Validation of 1,3-Dichloropropene (cis and trans)

Using SKC Cat. No. 575-002 Diffusive Samplers

Research Report

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Abstract

A sampling method using SKC Cat. No. 575-002 diffusive samplers has been partially validated for sampling 1,3-dichloropropene (cis and trans) in air. A desorption efficiency (DE) study was conducted at 0.05, 0.10, 0.50, 1, and 2 times ACGIH's limit of 1 ppm for an 8 hour period. Trans-1,3-dichlorpropene had an average DE of 99.4% with a relative standard deviation (RSD) of 5.88%. The average desorption efficiency for the cis isomer is 101% with a 6.22% RSD. The sampling rate was determined for samplers exposed to a 1,3-dichloropropene (cis and trans) level of 2 ppm at 60% relative humidity (RH) and 25°C. The Trans isomer has a mean sampling rate of 14.4 ml/min with an RSD of 7.79 % for 38 tests. The mean sampling rate for cis-1,3-dichloropropene is 13.6 ml/min with a 9.09% RSD for 31 tests. The trans isomer shows a 13% loss in recovery when stored for two weeks, even at freezer temperatures. Cis-1,3-dichlorpropene can be stored for up to two weeks at ambient temperatures with less than a 10% loss in recovery and in the freezer with less than a 5% loss in recovery. The Cat. No. 575-002 sampler was desorbed in 2 ml of carbon disulfide and analyzed by gas chromatography (GC) with flame ionization detection (FID).

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Introduction

1,3-Dichloropropene (cis and trans) is a liquid with a chloroform-like odor [(1)]. Potential symptoms of overexposure include irritation of skin, eyes and respiratory system, eye and skin burns, lacrimation, headache, dizziness, coma, gasping, refusal to breath, coughing, substernal pain, and possible liver, kidney, and heart injury. It is used as a soil fumigant and nematocide, as well as in the manufacturing of pesticides [(1)]. It has an ACGIH® guideline of 1 ppm based on an 8-hour time weighted average.

The purpose of this study was to partially validate 575-002 diffusive samplers for monitoring 1,3-dichloropropene (cis and trans) at 2 ppm. Critical parameters included analytical recovery, sampling rate, and storage.

Experimental

Desorption efficiency studies for the samplers were conducted by injecting a known amount of 1,3-dichloropropene (cis and trans) into the back of each sampler. The samplers were capped, equilibrated for 2 hours, and analyzed to determine the analytical recovery. The tests were conducted at mass loadings equivalent to an 8-hour TWA sample based on a calculated sampling rate of 15.2 ml/min at 0.05, 0.10, 0.50, 1, and 2 x the PEL under dry conditions.

1,3-Dichloropropene (cis and trans) (Aldrich, St. Louis, MO, U.S.) was used to prepare concentrations in the atmosphere chamber (Figure 1). A dynamic atmosphere was generated using a syringe pump and filtered airstreams to generate the concentration. The atmosphere was fed into an exposure chamber. The diffusive samplers were exposed on a rotating bracket inside of the chamber to simulate wind velocity. The sampling rate study was conducted at 2 x the PEL (2 ppm) for periods ranging from 15 minutes to 8 hours at 60% RH and 25°C. The concentration within the atmospheric chamber was verified with Cat. No. 226-01 sorbent tubes (SKC Inc., Eighty Four, PA, U.S.). SKC Cat. No. 575-002 diffusive samplers (SKC Inc., Eighty Four, PA, U.S.) were used for the study. After exposure the diffusive samplers and sorbent tubes were sealed until analysis.

The storage study consisted of injecting 21 samplers with known amounts of 1,3-dichloropropene (cis and trans). The samplers were capped and equilibrated for 2 hours. Three samplers were analyzed for a day zero while 9 samplers were stored at ambient temperatures and the remaining 9 samplers were stored in a freezer (-22°C). Three samplers each from the ambient and freezer lots were analyzed each week for three weeks to determine analytical recovery.

All diffusive samplers were desorbed in 2 ml of carbon disulfide and shaken on a flatbed shaker for 15 minutes. The extracts were analyzed by flame ionization detection gas chromatography. A chromatogram is shown in Figure 2.

SKC constantly reviews this data and conducts experiments to provide the most precise sampling rate. The rate published in these validation reports is the correct rate.

Results and Discussion

The desorption efficiency results for 1,3-dichloropropene (cis and trans) with the 575-002 diffusive samplers are shown in Tables 1 and 2. The mean recovery of the diffusive samplers was 99.4% (5.88% RSD) for the trans isomer and 101% (6.22% RSD) for the cis isomer. The sampling rate data is shown in Tables 3 and 4. The results of the 38 samplers show that trans-1,3-dichloropropene can be sampled with the 575-002 diffusive samplers at an average sampling rate of 14.4 ml/min with a 7.79% RSD. Cis-1,3-dichloropropene can be sampled with the 575-002 diffusive samplers at an average sampling rate of 13.6 ml/min with an RSD of 9.09% as shown by the results of the 31 samplers. The data indicates that the sampler can collect a 15 minute to 8 hour sample at 2 ppm of 1,3-dichloropropene (cis and trans). The two-week storage study, shown in Tables 5 and 6, suggests that trans-1,3-dichloropropene samples be analyzed as soon as possible, as they have a 13% loss in recovery after two weeks, even at freezer temperatures. The cis-1,3-dichloropropene storage data indicates that samples can be stored for two weeks at ambient temperatures with less than a 10% loss in recovery or in the freezer for two weeks with less than a 5% loss in recovery.

Conclusion

The 575-002 diffusive samplers have been partially validated for sampling 1,3-dichloropropene (cis and trans) in air. The trans isomer had a desorption efficiency of 99.4% with an RSD of 5.88% and a sampling rate of 14.4 ml/min with a 7.79% RSD. Cis-1,3-dichloropropene had a DE of 101% (RSD 6.22%) and a sampling rate of 13.6 ml/min with a 9.09% RSD. Trans-1,3-dichloropropene should be analyzed as soon as possible due to poor recovery when stored. Cis-1,3-dichloropropene showed good stability when stored for two weeks at ambient and freezer temperatures. 575-002 diffusive samplers can be used for measuring exposures of 1,3-dichloropropene (cis and trans) from 15 minutes to 8 hours at 2 ppm.

References

1. *Merck Index,* 13th Edition, p. 541

Table 1

Desorption Efficiency
trans-1,3-Dichloropropene

PEL	Spiked µg	Recovered µg	Recovery %
0.05	2.66	2.61	98.1
		2.25	84.7
		2.43	91.3
0.10	5.62	5.51	96.7
		5.57	97.7
		5.52	96.9
		6.19	109
0.50	16.0	17.1	107
		17.1	107
		15.7	98.2
		32.4	97.7
1.0	33.1	32.0	96.6
		31.9	96.2
		33.0	99.4
		55.3	102
		56.2	104
2.0	54.0	56.6	105
		54.7	101
		Mean	99.4
		Std. Dev.	0.0584
		RSD	5.88

Table 2

Desorption Efficiency
cis-1,3-Dichloropropene

PEL	Spiked µg	Recovered µg	Recovery %
0.05	2.91	2.65	91.0
		2.61	89.6
0.10	5.40	5.97	111
		5.88	109
		5.65	105
0.50	16.3	17.6	108
		17.3	106
		15.3	96.9
		33.5	98.5
1.0	34.0	33.0	97.0
		32.2	94.7
		33.2	97.6
		56.3	102
2.0	55.1	57.6	105
		57.9	105
		56.6	103
		Mean	101
		Std. Dev.	0.0629
		RSD	6.22

Table 3

Sampling Rate
2 ppm trans-1,3-Dichloropropene, 60% RH, and 25°C

Time (Hrs)	Sampling Rate (ml/min)
0.25	15.6
	16.0
	16.0
	13.7
	13.7
	13.3
	13.1
	14.1
0.50	15.2
	15.7
	13.2
	14.2
	13.5
	13.7
	13.3
1.00	14.5
	12.4
	13.3
	13.5
	14.5
	13.0
	12.9
2.00	13.9
	13.1
	13.3
	15.8
	13.5
	15.7
	14.9
4.00	15.0
	15.7
	15.4
6.00	14.9
	14.1
	15.3
8.00	15.6
	16.3
	15.8
Mean	14.4 ml/min
Std. Dev.	1.12
RSD	7.79%

Table 4

Sampling Rate
2 ppm cis-1,3-Dichloropropene, 60% RH, and 25°C

Time (Hrs)	Sampling Rate (ml/min)
0.25	12.4
	12.7
	13.0
	13.1
0.50	12.6
	12.5
	12.9
	13.0
	12.1
	12.4
1.00	12.5
	13.6
	12.4
	12.3
	12.5
	13.2
2.00	12.6
	13.9
	13.1
	13.5
	13.2
	13.2
	15.2
4.00	15.3
	15.9
	15.5
6.00	15.1
	14.3
	15.4
8.00	15.5
	15.6
Mean	13.6 ml/min
Std. Dev.	1.23
RSD	9.09%

Table 5

Storage Study
trans-1,3-Dichloropropene

Week	% Recovery Ambient	% Recovery Freezer (-22 C)
1	87.0	98.6
2	84.2	86.8

Table 6

Storage Study
cis-1,3-Dichloropropene

Week	% Recovery Ambient	% Recovery Freezer (-22 C)
1	102	105
2	92.2	96.5

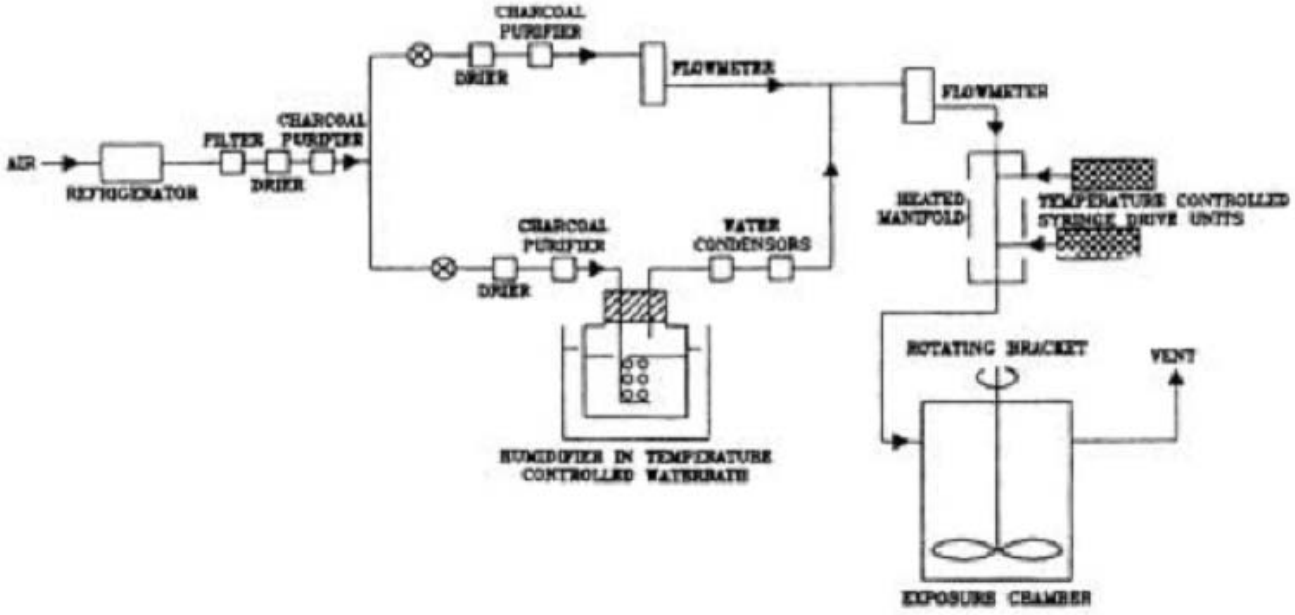

Figure 1. Test System

Appendix A

Atmosphere Generation Apparatus

The instrument is designed to expose a known concentration of a chemical hazard to a passive sampler under controlled conditions of: 1. Concentration, 2. Temperature, 3. Humidity, 4. Wind Velocity Effect, and 5. 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 at a known flow and selectable humidity.
3. An injection system composed of a precision motor driven syringe from 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. The chamber concentration can be actively verified by using solid sorbent tube sampling or gas analysis of the gas phase. The particular verification method used will depend on the analyte of interest. Means are also included to check the relative humidity.

Figure 2

Sample Chromatogram
1,3-Dichloropropene

Sample Chromatogram

Instrument: HP 5890 Gas Chromatograph

Column: 60 x 0.32mm, 1.0 micron film, Stabilwax

Temperatures:

Column: 80 c, hold for 1 minute, ramp up to 140 C at 10 C/min; hold for 1 minute

Injector: 220 C

FID Detector: 250 C

Retention times:

Cis-1,3-dichloropropene	5.2 minutes
Trans-1,3-dichloropropene	5.9 minutes