Validation of Crotonaldehyde

Using UME^{x} 100 Diffusive Samplers

Validation of Crotonaldehyde Using UME^{x} 100 Diffusive Samplers

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Abstract

A partial validation was performed using UME^{x} 100 diffusive samplers to determine the accuracy of the sampler when sampling crotonaldehyde in workplace air. A desorption efficiency (DE) study was conducted at 0.05, 0.10, 0.5, 1.0, and 2.0 times the in-house limit of 1 ppm for an 8-hour period. The average DE was 104% with a relative standard deviation (RSD) of 5.4%. The uptake rate (sampling rate) was determined for samplers exposed to a crotonaldehyde level of 4.5 ppm and at 80% relative humidity (RH) and 25 C. The mean sampling rate for 40 tests was 9.71 ml/min with an RSD of 9.0%. Samplers can be stored in a freezer (4 C) up to three weeks with less than a 5% loss in recovery.

Introduction

Crotonaldehyde is also known as crotonal, crotonic aldehydes, and b-methacrolein. It is a colorless to straw-color liquid with an irritating, pungent, and suffocating odor. Crotonaldehyde is flammable, highly reactive, and an irritant.[1,2] It occurs in a variety of foods such as soybean oils and is sometimes used as a warning agent in fuel gases and for locating breaks and leaks in pipes.[2] The main application for crotonaldehyde is as a precursor to fine chemicals. Sorbic acid, a food preservative, and trimethylhydroquinone, a precursor to vitamin E, are prepared from crotonaldehyde.[1]

Experimental

Reagents and Equipment

Crotonaldehyde (Aldrich, St Louis, MO, U.S.) was used to prepare concentrations in the test rig (Figure 1). A standard atmosphere of 4.5 ppm at 80% RH (25 C) was used for the validation. The concentration within the atmospheric chamber was verified with sorbent tubes containing silica gel coated with 2,4-dinitrophenylhydrazine (2,4-DNPH) (Cat. No. 226-119, SKC Inc., Eighty Four, PA U.S.). SKC UME^{x} 100 diffusive samplers (Cat. No. 500-100, SKC Inc., Eighty Four, PA U.S.) were used for the study. Each contained tape impregnated with 2,4-DNPH. The UME^{x} 100 samplers featured a sampling compartment and a blank compartment. A 2 x 2-cm piece of the coated filter paper was placed in each compartment. One piece was used for sampling, the other as a blank/correction for the sample. After exposure, the samplers were sealed until analysis. Each sampler was disassembled and the two pieces of tape placed in individual glass vials that were subsequently capped. The contents of each vial was desorbed with 3 ml of acetonitrile (Fisher Scientific, Fair Lawn, NJ, U.S.) and shaken for 20 minutes on a sample vibrator.

The samples were analyzed for crotonaldehyde by high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection at 365 nm (Appendix).

Calibration and Calculations

Certified crotonaldehyde-DNPH stock solutions (AccuStandard, New Haven, CT, U.S.) were used to prepare the calibration curve. A range of standards was prepared in 3 ml of acetonitrile to cover the expected target levels of crotonaldehyde. The following formula was used to calculate from micrograms (µg) of crotonaldehyde-DNPH to micrograms of crotonaldehyde:

µg crotonaldehyde-DNPH x 0.280 = µg crotonaldehyde

where 0.280 is the ratio of the molecular weight of crotonaldehyde to crotonaldehyde-DNPH.

Testing Procedures

The desorption efficiency study was conducted by preparing liquid solutions and spiking the samplers at levels based on approximate 8-hour exposures to 0.05, 0.10, 0.5, 1.0, and 2.0 times the in-house limit of 1 ppm. A dynamic atmosphere was generated using a syringe pump with crotonaldehyde and a filtered airstream to generate the concentration at a known humidity. Several sorbent tubes containing 2,4-DNPH-coated silica gel (Cat. No. 226-119, SKC Inc, Eighty Four, PA U.S.) were used to verify the concentration level during the atmospheric chamber run. The flow rate through each tube was set at 50 ml/min and the time varied depending on the concentration. Each tube was capped and placed in a freezer at 4 C until analysis. The calculated uptake rate for the samples of crotonaldehyde was verified at a concentration of 4.5 ppm and at a relative humidity of 80% (25 C). Four samplers were exposed simultaneously to the test concentration for each exposure period. The exposure periods consisted of 15 and 30 minutes and 1, 2, 4, 6, and 8 hours. After the exposure, the samplers were taken out of the chamber, sealed, and stored in a freezer at 4 C until analysis. The storage study was performed by exposing 16 samplers simultaneously to the test concentration. After the samplers were removed from the test chamber, four were analyzed that day and the remaining samplers were stored in a freezer (4 C) for up to three weeks. Four samplers were analyzed each week and the results were compared to the initial week.

Results and Discussion

The desorption efficiency results for crotonaldehyde with the diffusive samplers are shown in Table 1. The mean recovery of the diffusive samplers was 104% (RSD 5.4%). The sampling rate data is shown in Table 2. The results of the 40 samples show that crotonaldehyde can be sampled with UME^{x} 100 diffusive samplers at an average sampling rate of 9.71 ml/min (RSD 9.0%). The data indicates that the sampler can collect a 15-minute sample at 4.5 ppm of crotonaldehyde. The three-week storage study

(Table 3) indicates that the samplers can be stored for three weeks in a freezer (4 C) with less than a 5% loss in recovery.

Conclusion

UME^{x} 100 diffusive samplers have been partially validated for sampling crotonaldehyde with a mean sampling rate of 9.71 ml/min (RSD 9.0%). UME^{x} 100 diffusive samplers can be used for measuring exposures to crotonaldehyde for 15-minutes up to 8-hours. The samplers showed good stability when stored for three weeks in a freezer at 4 C.

References

[1] Schulz, R. P., Blumenstein, J., Kohlpaintner, C., "Crotonaldehyde and Crotonic Acid," *Ullmann's Encyclopedia of Chemical Technology*, Wiley-VEH, Weinheim, 2005

[2] *Merck Index*, 12th Edition, p. 2663

Table 1. Desorption Efficiency for Crotonaldehyde
Using UME^{x} 100 Diffusive Samplers

Mass Spiked (µg)	Recovery (%)
2.0	98.6
	95.4
	98.7
	106.5
4.3	96.2
	64.9
	102.7
	100.9
15.8	111.9
	111.7
	112.9
	113.3
24.1	102.4
	102.7
	101.9
	101.9
29.2	104.3
	105.5
	105.0
	105.7
Mean Recovery (± RSD)	104 (± 5.4 %)

Table 2. Sampling Rate and Capacity Study for Crotonaldehyde
Using UME^{x} 100 Diffusive Samplers

Time (hr)	Sample (µg)	Sampling Rate (ml/min)
0.25	1.85	8.87
0.25	2.16	10.34
0.25	1.98	9.48
0.50	4.13	9.89
0.50	3.50	8.38
0.50	4.43	10.60
0.50	4.62	11.07
0.50	4.30	10.30
1.0	8.39	10.05
1.0	8.41	10.07
1.0	8.99	10.77
1.0	9.49	11.36
2.0	13.39	9.43
2.0	13.63	9.60
2.0	14.71	10.36
2.0	13.14	9.26
4.0	31.73	9.50
4.0	29.79	8.92
4.0	33.18	9.93
4.0	25.06	7.50
4.0	31.56	9.45
4.0	28.81	8.62
4.0	26.47	7.92
4.0	28.28	8.47
4.0	32.45	9.72
4.0	33.27	9.96
4.0	28.44	8.52
4.0	33.08	9.90
4.0	33.45	10.02
4.0	34.58	10.35
4.0	33.43	10.01
4.0	34.12	10.22
6.0	37.43	8.79
6.0	44.68	10.49
8.0	55.00	9.68
8.0	58.52	10.31
8.0	56.04	9.87
8.0	63.01	11.10
	Mean Sampling Rate (± RSD)	9.71 (± 9.0 %)

Table 3. Storage Study for Crotonaldehyde
Using UME^{x} 100 Diffusive Samplers

Week	Recovery (%)
1	95
2	100
3	100

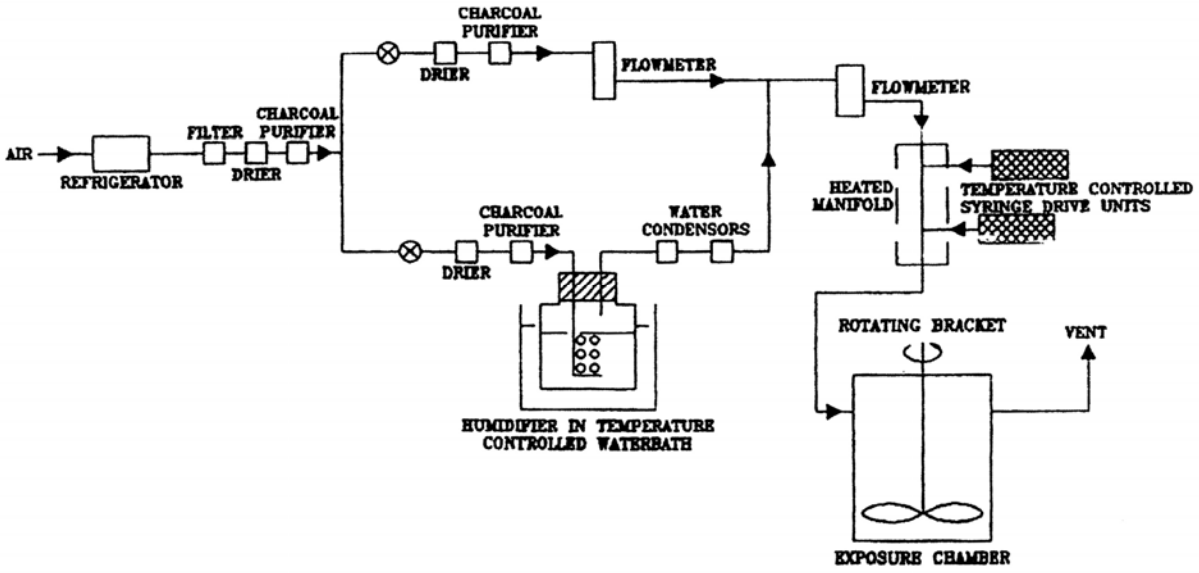

Figure 1. Test System

Appendix

Crotonaldehyde HPLC Conditions

Waters HPLC

Column:	BetaBasic-18 250 mm x 4.6 mm
Detector:	Chromteck 500 UV, 365 nm
Injection Volume:	20 µl
Eluent:	85/15 Methanol/DIUF Water