Full Validation of

Ammonia Using

SKC UME^{x} 300 Passive Sampler Cat. No. 500-300

Research Report

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Abstract

A full validation was performed using the UME^{x} 300 Passive Sampler (SKC, Inc., Eighty Four, PA, U.S.A., Cat. No. 500-300) from 0.1 to 100 ppm, 20 to 80% relative humidity (RH), and 22 to 40 C. The mean sampling rate for 182 tests was 39.92 ml/min with a relative standard deviation (RSD) of 11.4%. The average desorption efficiency was determined to be 99.4% with an RSD of 6.0%. A reverse diffusion study conducted at 25 ppm indicated no losses of ammonia. Samplers can be stored at both freezer (< 4 C) and ambient (22 C) temperatures with less than 12% loss in recovery after three weeks of storage.

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Introduction

Ammonia is a colorless corrosive gas with a pungent odor and has alkaline properties.[1] Ammonia is one of the most commonly produced industrial chemicals in the United States and is most commonly used as fertilizer, followed by household cleaners and fermentation.[2],[3] Minor uses and some new emerging uses are refrigeration, remediation, fuels, and the manufacture of plastics, explosives, pesticides, textiles, dyes, and other chemicals.[2] The most common route of exposure is inhalation of gas vapors but may also occur through skin contact.[1] Symptoms of overexposure include eye, nose, and throat irritation; dyspnea, bronchospasm, and chest pain; skin burns; and vesiculation.[1] In water, ammonia forms a strong alkaline solution that is especially irritating to the upper respiratory system. There is a strong odor at 50 ppm although there is no agreement on the odor threshold for ammonia. Eyes, nose, and throat are irritated at 50 ppm.[4]

Experimental

Reagents and Equipment

Certified cylinders ranging from 200 to 4000 ppm (Air Liquide Specialty Gases, Plumsteadville, PA, U.S.A.) were used to generate test concentrations in the atmospheric chamber. Standard atmospheres were created at different concentration levels, different temperature levels, and different relative humidities. The concentration within the test chamber was verified with a sorbent tube (SKC, Inc., Eighty Four, PA, U.S.A., Cat. No. 226-29) and with an ammonia detector tube (Dräger, Pittsburgh, PA, U.S.A., P/N 67-33-231, CH20501, and 81-01-941). The UME^{x} 300 passive sampler was placed in the test atmosphere under various test conditions. Each sampler had two compartments, each containing a 2 x 2-cm tape impregnated with sulfuric acid (H_2SO_4) to provide a sample and a blank/correction reference. After exposure, the samplers were sealed until analysis. Each sampler was disassembled and the two pieces of tape were placed in individual glass vials that were subsequently capped.

Analytical Conditions

The contents of each vial were desorbed with 3 ml of de-ionized ultra-filtered (DIUF) water. Shake the vial by hand and then let stand for 60 minutes without shaking. Excessive shaking causes the filter to break apart in the vial. After the extraction period, a portion of the sample was transferred to the auto sampler vials and analyzed for ammonium by ion chromatography (IC) with a Shimadzu CDD-10A VP Conductivity Detector, a Dionex 3 x 250-mm CS16 column, and a Dionex CSRS 300 2-mm Suppressor. The Cat. No. 226-29 sorbent tubes were desorbed in 3 ml of de-ionized ultra-filtered water, extracted on a sample vibrator for one hour, and analyzed under the same IC conditions as the UME^{x} 300 samplers.

Calibration and Calculations

Certified ammonia stock solutions (AccuStandard, New Haven, CT, U.S.A., P/N IC-NH4-100X-5 and IC-NH4-10X-5) were used to prepare the low and mid-level calibration curve. Higher

levels of the curve were made with ammonium chloride (Aldrich, St Louis, MO, U.S.A., P/N 326372-500G). The standards were prepared in 3 ml of DIUF water and analyzed under the same conditions as used with the UME^{x} 300 samplers. Ammonia standards were prepared to cover the expected target levels. The conversion factor required to calculate the micrograms of ammonia from micrograms of the ammonium is 0.944.

µg Ammonia = µg ammonium x 0.944

Note: *The ammonium curve is not linear. The standards were graphed using the Microsoft® Excel Scatter Chart. Other graphing programs can be used to plot the data.*

Testing Procedures

The desorption efficiency study was conducted by spiking at levels of 0.05, 0.1, 0.5, 1.0, and 2.0 times the PEL of 50 ppm for an eight-hour sample. Before placing samplers in the atmospheric chamber containing a known concentration of ammonia, the concentration level was tested with an ammonia detector tube (Dräger, Pittsburgh, PA, U.S.A., P/N 67-33-231, CH20501, and 81-01-941) to ensure proximity to the target level. The Cat. No. 226-29 sorbent tubes were used throughout the study along with the Dräger tubes to verify the concentration level of the atmospheric chamber.

The calculated uptake rate for the samples of ammonia was verified at the concentration range of 0.1 to 100 ppm, relative humidities ranging from 20 to 80%, and temperatures from 22 to 40 C. Four samplers at each time period were exposed simultaneously to the test concentration for time periods ranging from 15 minutes to 24 hours. After the exposure, the samples were taken out of the chamber, sealed, and stored at freezer (< 4 C) or ambient (22 C) temperature until analysis. Several of the Cat. No. 226-29 sorbent tubes were used to verify the concentration level of the atmospheric chamber. The flow through each tube was set at 100 ml/min and each tube sample was taken for one hour for concentrations above 5 ppm and for 24 hours for concentrations below 2 ppm. After exposure, each tube was capped and stored at freezer (< 4 C) or ambient (22 C) temperature until analysis.

Results and Discussion

The desorption efficiency results for ammonia with the diffusive samplers are shown in Table 1. The mean recovery of the samplers was 99.4% (6.0% RSD). Table 2 shows that reverse diffusion does not take place with the UME^{x} 300 samplers when exposed to 25-ppm ammonia. Tables 3 through 7 show the sampling rate results of all tests at various concentrations, times, temperatures, and relative humidities. The results of testing these 182 samplers show that ammonia ranging from 0.1 to 100 ppm can be sampled with the UME^{x} 300 at an average sampling rate of 39.92 ml/min (11.4% RSD). The data from the storage study (Table 8) shows that the samplers can be stored for up to three weeks at ambient (22 C) or freezer (< 4 C) temperature with less than a 12% loss in recovery.

Conclusion

The UME^{X} 300 diffusive sampler has been validated for sampling ammonia over a concentration range of 0.1 to 100 ppm, 22 to 40 C, and 20 to 80% RH. The mean sampling rate for the sampler was 39.92 ml/min (11.4% RSD) with a 99.4% recovery (6.0% RSD). The samplers showed good stability when stored for three weeks at ambient (22 C) and freezer (< 4 C) temperatures. The UME^{X} 300 diffusive sampler can be used for occupational exposures to ammonia over a range of 0.1 to 100 ppm and for 15-minute to 24-hour sampling periods.

References

1) *Merck Index*, 12th Edition, p. 87

2) New York Department of Health*; The Facts About Ammonia (Technical Information); http://www.health.ny.gov/environmental/emergency/chemical_terrorism/ammonia_tech.htm* Retrieved 2013-08-30

3) David Brown (2013-04-18), "Anhydrous ammonia fertilizer: abundant, important, hazardous," http://www.washingtonpost.com/national/health-science/anhydrous-ammonia-fertilizer-abundant-important-hazardous/2013/04/18/c2d4c69c-a85a-11e2-a8e2-5b98cb59187f_story.html
Retrieved 2013-08-30

4) U.S. Department of Labor, *OSHA-ID188, Ammonia in Workplace Atmospheres*

Table 1. Analytical Recovery
Ammonia

Spiked (µg)	Recovered (µg)	Recovery (%)
34	33.71	99.10
	33.15	97.50
	33.89	99.70
	33.43	98.30
68	67.04	98.60
	67.8	99.70
	67.24	98.90
	68.05	100.10
340	351.07	103.30
	368.77	108.50
	345.67	101.70
	315.58	92.80
	344.8	101.40
	336.5	99.00
	335.04	98.50
680	710.29	104.50
	720.00	105.90
	713.69	105.00
	714.03	105.00
	674.59	99.20
	696.63	102.40
	667.11	98.10
	714.68	105.10
1362	1477.97	108.50
	1390.6	102.10
	1186.24	87.10
	1196.7	87.90
	1181.37	86.70
	1200.80	88.10
	Mean	**99.40%**
	Std. Dev.	**0.06**
	RSD	**6.0%**

Table 2. Reverse Diffusion
Ammonia

Exposed for 4 hours to 25 ppm Ammonia (µg)		Exposed for 4 hours to 25 ppm and 4 hours to 0.0 ppm Ammonia (µg)	
105.11		104.00	
114.81		107.51	
101.03		115.10	
Mean	**106.98 µg**	**Mean**	**108.87 µg**
Std. Dev.	**7.07**	**Std. Dev.**	**5.67**
RSD	**6.6%**	**RSD**	**5.2%**

Table 3. Sampling Rate and Capacity:
Ammonia, 20% RH

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
50	120	137.94	43.74
		144.14	45.71
		136.87	43.41
50	240	287.62	45.61
		289.28	45.87
		287.93	45.66
100	60	268.33	37.99
		274.60	38.87
		243.59	34.48
		245.38	34.74
100	120	261.61	38.60
		271.02	39.99
		240.73	35.52
		254.41	37.54
100	240	616.02	45.30
		649.42	47.76
		592.70	43.59
		Mean	**41.43 ml/min**
		Std. Dev.	**4.43**
		RSD	**10.6%**

Table 4. Sampling Rate and Capacity
Ammonia, 60% RH

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
6.8	15	2.87	40.33
		2.80	40.77
		2.62	36.91
4.3	15	1.75	38.97
		1.49	33.25
		1.67	37.15
		1.41	31.38
7.16	30	6.70	44.79
		6.61	44.17
		5.90	39.42
5	30	4.79	38.18
		4.44	35.08
		4.83	38.54
5.24	60	8.82	40.27
		8.41	38.39
		9.21	42.07
		10.42	47.55
5	120	18.20	42.50
		17.86	41.70
		18.52	43.24
5	120	16.22	40.26
		17.37	43.12
		18.65	46.29
		16.34	40.55
5	240	40.31	46.83
		40.60	47.17
		40.88	47.49
5.24	360	49.71	37.83
		49.68	37.81
		42.89	32.64
		45.20	34.39
5.24	480	66.84	38.14
		61.22	34.94
		63.00	35.95
		59.09	33.72
13.33	15	4.87	34.94
		4.92	35.33

Table 4. Sampling Rate and Capacity (Cont)

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
20.04	15	9.58	45.74
		8.83	42.17
20.04	30	17.83	42.56
		17.82	42.55
		17.08	40.77
		17.55	41.90
17.4	30	11.27	31.46
		11.91	33.23
		12.34	34.44
12.33	60	16.38	31.77
		16.31	31.64
		18.19	35.29
13.13	120	40.24	36.67
		41.88	38.16
		49.80	45.38
		38.29	34.89
17.53	240	97.36	33.22
		110.59	37.73
		102.92	35.12
17.38	360	203.67	46.72
		200.35	45.96
		203.91	46.77
		190.50	43.70
17.19	480	252.10	47.25
		272.37	42.74
106.23	15	35.87	32.32
		43.81	39.47
		38.96	35.10
		34.35	30.94
106.23	30	84.83	38.21
		94.08	42.38
		89.90	40.49
		91.18	41.07
86.26	240	544.46	37.75
		563.88	39.10
		521.08	36.13
		616.30	42.73
97.97	360	849.48	34.57
		861.45	35.06
		818.29	33.30

Table 4. Sampling Rate and Capacity (Cont)

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
99.83	467.64	1170.83	35.07
		1034.03	30.97
		1069.06	32.02
		1022.84	30.64
		Mean	**38.73 ml/min**
		Std. Dev.	**4.83**
		RSD	**12.5%**

Table 5. Sampling Rate and Capacity
Ammonia, 60% RH, 40 C

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
50	120	183.54	44.67
		184.19	44.07
50	240	348.81	41.73
		481.45	45.63
		380.73	45.54
50	240	335.43	39.84
		363.18	43.13
		360.86	42.86
		314.34	37.33
		Mean	**42.75 ml/min**
		Std. Dev.	**2.75**
		RSD	**6.4%**

Table 6. Sampling Rate and Capacity
Ammonia, 80% RH

Level (ppm)	Time (min)	Collected (μg)	Sampling Rate (ml/min)
36.61	120	93.34	30.50
		133.72	43.70
		104.10	34.02
31	120	91.19	35.18
		102.30	39.47
		100.91	38.94
		94.10	36.31
31	240	196.86	37.98
		218.31	42.12
		197.78	38.16
		205.07	39.56
		Mean	**37.81 ml/min**
		Std. Dev.	**3.078**
		RSD	**9.8%**

Table 7. Sampling Rate and Capacity
Ammonia, 80% RH, 24-hour Exposure

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
2	1440	106.74	41.13
		106.25	41.93
		107.50	43.38
0.1	1440	4.19	42.14
		3.18	32.00
		3.98	40.08
		4.36	43.87
		Mean	**40.65 ml/min**
		Std. Dev.	**4.02**
		RSD	**9.8%**

Table 8. Storage Study
Ammonia, 340 µg spike

Week	Recovery (%)	
	< 4 C	**22 C**
0	100.0	100.0
1	97	100
2	91	91
3	88	90

Appendix A

Ammonia IC Conditions

Column: Dionex IonPac Analytical 3 x 250 mm, CS16

Run Time: 10.0 minutes

Detector: Shimadzu CDD-10A VP Conductivity Detector

Suppressor: Dionex CSRS 300, 3 mm, P/N 064557

Injector Volume: 25 µl