Research Report

Validation of Methyl tert-Butyl Ether using SKC Passive Sampler 575-001

Abstract

A sampling method for Methyl tert-Butyl Ether (MTBE) in air has been validated for concentration levels from 0.3 to 80 ppm and for exposure times from 8.5 minutes to 8 hours. The 575-001 passive sampler used has a sample medium of Lot 120 coconut charcoal. Desorption was with carbon disulfide and analysis by gas chromatography with flame ionization detection.

The analytical recovery over the range of 5 to 100 ppm for 8 hours (0.12 to 2.1 mg) was 97.4% (RSD 2.1%). There was no effect of humidity on recovery.

The sampling rate is 13.6 ml/min which was confirmed by the precision and accuracy calculations using 118 results (see Background; Sampling Rate Determination). Samples can be taken up to 40° C.

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

Samples were stable for up to two weeks in a refrigerator (≤ 39.2° F [4° C]).

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

Authors

Amy A. Fiore
Christina O'Lear
Martin Harper

Compiled by Martin Harper, Ph.D.

SKC Inc.
863 Valley View Road
Eighty Four, PA 15330 USA

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 4° 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.	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.

Factor effects test levels (item 5):

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)

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)[2], and the Comité Européen de Normalisation (CEN)[3,4] 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.[5]

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.[5] 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 EN 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 and temperature. 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 may be considered different, however, a paper showing that the results of the tests are 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 EN 838 and EN 482 for compliance monitoring. This conclusion is supported by a detailed comparison which has been submitted for publication.[7]

Full validation is equivalent to level 1A of EN 838. Partial validation, according to the Bi-level Theory of Validation, is equivalent to level 1B of EN 838.

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: Methyl tert-Butyl Ether (MTBE)

Matrix: Air

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

Exposure Guidelines:

ACGIH-TLV (1994/95)	40 ppm TWA
OSHA (1995)	None
NIOSH (1995)	None

Validation Range, Recovery:

Compound	Validation Range_ppm in air	Mean % Recovery
MTBE	5-100	97.4%

Detection Limits: Depending on the instrumentation, it is possible to determine at least 7 μg/sampler with a relative standard deviation of less than 10%. This corresponds to an air concentration of 0.3 ppm (v/v) based on an 8 hour sample at the validated sampling rate of 13.6 ml/min.

Temperature Effects: Samples could be taken up 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 styrene on the 575-001 passive sampler or the uptake rate.

Storage Effects: The passive sampler can store for at least 14 days in a refrigerator (≤ 39.2° F [4° C]) with no loss in recovery.

Interferences: Any compound that has the same retention time as MTBE will interfere with the analysis. A study was also conducted where passive samplers were exposed to 600 ppm iso-octane and 80 ppm MTBE and no significant loss in recovery was observed.

Validation Completion Date: January 1996

Physical Properties:

Mol. Weight (g/mole)	Boiling Pt. at 760 mm Hg	Density (g/ml)
88.15	54-55° C	0.740

Background

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

Research Purpose
The present work was to evaluate and validate the SKC 575 Series passive sampler containing Lot 120 coconut charcoal as a method for sampling Methyl tert-Butyl Ether (MTBE). The passive sampler was validated over a concentration range of 0.1 to 2 x 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. In addition, tests were carried out near the limit of detection for environmental sampling purposes.

Experimental
99.7% MTBE and HPLC-grade carbon disulfide (99.9%) were obtained from Aldrich Chemical Company. Iso-octane (2,2,4-trimethyl pentane) was obtained from Fisher Scientific. The 575 passive sampler containing Anasorb 120 (SKC Cat. No. 575-001) and the charcoal tubes used for atmosphere calibrations (SKC Cat. No. 226-37) are available from SKC, Inc.

A dynamic atmosphere generation apparatus was used to generate precise concentrations of MTBE 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 MTBE (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 expected sampling rate of 14.7 ml/min) at 0.1, 0.5, 1.0 and 2.0 TLV 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 TLV level. These passive samplers were all equilibrated overnight and analyzed the next day. Analytical recovery was also carried out at 0.01 TLV for low-level work.

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.

Analytical Recovery

NIOSH Requirements

Experimental Design	Interpretation of Results
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 3 higher levels require ≥ 75% recoveries with $S_r \leq 0.1$.

Results

TLV Level	Spike (µg)	Recovery (µg)	Recovery %	Mean	RSD %
0.01	7.4	12.9	87.1		
		14.0	94.5		
		13.7	92.5		
		13.6	91.8		
		12.9	87.1		
		12.8	86.4	89.9	3.8
0.02	14.8	6.1	82.4		
		7.2	97.3		
		6.7	90.5		
		6.8	91.9		
		6.6	89.2		
		6.8	91.9	90.5	5.4
0.1	118.5	119.9	101.0		
		115.8	97.8		
		120.0	102.0		
		118.5	100.0	100	1.7
0.5	592.4	582.2	98.3		
		592.4	100.0		
		578.9	97.7		
		589.2	99.5	98.9	1.1
1.0	1185	1163	98.2		
		1194	101.0		
		1126	95.1		
		1102	93.0	96.7	3.5
1.0*	1185	1123	94.8		
		1201	101.0		
		1039	87.7		
		1156	97.5	95.3	6.1
2.0	2222	2172	97.8		
		2137	96.2		
		2076	93.6	95.8	2.3

Mean of the results over the range 0.1 - 2 TLV is 97.4% (RSD 2.1%)

* Samplers pre-exposed to 80% humidity.

Sampling Rate and Capacity

NIOSH Requirements

Experimental Design

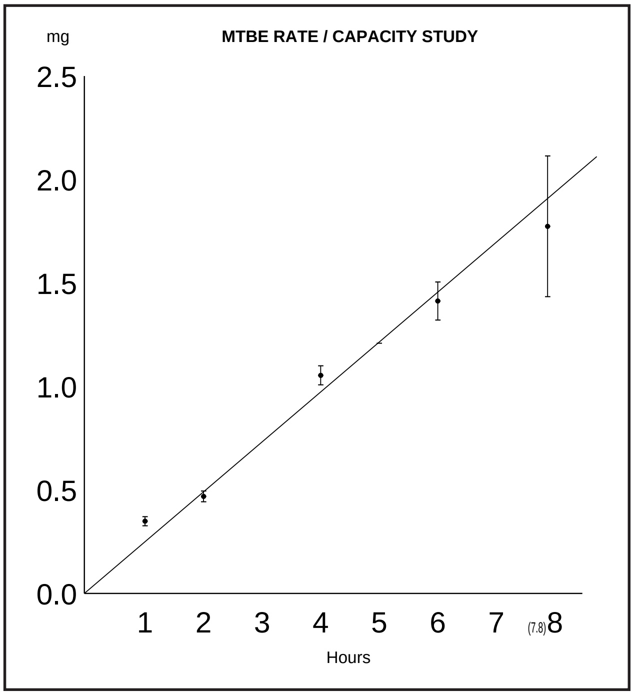
Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 and 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST.

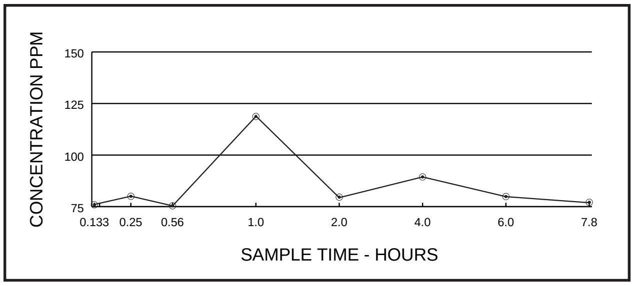
Interpretation of Results

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 (μg)	Mean (μg)	RSD%	DE Corr (μg)	Concn. (ppm)
0.133	28.5				
	29.4				
	28.5				
	29.6	29.0	2.0	29.8	75.9
0.25	56.4				
	57.5				
	59.2				
	56.8	57.5	2.2	59.0	80.0
0.56	122.2				
	122.6				
	122.6				
	118.7	121.5	1.6	124.7	75.4
1	328.1				
	349.2				
	349.5				
	337.8	341.2	3.0	350.3	118.7
2	463.6				
	467.2				
	461.4				
	438.3	457.6	2.9	469.9	79.6
4	1034.0				
	1055.0				
	1019.0				
	1002.0	1028.0	2.2	1055	89.4
6	1441.0				
	1349.0				
	1346.0				
	1375.0	1378.0	3.2	1414	79.9
7.8	1668.0				
	1590.0				
	1971.0				
	1686.0	1729.0	9.7	1775	77.1





Concentration values are calculated using the 1 through 8 hour time-weighted average sampling rate of 13.6 ml/min (2.95 μg/ppm/hr) based on a standard atmosphere of 82.4 ppm (calculated, checked by two reference methods).

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)

	MTBE Only Exposed 4 hours to analyte DE Corr (μg)	MTBE & iso-OCTANE Exposed 4 hours to analyte plus 4 hours at zero analyte concentration DE Corr (μg)
	1119	1065
	1120	1074
	1099	997
	1089	1041
	1043	999
	1221	1007
	1041	1065
	994	1066
Mean:	**1091**	**1039**
SD:	**68.5**	**33.2**
RSD:	**6.3**	**3.2**

Reverse diffusion in the presence of iso-OCTANE

	Exposed to 4 hours MTBE & iso-OCTANE (mg)		Exposed to 4 hours MTBE & iso-OCTANE Exposed to 4 hours iso-OCTANE only (mg)	
	MTBE DE Corr	iso-OCTANE	MTBE DE Corr	iso-OCTANE
	0.9547	10.24	0.8738	18.88
	0.9952	10.30	0.8671	18.57
	0.9863	10.49	0.9414	19.66
	0.9785	10.57	0.8911	19.46
	1.0010	10.84	0.8447	18.49
	1.0432	11.35	0.8168	18.80
	0.9896	10.70	0.8902	19.69
	0.9080	9.60	0.9168	19.82
Mean:	**0.9821**	**10.51**	**0.8802**	**19.17**
RSD:	**3.96**	**4.83**	**4.46**	**2.83**

Conditions: Exposure to 80 ppm MTBE and 600 ppm iso-octane for 4 hours (25˚C, 80% RH). 8 badges analyzed and 8 exposed for a further 4 hours to 600 ppm iso-OCTANE alone

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 4° 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 (≤ 39.2° F [4° C])		
	Uptake	**DE Corr**	**Mean DE Corr**		**Uptake**	**DE Corr**	**Mean DE Corr**
Day 1				Day 1			
	816.1	837.9			799.8	821.1	
	797.4	818.7			782.1	803.0	
	823.9	845.9	834.2		799.4	820.7	814.9
Day 4				Day 5			
	733.3	752.9			779.2	800.0	
	725.1	744.5			786.7	807.7	
	724.2	743.5	747.0		792.2	813.3	807.0
Day 8				Day 7			
	755.5	775.7			840.2	862.6	
	754.9	775.1			828.3	850.4	
	713.0	732.0	760.9		797.3	818.6	843.9
Day 15				Day 14			
	688.5	706.9			799.9	821.3	
	680.7	698.9			831.8	850.4	
	766.7	787.2	731.0		857.6	880.5	850.7

There is no significant loss of sample on refrigerated storage. However, the difference between the mean of the samplers stored at room temperature and those analyzed immediately is 10.5%. This is not significantly greater than the 10% allowed in the NIOSH protocol and so it is possible to store the samplers under either conditions.

Experiment altered to track storage closely and to extend storage to 14 days.
Samplers exposed for 7.75 hours for a more stringent test.

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

(All results in micrograms per ppm per minute).

Run #	Individual Monitor Results				Average*	%RSD
1	3.3233	3.2478	3.3010	3.3782	3.3188	4.7
2	3.4747	3.3869	3.5420	3.4690	3.4689	1.9
3	3.8639	3.7737	3.8332	3.9325	3.8564	2.4
4	2.7489	2.8770	2.9713	2.7201	2.8923	3.8
5	2.7496	2.9406	2.7306	2.7928	2.8032	3.8
6	3.6972	3.6507	3.6805	3.7653	3.6953	1.6
7	2.8742	2.8671	2.7111	2.8394	2.8005	3.6
8	2.4561	2.5285	2.5667	2.4793	2.5089	2.7
9	2.7375	3.0099	2.9530	2.9428	2.9089	5.9
10	2.2069	2.2069	2.1206	2.1733	2.1863	3.8
11	2.5431	2.6082	2.5413	2.5618	2.5565	1.8
12	3.8069	3.7875	3.2247	3.4818	3.6818	4.4
13	2.7207	2.7950	2.7961	2.5175	2.7065	5.8
14	2.7370	2.7573	2.6233	2.6641	2.6952	2.5
15	3.0634	3.0315	3.1476	3.1937	3.1091	2.6
16	3.5534	3.5583	3.8017	3.3447	3.5645	5.2

Notes:			
	Low face velocity	=	20 cm/sec
	Low concentration	=	0.1 TLV
	Minimum sample time	=	0.5 hours

• Averages are the mean of all analytical results

200 ppm Toluene used in the interference experiments.

Factorial Summary

Run Number			µg/ppm/hour
Run#	1	=	3.3188
Run#	2	=	3.4689
Run#	3	=	3.8564
Run#	4	=	2.8293
Run#	5	=	2.8032
Run#	6	=	3.6953
Run#	7	=	2.8005
Run#	8	=	2.5089
Run#	9	=	2.9089
Run#	10	=	2.1863
Run#	11	=	2.5565
Run#	12	=	3.6818
Run#	13	=	2.7065
Run#	14	=	2.6952
Run#	15	=	3.1091
Run#	16	=	3.5645
Average		**=**	**3.0431 = 14.1 ml/min**

	Factor	Effect	Percent	Significance
A -	Concentration	-0.14	4.6%	N.S.
B -	Relative Humidity	-0.46	15.2%	Significant
C -	Interferants	-0.30	9.9%	N.S.
D -	Time	-0.58	19.2%	Significant
E -	Face Velocity	0.18	5.9%	N.S.
F -	Orientation	-0.15	5.0%	N.S.
E1 -	ABC	0.17	5.6%	N.S.
E2 -	ABD	0.23	7.7%	N.S.
E3 -	AB + EF	-0.01	0.2%	N.S.
E4 -	AC + DF	0.19	6.2%	N.S.
E5 -	AD + CF	0.14	4.6%	N.S.
E6 -	AE + BF	-0.12	3.8%	N.S.
E7 -	CD + BE	-0.17	5.7%	N.S.
E8 -	BC + DE	-0.12	3.9%	N.S.
E9 -	BD + CE	0.07	2.3%	N.S.

Minimum Significant Effect (MSE) = ± 0.34

Significant factors were further investigated in accordance with the NIOSH protocol. Neither very short sampling periods (see rate experiment) nor very high humidities (see temperature effects experiment) showed any further effect. Therefore these effects are likely to be experimental artifacts rather than real effects.

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)

	40° C @ 2.0 x TLV
Sample (µg)	**DE Corr. (µg)**
974.2	1000.2
986.6	1012.9
989.7	1016.1
971.4	997.3
933.5	958.4
908.8	932.2

Mean:	**986.2**
RSD:	**3.4%**
Concentration[1]:	**85.5**
Uptake[2]:	**2.887**
Theoretical:	**3.025**

Uptake is within 10% of theoretical.

Experiment performed at 2 x TLV for more rigorous test.

[1] In ppm at the sampling temperature.

[2] Uptake rate measured as micrograms/ppm (sampling temperature)/hour.

Additional Tests

Additional storage study at "environmental" levels

Samples spiked with 14.8 µg and stored for 14 days at room temperature.

	µg	DE Corr (90.5%)
	14.2	15.7
	14.7	16.2
	14.8	16.3
	16.3	18.0
	16.5	18.3
	16.1	17.8
Mean		**17.1**
RSD		**6.5%**
Recovery		**115%**

Additional accuracy and precision study

Comparison With Charcoal Tubes

Exposure to 40 ppm at 25˚C (80% RH) for 196 minutes

	Monitors		Tubes	Gas Samples†
µg	**DE Corr**	**ppm**	**ppm**	**ppm**
409.5	420.4	43.6	45.9	43.0
419.2	430.4	44.6	48.1	42.4
456.3	468.5	48.6	42.7	44.4
458.5	470.6	48.8	44.8	41.7
416.1	427.2	44.3	43.7	
446.7	458.6	47.6	---*	
420.9	432.1	44.8	42.5	
413.1	424.1	44.0	46.7	
Mean		**45.8**	**44.9**	**42.9**
RSD		**4.7%**	**4.7%**	**3.3%**

† Average of 3

* Tube disconnected, sample lost

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 ≤ 10.5% for 0.5, 1 & 2 x STD levels.

All Values in µg/ppm/hr

Samplers run at 2.0 X PEL

Values for individual monitors for the Rate/Capacity Experiment

2 Hour -	2.8883	2.9108	2.8744	2.7306
4 Hour -	3.2194	3.2855	3.1748	3.1217
6 Hour -	2.9925	2.8010	2.7941	2.8546
8 Hour -	2.6643	2.5394	3.1480	2.6931

Values for individual monitors for the Factorial Experiment

Run #2 -	3.4747	3.3869	3.5421	3.4690
Run #4 -	2.7489	2.8770	2.9713	2.7201
Run #13 -	2.7206	2.7950	2.7961	2.5175
Run #15 -	3.0634	3.0315	3.1475	3.1937

Values for individual monitors for the Reverse Diffusion Experiment

4 Hours	3.3879	3.3912	3.3288	3.2970
MTBE only	3.1595	3.6977	3.1536	3.0105
4 + 4 Hours	3.1575	3.1856	2.9561	3.0857
MTBE only	2.9614	2.9864	3.1590	3.1625
4 Hours	2.8895	3.0121	2.9852	2.9616
MTBE + 10	3.0297	3.1574	2.9952	2.7482
4 + 4 Hours	2.6447	2.6244	2.8493	2.6970
MTBE + 10	2.5566	2.4722	2.6943	2.7748

Values for individual monitors for the Temperature Effects Experiment

2.8564	2.8927	2.9019	2.8481	2.7371	2.6623

Samplers run at 1.0 X PEL

Values for individual monitors for the Storage Stability Experiment

Storage - Refrigerated

Day 1 -	2.6355	2.5774	2.6342
Day 5 -	2.5678	2.5925	2.6105
Day 7 -	2.7687	2.7296	2.6275
Day 15-	2.6362	2.7411	2.7576

Storage - Ambient

Day 1 -	2.6344	2.5740	2.6595
Day 4 -	2.3671	2.3407	3.2769
Day 8-	2.4388	2.4369	2.3014
Day 21-	2.2225	2.1974	2.4750

Values for individual monitors for the charcoal tube comparison study

2.9995	3.0708	3.3427	3.3576
3.0480	3.2721	3.0830	3.0259

Samplers run at 0.1 X PEL

Values for individual monitors for the Factorial Experiment

Run #1 -	3.3265	3.2505	3.3023	3.3797
Run #3 -	3.8667	3.8783	3.8355	3.7564
Run #14 -	2.7370	2.7573	2.6233	2.6641
Run #16 -	3.5534	3.5583	3.8017	3.3447

Summary

PEL	Relative Standard Deviation	Degrees of Freedom
0.1	3.2%	12
1.0	3.9%	23
2.0	4.5%	57

Average Values in µg/ppm/hr

Experiment	Average	RSD
Rate/Capacity	2.9183	5.2%
Reverse Diffusion	3.0054	4.7%
Storage Stability	2.5334	3.1%
Factorial 0.1 PEL	3.3522	3.2%
Factorial, 2 PEL	3.0285	3.3%
Temperature Effects	2.8164	4.4%
Precision	3.1500	4.7%
Overall average	**2.9609**	**4.2%**

Overall sampling rate = 13.7 ml/min ± 1.1 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

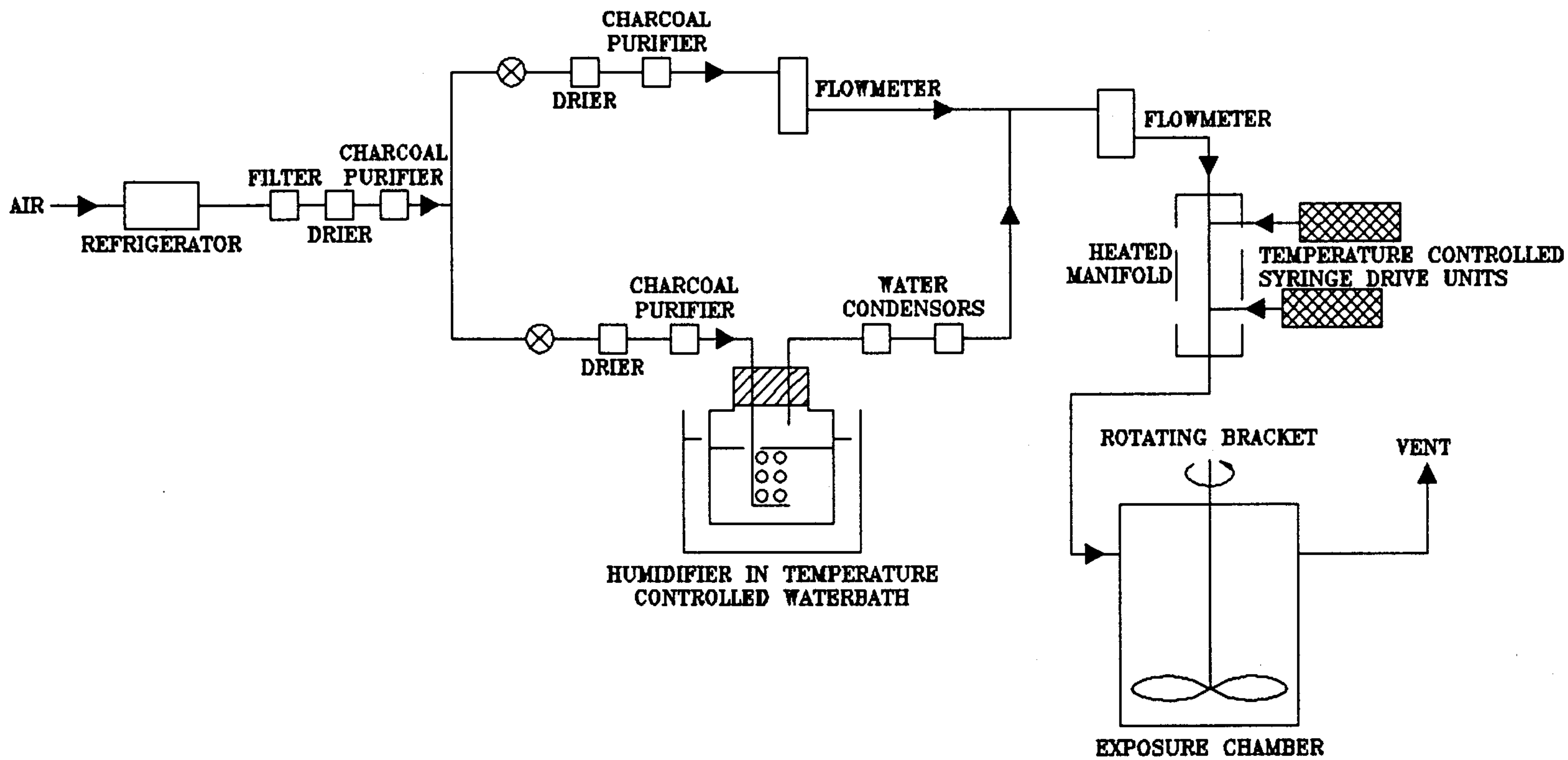
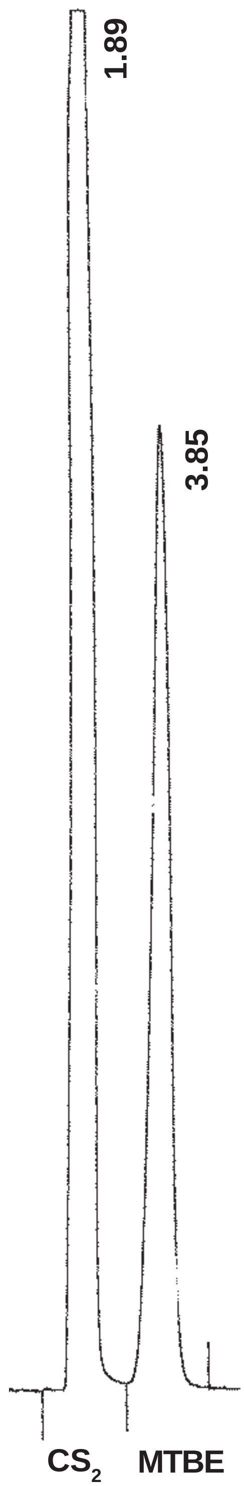


Figure 2
Analytical Instrument

Sample Chromatogram
MTBE in CS_2



GC Conditions

Column:	6 ft x 1/8" 60/80 mesh Porapak Q
Temperatures:	Column 170° C FID 150° C
Carrier Gas:	N_2
Injection:	1.75 µL

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.
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Validation of Methyl tert-Butyl Ether using SKC Passive Sampler 575-001

SKC Inc.
863 Valley View Road
Eighty Four, PA 15330 USA

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