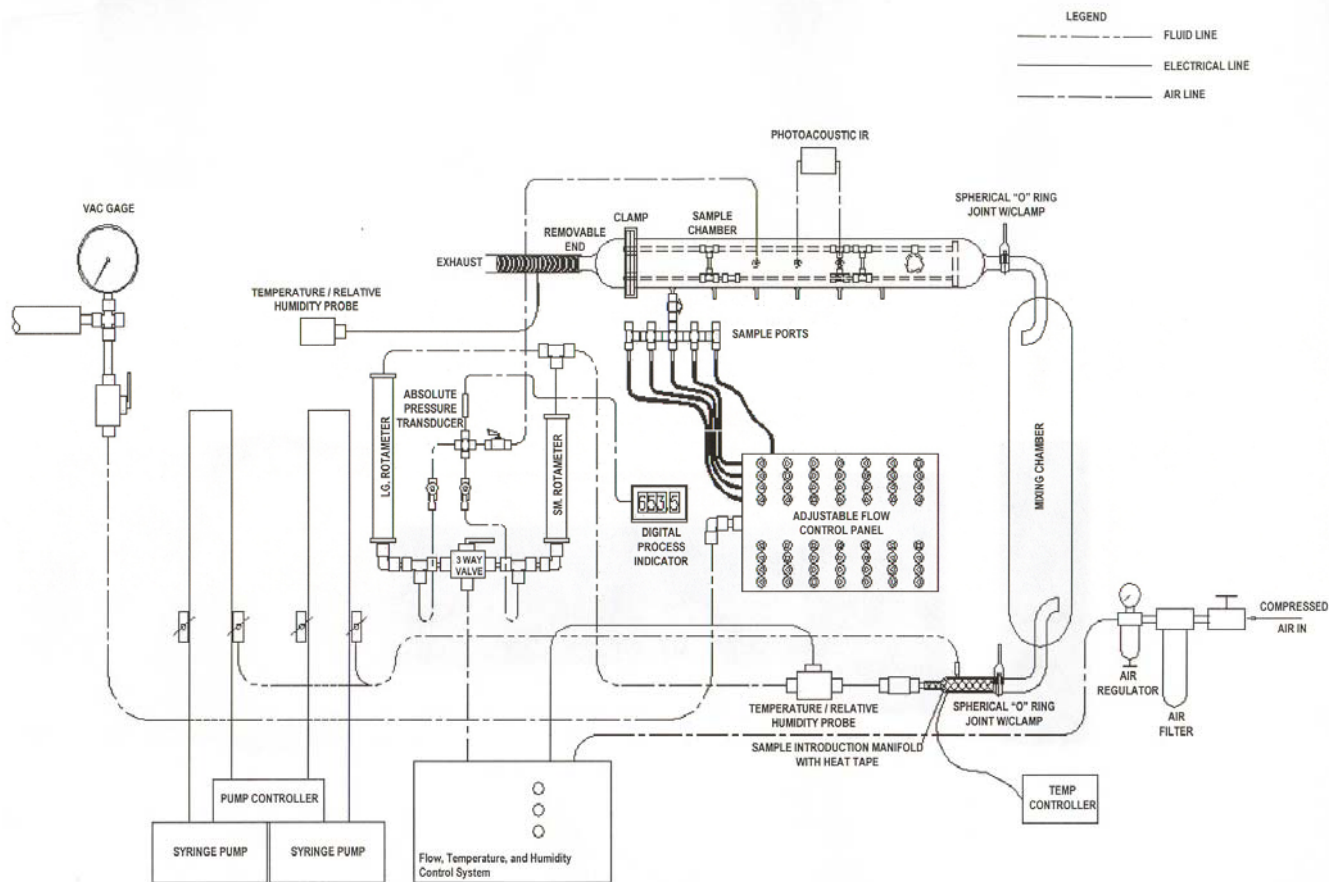


Figure 1. Dynamic Controlled Test Atmosphere Generation System

Sampling and Analysis

Six Dräger Type 50/a-L long-term detector tubes (LTDT) were tested at each combination RH and MC concentration. Each sampling train consisted of one Dräger Type 50/a-L LTDT, one scrubber (trap) tube, and an individual critical flow orifice. A scrubber tube was positioned with silastic tubing after each detector tube in order to protect the critical flow orifices from discharged chemicals. A vacuum between 20 and 24 inches of mercury was continually applied to the orifices to maintain a constant flow of approximately 20 mL/min during sampling. The sampling rates were measured immediately before and after sampling using a DryCal Primary Air Flow Meter (Bios International, Pompton Plains, NJ, 07444). Each detector tube was subjected to a 4-hour (4.8 Liter) sample of a test atmosphere. Sampling times were determined using a laboratory stopwatch. The detector tubes were immediately read under a fluorescent desk lamp after sampling was completed. Dräger Type 50/a-L LTDTs display the concentration of MC in absolute units (i.e. microliters). This scaled measurement is then converted to a TWA concentration (ppm) by the division of its associated air volume (Liters). The standard measuring range of Dräger Type 50/a-L LTDTs for a measuring time of 4 hours is 12.5 to 200 ppm. Dräger calibrates the 50/a-L LTDTs standard measuring ranges at 20 °C (operating range of 0 to 30 °C) and 1013 mbar (760 mmHg) (Dräger, 1998). Generated test atmosphere MC concentrations were equivalent to concentrations at 760 mmHg and 25 °C. Thus, ambient

conditions did not require the application of correction factors to detector tube readings. If the stain length is determined to be uneven (variation of stain length around the circumference of the tube at the interface between stained and unstained reagent) due to channeling of air flow, the appropriate reading is obtained by adding the maximum observed value to the minimum observed value and dividing the sum by two (OSHA, 2002a; AIHA, 1993; Roper, 1974).

RESULTS

Average Photoacoustic IR Readings vs. Reference Sampling and Analytical Method

Theoretical MC concentrations (ppm) collected by the photoacoustic infrared (PIR) analyzer were averaged and compared to average concentrations (ppm) using OSHA sampling and analytical method 59 (OSHA, 1986). This was the preferred reference method for the verification of test atmosphere concentrations in relation to respective average PIR readings. Six samples were performed with method 59 on each MC test atmosphere of 0.06x, 0.25x, 0.5x, 1x, 2x (performed twice), 5x, and 25x the TC at 40% RH_{eq}. A statistical linear relationship between the average PIR readings and average adsorbent tube readings ($R^2 = 0.999$, $p = 0.001$) was determined.

Detection Limit

The detection limit (DL) is defined as the minimal concentration that produces a discernible stain to most readers (OSHA, 2002a; AIHA, 1993). A stain length of 1 mm is arbitrarily considered the shortest length capable of being observed on a detector tube (OSHA, 2002a). For the lot of LTDTs evaluated, 1 mm is equivalent to approximately 7 uL of MC vapor. This absolute measurement from a 4.8 L sample is calculated to be approximately 1.5 ppm. The performance of the detector tubes at MC concentrations near the detection limit was verified by sampling from atmospheres <0.25x the TC. Table 1 illustrates the detector tube results and the respective theoretical MC concentrations. The detector tubes performed well at concentrations as low as 4.0 ppm MC. Thus, a detection limit of 1.5 ppm of MC for a 4.8 L is considered suitable.

Linearity, Range, and Interference from Water (relative humidity affects)

The linearity, range, and relative humidity effects were determined from dry, 40 % RH_{eq}, and 80% RH_{eq} test atmospheres containing MC at nominal concentrations of 0.5x, 1x, 2x, and 5x the TC. All samples were collected at a nominal flow rate of 20 mL/min for 4 hours. MC concentration data is displayed in Table 2 and graphically illustrated in Figure 2. Detector tube readings were linear over the range studied and independent of relative humidity. Independence from the affect of relative humidity is supported by comparing mean detector tube readings and PIR readings ($R^2 = 0.94$, $p = 0.001$). The slope of the line falls between 0.9 and 1.1 indicating the detector tubes are calibrated properly (OSHA, 2002a). The upper limit of the detector tube scale is 800 uL of MC vapor, which for a 4.8 L sample, is equal to approximately 167 ppm. Thus, the linearity of response for Dräger Type 50/a-L LTDTs is 1.5 to 167 ppm.

Table I. Detector Tube Results from Low MC Concentrations at dry, 40% RH_{eq}, and 80% RH_{eq}

Sample Number	Relative Humidity	Theoretical MC Concn., ppm	Tube Reading uL of MC	Air Volume Sampled, L	Calculated MC Concn, ppm
1	dry	5.7	32	4.86	6.6
2	dry	5.7	27	4.79	5.6
3	dry	5.7	30	4.67	6.4
4	dry	5.7	35	4.90	7.1
5	dry	5.7	25	4.91	5.1
6	dry	5.7	25	4.77	5.2
1	40% RH _{eq}	4.0	21	4.94	4.2
2	40% RH _{eq}	4.0	25	4.68	5.3
3	40% RH _{eq}	4.0	24	4.85	4.9
4	40% RH _{eq}	4.0	18	4.79	3.8
5	40% RH _{eq}	4.0	19	4.65	4.1
6	40% RH _{eq}	4.0	18	4.63	3.9
1	80% RH _{eq}	4.2	25	5.01	5.0
2	80% RH _{eq}	4.2	21	4.74	4.4
3	80% RH _{eq}	4.2	21	4.93	4.3
4	80% RH _{eq}	4.2	21	4.91	4.3
5	80% RH _{eq}	4.2	25	4.61	5.4
6	80% RH _{eq}	4.2	19	4.68	4.1

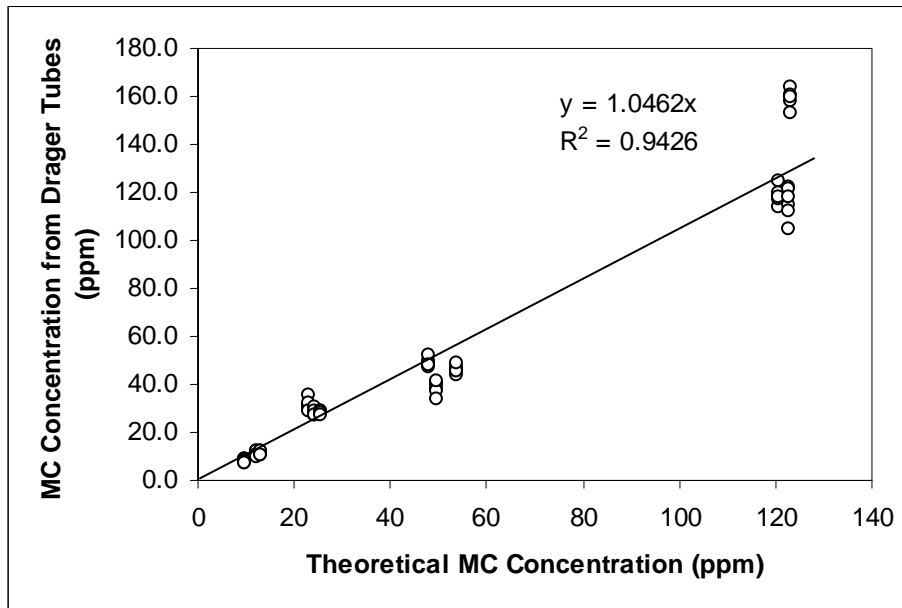


Figure 2. Dräger LTDT MC Concentration Readings vs. the Theoretical (true) Generated MC Concentrations

Table 2. Detector Tube Results from MC Atmospheres

Sample Number	Dry Atmospheres		40% RH _{eq} Atmospheres		80% RH _{eq} Atmospheres	
	Theoretical MC Conc., ppm	Calculated MC Conc., ppm	Theoretical MC Conc., ppm	Calculated MC Conc., ppm	Theoretical MC Conc., ppm	Calculated MC Conc., ppm
1	12.0	10.7	12.7	12.1	9.5	9.4
2	12.0	12.9	12.7	11.5	9.5	7.8
3	12.0	12.1	12.7	10.7	9.5	8.8
4	12.0	11.2	12.7	11.5	9.5	8.0
5	12.0	10.8	12.7	12.2	9.5	8.0
6	12.0	9.8	12.7	11.0	9.5	7.6
1	24.0	27.2	23.0	30.2	25.5	29.1
2	24.0	28.3	23.0	36.2	25.5	28.8
3	24.0	27.8	23.0	31.2	25.5	28.7
4	24.0	30.9	23.0	30.6	25.5	28.5
5	24.0	29.0	23.0	32.9	25.5	outlier
6	24.0	27.4	23.0	29.4	25.5	27.6
1	49.6	40.7	53.6	46.3	47.8	47.1
2	49.6	38.7	53.6	47.8	47.8	49.4
3	49.6	39.6	53.6	43.9	47.8	48.4
4	49.6	37.1	53.6	45.9	47.8	50.3
5	49.6	34.3	53.6	45.6	47.8	52.8
6	49.6	41.9	53.6	49.3	47.8	48.7
1	122.6	105.2	123.1	158.5	120.3	125.4
2	122.6	122.6	123.1	163.9	120.3	114.4
3	122.6	121.4	123.1	161.2	120.3	119.7
4	122.6	114.7	123.1	153.7	120.3	117.8
5	122.6	118.6	123.1	outlier	120.3	118.0
6	122.6	112.9	123.1	160.1	120.3	outlier

Stain Stability of Detector Tubes

The detector tubes' stain stability was determined by repeatedly, over a period of approximately two days, obtaining readings from test atmospheres containing 25 ppm MC. Samples were collected and evaluated from dry, 40% RH_{eq}, and 80% RH_{eq} atmospheres. Tables 3-5 illustrate the subsequent readings (microliters) and the respective percent variations from each tube's initial reading. The percent variation was calculated for each subsequent reading using

$$\frac{|R_i - R_s|}{R_i} \times 100 \quad (1)$$

where: R_i is the initial reading
 R_s is the subsequent reading

Table 3. Stain Stability at 25 ppm MC and a Dry Test Atmosphere

Approximate Hours After Initial Readings	Readings, microliters of MC											
	Tube 1 Readings	% Variation	Tube 2 Readings	% Variation	Tube 3 Readings	% Variation	Tube 4 Readings	% Variation	Tube 5 Readings	% Variation	Tube 6 Readings	% Variation
0	133	0	138	0	135	0	150	0	145	0	135	0
2.7	133	0	138	0	135	0	153	2.00	145	0	135	0
5.2	133	0	140	1.45	135	0	153	2.00	148	2.07	138	2.22
18.2	135	1.50	140	1.45	138	2.22	158	5.33	150	3.45	138	2.22
26.2	138	3.76	140	1.45	140	3.70	160	6.67	150	3.45	138	2.22
51.7	140	5.26	143	3.62	140	3.70	160	6.67	153	5.52	143	5.93

Table 4. Stain Stability at 25 ppm MC and a 40% RH_{eq} Test Atmosphere

Approximate Hours After Initial Readings	Readings, microliters of MC											
	Tube 1 Readings	% Variation	Tube 2 Readings	% Variation	Tube 3 Readings	% Variation	Tube 4 Readings	% Variation	Tube 5 Readings	% Variation	Tube 6 Readings	% Variation
0	145	0	175	0	150	0	150	0	160	0	143	0
2.2	148	2.07	178	1.71	148	1.33	153	2.00	158	1.25	143	0
6.2	148	2.07	178	1.71	148	1.33	155	3.33	160	0	145	1.40
18.2	150	3.45	185	5.71	150	0.00	155	3.33	168	5.00	148	3.50
23.7	150	3.45	185	5.71	153	2.00	158	5.33	168	5.00	148	3.50
51.2	150	3.45	190	8.57	155	3.33	163	8.67	170	6.25	150	4.90

Table 5. Stain Stability at 25 ppm MC and an 80% RH_{eq} Test Atmosphere

Approximate Hours After Initial Readings	Readings, microliters of MC											
	Tube 1 Readings	% Variation	Tube 2 Readings	% Variation	Tube 3 Readings	% Variation	Tube 4 Readings	% Variation	Tube 5 Readings	% Variation	Tube 6 Readings	% Variation
0	145	0	143	0	143	0	138	0	113	0	135	0
5.3	145	0	143	0	143	0	140	1.45	115	1.77	135	0
20.3	150	3.45	145	1.40	145	1.40	143	3.62	118	4.42	138	2.22
27.3	145	0	145	1.40	145	1.40	140	1.45	118	4.42	138	2.22
43.8	153	5.52	148	3.50	145	1.40	143	3.62	120	6.19	140	3.70
52.3	153	5.52	148	3.50	148	3.50	143	3.62	120	6.19	140	3.70

Stain Channeling of Detector Tubes

The evaluation of each detector tube's length of stain around its circumference due to airflow channeling was conducted (Roper, 1974). Samples were evaluated from 0.5x, 1x, 2x, and 5x the TC and all three levels of relative humidity as illustrated in Table 6. Variation in stain lengths (stain channeling) is expressed as

$$\frac{\Delta L}{M} \quad (2)$$

where:

$$\Delta L = L_2 - L_1$$

L_2 = the concentration value indicated by the length of stain at the side of the tube where the stain is farthest extended along the tube's longitudinal axis

L_1 = the concentration value indicated by the length of stain at the side of the tube where the stain is least extended along the tube's longitudinal axis

Table 6. Stain Channeling at all MC Concentrations and Levels of Relative Humidity

Sample Number	Dry			40% RH _{eq}			80% RH _{eq}		
	L ₁	L ₂	% Variation	L ₁	L ₂	% Variation	L ₁	L ₂	% Variation
1	52	52	0	55	60	8.70	41	51	21.74
2	63	63	0	50	60	18.18	35	41	15.79
3	59	59	0	50	54	7.69	38	48	23.26
4	55	55	0	54	60	10.53	34	44	25.64
5	53	53	0	55	65	16.67	35	45	25.00
6	47	47	0	50	57	13.08	30	43	35.62
1	125	140	11.32	140	150	6.90	140	150	6.90
2	135	140	3.64	165	185	11.43	135	150	10.53
3	125	145	14.81	150	150	0	135	150	10.53
4	150	150	0	145	155	6.67	130	145	10.91
5	140	150	6.90	155	165	6.25	100	125	22.22
6	130	140	7.41	135	150	10.53	125	145	14.81
1	195	200	2.53	215	230	6.74	230	230	0
2	190	195	2.60	225	250	10.53	235	245	4.17
3	200	205	2.47	210	220	4.65	225	250	10.53
4	180	180	0.00	225	225	0	230	260	12.24
5	170	170	0.00	220	230	4.44	250	270	7.69
6	200	205	2.47	230	250	8.33	225	250	10.53
1	500	510	1.98	775	775	0	600	625	4.08
2	595	610	2.49	800	815	1.86	550	575	4.44
3	590	600	1.68	780	795	1.90	590	600	1.68
4	550	575	4.44	725	775	6.67	570	580	1.74
5	570	590	3.45	515	535	3.81	575	590	2.58
6	530	575	8.14	765	800	4.47	700	750	6.90

Overall Uncertainty (Precision and Bias)

An overall uncertainty (OU) was determined for each sample set using a formula that simultaneously measures precision and bias (CEN, 1994).

$$OU = \frac{|\bar{x} - x_{ref}| + 2s}{x_{ref}} \times 100 \quad (3)$$

where: \bar{x} is the average result of the measurements
 x_{ref} is the theoretical or accepted concentration from the reference method
 s is the standard deviation of the measurements

Table 7 illustrates the reliability of the Dräger Type 50/a-L LTDTs at 0.5x, 1x, 2x, and 5x the TC and at all three levels of relative humidity. The pooled overall uncertainty was calculated for this sampling range as follows

$$OU_{pooled} = \sqrt{\frac{\sum OU^2 \times df}{\sum df}} \quad (4)$$

where: OU is the overall uncertainty of each sample set
 df is the degrees of freedom of each sample set

The Dräger Type 50/a-L LTDT's pooled overall uncertainty for these test parameters was calculated as 28.6%.

Table 7. Overall Uncertainties at Specified Test Atmospheres

MC concn., ppm	Relative Humidity	Mean (SD), ppm	Overall Uncertainty, %
12.0	dry	11.25 (1.100)	24.6
12.7	40% RH _{eq}	11.49 (0.581)	18.7
9.5	80% RH _{eq}	8.28 (0.696)	27.5
24.0	dry	28.44 (1.364)	29.9
23.0	40% RH _{eq}	31.76 (2.474)	59.4
25.5	80% RH _{eq}	28.55 (0.582)	16.6
49.6	dry	38.71 (2.697)	32.9
53.6	40% RH _{eq}	46.46 (1.865)	20.3
47.8	80% RH _{eq}	49.46 (1.948)	11.6
122.6	dry	115.91 (6.441)	16.0
123.1	40% RH _{eq}	159.48 (3.776)	35.7
120.3	80% RH _{eq}	119.06 (4.018)	7.7

Interferences

The color/stain produced on the detector tubes is based on the cleavage of MC by a chromate compound, followed by a reaction of the cleavage products with iodine pentoxide and sulfuric acid. Dräger reports that positive interferences are produced by other halogenated compounds, organic compounds, and carbon monoxide (Dräger, 1998). They reported that perchloroethylene at 25 ppm indicates about 60 ppm, n-butane at 25 ppm indicates about 10 ppm, and 25 ppm of carbon monoxide indicates about 30 ppm of MC. Additional interference studies were done for this evaluation by sampling from generated test atmospheres containing vapors from solvents commonly used with MC. Three samples were collected from each atmosphere. Sampling for four hours at about 20 mL/min from an atmosphere containing approximately 200 ppm of methanol resulted in an average response of 19 microliters of MC vapor (4 ppm, 4.8 L). Similarly, sampling from an atmosphere containing about 200 ppm of toluene resulted in an average response of 11 microliters of MC (2.3 ppm, 4.8 L). Tests on MC mixtures resulted in lower than anticipated responses based on the MC concentration in the mixture (approximately 125 ppm) according to the following: samples from a 125 ppm MC/200 ppm toluene atmosphere exhibited average responses about 16% lower than expected; samples from a 125-

ppm MC/200 ppm methanol atmosphere yielded responses about 9% low; and samples from a 125 ppm MC/200 ppm toluene/200 ppm methanol atmosphere exhibited levels about 18% low.

DISCUSSION

The measurement accuracy of theoretical (true) MC concentrations with a photoacoustic infrared (PIR) analyzer was verified with the reference OSHA Method 59. OSHA Method 59 is an active method in which air samples are collected on three sections of 350 mg coconut charcoal tubes (SKC Eighty-four, PA) followed by desorption of the individual charcoal sections with carbon disulfide. Samples are then analyzed using GC/FID. A satisfactory correlation between the PIR and reference method was found indicating that the PIR was calibrated properly and considered reliable for comparing detector tube results. An established detection limit for this sampling method indicates the minimum MC concentration that can be determined by most readers. Occupational safety and health practitioners will inevitably sample atmospheres containing minimal concentrations of MC. In these cases, MC concentrations are reported as <1.5 ppm in accordance with this sampling method's established detection limit. No measurement correction factors were required due to the linear slope equaling 1.05. The detector tubes' stain was deemed stable for a 48-hour period (<10% variation) at all three levels of relative humidity. Relative humidity was determined to not have an effect on stain stability. Excessive stain channeling indicates uneven airflow within detector tubes. Samples resulting in a length of stain variation $\geq 20\%$ should be thrown out (OHSA, 2002a; AIHA, 1993; Roper, 1974). With the exception of an outlier measurement (sample number 5) within the 1x TC/80% RH_{eq} sample set, stain channeling was deemed insignificant from 1x through 5x the TC over all levels of relative humidity. The statistical method of determining pooled overall uncertainty (method accuracy) has been used in previous MC air sampling method validation studies and compared to NIOSH accuracy recommendations (overall uncertainty of <25% of the "true" result) (Charron, 1998; Busch, 1980; NIOSH, 1990). Although this OSA sampling method's pooled overall uncertainty of 28.6% fell short of the NIOSH accuracy recommendation, OSHA considers the uncertainty to be acceptable and fully validated this on-site air sampling method for MC (OHSA, 2002b). The Dräger LTDTs only drawback is the possibility of chemical interference. Part of this study's literature review revealed historical research on the determination of MC workplace exposures and the development of effective control methods within organizations comprised of furniture stripping and/or general paint stripping operations (Estill, 2002; Riley, 2000; Estill, 1996; Hall, 1990). Toluene and methanol are two solvent components commonly found within industrial furniture strippers and consumer paint stripper products containing the active component methylene chloride. Subjecting the detector tubes to test atmospheres containing known concentrations of MC, toluene, and methanol resulted in lower than anticipated readings for MC. It is felt that the methanol and/or toluene solvent vapors in the atmospheres were reacting with and consuming the chemical agents on the detector tubes. This made the chemical agents unavailable to react with MC, thus resulting in lower than anticipated responses. Similar workplace atmospheres tested with this method may produce false-negative results and thus a false sense of safety.

CONCLUSION

Dräger Type 50/a-L LTDTs were subjected to rigorous criteria under the OSHA guidelines and testing protocol. This real-time on-site air sampling method for MC met OSHA established criteria and was fully validated for compliance purposes. In the event that this direct reading instrument reentered the market, this method would serve as a cost effective approach to evaluating MC workplace personal exposures.

REFERENCES

American Industrial Hygiene Association (AIHA). Direct-reading colorimetric indicator tubes manual. 2nd ed. Fairfax, Virginia: AIHA Gas and Vapor Detection Systems Committee, 1993.

Busch KA, Taylor, DG. Statistical protocol for the NIOSH validation test. In: Gangadhar Choudhary, ed. Chemical hazards in the workplace – measurement and control. ACS Symposium Series, No. 149. Washington, DC: American Chemical Society; 1980. p. 504-17.

Charron KA, Puskar MA, Levine SP. Field validation of passive monitors for the determination of employee exposures to methylene chloride in pharmaceutical production facilities. *Am Ind Hyg Assoc J.* 1998;59:353-58.

Dräger. Dräger tube handbook: Soil, water, and air investigations as well as technical gas analysis. 11th ed. Lübeck, Germany: Dräger Sicherheitstechnik GmbH; 1998.

Estill CF, Spencer AB. Case study: control of methylene chloride exposures during furniture stripping. *Am Ind Hyg Assoc J.* 1996;57(1):43-9.

Estill CF, Watkins DS, Shulman SA, Kurimo RW, Kovein RJ. Engineering controls for furniture strippers to meet the OSHA methylene chloride PEL. *Am Ind Hyg Assoc J.* 2002;63(3):326-33.

European Committee for Standardization (CEN). Workplace atmospheres – general requirements for the performance of procedures for the measurement of chemical agents. CEN: EN 482; 1994.

Hall AH, Rumack BH. Methylene chloride exposures in furniture-stripping shops: ventilation and respirator use practices. *J Occup Med.* 1990;32(1):33-7.

National Institute for Occupational Safety and Health (NIOSH). Development and validation of methods for sampling and analysis of workplace toxic substances (DHHS/NIOSH Pub. No. 80-133). Cincinnati, OH: NIOSH;1980.

Occupational Safety and Health Administration (OSHA). Evaluation guidelines, with testing and reporting protocols, for OSHA on-site air and surface sampling methods. OSHA Salt Lake Technical Center, Applied IH Chemistry Team; 2002a.

Occupational Safety and Health Administration (OSHA). Methylene chloride - 29 CFR 1910.1052. Washington D.C.: Occupational Safety and Health Administration, Department of Labor; 1997.

Occupational Safety and Health Administration (OSHA). Methylene chloride in workplace air by Dräger Type 50/a-L long-term detector tubes. OSHA Salt Lake Technical Center, Applied IH Chemistry Team; 2002b.

Occupational Safety and Health Administration (OSHA). Sampling and analytical method no. 59 – methylene chloride. OSHA Analytical Laboratory, Organic Methods Evaluation Branch, 1986.

Riley DM, Small MJ, Fischhoff B. Modeling methylene chloride exposure-reduction options for home paint-stripper users. *J Expo Anal Environ Epidemiol.* 2000;10(3):240-50.

Roper P. The NIOSH detector tube certification program. *Am Ind Hyg Assoc J.* 1974;35(7):438-42.

U.S. Department of Health and Human Services (DHHS). Toxicological Profile for Methylene Chloride (Update). Atlanta, Georgia: Agency for Toxic Substances and Disease Registry (ATSDR), Division of Toxicology/Toxicology Information Branch; 2000.