Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis

October 2005

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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 methods that utilize spectroscopic analytical techniques. The guidelines define sampling and analytical parameters, specify required laboratory tests, statistical calculations, criteria for acceptance, and provide a detailed outline for preparation of 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 clearly be defended with evaluation data. Other tests deemed necessary for any evaluation are permissible, and a description of these tests and the resultant experimental data shall be included in the back-up data section following the format prescribed in this document. Summary results of these tests shall be presented in the main body of the method.

These guidelines are continually open to examination by the OSHA Methods Development Team 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.

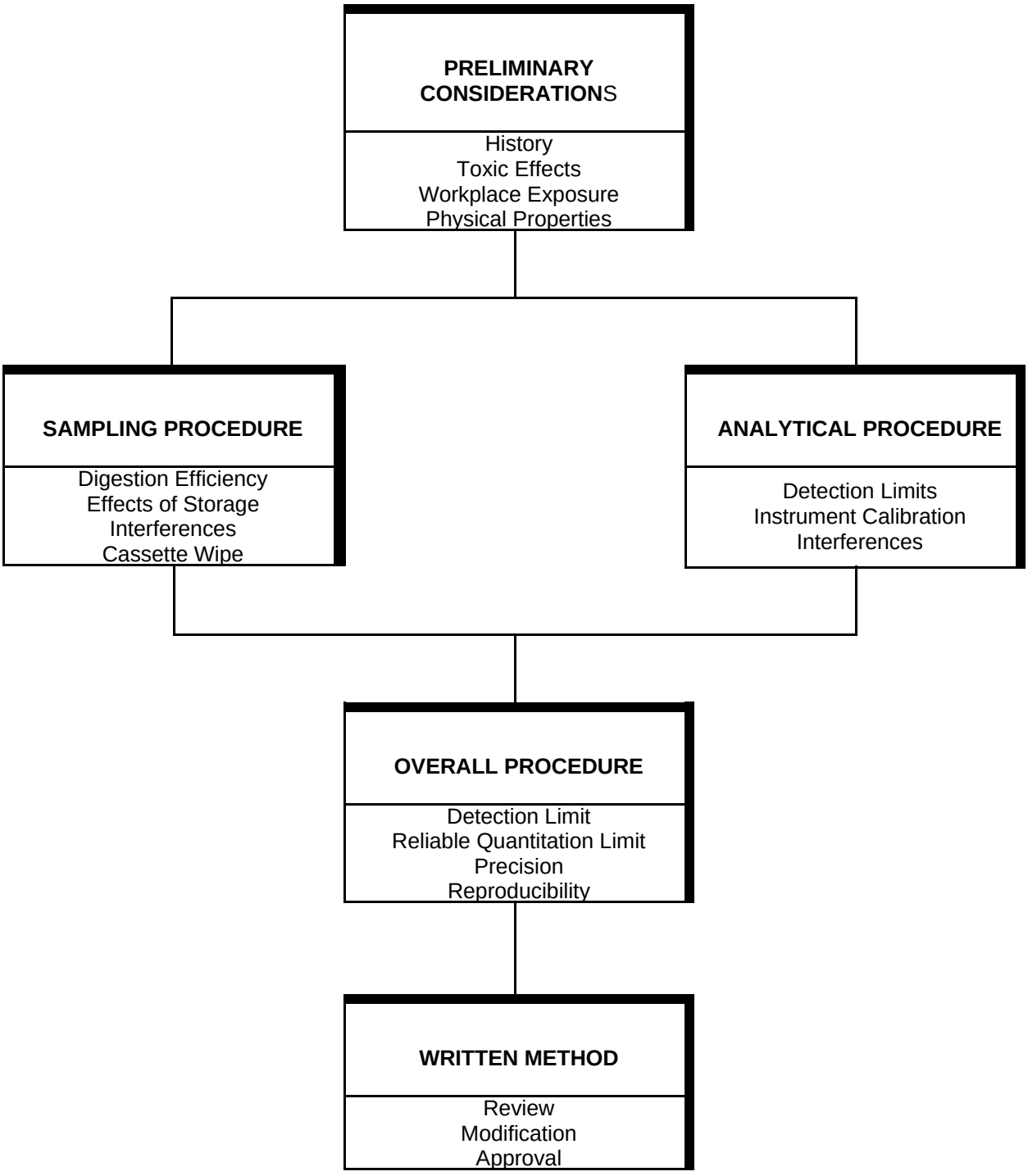

Figure 1. Evaluation scheme for OSHA spectroscopic methods.

EVALUATION GUIDELINES

I. Preliminary Considerations

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

The most common insoluble and soluble chemical forms of the substance
Sampling and analytical interferences
Existing or related sampling and analytical procedures and techniques
Toxic effects
Workplace exposure (what industries and how many people are involved)
Physical properties and other descriptive information
OSHA standards that may necessitate method validation at more than one level (General Industry, Construction, or Maritime; peak, STEL, ceiling, etc.)

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 some basis for selection.

Perform preliminary tests to determine the following parameters: sampling medium, analytical conditions, digestion acids, and internal standard (if used).

II. Analytical Procedure

These guidelines were written from the perspective of Inductively-Coupled Plasma/Mass Spectrometry or Inductively-Coupled Plasma/Opticial Emission Spectrometry analysis. Typically, 2 to 3 consecutive replicate readings are taken and averaged to obtain instrument response for a single sample. The format can be modified to accommodate analytical data from other instruments, but should be followed as closely as possible.

The substance being tested must be of known and confirmed purity whenever possible (NIST-traceable or other certified standard). Materials and reagents must be of high and acceptable quality.

The following sequence of experiments may be altered if necessary.

Instrument calibration and calculation of results is performed in a manner designed to provide the most accurate and consistent data for the evaluation parameter under study.

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.

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

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

Direct measurement of Y_{BR} and S_{BR} in spectroscopic methods is inconvenient and difficult when Y_{BR} is extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards (made with soluble salts) 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

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

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:

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

where $S_{Y•X(DLAP)}$ 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 linear regression

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
L_D is the detection limit
A is the analytical sensitivity (slope)
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

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

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 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 error of estimate from the data by plotting response versus concentration analyzed. Do not perform blank corrections.

4. Calculate the DLAP using Equation 2. Report the DLAP in the method as concentration of analyte.

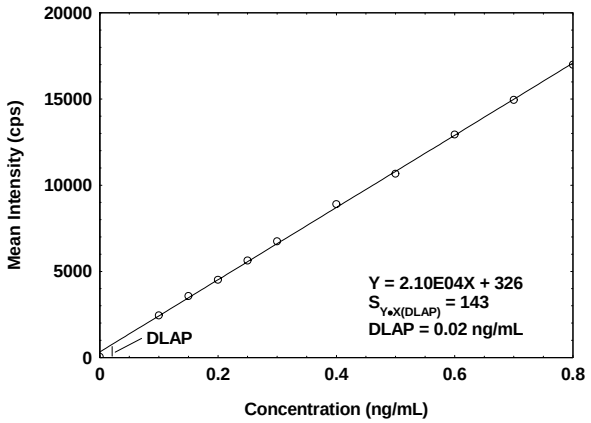

Figure 2. Example of plotted DLAP data.

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 simultaneously with this test. DLOP and RQL is determined in a similar test in which soluble standards are spiked on the sampling medium.

   Alternatively, if Y_{BR} is measurable, use the data from the analyses of 10 reagent blank samples to calculate Y_{BR} and S_{BR}. Use Equation 1 to determine Y_{DL}.

B. Instrument calibration

Calibrate the instrument over a range of 0.1 to 2 times the target concentration (TC) (0.1, 0.5, 1, 1.5, and 2×TC) representing the highest mass loading. Prepare the solutions from soluble salts. The data for the calibration is from three determinations (each determination is the average of two to three replicate readings) of five analytical standards.

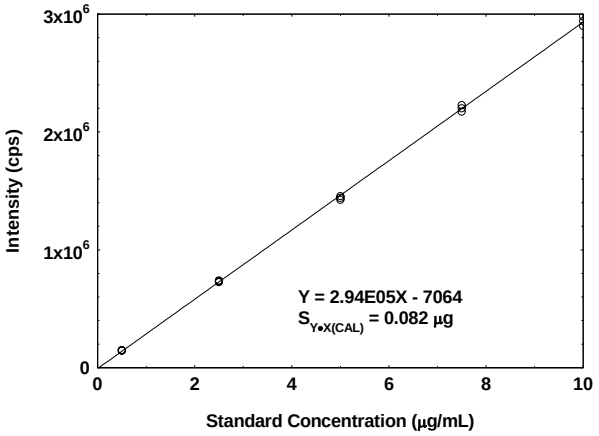

Figure 3. Example of a calibration curve.

1. Prepare one stock standard from a NIST-traceable or other certified standard (if possible). Dilute the stock to the required five (5) concentrations.

2. Report the concentration equivalent to the standard error of estimate from the linear regression of data points over a range that covers 0.1 to 2 times the target concentration with the highest mass loading. The standard error of estimate measures the variation or scatter about the line of regression.[2]

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

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

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

C. Interferences to the analytical procedure

1. Interferences to the analytical method may cause identification and quantitation of the analyte to be difficult or impossible. Such interferences may be identified in the literature search. Interferences can also be identified by looking for other elements that have spectral line overlap or mass/charge similarity. Evaluate the ability of analytical instrument software to correct for analytical interferences by the analysis of a sample containing both the interference and the analyte.

2. Determine the effects of suspected analytical interferences by analyzing spiked analytical standards. Add an appropriate amount of an interferent to a standard containing 10 times the RQL of the analyte. Perform this test at other appropriate levels of interferent and analyte.

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

3. If a reagent has been added to the sampling media, generate a spectral line chart (for inclusion in the method) of a sample at the target concentration showing the extra reagent's relationship to the analyte.

4. The presence of the analyte or of analytical interferences in blank samples is to be avoided if possible. Blank corrections are performed as appropriate.

5. The possibility exists that interferences may also be present in reference standards. Obtain certificates of analysis whenever possible.

D. Qualitative analysis

Analysis with alternative instruments or spectral lines may be useful in confirming the identity or purity of the analyte. Present a mass spectrum of the analyte if possible. Include this information in the method.

III. Sampling Procedure

These guidelines address the evaluation of samplers containing filters. There are different filter holders available such as IOM, Button Sampler, and 37-mm polystyrene cassette. Cyclones may be used to collect respirable particles and to exclude larger particles. Each sampler has different sampling characteristics and guidance for selection of the appropriate sampler to address the particle size issue under study might be found during the literature search. If no specific filter holder is identified, a 37-mm closed-face polystyrene cassette shall be used. These evaluation guidelines might require slight modification for 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.

Surface (wipe) sampling methods are validated using Evaluation Guidelines for Surface Sampling Methods[3].

If it is determined that a diffusive sampler can be used to collect the analyte, specific requirements that apply to the evaluation of diffusive samplers are found in Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis[4].

The use of controlled test atmospheres is the preferred technique to test candidate sampling methods. Preparation and generation of such atmospheres may not be possible due to safety or other reasons. If this is the case, then retention efficiency experiments provide a way to partially test sampler capacity.

A. Sampler 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 capacity or retention efficiency studies. For ceiling exposure limits listed in Table Z-1, determine if 15 minutes is practical as the recommended sampling time.

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[3] Evaluation Guidelines for Surface Sampling Methods, http://www.osha.gov/dts/sltc/methods/surfacesampling/t-006-01-0104-m.html (accessed 9/2005).

[4] Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 9/2005).

2. Select a sampling rate that is suitable for the sampler. The goal is to have an 8-hour recommended sampling time for TWA samples.

3. Sampler capacity is defined by the length of time a sampler can be used under a set of known test conditions without significant loss of analyte. It can also be described as a corresponding air volume or as mass collected at a specified sampling rate and at a known analyte concentration. An example of a sampler capacity test is shown in Figure 4.

4. If an atmosphere can be generated, sample at ambient temperature from a test atmosphere containing an analyte concentration equal to 2 times the target concentration. True concentration of test atmospheres could be the theoretical concentration or experimental concentration as determined by some method completely independent of the test sampling method. 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.

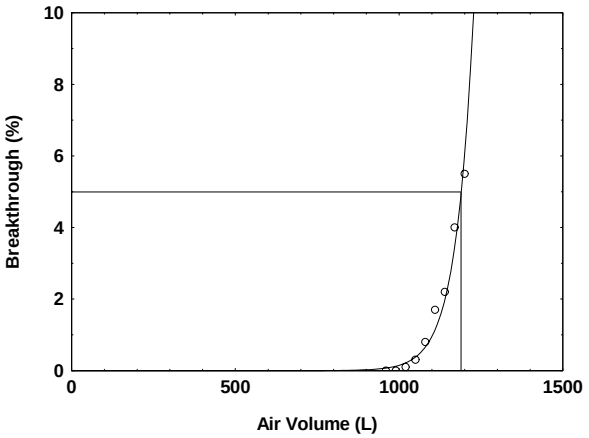

Figure 4. Example of sampler capacity test results.

5. The analytical procedure should include wiping the inside surfaces of the sampling device (such as the interior walls of a filter cassette) as part of routine analysis. The wipe shall be analyzed separate from the sample filter for methods development tests. The wipe sample can be digested along with the sample filter during routine analysis.

6. Retention efficiency

   Retention efficiency tests are useful when it is not possible to perform breakthrough tests with controlled test atmospheres. They will provide partial support of sampler capacity by showing that analyte present on the sampler is retained when the recommended sampling conditions are used. If possible, select volatile and water-soluble salts of the analyte and perform this test with each salt.

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

   a. Spike three samplers with an amount of analyte equivalent to two times the target concentration based on a tentative recommended air volume. Allow the spiked samplers to equilibrate for a sufficient time for the solvent to evaporate. Place a blank sampler immediately downstream of each spiked sampler to collect any analyte that is stripped from the front sampler.

   b. Spike three filters as in Step ‘a’ and place them in separate sealed cassettes, with backup pads, for the maximum sampling time 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.

   c. Select a recommended sampling time that is suitable for the samplers and draw air through the samplers prepared in Step ‘a’ for 1.25 times the maximum sampling time. The maximum sampling time recommended in the completed method is not to exceed 8 h. Perform further retention efficiency tests as necessary to support the sampling time and maximum air volume recommenced in the completed method.

d. 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).

e. Retention efficiency is determined by analyzing the spiked and backup samplers after air has been drawn through them. Wipe all interior walls of the spiked and backup samplers and digest the wipes separately from the sampling filter. Include wipe sample results in retention efficiency calculations. Digest and analyze filters, wipes, and support pads of the spiked and backup samplers separately. Apply digestion efficiency and blank sample corrections.

f. Retention efficiency is calculated as the percentage of analyte recovered from the front sampler in relation to the total amount of analyte spiked on the sampler. The total amounts found on the front and on the backup sampler should be the amount spiked.

7. Sampling interferences

Sampling interferences can reduce the capacity or ability of the sampling device to collect the analyte. Chemicals causing interferes can possibly be identified in the literature search.

a. Test the effects of low humidity on sample collection using a test atmosphere containing two times the target concentration of the analyte and having 3.9 milligrams of water per liter of air (about 20% relative humidity at 22.2 °C). Use spiked samplers in retention efficiency experiments if a test atmosphere cannot be generated.

b. Test the effects of low concentration on sample collection using a test atmosphere containing 0.1 times the target concentration of the analyte and with 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C). Use spiked samplers in retention efficiency experiments if a test atmosphere cannot be generated.

c. Test the effects of sampling interferences by sampling a test atmosphere containing one times the target concentration of analyte, an appropriate level of interferant and having 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C). Use spiked samplers in retention efficiency experiments if a test atmosphere cannot be generated.

B. Digestion efficiency

These tests will confirm that the selected acid matrix and digestion technique will adequately digest various chemical forms of the analyte.

1. Identify the most common insoluble chemical forms of the analyte. These forms shall include several insoluble salts, such as oxides, and Standard Reference Materials (SRM). Use masses equivalent to 0.5, 1, and 2 times the target concentration for this test. The analyte may have to be diluted by mixing with an inert interference-free substance for these tests. If the dilution technique is not feasible, determine the digestion efficiency at masses near as possible to the target mass that are consistent with those that can be accurately weighed using an analytical balance. Prepare 4 samples at each level. Include the sampling medium with the samples and analyze a blank sampler. Instrument calibration curves may have to be used in this test.

2. Normally, calibration curves are not used for the analysis of liquid-spiked digestion efficiency samples. Three standards are used to bracket the four samples for each level. In the case of liquid spiked samples, prepare the analytical standards with the same device (syringe, micropipet) used to spike the digestion efficiency samples. Use the corresponding standards and samples for calculation of results. For example, use 1× target concentration (TC) standards for 1× TC samples.

The digestion efficiency for the method is the mean percent of soluble analyte recovered from dry samplers and determined at the RQL, and 0.1, 0.5, 1, 1.5, and 2 times each target concentration,

based on the recommended air volume. {If there are several target concentrations, select the target concentration and recommended sampling time combination which will produce the highest mass loading on the sampler.} Prepare 4 samples at each level by spiking the sampling medium with soluble salts. Store the spiked samples at room temperature overnight unless a shorter time period can be justified. A dry sampler is one that is used as received from the manufacturer. The average of all four determinations will be the digestion efficiency for the analytical procedure providing the results are similar. If digestion efficiency does not remain constant at lower sample loadings attempts should be made to produce a digestion method that will provide constant digestion efficiency. If these attempts are not successful, a plot of digestion efficiency versus concentration shall be constructed and included in the method. Test the stability of digested samples by reanalyzing the 1 times the target concentration samples after 1and 7 days of ambient storage. The original analysis is “day 0". Use fresh standards and recalibrate the instrument for each analysis.

3. Perform a test of the digestion efficiency with wet samplers. Pull an air volume equivalent to the recommended sampling time through four samplers 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). Spike the wet samplers at one times the target concentration with a soluble salt. {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 digestion recovery from the mean dry sampler’s digestion 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 digestion scheme to minimize the difference.

4. Determine the digestion efficiency of support pads at 10 times the RQL (or 0.1× target concentration (TC), whichever is less) and at 1 times the target concentration. Spike 4 samples at each level. Allow these samples to stand overnight after spiking. A minimum digestion efficiency of 75% is required for this test.

5. Select a medium and a technique (wet or dry) to be used to wipe interior cassette walls. Spike the interior walls of 4 cassettes with 10 times the RQL (or 0.1×TC, whichever is less) and 4 separate cassettes with 1.0 times the target concentration of the analyte to determine the efficiency at which the analyte is removed by wiping. Allow these cassettes to stand overnight after spiking and then use the selected technique to perform the test. Determine the digestion efficiency of the wipe medium by spiking the medium separately and allowing them to stand overnight. Spike 4 samples at each level. A minimum recovery of 75% is required for this test.

6. Calculate the digestion efficiency as follows:

$$DE = \frac{100\ M_R}{M_S}$$

where DE is digestion efficiency
M_R is mass recovered
M_S is mass spiked

7. An average digestion efficiency of 75% is acceptable, but an average greater than 90% is preferred for all insoluble and soluble salts.

C. Effects of storage

Volatile salts, if identified, shall be used for storage tests.

A refrigerated-temperature storage stability test will not be performed unless the ambient temperature test gives unacceptable results.

1. Collect eighteen samples from a controlled test atmosphere containing the analyte at the target concentration. If the analyte has a ceiling, peak or STEL, generate another set of storage stability samples if the mass of analyte for the short-term sample is less than 10% of the mass collected for

a long-term sample. 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. 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 a closed laboratory drawer.

4. Analyze three samples 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 (not corrected for digestion 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 (not corrected for digestion 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 of a convenient sampler without restrictions on storage conditions, or time requirements for completion of analysis.

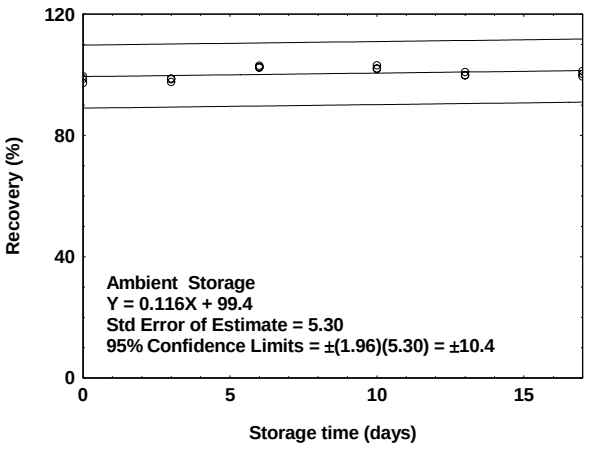

Figure 5. Example of a storage test.

7. Use alternate methods of preparing storage samples when safety considerations or other problems prevent generation of dynamically generated test atmospheres. The alternate methods include liquid-spiked samples, prepared by injecting the analyte directly onto the sampling device. Introduce water by drawing the recommended air volume of 80% humid air through the spiked sampler. In this latter method, a small volume of 80% humid air can be drawn through the sampler 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 5. Note that this figure includes data for the overall precision, which is defined in a following section. See Section C for required calculations to be included in the plot of storage data. 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. Use a series of spiked samplers instead of

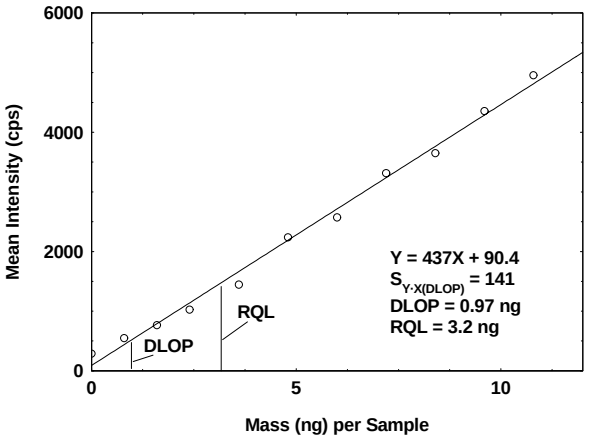

Figure 6. Example of plotted DLOP/RQL data.

analytical standards for Equation 2 (Section II.A). Use a soluble salt. Analyze a blank sampler but do not subtract blank results from spiked sampler results. Include a blank cassette wipe medium (Section A.5.) to determine if it affects results.

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 6.

B. Reliable quantitation limit (RQL)

1. Consider the RQL as the lower limit for precise quantitative measurements. Employ the regression line data used to calculate the DLOP. Determine the RQL with the following formula, providing the recovery from the sampler (including cassette wipe medium) for the mass closest to the RQL, is 100 ± 25% of its theoretical value.

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

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

Perform blank sample subtractions (if necessary) when calculating recovery. If the recovery from the closest spiked sampler is not within 25% of its theoretical value, then the RQL will be equal to the lowest spiked concentration that is within ±25% of its theoretical value. Determine this from a plot of recovery versus mass, as shown in Figure 7, 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.

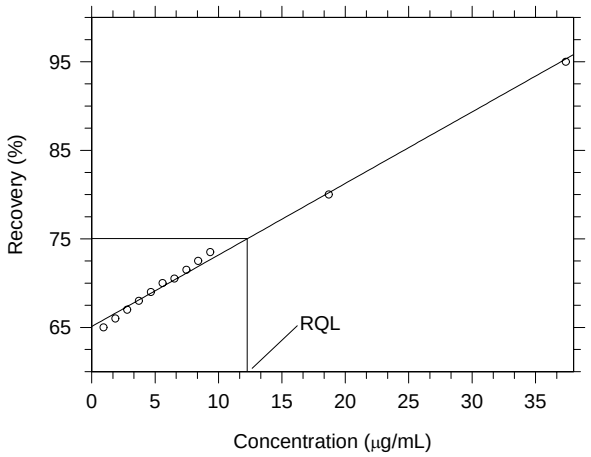

Figure 7. Example of a calculated RQL when recovery is the determining factor (Y = 0.808X + 65.1).

C. Precision of the method

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

2. Determine the standard error of estimate ($S_{Y|X}$) for the regression curve[5,6] of each storage test with the following formula.

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

where $S_{Y|X}$ 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 the storage test. Perform a refrigerated storage test if the ambient test fails. If the refrigerated storage test also

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

fails, restrictions must be set on the maximum storage time that will be allowed before samples must be analyzed.

Determine the standard error of the overall procedure (*SEE*) for each storage test by including the sampling pump variability (V_{SP}) (use a value of 5%) with the following formula:

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

where *SEE* is the total standard error of estimate
$S_{Y \cdot X}$ is the standard error of estimate from storage
V_{SP} is the sampling pump variability (±5%)

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 representing the precision of the method.

5. Represent the overall precision data graphically in the method as shown in Figure 5, 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 #25%.

D. Reproducibility

1. Using a soluble and an insoluble salt, prepare six samples for each salt (at the target concentration(s) on the sampler). Prepare these samples using the same technique used to prepare the storage stability samples. {Use humid air.} 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.

E. Method Review

Prepare written methods by following the format described in these Guidelines as closely as possible. Give each method a unique method number, a unique control number, and each draft version a unique draft number. Provide each member of the Methods Development Team (MDT) a copy of the draft method for review and comment. Schedule a review meeting to discuss the draft method. Revise the draft method considering comments from the review meeting. Continue this process until the consensus of MDT is that the method is suitable for examination by a review team external to MDT. Provide the external review team with copies of the method. Perform a final revision (remove the draft number) of the method after review by the external team for approval by the SLTC Director. Submit an electronic version of the completed method to the MDT team leader.

PREPARATION OF WRITTEN REPORTS

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

Written reports fall into three basic categories:

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

II. Partially Validated 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.

I. Fully Validated Methods

The following format provides a means of reporting data obtained during evaluation of spectroscopic 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 perspective of filter sample collection and ICP/MS (or ICP/OES) analysis.

Each fully validated method shall have a unique control number, for example: T-1xxx-FV-01-0501-M. See SLTC SOP “The Preparation of SOPs” (number A-001) for an explanation of the control number format. Place the control number immediately following the method number on the cover page and again in the lower right margin of each page as shown in these guidelines.

All fully validated methods completed by the Methods Development Team shall have the following statement on the cover page:

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

Page Numbering - Page number shall be at the bottom center, for example, 1 of XX. Use 8-point Arial.

Comments and instructions in these guidelines are for use by the author and are set off with braces "{ }", and shall not be not included in the final method.

Text shall be10 point Arial font with full justification with no hyphenation

Tabs shall be: method cover page: 2.0; main body of method: 0.2, 0.59, 1.12, 1.36

DOL logo shall be placed on the cover page - size = 0.500", attach to paragraph, 0" horizontal, 0" from top, right margin, wrap behind text

The following disclaimer shall be in 10-point Arial font and be placed immediately following Section 1:

{example}

1. General Discussion

“For assistance with accessibility problems in using figures and illustrations presented in this document, please contact OSHA Salt Lake Technical Center at (801) 233-4900. These Guidelines were developed for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.”

Table caption shall be 9-point Arial, 0.02" for left inside margin, right inside margin, top row margin, bottom row margin. Numbers shall be aligned on the decimal point.

Graphs shall be size = 3.1", attached to paragraph, 0" horizontal, 0" from top, right margin, wrap left, caption is 9-point Arial

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

References shall 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." If a reference is repeated, do not give it a new number.

{ANALYTE}
{as listed in CFR or ACGIH}

Method number:	1xxx
Control number:	T-1xxx-FV-01-yymm-M
Target concentration:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}}
OSHA PEL:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}} {None if no PEL}
ACGIH TLV:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}} {None if no TLV}

Procedure:

Samples are collected by drawing workplace air through 37-mm mixed cellulose ester filters (MCE) with cellulose support pads in closed-face polystyrene cassettes with personal sampling pumps. The samples are analyzed by wiping the interior walls of the cassette with a cellulose nitrate filter and combining it with the MCE filter for digestion. The filters and accompanying cassette wipes are digested with nitric acid and hydrogen peroxide using a microwave oven. Analysis is done by Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS). Other analytical techniques may be used after compatibility with the digestate of this method is demonstrated for the analytes of interest. These techniques include, but are not limited to, Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Those using a different analytical technique must consider the detection limits, precision, and sensitivity of the technique as it relates to each particular analyte.

Recommended sampling time and sampling rate:

___ min at___ L/min (___ L)
{If the sampling rate is less than 0.250 L/min, use mL/min.}

Reliable quantitation limit:

___ mg/m^3 {___ ppm(___ mg/m^3) {if appropriate}}

Standard error of estimate at the target concentration:

___ %

Special requirements:

{If none, delete this item}

Status of method:

Validated 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
Sandy UT 84070-6406

1. General Discussion

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

{The backup data section will be referenced throughout the method in the following manner: "(Section 4.____)". Literature citations will be footnotes. If a reference is repeated, do not give it a new number}

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[7] {These are to be used if applicable, other properties may be listed.}

CAS number:	___	vapor pressure:{kPa (mmHg)}	___
IMIS number:	___	8_{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 Spectroscopic Analysis"[8]. 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). {Delete previous sentence if not appropriate}

[7] This reference was used for most of the physical properties.
[8] Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 9/2005).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is ____ {concn}. This is the concentration 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 particular analyte must be altered, the altered definition shall appear in this section and the detailed explanation shall appear in Section 4.1. Also list any instrument parameter that can affect the mass of analyte detected.}

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is___ {mass} per sample (___ mg/m^3). This is the amount of {analyte} spiked on the sampler that will give a detector response that is significantly different from the response of a sampler blank. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is ___ {mass} per sample (___ mg/m^3). This is the amount of {analyte} spiked on the sampler that will give a detector response that is considered the lower limit for precise quantitative measurement. (Section 4.2)

1.2.4 Instrument calibration

The standard error of estimate for the calibration curve is ____ {concentration} over the range of ____ to ____ µg/mL. This range corresponds to 0.1 to 2 times the target concentration. (Section 4.3)

1.2.5 Precision

The precision of the overall procedure at the 95% confidence level for the ambient temperature {or reduced temperature (___°C)} 15-day storage stability test (at the target concentration) from {sampler} 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.}

1.2.6 Recovery

The recovery of {analyte} from samples used in a ___ -day storage test remained above __ % {the lowest points on the regression curve of Figure 4.5.} when the samples were stored at ____°C. (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

Samples collected from a controlled test atmosphere {or spiked by liquid injection, etc.} were submitted for analysis by the OSHA Salt Lake Technical Center. These samples included both soluble and insoluble chemical forms of the analyte. 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.}

{example}
Samples are collected with {description of the sampler, example} 37-mm diameter, 0.8-µm pore size, mixed cellulose ester membrane filters with a cellulose support pad contained in a 37-mm diameter, 2-piece, polystyrene cassette. For this evaluation, commercially prepared {sampler} were purchased from {Supplier}, Inc. (catalog no. ____).

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

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.}

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 top and bottom with plastic end plugs. Seal each sample end-to-end with an OSHA-21 form.

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.

Ship any bulk samples separate from the air samples.

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

The sampling capacity of ____ {sampler} was tested by sampling a dynamically generated test atmosphere containing ____ {analyte} at ____ mg/m^3 and 80% relative humidity at 22.2 °C. The samples were collected at ____ L/min. Five-percent loss from the sampling filter occurred after sampling for __ min. At this time, ___ L air had been sampled and ___ mg of {analyte} had been collected. {Use this format to completely describe alternative tests and conditions}

2.5 Recommended sampling time and sampling rate

Sample for up to__ min at__ L/min (__ L) when using ___ {sampler} to collect TWA (long-term) samples.

Sample for __ min at_ L/min (_ L) when using __ {sampler} to collect 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 {sampler} is ___ mg/m^3 for {analyte} when ___ L are collected.

2.6 Digestion efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine digestion efficiency because the chemical form of the analyte under analysis , acid matrix, and laboratory technique may be different than those listed in this evaluation and could influence analytical results.

Insoluble chemical forms

The mean digestion efficiencies for {list insoluble chemical forms of analyte} at 0.5, 1, and 2 times the target concentration were ___%, ___%, and ___%, respectively.

Soluble chemical form

The mean digestion efficiency for ___ {analyte} from dry __{sampler} over the range of the RQL to 2 times the target concentration (____ to ____ micrograms per sample) was ____%. The digestion 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.} {Also present mean digestion efficiency results for support pads, cassette wipes, and recovery from spiked cassette walls at 10 times the RQL mass (or 0.1× the target concentration, whichever is less) and 1 times the target concentration following the same format.}

Digested samples remain stable for at least ___days.

2.7 Interferences, sampling (Section 4.9)

Low humidity

The recovery for all samples was above ____% of theoretical {report the lowest value}, when {samplers} were used to sample a test atmosphere containing two times the target concentration of {analyte} and having about 20% relative humidity at 22.2 °C

Low concentration

The recovery for all samples was above ____% of theoretical {report the lowest value}, when {samplers} were used to sample a test atmosphere containing 0.1 times the target concentration of {analyte} and with 80% relative humidity at 22.2 °C.

Chemical {or other} interference

The recovery for all samples was above ___% of theoretical {report the lowest value}, when ___ {samplers} were used to sample a test atmosphere containing one times the target concentration of ___ {analyte} and ___ mg/m^3 of {interference(s) identified in literature search}, and with 80% relative humidity at 22.2 °C.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan as required by Occupational Exposure to Hazardous Chemicals in Laboratories[9] standard. Avoid skin contact and inhalation of all chemicals, and review all appropriate MSDSs before sample analysis. Follow any internal SOP or accreditation protocol necessary for proper instrument optimization and analysis.

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.}

3.1.1 Inductively coupled plasma - mass spectrometer (ICP-MS). A Perkin-Elmer Elan 6100 was used in this evaluation. Instrument accessories included: auto-sampler, peristaltic pump, mass flow controller, and water chiller. The Elan software controlled the instrument and provided the analytical results.

3.1.2 Laboratory quality microwave oven. A CEM MARS-5 microwave oven with accessories, including temperature probe and high throughput accessory set, was used in this evaluation.

3.1.3 Centrifuge. A Thermo IEC Centra CL3 centrifuge with accessories was used in this evaluation.

3.1.4 Plastic graduated centrifuge tubes, 50-mL, accuracy of ±2% or better at the 50-mL mark. Corning (accuracy of ±2%[10]) polypropylene centrifuge tubes were used in this evaluation.

3.1.5 Cellulose nitrate filters for use to wipe inside surfaces of cassettes. Whatman (Cat. No. 7184-004) , 0.45-: m pore size, 47-mm diameter filters were used in this evaluation.

3.2 Reagents

3.2.1 Nitric acid, [CAS no. 7697-37-2], for trace metal analysis. Nitric acid, 'Baker Instra-Analyzed', 69.0-70.0%, (lot V17032) purchased from JT Baker was used in this evaluation.

3.2.2 Hydrochloric acid, [CAS no. 7647-01-0], for trace metal analysis. Hydrochloric acid, 'Baker Instra-Analyzed', 36.5-38.0%, (lot T45036) purchased from JT Baker was used in this evaluation.

3.2.3 Calibration standards

3.2.3.1 Arsenic standard, [CAS no. 7440-38-2]. CPI International (CPI), 1000 : g/mL arsenic in 2% HNO_3 (lot 3AD064) was used in this evaluation.

3.2.3.2 Cadmium standard, [CAS no. 7440-43-9]. CPI 1000 : g/mL cadmium in 2% HNO_3 (lot 1LM044) was used in this evaluation.

3.2.3.3 Cobalt standard, [CAS no. 7440-48-4]. CPI 1000 : g/mL cobalt in 2% HNO_3 (lot 2JT116) was used in this evaluation.

3.2.3.4 Copper standard, [CAS no. 7440-50-8]. CPI 1000 : g/mL copper in 2% HNO_3, (lot 3AM188) was used in this evaluation.

---

[9] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2002.

[10] Personal communication from Connie MacDonald, Corning Life Sciences, 10/20/2004.

3.2.3.5 Lead standard, [CAS no. 7439-92-1]. CPI 1000 : g/mL lead in 2% HNO_3 (lot 2LF025) was used in this evaluation.

3.2.3.6 Nickel standard, [CAS no. 7440-02-0]. SPEX 1000 : g/mL nickel in 2% HNO_3 (lot PLNI2-2Y) was used in this evaluation.

3.2.4 Internal standards (IS). The elements and concentrations used may be specific for the particular instrument used and the elements in the calibration. Internal standards are used to correct for matrix interferences, instrument drift and short-term noise. The following were used for the evaluation of this method.

3.2.4.1 Germanium standard, [CAS no. 7440-56-4]. CPI 1000 : g/mL germanium in 2% HNO_3 (lot OBF145) was used in this evaluation. Germanium is used as an internal standard for arsenic, cobalt, copper, and nickel.

3.2.4.2 Indium standard, [CAS no. 7440-74-6]. CPI 1000 : g/mL indium in 2% HNO_3, (lot OBF173) was used in this evaluation. Indium is used as an internal standard for cadmium.

3.2.4.3 Lutetium standard, [CAS no. 7439-94-3]. CPI 1000 : g/mL, in 2% HNO_3 lutium (lot 1IF013) was used in this evaluation. Lutetium is used as an internal standard for lead.

3.2.4.4 Interference check sample. {describe using the format of this section}

3.2.5 De-ionized water (DIW), 18 megaohm. A Barnstead Model D11901 NANOpure DIamond water purifier was used in this evaluation.

3.2.6 Hydrogen peroxide, [CAS no. 7722-84-1], 30%. Mallinckrodt hydrogen peroxide solution, 30%, (lot 5240 T45A05) was used in this evaluation.

3.2.7 Ethanol, [CAS no. 64-17-5], 95%. AAPER Alcohol and Chemical Co. ethanol, 95%, (lot 98G23BB) was used in this evaluation.

3.3 Standard preparation

3.3.1 Match the matrix of standards to the final digested sample matrix of 4% nitric acid, 1% hydrochloric acid, 1% internal standard (IS) mix, and 1% ethanol. For this method, the IS and ethanol are added during preparation of the samples and standards. Alternatively, they could be added at the time of introduction into the instrument (e.g., using a mixing block just prior to the nebulizer).

3.3.2 Bracket sample concentrations with standard concentrations. If, upon analysis, sample concentrations are above the range of prepared standards, dilute the high samples with the proper acid matrix and reanalyze the samples.

3.4 Sample preparation

3.4.1 Transfer the sampling filter from the 37-mm cassette to the bottom of the plastic centrifuge tube. Wipe the interior walls of the cassette with a cellulose nitrate filter that has been moistened with 2-3 drops of DIW. Place the wipe at the bottom of the centrifuge tube with the sampling filter. If the support pad is visibly contaminated, digest and analyze it separately. Add 2 mL of concentrated nitric acid and 0.2 mL of 30% hydrogen peroxide to the centrifuge tube. Cap the tube loosely (no more than ¼ turn), to allow any excess pressure to vent around the cap. Swirl the tube to wet the filters contents. Place the tube

in the fast throughput carousel in the microwave oven. Digest the samples in the microwave. Samples are digested in the microwave using the following parameters:

First step
Maximum power = 600 W
Starting temperature = ambient
Ramp temperature to 104 °C over 9 min
Hold temperature at 104 °C for 3 min

Allow the samples to cool at least 10 min before removing from the microwave. Add 0.5 mL of concentrated hydrochloric acid. Recap the samples, return them to the microwave, and further digest them using the following parameters:

Second Step
Maximum power = 600 W
Starting temperature = ambient
Ramp temperature to 86 °C over 5 min
Hold temperature at 86 °C for 1 min

Allow the samples at least 10 minutes to cool before removing from the microwave. Add 0.5 mL of IS solution and 0.5 mL of 95% ethanol. Dilute the sample to the 50-mL mark with DIW. If solid particles remain after diluting to volume, filter the sample and digest the filter and particles in the microwave using the second step described above. Sample results shall be added together after both solutions have been analyzed separately. For this evaluation, the final matrix contains 4% nitric acid, 1% hydrochloric acid, 1% IS, and 1% ethanol.

Note: If volumes other than 50 mL are used, amounts of acids should be adjusted to keep the matrix approximately the same for samples and standards.

3.4.2 Digest a contaminated support pad, that has been identified by a discoloration on the white pad, separately using a modification of the above microwave procedure. Instead of using 2 mL of nitric acid, use 4 mL of nitric acid and 0.3 mL of 30% hydrogen peroxide. In the second step, use 1 mL of concentrated hydrochloric acid. Lastly, transfer the contents of the centrifuge tube to a 100-mL volumetric flask, add 1 mL of IS solution and 1 mL of 95% ethanol, and dilute to volume with DIW. Although the procedure may not completely digest all of the fibers present, a study was done to show that analytes spiked on the support pad do go into the solution (Section 4.8.2). Centrifuge the tubes at 2000 rpm for 10 min to compact the fibers, If necessary, before analyzing the sample.

3.5 Analysis

3.5.1 Analytical conditions

Number of replicates:	3
Integration time:	1 sec
Readings/replicate:	1
Detector mode:	dual
Auto lens:	on
Dwell time:	20 msec
Sweeps/reading:	50
Scan mode:	peak hopping

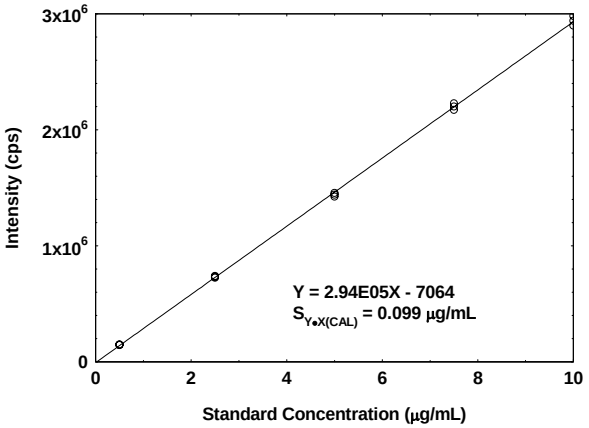

Figure 3.5. Calibration curve for {analyte}.

3.5.2 An internal standard (ISTD) calibration method is used. The calibration curve shown in Figure 3.5 was constructed by plotting ISTD-corrected response of standard determinations versus micrograms of analyte per milliliter. Bracket sample concentrations with freshly prepared analytical standards over the calibration range. The calibration curve was prepared with a soluble salt over the concentration range of 0.1 to 2 times the target concentration. The standard error of estimate for this curve is 0.099 : g/mL of {analyte} calculated from the precision of the calibration.

3.6 Interferences (analytical)

The following interferences, typically encountered with ICP-MS techniques, were addressed during the evaluation of this method:

Table 3.6
ICP-MS Analytical Interferences

analyte	interference	corrective measures
^{75}As	$^{40}Ar^{35}Cl$	mathematical correction factor
^{75}As	C	add ethanol to standards and samples
^{114}Cd	$^{98}Mo^{16}O$	adjust nebulizer flow to minimize oxides
^{114}Cd	^{114}Sn	mathematical correction factor
^{63}Cu	$^{31}P^{16}O_2$, $^{47}Ti^{16}O$	adjust nebulizer flow to minimize oxides
^{115}In	^{115}Sn	mathematical correction factor
^{60}Ni	$^{44}Ca^{16}O$	adjust nebulizer flow to minimize oxides
^{208}Pb	^{206}Pb, ^{207}Pb	mathematically combine all 3 isotopes*

*These three stable isotopes of lead are the endpoint of the radiologic decay of ^{232}Th, ^{235}U, and ^{238}U. The abundance ratio of these lead isotopes to each other may change slightly depending on the source of origin, but together they constitute 98.6% of all stable lead found. Summing the isotopes together cancels out ratio differences.

Although ICP-MS analysis has been found by analysts working in the field to be definitive for most of the elements examined in this method, other analytical techniques can be used if interferences are large and/or additional confirmation is needed. These techniques include, but are not limited to: FAAS, GFAAS, and ICP-AES.

3.7 Calculations

Air sample results are reported in units of mg/m^3. For analytes reported as a compound (such as lead sulfate), results are reported as mg/m^3 of that compound by using gravimetric factors. If it is necessary to analyze the support pad, it is analyzed separately from the combined sampling filter + cellulose nitrate wipe. The analytical results for each analyte are combined.

The concentration of analyte in the digestate is calculated from the appropriate calibration curve. The concentration (µg/mL) of an analyte in solution multiplied by its volume (mL) results in the mass per sample (µg). Analytical results are not normally corrected for digestion efficiency because the actual chemical compound being analyzed has not been identified. The final result, in mg/m^3, is calculated using the following formulas:

$$A = (C \times D \times H) - (E \times F \times I)$$

where
- A is combined mass of analytes (µg sample, blank corrected)
- C is result for sample filter plus cassette wipe (µg/mL)
- D is solution volume (mL)
- H is dilution factor (if any)
- E is result for sample blank plus cassette wipe blank
- F is solution volume for blank (µg/mL)
- I is dilution factor (if any)

$$B = (J \times K \times L) - (M \times N \times O)$$

where B is mass of analyte on support pad (µg sample, blank corrected)
J is result from support pad (µg/mL)
K is solution volume (mL)
L is dilution factor (if any)
M is result for support pad blank (µg/mL)
N is solution volume for blank (µg/mL)
O is dilution factor (if any)

$$X = \frac{A + B}{V}$$

where X is concn by weight (mg/m^3)
V is liters of air sampled

4. Backup data

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 Spectroscopic Analysis".[11] 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 in a graph.} {example:}
DLAP is measured as concentration of the analyte detected by the ICP/MS. Ten analytical standards were prepared with equally descending increments with the highest standard containing ___ µg/mL. This is the concentration that would produce a detector response peak approximately 10 times the response of a reagent blank. These standards, and the reagent blank were analyzed with the recommended analytical parameters ({list any analytical parameter that would affect the mass detected}), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of ____ and ____ were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be ng/mL.

Table 4.1
Detection Limit
of the Analytical Procedure

concn (ng/mL)	mean intensity (cps)
0.00	43
0.1	2449
0.15	3568
0.2	4513
0.25	5628
0.3	6744
0.4	8905
0.5	10664
0.6	12938
0.7	14945
0.8	16990

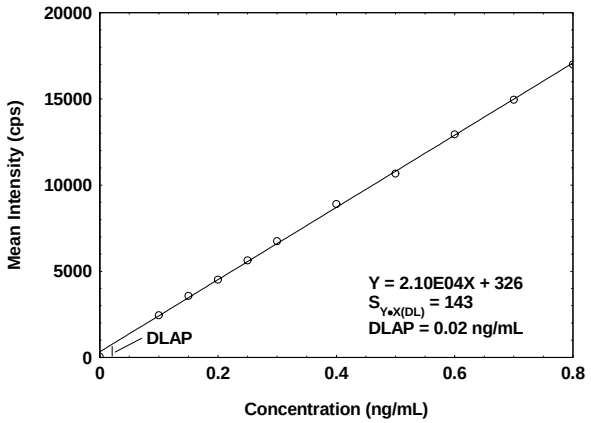

Figure 4.1. Plot of data to determine DLAP.

[11] Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 9/2005).

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:}
DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was ____ µg/sample. This is the amount spiked on a sampler that would produce a detector response 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 ___ µg/sample (___mg/m^3).

Table 4.2
Detection Limit of the Overall Procedure

mass per sample (ng)	mean intensity (cps)
0	286
0.8	545
1.6	764
2.4	1024
3.6	1443
4.8	2237
6	2572
7.2	3312
8.4	3647
9.6	4354
10.8	4954

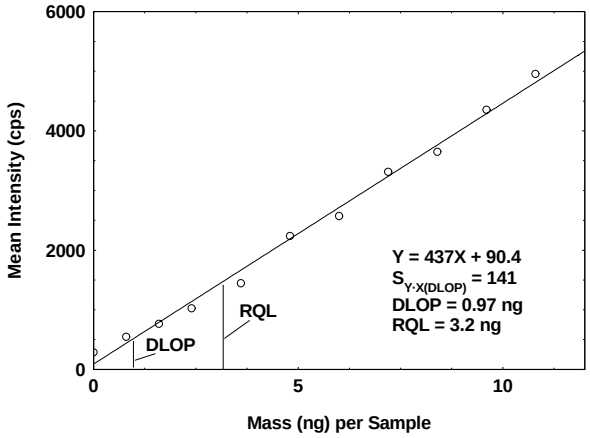

Figure 4.2. Plot of data to determine DLOP/RQL.

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____ µg per sample (____ µg/m^3). Recovery at this concentration is ____%.

4.3 Instrument calibration
{example:}
The standard error of estimate was determined from the linear regression of data points from the triplicate analysis of standards over a range that covers 0.1 to 2 times the target concentration (TC) for the sampler. Each analysis is the average of three replicates. A calibration curve was constructed from the three determinations of the five standards and it is shown in Section 3.5. The standard error of estimate is 0.099 µg/mL.

Table 4.3
Instrument Calibration

×TC	0.1×TC	0.5×TC	1×TC	1.5×TC	2×TC
µg/mL	0.5	2.5	5	7.5	10
mean	147000	733000	1440000	2200000	2940000
intensity	144030	726020	1423800	2171600	2899300
(cps)	149970	739980	1456200	2228400	2980700

4.4 Precision (overall procedure)

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, the 95% confidence interval is drawn about the regression line in the storage graph figure. The precision of the overall procedure is ±____ %. It was obtained from the standard error of estimate of __in Figure__. {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.}

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 a humidity of 80% at 22.2 °C. Eighteen samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the samples were stored in a closed drawer at ambient temperature (about 22 °C). At 2-5 day intervals {preferably 3-day intervals}, three samples were selected and analyzed. Sample results are not corrected for digestion efficiency.

Table 4.5
Ambient Temperature Storage Test
for {analyte}

time (days)	recovery (%)		
0	97.2	98.6	99.5
3	98.8	97.6	98.5
6	102.5	103	102.3
10	103.1	102.1	101.9
13	99.8	100.9	99.9
17	99.4	100.2	101.2

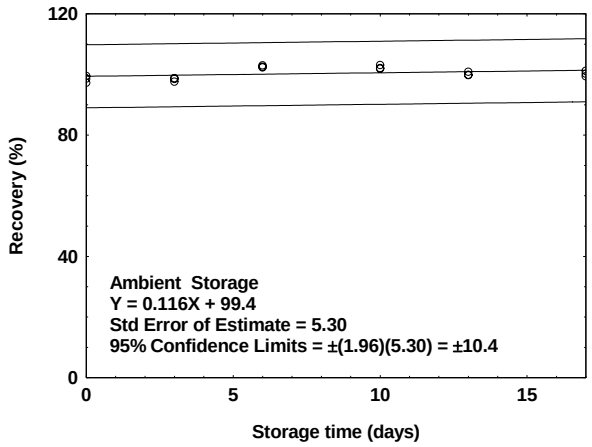

Figure 4.5. Ambient storage test for {analyte}.

4.6 Reproducibility {Describe reproducibility test and present data in Tables 4.6.1 and 4.6.2. {example:}
Samples were prepared for insoluble and soluble chemical forms of {analyte] 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. {specify if sample results were corrected for digestion 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
Insoluble {Analyte} on {Sampler}

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
50.0	45.5	91.0	-9.0
50.0	45.7	91.4	-8.6
50.0	45.3	90.6	-9.4
50.0	47.0	94.0	-6.0
50.0	46.2	92.4	-7.6
50.0	48.7	97.4	-2.6

Table 4.6.2
Reproducibility Data for
Soluble {analyte} on {Sampler}

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
50.0	47.2	94.4	-5.6
50.0	49.1	98.2	-1.8
50.0	49.1	98.2	-1.8
50.0	50.6	101.2	1.2
50.0	51.0	102.0	2.0
50.0	48.0	96.1	-3.9

4.7 Sampler capacity {Describe breakthrough, retention efficiency, or other studies used.}

The sampling capacity of a ____ {sampler} was tested by sampling from a dynamically generated test atmosphere of ___ {analyte} (____ mg/m^3) {2 times target concentration} with a relative humidity of 80% at 22.2 °C. The samples were collected at ____ L/min. {example} Three sets of two identical ___ {sampler} were connected in series and sampling was begun. Sampling was interrupted at 480 min and then the back sampler was regularly replaced with a fresh back sampler at 15 min intervals and sampling was resumed. Each section of the back samplers was analyzed separately to determine where on the sampling train the analyte was collected. Sampling was discontinued at 600 min and the front sampler was also analyzed. {or a direct-reading device was connected in-line with the {sampler} to detect breakthrough}. The recommended sampling time is ____ h.

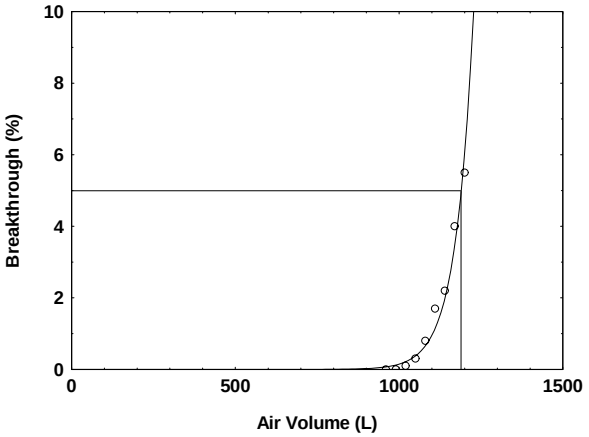

Figure 4.7. Sampler capacity test results.

Table 4.7
Sampler Capacity

	sampling time (min)			filter (µg)			support pad (µg)			cassette wipe (µg)		
sampler	1	2	3	1	2	3	1	2	3	1	2	3
back	480	480	480	0	0	0	0	0	0	0	0	0
	495	495	495	0	0	0	0	0	0	0	0	0.2
	510	510	510	0.1	0.1	0	0	0	0	0	0	0.1
	525	525	525	0.4	0.4	0.3	0	0	0	0.1	0	0.1
	540	540	540	1	0.9	0.9	0	0	0	0.1	0	1.3
	555	555	555	1.9	2.1	2	0	0	0	0	0	0.1
	570	570	570	2.7	2.7	2.6	0	0	0	0.1	0	0.4
	585	585	585	4.9	5	4.7	0	0	0	0.4	0.1	0.1
	600	600	600	6.7	6.8	6.5	0	0	0	0.2	0.5	2.1
front				122.6	124.4	118.2	0.9	0.3	0.5	0	0	0

4.8 Digestion efficiency and stability of digested samples

The digestion efficiency is dependent on the acid matrix, the digestion technique, and on any internal standards used. Other acids, techniques, and internal standards than those described in this method may be used, but they must be fully tested.

4.8.1 Insoluble forms

Digestion efficiency

The digestion efficiencies of insoluble forms of __ {analyte} were determined by {describe technique} at masses equivalent to 0.5, 1, and 2 times the target concentration (TC). {describe materials and spiking techniques}

Table 4.8.1
Digestion Efficiency for Insoluble Forms of {analyte} from {sampler}

				digestion efficiency (%)				
chemical compound	gravimetric factor	×TC	mass digested (µg)	1	2	3	4	mean
chemical 1	0.683	0.5	17.6	93.5	92.4	89.9	94.5	92.6
		1	35.1	92.9	94.9	95	97.6	95.1
		2	70.3	90.4	96.1	96.3	95.9	94.7
							ave	94.1
chemical 2	0.982	0.5	12.2	99.4	97.6	95.9	100.3	98.3
		1	24.4	98.9	96.9	99.2	98.9	98.5
		2	48.9	98.6	96.1	99.9	97.5	98
							ave	98.3
chemical 3	0.641	0.5	18.7	89.4	88.4	88.1	88.8	88.7
		1	37.4	90.6	85.9	86.6	85.6	87.2
		2	74.9	91.1	89.9	84.1	82.3	86.9
							ave	87.6

The gravimetric factor is the decimal equivalent of the percent of the analyzed element in the tested compound.

4.8.2 Soluble forms

The digestion efficiency of a soluble form of ____ {analyte} from ____ {sampler} was determined by liquid-spiking __ {sampler} with the analyte diluted with __ {acid matrix} at the RQL, 0.1, 0.5, 1, 1.5, and 2 times the target concentration. {describe materials and spiking techniques} An additional digestion efficiency test was performed with wet samplers at 1 times the target concentration. The spiked samples were all stored overnight at ambient temperature and then analyzed. The mean digestion 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 4.8.2.1
Digestion Efficiency for Soluble Form of {analyte} from {sampler} (%)

level	mass spiked (µg)	1	2	3	4	mean
RQL	0.32	93.5	90.4	91.1	87.2	90.6
0.1×	3.83	92	94.6	99.2	99.6	96.4
0.5×	19.2	94.7	96.4	97.2	98.7	96.8
1.0×	38.3	92.5	92.7	96.9	97.6	94.9
1.5×	57.5	95.4	89.6	97	99.9	95.5
2.0×	76.6	99.1	99.8	99.6	100.3	99.7
wet 1.0×	38.3	94.9	99.1	99.2	93.5	96.7

Stability of digested samples

The stability of extracted samples was investigated by reanalyzing the dry target concentration samples at 1 and again at 7 days after the initial analysis. These samples were stored at ambient temperature and fresh analytical standards were prepared and used each day. Results are presented as percent of the original analysis.

Table 4.8.2.2
Stability of Digested Samples at 1.0 × TC (%)

storage (days)	1	2	3	4	mean
1	93.5	98.9	100.5	98.6	97.9
7	95.5	99.4	92.9	100.5	97.1

4.8.3 Support pads and cassette wipes

The digestion efficiency of soluble ___ {analyte} from liquid-spiked support pads and from cassette wipes was determined at 10 times the RQL mass {or 0.1× the target concentration, whichever is less} and at 1 times the target concentration. {describe materials and spiking techniques} The samples were stored overnight at ambient temperature and then analyzed. The mean digestion efficiency from support pads was __%, and it was ___% from cassette wipes.

Table 4.8.3
Digestion Efficiency for {analyte} from Support Pads and from Cassette Wipes (%)

level	mass spiked (µg)	support pads				mean	cassette wipes				mean
		1	2	3	4		1	2	3	4	
10 times RQL	3.2	93.5	100.2	100	92.9	96.7	100.4	100	96.6	97.7	98.7
1.0 ×	38.3	100.9	103.1	92.2	94.9	97.8	100.4	100.1	98.6	92.2	97.8

4.8.4 Recovery from cassette interior walls

Recovery of soluble ___ {analyte} from liquid-spiked interior walls of ___ {sampler} was determined by {describe materials and technique} at the 10 times the RQL mass {or 0.1× the target concentration, whichever is less} and 1 times the target concentration. The __ {sampler} was spiked and then allowed to stand overnight before wiping the interior walls of ___ {sampler} with ___ {wipe medium} following the technique described in Section 3.4.

Table 4.8.4
Recovery of {analyte} from Cassette Walls

	mass spiked	recovery (%)				
level	(µg)	1	2	3	4	mean
10 times RQL	3.2	93.5	89.2	99.1	92.2	93.5
1.0×	38.3	94.6	96.6	99.7	95.9	96.7

4.9 Interferences (sampling)

Low humidity

The ability of a ___ {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} and 20% relative humidity at 22.2 °C. Three samplers had contaminated air drawn through them at _____ L/min for _____ min {the recommended sampling time}. All of the samples were immediately analyzed. The results were ___%, ___%, and ___% of theoretical.

Low concentration

The ability of a ___ {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 80% relative humidity and 22.2 °C. Three samplers had contaminated air drawn through them at ____ L/min for __ min {the recommended sampling time}. All of the samples were immediately analyzed. The results were ___%, ___%, and___% of theoretical.

Interference

The ability of a ___ {sampler} to collect ___ {analyte} was tested when other potential interferences were present by sampling an atmosphere containing __ mg/m^3 {one times the target concentration} of ___ {analyte} at 80% relative humidity and 22.2 °C and ___ {interference}, whose concentration was _ mg/m^3. Three samplers had contaminated air drawn through them at ___ L/min for ___ min {the recommended sampling time}. All of the samples were immediately analyzed. The results were ____%, ____% and, ____% of theoretical.

4.10 Qualitative analysis

{Present alternate spectroscopic and MS conditions that will aid in confirming the identity of the analyte or derivative. MS may provide the most conclusive identification. Analysis with alternate detectors and/or wavelengths may be useful. The format for mass spectrograms is shown in Figure 4.10.}

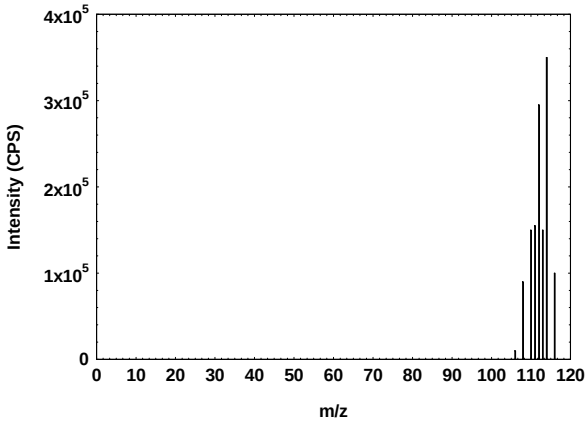

Figure 4.10. Mass Spectrum of {analyte}.

II. Partially Validated Methods - Data shall 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 fully validated procedure.

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

3. Reliable quantitation limit (RQL) - Determine this parameter in the same manner as in a fully validated procedure.

4. Digestion efficiency - Determine these parameters over the working rage of 0.5 to 2 times the target concentration plus the RQL, in the same manner as in a fully validated procedure.

5. Recommended sampling time and sampling rate - 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. Storage test - A storage test shall be performed with spiked samples at loadings equivalent to the target concentration. Draw the recommended air volume through the spiked samplers using humid air (80% relative humidity at 22.2°C). This test shall be performed for two weeks. The age of submitted samples could also be the basis for the length of a storage test.

7. Recommendation for further study - These include recommendations that shall be considered before a full validation is performed.

8. Method Review Prepare written methods by following the format described in these Guidelines as closely as possible. Give each method a unique method number, a unique control number, and each draft version a unique draft number. Provide the team leader of Methods Development Team (MDT) with four copies of the draft method for review and comment. Schedule a review meeting to discuss the draft method. Revise the draft method considering comments from the review meeting. Continue this process until the consensus of the reviewers is that the method is suitable. Perform a final revision (remove the draft number) of the method for approval by the IHC Director. Submit an electronic version of the completed method to the MDT team leader.

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

"Partially Validated 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 a Fully Validated Method.

{ANALYTE}
{as listed in CFR or ACGIH}

Method number:	PV2xxx
Control no:	T-PV2xxx-01-yymm-S
Target concentration:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}}
OSHA PEL:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}} {None if no PEL}
ACGIH TLV:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}} {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:	___ mg/m^3 {___ ppm (___ mg/m^3) {if appropriate}}
Special requirements:	{If none, delete this item}
Status of method:	Partially validated 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}

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

1. General Discussion

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

1.1 Background

1.1.1 History

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

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

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

1.1.3 Workplace exposure

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

1.1.4 Physical properties and other descriptive information {for example}[12]

CAS number:	____	vapor pressure:{kPa (mmHg)}	____
IMIS number:	____	8_{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 OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis"[13]. 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) {Present the test data in a table and in a graph.}
Example:
DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equally descending

[12] This reference was used for most of the physical properties.

[13] Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 9/2005).

increments of analyte, such that the highest sampler loading was ____ µg/sample. This is the amount spiked on a sampler that would produce a detector response 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 slope) for the calculation of the DLOP. Values of__ and ____ were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be ____ µg/sample (____ mg/m^3).

Table 1.2
Detection Limit of the Overall Procedure

mass per sample (ng)	mean intensity (cps)
0	286
0.8	545
1.6	764
2.4	1024
3.6	1443
4.8	2237
6	2572
7.2	3312
8.4	3647
9.6	4354
10.8	4954

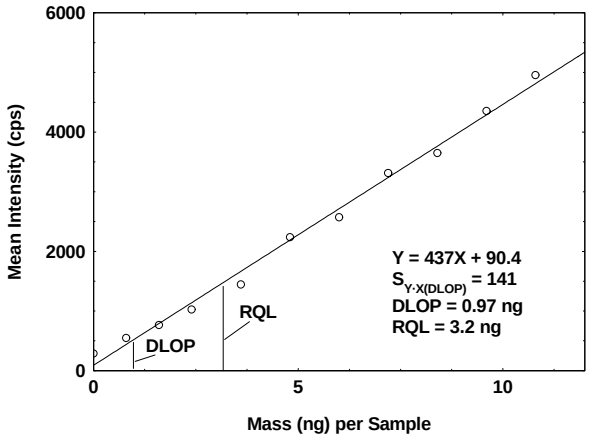

Figure 1.2. Plot of data to determine DLOP/RQL.

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____ µg per sample (____ µg/m^3) Recovery at this concentration is ___%.

2. Sampling Procedure {Refer to cited sections for format in Validated 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 19}

   2.2 Reagents {If no reagents are required, state "None required". Otherwise use the format described in Section 3.2, page 19.}

   2.3 Technique {Section 2.3, page 19}

   2.4 Digestion efficiency

   It is the responsibility of each analytical laboratory to determine digestion efficiency because the chemical form of the analyte under analysis , acid matrix, and laboratory technique may be different than the those listed in this evaluation and could influence analytical results.

.

{example}
Insoluble forms

The digestion efficiencies of insoluble forms of ____ {analyte} were determined by {describe technique} at masses equivalent to 0.5, 1, and 2 times the target concentration (TC). {describe materials and spiking techniques}

Table 2.4.1
Digestion Efficiency for Insoluble Forms of {analyte} from {sampler}

				digestion efficiency (%)				
chemical compound	gravimetric factor	×TC	mass digested (µg)	1	2	3	4	mean
chemical 1	0.683	0.5	17.6	93.5	92.4	89.9	94.5	92.6
		1	35.1	92.9	94.9	95	97.6	95.1
		2	70.3	90.4	96.1	96.3	95.9	94.7
							ave	94.1
chemical 2	0.982	0.5	12.2	99.4	97.6	95.9	100.3	98.3
		1	24.4	98.9	96.9	99.2	98.9	98.5
		2	48.9	98.6	96.1	99.9	97.5	98
							ave	98.3
chemical 3	0.641	0.5	18.7	89.4	88.4	88.1	88.8	88.7
		1	37.4	90.6	85.9	86.6	85.6	87.2
		2	74.9	91.1	89.9	84.1	82.3	86.9
							ave	87.6

The gravimetric factor is the decimal equivalent of the percent of the analyzed element in the tested compound.

Soluble forms

The digestion efficiency of a soluble form of ___ {analyte} from ___ {sampler} was determined by liquid-spiking {sampler} with the analyte diluted with __ {acid matrix} at the RQL, 0.5, 1, and 2 times the target concentration. {describe materials and spiking techniques} The spiked samples were all stored overnight at ambient temperature and then analyzed. The mean digestion efficiency over the working range of 0.5 to 2 times the target concentration is__%.

Table 2.4.2
Digestion Efficiency for Soluble Form of {analyte} from {sampler} (%)

level	mass spiked (µg)	1	2	3	4	mean
RQL	0.32	93.5	90.4	91.1	87.2	90.6
0.5×	19.2	94.7	96.4	97.2	98.7	96.8
1.0×	38.3	92.5	92.7	96.9	97.6	94.9
2.0×	76.6	99.1	99.8	99.6	100.3	99.7

Support pads and cassette wipes

The digestion efficiency of soluble ___ {analyte} from liquid-spiked support pads and from cassette wipes was determined at 10 times the RQL mass {or 0.1× the target concentration, whichever is less} and at 1 times the target concentration. {describe materials and spiking techniques} The samples were stored overnight at ambient temperature and then analyzed. The mean digestion efficiency from support pads was ___%, and it was ___% from cassette wipes.

Table 2.4.3
Digestion Efficiency for {analyte} from Support Pads and from Cassette Wipes (%)

	mass	support pads				mean	cassette wipes				mean
level	spiked (µg)	1	2	3	4		1	2	3	4	
10 times RQL	3.2	93.5	100.2	100	92.9	96.7	100.4	100	96.6	97.7	98.7
1.0 ×	38.3	100.9	103.1	92.2	94.9	97.8	100.4	100.1	98.6	92.2	97.8

Recovery from cassette walls

Recovery of soluble {analyte} from liquid-spiked interior walls of {sampler} was determined by {describe materials and technique} at the 10 times the RQL mass {or 0.1× the target concentration, whichever is less} and 1 times the target concentration. The cassette was spiked and then allowed to stand overnight before wiping the interior walls of the cassette with ___ {wipe medium} following the technique described in Section 3.5.

Table 2.4.4
Recovery of {analyte} from Cassette Walls

	mass spiked	recovery (%)				
level	(µg)	1	2	3	4	mean
10 times RQL	3.2	93.5	89.2	99.1	92.2	93.5
1.0×	38.3	94.6	96.6	99.7	95.9	96.7

2.5 Retention efficiency

{example}
Three ___ {samplers} were spiked with ___ µg (___ mg/m^3) of ___ {analyte} and allowed to equilibrate. An identical sampler was placed in series behind each test sampler as a backup. Next, ___ L {1.25 times the recommended volume} of humid air (___% relative humidity at ___°C) was drawn through the sampling train at____ L/min for___ min. Each section of the front and backup sampler was analyzed separately. The mean retention efficiency was ___%. There was ____% of ___ {analyte} found on the backup sampler.

Table 2.5
Retention Efficiency

	filter (µg)			support pad (µg)			cassette wipe (µg)		
sampler	1	2	3	1	2	3	1	2	3
front	122.6	124.4	118.2	0.9	0.3	0.5	0	0	0
back	0	0	0	0	0	0	0	0	0

2.6 Sample storage

{example}
Nine {samplers} were each spiked with _____ µg (___mg/m^3) of ___ {analyte}. _____ L of air with ___% relative humidity at 22.2 °C was 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, which are not corrected for digestion efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for {Analyte}

time (days)	1	2	3
0	100.2	101.5	98.4
7	99.8	100.8	100.5
14	97.6	101.4	99.1

2.7 Recommended air volume and sampling rate.
{example}
Based on the data collected in this evaluation, __ -L air samples should be collected at a sampling rate of ___ L/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[14]. Avoid skin contact and inhalation of all chemicals.

3.1 Apparatus {Section 3.1, page 22}

3.2 Reagents {Section 3.2, page 22}

3.3 Standard preparation {Section 3.3, page 23}

3.4 Sample preparation {Section 3.4, page 23}

3.5 Analysis {Section 3.5, page 24}

3.6 Interferences (analytical) {Section 3.6, page 25}

3.7 Calculations {Section 3.7, page 25}

4. Recommendations for Further Study

Cite sampling and analytical parameters that should receive more study.

III. Studies - Report studies using the following format:

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

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