EVALUATION GUIDELINES FOR SURFACE SAMPLING METHODS

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

CONTENTS

LIST OF FIGURES

INTRODUCTION

The following evaluation guidelines were developed to provide chemists with a uniform and practical means for evaluating surface sampling methods with regards to sampling media, sampling techniques, and sample preparation for analysis. These guidelines are intended to evaluate only the sampling and other procedures that differ from existing air sampling methods and are not intended to re-evaluate analytical procedures. Samples will be analyzed using procedures found in existing validated OSHA methods or other recognized and accepted analytical procedures. These guidelines specify required laboratory tests, statistical calculations, criteria for acceptance, and provide an outline for written reports. The overall goal of these guidelines is to provide surface sampling methods specifically suited to OSHA needs, whose credibility can be clearly defended with evaluation data.

These guidelines were adapted from the OSHA SLTC “Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis”[1] and “Evaluation Guidelines For Air Sampling Methods Utilizing Spectroscopic Analysis”[2], which set the criteria for SLTC methods evaluation protocol. All of these guidelines are open to examination by the chemists who are using them and any other interested parties. Refinements will be made as needed.

Techniques related to wipe sampling, using direct reading instruments or colorimetric means, might be investigated. When promising, these techniques may be developed into separate validated methods. A direct reading or colorimetric method will be evaluated following pertinent established protocols. Evaluated direct reading or colorimetric methods may become an appendix to the related surface sampling method, or referenced to it in some other manner.

Skin dosimetry techniques may provide desirable information that is not obtainable from skin wipe techniques. When applicable skin dosimetry techniques are available, they may be investigated. If a skin dosimetry method is developed, it should be evaluated according to an appropriate protocol. Such a method may be referenced to the related surface sampling method.

EVALUATION GUIDELINES

I. Preliminary Considerations

[1] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, 1999; www.osha.gov, analytical methods, (accessed May 2000).

[2] Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis (pending)

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

Related surface sampling techniques
Related colorimetric or direct reading instruments
Toxic effects
Exposure levels (i.e., NIOSH recommendations, other government standards, industry standard or recognized industrial hygiene literature)
Workplace exposure (what industries and how many people involved, typical routes of exposure (i.e., ingestion, skin absorption)
Biological monitoring techniques
Physical properties and other descriptive information (see list on page 11)

B. Determine the analyte concentration at which the evaluation will be performed. This value shall be known as the target concentration and will be based on a review of pertinent literature, industry standards, or other government standards when possible.

C. Select an existing analytical method to be used in evaluating the sampling medium and technique. This will usually be the method used to analyze air samples.

D. Select a promising sampling medium with which to begin the evaluation. DURX 670 (10×10 cm polyester and cellulose), Pro-Wipe 880 (20×25 cm polypropylene), Dissolving (Ghost) Wipes (12×12 cm cross linked polyvinyl alcohol) and AlphaWipe (23×23 cm polyester) clean room wipers are typical candidates. In some instances the wipes available from the supplier are too large to be useful and will need to be cut to a smaller size. If this is the case, select a cutting tool that will not introduce significant interferences. Wipe media in a size range of 7×7 cm to 10×10 cm are desirable.

E. Some compounds are highly reactive or unstable and will need to be treated with a stabilizing reagent immediately after sampling. After sampling, the media will be placed in vials containing a solution of the reagent required for these compounds.

F. Charcoal impregnated disks (such as are used in 3M diffusive samplers) will be the first choice for volatile organic solvents. Care must be taken that these media remain hermetically sealed until used and also resealed after sampling, as they will adsorb contaminants from the atmosphere by diffusion.

G. Consideration should be given to the appropriateness of using the surface sampling method for sampling directly from the skin (where appropriate), as well as from other workplace surfaces. Only water or a water-isopropanol mixture are currently recommended wetting solvents for use on skin.[3] No other solvents should be placed in contact with the skin. Liquids with molecular weights greater than 400, with no skin absorption potential, (i.e., mineral oil, corn oil, or polypropylene glycol) may be investigated for use as possible harmless wetting agents.[4] Other analytical methods may be used when an alternate sampling procedure is used.

[3] OSHA Technical Manual, Section II, Chapter 2, 1998; www.osha-slc.gov/dts/osta/otm/otm_ii/otm_ii_2html, (accessed Oct. 2000).

[4] Wester, R.; Hui, X.; Landry, T.; Maibach, H. *In Vivo Evaluation of MDI Skin Decontamination Procedures*; Department of Dermatology, UCSF; Health and Environmental Research Laboratory, The Dow Chemical Co., Presented at the Polyurethanes Expo., 1998

II. Sampling Procedure

The evaluation guidelines address the evaluation of surface sampling media (clean room wipes, glass fiber filters and charcoal impregnated pads) and modifications of the surface sampling method, if necessary, when taking samples directly from skin. Surface sampling techniques for some contaminants may require utilizing reactive reagents and, therefore, may require slight modification for adequate evaluation.

A. Surface sampler removal efficiency

1. The surface sampler removal efficiency refers to the ability of the wipe filter (or other medium) to absorb or otherwise capture surface contaminants when the medium is moved across a surface under firm pressure.

2. An ideal surface is one that is extremely smooth and non-porous. A glass plate or PTFE-coated surface will approach this ideal.

3. The contaminant will be introduced onto a glass or PTFE-coated surface at the target concentration (micrograms per 100 cubic centimeters). This implies that a template or other means of measuring the area of the surface must be used. One technique that has been used is to draw a 10 cm × 10 cm square with a marker on the reverse side of a glass plate.

4. The contaminant need not be uniformly distributed within the confines of the test area. Often the contaminant will have to be in solution with an appropriate solvent and delivered with a micro-syringe or micropipette onto the surface to achieve the desired surface contamination concentration.

5. If the contaminant being tested is delivered in solution onto the surface, allow the solvent to totally evaporate before proceeding. If the contaminant being tested is a volatile organic, be prepared to proceed as rapidly as possible. A portion of the volatile contaminant will be lost due to evaporation. This step will be performed in an area that has proper ventilation (i.e., an exhaust hood).

6. Wear the appropriate protective gloves and change them before each subsequent test.

7. Prepare the sampling medium if required. The sampling medium will be moistened with deionized water for investigating the removal efficiency of the medium for metals or metal compounds from surfaces. Prepare the sampling medium by wetting with deionized water or isopropanol (or mixture) for investigating the removal efficiency of the medium for non-volatile organic compounds. Some compounds may react with water or alcohols. In such cases, other appropriate solvents may need to be selected. Place the medium on the surface and apply firm pressure. To assure that all portions of the test area are wiped, start at an outside edge and progress toward the center making concentric squares of decreasing size. Fold the medium with the contaminant side in and repeat. Fold the medium once again (if possible) with the contaminant side in and place in a labeled vial for analysis.

8. Repeat removal efficiency tests on other prepared glass or PTFE surfaces to measure reproducibility. Six tests will be conducted.

9. Removal efficiency will be deemed adequate if $\geq$50% of the contaminant that was placed on an ideal surface was removed and accounted for by analysis. If removal efficiency is < 50%, try using a different solvent or medium.

B. Extraction efficiency (EE)

1. The EE is the percent of analyte that can be recovered from a spiked surface sampler, and shall be determined at sample loadings that represent concentrations of the RQL, 0.1, 1, and 10 times the target concentration. Always try to maintain a constant EE over the widest range of sample loadings possible through the judicious selection of extraction solvents and extraction techniques.

2. Four samplers shall be liquid spiked (analyte in solution), at each level, with an amount of analyte equivalent to the RQL,and 0.1, 1, and 10 times the target concentration.

3. For non-volatile analytes, sufficient time should be allowed for the evaporation of solvent used in the spiking solution from the sampling media.

4. Extract the spiked samples by adding an appropriate amount of solvent to each vial, and agitate for an adequate time. Transfer an adequate amount of solvent to vials that are appropriate to the analysis. Analyze the samples to determine the amount of recovered analyte. The analytical standards shall be prepared with the same microliter syringe or micropipette used in spiking the media. Two of the samples containing the target concentration amount of analyte shall be resealed immediately after analysis, the punctured septa of the other target concentration samples shall be retained. Use these samples for the test described in Step 7.

5. The EE shall be calculated as follows:

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

where E_E is the extraction efficiency
M_R is the mass of analyte recovered
M_S is the mass of analyte placed on the medium

6. An average extraction efficiency >75% is acceptable but >90% is preferred.

7. The stability of extracted samples will be determined by reanalyzing the target concentration extraction samples one day after the extraction efficiency is determined. Freshly prepared standards must be used in the reanalysis. The results obtained will determine if restrictions must be placed on how soon after extraction the samples must be analyzed. Extracted samples shall be considered stable if the difference between the average EE one day after extraction and the average EE from the initial determinations is not greater than 10%.

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

C. Analytical method recovery (AMR) (digestion, solubility, matrix effects)

1. Tests shall be conducted to ensure complete digestion of the sample media, solubility of the analyte, and to reveal any matrix effects (e.g., viscosity) of the digested sample, as compared to standards.

2. Microwave digestion with the acid matrix used to prepare the standards will be the first choice for sample preparation.

3. Prepare sixteen samples, four samples each spiked on the sampling media at four different concentrations, preferably at the RQL, 0.1, 1 and 10 times the target. The RQL and 0.1 times the target concentrations may be made with dilutions of soluble compounds. The higher spikes are usually done by weighing insoluble forms of the analyte “neat” rather than in solution. It may not be possible to quantitatively weigh the lower concentrations. This technique is used to test the solubility of the analyte in conjunction with the medium digestion.

4. Analyze the sixteen samples by the selected analytical procedure within 24 hours.

5. Perform analysis of the data to determine the Analytical Method Recovery (AMR, also known as analytical bias).

6. The analytical method must be capable of an overall AMR of >75% but >90% is preferred.

7. Hermetically seal two of the four target concentration samples after the initial analysis by installing the vial cap. The remaining two target concentration samples will be stored in the tubes that are

lightly covered with plastic wrap. Determine the stability of the digested samples by reanalyzing these four samples 5-7 days after the Analytical Method Recovery was determined. Use a new set of standards in the reanalysis. The results obtained will determine if restrictions must be placed on how soon after digestion the samples must be analyzed. Consider digested samples stable if the difference between the average results 5-7 days after digestion and the average results from the initial determinations, at the target concentration is not greater than 10% for each sample.

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

D. Effects of storage

1. Storage effects are studied for a series of spiked samples to determine any significant bias due to storage.

2. Twenty-one samples shall be prepared by spiking the analyte at the target concentration onto the sampling medium that has been moistened if required by the sampling procedure.

3. Three samples shall be analyzed on the day they are prepared.

4. Nine samples shall be stored at room temperature in the dark, and the remaining nine samples shall be stored under refrigeration at a temperature of 4-6°C.

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

6. Recovery will be measured from the regression curve obtained by plotting percent recovery (not corrected for EE or AMR) versus days of storage.

7. A drop in recovery of more than 10% shall be considered a significant uncorrectable bias and must be avoided. Also, the recovery (not corrected for EE or AMR) must remain above 75%, during storage. When these conditions are not met, they may be overcome by: use of an alternate sampling medium, use of reduced temperature storage requirements, or use of time requirements for completion of the analysis. The preferable goal is the use a convenient sampler without restrictions on storage conditions, or time requirements for completion of analysis. An attempt to achieve this goal should be made before temperature restrictions or time requirements are used.

E. Interferences to the sampling procedure

1. Interferences to the sampling procedure may manifest themselves in such a manner that collection, retention, recovery or stability of the analyte on the sampler is impaired.[5]

2. If any substance has the ability to alter the final concentration of analyte found, it can be considered an interference. An interference can be a modification of the analyte or analyte signal during a

[5] Care must be taken during the evaluation not to confuse a reactive substance with a potential sampling interference. If a substance on the surface simply reacts with the analyte of interest and converts it to another form, the amount of analyte is diminished. However, the amount of analyte actually available to produce a toxic effect may also be diminished. Therefore, an equivalence rather than an interference is established between that collected on the sampling medium and the surface where both the reactive substance and analyte coexist. Note that the product of the analyte and the reactive substance may be more toxic than the original analyte of interest. Sample stability problems may be enhanced by co-contaminants. Unstable contaminants that could breakdown to form the analyte of interest would be a positive interference.

specific portion of the analysis, a reaction with the medium, or an alteration of the collection efficiency.

3. Alternative sampling media may have to be used if a serious sampling interference is noted and if the interference can be considered a commonly found substance when sampling for the analyte of interest.

4. The effects of suspected interferences (if any) shall be determined by analyzing three samples that have been spiked with the analyte at the target concentration and with the suspected interference also added at an appropriate concentration. The concentration of any added interferant is determined in the same manner as the analyte target level was selected (Section I. B.).

5. Tests shall be conducted to determine interference due to contamination of the prepared media. Two blank wipe sampling media are moistened with the recommended solvent, placed in vials and analyzed. Two additional samples shall be prepared by wiping the same type of surface that was used for the removal efficiency test with media (moistened with reagent, if applicable). The surfaces shall not be spiked with analyte. The samples are analyzed.

III. Overall Procedure

A. Detection Limit of the Overall Procedure

Detection limits, in general, are defined as the amounts (or concentrations) of analyte that give a response (Y_{DL}) that is significantly different (three standard deviations (S_{BM})) from the response (Y_{BM}) of an extracted (or digested) medium blank.

$$Y_{DL} - Y_{BM} = 3S_{BM} \quad (1)$$

where S_{BM} is the standard deviation of the medium blank
Y_{DL} is the response at the detection limit
Y_{BM} is the response of the medium blank

1. Spectroscopic Methods

The response of a digested blank medium, and also its standard deviation, is usually measurable using spectroscopic methods. The response of the detection limit can then be determined as three standard deviations greater than the response of the digested blank medium. Analyze six digested blank media, and determine the standard deviation of the response. Use equation one to calculate the response of the detection limit. Calculate the detection limit and report the DLOP in the method as concentration or mass per sample.

2. Chromatographic Methods

The direct measurement of Y_{BM} and S_{BM} in chromatographic methods is typically inconvenient and difficult because Y_{BM} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of spiked samplers whose responses are in the vicinity of the response of the reagent blank. The regression curve obtained for a plot of instrument versus concentration of analyte will usually be linear. If it is clearly nonlinear, refer to Burkhart[6] for alternate calculations. Assuming S_{BM} and the precision of data about the curve are similar, the standard error of estimate for the regression curve can be substituted for S_{BM} in the above equation. The standard error of estimate of a line is the mathematical equivalent of the standard deviation for tabulated data. The following calculations derive a formula for the detection limit:

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

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

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

Y_{obs} is the observed response
Y_{est} is the estimated response from the regression curve
n is the total number of data points
k equals 2 for a linear regression

At point Y_{DL} on the regression curve

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

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

therefore

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

Substituting for Y_{DL} from Equation 1 gives

$$L_D = \frac{3S_{Y \cdot X}}{A} \quad (2)$$

Use the following procedure to assure that the concentrations of spiked samplers 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. For chromatographic methods, make the estimate near the elution time of the analyte.

b. Prepare five spiked samplers, in equally spaced intervals, with the highest spiked sampler producing a signal about ten times the background response.

c. Analyze the five spiked samplers and one blank sampler.

d. Determine the regression line and the standard estimate of error from the data by plotting response versus mass introduced into the instrument.

e. Calculate the DLOP using equation 2. Report the DLOP in the method as concentration or mass per sample.

B. Reliable Quantitation Limit (RQL)

1. Consider the RQL as the lower limit for precise analytical measurements. For spectroscopic methods using equation 1, the RQL is determined as ten standard deviations greater than the response of the medium blank. A sampler spiked at this level will be analyzed and determined to be the RQL providing the recovery from the sampler is 100 ± 25% of its theoretical value. If the recovery from this sampler is not 100 ± 25% of its theoretical value, use the chromatographic methods procedure (III. A. 2.) to determine the RQL. For chromatographic methods, employing the regression line data used to calculate the DLOP, the RQL is determined with the following formula, providing the recovery from the sampler which is closest to the RQL, is 100 ± 25% of its theoretical value.

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

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

If the recovery from the closest sampler is not 100 ± 25% of its theoretical value, then the RQL will be equal to the lowest spiked concentration that is 100 ± 25% of its theoretical value. Determine this from a plot of recovery versus mass, 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 or concentration.

3. Generate a plot of detector response of the RQL for inclusion in the method.

C. Sampling reproducibility

Prepare six surfaces of same type that was used for the removal efficiency test , by spiking them with the analyte at the target level as described in Section II A. A chemist, other than the one developing the surface sampling method, will conduct sampling on the surfaces using the technique as described in Section II A. The samples are analyzed. This test is repeated again with a third chemist performing the sampling. The results are a measure of the reproducibility of the sampling procedure under laboratory conditions.

D. Analytical reproducibility

Prepare six samples at the target concentration in the same manner as the extraction efficiency test (or in the same manner as the digestion, solubility, matrix effects test, if appropriate). Submit them to the SLTC for analysis. Include a draft copy of the procedure for analyst instructions. Relying on the draft copy for instructions, 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.

E. Qualitative analysis

The ability to confirm the presence or concentration of an analyte by a technique that is different than the one used to perform the analysis is desirable. There is a higher degree of confidence in the accuracy of the results of critical samples when these results can be confirmed by some other means. Alternate analysis to detect the presence of the analyte of interest will be identified (i.e., GC/MS, LC/MS, ICP/MS, CE) . Where the techniques and instruments are available, an analysis of the analyte will be performed. Spectrum and/or other figures and data are prepared for inclusion in the method.

PREPARATION OF WRITTEN REPORTS

Prepare each report in accordance with the following format:

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

All evaluated methods will have the following statement on the cover page:

"Evaluated method. This method has been subjected to the established evaluation procedures of {appropriate team name} team."

Methods numbered W4000's are reserved for surface contamination methods.

Page Numbering - The numbering of the pages begins with the cover page. Number pages at the bottom, centered, stating the page number of the total number of pages (i.e., 5 of 40).

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

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

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

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

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

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

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

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

{ANALYTE}
{as listed in CFR or ACGIH}

Method number: W4xxx

Target concentration: ____ µg/100 cm^2

Procedure: Samples are collected by using firm hand pressure to move the {type of collection media} across the surface of interest. Samples are extracted {digested} with ____ and analyzed by ____ using a ____ detector.

Reliable quantitation limit: ____ µg

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

____ {month year} {Chemist} ____

{Team}
{SLTC Division}
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1. General Discussion

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

1.1 Background

1.1.1 History

{Answer questions as to why this method is needed. 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 {Select information with a skin exposure emphasis. Include references to recognized biological monitoring techniques, if available.}(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 skin 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. Include available skin penetration information (permeability constants, absorption rates and dermal LD_{50} for theoretical, animal and human data) when applicable. Other properties may be listed.

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

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Surface Sampling Methods".[7] The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte surface concentrations throughout this method are based on the evaluated sampling area and analytical concentration parameters.

[7] Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001.

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure

The detection limit of the overall procedure is ____{mass} per sample. This is the smallest amount of {analyte} spiked on the wipe sampler that will give a detector a response that is significantly different from the response of the wipe sampler blank. (Section 4.1)

1.2.2 Reliable quantitation limit

The reliable quantitation limit is ____{mass} per sample. This is the amount of {analyte} spiked on the wipe sampler that will give a detector a response that is considered the lower limit for a precise quantitative measurement. (Section 4.1)

1.2.3 Recovery

The recovery of {analyte} from spiked samples used in a ____-day storage test remained above ____ % {the lowest point on the regression curve of Figure 4.2.1} 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 4.2)

1.2.4 Surface sampler removal efficiency

The removal efficiency of {name of the media} for {analyte} is ____%. This was the percentage of {analyte} that was removed from {specify type of surface that was used (i.e., a glass plate surface)} that was spiked at the target concentration. (Section 4.3)

1.2.5 Sampling reproducibility and analytical reproducibility

Six {state the type of surface, i.e., PTFE-coated} surfaces were spiked at the target concentration. A chemist, other than the one developing the method, conducted sampling on the {type of surface} surfaces as described in Section 2. The test was repeated with another chemist performing the sampling. The first chemist was able to achieve a removal efficiency of ____%. The second chemist was able to achieve a removal efficiency of ____%. (Section 4.5.1)

Six samples spiked at the target concentration by liquid injection were submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after ____ days of storage at ____ °C. The average analytical result was ____% of theoretical. (Section 4.5.2)

2. Sampling Procedure {When an alternate sampling procedure is used for taking samples from skin, include that information in 2.1-2.3}

All safety practices that apply to the work area being sampled should be followed. The sampling should be conducted 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.}

Samples are collected with {description of the wipe sampling media including wetting reagent if any}.

Samples are collected using firm hand pressure to wipe the sampling medium across a surface. Wear a clean pair of gloves for each sample. The gloves selected are to be resistant to penetration of the chemical being sampled and any other chemicals expected to be present.

Labeled vials {specify appropriate type}, one for each sample.

2.2 Reagents

Use the format described in Section 3.2.

2.3 Technique {Describe steps involved in media shipment, sample collection, preparation, and sample shipment.}
Example:
The media are received from the supplier in large packages, often containing 1200 wipes per package. Wear clean gloves and remove a sufficient number of wipes to perform the sampling. Remember to include extra wipes to serve as blanks. {In some instances the wipes available from the supplier are too large to be useful and will need to be cut to a smaller size. If this is the case, select a cutting tool that will not introduce significant interferences. Wipe media in a size range of 7 ×7 cm to 10 ×10 cm are desirable. Include any information regarding cutting the media to a useful size here, if pertinent.} Place the wipes in a 5"×7" recloseable polyethylene zipper bag. Place the remaining wipes in a large recloseable polyethylene zipper bag. The selected wipes can now be shipped or taken to the workplace for sampling.

Prepare the deionized water {or other reagents} that may be needed to moisten the wipe prior to sampling. Also prepare any derivatizing or stabilizing reagents that may be needed to be combined with the wipe sample after sampling.

Prepare a sufficient number of vials, each labeled with a unique number, for the projected sampling needs. It may be convenient to preload the vials with the appropriate media if no stabilizing reagent is being used. Wear clean gloves when handling the media. Do not wear powdered gloves.

Prepare a diagram of the area or rooms to be wipe sampled along with the locations of key surfaces.

Wear a new pair of clean gloves for each sample to prevent contamination of future samples as well as oneself. The gloves selected are to be resistant to penetration of the chemical being sampled and any other chemicals expected to be present. {__ type} gloves are recommended for sampling {analyte} based on a review of glove manufacturer's chemical resistivity and degradation information.

Record the sample vial number and the location where the sample is taken. Withdraw the medium from the vial with your fingers or clean tweezers. Moisten the medium with ____. {If a damp wipe sample is required.}

Depending on the purpose of the sample, it may be useful to determine the surface loading of the contamination (e.g., in micrograms of analyte per area). For these samples, it is necessary to record the area of the surface wiped (e.g., 100 cm^2). This would not be necessary for samples taken to simply show the presence of the contaminant.

Before taking any wipe samples from the skin, explain why you want the sample and ask the employee about possible skin allergies to the sampling medium or wetting solution. Employees may elect not to allow sampling from their skin.[8]

Firm pressure should be applied when wiping. Start at the outside edge and progress toward the center making concentric squares of decreasing size. Fold the medium with the contaminant side inward and repeat.

Without allowing the medium to come into contact with any other surface, fold the medium with the exposed side inward. Place the medium in a sample vial, cap and place a corresponding number at the sample location on the diagram. Include notes with the sketch giving any further description

[8] OSHA Technical Manual, Section II, Chapter 2, 1998; www.osha-slc.gov/dts/osta/otm/otm_ii/otm_ii_2html, (acessed Oct. 2000).

that may prove useful when evaluating the sample results (e.g., a description of the surface sampled, such as: pencil, doorknob, safety glasses, lunch table, inside respirator, employee's forehead or right or left hand, employees names, etc.).

{If this sampling method for this analyte requires the addition of a solvent or stabilizing reagent after sampling, include the information here.}

Submit at least one blank wipe medium, treated in the same fashion as the wipe samples, but without wiping.

Record sample location, employees names, surface area (if pertinent), work description, PPE, and any other necessary information, along with any potential interferences on the OSHA-91A form.

Submit the samples to the OSHA Salt Lake Technical Center together with OSHA-91A forms as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the surface samples.

2.4 Extraction efficiency {or Analytical Method Recovery, as the case may be} (Section 4.4)

It is the responsibility of each analytical laboratory to determine the extraction efficiency {or analytical method recovery} because the wipe sampling media, internal standard, reagents and laboratory techniques may be different than the those listed in this evaluation and influence the results.

2.4.1 The mean extraction efficiency {or analytical method recovery} for {analyte} from {name of wipe sampling media} over the range of {RQL or 0.1} to 10 times the target concentration (____ to ____ milligrams per sample) was ____%.

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

2.5 Interferences, sampling

Suspected interferences should be reported to the laboratory with submitted samples. {Include any information and observations here, regarding suspected interferences that have been tested.} (Section 4.6)

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan[9]. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure.

Analyze the samples using the analytical procedure in Method number ___ [10].{When possible, use an existing validated analytical procedure.}{If an alternate analytical method is used for samples taken from the skin, include that information here.}

3.1 Apparatus {Provide general descriptions of the required equipment. Follow each general description with a specific description of equipment actually used in the evaluation.}
Example:

3.1.1 High performance liquid chromatograph equipped with a fluorescence (FL) or an ultraviolet (UV) detector, manual or automatic injector, gradient flow programmer and chart recorder. A Waters M-6000A pump, Waters WISP 710B autosampler, Waters 660 solvent programmer, Schoeffel 970 FL detector, Waters 440 UV detector, and a Houston dual pen recorder were used in this evaluation.

3.1.2 LC column capable of separating PAHs from any interferences. A 25-cm × 4.6-mm i.d. DuPont Zorbax ODS (6 µm) column was used during this evaluation.

3.1.3 An electronic integrator, or some other suitable method of measuring detector response.

3.1.4 Vials, 4-mL with PTFE-lined caps.

3.1.5 Volumetric flasks, pipets, and syringes.

3.2 Reagents {Provide general descriptions of the required reagents. Follow each general description with a description of the specific reagent actually used in the evaluation.}
Example:

3.2.1 Acetonitrile (ACN), HPLC grade, lot, manufacturer, manufacturer location.

3.2.2 Water, HPLC grade. A Millipore Milli-Q system was used to prepare the water for this evaluation.

3.2.3 Benzene, HPLC grade, {etc.}.

3.3 Standard preparation {Describe preparation of standards in general and give an example.}
Example:

3.3.1 A stock standard solution is prepared by dissolving the selected PAHs in benzene. All dilutions of the stock solutions are made with benzene to arrive at the working range.

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

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

---

[9] Occupational Exposure to Chemicals in Laboratories. Code of Federal Regulations, Part 1910.1450, Tittle 29, 1998; http://www.osha-slc.gov/OshStd_data_1910_1450_APP_A.html, standards, (accessed May 2000).

[10]{Title of referenced method, number, date, web address and date accessed} (Example: Selected Polynuclear Aromatic Hydrocarbons (PAHs), Method 58,1986; http://www.osha-slc.gov/dts/ sltc /methods/organic/org058/org058.html, (accessed May 2000)).

3.4.1 The surface samples should be received in vials, if not, place the samples into scintillation vials. Pipet 4.0 mL of benzene into each vial and immediately seal the vials with polytetrafluoroethylene-lined caps.

3.4.2 Shake the vials vigorously several times during the 60 min extraction time.

3.4.3 Etc.

3.5 Analysis

Example:

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

Example:

HPLC conditions

column:	25-cm × 4.6-mm i.d. stainless steel column packed with 6-µm DuPont Zorbax ODS
mobile phase:	85:15 ACN/water (v/v)
flow rate:	1.0 mL/min for 5 min, Curve 10 (flow program) for 5 min to 1.5 mL/min, then hold for 10 min
FL detector:	254 nm excitation 370 nm emission
UV detector:	254 nm
injection size:	10 µL
retention time:	7-15 min
chromatogram:	Figure 3.5.1

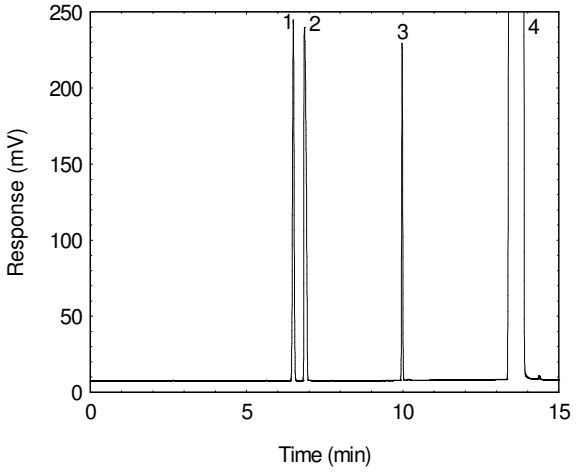

Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended conditions. (1 - Compound A; 2 - Compound B; 3 - Compound C; 4 - Compound D)

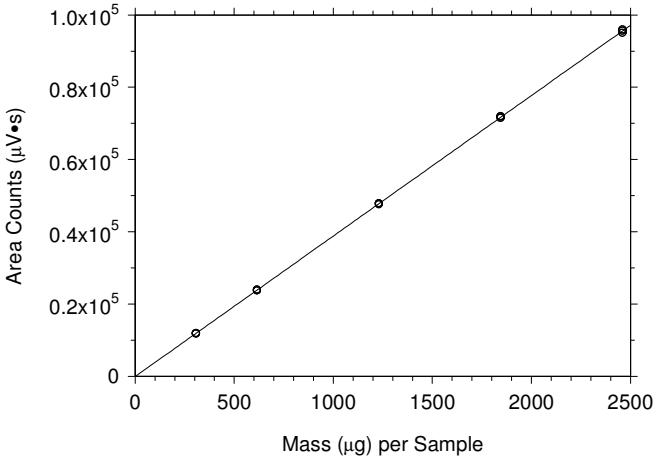

Figure 3.5.2. Calibration curve of {analyte}. (Y = 38.89X - 65.50)

3.5.2 An external standard (ESTD) calibration procedure is used to prepare a calibration curve using at least 2 stock standards from which dilutions are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards.

3.6 Interferences (analytical)
Example:

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

3.6.2 When necessary, the identity of an analyte peak may be confirmed with additional analytical data. Analysis by an alternate HPLC column, absorbance response ratioing, and mass spectrometry are additional means of identification (Section 4.8).

3.7 Calculations
Example:
The amount of {analyte} per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This amount is then adjusted by subtracting the amount (if any) found on the blank and corrected for extraction efficiency using the following formula.

$$M_S = \frac{M - M_B}{E_E}$$

where
M_S is the mass recovered from the sampled surface (µg)
M is micrograms per sample
M_B is the mass found on the blank (µg)
E_E is extraction efficiency, in decimal form

This amount may be expressed as micrograms {analyte} per 100 cm^2 if the surface area that was sampled was provided, by using the following formula.

$$C_S = 100\ \frac{M_S}{S}$$

where
C_S is the (µg) of {analyte} per 100 cm^2
M_S is the mass on the sampled surface (µg)
S is the surface area sampled (cm^2)
100 cm^2 is one hundred cubic centimeters

The surface that was sampled may be less ideal (more porous, less smooth) than the surface that was used to evaluate the removal efficiency of the sampling media. In this circumstance, the media will remove the surface contaminant less effectively. There may be significant amounts of contaminant remaining on the surface after sampling. Nevertheless, the amount found in the sample indicates that at least this amount of {analyte} was present on the surface.

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

General background information about the determination of detection limits and reproducibility of the overall procedure is found in the "Evaluation Guidelines for Surface Sampling Methods".[11] The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

4.1 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. The example is representative of chromatographic analysis. The DLOP and RQL of spectroscopic analysis may be determined by calculations based on direct response measurements of digested media blanks. If this is the case, present the measurements and calculations here.}
Example:
The DLOP is measured as mass per sample. Five samplers were spiked with equal descending increments

Table 4.1
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
0.841	178
1.68	375
2.52	696
3.36	810
4.21	1150

[11]Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001.

of analyte, such that the highest sampler loading was ____ µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers, and a 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.

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. Recovery at this concentration is ____%.

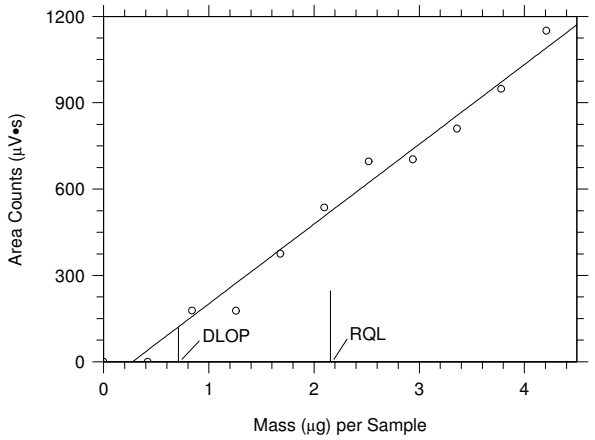

Figure 4.1.1. Plot of data to determine the DLOP/RQL. (Y = 277X - 75.8)

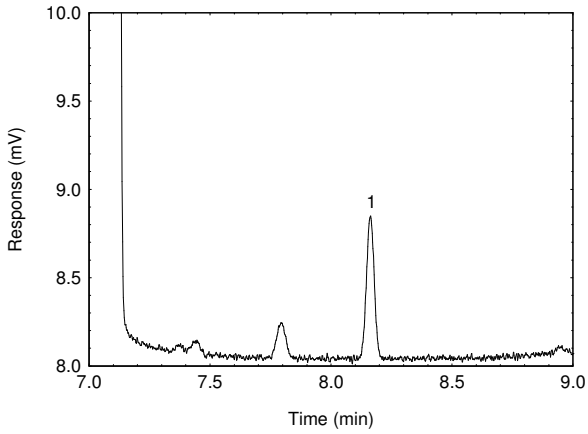

Figure 4.1.2. Chromatogram of the RQL. 1 - {Analyte}

4.2 Storage tests {Describe the storage tests, including preparation of samples.}

Storage samples were prepared by spiking media with {analyte}. The medium was spiked with the target concentration of {analyte} and allowed to dry. {If the analyte is a non-volatile compound, delivered to the surface in solution.} Twenty-one storage samples were prepared. Three samples were analyzed on the day prepared. Nine of the samples were stored at reduced temperature (4 ℃) and the other nine were stored in a closed drawer at ambient temperature (about 22 ℃). At 5-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency.

Table 4.2
Storage Test for {Analyte}

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	103.5	101.6	101.9	103.5	101.6	101.9
5	99.6	100.5	95.8	99.3	99.4	101.8
10	95.6	96.6	99.1	98.9	99.6	97.5
15	96.5	94.5	98.8	99.3	99.5	99.1

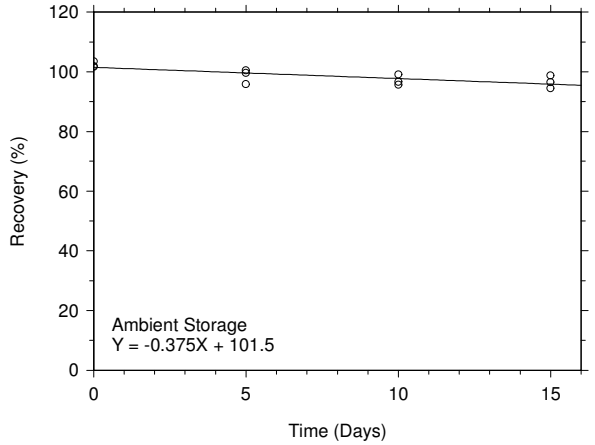

Figure 4.2.1. Ambient storage test for {analyte}

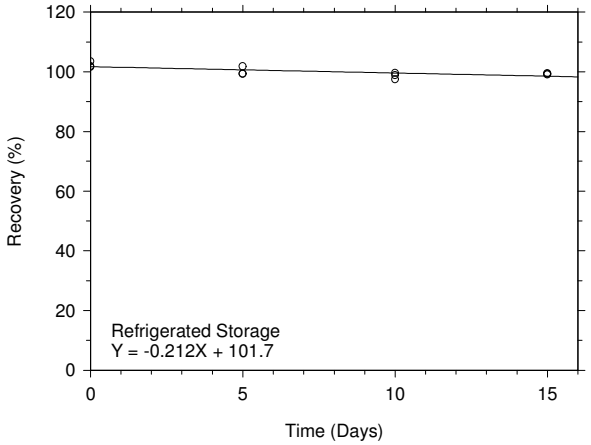

Figure 4.2.2. Refrigerated storage test for {analyte}

4.3 Sampler Removal Efficiency

Six surfaces were spiked at the target concentration of {analyte}, ____ µg /100 cm^2. Samples were collected from each surface using the technique described in Section 2.3 and analyzed. The results are shown in Table 4.3.

Table 4.3
Sampler Removal Efficiency
Data for {Analyte} on {Surface Sampler}

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
420.6	388.6	92.4
420.6	395.5	94.0
420.6	393.2	93.5
420.6	379.6	90.3
420.6	379.0	90.1
420.6	406.1	96.6

4.4 Extraction efficiency {or Analytical method recovery} and stability of extracted {digested} samples

The extraction efficiency is dependent on the extraction solvent as well as the internal standard. Other extraction solvents or internal standards may be used provided that the new extraction solution or internal standard is tested. The new extraction solvent or internal standard should be tested as described below. {The analytical method recovery is dependent on the acid used to digest the media and dissolve the analyte as well as physical characteristics, such as viscosity, of the resulting digestion matrix. Other acids may be used provided that standards are prepared in the same acids and concentrations as the prepared samples. The analytical method recovery of the new acid digestion procedures should be tested as described below.}

4.4.1 Extraction efficiency {Analytical method recovery}

The extraction efficiencies {analytical method recoveries} of {analyte} were determined by liquid-spiking {surface sampler} with the analyte at the RQL to 10 times the target concentration {0.1 to10 times the target concentration for acid digested metals} These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency {analytical method recovery} over the working range of the RQL {0.1 for metals} to 10 times the target concentration is ____%.

Table 4.4.1
Extraction Efficiency {Analytical Method Recovery} of {Analyte} from {Surface Sampler}

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	2	99.8	97.5	99.6	101.4	99.6
0.1	5	103.5	99.5	100.6	96.6	100.1
1.0	50	95.8	92.8	96.0	96.4	95.3
10.0	500	96.5	94.5	97.3	89.4	94.4

4.4.2 Stability of extracted {digested} samples

The stability of extracted {digested} samples was investigated by reanalyzing the four target concentration samples 24 h after initial analysis. {5-7 days for Acid digested metal samples} After the original analysis was performed,two of the vials were recapped with new septa, while the remaining two retained their punctured septa. {acid digested samples are stored in their auto sampler tubes, two are capped and hermetically sealed, the others lightly covered with plastic wrap} The samples were reanalyzed with fresh standards. The average percent change was ____% for the samples that were resealed and ____% for those that were stored (in their auto sampler tubes, lightly covered) with their septa punctured. (The septum was punctured ____ times for each injection.)

Table 4.4.2
Stability of Extracted {Digested} Samples for {Analyte}

punctured septa replaced {sealed}			punctured septa retained {lightly covered}		
initial (%)	after one day {5 days} (%)	difference (%)	initial (%)	after one day {5 days} (%)	difference (%)
95.8	100.3	4.7	96.0	104.3	8.6
92.8	96.5	4.0	96.4	104.2	8.1

4.5 Reproducibility

4.5.1 {Describe sampling reproducibility test and present data in Tables 4.5.1.1 and 4.5.1.2. Specify that the "amount found" is corrected for extraction efficiency.}
Example:
Six {type of surface} were spiked at the target level. A chemist, other than the one developing the method, conducted the surface sampling following the procedure described in the sampling procedure (Section 2.). The test was repeated with a third chemist performing the sampling. Sample results were corrected for extraction efficiency.

Table 4.5.1.1
Sampling Reproducibility
Data for {Analyte} on {Surface Sampler}

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
420.6	388.6	92.4
420.6	395.5	94.0
420.6	393.2	93.5
420.6	379.6	90.3
420.6	379.0	90.1
420.6	406.1	96.6

Table 4.5.1.2
Sampling Reproducibility
Data for {Analyte} on {Surface Sampler}

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
420.6	388.6	92.4
420.6	395.5	94.0
420.6	393.2	93.5
420.6	379.6	90.3
420.6	379.0	90.1
420.6	406.1	96.6

4.5.2 {Describe analytical reproducibility test and present data in Tables 4.5.2. Specify that the "amount found" is corrected for extraction efficiency.}
Example:
Six samples were prepared by spiking media in the same manner that was used in the preparation of samples for the storage study. The samples were submitted to the OSHA SLTC for analysis. The samples were analyzed after being stored for ____ days at ____ ℃. Sample results were corrected for extraction efficiency.

Table 4.5.2
Analytical Reproducibility
Data for {Analyte} on {Surface Sampler}

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
420.6	388.6	92.4
420.6	395.5	94.0
420.6	393.2	93.5
420.6	379.6	90.3
420.6	379.0	90.1
420.6	406.1	96.6

4.6 Interferences (sampling)

4.6.1 Media

Tests were conducted to determine interference due to contamination of the prepared media. Two blank wipe sampling media were moistened with the recommended solvent, placed in vials and analyzed. Two samples were prepared by wiping same type of surface that was used for the removal efficiency test with media moistened with {reagent} if applicable. The surfaces were not spiked with analyte. The samples were placed in vials and analyzed. The results are shown in Table 4.6.1.

Table 4.6.1
Interference to the Analysis of {Analyte}
from the Media or Surface (µg found)

sample	1	2	mean
blank	0.000	0.010	0.005
from surface	0.000	0.020	0.010

4.6.2 Tests were conducted to determine the effects of suspected interferences (if any). Three samplers were spiked with ____ µg {analyte} and also ____ µg {suspected interfering compound}. The samples were analyzed and the results are shown in Table 4.6.2.

Table 4.6.2
Interference to the Analysis of {Analyte},with {interferant compound} added.
(µg found)

amount of analyte spiked	1	2	3	mean
50.0 µg	51.1	49.7	50.0	50.2

4.7 Qualitative analysis

{Present alternate chromatographic and GC/MS conditions that will aid in confirming the identity of the analyte (or derivative) peak. GC/MS or LC/MS may provide the most conclusive identification and should be addressed in all cases, even if this amounts to an explanation why it is not possible or not available. Peak ratios and analysis with alternate detectors may be useful. The format for a mass spectrum is shown in Figure 4.7.}

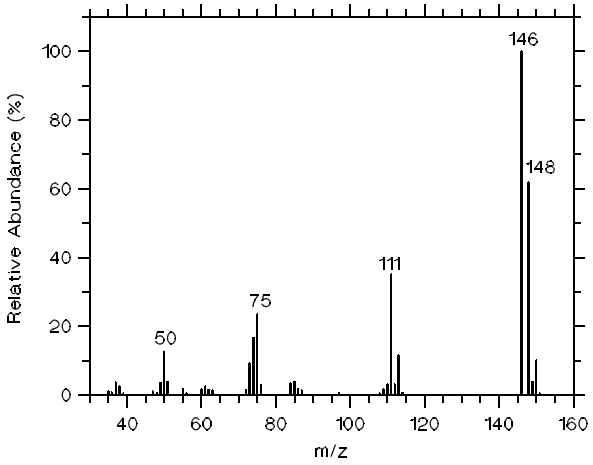

Figure 4.7. Mass spectrum of {analyte}.