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**Collection of Samples for Analysis of Formaldehyde and
Other Carbonyls in Indoor Air Using DNPH Cartridges**

BAA Guide 07-02

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Introduction

This guide is intended for indoor air quality (IAQ) investigations involving the sampling of formaldehyde and other low molecular weight carbonyl compounds onto commercially prepared cartridges for subsequent laboratory analysis by high performance liquid chromatography (HPLC). Determining the appropriate sampling strategy is a critical first step to achieving the study's objectives. Additionally, field air samples must be collected properly to obtain meaningful results. Specific procedures covered in this guide control and monitoring of the sampling process, reducing sources of contamination and interference, and sampler storage and transport. Sep-Pak XPoSure Aldehyde Samplers obtainable from Waters Corp. are recommended for most IAQ projects. The use of these Aldehyde Samplers for pumped collection of carbonyl compounds in air is covered in U.S. EPA Method TO-11A (see **BAA** website for a link to this method) and in ASTM Standard Test Method D 5197.

Sampling Strategy

1. For many typical building investigations, it is recommended that samples be collected from several indoor locations and one outdoor location. As an example, if you are investigating a complaint building, you may consider collecting samples from the areas in the building with the highest complaint levels and at least one sample from an area in the building with a low complaint level to serve as a control. An outdoor sample may be collected to serve as a background reference. The outdoor location should be carefully selected to be representative of the ventilation air entering the building. For example, avoid hanging samplers immediately outside of open windows since air may be flowing out of the building at the windows.
2. If a measure of sampling and analysis precision is required, collect two samples at one or more locations. These duplicate samples ideally should be co-located and collected simultaneously.

3. It may desirable to have a field blank in addition to an outdoor reference sample. Often only one blank sample is needed per building. The blank sampler should be handled, transported and stored identically to the other samplers.

Description of the Sampler

1. We recommend using Sep-Pak® XPoSure™ Aldehyde Samplers (Part No. WAT047205, Waters Corp.) as these come with a manufacturer's 'Certificate of Analysis' and have consistently low background levels of formaldehyde, acetaldehyde and acetone. XPoSure samplers are packed with 350 mg of acid treated 500-1000 µm chromatographic grade silica, coated with 1.0 mg of purified 2,4-dinitrophenylhydrazine (DNPH). The sampler is shown in Figure 1. The sampler body and internal filter discs are polyethylene. The external dimensions are 4.3 cm long and 2.0 cm diameter at the widest point. The sampler is configured with a male Luer connector at one end (the end nearest the silver-colored compression ring) and a female Luer connector at the other end. These connectors are sealed with a Luer cap and plug. It is recommended that the female Luer end serve as the air inlet end during sampling.
2. Waters™ Sep-Pak® XPoSure™ Aldehyde Samplers are available from Waters Corporation in Milford, MA. They can be ordered by phone at 1-800-252-4752. The part number is WAT047205. They are sold in boxes of 20 samplers. **BAA** usually can supply samplers in small quantities at cost.
3. Each sampler is packaged in a sealed, foil pouch with a label indicating the manufacturer's part number and production lot number. Carefully cut off the end of the pouch leaving the zip seal intact. Remove and save the Luer cap and plug by placing them in the pouch. The original pouches are effective and convenient for re-packaging samplers following field sample collection.

Handling, Storage and Transport

1. For long-term storage prior to use of the samplers, keep the factory sealed pouches in a refrigerator at 4° C. The maximum recommended storage time at this condition is six months. For short-term storage, the sealed pouches may be kept at room temperature (20-25° C). Best performance is obtained if samplers stored at this condition are used within one month.
2. After sample collection, tightly reseal the sampler with the Luer cap and plug. Place the sampler in the re-sealable foil-lined pouch and label the outside of the pouch. If possible, use a refrigerator for storage. Properly resealed samplers can be stored prior to analysis for two weeks at room temperature, or longer if refrigerated.
3. Avoid subjecting the samplers to elevated temperatures such as might occur in closed vehicles parked in the sun. It is recommended that samplers be transported and shipped in an ice chest using ice packs to keep the samplers cool. Return the samplers to **BAA** for analysis as soon as possible after the collection of samples.

4. When storing, transporting and shipping the samplers, make sure that they are well isolated from multisorbent samplers used for the collection of VOCs. The Aldehyde Samplers can be a source of acetonitrile contamination. At a minimum, it is recommended that these samplers and tightly capped multisorbent samplers be contained in separate, sealed polyethylene bags.
5. When submitting samplers to **BAA** for analysis, be sure to clearly indicate what services are desired. An IAQ services Chain-of-Custody Record is available from **BAA** for submitting samples if you do not already have an appropriate form.

Sampling Apparatus

1. If possible, draw air directly into the sampler to avoid connecting tubing to the inlet of the sampler. The only types of tubing that are acceptable for use upstream of the sampler are clean Teflon, stainless steel and copper. Prior to use, any inlet tubing should be cleaned by flushing it with methanol and then thoroughly dried.
2. The sampler should be connected upstream of the sample pump. In some cases, the sampler can be connected directly to the inlet of the pump. Often it is desirable to locate the sampler away from the pump and connect the sampler to the pump with tubing. Luer fittings with hose barbs and small diameter flexible tubing are available from Cole-Parmer Instrument Co., Chicago, IL (1-800-32-4340).
3. There are various AC and DC powered diaphragm and peristaltic pumps that are suitable for use with the sampler. The Aldehyde Sampler has a relatively low pressure drop so it may be used with many battery-operated personal sampling pumps.

Ozone Scrubber

1. Ozone reacts with the carbonyl-hydrazone derivative and can result in a significant negative interference for formaldehyde and other carbonyls when using the Aldehyde Sampler. This is an important consideration when sampling outdoors in urban environments with high ozone concentrations and also when sampling indoors in such environments.
2. A scrubber can be used upstream of the sampler to remove ozone from the sample-gas stream. It is most convenient to use the scrubber supplied by Waters Corp. for use with Aldehyde Samplers. These are Sep-Pak Ozone Scrubbers (Part No. WAT054420, Waters Corp.). Each Ozone Scrubber cartridge contains 1.4 grams of granular potassium iodide. When air containing ozone is drawn through this packed bed, iodide is oxidized to iodine, consuming the ozone.

Sample Volume and Flow Rate

1. It is imperative to know the flow rate of air through the sampler and the sampling interval elapsed time in order to calculate the sample volume. For highest precision, the flow rate through the sampler should be maintained at a constant rate and monitored continuously,

or at least frequently, during sampling. These objectives are best accomplished using electronic mass flow controllers in combination with a vacuum pump. Alternately, a pump with integrated flow control or a separate needle valve may be used to maintain constant flow rate. Electronic flow sensors, positive displacement flow sensors, bubble flow meters, or a rotameter may be used to monitor the flow rate.

2. The minimum sample volume is determined by the sensitivity of the analytical system, the blank level and the concentration of the target compound(s). Certified blank values are <50 ng of formaldehyde per sampler and typically are <20 ng. A sample volume of 60 L produces a lower limit of quantitation of about 1 ppb for formaldehyde assuming a blank value of <20 ng and using the criteria that the mass collected should be at least five times the mass of the blank.
3. Approximately 70 µg of formaldehyde will consume one half of the DNPH on the sampler which is a safe upper limit for DNPH depletion. This is equivalent to a formaldehyde concentration of about 13 ppm for a 60-L sample. However, the maximum safe sample volume is determined by the combined concentration of all of the carbonyl compounds in the sampled air. Therefore, if there are significant concentrations of other carbonyl compounds present (ppm levels), it will be necessary to use a smaller sample volume to prevent DNPH depletion and sample breakthrough.
4. For most indoor applications, a sample volume of 50-60 L is satisfactory. Limits of quantitation in the low ppb range are achieved for formaldehyde and sample breakthrough should not occur under most conditions.
5. Air flow rates are typically in the range of 0.125-1.5 L min⁻¹. A maximum flow rate of 1.0 L min⁻¹ is recommended for highest precision sampling. The lower air flow rates are used to collect integrated samples over longer time intervals. Collection efficiencies are greater than 95 percent within this flow rate range. The pressure drop across the sampler at a flow rate of 1.5 L min⁻¹ is about 20-in of water.
6. The sampling system should be leak checked prior to use, preferably with the sampler in place. With some types of pumps, this can be accomplished by capping the inlet of the sampler and checking that the flow rate at the outlet of the pump drops to zero.
7. The air flow rate through the sampler must be determined. For flow regulation schemes other than those using electronic mass-flow controllers, it is necessary to directly measure the flow rate. At a minimum, this measurement should be made both near the beginning and end of the sampling interval. If possible, the measurement should be made downstream of the sampler, preferably at the outlet of the pump. A bubble flow meter, calibrated rotameter or other flow measurement device may be used. Record the measurement data including the air temperature and the atmospheric pressure so that the flow rate can be converted to standard indoor conditions (*i.e.*, 25° C, 1 atm). If the measurement must be made upstream of the sampler, briefly use a calibrated rotameter following the precautions described above. Do **not**, under any circumstance, attach a bubble flow meter upstream of the sampler. This will contaminate the sampler.

Sample Collection

1. Be sure the Aldehyde Samplers are warmed to room temperature before use.
2. Remove the Luer cap and plug from a sampler and save these pieces as they are needed to reseal the sampler. Attach the end of the sampler with the male Luer connector (the end nearest the silver-colored ring) directly to the pump or to the sample tubing. Pull the air sample through the sampler at a flow rate up to 1.5 L min^{-1} .
3. After sampling, tightly reseal the sampler with the Luer cap and plug. Place the sampler in the reusable foil-lined pouch and label the pouch with the sample identification. If desired, the sampler can also be identified by placing a tape label on the metal ring. Do **not** write on the plastic body of the sampler.
4. The samplers contain residual acetonitrile which is used as the solvent in the coating of the silica with DNPH. During sampling, this acetonitrile is volatilized. If air samples also are being collected for the analysis of VOCs, the acetonitrile emitted to the air may contaminate the VOC samples. To prevent this contamination, it is recommended that a charcoal tube be attached to the exit of the pump to trap the acetonitrile.

Other Sampling Precautions

1. Do not expose samplers used outdoors to direct sunlight. Aluminum foil can be used to make a simple sun shield.
2. If possible, avoid collecting samples in the rain or in very high humidity situations.

Figure 1. XPoSure Aldehyde Sampler for Formaldehyde and Other Carbonyls

