



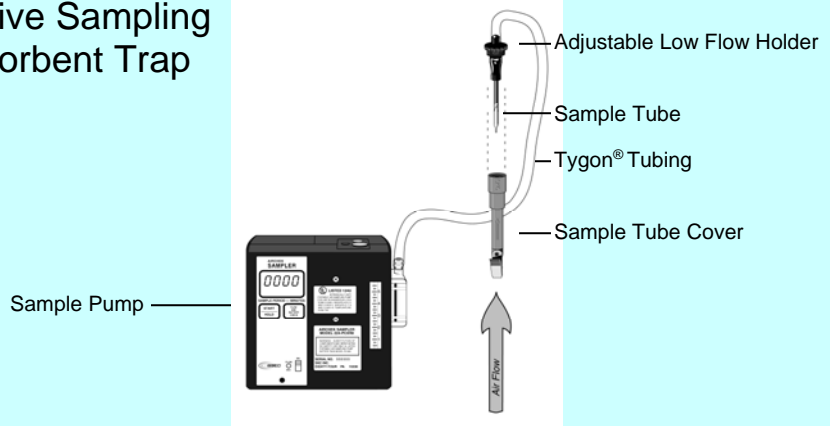
EPA IP-6 METHOD UPDATE

Year 2004
www.skcinc.com

This method update has been written by SKC as a guideline for users. The sampling apparatus specified in this SKC update reflects new technology that may not have been available at the time of the original publication. This method update by SKC has not been officially endorsed or approved by U.S. EPA.

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR

- Method IP-6A-Active Sampling Using a Solid Adsorbent Trap



- Method IP-6C-Passive (Diffusive) Sampler



1. Scope

This method update describes two methods for the determination of formaldehyde and other aldehydes in indoor air. The first method (IP-6A) references the revised Compendium Method TO-11A, which utilizes a solid adsorbent trap for sampling followed by high-performance liquid chromatography (HPLC) analysis. The second method (IP-6C) uses the same chemistry as the active method described in IP-6A. Method IP-6C, however, references the International Standard for Determination of Formaldehyde - Diffusive Sampling Method (ISO/FDIS 16000-2004). With this method, formaldehyde vapor diffuses into the sampler and is collected on silica gel filter paper that has been treated with 2,4-Dinitrophenylhydrazine (DNPH) with a phosphoric acid stabilizer. A stable hydrazone is formed which is desorbed with acetonitrile and analyzed by HPLC with ultraviolet (UV) detector.

2. Significance

2.1 Construction of more tightly sealed buildings and the use of synthetic building materials and furnishings can significantly increase the indoor levels of many pollutants. This is of particular concern because people spend as much as 90% of their time indoors. Monitoring indoor air pollutant levels is an essential part of evaluating potential health threats and identifying appropriate control measures.

2.2 Short-term exposures to formaldehyde and other specific aldehydes (i.e. acetaldehyde, acrolein, crotonaldehyde) are known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. Animal studies indicate that high concentrations can injure the lungs and other organs of the body. Formaldehyde may contribute to eye irritation and unpleasant odors that are common annoyances in polluted atmospheres. The International Agency for Research on Cancer (IARC) has designated formaldehyde as a known human carcinogen that causes nasopharyngeal cancer in humans.

2.3 Indoor sources of formaldehyde include particleboard, plywood, hardwood paneling, furniture, urea-formaldehyde foam insulation, tobacco smoke, and gas combustion. Some of the highest concentrations, exceeding 0.1 ppm, have been found in tightly constructed mobile homes where internal volumes are small compared with the surface area of formaldehyde-containing materials. Formaldehyde emissions increase with increasing temperature and humidity.

2.4 The procedures describe in this method provide the user with a choice of methodologies for the sampling and analysis of formaldehyde in indoor air. All sampling methods can be used in residential, commercial, industrial, or office environments for evaluating formaldehyde levels in a general area or in a microenvironment.

SKC Update to EPA Compendium Method IP-6A

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A SOLID ADSORBENT TRAP

METHOD IP-6A HIGHLIGHTS

Sampler - A glass cartridge containing a dual-bed configuration (300/150 mg) of DNPH-coated silica gel adsorbent (SKC Cat. No. 226-119 or 226-120 with ozone scrubber)

Flow rates - 100 to 1000 ml/min; flows less than 1 L/min will be required with most personal sampling pumps due to the pressure drop of the sampler

Sample time - Long-term (1 to 24 hours) or short-term (5 to 60 minutes)

Sampling temperature - 50 to 212 F (10 to 100 C)

Sample storage - Not to exceed 2 weeks at ≤ 39.2 F (4 C)

Analysis - HPLC-UV operated at 365 nm following desorption by acetonitrile

Background levels of samplers - Not to exceed 0.15 μg formaldehyde/cartridge

Capacity of samplers - Approximately 75 μg formaldehyde

Typical limits of detection - 0.03 μg formaldehyde per sample

Precision - Triplicate analysis of each of 12 identical samples of exposed DNPH cartridges provided formaldehyde measurements that agreed within 10.9% RSD. (Round robin test by EPA's Urban Air Toxics Program in Method TO-11A)

Analytical recovery - 89% at low levels of 0.5 μg aldehyde; 97.5% at high levels of 10 μg of aldehydes (Round robin test by EPA's Urban Air Toxics Program in Method TO-11A)

SKC Update to EPA Compendium Method IP-6A

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES
IN INDOOR AIR USING A SOLID ADSORBENT TRAP

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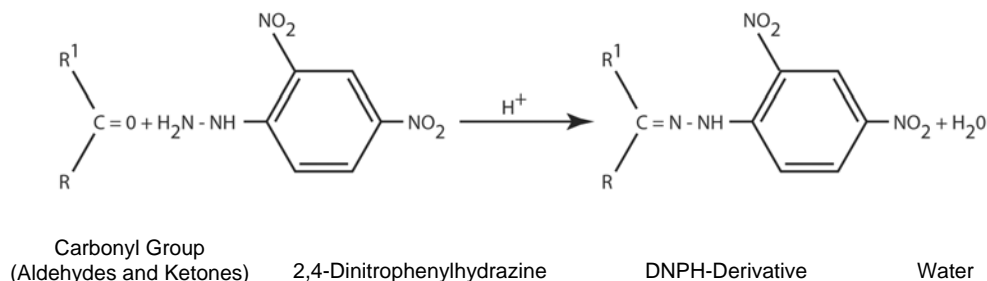
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1. Scope

1.1 This method describes a procedure for determination of formaldehyde and other aldehydes in indoor air. The method is specific for formaldehyde, but with modification, fourteen other aldehydes can be detected as per Compendium Method TO-11A (1).

1.2 The determination of formaldehyde and other carbonyl compounds in air using DNPH chemistry has been widely used and documented (2-5). For example, DNPH impingers are described in Compendium Method TO-5 to determine atmospheric aldehydes and ketones (6). The solid absorbent methodology in Compendium Method IP-6A, however, is a convenient alternative to impinger sampling.

1.3 This method is based on the specific reaction of carbonyl compounds (aldehydes and ketones) with DNPH-coated adsorbent (in traps) in the presence of an acid to form stable derivatives according to the following equation:



where R and R¹ are alkyl or aromatic groups (ketones) or either substituent is a hydrogen (aldehydes). The determination of formaldehyde from the DNPH-formaldehyde derivative is similar to Method TO-5 in incorporating HPLC.

1.4 Flow rates of 100 to 1000 ml/min can be employed to give a time-weighted average (TWA) sample. However, flow rates of 1 L/min or less will typically be required if using personal sampling pumps because of the pressure drop of the sampling media. This method can be used for long-term (1 to 24 hours) or short-term (5 to 60 minutes) sampling of indoor air for formaldehyde.

1.5 There are many commercially available DNPH-coated absorbent traps, which were fully described in the earlier version of this method (see Figure 1) (7). Sep-PAK[®] chromatographic-grade silica gel cartridges and similar items have a very high pressure drop. This method, therefore, describes only the use of DNPH-coated silica gel tubes.

1.6 The adsorbent tube (SKC Inc., Eighty Four, PA; Cat. No. 226-119/120) is a dual-bed configuration with 300 and 150 mg of DNPH-coated silica gel adsorbent in the primary and backup layers, respectively. The dual-bed configuration allows analysis of the backup layer for sample breakthrough.

1.7 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all the safety problems associated with its use. It is the user's responsibility to develop and implement appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
E682 Practice for Liquid Chromatography Terms and Relationships

2.2 Other Documents

Compendium of Methods for the Determination of Air Pollutants in Indoor Air
Compendium of Methods for the Determination of Organic Compounds in Ambient Air

3. Summary of Method

3.1 A known volume of indoor air is drawn through a tube prepacked with silica gel coated with acidified DNPH at a sampling rate of 100 to 1000 ml/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentration in the test atmosphere along with the application for the measurement. 24-hour sampling periods at a maximum rate of 1 L/min may be performed if the test atmospheres are not heavily loaded with particulates and the sampling pumps will work with the pressure drop of the sampling media.

3.2 After sampling, the adsorbent tubes are capped and packed for shipment to the laboratory. Store at ≤ 39.2 F (4 C) until analysis. Storage at ≤ 39.2 F (4 C) prior to analysis should not exceed 2 weeks. If samples are to be shipped to a laboratory for analysis, the duration of the ambient temperature period should be kept to a minimum, preferably less than two days.

3.3 The DNPH-formaldehyde derivative is determined using isocratic reverse phase HPLC with a UV detector operated at 360 nm. A blank sorbent tube is likewise desorbed and analyzed.

3.4 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak

areas with those of standard solutions (see Figure 4 for chromatogram and Figure 5 for sensitivity information).

4. Significance

4.1 This method uses an active sampling system that requires a pump to move sample air through a tube containing DNPH-coated adsorbent. The tubes are commercially prepared for ease of use. The manufacturer, SKC Inc., certifies that background levels of the DNPH-coated adsorbent do not exceed 0.15 µg formaldehyde per tube. The portable sampling system allows for employment of this method in general areas or in microenvironments.

4.2 Subsequent HPLC analysis provides a very accurate measure of indoor formaldehyde concentrations.

5. Definitions

Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356 and E682. All pertinent abbreviations and symbols are defined within this document at point of use.

6. Interferences

6.1 This procedure has been written specifically for the sampling and analysis of formaldehyde. Interferences in the method are certain isomeric aldehydes or ketones that may be unresolved by the HPLC system when analyzing for other aldehydes and ketones. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). In addition, other aldehydes and ketones can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acetone and propionaldehyde and the following higher molecular weight aldehydes and ketones (within an analysis time of approximately one hour) by utilizing two Zorbax ODS columns in series under a linear gradient program:

Acetaldehyde	Crotonaldehyde	Isovaleraldehyde	p-Tolualdehyde
Acetone	2,5-Dimethylbenzaldehyde	Propionaldehyde	Valeraldehyde
Benzaldehyde	Formaldehyde	m-Tolualdehyde	
Butyraldehyde	Hexanaldehyde	o-Tolualdehyde	

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram. The following gradient program was found to be adequate to achieve this goal: upon sample injection, linear gradient from 60 to 75% acetonitrile/40 to 25% water in 30 minutes, linear gradient from 75 to 100% acetonitrile/25 to 0% water in 20 minutes, hold at 100% acetonitrile for 5 minutes, reverse gradient to 60% acetonitrile/40% water in 1 minute, and maintain isocratic at 60% acetonitrile/40% water for 15 minutes.

6.2 Formaldehyde contamination of the DNPH reagent is a problem encountered frequently. Impurity levels of carbonyl compounds in DNPH are determined by HPLC prior to use and should be less than 0.15 µg per cartridge.

6.3 Ozone at high concentrations has been shown to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones). The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (2 and 40 ppb, respectively). In the indoor environment, ozone emission sources include electrostatic air cleaners and photocopying machines.

6.4 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the coated adsorbent. SKC Inc. offers a special tube containing DNPH-coated adsorbent and a built-in ozone scrubber for this application (SKC Inc., Eighty Four, PA; Cat. No. 226-120). The ozone scrubber in the SKC tube is granular potassium iodide.

6.5 Exposure of these sampling tubes to direct sunlight may produce artifacts and should be avoided.

7. Apparatus

7.1 Sampling

7.1.1 Sampling pump capable of accurately and precisely sampling 100 to 1000 ml/min of indoor air (see Figure 2). The sample pump should be capable of providing the required airflow through the sample tube at nominal pressure drops of 40 inches of water at 1 L/min. It is desirable for the sampling pump to incorporate automatic features such as an elapsed-time indicator to measure the actual time the sampling took place (SKC Inc., Eighty Four, PA; Cat. Nos. 224-PCXR4/8).

7.1.2 Calibrator for metering and setting the airflow rate through the sample tube.

7.1.3 DNPH-coated silica gel adsorbent tubes. The SKC adsorbent tube is a glass tube containing a front bed of 300 mg DNPH-coated silica gel and a back bed of 150 mg DNPH-coated silica gel. Airflow through the tube should be from front bed to back bed, as indicated by the arrows marked on the glass cartridge. Tubes are available with an ozone scrubber (SKC Inc., Eighty Four, PA; Cat. No. 226-120) or without the scrubber (SKC Inc., Eighty Four, PA; Cat. No. 226-119). SKC manufactures these tubes to meet the following criteria:

- Total formaldehyde concentration: <0.15 µg/tube

7.1.4 Sample mailers for shipment to a laboratory

7.2 Analysis

7.2.1 Isocratic HPLC system consisting of a mobile phase reservoir; a high pressure pump; an injection valve; a Zorbax ODS (25 cm X 4.6-mm ID) (DuPont® Instruments, Wilmington, DE) or equivalent C-18; a variable wavelength UV detector operating at 365 nm; and a data system. Most commercial HPLC analytical systems will be adequate for this application.

7.2.2 Laboratory glassware including Erlenmeyer and volumetric flasks, graduated cylinders, and sample vials

7.2.3 Laboratory accessories including dispensing pipettes of various sizes, syringes, and polyethylene gloves to handle the silica gel cartridges

8. Reagents and Materials

See Sections 8 in EPA Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>

9. Preparation of Reagents

See Sections 9 in EPA Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>

10. Sample Collection

10.1 The sampling train should be configured as shown in Figure 2 for area sampling or Figure 3 for microenvironmental sampling.

Note: The tester should ensure that the pump is capable of constant flow throughout the sampling period. Airflow through the tube may change during sampling as airborne particles deposit on the sampling media.

Note: Historically, the coated adsorbent cartridges have been used as direct probes and traps for sampling when the air temperature was above freezing. For sampling air below freezing, a short length (30 to 60 cm) of heated (50 to 60 F) stainless steel tubing must be added to condition the air sample prior to collection on the adsorbent tube.

10.2 Before sample collection, the system should be checked for leaks. This can be accomplished by plugging the inlet end of the tube so that no flow is indicated at the output end of the pump. The calibrator should not indicate any airflow through the sampling train.

10.3 The entire assembly (including a representative sampling tube) is installed and the flow rate checked at the desired sampling rate. In general, pump flow rate should be set at 100 to 1000 ml/min and measured using a calibrated flowmeter.

10.4 The flow rate is measured and recorded at the beginning and end of the sampling period to determine sample volume. For extended sampling times, the flow rate should be checked at intermediate points during the sampling period. A calibrated rotameter can be used to simplify this process.

10.5 Before sampling, let the adsorbent tube warm to ambient temperature and connect it to the sample train.

10.6 Using polyethylene gloves to avoid DNPH stains on skin, connect the opened DNPH-coated adsorbent tube to the sampling system. Ensure air is pulled through the tube in the direction noted on the tube by an arrow.

Record pertinent sampling parameters including: date, sampling location, time, ambient temperature, barometric pressure, relative humidity, flow rates, sample tube lot and sample identification numbers, and pump and calibrator serial numbers.

10.7 Turn on the pump and collect the sample for the desired time period with periodic review and recording of the flow rate and other pertinent variables.

10.8 At the end of the sampling period, stop the pump and check the flow rate. If the flow rate at the beginning differs by more than 15% from the flow rate at the end of the sampling period, the sample should be marked as suspect.

10.9 Immediately after sampling, don polyethylene gloves and remove the adsorbent tube from the sampling train. Cap tubes with the end caps provided. Store at ≤ 39.2 F (4 C) until analysis. Storage at ≤ 39.2 F (4 C) prior to analysis should not exceed 2 weeks.

10.10 The average sample flow rate is calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \dots + Q_N}{N}$$

Where: Q_A = average flow rate, L/min

Q_1, Q_2, \dots, Q_N = flow rates determined at beginning, end, and intermediate points during sampling, L/min

N = number of points averaged

10.11 The total volume sampled at measured temperature and pressure is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

Where: V_m = total volume sampled at measured temperature and pressure, L

T_2 = stop time, minutes

T_1 = start time, minutes

$T_2 - T_1$ = total sampling time, minutes

Q_A = average flow rate, L/min

10.12 The total volume (V_s) at EPA standard conditions, 25 C temperature and 760-mm Hg pressure, is calculated using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273} + T_A$$

Where: V_s = total sample volume at 25 C and 760 mm Hg pressure, L
 V_m = total sample volume at measured temperature and pressure, L
 P_A = average ambient pressure, mm Hg
 T_A = average ambient temperature, C

11. Sample Analysis

See Section 11 in EPA Compendium Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>.

12. Calculations

See Section 12 in EPA Compendium Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>.

13. Performance Criteria and Quality Assurance

See Section 13 in EPA Compendium Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>.

14. Detection of Other Aldehydes and Ketones

See Section 14 in EPA Compendium Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>.

15. Precision and Bias

See Section 15 in EPA Compendium Method TO-11A at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>.

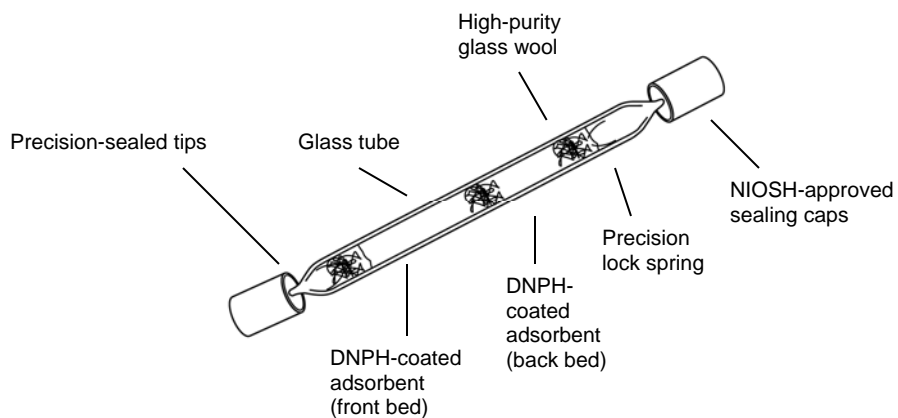
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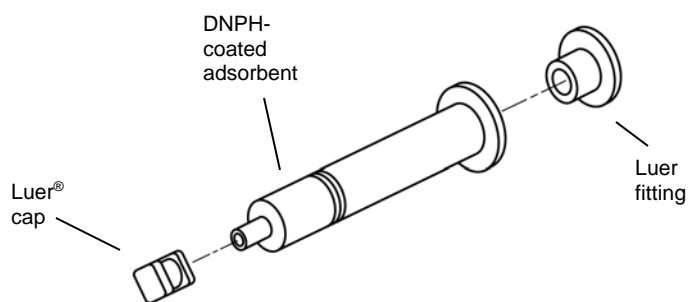
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3. Sirju, A., and Shempson, P.B., "Laboratory and Field Evaluation of the DNPH Cartridge Technique for the Measurement of Atmospheric Carbonyl Compounds," *Environ. Sci. Technol.*, Vol. 29, 1995, pp. 384-392
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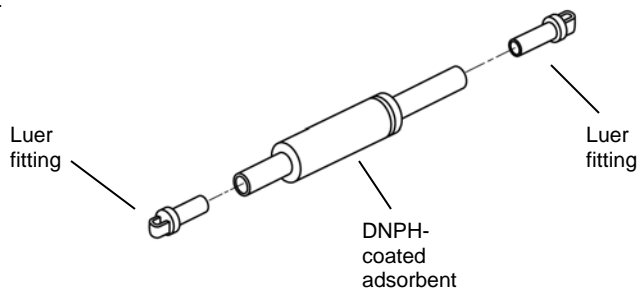
SKC



Supelco



ACC DNPH-C-18 Cartridge



Waters DNPH-Silica Gel Cartridge

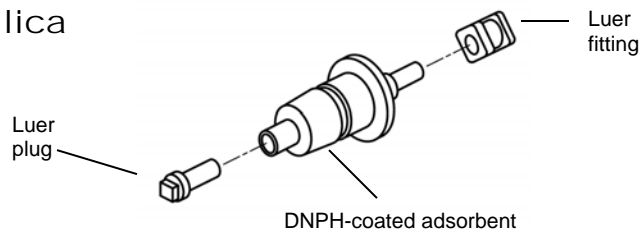


Figure 1. Examples of commercially available DNPH cartridges

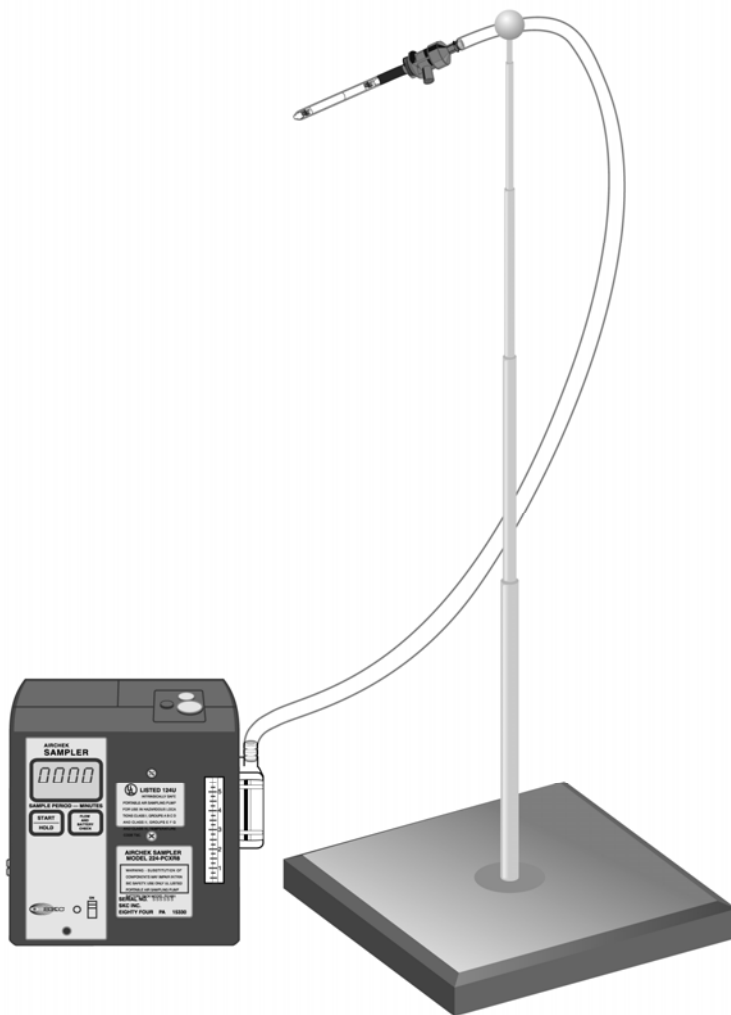
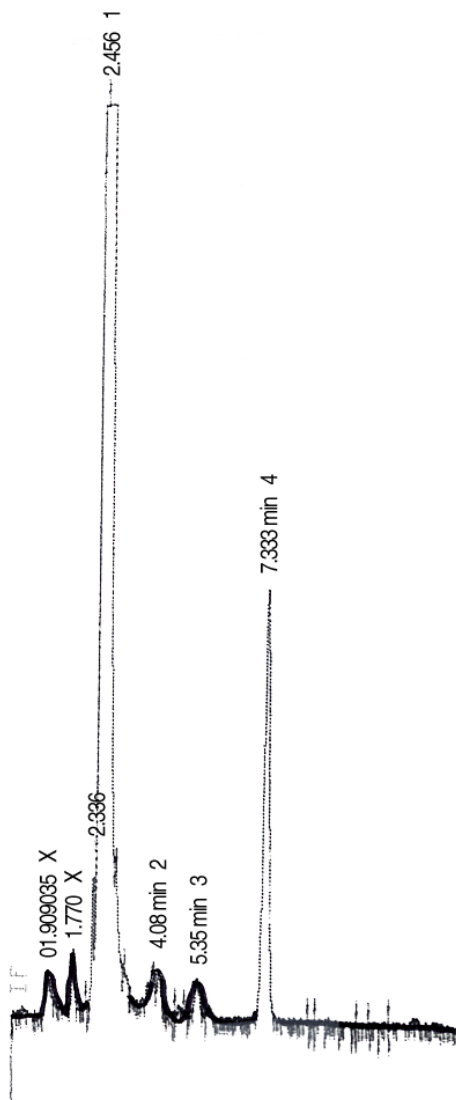


Figure 2. Portable area sampling system for solid adsorbent traps



Figure 3. Microenvironmental sampling system for solid adsorbent traps



X = Unknown
1 = DNPH
2 = Formaldehyde
3 = Acetaldehyde
4 = Acetone

Figure 4. Chromatogram of SKC 226-119 Tube without ozone scrubber

Sensitivity in ppb of Tube 226-119 for Sampling Aldehydes

Compound	Sample Volume (liters)						
	10	20	30	40	50	100	200
Formaldehyde	2.4	1.2	0.80	0.60	0.48	0.24	0.12
Acetaldehyde	1.7	0.83	0.57	0.42	0.34	0.17	0.085
Acetone	1.3	0.65	0.43	0.32	0.26	0.13	0.065

Figure 5. Sensitivity in ppb of Tube 226-119 for sampling aldehydes at various volumes

SKC Update to EPA Compendium Method IP-6C

DETERMINATION OF FORMALDEHYDE IN INDOOR AIR USING A PASSIVE (DIFFUSIVE) SAMPLER

METHOD IP-6C HIGHLIGHTS

Sampler - Silica gel filter paper treated with 2,4-dinitrophenylhydrazine (DNPH) placed in a polypropylene housing containing a number of inlet holes. The sampler is opened by sliding a cover to expose the holes to the air and is closed by replacing the sliding cover. The sampler contains 2 filter compartments. The treated filter beneath the diffusion holes is used for sample collection; the other filter is used as a blank/correction filter. (SKC Inc, Eighty Four, PA; Cat. No. 500-100.)

Sampling/uptake rate - For 15-minute to 24-hour sampling, the average sampling rate for formaldehyde is 28.6 ml/min with a relative standard deviation of 7.6%. The sampling rate is within 8% of theoretical and independent of concentration, relative humidity, sample time, orientation, and face velocity. For 1 to 7-day sampling, the average sampling rate for formaldehyde is 20.4 ml/min.

Sample time - 15 minutes to 24 hours at an average uptake rate of 28.6 ml/min, 1 to 7 days at an average uptake rate of 20.4 ml/min

Sampling conditions - Relative humidity from 10 to 80% and face velocities from 5 to 100 cm/s with either a parallel or a perpendicular orientation

Sample storage - Before use: Store at freezer temperatures (≤ 39.2 F [4 C]) for up to 12 months after manufacture
After use: Store at freezer temperatures (≤ 39.2 F [4 C]) not to exceed 3 weeks

Analysis - HPLC-UV operated at 365 nm following extraction with acetonitrile

Background levels of samplers - Not to exceed 0.085 μg formaldehyde per sampler

Capacity of samplers - Approximately 29 μg formaldehyde per sample

Typical limits of detection - 15-minute sample: 200 ppb
8-hour sample: 5 ppb
24-hour sample: 2 ppb
7-day sample: 0.2 ppb

Analytical recovery - Mean recovery is 100% with a relative standard deviation of 3.95%.

SKC Update to EPA Compendium Method IP-6C

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES
IN INDOOR AIR USING A PASSIVE (DIFFUSIVE) SAMPLER

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1. Scope

1.1 This method describes a procedure for determination of formaldehyde in indoor air. Other aldehydes can be determined, but a complete validation study of critical parameters including the experimental uptake rates of various aldehydes has not yet been completed by SKC Inc. or other agencies. See *the Passive Sampling Guide* at www.skcinc.com for calculated sampling rates for other aldehydes.

1.2 This method uses the same chemistry referenced in Section 1 of Method IP-6A. In this case, however, a silica gel filter paper is treated with DNPH. The treated filter paper is loaded into a polypropylene passive sampler, which collects the formaldehyde through the process of controlled diffusion (SKC Inc., Eighty Four, PA; Cat. No. 500-100). After sampling, the exposed filter papers are placed in a vial, extracted with acetonitrile, and analyzed by high-performance liquid chromatography with UV detection (HPLC-UV). (8-10)

Note: If sampling in an atmosphere containing formalin, see www.skcinc.com/instructions/1795.pdf for field study information. (13) (14)

1.3 The average uptake rate for formaldehyde using the SKC passive sampler was measured experimentally and found to be 28.6 ml/min with a relative standard deviation of 7.6%. The sampling rate was within 8% of theoretical and independent of concentration, relative humidity, sample time, orientation, and face velocity. The National Institute of Working Life in Sweden validated the SKC sampler for typical workplace sampling from 15 minutes to 8 hours. The sampler can easily detect levels as low as 5 ppb for an 8-hour exposure. (11)

1.4 Researchers at the National Institute of Working Life in Umea, Sweden have also validated the use of the sampler for indoor air sampling from 24 hours to 7 days. The sampler can detect levels as low as 2 ppb for a 24-hour exposure. (12)

1.5 The passive sampler is marketed as the UME^x 100 Passive Sampler for formaldehyde and is manufactured by SKC Inc. (Eighty Four, PA; Cat. No. 500-100). The sampler has 2 compartments for the treated filter paper, one serves as the sample and the other as the blank/correction. Designed for one-time use, the SKC UME^x 100 Passive Sampler is packaged in an aluminized pouch for easy transport. A shelf-life date is printed on the label on the outside of each pouch.

1.6 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all the safety problems associated with its use. It is the user's responsibility to develop and implement appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
E682 Practice for Liquid Chromatography Terms and Relationships

2.2 Other Documents

Compendium of Methods for the Determination of Air Pollutants in Indoor Air
Compendium of Methods for the Determination of Organic Compounds in Ambient Air

International Organization for Standardization (ISO) Standards for Environment, Health Protection and Safety (13.040 Air Quality)

3. Summary of Method

3.1 Formaldehyde vapor diffuses into the sampler at an experimentally determined rate and is collected on a silica gel filter paper, which has been treated with 2,4-dinitrophenylhydrazine (DNPH) with a phosphoric acid stabilizer. A stable hydrazone is formed which is desorbed with acetonitrile and analyzed by HPLC with an ultraviolet (UV) detector. The samplers have been validated for workplace sampling from 15 minutes to 8 hours and indoor air sampling from 24 hours to 7 days.

Note: If sampling in an atmosphere containing formalin, see www.skcinc.com/instructions/1795.pdf for field study information. (13) (14)

3.2 After sampling, the samplers are closed, sealed in the aluminized pouch provided, and packed for shipment to a laboratory. The samples should be stored at freezer temperatures (≤ 39.2 F [4 C]) until analysis. Storage at freezer temperatures (≤ 39.2 F [4 C]) prior to analysis should not exceed 3 weeks. If samples are to be shipped to a laboratory for analysis, the duration of the ambient temperature period should be kept to a minimum.

3.3 The DNPH-formaldehyde derivative is desorbed using 3.0 ml of acetonitrile in a 4-ml glass vial and is analyzed using HPLC with a UV detector at 365 nm for best results. The blank treated filter is likewise desorbed and analyzed.

3.4 Formaldehyde in the sample is identified and quantified by comparison of its retention times and peak heights or peak areas with those of standard solutions.

4. Significance

4.1 This method uses a passive sampling system with an uptake rate that depends on the diffusion coefficient of formaldehyde, and that is proportional to the cross-sectional area of the sampler opening and inversely proportional to the sampler diffusion zone length. The National Institute of Working Life in Sweden has experimentally verified this rate in the validation study. The samplers are available commercially from SKC Inc. and have a 12-month shelf life after date of manufacture if stored at freezer temperatures (≤ 39.2 F [4 C]). The manufacturer certifies that background levels of formaldehyde do not exceed 0.085 μg formaldehyde per sampler. The portable samplers allow for employment of this method in general areas with some minimal air movement or in microenvironments.

4.2 Subsequent HPLC analysis provides a very accurate measure of indoor formaldehyde concentrations.

5. Definitions

Note: Definitions used in this document and any user-prepared SOPs should be consistent with ASTM Methods D1356 and E682. All pertinent abbreviations and symbols are defined within this document at point of use.

6. Interferences

6.1 This procedure has been written specifically for the sampling and analysis of formaldehyde. When sampling, large amounts of airborne carbonyl compounds may reduce the uptake of formaldehyde. In laboratory analysis, interferences may result from isomeric aldehydes or ketones that may be unresolved by the HPLC system. Organic compounds that have the same retention time and significant absorbance at 365 nm as the DNPH derivative of formaldehyde will interfere. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions).

6.2 A negative interference caused by ozone has been reported with active sampling for formaldehyde using the DNPH chemistry. Only use passive sampling in atmospheres containing an ozone level < 0.5 ppm. (13)

Note: If sampling in an atmosphere containing formalin, see www.skcinc.com/instructions/1795.pdf for field study information. (13) (14)

7. Apparatus

7.1 Sampling

7.1.1 Passive (Diffusive) Sampler containing a DNPH-treated filter paper placed in a housing with inlet holes that allow for the controlled diffusion and collection of formaldehyde (see Figure 6). The sampler uptake rate is independent of concentration from 5 ppb to 5 ppm, humidity from 10 to 80% relative humidity, and wind velocity effects from 5 to 100 cm/sec. The sampler has a clip for positioning during sampling (SKC Inc., Eighty Four, PA; Cat. No. 500-100). SKC manufactures these samplers to meet the following criteria:

- Total formaldehyde concentration: <0.085 µg per sampler

Note: If sampling in an atmosphere containing formalin, see www.skcinc.com/instructions/1795.pdf for field study information. (13) (14)

7.1.2 The samplers are shipped from the manufacturer in a protective pouch, which can be used for shipment in an appropriate mailer to a laboratory.

7.2 Analysis

7.2.1 HPLC system consisting of solvent pump(s), solvent reservoir(s), solvent mixer, a reverse-phase column, a column oven, a pump controller, and a data-handling system. Most commercial HPLC analytical systems will be adequate for this application.

7.2.2 Ordinary laboratory glassware and accessories including volumetric flasks, cylinders, vials, pipettes, syringes, and forceps to handle the samples.

8. Reagents and Materials

9. Preparation of Reagents

Complete information for Sections 8 and 9 can be obtained in Section 4 of the ISO Standard ISO/FDIS 16000-4-2004. ISO standards for air quality can be purchased online at <http://www.iso.org> at ICS field 13.040 for air quality in the environment, health protection, and safety standards.

10. Sample Collection

10.1 The tester should open the pouch and remove the sampler. Enter the date, location, and start times in the space provided on the back of the sampler. Clip

the sampler in the desired location and slide the cover to the “on” position to begin sampling.

Note: Included in the pouch is a small length of tape similar to the tape inside the sampler. This tape protects the background of the sampler should any formaldehyde in the atmosphere enter the pouch. Leave the tape inside the pouch at all times and send along with the sample to the laboratory.

Note: The tester should check the expiration date on the label on the outside of the pouch. Do not use after the last day of the month indicated. Also, do not discard the pouch. Store it in a formaldehyde-free area and use after sampling for transport to a laboratory.

Note: ISO Standard 16000-2 provides guidance on sampler placement for area monitoring. The sampler should be at least 1 meter from the walls of the room at a height of 1.5 meters above the floor. Samplers should not be placed in areas of the room strongly influenced by local ventilation or near known sources of formaldehyde unless these sources are the target of the study.

10.2 At the end of the exposure period, slide the sampler cover to the “off” position to stop sampling. Enter the sample stop time in the space provided on the back of the sampler. Place the sampler into the original pouch immediately after sampling, seal it, and ship it to a laboratory in an appropriate mailing container with necessary supporting documentation. Use expedited shipping to avoid prolonged shipping time at ambient temperature.

10.3 There is no need to ship additional blank samplers to the laboratory as a treated blank/correction filter is contained within each UME^x sampler.

11. Sample Analysis

11.1 Desorption and Sample Preparation

11.1.1 Desorption of the DNPH-formaldehyde from the treated filter should be performed in a clean atmosphere, free of formaldehyde. Remove the sampler from the pouch and the sliding cover from the sampler. Remove the treated filters from each section of the sampler using forceps (cleaned with acetonitrile). Place each section in its own sealed vial.

Note: The blank/correction section has an indentation in the center of the filter paper for easy identification.

11.1.2 Pipette 3.0 ml of acetonitrile into each vial and hand agitate for 1 minute. Remove the treated filter from the vial and seal for analysis. The desorption efficiency will be at least 95% using this procedure.

11.1.3 If HPLC analysis is not going to be performed immediately, the DNPH-formaldehyde solution should be stored at freezer temperatures (≤ 39.2 F [4 C]) and analyzed within 3 days.

11.2 Derivative Preparation

Note: Prepared derivative standards are commercially available.

11.2.1 To prepare the derivative standards, add 10 ml concentrated hydrochloric acid to 2 grams of 2,4-DNPH while stirring. Dissolve the yellowish crystal mass in 200 ml ethanol (95%). Stir for 30 minutes and then cap the flask.

11.2.2 Filter the liquid to remove undissolved hydrazine hydrochloride. Add 0.8 ml 37% aqueous formaldehyde to form a yellowish precipitate. Filter and wash the crystals with 5 ml cold ethanol and recrystallize twice by adding boiling ethanol (95%). Prepare standard solutions in acetonitrile.

11.3 HPLC Analysis

11.3.1 A 10- μ l portion of the DNPH-formaldehyde solution is subjected to HPLC determination using an octadecylsilane (ODS) column and a mobile phase consisting of 33% water in methanol. Other conditions may also prove acceptable. Analysts should experiment with the on-site HPLC system to optimize chromatographic conditions for a specific application. Either a gradient or an isocratic elution program may be used (see Figure 7).

11.3.2 The formaldehyde 2,4-dinitrophenylhydrazone is detected with UV absorption between 230 and 370 nm. Tunable UV detectors should use 365 nm for optimum results. The detection limit will depend on instrument sensitivity.

11.3.3 When analyzing the derivative standards, it is suggested to start with the lowest concentration to avoid carry-over effects. After all the standards have been injected and the HPLC peak heights or areas have been obtained, prepare a calibration graph by plotting peak response against analyte concentration (μ g/ml).

11.3.4 Solutions produced by desorption of the exposed samples and blank treated filters are injected in the HPLC and analyzed in the same manner as the derivative calibration standards. Determine the peak responses and read the concentrations of DNPH-formaldehyde from the calibration graph.

12. Calculations

12.1 Amount of DNPH-formaldehyde on the filter

12.1.1 Calculate the mass of DNPH-formaldehyde desorbed from the sample or blank/correction filter by multiplying the concentration in the solution as read from the calibration curve by the volume of solution used for filter desorption:

$$\text{Total mass collected } (\mu\text{g}) = \text{Concentration } (\mu\text{g/ml}) \times \text{Desorption Volume (ml)}$$

12.2 Concentration of formaldehyde in air

12.2.2 Calculate the total air volume sampled using the following equation:

$$\text{Volume of air (liters)} = \frac{\text{Sample time (min)} \times \text{Sampling rate (28.6 ml/min)}}{1000}$$

Note: When calculating results from 1 to 7-day sampling, use a sampling rate of 20.4 ml/min.

12.2.3 The concentration of formaldehyde in mg/m³ can be determined as follows:

$$\text{Concentration (mg/m}^3\text{)} = \frac{\text{Total mass collected (mg)} \times 1000}{\text{Total volume sampled}}$$

12.2.4 The concentration can be converted to ppm, using the following:

$$\text{ppm in air} = (24.45/30.03) \times \text{mg/m}^3$$

13. Standard Operating Procedures

Information on reporting requirements and quality control can be obtained in Section 9 and 11, respectively, of the ISO Standard ISO/FDIS 16000-4-2004. ISO standards for air quality can be purchased online at <http://www.iso.org> at ICS field 13 for environment, health protection, and safety standards.

14. Precision and Bias

14.1 The sampling rate data was generated over a validation range of 0.06 to 3.0 ppm formaldehyde and at 10 to 80% relative humidity. The relative standard deviation of the mean sampling rate of 28.6 ml/min was 7.6%. The bias on the sampling rate ranged from - 2.3 to +1.5 or from 26.3 to 30.1 ml/min. ISO Standard ISO/FDIS 16000-4-2004 reported that the precision of replicate

measurement from field experiments performed with diffusive formaldehyde samplers using DNPH chemistry was typically less than 10%, expressed as a relative standard deviation.

15. References

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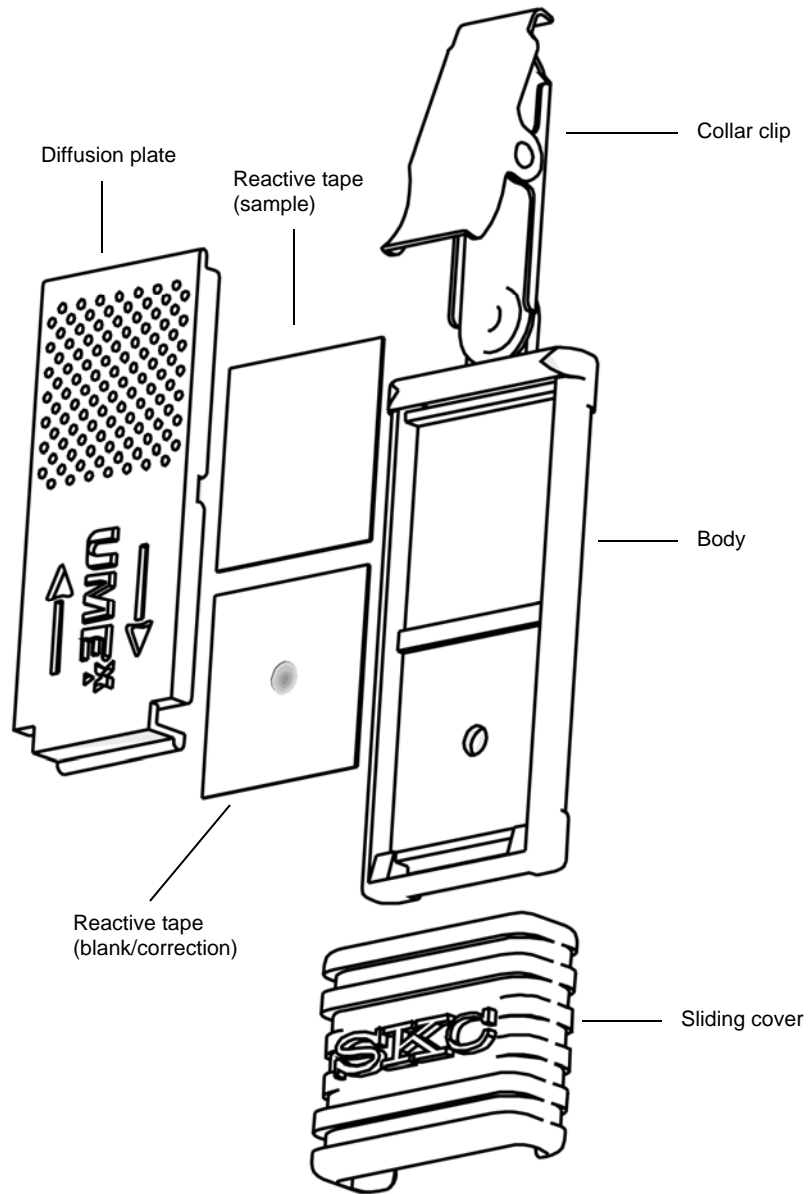


Figure 6. UME^x 100 Passive Sampler (exploded view)

Column: 250 mm x 4.6 mm, 5 micron, Betasil ODS, made by Keystone Scientific

Eluent: 60/40 Acetonitrile/DI Water at 1.5 ml/min

Injector: Waters 272 Autosampler, 20 microliters

Pump: SSI HPLC Pump, 222D

Detector: SSI 500 Variable UV/VIS, 365 nm

Integrator: HP 3396 Series II

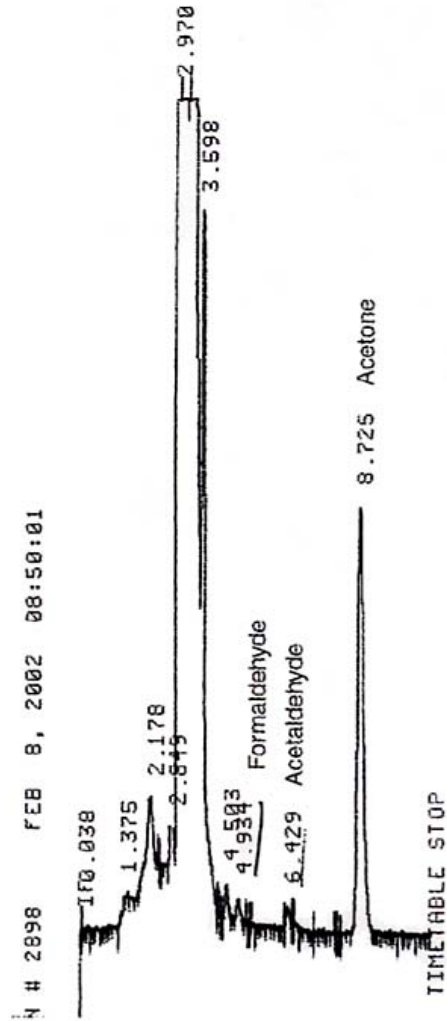


Figure 7. Sample chromatogram - blank DNPH-treated filter in acetonitrile