EVALUATION GUIDELINES
FOR AIR SAMPLING METHODS
UTILIZING CHROMATOGRAPHIC ANALYSIS

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INTRODUCTION

The following evaluation guidelines were developed to provide chemists of the Methods Development Team with a uniform and practical means for evaluating sampling and analytical methods that utilize chromatographic techniques. The guidelines define sampling and analytical parameters, specify required laboratory tests, statistical calculations, and criteria for acceptance, and provide a detailed outline for the written reports. 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 evaluation data.

These guidelines are continually open to examination by the OSHA Methods Development Team who are using them, and refinements are formally made on a periodic basis. The resulting evolution in the guidelines is apparent when comparing early methods to more recent ones. The evaluation guidelines have been effectively used and refined for more than twenty years. Revisions in this September 1999 update include the addition of evaluation tests for diffusive samplers.

Active sampling is defined as collection of an analyte using a sampling pump to draw air through an appropriate adsorbent. Diffusive sampling is a passive technique which collects the analyte without a sampling pump using the principles of diffusion.

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PRELIMINARY CONSIDERATIONS

History
Toxic Effects
Workplace Exposure
Physical Properties

SAMPLING PROCEDURE

Sampler Capacity
Sampling Rate
Extraction Efficiency
Effects of Storage
Interferences

ANALYTICAL PROCEDURE

Detection Limits
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OVERALL PROCEDURE

Detection Limit
Reliable Quantitation Limit
Precision
Reproducibility

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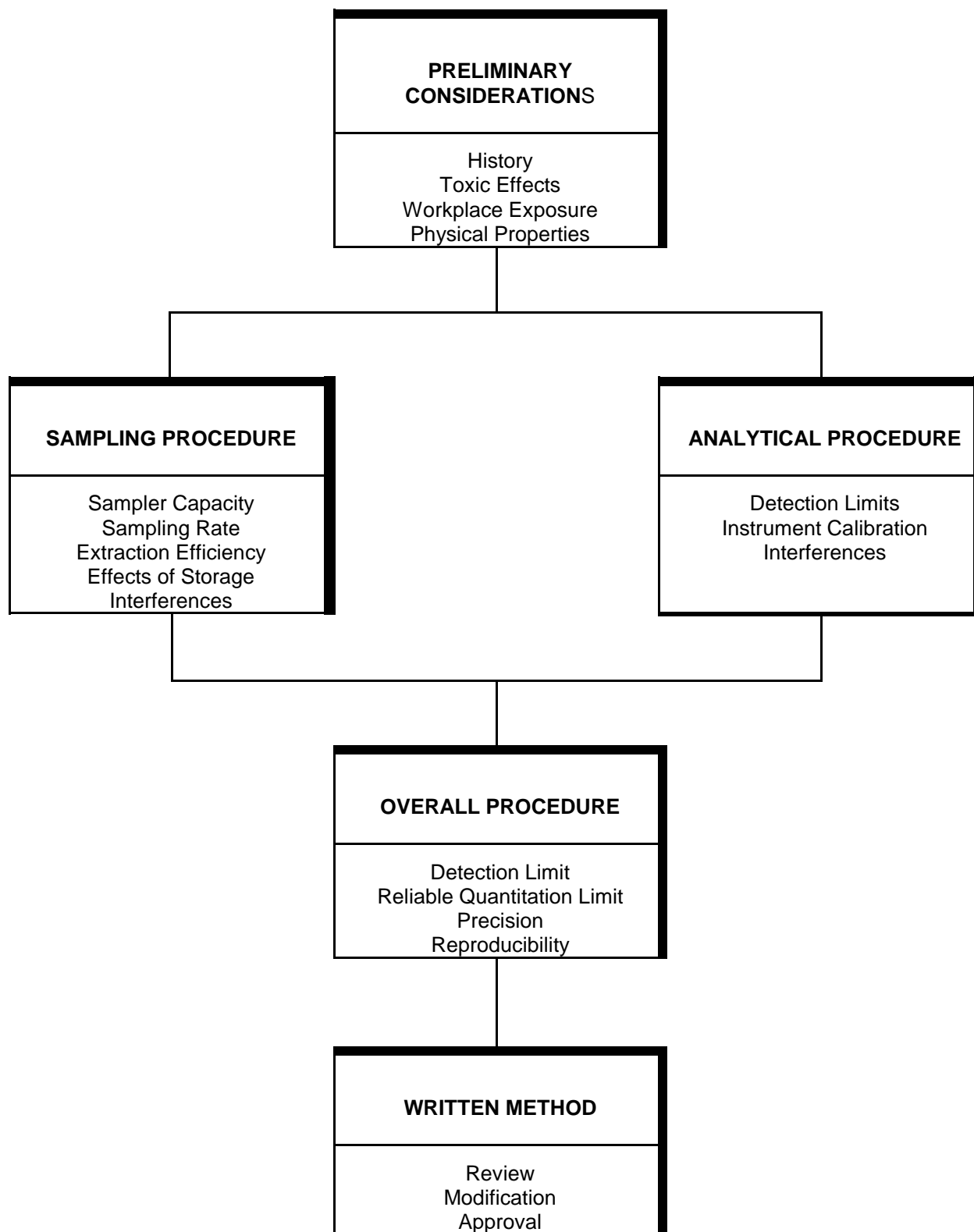
Review
Modification
Approval

Figure 1. Evaluation scheme for OSHA chromatography methods.

EVALUATION GUIDELINES

I. Preliminary Considerations

A. Review 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 evaluation will be performed. This value, which shall be known as the target concentration (TC), may be an OSHA PEL, an ACGIH TLV, or some other concentration for which there is a basis for selection.

C. 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 collecting aerosols.

Perform initial tests to determine the following parameters of the procedure: analytical conditions, capacity of the selected sampling device, extraction solvent, and internal standard (if used). Carbon disulfide shall be the first choice as an extraction solvent for adsorbent tubes and diffusive samplers analyzed by GC/FID. If this is inadequate, consider the solvent mixtures currently in use at SLTC before formulating a new extraction solvent (i.e., 60/40 dimethylforamide / carbon disulfide, 95/5 carbon disulfide / isopropyl alcohol or 95/5 methylene chloride / methanol).

II. 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.

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

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:

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

where $S_{Y \cdot X}$ is the standard error of estimate for the detection limit
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

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

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At point Y_{DL} on the regression curve

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

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

therefore

$$L_D = \frac{Y_{DL} - Y_{BR}}{A}$$

Substituting for Y_{DL} from Equation 1 gives

$$L_D = \frac{3S_{Y \bullet X}}{A} \qquad \textbf{(2)}$$

1. 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:

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

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

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

3. Determine the regression line and the standard estimate of error from the data by plotting response versus mass injected onto the column.

Figure 2. Example of plotted DLAP data ($Y = 3.28X + 20.5$).

4. Calculate the DLAP using Equation 2. Report the DLAP in the method as mass of analyte injected onto the head of the column.

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

6. 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

1. Report the standard error of estimate from the linear regression of data points over a range that covers 0.25 to 2 times the target concentration with the highest mass loading at the recommended sampling time for each sampler tested. The data for the line is determined from the triplicate analysis of analytical standards at the following concentrations: 0.25, 0.5, 1, 1.5, and 2

Figure 3. Example of a calibration curve ($Y = 38.89 X - 65.50$).

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times the target concentration. The standard error of estimate measures the variation or scatter about the line of regression.[2]

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

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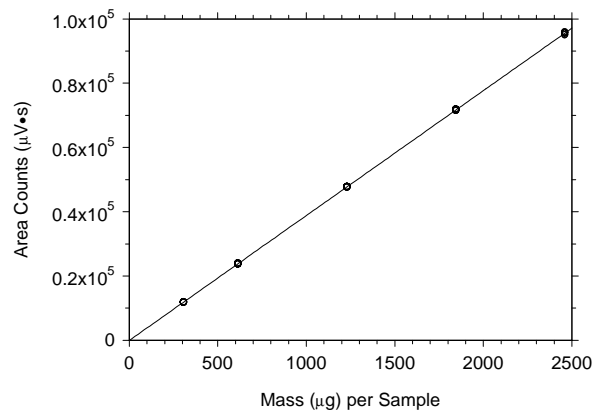Y_{obs} is observed response
Y_{est} is estimated response from regression curve
n is total number of data points
k is 2 for a linear regression

2. Prepare two stock standards from the same NIST-traceable (if possible) standard. Dilute each stock to the required five (5) concentrations. Inject each diluted standard three times.

3. Use the data collected to construct the calibration curve for inclusion in the method, as shown in Figure 3. (Section 3.5.2)

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

C. Interferences to the Analytical Procedure

1. Interferences to the analytical method make identification and quantitation of the analyte difficult or impossible.

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

3. If a reagent has been added to the sampling media, generate a chromatogram (for inclusion in the method) of a sample at the target concentration showing the extra peak'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 should 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)

III. Sampling Procedure

These evaluation guidelines address the evaluation of samplers containing adsorbent media or filters and may require slight modification for the adequate evaluation of more unique samplers such as those utilizing reactive reagents, or those containing both adsorbent and filter components. Modification may also be required for the evaluation of bubbler sampling procedures. Consider bubblers only as a sampling technique of last resort. Specific requirements which apply to the evaluation of diffusive samplers are included in the appropriate sections.

A. Active Samplers - Sampling Rate and Capacity

1. 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 or expanded health standards of 29 CFR 1910) at the selected sampling rate. If a short-term sample collected at the recommended 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

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

exposure limits listed in Table Z-1, determine if 15 minutes is practical as the recommended sampling time.

2. Select a sampling rate that is suitable for the active sampler. The goal is to have a 4-hour recommended sampling time for TWA samples. {Use 50-200 mL/min for tubes and 1-2 L/min for filters and OSHA Versatile Samplers (OVS).}

3. Sampler capacity is defined by the length of time a sampler {front adsorbent section only for two-section tubes} can be used under a set of known test conditions without significant loss of analyte. It can also be described as a corresponding air volume or as a collected analyte mass. 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 been established. When instrumental monitoring of the downstream effluent is not possible, monitor breakthrough with a backup sampler that is changed at measured time intervals and analyzed. Determine the analyte concentration in the effluent, at the midpoint of each time interval, from the air volume sampled in each interval.

4. Determine breakthrough at ambient temperature from a 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 22.2 C). All test atmospheres generated throughout these guidelines must be non-condensing.

5. Repeat breakthrough tests to assure reproducibility. {Three tests total.}

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

7. Select whichever is shorter, a recommended sampling time of 4 h or 80% of the time required to exceed the capacity of the sampler when challenged at two times the target concentration.
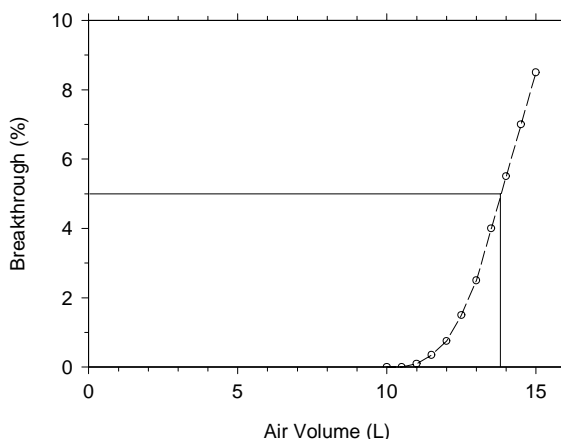
8. Retention Efficiency

Figure 4. Example of breakthrough data.

Retention efficiency is the percentage of analyte retained on a spiked sampler after a predetermined volume of appropriately conditioned air is drawn through it.

Test for retention of the analyte by using one set of six samplers to sample a 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 22.2 C) for one-quarter of the recommended sampling time. Discontinue sampling and set three samplers aside. Flush the generation system with contaminant-free air. Resume sampling with three samplers from contaminant-free humid air for three-quarters of the recommended sampling time. Analyze the six samplers. The test fails if the mean of the recoveries of the second half is 90% or less of the mean recovery of the first three samples. If the test passes, the recommended sampling time is the value from Paragraph III.A.7.

If the first test fails, repeat the test by using another set of six samplers to sample the same test atmosphere but reduce 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 90%

or less of the mean recovery of the first three samples, consider retention inadequate and an alternate sampling procedure must be considered.

If an atmosphere can not be generated, retention efficiency may be tested in the following manner:

For adsorbent tubes, spike the sampler in a manner that places the analyte at the head of the adsorbent bed. One way of accomplishing this, if the analyte is volatile, is to place the analyte on the glass wool plug immediately ahead of the adsorbent tube. The analyte will be rapidly leached to the head of the adsorbent bed when the test is started. If liquid injection of the analyte onto the adsorbent bed must be used, care should be taken to assure it is injected onto the head of the adsorbent bed. Retention efficiency tests are useful when it is not possible to perform breakthrough tests with controlled test atmospheres. They will provide partial support of a sampler capacity by showing that analyte present on the sampler can be retained when the recommended sampling conditions are used.

a. Spike six samplers with an amount of analyte equivalent to the two times the target concentration based on a tentative recommended air volume.

b. Select a recommended sampling time that is suitable for the samplers and draw air through them for 1.25 times the recommended sampling time.

c. The absolute humidity of the air drawn through the samplers shall be approximately 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C).

d. Retention efficiency is determined by analyzing (including extraction or extraction efficiency corrections) the spiked samplers after air has been drawn through them. During the test, the downstream effluent shall be monitored as it would in a breakthrough test.

e. Filters and support pads (if used) are extracted separately and the extractant of each is analyzed to determine the retention efficiency. If support pads are used, spike six filters as in Step 'a' and place in separate sealed cassettes, with backup pads, for 4 h with no air pulled through them. These filters will be used as controls to determine if contamination of the support pad occurs before air is pulled through the cassette.

9. Test for the effect of low humidity on collection efficiency by using a set of three samplers to sample a 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 22.2 C) or less using the recommended sampling time. Upon analysis, all three front sections of the individual samples should have collected enough analyte to be greater than 90% of the theoretical amount. If not, an alternate sampling procedure must be considered.

10. Test for the effect of low concentration on collection efficiency by using a set of three samplers to sample a 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 22.2 C) for the recommended sampling time. Upon analysis, all three front sections of the individual samples should have collected enough analyte to be greater than 90% of the theoretical amount. If not, an alternate sampling procedure must be considered.

11. Test for the effect of at least one suspected interference on collection efficiency by using a set of three samplers to sample for the recommended sampling time a test atmosphere at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C) containing the target concentration, and the suspected interference at a concentration set to an appropriate level. The appropriate level for the interference will be its PEL or TLV. If more than one interference is used, then the concentration of the interference will be divided by the number of interferences used. If two interferences are used, each will have a concentration equal to one-half of its PEL or TLV. Upon analysis, all three samples should have each collected 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 breakthrough test (Steps

3-8) with the interferences present in the atmosphere to determine a shorter recommended sampling time.

B. Diffusive Samplers - Sampling Rate and Capacity

{It is necessary to generate a controlled test atmosphere to determine sampling rates and capacities for diffusive samplers. Before making these determinations, the preliminary extraction efficiency from wet absorbent should be determined. Calculate the mass of analyte that will be collected on the diffusive sampler for four hours from an atmosphere containing the target concentration using an approximate sampling rate based on the manufacturer's literature (e.g., SKC is 13 mL/min or 3M is 31 mL/min). Spike at least two samplers with this amount of analyte and another two samplers with 5% of the amount. Upon analysis, the values should be ±10% 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. Using the final extraction efficiency, recalculate the final sampling rate and final recommended sampling time.}

1. 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 or expanded health standards of 29 CFR 1910). 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 minutes is practical as the recommended sampling time.

2. Determine sampling rates using replicate samples collected at increasing time intervals from a controlled test atmosphere. 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, use two times the TWA PEL. The 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 and the theoretical concentration do not agree. (Alternate methods may include an active sampling procedure and online monitoring with instruments such as GC or IR.) The face velocity of the test atmosphere over the samplers should be approximately 0.4 m/s. Record the temperature and pressure inside the sampling chamber. The 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 minute, and will be calculated by the following equation:

$$R_{SS} = \frac{M}{C \, t \, E_E}$$

where R_{SS} is sampling rate at sampling site
M is mass collected
C is concentration of the test atmosphere
t is sampling time
E_E is extraction efficiency

3. Convert the ambient sampling rates, which are determined at ambient temperature and atmospheric pressure, to equivalent sampling rates at the NTP conditions of 760 mmHg and 298 K with the following equation:[3]

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

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

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

4. Plot the sampling rates against sampling times as shown in the following example. Find the preliminary sampling rate by averaging the nine values for the 0.5, 1 and 2-h 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 of the sampling rates from 5 min through 10 h that are between the lines to determine the sampling rate. This range should contain at least four of the time intervals and the relative 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 of the data points used to determine the sampling rate.} Report the sampling rate as milliliters per minute at 101.3 kPa and 25 C and the range of time it covers, for example, 5 min to 4 h.

Table 1
Determination of Sampling Rate
and Recommended Sampling Rate

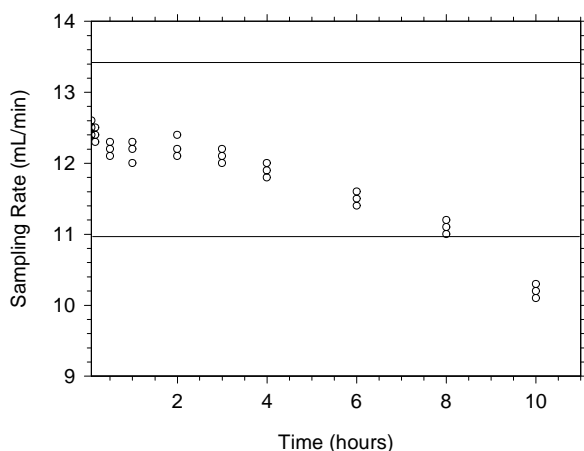| time (h)	sampling rate (mL/min)		
	first	second	third
5 min	12.4	12.5	12.6
10 min	12.3	12.4	12.5
0.5	12.1	12.2	12.3
1	12.0	12.2	12.3
2	12.1	12.2	12.4
3	12.0	12.1	12.2
4	11.8	11.9	12.0
6	11.4	11.5	11.6
8	11.2	11.0	11.1
10	10.2	10.3	10.1

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

5. 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. 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 h}. If this time is over 4 h, the recommended sampling time is 4 h. This will provide a conservative safety margin when samples are taken in complex work atmospheres where substances may compete for sites on the adsorbent. Report the sampler capacity as mass of analyte collected on the sampler if it is allowed to sample an atmosphere containing two times the target concentration for the recommended sampling time.

6. Test for reverse diffusion of the analyte by using one set of six samplers to sample a 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 22.2 C) for one-quarter of the recommended sampling time. Discontinue sampling and set three samplers aside. Flush the generation system with contaminant-free air. Resume sampling with the other three samplers from contaminant-free humid air for three-quarters of the recommended sampling time. Analyze the six samplers. The test fails if the mean of the recovered masses of the second half is 90% or less of the mean of 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 test atmosphere but reduce all time by one-half. If the test passes, the new recommended sampling time is one-half of the old value. If the mean of the recovered masses of the second half of the set is 90% or less of the mean of the first three samples, consider reverse diffusion significant and an alternate sampling procedure must be considered.

7. Test for the effect of low humidity on sampler performance by exposing a set of three samplers to a 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 22.2 C) or less for the recommended sampling time. Upon analysis, all three of the individual samples should have

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collected enough mass to be greater than 90% of the theoretical amount. If not, an alternate sampling procedure must be considered. Use sampling rate to calculate the theoretical amount.

8. Test for the effect of low concentration on sampler performance by exposing a set of three samplers to a 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 22.2 C) for the recommended sampling time. Upon analysis, each of the three individual samples should have collected enough mass to be greater than 90% of the theoretical amount. If not, an alternate sampling procedure must be considered. Use sampling rate to calculate the theoretical amount.

9. Test for the effect of at least one suspected interference on sampler performance by using a set of three samplers to sample for the recommended sampling time a test atmosphere containing the target concentration at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C), and the suspected interference at a concentration set at an appropriate level. The appropriate level for the interference will be its PEL or TLV. If more than one interference is used, then the concentration of the interference will be divided by the number of interferences used. If two interferences are used, each will have a concentration equal to one-half of its PEL or TLV. Upon analysis, all three of the individual samples should have collected enough mass to be greater than 90% of the theoretical amount. If not, repeat the breakthrough test (steps 1-4) with the interferences present in the atmosphere to determine a shorter recommended sampling time. Use sampling rate to calculate the theoretical amount.

C. Extraction Efficiency

1. First determine the minimum amount of time required to extract a constant amount from a sample. A series of spiked samplers are to be extracted and analyzed while increasing the amount of time between extraction and analysis. Shake each sample by hand for a few seconds shortly after adding the solvent. If the time exceeds 1 h, determine if mechanical agitation can reduce the time to fully extract the sample.

2. Perform a test of the extraction efficiency with wet samplers. Pull an air volume equivalent to the recommended sampling time through four active samplers and expose four diffusive samplers for the recommended sampling time using a contaminant-free atmosphere containing an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C) or spike each sampler with 50 L of water. 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.} If there is a significant difference in the mean of the wet sampler's extraction recovery from the mean dry sampler's extraction recovery, repeat the test. A significant difference is when the mean of the wet samplers is more than two standard deviations from the mean of the dry sampler at the same mass loading. If the difference persists, change the sampler or extraction solvent to minimize the difference.

3. The extraction efficiency is the mean percent of analyte recovered from dry samplers and determined at the RQL, and 0.25, 0.5, 1, 1.5, and 2 times the target concentration, based on the recommended air volume. A dry sampler is one that is used as received from the manufacturer. The average of all six determinations will be the extraction efficiency for the analytical procedure if they are similar. In the event the extraction efficiency does not remain constant at lower sample loadings, a plot of extraction efficiency versus concentration should be constructed and included in the method.

4. Prepare four samplers and three standards at each of the six concentrations.

5. 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.

6. Extract the spiked samples. After an appropriate amount of time for equilibrium to occur, analyze the samples. Reseal two of the dry samples containing the target concentration amount of analyte immediately after analysis for use in the test described in Step 9. Prepare the analytical standards with the same microliter syringe used in spiking the extraction samples. Compare the samples to the respective standards to determine the percent recovered.

7. Calculate the extraction efficiency as follows:

$$E_E = \frac{M_R}{M_S}$$

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

8. An average extraction efficiency >75% is acceptable but >90% is perferred.

9. Determine the stability of extracted dry samples by reanalyzing the four dry target concentration extraction samples one day after the extraction efficiency was determined. Reseal two of the four vials containing these samples with new septa after the initial analysis. The remaining two samples shall retain their punctured septa. Use freshly prepared standards in the 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 autosampler trays) for a period of time before reanalysis. Consider extracted samples stable if the difference between the extraction efficiency one day after extraction and the extraction efficiency from the initial determinations 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.

10. If storage instability is detected in Step 9, a 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 (or analysis) a valid analysis (or reanalysis) can be performed. Use the criteria for sample stability in Step 9.

11. If support pads are used in conjunction with filters, determine their extraction efficiency by spiking them with a sample loading equivalent to 0.05 times the target concentration.

D. Effects of Storage

1. Collect thirty-three samples from a 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 22.2 C). Use the recommended sampling time and sampling rate $_{NTP}$. If sample collection is extremely time consuming, increase the test atmosphere concentration or increase the 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.

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

4. Analyze three samples from each set approximately every third day so that the storage test is at least 15 days in length.

5. Measure recovery from the regression curve obtained by plotting percent recovery (corrected for extraction efficiency) versus days of storage.

6. A change in recovery of more than 10% in 15 days is a significant uncorrectable bias and must be avoided. Also, the recovery (corrected for extraction efficiency) must remain above 75% during storage. When these conditions are not met, they may be overcome by use of: an alternate sampling medium, refrigerated storage requirements, or time requirements for 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 effectiveness of ambient shipment to the laboratory and then storing the samples in a refrigerator 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.
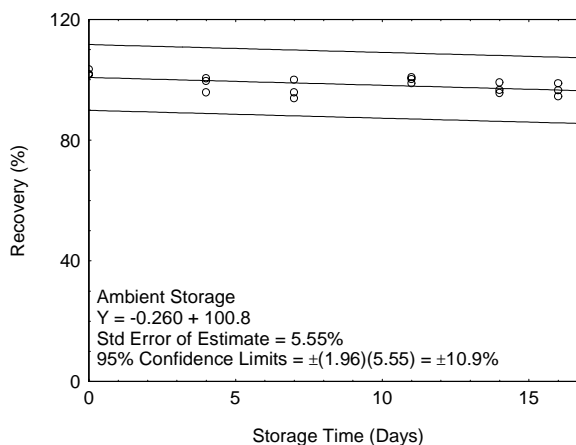

Figure 6. Example of a storage test.

7. Use alternate methods of preparing storage samples when safety considerations or other problems prevent generation of dynamically test atmospheres. The alternate methods include static test atmospheres, prepared in gas-sampling bags; vapor-spiked samples, volatilizing the analyte directly upstream from the sampling tube; and liquid-spiked samples, injecting the analyte directly onto the sampling tube. Introduce water by drawing the recommended amount of humid air through the spiked sampling tube. In this last method, a small volume of humid air can be drawn through the sampling tube so it has initial exposure to water before the analyte is introduced. These alternate methods may require that the analyte be contained in a solvent.

8. Plot 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 120%.

IV. 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 an equivalent air concentration 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.

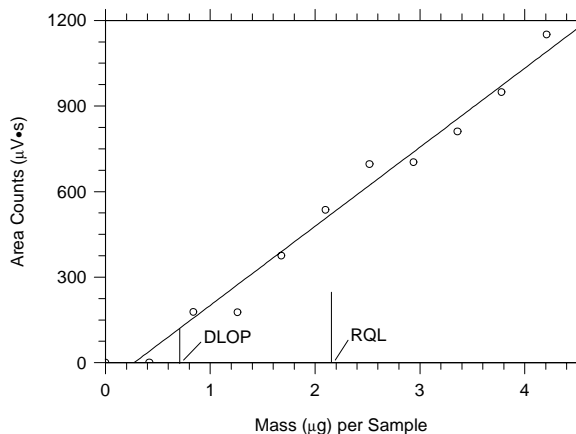Figure 7. Example of plotted DLOP/RQL data (Y = 277X - 75.5).

B. Reliable Quantitation Limit (RQL)

1. Consider the RQL as 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 the recovery from the sampler which is closest to the RQL, is 100 ± 25% of its theoretical value.

12

$$L_{RQ} = \frac{10 S_{Y \cdot X}}{A}$$

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

If the recovery from the closest sampler 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 are obtained by spiking a series of samplers with 2, 3, 4, or 5 times the highest mass spiked for the DLOP.
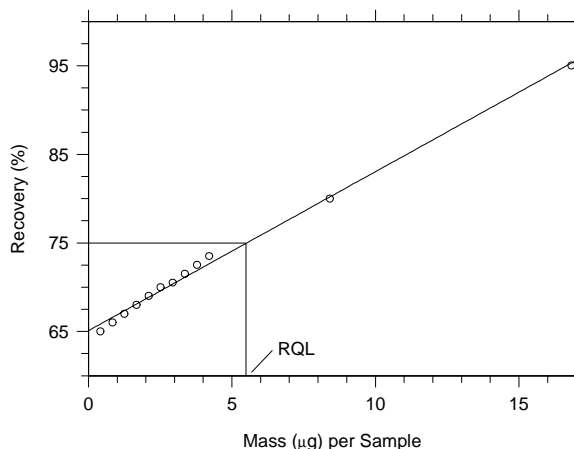
2. Report the RQL as mass per sample and as an equivalent air concentration based on the recommended sample air volume.

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

Figure 8. Example of a calculated RQL when recovery is the determining factor ($Y = 1.79X + 65.1$).

C. Determination of the Precision

1. Use data from Effects of Storage (Section III.D) in the determination of the overall precision.

2. Determine the standard error of estimate for the regression curve[4,5] of each storage test with the following formula.

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

where $S_{Y \cdot X}$ is the standard error of estimate
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. The standard error of estimate is determined for each sampler from the data used in both storage tests. Use the ambient test if the restrictions are satisfied in Section III.D.6. Use the 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.

i. Active Sampler

Determine the total standard error of the overall procedure for each storage test (S_{EE}) by including the sampling pump variability (V_{SP}) with the following formula, use an arbitrary value of 5%.

$$S_{EE} = \sqrt{S_{Y \cdot X}^2 + V_{SP}^2}$$

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

ii. Diffusive Sampler

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[4] Snedcor, G.W.; Cochran, W.G. *Statistical Methods*, 6th ed.; Iowa State University: Ames, Iowa, 1967; p 467.
[5] Arkin, H.; Colton, R.R. *Statistical Methods*, 5th ed.; Barnes and Noble: New York, 1970, p 85.

Modification of the calculation for standard error of estimate is required for diffusive samplers because V_{SP} is not an applicable parameter. In its place use sampling rate variability (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 pressure (P), the standard error of estimate must include additional uncertainty when these parameters are not determined at the sampling site.}

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

$$S_{EE} = \sqrt{S_{Y \cdot X}^2 + V_{SR}^2 + V_T^2 + V_P^2}$$

where S_{EE} is the overall standard error of estimate
$S_{Y \cdot X}$ is the standard error of estimate from storage
V_{SR} is the variability in the sampling rate
V_T is the variability in the sampling rate due to temperature
V_P is the variability in the sampling rate due to pressure

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

$$S_{EE} = \sqrt{S_{Y \cdot X}^2 + V_{SR}^2}$$

where S_{EE} is the standard error of estimate
$S_{Y \cdot X}$ is the standard error of estimate from storage
V_{SR} is the variability in the sampling rate

Determine the variability in the sampling rate from a factorial test, similar to that of the NIOSH protocol[6] or the SLTC protocol[7,8] for the validation for diffusive samplers. The variability in the sampling rate for SKC 575 Series Passive Sampler and the 3M 3520 Organic Vapor Monitor was determined to be 8.7%[9] and 7.4%[10], respectively.

4. Assuming a normal distribution of values about the regression curve and uniformity of variation about the entire range of the curve, ±1.96 times the overall standard error of estimate will represent the 95% confidence limits.

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

6. The confidence limits of the overall procedure must be equal to or less than 25%.

{The rest of this section is not related to the development of a method but is included as information that could be useful when analyzing field samples.}

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 variability in sampling rate caused by a temperature range of 22.2 ± 15 C (72 ± 27 F). 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 a value of 3% is used for V_P. This is the variability in pressure caused by

[6] Cassinielli, M.E.; Hull, R.D.; Crable, J.V.; and Teass, A.W., "Protocol for the Evaluation 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.

[7] Hendricks, W. *Development of a Protocol for Laboratory Testing of Diffusive Samplers*, OSHA Salt Lake Technical Center, Salt Lake City, UT. Unpublished work, 1996.

[8] Hendricks, W. *Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers*, OSHA Salt Lake Technical Center, Salt Lake City, UT. Unpublished work, 1998.

[9] Hendricks, W. *Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers*.

[10] Hendricks, W. *Development of a Protocol for Laboratory Testing of Diffusive Samplers*.

variations due to weather, which is based on the tracking of atmospheric pressure variations for a year at SLTC. When the pressure at the sampling site is known, V_P is equal to zero.

If the elevation of the sampling site is unknown, the elevation can be estimated by data found at the World Wide Web address 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.
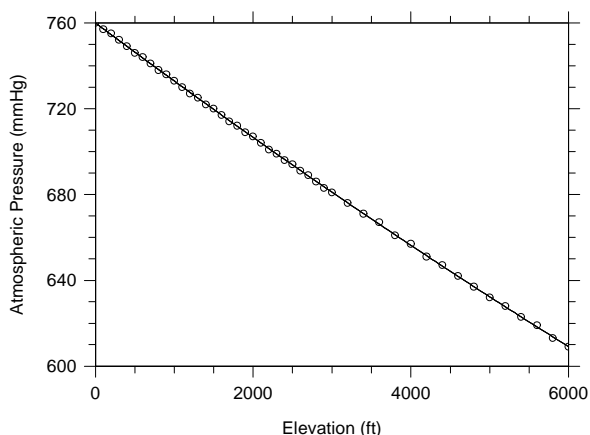

Figure 9. Plot of atmospheric pressure vs. elevation (Y = 3.887 E-7 X^2 - 0.02748 X + 760.0).

Table 2[11]
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	1900	709	2800	686	4400	647
100	757	1100	730	2000	707	2900	683	4600	642
200	755	1200	727	2100	704	3000	681	4800	637
300	752	1300	725	2200	701	3200	676	5000	632
400	749	1400	722	2300	699	3400	671	5200	628
500	746	1500	720	2400	696	3600	667	5400	623
600	744	1600	717	2500	694	3800	661	5600	619
700	741	1700	714	2600	691	4000	657	5800	613
800	738	1800	712	2700	689	4200	651	6000	609
900	736								

D. Reproducibility

1. Prepare six samples (for each target concentration and each sampler) in the same manner as storage samples. Submit them to SLTC for analysis. Include a draft copy of the analytical procedure for analyst instructions. Relying on the draft copy for instruction, the chemist will analyze the samples. 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 STEL, 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.

2. No individual analytical result should deviate from the theoretical value by more than 1.96 times the standard error of estimate. 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 reproducibility test must then be repeated.

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[11] Nelson, G.O. *Gas Mixtures: Preparation and Control*; Lewis: Boca Raton, 1992; Appendix M.

PREPARATION OF WRITTEN REPORTS

Written reports fall into three basic categories:

I. Evaluated Methods - Sampling and analytical methodology that has been thoroughly evaluated according to the evaluation guidelines.

II. Partially Evaluated Methods - Sampling and analytical procedures for which an in-depth evaluation has not been performed. The evaluation of these methods is often performed rapidly in order to meet the immediate need of field personnel when established methodology does not exist.

III. Studies - Investigations that involve a class or group of analytes, or an aspect of methodology that may be common to many methods in general. Unsuccessful evaluations will be reported as studies.

Prepare each type of report in accordance with the following respective formats:

I. Evaluated Methods

The following format provides a means of reporting data obtained during evaluation of chromatographic sampling and analytical methods. The cover page is intended as a quick reference that provides basic information. The backup data section contains tabulated and graphical laboratory data that are referenced throughout the report. This outline was prepared from the viewpoint of a chromatographic analysis.

All evaluated methods completed by the Methods Development Team will have the following statement on the cover page:

"Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team."

Page Numbering - Do not number the cover page. Number pages at the bottom, including the method number followed by a dash and then the page number. Example: The first page after the cover page of Method 1001 would be "1001-1".

Comments are set off with braces "{ }", and are not included in the method.

Text written in 10 point Arial font with full justification with no hyphenation

Tabs: Cover page - 2.0 - Method - 0.2, 0.59, 1.12, 1.36

OSHA logo on cover page - size = 0.500", paragraph anchor, 0" horizontal, 0" from top, right margin, wrap behind text

Tables - 9 point Arial font, 0.02" for left inside margin, right inside margin, top row margin, bottom row margin

Graphs - size = 3.1", paragraph anchor, 0" horizontal, 0" from top, right margin, wrap left, caption is 9 point Arial font

Table boxes - size = 3.1, paragraph anchor, 0" horizontal, 0" from top, left margin if next to a graph, wrap left or neither, 9 point Arial font

References will follow as closely as possible the format recommended by the American Chemical Society in their 1997 edition of "The ACS Style Guide - A Manual for Authors and Editors."

{ANALYTE}
{as listed in CFR or ACGIH}

Method number:	1xxx

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}

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 over 250 mL/min, use L/min.}
{Diffusive sampler}: ____ 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 samples where sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.4 for applicable standard errors of estimate.

Special requirements: When using a {diffusive sampler}, report the sampling site pressure and temperature. {If none, delete this item}

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

____ {month year}   {Chemist} ____

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1. General Discussion

{The backup data section will be referenced throughout the method in the following manner: "(Section 4.____)". Literature citations will be footnotes.}

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 to be used if applicable, others properties may be listed.}

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

This method was evaluated according to the OSHA SLTC "EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS"[12]. 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 25 C and 101.3 kPa (760 mmHg).

1.2   Limit defining parameters

    1.2.1   Detection limit of the analytical procedure

    The detection limit of the analytical procedure is ____ {mass}. This is the amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1) {If the definition for the analytical detection limit for a

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[12] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

particular analyte must be altered, the altered definition should appear in this section and the detailed explanation should appear in Section 4.1.}

1.2.2   Detection limit of the overall procedure

The detection limits of the overall procedure are _____ {mass} per sample (_____ ppm or _____ mg/m^3) and _____ {mass} per sample (_____ ppm or _____ mg/m^3) for {active sampler} and {diffusive sampler}, respectively. These are the amounts of {analyte} spiked on the respective sampler that will give detector responses that are significantly different from the responses of respective sampler blanks. (Sections 4.2)

1.2.3   Reliable quantitation limit

The reliable quantitation limits are _____ {mass} per sample (_____ ppm or _____ mg/m^3) and _____ {mass} per sample (_____ ppm or _____ mg/m^3) for {active sampler} and {diffusive sampler}, respectively. These are the amounts of {analyte} spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements. (Section 4.2)

1.2.4   Instrument calibration

{Active sampler}

The standard error of estimate is _____ {mass} over the range of _____ to _____ g. This range corresponds to 0.25 to 2 times the target concentration. (Section 4.3)

{Diffusive sampler}

The standard error of estimate is _____ {mass} over the range of _____ to _____ g. This range corresponds to 0.25 to 2 times the target concentration. (Section 4.3)

1.2.5   Precision

{Active sampler}

The precision of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (_____ C)} 15-day storage test (at the target concentration) from {adsorbent tube} is ± _____ %. This includes an additional 5% for sampling pump variability. (Section 4.4) {The precision cited must be based on the storage data that reflects the temperature recommended for shipment of samples.}

{Diffusive sampler}

The precisions of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (_____ C)} 15-day storage test (at the target concentration) from {diffusive sampler} are given in Table 1.2.5. They each include an additional

Table 1.2.5
Precision of the Overall Procedure

known conditions	precision (±%)
both T & P	_____
only T	_____
only P	_____
neither T nor P	_____

_____% for sampling rate variability. 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 ± 15 C (72 ± 27 F) 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. (Section 4.4) {The precision cited must be based on the storage data that reflects the temperature recommended for shipment of samples.}

1.2.6   Recovery

The recovery of {analyte} from samples used in a _____-day storage test remained above _____ % and _____% {the lowest points on the regression curves of Figure 4.5.} when the samples were stored at _____ C 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 _____ C.) (Section 4.5)

1.2.7   Reproducibility

Six samples for both samplers collected from a controlled test atmosphere {or spiked by liquid injection, etc.} were submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after _____ days of storage at _____ C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

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 such a manner that it 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 evaluation, if applicable.}

2.1.1   {Active sampler}
Example:
Samples are collected with {description of the sampler, 7-cm × 4-mm i.d. × 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 with glass wool plugs.} For this evaluation, commercially prepared {active samplers} were purchased from {Supplier}, Inc. (catalog no. _____).

Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.1.2   {Diffusive sampler}

Samples are collected with a {diffusive sampler}. For this evaluation, commercially available samplers were purchased from {Supplier}, Inc. (catalog no. xxx-xx).

A thermometer and barometer 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}

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

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

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

After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form 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 volume (liters), sampling time (minutes) and sampling rate (mL/min) for each sample, along with any potential interferences on the OSHA-91A form.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

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

Remove the sampler enclosed in an air-tight clear bag from the container. Keep the O-ring, press-on cover, cover retainer, port plugs and PTFE tube for later use.

Remove the sampler from the clear bag when ready to begin sampling. CAUTION - The monitor immediately begins to sample when it is removed from this bag.

Record the start time on the sampler label or on the Form OSHA-91A.

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

At the end of the sampling period, immediately detach the sampler from the worker and attach the cover with the O-ring in place 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 sampler label or on OSHA-91A form.

Prepare a blank by removing an unused sampler from its clear package and immediately attaching a cover with the O-ring in place onto it.

Seal each sampler with an OSHA-21 form.

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

Record the room temperature and atmospheric pressure of 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 samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples. Include all port plugs and PTFE tubes which will be used in the laboratory analyses.

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

2.3.3   {Filter cassette}

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.

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 an OSHA-21 form 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) for each sample, along with any potential interferences.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

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

The monitors 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 monitor. CAUTION - The monitor 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 monitor or on the OSHA-91A form.

Attach the monitor 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 monitor until the sampling period is terminated.

At the end of the sampling period, detach the monitor from the worker and remove the white film and retaining ring. Immediately snap a closure cap onto the primary (top) section of the monitor (where the white film and ring were removed). It is critical that this step be done as quickly as possible because the sampling rate is more than five times faster without the white film in place, which can be an important consideration, especially for short-term sampling. Assure that the attached port plugs are placed firmly into the port holes. The white film and ring can be discarded. Record the stop time on the back of the monitor or on the OSHA-91A form.

The following steps should be performed in a low background area for a set of monitors as soon as possible after sampling.

Ready a blank by removing the white film and ring and attaching a closure cap onto an unused monitor.

For each monitor (one at a time), separate the primary (top) and secondary (bottom) sections of the monitor using the edge of a coin as a pry.

Securely snap a cup onto the bottom of the primary section.

Snap a closure cap onto the secondary section of the monitor and assure that the attached port plugs are placed firmly into the port holes.

Return the sampler sections with closure caps and cup in place 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 an OSHA-21 form.

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

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

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

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

2.4   Sampler capacity (Section 4.7) {Describe test, conditions and results.}

    2.4.1   The sampling capacity of the front section of an {adsorbent} sampling tube was tested by sampling a dynamically generated test atmosphere of {analyte} (_____ mg/m^3 or _____ ppm) at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C). The samples were collected at _____ mL/min. The 5% breakthrough sampling time was determined to be _____ min.

    2.4.2   The sampling rate and capacity of the {diffusive sampler} were determined by sampling a dynamically generated test atmosphere of {analyte} (_____ mg/m^3 or _____ ppm) at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity

at 22.2 C) for increasing time intervals. A sampling rate of _____ mL/min and sampling time of _____ min were obtained from this test.

2.5   Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine the extraction efficiency because the adsorbent material, internal standard, reagents and laboratory techniques may be different than the those listed in this evaluation and influence the results.

2.5.1   {Active sampler}

The mean extraction efficiency for {analyte} from dry {adsorbent} over the range of {RQL or 0.05} to 2 times the target concentration (_____ to _____ milligrams per sample) was _____%. The extraction efficiency was not affected by the presence of water. {A significant difference is when the mean of the wet samplers is more than two standard deviations from the mean of the dry sampler at the same mass loading.}

Extracted samples remain stable for at least _____ h {or days}.

2.5.2   {Diffusive sampler}

The mean extraction efficiency for {analyte} from dry {diffusive sampler} over the range of {RQL or 0.05} to 2 times the target concentration (_____ to _____ milligrams per sample) was _____%. The extraction efficiency was not affected by the presence of water. {A significant difference is when the mean of the wet samplers is more than two standard deviations from the mean of the dry sampler at the same mass loading.}

Extracted samples remain stable for at least _____ h {or days}.

2.6   Recommended sampling time and sampling rate

2.6.1   {Active sampler}

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

Sample for _____ min at _____ mL/min (_____ L) when using {active sampler} to collect ceiling (short-term) samples.

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 are collected.

2.6.2   {Diffusive sampler}

Sample for up to _____ min when using {diffusive sampler} to collect TWA (long-term) samples. The sampling rate is _____ mL/min.

Sample for _____ min when using {diffusive sampler} to collect ceiling (short-term) samples. The sampling rate is _____ mL/min.

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

2.7   Interferences, sampling (Section 4.9)

   2.7.1   {Active sampler}

         The retention efficiency for all samples was above ____% {report the lowest value}, when
         {active samplers} containing ____ mg {½× TC} of {analyte} were allowed to sample ____
         L of contaminant-free air having an absolute humidity of 15.7 milligrams of water per liter
         of air (about 80% relative humidity at 22.2 C).

         The collection efficiency for all samples was above ____% of theoretical {report the
         lowest value}, when {active samplers} were used to sample a test atmosphere containing
         two times the target concentration of {analyte} and having an absolute humidity of 3.9
         milligrams of water per liter of air (about 20% relative humidity at 22.2 C).

         The collection efficiency for all samples was above ____% of theoretical {report the
         lowest value}, when {active samplers} were used to sample a test atmosphere containing
         0.1 times the target concentration of {analyte} and having an absolute humidity of 15.7
         milligrams of water per liter of air (about 80% relative humidity at 22.2 C).

         The collection efficiency for all samples was above ____% of theoretical {report the
         lowest value}, when {active samplers} were used to sample a test atmosphere containing
         one times the target concentration of {analyte}, ____ mg/m^3 of {interference} and having
         an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative
         humidity at 22.2 C).

   2.7.2   {Diffusive sampler}

         The mass for all samples was above ____% {report the lowest value}, when {diffusive
         samplers} containing ____ mg {½× TC} of {analyte} were used to sample for three-
         quarters of the recommended sampling time contaminant-free air having an absolute
         humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at
         22.2 C).

         The recovery for all samples was above ____% of theoretical {report the lowest value},
         when {diffusive samplers} were used to sample a test atmosphere containing two times
         the target concentration of {analyte} and having an absolute humidity of 3.9 milligrams of
         water per liter of air (about 20% relative humidity at 22.2 C).

         The recovery for all samples was above ____% of theoretical {report the lowest value},
         when {diffusive samplers} were used to sample a test atmosphere containing 0.1 times
         the target concentration of {analyte} and having an absolute humidity of 15.7 milligrams
         of water per liter of air (about 80% relative humidity at 22.2 C).

         The recovery for all sample was above ____% of theoretical {report the lowest value},
         when {diffusive samplers} were used to sample a test atmosphere containing one times
         the target concentration of {analyte}, ____ mg/m^3 of {interference} and having an absolute
         humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at
         22.2 C).

3. Analytical Procedure

   Adhere to the rules set down in your Chemical Hygiene Plan[13]. Avoid skin contact and inhalation of all
   chemicals and review all MSDSs.

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[13] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title
     29, 1998.

3.1 Apparatus {Provide general descriptions of the required equipment. Follow each general description with a specific description of equipment actually used in the evaluation.}
Example:
3.1.1 Gas chromatograph equipped with an FID. A Hewlett-Packard Model 6890 was used in this evaluation.

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 evaluation.}
Example:
3.2.1 Methylene chloride, [CAS no.], ___ grade or better. The methylene chloride used in this evaluation was A.C.S. HPLC grade (lot no. Q87C654) purchased from Aldrich (Milwaukee, WI).

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

3.3 Standard preparation {Describe preparation of standards in general and give an example.}
Example:
3.3.1 Prepare concentrated stock standards of {analyte} in CS_2. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1 mL of extracting solution delivered from the same dispenser used to extract samples. For example, to prepare a target level standard, inject ____ L of a stock solution containing ____ mg/mL of {analyte} in CS_2 into 1 mL of extracting solution.

3.3.2 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 extracting solution to each vial and immediately seal the vials with polytetrafluoroethylene-lined caps.

Shake the vials vigorously several times during the ____ min extraction time.

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 or sharp knife.

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 in the sampler rack (SKC Cat. No. 226-04-5) of a specialized shaker (SKC Cat. No. 226D-03-1) and shake the samplers for 1 hour.

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 sampler at 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.

Allow the sampler sections to extract for 30 min. Periodically apply gentle agitation to the sampler sections during the extraction period.

Transfer the solution from each sampler section by removing both plugs from the ports, inserting a decanting spout (a small section of PTFE tubing) into the rim port and pouring the liquid through the spout into a labeled autosampler vial. Immediately cap each vial.

3.5   Analysis
Example:
3.5.1   Analytical conditions {Provide detailed instrument settings, include chromatogram at the target concentration, and the calibration technique used.}
Example:

<u>GC conditions</u>

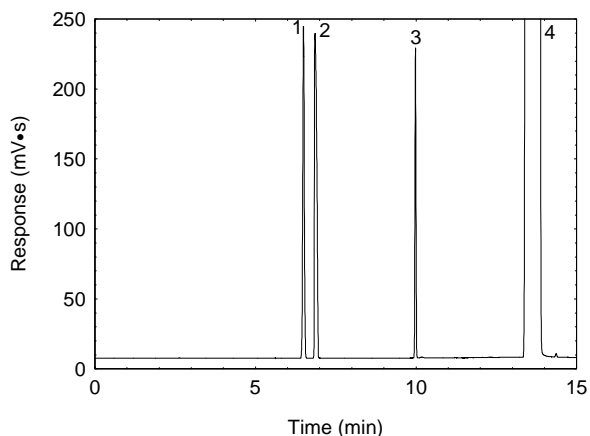|	
column temperature:	60 C (column)
zone temperatures:	250 C (injector) 300 C (detector)
run time:	15 min
column gas flow:	1.2 mL/min (hydrogen)
septum purge:	1.5 mL/min (hydrogen)
injection size:	1.0 L (12.5:1 split)
column:	6 0 - m × 0.32-mm i.d. capillary SPB-5 (d_f = 1.0- m)
retention times:	6.5 min (compound A) 6.9 min (compound B) 10.0 min (compound C) 13.6 min (compound D)

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

<pre>
                    FID conditions
                    hydrogen flow: 34 mL/min
                    air flow: 450 mL/min
                    nitrogen makeup
                    flow: 33 mL/min
</pre>

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.
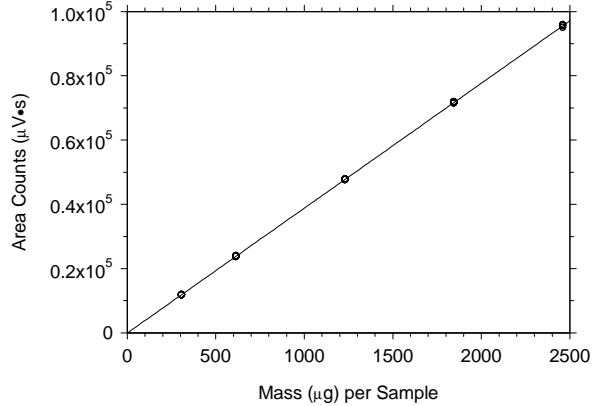

Figure 3.5.2. Calibration curve of {analyte}. (Y = 38.89X - 65.50)

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 an interference from the analyte.

      3.6.2   When necessary, the identity of an analyte peak may be confirmed with additional analytical data (Section 4.9).

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

              The amount of {analyte} per sampler 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. 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 concentration by weight (mg/m^3)
        M is micrograms per sample
        V is liters of air sampled
        E_E is extraction efficiency, in decimal form

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

where C_V is concentration by volume (ppm)
        V_M is molar volume at 25 C
        C_M is concentration by weight
        M_r is molecular weight

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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 is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, the amount is multiplied by 2.2 (as per manufacturer's instructions) and then added to the amount on the front section.} 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.

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

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

$$C_M = \frac{M}{tR_{SS}E_E}$$

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

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

where C_V is concentration by volume (ppm)
V_M is molar volume at 25 C
C_M is concentration by weight
M_r is molecular weight

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

$$P_{SS} = AE^2 - BE + 760.0$$

where P_{SS} is the approximate atmospheric pressure
E is the sampling site elevation, ft
A is 3.887×10^{-7} mmHg/ft^2
B is 0.02748 mmHg/ft

4. Backup Data {This section contains evaluation data which is referenced in the preceding sections.}

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"[14]. The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

4.1   Detection limit of the analytical procedure (DLAP) {Present the test data in a table and a graph.}
Example:
The DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equal increments with the highest standard containing _____ g/mL. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank near the elution time of the analyte. These standards, and the reagent blank were analyzed with the recommended analytical parameters (1- L injection with a __:1 split), and the data obtained were used to determine the required parameters (standard error

[14] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

of estimate and slope) for the calculation of the DLAP. Values of ____ and ____ were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be ____ pg.

Table 4.1
Detection Limit of the Analytical Procedure

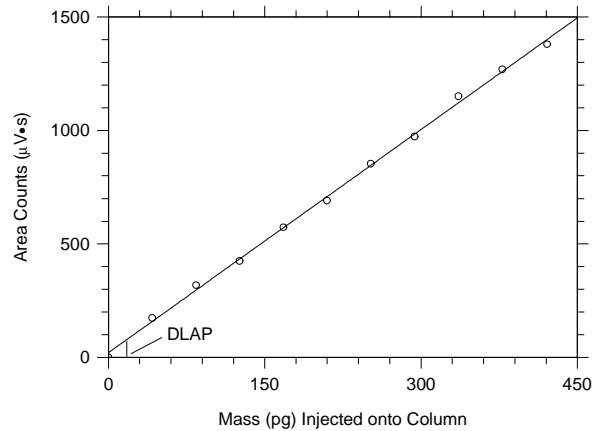| concentration (μg/mL)	mass on column (pg)	area counts (μV-s)
0	0	0
0.421	42.1	173
0.841	84.1	318
1.26	126	425
1.68	168	573
2.10	210	690
2.52	252	853
2.94	294	973
3.36	336	1150
3.78	378	1270
4.21	421	1380

Figure 4.1. Plot of data to determine the DLAP. (Y = 3.28X + 20.5)

4.2   Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL) {Present the test data in a table, graph and a chromatogram of the 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 equal descending increments of analyte, such that the highest sampler loading was ____ g/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. 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 ____ g/sample (____ ppm, ____ mg/m^3).

Table 4.2
Detection Limit of the Overall Procedure

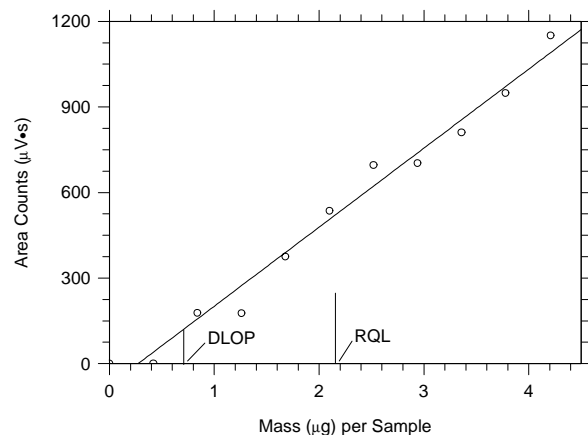| mass per sample (μg)	area counts (μV-s)
0	0
0.421	0
0.841	178
1.26	177
1.68	375
2.10	536
2.52	696
2.94	703
3.36	810
3.78	948
4.21	1150

Figure 4.2.1. Plot of data to determine the DLOP/RQL. (Y = 277X - 75.8)

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The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is ____ g per sample (____ ppm, ____ g/m³) Recovery at this concentration is ____%.
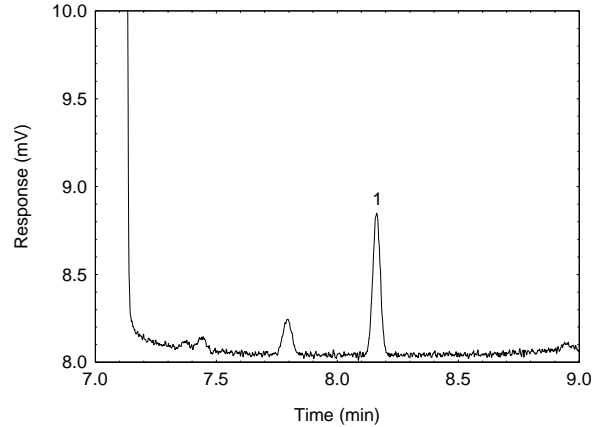

Figure 4.2.2. Chromatogram of the RQL. 1 - {Analyte}

4.3 Instrument calibration
Example:
The standard error of estimate was determined from the linear regression of data points from standards over a range that covers 0.25 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 six injections of five standards. The standard error of estimate is ____ {mass}.

Table 4.3.
Instrument Calibration

standard concn (μg/mL)	area counts (μV•s)					
307	11935	11795	11888	11735	11988	11895
615	23988	23738	23741	23938	23747	23788
1230	47783	47593	47895	47793	47595	47883
1845	71790	71490	71901	71795	71495	71990
2461	95054	95987	95616	95087	95916	95654

4.4 Precision (overall procedure)

4.4.1 {Active sampler}

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. The precision of the overall procedure of ±____ % was obtained from the standard error of estimate of ____ in Figure ____. {The standard estimate of error listed on the cover page of the method must be based on the storage data that reflects the temperature recommended for shipment and storage of samples.}

4.4.2 {Diffusive sampler}

The precisions of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (____ C)} 15-day storage test (at the target concentration) from {diffusive sampler} are given in Table 4.4.2. They each include an additional ____% for sampling rate variability.

Table 4.4.2
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	____	____

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 ± 15 C (72 ± 27 F) 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 must be based on the storage data that reflects the temperature recommended for shipment and storage of samples.}

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

4.5.1   {Active sampler}

Storage samples for {analyte} were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of {analyte} was at the target concentration with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 C). Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the tubes was stored at reduced temperature (4 C) and the other fifteen was stored in a closed drawer at ambient temperature (about 22 C). 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 corrected for extraction efficiency.

Table 4.5.1
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

Ambient Storage
Y = -0.260 + 100.8
Std Error of Estimate = 5.55%
95% Confidence Limits = ±(1.96)(5.55) = ±10.9%

Figure 4.5.1.1. Ambient storage test for {analyte}.

Refrigerated Storage
Y = -0.116 + 101.2
Std Error of Estimate = 5.60%
95% Confidence Limits = ±(1.96)(5.60) = ±11.0%
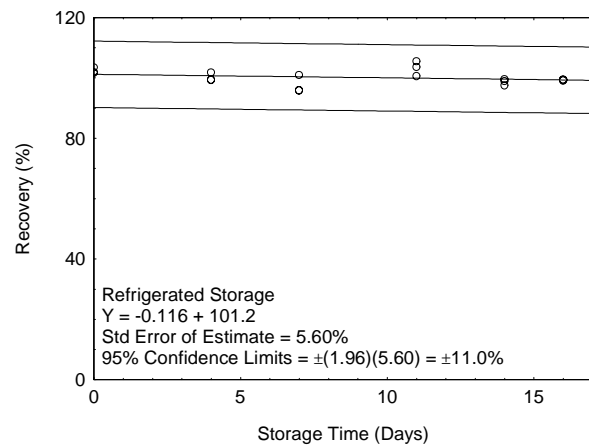
Figure 4.5.1.2. Refrigerated storage test for {analyte}.

4.5.2   {Diffusive sampler}

Storage samples for {analyte} were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of {analyte} was at the target concentration and the test atmosphere with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 C). Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the tubes was stored at reduced temperature (4 C) and the other fifteen was stored in a closed drawer at ambient temperature (about 22 C). 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 corrected for extraction efficiency.

Table 4.5.2
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

Ambient Storage
Y = -0.260 + 100.8
Std Error of Estimate = 5.55%
95% Confidence Limits = ±(1.96)(5.55) = ±10.9%

Refrigerated Storage
Y = -0.116 + 101.2
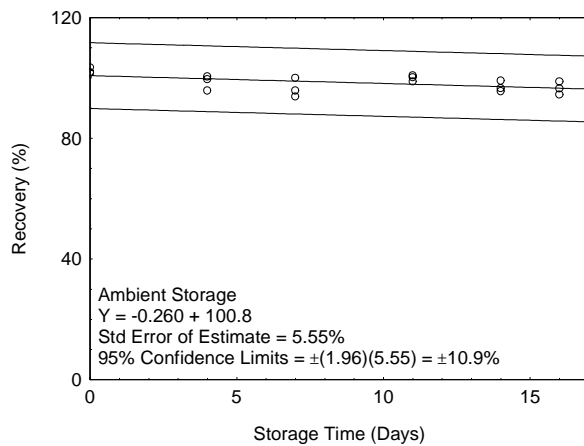Std Error of Estimate = 5.60%
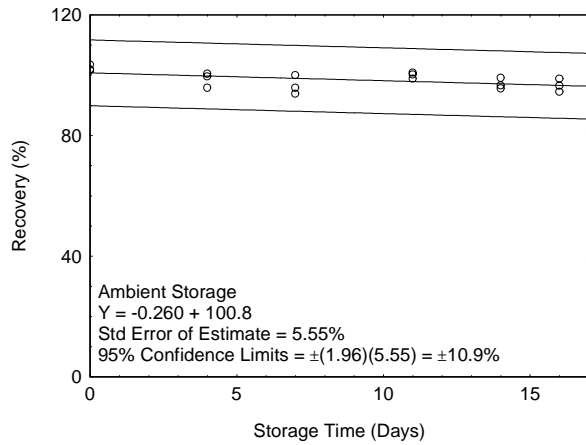95% Confidence Limits = ±(1.96)(5.60) = ±11.0%

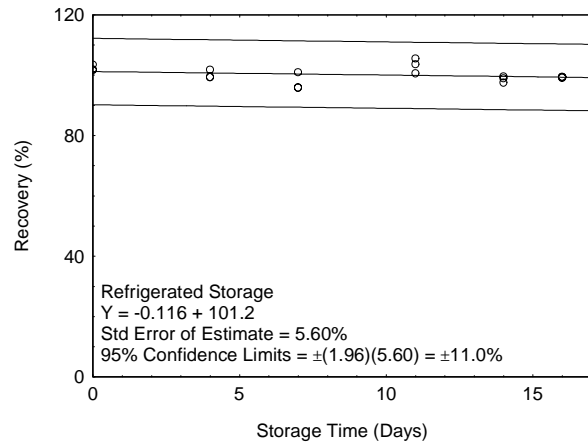Figure 4.5.2.1. Ambient storage test for {analyte}.   Figure 4.5.2.2. Refrigerated storage test for {analyte}.

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 collecting them from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for _____ days at _____ C. Sample results were corrected for extraction efficiency. No sample result for {analyte} had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6.1
Reproducibility
Data for {Analyte} 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} 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 {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 from a dynamically generated test atmosphere of {analyte} (_____ mg/m^3 or ____ ppm) with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C). 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 monitored the downstream air flow every 5 min. The recommended sampling time is _____ h.

Table 4.7.1
Breakthrough of {Analyte} with {Active Sampler}

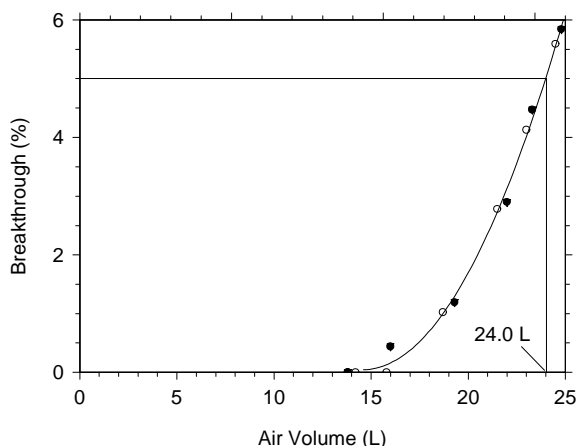| test no.	air vol (L)	sampling time (min)	downstream concn (mg/m^3)	break-through (%)
1	14.2	285	0.00	0.0
	15.8	315	0.00	0.0
	18.7	375	0.72	1.02
	21.5	430	1.96	2.78
	23.0	460	2.91	4.13
	24.5	490	3.94	5.59
2	13.8	275	0.00	0.0
	16.0	320	0.31	0.44
	19.3	385	0.84	1.19
	22.0	440	2.04	2.90
	23.3	465	3.15	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 are determined with samples collected at increasing time intervals from a controlled test atmosphere. Sampler capacity is exceeded when the sampling rate decreases. The concentration of the test atmosphere was two times the target concentration with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 C). The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and 2 h samples. Horizontal lines were placed 10% above and below the preliminary sampling rate. The sampling rate is _____ mL/min at 760 mmHg and 25 C 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 _____ h.

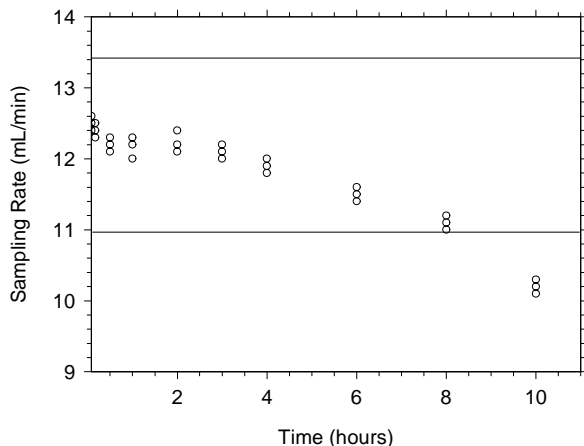| Table 4.7.2 Determination of Sampling Rate and Time			
	sampling rate (mL/min)		
time (h)	first	second	third
0.083	12.4	12.5	12.6
0.167	12.3	12.4	12.5
0.5	12.1	12.2	12.3
1	12.0	12.2	12.3
2	12.1	12.2	12.4
3	12.0	12.1	12.2
4	11.8	11.9	12.0
6	11.4	11.5	11.6
8	10.9	11.0	11.1
10	10.6	10.7	10.5

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

4.8   Extraction efficiency and stability of extracted samples

The extraction efficiency is dependent on the extraction solvent as well as the internal standard. Other extraction solvents or internal standards may be used provided that the new extraction solution or internal standard is tested. The new extraction solvent or internal standard should be tested as described below.

4.8.1   {Active sampler}

Extraction efficiency

The extraction efficiencies of {analyte} were determined by liquid-spiking {active sampler} with the analyte at the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is ____%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

Table 4.8.1.1 Extraction Efficiency of {Analyte} from {Active Sampler}						
level		sample number				
× target concn	μg per sample	1	2	3	4	mean
RQL	0.21	99.8	97.5	99.9	101.2	99.6
0.25	105	103.5	99.5	99.6	100.0	100.6
0.5	210	101.6	102.4	100.5	95.8	100.1
1.0	421	101.9	101.8	95.8	100.2	99.9
1.5	632	105.8	105.0	100.4	94.2	101.4
2.0	841	95.8	92.8	97.7	97.7	96.0
1.0 (wet)	421	102.8	103.7	101.1	100.4	102.0

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was ____% for samples that were resealed with new septa and ____%

for those that retained their punctured septa. Each septum was punctured _____ times for each injection.

Table 4.8.1.2
Stability of Extracted Samples for {Analyte}

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
92.8	89.1	−3.7	98.5	88.8	−9.7
97.3	88.3	−9.0	97.7	94.6	−3.1
	(mean)			(mean)	
95.1	88.7	−6.4	98.1	91.7	−6.4

4.8.2   {Diffusive sampler}

Extraction efficiency

The extraction efficiencies of {analyte} were determined by liquid-spiking {diffusive sampler} with the analyte at the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted and analyzed. The average extraction efficiency over the working range of RQL to 2 times the target concentration was _____%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

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

level		sample number				
× target concn	μg per sample	1	2	3	4	mean
RQL	0.21	99.8	97.5	99.9	101.2	99.6
0.25	42.1	101.6	102.4	100.5	95.8	100.1
0.5	84.1	101.9	101.8	95.8	100.2	99.9
1.0	421	95.8	92.8	97.7	97.7	96.0
1.5	632	102.8	103.7	101.1	100.4	102.1
2.0	841	96.8	99.8	98.7	98.7	98.5
1.0 (wet)	421	103.5	99.5	99.6	100.0	100.7

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was _____% for samples that were resealed with new septa and _____% for those that retained their punctured septa. Each septum was punctured _____ times for each injection.

Table 4.8.2.2
Stability of extracted Samples for {Analyte}

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
92.8	89.1	−3.7	99.5	96.8	−2.7
95.8	92.3	−3.5	97.7	88.7	−9.0
	(mean)			(mean)	
94.3	90.7	−3.6	98.6	92.8	−5.9

4.9   Interferences (sampling)

4.9.1   {Active sampler}

Retention

The ability of a {active sampler} to retain {analyte} after it has been collected was tested by sampling an atmosphere containing _____ mg/m^3 {two times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C).   Six samplers had

Table 4.9.1
Retention Efficiency (%) of {Analyte}
from {Active Sampler}

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	100.8	101.9	100.2	100.9

contaminated air drawn through them at _____ mL/min for _____ min {one-quarter of the recommended sampling time}. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples having contaminant-free air {relative humidity of 80% at 22.2 C} drawn through them at _____ mL/min for _____ h {three-quarters of the recommended sampling time} and then all six samplers were analyzed. All of the samples in the second set had retained more than _____% of the mean collected by the first three samples.

Low humidity

The ability of a {active sampler} to collect {analyte} from a relatively dry atmosphere was tested by sampling an atmosphere containing _____ mg/m^3 {two times the target concentration} of {analyte} at an absolute humidity of 3.9 milligrams of water per liter of air (about 20% relative humidity at 22.2 C). Three samplers had contaminated air drawn through them at _____ mL/min for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected _____%, _____% and _____% of theoretical.

Low concentration

The ability of a {active sampler} to collect {analyte} at low concentrations was tested by sampling an atmosphere containing _____ mg/m^3 {0.1 times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C). Three samplers had contaminated air drawn through them at _____ mL/min for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected _____%, _____% and _____% of theoretical.

Interference

The ability of a {active sampler} to collect {analyte} was tested when other potential interferences are present by sampling an atmosphere containing _____ mg/m^3 {one times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C) and {interference}, whose concentration was _____ mg/m^3. Three samplers had contaminated air drawn through them at _____ mL/min for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected ____%, ____% and ____% of theoretical.

4.9.2   {Diffusive sampler}

Reverse diffusion

The ability of a {diffusive sampler} to retain {analyte} after it has been collected was tested by sampling an atmosphere containing _____ mg/m^3 {two times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C). Six samplers were exposed to contaminated air for _____ min

Table 4.9.2
Reverse Diffusion of {Analyte}
from {Diffusive Sampler}

	mass (μg)			
set	1	2	3	mean
first	49.8	49.1	50.0	49.6
second	50.2	50.1	50.2	50.2
second/first	100.8%	102.0%	100.2%	101.2%

{one-quarter of the recommended sampling time}. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples being exposed to humid contaminant-free air for _____ h {three-quarters of the recommended sampling time} and then all six samplers were analyzed.

Low humidity

The ability of a {diffusive sampler} to collect {analyte} from a relatively dry atmosphere was tested by sampling an atmosphere containing _____ mg/m^3 {two times the target concentration} of {analyte} at an absolute humidity of 3.9 milligrams of water per liter of air (about 20% relative humidity at 22.2 C).   Three samplers are exposed to contaminated air for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected ____%, ____% and ____% of theoretical.

Low concentration

The ability of a {diffusive sampler} to collect {analyte} at low concentration was tested by sampling an atmosphere containing _____ mg/m^3 {0.1 times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C). Three samplers are exposed to contaminated air for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected ____%, ____% and ____% of theoretical.

Interference

The ability of a {diffusive sampler} to collect {analyte} when other potential interferences are present was tested by sampling an atmosphere containing _____ mg/m^3 {one times the target concentration} of {analyte} at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C) and {interference}, whose

concentration was _____ mg/m^3. Three samplers are exposed to contaminated air for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The samples had collected _____%, _____% and _____% of theoretical.

4.10   Qualitative analysis

{Present alternate chromatographic and GC/MS conditions that will aid in confirming the identity of the analyte (or derivative) peak. GC/MS or LC/MS may provide the most conclusive identification and should be addressed in all cases, even if this amounts to an explanation why it is not possible or not available. Peak ratios and analysis with alternate detectors may be useful.   The format for mass spectrograms is shown in Figure 4.10.}
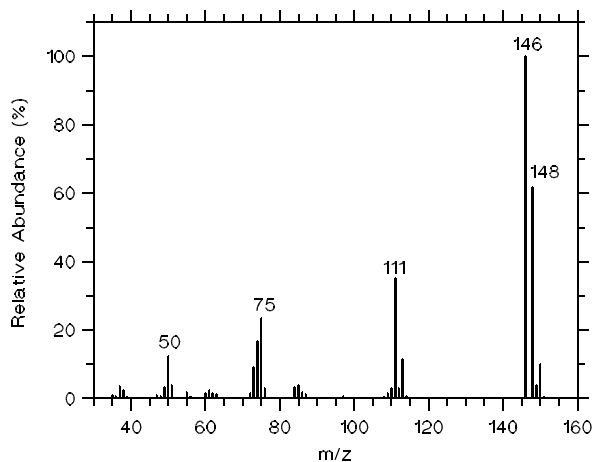

Figure 4.10. Mass spectrum of {analyte}.

II. Partially Evaluated Methods - Data must be included on the following items:

1. <u>Background information</u> - Include the purpose of the work, physical properties and other easily acquired information that would normally be reported in the Background Section of a thoroughly evaluated procedure.

2. <u>Detection limit of the overall procedure (DLOP)</u> - Determine this parameter in the same manner as in a thorough evaluation.

3. <u>Reliable quantitation limit</u> - Determine this parameter in the same manner as in a thorough evaluation.

4. <u>Extraction efficiency</u> - Determine these parameters over the working rage of 0.5 to 2 times the target concentration, in the same manner as in a thorough evaluation.

5. <u>Recommended sampling time and sampling rate</u> - The recommended sampling information will at least be based, in part, on retention efficiencies. Retention efficiencies must be performed with loadings equivalent to twice the target concentration and with humid air (80% relative humidity at 22.2 C).

6. <u>Storage test</u> - In order to determine sample stability, a storage test will be performed with spiked samples at loadings equivalent to the target concentration. This test should be performed for an amount of storage time considered necessary. The typical age of submitted samples could be the basis for the length of a storage test.

7. <u>Recommendation for further study</u> - Recommendations must be made that should be considered before a thorough evaluation is performed.

Report Partially Evaluated Methods according to the following outline. This outline is similar to that used for an Evaluated Method except the evaluation data is included in the various appropriate method sections instead of in a separate Backup Data section. The outline for Evaluated Methods can be a reference for more specific format details. All Partially Evaluated Methods will have the following statement of status on the cover page:

"Partially Evaluated Method". This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

Follow the formatting information of an Evaluated Method given on Page 17.

Method number: PV2<u>xxx</u>

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}

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 ____ L/min (____ L)

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

Special requirements: {If none, delete this item}

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

____ {month year}   {chemist}____

Chromatography Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1. General Discussion

   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[15]

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

This method was evaluated according to the OSHA SLTC "EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS"[16]. 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 25 C and 101.3 kPa (760 mmHg).

   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 equal descending increments of analyte, such that the highest sampler loading was ____ g/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 used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. Values of ____ and ____ were obtained for the slope and standard error of estimate respectively. DLOP was calculated to be ____ g/sample (____ ppm, ____ mg/m^3).

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[15] This reference was used for most of the physical properties.
[16] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

Table 1.2
Detection Limit of the Overall Procedure

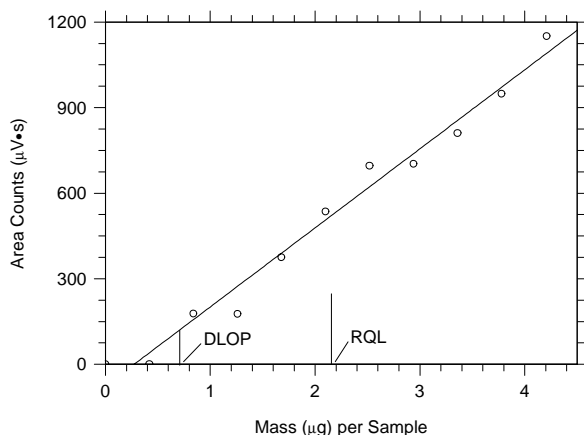| mass per sample (μg)	area counts (μV-s)
0	0
0.421	0
0.841	178
1.262	177
1.682	375
2.103	536
2.524	696
2.944	703
3.365	810
3.785	948
4.206	1151

Figure 1.2. Plot of data to determine the DLOP/RQL. (Y = 277X - 75.8)

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

2. Sampling Procedure {Refer to cited sections for format in Evaluated Methods for detail. Use paragraphs instead of using 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, page 21}

2.2   Reagents {If no reagents are required, state "None required". Otherwise use the format described in Section 3.2, page 27.}

2.3   Technique {Section 2.3, page 22}

2.4   Extraction efficiency
       Example:
       The extraction efficiencies of {analyte} were determined by liquid-spiking {sampler} with the analyte at 0.5 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 99.7% for {analyte}.

Table 2.4
Extraction Efficiency of {Analyte}

level		sample number				
× target concn	μg per sample	1	2	3	4	mean
0.25	105	103.5	99.5	99.6	100.0	100.6
0.5	210	101.6	102.4	100.5	95.8	100.1
1.0	421	101.9	101.8	95.8	100.2	99.9
1.5	632	105.8	105.0	100.4	94.2	101.4
2.0	841	95.8	92.8	97.7	97.7	96.0
1.0 (wet)	421	103.5	99.5	99.6	100.0	100.7

2.5 Retention efficiency
Example:
Six {samplers} were spiked with _____ mg (_____ mg/m^3) {analyte}, allowed to equilibrate for 6 h, and then had _____ L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 C) pulled through them. The samples were extracted and analyzed. The mean retention efficiency is _____%. There was _____% of {analyte} found on the backup portion of the {sampler}.

Table 2.5
Retention Efficiency of {Analyte}

section	sample number						mean
	1	2	3	4	5	6	
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 Sample storage
Example:
Nine {samplers} were each spiked with _____ g (_____ ppm) of {analyte}. They had _____ L of air with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 C) drawn through them. They were sealed and stored at room temperature. Three samples were analyzed immediately. Three more were analyzed after 7 days of storage and the remaining three after 14 days of storage. The amounts recovered,

Table 2.6
Storage Test for {Analyte}

time (days)	sample no.		
	1	2	3
0	100.2	101.5	98.4
7	99.8	100.8	100.5
14	97.6	101.4	99.1

which are corrected for extraction efficiency, indicate good storage stability for the time period studied.

2.7 Recommended air volume and sampling rate.
Example:
Based on the data collected in this evaluation, 10-L air samples should be collected at a sampling rate of 50 mL/min.

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 Chemical Hygiene Plan[17]. Avoid skin contact and inhalation of all chemicals.

3.1 Apparatus {Section 3.1, page 27}

3.2 Reagents {Section 3.2, page 27}

3.3 Standard preparation {Section 3.3, page 27}

3.4 Sample preparation {Section 3.4, page 27}

3.5 Analysis {Section 3.5, page 28}

3.6 Interferences (analytical) {Section 3.6, page 29}

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[17] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.7   Calculations {Section 3.7, page 29}

4. Recommendations for Further Study

III. Studies - Report studies using the following format:

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