

Ozone Titration Method for NIST-Traceable Calibration of Nitric Oxide Monitors™

Calibration of laboratory instruments requires well characterized and accurate gas standards. The accuracy of calibration gas mixtures, in turn, is largely dependent upon its analytical traceability to a reference material or reference instrument calibration. To achieve analytical traceability, there must be an unbroken link of comparisons between the measured value of the calibration gas mixture and a reference that is recognized in the international scientific community as being a true value. The U.S. National Institute of Standards and Technology (NIST) provide standard reference materials and calibration services that are internationally recognized for their accuracy.

The National Institute of Standards and Technology (NIST) provides calibration standards and services for many materials, but 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 Reference Source (20-200 ppb), the NIST gas standard is certified to an accuracy of only ± 15 ppb and has an unstable NO concentration that decreases over time.¹

Analytical traceability for a gas mixture can be achieved by using an instrument that has been calibrated against either a standard reference material or a standard reference instrument. The technique of gas phase titration (GPT) offers an analytical method for measuring nitric oxide using an ozone monitor, for which NIST offers calibrations with significantly higher accuracy than the NIST NO gas standard. In the technique of gas phase titration, NO is measured by monitoring the reaction with ozone and relies on the accurate detection of ozone. NIST offers calibration services for ozone monitors against their standard reference photometer, which has a minimum accuracy of ± 2 ppb in the range of 0 to 100 ppb and $\pm 2\%$ in the range of 100 to 1000 ppb.²

Measurements by gas phase titration are based on the quantitative reaction of nitric oxide with ozone (O_3):



This technique has long been used for the measurement of either NO or O_3 in a gas sample, and the reaction is stoichiometric; i.e., one O_3 molecule is consumed for every NO molecule oxidized to NO_2 in the reaction. A small concentration of ozone (≈ 3 -5 ppm) is added to the gas sample stream, and the mixture is given time for the ozone to be consumed through reaction 1. The resulting decrease in the ozone concentration is measured by the absolute method of UV absorption and is equal to the original concentration of NO in the gas stream, provided that adequate time has been allowed for the reaction to reach completion.

2B Technologies calibrates the NO Reference Sources through a series of analytical comparisons including gas phase titration measurements that are traceable to a NIST standard. The NO sources are directly calibrated using the NIOX[®] chemiluminescence instrument, which in turn is calibrated against gas standards prepared by our NO dynamic dilution manifold. The

NO dynamic dilution manifold is calibrated by an ozone titration in the range 0-200 ppb using a NIST-traceable ozone monitor.

Transfer standard. Our transfer standard is a Thermo Electron ozone calibrator, model 491-PS, serial number 0726724741. The transfer standard was calibrated by NIST against their Standard Reference Photometer, serial number 2, in Gaithersburg, MD on October 24, 2007. Measurements were collected at ten concentrations (25 to 1000 ppb) and two zero concentrations. A linear regression was fit to the data, and calibration factors were determined for the transfer standard.

Working Standard. Our working standard is a 2B Technologies Model 205 Dual Beam Ozone Monitor™, serial number 485DB. The working standard was calibrated by 2B Technologies by comparison to the NIST-calibrated transfer standard. Measurements were collected at six concentrations (50 to 300 ppb) and one zero concentration. A linear regression was fit to the data, and calibration factors were determined for the working standard.

Gas Phase Titration Apparatus. Our gas phase titration apparatus is designed to monitor the reaction of ozone with nitric oxide, Fig. 1. A flow of air containing ozone is added to the sample air flow at a mixing tee. Ideally, the flow from the ozone generator is less than 5% of the combined flow, so that dilution of NO by the sample air is small. As discussed below, both flows are measured, and an accurate correction is made for dilution of the sample.

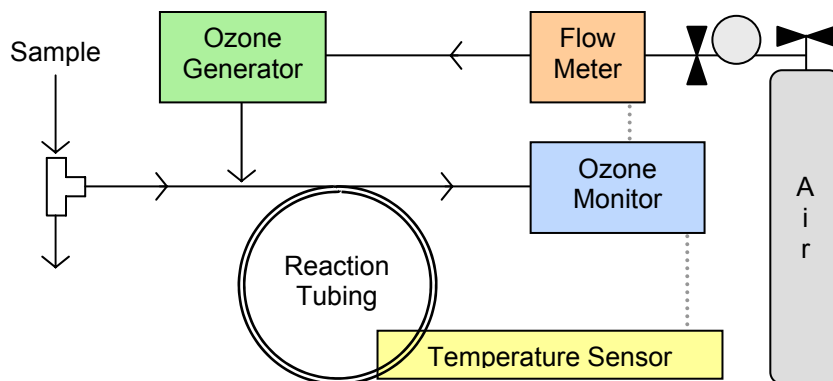


Fig. 1. Schematic diagram of the gas phase titration apparatus.

Ozone is produced by passing air through an aluminum housing thermostated at 42°C and containing a low pressure mercury lamp. The lamp has a fused silica window that passes highly energetic atomic emission near 185 nm in addition to the resonant emission at 254-nm. The wavelengths near 185-nm are absorbed by molecular oxygen (O₂) to produce oxygen atoms (O). Those oxygen atoms rapidly attach to O₂ via a termolecular reaction to form O₃:



Here, $h\nu$ indicates a photon of light having a wavelength near 185 nm, and M is any molecule, principally N₂, O₂, Ar and H₂O in air. The molecule M catalyzes the combination of O and O₂ by

removing excess translational energy. A cylinder of ultra high purity blended air (Scott) was equipped with a pressure regulator, a needle valve, and a flow meter to deliver a volumetric flow rate of 0.02 L/min to the ozone generator.

The flow out of the ozone generator was mixed with the sample air drawn into the apparatus by the working standard ozone monitor. The volumetric flow rate of the combined flow was 2.0 L/min. The resulting gas mixture contained 3.9 ppm ozone and passed through a 3.3 meter length of ¼" I.D. Kynar tubing before being drawn into the ozone monitor. Analog inputs on the ozone monitor were configured to read the ozone generator flow meter and a temperature sensor next to the reaction tubing.

The actual ozone concentration, the reaction temperature, and the flow rates are measured every 10 seconds. Alternating between the output of the NO dynamic dilution manifold and zero air every 5 minutes results in a square-wave modulation of the ozone concentration reaching the ozone monitor.

NO Dynamic Dilution Manifold. Our dynamic dilution manifold is made up of two mass flow controllers housed in a thermo-stated enclosure. A gas standard of 200 ppm nitric oxide in nitrogen is diluted in air from a compressed gas cylinder to generate gas mixtures with the mixing ratios in the low ppb range.

Results for Calibration of the Dynamic Dilution NO Gas Standard. The standing ozone concentration used in the GPT measurements was determined from the data collected using zero air. Minor drift in the ozone concentration was fit with a third order polynomial, Fig. 2. The calculated standing ozone concentration was subtracted from the raw data to determine changes in nitric oxide, Fig. 2.

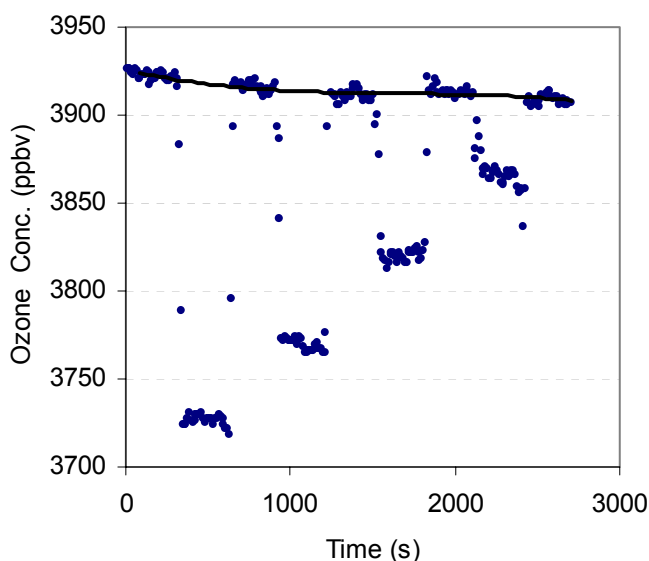


Fig. 2. Example of raw GPT data for NO concentrations of 200, 150, 100, and 50 ppb generated using a dilution manifold and fit to standing ozone concentration.

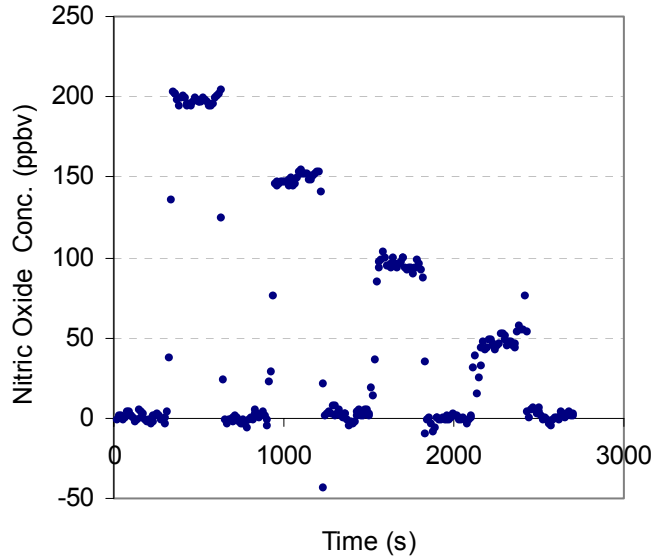


Fig. 3. Example of raw GPT data after subtracting calculated standing ozone concentration for 200, 150, 100, and 50 ppb NO generated using a dilution manifold.

Two small corrections are applied to the measured NO concentrations. The first, mentioned above, is a correction for dilution by the flow from the ozone generator. The correction factor, $f_{dilution}$, applied is:

$$f_{dilution} = \frac{F_{total}}{F_{total} - F_{ozone}} \quad (4)$$

where F_{total} is the total flow through the reactor, and F_{ozone} is the flow from the ozone generator. An average correction factor of 1.2% was made for dilution of the sample gas.

A small correction also is made for the possibility that the reaction between NO and O_3 is not 100% complete. Pseudo-first orders kinetics applies since the maximum concentration of the NO source is 200 ppb, which represents only 5% of the O_3 concentration. The correction factor for incomplete reaction, $f_{reaction}$, is then calculated from the formula:

$$f_{reaction} = \frac{1}{1 - \exp\left(-k[O_3]\left(\frac{298}{T}\right)\left(\frac{P}{760}\right)t\right)} \quad (5)$$

where k is the rate constant for the reaction between NO and O_3 at the temperature of the reaction coil, T is the absolute temperature, P is the pressure in torr, and t is the reaction time. The rate constant is well known and is given by:

$$k_{NO+O_3} = 3.0 \times 10^{-12} e^{-1500/T} \quad (6)$$

in units of $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ where T is the absolute temperature.³ The reaction time t is calculated from the total volumetric flow rate and reaction volume V_{reaction} , which is the measured volume of the reaction coil:

$$t = \frac{V_{\text{reaction}}}{F_{\text{total}}} \quad (7)$$

Based on the measurements of ozone concentration, temperature, pressure, volume of the reactor and volumetric flow rate, an average correction factor for incomplete reaction of 1.8% was applied to the data.

The output of the NO dynamic dilution manifold was measured by gas phase titration using this technique for concentrations of 50, 100, 150 and 200 ppb NO, as shown in Figs. 2-3. A linear regression was fit to the data, Fig. 4, and calibration factors were determined for the dynamic dilution manifold. The NO dilution manifold had been previously calibrated with a 200 ppb NIOX[®] NO standard in a compressed gas cylinder having a stated accuracy of 0.5%. The linearity of the calibration data (Fig. 4) verifies that the GPT response is linear, as expected. This gas phase titration was repeated twice with resultant slopes of 0.976 and 0.988 and intercepts of 4.4 and 5.4 ppb, respectively, where the GPT result is plotted against the expected NO concentration based on the previous calibration. At 200 ppb, the agreement of the average of the two results is within 1.4 ppb (0.7%) of the NIOX[®] gas standard previously used.