Determination of the Sampling Rate Variation for Supelco, Inc.
DSD-DNPH Diffusive Sampler for Aldehydes

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Introduction

The purpose of this study was to determine the sampling rate variation (SRV) for the Supelco, Inc. DSD-DNPH Diffusive Sampler for Aldehydes (DSD-DNPH). These samplers are intended by the manufacturer to measure the amount of formaldehyde and other aldehydes present in workplace air. The sampler uses 2,4-dinitrophenylhydrazine (DNPH) chemistry to produce a stable aldehyde derivative.

SRV has been established by OSHA as a measure of sampling error for diffusive samplers[1] SRV is the diffusive sampler equivalent of the often cited ±5% sampling pump error used for active samplers. It is a unique number that is experimentally determined for each individual design of diffusive sampler, because the SRV is presumed to be a function of sampler design. SRV provides the sampling error component of the Sampling and Analytical Error (SAE) calculations.[2]

SRV has been defined as the pooled relative standard deviation of sampling rates obtained in a modified version of the 16-run factor test described in the NIOSH testing protocol for diffusive samplers.[3] This test is based on determination of diffusive sampling rates for aldehydes in test atmospheres containing five different aldehydes. The test requires sample collection from 16 different combinations of high and low analyte concentration, short and long sampling time, high and low face velocity, high and low relative humidity, high and low interference level, and parallel and perpendicular sampler orientation to air flow direction in a sampling chamber.

The formaldehyde atmosphere was generated from a solution of formaldehyde in water freshly prepared from paraformaldehyde. Formaldehyde is sold commercially as a solution in water that is stabilized with methyl alcohol. The methyl alcohol can react with the formaldehyde forming methoxymethanol and dimethoxymethane (non-formaldehyde species).[4] These non-formaldehyde species are unstable and readily decompose back to formaldehyde and methyl alcohol.[5] These non-formaldehyde species readily react with the derivatizing agent, whether DNPH or 2-(hydroxymethyl)piperidine, to form the formaldehyde derivative. The test atmospheres produced from paraformaldehyde and from formaldehyde/water solution, contain mostly formaldehyde, while the atmospheres produced from formaldehyde that has been stabilized with methyl alcohol contain formaldehyde and non-formaldehyde species. The non-formaldehyde species are of higher molecular weight than formaldehyde and, therefore, they have different diffusive sampling rates. This difference in the sampling rates causes lower loadings of formaldehyde derivative on the diffusive samplers when compared to the active samplers taken from the same test atmosphere. This difference could result in formaldehyde results for the diffusive sampler which are as much as 35% lower than the active samplers.[6] Diffusive samplers, with sampling rates determined using test atmospheres prepared from paraformaldehyde, give analytical results similar to active samplers when sampling the same test atmosphere produced using paraformaldehyde. This study employed formaldehyde test atmospheres generated with formaldehyde solution (prepared from paraformaldehyde) to establish sampling rates for DSD-DNPH. Therefore, sampling rates shown here are for formaldehyde alone. Formaldehyde atmospheres in the workplace could result from formaldehyde stabilized with methyl alcohol, and would contain the non-formaldehyde species. Formaldehyde results from diffusive samplers would be lower than results from active samplers when both types of samplers were used to sample these atmospheres.

Reagents

Acetaldehyde, Aldrich Chemical Company, 99.5+%, lot CO 02962AO

Benzaldehyde, Aldrich Chemical Company, 99.5+%, lot 00208TI

Butyraldehyde, Aldrich Chemical Company, 99.5+%, lot BO 03519DI

Glutaraldehyde, Aldrich Chemical Company, 50%, lot 01907 CI

Paraformaldehyde, Aldrich Chemical Company, 95+%, lot 08710 AA

Acetonitrile, Fisher Chemical Company, 99.9%, lot 031027

Phosphoric acid, JT Baker, Baker-analyzed, 85.9%, lot D25821

2,4-Dinitrophenylhydrazine (DNPH), Aldrich Chemical Company, lot 7627JK (DNPH is light sensitive, so all solutions and samples should be protected from the light in light-impervious containers.)

Toluene, Alfa-Aesar, 99.8%, lot K06M13

N,N-Dimethylformamide (DMF), Aldrich Chemical Company, 99.8%, lot 04643LA

A freshly prepared solution of formaldehyde in water was prepared by heating paraformaldehyde at 80°C, and bubbling the vapor through deionized water. These mixtures were quantitated by titration[7] and diluted with deionized water to obtain the desired concentration before use in the vapor generation system.

Two different neat aldehyde mixtures were prepared. The first mixture was 1:1 (by volume) ratio of butyraldehyde:benzaldehyde, and the second mixture was 1:1:0.1 (by volume) of the formaldehyde solution:acetaldehyde:glutaraldehyde. These mixtures were used to generate the test atmospheres and to prepare standards.

DNPH extracting solution for extracting DSD-DNPH and DNPH coated glass fiber filters. The solution was composed of 1-g DNPH and 5-mL phosphoric acid in 1-L acetonitrile. The same solution was used to prepare analytical standards. The DNPH was purified by recrystallization from hot acetonitrile.

DNPH glass fiber filter coating solution. The solution was composed of 4-g DNPH and 20-mL phosphoric acid in 1-L acetonitrile. The DNPH was purified by recrystallization from hot acetonitrile

Adsorbent tube extracting solution. The solution was composed of 0.2 µL/mL DMF (used as internal standard) in toluene.

Sampling Media

Supelco, Inc. DSD-DNPH Diffusive Samplers for Aldehydes (DSD-DNPH), lot SP0403H01 containing a beaded silica gel coated with DNPH and phosphoric acid.

SKC 226-117 and 226-54 sampling tubes, lot 2952, containing XAD-2 coated with 10% (w/w) 2-(hydroxymethyl)piperidine (HMP XAD-2). These sampling tubes were packed with the same adsorbent, but contained differing amounts of the coated resin in the tubes, and thus have different amounts of formaldehyde background. The 226-54 has two sections containing 45- and 23-mg coated resin, and is used for short-term sampling. The 226-117 has two sections containing 150- and 75-mg coated resin, and is used for long-term samples. These sampling tubes were used to establish the concentrations of acetaldehyde, butyraldehyde, and formaldehyde in test atmospheres.

Glass fiber filters coated with 2-mg DNPH and 10-µL phosphoric acid (DNPH GFF). The cassette was loaded with three coated filters, with a spacer between each filter, and an extra spacer on the top to emulate open face sampling. These filters were used to establish the benzaldehyde and glutaraldehyde concentrations in the test atmospheres. The DNPH GFF were prepared by placing glass fiber filters on a clean glass plate and pipetting 0.5 mL of the DNPH glass fiber filter coating solution following the procedure found in OSHA Method 64 Glutaraldehyde.[8] The filters were allowed to dry 20 minutes in a hood, then they were placed in a light impervious container (brown glass jar) loosely sealed with a lid, allowed to dry completely overnight in a drawer. The next day the lid was tightly sealed and the jar was then placed into a freezer for storage.

Apparatus

Shaker. An Eberbach shaker was used to extract the adsorbent tubes.

Rotator. A Fisher Roto Rack was used to extract the DSD-DNPH and DNPH GFF samples.

Gas chromatograph (GC) with a nitrogen-phosphorus detector. An Agilent 6890 gas chromatograph with a 7683 injector, and 3396 Series II integrator was used for analysis of HMP XAD-2 samples. Separations were performed using a Restek Stabilwax DB capillary column (60-meter x 0.32-mm x 1-µm df). (Restek Corporation, Bellefonte PA).

An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium32 Data System was used in this evaluation.

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 analysis of DSD-DNPH and DNPH GFF samples. A 4.6- × 250-mm column packed with 5µm Pinnacle TO-11 (Restek Corporation, Bellefonte PA) was used in this evaluation.

Humid air generator. A Miller-Nelson Model HCS-401 Flow-Temperature-Humidity Control System was used to generate humid air for use with controlled test atmospheres. This instrument was equipped with a 500 L/min mass flow controller.

Relative humidity and temperature tester. An Omega Digital Thermo-hygrometer Model RH411 was used to determine the relative humidity and temperature of the test atmospheres within the exposure chamber. The probe was calibrated by the manufacturer.

Gas test meter. An Equimeter no. 750 gas meter was used to measure dilution flow rates. This meter had been checked at several flows against a Singer DTM 115 gas meter (that had been tested by the local natural gas distributor and found to be accurate).

Syringe pumps. The two aldehyde mixtures were metered into the system using two ISCO 100DM syringe pumps equipped with a cooling/heating jacket and an insulating cover. Both pumps were operated in the constant flow mode. The temperature of water in the cooling jacket was maintained at 19 °C with a Forma Scientific Model RH411 Bath and Circulator

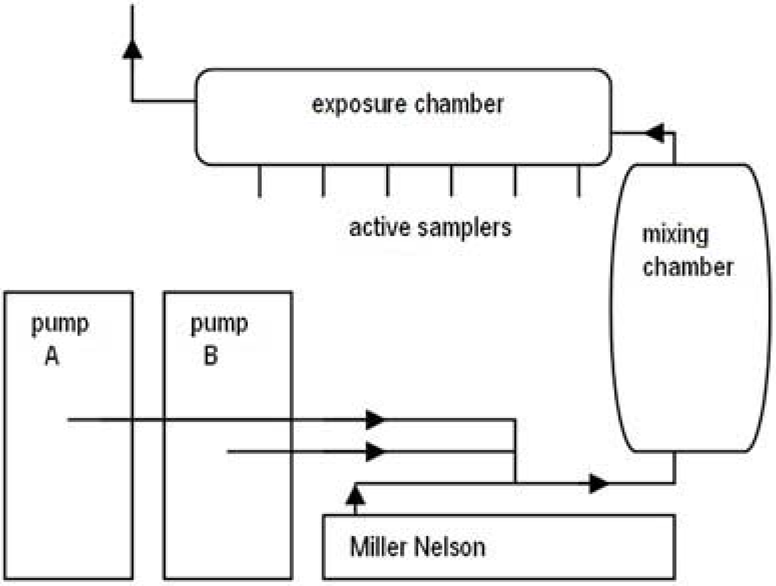

Figure 1. This is a diagram of the test atmosphere generation and sampling apparatus. The air stream of a known flow and humidity is introduced into the apparatus from the Miller Nelson Flow-Temperature-Humidity Control System. The aldehyde mixtures come from the ISCO syringe pumps and are teed into the air stream. The stream is heated to vaporize the aldehydes. The air and aldehydes flow into a glass mixing chamber to form a homogeneous test atmosphere. This test atmosphere then flows to the exposure chamber. The exposure chamber is large enough for the diffusive samplers to fit inside, and has side ports from which active samples can be taken. The test atmosphere then flows out of the exposure chamber into the exhaust.

The chemical vapors were generated by pumping the two aldehyde mixtures through a short length of 0.53-mm uncoated fused silica capillary tubing into a vapor generator where they were heated and evaporated into the dilution air stream (Figure 1). The entire apparatus was placed in a walk-in hood. The glass vapor generator consisted of a 15-cm length of 5-cm diameter piece of 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 mixture. A Miller Nelson Flow-Temperature-Humidity controller was used to regulate the humidity, temperature, and volume of the dilution stream of air. The test atmosphere passed into a glass mixing chamber (76-cm x 30-cm) from the vapor generator, and then into a glass exposure chamber (76-cm x 20-cm). The humidity and temperature were measured at the exit of the exposure chamber by 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.

Experimental

Sample Analysis

The HMP XAD-2 adsorbent tubes were opened, each section was placed into a separate 2-mL vial, and 1-mL of toluene with 0.25 µL/mL DMF as the internal standard was pipetted into each vial. The vials were sealed and were placed on a shaker for 1 hour. Standards were prepared by injecting microliter amounts of aldehyde spiking solutions, prepared by diluting both aldehyde mixture solutions, into vials containing 150 mg of the HMP XAD-2 resin for high standards, and 45-mg portions for low standards. Standards were prepared with the same amount of coated resin as was contained in the samples. Standard blanks of each amount of resin were analyzed, due to the background amount of formaldehyde present. The standards were allowed to react overnight. The standards were blank corrected before plotting in the calibration curve. The standards were extracted in the same manner as the samples.

Adsorbent tubes were analyzed by gas chromatography (GC) with a nitrogen-phosphorus detector. Separations were performed using a Restek Stabilwax DB capillary column (60-meter x 0.32-mm x 1-µm df). The injection volume was 1 µL with a 1:10 split. The GC temperature program was 60 °C for 4 min then 7 °C/min to 220 °C and hold for 2 min. The hydrogen carrier gas was 2.5 mL/min, hydrogen detector gas was 2 mL/min, the nitrogen auxiliary gas was 10 mL/min, and the detector air was 60 mL/min. The injector temperature was 220 °C and the detector temperature was 260 °C.

DNPH standards were prepared by injecting microliter amounts of spiking solutions, prepared by diluting both aldehyde mixture solutions, into 4-mL light-impervious (amber) vials containing 2 mL of DNPH extracting solution. Standards were allowed to react for 1 hour.

DSD-DNPH and the DNPH GFF were placed into amber 4-mL vials, 2 mL of the DNPH extracting solution was added, they were capped, and then they were extracted for 1/2 hour on a Fisher Roto Rack. The supernatant on the DSD-DNPH was immediately removed and placed into a separate vial for analysis. It is important to either dynamically extract the DSD-DNPH with the Supelco syringe filtering system or to use the procedure described above, as the concentration of DNPH derivatives decreases in solution with time when left in contact with the silica gel. It is not necessary to transfer the supernatant of the DNPH GFF samples.

DSD-DNPH and the coated glass fiber filters were analyzed using a liquid chromatograph equipped with a UV detector. A 4.6 × 250-mm column packed with 5-µm Pinnacle TO-11 was used in this study. The injection volume was 10 µL. The mobile phase was 65:35:0.02 acetonitrile:water:phosphoric acid pumped at 1 mL/min. The analytical wavelength was 365 nm.

Extraction efficiency

It was not necessary to perform an extraction efficiency study of the aldehydes from HMP XAD-2, as the same medium was spiked with the aldehydes in the mixture to make the analytical standards.[9]

The extraction efficiency study of the DNPH GFF was performed by spiking the five aldehydes onto the DNPH GFF, in amber vials, and allowing them to react overnight in a drawer. Six filters at each of six levels were spiked. The loadings studied were: acetaldehyde 1 to 86.4 µg/sample; benzaldehyde 1 to 208.4 µg/sample; butyraldehyde 1 to 141.6 µg/sample; formaldehyde 0.3 to 22 µg/sample; and glutaraldehyde 0.2 to 9.8 µg/sample.

The extraction efficiency study of the DSD-DNPH was performed by spiking the five aldehydes onto the coated silica gel, in amber vials, and allowing them to react overnight in a drawer. Six samples at each of six levels were spiked. The loadings studied were: acetaldehyde, 1 to 120 µg/sample; benzaldehyde, 1 to 187 µg/sample; butyraldehyde, 1 to 152 µg/sample; formaldehyde, 0.5 to 29.4 µg/sample; and glutaraldehyde, 0.3 to 9.8 µg/sample.

Sampling rate and capacity

The sampling rate and capacity of DSD-DNPH for each of the aldehydes was determined by exposing sets of three diffusive samplers to the aldehyde mixture for increasing time periods. The test atmosphere contained acetaldehyde (2 ppm or 3.6 mg/m^3), benzaldehyde (2 ppm or 8.82 mg/m^3), butyraldehyde (2 ppm or 5.9 mg/m^3), formaldehyde (0.75 ppm or 0.92 mg/m^3) and glutaraldehyde (0.2 ppm or 0.8 mg/m^3). This test atmosphere level will be referred to as the 1x, and the 1/10 of this level as 0.1x in this study. Unless otherwise noted, the sampler orientation was parallel to the flow direction of the test atmosphere. The average relative humidity, temperature, and face velocity of the test atmospheres, except in the factor tests, was 77%, 30 °C, and 0.4 m/s respectively. Six active samplers were collected with each set of three diffusive samplers. Active samplers consisted of three DNPH GFF and three HMP XAD-2. The sampling rates were 100 mL/min for DNPH GFF, and 50 mL/min for HMP XAD-2 samplers

Reverse diffusion tests were performed by sampling the 1x concentration for one-half the total sampling time, and then sampling clean humid air for the remainder of the sampling time. Eight diffusive samplers were exposed for 2 hours, four were removed and analyzed, and then the other four were exposed for 2 hours to clean, humid air and then analyzed. The relative humidity, temperature, and face velocity were 76%, 29 °C and 0.4 m/s respectively.

Factor tests

A 16-run factor test was performed using a modified version[10] of the NIOSH Factor Test.[11] NIOSH has identified six factors that can affect the performance of diffusive samplers: analyte concentration, face velocity, relative humidity, exposure time, interferant, and sampler orientation. Sixty-four experimental runs (26) would be required to fully evaluate combinations of each factor at two levels. NIOSH recognized that this would be an excessive number of tests, and has devised a 16-run fraction of the full factorial that is capable of revealing any of these factors having a significant effect, free of two-factor interactions, on sampler performance. Some of the two and three-factor interactions can also be screened by this design. The test is based on comparison of each factor effect to experimental error so that the significance of that effect can be determined. Experimental conditions are shown in Table 1. Interferant was provided by the components of the aldehyde mixture, for example if formaldehyde was examined, then acetaldehyde, benzaldehyde, butyraldehyde, and glutaraldehyde were the interferant, and the levels were either high (1x) or low (0.1x).

Table 1
Experimental Design of the Factor Test

run no.	analyte concn	RH (%, °C)	inter level	time (min)	face vel (m/s)	sampler orien
1	0.1x	21,30	low	120	1.9	perp
2	1x	19,29	low	30	0.2	perp
3	0.1x	80,30	low	30	2.0	paral
4	1x	80,30	low	120	0.2	paral
5	0.1x	21,30	high	120	0.2	paral
6	1x	20,30	high	30	1.8	paral
7	0.1x	79,30	high	30	0.2	perp
8	1x	79,30	high	120	1.8	perp
9	1x	80,29	high	30	0.2	paral
10	0.1x	77,30	high	120	1.8	paral
11	1x	20,30	high	120	0.2	perp
12	0.1x	21,31	high	30	1.9	perp
13	1x	77,30	low	30	1.8	perp
14	0.1x	78,30	low	120	0.2	perp
15	1x	21,29	low	120	1.8	paral
16	0.1x	20,29	low	30	0.2	paral

concn = concentration; inter = interference; face vel = face velocity; orien = orientation; perp = perpendicular; paral = parallel

Results and Discussion

Table 2
Extraction Efficiency (%)

acet = acetaldehyde; benz = benzaldehyde; buty = butyraldehyde; form = formaldehyde; and glut = glutaraldehyde

medium	acet	benz	buty	form	glut
DNPH GFF	100.0	100.1	100.0	100.0	100.0
DSD-DNPH	99.7	100.4	100.3	100.0	100.2

Extraction efficiency

A summary of the average extraction efficiencies is in Table 2. The extraction efficiencies were high and constant over the ranges studied.

Sampling rate and capacity

Sampling rates were calculated by dividing mass collected (corrected for extraction efficiency) by sampling time multiplied by the actual concentration of the test atmosphere (sampling rate = µg/(min x µg/L)). Sampling rate, in L/min, was converted to mL/min, the same units often used for adsorbent tubes. Theoretical concentrations were calculated from the test atmosphere generation apparatus operation parameters. The actual test atmosphere was determined from the HMP XAD-2 and DNPH GFF results. The actual test atmosphere was about 98% of the theoretical concentrations (Table 3). The selection of active medium used to establish actual test atmosphere concentrations was based on the existence of validated methodology and on technical considerations. The results from HMP XAD-2 tubes were used for acetaldehyde, butyraldehyde, and formaldehyde. The results for DNPH GFF were used for benzaldehyde and glutaraldehyde. The same sampling time was used for the active and passive samplers for each test run. All samples were analyzed as soon as possible after collection. Sampling rates and capacity results are in Table 4 and Figure 2. The sampling rates were determined at ambient temperature and pressure and converted to their equivalent at 25°C and 760 mmHg.

Table 3
Sampling Rate and Capacity Test Atmospheres (ppm)

source	acet	benz	buty	form	glut
theoretical concn	2.13	2.01	2.09	0.76	0.21
DNPH GFF results	1.83	1.98	2.01	0.72	0.20
HMP XAD-2 results	2.11	1.88	2.04	0.75	na

na = not applicable

Table 4
Sampling Rate and Capacity (mL/min)

time (min)	acet	benz	buty	form	glut
5	55.78	35.39	43.20	67.66	37.89
10	56.42	36.57	44.32	68.32	38.54
15	57.13	37.12	45.55	68.88	39.47
30	57.83	37.33	45.99	70.32	40.01
60	59.02	37.51	46.24	71.24	40.68
120	59.43	37.91	46.33	71.59	40.79
180	59.31	37.37	45.78	70.78	40.15
240	58.77	36.39	44.54	68.65	39.63
360	53.44	33.08	40.86	62.18	36.14
480	44.87	27.47	33.89	52.54	30.79

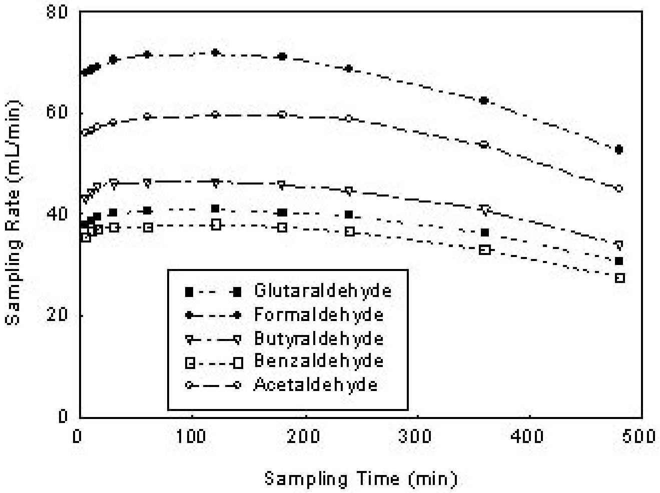

Figure 2. This is a plot of the sampling rate and capacity data presented in Table 4.

The sampling rates were fairly constant from 30 to 240 minutes. The capacity of the sampler for a component is presumed to be exceeded when the apparent sampling rate for that component decreases rapidly. It should be noted that the atmosphere of acetaldehyde was 2 ppm, while the PEL is 100 ppm, so the capacity results for a sampler at the PEL will be significantly lower than what appears in Table 4. Since the sampling rates were noticeably lower at 360 minutes, one could assume that the capacity at the PEL would be exceeded before 15 minutes of sampling. The average sampling rates for 30 to 240 minutes are listed in Table 5, along with their RSD. The DSD-DNPH sampling rates in Table 5 were obtained from Supelco, Inc.[12]

Table 5
Average Sampling Rate (mL/min) and RSD (%)

	acet	benz	buty	form	glut
30-240 min	58.87	37.30	45.78	70.52	40.25
RSD	1.18	1.16	1.21	0.91	1.12
DSD-DNPH sampling rate	59.4	38.2	46.4	71.9	na

na = not available

Reverse diffusion occurs when the compound is lost from the sampler after collection. All diffusive samplers have the potential for reverse diffusion. These DNPH derivatives are not volatile, but loss could occur through other means so this experiment was performed. The recovery was calculated by dividing the average recovery after 4 hours by the average recovery after 2 hours. The recoveries were all near 100%.

The effects of increasing face velocity on the sampling rates are shown in Figure 3. The most dramatic effects occur at low to medium velocities. The overall effect is similar to the ones observed for 3M 3520 OVMs[13], SKC 575-002.[14]

Table 6
Reverse Diffusion

	acet	benz	buty	form	glut
recovery (%)	100.2	100.3	100.0	100.2	99.3

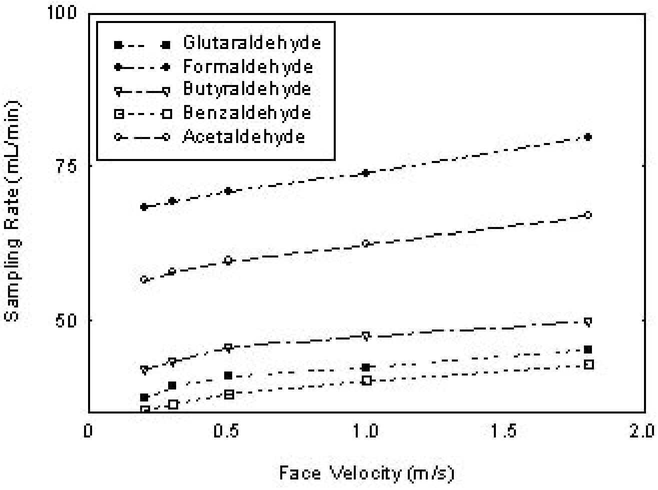

Figure 3. This is a plot of the effects of increasing face velocity on sampling rates from Table 7.

Table 7
Effect of Increasing Face Velocity on Sampling
Rates of DSD-DNPH (ml/min)

face vel (m/s)	acet	benz	buty	form	glut
0.2	56.53	35.49	42.15	68.45	37.33
0.3	58.38	36.30	43.24	69.25	39.28
0.5	59.66	38.07	45.62	70.99	40.86
1.0	61.66	40.12	47.48	73.98	42.39
1.8	66.94	42.76	49.85	79.84	45.28

Factor Test

The results of the factor test are presented in Table 8. The sampling rates were determined at ambient temperature and pressure, but are expressed at 25 °C and 760 mmHg.

Table 8
Factor Test Results (mL/min)

test	acet	benz	buty	form	glut
1	67.16	42.21	49.72	79.99	45.13
2	57.27	35.75	42.32	68.83	37.88
3	67.05	41.99	49.45	79.91	44.93
4	57.45	36.70	44.49	69.03	38.14
5	56.72	35.68	42.99	68.77	37.53
6	66.30	41.90	49.49	79.19	45.01
7	57.57	36.35	43.02	69.54	38.24
8	66.95	42.77	49.89	79.71	45.28
9	58.54	37.17	45.34	71.05	39.77
10	66.89	41.72	49.81	79.36	44.39
11	58.88	40.01	43.59	69.49	39.91
12	66.72	41.83	49.05	79.44	44.11
13	66.93	42.97	49.91	79.96	44.34
14	58.85	36.81	43.52	70.55	38.67
15	66.33	42.15	49.28	79.86	45.17
16	56.63	35.49	42.18	68.45	37.33

Average sampling rates and their percent RSDs are shown in Table 9. There percent RSDs were found to be homogenous by the Cochran Test at 95% confidence limits.[15] The pooled percent RSD, 7.49%, is the sampling rate variation for the DSD-DNPH as determined by this work.

The data in Table 8 was further analyzed to detect factor effects following the NIOSH protocol for diffusive samplers.[16] The minimum significant effect (MSE) was calculated for each component by multiplying experimental error of the factor test by the appropriate t statistic for the nine degrees of freedom (2.26 is the t statistic at the 95% confidence level for nine degrees of freedom). The MSE for each aldehyde is found in Table 10. The analysis gave a numerical factor effect result for each aldehyde component for each of the seven factors. The absolute value of the normalized ratio of effect/MSE is shown in Table 11. Any ratio above 1 is significant at the 95% confidence level, and that effect should be studied further in additional experiments. The results for interferant may be somewhat equivocal because the remainder of the mixture was considered the interference, such as acetaldehyde, benzaldehyde, butyraldehyde, and glutaraldehyde were interferents for formaldehyde. Face velocity had the most significant effect on the sampling rates, and humidity also had a significant effect for butyraldehyde.

Precision

The pooled relative standard deviations between sets of 3 sample results for each medium were calculated for each aldehyde from the factor tests. The precision data of the diffusive and active samplers for each component were comparable. While data is presented in Table 12 for both types of active samplers, the active sampler for acetaldehyde, butyraldehyde, and formaldehyde was HMP coated XAD-2 tubes, and the active sampler for benzaldehyde and glutaraldehyde was DNPH GFF.

Package integrity

Formaldehyde and acetaldehyde are common components in the air, especially in urban areas, as they are natural by-products of internal combustion engines. The integrity of unopened DSD-DNPH, lot SP0404H01, was checked by placing them in the exposure chamber, for 100 hours, while the 1x factor tests were performed. The diffusive samplers were exposed to 0.75 to 2 ppm for each component.

Conclusions

The sampling rate variation for DSD-DNPH is ±7.49% as determined by this work. Sampling rate variation is a function of the design of diffusive samplers, and is not dependent on the sorbent inside, or the chemical tested. This sampling rate variation may be used for other chemicals collected using this diffusive sampler under conditions that approximate conditions of these tests. This sampling rate variation would also apply if a different sorbent was placed inside the diffusive sampler for sampling other chemicals.

Sampling rate variation is used by OSHA as the sampling error component of the SAE (Sampling and Analytical Error).[17] The analytical error component is periodically updated from the analysis of quality control samples. Each analyte will have a unique SAE.

Table 9
Percent RSDs of Average Sampling Rates

	acet	benz	buty	form	glut
ave (mL/min)	62.27	39.47	46.50	74.57	41.61
RSD (%)	7.58	7.60	7.02	7.13	8.08
pooled RSD (%)			7.49		

Table 10
Analysis of Factor Data of Test Error

	acet	benz	buty	form	glut
error	0.32	0.48	0.31	0.35	0.37
MSE (mL/min)	0.73	1.09	0.70	0.80	0.85

Table 11
Analysis of Factor Data Effect Results

	acet	benz	buty	form	glut
concn	0.18	0.84	0.82	0.17	0.76
RH	0.73	0.17	1.22	0.79	0.25
interfer	0.16	0.38	0.42	0.01	0.39
time	0.38	0.53	0.46	0.06	0.39
lin vel	12.4	4.98	8.77	12.7	7.51
orient	0.76	0.68	0.36	0.30	0.19
interaction	none	none	none	none	none

Table 12
Precision Data (% RSD)

	acet	benz	buty	form	glut
HMP XAD-2	2.6	4.8	2.2	2.5	na
DNPH GFF	5.2	2.1	3.3	4.1	2.4
DSD-DNPH	2.9	2.4	2.6	2.5	2.9

na = not applicable DL = detection limit

Table 13
Package Integrity Test

	acet	benz	buty	form	glut
µg found	0.41	<DL	<DL	<DL	<DL
µg blank	<DL	<DL	<DL	<DL	<DL
DL (µg)	0.1	0.1	0.1	0.1	0.1

na = not applicable DL = detection limit

References

1 Hendricks, W., Development of a Protocol for Laboratory Testing of Diffusive Samplers, www.osha.gov, (accessed 11/24/03).

2 Hendricks, W., Development of a Protocol for Laboratory Testing of Diffusive Samplers, www.osha.gov, (accessed 11/24/03).

3 Hendricks, W., Development of a Protocol for Laboratory Testing of Diffusive Samplers, www.osha.gov, (accessed 11/24/03).

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

5 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.

6 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 OSHA Method 52 Formaldehyde, www.osha.gov, (accessed 11/24/03).

8 OSHA Method 64 Glutaraldehyde, www.osha.gov, (accessed 11/24/03).

9 OSHA Methods 52 and 64, www.osha.gov, (accessed 11/24/03)

10 Hendricks, W., Development of a Protocol for Laboratory Testing of Diffusive Samplers, www.osha.gov, accessed 11/24/03.

11 Cassinelli, M. E., Hull, R.D., Crable, J.V., and Teass, A.W, "Protocol for the Evaluation of Passive Monitors", Diffusive Sampling; An Alternative Approach to Workplace Air Monitoring, Berlin, A., Brown, R.H., Saunders, K.J., Eds., Royal Society of Chemistry, Burlinghouse, London, pp. 190-202, 1987.

12 DSD-DNPH Application Manual, www.sigma-aldrich.co.jp/supelco/pdf/DSD-DNPH_manual_V3.2.PDF, (accessed 12/11/03).

13 Hendricks, W., Development of a Protocol for Laboratory Testing of Diffusive Samplers, www.osha.gov, (accessed 12/11/03).

14 Hendricks, W., Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, www.osha.gov, (accessed 12/11/03).

15 Anderson, R.L., Practical Statistics for Analytical Chemists, Van Nostrand Reinhold Co., New York, 1987, p 62.

16 Cassinelli, M.E., Hull, R.D., Crable, J.V., and Teass, A.W., "Protocol for the Evaluation of Passive Monitors", Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring, Berlin, A., Brown, R.H., Saunders, K.J., Eds., Royal Society of Chemistry, Burlinghouse, London, pp 190-202, 1987.

17 Sampling and Analysis, www.osha.gov, (accessed 12/11/03).