Validation of

Nitrogen Dioxide Using

SKC UME^{X} 200 Passive Sampler Cat. No. 500-200

Research Report

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Abstract

A validation was performed using the UME^{x} 200 Passive Sampler (SKC, Inc., Eighty Four, PA, U.S.A., Cat. No. 500-200) to extend the validation range to include the new ACGIH-TLV of 0.2 ppm. The previous validation was done at the TLV of 3 ppm and covered a concentration range of 0.527 to 8.46 ppm at 20 to 80% relative humidity (RH). The extended uptake rate was determined at nitrogen dioxide levels ranging from 0.051 to 0.212 ppm and at 60% RH, 22 and 40 C, and sampling times from 15 minutes to 24 hours. The mean sampling rate when all data is combined from both validation studies was 17.3 ml/min with a relative standard deviation (RSD) of 11.5%. The average desorption efficiency was determined to be 97.4% with an RSD of 10.7%. A reverse diffusion study conducted at 2.37 ppm indicated no losses of nitrogen dioxide. A long term, 2-week, sampling and reverse diffusion study was conducted at 0.50 ppm exhibiting samplers can sample for up to 2 weeks with no significant losses. Samplers can be stored at both freezer and ambient temperatures with less than 5% loss in recovery after 3 weeks of storage. This study demonstrates the sampler can be used for occupational exposures from 15 minutes to 8 hours and indoor and ambient air environments for up to 24 hours.

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Introduction

Nitrogen dioxide (CAS No. 10102-44-0) is a reddish-brown or dark orange gas and usually co-exists with nitric oxide in industrial settings. Nitric oxide is reactive in air and produces nitrogen dioxide. Nitrogen dioxide is not flammable, however, it does support the combustion of carbon, phosphorus, and sulfur.[1,2]

Nitrogen dioxide is a major air pollutant in both indoor and outdoor air. Nitrogen oxides (NO_X) are a result of high-temperature combustion processes, such as those occurring in automobiles and in power plants, and NO_2 plays an important role in the atmospheric reactions that generate ozone. Indoor pollutants that produce substantial amounts of NO_2 include home heaters, gas stoves, welding, and tobacco smoke.[2]

Nitrogen dioxide is classified as a respiratory irritant, and the route of exposure is mainly inhalation. The lower solubility of nitrogen dioxide provides less warning and increases the potential for physiological damage when exposures occur; the symptoms of exposure may be delayed up to 12 hours. Exposure to nitrogen dioxide usually results in an increased susceptibility to respiratory infections.[3]

Nitrogen dioxide acts mainly as an irritant affecting the mucosa of the eyes, nose, throat, and respiratory tract. Extremely high-dose exposure, such as in a building fire, may result in pulmonary edema and diffuse lung injury. Continued exposure to high levels of nitrogen dioxide can contribute to the development of acute or chronic bronchitis. Low-level exposures may cause increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease, and increased risk of respiratory infections, especially in young children.[2]

Experimental

Reagents and Equipment

A 2-ppm and a 10-ppm nitrogen dioxide cylinder (Scott 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 and at 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. 226-40-02). The UME^X 200 sampler or badge was placed in the test atmosphere under various test conditions. Each badge had 2 compartments, each containing a 2 x 2-cm tape impregnated with triethanolamine (TEA) to provide a sample and a blank reference. After exposure, the samplers were sealed until analysis. Each sampler was disassembled and the 2 pieces of tape were placed in individual glass vials that were subsequently capped.

Analytical Conditions

The contents of each vial were desorbed with 2 ml of de-ionized ultra filtered (DIUF) water and shaken for 20 minutes on a sample vibrator. After the extraction period, a portion of the sample was transferred to the auto sampler vials and analyzed for nitrite by ion chromatography (IC) with a Shimadzu CDD-10A VP Conductivity Detector (Dionex CD20 Conductivity Detector for previous validation), a Dionex 4 x 250-mm AS14A column, and a Dionex ASRS 300 4-mm Suppressor. The Cat. No. 226-40-02 sorbent tubes were desorbed in 3 ml of a 1.5% TEA solution containing 0.05% butanol, extracted on a

sample vibrator for 1 hour, and analyzed under the same IC conditions as the UME^{x} 200 samplers. Sample injections from 0.05 to 0.2 ppm were increased from 20.0 µl to 70.0 µl to promote better reproducibility and better visibility at the low end.

Calibration and Calculations

Certified nitrite stock solutions (AccuStandard, New Haven, CT, U.S.A., P/N IS-16073-10x and P/N IC-NO2-1X-1) were used to prepare the calibration curve. The standards were prepared in distilled water and analyzed under the same conditions as used with the UME^{X} 200 samplers. Nitrite standards were prepared to cover the expected target levels of nitrogen dioxide. The conversion factor to calculate the micrograms of nitrogen dioxide from micrograms of the nitrite anion is:

$$\mu g\ NO_2 = \mu g\ NO_2^-$$

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 3.0 ppm for an 8-hour exposure as well as at 0.05 ppm, 0.10 ppm, and 0.20 ppm for the extended validation. Before placing samplers in the atmospheric chamber containing a known concentration of nitrogen dioxide, the concentration level was tested with a nitrogen dioxide detector tube (Dräger, Pittsburgh, PA, U.S.A., P/N CH30001) to ensure proximity to the target level. The Cat. No. 226-40-02 sorbent tubes were used throughout the study to verify the concentration level of the atmospheric chamber.

The calculated uptake rate for the samples of nitrogen dioxide was verified at the concentration range of 0.051 to 8.46 ppm and at relative humidities ranging from 20 to 80%. Four samplers at each time period were exposed simultaneously to the test concentration for time periods consisting of 15, 30, 120, 240, 360, 480, and 1440 minutes. The time of exposure was dependent on the concentration level of nitrogen dioxide in the chamber. After the exposure, the samples were taken out of the chamber, sealed, and stored in a freezer until analysis. Several of the Cat. No. 226-40-02 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 30 minutes for concentrations of 0.527 ppm and above. At the concentration range of 0.051 to 0.212 ppm, the flow through each tube was set at 50 ml/min and each tube sample was taken for 1 hour. Each test level was characterized using a minimum of 6 tubes. After exposure each tube was capped and placed in a freezer until analysis.

The storage study was performed by exposing 28 samplers simultaneously to the test concentration. After the samplers were removed from the test chamber, 4 were analyzed that day, 12 samplers were stored at ambient temperatures, and the remaining 12 samplers were stored in a freezer (-22 C) for 3 weeks. Four samplers from each storage temperature were analyzed each week, and the results were compared to the initial week to determine the analytical recovery.

The reverse diffusion study was conducted by exposing 6 samplers in the atmospheric chamber to 2.37 ppm of nitrogen dioxide for 4 hours. Three samplers were analyzed initially, and 3 samplers were placed back in the atmospheric chamber and exposed for another 4 hours to 0 ppm NO_2 to evaluate the effects of reverse diffusion. The 2-week sampling and reverse diffusion study was performed by exposing 4 samplers to 0.50 ppm for 4 hours. Two samplers were analyzed while the other 2 samplers were hung with the slider open for 2 weeks. The samplers hung for 2 weeks were compared to the samplers initially analyzed.

Results and Discussion

The desorption efficiency results for nitrogen dioxide with the diffusive samplers are shown in Table 1. The mean recovery of the samplers was 97.4% (10.7% RSD). Table 2 shows that reverse diffusion does not take place with the UME^X 200 samplers when exposed to nitrogen dioxide. Tables 3 through 6 show the sampling rate results of all tests at various concentrations, times, and relative humidities. The results of testing these 158 samplers show that nitrogen dioxide ranging from 0.051 to 8.46 ppm can be sampled with the UME^X 200 at an average sampling rate of 17.3 ml/min (11.5% RSD). The data from the storage study (Table 7) shows that the samplers can be stored for up to 3 weeks at either ambient or freezer temperatures.

Conclusion

The UME^X 200 diffusive sampler has been validated for sampling nitrogen dioxide over a concentration range of 0.051 to 8.46 ppm, at 20 to 80% RH, and 22 and 40 C. The mean sampling rate for the sampler was 17.3 ml/min (11.5% RSD) with a 97.4% recovery (10.7% RSD). The samplers showed good stability when stored for 3 weeks at either ambient or freezer temperatures. Samplers exposed to nitrogen dioxide levels of 0.50 ppm and 2.37 ppm showed no reverse diffusion. The UME^X 200 diffusive sampler can be used for concentrations of nitrogen dioxide ranging from 0.051 to 8.464 ppm for 15 minutes up to 24 hours.

References

1) U.S. Department of Labor, *Chemical Sampling Information – Nitrogen Dioxide, http://www.osha.gov/dts/chemicalsampling/data/CH_257400.html*

2) U.S. Environmental Protection Agency, *An Introduction to Indoor Air Quality – Nitrogen Dioxide*, *http://www.epa.gov/iaq/no2.html*

3) U.S. Department of Labor, *OSHA-ID182, Nitrogen Dioxide in Workplace Atmospheres*, *http://www.osha.gov/dts/sltc/methods/inorganic/id182/id182.html*

Table 1. Analytical Recovery
Nitrogen Dioxide

Spiked (µg)	Recovered (µg)	Recovery (%)
0.710	0.778	110.0
	0.774	109.0
	0.767	108.0
1.53	1.71	112.0
	1.46	95.8
3.22	3.50	109.0
	3.26	101.0
	3.37	105.0
	3.29	102.0
2.40	2.00	83.4
	1.79	74.6
	2.12	88.5
	2.41	101.0
4.60	3.80	84.3
	3.47	75.5
	3.63	78.9
	3.97	86.2
	4.05	88.0
	4.20	91.2
24.0	24.3	101.0
	23.7	98.8
	23.6	98.3
	22.4	93.3
46.0	46.7	102.0
	45.6	99.1
	46.6	101.0
	47.3	103.0
92.0	95.1	103.0
	95.0	103.0
	98.3	107.0
	97.8	106.0
	Mean	**97.4%**
	Std. Dev.	**10.4**
	RSD	**10.7%**

Table 2. Reverse Diffusion Studies

Exposed for 4 hrs to 2.37 ppm NO_2 (µg)		Exposed for 4 hrs to 2.37 ppm and 4 hrs to 0.0 ppm NO_2 (µg)	
16.8		14.1	
11.9		15.2	
12.2		12.8	
Mean	**13.6 µg**	**Mean**	**14.0 µg**
Std. Dev.	**2.75**	**Std. Dev.**	**1.20**
RSD	**20.1%**	**RSD**	**8.56%**
Exposed for 4 hrs to 0.50 ppm NO_2 (µg)		**Exposed for 4 hrs to 0.05 ppm and 2 weeks to 0.0 ppm NO_2 (µg)**	
4.34		4.11	
4.76		4.10	
Mean	**4.55 µg**	**Mean.**	**4.10 µg**
Std. Dev.	**0.297**	**Std. Dev**	**0.00490**
RSD	**6.52%**	**RSD**	**0.119%**

Table 3. Sampling Rate and Capacity
Nitrogen Dioxide, 20% RH

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
8.46	15	3.04	13.4
		3.48	15.3
8.46	30	7.23	15.9
		6.65	14.7
		8.18	18.0
		7.09	15.6
8.46	60	13.3	14.7
		13.6	15.0
		12.2	13.4
		14.1	15.5
8.46	120	30.5	16.8
		28.4	15.6
		32.9	18.1
		28.6	15.8
8.46	240	64.1	17.7
		61.8	17.0
		61.6	17.0
		54.4	15.0
2.37	240	11.9	17.3
		9.75	14.1
		12.2	18.1
2.37	240	14.1	20.5
		15.2	22.1
		12.8	18.6
2.37	360	19.6	19.0
		20.7	20.1
		19.1	18.5
8.46	360	83.4	15.3
		92.0	16.9
		101	18.5
		77.3	14.2
2.37	420	21.7	18.1
		22.0	18.3
		23.1	19.2
8.46	437	107	16.2
		108	16.3
		109	16.4
		118	17.8
		Mean	**16.8 ml/min**
		Std. Dev.	**1.99**
		RSD	**11.9%**

Table 4. Sampling Rate and Capacity
Nitrogen Dioxide, 60% RH

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
3.84	15	1.54	15.0
		1.62	15.8
		1.68	16.4
		1.50	14.6
3.84	30	2.79	13.6
		3.45	16.8
		3.35	16.3
		3.44	16.7
0.836	60	1.51	16.8
		1.62	18.1
		1.40	15.6
		1.68	18.7
3.84	60	6.29	15.3
		6.11	14.8
		6.75	16.4
		6.52	15.9
0.836	120	3.58	19.9
		2.70	15.1
		3.16	17.6
		3.34	18.6
3.84	120	14.5	17.6
		13.0	15.8
		13.4	16.3
		14.0	17.0
0.836	240	7.58	21.1
		6.54	18.2
		6.29	17.5
3.84	240	28.4	17.3
		29.2	17.8
		26.1	15.9
		27.2	16.6
0.133	240	0.976	16.3
		0.859	14.4
0.836	360	9.03	16.8
		10.3	19.2
		10.6	19.8
		11.0	20.3
3.84	360	39.8	16.1
		37.7	15.7
		42.5	17.2
0.171	360	2.24	19.3
		2.14	18.5
		1.91	16.5
		1.88	16.2

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
0.136	396	2.13	21.0
		1.90	18.7
		1.82	18.0
		1.94	19.1
0.051	420	0.666	16.6
		0.550	13.7
		0.649	16.2
		0.605	15.1
0.064	420	0.752	14.8
		0.752	14.8
		0.754	14.8
		0.869	17.1
0.136	450	1.79	15.5
		1.56	13.5
		1.89	16.3
		1.75	15.1
0.836	453	13.6	20.0
		14.6	21.5
		12.1	17.8
		16.3	24.1
3.84	480	50.7	15.4
		55.9	17.0
		52.4	15.9
		47.7	14.5
0.076	480	1.33	19.2
		1.25	18.1
		1.27	18.4
		1.22	17.7
0.212	480	2.76	14.4
		2.87	15.0
		3.15	16.5
		2.76	14.4
0.200	1440	8.66	16.0
		8.20	15.1
		8.54	15.8
		8.58	15.8
0.500	1440	15.1	18.3
		15.3	18.4
		14.7	17.7
		14.9	18.0
		Mean	**16.9 ml/min**
		Std. Dev.	**1.96**
		RSD	**11.6%**

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

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
0.200	390	3.01	20.5
		2.82	19.2
		2.74	18.7
		Mean	**19.5 ml/min**
		Std. Dev.	**0.924**
		RSD	**4.74%**

Table 6. Sampling Rate and Capacity
Nitrogen Dioxide, 80% RH

Level (ppm)	Time (min)	Collected (µg)	Sampling Rate (ml/min)
0.527	60	1.24	21.9
		1.04	18.4
1.89	60	3.19	15.8
		3.76	18.6
		3.44	17.1
		3.65	18.1
0.527	120	2.23	19.7
		2.09	18.5
		2.28	20.2
1.89	120	8.03	19.9
		6.85	17.0
		7.26	18.0
		6.91	17.1
0.527	240	4.09	18.1
		4.82	21.3
		3.66	16.2
1.89	240	14.8	18.4
		16.5	20.4
		15.2	18.9
		13.7	17.0
0.527	360	6.41	18.9
		6.26	18.4
		5.00	17.1
1.89	360	23.4	19.4
		24.5	20.2
		24.4	20.1
0.527	469	8.79	19.9
		7.60	17.2
		7.47	16.9
1.89	480	29.6	18.3
		30.6	19.0
		28.5	17.7
		30.9	19.1
		Mean	**18.6 ml/min**
		Std. Dev.	**1.45**
		RSD	**7.80%**

Table 7. Storage Study
Nitrogen Dioxide, 46 µg spike

Week	Recovery (%)	
	< 4 C	25 C
0	100.0	100.0
1	94.6	95.5
2	103.0	99.3
3	102.0	104.0

Appendix A

Nitrogen Dioxide IC Conditions

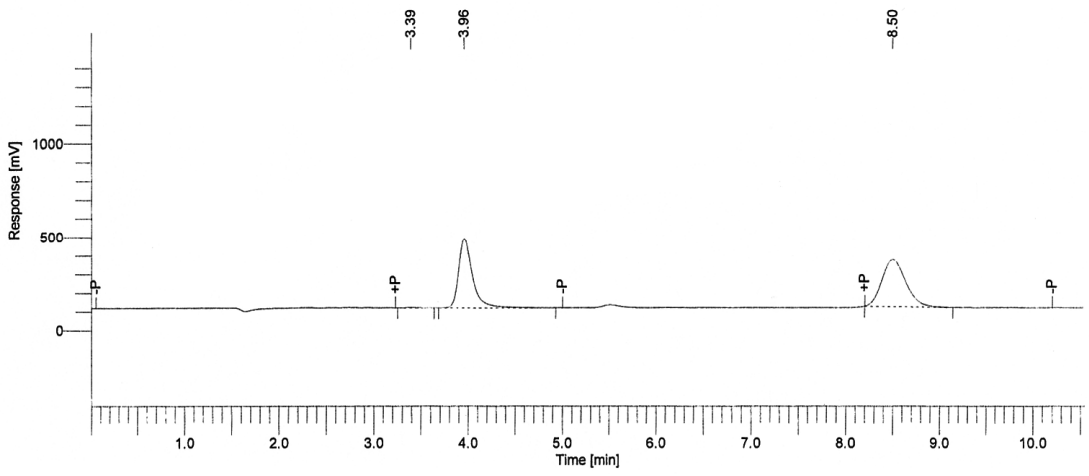
Column: Dionex IonPac Analytical 4 x 250 mm, AS14A

Run Time: 10.55 minutes

Detector: Dionex CD20 Conductivity Detector

Suppressor: Dionex ASRS 300 4 mm, P/N 064554

Injector Volume: 20 µl



Appendix B

Nitrogen Dioxide IC Conditions

Column:
Nitrite: Dionex IonPac Analytical
Sulfate: 4 x 250 mm, AS14A

Run Time: 15.5 minutes

Detector: Shimadzu CDD-10A VP Conductivity Detector

Suppressor: Dionex ASRS 300 4 mm, P/N 064554

Injector Volume: 70 µl