METHOD 0100

SAMPLING FOR FORMALDEHYDE AND OTHER CARBONYL COMPOUNDS IN INDOOR AIR

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the sampling of various carbonyl compounds in indoor air by derivatization with 2,4-dinitrophenylhydrazine (DNPH) in a silica gel cartridge. The method may be used in conjunction with Method 8315. The following compounds may be sampled by this method:

Compound Name	CAS No.[a]
Acetaldehyde	75-07-0
Acetone	67-64-1
Acrolein	107-02-8
Benzaldehyde	100-52-7
Butyraldehyde	123-72-8
Crotonaldehyde	123-73-9
2,5-Dimethylbenzaldehyde	5779-94-2
Formaldehyde	50-00-0
Hexanal	66-25-1
Isovaleraldehyde	590-86-3
Propionaldehyde	123-38-6
m-Tolualdehyde	620-23-5
o-Tolualdehyde	529-20-4
p-Tolualdehyde	104-87-0
Valeraldehyde	110-62-3

[a] Chemical Abstract Service Registry Number

1.2 This method is restricted to use by, or under the close supervision of, trained analytical personnel experienced in sampling organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A known volume of indoor air is drawn through a prepacked silica gel cartridge coated with acidified 2,4-dinitrophenylhydrazine (DNPH), at a predetermined sampling rate for an appropriate period of time. After sampling, the sample cartridges are capped and placed in borosilicate glass tubes with polypropylene caps and placed in cold storage until analysis. The compounds of interest may then be eluted from the cartridge with acetonitrile from a plastic syringe reservoir into a graduated test tube or a volumetric flask. The eluate is then topped to known volume and refrigerated until analysis. Analysis may be done High Performance Liquid Chromatography (HPLC), Method 8315, with an ultraviolet (UV/Vis) detector at 360 nm.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of analysis, by analyzing method blanks.

3.1.1 Glassware and plasticware must be scrupulously cleaned. Clean all glassware and plasticware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinsing with tap water, organic-free reagent water, and aldehyde-free acetonitrile. After cleaning, glassware and plasticware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.1.2 High purity reagents and solvents should be used to minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.1.3 Polyethylene gloves should be worn when handling the silica gel cartridges to reduce the possibility of contamination.

3.2 Contamination of the DNPH reagent is a frequently encountered problem. Formaldehyde, acetone, and 2,4-dinitroanaline (a decomposition product of DNPH) may be significant analytical impurities in the DNPH reagent at high concentrations. The DNPH must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40-60°C, by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV-grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined prior to the analysis of the samples and should be less than 0.025 µg/mL. Refer to Sec. 5.9 for a recrystallization procedure.

3.3 Ozone Interferences - Ozone at high concentration has been shown to interfere negatively by reacting with both DNPH and its hydrazone derivatives in the cartridge (Ref. 6).

3.3.1 The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds during sampling. The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde. Figure 1 shows chromatograms of samples of a formaldehyde-spiked air stream with and without ozone.

3.3.2 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the cartridge. This process entails constructing an ozone denuder or scrubber and placing it on the front of the cartridge. The denuder is constructed out of 1 m of 0.64 cm OD copper tubing, which is filled with a saturated solution of KI water, allowed to stand for approximately 5 minutes, and dried with a stream of clean air or nitrogen for about 1 hour. The capacity of the ozone denuder as described is about 10,000 ppb/hour of ozone. Test aldehydes that were dynamically spiked into an ambient sample air stream passed through the denuder with virtually no losses.

3.4 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field reagent blanks must be analyzed to determine when sampling and storage procedures have caused the contamination.

3.5 Matrix interferences may be caused by contaminants acquired by the sampling process. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If significant interferences occur due to organic compounds that have the same retention time, altering the separation conditions by using alternative HPLC columns or mobile phase conditions may resolve the problem.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Equipment

4.1.1 Sampling System - capable of accurately and precisely sampling 0.10 to 1.50 L/min of indoor air. The procedures given here assume use of a dry meter-equipped sampling system operated at flow rates of at least 0.5 L/min.

NOTE: A normal pressure drop through the sample cartridge approaches 19 kPa at a sampling rate of 1.5 L/min.

4.1.2 Thermometer and Barometer - to record indoor conditions at the time of sampling.

4.1.3 Stopwatch - to time sampling.

4.1.4 Rotameters - to allow observation of the flow rate without interruption of the sampling process.

4.1.5 Mass Flowmeters and Mass Flow Controllers - for metering and setting the air flow rate through the sample cartridge (0.50 to 1.20 L/min). These are necessary because cartridges have a high pressure drop and, at maximum flow rates, the cartridge behaves like a "critical orifice" and can display a flow rate drop over an extended sampling period (generally less than 5% over a 24 hour period).

4.1.6 Fittings and Plugs (Luer-Lok or equivalent) - to connect cartridges to the sampling system and to cap prepared cartridges.

4.1.7 Heated Probe - necessary when the temperature of sampled air is below 60°F, to insure effective collection of formaldehyde as a hydrazone.

4.1.8 Silica Gel Cartridges - chromatographic grade, 2 cm x 1.5 cm ID, with Luer-Lok type fittings on each end, for manual application of acidified DNPH coating (Sep-PAK from Waters Associates or equivalent). Commercially pre-packaged pre-coated cartridges are also available (Thermosorb/F cartridges from Thermedics Inc. and LpDNPH cartridges from Supelco, Inc. are examples).

4.2 Glassware

4.2.1 Volumetric Flasks - various sizes, 5 to 2000 mL.

4.2.2 Pipets - various sizes, 1 to 50 mL.

4.2.3 Sample Vials.

4.2.4 Borosilicate glass culture tubes (20 x 125 mm) with polypropylene screw caps - for transporting coated cartridges.

4.3 Liquid Syringes (polypropylene are adequate) - 10 mL, used to prepare DNPH-coated cartridges.

4.4 Syringe Rack - made of an aluminum plate with adjustable legs on all four corners. Circular holes of a diameter slightly larger than the diameter of the 10 mL syringes are drilled through the plate to allow batch processing of cartridges for cleaning, coating, and sample elution. A 0.16 x 36 x 53 cm plate with 45 holes in a 5x9 matrix is recommended. See Figure 2.

4.5 Cartridge Drying Manifold - has multiple standard male fittings (Luer-Lok or equivalent). See Figure 2.

4.6 Repetitive Dispensing Pipets - positive displacement, 0 to 10 mL range, with 1 L reagent bottles (Lab-Industries or equivalent).

4.7 Polyethylene Gloves - used to handle silica gel cartridges.

4.8 Sample Vial Holder - Friction-top metal can (e.g., 4 L paint can) or a styrofoam box lined with either polyethylene air bubble padding or granular charcoal to cushion the samples.

4.9 Soap Bubble Flowmeter or Calibrated Wet Test Meter - for calibrating the sampling flow rate.

4.10 Melting Point Apparatus (optional)

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Nitrogen gas, N_2 - high purity grade.

5.4 Acetonitrile, CH_3CN - UV grade.

5.5 Formaldehyde, CH_2O - ACS certified or assayed 36.5% solution (W/W).

5.6 Aldehydes and Ketones - analytical grade, used for preparation of DNPH derivative standards of target analytes other than formaldehyde. See list on page 1 for possible target analytes.

5.7 Perchloric Acid, $HClO_4$ - analytical grade.

CAUTION: Concentrated (69%) perchloric acid is a very strong oxidizing agent and presents a serious explosion hazard when combined with organic chemicals or materials. Any perchloric acid to be used in the preparation of DNPH, as per Sec. 5.9, must first be diluted with water to 3.8M as required in Sec. 5.9.5.

5.8 Hydrochloric Acid, HCl - analytical grade.

5.9 2,4-Dinitrophenylhydrazine (DNPH), $C_6H_6N_4O_4$ - recrystallize at least twice with UV grade acetonitrile using the following procedure:

NOTE: This procedure should be performed under a properly ventilated hood. Inhalation of acetonitrile can result in nose and throat irritation (brief exposure at 500 ppm) or more serious effects at higher concentration and/or longer exposures.

5.9.1 Prepare a saturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately 1 hour.

5.9.2 After 1 hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40 to 60°C. Maintain this temperature range until 95% of the solvent has evaporated leaving crystals.

5.9.3 Decant the solution to waste and rinse the remaining crystals twice with three times their apparent volume of acetonitrile.

5.9.4 Transfer the crystals to a clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let the crystals grow slowly at 40 to 60°C until 95% of the solvent has evaporated. Repeat the rinsing process as in Sec. 5.9.3.

5.9.5 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze by HPLC Method 8315). An acceptable impurity level is less than 0.025 mg/L of formaldehyde in recrystallized DNPH reagent or below the sensitivity (ppb, v/v) level indicated in Table 1 for the anticipated sample volume.

5.9.6 If the impurity concentration is not satisfactory, pipet off the solution to waste, repeat the recrystallization as in Sec. 5.9.4 but rinse with two 25 mL portions of acetonitrile. Prep and analyze the second rinse as in Sec. 5.9.5.

5.9.7 When the impurity concentration is satisfactory, place the crystals in an all-glass reagent bottle, add another 25 mL of acetonitrile, stopper, and shake the bottle. Use clean pipets when removing the saturated DNPH stock solution to reduce the possibility of contamination of the solution. Maintain only a minimum volume of the saturated solution adequate for day to day operation to minimize waste of the purified reagent.

5.10 Refer to the determinative method (Method 8315) for procedures regarding the preparation of DNPH derivatives, standards of the derivatives, and calibration standards for HPLC analysis. All standard solutions should be stored at about 4°C in a glass vial with a Teflon®-lined cap, with minimum headspace, and in the dark. They should be stable for about 6 weeks. All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.11 Preparation of DNPH-Coated Sep-PAK Cartridges (if pre-packaged pre-coated cartridges, as in Sec. 4.1.8, are not used)

NOTE: This procedure must be performed in an atmosphere with a very low aldehyde background. The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge to minimize contamination from laboratory air. All glassware and plasticware must be scrupulously cleaned and rinsed with deionized water and aldehyde free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.

5.11.1 DNPH Coating Solution

5.11.1.1 Pipet 30 mL of saturated DNPH stock solution into a 1000 mL volumetric flask, add 500 mL acetonitrile, and acidify with 1.0 mL of concentrated HCl.

5.11.1.2 Shake solution and dilute to volume with acetonitrile. Stopper the flask, invert, and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle equipped with a 0 to 10 mL range repetitive pipet dispenser. Prime the dispenser and slowly dispense 10 to 20 mL to waste.

5.11.1.3 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Sec. 7.2.

5.11.1.4 The impurity concentration should be less than 0.025 µg/mL formaldehyde, similar to that in the DNPH stock solution.

5.11.2 Coating of Sep-PAK Cartridges

5.11.2.1 Open the Sep-PAK package, connect the short end to a 10 mL syringe and place it in the syringe rack. The syringe rack used for coating and drying the sample cartridges is illustrated in Figures 2(a) and 2(b).

5.11.2.2 Using a positive displacement, repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

5.11.2.3 Let the liquid drain to waste by gravity. Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

5.11.2.4 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the acidified DNPH coating reagent into each of the syringes using the repetitive pipet dispenser.

5.11.2.5 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

5.11.2.6 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

5.11.2.7 Assemble a drying manifold as shown in Figure 2(b). This contains a previously prepared, DNPH-coated, cartridge at each of the exit ports (e.g., these

scrubber or "guard cartridges" can be prepared by drying a few of the newly coated cartridges as per the following sections, and "sacrificing" these few to assure the purity of the rest). The "guard cartridges" serve to remove traces of formaldehyde that may be present in the nitrogen gas supply.

5.11.2.8 Insert cartridge connectors (flared at both ends, 0.64 cm OD x 2.5 cm Teflon® FEP tubing with ID slightly smaller than the OD of the cartridge port) onto the long end of the scrubber cartridges.

5.11.2.9 Remove the cartridges from the syringes and connect the short ends of the cartridges to the open end of the cartridge connectors already attached to the scrubber cartridges.

5.11.2.10 Pass nitrogen through each of the cartridges at about 300 to 400 mL/min.

5.11.2.11 Rinse the exterior surfaces and outlet end of the cartridges with acetonitrile using a Pasteur pipet.

5.11.2.12 After 15 minutes, stop the flow of nitrogen, wipe the cartridge exterior free of rinse acetonitrile and remove the dried cartridges.

5.11.2.13 Plug both ends of the coated cartridge with standard polypropylene Luer-Lok male plugs and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

5.11.2.14 Put a serial number and a lot number label on each of the individual cartridge glass storage containers and refrigerate the prepared lot until use. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped culture tubes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Assemble the sampling system, and ensure that the pump is capable of constant flow rate throughout the sampling period. The coated cartridges can be used as direct probes and traps for sampling indoor air when the temperature is above 60°F.

6.1.1 If the temperature in below 60°F, use the heated probe, mentioned in Sec. 4.1.7, to warm the air entering the sampling equipment.

6.1.2 If necessary, add an ozone denuder (see Sec. 3.3).

6.2 Before sample collection, check the system for leaks. Plug the input (short end) of the cartridge so no flow is indicated at the output end of the pump. The mass flowmeter should not indicate any air flow through the sampling apparatus.

6.3 Install the entire assembly (including a "dummy" sampling cartridge) and check the flow rate at a value near the desired rate. In general, flow rates of 500-1200 mL/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH (2 mg or 0.01 mmole/cartridge). In general, a safe estimate of the sample size should be approximately 75% of the DNPH loading of the cartridge (approximately 200 µg as HCHO). Generally, calibration

is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.

NOTE: ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.

6.4 Ideally, a dry gas meter is included in the system to measure and record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Include a rotameter to allow observation of the flow rate without interruption of the sampling process.

6.5 Before sampling, remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to room temperature in the glass tube before connecting it to the sample train.

6.6 Using polyethylene gloves, remove the coated cartridge from the glass tube and connect it to the sampling system with a Luer adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that the short end becomes the sample inlet.

6.7 Turn the sampler on, record the start time, and adjust the flow to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two cartridges in tandem.

6.8 Operate the sampler for the desired period, with periodic recording of the sampling variables such as sample flow rate, pressure, and temperature.

6.9 At the end of the sampling period, stop the flow and record the stop time. If a dry gas meter or equivalent is not used, the flow rate must be checked just before stopping the flow. The average sample flow rate may be calculated using the equation in Sec. 9.1.1. If the flow rate at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

6.10 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with Teflon® tape, label the tube, and place it in a friction-top can containing 2-5 cm of granular charcoal or styrofoam box with appropriate padding. Refrigerate the culture tubes until analysis. The refrigeration period prior to analysis should not exceed 30 days.

NOTE: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.

6.11 Use the equations found in Secs. 9.1.2 and 9.1.3 to calculate the total volume of air sampled and the total volume of air sampled at standard conditions.

7.0 SAMPLE RECOVERY

7.1 The samples are returned to the laboratory in a friction-top can containing 2 to 5 cm of granular charcoal and stored in a refrigerator until analysis. Alternatively, the samples may also be

stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

7.2 Refer to the determinative method (Method 8315) for procedures regarding desorption of the sample from the cartridge and HPLC analysis preparation.

8.0 CALIBRATIONS

8.1 Refer to Sec. 6.0 for requirements regarding the calibration of the sampling system flow rate and equipment for the determination of total flow.

8.2 Refer to the determinative method for procedures regarding calibration of the HPLC analysis system.

8.3 Barometer - Adjust the barometer initially and before each test series to agree within ±2.5 mm Hg (±0.1 in Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level). Note that adjustment for elevation differences between the weather station and the sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase.

8.4 Thermometers

8.4.1 If a mercury-in-glass reference thermometer is to be used, it must conform to ATSM E-1 63C or 63F specifications.

8.4.2 If a thermocouple is to be used, it must be calibrated in the laboratory according to the manufacturer's specifications. The calibration should be done both with and without the use of any extension leads.

9.0 CALCULATIONS

9.1 Calculation of the total volume of air sampled at standard conditions.

9.1.1 If a dry gas meter or equivalent total flow indicator <u>is not</u> used, the average sample flow rate, FR_{ave} in mL/minute, may be calculated using the following equation:

$$FR_{ave} = \frac{FR_1 + FR_2 + ... + FR_N}{N}$$

where:

$FR_1, FR_2, ..., FR_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling

N = Number of flow rates averaged

9.1.2 The total volume of air sampled at the measured temperature and pressure, V_{Tot} in liters (L), may be calculated using the following equation:

$$V_{Tot} = \frac{(Time_2 - Time_1)(FR_{ave})}{1{,}000}$$

where:

$Time_2$ = Stop time (min)
$Time_1$ = Start time (min)
$(Time_2 - Time_1)$ = Total sampling time (min)
FR_{ave} = Average flow rate (mL/min)

9.1.3 The total volume of air sampled converted to standard conditions, V_{TotStd} in liter (L) at 25°C and 101.3 kPa, may be calculated using the following equation:

$$V_{TotStd} = V_{Tot} \times \frac{P_{ave}}{101.3\ kPa} \times \frac{298°C}{(273°C + T_{ave})}$$

where:

V_{Tot} = Total sample volume (L) at measured temperature and pressure
P_{ave} = Average indoor pressure (kPa)
T_{ave} = Average indoor temperature (°C)

10.0 DETERMINATION OF VOLUME TO BE SAMPLED

10.1 Refer to Table 1 for information regarding method "sensitivity" at various sampling volumes.

11.0 QUALITY CONTROL

11.1 Refer to Chapter One for quality control procedures.

11.2 Method Blanks - A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.3 Field Blanks - Field blanks must be submitted with the samples at each sampling site or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. It is desirable to analyze blank cartridges retained in the laboratory (method blanks) as well, to distinguish between possible field and laboratory contamination.

11.4 Blank and Matrix Spikes - A procedure for spiking air sampling cartridges is not yet established for this sampling technique. Refer to Appendix A for information regarding possible techniques for accomplishing sample spiking. Proper QC procedures require that a blank spike and matrix spike be processed for each batch of 10 samples or less. As the MDL becomes better established for this method, the representative spike concentration should be set at 10 times the MDL, for that matrix, to account for interferences.

12.0 METHOD PERFORMANCE

12.1 The method detection limit (MDL) is defined as the minimum concentration of the test compound that can be measured and reported with 99 percent confidence as being greater than zero. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects. The MDLs for the target analytes in the method have not yet been established.

12.2 Table 1 illustrates the sensitivity for the target analytes of interest found in ambient air that have been identified using two Zorbax ODS columns in series.

13.0 REFERENCES

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2. Tejada, S.B., "Standard Operating Procedure for DNPH-coated Silica Cartridges For Sampling Carbonyl Compounds in Air and Analysis by High-performance Liquid Chromatography," Unpublished, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1986.

3. Tejada, S.B., "Evaluation of Silica Gel Cartridges Coated in situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air," Intern. J. Environ. Anal. Chem., Vol. 26:167-185, 1986.

4. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods, EPA-600/4-77-027A, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1979.

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6. Arnts, R.R. and Tejada, S.B., "2,4-Dinitrophenylhydrazine-Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air", Env. Sci. and Tech. 23, 1428-1430 (1989).

TABLE 1

SENSITIVITY (PPB, V/V) OF SAMPLING AND ANALYSIS FOR ALDEHYDES AND KETONES IN AMBIENT AIR USING AN ADSORBENT CARTRIDGE FOLLOWED BY GRADIENT HPLC[a]

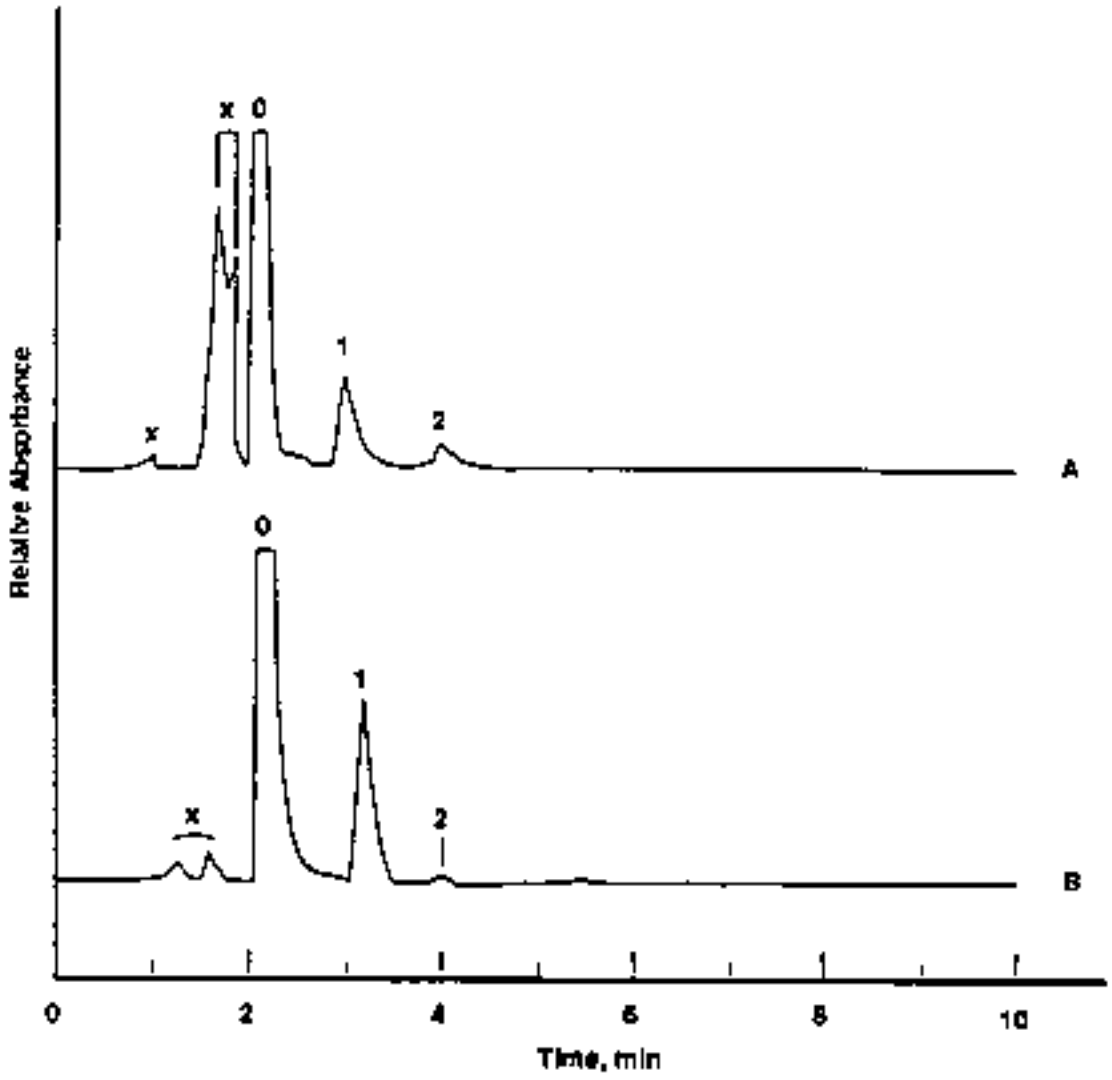
	Sample Volume (L)[b]									
Compound	10	20	30	40	50	100	200	300	400	500
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03
Acetone	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.11	0.05	0.04	0.03	0.02
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.12	0.06	0.04	0.03	0.02
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.12	0.06	0.04	0.03	0.02
2,5-Dimethyl-benzaldehyde	0.97	0.49	0.32	0.24	0.19	0.10	0.05	0.03	0.02	0.02
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03
Hexanal	1.09	0.55	0.36	0.27	0.22	0.11	0.05	0.04	0.03	0.02
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
m-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
o-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
p-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02

[a] The ppb values are measured at 1 atm and 25°C. The sample cartridge is eluted with 5 mL acetonitrile and 25 µL is injected into the HPLC. The maximum sampling flow through a DNPH-coated Sep-PAK is about 1.5 L/minute.

[b] A sample volume of 1000 L was also performed. The results show a sensitivity of 0.01 ppb for all the target analytes.

FIGURE 1

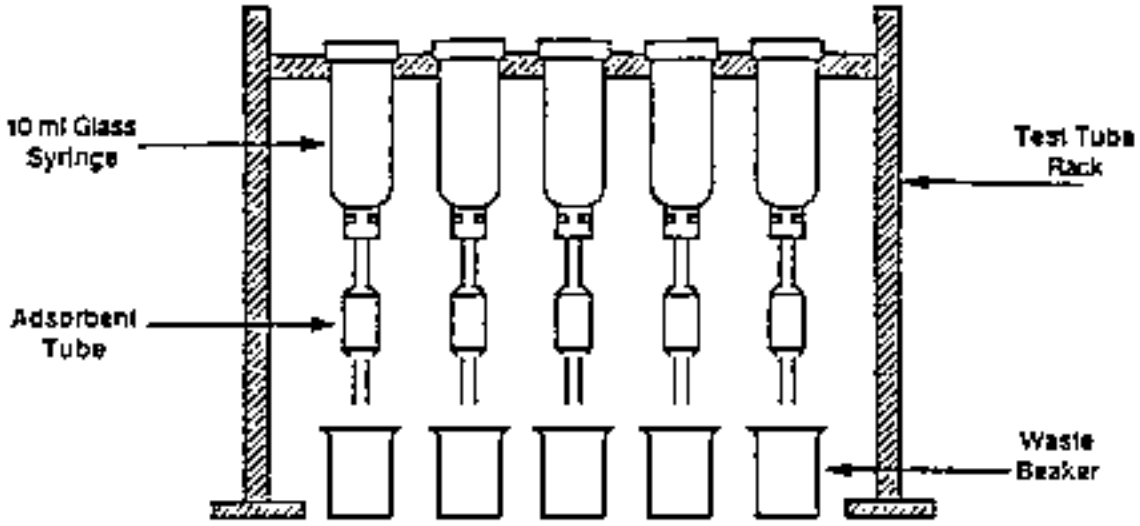
CARTRIDGE SAMPLES OF A FORMALDEHYDE AIR STREAM
WITH (A) AND WITHOUT (B) OZONE



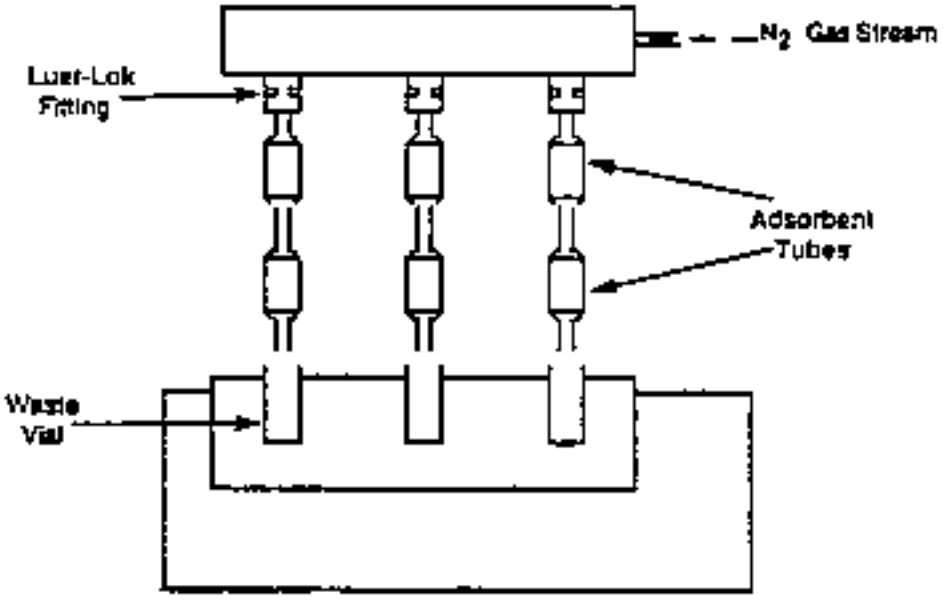
x = unknown
0 = DNPH
1 = formaldehyde
2 = acetaldehyde

FIGURE 2

SYRINGE RACKS FOR COATING AND DRYING SAMPLE CARTRIDGES



(a) RACK FOR COATING CARTRIDGES



(b) RACK FOR DRYING DNPH-COATED CARTRIDGES

This method does not contain a procedure for spiking cartridges for blank spikes and matrix spikes to determine percent recovery. Two suggested techniques for spiking cartridges are as follows:

1) A spike may be performed by introducing an aliquot of a solution containing the target analytes by pipet or syringe directly onto a cartridge in the field or in the laboratory. Standard spike and recovery procedures are followed and the field spike sample is returned to the laboratory for analysis. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

2) Another technique would include spiking the sampling cartridge using a TGM 555 analyzer which produces gaseous formaldehyde standards. However, it should be noted that the procedures required to produce accurate, dynamic, low-level standard mixtures of organics in air are non-routine. The techniques developed for use in evaluating other air sampling procedures employ a 3-stage dynamic gas dilution system coupled with a constant-rate vapor generation assembly containing a trioxane permeation tube (VICI Medtronics Dynacal permeation device or equivalent) that is maintained at 55°C. Trioxane vapor is converted stoichiometrically to formaldehyde vapor using a special high-temperature (160°C) catalytic converter assembly. This method of sample introduction has been used when testing continuous sampling apparatus.