METHOD EVALUATION GUIDELINES

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ACKNOWLEDGMENTS

NIOSH protocol for the Standards Completion Program was a significant influence on the development of these guidelines. Also, the members of the Organic Methods Evaluation Branch provided a significant contribution and are a continuing source of suggestions for refinements.

CONTENTS

LIST OF FIGURES

INTRODUCTION

The following evaluation guidelines were developed to provide chemists of the Organic Methods Evaluation Branch with a uniform and practical means for evaluating air sampling and analytical methods. The guidelines define analytical parameters, specify required laboratory tests, specify statistical calculations, specify criteria for acceptance, and provide a detailed outline for the written reports. The overall goal of these guidelines is to provide sampling and analytical methods specifically suited to OSHA needs, whose credibility can be clearly defended with evaluation data.

These guidelines are continually open to examination by the chemists who are using them, and refinements are formally made on a periodic basis. The resulting evolution in the guidelines is easily detected when comparing the early methods to the more recent ones. The evaluation guidelines have been effectively used and refined by the Organic Methods Evaluation Branch for more than fourteen years, resulting in the evaluated organic methods that are now available. Revisions included in this June 1993 update involve a change in detection limit definitions and format modifications made possible by expanded word processing capabilities.

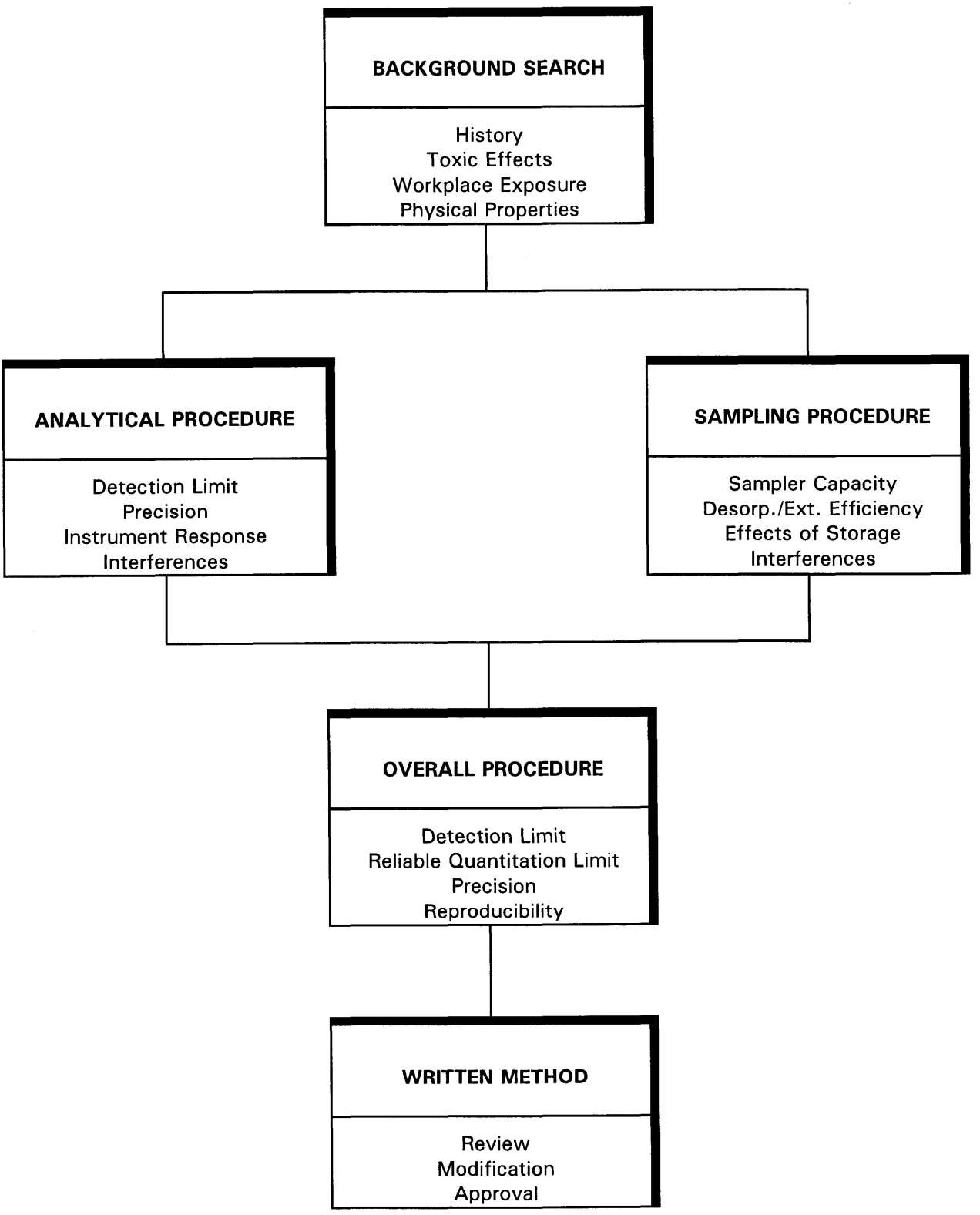

Figure 1. Evaluation scheme for OSHA organic methods.

EVALUATION GUIDELINES

I. Background Search

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

   Related sampling and analytical advances
   Toxic effects
   Workplace exposure (what industries and how many people involved)
   Physical properties and other descriptive information (see list on page 15)

2. Determine the analyte concentration at which the evaluation will be performed. This value, which shall be known as the target concentration, may be an OSHA PEL, an ACGIH TLV, or some other concentration for which there is a basis for selection.

3. Determine the most promising sampling and analytical technique with which to begin the evaluation.

II. Analytical Procedure

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 (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{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 or samples whose responses are in the vicinity of the background response. 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 Reference 1 for alternate calculations.) Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

$\mathbf{Y_{obs}}$ = observed response
$\mathbf{Y_{est}}$ = estimated response from regression curve
$\mathbf{n}$ = total no. of data points
$\mathbf{k}$ = 2 for a linear regression curve

At point Y_{DL} on the regression curve

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

$\mathbf{A}$ = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

1. The following procedure shall be used to assure that the concentrations of analytical standards used to determine the regression curve will produce responses in the vicinity of the blank signal:

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

   b. Prepare ten standards, in equally spaced decreasing increments, 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 SEE for the data.

4. Calculate the DLAP with the above equation for DL. The DLAP shall be reported in the written method as mass of analyte injected onto the head of the column.

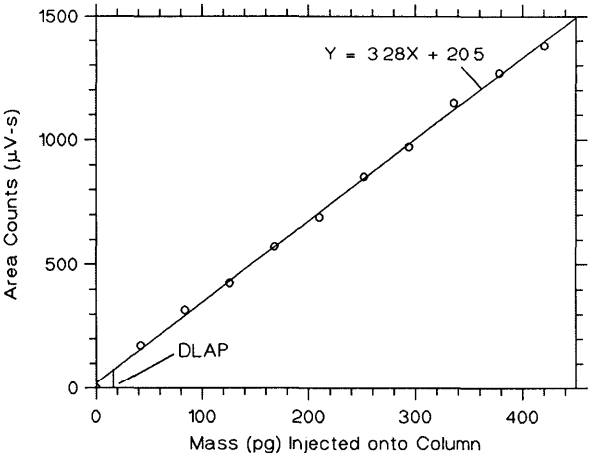

Figure 2. Example of plotted DLAP data.

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

Precision of the Analytical Procedure

1. The precision of the analytical procedure shall be measured as 1.96 (95% confidence) times the pooled relative standard deviation (pooled coefficient of variation). It shall be determined from the replicate analysis of analytical standards.

2. Determine relative standard deviations (RSDs) at concentrations representing 0.5, 0.75, 1, 1.5, and 2 times the target concentration based on the recommended air volume. Use six replicate injections at each concentration.

3. Test the five RSDs for homogeneity. The Cochran test (Ref. 2) can be applied by using the following formula to determine the *g* statistic:

$$g = \frac{\text{largest } RSD^2}{RSD_{0.5}^2 + RSD_{0.75}^2 + RSD_1^2 + RSD_{1.5}^2 + RSD_2^2}$$

4. If the *g* statistic does not exceed the critical value of 0.5065 (The critical value at the 95% confidence level for five variances, each based on six observations.), the RSDs can be considered, with 95% confidence, to be equal, and can be pooled to obtain an estimated RSD for the concentration range of 0.5 to 2 times the target concentration.

5. Calculate the pooled RSD using the following formula:

$$RSD_p = \sqrt{\frac{\sum_{i=1}^{5} f_i (RSD_i)^2}{\sum_{i=1}^{5} f_i}}$$

RSD_p = pooled relative standard deviation
i = index for the 5 concentration levels
RSD_i = relative standard deviation of the observations (injections) at the *i* th level
f_i = degrees of freedom, which is equal to the number of observations (injections) minus 1, at the *i* th concentration level

6. The following calculations, using the data tabulated below, show how to apply the above formulae:

× target concn	0.5 ×	0.75 ×	1 ×	1.5 ×	2 ×
(μg/sample)	72.7	109.1	145.4	218.1	290.7
area counts	25033	33561	44415	67123	80845
(μV-s)	24988	33689	44831	67524	81054
	24738	33235	44974	66790	80987
	24741	33701	44783	67490	80616
	24854	33206	44593	66901	80534
	24431	33181	44895	67450	79934
$\overline{X}$	24798	33429	44749	67213	80662
SD	217.3	248.2	207.7	320.6	410.1
RSD (%)	0.876	0.742	0.464	0.477	0.508

$$g = \frac{0.876^2}{0.876^2 + 0.742^2 + 0.464^2 + 0.477^2 + 0.508^2} = 0.3798$$

The critical value of the *g* statistic, at the 95% confidence level, for five variances, each associated with six observations is 0.5065. Because the *g* statistic does not exceed this value, the RSDs can be considered equal and they can be pooled (RSD_p) to give an estimated RSD for the concentration range studied.

$$RSD_p = \sqrt{\frac{5[(0.876)^2+(0.742)^2+(0.464)^2+(0.477)^2+(0.508)^2]}{5+5+5+5+5}} = 0.64\%$$

These calculations can be performed with area counts or concentration units. The type of calibration (external or internal standard) used in the analytical procedure will determine which option is preferable.

7. If the critical value for the *g* statistic is exceeded, the analytical procedure is unacceptable.

Instrument Response to the Analyte

1. The data collected for the determination of the precision of the analytical procedure shall be used to construct the calibration curve for the written report, as shown in Figure 3.

2. Generate a chromatogram of the analyte at the target concentration for use in the written report. (see page 19)

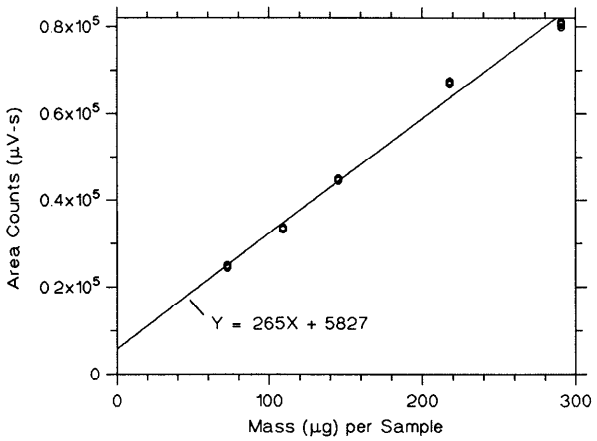

Figure 3. Example of a calibration curve.

Interferences to the Analytical Procedure

1. Interferences to the analytical method manifest themselves by making quantitation of the analyte difficult or impossible.

2. The effects of suspected interferences shall be determined by analyzing spiked analytical standards. Serious interferences to the analytical method shall be avoided.

Qualitative Analysis

1. The qualitative identification of an analyte (or its derivative) should be investigated to the extent that the requirements of Section 4.11 on page 27 can be satisfied.

III. Sampling Procedure

The evaluation guidelines address the evaluation of samplers containing adsorbent media or filters and therefore 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 passive samplers, or the evaluation of bubbler sampling procedures. Bubblers shall be considered only as a sampling technique of last resort.

Sampler Capacity

1. The sampler capacity is the basis for the recommended sample air volume and shall be defined by the length of time a sampler (front section only) can be used under a set of known test conditions without significant loss of analyte. It can also be presented as a corresponding sample air volume or as a collected analyte mass. Breakthrough tests will be used to determine the sampler capacity. Breakthrough shall be considered to have occurred when the effluent from the sampling tube 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 caused by the upstream concentration has been established. When instrumental monitoring of the downstream effluent is not possible, breakthrough can be monitored with a backup sampling tube that is changed at measured time intervals and analyzed. The analyte concentration in the effluent, at the midpoint of each time interval, can be determined from the air volume sampled in each interval.

2. Breakthrough shall be determined at ambient temperature, with a test atmosphere containing an analyte concentration equal to 2 times the target concentration. The relative humidity of the test atmosphere shall be about 80%.

3. A flow rate shall be selected that is suitable for the sampling tube.

4. Only the front portion of the adsorbent in the sampling tube shall be used in breakthrough studies.

5. Breakthrough tests shall be repeated to assure reproducibility.

6. Prepare a plot of breakthrough data for the written report as shown in Figure 4.

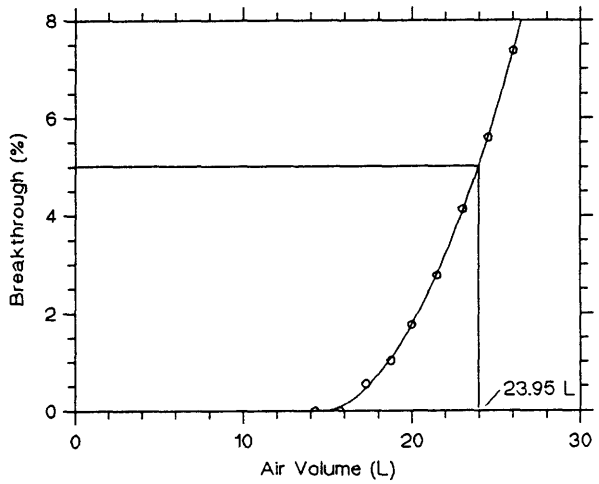

Figure 4. Example of breakthrough data.

7. The recommended sample air volume should be at least 20% less than the breakthrough volume at 2 times the target concentration.

8. For those substances that have a peak, ceiling, or short-term exposure limit, the limitations of taking a short-term sample (15 min, or shorter if feasible) at the recommended sampling rate should be determined. If a short-term sample at the recommended sampling rate is unfeasible, the use of a higher flow rate, should be studied through additional breakthrough studies.

9. When generated test atmospheres cannot be used for breakthrough determinations, other techniques which provide data that partially or indirectly describe sampler capacity shall be used to provide a convincing argument for a recommended sample air volume and flow rate. These techniques may include retention efficiencies and literature data for particle size collection efficiencies. These other techniques may require comparing amounts of analyte on front and backup samplers instead of air concentrations upstream and downstream from the sampling tube.

Retention Efficiency (RE)

1. Retention efficiency is the percentage of analyte retained on a spiked sampler after a predetermined volume of appropriately conditioned air is drawn through it. For sampling tubes, the sampler shall be spiked 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 a 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 must 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 for a samplers capacity by showing that analyte present in the sampler can be retained when the recommended sampling conditions are used.

2. Six samplers shall be liquid spiked with an amount of analyte equivalent to the 2 times the target concentration based on a tentative recommended air volume.

3. A recommended flow rate will be selected that is suitable for the samplers and the recommended air volume drawn through each of them.

4. The air drawn through the samplers should have a relative humidity of approximately 80%.

5. The RE is determined by analyzing (including desorption or extraction efficiency corrections) the spiked samplers after the recommended volume of air has been drawn through it. During the test, the downstream effluent may be monitored as it would be in a breakthrough test.

6. Filters and support pads (if used) are extracted separately and the extractant of each is analyzed to determine the percent retention. If support pads are used, 6 filters will be spiked as in Step 1 and placed in separate sealed cassettes, with backup pads, for 1 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.

Desorption Efficiency (DE) (adsorbent tubes)

1. The DE is the percent of analyte that can be recovered from an adsorbent sampler and shall be determined at 0.05, 0.1, 0.2, 0.5, 1, and 2 times the target concentration, based on the recommended air volume. The average of determinations made at 0.5, 1, and 2 times the target concentration shall define the working range DE. The determinations at 0.05, 0.1 and 0.2 times the target concentration describe the DE at lower sample loadings. Sometimes the DE does not remain constant at lower sample loadings and special precautions may be required for accurate DE corrections. Always try to maintain a constant DE over the widest range of sample loadings possible through the judicious selection of sampling materials and desorption solvents.

2. Six liquid-spiked portions of sampling medium containing the amount of adsorbent that will be used in the sampling procedure (front section of an adsorbent tube) shall be prepared at each concentration.

3. The spiked samples shall be stored at room temperature for a sufficient amount of time to assure complete adsorption of the analyte onto the surface of the adsorbent. Although the amount of time required may vary with each particular analyte, one day shall be the standard amount of time used unless a shorter time period can be justified.

4. The spiked sampling tubes shall be desorbed. After an appropriate amount of time for equilibrium to occur, the samples shall be analyzed. Three of the samples containing the target concentration amount of analyte shall be resealed immediately after analysis for use in the test described in Step 7. The analytical standards shall be prepared with the same microliter syringe used in spiking the desorption tubes.

5. The DE shall be calculated as follows:

$$DE = \frac{\text{Amount of Analyte Recovered}}{\text{Amount of Analyte Placed on Adsorbent}} \times 100\%$$

6. An average DE of 75% or lower in the range of 0.5 to 2 times the target concentration shall be avoided.

7. The stability of desorbed samples will be determined by reanalyzing the six target concentration desorption samples one day after the DE was determined. Three of the six vials containing these samples shall have been resealed with new septa after the initial analysis; the remainder shall retain their punctured septa. Freshly prepared standards must be used in the reanalysis. The results obtained from the resealed samples will determine if restrictions must be placed on how soon after desorption 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. Desorbed samples shall be considered stable if the difference between the average DE one day after desorption and the average DE from the initial determinations is not greater than 10%.

8. If storage instability is detected in Step 7, a time study may be necessary in which desorbed samples are reanalyzed at sufficiently short time intervals. These data will be used to determine how long after desorption (or analysis) a valid analysis (or reanalysis) can be performed. The criteria for sample stability shall be the same at that used in Step 7.

Extraction Efficiency (EE) (filters)

1. The EE is the percent of analyte that can be recovered from a spiked filter sampler, and shall be determined at sample loadings that represent air concentrations of 0.05, 0.1, 0.2, 0.5, 1, and 2 times the target concentration, based on the recommended air volume. The average of determinations made at 0.5, 1, and 2 times the target concentration shall define the working range EE. The determinations at 0.05, 0.1 and 0.2 times the target concentration describe the EE at lower sample loadings. Sometimes the EE does not remain constant at lower sample loadings and special precautions may be required for accurate EE corrections. Always try to maintain a constant EE over the widest range of sample loadings possible though the judicious selection of sampling materials and extraction solvents.

2. Six filters shall be liquid spiked, at each level, with an amount of analyte equivalent to 0.05, 0.1, 0.2, 0.5, 1, and 2 times the target concentration based on the recommended air volume.

3. Sufficient time should be allowed for the evaporation of solvent used in the spiking solution.

4. The filters shall be extracted and the extractant analyzed to determine the amount of recovered analyte. The analytical standards shall be prepared with the same microliter syringe used in spiking the filters. Three of the samples containing the target concentration amount of analyte shall be resealed immediately after analysis for use in the test described in Step 7.

5. The EE shall be calculated as follows:

$$EE = \frac{\text{Amount of Analyte Recovered}}{\text{Amount of Analyte Placed on Filter}} \times 100\%$$

6. An average EE of 75% or lower, in the range of 0.5 to 2 times the target concentration shall be avoided.

7. The stability of extracted samples will be determined by reanalyzing the six target concentration extraction samples one day after the extraction efficiency is determined. Three of the six vials containing these samples should be resealed with new septa immediately after the initial analysis; the remainder shall retain their punctured septa. Freshly prepared standards must be used 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. Extracted samples shall be considered stable if the difference between the average EE one day after extraction and the average EE from the initial determinations is not greater than 10%.

8. If storage instability is detected in Step 7, a time study may be necessary in which extracted samples are reanalyzed at sufficiently short intervals. These data will be used to determine how long after extraction (or analysis) a valid analysis (or reanalysis) can be obtained. The criteria for sample stability shall be the same at that used in Step 7.

9. If support pads are used, their extraction efficiency should be determined by spiking them with a sample loading equivalent to 5% of the target concentration, based on the recommended air volume.

Effects of Storage

1. Thirty-six samples shall be collected from a controlled test atmosphere containing the analyte at the target concentration. The relative humidity shall be about 80%. The recommended air volume and sampling rate shall normally be used. If sample collection is extremely time consuming, the test atmosphere concentration may be increased or the sampling flow rate may be increased in order to obtain the correct analyte loading on the samplers in a more timely manner. If this approach is taken, it must be made certain that sampler capacity is not exceeded due to the altered sampling conditions.

2. Six samples shall be analyzed on the day they are collected.

3. Fifteen samples shall be stored at room temperature in the dark, and the remaining 15 samples shall be stored under refrigeration at a temperature of 0-2°C.

4. Three samples from each set shall be analyzed approximately every third day, resulting in a storage test 15 to 18 days in length.

5. Recovery will be measured from the regression curve obtained by plotting percent recovery (uncorrected for DE or EE) versus days of storage.

6. A drop in recovery of more than 10% shall be considered a significant uncorrectable bias and must be avoided. Also, the recovery (uncorrected for DE or EE) must remain above 75%, during storage. When these conditions are not met, they may be overcome by: use of an alternate sampling medium, use of reduced temperature storage requirements, or use of 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. An exhaustive attempt to achieve this goal should be made before temperature restrictions or time requirements are used. The effectiveness of ambient shipment of samples to the laboratory and then refrigerated storage until analysis can be estimated by tracking cumulative sample loss initially on the plot of the ambient storage test for the first 5 days and then transferring to the plot of the reduced temperature test for the remainder of the storage time.

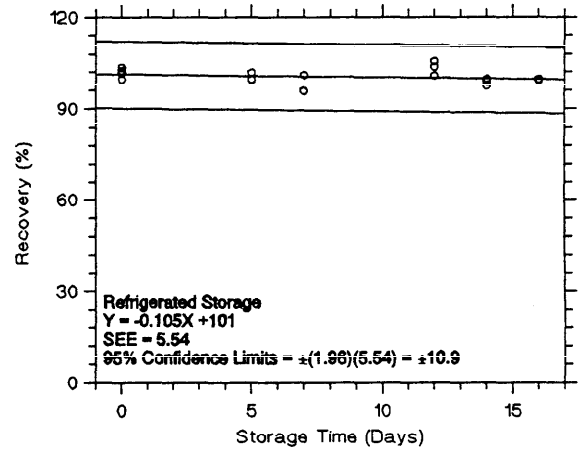

Figure 5. Example of a storage test.

7. Alternate methods of preparing storage samples must be used when safety considerations or other problems prevent the use of dynamically generated test atmospheres. The alternate methods include: the use of static test atmospheres, which can typically be prepared in gas-sampling bags; the use of vapor-spiked samples, where a known amount of analyte is allowed to volatilize directly upstream from the sampling tube, through which the recommended amount of humid air is being drawn; and the use of liquid-spiked samples, where a known amount of analyte is injected directly onto the sampling tube, and water is introduced 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. Storage test data will be plotted as shown in Figure 5. Note that this figure includes data for the overall precision, which is defined in a following section.

Interferences to the Sampling Procedure

1. Interferences to the sampling procedure may manifest themselves in such a manner that collection, retention, recovery or stability of the analyte on the sampler is impaired.

2. The effects of suspected interferences shall be determined by analyzing samples prepared as in the previous section, except with the suspected interference also added at an appropriate concentration.

IV. Overall Procedure

Detection Limit of the Overall Procedure (DLOP)

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

2. The DLOP shall be reported 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 the written report as shown in Figure 6.

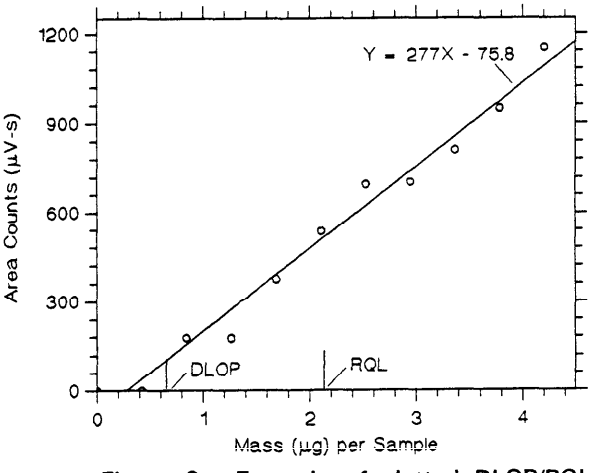

Figure 6. Example of plotted DLOP/RQL data.

Reliable Quantitation Limit (RQL)

1. The RQL shall be considered as the lower limit for precise quantitative measurements. Employing the regression line data used to calculate the DLOP, the RQL shall be determined with the following formula, providing at least 75% of the analyte is recovered.

$$RQL = \frac{10(SEE)}{A}$$

If the recovery of analyte is less than 75% at the concentration obtained with the above formula, then the RQL shall be the concentration at which at least 75% of the analyte is recovered. This can be determined from a plot of spiked samples that bracket 75% recovery, as shown in Figure 7, which shall be included in the written report.

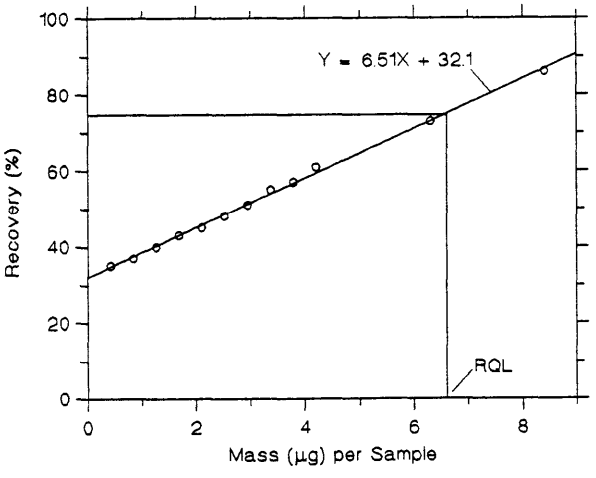

Figure 7. Example of a calculated RQL when recovery is the determining factor.

2. The RQL shall be reported 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 use in the written report.

Determination of the Precision of the Overall Procedure

1. Data from Effects of Storage Section shall be used in the determination of the overall precision.

2. Determine the standard error of estimate for the regression curve (SEE_R) (Refs. 3 and 4) of each storage test with the following formula.

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{est} = estimated recovery taken from the regression curve
Y_{obs} = observed recovery, the experimental data
n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression

3. Determine the total standard error of the overall procedure for each storage test (SEE) by including the sampling pump variability (SP) with the following formula. An arbitrary value of 5% shall be used for SP.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

4. Assuming a normal distribution of values about the regression curve and uniformity of variation about the entire range of the curve, ±1.96 SEE will represent the 95% confidence limits. The value of 1.96 SEE shall be the precision for the overall procedure.

5. The overall precision data, shall be presented graphically in the written report as shown in Figure 5, page 10, and the value (SEE) derived from the data that reflects the recommended temperature for sample shipment shall be used to describe the method.

6. The precision of the overall procedure must be 25% or better.

Reproducibility

1. Six samples prepared in the same manner as the storage samples, along with a draft copy of the analytical procedure, shall be given to a chemist unassociated with the evaluation. Relying on the draft copy for instruction, the chemist shall proceed to 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.

2. No individual analytical result should deviate from the theoretical value by more than 1.96 SEE. If this does occur, steps must be taken to determine and eliminate the cause of the excessive imprecision, be it 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.

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.

Each type of report will be prepared in accordance with the following respective formats:

I. Evaluated Methods

The following format provides a means of reporting data obtained during evaluation of organic 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 adsorbent tubes, therefore it should be modified accordingly when other sampling devices are considered.

All evaluated methods completed by the Organic Methods Evaluation Branch will have the following statement on the cover page:

"Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch."

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 07 would be "07-1".

Editorial comments are set off with braces "{ }".

(NAME OF ANALYTE)

Method number:	___
Matrix:	Air {or other, such as Bulk Material}
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 a known volume of air through ___. Samples are desorbed (or extracted) with ___ and analyzed by ___ using a ___ detector.
Recommended air volume and sampling rate:	___ L at ___ L/min
Reliable quantitation limit:	___ ppm (___ mg/m^3)
Standard error of estimate at the target concentration:	___%
Special requirements:	{If none, delete this item}
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: _____ {month year}

Chemist: _____

Organic Methods Evaluation Branch
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

{The backup data section will be referenced throughout the method in the following manner: "(Section 4._)". Literature references throughout the method will be denoted in the following manner: "(Ref. 5._)".}

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 other descriptive information (Ref. 5._ unless otherwise indicated)

CAS number:	___	vapor pressure:{kPa (mmHg)}	___
molecular weight:	___	flash point:	___
boiling point:	___	odor:	___
melting point	___	lower explosive limit:	___
color:	___	synonyms:	___
specific gravity:	___	structural formula:	___
molecular formula:	___		

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 response that is significantly different from the background response of a reagent blank. (Sections 4.1 and 4.2) {If the definition for the analytical detection limit for a particular analyte must be altered, the altered definition should appear in this section and the detailed explanation should appear in Section 4.2.}

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is ___ {mass} per sample (___ ppm or ___ mg/m^3). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is ___ {mass} per sample (___ ppm or ___ mg/m^3). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precision of the analytical procedure, measured as the pooled relative standard deviation over a concentration range equivalent to the range of 0.5 to 2 times the target concentration, is ___%. (Section 4.5)

1.2.5 Precision (overall procedure)

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) is ± ___ %. This includes an additional 5% for sampling error. (Section 4.6) {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 name} from samples used in a 15-day storage test remained above ___ % {the lowest point on the regression curve of Figure 4.7._} when the samples were stored at ___°C. (or if the case requires: The recovery of {analyte name} from samples used in a 15-day storage test remained above 75% for the first ___ days when samples were stored at ___°C.) (Section 4.7)

1.2.7 Reproducibility

Six samples collected from a controlled test atmosphere {or: spiked by liquid injection, etc.}, with a draft copy of this procedure, were submitted for analysis by one of the OSHA Salt Lake Technical Center's service branch laboratories. The samples were analyzed 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 4.8)

2. Sampling Procedure

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

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

2.1.2 Samples are collected with 7-cm × 4-mm i.d. × 6-mm o.d. glass sampling tubes packed with two sections of *adsorbent ABC*. The front section contains 110 mg and the back section contains 55 mg of *adsorbent ABC*. The sections are held in

place with glass wool plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-73).

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.}
Example:

2.3.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.3.2 Attach the sampling tube to the sampling pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air first passes through the 110-mg section.

2.3.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.3.4 Attach the sampler vertically with the 110-mg section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.3.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.6 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.

2.3.7 Record sample air volumes (in liters) for each sample, along with any potential interferences.

2.3.8 Ship any bulk samples separate from the air samples.

2.3.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at reduced temperature.

2.4 Sampler capacity {Describe test, conditions and results.}
Example:
The sampling capacity of the front section of an *adsorbent ABC* sampling tube was tested by sampling from a dynamically generated test atmosphere of *analyte XYZ* (70.5 mg/m^3 or 20.0 ppm). The samples were collected at 0.05 L/min and the relative humidity was 80% at 25°C. The 5% breakthrough air volume was determined to be 23.95 L. (Section 4.9)

2.5 Desorption efficiency {Extraction efficiency reported similarly.}

2.5.1 The average desorption efficiency for {analyte name} from {the sampling medium} over the range of 0.5 to 2.0 times the target concentration was ___%. (Section 4.10.1)

2.5.2 The desorption efficiency at 0.2, 0.1, and 0.05 times the target concentration was found to be ___%, ___%, and ___% respectively. (Section 4.10.1) {If these values differ significantly from the working range average, recommend steps to be taken for accurate corrections at these lower levels.}

2.5.3 Desorbed {or extracted} samples remain stable for at least __ h {or days}. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1 For long-term samples collect ____ L {recommended air volume} at ____ L/min {recommended sampling rate}.

2.6.2 For short-term {usually a 15-min sample} samples collect ___ L {recommended air volume} at ___ L/min {recommended sampling rate}.

2.6.3 When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is ____ ppm (____ mg/m^3) for {analyte name} when {recommended air volume of Section 2.6.2} is collected.

2.7 Interferences (sampling)
Example:

2.7.1 It is not known if any compounds will severely interfere with the collection of *analyte XYZ* on *adsorbent ABC*. In general, the presence of other contaminant vapors in the air will reduce the capacity of *adsorbent ABC* to collect *analyte XYZ*.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling) {emphasize any unique safety considerations}
Example:

2.8.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 All safety practices that apply to the work area being sampled should be followed.

2.8.3 Protective eyewear should be worn when breaking the ends of the glass sampling tubes.

3. Analytical Procedure

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 with an FID. A Hewlett-Packard Model 5890 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, reagent grade or better. The methylene chloride used in this evaluation was b&j brand HIGH PURITY SOLVENT, purchased from American Burdick & Jackson (Muskegon, MI).

3.2.2 Carbon disulfide (CS_2), reagent grade or better. The carbon disulfide used in this evaluation was 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 XYZ* in CS_2. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1 mL of desorbing solution delivered from the same dispenser used to desorb samples. For example, to prepare a target level standard, inject 10 µL of a stock solution containing 42 mg/mL of *analyte XYZ* in CS_2 into 1 mL of desorbing solution.

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

3.4.1 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.

3.4.2 Add 1.0 mL of desorbing solution to each vial and immediately seal the vials with polytetrafluoroethylene-lined caps.

3.4.3 Shake the vials vigorously several times during the next 30 min.

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 temperatures:	60°C (column)
zone temperatures:	250°C (injector) 300°C (detector)
run time:	10 min
column gas flow:	1.2 mL/min (hydrogen)
septum purge:	1.5 mL/min (hydrogen)
injection size:	1.0 µL (12.5:1 split)
column:	60-m × 0.32-mm i.d. capillary SPB-5 (1.0-µm film thickness)
retention times:	5.4 min (*compound XYZ*) 5.9 min (*compound UVW*) 6.5 min (*compound RST*) 8.2 min (n-decane)

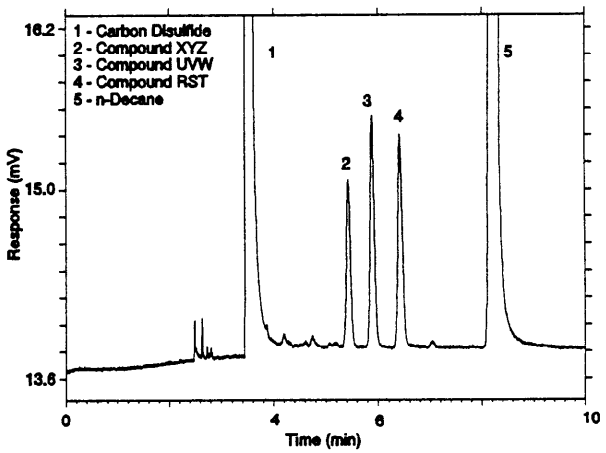

Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended conditions.

<u>FID conditions</u>

hydrogen flow:	34 mL/min
air flow:	450 mL/min
nitrogen makeup flow:	33 mL/min

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

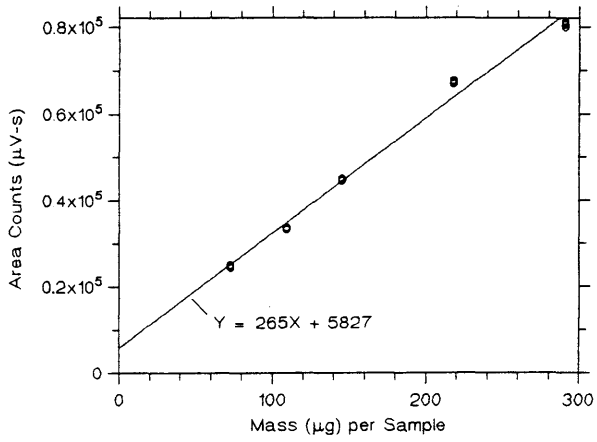

Figure 3.5.2. Calibration curve of *analyte XYZ* made from the data of Table 4.5.

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 desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data (Section 4.11).

3.7 Calculations {Use 24.46 [(22.41)(298.2)/273.2] for the molar volume.}
Example:
The amount of *analyte XYZ* per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample uncorrected for desorption efficiency. The back (55-mg) 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 formulae.

$$\text{mg/m}^3 = \frac{\text{micrograms of analyte per sample}}{\text{liters of air sampled} \times \text{desorption efficiency}}$$

$$\text{ppm} = \frac{24.46 \times \text{mg/m}^3}{\text{molecular weight of analyte}}$$

3.8 Safety precautions (analytical) {emphasize any unique safety considerations}
Example:

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan (which is mandated by the OSHA laboratory standard).

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

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

4.1 Determination of detection limits

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 (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{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 or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DL} on the regression curve

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

A = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

4.2 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 actually introduced into the chromatographic column. Ten analytical standards were prepared in equal descending increments with the highest standard containing 4.206 μg/mL. This is the concentration that would produce a peak approximately 10 times the background 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-μL injection with a 10:1 split), and the data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP. Values of 3.28 and 17.83 were obtained for A and SEE respectively. DLAP was calculated to be 16.3 pg.

Table 4.2
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
1.262	126.2	425
1.682	168.2	573
2.103	210.3	690
2.524	252.4	853
2.944	294.4	973
3.365	336.5	1149
3.785	378.5	1270
4.206	420.6	1380

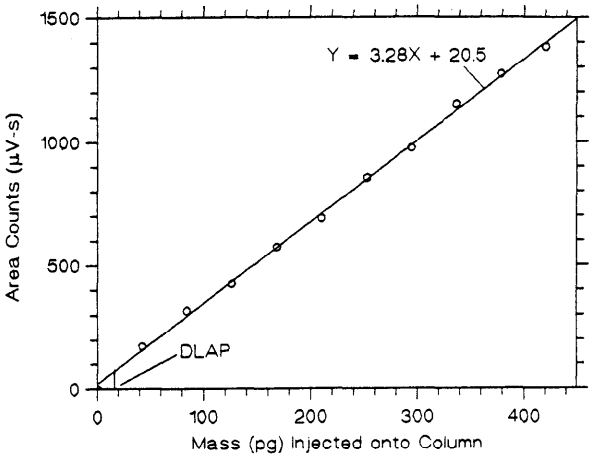

Figure 4.2. Plot of data to determine the DLAP.

4.3 Detection limit of the overall procedure (DLOP) {Present the test data in a table and a graph.}

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 4.206 μg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the background 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 (A and SEE) for the calculation of the DLOP. Values of 277 and 59.14 were obtained for A and SEE respectively. DLOP was calculated to be 0.641 μg/sample (5 ppm, 3 mg/m^3).

Table 4.3
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

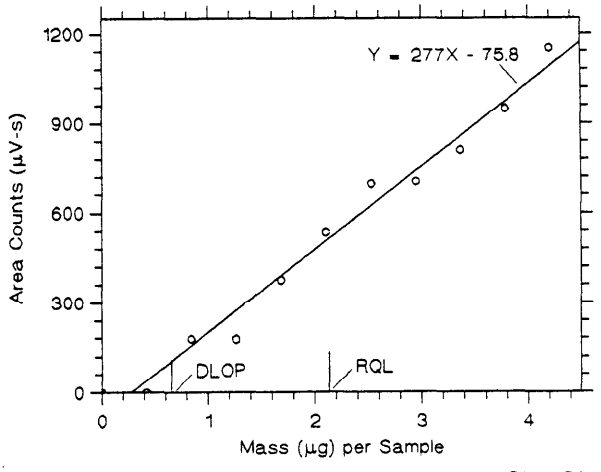

Figure 4.3. Plot of data to determine the DLOP/RQL.

4.4 Reliable quantitation limit (RQL) {Present chromatogram and specified data when required.}

Example:

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 (Section 4.3), providing at least 75% of the analyte is recovered. The RQL is defined as the amount of

analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

Otherwise, the RQL is the lowest loading at which 75% of the analyte can be recovered as determined from the regression line of the plotted data. {If this applies, show the determination as in the following figure:}

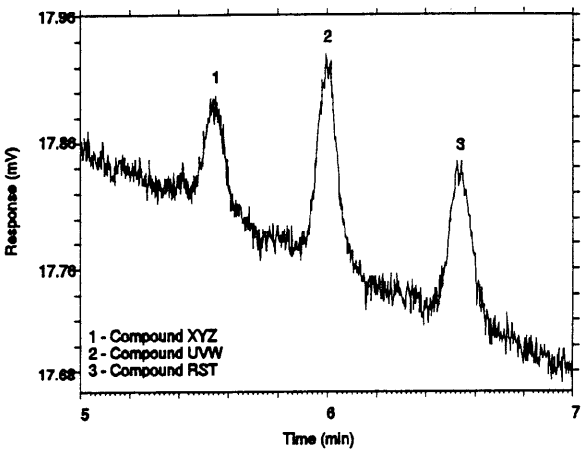

Figure 4.4.1. Chromatogram of the RQL.

RQL = ___ µg per sample (___ ppm, ___ µg/m³) Recovery at this concentration is 90%.

{or}

RQL = ___ µg per sample (___ ppm, ___ µg/m³)
This value is based on the 75% recovery requirement.

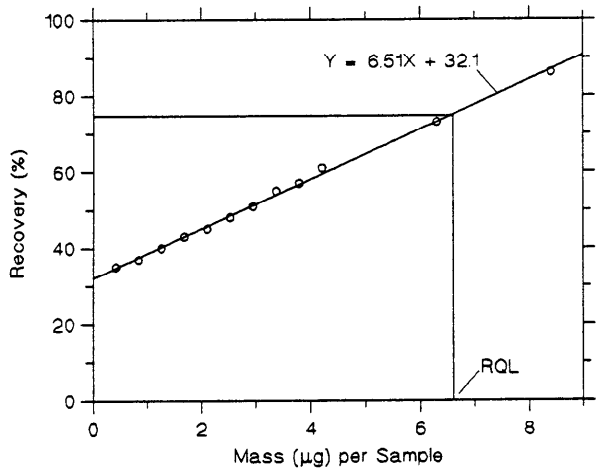

Figure 4.4.2. Plot of data to determine the RQL.

Table 4.4
Reliable Quantitation Limit

mass per sample (µg)	mass recovered (µg)	recovery (%)
0.421	0.147	35
0.841	0.311	37
1.262	0.505	40
1.682	0.723	43
2.103	0.946	45
2.524	1.212	48
2.944	1.501	51
3.365	1.851	55
3.785	2.157	57
4.206	2.566	61
6.306	4.603	73
8.409	7.232	86

4.5 Precision (analytical method)

Example:

The precision of the analytical procedure is measured the pooled relative standard deviation (RSD_p). Relative standard deviations are determined from six replicate injections of *analyte XYZ* standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, RSD_p was calculated to be 0.64% for *analyte XYZ*.

Table 4.5
Instrument Response to *Analyte XYZ*

× target concn (μg/mL)	0.5 × 72.7	0.75 × 109.1	1 × 145.4	1.5 × 218.1	2 × 290.7
area counts (μV-s)	25033	33561	44415	67123	80845
	24988	33689	44831	67524	81054
	24738	33235	44974	66790	80987
	24741	33701	44783	67490	80616
	24854	33206	44593	66901	80534
	24431	33181	44895	67450	79934
$\bar{X}$	24797.4	33429	44749	67213	80662
SD	217.3	248.2	207.7	320.6	410.1
RSD (%)	0.876	0.742	0.464	0.477	0.508

The Cochran test for homogeneity:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5\times}^2 + RSD_{0.75\times}^2 + RSD_{1\times}^2 + RSD_{1.5\times}^2 + RSD_{2\times}^2} = 0.3798$$

The critical value of the *g* statistic, at the 95% confidence level, for five variances, each associated with six observations is 0.5065. Because the *g* statistic does not exceed this value, the RSDs can be considered equal and they can be pooled (RSD_p) to give an estimated RSD for the concentration range studied.

$$RSD_p = \sqrt{\frac{5(RSD_{0.5\times}^2+RSD_{0.75\times}^2+RSD_{1\times}^2+RSD_{1.5\times}^2+RSD_{2\times}^2)}{5+5+5+5+5}} = 0.64\%$$

4.6 Precision (overall procedure) {The following text should be used without modification, and the appropriate values for precision and figure number filled in.}

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE_R is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1 and 4.7.2. The precision of the overall procedure of ±__.__% was obtained from Figure ___. {The SEE listed on the cover page of the method must be based on the storage data that reflects the temperature recommended for shipment of samples.}

4.7 Storage test {Describe the storage test, including preparation of samples.}
Example:
Storage samples for *analyte XYZ* were prepared by drawing samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of analyte was at the target concentration and the test atmosphere relative humidity was 80% at 22°C. Thirty-six storage samples were prepared. One-half of the tubes was stored at reduced temperature (2°C) and the other half was stored in a closed drawer at ambient temperature (about 22°C). At 2-5 day intervals {preferably three day intervals}, three samples were selected from each of the two storage sets and analyzed.

Table 4.7
Storage Test for *Analyte XYZ*

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	103.5	101.6	101.9	103.5	101.6	101.9
	99.5	102.4	101.8	99.5	102.4	101.8
5	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
12	100.8	98.8	100.2	100.6	103.6	105.5
14	95.6	96.6	99.1	98.9	99.6	97.5
16	96.5	94.5	98.8	99.3	99.5	99.1

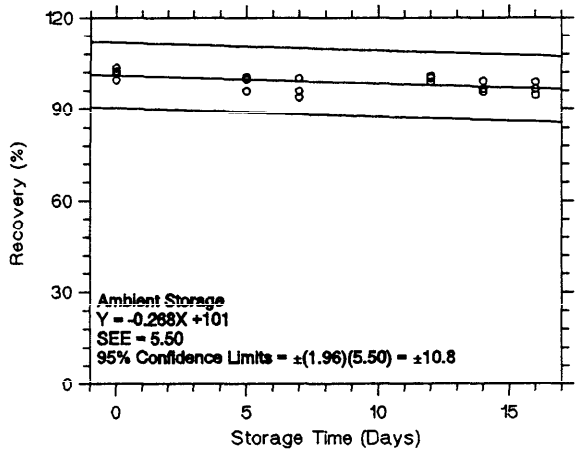

Figure 4.7.1. Ambient storage test for *analyte XYZ*.

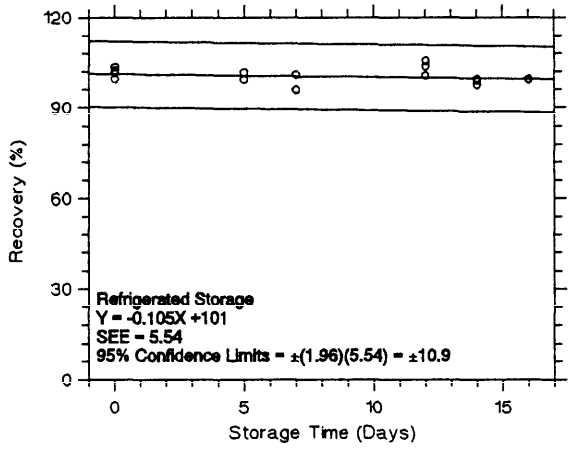

Figure 4.7.2. Refrigerated storage test for *analyte XYZ*.

4.8 Reproducibility {Describe reproducibility test and present data in Table 4.8. Specify that the "amount found" is corrected for desorption efficiency.}
Example:
Six samples were prepared 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 a OSHA Salt Lake Technical Center service branch for analysis. The samples were

analyzed after being stored for 11 days at 2°C. Sample results were corrected for desorption efficiency. No sample result for *analyte XYZ* had a deviation greater than the precision of the overall procedure determined in Section 4.6, which is ±10.8%.

Table 4.8
Reproducibility
Data for *Analyte XYZ*

spiked (μg/sample)	recovered (μg/sample)	recovered (%)	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

4.9 Sampler capacity {Describe breakthrough or other studies used and present data in Table 4.9 and Figure 4.9.}
Example:
The sampling capacity of the front section of an *adsorbent ABC* sampling tube was tested by sampling from a dynamically generated test atmosphere of *analyte XYZ* (70.5 mg/m³ or 20.0 ppm). The samples were collected at 0.05 L/min and the relative humidity was 80% at 23°C. A complete *adsorbent ABC* sampling tube was placed in-line behind the front test section and changed at measured intervals. The 5% breakthrough air volume was determined to be 23.95 L.

Table 4.9
Breakthrough of *Analyte XYZ*
with *Adsorbent ABC* Sampling Tubes

air volume (L)	sampling time (min)	downstream concentration (mg/m³)	breakthrough (%)
14.25	285	0.00	0.0
15.75	315	0.00	0.0
17.25	345	0.38	0.54
18.75	375	0.72	1.02
20.00	400	1.24	1.76
21.50	430	1.96	2.78
23.00	460	2.91	4.13
24.50	490	3.94	5.59
26.00	520	5.20	7.37

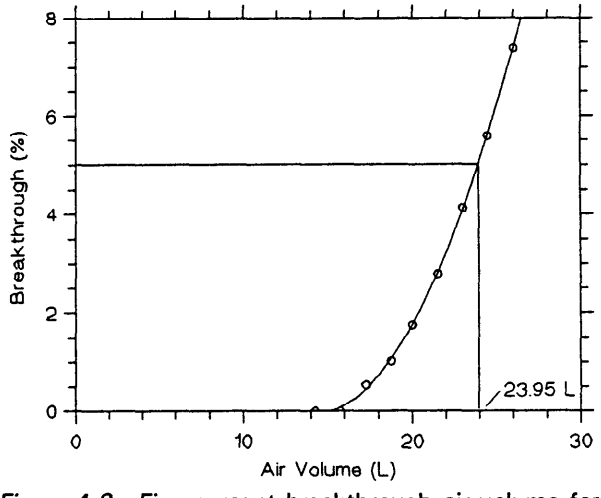

Figure 4.9. Five percent breakthrough air volume for *analyte XYZ*.

4.10 Desorption efficiency and stability of desorbed samples {or extraction efficiency}
{Describe desorption efficiency test and present data in Table 4.10.1}
Example:
4.10.1 Desorption efficiency

The desorption efficiencies (DE) of *analyte XYZ* were determined by liquid-spiking 110-mg portions of *adsorbent ABC* with the analyte at 0.05 to 2 times the target concentration. These samples were stored overnight at ambient temperature and

then desorbed and analyzed. The average desorption efficiency over the working range of 0.5 to 2 times the target concentration was 99.7%.

Table 4.10.1
Desorption Efficiency of *Analyte XYZ*

× target concn (μg/sample)	0.05× 21.03	0.1× 42.06	0.2× 84.12	0.5× 210.3	1.0× 420.6	2.0× 841.3
DE (%)	103.5	101.6	101.9	99.3	97.3	102.8
	99.5	102.4	101.8	105.8	95.8	103.7
	99.6	100.5	95.8	105.0	92.8	101.1
	100.0	95.8	100.2	100.4	97.7	100.4
	100.8	98.8	99.1	94.2	97.7	99.5
	95.6	96.6	98.8	105.7	99.5	96.4
$\bar{X}$	99.8	99.3	99.6	101.7	96.8	100.6

4.10.2 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed three vials were recapped with new septa while the remaining three retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was −5.4% for samples that were resealed with new septa, and −8.3% for those that retained their punctured septa.

Table 4.10.2
Stability of Desorbed Samples for *Analyte XYZ*

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
92.8	89.1	−3.5	99.5	86.8	−12.7
95.8	92.3	−3.5	97.7	88.7	−9.0
97.3	88.3	−9.0	97.7	94.6	−3.1
	(averages)			(averages)	
95.3	89.9	−5.4	98.3	90.0	−8.3

4.11 Qualitative analysis {Present alternate chromatographic and GC/MS conditions that will aid in confirming the identity or purity of the analyte (or derivative) peak. GC/MS provides 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 ratioing and analysis with alternate detectors may be useful in HPLC methods. Use the format of Section 3.5.1 to present analytical conditions with chromatograms, mass spectrograms and HPLC detector spectra. The format for mass spectrograms is shown in Figure 4.11.}

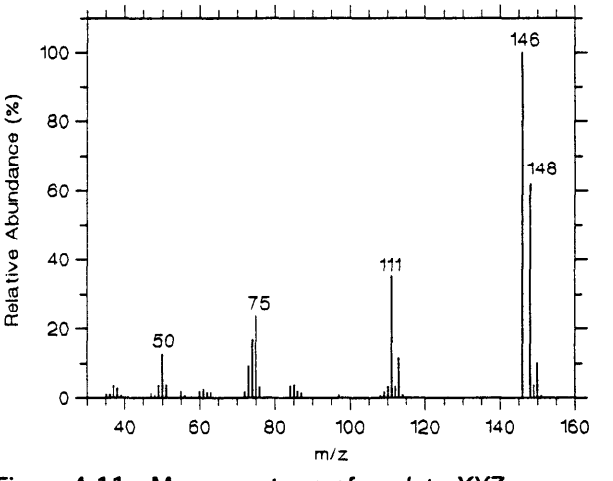

Figure 4.11. Mass spectrum of *analyte XYZ.*

5. References

{References will follow as closely as possible the format recommended by the American Chemical Society in their 1986 edition of "Handbook for Authors." The following are examples of various types of references:}

5.1 "Criteria for a Recommended Standard...Occupational Exposure to Diisocyanates"; Department of Health, Education and Welfare, National Institute for Occupation Safety and Health: Cincinnati, OH, 1978.

5.2 *Fed. Regist.* **1977**, 42 (No. 240), 62869-62869A.

5.3 *NIOSH Manual of Analytical Methods*, 2nd ed.; Department of Health, Education and Welfare, National Institute for Occupational Safety and Health: Cincinnati, OH, 1977; Vol. 1, Method no. P&CAM 141; DHEW (NIOSH) Publ. (U.S.), 77-157-A.

5.4 Walker, R.F.; Guiver, R. *Am. Ind. Hyg. Assoc. J.* **1981**, *42*, 559-565.

5.5 Billmeyer, F. W., Jr. *Textbook of Polymer Science*, 2nd ed.; Wiley-Interscience: New York, 1971; Chapter 7.

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

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

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

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

4. Desorption or extraction efficiency - 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. Recommended air volume and sampling rate - The recommended sampling information shall 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).

6. Storage test - In order to determine sample stability, a storage test shall 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. Interferences - The partial evaluation must consider if potential interferences exist and if they can be circumvented. Those that may seriously hamper the method must be checked.

8. Recommendation for further study - Recommendations must be made that should be considered before a thorough evaluation is performed.

Partially Evaluated Methods shall be reported 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 shall have the following statement of status on the cover page:

"Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

Editorial comments are set off with braces "{ }".

(NAME OF ANALYTE)

Matrix:	Air {or other, such as Bulk Material}
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 a known volume of air through a ___. Samples are desorbed (or extracted) with ___ and analyzed by ___ using a ___ detector.
Recommended air volume and sampling rate:	___ L at ___ L/min
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, and is presented for information and trial use.

Date: _____ {month year}

Chemist:_____

Organic Service Branch _
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

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 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 (Ref. 5._ unless otherwise indicated)

CAS number:	___	vapor pressure:{kPa (mmHg)}	___
molecular weight:	___	flash point:	___
boiling point:	___	odor:	___
color:	___	lower explosive limit:	___
specific gravity:	___	synonyms:	___
molecular formula:	___	structural formula:	___
melting point	___		

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 overall procedure (DLOP)

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{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 samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are

similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$ A = analytical sensitivity (slope)

therefore

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

{Present the test data in a table and a graph.}
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 4.206 μg/sample. This is the amount, when spiked on a sampler, would produce a peak approximately 10 times the background 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 (A and SEE) for the calculation of the DLOP. Values of 277 and 59.14 were obtained for A and SEE respectively. DLOP was calculated to be 0.641 μg/sample (5 ppm, 3 mg/m³).

Table 1.2.1
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

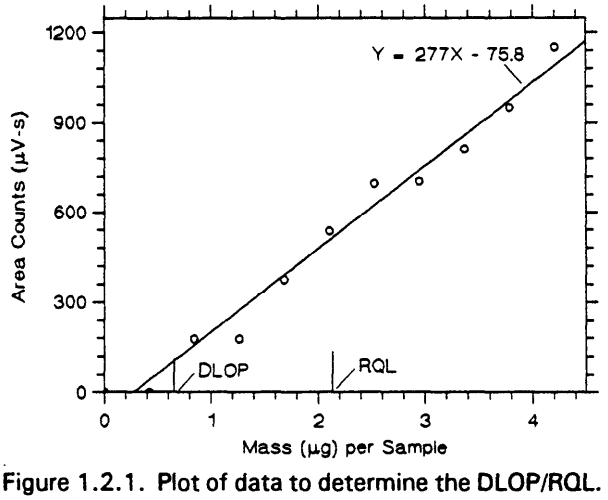

Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL) {Present specified data when required.}
Example:
The RQL is considered the lower limit for precise quantitative measurements. It is determined from in the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

{Otherwise, the RQL is the lowest loading at which 75% of the analyte can be recovered as determined from the regression line of the plotted data. {If this applies, show the determination as in Figure 1.2.2, and include the data in Table 1.2.2.}

RQL = ___ µg per sample (___ ppm, ___ µg/m^3)

Recovery at this concentration is 90%.

{or}

RQL = ___ µg per sample (___ ppm, ___ µg/m^3)

This value is based on the 75% recovery requirement.

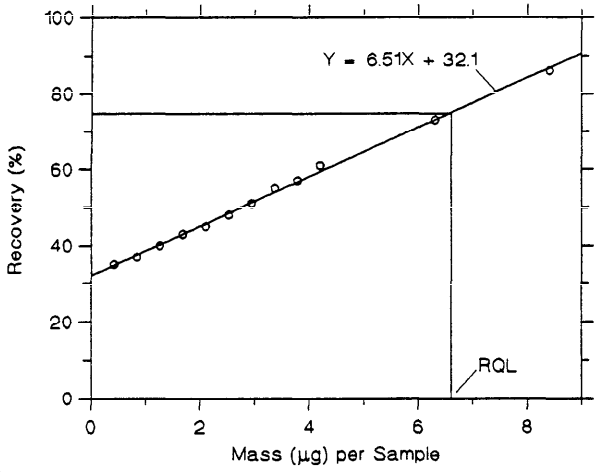

Figure 1.2.2. Plot of data to determine the RQL.

Table 1.2.2
Reliable Quantitation Limit

mass per sample (µg)	mass recovered (µg)	recovery (%)
0.421	0.147	35
0.841	0.311	37
1.262	0.505	40
1.682	0.723	43
2.103	0.946	45
2.524	1.212	48
2.944	1.501	51
3.365	1.851	55
3.785	2.157	57
4.206	2.566	61
6.306	4.603	73
8.409	7.232	86

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

2.1 Apparatus {Section 2.1, page 16}

2.2 Reagents {If no reagents are required, state "None required". Otherwise use the format described in Section 3.2, page 18.}

2.3 Technique {Section 2.3, page 17}

2.4 Extraction {or desorption} efficiency

Example:

The desorption efficiencies (DE) of *analyte XYZ* were determined by liquid-spiking 110-mg portions of *adsorbent ABC* with the analytes at 0.5 to 2 times the target concentrations. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the studied range was 99.7% for *analyte XYZ*.

Table 2.4
Desorption Efficiency of *Analyte XYZ*

× target concn (μg/sample)	0.5× 210.3	1.0× 420.6	2.0× 841.3
DE (%)	99.3	97.3	102.8
	105.8	95.8	103.7
	105.0	92.8	101.1
	100.4	97.7	100.4
	94.2	97.7	99.5
	105.7	99.5	96.4
mean	101.7	96.8	100.6

2.5 Retention efficiency

Example:

The filter of six OVS-*ABC* tubes were spiked with 1.0 mg (10 mg/m^3) *analyte XYZ*, allowed to equilibrate for 6 h, and then had 100 L humid air (89% RH at 22°C) pulled through them. The glass fiber filter was placed before the Teflon spacer to insure that no *analyte XYZ* spiked onto the filter was in contact with the *adsorbent ABC* sections before the humid air was drawn. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.3%. There was no *analyte XYZ* found on the backup portions of the tubes. The amount found on the front adsorbent portion of the OVS-*ABC* tubes indicates that *analyte XYZ* is too volatile to be collected on glass fiber filters.

Table 2.5
Retention Efficiency of *Analyte XYZ*

Tube #	filter recovery (%)	A section recovery (%)	B section recovery (%)	total recovery (%)
1	65.7	34.4	0.0	100
2	65.9	34.3	0.0	100
3	53.1	44.7	0.0	97.8
4	65.9	34.5	0.0	100
5	71.7	28.5	0.0	100
6	73.2	25.0	0.0	98.2
mean				99.3

2.6 Sample storage

Example:

The front sections of six *adsorbent ABC* sampling tubes were each spiked with 10.8 mg (205 ppm) of *analyte XYZ*. They were sealed and stored at room temperature. Three samples were analyzed after 7 days and the remaining three after 14 days. The amounts recovered, which are not corrected for desorption efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for *Analyte XYZ*

time (days)	recovery (%)	time (days)	recovery (%)
7	100	14	99.3
7	99.7	14	100
7	101	14	98.7
mean	100	mean	99.7

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 0.05 L/min.

2.8 Interferences (sampling) {Section 2.7., page 18}

2.9 Safety precautions (sampling) {Section 2.8., page 18}

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

3.1 Apparatus {Section 3.1, page 18}

3.2 Reagents {Section 3.2, page 18}

3.3 Standard preparation {Section 3.3, page 19}

3.4 Sample preparation {Section 3.4, page 19}

3.5 Analysis {Section 3.5, page 19}

3.6 Interferences (analytical) {Section 3.6, page 20}

3.7 Calculations {Section 3.7, page 20}

3.8 Safety precautions (analytical) {Section 3.8, page 20}

4. Recommendations for Further Study

5. References

5.1 {Section 5., page 28}

III. Studies - Studies shall be reported using the following format:

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

REFERENCES

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

2. Anderson, R. L. *Practical Statistics for Analytical Chemists*; Van Nostrand Reinhold: New York, 1987, p 62.

3. Snedcor, G.W.; Cochran, W.G. *Statistical Methods*, 6th ed.; The Iowa State University: Ames, Iowa, 1967; p 467.

4. Arkin, H.; Colton, R.R. *Statistical Methods*, 5th ed.; Barnes & Noble: New York, 1970, p 85.