Validation of Methanol

Using SKC Cat. No. 575-007 Diffusive Samplers

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Methanol

Research Report

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Abstract

A sampling method using the SKC Cat. No. 575-007 diffusive sampler, which contains 500 mg of Anasorb® 747 and incorporates a green secondary diffusion barrier, has been validated for sampling methanol in workplace air. The desorption efficiency (DE) was 101% with a 4.2% relative standard deviation (RSD). The sampling rate was determined for Cat No. 575-007 samplers at a methanol level of 400 ppm at 80% relative humidity (RH) and 22 C. The mean sampling rate for 38 tests was 1.20 ml/min with a 10.0% RSD. Cat. No. 575-007 samplers can be stored at ambient (22 C) temperature for one week with a 10% or less loss of recovery or at freezer temperatures (< 4 C) for up to 3 weeks with no loss in recovery. A reverse diffusion study shows that reverse diffusion does not take place. All diffusive samplers were desorbed in 2 ml of 50:50 carbon disulfide:dimethylformamide (DMF) and analyzed by gas chromatography (GC) with flame ionization detection (FID). The limit of detection is 5.0 ppm (3.8 ug) based on an 8-hour sample.

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Introduction

Methanol, also known as methyl alcohol, carbinol, wood alcohol, wood naphtha, or wood spirit, is a clear flammable liquid with an odor similar to ethanol. Methanol is the simplest alcohol and is light, volatile, and very toxic. Methanol was originally manufactured by the destructive distillation of wood but now is usually manufactured from hydrogen and carbon monoxide or carbon dioxide and also by the oxidation of hydrocarbons. Methanol is used as an industrial solvent and dissolves many organic salts better than ethanol. Methanol is also used to manufacture formaldehyde and methyl esters, as antifreeze for automotive radiators and air breaks, and as an octane booster in gasoline. Other uses include fuel for picnic stoves and soldering torches, and denaturing ethanol.[1] Poisoning can occur from ingestion and inhalation or through absorption. The effects of exposure to methanol include headache, fatigue, nausea, visual impairment or blindness, convulsions, acidosis, circulatory collapse, respiratory failure, and death. A 100 to 250-ml dose of methanol is usually fatal but deaths have been reported from ingestion of less than 30 ml.[1,2] In the body, methanol is converted to formaldehyde, which is then converted to formic acid. Both of these are toxic and attack the liver and optic nerve.[3,4]

The purpose of this study was to validate SKC Cat. No. 575-007 diffusive samplers for monitoring methanol at 400 ppm.

Experimental

Methanol (Sigma Aldrich, St. Louis, MO, USA) was used to prepare concentrations in the test chamber. A dynamic atmosphere was created at two times the permissible exposure limit (PEL) (200 ppm) using a syringe pump and filtered air streams to generate the concentrations. The system is shown in Figure 1. The atmosphere was fed into an exposure chamber and the diffusive samplers were exposed on a rotating bracket inside the chamber to stimulate wind velocity. The sampling rate testing was conducted at 400 ppm for periods from 15 minutes to 8 hours at 80% RH and 22 C. The concentration within the atmospheric chamber was verified with SKC Cat. No. 226-82 sorbent tubes. The Cat. No. 575-007 diffusive sampler, which incorporates a green secondary diffusion barrier to lower the sampling rate, was used for the study. After exposure, samplers were sealed until analysis.

The DE for the samplers was determined by injecting a known amount of methanol into the back of each sampler. The samplers were capped and allowed to equilibrate overnight and then analyzed the next day to determine the analytical recovery. The test was conducted at mass loadings equivalent to an 8-hour time-weighted average (TWA) sample based on a validated sampling rate (1.2 ml/min) at 0.1, 0.5, 1.0, and 2.0 times the PEL under dry conditions. A reverse diffusion study was performed by exposing four badges to 400 ppm of methanol for 2 hours and another four badges to the same 400 ppm of methanol for 2 hours followed by 6-hour exposure to 0 ppm of methanol. Both exposures were at 80% RH and 22 C.

The storage study consisted of injecting 28 Cat. No. 575-007 passive samplers with known amounts of methanol. The samplers were capped and allowed to equilibrate for 2 hours. Four samplers were analyzed while 12 samplers were stored at ambient (22 C) temperature and the remaining 12 samplers were stored in a freezer (< 4 C). Four samplers from both temperatures were analyzed each week for 3 weeks to determine the analytical recovery.

All diffusive samplers were desorbed in 2 ml of 50:50 carbon disulfide: DMF and shaken on a flatbed shaker for 15 minutes. The extracts were then analyzed by GC with FID. A chromatogram is shown in Figure 2.

Because SKC Inc. constantly reviews this data and conducts experiments to provide the most precise sampling rate, the rate published in this validation report is correct.

Results and Discussion

The DE was 101% (RSD 4.2%) as shown in Table 1. The sampling rate data are shown in Table 2. The results of the 38 samplers show that methanol can be sampled with the Cat. No. 575-007 diffusive sampler at an average sampling rate of 1.20 ml/min (RSD 10.0%). The data indicate that the sampler can collect a 15-minute to 8-hour sample at 20 to 400 ppm of methanol. The 3-week storage study, shown in Table 3, suggests that samplers can be stored at ambient (22 C) temperature for one week with less than 10% loss in recovery or in a freezer (< 4 C) for 3 weeks with no loss in recovery. Table 4 shows that reverse diffusion does not take place. The limit of detection is 5.0 ppm (3.8 ug) based on an 8-hour sample.

Conclusion

The Cat. No. 575-007 diffusive sampler has been partially validated for sampling methanol with a DE of 101% (RSD 4.2%). The diffusive sampler samples at a rate of 1.20 ml/min (RSD 10.0%). The sampler showed good stability when stored for one week at ambient (22 C) temperature with a < 10% loss in recovery or for 3 weeks at freezer (< 4 C) temperatures with no loss in recovery. Cat. No. 575-007 diffusive samplers can be used for measuring exposures of methanol from 15 minutes to 8 hours at 20 to 400 ppm at 80% RH. Reverse diffusion does not take place.

References

1. *Merck Index,* 12th Edition, 1996, p. 1018
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4. McMartin, K.E., et al., "Lack of a role for formaldehyde in methanol poisoning in the monkey," *Biochen. Pharmacol.* **28** (5), 1979, pp. 645-9. Doi:10.1016/0006-2952(79)90149-7 (http://dx.doi.org/10.1016%2F0006-2952%2897%2990149-7> PMID 109089 (https://www.ncbi.nlm.nih.gov/pubmed/109089).

Figure 1

Atmospheric Chamber

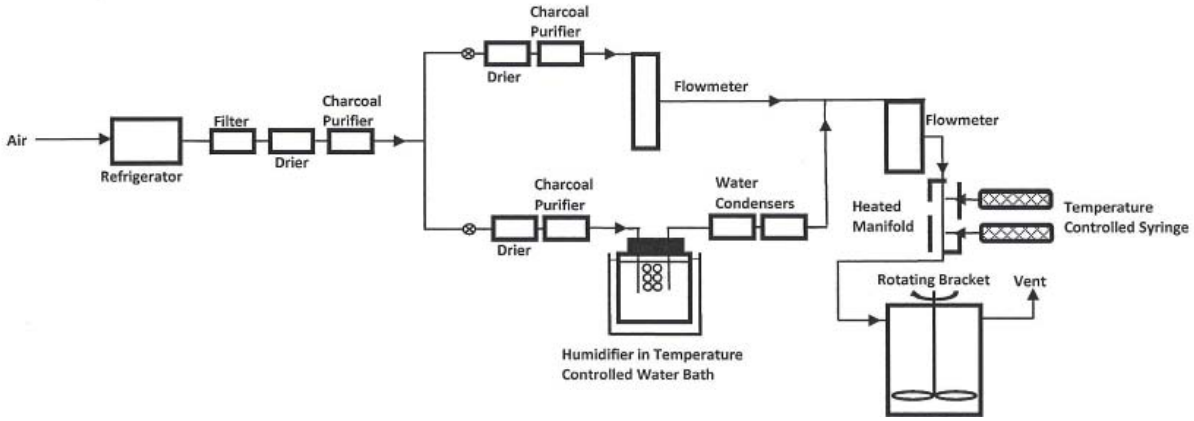
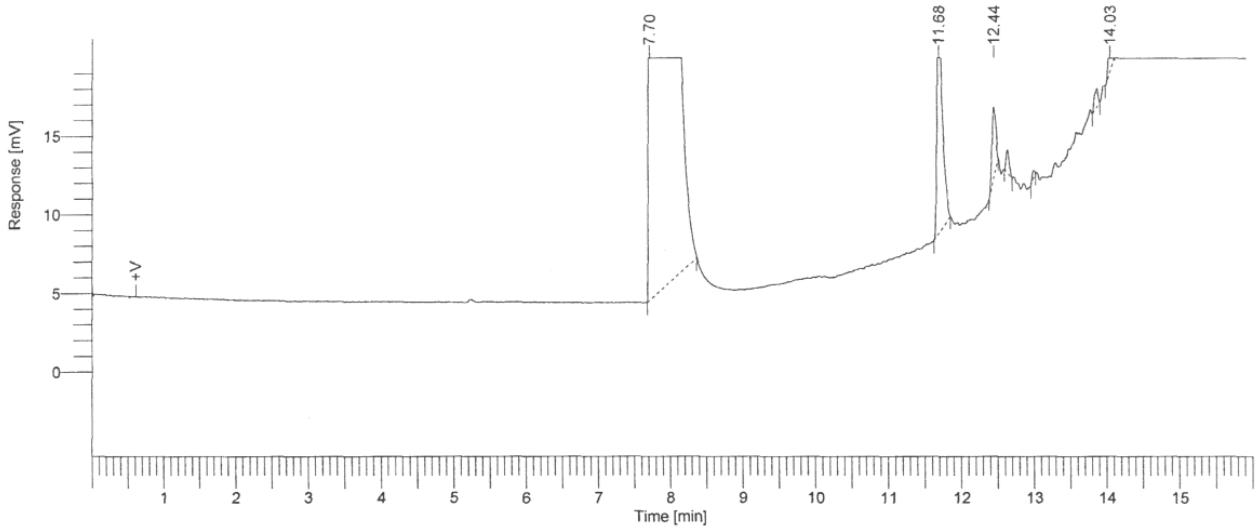


Figure 2

Methanol Sample Chromatogram



Column: StabilWax, 60 m x 0.32 mm ID x 1.0 µm film

Temperature:

Injector:	250 C
Detector:	FID at 300 C
Column:	50 C hold 2.4 min, ramp 15 C/min to 240 C hold 5 min

Retention times (minutes):

Carbon disulfide:	7.70
Methanol:	11.68
Impurity:	12.44
DMF:	14.03

Table 1

Analytical Recovery
Methanol

µg Spiked	µg Recovered	% Recovery
13.6	13.83	102
	12.53	92.3
	12.72	93.7
65.0	68.6	106
	68.3	105
	67.0	103
150	155	103
	158	105
	155	103
360.57	353	100
	361	102
	360	102
	Mean (%)	101
	Standard Deviation	426
	RSD (%)	4.2

Table 2

Sampling Rate
400 ppm of Methanol at 80% RH, 22 C

Time	Sampling Rate (ml/min)
15 Min	1.58
	1.40
30 Min	1.16
	1.36
	0.96
	1.40
1 Hour	1.03
	1.21
	1.12
	1.13
2 Hours	1.20
	1.18
	1.04
	1.10
	1.09
	1.25
	1.30
	1.16
	1.09
	1.10
	1.21
4 Hours	1.13
	1.16
	1.19
	1.22
	1.19
	1.14
6 Hours	1.20
	1.30
	1.21
	1.32
8 Hours	1.16
	1.19
	1.21
	1.32
Mean	1.20
Standard Deviation	0.125
RSD (%)	10.0

Table 3

Storage Study
Methanol

Week	Ambient (22 C) % Recovery	Freezer (< 4 C) % Recovery
1	93	104
2	80	97
3	74	100

Table 4

Reverse Diffusion
Methanol
Exposed for 2 Hours at 400 ppm

Methanol (µg)		Exposed for 2 Hours at 400 ppm Methanol plus 6 Hours at 0.0 ppm (µg)	
62.82		66.95	
72.37		63.18	
75.15		63.73	
		70.10	
Mean (µg)	70.11	**Mean (µg)**	65.99
Standard Deviation	6.47	**Standard Deviation**	3.21
RSD (%)	9.2	**RSD (%)**	4.9

Appendix A

Atmosphere Generation Apparatus

The instrument is designed to expose a known concentration of a chemical hazard to a diffusive sampler under controlled conditions of concentration, temperatures, humidity, wind velocity effect, and time.

Description

The instrument consists of:

1. An exposure chamber in which the wind velocity effects are controlled by internal rotating holders.
2. An air supply and purification train such that dry air is blended with saturated air under desired temperature conditions so as to provide air known at a known flow and selectable humidity.
3. An injection system comprising a precision motor-driven syringe in which the chemical hazard can be injected into the flow system and in which the temperature of the injector is closely controlled.
4. An electrical control system that controls the entire instrument operation.
5. A chamber concentration that can be verified by either solid sorbent sampling tubes actively sampled or by gas analysis of the gas phase. The particular verification method used will depend on the analyte of interest.

Means of checking the RH are also included.