Development of a Portable Nitric Oxide Calibration Source

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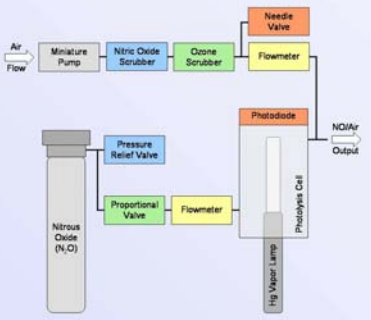


Schematic of the Nitric Oxide Calibration Source.

A new method of generating nitric oxide (NO) calibration gas has been developed for accurate field calibrations in the range of 20-1,000 ppbv. NO is produced through the photolysis of nitrous oxide (N_2O) using a low-pressure mercury vapor lamp. The vacuum UV emission lines of mercury near 185 nm are absorbed by N_2O to produce electronically excited oxygen atoms, $O(^1D_2)$. These highly energetic oxygen atoms react with N_2O to form NO:

$$N_2O + h\nu \rightarrow N_2 + O(^1D_2)$$
$$O(^1D_2) + N_2O \rightarrow 2\ NO$$
$$\text{Net:}\quad 2\ N_2O + h\nu \rightarrow N_2 + 2\ NO$$

where hν symbolizes a photon of light. Other reactions produce a small amount of molecular oxygen as well.

Ambient air is scrubbed of NO and used to dilute the N_2O /NO gas flow, resulting in a N_2O concentration of 2% in the final mixture. The mixing ratio of NO depends on the intensity of the photolysis lamp, the concentration of N_2O (determined by pressure and temperature), and the residence time in the photolysis cell (determined by volumetric flow rate and cell volume). By adjusting the lamp intensity to account for changes in the total flow rate, it is possible to produce a flow of air containing a constant concentration of nitric oxide.

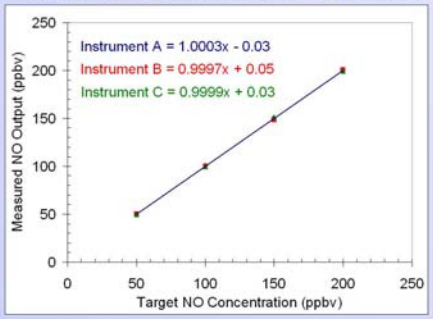
Reproducible NO mixing ratios were achieved using a thermostated lamp housing and feed-back control of the power to the photolysis lamp based on the measured light intensity. An electronic proportional valve was used in conjunction with a mass flow meter to control the N_2O flow. Test data show that the NO mixing ratio is independent of ambient temperature, pressure and humidity. The rise time was measured to be less than 30 seconds to reach 95% of the selected concentration. Precisions and accuracies for the NO mixing ratio were better than 2.0 ppbv.

The Model 408 Nitric Oxide Calibration Source™ is well suited for in field calibrations. The calibration source is extremely portable with dimensions of 3.8" x 7.5" x 8.5", weight of 5.2 lbs, and maximum power draw of 18 W at 12 VDC. A puncture device and regulator are supplied for use of disposable, 16 g N_2O cylinders that allow for up to 6 hours of use in the field. The source can be programmed to generate up to 10 individual NO step concentrations over a chosen time interval, including zero, which corresponds with the photolysis lamp turned off. With an output mass flow rate adjustable up to 3.0 L/min, the calibration source can be used to calibrate any nitric oxide analyzer. Each Nitric Oxide Calibration Source™ is calibrated against a NIST traceable standard. The user can recalibrate the source against a separately maintained standard and enter calibration data into the software to use the source as a transfer standard.

High Accuracy and Precision

The performance of the NO calibration source was evaluated using a chemiluminescence NO analyzer. Independent validation of the instrument was performed by Prevas AB in Sweden.

	50 ppb NO			100 ppb NO			150 ppb NO			200 ppb NO		
Instrument ID	A	B	C	A	B	C	A	B	C	A	B	C
NO Calibration Source Output	49.6	48.8	51.2	102.5	101.4	100.2	152.4	150.1	153.7	196.6	204.0	197.0
	50.5	49.2	50.0	100.7	103.1	98.8	152.9	145.3	152.6	205.0	201.8	196.1
	50.1	51.4	49.6	98.0	101.2	98.4	144.2	148.6	151.4	198.5	201.4	199.7
	48.0	49.5	49.7	102.9	96.9	99.1	148.3	146.8	151.6	201.2	203.3	198.8
	48.7	52.0	49.0	98.2	99.7	99.7	152.2	152.0	149.4	202.3	196.4	196.2
	47.6	50.5	49.1	99.3	101.8	100.1	149.5	151.0	148.3	200.5	193.4	199.5
	49.9	50.8	49.1	100.9	101.4	97.7	151.5	149.7	151.2	199.8	210.5	200.8
	50.8	50.8	50.1	101.4	96.0	98.6	152.9	143.4	153.5	197.1	203.3	198.6
	47.8	48.1	49.1	100.0	103.3	103.4	150.4	148.6	150.6	194.5	198.8	205.3
	49.9	50.1	50.4	103.4	102.2	101.3	152.4	148.4	152.4	198.0	195.5	199.3
Mean:	49.3	50.1	49.7	100.7	100.7	99.7	150.7	148.4	151.5	199.4	200.8	199.1
Accuracy:	49.3	50.1	49.7	100.7	100.7	99.7	150.7	148.4	151.5	199.4	200.8	199.1
Precision:	1.2	1.2	0.7	1.9	2.5	1.7	2.7	2.6	1.7	3.0	5.0	2.7



NO Concentrations Independent of Ambient Conditions

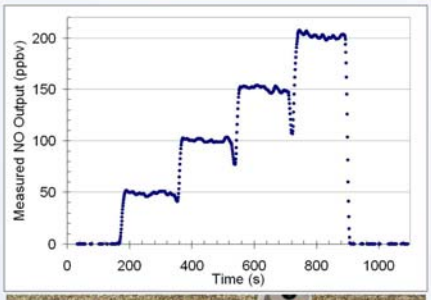
Pressure (Altitude) Testing. Testing shows that an NO calibration source calibrated in Boulder (1.6 km, 844 mbar) gave the correct NO output in Stockholm (0 km, 1013 mbar). NO output measurements at Fritz Peak (2.7 km, 745 mbar) were the same as in Boulder within experimental uncertainty. It appears that there is no significant effect (≤2.5%) of altitude for the range 0-2.7 km.

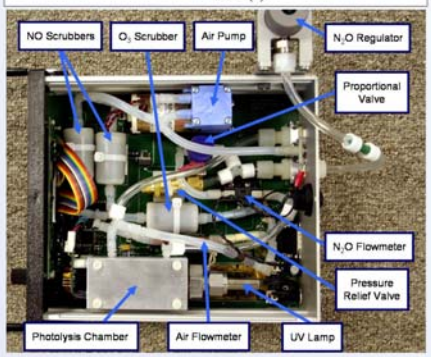
Humidity Testing. A very slight humidity effect on the NO output would be expected because the mass flow meter in the instrument is calibrated using ambient air. Since water has a different heat capacity than air, the mass flow rate will not be measured correctly at a different ambient humidity. The NO calibration source uses the measured mass flow rate to adjust the lamp intensity and produce nitric oxide in proportion to the dilution factor. As a result, we might expect the NO output to be about 1% higher at 100% RH than at 0% RH at 25 ºC. No significant difference in measured NO output was observed between dry tank air and 100% RH tank air.

Total Flow Testing. The instrument continuously measures the mass flow rate and adjusts the lamp intensity so as to produce a constant concentration of NO. No effect of the total flow rate on the NO output was observed over the flow rate range of 2.3 to 4.5 L/min.

Nitrous Oxide Flow Testing. The photolysis chamber was designed to be optically thick so that the NO output would not change significantly over a wide range of N_2O flow rates. In measurements of the NO output collected over the flow rate range 40-60 cc/min, no significant effect of N_2O flow rate was observed.

Temperature Testing. The photolysis chamber is regulated to better than 0.1 ºC so that external temperature does not affect the efficiency of NO production. Furthermore, the output was found to be the same at room temperature (21.5 ºC) as at 40 ºC. This is because the lamp intensity is continuously measured and regulated in a feedback loop. Also, the N_2O and air flow are measured by mass flow meters, which measure flow rate in a way that is virtually independent of temperature.





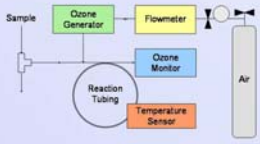
NIST Traceable Calibration

The National Institute of Standards and Technology (NIST) offers only one nitric oxide standard in the ppb range, which is prepared in a compressed gas cylinder with a concentration of 500 ppb. In addition to being outside of the typical working range of the NO calibration source, the NIST standard is certified to an accuracy of only ± 15 ppb and has an unstable NO concentration that decreases over time.[1]

Analytical traceability can also be achieved by using an instrument that has been calibrated against a NIST standard reference instrument. The technique of gas phase titration (GPT) offers an analytical method for measuring nitric oxide using an ozone monitor, which is calibrated against a NIST standard reference photometer with a minimum accuracy of ±2 ppb in the range of 0 to 100 ppb and ±2% in the range of 100 to 1000 ppb.[2] GPT measurements are made by monitoring the quantitative reaction of nitric oxide with ozone (O_3) and relies on the accurate detection of ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

1. NIST, Certificate of Analysis, Standard Reference Material® 2737, January 2006.
2. Paur, R.J., et al., Standard Reference Photometer for the Assay of Ozone in Calibration Atmospheres, NIST Internal Report 6963, February 2003.



Schematic of the Gas Phase Titration Apparatus.

Model 408 Nitric Oxide Calibration Source™ Specifications

Power Requirements	11-14 V DC or 110/220 V AC , 18 watt
Dimensions	3.8" x 7.5" x 8.5" (10 x 19 x 22 cm)
Weight	5.2 lbs (2.4 kg)
NO Output	0 ppb and 20-1,000 ppb
Output Flow Rate	3.0 L/min volumetric
Precision	3.0 ppb or 3.0%, whichever is greater
Accuracy	3.0 ppb or 3.0%, whichever is greater
Rise Time (95%)	< 30s to reach 95% of concentration
Data Outputs	RS232, LCD Display