VALIDATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS

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INTRODUCTION

Work performed by the OSHA Methods Development Team usually results in fully validated sampling and analytical methods for a single toxic substance or for a group of chemicals that are related to one another. When field personnel have a need of to perform workplace monitoring for a certain toxic substance and when established methodology does not exist, partially validated methods can be rapidly developed using similar, but condensed, evaluation tests as those used for fully validated methods. Validation tests for partially validated methods are further described in the section immediately after "PREPARATION OF WRITTEN REPORTS FOR FULLY VALIDATED METHODS". Candidate sampling and analytical methods that cannot meet acceptance criteria for validated methods are published in analytical study format. Studies are also used to report investigations that involve a class or group of analytes, or an aspect of sampling and/or analytical methodology that may be useful for possible future methods development work.

The following guidelines were developed to provide chemists of the Methods Development Team with a uniform and practical means for validating sampling and analytical methods that utilize chromatographic analysis. The guidelines define sampling and analytical parameters, specify required laboratory tests, statistical calculations and criteria for acceptance, and provide a detailed outline for the format of written reports for fully validated methods, partially validated methods, and studies. An overview of the guidelines is shown in Figure 1. The overall goal of these guidelines is to provide OSHA with sampling and analytical methods that can be clearly defended with validation data. The validation tests are presented in logical order in these guidelines, but the person performing the validation work can change the order in which the tests are completed if so desired.

These guidelines are open to examination by the OSHA Methods Development Team and refinements are officially made on a periodic basis. The resulting evolution in the guidelines is apparent when early methods are compared to more recent ones. The validation guidelines have been effectively used and refined for more than twenty-five years.

Fully-validated methods are peer-reviewed by a SLTC methods review committee to assure that methods are clearly written and that they comply with the validation tests and acceptance criteria specified in the guidelines. The guidelines are used by the review committee to review methods. The methods review committee will also verify that any deviation from the guidelines is documented in the method. Partially-validated methods do not have the same status as fully-validated methods and are usually not reviewed by the entire methods review committee.

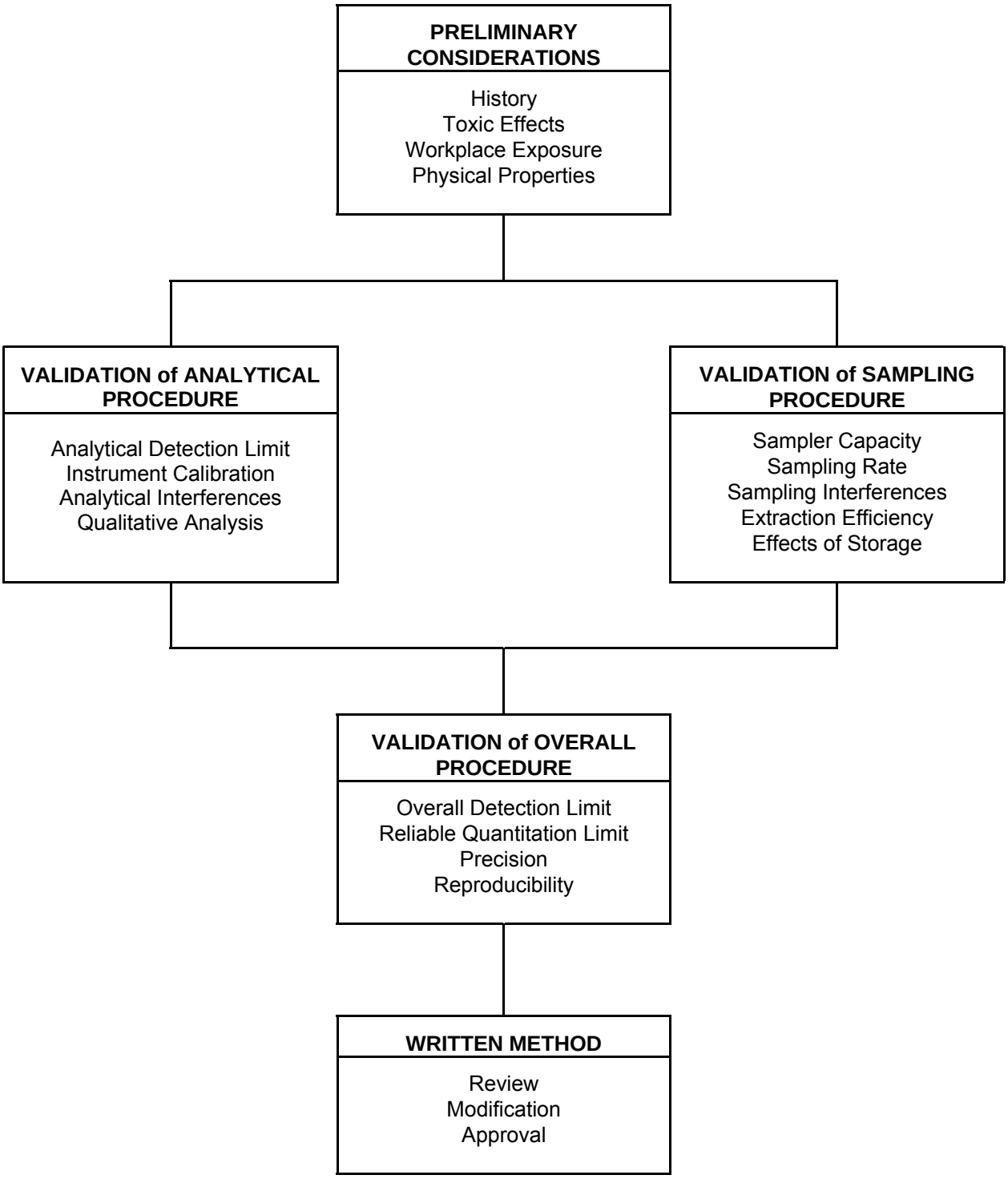

Figure 1. Validation of OSHA methods utilizing chromatographic analysis.

VALIDATION GUIDELINES

I. Preliminary Considerations

A. Review the literature and consult appropriate sources for information on the following:

Existing or related sampling and analytical procedures
Toxic effects
Workplace exposure (what industries and how many people involved)
Physical properties and other descriptive information
Potential interferences

B. Determine the analyte concentration at which the validation will be performed. This value, which shall be known as the target concentration, may be an OSHA PEL, an ACGIH TLV, or some other concentration for which there is a basis for selection. It may be necessary to validate the method at more than one level if the PEL for the analyte has multiple exposure limits such as TWA, ceiling, peak, short-term exposure limit, or action level.

Consider both active and diffusive samplers for vapors. The ideal goal is to provide sampling options for both types of samplers, if possible. Filters or OSHA Versatile Samplers (OVS) are to be considered for sampling aerosols or particulates. Active sampling is defined as collection of an analyte using a sampling pump to draw air through an appropriate sampling medium such as an adsorbent tube or filter. Diffusive sampling is a passive technique that collects the analyte using a sampler that employs the principles of diffusion and does not require the use of a sampling pump.

C. Perform initial tests. Assure that the analytical instrumentation is functioning properly, use either a new analytical column or a column that is known to be functioning properly, determine analytical conditions, estimate capacity of the selected sampling device, identify possible extraction solvents and internal standards (if used) to be tested. If adsorbent tubes and diffusive samplers are to be analyzed by GC/FID, first consider 99/1 carbon disulfide/dimethylformamide as the extraction solvent. If the resulting extraction efficiency is low, test solvent mixtures currently in use at SLTC (i.e., 95/5 ethanol/water, 60/40 dimethylformamide/carbon disulfide, 95/5 acetone/methanol, 95/5 methylene chloride/methanol, or one of several neat solvents) before formulating a new extraction solvent. Overall average extraction efficiency greater than 75% is acceptable but an average greater than 90% is preferred.

D. Use NIST-traceable or other high-quality reagent sources to prepare analytical standards and spiked samples. Use reagent-grade chemicals in validation tests and record lot numbers of chemicals used in the tests.

II. Validation of Analytical Procedure

A. Detection limit of the analytical procedure (DLAP)

Detection limits, in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (S_{BR})) from the response (Y_{BR}) of a reagent blank.

(1) $Y_{DL} - Y_{BR} = 3S_{BR}$

where S_{BR} is the standard deviation of a reagent blank
Y_{DL} is the response at the detection limit
Y_{BR} is the response of the reagent blank

The direct measurement of Y_{BR} and S_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards whose responses are in the vicinity of the response of a reagent blank. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. If it is clearly nonlinear, refer to Burkhart[1] for alternate calculations. Assuming S_{BR} and the precision of data about the curve are similar, the standard error of estimate for the regression curve can be substituted for S_{BR} in the above equation. The standard error of estimate of a line is the mathematical equivalent of the standard deviation for tabulated data. The following calculations derive a formula for the detection limit:

$$(2)\ S_{Y\cdot X(DLAP)} = \sqrt{\frac{\sum (Y_{OBS}-Y_{EST})^2}{n-k}}$$

where $S_{Y\cdot X(DLAP)}$ is the standard error of estimate for the DLAP
Y_{OBS} is observed response
Y_{EST} is estimated response from regression curve
n is total number of data points
k is 2 for linear regression

at point Y_{DL} on the regression curve

$$(3)\ Y_{DL} = A(L_D) + Y_{BR}$$

where Y_{DL} *is th*e response at the detection limit
A is the analytical sensitivity (slope)
L_D is the DLAP
Y_{BR} is the response of the background

substituting for Y_{DL} from Equation 1 gives

$$(4)\ L_D = \frac{3S_{Y\cdot X(DLAP)}}{A}$$

where L_D is the DLAP
$S_{Y\cdot X(DLAP)}$ is the standard error of estimate for the DLAP
A is the analytical sensitivity (slope)

Use the following procedure to assure that the concentrations of analytical standards used to determine the regression curve will produce responses in the vicinity of the background response:

1. Estimate the background response near the elution time of the analyte from a reagent blank.

2. Prepare ten standards, in equally spaced intervals, with the highest standard producing a signal about ten times the background response.

3. Analyze the ten analytical standards and one reagent blank.

[1] Burkhart, A.J. *Appl. Ind. Hyg.* **1986**, 1, 153-155.

4. Determine the regression line and then the standard estimate of error for the DLAP from the data by plotting response versus mass injected onto the column. Calculate mass injected onto the column by multiplying the concentration of the standard by the volume injected; and then by the split ratio (if any).

5. Calculate the DLAP using Equation 4. Report the DLAP in the method as mass of analyte injected onto the column.

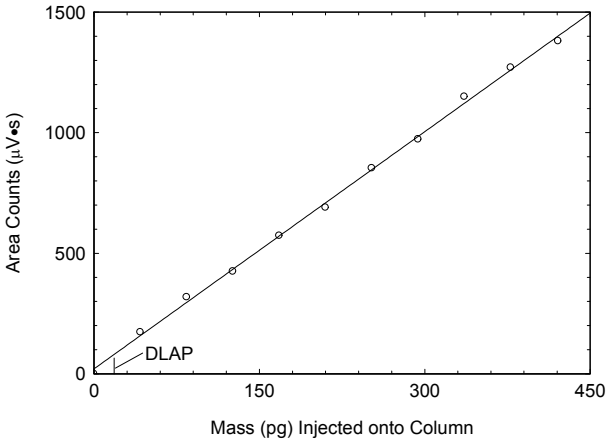

Figure 2. Example of plotted DLAP data (y = 3.28x + 20.8).

6. Prepare a graph of the DLAP data as shown in Figure 2 for inclusion in the method.

7. The detection limit of the overall procedure (DLOP) and the reliable quantitation limit (RQL), described in Sections IV.A and IV.B, can be determined in conjunction with this test.

B. Instrument calibration

Report the standard error of estimate (defined as the mass equivalent to $S_{y \cdot x(cal)}$ in Equation 5) from the linear regression of data points over a range that covers 0.1 (or RQL whichever is higher) to 2 times the target concentration. If there are several target concentrations, select the target concentration and the sampler with the recommended sampling time and sampling rate combination that will produce the highest mass loading. The regression line is determined from the triplicate analysis of analytical standards at working range concentrations of 0.1 (or RQL, whichever is less), 0.5, 1, 1.5, and 2 times the target concentration as follows:

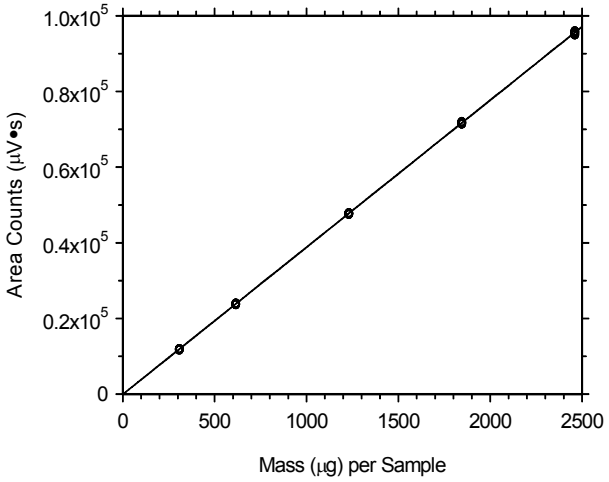

Figure 3. Example of a calibration curve (y = 38.89x - 65.50).

1. Prepare and dilute analytical standards as necessary. Analyze each standard three times.

2. Use the data collected to calculate $S_{y \cdot x(cal)}$ as shown in Equation 5 and to construct the calibration curve (as shown in Figure 3) for inclusion in the method.

3. Generate a chromatogram of a standard at the target concentration for inclusion in the method. (Section 3.5.1 in the text of the method)

The standard error of estimate is a measure of variation or scatter about the line of regression[2] and it is calculated as follows:

$$(5)\quad S_{Y\cdot X(CAL)} = \sqrt{\frac{\sum (Y_{OBS} - Y_{EST})^2}{n-k}}$$

where $S_{Y\cdot X(CAL)}$ is the standard error of estimate for the calibration
Y_{OBS} is the observed response
Y_{EST} is estimated response from the regression curve
n is the total number of data points
k = 2 for linear regression
k = 3 for quadratic regression

C. Analytical interferences

Analytical interferences become evident if they interfere with quantitation of the analyte. The interferences selected for testing should be based, in part, on interferences present in workplaces similar to those in which the new method may be used. The literature should also be reviewed to identify possible interferences. These potential interferences can often be resolved by changing chromatographic conditions or by using a more selective analytical detector.

1. Determine the effects of suspected interferences by analyzing spiked analytical standards. Avoid serious interferences to the analytical method by modifying the analytical method or the sampling procedure.

2. If a reagent has been added to the sampling medium, generate an additional chromatogram at the target concentration for inclusion in the method showing the reagent's relationship to the analyte. (Section 3.5.1)

D. Qualitative analysis

Present a mass spectrum or alternate chromatographic conditions that will aid in confirming the identity or purity of the analyte (or derivative) peak. Mass spectrometry may provide the most conclusive identification and shall be addressed in all cases, even if this amounts to an explanation why it is not possible or not available. Peak response ratios and analysis with alternate detectors may also be useful. Use the format of Section 3.5.1 to present analytical conditions with chromatograms, UV spectra, or mass spectra. Include this information in the method. (Section 4.10) If the mass spectrum was taken from a spectral library, it is not necessary to include analytical conditions.

III. Validation of Sampling Procedure

Use dynamically generated controlled test atmospheres whenever possible to prepare samples for validation tests. All test atmospheres generated throughout these validation tests must be non-condensing. It may be necessary, however, to use static test atmospheres such as those prepared in gas-sampling bags when safety considerations or other problems prevent use of dynamically generated controlled test atmospheres. It might be necessary to use vapor-spiked samples where the analyte is volatilized directly upstream of the sampler while drawing air through the sampler. Water can be added to the sampler by using humid air in these tests. These alternative and other innovative techniques used to prepare samples may require that the analyte be contained in a non-interfering solvent. Gary O. Nelson's book "Gas Mixtures Preparation and Control" is a useful

[2] Arkin, H.; Colton, R.C. *Statistical Methods*, 5th ed.; Barnes & Noble: New York, 1970; pp 84-88.

resource when generating test atmospheres.[3] Procedures used to generate samples should be fully described in the backup data section of the validated method. (Section 4.11)

This section of the guidelines address validation of samplers containing adsorbent media or filters, and may require slight modification for validation of more unique samplers such as those utilizing reactive reagents, or those containing both adsorbent and filter components such as OSHA Versatile Samplers (OVS). Modification may also be required for the validation of bubbler sampling procedures. Consider bubblers only as a primary sampling technique of last resort. Specific requirements which apply to the validation of diffusive samplers are included in the appropriate sections. The overall extraction efficiency, determined in Section III.C, shall be applied to analytical results from capacity, interference, and reproducibility validation test results.

A. Active samplers

1. Sampling rate

a. For those substances that have a peak, ceiling, or short-term exposure limit, determine the limitations of taking a short-term sample (applicable time from Table Z-2 of 29 CFR 1910 or expanded health standards) at the proposed sampling rate. If a short-term sample collected at the proposed sampling rate does not result in a mass of analyte equal to or greater than 10 times the RQL, study the use of a higher flow rate through additional breakthrough studies. For ceiling exposure limits listed in Table Z-1 or in expanded standards, determine if 15 min is a practical recommended sampling time.

b. Select a sampling rate that is suitable for the active sampler. In general, use 50-200 mL/min for adsorbent tubes and 1-2 L/min for filters and OSHA Versatile Samplers (OVS). The sampling rate for samplers that utilize reagent coated sampling media may depend on reaction kinetics. The goal is to have a 4-hour recommended sampling time for TWA samples. Measure the pressure drop across the sampler at each recommended sampling rate and confirm that a sampling pump is commercially and commonly available that is capable of maintaining constant flow at the measured pressure drop.

2. Capacity

a. Sampler capacity is defined by the length of time a sampler can be used under a set of known test conditions without significant loss of analyte. Capacity can also be described as a corresponding air volume or as a collected analyte mass. Capacity tests employ only the front adsorbent section of two-section absorbent tubes. Use breakthrough tests to determine sampler capacity. Consider breakthrough to have occurred when the effluent from the active sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). This can be determined by monitoring the downstream effluent with an instrument such as a total hydrocarbon analyzer, a gas chromatograph, or an infrared spectrophotometer, after the response of the upstream concentration has first been established. When use of an instrument is not possible, breakthrough can be determined with a series of backup samplers that are changed at measured time intervals. The time intervals will vary with the sampling medium and with the analyte, but they must be sufficiently short so that the 5% breakthrough point can be accurately determined. Analyze each backup sampler separately. If sampler

[3] Nelson, G.O., *Gas Mixtures Preparation and Control*, Lewis Publishers, Boca Raton, 1992.

capacity is not exceeded after 10 hours of sampling at two times the target concentration, discontinue the sampling capacity test and report this fact in the method.

b. Determine breakthrough at ambient temperature from a dynamically generated controlled test atmosphere containing an analyte concentration equal to 2 times the target concentration. Use an absolute humidity for the test atmosphere of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC).

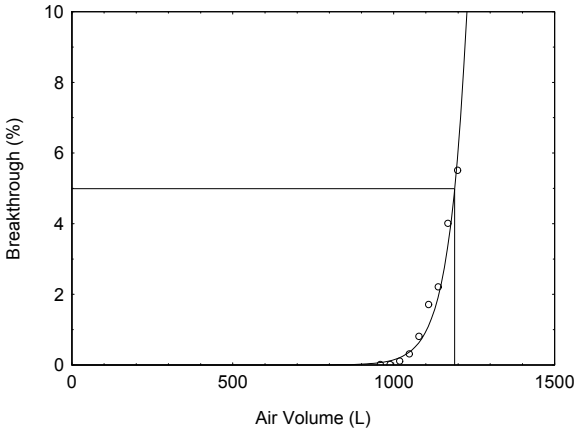

Figure 4. Example of breakthrough data.

c. Perform three separate breakthrough tests to assure that sampler capacity has adequately been determined.

d. Prepare a plot of breakthrough data for inclusion in the method as shown in Figure 4.

e. Set the recommended sampling time for the method at whichever time is shorter, 4 hours or 80% of the time required to exceed the capacity of the sampler when challenged at two times the target concentration.

f. Retention efficiency

Retention efficiency tests are performed when it is not possible to use a dynamically generated controlled test atmosphere. They are designed to provide partial support for sampler capacity by showing that analyte when preloaded on the sampler is retained when the recommended sampling conditions are used to draw humid air through the sampler.

Perform retention efficiency tests for adsorbent tubes in the following manner: Use only the front section of two-section tubes, and spike the sampler in a manner that places the analyte at the head of the adsorbent bed. This can be accomplished for volatile substances by placing the analyte on the glass wool plug immediately ahead of the adsorbent tube while drawing air through the sampler. The analyte will be rapidly transferred to the head of the adsorbent bed when the test is started. An alternative technique that can be used for less volatile substances is to spike the analyte directly onto the head of the adsorbent bed. No more than about 20 µL of liquid should be used in these tests.

Perform retention efficiency tests for filters and for samplers that contain both a filter and an adsorbent (such as OVS tubes) in a similar manner. Be certain to spike the samplers in such a way that the analyte is not immediately transferred to the support pad or to the absorbent bed. Volatile substances can be spiked on a medium that only weakly retains the analyte which is connected in-series upstream to the sampling cassette or OVS tube. The analyte will be rapidly transferred to the sampler when the test is started. Nonvolatile substances must be directly spiked

on the filter surface. This can be accomplished by placing the filter (without any support pad) on a suitable support such as the rim of a small beaker so that only the outside edge of the filter is supported and then spiking the liquid in about 5-10 small spots randomly spaced over the face of the filter. This is especially important if a reagent is coated on the filter.

If filters are used with support pads (back-up pads), they are extracted and analyzed separately when retention efficiency tests are performed. If backup pads are used, spike six filters and place them in separate sealed cassettes together with backup pads for 4 hours with no air drawn through them. These filters will be used as controls to determine if the analyte is transferred to the support pad by contact without air being drawn through the cassette.

Perform retention tests as follows:

i. Spike six samplers with an amount of analyte equivalent to two times the target concentration based on a tentative recommended air volume. Use only the front section of two-section adsorbent tubes. Do not spike the samples with more than 20 µL of liquid in order to avoid saturation of the sampling medium.

ii. Select a recommended sampling rate that is suitable for the samplers. The absolute humidity of the air shall be approximately 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC). The test must be conducted for a sufficient time to draw at least 1.25 times the tentative recommended air volume through the samplers.

iii. Monitor the downstream effluent of the sampler with an instrument as in a breakthrough test using a dynamically generated controlled test atmosphere if possible. If it is not possible to use an instrument, monitor breakthrough with a series of backup samplers that are changed at measured time intervals and then analyzed. The time intervals will vary with the sampling medium and with the analyte, but they must be sufficiently short so that the 5% breakthrough point can be accurately determined. Analyze the spiked samplers at the completion of the test.

iv. Express the analytical results of the backup sampler as percent breakthrough by dividing them by the amount spiked on the sampler and plot the results against air volume sampled as shown in Figure 4. Report the recovery of the spiked samplers determined at the end of the test.

3. Sampling interferences

Sampling interferences may affect sampler capacity, may chemically react with the analyte and affect recovery of the analyte, and may result in analytical interferences. The interferences selected for testing should be based, in part, on interferences present in workplaces similar to those in which the new method may be used. The literature should also be reviewed to identify possible interferences.

a. Test for retention of the analyte by using one set of six samplers to sample a dynamically generated controlled test atmosphere containing two times the target concentration at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for one-quarter of the recommended sampling time. Discontinue sampling and set three samplers aside. Flush the generation system with contaminant-free air. Contaminant-free air is laboratory

conditioned air at known relative humidity but without any added chemical except water. Sample the contaminant-free humid air for three-quarters of the recommended sampling time using three of the six samplers. Analyze the six samplers. Upon analysis, the mean recovery for the second three samplers must be greater than 90% of the mean recovery for the first three samples.

If the first test fails, repeat the test by using another set of six samplers to sample the same dynamically generated controlled test atmosphere but reduce the two sampling times by one-half. If the test passes, the new recommended sampling time is one-half of the old value. If the mean of the recoveries of the second half of the set is still less than 90% of the mean recovery of the first three samples, consider retention inadequate and an alternate sampling medium must be found and tested.

b. Test for the effect of low humidity on analyte recovery by using a set of three samplers to sample a dynamically generated controlled test atmosphere containing two times the target concentration at an absolute humidity of 3.9 milligrams of water per liter of air (about 20% relative humidity at 22.2EC) using the recommended sampling time. Upon analysis, all three front sections of the individual samples shall have collected enough analyte to be greater than 90% of the theoretical amount. If not, perform the test at a higher absolute humidity (i.e., 5.8 milligrams of water per liter of air or about 30% relative humidity at 22.2EC) and list the restriction in the Special Requirements Section on the cover page of the method.

c. Test for the effect of low concentration on analyte recovery by using a set of three samplers to sample a dynamically generated controlled test atmosphere containing 0.1 times the target concentration at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for the recommended sampling time. Upon analysis, all three front sections of the individual samples shall have collected enough analyte to be greater than 90% of the theoretical amount. If not, an alternate sampling and/or analytical procedure that provides at least 90% recovery must be found and tested.

d. Test for the effect of at least one suspected chemical sampling interference on recovery by using a set of three samplers to sample a dynamically generated controlled test atmosphere containing one times the target concentration of the analyte at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for the recommended sampling time. The suspected interference shall be set at an appropriate level which may be its PEL, TLV, or level anticipated to be found in the workplace. If more than one interference is tested, then the concentration of the interference should be divided by the number of interferences so that the sampler will not be overloaded. If two interferences are used, each could have a concentration equal to one-half of its PEL, TLV, or anticipated level. Upon analysis, all three front sections of the individual samplers shall have each collected enough analyte to be greater than 90% of the theoretical amount of the analyte. If 10% or more of the analyte is found on the back section, the recommended sampling time may be too long. Repeat the sampler capacity test with the interferences present in the dynamically generated controlled test atmosphere, reduce the sampling time, and determine if the shorter sampling time is appropriate.

B. Diffusive samplers

1. Sampling rate and capacity

It is necessary to generate controlled test atmospheres to determine sampling rates and capacities for diffusive samplers. The face velocity of the test atmosphere over the samplers should be 0.4 m/second. Before determining sampling rate and capacity, the preliminary extraction efficiency from wet absorbent should be determined as follows: Calculate the mass of analyte that would be collected on the diffusive sampler after sampling a dynamically generated controlled test atmosphere containing the target concentration using an approximate sampling rate based on the manufacturer's literature (e.g., SKC is 13 mL/min and 3M is 31 mL/min) for four hours. Spike at least two samplers with this amount of analyte and another two samplers with 5% of the amount. Upon analysis, the preliminary extraction efficiencies should be sufficiently high and within $\forall$5% of each other. Use the average as the preliminary extraction efficiency. After the preliminary sampling rate and preliminary recommended sampling time are determined with the preliminary extraction efficiency, perform the final extraction efficiency studies in Section III.C. Recalculate the final sampling rate and final recommended sampling time using the final extraction efficiency.

a. For those substances that have a peak, ceiling, or short-term exposure limit, determine the limitations of taking a short-term sample (applicable time from Table Z-2 of 29 CFR 1910 or expanded health standards). The shortest recommended sampling time for a short-term sample should result in a mass of analyte equal to or greater than 10 times the RQL. For ceiling exposure limits listed in Table Z-1, determine if 15 min is practical as the recommended sampling time.

b. Determine sampling rates by using replicate samples to sample a dynamically generated controlled test atmosphere for increasing time intervals. Collect three samples for each time interval. The time intervals will normally be 5, 10, and 30 min plus 1, 2, 3, 4, 6, 8, and 10 hours. The concentration of the test atmosphere should be two times the target concentration. If the analyte is in Table Z-2 or in an expanded standard, use two times the TWA PEL. An absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C) should be used. The concentration of the test atmosphere should be verified with an alternate method. Two alternate methods are needed if the first alternate method does not agree with the theoretical concentration. Alternate methods may include an active sampling method and an on-line instrument such as a GC or an IR. The theoretical concentration shall be used in subsequent calculations if it is verified. Record the temperature and atmospheric pressure inside the chamber. The sampler masses are corrected for extraction efficiency as determined in Section III.C. Analytical data from only the primary sorbent section of samplers that have a secondary sorbent section should be used in these tests. Sampling rate is expressed in milliliters per min, and will be calculated by the following equation:

$$(6)\ R_{SS} = \frac{1000\,M}{C\,t\,E_E}$$

where R_{SS} is sampling rate at sampling site (mL/min)
M is mass collected (µg)
C is concn of the test atmosphere (µg/L)
t is sampling time (min)
E_E is extraction efficiency (decimal form)
1000 is unit conversion from L to mL

c. Convert the ambient sampling rates that are determined at sampling site temperature and atmospheric pressure to equivalent sampling rates at NTP conditions of 760 mmHg and 298.2 K with the following equation[4]:

$$(7)\ R_{NTP} = R_{SS}\left(\frac{T_{NTP}}{T_{SS}}\right)^{\frac{3}{2}}\left(\frac{P_{SS}}{P_{NTP}}\right)$$

where R_{NTP} is the sampling rate at NTP conditions
R_{SS} is the sampling rate at sampling site
T_{SS} is the sampling site temperature in K
T_{NTP} is 298.2 K
P_{SS} is the pressure at the sampling site
P_{NTP} is 760 mmHg

d. Plot the sampling rates against sampling times as shown Figure 5. Find the preliminary sampling rate by averaging the nine values for the 0.5, 1, and 2 hour samples (12.2 mL/min). Draw horizontal lines that are 10% above and below the preliminary sampling rate (13.42 and 10.98 mL/min). Average all the values from 5 min to 10 hours that are between the lines to determine the sampling rate. The range should contain at least four of the time intervals and the standard deviation of the sampling rate should be no more than 5%. Report the mean (12.1 mL/min), standard deviation (0.445 mL/min) and the relative standard deviation (3.7%) for all the data points used to determine the sampling rate. Report the sampling rate as milliliters per min at 760 mmHg and 25 °C and report the range of time it covers for example: 5 min to 4 hours.

Table 1
Determination of Sampling Rate
and Recommended Sampling Time

time (h)	first	second	third
5 min	12.4	12.5	12.6
10 min	12.3	12.4	12.5
0.5	12.1	12.2	12.3
1	12.0	12.2	12.3
2	12.1	12.2	12.4
3	12.0	12.1	12.2
4	11.8	11.9	12.0
6	11.4	11.5	11.6
8	11.2	11.0	11.1
10	10.2	10.3	10.1

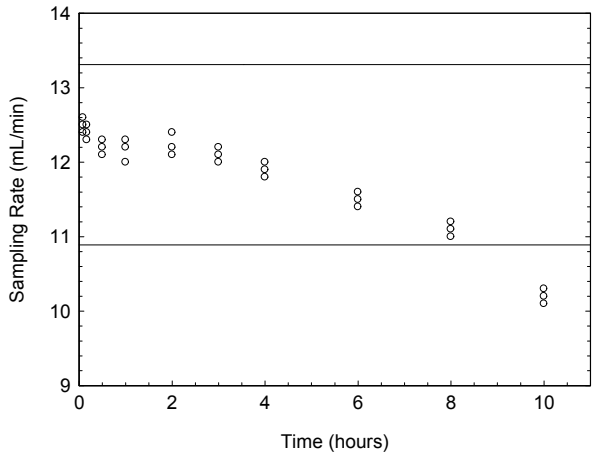

Figure 5. Example of plotted data to determine the recommended sampling time and sampling rate.

e. To determine the recommended sampling time, use the data from the previous paragraph. Sampler capacity is defined to be exceeded when the sampling rate appears to decrease rapidly. Sampler capacity was not been exceeded if the sampling rate does not appear to decrease. The sampling rate remains constant, but analyte can no longer be quantitatively retained because capacity has been exceeded. Find the data point with the longest time that is between the horizontal lines. Multiply this time by 0.80 to determine the maximum sampling time (6.4 hours). If this time is greater than 4 hours, the sampling time recommended in the method will be 4 hours. This will provide a conservative safety margin when samples are taken in complex work atmospheres where substances may compete for sites on the adsorbent.

[4] Shulsky, M. "Review of Calculations with Solid Sorbent Passive Monitors to Determine Air Contaminant Concentrations", OSHA Salt Lake Technical Center, Salt Lake City, UT. Unpublished work, 1983.

2. Sampling interferences

a. Test for reverse diffusion of the analyte by using one set of six samplers to sample a dynamically generated controlled test atmosphere containing two times the target concentration at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for one-quarter of the recommended sampling time. Discontinue sampling and set three samplers aside. Flush the generation system with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity but without any added chemical except water. Sample the contaminant-free humid air for three-quarters of the recommended sampling time with the other three samplers. Analyze the six samplers. Upon analysis, the mean recovery for the second three samplers must be greater than 90% of the mean recovery for the first three samples. If the test passes, the recommended sampling time is the value from the previous paragraph.

   If the first test fails, repeat the test by using another set of six samplers to sample the same dynamically generated controlled test atmosphere but reduce the two sampling times by one-half. If the test passes, the new recommended sampling time is one-half of the old value. If the mean of the recoveries of the second three samplers is still less than 90% of the mean recovery of the first three samples, then reverse diffusion is significant and an alternate sampler must be considered.

b. Test for the effect of low humidity on sampler performance by exposing a set of three samplers to a dynamically generated controlled test atmosphere containing two times the target concentration at an absolute humidity of 3.9 milligrams of water per liter of air (about 20% relative humidity at 22.2EC) for the recommended sampling time. Upon analysis, all three of the individual samples shall have collected enough analyte to be greater than 90% of the theoretical amount. If not, perform the test at a higher absolute humidity (i.e., 5.8 milligrams of water per liter of air or about 30% relative humidity at 22.2EC) and list the restriction in the Special Requirements Section on the cover page of the method. Use the average diffusive sampling rate determined in Section III.B converted to its equivalent sampling rate at sampling site temperature and pressure to calculate results.

c. Test for the effect of low concentration on sampler performance by exposing a set of three samplers to a dynamically generated controlled test atmosphere containing 0.1 times the target concentration at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for the recommended sampling time. Upon analysis, each of the three individual samples shall have collected enough analyte to be greater than 90% of the theoretical amount. If not, an alternate sampler must be considered. Use the average diffusive sampling rate determined in Section III.B converted to its equivalent sampling rate at sampling site temperature and pressure to calculate results.

d. Test for the effect of at least one suspected chemical sampling interference on recovery by using a set of three samplers to sample a dynamically generated controlled test atmosphere containing one times the target concentration of the analyte at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) for the recommended sampling time. The suspected interference shall be set at an appropriate level which may be its PEL or TLV. If more than one interference is used, then the concentration of the interference should be divided by the number of interferences used so that the sampler will not be overloaded. If two interferences are used, each could have a concentration equal to one-half of its PEL or TLV. Upon analysis, all three samples

shall have each collected enough analyte to be greater than 90% of the theoretical amount of the analyte. If results are less than 90%, then the recommended sampling time may be too long. Repeat the sampler capacity test with the interferences present in the atmosphere to determine if a shorter sampling time is appropriate. Use the average diffusive sampling rate determined in Section III.B converted to its equivalent sampling rate at sampling site temperature and pressure to calculate results.

C. Extraction efficiency and stability of extracted samples

The following section was written primarily for adsorbent media, but the same procedures can be used for filter media. Determine the extraction efficiency for support pads (if they are used with filters) as described in Step 9 of this Section. Determine the extraction efficiency for cassette wipes as described in Step 10 of this Section when sampling is performed using 25- or 37-mm cassettes. If both filter and adsorbent media are used in the same sampler (e.g. OVS sampler), determine the extraction efficiency for each medium separately.

Determine extraction efficiency using only the front sections of two-section adsorbent tubes. It may be convenient to place the sampling medium in an extraction vial that has a septum cap and then spike it in the vial.

1. Determine the amount of time required to fully extract a constant amount of analyte from spiked samples. Extract and analyze a series of spiked samplers that covers the range of from the RQL to 2 times the target concentration for each sampler while increasing the amount of time between addition of the extraction solvent and analysis. Shake each sample by hand for a few seconds shortly after adding the solvent. If the extraction time is excessive, determine if mechanical agitation can reduce the time to fully extract the sample. SKC Passive Samplers are extracted using a specialized mechanical shaker.

2. The overall extraction efficiency is the mean percent of analyte recovered from dry samplers determined at 0.1, 0.25, 0.5, 1, 1.5, and 2 times the target concentration, based on the recommended air volume. If there are several target concentrations, select the target concentration and recommended sampling time combination which will produce the highest mass loading on the sampler. A dry sampler is one that is used as received from the manufacturer. The average of all the levels will be the overall extraction efficiency for the analytical procedure, provided they are similar. The average extraction efficiencies for each level tested should be within ±5% of the overall average. The individual extraction efficiencies within a level should agree to within ±5%. If the extraction efficiency does not remain constant, determine if a different extraction solvent or extraction technique will provide constant results. If another extraction solvent does not provide constant results, a plot of extraction efficiency versus concentration shall be constructed and included in the method. Determine extraction efficiency at the RQL but do not include these results in the overall average.

   Perform a test of the extraction efficiency with wet samplers but do not include the results in the overall average for dry samplers as follows:

   a. Sample contaminant free humid air at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC) at the recommended sampling rate for the recommended sampling time using four active samplers. Also expose four diffusive samplers to the humid air for the recommended sampling time.

b. Spike the wet active and diffusive samplers at one times the target concentration. If there are several target concentrations, select the target concentration and recommended sampling time combination which will produce the highest mass loading on the sampler.

c. Extract and analyze the samples. If there is a significant difference in the mean of the extraction efficiency for wet samplers and the overall extraction recovery for dry samplers, repeat the test. A significant difference is when the mean of the wet samplers is 5 to 10% different from the mean of the dry sampler at the same mass loading. A difference of ≤5% is preferred. For GC analysis, the difference may be an analytical issue and it might be possible to resolve it by changing analytical method parameters such as the internal standard or the GC injector liner. If the difference persists, investigate changing the sampler or extraction solvent to minimize the difference.

d. An alternative, but less exact, way to simulate wet sampling media is to spike the medium with 50 µL of deionized water before spiking it with the analyte.

3. Prepare four samplers at each of the six concentrations. Prepare four samplers at the target concentration using wet media. Prepare an additional four samplers at the RQL. Store the spiked samples at room temperature for a sufficient time to assure complete adsorption of the analyte. Although the time required may vary with each particular analyte, the samples should be stored overnight unless a shorter time period can be justified.

4. Prepare three analytical standards at each of the six concentration levels. Prepare the analytical standards with the same microliter syringe used in spiking the extraction samples.

5. Extract the spiked samples using the selected technique. After an appropriate amount of time for equilibrium to occur, analyze the samples. Analyze standards and samples for each level in the following order: standard no. 1; samples no. 1 and no. 2; standard no. 2; samples no. 3 and no. 4; standard no. 3. Reseal two of the dry samples containing the target concentration amount of analyte immediately after analysis for use in the test described in Step 7 of this Section.

6. For each level, separately calculate the extraction efficiency for each of the spiked samples using the average of the three analytical standards as follows:

(8) $$E_E = \frac{M_R}{M_S} 100$$

where E_E is extraction efficiency
M_R is mass recovered
M_S is mass spiked

Overall average extraction efficiency greater than 75% is acceptable but an average greater than 90% is preferred.

7. Determine the stability of extracted dry samples by reanalyzing the four dry target (2 samples with resealed vials, and 2 samples with punctured septa) concentration extraction samples approximately 24, 48, and 72 hours after the extraction efficiency was initially determined. Reseal two of the four vials containing these samples with new septa after each analysis. The remaining two samples shall retain their punctured septa throughout the test. Use freshly prepared standards for each reanalysis. The results obtained from the resealed samples will determine if restrictions must be placed on how soon after extraction the samples must be analyzed. The results from the

samples stored with punctured septa will determine if restrictions must be placed on the reanalysis of samples that may sit (as in an autosampler tray) before reanalysis. Consider extracted samples stable for the length of time that the difference between results for the initial analysis and results for the reanalysis is not greater than 10% for each sample. Also determine the number of punctures in each septum during the injection of the sample and report this number.

8. If storage instability after 24 hours is detected in Step 7, a reduced time study may be necessary in which extracted samples are reanalyzed at sufficiently short time intervals. Use this data to determine how long after extraction a valid analysis (or reanalysis) can be performed. Use the same criteria for sample stability as above.

9. If support pads are used in conjunction with 25 or 37-mm filters, determine their extraction efficiency by spiking them with a sample loading equivalent to the RQL or 0.05 times the target concentration whichever is higher. If a reactive reagent is used on the sampling filter it may be necessary to use the reagent in this test.

10. Select a medium and a technique (wet or dry) to be used to wipe interior walls of 25- or 37-mm filter cassettes used for particulate sampling. Spike the interior walls of 4 cassettes with 10 times the RQL or 0.1× target concentration (whichever is less), and 4 separate cassettes with 1.0 times the target concentration of the analyte to determine the efficiency at which the analyte is removed by wiping. Allow these cassettes to stand for a sufficient time (overnight for nonvolatile analytes) and then use the selected technique to perform the test. Determine the extraction efficiency from the wipe medium by spiking the medium separately and allowing them to stand overnight. A minimum recovery of 75% is required for this test. If results are less than 75%, determine if a second wipe performed with the same wipe medium used to collect the first wipe sample and with the same spiked cassette used for that test will provide total results greater than 75%. Fold the wipe medium so that the first collected sample is inside the folded wipe to perform the second wipe. If the second wipe does not provide recovery greater than 75%, perform the second cassette wipe using a fresh wipe medium. If a reactive reagent is used on the sampling filter it may be necessary to use the reagent in this test.

D. Effects of storage

1. Ambient and refrigerated temperature storage tests are performed simultaneously if stability of the analyte on the collection medium is unknown or if recovery is expected to decrease over time. The refrigerated storage test is optional if the samples are stable at ambient temperature. Collect 33 samples if a refrigerated temperature test is performed or 18 samples if only an ambient test is performed, from a dynamically generated controlled test atmosphere containing the analyte at the target concentration. The absolute humidity should be 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2EC). Use the recommended sampling time; and the recommended sampling rate for active samplers. If sample collection is extremely time consuming, increase the test atmosphere concentration or increase the active sampling rate in order to obtain the correct analyte loading on the samplers within a reasonable time. If this approach is taken, make certain that sampler capacity is not exceeded due to the altered sampling conditions.

2. Analyze three samples on the day they are collected. Use the average diffusive sampling rate determined in Section III.B converted to its equivalent sampling rate at sampling site temperature and pressure to calculate results for diffusive samplers. Do not correct sample results for extraction efficiency.

3. Store fifteen samples at ambient temperature in the dark, and store the remaining 15 samples under refrigeration at a temperature of 2-6 EC.

4. Analyze three samples from each set approximately every third day so that the storage test is at least two weeks in length.

5. Measure recovery from the regression curve obtained by plotting percent recovery (not corrected for extraction efficiency) versus days of storage.

6. A change in recovery of more than 10% in the two weeks is a significant uncorrectable bias and must be avoided. Also, the recovery (not corrected for extraction efficiency) must remain above 75% during storage and the 95% confidence limits must be within ±25% (see Section IV.C). When these conditions are not met, they may be overcome by use of an alternate sampling medium, by refrigerated sample storage, or by time requirements placed on completion of the analysis. The preferable goal is the use a convenient sampler without restrictions on storage conditions, or time requirements for completion of analysis. The effect of ambient shipment to the laboratory and then refrigerated storage of samples until analysis can be estimated. This is done by tracking cumulative sample loss on the plot for the ambient storage test for the first five days and then switching to the plot for the reduced temperature test for the remainder of the storage time. If the change in recovery remains greater than 10%; or if recovery is still less than 75%; or if the 95% confidence limits are greater than ±25% even after sample refrigeration, an alternate sampling procedure must be found and tested.

7. Plot the storage test data as shown in Figure 6. Note that this figure includes data for the overall precision, which is defined in a following section. The scale on the vertical axis is from 0% to 125%. The 95% confidence limits are ±1.96 times the overall standard error of estimate (equation 11) for the regression line for the storage data.

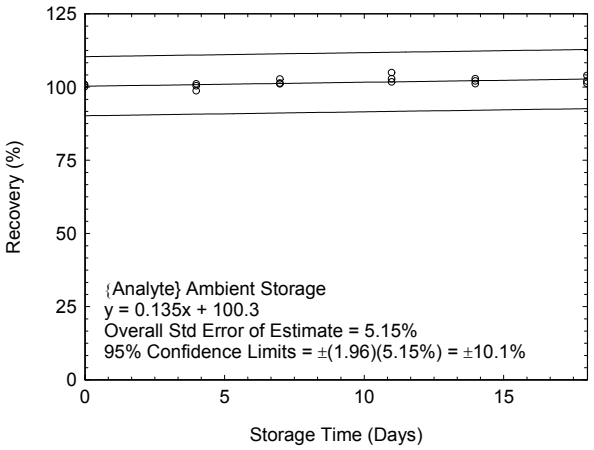

Figure 6. Example of a storage test.

IV. Validation of Overall Procedure

A. Detection limit of the overall procedure (DLOP)

1. Determine DLOP using the same procedure that was used to determine DLAP (Section II.A), except data shall be obtained from spiked samplers instead of analytical standards.

2. Report the DLOP as mass per sample and as equivalent air concentrations based on the recommended sample air volume.

3. Prepare a plot of the DLOP data for inclusion in the method as shown in Figure 7.

B. Reliable Quantitation Limit (RQL)

1. The RQL is the lower limit for precise quantitative measurements. Employing the regression line data used to calculate the DLOP, determine the RQL with the following formula, providing recovery from the sampler with mass closest to the RQL, is 100 ±25% of its theoretical value.

$$(9)\ L_{RQL} = 10\frac{S_{Y\cdot X(DLOP)}}{A}$$

where L_{RQL} is the reliable quantitation limit
$S_{Y\cdot X(DLOP)}$ is the standard error of estimate for the regression line for DLOP
A is the analytical sensitivity (slope)

If the recovery from the sampler with mass closest to the RQL is not within ±25% of its theoretical value, then the RQL will be equal to the lowest spiked concentration that is ±25% of its theoretical value. Determine this from a plot of recovery versus mass as shown in Figure 8, for inclusion in the method. Additional data points can be obtained by spiking a series of samplers with 2, 3, 4, or 5 times the highest mass spiked for the DLOP.

2. Report the RQL as mass per sample and as an equivalent air concentration based on the recommended sample air volume.

3. Generate a chromatogram of the RQL for inclusion in the method.

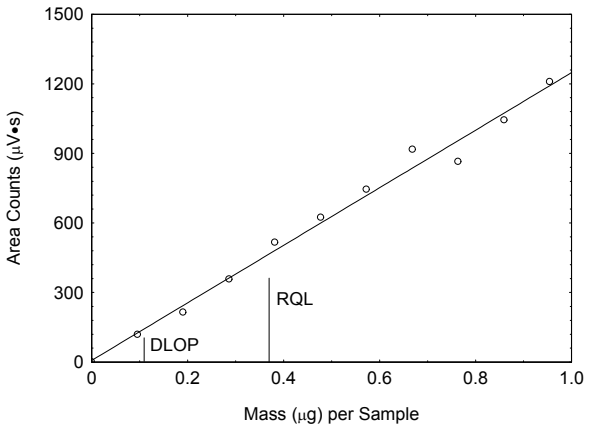

Figure 7. Example of plotted DLOP/RQL data (y = 1241x + 7.3).

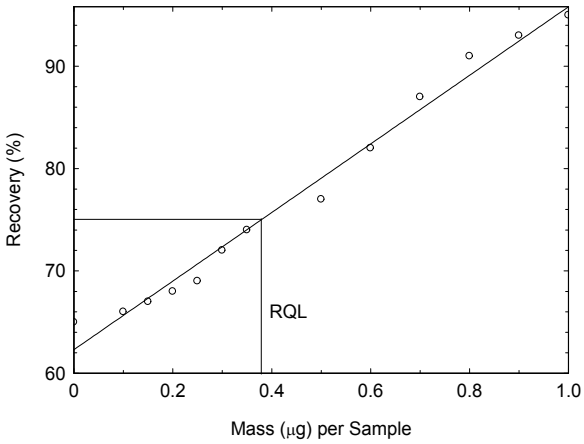

Figure 8. Example of a calculated RQL when recovery is the determining factor (y = 33.5x + 62.3).

C. Determination of the precision

1. Use data from Effects of Storage (Section III.D) in the determination of the overall precision. The precision cited for the method is based on the storage data that reflects the temperature recommended for shipment of samples.

2. Determine the standard error of estimate for the regression curve[5,6] of each storage test with the following formula.

[5] Snedcor, G.W.; Cochran, W.G. *Statistical Methods*, 6th ed.; Iowa State University: Ames, Iowa, 1967; p 467.
[6] Arkin, H.; Colton, R. C. *Statistical Methods*, 5th ed.; Barnes & Noble: New York, 1970; pp 84-88.

(10) $S_{Y \cdot X(STO)} = \sqrt{\frac{\sum (Y_{OBS} - Y_{EST})^2}{n-k}}$

where $S_{Y \cdot X(STO)}$ is the standard error of estimate from storage
Y_{obs} is observed response
Y_{est} is estimated response from regression curve
n is total number of data points
k is 2 for a linear regression
k is 3 for quadratic regression

3. Determine the overall standard error of estimate for each sampler type from the data used in both storage tests. Use the ambient test if the restrictions in Section III.D.6. are satisfied. Use the overall standard error of estimate from the refrigerated storage test if the ambient test fails. If the refrigerated storage test also fails, restrictions must be set on the maximum storage time that will be allowed before samples must be analyzed. List the overall standard error of estimate on the cover page of the completed method.

   a. Active sampler

      Determine the overall standard error of estimate for the overall procedure for each storage test (S_{EE}) by including the sampling pump variability (V_{SP}) with the following formula. Use 5% for V_{SP}.

(11) $S_{EE} = \sqrt{S^2_{Y \cdot X(STO)} + V^2_{SP}}$

where S_{EE} is the overall standard error of estimate
$S_{Y \cdot X(STO)}$ is the standard error of estimate from storage
V_{SP} is the sampling pump variability (5%)

   b. Diffusive sampler

      Modification of the calculation for overall standard error of estimate is required for diffusive samplers because V_{SP} is not an applicable parameter. In its place use sampling rate variation (V_{SR}), which is considered a function of sampler design and must be determined before methods development work with the sampler is performed. Because diffusive sampling rates are a function of temperature (T) and atmospheric pressure (P), the standard error of estimate must include additional uncertainty when these parameters are not determined at the sampling site. (See Sections IV.C.7 and 8.)

      The formula for the determination of the total standard error of estimate for diffusive samplers thus becomes:

(12) $S_{EE} = \sqrt{S^2_{Y \cdot X(STO)} + V^2_{SR} + V^2_T + V^2_P}$

where S_{EE} is the overall standard error of estimate
$S_{Y \cdot X(STO)}$ is the standard error of estimate from storage
V_{SR} is the sampling rate variation
V_T is the sampling rate uncertainty due to unreported temperature (7.7%)
V_P is the sampling rate uncertainty due to unreported pressure (3%)

but when the sampling site temperature and pressure are known, it simplifies to:

$$(13)\ S_{EE} = \sqrt{S^2_{Y \cdot X(STO)} + V^2_{SR}}$$

where S_{EE} is the overall standard error of estimate
$S_{Y \cdot X(STO)}$ is the standard error of estimate from storage
V_{SR} is the sampling rate variation

The sampling rate variation must be determined for any manufacturer's unique diffusive sampling product (such as 3M Organic Vapor Monitor, or SKC 575 Series Passive Sampler) before that sampler can be used by OSHA. Determine the sampling rate variation using a factorial test, similar to that of the NIOSH diffusive sampler testing protocol[7] or the SLTC protocol[8,9] for the validation for diffusive samplers. The sampling rate variation for SKC 575 Series Passive Sampler and the 3M 3520 Organic Vapor Monitor was determined to be 8.7%[10] and 6.4%[11], respectively.

4. Assuming a normal distribution of values about the regression curve and uniformity of variation about the entire range of the storage stability curve, ±1.96 times the overall standard error of estimate will represent the 95% confidence limit which is the precision of the method.

5. Represent the overall precision data graphically as shown in Figure 6, and cite the overall standard error of estimate derived from the data that reflects the recommended temperature for sample shipment as the precision of the method.

6. The two-sided 95% confidence limits of the overall procedure must be within ∀25%.

7. When the temperature at the sampling site is unknown, a value of 7.7% is used for V_T. This is an estimate of the maximum variation in sampling rate caused by a temperature range of 22.2 ∀ 15EC (72 ∀ 27EF). When the sampling site temperature is known, V_T is equal to zero.

8. When the pressure at the sampling site is unknown, determine it from the estimated elevation of the sampling site, and use a value of 3% for V_P. This is the variation in pressure due to changing weather conditions, which was determined by tracking atmospheric pressure at SLTC for a year. When the pressure at the sampling site is known, V_P is equal to zero.

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[7] Cassinielli, M.E.; Hull, R.D.; Crable, J.V.; and Teass, A.W., "Protocol for the Validation of Passive Monitors", *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring*, Berlin, A.; Brown, R.H.; and Saunders, K.J., Eds., Royal Society of Chemistry, Burlington House, London, pp 190-202, 1987.

[8] Hendricks, W. Development of a Protocol for Laboratory Testing of Diffusive Samplers, 1996. United States Department of Labor, Occupational Safety & Health Administration web site. http://osha.gov/dts/sltc/methods/studies/3movm/3movm.html (accessed January 7, 2009).

[9] Hendricks, W. Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, 1998. United States Department of Labor, Occupational Safety & Health Administration. http://osha.gov/dts/sltc/methods/studies/skc575/skc575.html (accessed January 7, 2009).

[10] Hendricks, W. Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, 1998. United States Department of Labor, Occupational Safety & Health Administration. http://osha.gov/dts/sltc/methods/studies/skc575/skc575.html (accessed January 7, 2009).

[11] Hendricks, W. Development of a Protocol for Laboratory Testing of Diffusive Samplers, 1996. United States Department of Labor, Occupational Safety & Health Administration web site. http://osha.gov/dts/sltc/methods/studies/3movm/3movm.html (accessed January 7, 2009).

9. If the elevation of the sampling site is unknown, the elevation can be estimated by data found on the internet. One internet source is: http://www.airnav.com. Select the AIRPORTS button. Select LOOK BY TOWN/REGION. Enter the city name. Check HELIPORTS and PRIVATE. This will identify all public airports, military airfields, private landing strips and all locations that accept helicopters. Select the radius of the search area. Select an airfield that is close to the sampling site. Maps are displayed to help with the selection of the nearest airfield. The elevation will be listed near the top of the airfield's information. Use the equation in Figure 9 to estimate the atmospheric pressure of the sampling site.

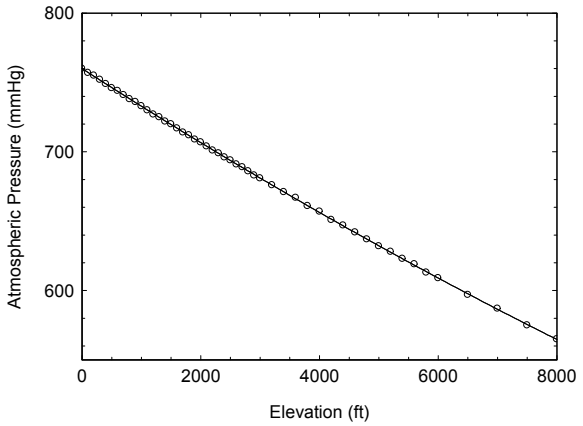

Figure 9. Plot of atmospheric pressure vs. elevation ($y = 3.768E\text{-}07x^2 – 2.741E\text{-}02x + 760$).

Table 2[12]
Atmospheric Pressure Versus Elevation

elevation (ft)	pressure (mmHg)	elevation (ft)	pressure (mmHg)	elevation (ft)	pressure (mmHg)	elevation (ft)	pressure (mmHg)	elevation (ft)	pressure (mmHg)
0	760	1000	733	2000	707	3000	681	5000	632
100	757	1100	730	2100	704	3200	676	5200	628
200	755	1200	727	2200	701	3400	671	5400	623
300	752	1300	725	2300	699	3600	667	5600	619
400	749	1400	722	2400	696	3800	661	5800	613
500	746	1500	720	2500	694	4000	657	6000	609
600	744	1600	717	2600	691	4200	651	6500	597
700	741	1700	714	2700	689	4400	647	7000	587
800	738	1800	712	2800	686	4600	642	7500	575
900	736	1900	709	2900	683	4800	637	8000	565

D. Reproducibility

1. Prepare six samples for each target concentration and for each sampler type in the same manner as used to prepare storage samples. Submit them to SLTC for analysis. Include a complete draft copy of the method for analyst instruction. The analyst will analyze the samples relying solely on the draft method for guidance to reproduce the analytical conditions. If possible, the analyst will use different analytical equipment to analyze the samples than was used to develop the method. If the samples are stored before analysis, the conditions under which they are stored should correspond to the recommended storage conditions of the method. If the analyte has a ceiling, peak or short term exposure limit, generate another set of reproducibility samples if the mass of analyte for the short-term sample is less than 10% of the mass collected for a long-term sample.

[12] Nelson, G.O., *Gas Mixtures Preparation and Control*, Lewis Publishers, Boca Raton, 1992, p. 265-266.

2. No individual analytical result shall deviate from the theoretical value by more than 1.96 times the standard error of estimate determined in Section IV.C. If this does occur, steps must be taken to determine and eliminate the cause of the excessive imprecision (e.g., an unanticipated technical problem or a lack of clarity in the analytical instructions provided in the draft copy). The analyst will discuss any problem or concern that arises from analysis of the reproducibility samples with the person that developed the method. The reproducibility test must then be repeated.

3. The analyst will discuss the analysis of the reproducibility samples with the Methods Development Team supervisor or team leader.

PREPARATION OF WRITTEN REPORTS FOR FULLY VALIDATED METHODS

The following format provides a means of reporting data obtained during validation of sampling and analytical methods that employ chromatographic analysis. The cover page is intended as a quick reference that provides basic information. The Method Validation Section contains tabulated and graphical laboratory data that may be referenced throughout the report.

Each fully validated method will be assigned a version number beginning with the number "1.0". Significant changes or revisions to the method require that a new version number be assigned, for example "2.0". If the document is revised, the date revised will be placed on the cover page and a discussion concerning the revision included in Section 1.1.1 History.

Required statements concerning the status of the method, accessibility problems, intended use of the method, manufacturer disclaimer, toxic effects disclaimer, reference to OSHA Methods Development Guidelines, basis of cited air concentrations, sampling safety, chemical hygiene plan, analytical safety, and QA practices are placed at certain points in the method text. These required statements will not be altered and will be inserted in the locations shown in the example fully validated method.

Text formatting, instructions for field and laboratory personnel, and descriptive discussion shown in the example fully validated method will not be altered unless such text in clearly inaccurate or inappropriate.

The purpose of section and paragraph indents is to delineate text and to provide a convenient way to reference sections and paragraphs in subsequent sections and paragraphs. Indents should be used as shown in the example fully validated method unless additional indents are necessary for clarity. Quaternary indents , for example 3.4.1.1, will be avoided whenever possible.

Page Numbering - Number the cover page. Number pages in the center of the footer in 8 point Arial font. Example: The first page of Method 1001 would be "1 of 38".

Editorial comments and text locations requiring the author to insert information are set off with braces "{ }". The note in braces is not itself intended to be inserted in the method.

Text will be written in 10 point Arial font with full justification with no added hyphenation.

Tabs: Cover page - 2.0 - Method - 0.25, 0.63, 1.13, 1.38

OSHA logo on cover page - size = 0.500", right margin, wrap behind text.

Graphs - size = 3.1", caption is 9 point Arial font.

Tables- size = 3.1, 9 point Arial font.

References will follow as closely as possible the format recommended by the American Chemical Society in the 3rd edition of "The ACS Style Guide - A Manual for Authors and Editors."

{ANALYTE}
{as listed in CFR or ACGIH}

Method number: 1xxx

Version: x.0

Target concentration: ____ ppm (____ mg/m^3)
OSHA PEL: ____ ppm (____ mg/m^3) {None if no PEL}
ACGIH TLV: ____ ppm (____ mg/m^3) {None if no TLV}
{Include skin designations when applicable}

Procedure: Active samples are collected by drawing workplace air through ____ {active sampler} with personal sampling pumps. Diffusive samples are collected by exposing ____ {diffusive sampler} to workplace air. Samples are extracted with ____ and analyzed by ____ using a ____ detector.

Recommended sampling time and sampling rate:
____ {Active sampler}: ____ min at ____ mL/min (____ L)
{If the sampling rate is greater than 250 mL/min, use L/min}
____ {Diffusive sampler}: ____ min (sampling rate at 760 mmHg and 25 °C ____ mL/min)

Reliable quantitation limit:
____ {Active sampler}: ____ ppm (____ mg/m^3)
____ {Diffusive sampler}: ____ ppm (____ mg/m^3)

Standard error of estimate at the target concentration:
____ {Active sampler}: ____%
____ {Diffusive sampler}: ____%*
*For diffusive samplers when sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.5 for applicable standard errors of estimate.

Special requirements: When using a ____ {diffusive sampler}, report the temperature and uncorrected sampling site atmospheric pressure. {If there are no special requirements, delete this item}

Status of method: Fully validated method. This method has been subjected to the established validation procedures of the Methods Development Team.

____ {month year} {Chemist} ____
Date revised ____ {month year}

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

{Explain why past methodology is inadequate, and how the new procedure is superior. Also, obvious questions that may be raised by knowledgeable readers should be addressed. Keep length to 1.5 pages or less.}

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

{Cite sources for presented information. If both animal data and human data are presented, present the animal data first. If the entire section is taken from one reference, the reference notation can be placed behind the qualifying statement in the heading.}

1.1.3 Workplace exposure

{Report major sources of exposure in the workplace and, if available, the size of the work population that is exposed. If the entire section is taken from one reference, the reference notation can be placed behind the heading.}

1.1.4 Physical properties and descriptive information {these are examples and can be used if applicable, other physical properties can also be listed.}

synonyms:	____		
solubility:	____		
IMIS number[13]:	____	appearance:	____
CAS number:	____	vapor pressure: {kPa (mmHg)}	____
molecular weight:	____	flash point:	____
boiling point:	____	odor:	____
melting point:	____	lower explosive limit:	____
δ_{max}:	____	specific gravity:	____
structural formula:	____	molecular formula:	____

[13] Chemical Sampling Information. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html (accessed March 11, 2009).

This method was validated according to the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[14]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations, and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25EC and 760 mmHg (101.3 kPa).

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

2.1 Apparatus {Provide general descriptions of the required equipment followed by a description of specific equipment actually used in the validation, if applicable.}

2.1.1 ____ {Active sampler}
Example:
Samples are collected with {description of the sampler, 7-cm H 4-mm i.d. H 6-mm o.d. glass sampling tubes packed with two sections of ____ {adsorbent}}. The front section contains 110 mg and the back section contains 55 mg of ____ {adsorbent}. The sections are held in place and separated with glass wool plugs. For this validation, commercially prepared ____ {active samplers} were purchased from ____ {Supplier} (catalog no. ____, lot no._____).

A sampling tube holder is required to protect the worker from the sharp end of the glass sampling tube.

Samples are collected using a personal sampling pump calibrated to within ∀5% of the recommended flow rate with the sampling device in-line.

2.1.2 ____ {Diffusive sampler}

Samples are collected with a ____ {diffusive sampler}. For this validation, commercially available samplers were purchased from ____ {Supplier} (catalog no. _____, lot no. _____).

2.1.3 A thermometer and barometer are required to determine the sampling site air temperature and atmospheric pressure.

2.2 Reagents {If no reagents are required, state "None required". Otherwise use the format described in Section 3.2.}

2.3 Technique {Describe steps involved in sample collection, preparation, and shipment.}

2.3.1 ____ {Adsorbent tube}

[14] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking ends. Use sampling tube holders to minimize the hazard to the worker from the broken ends of the tubes. All tubes should be from the same lot.

The smaller section of adsorbent in the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder (with the adsorbent tube) to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down in the worker's breathing zone during sampling. Position the sampling pump, tube holder, and tubing so they do not impede work performance or safety.

Draw air directly into the inlet of the sampling tube holder. The air being sampled should not pass through any hose or tubing before entering the sampling tube.

Sample for up to ____ min at ____ mL/min (____ L) when using ____ {sampler} to collect TWA (long-term) samples.

Sample for ____ min at ____ mL/min (____ L) when using ____ {sampler} to collect {short-term, ceiling, or peak whichever is appropriate} samples.

After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with a Form OSHA-21 as soon as possible.

Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (min) and sampling rate (mL/min) for each sample, along with any potential interference on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator as a precaution.

Ship any bulk sample(s) separate from the air samples.

2.3.2 ____ {Filter sampler}

Remove the plastic end plugs from the filter cassette immediately before sampling. {Remove the rear plastic plug and the top piece of the filter cassette for open-face sampling.}

Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, cassette, and tubing so it does not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the cassette. The air being sampled is not to be passed through any hose or tubing before entering the cassette.

Sample for up to ____ min at ____ L/min (____ L) when using ____ {sampler} to collect TWA (long-term) samples.

Sample for ____ min at ____ L/min (____ L) when using ____ {sampler} to collect {short-term, ceiling, or peak whichever is appropriate} samples.

After sampling for the appropriate time, remove the sample and seal the cassette with plastic end plugs {plug and top piece}. Seal each sample end-to-end with a Form OSHA-21 as soon as possible.

Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

Record sample air volumes (liters), sampling time (min), and sampling rate (L/min) for each sample, along with any potential interference.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator as a precaution.

Ship any bulk sample(s) separate from the air samples.

2.3.3 SKC 575-002 Passive Samplers (In general, follow the manufacturer's instructions.)

Remove the sampler from its air-tight package.

Record the start time on the sampler label and on the Form OSHA-91A. Remove the cover and cover retainer when ready to begin sampling. CAUTION - The sampler immediately begins to sample when the cover is removed. Keep the O-ring, press-on cover, cover retainer, port plugs and poly(tetrafluorethylene) (PTFE) tube in the package for later use.

Attach the sampler to the worker near his/her breathing zone with the perforations in the sampler facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

Sample for up to ____ min when using ____ {sampler} to collect TWA (long-term) samples. The sampling rate for ____ {analyte} using ____ {sampler} is ____ mL/min at 760 mmHg and 25 °C.

Sample for ____ min when using ____ {sampler} to collect {short-term, ceiling, or peak whichever is appropriate} samples. The sampling rate for ____ {analyte} using ____ {sampler} is ____ mL/min at 760 mmHg and 25 °C.

At the end of the sampling period, immediately detach the sampler from the worker and attach the O-ring and cover onto the side of the sampler with the perforations. Secure the cover onto the sampler using the cover retainer. Visually inspect the O-ring to be sure it is forming a proper seal around the entire circumference of the sampler. Record the stop time on the sampler label and also on the Form OSHA-91A. Return each sampler to its package, close the package, and seal it with a Form OSHA-21.

Prepare a blank in a low background area by removing an unused sampler from its package. Then remove the cover and the cover retainer. Immediately attach an O-ring, a cover, and a cover retainer onto the sampler. Return the blank sampler to its package, close the package, and seal it with a Form OSHA-21.

Verify that the sampling times are properly recorded on the Form OSHA-91A for each sample. Also, identify blank samples on this form.

Record the room temperature and atmospheric pressure at the sampling site on the Form OSHA-91A.

List any compounds that could be considered potential interferences, especially solvents that are being used in the sampling area.

Submit the samplers to the laboratory for analysis as soon as possible. Include all port plugs and PTFE tubes which will be used in the laboratory analyses in the bag with the sampler. If delay is unavoidable, store the samples in a refrigerator as a precaution.

Ship any bulk sample(s) in a container separate from the air samples.

2.3.4 3M 3520 OVMs (In general, follow the manufacture's instructions.)

The samplers come individually sealed in small metal cans. When ready to begin sampling, remove the plastic lid from the can and lift up on the revealed ring. Pull back on the ring to open the can. Discard the metal top of the can and remove the sampler. CAUTION - The sampler immediately begins to sample when the can is unsealed.

Keep the two closure caps with attached port plugs, cup and PTFE tubes in the can for later use. Close the can with the plastic lid.

Record the start time on the back of the sampler and on the Form OSHA-91A.

Attach the sampler to the worker near his/her breathing zone with the white face forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period. Do not remove the white film and ring from the sampler until the sampling period is terminated.

Sample for up to ____ min when using ____ {sampler} to collect TWA (long-term) samples. The sampling rate for ____ {analyte} using ____ {sampler} is ____ mL/min at 760 mmHg and 25 °C.

Sample for ____ min when using ____ {sampler} to collect {short-term, ceiling, or peak whichever is appropriate} samples. The sampling rate for ____ {analyte} using ____ {sampler} is ____ mL/min at 760 mmHg and 25 °C.

At the end of the sampling period, detach the sampler from the worker and remove the white film and retaining ring. For each sampler (one sampler at a time), **immediately** after removing the white film and retaining ring, separate the primary (top), and secondary (bottom) sections of the sampler using the edge of a coin as a pry. Snap a closure cap onto the top of the primary section. Snap a cup onto the bottom of the primary section. Snap a closure cap onto the secondary section of the sampler. Assure that the attached port plugs are all placed firmly into the port holes. Return the sampler sections (with their closure caps, cup, and port plugs all securely affixed) to the metal can which contains the PTFE tubes (which will be used by the laboratory). Close the can with the plastic lid, and seal it with a Form OSHA-21.

Perform the following in a low background area for a set of samplers as soon as possible after sampling. Prepare a blank by removing the white film and ring and attaching a closure cap onto an unused sampler. For the blank sampler, separate the primary (top), and secondary (bottom) sections of the sampler using the edge of a coin as a pry. Snap a cup onto the bottom of the primary section. Snap a closure cap onto the secondary section of the sampler. Assure that the attached port plugs are all placed firmly into the port holes. Return the blank sampler sections (with their closure caps, cup, and port plugs all securely affixed) to the metal can which contains the PTFE tubes (which will be used by the laboratory). Close the can with the plastic lid, and seal it with a Form OSHA-21.

Verify that the sampling times are properly recorded on the Form OSHA-91A for each sample. Also, identify blank samples on this form.

Record the room temperature and atmospheric pressure of the sampling site on Form OSHA-91A.

List any compounds that could be considered potential interferences, especially solvents that are being used in the sampling area.

Submit the samplers to the laboratory for analysis as soon as possible. If delay is unavoidable, store the samples in a refrigerator as a precaution.

Ship any bulk sample(s) in a container separate from the air samples.

3. Analytical Procedure

Adhere to the rules set down in your laboratory's Chemical Hygiene Plan[15] (for instance: OSHA SLTC adheres to the rules set down in the OSHA SLTC Chemical Hygiene Plan). Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure. Follow all applicable quality assurance practices established in your laboratory's internal quality system (for instance: OSHA SLTC follows the quality assurance practices established in the OSHA SLTC Quality Assurance Manual).

3.1 Apparatus {Provide general descriptions of the required equipment. Follow each general description with a specific description of equipment actually used in the validation.}
Example:
Gas chromatograph equipped with an FID. An Agilent 6890 Series GC System was used in this validation.

3.2 Reagents {Provide general descriptions of the required reagents. Follow each general description with a description of the specific reagent actually used in the validation.}
Example:
Methylene chloride, [CAS no.], ___ grade or better. The methylene chloride used in this validation was A.C.S. HPLC grade (lot no. Q87C654) purchased from Aldrich (Milwaukee, WI).

Carbon disulfide (CS_2), [CAS no.], ____ grade or better. The CS_2 used in this validation was low benzene grade (lot no. 37529) purchased from JT Baker Chemical Co. (Phillipsburg, NJ).

N,N-Dimethylformamide (DMF), [CAS no.], ____ grade or better. The DMF used in this validation was 99+% (lot no. LP642) purchased from Aldrich (Milwaukee, WI).

p-Cymene, [CAS no.], The *p*-cymene used in this validation was 99+% (lot no. SW 9180SU) purchased from Aldrich (Milwaukee, WI).

Extraction solvent. The extraction solvent used in this validation consisted of ____ {list volume} µL/mL *p*-cymene in 99/1 (V/V) CS_2/DMF. The *p*-cymene was added as an internal standard. The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.[16]

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[15] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

[16] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

3.3 Standard preparation {Describe preparation of standards in general and give an example.}
Example:
Prepare concentrated stock standards of ____ {analyte} in the extraction solvent. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1 mL of extraction solvent delivered from the same dispenser used to extract samples. For example, to prepare a target level standard, inject ____ µL of a stock solution containing ____ mg/mL of ____ {analyte} into 1 mL of extraction solvent.

Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

3.4 Sample preparation {Describe steps involved in preparing samples for analysis.}

Example:
3.4.1 ____ {Active sampler}

Remove the plastic end caps from the sample tube and carefully transfer each section of the adsorbent to separate 2-mL vials. Discard the glass tube and glass wool plugs.

Add 1.0 mL of extraction solution to each vial and immediately seal the vials with PTFE-lined caps.

Extract the samples for ____ {30 min} by {describe technique}.

3.4.2 SKC 575-002 Samplers (In general, follow the manufacturer's instructions.)

Cut off the ends of the two protruding tubes of each sampler with a razor blade, sharp knife, or scissors.

Slowly add 1.0 mL of extraction solvent through one of the protruding tubes (ports). After about 30 seconds, slowly add another 1.0 mL of extraction solvent.

Immediately insert plugs into the ports.

Mount the samplers on the sampler rack (SKC Cat. No. 226-04-5) of a specialized shaker (SKC Cat. No. 226D-03-1) and shake the samplers for ____ {time}.

Do not leave the extracted sample in the sampler. Transfer each extracted sample by removing the plugs from the sampler ports, firmly inserting the tapered end of a supplied PTFE tube into the outer port and carefully pouring the solution through the PTFE tube into a labeled autosampler vial.

3.4.3 3M 3520 OVMs (In general, follow the manufacturer's instructions.)

Remove both sampler sections from the metal cans, along with the sections of PTFE tubing. Assure that the closure caps are firmly snapped to the primary and secondary sections of all the samplers. Also assure that all cap plugs are firmly seated in the cap ports. Any deviations must be noted.

Prepare one section of the sampler at a time by temporarily removing the cap plugs from the ports and adding 2.0 mL of extraction solvent through the center port. This is most easily done by dispensing two 1.0-mL aliquots of extraction solvent using a dispenser. Immediately replace the plugs in the ports. {An alternate means of

preparation for 3M 3520 OVMs is to remove the cap, remove the interior retaining ring, remove the front charcoal pad, and place it into a 4-mL vial. Remove the pad from the second section of the sampler in similar fashion and place it in a separate 4-mL vial. Add 2-mL of the extraction solvent to each vial and cap the vials.} Extract the sample for ____ {min} by {describe technique}.

Transfer the solution from each sampler section by removing both plugs from the ports, inserting a supplied decanting spout (a small section of PTFE tubing) into the outer port and pouring the liquid through the spout into a labeled autosampler vial. {or by transferring the solution from the extraction vial to a labeled autorampler vial}. Immediately cap each vial.

3.5 Analysis

{Provide detailed instrument settings; include a chromatogram at the target concentration, a calibration curve, and the calibration technique used.}

3.5.1 Analytical conditions

Example:

GC conditions

oven temperature:	60 °C (hold 1 min), ramp to 225 °C at 15 °C/min (hold 3 min)
injector temperature:	250 °C
detector temperature:	300 °C
run time:	15 min
column:	Supelco SPB-5 capillary column, 60-m × 0.32-mm i.d, d_f = 1.0-µm, or equivalent
column mode:	constant pressure (14 psi) {or constant flow}
initial column gas flow:	1.2 mL/min (hydrogen)
septum purge:	1.5 mL/min (hydrogen)
injection size:	1.0 µL (10 to 1 split)
inlet liner:	Agilent 5183-4647 or equivalent
retention times:	6.5 min (compound A) 6.9 min (compound B) 10.0 min (compound C) 13.6 min (compound D)

FID conditions

hydrogen flow:	30 mL/min
air flow:	450 mL/min
nitrogen make up flow:	45 mL/min

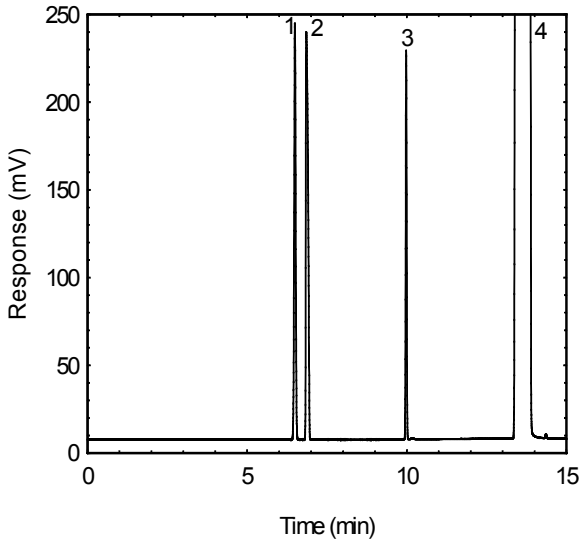

Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended analytical conditions (1: compound A; 2: compound B; 3: compound C; 4: compound D).

3.5.2 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

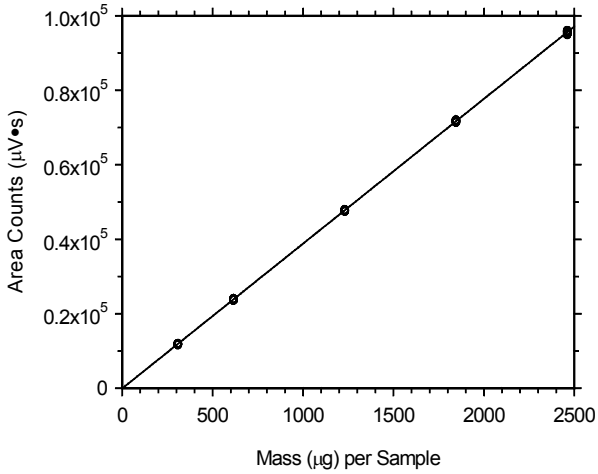

Figure 3.5.2. Calibration curve for ____ {analyte} (y = 38.89x -65.50).

3.6 Interferences (analytical)

Example:

3.6.1 Any compound that produces an FID response and has a similar retention time as the analyte or internal standard is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate interferences from the analyte.

3.6.2 When necessary, the identity of an analyte peak can be confirmed with additional analytical data or procedures (Section 4.10).

3.7 Calculations {Use 24.46 L/mole [(22.41 L/mole)(298.2 K)/273.2 K] for the molar volume.}
Example:

3.7.1 ____ {Active sampler}

The amount of ____ {analyte} per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The back section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, it is added to the amount on the front section. If more than 20% of the total amount is found on the back section, report that the sampler may have been saturated on the Form OSHA-91B. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concn by weight in air (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

$$C_V = \frac{C_M V_M}{M_r}$$

where C_V is concn by volume (ppm)
C_M is concn by weight in air (mg/m^3)
V_M is 24.46 (molar volume at NTP)
M_r is molecular weight

3.7.2 ____ {Diffusive sampler}

The amount of ____ {analyte} for the samples is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The back section of a 3M 3520 OVM is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, this amount is multiplied by 2.2 (as per manufacturer's instructions) and then added to the amount on the front section. If more than 20% of the total amount is found on the back section, report that the sampler may have been saturated on the Form OSHA-91B. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$R_{SS} = R_{NTP}\left(\frac{T_{SS}}{T_{NTP}}\right)^{\frac{3}{2}}\left(\frac{P_{NTP}}{P_{SS}}\right)$$

where R_{SS} is the sampling rate at the sampling site (mL/min)
R_{NTP} is the sampling rate at NTP (mL/min)
T_{SS} is the temp at the sampling site (K)
T_{NTP} is 298.2 K
P_{SS} is the sampling site pressure (mmHg)
P_{NTP} is 760 mmHg

$$C_M = \frac{M1000}{R_{SS}\, t\, E_E}$$

where C_M is concn by weight in air (mg/m^3)
M is micrograms per sample
R_{SS} is the sampling rate at the sampling site (mL/min)
t is the sampling time (min)
E_E is extraction efficiency in decimal form

$$C_V = \frac{C_M V_M}{M_r}$$

where C_V is concentration by volume (ppm)
V_M is 24.46 (molar volume at NTP)
C_M is concentration by weight (mg/m^3)
M_r is molecular weight

If the sampling site temperature is not provided, assume that it is 22.2EC. If the sampling site atmospheric pressure is not given, calculate an approximate value based on the sampling site elevation from the following equation.

$$P_{SS} = AE^2 - BE + 760$$

Pss is the approximate atmospheric pressure (mmHg)
E is the sampling site elevation (ft)
A is 3.768×10^{-7} mmHg/ft^2
B is 0.02741 mmHg/ft

4. Method Validation

General instruction for the laboratory validation of OSHA sampling and analytical methods that employ chromatographic analysis is presented in "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[17]. These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

4.1 Detection limit of the analytical procedure (DLAP) {Present test data in a table and in a graph. {Use a single summary paragraph, and separate tables and graphs for multiple analytes.}
Example:
The DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments of ____ {analyte} with the highest standard containing ____ µg/mL. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. These standards and the reagent blank were analyzed with the recommended analytical parameters (1-µL injection with a __:1 split). The data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of ____ and ____ were obtained for the slope and standard error of estimate respectively. The DLAP was calculated to be ____ pg.

Table 4.1
Detection Limit of the Analytical Procedure

concentration (µg/mL)	mass on column (pg)	area counts (µV-s)
0	0	0
0.421	42.1	173
0.841	84.1	318
1.26	126	425
1.68	168	573
2.10	210	690
2.52	252	853
2.94	294	973
3.36	336	1150
3.78	378	1270
4.21	421	1380

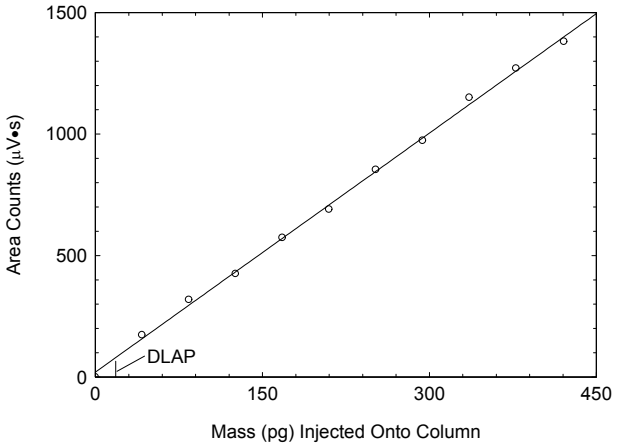

Figure 4.1. Plot of data to determine the DLAP (y = 3.28x + 20.8).

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL) {Present test data in a table, in a graph, and in a chromatogram of the RQL. Use a single summary

[17] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

paragraph and separate tables and chromatograms for multiple analytes and samplers. Present DLOP and RQL values in separate summary tables if there are multiple analytes or samplers}

The DLOP is measured as mass per sample and expressed as equivalent air concentrations based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was ____ µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of ____ and ____ were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be ____ µg/sample (____ ppm or ____ mg/m^3).

Table 4.2
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
0.096	118
0.191	214
0.287	357
0.232	515
0.478	623
0.573	744
0.669	916
0.764	864
0.860	1043
0.955	1208

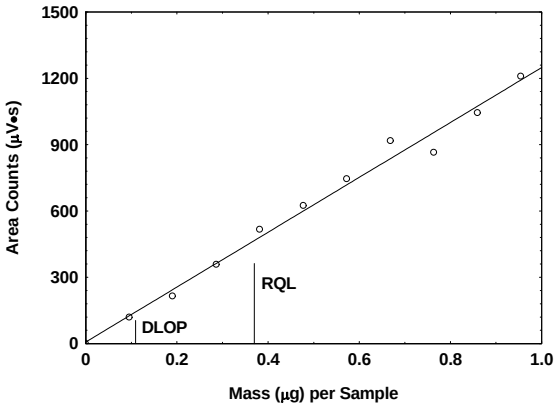

Figure 4.2.1. Plot of data to determine the DLOP/RQL (y = 277x – 75.5).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of DLOP providing 75% to 125% of the analyte is recovered. The RQL is ____ µg/sample (____ ppm or ____ µg/m^3). Recovery at this concentration is ____%.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for ____ {active sampler} is ____ ppm (____ mg/m^3) for ____ {analyte} when ____ L is sampled.

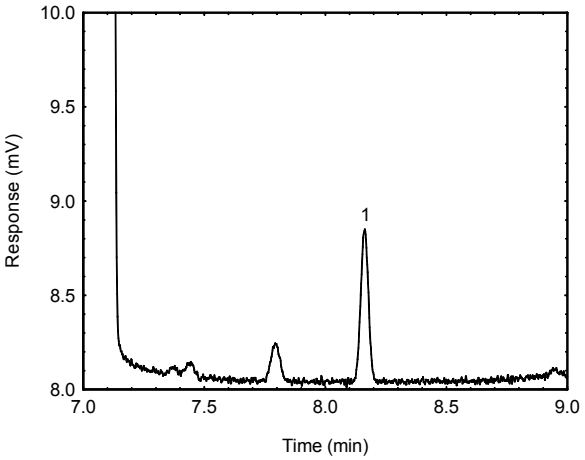

Figure 4.2.2. Chromatogram of the RQL (1: ____ {analyte}).

4.3 Precision of the analytical method

Example:

The precision of the analytical method measured as the mass equivalent to the standard error of estimate determined from the {list type of curve, example: linear} regression of data points from standards over a range that covers 0.1 {or RQL whichever is higher} to 2 times the target

concentration for the sampler with the highest mass loading. A calibration curve was constructed and shown in Section 3.5.2 from the three injections of five standards. The standard error of estimate was ____ {mass}.

Table 4.3
Instrument Calibration

H target	0.1H	0.5H	1.0H	1.5H	2.0H
concn (µg/sample)	123	615	1230	1845	2461
area counts (µV·s)	4772	23988	47783	71790	95054
	4770	23738	47593	71490	95987
	4799	23741	47895	71901	95616

4.4 Storage stability test {Describe the storage test, including preparation of samples.}

4.4.1 ____ {Active sampler}

Storage samples for ____ {analyte} were prepared by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentration of ____ {analyte} in the test atmosphere was the target concentration (____ppm or ____mg/m^3), and the relative humidity was ____ {RH} at ____ {temp} EC. Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen samples were stored at reduced temperature (4EC) and the other fifteen were stored in a closed drawer at ambient temperature (about ____ {temp}EC). At 2-5 day intervals {preferably 3-day intervals}, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.4.1
Storage Test for ____ {Analyte}

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.5	99.9	100.7	100.5	99.9	100.7
4	98.6	100.9	100.3	97.4	96.2	98.7
7	102.6	100.9	101.2	101.5	98.8	100.9
11	102.7	104.8	101.6	101.9	101.9	102.4
14	101.9	101.0	102.7	100.2	98.8	103.2
18	101.1	103.8	101.9	100.7	98.4	102.8

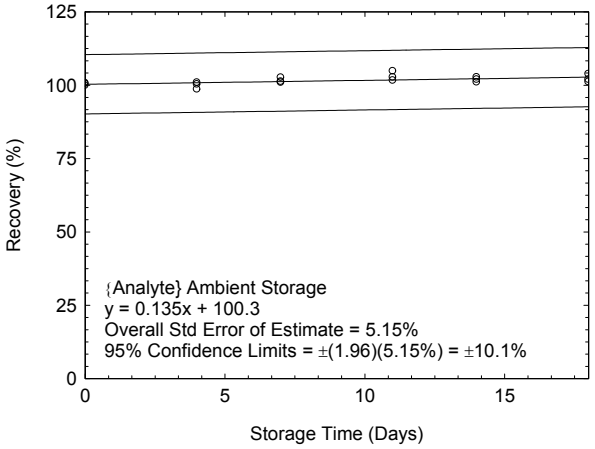

Figure 4.4.1.1. Ambient storage test for ____ {analyte}.

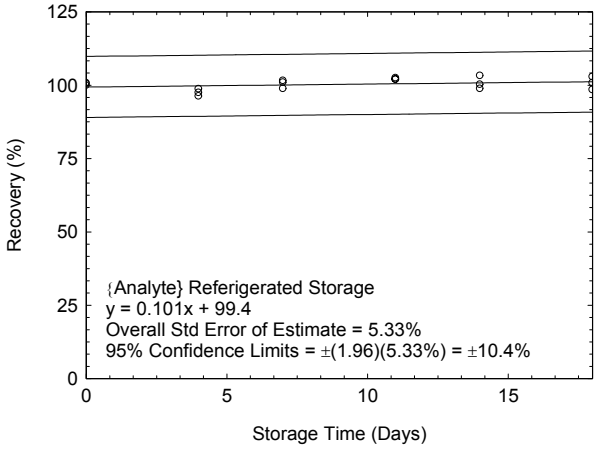

Figure 4.4.1.2. Refrigerated storage test for ____ {analyte}.

4.4.2 ____ {Diffusive sampler}

Storage samples for ____ {analyte} were prepared sampling a dynamically generated controlled test atmosphere using the recommended sampling time. The concentration of ____ {analyte} in the test atmosphere was the target concentration (____ ppm or ____mg/m^3), and the relative humidity was ____ {RH} at ____ {temp} EC. Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the samplers were stored at reduced temperature (4EC) and the other fifteen were stored in a closed drawer at ambient temperature (about ____ {temp} EC). At 2-5 day intervals {preferably 3-day intervals}, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency. Results were calculated using the sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure.

Table 4.4.2
Storage Test for ____ {Analyte}

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	103.5	101.6	101.9	103.5	101.6	101.9
4	99.6	100.5	95.8	99.3	99.4	101.8
7	100.0	95.8	93.8	95.9	100.9	95.8
11	100.8	98.8	100.2	100.6	103.6	105.5
14	95.6	96.6	99.1	98.9	99.6	97.5
16	96.5	94.5	98.8	99.3	99.5	99.1

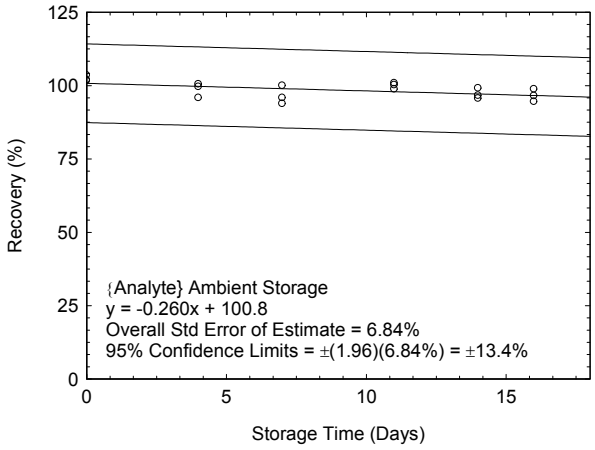

Figure 4.4.2.1. Ambient storage test for ____ {analyte}.

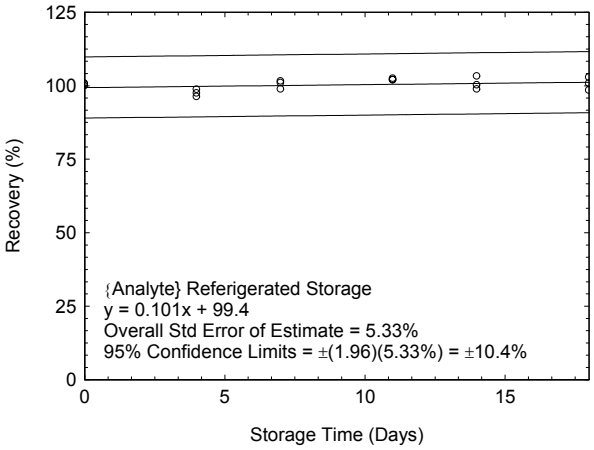

Figure 4.4.2.2. Refrigerated storage test for ____ {analyte}.

4.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). Ninety-five percent confidence intervals are drawn about the regression lines in the storage stability figures shown in Section 4.4.

4.5.1 ____ {Active sampler}

The precession of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (____EC)} 15-day storage test (at the target concentration) is ∀____ %. It was obtained from the overall standard error of estimate (____ %) of the data shown in Figure ____. It contains an additional 5% for sampling pump error. {The standard error of estimate listed on the cover page of the method and in this section must be based on the storage data that reflects the temperature recommended for shipment and storage of samples.}

4.5.2 ____ {Diffusive sampler}

The precisions of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (____ EC)} 15-day storage test (at the target concentration) for ____ {diffusive sampler} are given in Table 4.5.2. They each include an additional ____% for sampling rate variation[18,19]. There are different values given, depending on whether both, either, or neither temperature (*T*) or atmospheric pressure (*P*) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15EC (72 ± 27 EF) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included. {The standard error of estimate listed on the cover page of the method and in this section must be based on the storage data that reflects the temperature recommended for shipment and storage of samples. Temperature and barometric pressure are known conditions for storage samples.}

Table 4.5.2
Overall Standard Error of Estimate
and Precision of the Overall Procedure

known condition	error (%)	precision (∀%)
both *T* & *P*	____	____
only *T*	____	____
only *P*	____	____
neither *T* nor *P*	____	____

4.5.3 Recovery

The recovery of ____ {analyte} from samples used in a ____-day storage test remained above ____ % and ____% {the lowest points on the respective regression curves of Section 4.5} when the samples were stored at ____EC for ____ {active sampler} and ____ {diffusive sampler}, respectively. (Or if the case requires: The recovery of ____ {analyte} from samples used in a ____-day storage test remained above 75% for the first ____ days when samples were stored at ____EC.) {Use the same storage data as used for precision to calculate recovery}

4.6 Reproducibility {Describe reproducibility test and present data in Tables 4.6.1 and 4.6.2. Specify that the "amount found" is corrected for extraction efficiency.}
Example:
Six samples were prepared for both types of sampler by sampling a dynamically generated controlled test atmosphere similar to that used in the collection of the storage samples. The concentration of ____ {analyte} in the test atmosphere was the target concentration (____ ppm or ____mg/m^3), and the relative humidity was ____ {RH} at ____ {temp} EC. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for ____ days at ____EC. Sample results were corrected for extraction efficiency. No sample result for ____ {analyte} had a deviation greater than the

[18] Hendricks, W. Development of a Protocol for Laboratory Testing of Diffusive Samplers, 1996. United States Department of Labor, Occupational Safety & Health Administration. http://osha.gov/dts/sltc/methods/studies/3movm/3movm.html (accessed January 7, 2009).
[19] Hendricks, W. Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, 1998. United States Department of Labor, Occupational Safety & Health Administration. http://osha.gov/dts/sltc/methods/studies/skc575/skc575.html (accessed January 7, 2009).

precision of the overall procedure determined in Section 4.5. Theoretical masses for ____ {diffusive sampler} were determined using the sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and atmospheric pressure.

Table 4.6.1
Reproducibility Data for ____ {Analyte}
Collected on ____ {Active Sampler}

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
420.6	388.6	92.4	!7.6
420.6	395.5	94.0	!6.0
420.6	393.2	93.5	!6.5
420.6	379.6	90.3	!9.7
420.6	379.0	90.1	!9.9
420.6	406.1	96.6	!3.4

Table 4.6.2
Reproducibility Data for ____ {Analyte}
Collected on ____ {Diffusive Sampler}

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
420.6	388.6	92.4	!7.6
420.6	395.5	94.0	!6.0
420.6	393.2	93.5	!6.5
420.6	379.6	90.3	!9.7
420.6	379.0	90.1	!9.9
420.6	406.1	96.6	!3.4

4.7 Sampler capacity {add "and sampling rate for ____diffusive samplers}" if appropriate {Describe breakthrough or other studies used.}

4.7.1 ____ {Active sampler}

The sampling capacity of the front section of an ____ {active sampler} was tested by sampling a dynamically generated controlled test atmosphere containing ____ {analyte} at two times the target concentration (____ppm or ____ mg/m^3) and ____ {RH} relative humidity at ____ {temp} EC. The samples were collected at ____ mL/min. A GC equipped with a gas sampling valve and an FID was placed in-line behind the front test section and was used to monitor the effluent from the sampling tube every 5 min. The recommended sampling time is ____ hours.

Table 4.7.1
Breakthrough of ____ {Analyte}
From Front Section of ____ {Active Sampler}

test no.	air vol (L)	sampling time (min)	downstream concn (mg/m^3)	break-through (%)
1	14.2	285	0.00	0.0
	15.8	315	0.00	0.0
	18.7	375	0.72	1.02
	21.5	430	1.96	2.78
	23.0	460	2.91	4.13
	24.5	490	3.94	5.59
2	13.8	275	0.00	0.0
	16.0	320	0.31	0.44
	19.3	385	0.84	1.19
	22.0	440	2.04	2.90
	23.3	465	3.15	4.47
	24.8	495	4.11	5.84
3	13.5	270	0.00	0.0
	15.5	310	0.21	0.30
	18.5	370	0.75	1.07
	21.8	435	1.85	2.63
	22.5	450	3.20	4.55
	25.0	500	4.20	5.97

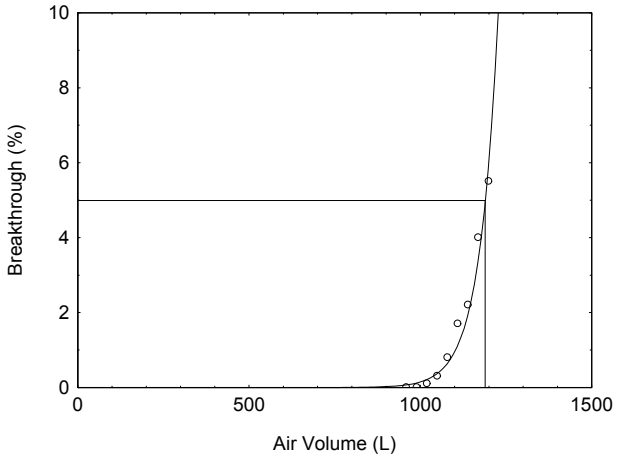

Figure 4.7.1. Five-percent breakthrough air volume for ____{analyte}.

4.7.2 ____ {Diffusive sampler}

The sampling rate and sampler capacity for ____ {diffusive sampler} were determined by sampling a dynamically generated controlled test atmosphere for increasing time intervals. Sampler capacity is exceeded when the plotted sampling rate decreases rapidly as the sampler becomes saturated. The concentration of the test atmosphere was two times the target concentration (____ ppm or ____ mg/m^3) at ____ {RH} relative humidity and ____ {temp} EC. The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and 2 hour samples. Horizontal lines were placed 10% above and 10% below the preliminary sampling rate. The sampling rate is ____ mL/min at 760 mmHg and 25EC and represents the average of all values between the lines. The standard deviation and RSD are ____ mL/min and ____%, respectively. The data obtained are shown in Table 4.7.2 and Figure 4.7.2. Mass collected is corrected for extraction efficiency. The recommended sampling time is ____ hours.

Table 4.7.2
Determination of Sampling Rate and Time

	sampling rate (mL/min)		
time (h)	first	second	third
0.083	12.4	12.5	12.6
0.167	12.3	12.4	12.5
0.5	12.1	12.2	12.3
1	12.0	12.2	12.3
2	12.1	12.2	12.4
3	12.0	12.1	12.2
4	11.8	11.9	12.0
6	11.4	11.5	11.6
8	10.9	11.0	11.1
10	10.6	10.7	10.5

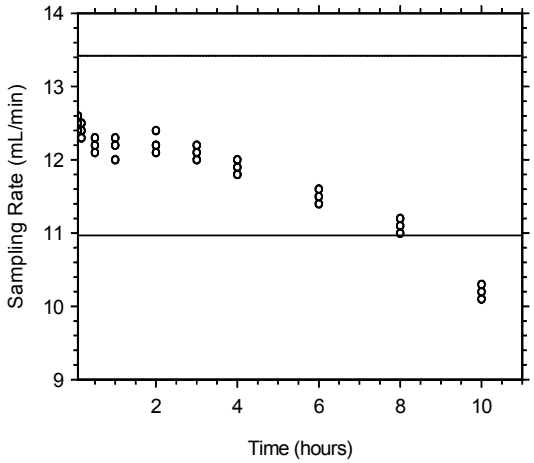

Figure 4.7.2. Example of plotted data to determine the sampling rate and recommended sampling time.

4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.[20]

4.8.1 ____ {Active sampler}

Extraction efficiency

The extraction efficiency of ____ {analyte} was determined by liquid-spiking four ____ {active sampler} at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The overall mean extraction efficiency over the working range of 0.1 to 2 times the target concentration was ____%. The

[20] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

extraction efficiency at the RQL was ____%. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies for the RQL and for the wet samplers are not included in the overall mean. Wet media were prepared by drawing humid air (____ {RH} relative humidity at ____ {temp} °C) at ____ {recommended sampling rate} for ____ {recommended sampling time}. The data obtained are shown in Table 4.8.1.1.

Table 4.8.1.1
Extraction Efficiency of ____ {Analyte} from ____ {Active Sampler}

level		sample number				
H target concn	µg per sample	1	2	3	4	mean
0.1	21.0	99.8	97.5	99.9	101.2	99.6
0.25	52.5	103.5	99.5	99.6	100.0	100.6
0.5	105	101.6	102.4	100.5	95.8	100.1
1.0	210	101.9	101.8	95.8	100.2	99.9
1.5	315	105.8	105.0	100.4	94.2	101.4
2.0	420	95.8	92.8	97.7	97.7	96.0
RQL	2.08	90.4	95.1	87.6	90.0	90.8
1.0 (wet)	210	104.3	99.6	94.7	100.5	99.8

Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were allowed to stand in the autosampler tray at {ambient} temperature. The samples were reanalyzed with freshly prepared standards. Diff is the difference between the initial analysis and the subsequent analysis. Each septum was punctured ____ times for each injection. The data obtained are shown in Table 4.8.1.2.

Table 4.8.1.2
Stability of Extracted Samples for ____ {Analyte}

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
101.9	99.9	-2.0	103.5	+1.6	100.5	-1.4	95.8	95.9	+0.1	99.8	+4.0	100.6	+4.8
101.8	101.2	-0.6	99.5	-2.3	97.8	-4.0	100.2	97.9	-2.3	97.5	-2.7	102.4	+2.2
			mean							mean			
101.9	100.6	-1.3	101.5	-0.4	99.2	-2.7	98.0	96.9	-1.1	98.6	+0.6	101.5	+3.5

4.8.2 ____ {Diffusive sampler}

Extraction efficiency

The extraction efficiency of ____ {analyte} was determined by liquid-spiking four ____ {diffusive sampler} at each concentration level. These samples were stored overnight at ambient temperature and then extracted and analyzed. The overall mean extraction efficiency over the range of 0.1 to 2 times the target concentration was ____%. The extraction efficiency at the RQL was ____%. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies for the RQL and for the wet samplers are not included in the overall mean. Wet media were prepared by exposing

the samplers to humid air (____ {RH} relative humidity at ____ {temp} °C) for ____ {recommended sampling time}. The data obtained are shown in Table 4.8.2.1.

Table 4.8.2.1
Extraction Efficiency of ____ {Analyte} from ____ {Diffusive Sampler}

level		sample number				
H target concn	µg per sample	1	2	3	4	mean
0.1	12.6	98.8	99.1	99.0	100.0	99.2
0.25	31.5	101.6	103.4	100.9	96.7	100.7
0.5	63.0	102.4	99.9	95.7	98.0	99.0
1.0	126	101.2	100.8	95.9	101.0	99.7
1.5	189	95.8	92.8	97.7	97.7	96.0
2.0	252	102.8	104.0	100.1	99.4	101.6
RQL	4.06	96.8	99.8	98.7	98.7	98.5
1.0 (wet)	126	103.5	99.5	99.6	100.0	100.6

Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were allowed to stand in the autosampler tray at {ambient} temperature. The samples were reanalyzed with freshly prepared standards. Diff is the difference between the initial analysis and the subsequent analysis. Each septum was punctured ____ times for each injection. The data obtained are shown in Table 4.8.2.2.

Table 4.8.2.2
Stability of Extracted Samples for ____ {Analyte}

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
101.2	99.8	-1.4	97.7	-3.5	98.2	-3.0	95.9	100.8	+4.9	100.1	+4.2	97.1	+1.2
100.5	98.8	-1.7	97.7	-2.8	98.6	-1.9	101.0	99.4	-1.6	99.4	-1.6	99.8	-1.2
			mean							mean			
100.9	99.3	-1.6	97.7	-3.2	98.4	-2.5	98.5	100.1	+1.6	99.8	-1.3	98.5	0.0

4.9 Sampling interferences {use tables to present data when appropriate}

The tested sampling interferences had no significant effect on the ability of {sampler} to collect or retain ____{analyte}. {Or if any of the tested interferences has a significant effect on sampling, this fact and the remedy must be listed here and in the appropriate subsection(s) of Section 2.}

4.9.1 ____ {Active sampler}

Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (____ ppm or____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC. The test atmosphere was sampled with six ____ {sampler} at ____ mL/min for ____ min. {one-quarter of the recommended sampling time}. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemical except water. Sampling was resumed with a set of three samples and contaminant-free air at ____ {RH} relative humidity and ____ {temp} EC at ____ mL/min for ____ min {three-quarters of the recommended sampling time} and then all six samplers were analyzed. The data obtained are shown in Table 4.9.1.

Table 4.9.1
Retention of ____ {Analyte}
on ____ {Active Sampler}

	recovery (%)			
set	1	2	3	mean
first	99.6	98.2	100.0	99.3
second	100.4	100.1	100.2	100.2
second/first				100.9

Low humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC. The test atmosphere was sampled with three ____ {sampler} at ____ mL/min for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Sample results were ____%, ____%, and ____% of theoretical.

Low concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 0.1 times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} °C. The test atmosphere was sampled with three ____ {sampler} at ____ mL/min for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Sample results were ____%, ____%, and ____% of theoretical.

Chemical interference

The effect of potential chemical sampling interference(s) was tested by sampling a dynamically generated controlled test atmosphere containing one times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC and the interference(s). The interference(s) were {list interference(s) and concn(s)}. The test atmosphere was sampled with three ____ {sampler} at ____ mL/min for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Sample results were ____%, ____%, and ____% of theoretical.

4.9.2 ____ {Diffusive sampler}

Reverse diffusion

Reverse diffusion was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC. Six samplers were exposed to the test atmosphere for ____ min {one-quarter of the recommended sampling time}. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Sampling was resumed with a set of three samples exposed to contaminant-free air at ____ {RH} relative humidity and ____ {temp} EC for ____ min {three-quarters of the recommended sampling time} and then all six samplers were analyzed. The data obtained are shown in Table 4.9.2. Reverse diffusion was less than ____%.

Table 4.9.2
Reverse Diffusion of
____ {Analyte} From ____ {Diffusive Sampler}

	mass (µg)			
set	1	2	3	mean
first	212.0	209.2	204.0	208.4
second	203.4	201.1	204.2	202.9
second/first				97.4

Low humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC. Three samplers were exposed to the test atmosphere for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were ____%, ____%, and ____% of theoretical.

Low concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 0.1 times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC. Three samplers were exposed to the test atmosphere for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were ____%, ____%, and ____% of theoretical.

Chemical sampling interference

The effect of potential chemical sampling interference(s) was tested by sampling a dynamically generated controlled test atmosphere containing one times the target concentration (____ ppm or ____ mg/m^3) of ____ {analyte} at ____ {RH} relative humidity and ____ {temp} EC and the interference(s). The interference(s) were {list interference(s) and concn(s)}. Three samplers were exposed to the test atmosphere for ____ min {the recommended sampling time}. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were ____%, ____%, and ____% of theoretical.

4.10 Qualitative analysis

{GC/MS may provide conclusive peak identification and should be addressed in all cases, even when the discussion amounts to why it is not possible or not available. Use the format of Section 3.5.1 to present GC/MS conditions if the mass spectrum was generated using in-house instrumentation. Be sure to include relevant MS conditions. The format for mass spectra is shown in Figure 4.10. Include a citation if the included mass spectrum was taken from a library. It is not necessary to list GC/MS conditions if the spectrum was taken from a library. Use the same format to present analytical conditions if alternate means for qualitative analysis are presented.}

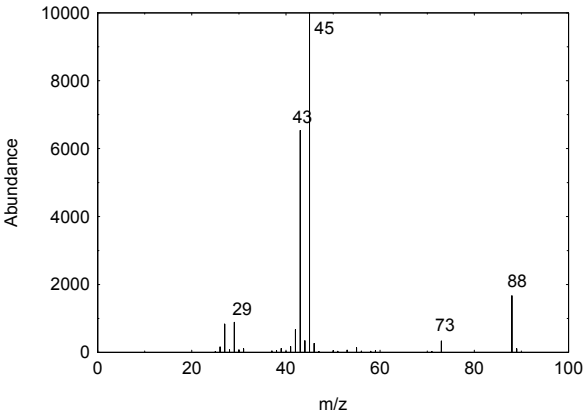

Figure 4.10. Mass spectrum of ____ {analyte}.

Example
GC/MS conditions

oven temperature:	60 °C (hold 1 min), ramp to 225 °C at 15 °C/min (hold 3 min)
injector temperature:	250 °C
detector temperature:	300 °C
run time:	15 min
column:	Supelco SPB-5 capillary column, 60-m × 0.32-mm i.d, d_f = 1.0-µm, or equivalent
column mode:	constant pressure (14 psi) {or constant flow}
initial column gas flow:	1.2 mL/min (helium)
septum purge:	1.5 mL/min (helium)
injection size:	1.0 µL (10 to 1 split)
inlet liner:	Agilent 5183-4647 or equivalent

MS conditions

MS temperatures
mass range
etc.

4.11 Generation of test atmospheres
{Describe the apparatus used to generate and sample test atmospheres and include a diagram if possible.}

Example
Test atmospheres were generated from ____ solutions containing ____ {analyte}.

The apparatus was placed in a walk-in hood. Test atmospheres were generated by pumping low microliter volumes of the ____ {analyte} solution with an Isco precision HPLC pump through a short length of 0.53-mm diameter uncoated fused silica capillary tubing into a vapor generator where it was heated and evaporated into a dilution air stream (Figure 4.11). The vapor generator was a short length of glass tubing with a side port for introduction of the capillary tubing. The vapor generator was heated with a variable voltage-controlled heating tape to evaporate the ____ {analyte} solution. The humidity, temperature, and volume of dilution air of were regulated by use of a Miller Nelson Flow-Temperature-Humidity controller. The test atmosphere passed from the vapor generator into a glass mixing chamber, and then into a glass exposure chamber where samples could be collected. Active samplers were connected to glass ports extending from the exposure chamber and diffusive samplers were placed inside the chamber. The air velocity through the exposure chamber was approximately 0.4 m/sec. The humidity and temperature were measured at the exit of the exposure chamber with an Omega Digital Thermo-hygrometer.

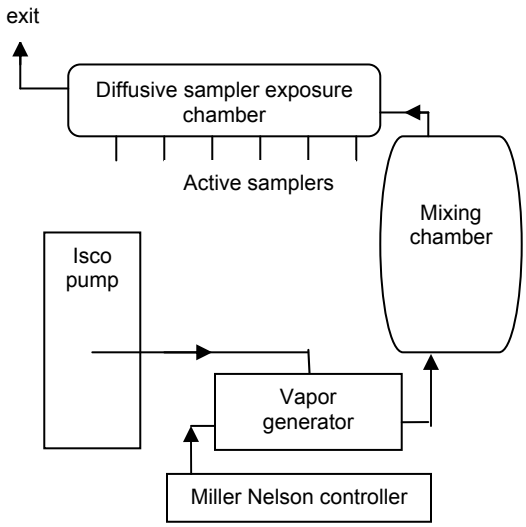

Figure 4.11. The test atmosphere generation and sample collection apparatus.

PREPARATION OF WRITTEN REPORTS FOR PARTIALLY VALIDATED METHODS

Each partially validated method will be assigned a version number beginning with the number "1.0". Significant changes or revisions to the method require that a new version number be assigned, for example "2.0". If the document is revised, the date revised will be placed on the cover page and a discussion concerning the revision included in Section 1.1.1 History.
.

Partially validated methods will include data on the following items:

1. Background information - Include the purpose of the work, physical properties, and other easily acquired information that would normally be reported in the Background Section of a fully validated method.

2. Detection limit of the overall procedure (DLOP) - Determine this parameter in the same manner as in a full validation.

3. Reliable quantitation limit (RQL) - Determine this parameter in the same manner as in a full validation.

4. Extraction efficiency - Determine these parameters over the working rage of 0.1 to 2 times the target concentration in the same manner as in a full validation. Determine the extraction efficiency at one times the target concentration using wet media. Determine the extraction efficiency at the RQL. Do not include the extraction efficiency from wet media or at the RQL in the overall average.

5. Retention efficiency - The recommended sampling time and sampling rate will be based, at least in part, on retention efficiency. Perform retention efficiency tests with loadings equivalent to two times the target concentration using humid air at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 EC). The minimum length of time that the retention efficiency test must be conducted is 1.25 times the sampling time recommended in the method.

6. Storage stability test – Perform a storage stability test with spiked samples at loadings equivalent to the target concentration. The recommended volume of humid air (absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 EC)) will be drawn through the samplers at the recommended sampling rate before storage. Prepare 12 spiked samples, store them at ambient temperature in the dark, and analyze three samples approximately every five days over two weeks. It may be necessary to perform another storage stability test at refrigerated temperature if instability is observed at ambient temperature.

7. Recommendation for further study - Recommendations will be made that should be considered before a full validation is performed.

Prepare written partially validated methods according to the following outline. This outline is similar to that used for a fully validated method except that the validation data is included in the various method sections instead of in a separate Backup Data section. Use the guidelines for Fully Validated Methods as a reference for more specific format details.

Required statements concerning the status of the method, accessibility problems, intended use of the method, manufacturer disclaimer, toxic effects disclaimer, reference to OSHA Methods Development Guidelines, basis of cited air concentrations, sampling safety, chemical hygiene plan, analytical safety, and QA practices are placed at certain points in the method text. These required statements will not be altered and will be inserted in the locations shown in the example partially validated method.

Text formatting, instructions for field and laboratory personnel, and descriptive discussion shown in the example partially validated method will not be altered unless such text in clearly inaccurate or inappropriate.

The purpose of section and paragraph indents is to delineate text and to provide a convenient way to reference sections and paragraphs in subsequent sections and paragraphs. Indents should be used as shown in the example partially validated method unless additional indents are necessary for clarity. Quaternary indents, for example 3.4.1.1, will be avoided whenever possible.

{ANALYTE}
{as listed in CFR or ACGIH}

Method number: PV2xxx

Version: x.0

Target concentration: ____ ppm (____ mg/m^3)
OSHA PEL: ____ ppm (____ mg/m^3) {None if no PEL}
ACGIH TLV: ____ ppm (____ mg/m^3) {None if no TLV}
{Include skin designations when applicable}

Procedure: Samples are collected by drawing workplace air through ____ with personal sampling pumps. Samples are extracted with ____ and analyzed by ____ using a ____ detector.

Recommended sampling time and sampling rate: ____ min at ____ mL/min (____ L)

Reliable quantitation limit: ____ ppm (____ mg/m^3)

Special requirements: {If none, delete this item}

Status of method: Partially validated method. This method has been subjected to the established validation procedures of the Methods Development Team and is presented for information and trial use.

____ {month year} {Chemist} ____
Date revised: ____ (month year}

{Branch} Analytical Services
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

{Explain the purpose of this work. Also, obvious questions that may be raised by knowledgeable readers should be addressed. Keep length at 1 to 1.5 pages or less.}

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

{Cite sources for presented information. If both animal data and human data are presented, present the animal data first. If the entire section is taken from one reference, the reference notation can be placed behind the qualifying statement in the heading.}

1.1.3 Workplace exposure

{Report major sources of exposure in the workplace and, if available the size of the work population that is exposed. If the entire section is taken from one reference, the reference notation can be placed behind the heading.}

1.1.4 Physical properties and other descriptive information[21] {these are examples that can be used if applicable, other physical properties can also be listed.}

synonyms:	____		
solubility:	____		
IMIS number[22]:	____	appearance:	____
CAS number:	____	vapor pressure: {kPa (mmHg)}	____
molecular weight:	____	flash point:	____
boiling point:	____	odor:	____
melting point:	____	lower explosive limit:	____
8_{max}:	____	specific gravity:	____
structural formula:	____	molecular formula:	____

This method was validated according to the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[23]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations, and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25EC and 760 mmHg (101.3 kPa).

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[21] This reference was used for most of the physical properties.
[22] Chemical Sampling Information. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html (accessed March 11, 2009).
[23] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)
Example:
The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was ____ µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response for a sample blank. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained were used to calculate the DLOP. Values of ____ and ____ were obtained for the slope and SEE respectively. The data obtained are shown in Table 1.2 and Figure 1.2.1. DLOP was calculated to be ____ µg/sample (____ ppm or ____ mg/m^3).

Table 1.2
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
0.421	0
0.841	178
1.26	177
1.68	375
2.10	536
2.52	696
2.94	703
3.36	810
3.78	948
4.21	1150

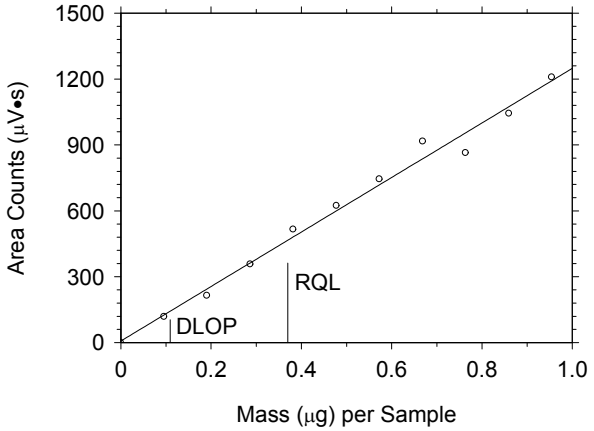

Figure 1.2.1. Plot of data to determine the DLOP/RQL (y = 277x – 75.5).

The RQL is the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained from the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is ____ µg per sample (____ ppm or ____ mg/m^3). Recovery at this concentration is ____%.

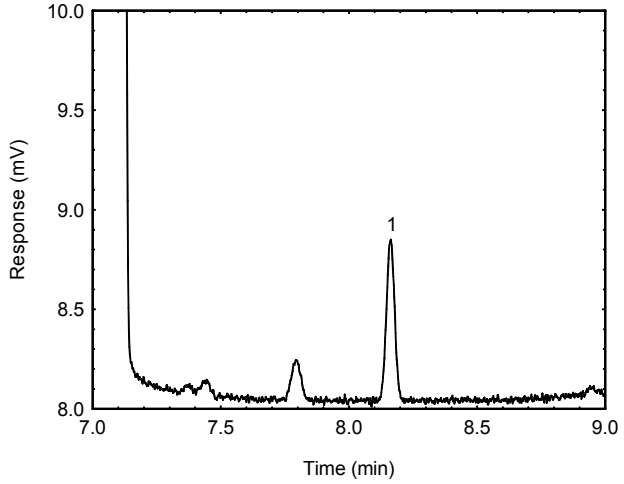

Figure 1.2.2. Chromatogram of the RQL (1: ____ {analyte}).

2. Sampling Procedure {Refer to the cited sections in the Fully Validated Method example for format detail. Use paragraphs instead of tertiary subsections}

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with the work performance or safety.

2.1 Apparatus {Section 2.1}

2.2 Reagents {if no reagents are required, state "None required". Otherwise use the format described in Section 3.2}

2.3 Technique {Section 2.3}

2.4 Extraction efficiency

The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.[24]

Example
The extraction efficiencies of ____ {analyte} were determined by liquid-spiking ____ {sampler} with the analyte at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted and analyzed. The mean extraction efficiency over the studied range was 98.7% for ____ {analyte}. The results for the RQL and the wet samplers were not included in the overall average. Wet samplers were prepared by sampling humid air (____ {RH} relative humidity at ____ {temp} °C) at {recommended sampling rate} for {recommended sampling time}. The data obtained are shown in Table 2.4.

Table 2.4
Extraction Efficiency of ____ {Analyte} from ____ {Active Sampler}

level		sample number				
H target concn	µg per sample	1	2	3	4	mean
0.1	21.0	99.8	97.5	99.9	101.2	99.6
0.25	52.5	103.5	99.5	99.6	100.0	100.6
0.5	105	101.6	102.4	100.5	95.8	100.1
1.0	210	101.9	101.8	95.8	100.2	99.9
1.5	315	105.8	105.0	100.4	94.2	101.4
2.0	420	95.8	92.8	97.7	97.7	96.0
RQL	2.08	90.4	95.1	87.6	90.0	90.8
1.0 (wet)	210	104.3	99.6	94.7	100.5	99.8

2.5 Retention efficiency
Example:
Six ____ {samplers} were spiked with ____ µg of ____ {analyte} and then ____ L {1.25 times recommended volume} of humid air at ____ {RH} relative humidity and ____ {temp} EC was sampled. The samples were extracted and analyzed. The mean retention efficiency was

[24] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March 11, 2010).

____%. There was ____% of ____ {analyte} found on the backup portion of the ____ {sampler}. {The amount spiked will be equivalent to two times the target concentration based on the recommended air sample volume}. The data obtained are shown in Table 2.5.

Table 2.5
Retention Efficiency of ____ {Analyte}

	sample number						
section	1	2	3	4	5	6	mean
front	99.1	95.2	97.3	99.5	99.6	100.0	98.4
rear	0	1.2	1.1	0	0	0	0.4
total	99.1	96.4	98.4	99.5	99.6	100.0	98.8

2.6 Recommended air volume and sampling rate
Example:
Sample for up to ____min at ____mL/min for to collect TWA samples.

2.7 Sample stability
Example:
Twelve ____ {samplers} were each spiked with ____ µg of ____ {analyte} which is equivalent to ____ ppm (____ mg/m^3). The spiked samplers were used to sample ____L {recommended air volume} of humid air at ____ {RH} relative humidity and ____ {temp} EC. The samples were then sealed and stored at ambient temperature. Three samples were analyzed immediately after preparation and three samples were analyzed every five days over the next 15 days. The data obtained are shown in Table 2.7.

Table 2.7
Storage Test for ____ {Analyte}

	sample number		
time (days)	1	2	3
0	100.2	101.5	98.4
5	99.8	100.8	100.5
10	97.6	101.4	99.1
15	93.7	91.8	95.2

3. Analytical Procedure {Refer to cited sections of format for Evaluated Methods for detail. Use paragraphs instead of using tertiary subsections}

Adhere to the rules set down in your laboratory's Chemical Hygiene Plan[25] (for instance: OSHA SLTC adheres to the rules set down in the OSHA SLTC Chemical Hygiene Plan). Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure. Follow all applicable quality assurance practices established in your laboratory's internal quality system (for instance: OSHA SLTC follows the quality assurance practices established in the OSHA SLTC Quality Assurance Manual).

3.1 Apparatus {Section 3.1}

3.2 Reagents {Section 3.2}

3.3 Standard preparation {Section 3.3}

3.4 Sample preparation {Section 3.4}

3.5 Analysis {Section 3.5}

3.6 Interferences (analytical) {Section 3.6}

[25] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

PREPARATION OF WRITTEN REPORTS FOR ANALYTICAL STUDIES

Follow the format of articles published in the ACS journal "Analytical Chemistry" as closely as possible and include sections on the following items:

1. Introduction (include purpose)
2. Experimental
3. Results and Discussion
4. References