Research Report

Determination of Formaldehyde Using the SKC UME^{X} 100 (Cat. No. 500-100) Passive Sampler

Abstract

A sampling method for formaldehyde in air using a UME^{X} 100 Passive Sampler has been validated for concentrations ranging from 0.06 to 3.0 ppm and for exposures ranging from 15 minutes to 24 hours. The UME^{X} 100 passive sampler consists of a Whatman silica gel filter paper treated with 2,4-dinitrophenylhydrazine (2,4-DNPH) in a polypropylene housing. The sampler contains 2 compartments, one for the sample and the other for the blank/correction. After sampling, each tape is placed in a vial, extracted with acetonitrile, and analyzed by High Performance Liquid Chromatography (HPLC) with UV detection at 365 nm.

The average sampling rate of 28.6 ml/min has a relative standard deviation (RSD) of 7.6%. The sampling rate was within 8% of theoretical and independent of concentration, relative humidity, sample time, orientation, and face velocity. Samples are stable for up to 3 weeks in the refrigerator.

The UME^{X} 100 passive sampler can detect 5 ppb in an 8-hour sample. Field studies comparing the passive sampler with pumped sampling indicated it is useful and accurate for 24-hour monitoring in indoor air environments. Additional studies show that the UME^{X} 100 passive sampler is also suitable for up to 7-day monitoring at a lower average uptake rate of 20.4 ml/min.

This validation work was supervised by Dr. Jan-Olaf Levin of the National Institute of Working Life in Umea, Sweden.

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Introduction

The International Agency for Research on Cancer (IARC) recently found sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans. Occupational exposures occur in the range of 0.1 to 5 ppm. In addition to industrial and commercial applications, formaldehyde is also found in a variety of construction materials and consumer products; people are exposed to formaldehyde in their homes as well. A sampler developed by the National Institute of Working Life was evaluated for its ability to monitor for formaldehyde under a variety of conditions including concentration, relative humidity, orientation, face velocity, and 24-hour sampling.

Experimental

Standard atmospheres of formaldehyde were generated in a dynamic system by decomposition of paraformaldehyde at 25 to 30 C. Six samplers were exposed in a sampling chamber to formaldehyde levels from 0.06 to 3.0 ppm, with sampling times between 15 minutes and 8 hours. Relative humidity was varied between 10 and 80% and face velocities between 5 and 100 cm/sec. Samplers were oriented parallel to the airstream. Atmospheres were verified using coated filters with battery-operated pumps.

The sampler housing was made from polypropylene. Two treated Whatman (SG-81) filters were in compartments below the screen. The treated filter beneath the diffusion holes was used for sampling; the other half was used as a blank/correction filter. The blank/correction section contained a small indentation so that it could be distinguished from the sample. A sliding cover sealed the holes when the sampler was not in use.

When sampling was complete, the 2 coated-filter samples were placed in vials and capped. The 2,4-dinitrophenylhydrazine derivative was extracted using 3.0 milliliters of acetonitrile and hand shaken for 1 to 2 minutes. The extract was analyzed by HPLC using UV detection at 365 nm. The analytical conditions with chromatogram are shown in Figure 1. Quantitation was performed by using prepared formaldehyde-DNPH standard solutions purchased from AccuStandard, Inc. (New Haven, CT).

Results and Discussion

The recoveries were calculated using an average sampling rate of 28.6 ml/min (Table 1). The concentrations ranged from 0.06 to 3.0 ppm and time intervals from 15 minutes to 8 hours. The face velocity was at 30 cm/sec. The mean recovery was 100% with a relative standard deviation of 3.95%. These data represent an average of 72 determinations over this concentration range.

The face velocity and orientation data (Table 2) indicate that there is no change in sampling rate over a range of 5 to 100 cm/sec or with either a parallel or perpendicular orientation.

UME^X 100 passive samplers must be stored at temperatures $\leq$39.2 F (4 C) to keep the background to a minimum. The exposed sampler is stable for 3 weeks, provided it is stored in the resealable aluminized pouch at temperatures $\leq$39.2 F (4 C) to keep the background to a minimum. The formaldehyde-hydrazone derivative is stable.

Summary

The UME^X 100 (Cat. No. 500-100) has been validated for formaldehyde over a concentration range of 0.06 to 3.0 ppm and at relative humidities from 10 to 80%. The sampler can sample from 15 minutes to 24 hours (Table 3) and has a mean sampling rate of 28.6 ml/min. Further studies indicate that the UME^X 100 passive sampler is suitable for up to 7-day indoor air sampling at an average sampling rate of 20.4 ml/min (wind velocities < 5 cm/sec).

Face velocities from 5 to 100 cm/sec and various orientations had no effect on sampling rate. The sampler was field tested and showed good correlation against a pumped filter method.

This sampler utilizes the popular DNPH chemistry and can easily detect 5 ppb for an 8-hour exposure. The sampler can be used for 24-hour to 7-day monitoring of contaminants found in indoor environments as well as 12-hour personal monitoring in industrial environments.

Table 1

Recovery of Formaldehyde on the UME^{X} 100 Passive Sampler

Level (ppm)	RH (%)	Sampling Time (min)	Recovery[1] (%)	RSD[2]
0.057	10	480	105.2	4.0
0.092	20	15	99.6	6.1
0.092	75	480	96.5	6.9
0.0978	80	120	105.2	14.0
0.106	10	120	99.6	9.0
0.114	80	480	102.8	7.0
1.70	75	15	101.7	1.8
1.70	20	480	102.1	1.6
2.1	80	15	98.4	2.0
2.4	80	480	102.3	4.0
2.4	10	480	92.1	3.0
3.0	10	15	95.6	3.0

1) Recovery calculated based on a sampling rate of 28.6 ml/min.
2) RSD = relative standard deviation on 6 determinations

Table 2

The Effect of Face Velocity and Orientation on the Sampling Rate (SR) of the UME^{X} 100 Passive Sampler for Formaldehyde

Concentration (ppm)	Wind Velocity (cm/sec)	Orientation	Sampling Rate (ml/min)
1.22	30.0	Perpendicular	33.5
1.47	5.0	Parallel	28.3
2.69	10.0	Parallel	30.1
2.69	10	Perpendicular	27.2
2.11	30	Parallel	28.1
0.98	50	Parallel	28.6
0.65	100	Parallel	31.1
0.65	50	Perpendicular	32.5
		Mean SR	29.9

Table 3

24-hour Field Study of Pumped Tube Method and Passive Samplers
(*Results reported in mg/m^3*)

Indoor Air Location	Pumped Tube (mg/m^3) (n=6)	Passive (UME^X 100) Sampler (mg/m^3) (n=6)
Office Room	0.027	0.027
Factory 1	0.155	0.141
Factory 2	1.10	1.04

Figure 1
Sample Chromatogram
Blank Sampler in Acetonitrile

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

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

Injector: Waters 717 Autosampler, 20 microliters

Pump: SSI HPLC Pump, 222D

Detector: SSI 500 Variable UV/VIS, 365 nm

Integrator: HP 3396 Series II