Validation of Methylene Chloride using SKC Passive Sampler 575-001

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Contents

Research Report

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Abstract

A sampling method for Methylene Chloride in air has been validated for concentration levels from 2.5 to 50 ppm and for exposure times from 7.5 minutes to 12 hours. The 575-001 passive sampler used has a sample medium of coconut charcoal. Desorption was with carbon disulfide and analysis by gas chromatography with flame ionization detection.

The analytical recovery over the range of 2.5 to 50 ppm (53 to 1270 µg) was 96.0% with a relative standard deviation of 4.5%.

The sampling rate is 14.7 ml/min which was confirmed by the precision and accuracy calculations using 138 results (see Background; Sampling Rate Determination)*. Samples can be taken from 10°C to 40° C.

Minimum recommended sampling time is 15 minutes. Maximum recommended sampling time is 8 hours.

Storage stability at freezer (-8° C), refrigerator (3° C) or room temperature showed no significant loss in recovery after 21 days.

A full validation of Methylene Chloride was done according to NIOSH Protocol.[1]

This report updates the publication of initial results.[2]

** This rate is most accurate for samples taken for a period greater than 4 hours and used to determine a TWA concentration for comparison with a PEL or 8-hour TLV. The most accurate rate for samples taken for periods up to 4 hours and used for comparison with a STEL is 16.0 ml/min.*

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Importance of Validation of Passive Samplers

There are distinct differences between a passive sampler and a sample tube.

The most important difference is that a passive sampler does not have a foolproof back up section that guarantees that all the chemical hazard has been collected and there is a true and total measure of the worker exposure.

Secondly, the sorbent media is exposed to the external environment and this poses problems not associated with a sample tube where the air sample passes into the sample tube directly contacting the sorbent media. That is why it is critical to use a strong sorbent medium in passive samplers to assure complete capture and retention.

Therefore, for compliance purposes a passive sampler must be laboratory tested and validated under worst case field conditions for all factors that affect sampling accuracy as well as interaction between affects.

NIOSH has laid out a rigorous and complete validation protocol to assure that the sample collected is a complete and true measure of worker exposure. The following are the factors that the NIOSH protocol addresses:

Factors That Affect Complete Sample Uptake & Retention

Chemical Hazard Concentration	Temperature
Time of Exposure	Humidity
Sorbent Capacity	Interfering Chemicals
Sorbent Strength	Reverse Diffusion from Sorbent Surface
Wind Velocity	Sampler Orientation

Interaction of Any of the Above Factors

Validation by NIOSH protocol assures that the sample results are a true and total measure of worker exposure.

**SKC Validation follows the NIOSH Validation Protocol.
Certain experiments may have been modified for practical
reasons, or to provide more rigorous tests.**

User Responsibility

The sampler manager should be a professional trained in air sampling and aware of the limitations and advantages of the method being used. It is also very helpful if they have a working relationship with the analytical techniques being used and the requirements of record keeping.

In accordance with ASTM D6346-98 and ANSI 104-1998 standards, use of samplers outside the range of conditions used in these validation tests does not assure accurate results and is not recommended. It is the user's responsibility to determine whether the conditions of the sampling site fall within the range tested. For bi-level validations it can be assumed that the applicable range is that used for testing the lower member of the homologous series.

Workers should be trained in the use of the equipment. In collecting the sample, care should be taken in the location of the sampler on the worker. It is to be openly exposed near the breathing zone. Exact times of exposure must be recorded. No moisture condensation should occur on the sampler. Workers should not be allowed to touch the sampler as they may transfer contamination. Particular attention must be paid to environments where liquid aerosols may be present, since droplets of liquid solvent on the sampler face will invalidate the sample. Any other field conditions outside of the limits used in the NIOSH protocol, such as extreme temperatures or stagnant air conditions which might affect the sampler operation should be recorded.

Good laboratory practice must be followed. Follow the operating instructions for the desorption time needed for complete desorption. Use only the correct desorption instrument. If gas chromatography is used as the analysis method, base line separation should occur with the chemical hazard of interest and proper instrument calibration procedures used.

NIOSH or OSHA analytical methods should be used.

Summary of NIOSH Validation Protocol[1]

Characteristic	Experimental Design	Interpretation of Results
1. Analytical Recovery	Spike 16 samplers, 4 at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 x STD) Equilibrate about 12 h and analyze.	For the higher 3 levels require ≥ 75% recoveries with $S_r \leq 0.1$.
2. Sampling Rate and Capacity	Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 & 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST.	Verify sampling rate. State useful range at 80% RH & 2 x STD. Capacity - sample loading corresponding to the downward break in conc. vs time curve from constant concentration. SRST - time linear uptake rate achieved. MRST-0.67 x capacity (1 analyte) MRST-0.33 x capacity (Multi-analyte)
3. Reverse Diffusion	Expose 20 samplers to 2 x STD. 80% RH for 0.5 x MRST. Remove and analyze 10 samplers. Expose others to 80% RH and no analyte for remainder of MRST.	Require ≤ 10% difference between means of the two sampler sets at the 95% CL.
4. Storage Stability	Expose 3 sets of samplers (10 per set) at 80% RH, 1 x STD, and 0.5 x MRST. Analyze first set within 1 day, second set after 2 weeks storage at about 25° C, third set after 2 weeks storage at about 5° C.	Require ≤ 10% difference at the 95% CL between means of stored sampler sets and set analyzed within 1 day.
5. Factor Effects	Test the following factors at the levels shown. Use a 16 -run fractional factorial design (4 samplers per exposure) to determine significant factors. Factor — Test Levels analyte concentration — 0.1 & 2 x STD exposure time — SRST & MRST face velocity — 10 & 150 cm/s relative humidity — 10 & 80% RH interferant — 0 & 1 x STD sampler orientation — parallel & perpendicular (to air flow)	Indicate any factor that causes a statistically significant difference in recovery at the 95% CL. Investigate further to characterize its effect.
6. Temperature Effects	Expose samplers (10 per temp) to 0.5 x STD at 10, 25, & 40° C for 0.5 x MRST	Define temperature effect and verify correction factor, if provided.
7. Accuracy and Precision	Calculate precision and bias for samplers (10 per conc. level) exposed to 0.1, 0.5, 1 & 2 x STD at 80% RH for ≥ MRST. Use data from previous experiments.	Require bias within ± 25% of true value at 95% CL with precision $S_r \leq 10.5\%$ for 0.5, 1, & 2 x STD levels.

Summary of NIOSH Validation Protocol (cont.)

Characteristic	Experimental Design	Interpretation of Results
8. Shelf Life	Observe samplers throughout evaluation for changes in blank values, physical appearance, etc. Test samplers from more than one lot, if possible.	Note shelf storage time at which changes begin to occur. Indicate whether correctable or not.
9. Behavior in the Field	Consider problems not predictable from laboratory experiments.	Record temperature, humidity, air velocity, other contaminants, etc.
Area Sampling:	Expose passive samplers and independent method samplers (13 each) to the same environment.	Calculate precision and bias. Compare with laboratory results.
Personal Sampling:	Conduct personal sampling with $\geq$ 25 sampler pairs. Place pairs of passive samplers and independent samplers on the same lapel of each worker.	Calculate bias. Compare with area sampling and laboratory results

Bi-Level Validation (previously designated by SKC as 5B)

Validation of passive samplers is essential to ensure accurate determination of airborne chemical levels. To assist manufacturers and users, the National Institute for Occupational Safety and Health (NIOSH), the Health and Safety Executive (HSE)[3], and the Comité Européen de Normalisation (CEN)[4,5] have developed comprehensive protocols for the validation of passive samplers.

Bi-level validation can also be used to assure a sample that gives the total and complete exposure to a chemical hazard.

Bi-level validation is only for a series of chemically related compounds, i.e., members of a homologous series. Bi-level validation includes a full protocol validation on key compounds followed by a partial validation on other members of the series.

The concept of a bi-level validation of chemically related compounds for a given sorbent and sampler design is based on the following premises and has been studied by Guild et al.[6]

1. Full validation by NIOSH, HSE, or CEN Protocol of a lower member of the series is essential to assure accurate, routine sampling under all field conditions without the need for error-corrective measures.

2. Capacity and retentivity are directly related to the affinity of a sorbent for a specific chemical. For a series of chemically related compounds, the affinity of a sorbent for a particular member compound will increase with the molecular weight and boiling point of the member. If a sorbent is suitable for collecting a low molecular weight member of the series, it will be suitable for the higher molecular weight members of the series as well.

3. For chemically stable compounds, sample loss by reverse diffusion and loss during storage are inversely related to the affinity of the sorbent for the adsorbate. Therefore, compounds with higher molecular weights and boiling points will exhibit less loss by reverse diffusion and storage. Again, if a sorbent is suitable for a member with a lower molecular weight and boiling point, it will be suitable for the higher members.

4. The linearity of uptake with time is also a function of sorbent affinity and capacity. Uptake becomes increasingly linear as the molecular weight and boiling point increases and the sample load decreases. (Protocol validation requires study of concentrations ranging from 0.1 to 2.0 x the permissible exposure limit.)

Bi-Level Validation (cont.)

5. Temperature affects the accuracy of passive samplers in two different ways; the relation of temperature to adsorption affinity and the relation of the molecular diffusion of the sample to the sampler.

   a. It is well known that the affinity of a sorbent for a chemical decreases with increasing temperature. If the sorbent has adequate affinity for a low molecular weight member of the series at 40° C (the maximum temperature tested under protocol), it will also be adequate at lower temperatures, and for higher molecular weight members of the series.

   b. The effects of temperature on sample uptake follow established mathematical relationships and are not significant compared to other random sampling errors.

6. The effects of humidity because of competition or modification of sorbent affinity will be most pronounced for lower members of the series.

7. Adsorption affinity decreases with the mass adsorbed. Therefore, the "key" member chosen for full validation should have a high PEL relative to the other members of the series.

8. Air velocity and sampler-orientation effects are functions of sampler design and will be similar for all compounds.

9. If all the factors affecting sampling accuracy improve with increasing molecular weight and boiling point and there are no interacting effects of these parameters with a lower member of the series, then there will be no interacting effects with higher members.

10. The accuracy of a sampler is determined by its bias and precision. For most passive samplers, the bias is the result of the deviation of the calculated sample rate from the actual rate. By determining the sample rate under known conditions at 1 PEL, the bias is reduced to zero. Therefore, measured sample rates should be determined for all compounds.

11. The precision of a sampler is a function of the consistency of sampler manufacture and the analytical procedures in the laboratory.

12. Analytical recovery tends to decrease with increased sorbent affinity and is a function of the chemical compound, the concentration, and the sorbent. Therefore, analytical recovery should be determined for every compound over the concentration range of 0.1 to 2.0 PEL, as recommended by protocol.

Conclusion: The above premises have been verified, peer reviewed and published.[6] Therefore, Bi-Level validation (5B) is an excellent way to assure accurate performance of a passive sampler for higher members of a homologous series.

Comments on the Relationship Between the NIOSH and CEN Diffusive Sampler Evaluation Protocols

The Comité Européen de Normalisation (CEN) is engaged in writing standards for air sampling equipment which include the limitations on precision and accuracy (EN 482) and the required performance tests. In the case of passive samplers the relevant performance test standard is yet to be published, but draft copies are available (prEN 838).

The precision and accuracy requirements in EN 482 are based on the use that will be made of the results, principally either for problem identification or compliance purposes. The standard for compliance purposes is a combined precision and accuracy of less than 30%, which is a looser standard than the 25% in the NIOSH protocol.

The performance tests are closely related to those in the NIOSH protocol, as might be expected, since they are trying to confirm the performance of the samplers over a similar range of environmental conditions. As in the NIOSH protocol there are tests for desorption efficiency, uptake rate at different concentrations and for different time-periods, reverse diffusion, storage stability, wind velocity and orientation, humidity, temperature, and the presence or absence of interferences. As in the NIOSH protocol these factors are normally tested using a "high" and a "low" measure, whether alone or in combination. Since there is little difference between workplace conditions in the U.S.A. and Europe, these "high" and "low" conditions are very similar in the two protocols. In general, the NIOSH test provides the more stringent conditions (e.g. 7.5 minutes up to 12 hours in the NIOSH uptake rate experiment versus 30 minutes and 8 hours in the CEN equivalent). In addition, for the majority of the experiments, the NIOSH protocol requires more samples to be taken for each data point (typically 10 rather than 6). The reverse diffusion test is one test that might be considered significantly different, and a paper showing that the results of the tests are actually comparable has been submitted for publication.[6]

In addition, the CEN protocol requires tests for shelf-life and packaging integrity that have been carried out for one analyte (n-Hexane) only. The 575 Series passive sampler successfully passed these tests.

For the reasons given above, SKC considers the validations presented in these research reports to be at least sufficient to meet the requirements of the European Standards prEN 838 and EN 482 for compliance monitoring. This conclusion is supported by a detailed comparison which has been submitted for publication.[8]

The CEN protocol supports the Bi-level theory of validation.

SHELF-LIFE STUDY ON 575 SERIES PASSIVE SAMPLERS

Protocol: 4 expired and 2 unexpired 575-001 samplers were exposed to an atmosphere 100 ppm n-Hexane (2 X PEL) at 80% relative humidity (25° C) for 30 minutes, and then analyzed. Study was conducted August 1995.

Results:

Calculated atmosphere concentration:	106 ppm
Gas sample analysis concentration:	102 ppm (RSD = 7.0%)
Sorbent tube analysis concentration:	115 ppm (RSD = 3.2%)
Sampler analysis concentration:◊	
Sampler expired 12/92:	106 ppm
Sampler expired 4/94:	106 ppm
Sampler expired 10/94:	108 ppm
Sampler expired 10/94:	110 ppm
Sampler unexpired (7/96):	100 ppm
Sampler unexpired (7/96):	100 ppm

◊ Based on 111.6% desorption efficiency

Conclusion: Samplers will perform as expected up to their expiration date.

PACKAGING INTEGRITY STUDY ON 575 SERIES SAMPLERS

Protocol: 6 575-001 samplers in unopened Tedlar® pouches were exposed to an atmosphere of 100 ppm n-Hexane (2 X PEL) at 80% relative humidity (25° C) for four hours, and then opened and analyzed.

Results:

Calculated atmosphere concentration:	103 ppm
Gas sample analysis concentration:	104 ppm (RSD = 8.7%)
Sorbent tube analysis concentration:	103 ppm (RSD = 2.7%)

Sampler analysis: No detectable n-Hexane in any sampler.

(estimated LOD = 1.5 micrograms, equivalent to 0.125 ppm)

Conclusion: Packaging will prevent contamination of stored samplers.

Scope of the Method

Analyte: Methylene Chloride

Matrix: Air

Procedure: Adsorption on a 575-001 SKC passive sampler, desorption with 2 ml of CS_2, and analysis by GC-FID.

Sampling Rate: 14.7 ml/min valid for PEL samples greater than 4 hours duration.
16.0 ml/min valid for STEL samples up to 4 hours.

Exposure Guidelines:

ACGIH-TLV (1994/95)	50 ppm TWA; suspect carcinogen
OSHA (1995)	500 ppm TWA, 1000 ppm C
Proposed (1992)	25 ppm TWA, 125 ppm STEL*
NIOSH (1994)	Lowest feasible; carcinogen

Validation Range, Recovery:

Compound	Validation Range ppm in air	Mean % Recovery
Methylene Chloride	2.5-50	96.0

Detection Limits: 0.1 PEL concentration was easily determined. No studies were made to determine the absolute detection limit.

Temperature Effects: Samples could be taken from 10° C to 40° C.

Factorial: No significant effects were found due to the interaction of factors that affect sampling accuracy.

Humidity Effects: High humidity conditions (80% RH at 25° C) did not affect the recovery of Methylene Chloride on the 575-001 passive sampler, or the uptake rate.

Storage Effects: The passive sampler can store for at least 21 days at freezer (-8° C), refrigerator (3° C) or room temperatures with no loss in recovery.

Interferences: Any compound that has the same retention time as Methylene Chloride will interfere with the analysis. A study was also conducted where passive samplers were exposed to 100 ppm toluene and 50 ppm Methylene Chloride and no significant loss in recovery was observed.

Validation Completion Date: December 1989

Physical Properties:

Mol. Weight (g/mole)	Boiling Pt. at 760 mm Hg	Density (g/ml)
84.94	40 ° C	1.3266

* Federal Register 57, p 36965 (August 17, 1992)

Background

History of Methodology
Previous methodologies have used activated charcoal SKC Lot 120 or carbon molecular sieve in a sample tube.

Research Purpose
The present work was to evaluate and validate the SKC 575 Series passive sampler containing coconut charcoal as a method for sampling Methylene Chloride. The passive sampler was validated over a concentration range of 0.1 to 2 x the proposed 25 ppm PEL. Critical parameters such as analytical recovery, concentration, relative humidity, reverse diffusion, storage stability, temperature, sampling time, wind speed and orientation, and the presence of interfering compounds were addressed.

Experimental
Optima-grade Methylene Chloride (Fisher Scientific) was used. The HPLC-grade carbon disulfide (99.9%) was obtained from Aldrich Chemical Company. The 575 passive sampler containing coconut charcoal (SKC Cat. No. 575-001) is available from SKC, Inc.

A dynamic atmosphere generation apparatus was used to generate precise concentrations of Methylene Chloride in air for exposure of the passive samplers. The system is described in Appendix A and Figure 1. The atmosphere was fed into an exposure test chamber. The passive samplers were exposed on a rotating bracket inside the test chamber to simulate wind velocity and orientation.

Analytical recoveries for the passive samplers were conducted by injecting a known amount of Methylene Chloride (as a CS_2 solution) into the back of each sampler. The passive samplers were capped, allowed to equilibrate overnight, and analyzed the next day to determine analytical recovery or desorption efficiency. The tests were conducted at mass loadings equivalent to an 8-hour time weighted average sample (7.06 L at the experimentally determined sampling rate of 14.7 ml/min) at 0.1, 0.5, 1.0 and 2.0 PEL (25 ppm) and 0.5, 1.0 and 2.0 STEL (125 ppm) under dry conditions. A wet desorption efficiency was conducted by first exposing the passive sampler to 80% RH air for eight hours and then spiking the passive sampler at a mass loading equivalent to the 1 PEL (25 ppm) level. These passive samplers were all equilibrated overnight and analyzed the next day.

The sampling rate, reverse diffusion and storage stability experiments on the passive sampler were conducted under dynamic conditions in the test chamber described above. In the storage stability study, recovery is referred back to the reference samples analyzed on Day 1.

The passive samplers were desorbed (in situ) with 2 ml of CS_2 and shaken on a flatbed shaker for 30 minutes. All extracts were transferred to autosampler vials and analyzed by flame ionization gas chromatography. A chromatogram with analytical conditions is shown in Figure 2.

Sampling Rate Determination
Sampling rates can be determined by one of several statistical methods from the experimental data and they differ by only a small amount. Any bias taken is toward the protection of the worker.

We use the time-weighted average from one to eight hours where results fall within NIOSH criteria.

We constantly review our data and conduct experimental work to provide the most precise sampling rate. This rate may differ slightly from previously published sampling rates. Use the rate listed in this report.

During the final stages of this study a paper was published in Applied Occupational and Environmental Hygiene [2] presenting the initial results. In reviewing the data for this work, some minor differences have arisen in the results. These differences result from correction of errors in the original publication, or refinement of data handling techniques, or inclusion of additional data. They do not materially affect the conclusions.

Analytical Recovery

NIOSH Requirements

Experimental Design

Spike 16 samplers, 4 at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 x STD) Equilibrate about 12 h and analyze.

Interpretation of Results

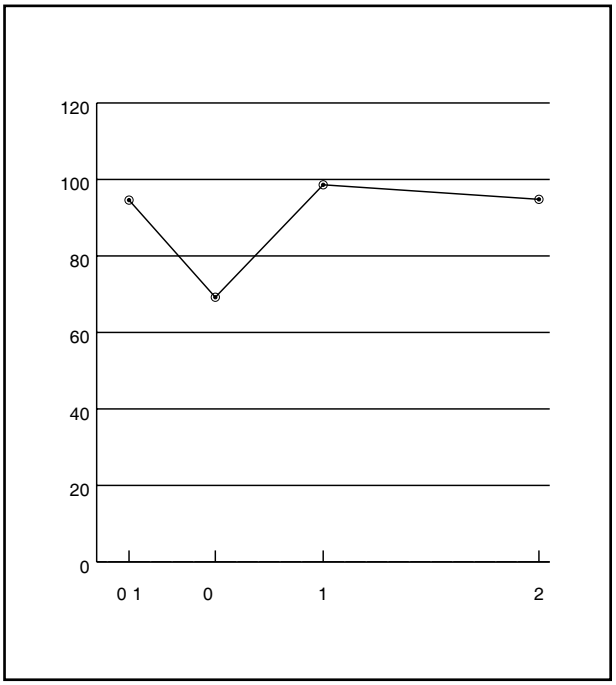
For the 3 higher levels require ≥ 75% recoveries with $S_r \leq 0.1$.

Results

PEL Level	Spike (mg)	Recovery (mg)	Recovery %	Mean	RSD %
0.1	52.9	54.6	103		
		51.8	97.9		
		49.2	93.0		
		48.2	91.1		
		48.8	92.2		
		48.0	90.7	94.6	5.1
0.5	318	305	95.9		
		306	96.2		
		299	94.0		
		311	97.8		
		308	96.9		
		307	96.5	96.2	1.3
1.0	635	634	100		
		620	97.6		
		622	98.0		
		624	98.3		
		625	98.4		
		629	99.1	98.6	0.9
1.0 (humidified)	635	616	97.0		
		615	96.9		
		615	96.9		
		629	99.1		
		637	100		
		629	99.1	98.2	0.9
2.0	1323	1298	98.1		
		1226	92.7		
		1294	97.8		
		1204	91.0		
		1248	94.3	94.8	3.3
2.0	1270	1347	106		
		1201	94.6		
		1163	91.6		
		1156	91.0		
		1130	89.0		
		1175	92.5	94.1	6.5

STEL Level	Spike (mg)	Recovery (mg)	Recovery %	Mean	RSD %
0.5	52.9	54.0	102		
		55.4	105		
		53.1	100		
		50.7	95.8		
		54.0	102		
		51.0	96.4	100	3.6
1.0	106	100	94.5		
		96.8	91.5		
		88.2	83.4		
		99.5	94.0		
		102	95.9		
		89.6	84.7	90.7	5.9
2.0	185	177	95.7		
		180	97.3		
		175	94.6		
		179	96.8		
		180	97.3		
		178	96.2	96.3	1.1

Pooled mean (all levels) 96.0%



Sampling Rate and Capacity

NIOSH Requirements

Experimental Design

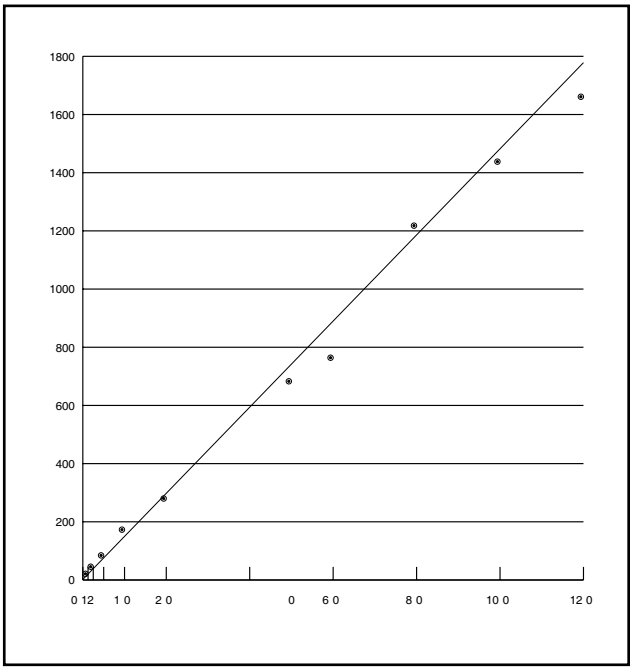
Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 and 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST.

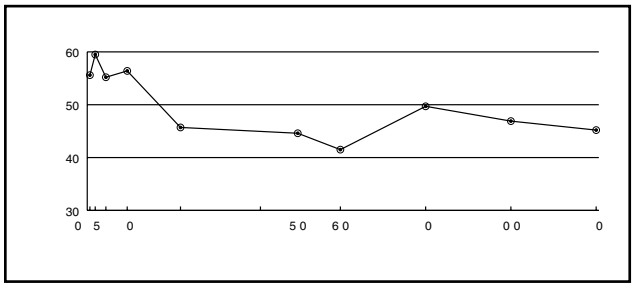
Interpretation of Results

Verify sampling rate. State useful range at 80% RH and 2 x STD. Capacity - sample loading corresponding to the downward break in conc. vs time curve from constant concentration. SRST-time linear uptake rate achieved. MRST - 0.67 x capacity (1 analyte)
MRST-0.33 x capacity (Multi-analyte)

Results

Time (hrs)	Uptake (mg)	Mean	RSD %	DE Corr (mg)	Concn. (ppm)
0.125	20.9				
	21.5				
	20.1				
	19.4	20.5	4.5	21.3	55.6
0.25	43.8				
	44.4				
	42.3				
	44.5	43.8	2.3	45.6	59.5
0.5	79.9				
	80.3				
	81.3				
	83.2	81.2	1.8	84.6	55.2
1	165				
	165				
	168				
	165	166	0.9	173	56.4
2	271				
	260				
	272				
	271	269	2.2	280	45.7
5	655				
	661				
	651				
	655	656	4.1	683	44.6
6	710				
	713				
	763				
	746	733	3.5	764	41.5
8	1159				
	1161				
	1185				
	1172	1169	1.0	1218	49.7
10	1432				
	1379				
	1360				
	1350	1380	2.6	1438	46.9
12	1579				
	1587				
	1607				
	1606	1595	0.9	1661	45.2





Concentration values are calculated using the 1, 2, 5, and 8-hour time-weighted average sampling rate of 14.7 ml/min (3.0628 µg ppm^{-1} hr^{-1})based on a standard atmosphere of 48 ppm.

Reverse Diffusion

NIOSH Requirements

Experimental Design

Expose 20 samplers to 2 x STD 80% RH for 0.5 x MRST. Remove and analyze 10 samplers. Expose others to 80% RH and no analyte for remainder of MRST.

Interpretation of Results

Require ≤ 10% difference between means of the two sampler sets at the 95% CL.

Results (in micrograms)

Exposed 4 hours to analyte hours at zero analyte concentration		Exposed 4 hours to analyte plus 3.5	
Uptake (µg)	**DE Corr. (µg)**	**Uptake (µg)**	**DE Corr. (µg)**
640.3	667.0	526.4	548.3
658.1	685.5	627.7	653.8
601.2	626.2	640.0	666.7
614.1	639.6	555.4	578.5
619.1	644.9	600.3	625.4
632.6	659.0	583.0	607.3
659.5	687.0	629.0	655.3
633.5	659.9	640.5	667.2
558.3	581.6	629.0	655.2
650.0	677.1	642.6	669.4
Mean:	**652.8**		**632.7**
SD:	**31.86**		**42.05**
RSD:	**4.9%**		**6.6%**

The difference between the two sets of results is less than 10%.

2 x PEL used as a more stringent test.

Storage Stability

NIOSH Requirements

Experimental Design

Expose 3 sets of samplers (10 per set) at 80% RH, 1 x STD, and 0.5 x MRST. Analyze first set within 1 day, second set after 2 weeks storage at about 25° C, third set after 2 weeks storage at about 5° C.

Interpretation of Results

Require ≤ 10% difference at the 95% CL between means of stored sampler sets and set analyzed within 1 day.

Results (in micrograms)

	Room Temp		Refrigerator		Freezer	
	Uptake (µg)	DE Corr. (µg)	Uptake (µg)	DE Corr (µg)	Uptake (µg)	DE Corr. (µg)
Day 1	1171	1220	1284	1337	1235	1286
	1178	1227	1244	1285	1305	1359
Day 3 (Refrigerated Day 4)						
	1233	1285	1309	1363	1154	1202
	1237	1288	1311	1365	1113	1159
	1217	1268	1291	1345	1185	1234
Day 7	1275	1328	1233	1284	1011	1053
	1241	1293	1253	1305	1130	1177
	1246	1298	1284	1338	1005	1047
Day 10 (Refrigerated Day 11)						
	1217	1268	1004	1046	1078	1123
	1221	1272	1059	1104	1123	1170
	1230	1281	1046	1090	1093	1138
Day 14	1087	1132	1259	1310	1313	1368
	1066	1110	1299	1353	1189	1239
	1045	1089	1311	1366	1313	1368
Day 21	1152	1200	1284	1338	1210	1260
	1244	1296	1297	1351	1295	1349
	1187	1237	1296	1350	1137	1184
Mean: Day 3-21		**1243**		**1287**		**1205**
RSD:		**6.3%**		**8.6%**		**8.4%**

No significant effect of temperature or time on sample storage stability. Eight-hour exposure at 2 x PEL (50 ppm) represents a more stringent test than the NIOSH protocol.

Ambient results normalized to 480 minutes from 439 minute exposure. Refrigerated results normalized to 480 minutes from 477 or 483 minutes.

* Samplers stored at room temperature lost 12.5% compared to Day 1. The observed difference (0.829 mg) is slightly greater than the 95% confidence interval test difference of 0.814 indicating a loss significantly greater than 10%.

Factorial Results

NIOSH Requirements

Experimental Design

Test the following factors at the levels shown. Use a 16 run fractional factorial design (4 samplers per exposure) to determine significant factors.

Factor	Test Levels
analyte concentration	0.1 & 2 x STD
exposure time	SRST & MRST
face velocity	10 & 150 cm/s
relative humidity	10 & 80% RH
interferant	0 & 1 x STD
sampler orientation	parallel & perpendicular (to air flow)

Interpretation of Results

Indicate any factor that causes a statistically significant difference in recovery at the 95% CL. Investigate further to characterize its effect.

Results (in micrograms per ppm per hour ($\mu g\ ppm^{-1}\ h^{-1}$), desorption efficiency corrected)

Run #	Individual Monitor Results				Average	%RSD
1	3.7446	3.9981	4.0361	3.9105	3.9223	3.3
2	3.4554	3.4092	3.4246	3.7940	3.5208	5.2
3	2.7563	3.0476	2.7115	2.6218	2.7843	6.6
4	2.6683	2.6424	3.1024	2.8724	2.8214	7.6
5	2.8601	2.7786	2.7379	3.1043	2.8702	5.7
6	2.8079	2.8647	2.7673	2.6861	2.7815	2.7
7	2.9521	2.8365	3.3323	3.0646	3.0463	6.7
8	-.-----*	2.4894	2.4535	2.4509	2.4646	0.9
9	3.0951	2.9882	3.1736	-.-----*	3.0856	3.0
10	3.1955	3.4041	3.3147	2.7337	3.1620	9.4
11	3.1169	3.2612	3.3582	3.1045	3.2102	3.8
12	3.3225	3.4714	3.2482	3.1242	3.2916	4.4
13	3.1889	3.2525	3.1968	3.3161	3.2386	1.8
14	3.8938	3.2307	4.0678	3.7767	3.7423	9.6
15	3.8107	3.7736	4.0678	3.7764	3.8571	3.7
16	3.3228	3.1111	3.4497	3.1323	3.2540	5.0

Notes:
- Low face velocity = 20 cm/s
- Low concentration = 0.1 PEL
- Minimum sample time = 2.5 hours

100 ppm Toluene used in the interference experiments.

* Outlier result not used.

Factorial Summary

Run Number		µg/ppm/hour
Run#	1	= 3.9223
Run#	2	= 3.5208
Run#	3	= 2.7843
Run#	4	= 2.8214
Run#	5	= 2.8702
Run#	6	= 2.7825
Run#	7	= 3.0463
Run#	8	= 2.4335
Run#	9	= 3.2770
Run#	10	= 3.1620
Run#	11	= 3.2102
Run#	12	= 3.2916
Run#	13	= 3.2386
Run#	14	= 3.7423
Run#	15	= 3.8571
Run#	16	= 3.2540
Average		**= 3.2009 = 15.4 ml/min^{-1}**

	Factor	Effect	Percent	Significance
A -	Concentration	-0.12	3.6%	N.S.
B -	Relative Humidity	-0.28	8.6%	N.S.
C -	Interferants	-0.38	12.0%	N.S.
D -	Time	0.10	3.2%	N.S.
E -	Face Velocity	-0.03	1.1%	N.S.
F -	Orientation	0.20	6.2%	N.S.
E1 -	ABC	0.04	1.3%	N.S.
E2 -	ABD	-0.36	11.1%	N.S.
E3 -	AB + EF	-0.12	3.9%	N.S.
E4 -	AC + DF	-0.05	1.6%	N.S.
E5 -	AD + CF	-0.23	7.1%	N.S.
E6 -	AE + BF	-0.10	3.0%	N.S.
E7 -	CD + BE	-0.28	8.9%	N.S.
E8 -	BC + DE	0.22	6.8%	N.S.
E9 -	BD + CE	-0.15	4.7%	N.S.

Minimum Significant Effect (MSE) = ± 0.45

No significant effect of factors or their tested interactions.

Temperature Effects

NIOSH Requirements

Experimental Design

Expose samplers (10 per temp) to 0.5 x STD at 10, 25, & 40° C for 0.5 x MRST.

Interpretation of Results

Define temperature effect and verify correction factor, if provided.

Results (in micrograms)

10° C		25° C		40° C	
Uptake (µg)	**DE Corr. (µg)**	**Uptake (µg)**	**DE Corr (µg)**	**Uptake (µg)**	**DE Corr. (µg)**
212.1	221.0	146.7	152.8	146.7	152.8
212.8	221.7	156.3	162.8	142.2	148.1
185.6	193.3	157.1	163.7	143.9	149.9
219.5	228.7	144.8	150.8	159.2	165.8
----.-*	----.-*	148.6	154.7	133.5	139.0
184.2	191.9	141.4	147.3	152.2	158.5
196.3	204.5	162.4	169.1	136.3	142.0
177.9	185.3	149.4	155.6	140.1	145.9
208.0	216.6	141.6	147.5	164.6	171.5
221.5	230.7	152.3	158.6	140.2	146.0
Mean:	**210.4**		**156.3**		**152.0**
RSD:	**8.1%**		**4.6%**		**6.8%**
Concentration:[1]	**18.236**		**12.313**		**13.265**
Uptake rate:[2]	**2.8846**		**3.1735**		**2.8647**
Theoretical:[3]	**3.0942**				**3.2528**

Uptake is within 10% of theoretical (based on 25° C result) at 10° C and within 20% of theoretical at 40° C.

10° C results normalized to 240 minutes from 300 minutes
25° C results normalized to 240 minutes from 304 minutes
40° C results normalized to 240 minutes from 272 minutes

* Sampler lost.

[1] In ppm at the sampling temperature

[2] Uptake rate measured as micrograms/ppm (sampling temperature)/hour (µg ppm^{-1} h^{-1})

[3] Theoretical uptake rate is based on 25° C result

Accuracy and Precision

NIOSH Requirements

Experimental Design

Calculate precision and bias for samplers (10 per conc. level) exposed to 0.1, 0.5, 1 & 2 x STD at 80% RH for ≥ MRST. Use data from previous experiments.

Interpretation of Results

Requires bias within ± 25% of true value at 95% CL with precision $S_r \leq 10.5\%$ for 0.5, 1 & 2 x STD levels.

All Values in µg/ppm/hr

Monitors run at 2.0 X PEL

Values for individual monitors for the Rate/Capacity Experiment

5 Hour -	2.8429	2.8689	2.8255	2.8429
8 Hour -	3.1440	3.1494	3.2145	3.1793
10 Hour -	3.1076	2.9926	2.9514	2.9297

Values for individual monitors for the Reverse Diffusion Experiment

4 Hour -	2.3350	3.4275	3.1310	3.1980	3.2245
	3.2950	3.4350	3.2995	2.9080	3.3855
4 Hour -	2.7415	3.2690	3.3335	2.8925	3.1270
+ zero	3.0365	3.2765	3.3360	3.2760	3.3470

Values for individual monitors for the Storage Stability Experiment

Room T -	3.2125	3.2200	3.1700	3.3200	3.2325
	3.2450	3.1700	3.1800	3.2025	2.8300
	2.7750	2.7225	3.0000	3.2400	3.0925
Refrig -	3.4075	3.4125	3.3625	3.2100	3.2625
	3.3450	2.6150	2.7600	2.7250	2.2750
	3.3825	3.4150	3.3450	3.3775	3.3750
Freezer -	3.0050	2.8975	3.0850	2.6325	2.9425
	2.6175	2.8075	2.9250	2.8450	3.4200
	3.0975	3.4207	3.1500	3.3725	2.9600

Values for individual monitors for the Factorial Experiment

Run #2 -	3.4554	3.4092	3.4246	3.7940
Run #4 -	2.6683	2.6424	3.1024	2.8724
Run #13 -	3.1889	3.2525	3.1968	3.3161
Run #15 -	3.8107	3.1111	3.4497	3.1323

Monitors run at 0.5 x PEL

Values for individual monitors for the Temperature Effects Experiment

10 deg -	3.1055	3.1153	2.7162	3.2137	
	2.6966	2.8736	2.6038	3.0436	3.2418
25 deg -	3.1024	3.3054	3.3237	3.0618	3.1410
	2.9907	3.4334	3.1593	2.9948	3.2202
40 deg -	2.8078	2.7214	2.7545	3.0466	2.5542
	2.9125	2.6093	2.6810	3.1514	2.6828

Monitors run at 0.1 x PEL

Values for individual monitors for the Factorial Experiment

Run #1 -	3.7446	3.9981	4.0361	3.9105
Run #3 -	2.7563	3.0476	2.7115	2.6218
Run #14 -	3.8938	3.2307	4.0678	3.7767
Run #16 -	3.3228	3.1111	3.4497	3.1323

Summary

PEL	Relative Standard Deviation	Degrees of Freedom
0.1	6.6%	12
0.5	6.6%	26
2.0	6.1%	83

Average Values in µg/ppm/hr

Experiment	Average	RSD
Rate/Capacity	3.0041	1.7%
Factorial, 2.0 PEL	3.2392	6.7%
Storage Stability 2.0 PEL	3.1125	7.8%
Temperature 0.5 PEL	2.9741	6.6%
Reverse Diffusion 2.0 PEL	3.2138	5.8%
Factorial 0.1 PEL	3.4257	6.6%
Overall average	**3.1768**	**6.3%**

Overall sampling rate = 15.2 ml/min ± 1.9 ml/min

Appendix A

Atmosphere Generation Apparatus

The instrument is designed to expose a known concentration of a chemical hazard to a passive sampler under controlled conditions of: 1. Concentration, 2. Temperature, 3. Humidity, 4. Wind Velocity Effect, 5. Time, and 6. Up to four multicomponent hazards.

Description

The instrument consists of:

1. an exposure chamber in which the wind velocity effects are controlled by internal rotating holders,

2. an air supply and purification train such that dry air is blended with saturated air under desired temperature conditions so as to provide air at a known flow and selectable humidity,

3. an injection system composed of precision motor driven syringes in which 1 to 4 chemical hazards can be injected into the flow system and in which the temperature of the injectors is closely controlled,

4. an electrical control system that controls the entire instrument operation,

5. the chamber concentration can be verified by either solid sorbent sampling tubes actively sampled or by gas analysis of the gas phase. The particular verification method used will depend on the analyte of interest.

Means are also included to check the relative humidity.

Figure 1
Atmosphere Generation Apparatus

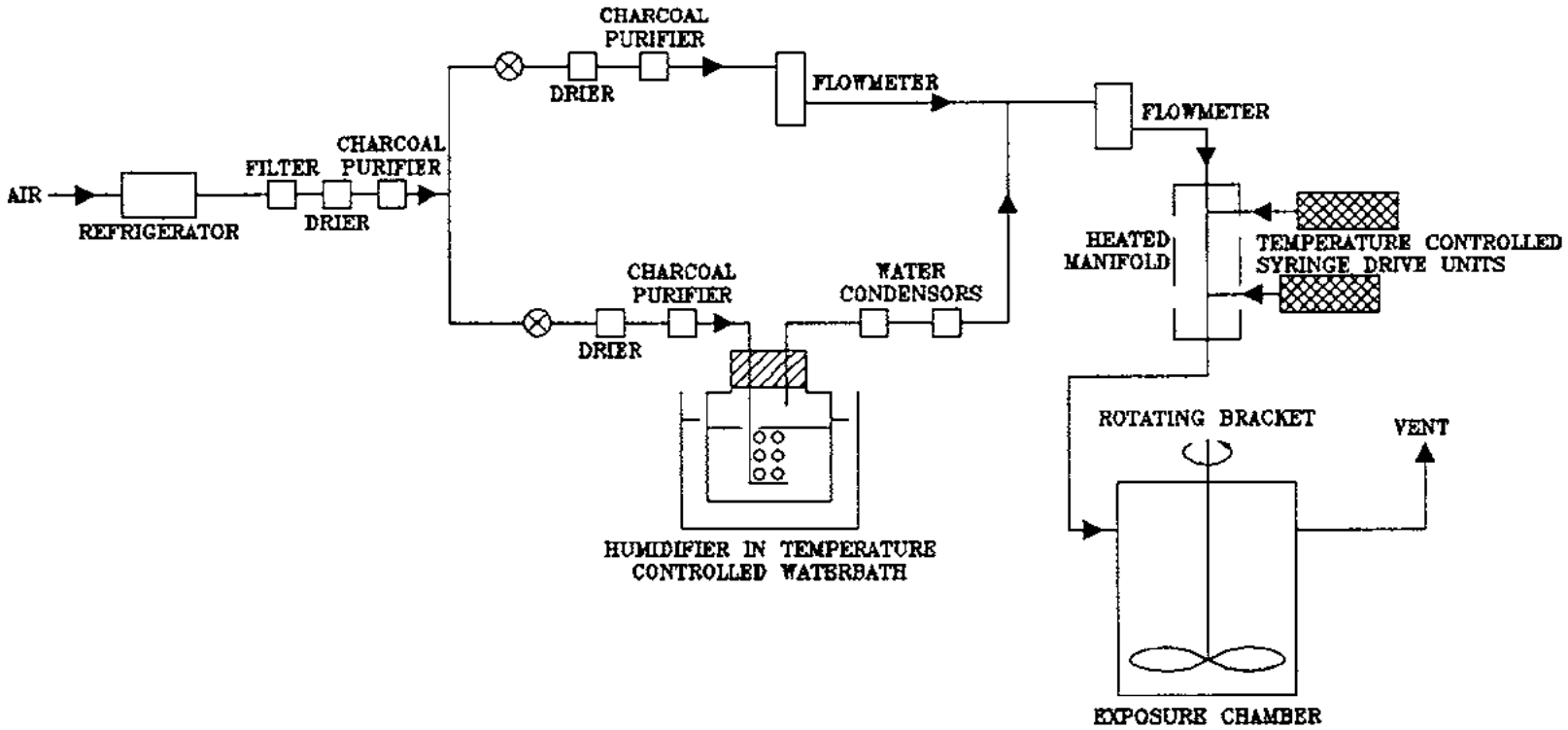
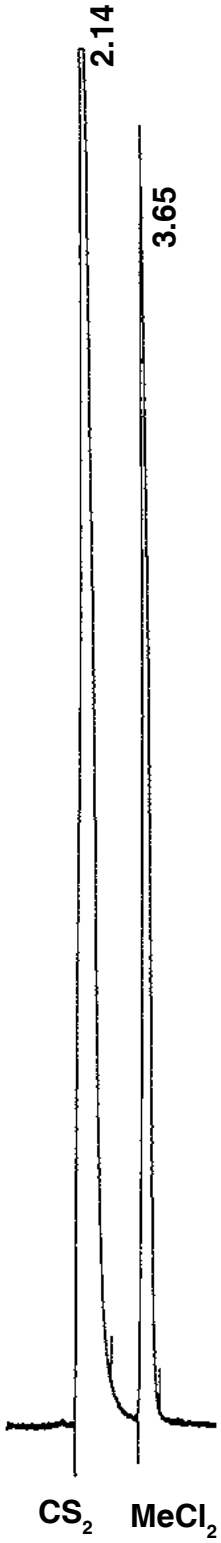


Figure 2
Analytical Instrument

Sample Chromatogram
Methylene Chloride in CS_2



GC Conditions

Column:	10 ft x 1/8 " 10% SP-1000 on 100/120 mesh Chromosorb AW
Temperatures:	Column 85° C FID 150° C
Carrier Gas:	N_2
Injection:	1µL

Abbreviations

C	Celsius
CL	confidence level
cm	centimeter
ml	milliliter
min	minute
g	gram
GC-FID	gas chromotography - flame ionization detector
h	hour
L	liter
LOD	limit of detection
MRST	maximum recommended sampling time
N.S.	not significant
PEL	permissible exposure limit
RH	relative humidity
TLV	threshold limit value
TWA	time-weighted average
RSD	relative standard deviation
SD	standard deviation
SRST	shortest recommended sampling time
STD	the appropriate exposure standard (OSHA PEL, ACGIH TVA , or NIOSH recommended standard)
S	second
S_r	Pooled relative standard deviation
V	volume

Trademarks

Anasorb is a registered trademark of SKC Inc.
Tedlar is a registered trademarik of DuPont Corporation.
Porapak is a registered trademark of Waters Associates, Inc.

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