Development of a Protocol for Laboratory Testing of Diffusive Samplers

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Introduction

There is continued interest in the use of diffusive samplers as replacements, alternatives, and supplements to active samplers. Their use is attractive because diffusive samplers are small, intrinsically safe, easy to use, and do not require sampling pumps. Numerous citations of diffusive samplers in the industrial hygiene literature and their widespread promotion has helped prompt this work.

OSHA presently has only a few methods, which require the use diffusive samplers. OSHA has been hesitant to pursue their use for several reasons. Early studies showed little correlation of results between side-by-side active and diffusive samplers. Diffusive samplers cost substantially more to use than active samplers, even when the issue of sampling pumps is considered. There is no consensus on the effects of environmental conditions, such as temperature and pressure, on sampling performance. Their relatively low sampling rates and high cost could limit their usefulness for short-term sampling. Sampling rates for diffusive samplers are not easily determined, and cannot be verified in the field.

Diffusive samplers require investment beyond their initial cost in terms of work to evaluate their performance under the varied environmental conditions, which may be encountered in their use. An evaluation protocol is necessary to systematically and efficiently test their performance. Two such protocols, the NIOSH and the CEN protocols (Refs. 1 and 2), are often cited in the literature. The NIOSH Protocol is especially comprehensive, but it is time-consuming and expensive to implement. The CEN Protocol is also very comprehensive, some tests are similar to the NIOSH Protocol, and is in the final stages of development by the European community. One intent of this work was to develop the basis for a protocol, which requires less laboratory testing, but would still provide a defensible evaluation of sampler performance. This approach has been taken by others (Ref. 3), but their testing does not fully address the needs of OSHA.

This work was performed by examining the characteristics of 3M Model 3520 Organic Vapor Monitors (OVM) used to sample a solvent mixture. The 3M OVM was selected because it has found widespread user acceptance especially in the private sector, and it has been marketed for several years. The solvent mixture contained different classes of chemicals anticipated to provide a difficult challenge to the OVM. The NIOSH Protocol was generally followed except when it was judged that an experiment could be changed to provide more efficient or more convenient testing of the performance factor under investigation. Additional experiments were conducted when deemed appropriate. It was anticipated that experience gained as a result of this work would culminate in a hybrid protocol that could be applied to diffusive samplers in general.

Reagents

Methyl ethyl ketone (MEK), Burdick & Jackson Laboratories, Inc., Distilled-In-Glass grade, Lot 7938.

2-Propanol (IPA), Fisher Scientific, Optima grade, Lot 936625.

Methylene chloride (MeCL), Baxter Burdick & Jackson, B&J Brand High Purity Solvent, Lot 946571.

Toluene (Tol), Baxter Burdick & Jackson, B&J Brand High Purity Solvent, Lot BA 297.

Butyl Acetate (BA), Sigma-Aldrich Chemical Co., 99.7% HPLC Grade, Lot 00824 PF.

A solvent mixture was prepared in the following ratio: 184-mL MEK, 306-mL IPA, 54-mL MeCL, 234-mL Tol, and 222-mL BA. This mixture was used to generate test atmospheres, and to prepare test samples and analytical standards.

Sample desorbing solution. The solution was composed of 50% (v/v) carbon disulfide and 50% (v/v) N,N-dimethylformamide (DMF) with internal standard (0.25 µL/mL p-cymene). This solution was prepared from reagent grade chemicals of various lot numbers.

Sampling Media

Organic Vapor Monitors, 3M Model 3520 with back-up section, various lot numbers including Lot 4158 009 (expiration date: 12/07/95). None of the monitors used in this work exceeded their expiration date. Blank coconut-shell charcoal pads identical to those in the monitors were obtained from 3M. These pads were used for desorption efficiency experiments.

Carbosieve S-III adsorbent tubes, carbon molecular sieve, Orbo 91, 130/65 mg sections, Supelco, Inc., Lot 1001. These sampling tubes were used as an independent means to monitor concentrations of test atmospheres.

Apparatus

Samples were analyzed by gas chromatography. A Hewlett-Packard Model 5890 GC equipped with a Chem-Station, an automatic sample injector, and an FID were used. Separations were performed on a Restek Stabilwax® (60-m × 0.32-mm ID × 1.00-µm df) column. The injection volume was 1 µL with a 50 to 1 split. The GC was temperature programmed from 40 to 220°C in three ramps: 40 to 90°C at 5°/min, 90 to 170°C at 10°/min, and 170 to 220°C at 15°/min. The GC oven was maintained at 40°C for 1 min following injection, and held at 220°C for 5 min following completion of the temperature program. The hydrogen carrier gas flow rate was 1.2 mL/min, the nitrogen auxiliary gas flow rate was 36.1 mL/min, the septum purge flow rate was 2.1 mL/min, the detector hydrogen gas flow rate was 29.1 mL/min, and the detector air gas flow rate was 370 mL/min.

Samples were collected from dynamically-generated test atmospheres using an apparatus constructed from stainless steel. The apparatus consisted of two chambers which were connected in series, and which were designed to permit simultaneous exposure of a large number of samplers to the same test atmosphere at two significantly different linear (face) velocities. A complete set of drawings and specifications is included in Ref. 4.

Humid air (for use with controlled test atmospheres) was generated using a Miller-Nelson Model HCS 301 Flow-Temperature-Humidity Control System. This system was equipped with a 500 L/min mass flow controller.

Relative humidity and temperature of the test atmospheres within the exposure apparatus were monitored with a Solomat MPM 500e meter equipped with a Model 355RHX humidity/temperature probe and with a EG&G Model 911 Dew-All Digital Humidity Analyzer. The probes were calibrated by the manufacturer.

Dilution air flow rates (50-360 L/min) were measured with a Equimeter No. 750 gas meter. The meter readings for several different flow rates were compared to those of a Singer DTM 115 gas meter (which had been tested by the local natural gas distributor and found to be accurate) that was connected in series before the Equimeter. Both meters gave very similar readings.

The solvent mixture was metered into the system with an Isco 100 DM syringe pump equipped with a cooling/heating jacket and an insulation cover package. The pump was operated in the constant flow mode. The temperature of water in the cooling/heating jacket was maintained at 23 °C with a Forma Scientific Model 2006 CH/P Bath and Circulator.

Solvent vapors were generated by pumping the liquid into a vapor generator where it evaporated into the dilution air stream (Figure 1). The vapor generator consisted of a 10-cm length of ¼-inch diameter glass tubing with a small hole in the side. The hole was just large enough for 1/16-inch diameter tubing to be inserted. The glass tubing was placed inside a ½-inch stainless steel Swagelok tee wrapped with heating tape. The 1/16-inch tubing entered the third port of the tee through an adaptor and was inserted about 1/8-inch (approximately in the center) into the glass tubing through the small hole. Solvent was pumped through the steel tubing and into the glass tubing. The liquid flow rate was adjusted so that liquid did not accumulate in the evaporation tube. The entire dilution air stream passed through the tee and swept generated vapors into the apparatus.

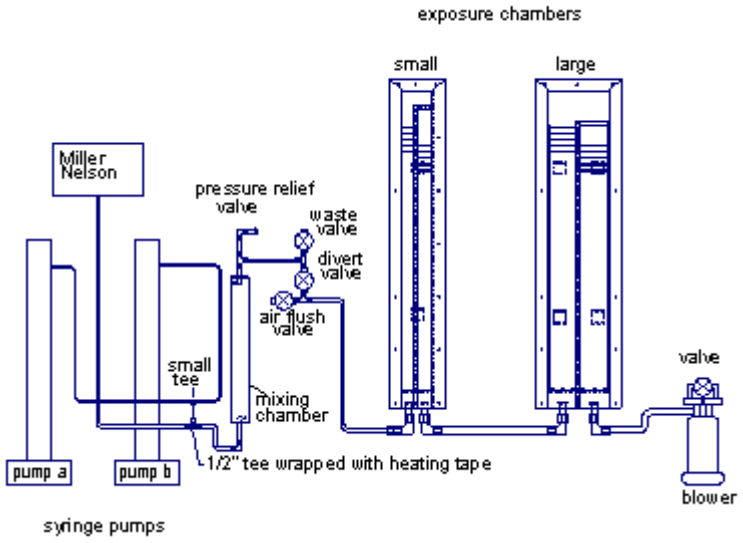

Figure 1. Test atmosphere generation and sample collection apparatus.

The following is a description of the arrangement of the apparatus which was placed in a walk-in hood. Liquid from which vapors were to be dynamically generated was pumped with a precision Isco syringe pump (an identical pump and a small solvent mixing tee was available when its use was desired) into a heated manifold where it evaporated. The generated vapors were swept from the manifold with dilution air. Stainless steel tubing (½-inch O. D.) connected with stainless steel Swagelok fittings was used to transfer the test atmosphere. The dilution air was humidified (if desired) using a Miller-Nelson Flow-Temperature-Humidity controller. The vapor/dilution air mixture then passed into a 3×24-inch stainless steel mixing chamber which could be removed from the system. The test atmosphere next passed through ½-inch ball valves where it could be either diverted to waste, or directed into the exposure chambers. An additional ball valve allowed the chambers to be purged with room air. The transfer tubing diameter was increased from ½ inch to 1 inch at this point using a Swagelok adaptor attached to the chamber inlet. Tube and fitting diameter was increased to 1 inch after this fitting to help reduce any increased pressure to ambient. The 1-inch O. D. chamber inlets have small stainless steel deflectors to help insure that the test atmosphere completely fills the

sampling chambers. Stainless steel screens were placed inside the chambers for the same purpose. This design should cause air flow through the chambers to be somewhat turbulent. A Gast Model R1102 blower was used to move the test atmosphere through the apparatus. A gate valve was used to help regulate pressure by adding make-up air to the blower. Pressure (positive as well as negative) within the chambers was monitored with U.S. Gauge (0 to 15 inches of water), Noshok (0 to -30 inches of water), and Marsh (0 to -35 inches of water) gauges. Linear velocities of the test atmospheres were calculated by dividing the volumetric flow of each atmosphere by the cross-sectional area available for air flow in each chamber. The cross-sectional area available for air flow was the cross-sectional area of each chamber reduced by the cross-sectional areas of the OVMs. Humidity and temperature were monitored only within the large chamber because of access port limitations. This arrangement of the apparatus is shown in Figure 1.

A glass exposure chamber (approximately 3×4×24 inches) contained within a glass water jacket was used for the temperature experiments. The temperature of water pumped through the water jacket was controlled with a Forma Scientific CH/P Model 2067 Temperature Control System Bath and Circulator. Diffusive samplers were suspended within the chamber from a sampling tree which was constructed of glass tubing. Active sampling tubes were attached to Y-tubes on the tree with silicone tubing. This chamber and sampling tree are shown in Figure 2.

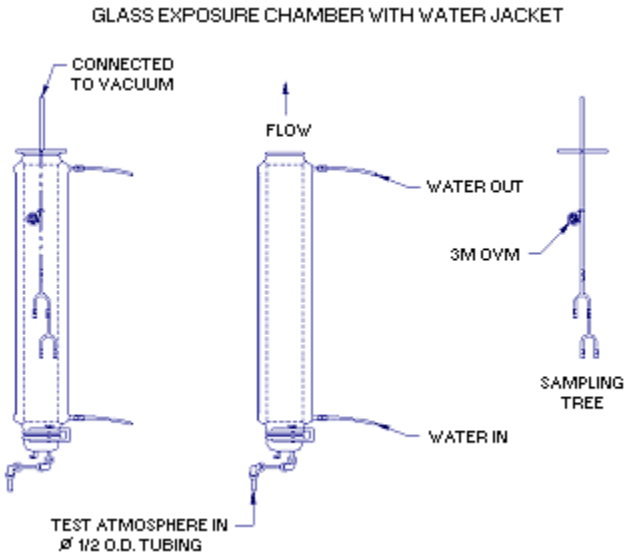

Figure 2. Glass exposure chamber.

Experimental

The following include a synopsis of elements of the NIOSH Protocol, and summary conditions under which associated experiments were performed. Complete experimental conditions are included in a separate Back-up Data document.

Analytical Recovery

The NIOSH Protocol requires that analytical recovery (desorption efficiency) be determined from the sampling medium by liquid spiking four monitors at each concentration level of 0.1, 0.5, 1.0 and 2.0 times the exposure standard (STD). A minimum of 75% recovery is required at each of the three

higher levels. The term STD should be interpreted for this work simply as tested levels of analytes (target concentrations).

Desorption efficiency experiments were performed in this study by liquid spiking individual 3M coconut charcoal pads and 130-mg portions of Carbosieve S-III adsorbent (each medium contained in separate sealed glass vials) with the solvent mixture, allowing the spiked samples to equilibrate overnight, and then desorbing the samples the next day. Dry media were used as received from the vendors. Some media were pre-conditioned with humid air before liquid spiking by drawing approximately 6 L of humid air (80 % RH and 25°C) through Carbosieve S-III adsorbent tubes, and by exposing monitors to humid air (80 % RH and 25°C) for 2 hours.

All samples were analyzed by GC following desorption with 2 mL of a solvent mixture containing 50% DMF in carbon disulfide with 0.25 µL/mL of p-cymene internal standard. The charcoal pads were removed from the 3M monitors and placed in separate 4-mL glass vials to be desorbed for 1 hour on a tube rotator. 3M OVMs are designed to be desorbed in-situ, but this feature was not used to avoid possible solvent leakage from the monitor cases. The contents of the Carbosieve S-III sampling tubes were desorbed in a similar manner as the monitors.

Sampling Rate and Capacity

The NIOSH Protocol requires that sampling rate and capacity be established by plotting analyte concentration of the test atmosphere (as determined with the monitor) against time. The Protocol specifies that test atmospheres will contain two times the exposure standard (2× STD) at 80% relative humidity, and that the face velocity be at least 0.2 m/s. The linear horizontal portion of the curve indicates constant sampling rate, and capacity is exceeded when the apparent concentration rapidly decreases. The time at which sampling rate becomes constant is defined as the point where the determined concentration is ±25% of the true concentration of the test atmosphere. This point is the shortest recommended sampling time (SRST). The maximum recommended sampling time (MRST) is defined as 0.67× the time at which capacity is exceeded for a single analyte, and 0.33× capacity for multiple analytes.

Sampling rates and capacities of 3M OVMs for the solvent mixture were determined in this study by sampling controlled test atmospheres for increasing periods of time (Table 1), and then analyzing the monitors to determine the mass of analyte collected. The capacity of the OVMs was quickly exceeded when test atmospheres contained 2× STD (approximately 2× OSHA PEL) of each component, therefore, the concentration was reduced to about 1× STD for each component (with the exception of methylene chloride) so that the sampling time could be extended. Seventy-five ppm was used as the STD for methylene chloride (current OSHA PEL is 500 ppm) to help prevent premature sampler saturation. The total challenge was about 4× STD, based on the sum of the PEL fractions (analyte concn/PEL). Four monitors per time period were exposed for ten time periods of from 7.5 min to 12 hours.

Similar experiments were performed to test the effects of increasing face velocity on sampling rates for the mixture (Table 1), and also for individual components of the mixture (Table 1). Linear velocity (lin vel) was controlled by changing the dilution air flow rate. Average analyte concentrations used in sampling rate experiments, and OSHA PELs are shown below. Sampling time was approximately two hours.

Table 1
Concentrations (µg/L) of Analytes Used in Sampling Rate experiments

	MEK	IPA	MeCL	Tol	BA
OSHA PEL	590	980	1740	755	710
mixture sampled for increasing time	550	890	265	750	725
mixture sampled at increasing lin vel	550	890	265	750	725
individual components sampled at increasing lin vel	610	980	175	755	720

Reverse Diffusion

The NIOSH Protocol specifies that 20 monitors be exposed to 2× STD and 80% relative humidity for 0.5× MRST, that 10 monitors be removed and analyzed after 0.5× MRST, and that the other set of 10 monitors be exposed to clean air at 80% relative humidity for the remainder of MRST.

Twenty-eight monitors were exposed in this study by sampling the solvent mixture for the two-hour MRST determined for the solvent mixture. The analyte concentration was 1× STD and the relative humidity was 68%. Fourteen monitors were then removed from the sampling chambers and analyzed. Sampling was continued with the remaining fourteen monitors exposed to humid air without analytes for another two hours. Sample results from the OVMs exposed for two hours to the solvent mixture were compared to those exposed for the original two hours and an additional two hours of clean air. Samples were collected at linear velocities of 0.2 and 1.1 m/s.

Additional experiments designed to evaluate the ability of the monitor to respond to intermittent high levels (pulses) of the mixture were performed. Monitors were exposed to cyclic concentrations of the mixture, which were abruptly increased from 0.1× STD to 2× STD, maintained at 2× STD for a few minutes, and then decreased to the initial level until the next pulse. One test had three five-min pulses over 90 min total sampling time, and the second had one five-min and four three-min pulses over 116 min. The relative humidity of the test atmospheres was 68.2 % and the linear velocity was 0.3 m/s.

Storage Stability

The NIOSH Protocol requires that three sets of ten storage stability samples be collected from a test atmosphere at 1× STD and 80% relative humidity for 0.5× MRST. The first set is analyzed within one day, the second set following two weeks storage at about 25°C, and the third set after two weeks storage at about 5°C. Storage stability is acceptable if there is <10% (at the 95% confidence level) difference between the means of stored samples and the set analyzed within one day of generation.

Storage tests for this work were conducted in this study following OSHA OME Method Evaluation Guidelines (Ref. 5) because those tests provide better documentation of storage stability over time. OME guidelines stipulate that storage loss following two weeks storage be no more than 10%, that recovery following two-weeks storage be at least 75%, and that storage test results and sampling error be used to calculate sampling and analytical error. Storage loss is calculated relative to samples analyzed on the same day they are generated (Day Zero).

Thirty-six samples were simultaneously collected by sampling the solvent mixture at 1× STD, 66% relative humidity, and 0.2 m/s for two hours. The samples were prepared for storage after removal

from the exposure apparatus by complying with 3M's instructions (Ref. 6): separate individual monitors into their two component sections, install cup and closure cap, place the two sections in the aluminum can, and seal the can with its plastic cap. Six of the samples were analyzed immediately after collection, and the remaining samples separated into two sets. One set was stored at ambient temperature (about 25°C), and the other set stored in a refrigerator at about 4°C. Three samples were selected from each set every three or four days and were analyzed.

Factor Effects

NIOSH has identified six factors (analyte concentration, exposure time, face velocity, relative humidity, interferant, and monitor orientation) that can affect monitor sampling performance. Sixty-four experimental runs (26) would be required to evaluate combinations of each factor at two levels per factor. NIOSH has recognized that this is an excessive number of experimental runs, and has devised a 16-run fraction of the full factorial experiment that is capable of revealing any of these factors having a significant effect on performance, free of two-factor interactions. Some two and three-factor interactions, in which the combined effect of certain factors are compared to their separate effects, can also be tested by this experimental design. This fraction of the full factorial is based on the Plackett-Burman screening design. A Plackett-Burman screening design is a specific fraction of the full factorial that has properties, which allow efficient estimation of the effects of the variables under study (Ref. 13). The following is a representation of the experimental design, and this format is suitable for use in an electronic spreadsheet. The effects of the factors are examined at two levels. The two levels are a high level (designated by a "1"), and a low level (designated by a "-1"). Columns ×1 through ×6 represent the factors, for example, ×1 is analyte concentration. The E columns provide an estimate of experimental error, a means to calculate minimum significant effect (MSE), and estimates of two and three-factor interactions. Columns E1 and E2 depict the three-factor interactions, and columns E3 through E9 represent two-factor interactions. Rows 1 through 16 are the experimental trials. Experiments are performed under the conditions specified in the appropriate row. For example: experiment 1 is conducted at low analyte concentration, low relative humidity, low interference level, high exposure time, high linear velocity, and perpendicular monitor orientation. Four monitors are exposed under the required conditions for each experimental trial. The analytical results are calculated in percent recovery based on amount of analyte present in the test atmosphere, and are placed in the R column (or in a separate array with the same format). Each experimental result (R) is multiplied by the number (either 1 or -1) in each cell, and that cell content is replaced by the result. For example, if the result for trial 1 was 95%, ×1 (trial 1) would become -95, ×2 (trial 1) become -95, ×3 (trial 1) become -95, ×4 (trial 1) become 95...E9 (trial 1) become -95. Alternatively, the results could be entered in another table. The sum of the positive numbers in a column (for example: the ×1 Column) is entered in the "Sum+" row under each column. The sum of the negative numbers in a column (for example: the ×1 Column) is entered in the "Sum-" row under each column. Add the absolute values of the "Sum+" and "Sum-" numbers for each column and place that result in the "Total" row. The "Total" result should be the same for all columns. Add the "Sum+" number and the "Sum-" number and place that result in the "Diff" row. Divide the "Diff" number by 8 (the number of positive numbers in each column, and put that result in the "Effect" row. The "Effect" number is the factor effect for the × columns, and an estimate of experimental error for the E columns. The experimental error is calculated by the following equation:(1/9×(E12+E22+E32+.. .+E92))0.5. The minimum significant effect (MSE) is calculated by multiplying the experimental error by the t statistic at the 95% confidence level for the number of E columns (degrees of freedom). In this case the t statistic is 2.26 because there are nine degrees of freedom. Factors with "Effect" numbers (absolute value) exceeding "MSE" have significant effect on the sampling performance of the monitors and should be further studied. E columns with "Effect" numbers (absolute value) exceeding "MSE" are an estimate of factor interactions. The interactions (Refs. 1 and 13) are shown in Table 23. A worked example is presented below, as are others in a Back-up Data document for this work.

Table 2
Factor Effects Experimental Design

	×1	×2	×3	×4	×5	×6	E1	E2	E3	E4	E5	E6	E7	E8	E9	R
trial	concn	RH	inter	time	lin vel	orien										
1	-1	-1	-1	1	1	1	-1	1	1	1	-1	-1	-1	1	-1	
2	1	-1	-1	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	
3	-1	1	-1	-1	1	-1	1	1	-1	1	1	-1	1	-1	-1	
4	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	-1	-1	1	
5	-1	-1	1	1	-1	-1	1	1	1	-1	-1	1	1	-1	-1	
6	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	-1	1	
7	-1	1	1	-1	-1	1	-1	1	-1	-1	1	1	-1	1	-1	
8	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
9	1	1	1	-1	-1	-1	1	-1	1	1	-1	-1	-1	1	-1	
10	-1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1	1	
11	1	-1	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	-1	
12	-1	-1	1	-1	1	1	1	-1	1	-1	1	-1	-1	-1	1	
13	1	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1	-1	-1	
14	-1	1	-1	1	-1	1	1	-1	-1	1	-1	1	-1	-1	1	
15	1	-1	-1	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	
16	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	
Sum+																
Sum-																
Total																
Diff																
Effect																
Error																
MSE																

Table 3
Worked Example of Factor Tests Results for MEK

	×1	×2	×3	×4	×5	×6	E1	E2	E3	E4	E5	E6	E7	E8	E9	R
trial	concn	RH	inter	time	lin vel	orien										
1	-104.7	-104.7	-104.7	104.7	104.7	104.7	-104.7	104.7	104.7	104.7	-104.7	-104.7	-104.7	104.7	-104.7	104.7
2	102.9	-102.9	-102.9	-102.9	-102.9	102.9	102.9	102.9	-102.9	-102.9	-102.9	-102.9	102.9	102.9	102.9	102.9
3	-107.5	107.5	-107.5	-107.5	107.5	-107.5	107.5	107.5	-107.5	107.5	107.5	-107.5	107.5	-107.5	-107.5	107.5
4	97.9	97.9	-97.9	97.9	-97.9	-97.9	-97.9	97.9	97.9	-97.9	97.9	-97.9	-97.9	-97.9	97.9	97.9
5	-90.6	-90.6	90.6	90.6	-90.6	-90.6	90.6	90.6	90.6	-90.6	-90.6	90.6	90.6	-90.6	-90.6	90.6
6	107.9	-107.9	107.9	-107.9	107.9	-107.9	-107.9	107.9	-107.9	107.9	-107.9	107.9	-107.9	-107.9	107.9	107.9
7	-101.3	101.3	101.3	-101.3	-101.3	101.3	-101.3	101.3	-101.3	-101.3	101.3	101.3	-101.3	101.3	-101.3	101.3
8	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7	107.7
9	97.2	97.2	97.2	-97.2	-97.2	-97.2	97.2	-97.2	97.2	97.2	-97.2	-97.2	-97.2	97.2	-97.2	97.2
10	-109.6	109.6	109.6	109.6	109.6	-109.6	-109.6	-109.6	-109.6	-109.6	-109.6	-109.6	109.6	109.6	109.6	109.6
11	102.5	-102.5	102.5	102.5	-102.5	102.5	-102.5	-102.5	-102.5	102.5	102.5	-102.5	102.5	-102.5	-102.5	102.5
12	-103.1	-103.1	103.1	-103.1	103.1	103.1	103.1	-103.1	103.1	-103.1	103.1	-103.1	-103.1	-103.1	103.1	103.1
13	103.3	103.3	-103.3	-103.3	103.3	103.3	-103.3	-103.3	103.3	-103.3	-103.3	103.3	103.3	-103.3	-103.3	103.3
14	-95.9	95.9	-95.9	95.9	-95.9	95.9	95.9	-95.9	-95.9	95.9	-95.9	95.9	-95.9	-95.9	95.9	95.9
15	105.5	-105.5	-105.5	105.5	105.5	-105.5	105.5	-105.5	-105.5	-105.5	105.5	105.5	-105.5	105.5	-105.5	105.5
16	-92.3	-92.3	-92.3	-92.3	-92.3	-92.3	-92.3	-92.3	92.3	92.3	92.3	92.3	92.3	92.3	92.3	92.3
Sum +	825	820.5	819.9	814.5	849.4	821.4	810.3	820.5	796.8	815.7	817.8	804.4	816.4	821.2	817.2	
Sum -	-805	-809	-810	-815	-781	-809	-820	-809	-833	-814	-812	-826	-814	-809	-813	
Total	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	1630	
Diff	20.07	11.1	9.833	-0.99	68.84	12.9	-9.25	11.07	-36.3	1.485	5.727	-21.1	2.894	12.46	4.553	
Effect	2.509	1.387	1.229	-0.12	8.605	1.613	-1.16	1.384	-4.53	0.186	0.716	-2.64	0.362	1.558	0.569	
Error	1.949															
MSE	4.404															

Both linear velocity and the E3 interaction were significant factors which influence the sampling performance of OVMs used to collect MEK. The E3 interaction is completely confounded between concentration and relative humidity or between linear velocity and monitor orientation. The six factors and their respective levels required in the NIOSH Protocol are shown in Table 4.

Table 4.
Levels Required In NIOSH Protocol

Factor	high level (1)	low level (-1)
Concn	2× STD	0.1× STD
relative humidity	80%	10%
Interference	1× STD	absent
exposure time	MRST	SRST
linear velocity	1.5 m/s	0.1 m/s
monitor orientation	perpendicular	parallel

Experimental conditions for this work are shown in Tables 5 and 6. Low (-1) concentration was approximately 0.1× STD, high (1) 1× STD; 1 monitor orientation was the monitor face positioned perpendicular (perp) to the air flow direction, -1 was parallel (paral); interferant was provided by the components of the mixture and was 1 or -1 by declaration.

Table 5
Average Concentrations

concn level	MEK	IPA	MeCL	Tol	BA
low (µg/L)	56	98	26	76	76
high (µg/L)	556	892	268	751	776

Table 6
Experimental Conditions

trial no.	Concn	RH (%)	time (min)	lin vel (m/s)	orientation
1	Low	6.8	121	2.0	perp
2	High	11.6	30	0.1	perp
3	Low	76.0	30	1.9	paral
4	High	71.5	120	0.1	paral
5	Low	12.4	120	0.1	paral
6	High	5.5	30	1.9	paral
7	Low	71.2	30	0.1	perp
8	High	80.0	120	2.0	perp
9	High	71.5	30	0.1	paral
10	Low	80.4	121	1.8	paral
11	High	11.6	120	0.1	perp
12	Low	18.6	30	2.0	perp
13	High	80.0	30	2.0	perp
14	Low	71.2	120	0.1	perp
15	High	5.5	120	1.9	paral
16	Low	12.4	31	0.1	paral

Temperature Effects

The NIOSH protocol requires three experiments in which 10 monitors each are exposed to 0.5× STD at 10, 25, and 40°C for 0.5 MRST. The data are normalized prior to examination. The high and low temperature results are compared to theoretical, or to results from a reference method shown to be temperature independent (or temperature correctable).

Three experiments were performed in this study using the glass-jacketed apparatus shown in Figure 2. The temperature of the sampled air, and of the sampling media can be controlled with this apparatus. The experiments were conducted at 8, 25, and 40°C. The concentration of the test atmosphere was about 1× STD, the linear velocity about 0.1 m/s, and the relative humidity of the Miller-Nelson humid air generator was set at 80%. The relative humidity of the air inside the sampling chamber depended on the temperature of the test atmosphere. Four monitors were exposed in each of the tests.

Accuracy and Precision

The NIOSH Protocol acceptability criterion for accuracy is results within ±25% of the reference value at the 95% confidence level over the range 0.5 to 2× STD. Data at the 0.1× STD level are not included in the computations, however, its importance is emphasized when used for purposes like the ACGIH fractional treatment of exposure to mixtures (Ref. 7). Several of the NIOSH concentration levels were designed to provide data for accuracy and precision calculations. The source of the data to be used for this purpose is as follows: 2× STD data from the 4 to 8 hour samples of the Sampling Rate and Capacity Experiment, the Reverse Diffusion Experiment, runs 2, 4, 13, and 15 of the Factor Experiment; 1× STD data from the Storage Stability Experiment; 0.5× STD data from the Temperature Effects Experiment. Runs 1, 3, 14, and 16 of the Factor experiments could be used to evaluate monitor performance at 0.1× STD.

It was not possible to pool relative standard deviations over the range 0.5 to 2× STD in this study because most runs were performed at 1× STD. The data for 1× STD and for 0.1× STD were pooled separately. NIOSH specified which data to pool and those instructions were followed as closely as feasible. At least four samples were collected for each test and the RSD of the four samples was calculated. RSDs were pooled after first subjecting them to the Cochran Test for homogeneity (Ref. 5). The 1× STD data source was 6 and 8 hour samples from Sampling Rate and Capacity experiment; first set of samples (0.21 m/s) from Reverse Diffusion experiment; trials 2, 4, 13, and 15 from Factor Effects experiment; day zero samples from Storage Stability experiment; and 8, 25, and 40°C samples from Temperature Effect experiment. The 0.1× STD data source was trials 1, 3, 14, and 16 of the Factor Effects experiment.

Accuracy and precision was also assessed in terms of sampling rate variation using those obtained for the factor tests. Another way to examine sampler accuracy and precision would be to use the convention presented in the SLTC OME Method Evaluation Guidelines (Ref. 5). OME Guidelines utilize storage stability test data to calculate a sampling and analytical error (SEE) number which is representative of the method. SEE is not statistically sophisticated, but it has served the needs of OSHA for several years. SEEs were calculated from the storage stability data for this work.

Shelf Life

The NIOSH Protocol requires that the monitors be continuously examined throughout the evaluation to detect changes in physical appearance, sampler blank values, and etc.

No changes were observed in 3M OVMs tested during this work. The duration of the work was about one year.

Behavior in the Field

The NIOSH Protocol specifies that field sampling studies be performed in which diffusive sampler results are compared to results from a reference method. Field environmental conditions, having significant effect on monitor performance, may exist which were not considered in laboratory tests. No field samples were collected during this work.

Results and Discussion

The following include graphs and summary tables of the results from the experiments. Complete experimental results are included in the separate Back-up Data document for this work.

Desorption Efficiency

The results of the desorption efficiency studies are summarized in Table 7. These overall averages were used in subsequent work. All samples were desorbed with a 50/50 mixture of carbon disulfide and DMF for 1 hour on a tube rotator. This mixture was used because the presence of collected water has been observed to cause low apparent recoveries for water soluble compounds by partitioning the analyte in the water phase when samples were desorbed with pure carbon disulfide, or with 1% DMF in carbon disulfide. The high level of DMF served to prevent two-phase systems. Also, it is very desirable to use a common desorption solvent for organic vapor diffusive samplers because they are intended to be general samplers used for a wide variety of chemicals. The desorption efficiencies obtained from 3M pads were high and constant, except for very high levels of MeCL (>5 mg) and MEK (>11 mg). Results from these very high levels were low, and were not included in the overall averages. The presence of water had no significant effect on desorption efficiency. Desorption efficiencies obtained for Carbosieve S-III were also constant and adequately high.

Table 7
Percent Desorption Efficiency

	MEK	IPA	MeCL	Tol	BA
Carbosieve S-III	95.0	79.3	101.2	94.8	88.0
3M Pads	99.6	99.8	99.7	96.1	98.6

Sampling Rate and Capacity

Sampling rates, for this work, were calculated by dividing mass collected (µg) by sampling time (min) multiplied by concentration of the test atmosphere (µg/L): sampling rate=µg/((µg/L)×min). The result (L/min) is expressed in mL/min, the same units often used for adsorbent tubes, although it should be recognized that no air actually flows through diffusive samplers. Four variations of this calculation were performed: (1) test atmosphere concentrations determined from active samples, amount found on back-up pad multiplied by 2.2 and added to the amount collected on front pad; (2) same as 1, but concentrations of test atmosphere determined from pump rate, concentration of analyte in solution, and dilution air volume; (3) same as 1, but amount collected on back-up pad ignored; and (4) same as 2, but amount collected on back-up pad ignored.

The use of back-up pads in diffusive samplers does not entirely parallel the use of back-up sections in active sampling tubes. In addition to providing evidence that capacity of the front pad has been exceeded, monitor back-up pads can reveal a condition known as reverse diffusion. Reverse diffusion is caused by use of an unsuitable adsorbent, and is characterized by unsatisfactory retention of the analyte on the front pad. 3M specifies that the amount of any analyte found on the secondary adsorbent section (back-up) be multiplied by 2.2 to compensate for a reduction in sampling rate caused by the increased path length from the front to the back section. The corrected amount found on the back-up is added to the amount found on the primary adsorbent. The ratio of uncorrected secondary to primary results must be <0.50 for the sample to be considered valid. The use of back-ups in diffusive samplers has been criticized, and the required 2.2 factor attributed to loss of a portion of the analyte from the sampler (reverse diffusion) (Ref. 8), but comparison of Figures 3-6 show their utility.

Results for the sampling rate and capacity experiments (conducted at a linear velocity of 0.3 m/s) are presented in Figures 3-6. Note that the x-axes of these Figures are constructed in log scale to better show the results from short and medium sampling times. All these figures show that sampling rates for Tol, IPA, and BA did not become constant (linear) until 31 min, therefore, the shortest

recommended sampling time (SRST) for the mixture is 30 min. Figures 5 and 6 show that the capacity of the front pad of the monitors for MeCL is exceeded by 120 min, and that the maximum recommended sampling time (MRST) for the mixture should be less than 120 min. Figures 3 and 4 show that MRST can be extended past 120 min if the amounts found on the back-up are included in the total amount. MRST was set at 120 min. Figures 3 and 5 depict somewhat less variation in sampling rates between 31 and 120 min than do Figures 4 and 6. These figures show that determination of test atmosphere concentrations from active samples gave slightly more consistent results than did determination of concentrations from experimental parameters, and illustrate that an independent means of concentration determination/verification is useful to detect minor variation from theoretical concentration.

A consequence of this strategy (test atmosphere concentration determined from active samples) is that results from diffusive samplers would be forced to be comparable to active samplers. Obviously, there would be no bias between the two methods. The technique should not be employed if active sample results show uncorrectable bias. An example of uncorrectable sampling bias is instability of the analyte on the collection medium. Correction of sample results for desorption efficiency is an example of correctable bias. Evidence of uncorrectable bias, either in sampling or in test atmosphere generation, could be active results which are not close to the theoretical level. More than one independent means may have to be employed if generation of test atmospheres is not quantitative. Active sampler bias ((average of active results/true concentration)-1) was no more than 5% when concentration calculated from experimental parameters was considered the true concentration. No significant uncorrectable bias in active results was observed during this work, perhaps because all active samples were analyzed immediately after collection. A summary of active results, calculated in percent of theoretical based on experimental parameters, is presented in Table 8.

Table 8
Summary of Active Sample Results

	MEK	IPA	MeCL	Tol	BA
percent of theoretical	96.6	99.4	96.5	95.1	100.0
RSD	4.63	6.56	4.94	4.51	5.12

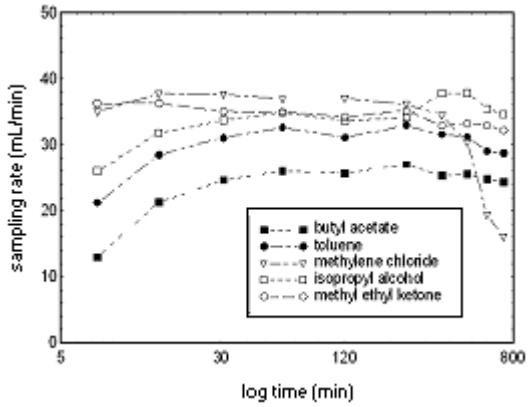

Figure 3. Test atmosphere concentrations determined from active samples, amounts found on back-up included in total amount.

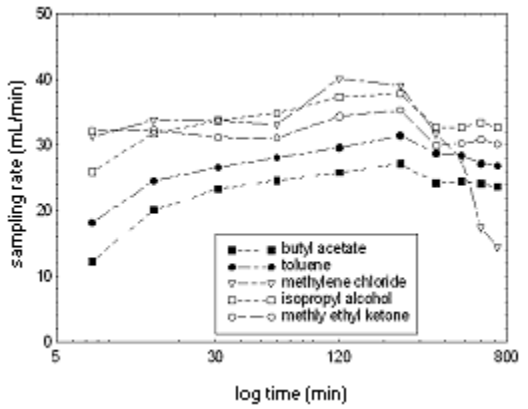

Figure 4. Test atmosphere concentrations determined from experimental parameters, amounts found on back-up included in total amount.

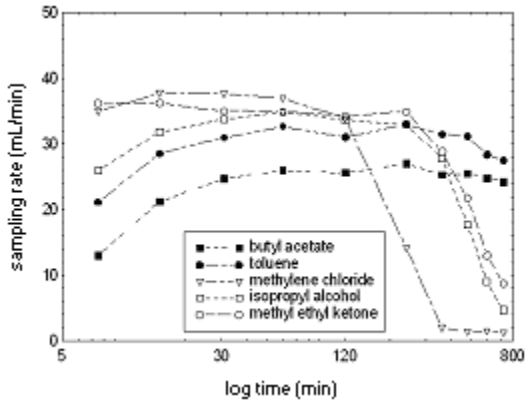

Figure 5. Test atmosphere concentrations determined from active samples, amounts found in back-up not included in total amount.

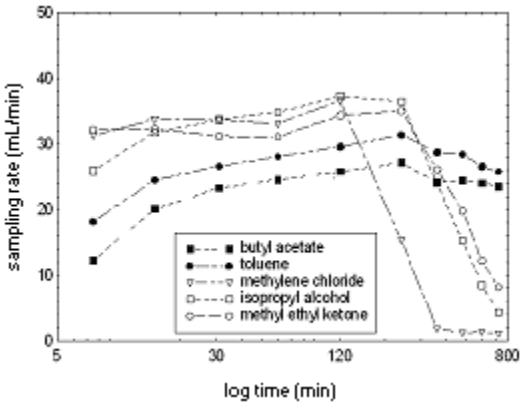

Figure 6. Test atmosphere concentrations determined from experimental parameters, amounts found on back-up included in total amount.

Averages of the sampling rates determined from 31 to 120 min are presented in Table 9.

Table 9
Sampling Rates (mL/min)

calculation method	MEK	IPA	MeCL	Tol	BA
1 concn from active samps, amt on OVM back-up inc	34.74	34.09	37.21	31.58	25.42
2 theo concn, amt on OVM back-up inc	32.21	35.30	35.61	28.08	24.53
3 concn from active samps, amt on OVM back-up not inc	34.74	34.09	36.17	31.58	25.42
4 theo concn, amt on OVM back-up amt not inc	32.21	35.30	34.48	28.08	24.53

(theo concn is calculated from pump rate, concn of analyte in solution, and dilution air volume)

Differences in the above sampling rates for the same analyte are primarily due to the method used to calculate the concentration of test atmospheres. Calculation method 1 (test atmosphere concentration determined from active samples, amount found on back-up pad multiplied by 2.2 and added to amount collected on front pad) was selected for the purposes of this work and will be used in ensuing sampling rate determinations.

During the course of this work, it became apparent that the linear velocity of the sampled air past the OVM had a significant effect on sampling rate. This phenomenon has also been reported in the literature (Ref. 9). NIOSH suggests that 0.1 to 1.5 m/sec should encompass air speeds encountered in a typical indoor workplace. The range of from 0.1 to 1.0 m/s has been proposed by OSHA personnel. Experiments were performed in which sampling rates were determined, both for the mixture and for individually generated components, at increasing linear velocities. The results of these experiments are shown in Figures 7 and 8.

The sampling rates for IPA and MeCL were higher when determined from individually generated components than when determined from the solvent mixture. The difference was greater for MeCL and was especially apparent at higher face velocities. Fifty-ppm MeCL was used in the individual

components experiment, while 75 ppm was used in the mixture experiment. The Factor Effects Experiment did not predict concentration to be a significant factor affecting sampling rate for MeCL, therefore, it is unlikely that the relatively small difference in analyte concentrations caused the results of the two tests to be different.

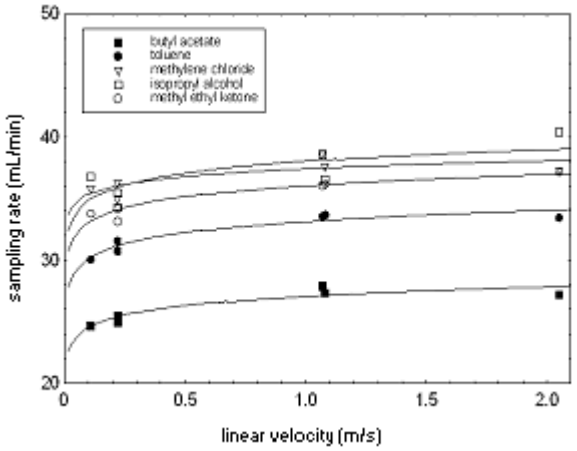

Figure 7. Sampling rate v linear velocity for the solvent mixture. Test atmosphere concentration determined from active samples.

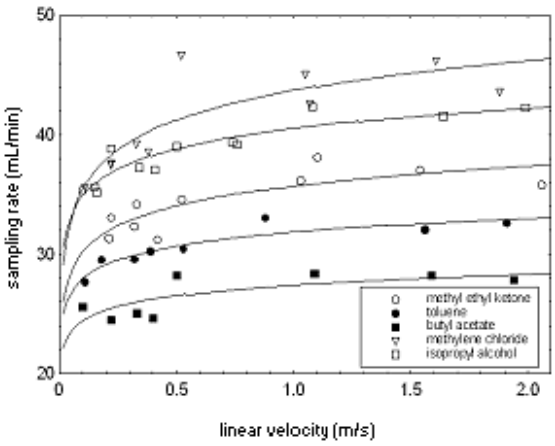

Figure 8. Sampling rate v linear velocity for individual analytes. Test atmosphere concentration determined from active samples

Results from the Sampling Rate v Linear Velocity experiments were used to estimate sampling rate variation due to face velocity. The equations of the regression lines were used to calculate sampling rates at 0.1 m/s and 1.5 m/s. The sampling rates at 0.1 and 1.5 m/s were averaged. The average sampling rate occurred at approximately 0.4 m/s. The sampling rate at 0.1 m/s was subtracted from the average sampling rate, and the difference was divided by the average. Results from both experiments were averaged. The average variation for the all the components of the mixture was 7.4%.

Determination of sampling rates at 0.2 m/s is inappropriate if sampling rate variations determined from this work are to be used as estimated variations for future work. A linear velocity of 0.4 m/s would be more suitable because average sampling rates for the Sampling Rate v Linear Velocity experiments occurred at approximately 0.4 m/s. Sampling rates at 0.4 m/s (760 mmHg and 25°C) were calculated and are presented below.

Table 10
Sampling Rates at 0.4 m/s and Their Variations Due to Face Velocity

	MEK	IPA	MeCL	Tol	BA
sampling rate (mL/min)	34.47	37.84	38.70	31.33	26.21
variation (%)	7.41	7.57	8.04	7.10	6.75

Sampling rates at other linear velocities were calculated and are shown in Table 11. These sampling rates were used to calculate results from some of the experiments performed in this work, such as the storage stability test.

Table 11
Sampling Rates at 0.1, 0.2, and 0.3 m/s

	MEK	IPA	MeCL	Tol	BA
samp rate at 0.1 m/s (mL/min)	31.86	34.91	35.52	29.06	24.32
samp rate at 0.2 m/s (mL/min)	33.16	36.38	37.11	30.20	25.36
samp rate at 0.3 m/s (mL/min)	33.61	36.95	37.80	30.67	25.75

Hirschfelder Diffusion Coefficients were calculated and were used to calculate sampling rates for components of the solvent mixture. These calculations were performed using the formulas and data provided by 3M (Ref. 11). The linear velocity at which the data was gathered was not specified by 3M. Hirschfelder Diffusion Coefficients, calculated sampling rates, experimentally determined sampling rates (0.4 m/s), and ratios of the sampling rates are shown in Table 12. Sampling rates published by 3M (Ref. 10) are included for comparison. Sampling rates (3M) with an asterisk were determined experimentally, and the others were calculated.

Table 12
Calculated, Experimental, and 3M Sampling Rates

	MEK	IPA	MeCL	Tol	BA
Hirschfelder (cm^2/s)	0.0942	0.1008	0.1098	0.0826	0.0725
calculated (mL/min)	36.31	38.56	37.71	30.76	28.81
experimental (mL/min)	34.47	37.84	38.70	31.33	26.21
exper/calculated	0.949	0.981	1.026	1.019	0.910
3M (mL/min)	36.3*	39.4	37.9*	31.4*	31.6

*3M experimentally determined sampling rate from laboratory work

The calculated and experimentally determined sampling rates, with the exception of BA, were well within the ±7.4% sampling rate variation for sampling rates.

Other environmental factors known to affect sampling rates are temperature and barometric pressure (Refs. 11 and 12). There is, however, some disagreement if it is appropriate to correct sampling rate for pressure. Sampling rates presented in this work are generally referenced (corrected) to 760 mmHg and 298K. They were determined at ambient temperature and pressure which was measured and recorded for each experimental trial.

Sampling rate at any temperature (T) and pressure (P) can be calculated from the sampling rate at reference temperature and pressure by use of the following equation:

$$\text{sampling rate} = \text{sampling rate}_{ref} \, (T/T_{ref})^{3/2} \, (P_{ref}/P)$$

There is additional uncertainty in results from diffusive samplers unless appropriate correction is made for the temperature and pressure under which the sample is collected. Either a 10K or a 40 mmHg deviation from reference conditions will cause a 5% deviation in sampling rate (Ref. 12). Sampling site temperature and pressure is basic information that should be provided to the analytical laboratory by the person collecting the samples.

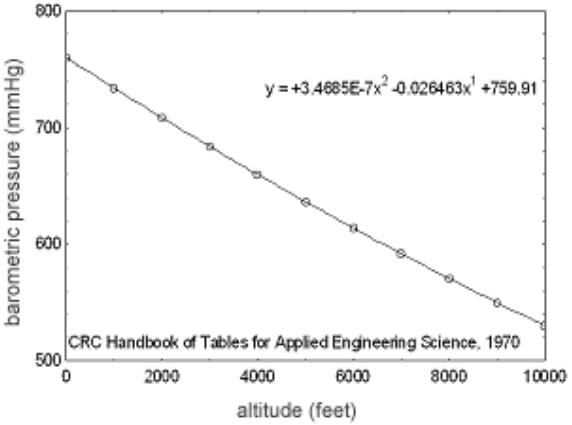

Figure 9. Barometric pressure v altitude

Barometric pressure at SLTC was tracked for approximately one year, and the average was 654.2 mmHg with a standard deviation of 5.2 mmHg. Four standard deviations (3.2%) would bracket all observed pressures. The pressure variation was due to changing weather conditions, and would presumably apply to other locations.

Barometric pressure can be estimated from altitude (Figure 9), and its uncertainty caused by changing weather conditions estimated to be ±3.2%. The pressure predicted for SLTC from its altitude (4235 feet) is 653.2 mmHg. The altitude of a sampling site might be determined from the altitude of a nearby airport or other reference point.

Reverse Diffusion

This test is performed to detect loss of a collected but inadequately retained analyte during sampling. Effective diffusive sampling requires that the residual vapor concentration of the analyte at the surface of the collection medium be very small in comparison to the ambient concentration. Significant loss of analyte could occur if the residual concentration becomes too large.

Test results were evaluated by testing the means (X) and variances (s^2) of the data sets to determine if their difference (d_o) is greater than a set value ($d_0 = 0.1X$). NIOSH specifies that the difference be <10% at the 95% confidence limit. MRST, rather than 0.5 MRST, was used in this work. No specific face velocity was stipulated in the NIOSH Protocol, however, the effects at two face velocities were studied. Any analyte found on the back-up section was multiplied by 2.2 and added to that on the primary section.

$$t' = ((X_1 - X_2)-d_o))/(s^2_1/n_1+ s^2_2/n_2)^{0.5}$$

$$\text{degrees of freedom} = (s^2_1/n_1+ s^2_2/n_2)^2/((s^2_1/n_1)/(n^1-1)+ (s^2_2/n^2)/(n^2-1))$$

Table 13
Reverse Diffusion at 0.2 m/s

	MEK	IPA	MeCL	Tol	BA
t'	-4.81	-7.04	-5.00	-6.30	-6.60
deg of free	14	14	16	14	16
T'	2.145	2.145	2.120	2.145	2.120

The distribution of T is usually called the Student-t distribution, or simply the t distribution

Table 14
Reverse Diffusion at 0.8 m/s

	MEK	IPA	MeCL	Tol	BA
t'	-7.13	-7.62	-9.55	-7.97	-8.04
deg of free	14	17	9	16	18
T'	2.145	2.110	2.262	2.120	2.093

The differences between the means of the data sets for both velocities are less than d_0 because all the calculated t' values are less than the tabulated T' values (-T').

More than 50% of the total MeCL was found on the back-up sections of the second set of samples (exposed to clean air for an additional two hours) at 0.2 m/s, and the percentage was even higher at 0.8 m/s. Low amounts of MEK and IPA were also found on the back-up sections of the second set, with slightly higher levels at 0.8 m/s than at 0.2 m/s. This study confirms the value of back-up sections for 3M OVMs. Reverse diffusion can be a serious problem for MeCL, and sample results for the second set would have been invalid had they been from field samples.

Two additional experiments were performed in which the concentration of the test atmosphere was abruptly and periodically increased from 0.1× STD to 2× STD, maintained at 2× STD for a few minutes, and then decreased to 0.1× STD until the next period (pulse). The analyte levels and durations of the periods are presented in Tables 15 and 17. Four monitors were exposed for each test and the results were averaged. Sampling rates at 0.3 m/s were converted to their SLTC equivalents and used to calculate results. The average concentrations of the test atmospheres were calculated using the mixture experimental parameters and the durations of the periods. The calculated and the experimentally determined concentrations are presented in Tables 16 and 18. The test results show the OVMs to be capable of providing accurate sampling results for atmospheres of rapidly changing concentration.

Table 15
Pulse Test One

concn (× STD)	0.1×	2×	0.1×	2×	0.1×	2×	0.1×
time (min)	32	5	10	5	10	5	23

Table 16
Test One Results

	MEK	IPA	MeCL	Tol	BA
calc concn (µg/L)	230.41	373.42	111.11	316.28	305.52
exper concn (µg/L)	238.83	385.56	108.21	312.51	308.12
ratio of calc to exp	0.96	0.97	1.01	1.01	0.99

Table 17
Pulse Test Two

concn (× STD)	0.1×	2×	0.1×	2×	0.1×	2×	0.1×	2×	0.1×	2×	0.1×
time (min)	23	5	11	3	10	3	10	3	10	3	35

Table 18
Test Two Results

	MEK	IPA	MeCL	Tol	BA
calc concn (µg/L)	213.82	346.53	103.11	293.51	283.52
exper concn (µg/L)	214.36	344.86	98.49	280.85	279.04
ratio of calc to exp	1.00	1.00	1.05	1.05	1.02

Storage Stability

Masses collected on Day Zero were determined by GC, analyte concentrations were calculated using the sampling rates at 0.2 m/s presented in Table 11, and percent recoveries were calculated relative to active sample results. Recoveries for stored samples were subsequently determined in a similar manner. The results are not corrected for desorption efficiency. Results for the storage tests are presented in Tables 19 and 20, and in Figures 10 and 11. Statistical data are shown in Table 21.

Table 19
Ambient Storage Test

time (days)	MEK (%)			IPA (%)			MeCL (%)			Tol (%)			BA (%)		
0	98.0	101.5	102.9	95.6	99.4	101.0	96.2	95.2	96.3	96.4	99.7	101.3	95.6	98.9	100.1
0	95.6	97.0	102.9	93.3	94.6	99.9	90.9	90.9	96.7	93.6	95.4	100.7	92.6	94.2	99.4
3	88.9	97.4	96.0	89.5	97.8	96.9	84.4	86.3	89.8	88.2	98.1	99.9	87.5	99.5	100.6
7	95.1	93.8	93.0	98.9	96.3	94.8	93.9	89.7	89.6	97.5	95.5	94.2	97.5	96.2	95.3
10	92.6	85.4	93.6	102.0	88.7	99.7	94.2	83.3	93.6	99.9	86.9	97.9	99.1	86.8	97.1
14	92.1	90.0	90.9	100.9	93.3	93.3	90.8	90.6	90.2	99.5	92.2	92.3	98.7	91.6	91.7
17	92.9	92.1	83.9	95.9	95.8	94.2	90.0	91.5	90.9	94.2	93.9	91.9	92.2	91.9	92.8
ave day 0	99.7			97.3			94.4			97.9			96.8		

Table 20
Refrigerated Storage Test

time (days)	MEK (%)			IPA (%)			MeCL (%)			Tol (%)			BA (%)		
0	98.0	101.5	102.9	95.6	99.4	101.0	96.2	95.2	96.3	96.4	99.7	101.3	95.6	98.9	100.1
0	95.6	97.0	102.9	93.3	94.6	99.9	90.9	90.9	96.7	93.6	95.4	100.7	92.6	94.2	99.4
3	100.5	98.2	96.3	99.1	96.5	94.8	96.6	91.9	90.4	96.8	98.5	96.0	99.6	97.5	95.6
7	92.4	97.3	99.1	91.2	96.6	97.4	87.8	89.9	92.7	90.4	95.5	96.8	91.3	96.4	97.0
10	99.4	97.5	93.8	92.9	99.7	97.5	90.5	94.3	91.5	91.0	94.8	95.2	90.0	96.4	94.9
14	88.1	92.6	94.8	87.7	91.1	94.6	86.4	90.6	92.3	85.4	89.2	92.5	84.8	88.8	92.3
17	93.7	91.7	92.2	94.0	90.8	90.9	92.5	90.2	89.4	91.2	88.7	89.5	90.3	87.2	88.1

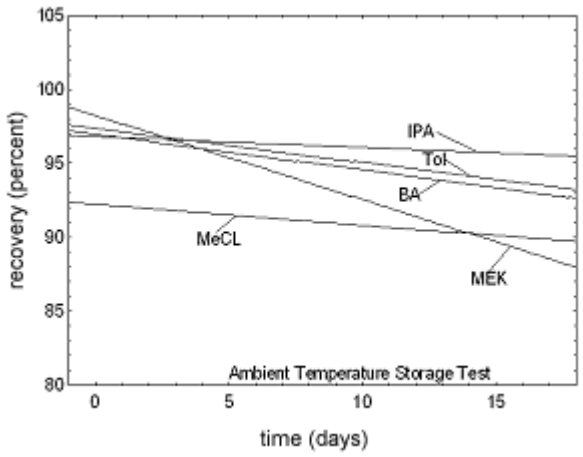

Figure 10. Ambient temperature storage stability tests

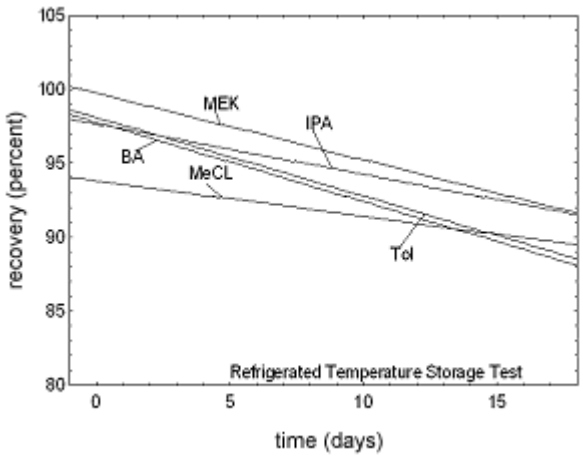

Figure 11. Refrigerated temperature storage stability tests

Statistical data from the storage tests are presented in Table 21. OME Guidelines define SEE as the square root of the sum of the standard error of estimate (SEER) of the regression line for the storage data squared, and the sampling error squared, therefore, for the storage tests here: SEE = ((SEER)2+(7.4)2)0.5. The 95% confidence interval (conf int) is defined as 1.96×SEE. OME Guidelines also require that storage loss be no more than 10% over the two-week storage period. The ambient storage loss for MEK was near 10%, therefore, MEK samples should be refrigerated and analyzed as soon as possible.

Table 21
Storage Tests Statistical Data

Analyte	equation of line	SEER (±%)	SEE (±%)	95% conf int (±%)
MEK (ambient)	Y = -0.570X+98.2	3.50	8.19	16.0
MEK (refrigerated)	Y = -0.451X+99.7	2.74	7.89	15.5
IPA (ambient)	Y = -0.0717X+96.8	3.67	8.26	16.2
IPA (refrigerated)	Y = -0.342X+97.7	2.95	7.97	15.6
MeCL (ambient)	Y = -0.140X+92.2	3.60	8.23	16.1
MeCL (refrigerated)	Y = -0.241X+93.8	2.52	7.82	15.3
Tol (ambient)	Y = -0.229X+97.3	3.82	8.33	16.3
Tol (refrigerated)	Y = -0.532X+98.1	3.08	8.02	15.7
BA (ambient)	Y = -0.240X+97.0	3.85	8.34	16.4
BA (refrigerated)	Y = -0.538X+97.8	2.89	7.94	15.6

Factor Effects

The results of the Factor Effects Experiment are presented in Table 22. Results were calculated by dividing Effect by MSE. Experimental error was approximately 2%, which was sufficiently low to be capable of revealing factor effects on the order of 5%. Any main effect or E column interaction is significant if its absolute value exceeds 1, or nearly significant at 0.9 (arbitrary). NIOSH Protocol requires that any factor shown to be significant be further investigated. These tests confirmed that face velocity had a significant effect on monitor sampling performance for all analytes. The average face velocity Effect was 8%, which is in line with the ±7.4% sampling rate variation proposed earlier in this report. E3 Interaction was significant for MEK and nearly significant for the other analytes except MeCL. The E3 Interaction is completely confounded between some interaction of concentration and relative humidity, or between face velocity and monitor orientation. Analyte concentration was significant for IPA, and nearly significant for Tol and BA. The effects of the interference factor may be somewhat equivocal because the remainder of the mixture was considered the interferant. That is: IPA, MeCL, Tol, and BA was declared the interference factor in MEK tests; MEK, MeCL, Tol, and BA interference in IPA tests...etc. Ranking the factor effects in order of significance could provide the basis for additional experiments.

Table 22
Factor Experiment Results

	effect/MSE														
	×1	×2	×3	×4	×5	×6	E1	E2	E3	E4	E5	E6	E7	E8	E9
	concn	RH	inter	time	vel	orien									
MEK	0.57	0.31	0.28	-0.028	1.95	0.37	-0.26	0.31	-1.03	0.042	0.16	-0.60	0.082	0.35	0.13
IPA	2.07	0.004	0.24	-0.06	1.61	0.16	0.047	0.49	-0.95	0.34	0.29	-0.46	-0.26	0.32	0.15
MeCL	-0.27	-0.51	-0.059	-0.64	1.40	0.14	-0.081	0.51	-0.69	-0.055	0.81	-0.49	-0.24	-0.006	-0.24
Tol	0.90	0.023	0.38	0.69	1.82	0.23	-0.45	0.34	-0.94	0.040	-0.16	-0.076	-0.28	0.64	0.21
BA	0.98	-0.12	0.025	0.29	1.47	0.069	-0.31	0.36	-0.94	0.39	-0.28	0.063	-0.21	0.53	0.30

The factor interactions are shown in Table 23.

Table 23
Factor Interactions

E column	factor interaction	E column	factor interaction
E1	X1X2X3	E6	X1X5 or X2X6
E2	X1X2X4	E7	X3X4 or X2X5
E3	X1X2 or X5X6	E8	X2X3 or X4X5
E4	X1X3 or X4X6	E9	X2X4 or X3X5
E5	X1X4 or X3X6		

Another way to examine results of the Factor Effects Experiment would be to compare percent recovery for each of the experiments. No statistical evaluation of individual factors known to influence monitor performance can be made, however, the overall effects are readily apparent. Results from the tests were calculated in terms of percent of actual concentration based on active samples. The sampling rates were those at 0.4 m/s and converted to their equivalent under prevailing SLTC temperature and pressure. The RSD values are similar to the numbers obtained in the Sampling Rate v Linear Velocity experiments. The imprecision here may be due to elements in addition to face velocity, but the overall effect is comparable.

Table 24
Percent Recovered for Factor Effects Experiment

factor exp no.	MEK (%)	IPA (%)	MeCL (%)	Tol (%)	BA (%)
1	104.7	96.7	102.8	104.2	101.5
2	102.9	101.8	97.7	98.3	99.4
3	107.5	99.6	110.1	97.1	97.5
4	97.9	97.1	92.5	95.9	94.1
5	90.6	83.0	88.4	89.2	87.9
6	107.9	108.8	103.7	108.0	108.2
7	101.3	92.6	101.3	97.4	94.4
8	107.7	106.7	96.2	106.8	103.7
9	97.2	97.4	88.6	93.6	93.9
10	109.6	97.2	97.0	107.3	102.1
11	102.5	100.8	96.9	99.4	97.3
12	103.1	95.0	106.7	96.0	92.9
13	103.3	97.9	94.8	98.8	97.5
14	95.9	88.4	87.3	94.0	94.5
15	105.5	105.8	103.2	106.8	104.2
16	92.3	84.8	93.3	88.2	90.6
Ave	101.9	97.1	97.5	98.8	97.5
RSD	5.6	7.5	6.9	6.3	5.6

The data in Table 25 are the sampling rates determined from the Factor Effects experiments. Factor effects would be an excellent means to determine average sampling rates because the effects of several environmental factors which can influence sampling rate are studied at two levels. The RSDs were pooled after first assuring that they were homogeneous. The pooled relative standard deviation of these sampling rates is 6.4%, which is comparable to the 7.4% sampling rate variation determined previously. Factor Effects experiments cannot replace Sampling Rate/Capacity tests, because factor tests provide no capacity information and it is necessary to know MRST and SRST in order to perform factor tests.

Table 25
Sampling Rates from Factor Effects Experiment (mL/min)

factor exp no.	MEK (mL/min)	IPA (mL/min)	MeCL (mL/min)	Tol (mL/min)	BA (mL/min)
1	36.10	36.58	39.78	32.65	26.60
2	35.46	38.53	37.81	30.81	26.07
3	37.06	37.70	42.60	30.43	25.54
4	33.76	36.74	35.80	30.05	24.66
5	31.22	31.40	34.22	27.96	23.05
6	37.19	41.18	40.13	33.82	28.36
7	34.92	35.04	39.19	30.50	24.74
8	37.12	40.36	37.25	33.45	27.17
9	33.51	36.87	34.27	29.34	24.62
10	37.79	36.78	37.53	33.63	26.76
11	35.34	38.16	37.51	31.14	25.49
12	35.53	35.93	41.28	30.08	24.35
13	35.62	37.05	36.67	30.95	25.55
14	33.05	33.44	33.79	29.46	24.78
15	36.37	40.05	39.96	33.45	27.32
16	31.80	32.09	36.09	27.62	23.76
Ave	35.12	36.74	37.74	30.96	25.55
RSD	5.6	7.5	6.9	6.3	5.6
pooled RSD	6.4				

A summary of sampling rates from various experiments is presented in Table 26. Sampling rates were taken from calculation method 1 of the Sampling Rate and Capacity experiments (Table 9), Sampling Rates v Linear Velocity experiments (Table 10), and Factor Effects experiments (Table 25).

Table 26
Sampling Rate Summary

data source	MEK	IPA	MeCL	Tol	BA
Table 9 (mL/min)	34.74	34.09	37.21	31.58	25.42
Table 10 (mL/min)	34.47	37.84	38.70	31.33	26.21
Table 25 (mL/min)	35.12	36.74	37.74	30.96	25.55
ave (mL/min)	34.78	36.22	37.88	31.29	25.73
RSD (%)	0.76	4.28	1.63	0.82	1.35

Temperature Effects

The NIOSH Protocol presents the following equation comparing analyte concentrations found at low and high absolute temperatures:

$$CL/CH=(T_L)^{0.5}/(T_H)^{0.5}$$

The results of the three separate temperature tests were calculated in terms of analyte concentration and are presented in Table 27. The sampling rates used were those at 0.1 m/s from the Sampling Rates v Linear Velocity experiments converted to their equivalent under prevailing SLTC pressure and 25°C.

Table 27
Experimentally Determined Analyte Concentrations

	MEK	IPA	MeCL	Tol	BA
concn at 8°C (µg/L)	506.45	806.47	219.38	666.67	676.03
concn at 25°C (µg/L)	539.28	865.62	251.18	719.96	729.96
concn at 40°C (µg/L)	521.71	839.29	242.16	701.80	744.20

The analyte concentrations in Table 28 were calculated at 8 and 40°C using the NIOSH equation based on the experimental concentration at 25°C, and the ratio of experimental to calculated concentrations was determined. The average of the ratios was 1.05 with a relative standard deviation of 0.026. The validity of the NIOSH equation was confirmed under the experimental conditions.

Table 28
Calculated Analyte Concentrations

	MEK	IPA	MeCL	Tol	BA
concn at 8°C (µg/L)	523.81	840.79	243.97	699.31	709.02
calculated/experimental (8°C)	1.03	1.04	1.11	1.05	1.05
concn at 40°C (µg/L)	552.82	887.35	257.48	738.03	748.28
calculated/experimental (40°C)	1.06	1.06	1.06	1.05	1.00

Another way to evaluate temperature effects would be to compare experimentally determined ambient sampling rates to previously determined sampling rates converted to their equivalent under experimental conditions. Sampling rates at 0.1 m/s were calculated from the Sampling Rate v Linear Velocity experiments and were converted to their equivalent under experimental temperature and pressure by applying the following equation:

$$sampling\ rate = sampling\ rate_{ref}\,(T/T)^{3/2}\,(P_{ref}/P)$$

They are presented, together with the experimentally determined ambient sampling rates and the ratios of the equivalent to the experimental sampling rate, in Tables 29-31.

Table 29
Experiment Performed at 8°C

	MEK	IPA	MeCL	Tol	BA
pre-determined equivalent (mL/min)	33.94	37.19	37.84	30.96	25.91
experimental (mL/min)	33.53	35.16	34.59	30.32	24.40
equivalent/experimental	1.01	1.06	1.09	1.02	1.06

Table 30
Experiment Performed at 25°C

	MEK	IPA	MeCL	Tol	BA
pre-determined equivalent (mL/min)	37.18	40.74	41.45	33.91	28.38
experimental (mL/min)	36.23	39.27	39.55	33.11	27.03
equivalent/experimental	1.03	1.04	1.05	1.02	1.05

Table 31
Experiment Performed at 40°C

	MEK	IPA	MeCL	Tol	BA
pre-determined equivalent (mL/min)	40.05	43.88	44.65	36.53	30.57
experimental (mL/min)	40.99	43.87	42.71	36.16	30.39
equivalent/experimental	0.98	1.00	1.05	1.01	1.01

The average ratio was 1.03 and the relative standard deviation was 0.028. These experiments show that variation in sampling rate caused by exposure temperature is a correctable bias in the studied range.

MeCL and IPA (at much lower levels than MeCL) were found on the back-up section in greater amounts as the temperature increased. It was apparent that capacity decreased as sampling temperature increased. MRST should be reduced in hot environments.

Precision and Accuracy

The NIOSH method acceptability criterion for accuracy is results within ±25% of the reference value at the 95% confidence level over the range 0.5 to 2× STD. It was not possible to perform these calculations because most the experiments in this work were not conducted over the specified concentration range because of capacity limitations.

The 0.1× and 1× STD data were tested separately to estimate precision at those levels. NIOSH specified which data to evaluate and those instructions were followed as closely as feasible. At least four samples were collected for each test and the RSD of the four samples was calculated. The 1× STD data source was 6 and 8 hour samples from Sampling Rate and Capacity Experiment; first set of samples (0.21 m/s) from Reverse Diffusion Experiment; trials 2, 4, 13, and 15 from Factor Effects Experiment; day zero samples from Storage Stability Experiment; and 8, 25, and 40°C samples from Temperature Effect Experiment. The 0.1× STD data source was trials 1, 3, 14, and 16 of the Factor Effects Experiment. The RSDs were pooled, with the exception of Factor Trial 4 for MeCL (1× STD Data) which was non-homogenous as determined by the Cochran Test for homogeneity. The other RSDs were homogenous.

The pooled standard deviations were 3-5%. These low results imply that individual 3M OVMs will provide reliable sampling results over the tested conditions.

Table 32
Relative Standard Deviations for 1× STD Data

data source	MEK	IPA	MeCL	Tol	BA
SR/cap 6 hour	1.86	1.73	2.33	2.09	2.56
SR/cap 8 hour	3.12	2.36	4.24	3.23	3.31
first set rev diff (0.21 m/s)	3.79	3.37	3.74	3.68	3.21
Factor trial 2	1.18	1.38	1.07	1.27	1.26
Factor trial 4	2.43	2.26	8.24	2.72	2.70
Factor trial 13	2.54	2.59	2.98	2.04	1.81
Factor trial 15	1.62	1.71	1.03	1.53	1.27
Storage day zero	3.22	3.30	2.82	3.24	3.21
Temp 8°C	4.01	4.25	3.96	3.60	3.75
Temp 25°C	2.95	3.07	2.47	2.92	2.81
Temp 40°C	3.88	4.03	3.12	4.07	3.27
pooled RSD	2.93	2.88	2.83	2.90	2.77

Table 33
Relative Standard Deviations for 1× STD Data

data source	MEK	IPA	MeCL	Tol	BA
Factor trial 1	5.24	4.88	7.54	5.06	8.10
Factor trial 3	1.96	1.77	2.80	2.14	2.95
Factor trial 14	3.05	2.79	3.96	2.48	3.46
Factor trial 16	3.57	3.49	6.27	3.09	3.50
pooled RSD	3.65	3.42	5.47	3.39	4.96

Conclusions

The 3M OVM has been shown to provide generally effective sampling and analytical results for the test mixture. Precision was similar to active samplers. Diffusive sampling has similar limitations as active sampling including limited capacity and the potential for storage instability. The technique also has intrinsic liabilities such as the sampling rate for every analyte must be determined, the

temperature and barometric pressure of the sampled air must be known or estimated, and environmental factors such as face velocity and analyte concentration may affect sampling results. These and other liabilities can be addressed through development of sampling precision and accuracy data. Results from diffusive samplers have the potential to be as easily interpreted and defended as results from active samplers, providing support data exists.

Cost is an important issue that inhibits overall acceptance of diffusive samplers. Diffusive samplers are more expensive than active samplers, even when the cost of purchasing and maintaining sampling pumps is considered. Performance aspects of diffusive samplers must be known to correctly interpret sampling results, and costs of obtaining that knowledge will be borne by users. Analytical costs are similar for active and diffusive samplers. They are, however, convenient and easy to use such that one person can deploy several samplers to fully characterize exposure to toxic chemicals at a particular workplace.

Experimental determination of the effects of environmental conditions on sampling rates require the use of systematic experiments outlined in an evaluation protocol. The NIOSH and CEN Protocols are often cited in the literature. The NIOSH Protocol is especially comprehensive, but it is time-consuming and expensive to implement. The NIOSH Protocol requires roughly 31 experimental runs using 184 monitors. The main intent of this work was to determine if it was feasible to create a new protocol for OSHA needs using experience gained by applying the NIOSH Protocol to a solvent mixture. It was judged that some of the NIOSH tests could be modified or eliminated. The primary deletions are some of the factor experiments and the reverse diffusion experiment. The proposed OSHA Protocol requires about 15 experimental runs utilizing 81 samplers in which test atmospheres are generated. Additionally, the protocol requires that desorption efficiency and detection limit parameters be determined using spiked sampling media. Both protocols require additional work to be performed when monitor performance inconsistencies are detected.

It was concluded that the ±6.4% pooled relative standard deviation from the Factor Effects experiments provided a more sound basis to describe sampling rate variation than did the ±7.4% value from the Sampling Rates v Linear Velocity experiments because Factor Effects addressed more variables than did the Sampling Rates experiments. It is recommended that ±6.4% be adopted as estimated sampling rate variation (error) for future evaluations of other analytes collected on 3M OVMs. Other monitors may have different variation.

Precision values for the storage stability tests were recalculated substituting ±6.4% for ±7.4%. Recalculated values for total standard error of estimate (SEE) and 95% confidence interval (95% CI) are presented below.

Table 34
Recalculated SEE (±%) and 95% CI (±%) for Storage Stability Tests

	MEK amb	MEK ref	IPA amb	IPA ref	MeCL amb	MeCL ref	Tol amb	Tol ref	BA amb	BA ref
SEE	7.29	6.96	7.38	7.05	7.34	6.88	7.45	7.10	7.47	7.02
95% CI	14.30	13.65	14.46	13.81	14.39	13.48	14.61	13.92	14.64	13.76

(amb = ambient, ref = refrigerated)

It is reasonable that OSHA Methods, which employ diffusive samplers, have a similar infrastructure as OSHA Methods, which use active samplers. The main differences between the proposed protocol and OSHA Method Evaluation Guidelines for active samplers are certain tests for determination of

monitor sampling rate and capacity. Those parameters which describe aspects of the analytical and overall procedures will be evaluated in a similar manner for diffusive samplers as active samplers.

OME Guidelines utilize sampling pump variability (±5%) added to precision of storage stability tests (by the addition of variances) to calculate Standard Error of Estimate (SEE) which is an estimate of the overall precision of the method. SEE for OME Methods published from June 1991 to present has averaged ±6% (RSD=0.2%). The precision of those storage tests was calculated to be ±3.3% using this SEE. The precision at the 95% confidence level is calculated by multiplying the SEE by 1.96. The ±6.4% sampling rate variation proposed for diffusive samplers is comparable to the ±5% sampling pump error used by OSHA for active methods. It is anticipated that future OSHA methods for diffusive samplers would have precision at the 95% confidence level of about ±14-16% if the proposed sampling rate variation is adopted. Barometric pressure and temperature have known effects on sampling rate, and if sampling site pressure and temperature are not known, an appropriate modification of sampling rate variation must be made. Barometric pressure can be calculated from sampling site altitude (which can be inferred from the altitude of a nearby airport), and its day-to-day variation caused by changing weather has been estimated to be ±3.2%. Pressure variation could be combined with sampling rate variation by the addition of variances to give a sampling rate variation of ±7.2%. An additional factor to compensate for unknown temperature would have to be included to obtain a total sampling rate variation.

OSHA CSHOs use sampling and analytical error (SAE) to compare sampling results to OSHA PELs to help determine if the standard has been exceeded. SAEs are presently calculated using sampling pump variation (±5%) and QC Division sample results. Use of a standard figure for diffusive sampler sampling rate variation is attractive because calculation of SAE for diffusive samplers would then parallel that for active samplers. There would be no immediate change in QC Division operations for methods which use diffusive samplers other than use of a different number in SAE calculations for diffusive samplers.

Proposed Protocol For The Laboratory Evaluation Of Diffusive Samplers

The author has liberally borrowed concepts and terms from other protocols including the NIOSH Protocol, OME Guidelines, CEN Protocol, and the SKC Bi-Level Validation. This protocol will undoubtedly be refined through future work. The more comprehensive NIOSH Protocol (with appropriate modification) should be applied using a mixture of representative analytes when a monitor is first tested, or when construction (or components) of a previously evaluated monitor is sufficiently altered that full re-evaluation becomes necessary.

Fundamental considerations which influence the performance of methods using active samplers also affect methods which use diffusive samplers. These considerations include desorption efficiency, detection limits, analytical precision, and storage stability. Perhaps the greatest difference between laboratory evaluations of active and diffusive samplers is that the sampling rate must be determined for every analyte collected on every different brand of diffusive sampler, while an appropriate sampling rate is merely selected for active samplers.

Provisional sampling rates can be calculated from an analyte’s chemical and physical properties if there is adequate knowledge regarding sampling rates for related compounds collected on a specific monitor such as the 3M OVM. Accurate sampling rates cannot be calculated from the analyte's properties and the internal dimensions of a diffusive sampler.

Stability of sampling rate in response to different environmental conditions can be used to describe most aspects of the sampling performance of diffusive samplers. Sampling rates must be experientially determined under controlled conditions. These sampling rates are without bias when compared to the method used to determine the concentration of the test atmosphere.

The following experimental conditions are general and will be adhered to as closely as practical.

A common desorption solvent and technique will be selected and utilized. It is vital that the same solvent and technique apply to most analytes collected on a specific monitor (for example: 3M OVM) so that methodology can be standardized.

Sampling rates and desorption efficiency should be verified from time-to-time. Generated (not spiked) QC samples could be used as indicators of when re-determination of sampling rate becomes necessary.

Test atmospheres will be prepared and a face velocity of 0.4 m/s maintained while samples are collected. The relative humidity and temperature of the test atmosphere must be known and controlled. Pressure of the test atmosphere will be ambient barometric pressure.

The concentration of the test atmosphere will be confirmed through use of at least one independent means. The benchmark is calculation of concentration from experimental parameters. One means of confirmation could be real-time monitoring with a calibrated instrument such as an IR analyzer or a GC, and another could be active samples, which were collected simultaneously with diffusive samplers. The independent means can be used to establish the concentration of the test atmosphere, providing that method is essentially bias-free. Maximum acceptable bias is about 5%. The NIOSH definition for bias is:

(average of results for test method/true concentration of test atmosphere) -1.

At least one other independent means to confirm or establish concentration is necessary if the calculated concentration does not agree with the independent means. Results from the two independent methods must agree to establish concentration. This necessity may occur when test atmosphere generation is not quantitative based on experimental parameters.

Desorption Efficiency

Sampling rate and desorption efficiency experiments are linked because knowledge of desorption is necessary to calculate sampling rate, and knowledge of capacity is required to calculate mass for desorption experiments. It may be necessary to refine sampling rate calculations as desorption efficiency becomes better known. Preliminary desorption experiments could be performed using estimated sampling rate and capacity.

Desorption efficiency will be determined as outlined in OME Method Evaluation Guidelines, with the exception that an additional determination will be performed at the mass equivalent to 1× target concentration collected for Maximum Recommended Sampling Time (MRST, see Sampling Rate and Capacity) using wet sampling media. Wet media can be prepared by exposing dry media to humid air (80% relative humidity at 25°C) for MRST. The determination using wet media is performed to ascertain if the presence of water has a detrimental effect on recovery. Low or inconsistent recovery problems must be resolved.

The following has been found to be an acceptable technique of preparing desorption efficiency samples for 3M coconut charcoal pads: charcoal pads were obtained from 3M and were individually placed in 4-mL glass screwcap vials which were sealed with septum caps. The pads were liquid spiked with the analyte and allowed to equilibrate overnight at room temperature before desorption and analysis.

Sampling Rate and Capacity

Sampling rate will be determined by collection of replicate samples from test atmospheres for increasing time intervals. The time intervals will normally be 0.125, 0.25, 0.5, 1, 2, 4, 6, 8,10, and 12 hours. Three samples will be simultaneously collected during each time interval. The feasibility of STEL samples will be determined by 7.5 and 15-min time intervals. The concentration of the test atmosphere will be 2× target concentration and the relative humidity about 80% at 25°C. Mass

collected is corrected for desorption efficiency. Analyte detected on the back-up section (if applicable) will not normally be included in the mass collected. Sampling rate is usually expressed in mL/min, and will be calculated by the following equation:

ambient sampling rate = average mass collected/(concn of test atm × sampling time)

The experimental sampling rate is determined at ambient temperature and barometric pressure, and will be converted to its equivalent at 760 mmHg and 298K by the following equation:

$$\text{sampling rate}_{760\ mmHg,\ 298K} = \text{sampling rate}_{amb}(298/T_{amb})^{3/2}(P_{amb}/760)$$

Sampling rates for each interval will be plotted against time. The time at which the sampling rate becomes constant is the shortest recommended sampling time (SRST). Sampler capacity is exceeded when the sampling rate decreases rapidly. SRST and the time at which sampler capacity has been exceeded is determined graphically. Professional judgement must be used to declare when these events have occurred. A sampling rate decrease of five percent could be used as an indicator of sampler saturation. The time at which capacity is exceeded is multiplied by 0.8, and this result is the maximum recommended sampling time (MRST). The factor 0.8 is appropriate to provide reserve capacity for single analytes, however, an increased safety margin may be necessary in cases where competition for sampler capacity is anticipated. Analytes with MRST less than about two hours are not good candidates for the tested medium, and another collection medium should be selected.

Reverse diffusion, caused by use of an inadequate collection medium and revealed by poor analyte retention, should become apparent during the sampling rate and capacity tests. Reverse diffusion is due to the vapor concentration of the analyte at the surface of the collection medium being too high, and can be easily misinterpreted as sampler saturation. The net effect is the same. Reverse diffusion is revealed by earlier than anticipated sampling rate decrease in the sampling rate experiments, and analyte appearance on the back-up section (if applicable). Storage migration of the analyte from the front to the back-up section of an unseparated two-section sampler is indicative of reverse diffusion. Reverse diffusion can be confirmed by exposing two sets monitors to a test atmosphere containing 2× target concentration of the analyte in humid air, removing one set of samples, and then exposing the remaining set to clean humid air. Reverse diffusion has likely occurred if the results are more than about 10% different for the two sets of samplers.

The overall sampling rate is calculated by averaging the individual sampling rates between SRST and the point at which sampling rate begins to decrease rapidly, or alternatively at MRST. This range should contain at least four individual sampling rates, and their relative standard deviation should be no more than about 3%. Sampling rate is reported in mL/min at 760 mmHg and 25°C. Sampler capacity is reported in mass per sample.

Three additional sampling rate experiments will be performed in which the effects of low relative humidity, and low analyte concentration will be screened. (1) Relative humidity will be set at 10% at 25°C, the analyte at 2× target concentration, and samples collected for MRST. (2 and 3) Concentration will be maintained at 0.1× target concentration, the relative humidity set at 80% and 25°C, a set of samples collected for SRST, another set collected for MRST. Additional data may have to be collected to fully determine the extent of adverse effects if sampling rates from these experiments are more than about 10 to 15% different than the overall sampling rate. The effects of relative humidity, concentration, and sampling time can be fully evaluated at two levels in eight experiments. Restrictions may have to be placed on field use of the sampler.

If appropriate, an experiment will be performed in which the sampling rate for the analyte and the capacity of the sampler for the analyte will be verified in the presence of a suspected sampling interference. One example of an appropriate situation is the potential gasoline matri× interference to a sampling method for benzene in a gasoline refinery. The concentration of analyte in the test

atmosphere will be 1× target concentration, and the relative humidity 80% at 25°C. The concentration of the interferant will be 1× its exposure standard, or another suitable level.

Variations in sampling rates caused by exposure temperatures in the range of 10 to 40°C are a correctable bias. MRST should be reduced in hot environments to compensate for reduced capacity.

Storage Stability Test

Perform a storage stability test following the procedure in OME Guidelines. The concentration of the test atmosphere will be 1× target concentration, and the relative humidity approximately 80% at 25°C. Collect 36 samples simultaneously (if possible) for MRST. Samples analyzed immediately after collection can be used to verify that the overall sampling rate is constant at 1× target concentration. Percent recovery will be calculated from the concentration of the test atmosphere, the mass of analyte collected on the monitor (uncorrected for desorption efficiency), and the sample air volume calculated using the overall sampling rate determined in Sampling Rate and Capacity experiments. Substitute ±6.4% sampling error for the ±5% figure in the SEE calculation. The ±6.4% value is estimated sampling rate variation for samples collected at known barometric pressure and temperature. The ±6.4% value is appropriate for the 3M 3520 diffusive sampler only.

OSHA CSHOs use sampling and analytical error (SAE) to compare sampling results to OSHA PELs to help determine if the standard has been exceeded. SAEs are presently calculated for active samplers using sampling pump variation (±5%) and QC Division sample results. Similar SAEs can be calculated for diffusive samplers by substitution of ±6.4% for sampling rate variation. Sampling rate variation of ±6.4% is appropriate only if sampling site barometric pressure and temperature were reported to SLTC, and were used to calculate field sample results. The ±6.4% value is used for the 3M 3520 diffusive sampler only.

Detection Limits, RQL, Precision, Reproducibility

Detection limits, reliable quantitation limit (RQL), analytical precision, and reproducibility will be determined as specified in OME Guidelines.

Written Report

Observe the format specified in the OME Guidelines as closely as possible. Document the tests performed for sampling rate and capacity completely.

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