

PART B - CHAPTER 8

INHALATION EXPOSURE

GUIDELINE 875.2500	B8-1
8.1 INTRODUCTION	B8-1
8.2 SAMPLE COLLECTION	B8-1
8.2.1 <u>Test Substance</u>	B8-1
8.2.2 <u>Timing of Application</u>	B8-1
8.2.3 <u>Pesticide Application Rate and Frequency</u>	B8-2
8.2.4 <u>Sampling Parameters</u>	B8-2
8.2.5 <u>Monitoring Selection Criteria</u>	B8-3
8.2.5.1 <i>General Considerations</i>	B8-3
8.2.5.2 <i>Method Sensitivity</i>	B8-5
8.2.5.3 <i>Sampling Pump Flow Rates</i>	B8-5
8.2.5.4 <i>Method Validation Considerations</i>	B8-6
8.2.5.5 <i>Study Validation Requirements</i>	B8-6
8.2.5.6 <i>Novel Sampling and Analysis Methodologies</i>	B8-8
8.2.6 <u>Sampling Techniques</u>	B8-8
8.2.6.1 <i>Personal vs. Area Monitoring Techniques</i>	B8-8
8.2.6.2 <i>General Considerations</i>	B8-10
8.2.6.3 <i>Monitoring Equipment</i>	B8-12
8.2.6.4 <i>Sampling Media</i>	B8-15
8.2.6.5 <i>Small Scale Environmental Chambers</i>	B8-24
8.3 SAMPLE STORAGE	B8-25
8.4 SAMPLE ANALYSIS	B8-25
8.5 CALCULATIONS	B8-25
8.6 DATA PRESENTATION	B8-25

REFERENCES FOR PART B, CHAPTER 8	B8-27
----------------------------------	-------

PART B - CHAPTER 8
INHALATION EXPOSURE
GUIDELINE 875.2500

8.1 INTRODUCTION

This Guideline provides a description of the techniques that can be used to measure inhalation exposure and ambient air concentrations of pesticides. The data obtained are needed to assess risks associated with the inhalation of airborne particulates containing pesticide residues and gases/vapors resulting from the previous application of a pesticide product (i.e., to assess postapplication inhalation exposures).

8.2 SAMPLE COLLECTION

This section describes the sample collection procedures required for developing inhalation exposure data. See Part B, Chapter 2 - Study Design, for more details pertaining to protocol development and study conduct.

8.2.1 Test Substance

As stated at 40 CFR 158.390, the test substance to be used for inhalation exposure measurements must be a typical end-use product. Where metabolites, breakdown components, or contaminants of pesticide end-use products pose a potential toxicological concern, investigators may need to consider sampling for them on a case-by-case basis.

8.2.2 Timing of Application

Sample collection should be conducted during the intended use season or under climatic conditions that are essentially identical to those encountered during the intended use season. Weather forecasts should be studied to avoid initiating the testing immediately (e.g., within 24 hours) before a precipitation event. For further information on climatological consideration, see Part B, Chapter 2 - Study Design.

8.2.3 Pesticide Application Rate and Frequency

Generally, the end-use product chosen for the study should be applied at the maximum rate specified on the label. Monitoring at more than one rate will provide additional information about the relationship between the application rates and exposure concentrations. Also, testing at a lower rate may prove to be beneficial in the event that the data from use of the product at the maximum application rate results in an unacceptable risk.

Where multiple applications are recommended, the minimum time interval between applications should be used. Also, the potential accumulation of residues from multiple applications should be considered. The application method and equipment typical for the selected test substance should be used.

8.2.4 Sampling Parameters

Sampling parameters should be based on the following criteria:

- A sufficient number of replicates should be generated to address the exposure issues associated with each population of interest. In general, each study should include a minimum of 15 replicates per activity. Where possible, these replicates should be distributed as follows: 5 replicates (e.g., individuals) on each of three monitoring periods (e.g., "n" days after application). Investigators must be flexible concerning the number and distribution (e.g., locations and intervals after application) of the monitoring replicates. Because the aforementioned guideline cannot be expected to apply to all potential scenarios, the Agency requires investigators to submit protocols for review purposes prior to the inception of a study.
- The exposure monitoring period must be of sufficient duration, and the analytical method must have adequate sensitivity to ensure that each monitored activity has been sufficiently evaluated. Minimum sample volume and analytical quantification limits should be reflective of appropriate toxicology endpoints. (See Part C - QA/QC for a discussion of determining appropriate limits of quantification). The activity must be well defined and be representative of typical practice. Most postapplication activities range from 4 hours (e.g., homeowner lawn and garden maintenance) to 8 hours (e.g., harvesting strawberries). Thus, a representative monitoring duration based on typical activities is recommended for each replicate. Justifications for determining monitoring durations should be provided in the study protocol.
- Inhalation exposure studies must be carried out concurrently with dermal exposure and transferable residue studies. Refer to the appropriate chapters for guidance concerning the types and numbers of transferable residue and dermal samples that are appropriate.
- The selected sites and seasonal timing of monitoring must be appropriate to the activity.

- When appropriate to conduct ambient (i.e., area or stationary) monitoring in conjunction with, or in lieu of, personal monitoring, each study should contain sufficient samples to characterize the likely range of possible exposure concentrations resulting from the use of the chemical of interest. Guidance on sampler location is included in this chapter. Additionally, samples should be collected to ensure that the reentry exposure scenario can be addressed with the resulting data (e.g., sampling should be completed concurrently with harvesting activity).
- Along with gas and vapor phase monitoring, total (i.e., rather than respirable) airborne particulate levels should be monitored in all scenarios unless there is justification for doing otherwise. Typically, the Agency is concerned with quantifying total airborne concentrations of materials as opposed to quantifying only inspirable or respirable fractions of airborne contaminants because of the potential for the absorption of chemical residues via the upper respiratory tract and/or through the gastrointestinal tract. The relationship between particle sizes and inhalation exposure is illustrated in Figure B8-1.

8.2.5 Monitoring Selection Criteria

8.2.5.1 *General Considerations*

Selecting the proper method for monitoring inhalation exposure depends on several factors including, but not limited to, the following: (1) typical pesticide usage practices; (2) the range of air concentration anticipated; (3) minimum quantification limit required; (4) the anticipated durability of the devices/dosimeters under consideration; (5) the physical and chemical properties of the pesticide (e.g., stability and vapor pressure); (6) the anticipated physical state (e.g., gas, aerosol, particulate) of the airborne contaminant; and (7) sampling device flow rate (as applicable).

The Agency recognizes that there are shortcomings inherent with the use of almost any monitoring technology. Understanding the conditions under which the pesticide is used and the practices associated with its use will contribute greatly to the investigator choosing the appropriate monitoring method. A principal concern related to the monitoring of airborne pesticide residues is the anticipated physical nature in the ambient environment after the application of a pesticide product.

Investigators must select the equipment and sample matrices that are to be used in any study by careful consideration of the general criteria described above and considering both the positive and negative attributes of each type of sampling equipment/matrix.

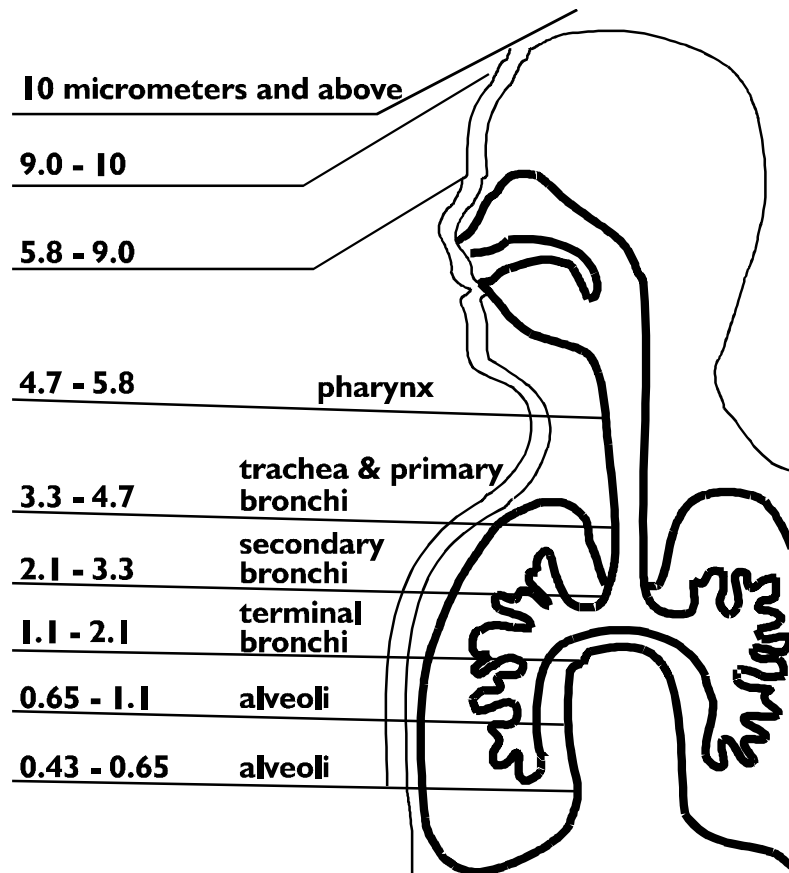


Figure B8-1. Relationship Between Particle Size and Deposition in the Respiratory Tract

Source: Graseby Anderson, 1985.

8.2.5.2 Method Sensitivity

The investigator will need to anticipate what the maximum and minimum expected concentrations may be in the field over the time period of interest, whether levels are likely to vary significantly during the sampling period, and whether the chosen methodology can be expected to be adequate to deliver the required information under actual field conditions, given the nature of the contaminants being monitored. For more information on the selection of maximum detection limits, see Part C - QA/QC.

Additional guidance is available from several sources on the health-based limits associated with various chemicals. These values may be useful in determining the range in which detection/ quantification limits need to be set. For an occupational exposure study, it is appropriate to consult: (1) The Occupational Safety and Health Administration's (OSHA's) Permissible Exposure Limits (see 29 CFR 1910.1000) for legal limits; (2) American Conference for Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) (ACGIH, 1996); and (3) the National Institute of Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards (NIOSH, 1994b). The NIOSH Recommended Exposure Limits are guidelines only and are not legally enforceable. Although ACGIH TLVs do not have the force of law either, they are peer-reviewed, well-accepted, and widely used guidelines. OSHA's ongoing 1970 PELs were in fact adopted from the ACGIH TLVs of that day. A complete discussion of the derivation of the TLVs is available in ACGIH (1991).

8.2.5.3 Sampling Pump Flow Rates

Establishing the proper flow rate is critical to the design of any inhalation exposure study. Minimum flow rates can be calculated in advance based on anticipated exposure monitoring periods, anticipated collection efficiency (if available), and the quantification limit of the analytical method. If the flow rate is too low, an insufficient sample volume will be collected over the specified exposure monitoring period; or the chemical residue may not be collected on the sorption media. If the flow rate is too high, the pump battery charge may be inadequate to last an entire exposure monitoring period, and excessively high flow rates may result in sample losses or artifact formation. Furthermore, when sampling particulates, it is important to consider capture velocities. Flow rates or sampling times may need to be adjusted when monitoring in an area containing extremely high contaminant concentrations (e.g., due to filter overloading). Additionally, recommendations from sampling media manufacturers should be heeded when defining flow rates (e.g., several sorbent tube manufacturers limit flow rates - generally 1 Lpm or less).

8.2.5.4 Method Validation Considerations

The investigator bears the primary responsibility for the choice and proper application of an appropriate sampling and analytical methodology. When designing a study, it is recommended that investigators review available methods contained in several sources of validated sampling and analytical methods (NIOSH, 1994a; OSHA, 1990; OSHA, 1993; ASTM, 1996; ASTM, 1997a; ASTM, 1997b). However, it must be stressed that available methods were likely developed for application in an occupational setting. Therefore, they may not be sensitive enough for residential exposure scenarios.

If the investigator finds that a pre-validated methodology from a recognized, peer-reviewed, source is not available for the pesticide analyte of interest, or if an available pre-validated methodology is not sensitive enough, then the study design will need to include data which demonstrate the validity of the chosen method under the conditions of the study. This is particularly likely to be necessary if the method chosen is a proprietary, unpublished method, or a method available in the general published literature. For information on standards used by NIOSH, OSHA, and ASTM for data validation, the reader should consult published methods found in NIOSH (1994a), OSHA (1990), and ASTM (1997).

Development of an inhalation exposure monitoring method should include three phases: (1) selection of several sample collection protocols to be considered for validation, based on the physical nature of the contaminant (e.g., particulate or vapor), a literature review, Agency recommendations, experience, etc.; (2) performance of a rangefinder retention/breakthrough (e.g., volatilization) study to narrow the selection process; and (3) final method validation based on a definitive pre-field phase breakthrough/retention study and an in-field recovery study. (See Part C - QA/QC.)

8.2.5.5 Study Validation Requirements

At least two critical validation requirements must be completed for every study. These are: (1) pre-field phase retention and breakthrough/volatilization trials and (2) field recovery studies.

Retention. Retention efficiency studies are required to validate the performance of sample collection media prior to field trials. Retention samples are inhalation sampling media that have been fortified with several concentrations of the analyte of interest, allowed to dry for a sufficient time (e.g., to permit solvent evaporation from fortifying solution to prevent volatilization due to coevaporation of analyte with solvent), and that have had air drawn through them for a period of time, at a flow rate similar to that anticipated in the field study under similar conditions. Tests must be performed at high residue levels (e.g., 10x and 100x to 1,000x LOQ) to accurately determine the percentage of retention that will occur. These

samples, coupled with breakthrough samples described below are intended to assess the utility and performance of the methodology.

Breakthrough. Breakthrough samples are blank (e.g., not fortified) sample collection media that have been placed in-line between the fortified retention sampling media and the pump (e.g., personal sampling pump) to entrap residues which may volatilize from the fortified media. (Melcher et al., 1978) Tests must be performed at high residue levels (e.g., 10X and 100X to 1,000X LOQ) to accurately determine the percentage of breakthrough that will occur. Low concentrations make it more difficult to accurately quantitate breakthrough levels because anticipated levels may approach the LOQ or LOD and make quantification of available residues difficult. Note that the same technique should be routinely employed during field sampling, as a quality control measure to ensure that collected chemical residues are not lost from the media during sampling. According to standard industrial hygiene practice, if the back-up section contains more than 20 percent of the concentration in the front part of the tube, the sample should be considered suspect (NIOSH, 1980; ACGIH, 1995; OSHA, 1995).

Retention and breakthrough studies should be performed under conditions similar to those anticipated in the field phase of the study. Laboratory incubators can be used to simulate field temperature and humidity conditions. If environmental conditions are anticipated to change during exposure monitoring periods, then a worst-case scenario (e.g., most chances for volatilization and degradation) should be simulated (e.g., relative humidity typically drops drastically in the San Joaquin Valley of California as the sun rises). Worst-case scenarios should be supported by investigators based on the physical/chemical characteristics of the pesticide(s) being studied.

Field Recovery. Inhalation monitoring media are fortified and allowed to dry as above, then exposed to identical environmental conditions as the actual field samples (e.g., all tests done concurrently). Air is drawn through them at flow rates and volumes similar to actual field samples. Field recovery samples are required in conjunction with any retention/breakthrough study to determine the effect of ambient environmental conditions (e.g., volatilization and other dissipation or degradation effects) on the field recovery of residues collected on the inhalation monitoring media. (See Part C - QA/QC for further details.)

Trapping Efficiency. While it would be desirable to know the trapping efficiency of media using actual airborne particulates containing the chemical analytes of interest, no completely satisfactory procedure is currently available for this type of testing. Investigators are strongly urged to develop and enhance procedures for determining trapping efficiency. Unless the chemical of interest can be introduced directly to test the sample media, investigators will have to determine the retention efficiency of fortified media rather than the trapping efficiency as described for the retention/breakthrough samples above.

8.2.5.6 *Novel Sampling and Analysis Methodologies*

Although the Agency encourages investigators to develop and use novel approaches for monitoring inhalation exposure levels, the Agency would like the opportunity to review and approve such technologies prior to the initiation of any field experiments. Historically, investigators have developed protocols based on the types of monitoring techniques that they have used most often (e.g., personal sampling pump in conjunction with a filter cassette and resin tube). Investigators must determine and justify their selections of specific sampling methods, the appropriate sampling medium, conditions for storage of samples, and analytical procedure (NIOSH, 1995). Investigators should make selections based largely on the pesticide(s) and use patterns being studied. Additionally, as indicated above, investigators may need to develop sampling regimens that are capable of monitoring both gas phase and particulate airborne contaminants (NIOSH, 1984).

8.2.6 Sampling Techniques

This section describes the available sample collection techniques, monitoring equipment, and sampling media that can be used in obtaining inhalation exposure data. Where possible, recommendations are also made with regard to the selection of specific techniques that could be used to evaluate specific exposure scenarios. See Part B, Chapter 2 - Study Design for further information pertaining to protocol development and study conduct. The Agency prefers that personal sampling be conducted using personal sampling pumps, and sampling trains consisting of filter cassettes and resin tubes or polyurethane foam filters. The Agency considers personal sampling to be appropriate for most occupational exposure scenarios and for some residential scenarios. In cases where personal sampling is not appropriate, the Agency requires that stationary sampling be conducted using equipment/matrix combinations that maximize the potential sample volume collected for that scenario. Passive monitors may be used under certain circumstances, as appropriate (e.g., volatile compounds). Use of grab sampling or direct technologies may also be useful in specialized situations. Further information is available in ACGIH, 1995; National Safety Council, 1996; NIOSH, 1995; OSHA, 1995; Lodge, 1989).

8.2.6.1 *Personal vs. Area Monitoring Techniques*

Both personal and area monitoring can provide airborne concentration data that may be useful in the risk assessment process. Personal monitoring is generally performed using battery-powered pumps/devices, which generally operate within a range of flow rates. Area monitoring (also known as stationary monitoring) can be performed using personal sampling pumps; mid- and high-flow rate stationary air samplers; grab sampling devices; passive monitors; or direct-reading instruments. Specific requirements of each approach

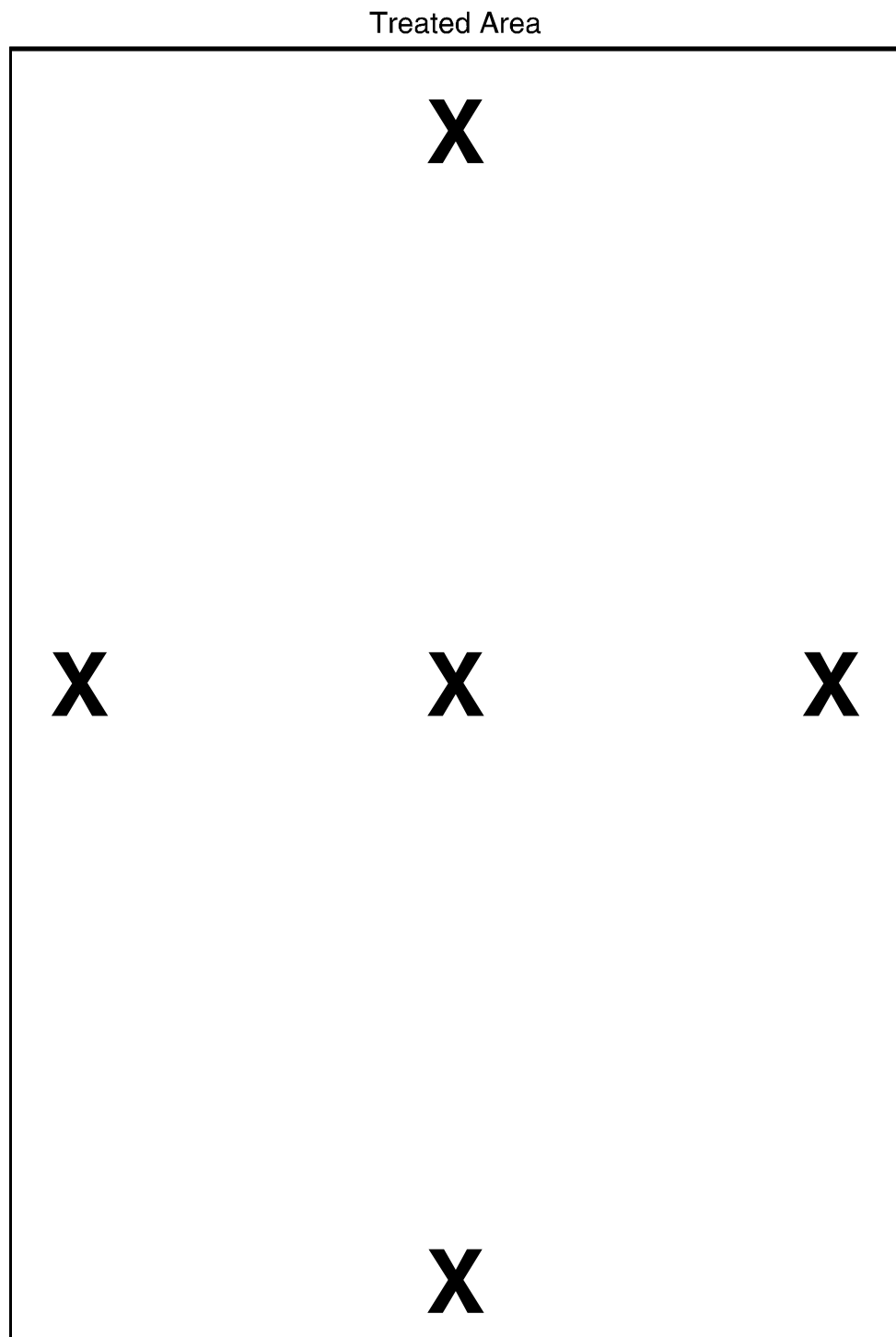
and the corresponding inadequacies are addressed below. Additionally, general requirements that are pertinent to either approach are also presented.

Personal Monitoring. The Agency considers the use of battery powered, personal sampling pumps to be the most effective method for quantifying inhalation exposure levels. Investigators should use personal air sampling pump methods unless it has been determined that this approach would not be effective or there is a more effective approach available. Personal sampling pumps should be attached to test subjects in the least obtrusive, most comfortable manner possible. For the test subject's comfort and safety, it is necessary to ensure that the pumps, hoses, and sample media are secured to minimize movement/shifting and the potential for snagging. For the vast majority of exposure scenarios, the use of personal sampling pumps will be the most appropriate. In certain specialized situations, other devices such as passive monitors, may be appropriate. Manufacturers of passive monitors generally provide very explicit direction concerning the scenarios that are appropriate for their use.

Devices which contain the sampling media attached to personal sampling pumps (e.g., 37-mm cassettes containing filters in conjunction with the appropriate resin tube or cylindrical holders containing PUF plugs) should be clipped to the collar in the breathing zone of test subjects so that the sample air inlet is facing slightly downward whenever possible (ACGIH, 1995; OSHA, 1995).

Area Monitoring. Area monitoring provides another potentially useful approach for quantifying ambient air levels that may be useful in the risk assessment process. Several types of equipment and sample media combinations can be used during area monitoring studies (e.g., high-volume air samplers, personal sampling pumps, passive monitors, grab sampling, and alternative technologies such as real-time gas chromatography). If area monitoring is performed, samples should generally be collected within the treatment area. [There are notable exceptions such as after public health applications of mosquito control agents.] Additionally, samples should be collected in zones of the treatment area that are typical of the exposure scenario being monitored. For example, samples should be collected from the center of a chemically treated field and from at least four other locations, preferably at the cardinal compass points from the center location (e.g., recreational turf application on parkland). (See Figure B8-2.) Note that appropriate climatological data must also be collected concurrently with any stationary air sampling as described in Part C.

Indoor sampling strategies should be designed based on the nature of the exposure scenario and the building construction type (e.g., for residences: plenum, slab, crawl space, or basement). Investigators must be careful not to design a study in which sampled indoor air will be altered by



X = Sampling Location

Figure B8-2. Suggested Outdoor Stationary Sampling Regimen

Working Draft -- Do Not Quote or Cite

scavenging or cleaning the ambient air near the sampler or by altering any airflows or mixing conditions within the residence. Additionally, for indoor scenarios, samples should be collected at heights that represent the breathing zones of infants/children and adults (e.g., 18 and 48 inches). Generally, it is recommended that indoor air monitoring protocols be developed after consultation with the Agency.

8.2.6.2 General Considerations

Various issues must be addressed in the design of an inhalation exposure monitoring study regardless of whether the study is performed using a personal or stationary monitoring approach.

Equipment Maintenance. Air samplers are mechanical devices. As a result, they can be expected to break down during use or otherwise malfunction (e.g., overheating, calibration adjustments, power supply failures, etc.). Investigators should anticipate these occurrences and take the appropriate precautions. Mechanical air samplers should be maintained according to manufacturer specifications.

Sample Integrity. Sampling media must remain intact throughout the duration of an exposure monitoring period to ensure the integrity of the sample. Therefore, sampling media must be designed and used in a manner that is consistent with: (1) the sampler's surviving the exposure monitoring period intact; (2) obtaining a valid, representative sample; and (3) not interfering with the normal work functions of the test subjects. If a sample should leak, spill, tear, or otherwise disintegrate during the exposure monitoring period, the investigator should assume that the integrity of the sample is compromised. If the sample is compromised, it must be identified as such and, in most cases, should be voided. For example, monitors can be reattached to clothing or replaced with a fresh, unexposed monitor as long as it is accompanied by appropriate documentation.

If samplers break or otherwise obviously malfunction during operation, the devices should be replaced and the sampling should continue, if the integrity of the sample can be assured. The investigator should use any means available to obtain field samples when malfunctioning equipment is involved unless the integrity of the sample is unquestionably compromised (e.g., discretion is called for on the part of the investigator). If questions regarding the integrity of the sample cannot be answered, the sample should be discarded or any results based on that sample must be explained with the appropriate caveats.

Sample Volume. Studies should be designed to maximize the duration of the sampling interval and air flow rates within the appropriate flow rate range in order to increase the potential for capturing enough of the chemical of concern in a sampling event to be quantifiable (e.g., the total sample volume should be maximized as appropriate).

Sampling Pump Calibration. It is necessary to check flow rates at the beginning and end of each exposure monitoring period. Several types of equipment are available for calibrating inhalation exposure monitoring equipment. All equipment used to calibrate personal sampling pumps must be a primary standard or be traceable to a primary standard (e.g., electronic soap film meters or dry gas meters). A rotameter may be used as a secondary method in the field provided it is traceable to a primary standard. If flows change during the exposure monitoring period, the mean flow rate should be used for all calculations unless otherwise justified by the investigator. The flow rate must always remain within the acceptable flow rate range determined for that sampling method (e.g., changes in air flow over the monitoring period must be minimized or a sample is considered invalid; acceptable variations in air flow rate is generally limited to ± 10 percent).

Airflow rates should be recorded at the initiation and termination of the monitoring period, with the average being used in all calculations unless otherwise justified by the investigator. Intervals where the sampling process has been interrupted should be described in submissions to the Agency (e.g., fueling portable gasoline powered generators to operate air samplers, changing filters, checking flows, etc.).

8.2.6.3 Monitoring Equipment

Several types of equipment are available to monitor inhalation exposure levels. The most commonly available types are described below and in ACGIH (1995) and National Safety Council (1996). Each type of equipment, when used in conjunction with the proper sample collection media, can be used to monitor inhalation exposure levels to airborne chemical residues. Each type of equipment has particular applications and limitations associated with its use.

Personal Sampling Pumps. Several brands of commercially produced, battery-powered, personal sampling pumps are available for use in monitoring inhalation exposure. These pumps typically consist of a battery-powered motor that operates a diaphragm pump capable of performing for up to 8 hours at air flow rates in the 1.0 to 4.0 L/minute range. Modern personal sampling pumps often have the capability to maintain a flow rate set point, within a specified tolerance (e.g., ± 10 percent) that adjusts to the actual pressure drop across the sampling media even as head pressure fluctuates due to loading on the sampling media. Additionally, these modern devices electronically record flow rates and sample times for exposure intervals. Most sample collection methods are based on flow rates that range from 0.5 to 2.0 L/minute.

High Volume Monitoring Pumps. Several brands of commercially produced sampling pumps are available for use in monitoring ambient airborne chemical residues. These air samplers are usually based on one of two common designs. The first design is a high volume, centrifugal, electric-powered fan that draws air through a filter directly attached to the device at flow rates ranging from 20-50 ft³/minute (CFM) or >250

LPM (e.g., as described in ASTM, 1996 or 40 CFR 50). The second common type of stationary monitor is the rotary-vane vacuum pump that can typically operate at lower average flow rates (e.g., “Anderson” 1 CFM sampler). Higher flow rate stationary air samplers should be selected and used with caution so not to modify the sampled environment by scavenging/cleaning the air within that environment (e.g., inside residences).

Passive/Diffusion Monitors. Passive monitors are commonly used by industrial hygienists and other health and safety personnel to monitor ambient levels of certain highly volatile workplace gases and vapors, generally indoors (e.g., 3M-type and polyacrylate film fiber by Supelco). (See Figure B8-3.) These devices should be used with caution in pesticide exposure studies for two reasons: (1) most pesticides are insufficiently volatile and/or have diffusion coefficients which are too low for efficient collection, and (2) passive dosimeters measure only gas and/or vapor phase contaminants (i.e., particulate or particulate-bound residues are not quantified). It is recommended that the manufacturers of these devices be consulted for technical assistance when considering the use of these devices for pesticides because of the limitations associated with their use. Generally, the primary concern over the use of passive monitors is the lack of appropriate validation data for the chemical of concern, including the accuracy and precision of the dosimeters.

Direct-reading Technologies. Investigators are encouraged to also consider using other approaches for monitoring inhalation exposure levels and/or ambient air concentrations, when appropriate. Direct-reading technologies may include direct-reading instruments (e.g., portable gas chromatography; real time aerosol monitoring; colorimetric tubes commonly used in industrial hygiene; or immunoassay techniques). Thorough documentation must be provided to justify the use of direct-reading technology.

Grab Sampling. Grab sampling should only be used in environments where other technologies are not functional or the use of this approach can be otherwise justified. This technique, which is only applicable to collection of samples containing volatile compounds in the gas phase (e.g., sulfuryl fluoride, methyl bromide), involves drawing a bulk volume of air into a sample collection container (e.g., bag or metal canister) either passively or actively (e.g., using a pump), followed by laboratory analysis and quantification of the analyte in the laboratory. Grab sampling is not intended for environments where airborne particulate contaminants are of concern. Samples can be retained and analyzed by a direct method or the captured residues can be trapped on a sorbent and then analyzed. Several sample collection containers are commercially available that are appropriate for bulk sampling purposes. These containers are of known volume and are typically made from a well characterized

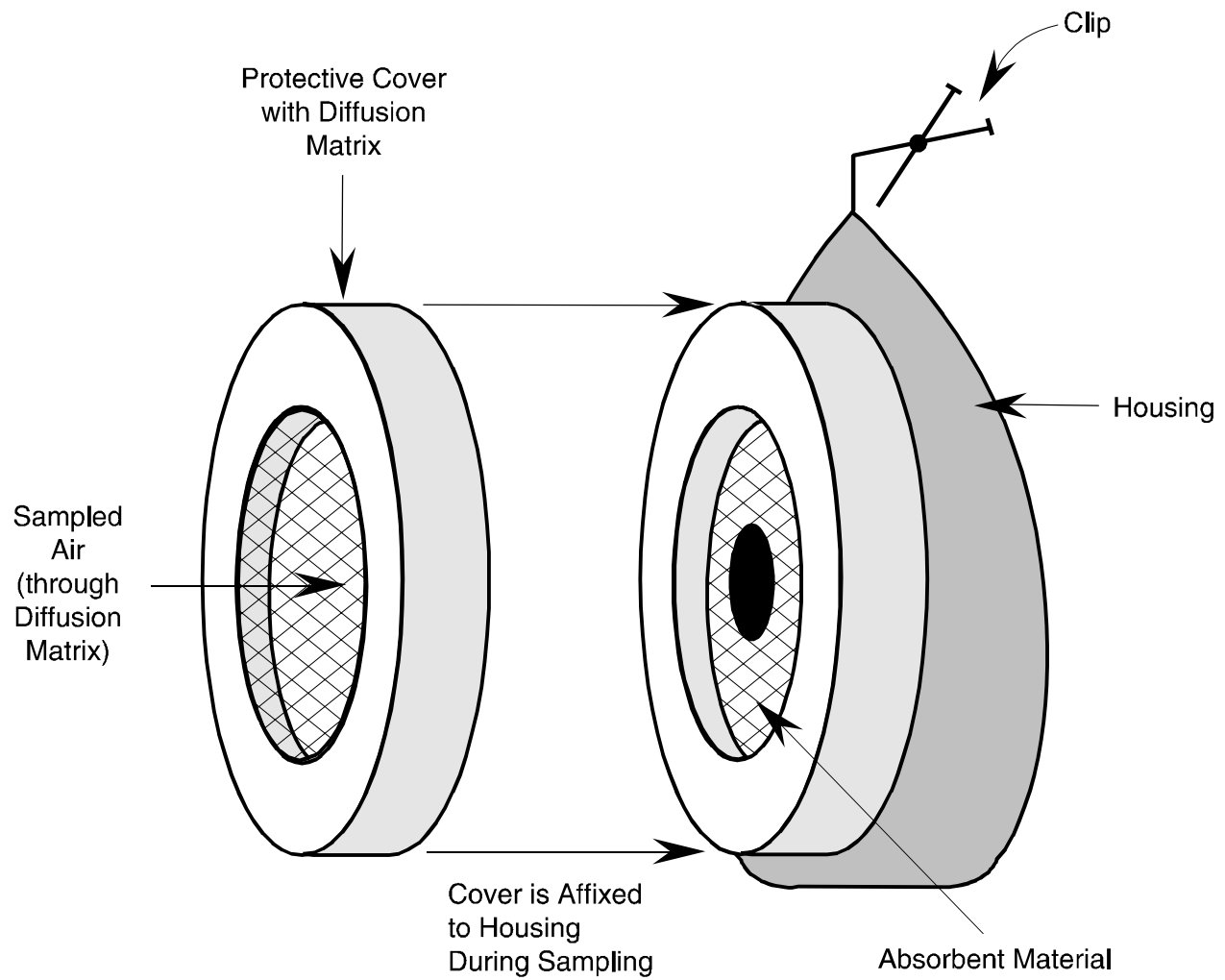


Figure B8-3. Schematic of Typical Passive Monitor/Badge

material (e.g., mylar, polyethylene bags, or evacuated stainless steel canisters). Flow rates are not as important in this technique, since the purpose is to collect a bulk sample and not to characterize inhalation exposure levels over the duration of the exposure monitoring period.

8.2.6.4 Sampling Media

A large variety of sampling media are available to monitor inhalation exposure and ambient air concentrations. Various types of media and sample holders are described below. In general, (1) filters or membrane filters (e.g., mixed cellulose ester, glass fiber, PVC, etc.) are used to trap particulates; (2) sorbent resins (e.g., silica gel, activated charcoal, Chromosorb, etc.) are used to trap gases and vapors; (3) PUF (e.g., polyurethane plugs) is useful to trap particulates as well as gases and vapors (combinations of filters and sorbent resins in series are an acceptable alternative); (4) particle sizing devices may be employed to differentiate total particles from respirable particles; (5) evacuated sample collection vessels (e.g., Tedlar bags or metal canisters) may be useful to monitor gaseous fumigants (e.g., methyl bromide or sulfuryl fluoride). One other sampling medium is briefly discussed reflecting its limited applicability. Glass impingers containing trapping solutions are occasionally, but rarely, employed in pesticide monitoring studies. For summarized information on recommended techniques and equipment to use to analyze specific analytes, investigators may consult OSHA (1991).

Identifying the most suitable medium for a particular investigation will depend on the physical/chemical properties of the analyte. Investigators must rationalize the selection and use of a method that is not designed to simultaneously collect both gas/vapor and particulate phase contaminants in any study. For most exposure scenarios, the Agency believes there may be a potential hazard/risk from both gaseous phase or particulate airborne contaminants (NIOSH, 1984).

Many sample holder devices are available for the different types of media used for entrapping airborne chemical residues while monitoring inhalation exposure levels including, but not limited to, the following: spill-proof microimpingers; 37-mm cassettes containing a filter; glass tubes that contain various sorbent resins; and plastic/glass tubes to contain polyurethane foam plugs. Most sample holders are of the same general design: a fitting for attachment of flexible tubing at each end of the holder (e.g., to attach personal sampling pump and resin tube used in series); rubber grommets to hold the resin tube in place at both ends of a metal holder that allow air to flow across the resin bed and that hold the tube in place; and an alligator-type clip to affix the device to the test subject during sampling. (See Figure B8-4.)

Sorbents. A wide variety of sorbents are available for use as inhalation monitoring media. These sorbents are typically contained in small diameter glass tubes, approximately 10 cm in length, that are open at both ends to allow air flow through the sorbent bed. (See Figure B8-4.) Sorbent tubes are usually designed

only for the measurement of airborne chemical residues present as a gas or vapor. Additionally, these devices are typically designed exclusively for use in conjunction with a personal sampling pump. A large variety of sorbents are available in commercially produced tubes including, but are not limited to, the following: XAD, chromosorb, tenax, silica, alumina, activated charcoal, and florisol. Flow rates for personal sampling pumps typically average 0.8 to 1.0 L/minute when sampling with these devices.

Filters and Membrane-filters. Filters, for the purposes of this guideline, are porous structures with definable external dimensions such as thickness and cross section normal to laminar air flow. Filters remove particles from a gas stream by various mechanisms depending on flow rate, structure of the filter, and the nature of the contaminant. One of the oldest and most common filter types is the fibrous filter, which is comprised of mats of cellulose, glass, quartz, asbestos, or plastic fibers in random orientation within the plane of the filter sheet. A wide variety of commercially produced filters are available. Common filter types include, but are not limited to, the following: mixed alpha-cellulose ester, glass fiber, and coated filters (e.g., charcoal impregnated).

According to ACGIH (1995), "the term "membrane filter" was originally applied to discs of a cellulose ester gel having interconnected pores of uniform size. Gel type membrane filters are now also available in polyvinyl chloride (PVC), nylon, and other plastics. The Nucleopore® filter, a polycarbonate pore filter, is generally considered to be a membrane filter, but it has a radically different structure (i.e., a series of nearly parallel straight-through holes). Whereas the methods of production are different, the flow pathways through [both] types of [media] are quite similar in terms of the tortuosity of the flow pathways."

Filters can be utilized with either personal sampling pumps or with stationary sampling devices. Filters for use in conjunction with personal sampling pumps typically are intended for flow rates of 0.5 to 4.0 L/minute, while flow rates as high as 40 or 50 ft³/minute are typical for filters used in conjunction with high-volume air samplers (e.g., TSP, as specified in 40 CFR 50). As with the resin tube holders described above, filter holders are widely available, generally from the same manufacturers as the filters. For personal sampling pumps, 37-mm filter cassettes are widely used as sample medium holders (i.e., they are the standard accepted in the United States). As illustrated in Figure B8-5, filter cassettes typically consist of a three piece plastic ring "sandwich" in which the filter resides. These devices can be used open-faced (e.g., the actual diameter of the filter) or closed-faced (e.g., air flows through a 4-mm diameter orifice in the center of the cassette). Larger diameter, circular filters and cassettes of similar design are often used with rotary vane vacuum pumps for velocity considerations or trapping particulates. [Note: When used as an open-faced device, the third piece of the filter cassette is added

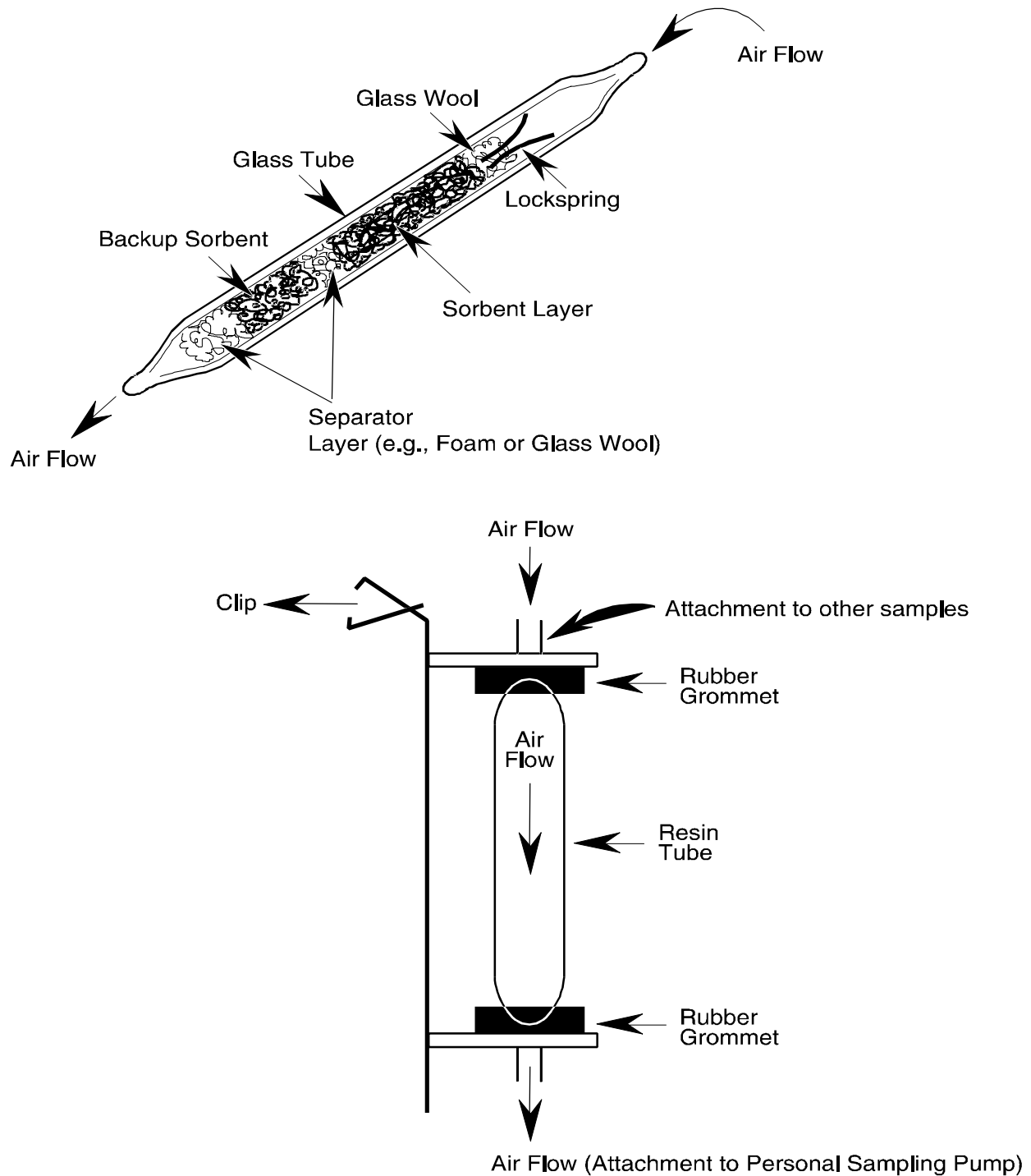


Figure B8-4. Schematic of Typical Resin Tube/Holder

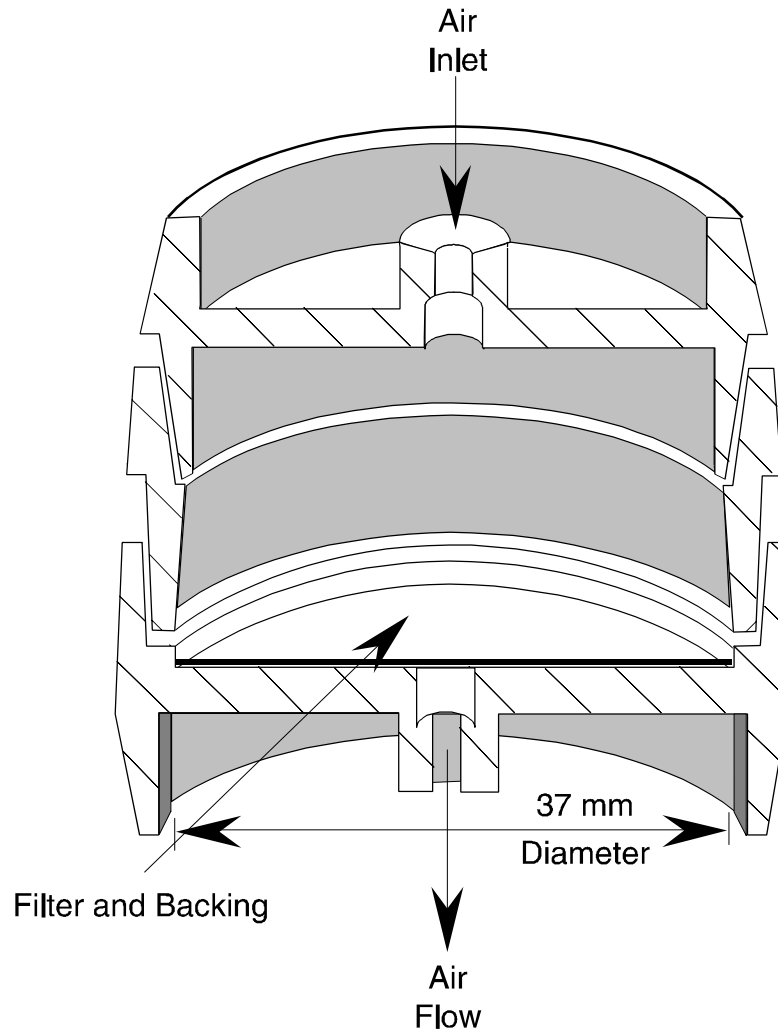


Figure B8-5. Schematic of Typical 37 mm Filter Cassette

after sampling to seal the cassette and is not utilized during sampling.] Filters are usually attached to the high-volume air samplers using a device produced by the manufacturer which is specific to the device (e.g., rectangular filter cassette for TSP sampling).

Polyurethane Foam (PUF). PUF media are available in several physical configurations. Regardless of the configuration, PUF provides a medium through which ambient air is drawn (using either low flow personal monitoring pumps or high volume stationary sampling devices) to trap chemical residues in the gas, vapor, and/or the particulate phases. Cylindrical PUF plugs (e.g., 0.5-inch diameter x 1.5 inches long for personal sampling and 2.2 x 76 cm long for ambient air) are typically placed in some type of holder that can either be positioned in-line with other devices or used without a pre-filter. PUF used in stationary, high-volume air samplers is generally larger (e.g., 6 cm diameter plugs; ASTM, 1997b). These PUF filters are affixed to the samplers with a threaded or snap-on arrangement. For high-volume air samplers, sampling flow rates are generally in the 20 ft³/minute range.

Particulate Sizing Devices. Inhalation of particle-bound chemical residues may result in a biologically effective dose even when inhaled particulates are too large to penetrate the lungs, due to absorption through the gastrointestinal tract (ACGIH, 1995). Therefore, in the majority of pesticide exposure scenarios, the Agency is interested in total airborne particulate levels rather than just the respirable fraction. The total airborne contaminant may be defined as airborne particles for which the aerodynamic diameter is <100 µm (ACGIH, 1995). However, there are a limited number of postapplication scenarios (e.g., respirable particulate fractions of wind blown chemical laden soil particles or residue laden house dust) for which knowledge of the respirable particulate levels may be important. The respirable fraction of a contaminant may be defined as airborne particles for which the aerodynamic diameter is <10 µm, although generalizations regarding the site of deposition of particles of a given size are problematic. However, in the average adult, most particles larger than 10 µm aerodynamic diameter are deposited in the nose or oral pharynx and cannot penetrate to tissues distal to the larynx, and the alveolar region has significant deposition efficiencies for particles smaller than 5 µm and larger than 0.003 µm (Casarett et al., 1995). Where exposure to respirable particulates is likely to be of toxicological significance, the Agency reserves the right to require that respirable particulate levels be measured .

The respirable particle fraction can be quantified using devices of two basic designs, the cyclone or the inertial impactor. (See Figures B8-6 and B8-7.) Both devices operate on the principles of momentum and force. In cyclones, airborne particulates are drawn into a cylinder where the air is flowing in a circular pattern. As the entrapped particulates move around the cylinder in a circular motion, the lighter, respirable particles are carried to the outlet and are collected on a filter contained in

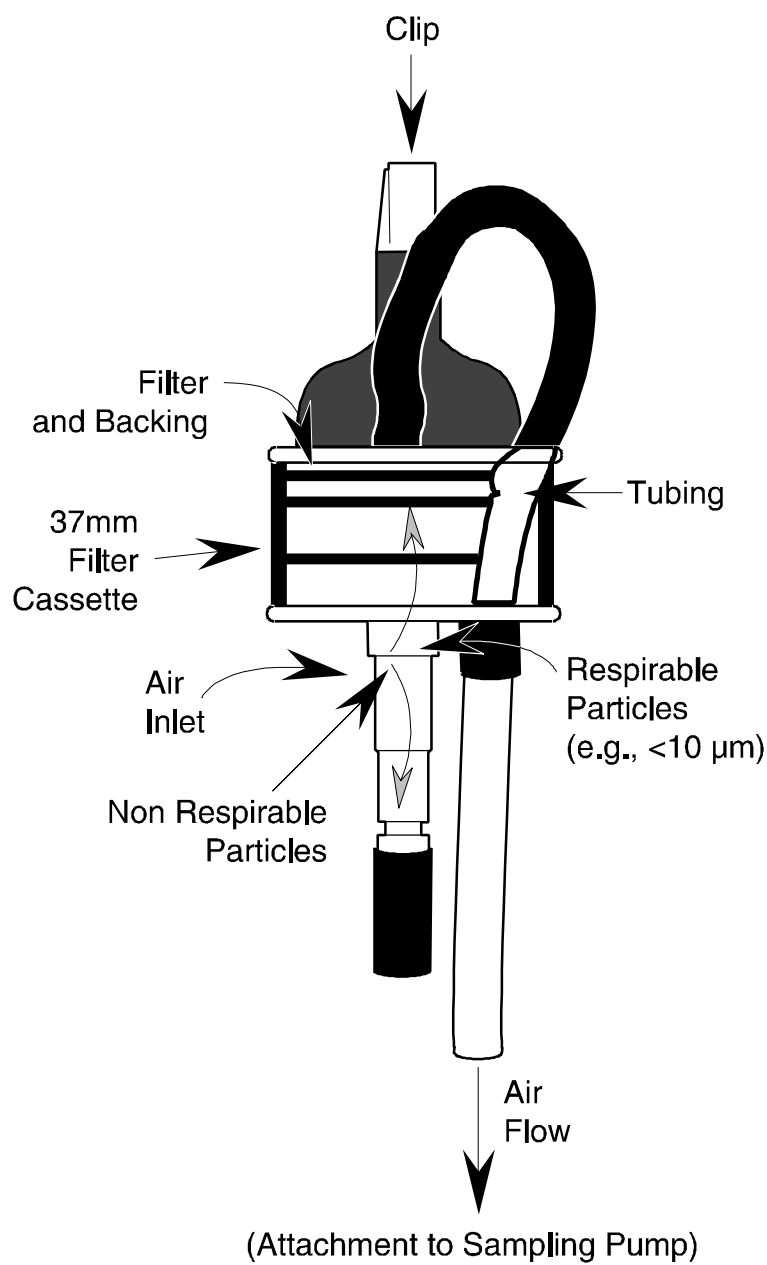


Figure B8-6. Schematic of Typical Cyclone Device

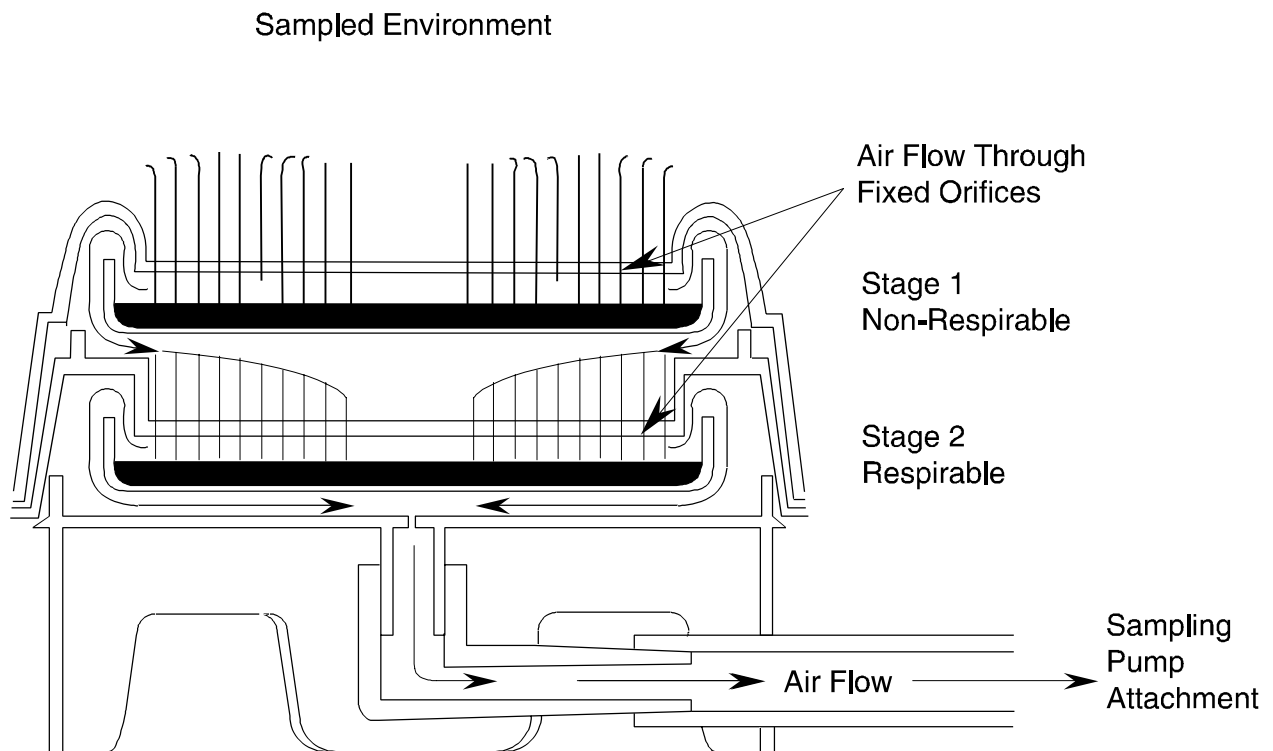


Figure B8-7. Schematic of a Typical Inertial Impactor

a typical 37-mm cassette. (See Figure B8-6.) The heavier particles are retained in the cylinder and are discarded. Size separation is now often also achieved using inertial impactors. In these devices, air is drawn through a series of orifices that limit particle sizes in sequentially smaller fractions as illustrated in Figure B8-7. Inspirable aerosol samplers are also available that are based on the concept of inertial impaction (Vincent and Mark, 1987).

Trapping Solutions (e.g., impingers and diffusers). Trapping solutions are used in conjunction with impingers or diffusers to entrap airborne chemical residues in various phases (e.g., gas, typically a gas or vapor, potentially particulates) during either personal or area monitoring. Impingers are suited for monitoring aerosols and other airborne particulates, while diffusers are better for quantifying gases, vapor phase contaminants, aerosols, or liquids. The design of both types of devices is similar. Essentially, both devices consist of a graduated cylinder (e.g., ~25 mL volume) outfitted with an air sampler attachment orifice and a ground-glass or threaded stopper through which a tube runs from the ambient air down into the trapping solution. (See Figure B8-8.) In both types of devices, sampled air is drawn through the tube directly into the trapping solution. As the sampled air exits the end of the tube into the solution, bubbles are formed by the vacuum placed on the device by the attached sampling pump. The design of the end of the tube which is placed in the trapping solutions differentiates the two types of devices. In impingers, an open-ended tube is placed directly in the trapping solution so that the tube end is at a fixed distance from the bottom of the flask. (See Figure B8-8.) As a result, airborne particulates can pass through the tube and are trapped in solution. Impingers may also trap gases or vapors. However, impingers may not as efficiently collect gases that have a low reactivity with the trapping solution. Diffusers are suited for monitoring only gases, vapors, and aerosols (e.g., liquid particulates). The design of a diffuser is intended to absorb or collect gaseous contaminants. A fritted glass diffuser head may be attached to the end of the tube that is immersed in the trapping solution. As air passes through the diffuser head, the total surface area of the bubbles created is much larger, thus, enhancing the probability that a gas or vapor may be absorbed into the trapping solution. The total surface area is larger for diffusers because larger numbers of smaller bubbles are created due to the number of orifices in the diffuser head in comparison to the single immersed tube that is characteristic of an impinger. Typically, individual orifices in diffuser heads are extremely small in diameter, thus, inhibiting the passage of particulate materials into the trapping solution. A variety of trapping solutions can be used with impingers and diffusers. Selection of the appropriate trapping solution depends upon the physical/chemical characteristics of the analyte. Commonly used solutions include, but are not limited to, the following: ethylene glycol, weak acid/base solutions, common organic solvents (e.g., hexane, xylene and acetonitrile), and various buffer solutions. For most monitoring purposes, the use of impingers/diffusers is appropriate only for personal monitoring in conjunction with personal sampling pumps operating at flow rates of 0.5 to 2.0 L/minute. Impingers/diffusers are typically filled to

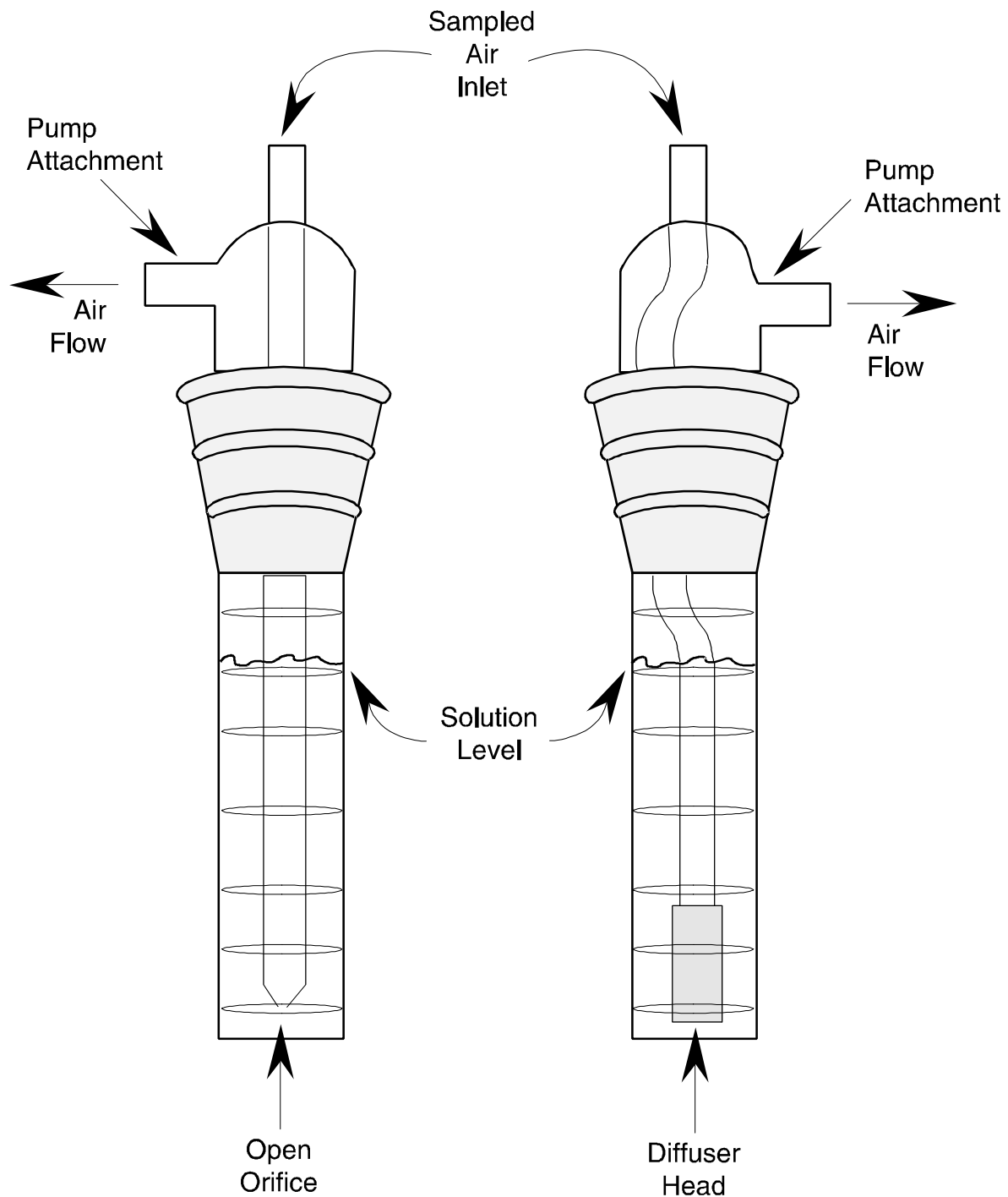


Figure B8-8. Schematic of a Typical Impinger and Diffuser

Working Draft -- Do Not Quote or Cite

approximately 80 percent of their total volume during sampling to ensure that the sampled air will bubble through a sufficient volume of trapping solution.

8.2.6.5 *Small Scale Environmental Chambers*

Small environmental test chambers are often used to evaluate and characterize the emission of organic compounds, under controlled conditions, from a variety of materials and products into indoor air. The source emissions data from these studies can be used to predict indoor air concentrations of the compounds emitted from the tested material, and subsequently to estimate inhalation exposure. The standard exposure chamber for evaluation of emissions is typically constructed of a nonabsorbent, chemically-inert, smooth interior substance, most commonly glass or stainless steel, so that the emitting substance does not adsorb to or react with the interior surface of the exposure chamber. Studies using glass or stainless steel environmental test chambers have been typically carried out for three reasons (Sollinger and Levsen, 1993): (1) to identify parameters which influence the rate of chemical emissions from a given source; (2) to rapidly screen materials used indoors in order to determine the emission potential; and (3) to simulate as closely as possible real indoor conditions thus allowing the estimation of the contribution of the emission of a given product to the total indoor air concentrations. Once a generation rate (G) for a given material is determined, it can be used in indoor air models to predict indoor air concentrations. This generation rate could be a function of time, concentration, or other parameters. Small environmental test chambers are designed to permit testing of various types of building materials and consumer products. They typically range in size from a few liters to 5 m³. Chambers greater than 5 m³ are considered large (ASTM, 1990). The standard exposure chamber has an access door with air-tight, non-absorbent seals, and is fitted with inlet and outlet ports for airflow. Currently, the ASTM standard (ASTM D5116-90) for small environmental chamber testing advises that the test chambers be designed to ensure (1) adequate mixing of the chamber air, (2) the air velocity around the tested material is not excessive, and (3) temperature, relative humidity, and light are appropriately controlled.

The limitations of current small scale chamber designs include the following:

- (1) They cannot be used to directly measure the airborne concentration of an off-gassed material that can be expected in an indoor environment. Chambers with nonabsorbent surfaces may give erroneous and unrealistically high results relative to actual concentrations of some compounds found in the indoor environment. The actual concentration will depend on the amount of product applied or the material loading ratio, as well as effects of indoor sinks; and

- (2) They should not be used to measure generation rates (G) when there is evidence that degradation of the compound of interest takes place on the walls of the chamber. In those situations, erroneously low results relative to actual source rates will be measured.

A true maximum emission rate (G_{max}) for a given product or material may be determined by measuring the amount of active ingredient in the air, and possibly on the walls of the chamber, during the first few hours of the experiment. Comparison of total mass emitted over a longer period of measurement with mass applied, if known, will enable estimation of losses due to degradation.

Several resources are available for the planning and conduct of small scale environmental chamber testing. These include, but are not limited to, the following: ASTM accessible on the Internet at <http://www.astm.org>; ASTM (1992); and ASTM (1996).

8.3 SAMPLE STORAGE

Samples should be stored in a manner that will minimize deterioration and loss of analyte between collection and analysis; more detailed information on sample storage is provided in Part C, Quality Assurance and Quality Control. The study investigator is responsible for demonstrating the stability of the samples under the storage duration and conditions used.

8.4 SAMPLE ANALYSIS

Appropriate cleanup procedures should be used and the pesticide residues quantified by the best available method. See Part C, Quality Assurance and Quality Control for more detailed information on sample analysis.

8.5 CALCULATIONS

Refer to Part D of this document for a description of the calculations needed for estimating exposure and risk.

8.6 DATA PRESENTATION

Inhalation exposure residue data should be reported in tabular form. These data should be reported as total µg/sample and as an airborne concentration (µg/m³). Additionally, all other sampling parameter data generated concurrently with the residue data must be reported (e.g., pump flow rates--Lpm, pump calibration

PART B - GUIDELINES
Inhalation Exposure (Guideline 875.2500)

data--Lpm before and after exposure replicate, and the duration of the exposure replicate--minutes).
Distribution data should be provided, to the extent possible.

REFERENCES FOR PART B, CHAPTER 8

ACGIH. (1991). Documentation of Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs). 6th ed. Cincinnati, OH.

ACGIH. (1995). Air Sampling Instruments for Evaluation of Atmospheric Contamination, 8th ed. B.S. Cohen & S.V. Hering eds., American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, OH.

ACGIH (American Conference of Governmental Industrial Hygienists). (1996). Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH.

ASTM (American Society for Testing and Materials) (1990). Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products. ASTM Designation: D5116-90.

ASTM (1992). Modeling of Indoor Air Quality and Exposure. ASTM Special Technical Publication (STP) 1205, Niren L. Nagda, Editor. ASTM (1996). Characterizing Sources of Indoor Air Pollution and Related Sink Effects. ASTM Special Technical Publication (STP) 1287, Bruce A. Tichenor, Editor.

ASTM. (1996). "Standard Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air." [ASTM D 4861-94a. In: 1996 Annual Book of ASTM Standards, Volume 11.03: Atmospheric Analysis; Occupational Health & Safety. West Conshohocken, PA.

ASTM. (1997a). "Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorbent Method)." [ASTM D 3686-95]. In: 1997 Annual Book of ASTM Standards, Volume 11.03: Atmospheric Analysis; Occupational Health & Safety. West Conshohocken, PA.

ASTM. (1997b). "Standard Method for Chlordane and Heptachlor Residues in Indoor Air." [ASTM D 4947-94]. In: 1997 Annual Book of ASTM Standards, Volume 11.03: Atmospheric Analysis; Occupational Health & Safety. West Conshohocken, PA.

ASTM. (1997c). "Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)." [ASTM D5466-95]. In: 1997 Annual Book of ASTM Standards, Volume 11.03: Atmospheric Analysis; Occupational Health & Safety. West Conshohocken, PA.

ASTM. (1998). Home Page, Jan. 2, 1998. West Conshohocken, PA: American Society for Testing and Materials. Internet address: <http://www.astm.org/>.

Casarett, L.J.; Amdur, M.O.; Klaassen, D.C. (1995). Casarett and Doull's Toxicology: The Basic Science of Poisons, 5th ed. McGraw Hill, New York, NY.

Graseby Anderson (1985) Operating Manual for Anderson 1 ACFM Non-vible Ambient Particle Sizing Samplers. Smyrna, GA: Graseby Anderson. TR #76-900016.

PART B - GUIDELINES
Inhalation Exposure (Guideline 875.2500)

Lodge, J.P.. (1989). *Methods of Air Sampling and Analyses*, 3rd ed. Lewis Publishers, Chelsea, Michigan.

Melcher, R.G.; Garner, W.L.; Severs L.W.; Vaccaro, J.R. (1978) Collection of Chlorpyrifos and Other Pesticides in Air on Chemically Bonded Sorbents. *Anal. Chem* 50(2):251-255.

National Safety Council. (1996). Fundamentals of Industrial Hygiene. Plog, B.A., et al. eds. Itasca, IL: National Safety Council.

NIOSH. (1980) Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, Research Report. U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133.

NIOSH. (1984) General Considerations for Sampling Airborne Contaminants, NIOSH Manual of Analytical Methods, 3rd ed., Vol. I, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 84-100 (1984).

NIOSH. (1994a). NIOSH Manual of Analytical Methods, 4th ed. Department of Health and Human Services (DHHS) Publication 94-113 (August, 1994), Eller, P. & Cassinelli, M., eds. Washington, D.C.: U.S. Government Printing Office.

Methods 0500 (total particulates -GRAV) and 0600 (respirable particulates)

NIOSH. (1994b). Pocket Guide to Chemical Hazards. Department of Health and Human Services (DHHS). Public Health Service. Centers for Disease Control and Prevention. DHHS (NIOSH) Pub. No. 94-116. Washington, D.C.: U.S. Government Printing Office.

NIOSH. (1995). NIOSH Guidelines for Air Sampling and Analytical Methods and Evaluation. Department of Health and Human Services (DHHS) Publication 95-117. [PB-96-134-564] Washington, D.C.: Government Printing Office.

OSHA. (1990). OSHA Analytical Methods Manual, 2nd ed, Vol. 1-3. Salt Lake City, UT: Dept. Labor, Directorate of Technical Support, Salt Lake Technical Center.

OSHA. (1991). Chemical Information Manual. OSHA CPL 2-2.43A, July 1, 1991. Washington, D.C.: Directorate of Technical Support.

OSHA. (1993). OSHA Analytical Methods Manual, 2nd ed, Vol. 4. Salt Lake City, UT: Dept. Labor, Directorate of Technical Support, Salt Lake Technical Center.

OSHA. (1995). OSHA Technical Manual (OTM). OSHA Instruction TED 1.15, September 22, 1995. Washington, D.C.: Office of Science and Technology.

Sollinger, S.; Levsen, K. (1993). Indoor Air Pollution by Organic Emissions from Textile Floor Coverings Climate Chamber Studies Under Dynamic Conditions. *Atmos. Environ.* 27B:183-192.

Vincent, J.H.; Mark, D. (1987) Comparison of Criteria for Defining Irrespirable Aerosol and the Development of Appropriate Samplers. *Am. Ind. Hyg. Assoc. J.* 48(5):454-457.

Working Draft -- Do Not Quote or Cite