

Formaldehyde
(Diffusive Samplers)



Method no: 1007
Control no.: T-1007-FV-01-0505-M

Target concentration: 0.75 ppm (0.92 mg/m³)
OSHA PEL: 0.75 ppm (0.92 mg/m³) (TWA); 2 ppm (2.5 mg/m³) (STEL)
OSHA Action level: 0.5 ppm (0.61 mg/m³) (TWA)
ACGIH TLV: 0.3 ppm (0.37 mg/m³) (ceiling)

Procedure: Diffusive samples are collected by exposing either Assay Technology ChemDisk Aldehyde Monitor 571 (ChemDisk-AL), SKC UME_x 100 Passive Sampler (UMEx 100), or Supelco DSD-DNPH Diffusive Sampling Device (DSD-DNPH) to workplace air. Samples are extracted with acetonitrile and analyzed by LC using a UV detector.

Recommended sampling time
For UME_x 100, ChemDisk-AL,
and DSD-DNPH: 240 min (TWA); 15 min (STEL)

Reliable quantitation limit:

sampler	RQL		SEE*
	(ppb)	(µg/m ³)	(%)
ChemDisk-AL	1.88	2.30	7.8
UMEx 100	5.68	6.93	8.2
DSD-DNPH	0.58	0.70	7.5

*For samples where sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.4 for applicable standard errors of estimate.

Special requirements: Report sampling site atmospheric pressure and temperature when using diffusive samplers.
Store samplers in a refrigerator both before and after sampling.
For quantitative results, use an active sampling procedure such as OSHA Method 52 when monitoring exposures resulting from the use of formalin solutions. These diffusive samplers failed validation when formalin was the source of formaldehyde. (Section 4.9)
Do not use these diffusive samplers if the ozone level is greater than 0.5 ppm. (Section 4.9)
Do not use these diffusive samplers if the humidity is 10% or less. (Section 4.9)
Place samples into manufacturer-supplied aluminized bags immediately after sampling.

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

May 2005

Mary Eide

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

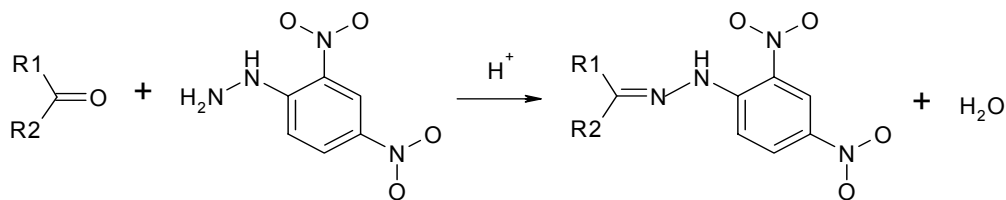
1. General Discussion

For problems with accessibility in using figures and illustrations in this method, please contact the author at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

The purpose of this work was to validate a diffusive sampler for formaldehyde. The 3M formaldehyde monitor 3721, used in OSHA Method ID-205¹, adsorbed the formaldehyde onto a bisulfite-impregnated paper, and used chromotropic acid to detect formaldehyde. These samplers could be used for only TWA sampling with a minimum of 4 hours sampled. The PEL for formaldehyde has a 2 ppm STEL, so a diffusive sampler that could measure STEL level was desired. The three diffusive sampling devices used in this method are Assay Technology ChemDisk 571 Aldehyde Monitor (ChemDisk-AL), SKC UMEEx 100 Passive Sampler (UMEEx 100), and Supelco DSD-DNPH Diffusive Sampling Device (DSD-DNPH). All three of these samplers use 2,4-dinitrophenyl hydrazine (DNPH), in the presence of a strong acid, to derivatize the formaldehyde into a unique derivative. Other aldehydes and ketones will form their own unique derivative. The analysis is by liquid chromatography (LC) with a UV detector at 365 nm. The sensitivity of these samplers was much greater than the bisulfite impregnated paper, so these samplers can be used for STEL sampling. The reaction of the carbonyl containing chemical with DNPH to form the hydrazone derivative and water is shown below:



In the case of formaldehyde R1 and R2 are hydrogens.

The test atmospheres used in this work were dynamically generated by introducing the formaldehyde/water solution into a heated manifold, and then diluting the resultant vapor with a measured stream of air at a known flow, temperature, and humidity. The formaldehyde/water solution was freshly prepared by bubbling formaldehyde gas produced by heating paraformaldehyde into deionized water. A nitrogen gas stream carried the formaldehyde gas into the water. The concentration of the formaldehyde in solution was determined by titration following the procedure in OSHA Method 52.² This solution was stable for at least 1 week. Theoretical test atmosphere concentration was calculated from the test atmosphere generation parameters, and it was confirmed using OSHA Method 52.² The average of active sampling method results was 99.4% of theoretical for side-by-side samples that were collected simultaneously for every diffusive sampler test. Theoretical test atmosphere concentrations (verified by active sample results) were used in subsequent calculations.

¹ Formaldehyde OSHA Method ID-205. www.osha.gov (accessed 9/03/03).

² Acrolein and/or Formaldehyde OSHA Method 52. www.osha.gov (accessed 9/03/03).

Sampling test atmospheres generated using formalin (formaldehyde/water solution stabilized with methyl alcohol) at ambient temperatures can produce low results for diffusive samplers that have been calibrated with formaldehyde when compared to results from active samplers. This discrepancy has been cited in the literature and it was confirmed by experimental work performed in this method (Section 4.9), and may be as much as 35%.^{3,4} The root cause of the inconsistency is the reversible chemical reaction of formaldehyde and methyl alcohol to form primarily methoxymethanol and trace levels of dimethoxymethane.⁵ Both formaldehyde and methoxymethanol react to form the formaldehyde derivative on reagent coated active and diffusive samplers. Methoxymethanol and dimethoxymethane have different diffusive sampling rates than formaldehyde. Sampling rate for diffusive samplers is dependant on the chemical being sampled, while sampling rate for active samplers is independent of the chemical being sampled, as the sampling rate is the flow rate of the sampling pump.

This uncorrectable bias for formaldehyde diffusive samplers will always exist in workplaces where formalin is used, and may be greater than the accuracy requirement of $\pm 25\%$ for TWA samples and $\pm 35\%$ for STEL samples, required by the OSHA standard for formaldehyde.⁶ For quantitative results, an active sampling procedure such as OSHA Method 52⁷ should be used when monitoring exposures resulting from the use of formalin solutions.

The laboratory test atmosphere issue can be resolved by increasing the temperature of the vapor generator such that it is sufficient to reverse the formation of methoxymethanol and dimethoxymethane and accordingly reform formaldehyde. Diffusive and active sampling results from such a test atmosphere are similar. This effect was also confirmed in this work (Section 4.11). Conditions in the workplace may not be sufficient to reverse the formation of methoxymethanol and dimethoxymethane, and their unknown proportions in workplace atmospheres can cause erroneous diffusive sampling results for formaldehyde.

Ozone is an interference for samplers using DNPH derivatization. Ozone can react with the DNPH, decreasing the amount available for derivatizing the formaldehyde, or it can decrease the amount of formaldehyde-DNPH already produced.⁸ Most urban pollution levels are below 0.5 ppm ozone. Tests of an atmosphere of 0.577 ppm ozone showed a recovery of 92.5% for ChemDisk-AL, 92.6% for UMEx 100, and 92.5% for DSD-DNPH. Higher ozone levels showed more of a loss (Section 4.9).

The diffusive samplers in this work performed best in relative humidities (RH) above 10% (Section 4.9). At relative humidities lower than 10% the tested results were significantly lower when compared to theoretical. This indicates that water is a necessary component of the reaction between formaldehyde and DNPH.

Storing samplers at elevated temperatures causes the DNPH to decompose, forming 2,4-dinitroaniline, which may co-elute with the DNPH-formaldehyde derivative. EPA recommends storing samplers both before and after sampling at 4 °C.^{7,9} This

³ Pengelly, I, Groves, J.A., Levin, J.O., and Lindahl, R. An Investigation into the Differences in Composition of Formaldehyde Atmospheres Generated from Different Source Materials and the Consequences for Diffusive Sampling, *Ann. Occup. Hyg.*, 1996, Vol. 40, No. 5, pp 555-567.

⁴ Formaldehyde in Air, MDHS 78. www.hse.gov.uk (accessed 9/10/03).

⁵ Walker, J. *Formaldehyde*, Reinhold Publishing Corporation: New York, 1953, p 74.

⁶ CFR 1926.1148 Formaldehyde. www.osha.gov (accessed 9/03/03).

⁷ Acrolein and/or Formaldehyde OSHA Method 52. www.osha.gov (accessed 9/03/03).

⁸ Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC). www.epa.gov (accessed 4/15/04).

⁹ Compendium Method 0011, Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources. www.epa.gov (accessed 4/15/04).

decomposition was also observed by NIOSH, a significant increase of a peak at the retention time of the formaldehyde-DNPH derivative was observed when DNPH coated silica gel air samplers were stored at 40 °C (104 °F) overnight.¹⁰

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)⁶

OSHA has stated “Formaldehyde has the potential to cause cancer in humans.” Concentrations of 0.5 to 2 ppm may cause eye, respiratory, and skin irritation. Rats exposed to 2 ppm formaldehyde developed benign nasal tumors. Structural changes in epithelial cells in human nasal passages have been observed. The perception of formaldehyde by odor and/or eye irritation may diminish with time as the body adapts to the formaldehyde concentration in the workplace air. It can cause skin sensitization. Formaldehyde is genotoxic showing properties of both an initiator and a promoter.

1.1.3 Workplace exposure¹¹

Formaldehyde is consistently listed in the top 25 chemicals produced in the U.S. Some of the formaldehyde produced in the U.S. is produced and consumed in the same facility through a closed system. Most of the commercial production is as formalin solution. The rest of the commercial production is as formaldehyde gas and paraformaldehyde. Formaldehyde is used in the production of urea-formaldehyde, phenol-formaldehyde, melamine, and polyacetal resins. It is used in the production of many organic chemicals, including dyes, fertilizers, disinfectants and germicides. It is used as a preservative for shampoos, conditioners, and paints, as an embalming fluid, as a hardening agent, as an oil well corrosion inhibitor, as a reducing agent in the recovery of gold and silver, as a fungicide for other plant products, as a component in the manufacture of fiberboard, particle board and plywood, and as a permanent-press treatment for fabrics. Formaldehyde exposure may come from the vapors from formaldehyde gas, formalin solution, or solid paraformaldehyde. Exposures also come from cutting, heating, and other manipulations of the formaldehyde containing resins, fiber products and wood products. Formaldehyde is a component of diesel exhaust.

1.1.4 Physical properties and other descriptive information^{10, 12, 13}

synonyms:	formic aldehyde; methyl aldehyde; methylanal; methylene oxide; oxomethane; oxymethylene
IMIS ¹⁴	1290
CAS number:	50-00-0
boiling point:	-19.5 °C (-3.1 °F)
melting point:	-92 °C (-133.6 °F)
molecular weight:	30.03
vapor pressure:	1.33 kPa @ -88 °C
flash point:	50 °C (122 °F) (closed cup aqueous solution with 15% methyl alcohol)
appearance:	colorless gas; aqueous solutions with methyl alcohol are clear liquid

⁶ CFR 1926.1148 Formaldehyde. www.osha.gov (accessed 9/03/03).

¹⁰ Harper, M. NIOSH. Private communication, 2005.

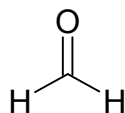
¹¹ *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; American Conference of Governmental Industrial Hygienists Inc.: Cincinnati, OH, 2001, Vol. II, p Formaldehyde 1-25.

¹² Lewis, R. J. Sr., Ed. *Hawley's Condensed Chemical Dictionary*, 14th ed.; Van Nostrand Reinhold Co.: New York, 2001, p 511.

¹³ Budavari, S., Ed. *The Merck Index*, 13th ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 751.

¹⁴ OSHA Chemical Sampling Information, www.osha.gov (accessed 11/15/03).

vapor density: 1.08 (air = 1.0)
 molecular formula: CH₂O
 odor: pungent, slightly musty
 lower explosive limit: 7 to 73% by volume
 specific gravity: 0.815 at -20/4 °C
 solubility: very soluble in water, up to 55%; soluble in alcohol, ether
 structure:



This method was evaluated according to the OSHA SLTC “Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis”¹⁵. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure (DLAP) is 4.26 pg. This is the amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure (DLOP) are shown in Table 1.2.2. These are the amounts of formaldehyde spiked on the respective sampler that will give detector responses that are significantly different from the responses of the respective sampler blanks. (Section 4.2)

Table 1.2.2
Detection Limits of the Overall Procedure

sampler	ng	ppb	µg/m ³
ChemDisk-AL	2.25	0.56	0.69
UMEx 100	14.9	1.70	2.08
DSD-DNPH	3.56	0.17	0.21

1.2.3 Reliable quantitation limit

The reliable quantitation limits (RQL) are shown in Table 1.2.3. These are the amounts of formaldehyde spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements. (Section 4.2)

Table 1.2.3
Reliable Quantitation Limits

sampler	ng	ppb	mg/m ³	E _E
ChemDisk-AL	7.49	1.88	2.30	99.5
UMEx 100	49.5	5.68	6.93	99.3
DSD-DNPH	11.9	0.58	0.70	99.5

E_E = extraction efficiency

¹⁵ Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, www.osha.gov (accessed 11/15/03).

1.2.4 Instrument calibration

The standard error of estimate is 0.051 µg over the range of 3.92 to 31.34 µg/sample. This range corresponds to 0.25 to 2 times the TWA target concentration for DSD-DNPH. (Section 4.3)

1.2.5 Precision

The precisions of the overall procedure at the 95% confidence level were calculated from the ambient temperature 17-day storage test for samples collected from a dynamically generated atmosphere of 0.75 ppm (0.92 mg/m³) formaldehyde. The precision includes the sampling rate variability of 7.71% for ChemDisk-AL, 8.06% for UME_x 100, and 7.54% for DSD-DNPH. There are different precision values given, depending on whether both, either, or neither temperature (*T*) or atmospheric pressure (*P*) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included. (Section 4.4)

Table 1.2.5
Precision of the Overall Procedure

known conditions	ChemDisk-AL precision (± %)	UMEx 100 precision (± %)	DSD-DNPH precision (± %)
both <i>T</i> & <i>P</i>	15.3	16.0	14.8
only <i>T</i>	16.3	17.0	15.9
only <i>P</i>	21.6	22.0	21.2
neither <i>T</i> nor <i>P</i>	22.3	22.7	22.0

1.2.6 Recovery

The recovery of formaldehyde from samples used in a 17-day storage test remained above 95.2, 94.6, and 95.8% when the samples were stored at 23 °C for ChemDisk-ALs, UME_x 100s, and DSD-DNPHs, respectively. All samples were stored in manufacturer-supplied aluminized bags to protect them from ambient formaldehyde. (Section 4.5)

1.2.7 Reproducibility

Six samples for each of the three types of samplers were collected from a controlled test atmosphere and submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after 27 days of storage at 4 °C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5 for known temperature and pressure. (Section 4.6)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

ChemDisk 571 Aldehyde Monitor, containing a glass fiber filter coated with DNPH and phosphoric acid (Assay Technology, Inc., catalog no. 571, lot 571AT1D03).

SKC UME_x 100 Passive Sampler, containing a silica tape coated with DNPH and phosphoric acid (SKC, Inc., catalog no. 500-100, lots 2527A, 2233C, and 2756).

DSD-DNPH Diffusive Samplers for Aldehydes, containing a beaded silica gel coated with DNPH and phosphoric acid (Supelco, Inc., lot SP0403H01). A reusable sampler holder was used to hold DSD-DNPH (Supelco, Inc., catalog no. 21019-U).

A thermometer and barometer to determine the sampling site air temperature and atmospheric pressure while sampling.

2.2 Reagents

None required

2.3 Technique

Refrigerate all samplers before and after use.

2.3.1 ChemDisk-AL (In general, follow the manufacture's instructions supplied with the samplers.)

Immediately before sampling, tear open the aluminum foil pouch at the notches, and remove the sampler. Remove the plastic cover from the face that has the holes, and save the cover. Place the sampler in the holder. Save the plastic disc-shaped sampler cover to put on the sampler after sampling is completed. If the sampler is the ChemDisk II design, tear open the aluminum foil pouch, attach the clip to the sampler, and open the cover. **Caution - The sampler begins to sample immediately after the foil pouch is opened and plastic cover is removed.**

Record the start time on the OSHA 91A form or equivalent monitoring record.

Attach the sampler to the worker near his/her breathing zone with the side that has the holes facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

At the end of the sampling period, detach the sampler from the worker and replace the cover. Place the sampler immediately into the plastic disc-shaped sampler holder and snap it shut. (In newer models, close the attached lid securely.) Then place it into the unused manufacturer-supplied aluminized bag, pull off the protective strip from the adhesive, and close it securely. Fold the sealed flap one more time. Any failure to seal the sample in the manufacturer-supplied aluminized bag could result in the sample continuing to collect formaldehyde from the workplace and from ambient air while in transit. Label the aluminized bag with pertinent sampling information. Place a form OSHA-21 seal across the folded top of the bag. Record the stop time on the OSHA 91A form.

Verify that the sampling times are properly recorded on OSHA 91A form for each sample. Also, identify blank samples on this form.

The following steps should be performed in a low background area for a set of samplers as soon as possible after sampling.

Submit at least one blank sample with each set of samples. Ready a blank by removing the sampler from its pouch and place it in an unused aluminized bag, seal the bag, label properly, fold the closure side of the bag down, and place the form OSHA-21 seal across the folded top of the bag.

Record the room temperature and atmospheric pressure or elevation above sea level of the sampling site on OSHA 91A form.

List any chemical compounds that could be considered potential interferences that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.3.2 UME_x 100 (In general, follow the manufacture's instructions supplied with the samplers.)

The samplers come individually sealed in manufacturer-supplied aluminized bags. When ready to begin sampling, tear the top off at the notches, being careful to not tear the bag on the sampler side of the closure. Save the aluminized bag to place the sampler in after sampling. Open the closure and pull out the sampler. Pull the green band down to the opposite end from the clip, exposing a face covered with holes. **Caution - The sampler begins to sample immediately after the green band is moved to expose the face covered with holes.**

Record the start time on the back of the sampler and on the OSHA 91A form or equivalent monitoring record.

Attach the sampler to the worker near his/her breathing zone with the side covered with holes facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

At the end of the sampling period, detach the sampler from the worker and slide the green band over the face with holes. Record the stop time on the back of the sampler and on the OSHA 91A form. Place the sampler back into the manufacturer-supplied aluminized bag and close it securely. Fold the top of the bag under the closure and then seal each sampler with a form OSHA-21 seal over the folded top of the aluminum bag. Any failure to seal the sample in the manufacturer-supplied aluminized bag could result in the sample continuing to collect formaldehyde from the workplace and from ambient air in transit.

Verify that the sampling times are properly recorded on the OSHA 91A form for each sample. Also, identify blank samples on this form.

The following steps should be performed in a low background area for a set of samplers as soon as possible after sampling.

Send at least one blank sampler with each set of samplers. Ready a blank by opening the manufacturer-supplied aluminized bag, removing the sampler, open then immediately close the green band, replace it in the manufacturer-supplied aluminized bag, close the bag, fold the bag at the closure, and place a form OSHA-21 seal over the folded edge of the bag.

Record the room temperature and atmospheric pressure or elevation above sea level of the sampling site on OSHA 91A form.

List any chemical compounds that could be considered potential interferences that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.3.3 DSD-DNPH (In general, follow the manufacturer's instructions.)

The sampler comes in an aluminized bag. A re-useable sampler holder is also needed to perform sampling. The Supelco re-useable sampler holder looks like an open tube with large holes all over it, and a pen-clip on one side. Open the manufacturer-supplied aluminized bag by cutting with scissors along the dashed line. Remove the sampler from the aluminized bag and place into the holder. Save the aluminized bag to put the sampler back in for shipment. **Caution- The sampler begins to sample immediately after the aluminized bag is opened.**

Record the start time on the OSHA 91A form or equivalent monitoring record.

Attach the sampler to the worker near his/her breathing zone. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

At the end of the sampling period, immediately detach the sampler from the worker, remove from the holder, and place it in the manufacturer-supplied aluminized bag, close it securely, fold the bag near the closure, and place the form OSHA-21 seal across the folded top of the bag. Record the stop time on OSHA 91A form. Any failure to seal the sample in the manufacturer-supplied aluminized bag could result in the sample continuing to collect formaldehyde from the workplace and from ambient air in transit.

Verify that the sampling times are properly recorded on the OSHA 91A form for each sample. Also, identify blank samples on this form.

Prepare a blank in a contaminate-free area by removing an unused sampler from its manufacturer-supplied aluminized bag, immediately replacing it, close the bag, fold the top of the bag, and seal with the form OSHA-21 seal over the folded top of the bag.

Record the room temperature and atmospheric pressure or elevation above sea level of the sampling site on the OSHA 91A form.

List any chemical compounds that could be considered potential interferences which are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.4 Sampler capacity (Section 4.7)

The sampling rate and capacity of the ChemDisk-AL, UMEx 100, and DSD-DNPH were determined by sampling a dynamically generated test atmosphere of formaldehyde (1.5 ppm) at an average of 78% relative humidity and 23°C for increasing time intervals. A sampling rate of 13.56 mL/min for ChemDisk-ALs, 29.77 mL/min for UMEx 100s, and 70.45 mL/min for DSD-DNPHs was determined. The sampler capacity was not exceeded after more than 10 hours of sampling at 1.5 ppm formaldehyde.

2.5 Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine the extraction efficiency because the laboratory techniques may be different than those listed in this evaluation and may influence the results.

2.5.1 ChemDisk-AL

The mean extraction efficiency for formaldehyde from dry ChemDisk-AL over the range of RQL to 2 times the target concentration (0.007 to 5.74 micrograms per sample) was 100.1%. The extraction efficiency was not affected by the presence of water.

Extracted samples remain stable for at least 24 h.

2.5.2 UMEEx 100

The mean extraction efficiency for formaldehyde from dry UMEEx 100 over the range of RQL to 2 times the target concentration (0.05 to 12.36 micrograms per sample) was 99.8%. The extraction efficiency was not affected by the presence of water.

Extracted samples remain stable for at least 24 h.

2.5.3 DSD-DNPH

The mean extraction efficiency for formaldehyde from dry DSD-DNPH over the range of RQL to 2 times the target concentration (0.012 to 31.34 micrograms per sample) was 100.0%. The extraction efficiency was not affected by the presence of water.

Extracted samples remain stable for at least 24 h.

2.6 Recommended sampling time and sampling rate

2.6.1 ChemDisk-AL

Sample with ChemDisk-AL for up to 240 min to collect TWA (long-term) samples, and for 15 min to collect STEL (short-term) samples. The sampling rate is 13.56 mL/min at NTP.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for ChemDisk-AL is 0.03 ppm (0.037 mg/m³) for formaldehyde when 0.2 L (15 min) is sampled.

2.6.2 UMEEx 100

Sample with UMEEx 100 for up to 240 min to collect TWA (long-term) samples, and for 15 min to collect STEL (short-term) samples. The sampling rate is 29.77 mL/min at NTP.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for UMEEx 100 is 0.09 ppm (0.11 mg/m³) for formaldehyde when 0.45 L (15 min) is sampled.

2.6.3 DSD-DNPH

Sample with DSD-DNPH for up to 240 min to collect TWA (long-term) samples, and for 15 min to collect STEL (short-term) samples. The sampling rate is 70.45 mL/min at NTP.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for DSD-DNPH is 0.0092 ppm (0.011 mg/m³) for formaldehyde when 1.06 L (15 min) is collected.

2.7 Interferences, sampling (Section 4.9)

Reverse diffusion

Reverse diffusion is a measure of the ability of the sorbent within a diffusive sampler to retain the analyte collected. Reverse diffusion was measured by first exposing two sets of samplers to humid air containing the analyte for one hour and then additionally exposing one of the sets for three hours to contaminate free humid air with an average humidity of 76% at 23°C. Comparison of the two sets showed an average recovery of 100.7% for ChemDisk-AL, 101.3% for UME_x 100, and 100.6% for DSD-DNPH, indicating no loss to reverse diffusion.

Low humidity

The recovery for ChemDisk-AL was 93.5% of theoretical, UME_x 100 was 95.5% of theoretical, and DSD-DNPH was 95.4% of theoretical of a test atmosphere of two times the target concentration of formaldehyde and having an average relative humidity of 20% at 23°C for four hours.

At humidities lower than 20% the samplers had lower recoveries when compared with theoretical, the lower the humidity the lower the recovery. The recoveries ranged from 85.4% at 15% relative humidity to 66.1% at 5% relative humidity for ChemDisk-AL, from 89.7% at 15% relative humidity to 76.2% at 5% relative humidity for UME_x 100, and 89.4% at 15% relative humidity to 77.2% at 5% relative humidity for DSD-DNPH.

Low concentration

The average recovery for ChemDisk-AL was 96.7% of theoretical, UME_x 100 was 98.5% of theoretical, and DSD-DNPH was 99.6% of theoretical when sampling a test atmosphere containing 0.075 ppm formaldehyde and having an average relative humidity of 79% at 23°C.

Interference

The ability of diffusive samplers to collect formaldehyde in the presence of an interference was determined by sampling a test atmosphere containing an average relative humidity of 78% at 23°C and containing 2 ppm formaldehyde along with 2 ppm acetaldehyde, 2 ppm butyraldehyde, 2 ppm benzaldehyde, and 0.2 ppm glutaraldehyde. The formaldehyde concentration from the samples remained above 99.7% of theoretical for ChemDisk-AL, 99.3% for UME_x 100, and 100.0% for DSD-DNPH.

Ozone is a known interference for active samplers using DNPH to derivatize formaldehyde.⁷ The ozone can react with the DNPH decreasing the amount available to react, or it can decrease the amount of formaldehyde-DNPH derivative already formed. Tests were conducted

⁷ Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC). www.epa.gov (accessed 4/15/04).

by exposing samplers to an atmosphere of 0.78 ppm formaldehyde at an average relative humidity of 79% at 23 °C for 240 min and then exposing them to ever increasing concentrations of ozone, for 240 minutes, to determine the extent of the ozone interference. ChemDisk-AL recoveries ranged from 96.6% at an ozone concentration of 0.154 ppm to 87.3% at an ozone concentration of 0.719 ppm. UMEEx 100 recoveries ranged from 96.9% at an ozone concentration of 0.154 ppm to 87.3% at an ozone concentration of 0.719 ppm. DSD-DNPH recoveries ranged from 97.1% at an ozone concentration of 0.154 ppm to 87.0% at an ozone concentration of 0.719 ppm.

Formaldehyde solutions stabilized with methyl alcohol (formalin) allow formaldehyde to react with methyl alcohol to form mainly methoxymethanol and some dimethoxymethane, which have different sampling rates than formaldehyde. Four different formaldehyde solutions, containing differing concentrations of methyl alcohol, were tested to determine the percentage from theory of the recovery for each diffusive sampler. For the solution containing 7-8% methyl alcohol the recovery was 86.8% of theory for ChemDisk-AL, 86.6% for UMEEx 100, and 86.4% for DSD-DNPH. For the three solutions containing 10-15% methyl alcohol the recoveries ranged from 69.3% to 72.7% of theory on ChemDisk-AL, 68.7% to 70.9% for UMEEx100, and 69.0% to 71.5% for DSD-DNPH. The active sampler recoveries from these tests averaged 99.8%. These variations indicate an uncorrectable bias in sampling with these diffusive samplers.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan¹⁶. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning this analytical procedure.

3.1 Apparatus

A liquid chromatograph equipped with a UV detector. A Waters 600 Controller and pump, with a Waters 2487 Dual wavelength absorbance Detector, and a Waters 717 plus Autosampler was used for this evaluation. A Pinnacle TO-11 5 µm 250 × 4.6-mm column (Restek Corporation, Bellefonte, PA) was used in this evaluation.

An electronic integrator or other suitable means of measuring LC detector response for analysis of the active samplers. A Waters Millennium³² Data System was used in this evaluation.

Light-impervious (amber) glass vials with PTFE-lined caps. In this evaluation, 4-mL vials were used. The DSD-DNPH and UMEEx100 samples also required 1-mL inserts to place the supernatant into after extraction.

A dispenser capable of delivering 2.0 mL of extracting solvent to prepare standards and samples. If a dispenser is not available, a 2.0-mL volumetric pipet may be used.

Class A volumetric flasks - 10-mL and other convenient sizes for preparing standards.

Class A volumetric pipets for making analytical standards.

Calibrated 10-µL syringe for preparing standards.

Rotator. A Fisher Roto Rack was used to extract the samples.

¹⁶ Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.2 Reagents

Formaldehyde-DNPH derivative, [CAS no. 1081-15-8], reagent grade or better. The formaldehyde-DNPH derivative used in this evaluation was A.C.S. reagent grade (lot no. LB18595) purchased from Supelco (Bellefonte, PA). The derivative is light sensitive, so all solutions must be protected from light.

Acetonitrile, [CAS no. 75-05-8], reagent grade or better. The acetonitrile used in this evaluation was 99.9+% HPLC grade (lot no. 042316) purchased from Fisher (Pittsburg, PA).

Phosphoric acid, [CAS no. 7664-38-2], reagent grade or better. The phosphoric acid used in this evaluation was 85.9% Baker-Analyzed (lot no. D25821) purchased from J.T. Baker (Phillipsburg, NJ).

Deionized water, 18 megaohm. A Barnstead NANOpure Diamond water deionizer was used in this evaluation.

The LC mobile phase consisted of 65% acetonitrile/35% deionized water/0.2% phosphoric acid by volume.

If the formaldehyde-DNPH derivative is not used as an analytical standard, the analytical standards can be prepared with the following chemicals:

Formaldehyde [CAS no. 50-00-0], reagent grade or better. The formaldehyde used in this evaluation was 37% (lot no. 15902 CO) purchased from Aldrich Chemical Company (Milwaukee, WI). The formaldehyde solution should be titrated every 6 months following the procedure found in OSHA Method 52.²

2,4-Dinitrophenylhydrazine (DNPH), [CAS no. 119-26-6], moist solid containing >30% water, reagent grade or better. The DNPH used in this evaluation was 99% (lot no. 7627JK) purchased from Aldrich Chemical Company (Milwaukee, WI). DNPH is light sensitive, so all solutions and samples should be protected from the light in light-impervious containers. The DNPH was purified by recrystallization from hot acetonitrile and dried with a nitrogen stream. There is formaldehyde in ambient air that can react with DNPH as it dries if air is used to dry the crystals, so it is important to use a nitrogen atmosphere when recrystallizing the DNPH. The DNPH will need to be recrystallized when a significant background of formaldehyde-DNPH is found in reagent blank. Store DNPH under a nitrogen blanket.

DNPH standard solution. The solution was composed of 1-g recrystallized DNPH and 5-mL phosphoric acid in 1 L acetonitrile. This solution was used to prepare analytical standards by injecting the formaldehyde stock solution into this solution. All solutions and containers are placed under a nitrogen blanket to prevent absorption of ambient formaldehyde.

3.3 Standard preparation

Prepare concentrated stock standards of formaldehyde-DNPH in acetonitrile. Concentrated stock standards keep at least two weeks in the freezer if protected from light. Prepare working analytical standards by diluting these stock standards with the extracting solution delivered from the same dispenser used to extract the samples. Prepare fresh dilutions with each analysis. The concentration of the stocks are corrected for the difference in the molecular weights of the formaldehyde (MW = 30.03) and formaldehyde-DNPH (MW = 210.15). Dilutions

² Acrolein and/or Formaldehyde OSHA Method 52. www.osha.gov (accessed 9/03/03).

of the stock standards are prepared, the concentration range for standards used to analyze DSD-DNPH for this evaluation was 0.01 to 109.7 µg/mL formaldehyde-DNPH or the equivalent as formaldehyde was 0.002 to 15.67 µg/mL (0.004 to 31.34 µg/sample when multiplied by the 2-mL extraction volume).

An alternate procedure for preparing analytical standards is to use the commercially available formaldehyde and a solution of recrystallized DNPH in acetonitrile (DNPH standard solution contains 1-g DNPH, 5-mL phosphoric acid in 1-L acetonitrile). It is important that DNPH be recrystallized and dried with nitrogen to prevent the formaldehyde in the ambient air from reacting with DNPH as it dries, causing contamination. Stock solutions of formaldehyde are prepared in water, and microliter amounts are spiked into 2 mL of DNPH standard solution. A stock solution of 10 µL/mL formalin in water is equivalent to 4.01 mg/mL or 4.01 µg/µL (for a density of 1.083 and 37% w/w formaldehyde in the solution). A spike of 3 µL of this stock solution into 2 mL of DNPH standard solution is equivalent to 6.02 µg/mL formaldehyde (12.04 µg/sample) in DNPH standard solution.

Bracket sample concentrations with standard concentrations. If, upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to include in the calibration curve or dilute high samples with extraction solvent and reanalyze the diluted samples.

The calibration curve is plotted by comparing area counts to µg/mL. To obtain the mass per sample the concentration in µg/mL is multiplied by the 2 mL extraction volume.

3.4 Sample preparation

3.4.1 ChemDisk-AL (In general, follow the manufacturer's instructions.)

Remove the sampler from the aluminized bag.

Pry the back end cap off with tweezers or a small screwdriver, remove the coated glass fiber filter, and place into a light-impervious (amber) 4-mL vial.

The newer Chemdisk II model comes with an attached cap. Open the cap, place a probe or pointed forceps in one of the holes of the diffusion screen and pry off the diffusion screen. Remove the coated filter and place into a light-impervious 4-mL vial.

Add 2.0 mL of acetonitrile to each vial and immediately cap the vials with PTFE-lined caps.

Rotate on a rotator for 15 min.

3.4.2 UMEEx 100 (In general, follow the manufacturer's instructions.)

Remove the sampler from the aluminized bag.

Push the green closure band to the center of the sampler and pry it off from the side (pliers work well to grab the edge of the green band to pry it off). At the bottom of the sampler there is a tab which you push in to make the top of the sampler come off. Inside are two squares of coated silica tape. Remove each one and place each into its own light-impervious (amber) 4-mL vial. While the manufacturer says the second, inner section, is a blank, tests in this method showed that the amount of formaldehyde found on the inner section increased with higher concentrations in the test atmospheres, so it was assumed to be part of the sample, not a back-up or blank.

Add 2.0 mL of acetonitrile to each vial and immediately seal the vials with PTFE-lined caps.

Place samples on a rotator for 15 min. Immediately pour the supernatant (liquid in the vial) into a 1-mL insert for the 4-mL vial, place the insert back into the vial, and cap the vial. The formaldehyde-DNPH derivative will decrease in solution with time if left in contact with the silica tape. If samples are not transferred within 5 minutes after completing rotation, re-rotate the samples for 5 min, and immediately transfer the sample supernatant.

3.4.3 DSD-DNPH (In general, follow the manufacturer's instructions.)

Remove the sampler from the aluminized bag.

Remove the white translucent part. Dynamically extract the DNPH-coated silica gel inside the sampler using a syringe filter with 2 mL of acetonitrile into a light-impervious (amber) 4-mL vial.

Alternately, place the DNPH-coated silica gel into a light-impervious (amber) 4-mL vial, add 2.0 mL of acetonitrile to each vial and immediately seal the vials with PTFE-lined caps. Rotate samples on a rotator for 15 min. Immediately pour the supernatant into a 1-mL insert for the 4-mL vial, separate from the silica gel, and place the insert back into the vial and cap. The formaldehyde-DNPH derivative will decrease in solution with time if left in contact with the silica gel. If samples are not transferred within 5 min after completing rotation, re-rotate the samples for 5 min, and immediately transfer the sample supernatant.

3.5 Analysis

Liquid chromatograph conditions:

mobile phase: 1 mL/min of 35% water/
65% acetonitrile/0.2%
phosphoric acid (v/v/v)

detector
wavelength: 365 nm
injection volume: 10 μ L
output range: 2 AUFS
column: Restek Pinnacle TO-11
5 μ m 250 \times 4.6 mm
retention times: DNPH (3.9 min);
formaldehyde (4.8 min)

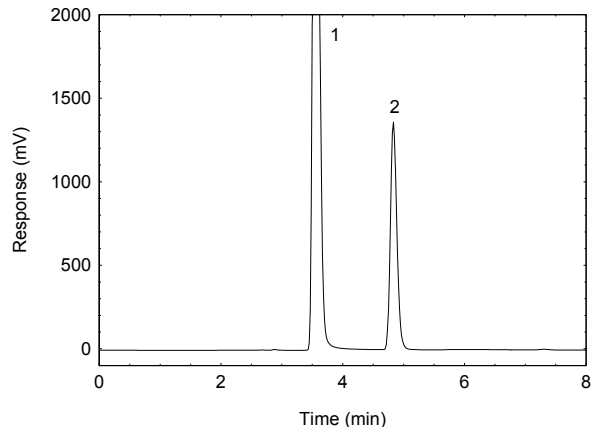


Figure 3.5.1 A chromatogram of 18.9 μ g/mL formaldehyde in acetonitrile with DNPH. [Key: 1) DNPH, 2) formaldehyde as the DNPH derivative.]

An external standard (ESTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms/milliliter of analyte. (Note: the samples are extracted with 2 mL of acetonitrile so the mass per sample is the μ g/mL \times 2 mL.) Bracket the samples with freshly prepared analytical standards over the range of concentrations. (Section 3.3)

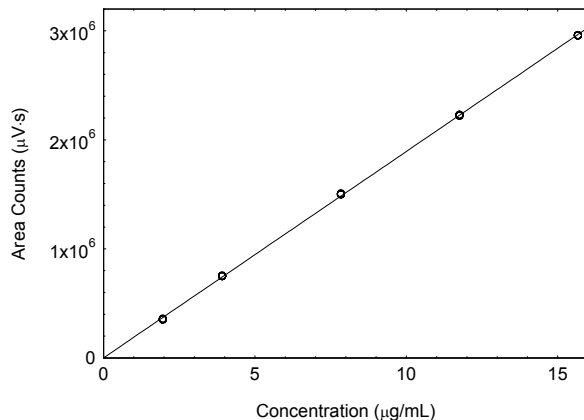


Figure 3.5.2 Calibration curve for formaldehyde.
 $(y = 1.89E5x = 752)$

3.6 Interferences (analytical)

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

When necessary, the identity or purity of an analyte peak may be confirmed by additional analytical data, such as GC-mass spectrometry, or monitoring an alternant wavelength such as 254 or 280 nm (Section 4.10).

3.7 Calculations

The amount of analyte for the samples is obtained from the appropriate calibration curve in terms of micrograms per milliliter, uncorrected for extraction efficiency. This amount is then corrected by subtracting the total amount (if any) found on the blank. Blank correct each section of the UME_x 100 with its corresponding section in the blank, then add the results together. The air concentration is calculated using the following formulas.

$$M = [(C_a - C_{bka}) + (C_b - C_{bkb})](2mL)$$

where: *M* is micrograms per sample

C_a is µg/mL found on main section of sample from calibration curve

C_b is µg/mL found on second section of sample (UMEx 100 only) from calibration curve

C_{bka} is µg/mL found on main section of blank sample from calibration curve

C_{bkb} is µg/mL found on second section of blank (UMEx 100 only) from calibration curve

2mL is the extraction volume

$$R_{SS} = R_{NTP} \left(\frac{T_{SS}}{T_{NTP}} \right)^3 \left(\frac{P_{NTP}}{P_{SS}} \right)$$

where: R_{SS} is the sampling rate at sampling site
 R_{NTP} is the sampling rate at NTP conditions (ChemDisk-AL=13.56 mL/min, UME_{x100}=29.77 mL/min, and DSD-DNPH=70.45 mL/min)
 T_{SS} is the sampling site temperature in K
 T_{NTP} is 298.2 K
 P_{SS} is the sampling site pressure in mmHg
 P_{NTP} is 760 mmHg

$$C_M = \frac{M1000}{tR_{SS}E_E}$$

where: C_M is concentration by weight ($\mu\text{g/L} = \text{mg/m}^3$)
 M is micrograms per sample
 R_{SS} is the sampling rate at the sampling site
 t is the sampling time
 E_E is extraction efficiency, in decimal form
1000 is a conversion factor to convert the sampling rate mL/min to L/min

$$C_V = \frac{V_M C_M}{M_r}$$

where: C_V is concentration by volume (ppm)
 $V_M = 24.46$ at NTP
 C_M is concentration by weight
 M_r is molecular weight of 30.0

If the sampling site temperature was not given, assume that it is 22.2°C. If the sampling site atmospheric pressure was not given, calculate an approximate value based on the sampling site elevation level from the following equation.

$$P_{SS} = AE^2 - BE + 760$$

where: P_{SS} is the approximate atmospheric pressure in mmHg
 E is the sampling site elevation, ft
 A is 3.887×10^{-7} mmHg/ft²
 B is 0.02748 mmHg/ft

4. Backup data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"¹⁸. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria.

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments with the highest standard containing 11.3 ng/mL. This is the concentration that would produce a peak at least 10 times the response of a reagent blank near the elution time of the analyte. These standards, and the reagent blank were analyzed with the recommended analytical parameters (10- μL injection), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 22.75 and 32.31 were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be 4.26 pg.

¹⁸ Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis. www.osha.gov (accessed August 2001).

Table 4.1
Detection Limit of the Analytical Procedure

concentration (ng/mL)	mass on column (pg)	area counts ($\mu\text{V}\cdot\text{s}$)
0	0	0
1.13	11.3	256
2.26	22.6	494
3.39	33.9	796
4.52	45.2	1017
5.65	56.5	1338
6.78	67.8	1557
7.91	79.1	1780
9.04	90.4	2046
10.17	101.7	2372
11.30	113.0	2531

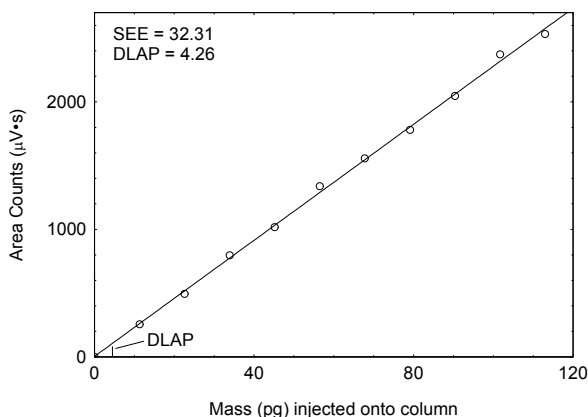


Figure 4.1 Plot of data in Table 4.1 used to determine the DLAP. ($y = 22.75x + 4.14$)

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was 56.5 ng/sample for ChemDisk-AL and DSD-DNPH, and 452 ng/sample for SKC UME_x 100. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 111 and 83.2 were obtained for the slope and standard error of estimate for ChemDisk-AL, respectively. The DLOP for ChemDisk-AL was calculated to be 2.25 ng/sample (0.56 ppb based on 240 min). Values of 120 and 594 were obtained for the slope and standard error of estimate for UME_x 100, respectively. The DLOP for UME_x 100 was calculated to be 14.9 ng/sample (1.7 ppb). Values of 112 and 133 were obtained for the slope and standard error of estimate for DSD-DNPH, respectively. The DLOP for DSD-DNPH was calculated to be 3.56 ng/sample (0.17 ppb).

Table 4.2.1
Detection Limit of the Overall Procedure for ChemDisk-AL

mass per sample (ng)	area counts ($\mu\text{V}\cdot\text{s}$)
0	313
5.65	967
11.3	1612
17.0	2101
22.6	2945
28.3	3504
33.9	3954
39.6	4804
45.2	5414
50.9	5913
56.5	6639

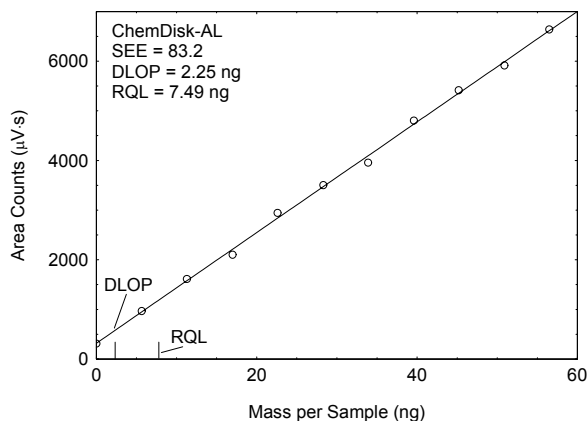


Figure 4.2.1 Plot of data in Table 4.2.1 used to determine the DLOP/RQL for ChemDisk-AL. ($y = 111x + 322$)

Table 4.2.2
Detection Limit of the Overall Procedure for UME_x 100

mass per sample (ng)	area counts (μV·s)
0	5612
45.2	11224
90.4	16356
136	21235
181	26541
226	33052
271	36647
316	43851
362	48654
407	54673
452	59534

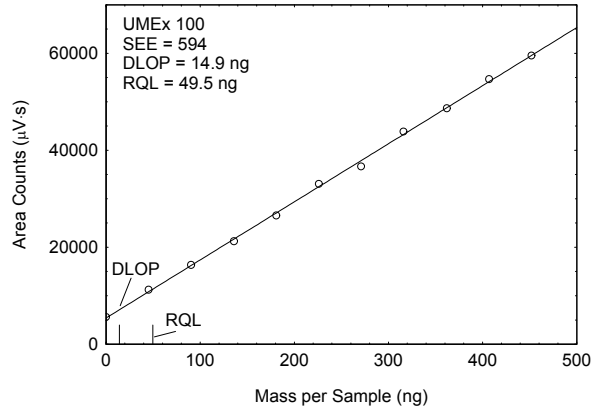


Figure 4.2.2 Plot of data in Table 4.2.2 used to determine the DLOP/RQL for UME_x 100. ($y = 120x + 5408$)

Table 4.2.3
Detection Limit of the Overall Procedure for DSD-DNPH

mass per sample (ng)	area counts (μV·s)
0	300
5.65	919
11.3	1596
17.0	2297
22.6	3014
28.3	3412
33.9	3912
39.6	4919
45.2	5582
50.9	6014
56.5	6533

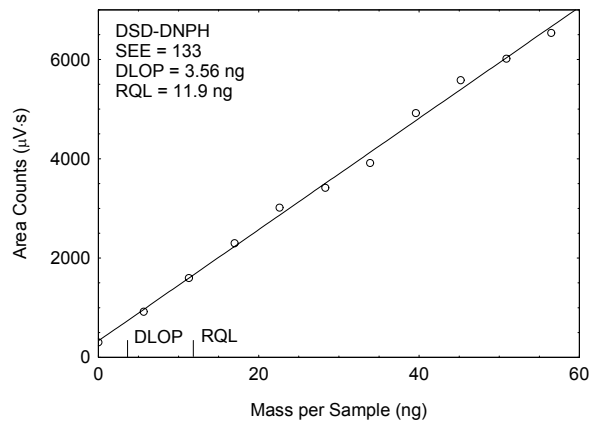


Figure 4.2.3 Plot of data in Table 4.2.3 used to determine the DLOP/RQL for DSD-DNPH. ($y = 112x + 333$)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQLs for the various media are listed in Table 4.2.4.

Table 4.2.4
Reliable Quantitation Limits

sampler	ng	ppb	μg/m ³	E _E
ChemDisk-AL	7.49	1.88	2.30	99.5
UMEx 100	49.5	5.68	6.93	99.3
DSD-DNPH	11.9	0.58	0.70	99.5

E_E = extraction efficiency

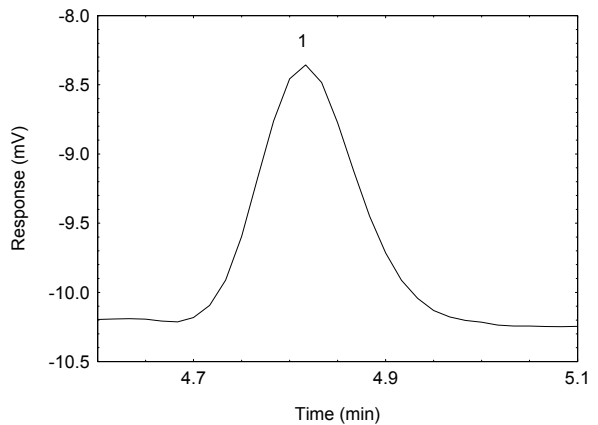


Figure 4.2.4 Chromatogram of a peak near the RQL on ChemDisk-AL. (Key: 1 = formaldehyde)

4.3 Instrument calibration

The standard error of estimate was determined from the linear regression of data points from standards over a range that covers 0.25 to 2 times the TWA target concentration. A calibration curve for DSD-DNPH samples was constructed and shown in Figure 3.5.2 from the six injections of five standards. The standard error of estimate is 0.069 µg/mL.

Table 4.3
Instrument Calibration for DSD-DNPH Samples

standard concn (µg/mL)	area counts (µV·s)					
1.96	350361	361024	350982	354675	353392	358132
3.92	750107	750992	748941	749243	750123	755923
7.84	1501151	1498251	1509918	1502208	1498322	1503128
11.76	2229123	2226189	2218391	2228424	2230119	2219872
15.67	2959210	2954912	2960123	2958381	2961022	2955670

4.4 Precision (overall procedure)

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test (at the target concentration) for the diffusive samplers are given in Table 4.4. They each include the sampling rate variability of 7.71% for ChemDisk-AL, 8.06% for UME_x 100, and 7.49% for DSD-DNPH. There are different values given, depending on whether both, either, or neither temperature (*T*) or atmospheric pressure (*P*) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15°C (72 ± 27°F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included.

Table 4.4
Standard Error of Estimate and Precision of the Overall Procedure

known conditions	ChemDisk-AL error (%)	ChemDisk-AL precision (± %)	UMEx 100 error (%)	UMEx 100 precision (± %)	DSD-DNPH error (%)	DSD-DNPH precision (± %)
both <i>T</i> & <i>P</i>	7.78	15.3	8.15	16.0	7.54	14.8
only <i>T</i>	8.34	16.3	8.68	17.0	8.12	15.9
only <i>P</i>	11.0	21.6	11.2	22.0	10.8	21.2
neither <i>T</i> nor <i>P</i>	11.4	22.3	11.6	22.7	11.2	22.0

4.5 Storage test

4.5.1 ChemDisk-AL

Storage samples for formaldehyde were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of formaldehyde was at the target concentration with an average relative humidity of 78% and temperature of 23 °C. Thirty-three storage samples were prepared and all were stored in aluminized bags. Three samples were analyzed on the day of generation. Fifteen of the samples were stored at refrigerated temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 3-4 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.1
Storage Test for Formaldehyde on ChemDisk-AL

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.2	99.7	98.9			
3	97.7	100.3	98.6	98.6	100.4	99.8
7	99.7	98.8	96.8	98.9	99.7	98.8
10	98.4	97.9	95.9	98.5	98.1	99.9
14	97.2	94.9	95.6	96.9	99.3	98.6
17	95.8	93.9	94.9	97.8	98.3	98.9

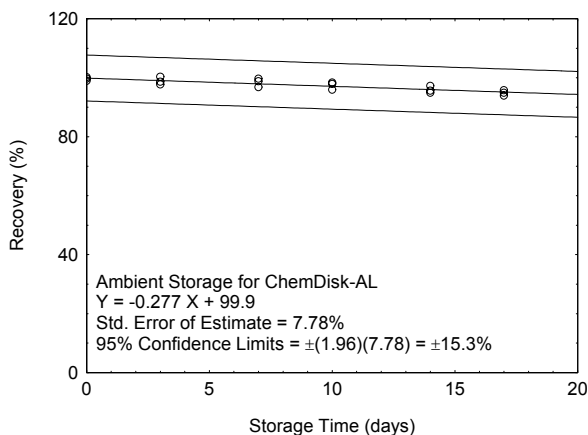


Figure 4.5.1.1 Ambient storage test for formaldehyde collected on ChemDisk-AL.

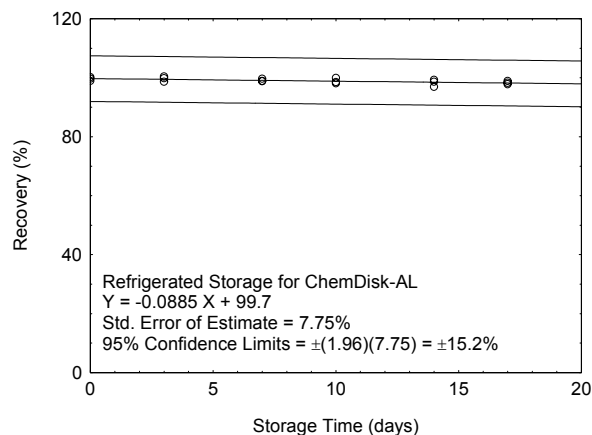


Figure 4.5.1.2 Refrigerated storage test for formaldehyde collected on ChemDisk-AL.

4.5.2 UMEEx 100

Storage samples for formaldehyde were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of formaldehyde was at the target concentration with an average relative humidity of 78% and temperature of 23 °C. Thirty-three storage samples were prepared and all were placed in aluminized bags. Three samples were analyzed on the day of generation. Fifteen of the samples were stored at refrigerated temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 3-4 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.2
Storage Test for Formaldehyde on UMEEx 100

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.9	98.3	99.4			
3	99.9	98.4	97.0	98.1	97.9	99.6
7	98.2	99.6	97.2	99.9	98.3	97.4
10	98.4	96.7	97.4	98.4	99.2	97.2
14	96.5	94.4	93.9	98.0	97.5	96.9
17	95.3	94.1	93.8	96.1	95.2	94.3

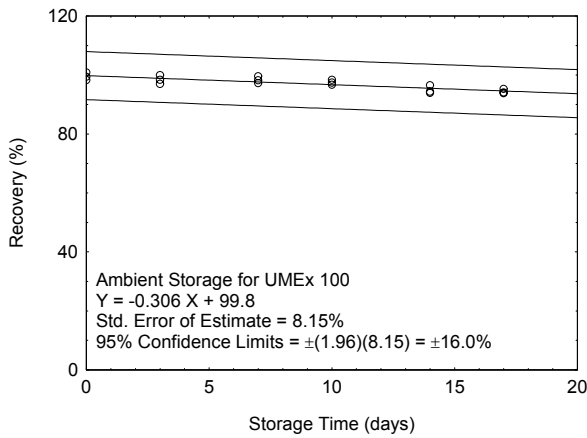


Figure 4.5.2.1 Ambient storage test for formaldehyde collected on UMEEx 100.

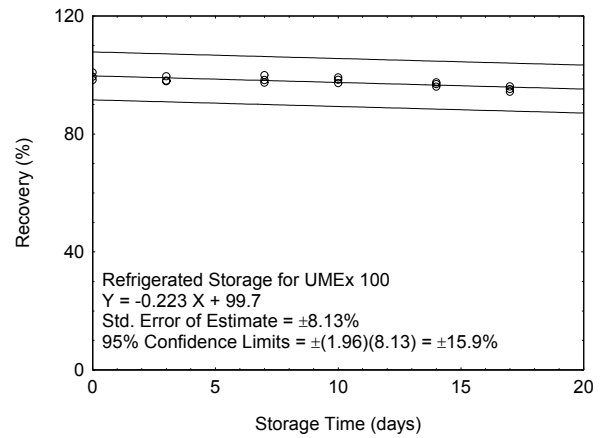


Figure 4.5.2.2 Refrigerated storage test for formaldehyde collected on UMEEx 100.

4.5.3 DSD-DNPH

Storage samples for formaldehyde were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of formaldehyde was at the target concentration with an average relative humidity of 78% and temperature of 23 °C. Thirty-three storage samples were prepared and all were stored in aluminized bags. Three samples were analyzed on the day of generation. Fifteen of the tubes were stored at refrigerated temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 3-4 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.3
Storage Test for Formaldehyde on DSD-DNPH

time (days)	ambient storage			refrigerated storage		
		recovery (%)			recovery (%)	
0	100.4	99.5	98.7			
3	97.0	98.5	99.6	97.1	99.9	98.9
7	97.4	97.0	98.3	99.5	99.8	98.3
10	97.1	98.4	96.9	99.0	98.6	97.8
14	97.9	95.7	96.1	98.3	97.3	99.1
17	94.4	96.5	95.9	98.9	99.3	97.9

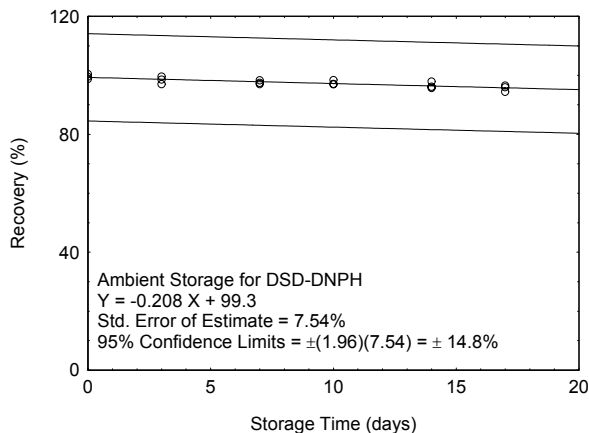


Figure 4.5.3.1 Ambient storage test for formaldehyde collected on DSD-DNPH.

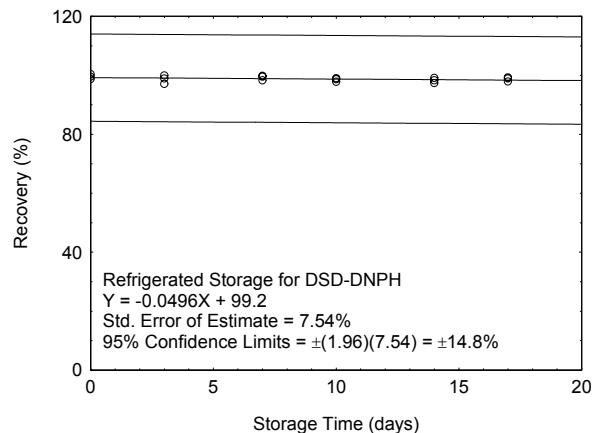


Figure 4.5.3.2 Refrigerated storage test for formaldehyde collected on DSD-DNPH.

4.6 Reproducibility

Six samples of each of the three types of samplers were prepared by collecting them from a controlled test atmosphere that was similar to that which was used in the collection of the storage samples. The samples were submitted to the OSHA Salt Lake Technical Center for analysis, along with a draft copy of this method. The samples were analyzed after being stored for 27 days at 4 °C. Sample results were corrected for extraction efficiency. No sample result for formaldehyde had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6.1
Reproducibility Data for Formaldehyde using ChemDisk-AL

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
2.99	2.87	96.0	-4.0
2.99	3.03	101.3	+1.3
2.99	2.95	98.6	-1.4
2.99	2.88	96.3	-3.7
2.99	3.09	103.3	+3.3
2.99	2.83	94.6	-5.4

Table 4.6.2
Reproducibility Data for Formaldehyde using UME_x 100

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
6.24	6.34	101.6	+1.6
6.24	5.86	93.9	-6.1
6.24	5.98	95.8	-4.2
6.24	6.28	100.6	+0.6
6.24	5.87	94.1	-5.9
6.24	5.79	92.8	-7.2

Table 4.6.3
Reproducibility Data for Formaldehyde using DSD-DNPH

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
16.3	16.7	102.5	+2.5
16.3	15.1	92.6	-7.4
16.3	15.6	95.7	-4.3
16.3	16.6	101.8	+1.8
16.3	15.5	95.1	-4.9
16.3	15.9	97.5	-2.5

4.7 Sampler capacity

The sampling rate and sampler capacity are determined with samples collected for increasing time intervals from a controlled test atmosphere. Sampler capacity is exceeded when the sampling rate decreases. The capacity of these samplers was not exceeded after 10 hours. The concentration of the test atmosphere was two times the target concentration with an average relative humidity of 78% and temperature of 23 °C. The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and 2 h samples. Horizontal lines were placed 10% above and below the preliminary sampling rate. For an atmosphere of 1.5 ppm the

sampling rate for ChemDisk-AL is 13.56 mL/min at 760 mmHg and 25°C and represents the average of all values between the lines. The standard deviation and relative standard deviation (RSD) are 0.45 mL/min and 3.3%, respectively. The data obtained are shown in Table 4.7.1 and Figure 4.7.1. For an atmosphere of 1.5 ppm the sampling rate for UME_x 100 is 29.77 mL/min at 760 mmHg and 25°C and represents the average of all values between the lines. The standard deviation and RSD are 0.62 mL/min and 2.1%, respectively. The data obtained are shown in Table 4.7.2 and Figure 4.7.2. For an atmosphere of 1.5 ppm the sampling rate for DSD-DNPH is 70.45 mL/min at 760 mmHg and 25°C and represents the average of all values between the lines. The standard deviation and RSD are 1.58 mL/min and 2.2%, respectively. The data obtained are shown in Table 4.7.3 and Figure 4.7.3. Mass collected is corrected for extraction efficiency. The recommended sampling time is 4 h for TWA samples and 15 min for STEL samples.

Table 4.7.1
Determination of Sampling Rate and Sampling Time
for Chemdisk-AL

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	12.77	12.89	12.62
0.167	13.09	12.95	12.92
0.25	13.26	13.28	13.13
0.5	13.35	13.51	13.49
1	13.78	13.84	13.99
2	14.13	13.92	14.07
3	14.29	13.88	14.14
4	13.87	14.22	13.95
6	13.90	13.72	13.81
8	13.51	13.47	13.68
10	13.29	13.33	13.45

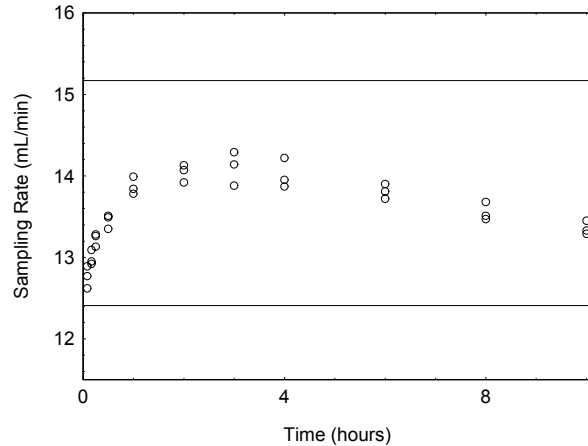


Figure 4.7.1 The ChemDisk-AL data in Table 4.7.1 plotted to determine the recommended sampling time and sampling rate from a 1.5-ppm atmosphere.

Table 4.7.2
Determination of Sampling Rate and Sampling Time
for UME_x 100

time (h)	sampling rate mL/min		
	first	second	third
0.083	28.46	28.71	28.55
0.167	28.88	28.92	28.74
0.25	29.35	29.44	29.54
0.5	29.73	30.01	29.93
1	30.20	30.35	30.07
2	30.47	30.73	30.49
3	30.49	30.26	30.38
4	30.36	30.15	30.21
6	29.81	30.13	30.05
8	29.78	29.80	29.98
10	29.68	29.43	29.55

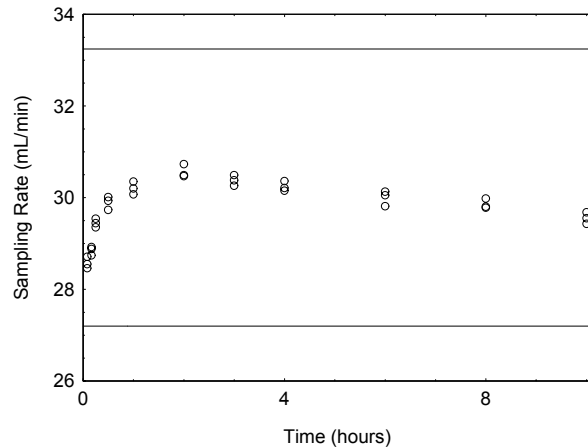


Figure 4.7.2 The UME_x 100 data in Table 4.7.2 plotted to determine the recommended sampling time and sampling rate from a 1.5-ppm atmosphere.

Table 4.7.3
Determination of Sampling Rate and Sampling Time
for DSD-DNPH

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	68.54	68.21	67.87
0.167	69.24	69.01	69.43
0.25	69.82	69.96	70.16
0.5	70.43	70.77	70.99
1	71.85	72.12	72.39
2	72.68	72.52	72.92
3	72.18	72.35	72.59
4	71.99	71.54	71.32
6	70.29	70.55	70.83
8	69.16	68.33	69.62
10	67.79	68.56	68.93

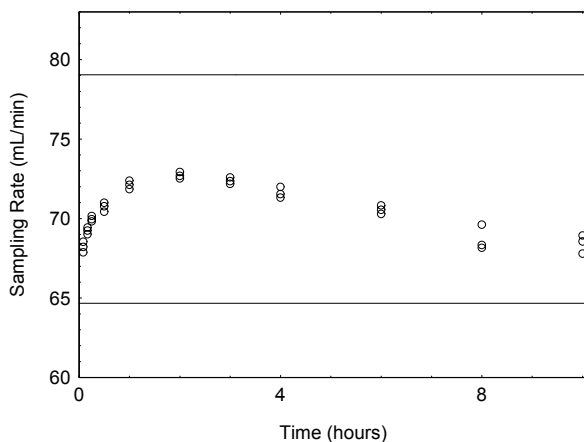


Figure 4.7.3 The DSD-DNPH data in Table 4.7.3 plotted to determine the recommended sampling time and sampling rate from a 1.5-ppm atmosphere.

4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is dependent on the extraction solvent. The extraction solvent used for this evaluation was acetonitrile. An alternate extraction solvent is the DNPH standard preparation solution (Section 3.2). Other extraction solvents may be used provided that the new extraction solution is tested. The new extraction solvent should be tested as described below. The extraction studies listed below are results of spiking formaldehyde onto the samplers; similar results were obtained from spiking with the formaldehyde-DNPH derivative.

4.8.1 ChemDisk-AL

Extraction efficiency

The extraction efficiencies of formaldehyde were determined by liquid-spiking four ChemDisk-AL with formaldehyde at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 100.1%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if water would affect the extraction efficiency and it did not affect it.

Table 4.8.1.1
Extraction Efficiency (%) of Formaldehyde from ChemDisk-AL

level		sample number				mean
× target concn	µg per sample	1	2	3	4	
RQL	0.007	100.1	99.9	99.2	98.8	99.5
0.25	0.72	99.3	100.3	98.9	100.5	99.8
0.5	1.44	100.3	99.6	99.4	100.6	100.0
1.0	2.87	100.1	100.4	99.8	100.5	100.2
1.5	4.31	99.9	100.3	101.1	100.6	100.5
2.0	5.74	100.5	100.6	101.2	99.6	100.5
1.0 (wet)	2.87	100.2	99.5	101.0	99.4	100.0

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -0.2% for samples that were resealed with new septa and 0.4% for those that retained their punctured septa. Each septum was punctured 5 times for each injection.

Table 4.8.1.2
Stability of Extracted Samples for Formaldehyde on ChemDisk-AL

<u>punctured septa replaced</u>			<u>punctured septa retained</u>		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
100.1	100.0	-0.1	99.8	100.4	+0.6
100.4	100.2	-0.2	100.5	100.7	+0.2
	(mean)			(mean)	
100.3	100.1	-0.2	100.2	100.6	+0.4

4.8.2 UMEEx 100

Extraction efficiency

The extraction efficiencies of formaldehyde were determined by liquid-spiking four UMEEx 100 with formaldehyde at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 99.8%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if water would affect the extraction efficiency and it did not affect it.

Table 4.8.2.1
Extraction Efficiency (%) of Formaldehyde from UMEEx 100

<u>level</u>		<u>sample number</u>				<u>mean</u>
× target concn	µg per sample	1	2	3	4	
RQL	0.05	99.4	98.7	99.8	99.2	99.3
0.25	1.55	99.8	100.2	99.3	99.1	99.6
0.5	3.09	100.3	99.2	99.8	99.5	99.7
1.0	6.18	99.5	99.1	100.1	100.4	99.8
1.5	9.27	100.2	100.0	99.4	100.5	100.0
2.0	12.36	99.8	100.2	100.4	100.6	100.3
1.0 (wet)	6.18	99.1	100.2	99.8	100.4	99.9

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was 0.2% for samples that were resealed with new septa and

0.3.% for those that retained their punctured septa. Each septum was punctured 5 times for each injection.

Table 4.8.2.2
Stability of Extracted Samples for Formaldehyde on UME_x 100s

<u>punctured septa replaced</u>			<u>punctured septa retained</u>		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
99.5	99.6	+0.1	100.1	100.4	+0.3
99.1	99.3	+0.2	100.4	100.7	+0.3
	(mean)			(mean)	
99.3	99.5	+0.2	100.3	100.6	+0.3

4.8.3 DSD-DNPH

Extraction efficiency

The extraction efficiencies of formaldehyde were determined by liquid-spiking four DSD-DNPH with formaldehyde at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 100%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if water would affect the extraction efficiency and it did not affect it.

Table 4.8.3.1
Extraction Efficiency (%) of Formaldehyde from DSD-DNPH

<u>level</u>		<u>sample number</u>				<u>mean</u>
× target concn	µg per sample	1	2	3	4	
RQL	0.012	99.4	100.0	98.9	99.7	99.5
0.25	3.92	99.1	100.3	99.9	99.7	99.8
0.5	7.84	100.4	100.5	99.2	98.9	99.8
1.0	15.67	100.3	100.1	99.8	100.2	100.1
1.5	23.51	100.4	99.5	100.4	100.1	100.1
2.0	31.34	100.1	99.7	101.2	101.3	100.6
1.0 (wet)	15.67	100.1	99.8	100.4	100.3	100.2

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was +0.6% for samples that were resealed with new septa and +0.7% for those that retained their punctured septa. Each septum was punctured 5 times for each injection.

Table 4.8.3.2
Stability of Extracted Samples for Formaldehyde on DSD-DNPH

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
100.3	101.1	+0.8	99.8	100.4	+0.6
100.1	100.5	+0.4	100.2	101.0	+0.8
	(mean)			(mean)	
100.2	100.8	+0.6	100.0	100.7	+0.7

4.9 Interferences (sampling)

Reverse diffusion

Reverse diffusion is a measure of the ability of the sorbent within a diffusive sampler to retain the collected analyte. Reverse diffusion is measured by first exposing two sets of samplers to humid air containing formaldehyde and then additionally exposing one of the sets to contaminate free humid air of an average relative humidity of 76% and temperature of 23°C. Six samplers were exposed to humid air containing 1.56 ppm formaldehyde for 60 min. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples being exposed to humid contaminant-free air for 180 min and then all six samplers were analyzed. Comparison of the two sets of samplers showed no loss to reverse diffusion (Table 4.9.1).

Table 4.9.1
Reverse Diffusion of Formaldehyde

set	mass (µg) found on <u>ChemDisk-AL</u>				mass (µg) found on <u>UMEx 100</u>				mass (µg) found on <u>DSD-DNPH</u>			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
first	1.47	1.39	1.42	1.43	3.06	3.12	3.04	3.07	8.05	8.09	8.12	8.09
second	1.40	1.44	1.48	1.44	3.11	3.15	3.07	3.11	8.12	8.13	8.17	8.14
second/first	100.7%				101.3%				100.6%			

Low humidity

The ability of the diffusive samplers to collect formaldehyde from a relatively dry atmosphere was tested by sampling an atmosphere containing 1.56 ppm of formaldehyde at an average relative humidity of 20% at 23°C. Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The average percent of theoretical for the sampling rates were 93.5% for ChemDisk-AL, 95.5% for UMEx 100, and 95.4% for DSD-DNPH. Most workplaces have a relative humidity between 20% and 80%, so in this range there should be no adverse effect on recovery from humidity. The effects of lower relative humidity on the recovery were studied. A test was performed with a relative humidity of 5%, and a much lower recovery was found. Further tests with lower humidities indicated that, the lower the humidity, the lower the recovery due to the need for water for the derivatization to occur (Table 4.9.2).

Table 4.9.2
Low Humidity Effect on Recovery

% relative humidity	% of theoretical for ChemDisk-AL				% of theoretical for UMEEx 100				% of theoretical for DSD-DNPH			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
20	92.1	93.6	94.8	93.5	94.3	95.9	96.3	95.5	94.2	95.4	96.6	95.4
15	83.7	86.7	85.9	85.4	89.1	89.7	90.4	89.7	90.2	89.1	88.9	89.4
10	77.2	78.9	76.6	77.6	84.5	82.7	83.7	83.6	83.8	81.9	82.5	82.7
5	65.4	68.2	64.7	66.1	76.9	73.9	77.8	76.2	77.9	76.3	77.4	77.2

Low concentration

The ability of the diffusive samplers to collect formaldehyde at low concentration was tested by sampling an atmosphere containing 0.075 ppm of formaldehyde at an average relative humidity of 79% and temperature of 23°C. The formaldehyde concentration was achieved by diluting the formaldehyde solution with deionized water. Three samplers, from each type of samplers, were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The recovery, as a percentage of theoretical, was 96.1%, 95.2% and 98.8% for ChemDisk-AL, 98.6%, 99.4% and 97.4% for UMEEx 100, and 99.2%, 99.5% and 100.1% for DSD-DNPH.

Interference

The ability of the diffusive samplers to collect formaldehyde when other potential interferences are present was tested by sampling an atmosphere containing 2 ppm of formaldehyde at an average relative humidity of 81% and temperature of 24°C along with 2 ppm acetaldehyde, 2 ppm butyraldehyde, 2 ppm benzaldehyde, and 0.2 ppm glutaraldehyde. Three of each type of samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The recovery as a percentage of theoretical was 100.1%, 100.2% and 99.7% for ChemDisk-AL, 100.2%, 99.3% and 100.1% for UMEEx 100, and 100.0%, 100.1% and 100.3% for DSD-DNPH. This indicates that formaldehyde may be collected with other aldehydes but methods have not yet been validated for these aldehydes.

Ozone is a known interference for active samplers using DNPH to derivatize formaldehyde. EPA has a target ambient air concentration of 0.1 ppm ozone, with most communities in the U.S. measuring between 0.05 and 0.5 ppm.⁷ Ozone can react with DNPH decreasing the amount available to react, or it can decrease the amount of formaldehyde-DNPH already formed. Tests were conducted using samplers that had been exposed to an atmosphere of 0.78 ppm formaldehyde for 240 minutes at an average relative humidity of 79% and temperature of 23°C. These samplers were then exposed to ozone using ever increasing concentrations, for 240 minutes, to determine the extent of the ozone interference. Thermo Electron Instruments Model 565 Ozone Generator was used to generate the ozone atmospheres.

Table 4.9.3
Ozone Effect on Formaldehyde Recovery

ozone (ppm)	% of theoretical for ChemDisk-AL				% of theoretical for UMEEx 100				% of theoretical for DSD-DNPH			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
0.154	95.9	97.1	96.8	96.6	96.1	97.9	96.7	96.9	96.1	97.5	97.7	97.1
0.304	93.8	94.6	95.1	94.5	93.3	93.9	94.8	94.0	94.2	94.9	95.4	94.8
0.577	91.5	93.1	92.9	92.5	93.5	92.4	91.9	92.6	92.6	93.4	91.5	92.5
0.719	87.4	88.1	86.4	87.3	85.5	88.9	86.3	87.3	88.3	87.1	85.5	87.0

² Acrolein and/or Formaldehyde OSHA Method 52, www.osha.gov (accessed 9/03/03).

Formaldehyde solutions stabilized with methyl alcohol (formalin) react to form mainly methoxymethanol and a trace dimethoxymethane. These chemicals have different sampling rates than the formaldehyde. It has been reported that the recovery of formaldehyde can be as much as 35% low when formaldehyde solutions stabilized with methyl alcohol are used to generate the test atmosphere.³ Four formaldehyde solutions, containing differing concentrations of methyl alcohol, were tested to determine the amount of change in the recovery at an average relative humidity of 79% and temperature of 30° C. The formaldehyde solutions tested were: Aldrich Chemical Co. lot 18829MB 37% solution, 7-8% methyl alcohol; Acros Organics lot B0505213 37% solution, 10-15% methyl alcohol; Aldrich Chemical Co. lot 15902CO 37% solution, 10-15% methyl alcohol; and Sigma Chemical Co lot 072K0885 37% solution, 10-15% methyl alcohol. This test shows that the amount of methyl alcohol affects the recovery. The amount of formaldehyde found from the active samplers using the HMP-XAD-2 tubes following OSHA Method 52² averaged 99.9% of theoretical for all tests.

Table 4.9.4
Methyl Alcohol in the Formaldehyde Solution Effect on Recovery

source (% methyl alcohol)	% of theoretical for ChemDisk-AL				% of theoretical for UME _x 100				% of theoretical for DSD-DNPH			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
Aldrich (7-8)	85.5	87.1	87.7	86.8	85.5	87.4	86.9	86.6	85.6	87.3	86.2	86.4
Acros (10-15)	71.7	73.9	72.6	72.7	72.5	69.3	70.9	70.9	72.2	70.6	71.8	71.5
Aldrich (10-15)	71.6	70.9	68.1	70.2	70.8	71.9	69.3	70.7	71.9	68.4	70.8	70.3
Sigma (10-15)	70.4	69.7	67.9	69.3	68.6	69.6	67.8	68.7	70.5	68.6	67.8	69.0

4.10 Qualitative analysis

When necessary, the identity or purity of an analyte peak can be confirmed by GC-mass spectrometry or by another analytical procedure. The mass spectrum in Figure 4.10 was taken from the NIST spectral library. Mass spectrometry analysis can be performed using the following parameters: an Agilent 6890 gas chromatograph with a 5973 mass selective detector, a 30 m x 0.25 mm HP-5MS capillary column with 0.25 µm d.f., a temperature program of 35 °C, 5 min hold, then program at 10 °/min to 270 °C and hold 5 min. The retention time of the formaldehyde-DNPH derivative was 23 min.

³ Pengelly, I, Groves, J.A., Levin, J.O., and Lindahl, R., An Investigation into the Differences in Composition of Formaldehyde Atmospheres Generated from Different Source Materials and the Consequences for Diffusive Sampling, *Ann. Occup. Hyg.*, 1996, Vol. 40, No. 5, pp 555-567.

⁷ Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC). www.epa.gov (accessed 4/15/04).

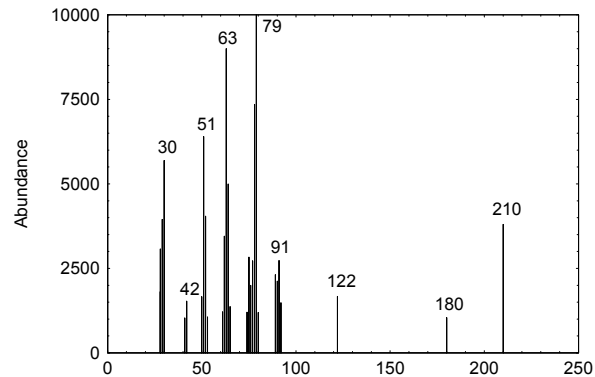


Figure 4.10 Mass spectrum of formaldehyde-DNPH derivative.

4.11 Generation of test atmospheres

The test atmosphere of formaldehyde was generated from a solution of formaldehyde gas in water freshly prepared by heating paraformaldehyde and collecting it in de-ionized water.

The following apparatus was placed in a walk-in hood. The formaldehyde vapors were generated by pumping the formaldehyde/water solution, using the Isco pump, through a short length of 0.53-mm uncoated fused silica capillary tubing into a vapor generator where it was heated and evaporated into the dilution air stream (Figure 4.11). The vapor generator consisted of a 15-cm length of 5-cm diameter glass tubing with a side port for introduction of the capillary tubing. The glass tube of the vapor generator was wrapped with heating tape to evaporate the chemicals in the solution. The humidity, temperature, and volume of the dilution stream of air were regulated by use of a Miller Nelson Flow-Temperature-Humidity controller. The test atmosphere passed into a glass mixing chamber (76-cm × 30-cm) from the vapor generator, and then into a glass exposure chamber (76-cm × 20-cm). Diffusive samplers were placed inside the exposure chamber and active samplers were attached to glass tubes extending from the exposure chamber. The humidity and temperature were measured at the exit of the exposure chamber with an Omega Digital Thermo-hygrometer. Face velocities of the test atmospheres were calculated by dividing the volumetric flow of each atmosphere by the cross-sectional area available for the air flow in each chamber. The cross-sectional area available for the air flow was the cross-sectional area of the chamber reduced by the cross-sectional areas of the samplers. The face velocity was maintained at 0.4 m/s.

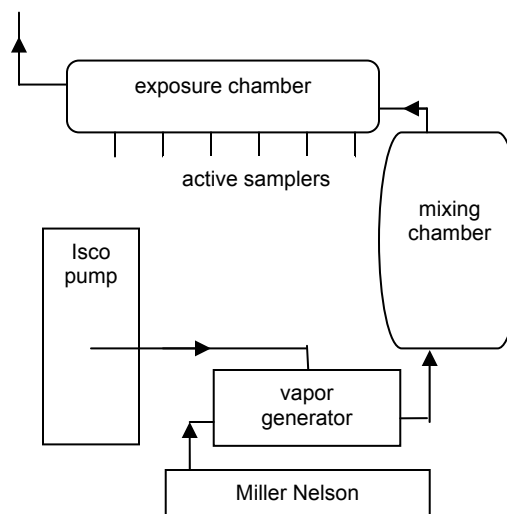


Figure 4.11 The test atmosphere generation and sampling apparatus.

Tests of the generation of formaldehyde from formalin solution were performed by heating the vapor generator at different temperatures to determine the effect temperature had on the recovery of formaldehyde. These tests were performed using the 37% formalin solution from Aldrich (lot 15902CO). It was found that the higher the temperature of the vapor generator, the

higher the recovery. These tests show heating the vapor generator to 100 °C causes the recovery of formaldehyde to be greater than 97% indicating that most of the formaldehyde was regenerated from the methoxymethanol.

Table 4.11.1
Temperature Effect on Recovery using a 37% Formalin Solution

temperature	% of theoretical for ChemDisk-AL				% of theoretical for UMEx 100				% of theoretical for DSD-DNPH			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
30 °C (86 °F)	71.6	70.9	68.1	70.2	70.8	71.9	69.3	70.7	71.9	68.4	70.8	70.3
40 °C (104 °F)	80.6	81.1	82.6	81.4	80.0	79.4	81.5	80.3	80.8	79.9	81.8	80.8
50 °C (122 °F)	88.4	90.5	89.8	89.5	89.7	90.4	88.8	89.6	90.9	89.3	88.9	89.7
100 °C (212 °F)	98.5	97.2	97.7	97.8	97.3	98.1	98.4	97.9	97.9	98.4	97.8	98.0