A Single (Three-section) Sorbent Tube for Sampling Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) in Air

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Abstract

SKC sorbent tube Cat. No. 226-182 was validated for sampling nitric oxide (NO). The test concentrations ranged from 1.0 to 44 ppm at 60 to 80% relative humidity and at a temperature range of 20 to 25 C. The samples were collected at a flow rate of 100 ml/min for 1.7 to 4 hours. The SKC oxidizer sorbent oxidizes NO to nitrogen dioxide (NO_2), which is collected on a triethanolamine (TEA)-treated molecular sieve and converted to nitrite ion. Because the conversion of NO_2 to nitrite ion is concentration dependent, conventional methods for calculating micrograms and ppm are not appropriate. The data plotted from 1.0 to 12.5 ppm is calculated using a correction factor of 0.601 with a percent relative standard deviation of 12.6. The data plotted from 12.5 to 44 ppm is calculated using a linear curve that produces a correlation coefficient of 0.998. The data indicates that NO can be sampled reliably with this method.

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Introduction

Methods for sampling both nitric oxide (NO) and nitrogen dioxide (NO_2) specify a sampling train that includes an oxidizer sorbent tube to convert NO to NO_2 for collection on a TEA-treated molecular sieve and subsequent analysis. NO_2 has been validated in OSHA Method ID-182 and was not a part of this validation.[1] Validated methods for NO used SKC sorbent tube 226-40A and have been described in OSHA ID-190 and in NIOSH 6014[2, 3] and in an SKC Inc. research report.[4] In late 2017, the oxidizer tube described in these previous methods was discontinued by the vendor. This study was conducted to validate a new SKC oxidizer sorbent contained in SKC sorbent tube Cat. No. 226-182 for NO and NO_2, which contains a 400 mg TEA-treated molecular sieve, 400 mg of SKC oxidizer, and a 600 mg TEA-treated molecular sieve in a single tube (*Figure 1*).

Experimental

Two certified NO cylinders, one 25.5 ppm and one 110 ppm (Airgas, Radnor, PA), were blended with clean air to generate different test concentrations at different levels of relative humidity. The 226-182 tube samples were collected at 100 ml/min using calibrated pumps for 1.7 to 4 hours. The concentrations generated from the certified cylinder were verified with SKC Cat. No. 810-10 Gastec detector tubes (SKC Inc., Eighty Four, PA).

Analytical/Calibration

The contents of each TEA-treated tube were desorbed in 10 ml of 1.5% TEA in a water solution containing 0.05% n-butanol. Each vial was shaken by hand for 1 to 2 minutes and then set for 60 minutes prior to analysis. The sorbent tubes were analyzed for nitrite ion using a Dionex Aquion IC System equipped with the following: DRS 600 Regenerative Suppressor, Dionex NG1 Guard Column, and AS14A 4 x 250 mm Ion Pac column.

Certified nitrite ion stock solutions (AccuStandard, New Haven, CT) were used to prepare the calibration curves. The standards were prepared in distilled deionized water and analyzed under the same conditions as the tube extracts.

Calculations

At levels from 12.5 to 44 ppm NO in the air, divide the micrograms (µg) of nitrite ion by the air volume in liters; enter that value into the following equation:

$$y = 0.439x + 8.7568$$

where y = µg of nitrite ion/liters of air

and x = ppm of NO

At levels from 1 to 12.5 ppm NO in the air, a conversion factor of 0.601 can be used as discussed below.

1 µg NO_2 gas = 0.601 µg of nitrite ion

or conversely

1 µg of nitrite anion = 1.664 µg NO_2 gas

To calculate ppm of NO over a range of 1 to 12.5 ppm, use the following equation:

$$\text{ppm NO} = \frac{(\text{MV}) \times (\mu\text{g/ml nitrite ion}) \times (\text{solution volume in ml}) \times \text{Conversion} \times \text{GF}}{(\text{Formula Weight}) \times (\text{Air Volume in liters})}$$

Where:

MV = molar volume	=	24.45 (25 C and 760 mmHg)
µg/ml nitrite ion	=	Blank correct sample result
Conversion (NO_2 gas/nitrite anion)	=	1.664
GF (Gravimetric factor NO/NO_2)	=	0.6522
Formula Weight (NO)	=	30.01

Results and Discussion

Tables 1 and 2 show the data collected at six concentrations (1.0 to 44 ppm NO) and at relative humidity levels ranging from 60 to 80% (20 to 25 C). The flow rate for this study was set at 100 ml/min; sample volumes ranged from 10 to 24 liters. The 100 ml/min flow rate was chosen because data generated at 25 ml/min, as described in OSHA ID-190, did not produce consistent data. For each group of data, the mean µg of nitrite ion/air volume (liters) was calculated.

The data from Table 1 (1.0 to 12.5 ppm) was calculated using a correction factor with the formula above. Correction factors were originally used in OSHA ID-190 and NIOSH 6014 for NO. It was shown that from 1.0 to 12.5 ppm NO, the correction factors averaged 0.601 with a relative standard deviation of 12.6%. In discussions with labs that use this method, it was stated that most data calculated over the years has been at levels less than 10 ppm. Therefore, correction factors can be used to calculate levels up to 12.5 ppm. For levels greater than 12.5 ppm, it is recommended that the linear curve calculation be used.

Table 2 shows data collected at 12.5 to 44 ppm of NO. The correction factors were not consistent over this range. However, when this data was plotted, it did show a linear response with a correlation coefficient of 0.998 (*Figure 2*).

For calculating levels of NO_2, correction factors outlined in OSHA-ID 190 and NIOSH 6014 can be used.

Conclusions

SKC sorbent tube Cat. No. 226-182 has been validated for sampling NO over a concentration range of 1.0 to 44 ppm at 60 to 80% relative humidity and 20 to 25 C. The sampling rate used was 100 ml/min and sample volumes ranged from 10 to 24 liters. This new method can be used to sample for both NO and NO_2 in one sample tube.

References

1. *U.S. Department of Labor, OSHA Method ID-182, Nitrogen Dioxide in Workplace Atmospheres, www.osha.gov/dts/sltc/methods/inorganic/id182/id182.pdf*
2. *U.S. Department of Labor, OSHA Method ID-190, Nitric Oxide in Workplace Atmospheres, www.osha.gov/dts/sltc/methods/inorganic/id190/id190.html*
3. *Centers for Disease Control, NIOSH Method 6014, Nitric Oxide and Nitrogen Dioxide, www.cdc.gov/niosh/docs/2003-154/pdfs/6014-1.pdf*
4. *Elder, J. and Coyne, L., A New Oxidizer Tube for Sampling Nitric Oxide and Nitrogen Dioxide in Air, SKC Inc., June 2019, https://www.skcinc.com/media/documents/1985.pdf*

Figure 1. Sorbent Tube 226-182

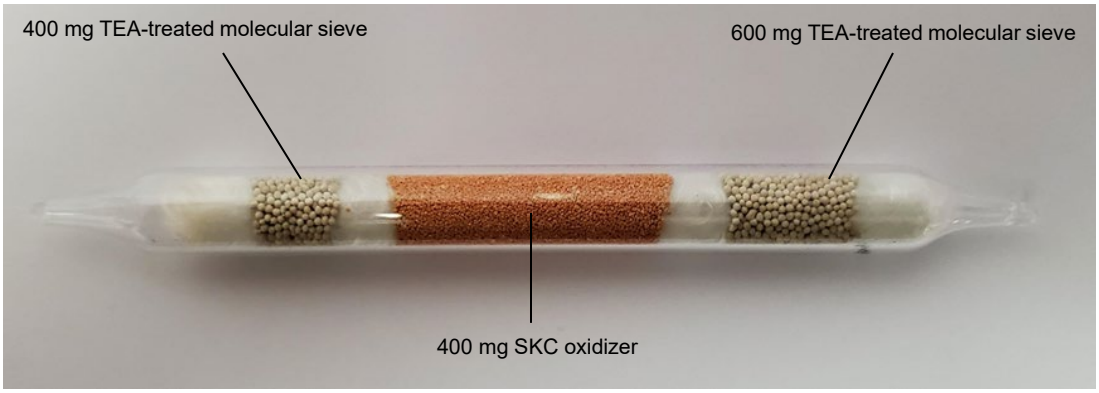

Table 1. Validation Data for NO Using SKC Cat. No. 226-182
1.0 to 12.5 ppm NO

Test Level (ppm)	µg of Nitrite Ion/Tube	% Relative Humidity	Air Volume (liters)	µg of Nitrite Ion/Liters of Air
1.0	28.7	80	24	1.20
	32.1	80	24	1.34
	32.4	80	24	1.35
			Mean	**1.29**
2.0	63.7	80	24	2.65
	58.3	80	24	2.43
	59.8	80	24	2.49
			Mean	**2.53**
2.5	27.5	80	10	2.75
	24.0	80	10	2.40
	29.2	80	10	2.92
	28.1	80	10	2.81
			Mean	**2.60**
6.5	167.0	80	24	6.96
	159.7	80	24	6.65
	156.7	80	24	6.53
	98.2	80	18	5.46
	103.0	80	18	5.72
			Mean	**6.26**
12.5	262.8	80	18	14.6
	256.6	80	18	14.3
	271.9	80	18	15.1
	262.2	80	16	16.4
	225.4	80	17	13.3
			Mean	**14.5**

Table 2. Validation Data for NO Using SKC Cat. No. 226-182
12.5 to 44 ppm NO

Test Level (ppm)	µg of Nitrite Ion/Tube	% Relative Humidity	Air Volume (liters)	µg of Nitrite Ion/Liters of Air
12.5	262.3	80	18	14.6
	256.6	80	18	14.3
	271.9	80	18	15.1
	262.2	80	17	16.4
	225.4	80	17	13.3
			Mean	**14.5**
22	417.7	80	24	17.4
	400.0	80	24	16.7
	420.8	80	24	17.5
	154.7	80	10	15.5
	161.6	80	10	16.2
	386.1	80	18	21.4
	388.8	80	18	21.6
			Mean	**18.0**
33	603.6	80	24	25.2
	603.6	80	24	25.2
	545.1	80	24	22.7
	221.4	80	10	22.1
	236.8	80	10	23.7
	234.2	80	10	23.4
	231.3	80	10	23.1
	223.0	80	10	22.3
	394.8	80	18	21.9
	400.0	80	18	22.2
			Mean	**23.2**
44	736.2	60	24	30.7
	606.7	60	24	25.3
	669.2	60	24	27.9
	769.3	60	24	32.1
	666.3	60	24	27.7
	586.3	60	24	24.4
	637.0	60	24	26.5
	444.0	60	18	24.7
	533.5	60	18	29.6
	478.1	60	18	26.6
	565.3	60	18	31.4
	305.9	60	10	30.6
	297.3	60	10	29.7
	266.1	60	10	26.6
	305.3	60	10	30.5
	272.5	60	10	27.2
			Mean	**28.2**

Figure 2. Plot of Validation Data 12.5 to 44 ppm for Nitric Oxide Using SKC Cat. No. 226-182