A New Oxidizer Tube for Sampling Nitric Oxide and Nitrogen Dioxide in Air:

A Modified OSHA ID-190 and NIOSH 6014 Method Using a New Sampling Train with Different Sampling Parameters and Calculations

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Nitric Oxide

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Abstract

SKC Cat. No. 226-40A sorbent tubes were validated for sampling nitric oxide (NO). The test concentrations ranged from 1 to 44 ppm at 20 to 80% relative humidity and a temperature range of 20 to 25 C. The samples were collected at a flow rate of 100 ml/min for 30 minutes to 4 hours. The SKC oxidizer sorbent oxidizes NO to nitrogen dioxide (NO_2), which is collected on a triethanolamine (TEA)-treated molecular sieve tube 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 conversion factors for the range of 1 to 44 ppm NO did not follow exactly those listed in OSHA Method ID-190 and NIOSH Method 6014. At levels from 1 to 12.5 ppm, the average conversion factor was 0.661 with a relative standard deviation (RSD) of 11%. For levels above 12.5 ppm, the conversion factors were inconsistent and thus the logarithmic curve generated by the data from 2.5 ppm to 44 ppm NO should be used to calculate the ppm NO. The ppm NO is calculated by using the appropriate conversion factor or curve, depending on the concentration level. 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 triethanolamine (TEA)-treated molecular sieve and subsequent analysis. NO_2 has been validated in OSHA Method ID-182 and, therefore, was not part of this validation.[1] Validated methods for NO used SKC Cat. No. 226-40 and are described in OSHA Method ID-190 and NIOSH Method 6014.[2, 3] In late 2017, the oxidizer tube described in these two methods was discontinued by the vendor. This study was conducted to validate a new SKC oxidizer sorbent contained in the SKC Cat. No. 226-40A sorbent tube sampling train for NO and NO_2, which contains 400 mg of TEA-treated molecular sieve, 400 mg of SKC oxidizer, and 600 mg of TEA-treated molecular sieve (*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. Cat. No. 226-40A tubes were used to collect samples at 100 ml/min using calibrated pumps for 30 minutes 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 Shimadzu CDD-10A Conductivity Detector, a Dionex 4 x 250-mm AS14A column, and a Dionex ASRS 300 4-mm Suppressor.

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 air, divide the micrograms (µg) of nitrite ion by the air volume in liters; enter that value into the following equation and calculate the ppm NO.

$$y = 7.0361 \ln(x) - 3.6157$$

where y = µg of nitrite ion/liters of air

and x = ppm of NO

At levels from 1 to 12.5 ppm NO in air, a conversion factor of 0.661 can be used and is discussed below.

$$1\ \mu g\ NO_2 \text{ gas} = 0.661\ \mu g \text{ of nitrite anion}$$

or conversely,

$$1\ \mu g \text{ nitrite anion} = 1.513\ \mu g\ NO_2 \text{ gas}$$

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

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

Where:

MV (Molar Volume)	=	24.45 (25 C and 760 mmHg)
µg/ml nitrite anion	=	Blank corrected sample result
Conversion (NO_2 gas/nitrite anion)	=	1.513
GF (Gravimetric Factor, NO/NO_2)	=	0.6522
Formula Weight (NO)	=	30.01

Results and Discussion

The flow rate for this study was set at 100 ml/min; sample volumes ranged from 3 to 25 liters. The 100 ml/min flow rate was chosen because data generated at 25 ml/min, as described in OSHA ID-190, was inconsistent.

Tables 1 and 2 show the data collected at six concentrations from 2.5 to 44 ppm NO and at relative humidity levels ranging from 20 to 80% (20 to 25 C). For each group of data, the mean micrograms (µg) of nitrite ion/air volume (liters) were calculated and then plotted versus the NO test level concentration in ppm (*Figure 2*). The results showed a logarithmic curve with a correlation coefficient of 0.995.

Table 3 shows data collected at concentrations from 1 to 2.5 ppm NO and at relative humidity levels ranging from 20 to 80% (20 to 25 C). When calculated using the logarithmic curve shown in Figure 2, the data showed a high degree of bias relative to the actual test level.

Conversion factors were originally used in OSHA ID-190 and NIOSH 6014 for NO. The conversion factors from this study did not follow exactly the factors listed in the OSHA and NIOSH methods. However, Table 4 shows that from 1 to 12.5 ppm NO, the conversion factors averaged 0.661 with a relative standard deviation (RSD) of 11%. This is very similar to the value of 0.63 listed in the OSHA method. 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, a conversion factor can be used to calculate levels up to 12.5 ppm. For levels greater than 12.5 ppm, the conversion factors were inconsistent, with an average of 0.353 and an RSD of 21.4%. Therefore, it is recommended that the logarithmic curve shown in Figure 2 be used to calculate levels greater than 12.5 ppm.

To calculate levels of NO_2, the conversion factors in OSHA ID-182 and NIOSH 6014 should be used.

Conclusions

Cat. No. 226-40A has been validated for sampling NO over a concentration range of 1 to 44 ppm at 20 to 80% relative humidity and 20 to 25 C. The sampling rate used was 100 ml/min and sample volumes ranged from 3 to 25 liters. This new method can be used to sample both NO and NO_2 in one sampling train and, with the appropriate curves and/or conversion factors, to reliably sample NO.

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.pdf*
3. *Centers for Disease Control, NIOSH Method 6014, Nitric Oxide and Nitrogen Dioxide,* *www.cdc.gov/niosh/docs/2003-154/pdfs/6014-1.pdf*

Figure 1. SKC Cat. No. 226-40A Sampling Train for NO_2 and NO

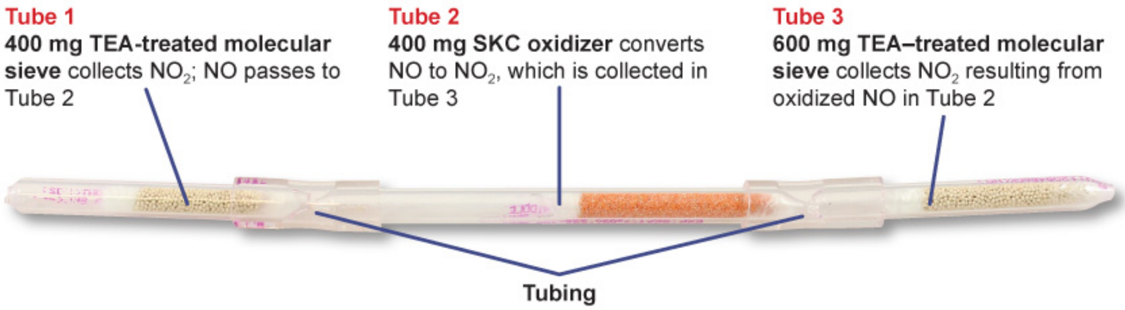

Table 1. Validation Data for NO Using SKC Cat. No. 226-40A
2.5 to 12.5 ppm NO

Test Level (ppm)	µg of Nitrite Ion/Tube	% Relative Humidity	Air Volume (liters)	µg of Nitrite Ion/Liters of Air
2.5	90.8	20	24	3.78
	92.7	20	24	3.86
	86.1	20	24	3.59
	80.3	20	24	3.34
	100.3	20	24	4.18
	76.4	20	24	3.18
	10.0	20	3.0	3.33
	9.17	60	3.0	3.06
	9.86	60	3.0	3.29
	82.6	80	24	3.44
	68.6	80	24	2.86
	77.5	80	24	3.23
	74.0	80	24	3.08
				Mean 3.40
6.5	165.7	20	19	8.72
	239.2	60	27	8.86
	242.6	60	27	8.99
	225.6	60	25	9.02
	233.0	60	26	8.96
	215.1	80	24	8.96
	204.1	80	24	8.50
	211.7	80	24	8.82
	200.0	80	24	8.33
	208.5	80	24	8.69
	250.8	80	24	10.4
				Mean 8.94
12.5	44.9	20	3.0	15
	43.0	20	3.0	14.3
	43.8	20	3.0	14.6
	208.5	80	14.0	14.9
	328.8	80	24	13.7
	339.1	80	24	14.1
	317.0	80	24	13.2
	318.5	80	24	13.3
	307.8	80	24	12.8
	313.4	80	24	13.1
	289.5	80	24	12.1
	289.8	80	24	12.1
				Mean 13.6

Table 2. Validation Data for NO Using SKC Cat. No. 226-40A
22 to 44 ppm NO

Test Level (ppm)	µg of Nitrite Ion/Tube	% Relative Humidity	Air Volume (liters)	µg of Nitrite Ion/Liters of Air
22	459.1	20	24	19.1
	432.6	20	24	18
	53.5	60	3.0	17.8
	56.8	60	3.0	18.9
	48.8	60	3.0	16.3
	51.5	60	3.0	17.2
	459.6	60	24	19.2
	459.7	60	24	19.2
	452.8	60	24	18.9
	428.4	60	24	17.8
	428.4	80	24	17.8
	374.6	80	24	15.6
	452.6	80	24	18.9
	401.4	80	24	16.7
				Mean 18.0
33	460.9	20	24	19.2
	507.2	20	24	21.1
	493.2	20	24	20.6
	517.7	20	24	21.6
	551.3	60	25	22.1
	589.3	60	25	23.6
	529.8	60	25	21.2
	503.8	60	25	20.2
				Mean 21.2
44	68.9	60	3.0	23.0
	59.1	60	3.0	19.7
	74.5	60	3.0	24.8
	595.4	60	24	24.8
	580.1	60	24	24.2
	571.3	60	24	23.8
	571.1	60	24	23.8
	572.1	60	24	23.8
				Mean 23.5

Figure 2. Plot of Validation Data for NO Using SKC Cat. No. 226-40A
2.5 to 44 ppm NO

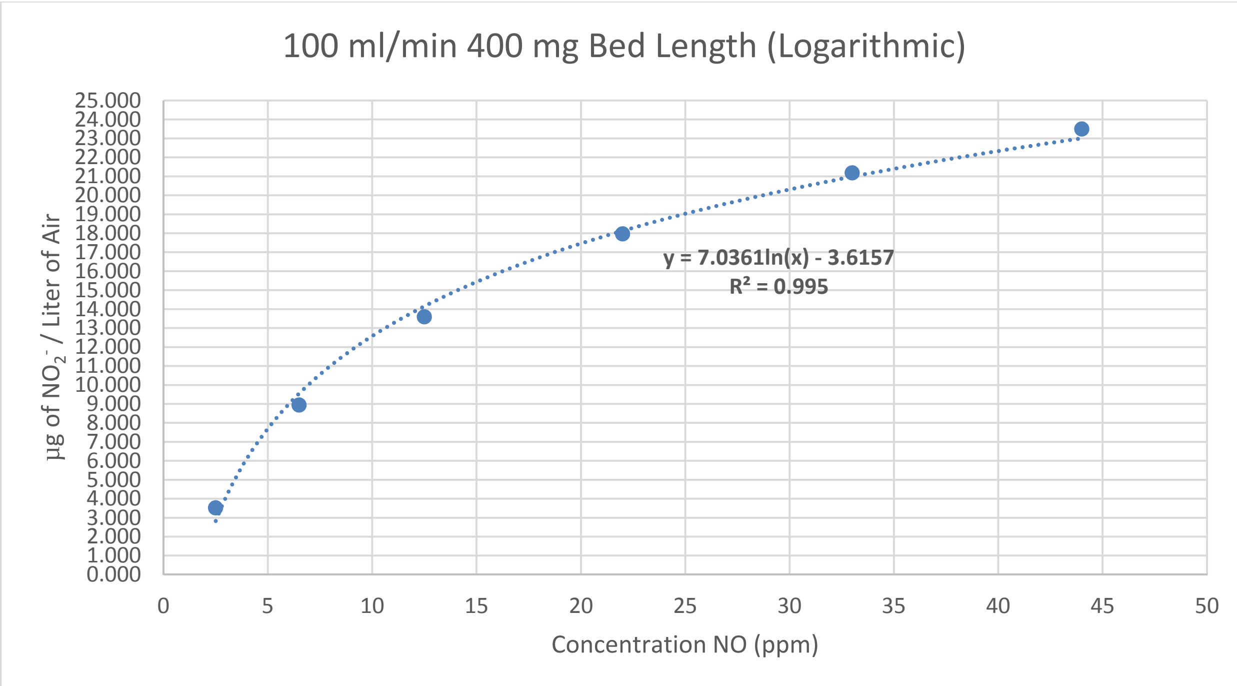

Table 3. Validation Data for NO Using SKC Cat. No. 226-40A
1 to 2.5 ppm NO

Test Level (ppm)	µg of Nitrite Ion/Tube	% Relative Humidity	Air Volume (liters)	µg of Nitrite Ion/Liters of Air
1.0	21.3	60	21	1.01
	25.4	60	21	1.21
	29.0	60	21	1.38
	22.4	60	21	1.07
	23.3	60	21	1.11
	27.8	60	21	1.32
	26.0	80	24	1.08
	26.4	80	24	1.10
				Mean 1.16
2.0	58.4	60	22	2.65
	57.7	60	22	2.62
	59.7	60	22	2.71
				Mean 2.66
2.5	9.86	80	3.0	3.29
	9.17	60	3.0	3.06
	10.0	20	3.0	3.33
	90.8	20	24	3.78
	92.7	20	24	3.86
	86.1	20	24	3.59
	80.3	20	24	3.34
	100.3	20	24	4.18
	76.4	20	24	3.18
	82.7	80	24	3.44
	68.6	80	24	2.86
	77.5	80	24	3.23
	74.0	80	24	3.08
				Mean 3.40

Table 4. Conversion Factor for Nitrite Anion from 1 µg of NO_2 Gas

Test Level (ppm)	Conversion Factor
1.0	0.623
2.0	0.708
2.5	0.730
6.5	0.730
10.0	0.620
12.5	0.554
Average	0.661*
Standard Deviation	0.073
% RSD	11.0

**The 0.661 conversion factor can also be listed as 1 µg nitrite anion = 1.513 µg NO_2*