



Portable calibrator for NO based on the photolysis of N₂O and a combined NO₂/NO/O₃ source for field calibrations of air pollution monitors

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Abstract. A highly portable calibration source of nitric oxide (NO) based on the photolysis of nitrous oxide (N₂O) supplied by 8 or 16 g disposable cartridges is demonstrated to serve as an accurate and reliable transfer standard for the calibration of NO monitors in the field. The instrument provides output mixing ratios in the range 0–1000 ppb with a precision and accuracy better than the greater of 3 ppb or 3 % of the target NO mixing ratio over a wide range of environmental conditions of ambient temperature (8.5–35.0 °C), pressure (745–1015 mbar corresponding to 2.7–0.0 km of elevation), and relative humidity (0 %–100 % RH). The combination of the NO calibration source with a previously described ozone calibration source based on the photolysis of oxygen in air provides a new instrument capable of outputting calibrated mixing ratios of NO, ozone (O₃), and nitrogen dioxide (NO₂), where the NO₂ is produced by the stoichiometric gas-phase reaction of NO with O₃. The portable NO₂/NO/O₃ calibration source requires no external gas cylinders and can be used for calibrations of NO, NO₂, and O₃ instruments for mixing ratios up to 1000, 500, and 1000 ppb, respectively. This portable calibrator may serve as a convenient transfer standard for field calibrations of ozone and NO_x air pollution monitors.

chemical interactions between NO_x (NO+NO₂) and organic compounds in sunlight (Haagen-Smit, 1957). Both NO₂ and O₃ are known to produce several cardiac and respiratory ailments (both acute and chronic) and are classified as “criteria pollutants”; their atmospheric levels are regulated by the U.S. Environmental Protection Agency (U.S. EPA) and corresponding regulatory agencies around the world. Verification of compliance with these regulations requires a comprehensive and continuous monitoring system of both ambient atmospheric levels and NO_x emissions from industrial combustion sources (often referred to as CEMS – continuous emissions monitoring). Routine NO_x monitoring is also required for safety reasons in settings where diesel engines and machinery are used in confined areas, such as in the mining industry. Nitric oxide is used in the medical field where it is approved by the U.S. Food and Drug Administration for the treatment of adult pulmonary arterial hypertension (Abman, 2013) and for persistent pulmonary hypertension in hypoxic-term and near-term newborns (“blue babies”) (Clark et al., 2000). During this inhalation therapy, the concentration of NO (typically 20 ppm) must be continuously monitored during administration, and, very importantly, the concentration of its toxic impurity NO₂ must also be continuously monitored and kept below 3 ppm (preferably much lower due to the acute NO₂ toxicity).

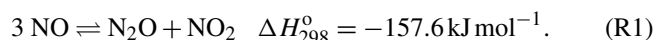
In all these applications, accurate monitoring of NO, NO₂, and O₃ not only requires stable, robust chemical analyzers, but also a way to test the validity of the analyzer response periodically using a standardized calibration method. Ideally, this is done by introducing gaseous standards with well-known concentrations of the analyte of interest. The fre-

1 Introduction

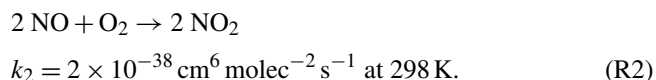
Measurements of gaseous nitric oxide (NO), nitrogen dioxide (NO₂), and ozone (O₃) are critical in numerous fields. NO is a direct combustion product that is readily oxidized in air to form NO₂. Ground-level ozone is produced by the photo-

quency of calibration depends upon the species being measured and the instrumental approach. A detailed discussion of ozone detection methods and calibration protocols is given in a previous publication describing a portable ozone calibrator (Birks et al., 2018b) and will not be repeated here. In the past, NO_x calibration methods were developed primarily for use with analyzers based on the chemiluminescence (CL) reaction of NO with an excess of ozone, which is the most widely used method for quantifying NO and, following its conversion to NO₂ (Fontijn et al., 1970; Ridley and Howlett, 1974; Kley and McFarland, 1980; Steffenson and Stedman, 1974; Demerjian, 2000). These analyzers require relatively frequent calibrations to assess both the basic instrumental sensitivity drift for NO and the NO₂ conversion efficiency.

The calibration of monitors for NO is typically achieved by the use of gas standards. A well-known problem with NO gas standards is that NO is unstable in gas cylinders at low concentrations; when NO standards are prepared at low parts per billion (ppb) levels, there is a strong tendency for the concentration of NO in the cylinder to decline with time even though the NO is diluted into an unreactive gas such as nitrogen (e.g., Robertson et al., 1977). This is because NO is thermodynamically unstable with respect to disproportionation to form N₂O and NO₂ according to the equilibrium (Burkholder et al., 2015):



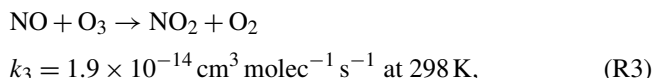
Although extremely slow in the gas phase, this reaction may be catalyzed on the interior walls of compressed gas cylinders. The walls may be treated to slow the reaction, but the treatment is not always effective, and one cannot be certain that the concentration of NO in a gas cylinder is what it was when the cylinder was last analyzed. Furthermore, even trace amounts of oxygen (O₂) in the diluent gas can react to oxidize NO to NO₂ according to the reaction (Atkinson et al., 2004)



Because of Reaction (R2), compressed gas standards for NO cannot be made with air as the diluent. This is a disadvantage since it is desirable to calibrate NO instruments using the same diluent gas as the gas being analyzed, which most commonly is air. Nitric oxide standards are much more stable at high concentrations; thus, it is common to prepare gas standards at a high parts per million level in an unreactive diluent gas such as N₂ and then dynamically dilute that standard with air prior to entering the analytical instrument being calibrated. Even at high parts per million levels, NIST-certified NO gas standards are typically only certified for 1–2 years. Although the dynamic dilution method works quite well, it is difficult to use as a portable transfer standard due to the need

for a cylinder of certified NO gas mixture and the need for accurately calibrated flowmeters, whose response can vary with temperature.

Nitrogen dioxide gas standards in standard passivated aluminum cylinders are known to degrade over a relatively short period of time regardless of concentration (U.S. EPA, 2019). The development of an NO₂ primary reference standard and subsequent calibration traceability protocols is an ongoing project (U.S. EPA, 2019). Historically, the U.S. EPA has recommended two methods for the dynamic multipoint calibration of NO₂ analyzers based on chemiluminescence (Ellis, 1975; U.S. EPA, 1983): one based on a permeation tube source of NO₂ and another based on the gas-phase titration (GPT) technique. Although the permeation tube source has found acceptance in certain areas (e.g., mine safety; Chilton et al., 2005), the difficulty of producing stable and reproducible NO₂ outputs from permeation tubes has precluded them from widespread use. The GPT technique is almost exclusively used for calibrating analyzers for compliance with the U.S. Clean Air Act. In the GPT method, the instrument is first calibrated for NO by the dynamic dilution of a high-concentration NO/N₂ gas standard traceable to a NIST Standard Reference Material (SRM) with NO_x-free air. The instrument is then calibrated for NO₂ by the addition of varying concentrations of ozone to an excess of NO. The 1 : 1 stoichiometric conversion of NO to NO₂ via the reaction of NO with O₃ (Burkholder et al., 2015),



forms the basis of the calibration. Ozone concentrations are generated by the photolysis of O₂ (typically from air) and added to an excess of NO while allowing for sufficient mixing time so that Reaction (R3) goes to completion. Nitrogen dioxide is calibrated based on the increase in NO₂ signal (NO_x – NO in CL analyzers) relative to the decrease in the NO signal (U.S. EPA, 2002). The NO₂ formed should equal the NO consumed if the NO₂ conversion efficiency to NO of the analyzer to be calibrated is unity. Incomplete conversion yields [NO₂]_{formed} < [NO]_{consumed} such that using the GPT reaction as a calibration incorporates a measure of the conversion efficiency in analyzers for which NO is monitored (i.e., CL analyzers). However, as with the case above concerning NO, a portable means of NO₂ calibration via the GPT method requires a NIST SRM NO gas mixture, a source of purified air, some type of ozone generator, and accurate mass flow controllers.

More recently, several new techniques that directly measure NO₂ based on variations of UV absorption (e.g., cavity ring-down and cavity-attenuated phase-shift spectroscopy) have become available (Paldus and Kachanov, 2006; Keababian et al., 2005, 2008). However, many of these do not measure NO. Therefore, for NO₂-only analyzers the GPT calibration method requires either (1) a second instrument

that can measure the loss of NO or (2) a NIST-traceable ozone source such that the loss of ozone can be correlated with the formation of NO₂. Note that the standard GPT calibration procedures can still be applied to methods that directly measure NO₂ and then indirectly measure NO (the opposite of the chemiluminescence technique) – such as in the long-path folded tubular photometer (FTP) developed in our group that measures direct NO₂ absorbance at 405 nm (Birks et al., 2018a).

In this paper we will initially describe and evaluate a portable calibration source for nitric oxide based on the photolysis of N₂O (the 2B Technologies Model 408 Nitric Oxide Calibration Source™; Andersen et al., 2019) and show that it is suitable to be used as a field transfer calibration standard. An advantage of this approach to NO calibration is that the nitrous oxide can be supplied by an 8 or 16 g cartridge (e.g., whipped-cream chargers), thereby eliminating the need for a compressed gas cylinder. The result is a highly portable NO calibrator. Recently, we have combined this Model 408 NO Calibration Source with a Model 306 O₃ Calibration Source™ (described in Birks et al., 2018b) to produce a GPT NO₂ calibrator (the Model 714 NO₂/NO/O₃ Calibration Source™). Here we evaluate the feasibility of using this instrument as a portable transfer standard for NO₂ without the requirements of having a certified gas standard and accurately calibrated mass flow controllers, thus increasing the portability of the transfer standard. Finally, we show that combining the O₃ calibrator and the NO calibrator into one instrument enables the user to perform robust calibrations for all three gases (NO₂, NO, and O₃) using just one highly portable instrument suitable for laboratory or field applications.

2 Theory of operation

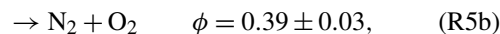
2.1 Nitric oxide (NO) calibration

The Model 408 Nitric Oxide Calibration Source™ (2B Technologies, Boulder, Colorado) makes use of a low-pressure mercury (Hg) lamp to photolyze pure nitrous oxide (N₂O) to produce NO. The vacuum UV emission lines of mercury near 184.9 nm are absorbed by N₂O to produce electronically excited oxygen atoms, O(¹D),



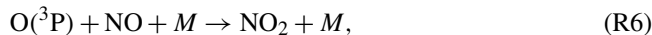
where $h\nu$ symbolizes a photon of light. These highly energetic oxygen atoms react with N₂O with a near-collisional reaction rate coefficient ($k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)

to form three different sets of products:



with the branching ratios (ϕ) shown (Burkholder et al., 2015). Since Reaction (R5a) produces two NO molecules, the overall quantum yield for NO production is approximately 1.22. The NO calibration source is similar in design to our ozone calibrator (Birks et al., 2018b), as both make use of the 184.9 nm line of a low-pressure mercury lamp. An important fundamental difference is that the 184.9 nm absorption cross section for N₂O is approximately 14 times larger than that of O₂. The absorption cross section, σ , of N₂O at the 184.9 nm mercury emission line is $\sim 1.4 \times 10^{-19} \text{ cm}^2 \text{ molec}^{-1}$ (Creasey et al., 2000; Cantrell et al., 1997) compared to $\sim 1 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ for O₂ (Yoshino et al., 1992; Creasey et al., 2000). Also, O₂ is only 21 % of the air that passes through the photolysis chamber in the ozone calibrator, while N₂O is supplied to the photolysis chamber by a source that is > 99 % N₂O. The result is that the N₂O gas absorbs the 185 nm light ~ 70 times stronger than does O₂ in air. At 298 K and 1 atm, the molecular concentration, c , is $2.46 \times 10^{19} \text{ molec cm}^{-3}$; thus, the absorption of 184.9 nm light from the low-pressure mercury lamp becomes optically thick ($1/e$ attenuation) at a path length, $1/(\sigma c)$, of 0.3 cm, and 99 % of the light is absorbed for a path length of 1.35 cm. Under such conditions, the rate of production of NO ($\text{molec cm}^{-3} \text{ s}^{-1}$) depends almost entirely on the lamp intensity and is independent of flow rate (i.e., residence time in the photolysis cell). The NO/N₂O stream exiting the photolysis chamber is diluted into NO_x-scrubbed air to produce the desired output concentration of NO in air. At constant flow rates of N₂O and the dilution air, the concentration of NO in the calibrator's output is varied by merely changing the lamp intensity.

We typically observe a small amount of NO₂ produced from the NO photolytic generator (≤ 3 % of the NO produced). This is likely due to the formation of O(³P) atoms in the photolysis cell, which combine with NO via the reaction



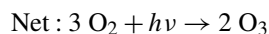
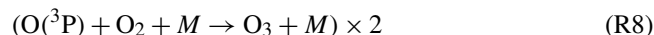
where M is a third body, most likely N₂O in this case. O(³P) atoms can arise from several possible sources. Nishida et al. (2004) report a quantum yield for O(³P) from N₂O photolysis of 0.005 ± 0.002 (i.e., NO₂/NO = $0.005/1.22 \sim 0.4$ %). Quenching of O(¹D) to O(³P) by N₂O (Reaction R5c) likely contributes up to another 0.8 % (Vranckx et al., 2008, report a limit of $\phi_{5c} < 0.01$ at 298 K). Oxygen (O₂), which is a typical N₂O impurity, can also photolyze to produce two O(³P) atoms. Even NO itself could be photolyzed at 184.9 nm ($\sigma \sim 3 \times 10^{-18} \text{ cm}^2 \text{ molec}^{-1}$, thermodynamic dissociation threshold of 189.7 nm; Iida et al., 1986

and Burkholder et al., 2015) to produce $O(^3P)$ atoms; however, this would be expected to be of lesser importance due to the relatively lower NO concentrations (ppm) within the photolysis cell. In all of these cases, the amount of NO_2 formed relative to NO should be small and approximately constant over time.

A final issue pertains specifically to CL NO analyzers for which the presence of N_2O can lead to collisional quenching of the chemiluminescence signal. Clyne et al. (1964) report that N_2O quenches the NO/O_3 chemiluminescence 2.6 and 2.9 times more efficiently than O_2 and N_2 , respectively. Therefore, a mixture of 1.5 % N_2O in air (typical conditions – see Sect. 3) would be expected to reduce the observed chemiluminescent signal by ~ 2.7 % relative to pure air. In practice, this is typically slightly less (2.2 %–2.4 %) as the sample flow in a CL analyzer is diluted by the addition of a reagent O_3 /air flow (10 %–25 % of the total flow). This correction term can be explicitly calculated from the measured flows in the photolytic NO calibration source and the flow rates in the CL analyzers (as in the example given here) or it can be eliminated depending upon the analyzer used during the initial calibration of the relationship between lamp intensity and NO output (see Sect. 3.1). If a CL analyzer is used to determine this relationship, then quenching by N_2O is intrinsically included in the calibration of the photolytic source.

2.2 Ozone calibration

The photolytic ozone calibration source has been described in detail previously (Birks et al., 2018b) and the following is only meant to briefly highlight the important points of this calibrator since it plays a key role in the NO_2 calibration device described in the following section. In the photolytic ozone calibration source that is used in the Model 306 Ozone Calibration Source™ (2B Technologies, Boulder, Colorado), a low-pressure mercury lamp produces calibrated concentrations of ozone by the photolysis of oxygen in air.



A key difference compared to the NO photolytic source described above (Sect. 2.1) is that for a 1 cm path length (and at 1 atm and 25 °C), the O_2 absorption in air is nearly optically thin (~ 5 % light absorbed). For an optically thin system, the mixing ratio of ozone produced depends linearly on the residence time within the photolysis chamber; thus, it varies with volumetric flow rate. In the Model 306 Ozone Calibration Source, the mass flow rate, temperature, and pressure are continuously measured to compute the volumetric flow rate (and therefore the residence time), and the lamp intensity is adjusted in a feedback loop to maintain a constant ozone output mixing ratio. A further key point in the ozone

calibration source is that the photolysis cell must be maintained at a constant (slightly heated) temperature to ensure constant overlap between the Hg lamp emission lines and the O_2 absorption lines and to maintain a constant ratio of lamp intensities between the 184.9 nm Hg line and the 253.7 nm Hg line that is monitored in the feedback loop to maintain a constant photolysis rate (Birks et al., 2018b). The main difference between the previously described Model 306 Ozone Calibration Source and the one used for the NO_2 calibrator described below (Sect. 2.3) is that the flow rate through the photolysis cell is much lower ($\sim 50 \text{ cm}^3 \text{ min}^{-1}$ as opposed to $3000 \text{ cm}^3 \text{ min}^{-1}$). This increases the cell residence time from 0.06 to ~ 3.6 s and consequently results in the production of much higher ozone mixing ratios (up to 15 ppm) exiting the photolysis cell in the Model 714. However, control of the lamp intensity and volumetric flow rate (as described in Birks et al., 2018b) still allows for precise control of the output ozone mixing ratio that is independent of pressure and temperature. The longer residence time and higher mixing ratios in the O_3 photolysis cell do lead to complications due to water vapor that were not found in the individual O_3 calibration source (the Model 306). A solution to this potential problem will be discussed in Sect. 4.2.

2.3 NO_2 calibration in a combined calibrator

Combining the above two calibrators into a single unit (the Model 714 $NO_2/NO/O_3$ Calibration Source™, 2B Technologies, Boulder, Colorado) makes it possible to calibrate not only for NO and O_3 , but also a third gas, NO_2 . The calibrated concentrations of NO and O_3 are produced as described above. Calibration of NO_2 is accomplished via the gas-phase titration (GPT) technique (Reaction R3), making use of the NO and O_3 produced in the combined calibration source. Here, O_3 is reacted with an excess of NO to produce known concentrations of NO_2 under conditions such that $[NO]_{\text{consumed}} = [NO_2]_{\text{produced}}$. A key difference in the Model 714 from the two individual calibrators is that Reaction (R3) must be carried out at high concentrations (parts per million level) to drive Reaction (R3) to completion; therefore, the NO and O_3 reagents are mixed before subsequent dilution. Modeling the second-order kinetics of Reaction (R3) (see Fig. 1) shows that with $[NO] = 2 \times [O_3]$ (i.e., NO a factor of 2 in excess of O_3), ~ 5 ppm of NO is required to consume 99.6 % of the ozone for a reaction time of 4 s. Increasing the reaction time allows for lower [NO] to be used to obtain the same completeness of reaction. It should be noted that for NO_x analyzers that measure both NO and NO_2 , it is not necessary for Reaction (R3) to go to completion because one measures the consumption of NO relative to the production of NO_2 . However, residual ozone complicates the calibration protocol as Reaction (R3) continues to alter the NO/ NO_2 ratio (at a reduced rate after dilution) as the gas mixture is transported to the analyzer to be calibrated. Thus, the NO/ NO_2 ratio would depend on the residence time of the

connection tubing. For NO₂-only analyzers, it is critical to have > 99 % conversion as the NO₂ signal produced may be correlated with the loss of ozone (which is assumed to be at the calibrated target concentration and typically not explicitly measured). The calculations described in Fig. 1 can be used as a guide to the required concentrations and residence times of a GPT reactor.

One more point concerning the GPT chemistry is that NO must be maintained in excess over ozone (Ellis, 1975; U.S. EPA, 2002). If ozone is used in excess, NO₂ can react with the excess ozone to produce NO₃,



and NO₃ can subsequently form N₂O₅ rapidly via (Bertram et al., 2012)



Reaction (R9) is ~ 600 times slower than Reaction (R3) ($k_9 = 3.22 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K; Burkholder et al., 2015) but can proceed to a small extent at parts per million levels of NO₂ and O₃. At room temperature and NO₂ concentrations greater than about 25 ppb, Reaction (R10) favors N₂O₅ formation and proceeds relatively rapidly ($k_{10} \sim 1.4 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ s}^{-1}$; Burkholder et al., 2015), thus resulting in a net loss of two NO₂ molecules. In typical CL analyzers that use heated molybdenum to convert NO₂ to NO, N₂O₅ production is not observable, since the heated catalyst will thermally decompose N₂O₅ rapidly (Reaction R10r), followed by the reduction of both NO₂ and NO₃ to NO, thus not affecting the observed $[\text{NO}]_{\text{consumed}} = [\text{NO}_2]_{\text{produced}}$. However, in the case of photolytic NO₂ converters and the long-path FTP method mentioned in the previous section, the formation of N₂O₅ would cause an underestimate in the calibration (i.e., $[\text{NO}]_{\text{consumed}} > [\text{NO}_2]_{\text{produced}}$). For photolytic converters, there would be no way to elucidate the error as the lower observed NO₂ would likely be incorporated into an incorrect conversion efficiency.

3 Experimental design

3.1 Portable nitric oxide calibration source

Figure 2 is a schematic diagram of the NO calibration source. An air pump draws ambient air into the instrument through NO_x and ozone scrubbers (a mixture of Carulite® and activated carbon) to produce the diluent air stream. The airflow rate is measured by a mass flowmeter and is controlled by the use of restrictors (not shown) and a needle valve that vents part of the flow. The needle valve is adjusted to produce diluent air at a total output volumetric flow rate of $\sim 3 \text{ L min}^{-1}$. In the most portable configuration of the instrument, nitrous oxide is supplied by a cartridge containing either 8 or 16 g of liquid N₂O with a headspace pressure of

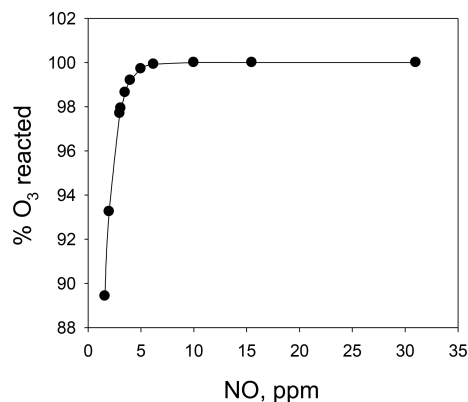


Figure 1. A plot of the percent of O₃ consumed vs. the initial NO concentration for the conditions of $[\text{NO}] = 2 \times [\text{O}_3]$ and a total reaction time of 4 s.

$\sim 50 \text{ atm}$ at 20°C . A combined cracker–regulator punctures the cartridge as it is tightened and also drops the outlet delivery pressure to below 25 psig. A 25 psig pressure-relief valve is installed inside the instrument housing to prevent over-pressurization. The valve on the cracker–regulator provides a coarse adjustment of the N₂O flow rate. A voltage-sensitive orifice (VSO) valve is then used to provide fine control of the N₂O flow rate to $60 \pm 1 \text{ cm}^3 \text{ min}^{-1}$ in a feedback loop. Pressure within the gas stream is measured but not controlled. The N₂O then passes through an aluminum photolysis cell (volume $\sim 6 \text{ cm}^3$) where a small fraction of the N₂O is converted to NO (and N₂ + O₂) by a low-pressure mercury discharge lamp. As discussed above, because the system is optically thick (essentially every photon is absorbed), the NO production rate (molec s^{-1}) is independent of photolysis cell pressure and N₂O flow rate, the production rate depending only on the lamp intensity. NO output is varied by changing the pulse-width-modulated duty cycle to the Hg lamp while monitoring its intensity with a photodiode. Since nearly all of the 184.9 nm light is absorbed by the N₂O in the cell, the lamp intensity at the 253.7 nm mercury line is monitored by the photodiode and controlled by the microprocessor. As the monitoring wavelength (253.7 nm) and the photolysis wavelength (184.9 nm) are different, it is important to maintain a constant ratio of lamp emission at these two wavelengths. This is accomplished by regulating the photolysis cell (which houses the lamp) at a constant temperature of 40°C . Even as the lamp duty cycle is varied, the temperature regulation maintains a constant lamp temperature, thus ensuring a stable 184.9/253.7 nm output. The NO/N₂O stream exiting the photolysis chamber is diluted into the $\sim 3 \text{ L min}^{-1}$ flow of NO_x-scrubbed air to produce the desired output concentration of NO in air.

For the NO calibration source to be a valid transfer standard, the photolytic NO source must be validated against a NIST-traceable NO standard to provide a lamp intensity vs. NO output concentration working curve. Therefore, the pho-

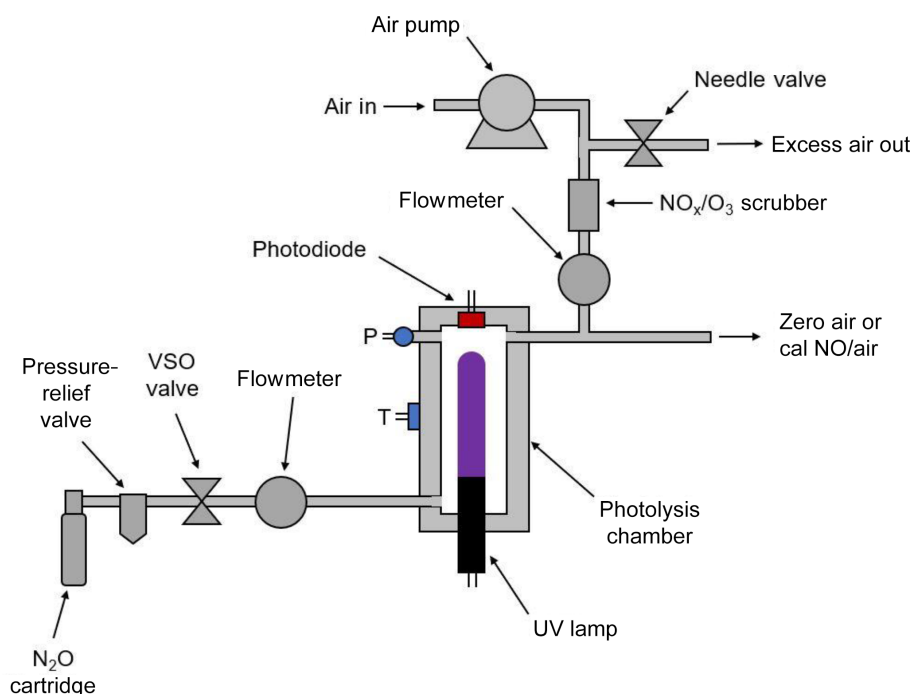


Figure 2. Schematic diagram of the 2B Technologies Model 408 Nitric Oxide Calibration Source.

todiode voltage (i.e., a measurement of lamp intensity) must be calibrated against the output NO concentration as measured by an NO analyzer that has been recently calibrated using a NIST SRM NO gas standard dilution system.

Nitrous oxide can be supplied to the instrument either by means of N₂O cartridges (commercially available and often used as whipped-cream chargers) as shown in Fig. 2 or by connection to a lecture bottle or gas cylinder containing N₂O. The cartridge holder and cracker allow the use of either 8 or 16 g cartridges containing liquid N₂O and will supply a gas flow of N₂O of 60 cm³ min⁻¹ for approximately 1.2 or 2.5 h, respectively. Alternatively, a lecture bottle or tank of N₂O may be used, allowing for continuous operation of 1.5 d for a lecture bottle containing 227 g or 174 d for a typical containing 27 kg of N₂O.

3.2 Combined NO₂, NO, and O₃ calibration source

A portable calibrated source of NO₂ can be achieved by combining the NO photolytic calibration source (described in Sects. 2.1 and 3.1) with the photolytic ozone calibration source (described in Sect. 2.2 and in Birks et al., 2018b). This is commercially available as the 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source™, which is capable of providing calibrated mixing ratios of NO₂, NO, or O₃. A schematic diagram of the Model 714 NO₂/NO/O₃ Calibration Source is shown in Fig. 3. The instrument produces O₃ by the photolysis of oxygen in air, NO by the photolysis of N₂O, and NO₂ by the gas-phase titration (GPT) of known concentrations of O₃ in an excess of NO.

An air pump pushes ambient air through an O₃/NO_x scrubber; thereafter the flow is split using a restrictor to send a volumetric flow of $\sim 50 \text{ cm}^3 \text{ min}^{-1}$ through an ozone photolysis chamber, with the bulk of the flow, $\sim 2.7 \text{ L min}^{-1}$, serving as a diluent gas. This main flow combines with the effluent of the photolysis cells just prior to the outlet. A voltage-sensitive orifice (VSO) valve controls the flow, as measured by a mass flowmeter, through the photolysis chamber. For the production of NO, a pressurized source of N₂O passes through a mass flow controller and into an NO photolysis chamber at a volumetric flow rate of $\sim 40 \text{ cm}^3 \text{ min}^{-1}$. Flows through the O₃ and NO photolysis chambers join at a tee prior to entering a reaction zone having a volume of 6.5 cm³ consisting of 20.3 cm of 6.4 mm i.d. Teflon tubing. For the generation of NO₂, the outputs of the NO and O₃ photolysis cells are mixed and allowed to react in the Teflon reaction volume. The total flow rate passing through this reactor is 90 cm³ min⁻¹ (40 cm³ min⁻¹ of NO/N₂O and 50 cm³ min⁻¹ of O₃/air), giving a reaction time of 4.3 s. The O₃ is quantitatively converted to NO₂ during this time. The high-concentration O₃, NO, or NO/NO₂ mixture is diluted by a factor of ~ 30 –54 (the larger being in the absence of the N₂O flow for outputting only O₃) with O₃/NO₂-scrubbed ambient air at a tee just prior to the instrument outlet. Ozone or NO is produced at calibrated concentrations by turning the corresponding lamps on and adjusting their intensities as measured by photodiode measurements in the respective chambers. Typically, the N₂O flow is turned off when only ozone is being output to conserve N₂O usage. To produce

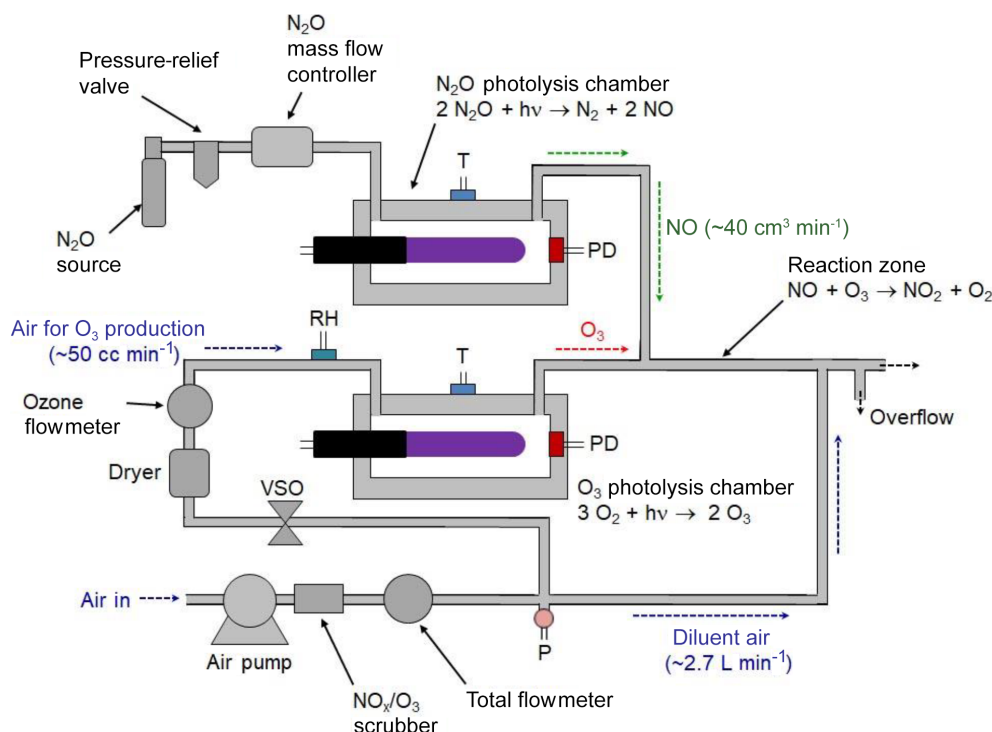


Figure 3. Schematic diagram of the 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source.

known mixing ratios of NO₂, calibrated amounts of O₃ (corrected for the slight dilution by N₂O) are produced in the range 0–500 ppb with the NO output set at least twice the output ozone (e.g., 1000 ppb of NO is required for 500 ppb of O₃ to be converted to NO₂). Note that these are the concentrations exiting the calibrator as opposed to the much higher concentrations found within the reaction zone. For example, a final output concentration of 200 ppb of NO would give a concentration of 6 ppm of NO within the reaction zone.

3.3 Validation as a suitable transfer standard

As described in Sect. 1, the U.S. EPA sets out procedural guidelines for the calibration of monitors used for the regulatory monitoring of ambient O₃ and NO₂ (U.S. EPA, 2002; U.S. EPA, 2013). Since most NO₂ monitors actually monitor NO (CL analyzers), their guidelines also describe the calibration of NO as a matter of necessity even though NO is not a criteria pollutant. For NO_x, the basis of these procedures ties NO and NO₂ calibrations to a NIST-traceable SRM gas mixture of NO. However, the U.S. EPA does not provide guidance for transfer standards that do not include the direct use of either a NIST SRM gas mixture or a gas mixture that is somehow traceable to a NIST SRM (as with the photolytic NO₂ calibrator described here). In contrast, specific statistical requirements are established for the use of either photolytic generators or analyzers based on photometry for use as transfer standards in the calibration of ozone monitors (U.S. EPA, 2013; Birks et al., 2018b). In lieu of direct

statistical requirements for a photolytic NO and NO₂ transfer standard, we have applied the same requirements that are established for a Level 4 ozone transfer standard (U.S. EPA, 2013). Level 4 ozone transfer standards must undergo a “6 × 6” verification in which six calibration curves, each consisting of six approximately equally spaced concentrations in a range including 0 % and 90 % (±5 %) of the upper range of the reference standard, are obtained on six different days (U.S. EPA, 2013). The relative standard deviations of the six slopes of the calibration plots must not exceed 3.7 %, and the standard deviation of the six intercepts cannot exceed 1.5 ppb.

The 6 × 6 verification requires an analyzer whose calibration is traceable to a NIST standard. For the measurements presented here, a 2B Technologies Model 205 or 202 ozone monitor was used as a reference photometer for O₃, and a 2B Technologies Model 400 (for NO only) or a Model 405 (NO and NO₂) was used as a reference analyzer for NO_x. The ozone monitors (Model 202 or 205) are each certified as an ozone Federal Equivalent Method (FEM) by the U.S. EPA (EQOA-0410-190) and are NIST-traceable through comparison with a currently accredited ozone calibrator (Thermo Scientific model 49i-PS). The Model 405 also is designated as an FEM for NO₂ (EQNA-0217-243), and it and the Model 400 were calibrated using a Teledyne-API model 700 Dynamic Dilution NO/NO₂ calibrator using a NIST-traceable NO gas mixture (Scott Specialty or Airgas). Furthermore, the ozone photometer (used to measure the ozone for the GPT re-

Table 1. NO mixing ratios measured from a Model 714 NO₂/NO/O₃ Calibration Source as a function of the N₂O flow rate.

N ₂ O flow rate cm ³ min ⁻¹	NO mixing ratio* ppb (±1σ)
5.1	394.5 ± 6.1
7.7	396.9 ± 1.4
10.1	397.9 ± 1.1
15.3	397.8 ± 3.9
20.4	398.4 ± 3.0
25.4	399.2 ± 4.1
30.4	397.1 ± 2.4
35.5	397.9 ± 1.9
39.6	394.7 ± 2.7
45.6	396.4 ± 2.6
47.7	396.2 ± 1.8

* NO measured using a Model 405 NO/NO₂/NO_x monitor.

action) within the model 700 was also calibrated against the NIST-traceable Thermo Scientific ozone standard.

Because a goal of the calibration sources is their use in the field calibrations of analyzers, one also needs to consider the effect of environmental factors such as temperature, pressure, and humidity on the output mixing ratios of the photolytically generated analytes. The factors of optical opacity and the photochemistry discussed above in Section 2 imply that environmental variables such as temperature, pressure, and relative humidity should have minimal effects on the performance of the ozone and NO calibrators. However, this assumes that the N₂O is completely optically thick and that the sensors for temperature, pressure, and mass flow rate are perfectly linear and independent of one another. For example, as pointed out below, mass flowmeters depend on molecular composition and will not be perfectly accurate when the water vapor mixing ratio changes. Similar tests of the ozone calibrator have been described previously (Birks et al., 2018b), and here we carry out additional environmental tests of the NO calibration source. Furthermore, temperature certainly affects the GPT chemistry (Reaction R3) and can place limitations on the usable concentration ranges – typically at low concentrations for which Reaction (R3) may not go to full completion. The methods for varying the temperature, pressure, and humidity will be described as the results are presented in the following section.

4 Results and discussion

4.1 NO calibration source

The Model 408 Nitric Oxide Calibration Source was first introduced as a product by 2B Technologies in 2007 but has not been described in the scientific literature. Applications of this highly portable NO calibrator have been lim-

ited primarily because users need an instrument that also calibrates for NO₂ measurements. The photolytic NO generator described here has since been used in the 2B Technologies Model 211 Scrubberless Ozone Monitor, wherein NO serves as a gas-phase scrubber, and more recently the Model 714 NO₂/NO/O₃ Calibration Source. The NO generator is identical in all three instruments – the only differences being the N₂O flow rates used and the degree of dilution. Since, as discussed in Sect. 2.1, 1 atm of N₂O is optically thick at 184.9 nm, the flow rate of N₂O through the chamber is not critical. Because essentially every photon is absorbed, the production rate of NO is determined only by the lamp intensity – a low flow rate of N₂O through the chamber produces the same number of molecules of NO per second as a high flow rate. The effect of changing the N₂O flow rate is only to change the total flow into which the NO produced is diluted, which is small since the N₂O flow rate is only 1 %–2 % of the total flow. Optical opacity was verified experimentally by using the NO calibration source in a Model 714, varying the N₂O flow rate through the photolysis chamber from 5 to 50 cm³ min⁻¹, and setting the lamp intensity to output a constant 400 ppb of NO. The resulting NO mixing ratios measured are given in Table 1. As is readily apparent, there is no observable dependence of the NO concentration produced on the flow rate of N₂O within the measured uncertainties. Due to this invariance with N₂O flow, this flow rate is often set based on the balance between N₂O usage and the response time to a change in NO concentration. Faster flow rates result in a quicker flush time of the photolysis cell and lead to more rapid changes in NO concentration. For example, in the 2B Technologies Model 211 Scrubberless Ozone Monitor, only a constant amount of excess NO is required, and thus a small flow rate (10–15 cm³ min⁻¹) serves to conserve N₂O usage. However, in both the NO calibrators (the Model 408 and 714), higher flow rates (40–60 cm³ min⁻¹) are used to allow for more rapid concentration changes (< 1 min).

The NO calibration source is typically configured to deliver a calibration gas at a volumetric flow rate of 2.5 to 3.0 L min⁻¹. A change in the flow rate of diluent air would be expected to change the concentration of NO produced. However, the instrument continuously measures the total mass flow rate and adjusts the lamp intensity to compensate for changes in dilution so as to produce a constant output mixing ratio of NO. In typical operation, these intensity adjustments are small as the total flow rate is usually rather constant (within ±5 %). However, the intensity vs. total flow rate feedback loop was tested by measuring the NO output (at 200 ppb) as the total flow rate was varied between 2.2 and 4.5 L min⁻¹. There was no measurable difference in the NO mixing ratios (< ±2 % or 4 ppb; data not shown).

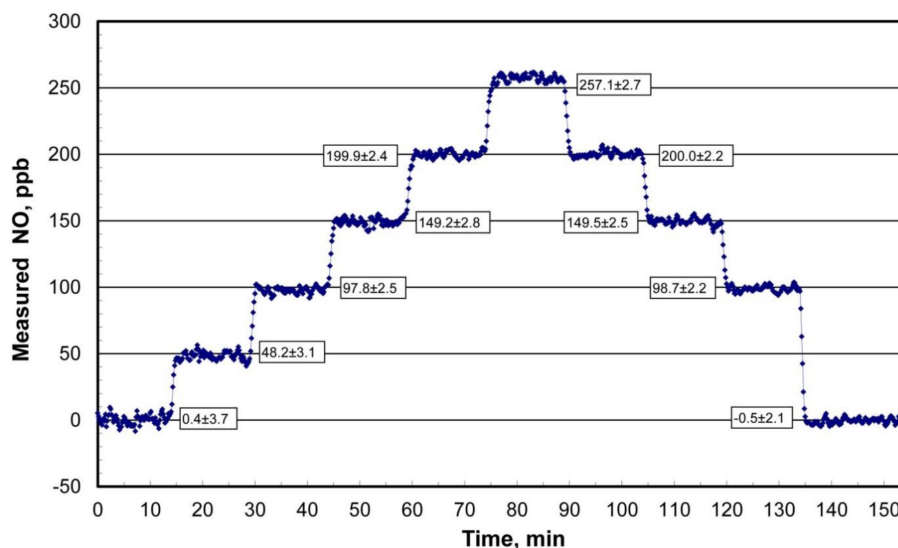


Figure 4. Measured output from the Model 408 NO Calibration Source for programmed NO mixing ratios of 0, 50, 100, 150, 200, 250, 200, 150, 100, and 0 ppb and time steps of 15 min. Average concentrations after the 1 min step changes are shown along with standard deviations.

4.1.1 Precision, accuracy, stability, and reproducibility of the photolytic NO calibration source

An example of the NO output concentration of a Model 408 NO Calibration Source as measured with a recently calibrated 2B Technologies Model 400 Nitric Oxide Monitor™ (2B Technologies, Boulder, Colorado; Birks and Bollinger, 2006) over 2.5 h is shown in Fig. 4. The NO calibrator was programmed to run through a series of 10 target concentration steps of 0, 50, 100, 150, 200, 250, 200, 150, 100, and 0 ppb with a hold time of 15 min at each concentration. As can be seen the rise (or fall) time between steps is on the order of 1 to 1.5 min (samples are every 10 s) before stable NO outputs are established. Precisions (1σ) averaged 2.6 ppb at nonzero target concentrations and were not significantly different from the 2.9 ppb average of precisions of the first and last steps with the lamp off. This implies that the observed variability was almost entirely due to the NO monitor used – thus, NO output concentrations from the photolytic calibrator are stable to considerably better than ± 2.6 ppb. All output concentrations agreed with the target concentrations within 1 standard deviation, with the exception of the 250 ppb level at which the measured output concentration was higher by 7.1 ± 2.7 ppb or 2.8 %.

Figure 5 shows the temporal behavior and stability of NO produced from the NO calibration source over the entire usable time period of an 8 g N_2O cartridge (~ 160 min) for a set point of 800 ppb. The small amount of NO_2 produced (NO_2/NO of 1.6 %) is also shown (note the break in the y axis). Both NO and NO_2 were measured using a 2B Technologies Model 405 $\text{NO}_2/\text{NO}/\text{NO}_x$ monitor. There is a slight increase in the measured NO (4.4 ppb h^{-1}) with a total NO increase of ~ 12 ppb (1.5 % of the 800 ppb set

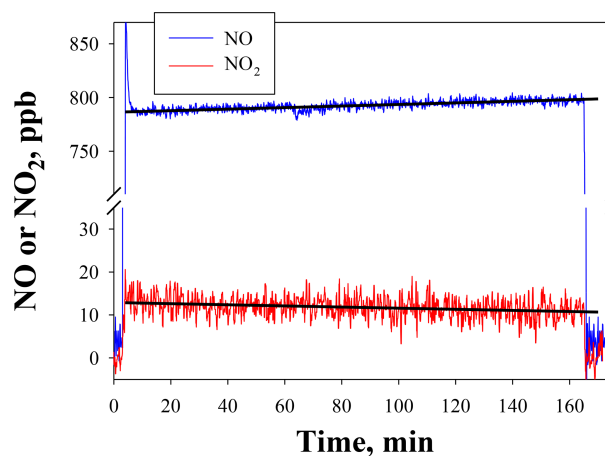


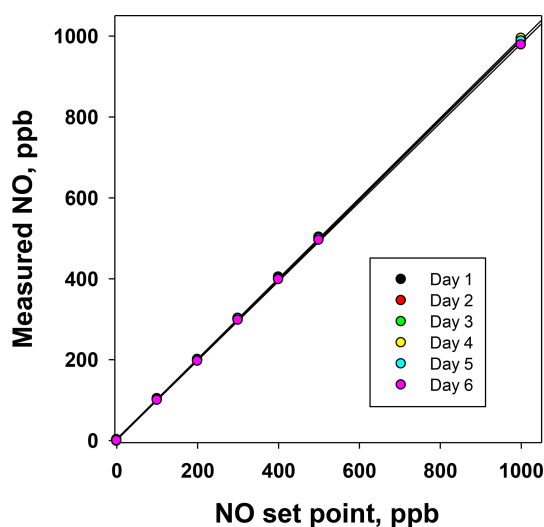
Figure 5. NO and NO_2 output by the NO calibration source over the time to use an entire 8 g N_2O cartridge. The NO set point was 800 ppb. Lines drawn are linear fits to data between 15 and 165 min.

point) over the lifetime of the N_2O cartridge. A similar experiment at a set point of 200 ppb (data not shown) gave a similar percentage increase (3.8 ppb or +1.9 %). However, when using a 27 kg N_2O cylinder with similar stated purity (99.5 %), no increase in NO was measured (< 0.3 % at a set point of 800 ppb) over the same 2.7 h time frame. This suggests that the small 1 %–2 % increase in the NO signal may arise from preferential volatilization of the small amount of impurities in the N_2O (likely N_2 and O_2), leading to a slightly more purified N_2O over the lifetime of the 8 g cartridge. This would be expected to be very slow and unobservable when using a larger cylinder. Overall this suggests that the NO calibration source is stable to about 2 % over the 2 to 3 h

Table 2. Results from the 6×6 validation over six consecutive days for the NO photolysis source in the 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source.

NO set point (ppb)	NO measured Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Average (ppb)	SD (ppb)
1000	988.9	986.4	988.1	994.2	987.4	978.1	987.2	5.2
500	498.1	498.2	501.1	502.6	499.6	495.2	499.1	2.6
400	400.2	400.2	402.4	403.8	401.2	397.8	400.9	2.1
300	299.0	299.2	301.6	302.0	301.2	297.3	300.1	1.8
200	197.0	197.1	199.0	200.1	199.1	196.1	198.1	1.6
100	101.7	101.3	103.0	103.0	102.7	99.6	101.9	1.3
0	-1.5	-0.1	1.0	1.5	2.1	-0.6	0.4	1.4
Intercept	1.3	2.2	4.0	3.6	4.2	2.2	2.9	1.2
Slope	0.9897	0.9866	0.9872	0.9930	0.9856	0.9791	0.9869	0.004
R ²	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	

SD = standard deviation.

**Figure 6.** Plots of the NO measured (ppb) from the NO photolysis source of a 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source vs. the NO set point on six consecutive days.

time span needed for conducting calibrations regardless of the N₂O source.

NO₂ showed a corresponding decrease of -0.8 ppb h^{-1} (total of 2.2 ppb) over the course of depleting the 8 g N₂O cartridge (see Fig. 5). This small decrease is within the measurement precision of the NO₂ analyzer. No decrease in NO₂ could be detected at lower NO set points (e.g., 200 ppb) or when using a larger cylinder. Therefore, the NO₂ produced at a given NO set point is essentially constant over several hours and would have a minimal effect ($< 1 \%$) on the NO₂ calibrations described in Sect. 4.2.

Using the NO calibration source from a Model 714 NO₂/NO/O₃ calibrator ($S/N = 1014$), a 6×6 verification was undertaken to ascertain whether it could be used as a

traceable transfer standard for NO. Figure 6 shows the calibration plots obtained over 6 d using a recently calibrated 2B Technologies Model 405 NO₂/NO/NO_x monitor to detect the generated NO. Due to the high reproducibility, the results are also given in tabular form (Table 2), including the measured slopes, intercepts, and correlation coefficients from a linear regression. As can be seen, day-to-day variations are not statistically different from the precision of the measuring analyzer ($\sim \pm 2 \text{ ppb}$) with the exception of the highest (1000 ppb) point, which has a slightly higher standard deviation ($\pm 5.2 \text{ ppb}$). However, this is still a precision that is $< 1 \%$ of the measured value. From the linear regressions it can be seen that the standard deviation in the intercepts is 1.2 ppb, below the 1.5 ppb required of Level 4 ozone transfer standards. Also, the standard deviation in the slopes is only ± 0.004 or 0.4 %, which is substantially below the required level of 3.7 %. Therefore, it is obvious that the photolytic NO calibrator is highly stable and reproducible, and it successfully meets the same criteria set forth for the establishment of an ozone transfer standard.

4.1.2 Effects of temperature, pressure, and humidity on the photolytic NO calibration source

In order to test for the effect of temperature on the NO concentrations produced, the output mixing ratio of a Model 408 NO Calibration Source was measured using a program consisting of steps of 0, 50, 100, 150, and 200 ppb at ambient temperatures of 23.5 and at 8.5 °C. Mixing ratios were measured using a 2B Technologies Model 400 NO monitor. The low temperature was achieved by placing the calibrator in an ice chest, allowing it to cool, and then powering the instrument on. The output was directed out of the ice chest and sampled by the NO monitor at room temperature. At start-up, the instrument showed that the photolysis chamber was at 8.5 °C. Results of measurements at the two temperatures are

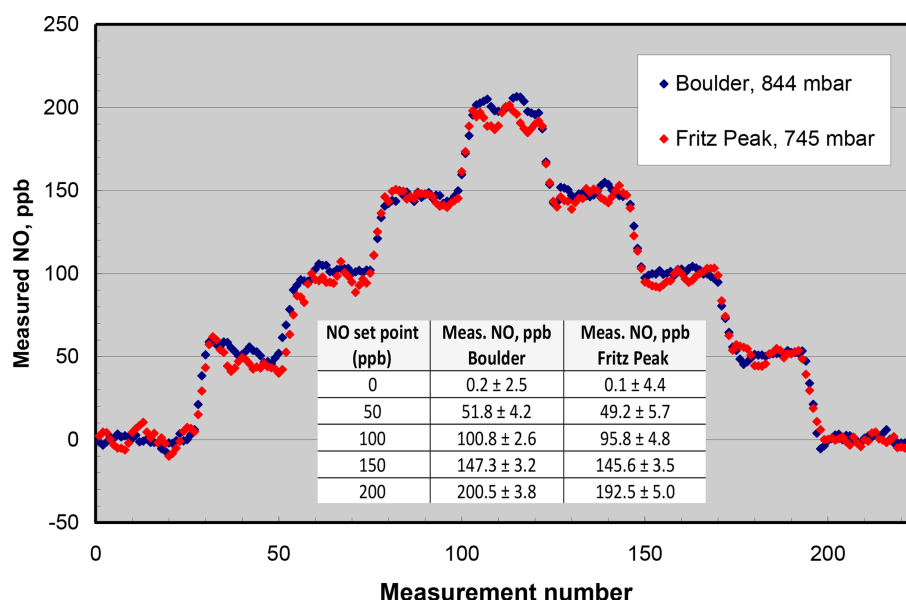


Figure 7. NO measured from the output of a Model 408 NO Calibration Source in Boulder, CO (elevation 1.6 km), and Fritz Peak, CO (elevation 2.7 km). The inset panel gives the averages and standard deviations (1σ) at the different NO set points of the calibrator. Measurements were made every 10 s.

Table 3. Summary of the effect of temperature on the NO output concentration from a 2B Technologies Model 408 NO Calibration Source.

Target NO, ppb	Measured NO, ppb $T = 23.5^\circ\text{C}$	Measured NO, ppb $T = 8.5^\circ\text{C}$	Difference ppb
0	0.0 ± 2.8	0.0 ± 3.4	0.0
50	53.4 ± 2.9	55.9 ± 4.5	2.5
100	101.0 ± 2.7	101.1 ± 4.6	0.1
150	149.7 ± 2.8	151.8 ± 5.9	2.1
200	201.0 ± 1.9	198.5 ± 2.9	-2.5
Average difference			0.5 ± 2.0

summarized in Table 3. Data at the two temperatures agree very well within the standard deviation of the measurements.

The average difference between measurements at the two temperatures is 0.5 ± 2.0 ppb, i.e., well within the noise of the measurements. The average precision at 8.5°C was ± 4.3 ppb compared to ± 2.6 ppb at 23.5°C . Although a large fraction of this imprecision can be attributed to the 2B Technologies Model 400 Nitric Oxide monitor, it does appear that there is an increase in the measured standard deviations at the lower temperature from the output of the calibrator. The increased power draw from heating the photolysis chamber may affect the Hg lamp stability, causing this decrease in precision at lower temperatures. Thus, it appears that there is no significant dependence of the output concentration of the NO calibrator on temperature in the range 8.5 to 23.5°C ; however, there is small loss of precision at lower temperatures.

Lack of significant dependence of the NO calibrator on ambient pressure has been confirmed many times by measuring the output NO mixing ratio of instruments calibrated in Boulder, Colorado (1.6 km elevation, 844 mbar pressure), and shipped to other locations, typically at much lower elevations. In order to extend the range of pressure testing to lower pressures, the NO output was measured in Boulder and at Fritz Peak (2.7 km elevation, 745 mbar) near Rollinsville, Colorado. The NO calibrator and Model 400 NO monitor were battery-powered at the Fritz Peak location. Again, concentrations from 0 to 200 ppb were measured at the two locations (see Fig. 7). As can be seen in the figure, within the precision of the measurements, there is no discernible difference between the measurements at the two different altitudes. Linear regressions of the measured NO values vs. NO set point (given in the inset panel in Fig. 7) indicate a slightly lower slope ($\sim 3\%$) at the higher-elevation site. If there is a slight falloff in output concentration at high altitudes, it could be explained by the lack of optical thickness within the N_2O photolysis chamber due to the reduced pressure. The pressure and therefore molecular concentration are only slightly higher in the photolysis chamber than that of ambient air, so the fraction of 185 nm light absorbed decreases slightly as ambient pressure decreases.

Since pure N_2O is the only gas passing through the photolysis chamber, ambient humidity should have no effect on the NO output rate. Humidity can only affect the overall NO output by affecting the output of the airflow mass flowmeter, causing small errors in the calculated dilution. Because water has a different heat capacity than air ($\sim 30\%$ larger), an airflow saturated with water vapor at 1 atm and 25°C (sat-

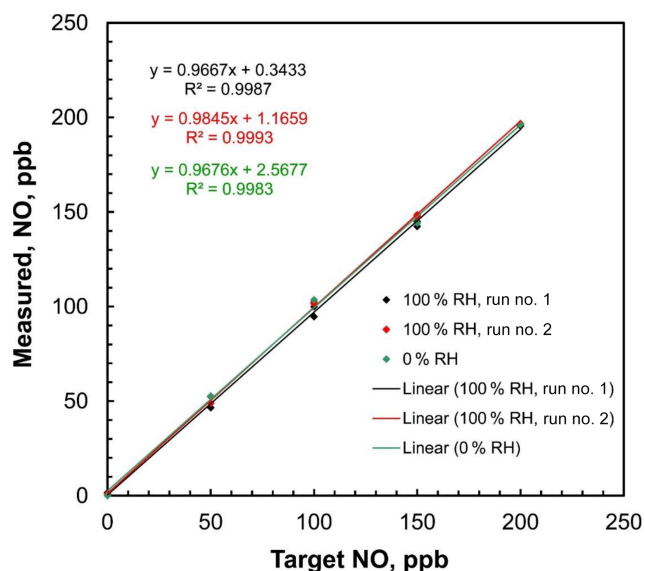


Figure 8. Linear regressions of measured NO concentrations vs. target concentrations of the 2B Technologies Model 408 NO Calibration Source with dilution air containing both 0 % and 100 % relative humidity at 23.5° C.

uration vapor pressure 31.7 mbar, H₂O mole fraction 3.1 %) has a heat capacity that is about 0.9 % higher than that of dry air. Since the mass flow rate measurement is proportional to heat capacity and the NO calibration source adjusts the lamp intensity to produce NO in proportion to the measured total mass flow rate, one could expect a small (~ 1 %) error in the output mixing ratio. This would likely be within the uncertainties of most analytical NO monitors. The effect of humidity on the NO calibration source output was tested by using a 2B Technologies Model 400 Nitric Oxide Monitor to measure step profiles of 0, 50, 100, 150, and 200 ppb at both 0 % and 100 % relative humidity (RH). The target humidities were generated by supplying the air inlet of the NO calibration source with zero air from a compressed gas cylinder (0 % RH) and then humidifying that flow to ~ 100 % RH by passing it through a Nafion tube submerged in warm water. The 100 % RH experiment was run twice. Ambient temperature was 23.5 °C. For all experiments, the relative humidity was measured using a Cole–Parmer model 37951-00 thermohygrometer inserted in line with the supply airflow. Plots of measured NO concentration vs. target concentration are shown in Fig. 8. The slopes of the regression lines were 0.968 at 0 % RH and 0.967 and 0.985 for two sequential calibrations made at 100 % RH. Within measurement error, there was no statistical difference between dry air and 100 % RH air, confirming the expectations that any humidity effect is within the statistical uncertainty of the analyzer.

4.2 NO₂/NO/O₃ calibration source

The 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source is a combination of a Model 306 Ozone Calibration Source and a Model 408 NO Calibration Source (Sect. 4.1) that allows for the generation of calibrated mixing ratios of either O₃, NO, or NO₂ (the latter via the GPT Reaction R3). The NO source is identical to the one described in Sects. 3.1 and 4.1, except the N₂O flow rate is typically lowered to around 40 cm³ min^{−1} compared to the earlier Model 408 NO Calibration Source. As noted in Sect. 3.1, the NO output is not affected by the choice of N₂O flow rate due to the optical opacity of the N₂O. The ozone calibration source in the Model 714 differs from that described previously for the Model 306 (Birks et al., 2018b) in that only a small fraction of the airflow passes through the photolysis cell (described in Sect. 2.2). For the generation of NO₂, the outputs of the NO and O₃ photolysis cells are mixed and allowed to react within a Teflon reaction volume (described in Sect. 3.3) to quantitatively convert O₃ (which is lower in concentration) to NO₂ before final dilution to the prescribed set point concentration.

4.2.1 Water vapor effects and verification of the modified photolytic O₃ calibration source

Section 4.1.2 showed that the effects of water vapor are very small (< 0.5 %) on the NO output from dry air up to air saturated with water vapor. Since the NO photolytic generator is unchanged in the NO₂/NO/O₃ calibrator, it also shows minimal effects due to changing humidity. However, the stand-alone ozone calibrator (Model 306) operates using rather different flow rates (and therefore residence times) than the ozone photolysis cell in the NO₂/NO/O₃ calibrator described here. Birks et al. (2018a) found that the chemical loss of ozone due to OH and HO₂ radicals (generated either by water photolysis at 184.9 nm or by ozone photolysis and subsequent reaction of O(¹D) with H₂O) was a negligible effect on the ozone output in the stand-alone ozone calibrator (the Model 306). The only effect of water vapor was the small dilution of the O₂ precursor by water vapor in the photolysis cell that results in a small reduction of the ozone generated (up to ~ 2 %). But the flow rate through the ozone photolysis cell in the NO₂/NO/O₃ calibrator is ~ 60 times slower than in the stand-alone Model 306 (50 cm³ min^{−1} compared to 3 L min^{−1}). Therefore, the longer residence time generates considerably higher concentrations of ozone, resulting in higher concentrations of HO_x (OH and HO₂) radicals when water vapor is present, which, in turn, can catalyze ozone depletion.

Modeling of the photolysis chemistry using the reaction kinetics model described in Birks et al. (2018b) suggested that at a relative humidity of 25 % (at 298 K), the ozone output in the NO₂/NO/O₃ calibrator would be reduced by 3.4 % when attempting to output 500 ppb (a loss of 17 ppb). The ozone loss was also nonlinear – a smaller percent loss at

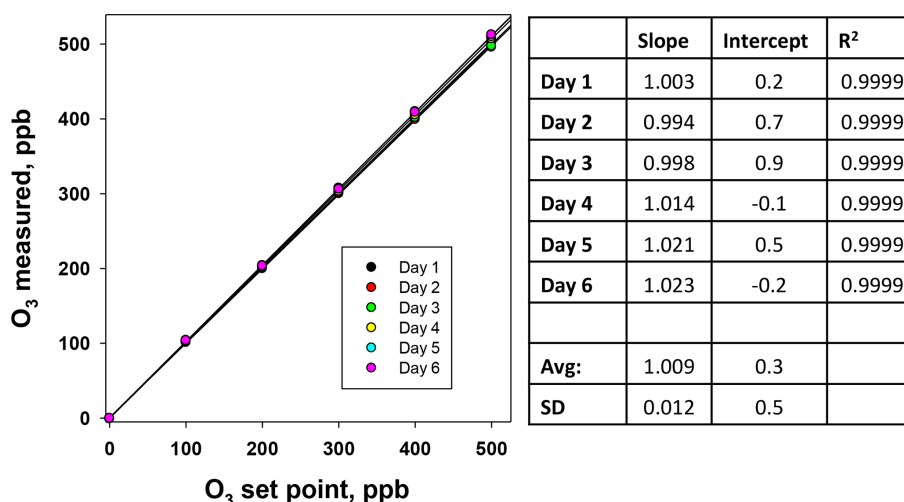
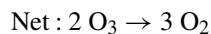


Figure 9. Plots of the O₃ measured vs. the O₃ set point in a Model 714 NO₂/NO/O₃ calibrator on six consecutive days. Regression slopes and intercepts are given in the panel on the right.

lower O₃ set points. This is due to the nonlinear nature of the HO_x catalytic ozone destruction cycle that is driven by the high concentrations of ozone in the photolysis chamber.



Experimental results showed that at low RH (RH = 6 %–10 %), the observed decreases in ozone output in the NO₂/NO/O₃ calibrator relative to dry air (RH < 1 %) were on the order of 2 %–3 % for an output concentration of 500 ppb (i.e., 11 to 16 ppb). This is in reasonable agreement with the ~1.5 % decrease predicted by the photochemical model. However, at a more typical relative humidity level of 25 %, observed ozone decreases were significantly greater than those predicted. As mentioned above, predicted losses suggested a 3.4 % loss at 500 ppb; however, observations ranged from 6 % to 12 % (34 to 60 ppb). Therefore, it appears there is even greater chemical loss than expected. As a result of the very nonlinear nature of the chemistry when water vapor was present, it was necessary to dry the air prior to entering the ozone photolysis chamber of the NO₂/NO/O₃ calibrator. An 80 cm³ silica gel trap (United Filtration, IACH-38-150-80-SG) was added in line to reduce the RH to < 1 % in the O₃-precursor airflow (see Fig. 3). A relative humidity and temperature sensor was also placed just before the ozone photolysis chamber to monitor the RH and warn the user if the humidity rose to significant levels (RH > 2 %) such that ozone outputs could be impacted by more than 1 %. At the typical flow rate of 50 cm³ min⁻¹, this trap maintained the RH below 2 % for more than 24 h of continuous operation. It should also be noted that once the air for the ozone photolysis has been dried, there is no significant amount of water

vapor present in the GPT reaction zone, as the flow consists only of dry air/O₃ and dry N₂O/NO, thereby eliminating any possibility of water vapor affecting the GPT chemistry.

After the insertion of the dryer, a 6 × 6 verification was performed for this slightly modified ozone calibration source used in the NO₂/NO/O₃ calibrator. Ozone concentrations were measured with a 2B Technologies Model 205 Ozone Monitor that had been recently calibrated relative to our primary ozone standard (Sect. 3.3). Calibration plots and results of the linear regressions are shown in Fig. 9. Both the standard deviations in the slopes and intercepts are well within the U.S. EPA transfer standard requirements ($\sigma_{\text{slope}} < 3.7 \%$, $\sigma_{\text{intercept}} < 1.5 \text{ ppb}$), thereby confirming that the adaptations made in the O₃ photolysis system for use in the NO₂/NO/O₃ calibrator do not adversely impact its use as an O₃ transfer standard.

4.2.2 Precision, accuracy, and reproducibility of the NO₂ calibration source

Figure 10 shows mixing ratios of NO and NO₂ produced by a Model 714 NO₂/NO/O₃ Calibration Source (as measured by a Model 405 NO₂/NO/NO_x monitor) for an automated sequence of several NO₂ concentrations. The NO set point remained constant at 1000 ppb from 5 to 80 min during the sequence. Six different ozone concentrations (i.e., equal to the target NO₂ concentrations) were then generated (set points 0, 80, 180, 280, 380, 480 ppb of ozone), each lasting 10 min (note that the use of 480 ppb instead of 500 ppb allows for visual clarity in the time series graph at the highest concentration). As seen in the figure, NO₂ increases as NO decreases due to its reaction with ozone. The time required to reach a new set point is typically < 45 s. The measured concentrations averaged over the last 5 min of each step are shown in the panel to the right of the figure along with ob-

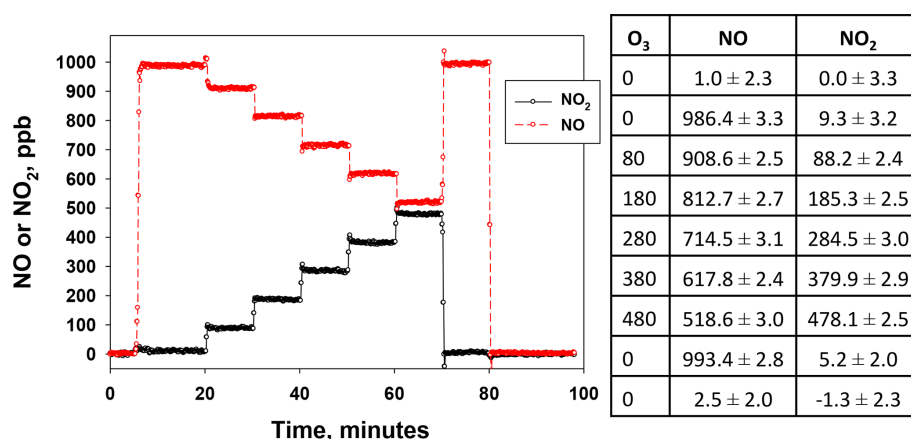


Figure 10. NO and NO₂ measured from the output of a Model 714 GPT calibrator. At time 5 min, NO was set to 1000 ppb. At time 20 min, ozone was added and set points were varied between 80 and 480 ppb in steps of 100 ppb (this allowed for visual clarity of both NO and NO₂ at the highest [O₃]). O₃ was changed every 10 min. Finally, data for [O₃] = 0 and [NO] = 0 were repeated for completeness. NO and NO₂ were measured using a calibrated 2B Tech Model 405.

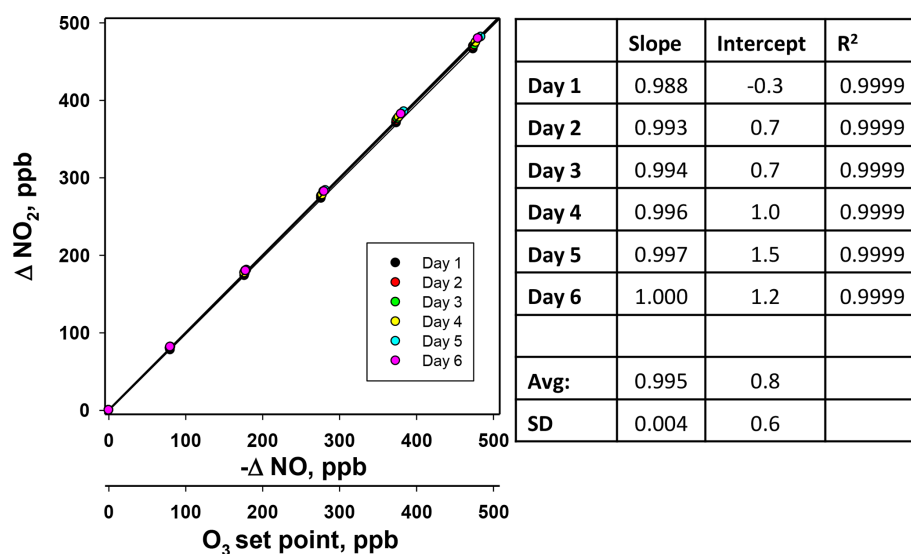


Figure 11. Calibration curves for NO₂ made on six consecutive days. $\Delta\text{NO}_2 = \text{NO}_2 - \text{NO}_2(\text{O}_3=0)$ and $-\Delta\text{NO} = \text{NO}(\text{O}_3=0) - \text{NO}$ at each ozone set point. Slopes, intercepts, and correlation coefficients are reported in the panel to the right.

served precisions (1σ). Note that the precisions for steps 2–8 are nearly the same as those in steps 1 and 9, in which no reagent gases were being produced. This suggests that the observed precisions are limited by the measuring analyzer and that the actual precisions of the output NO and NO₂ concentrations from the calibrator are lower ($\leq \pm 2.8$ ppb for NO, $\leq \pm 2.6$ ppb for NO₂, the average precision from Fig. 10).

Also note the small amount of NO₂ produced by the NO photolysis source (9.3 ppb, $\sim 0.9\%$ of the NO; see Fig. 10). As discussed in Sect. 4.2.3, this NO₂ is typically small ($\leq 2\%$ of the NO produced), and it is also constant over a given calibration with a set NO concentration. Therefore, a step in which NO is present with no accompanying O₃ must be

included to measure and subtract out this small amount of photolytically produced NO₂.

Figure 11 shows the results of a 6×6 verification for NO₂ produced by the Model 714 NO₂/NO/O₃ calibrator along with the results from the linear regressions. As seen in the figure, plots were extremely linear (high R^2), with slopes near unity, and reproducible from day to day. Relative standard deviations of the slope and intercepts were 0.4 % (compared with the required $< 3.7\%$) and 0.6 ppb (compared with the required < 1.5 ppb), respectively. Thus, all three reactants (O₃, NO, and NO₂) produced in the Model 714 NO₂/NO/O₃ calibrator pass the statistical tests established for a Level 4 ozone transfer standard.

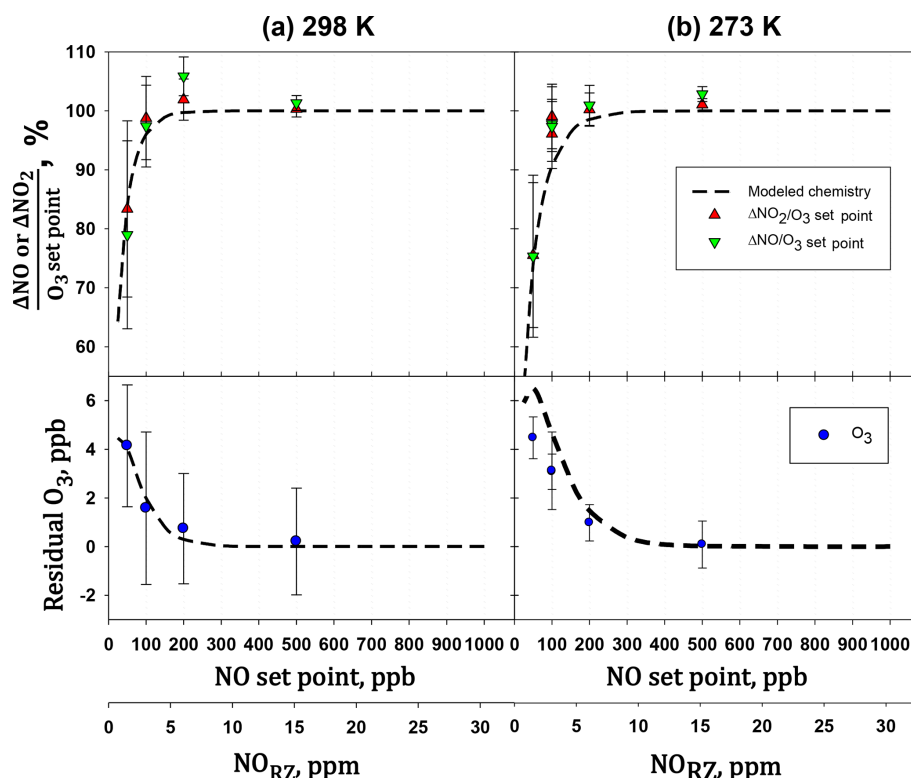


Figure 12. Plots of the amount of NO consumed ($\Delta\text{NO}/\text{O}_3$ set point) and NO₂ formed ($\Delta\text{NO}_2/\text{O}_3$ set point) vs. the NO set point. A second x axis of the NO concentration in the reaction zone (NO_{RZ}) is also given as a reference to Fig. 1. Measurements were made with the reaction zone at (a) 298 K and (b) 273 K.

4.2.3 Completeness of reaction and effects of temperature and pressure

Complete conversion of ozone to NO₂ is not critical if NO is measured as well (then $-\Delta[\text{NO}]=\Delta[\text{NO}_2]$ and the NO₂ signal can be calibrated relative to NO); however, the conversion efficiency is important for cases in which the NO₂ produced must be compared to the ozone generated by the calibrated photolysis source. In a general sense, complete conversion also simplifies the chemical system and reduces the chance for undesirable chemistry. It is also important to limit the amount of ozone exiting the calibrator in the case of NO_x analyzers that use a photolytic NO₂ converter as the conversion efficiency of these converters is known to depend upon ozone concentration (see, e.g., Pätz et al., 2000). The modeling exercise described earlier (see Fig. 1) suggests $> 99\%$ reaction of the ozone for NO output concentrations greater than about 130 ppb (or ~ 4 ppm in the reactor) at 1 atm (1013 mbar), 298 K, and a reaction time of 4 s. Although the temperature and pressure do not affect the output mixing ratios from the photolytic sources of ozone and NO, these factors can impact the GPT chemistry occurring within the reaction zone. Reaction (R3) has a rather substantial activation energy ($E/R = 1500 \text{ K}^{-1}$; Burkholder et al., 2015), resulting in a smaller rate coefficient with decreasing temper-

ature. Lower pressures have the effect of reducing the overall number density of the reactants, which is key to driving Reaction (R3) to completion. Although the photolytic sources (O₃ and NO) described here output constant mixing ratios with varying pressure, the number density (molec cm^{-3}) of ozone and nitric oxide do vary with overall pressure changes.

The extent of reaction was tested by measuring all three components (O₃, NO, and NO₂) for a variety of set point concentrations from the calibrator ([NO] varied from 50 to 500 ppb, [O₃] from 24 to 240 ppb) while maintaining $[\text{NO}] > 2 \times [\text{O}_3]$. Changes in O₃, NO, and NO₂ were measured relative to when $[\text{O}_3] = 0$ (i.e., $\Delta\text{NO} = \text{NO}_{\text{meas}, \text{O}_3 > 0} - \text{NO}_{\text{meas}, \text{O}_3 = 0}$). Table 4 shows the results from two experiments conducted at room temperature (25 °C, 298 K) and at 0 °C (273 K). Both experiments were conducted at a total pressure of 830 mbar (ambient pressure at our location in Boulder, Colorado, USA). Note that total pressure closer to 1 atm (as would be typical) results in larger number densities, thus driving a higher extent of reaction. The temperature of the reaction zone was maintained by wrapping the reaction zone tubing in a flexible ice pack. The temperature was measured by attaching two thermocouples to the outside of the reaction zone tubing (one on each end). The extent of the conversion of NO to NO₂ can be quantified by looking at either the loss of NO ($-\Delta\text{NO}/\text{O}_3$ generated) or the forma-

Table 4. O₃, NO, and NO₂ measured at the output of a Model 714 for the NO and O₃ set points given in columns 1 and 2. The pressure was 830 mbar. All units are in parts per billion.

NO set point	O ₃ set point (= NO ₂)	ΔNO ^a	ΔNO ₂ ^a	ΔO ₃ ^a	Predicted ^b O ₃ left
298 K					
500	240	243.2 ± 2.9	240.7 ± 3.2	0.2 ± 2.2	< 0.1
200	96	101.6 ± 3.3	97.8 ± 3.4	0.7 ± 2.3	0.2
100	48	46.8 ± 3.0	47.4 ± 3.3	1.6 ± 3.1	1.8
50	24	19.0 ± 3.3	20.0 ± 3.0	4.1 ± 2.5	3.8
273 K					
500	240	246.8 ± 3.1	242.5 ± 2.4	0.1 ± 1.0	< 0.1
200	96	96.9 ± 3.3	96.2 ± 2.7	1.0 ± 0.7	1.3
100	48	46.9 ± 3.0	47.5 ± 2.6	3.1 ± 0.7	4.3
50	24	18.1 ± 2.5	18.1 ± 2.5	4.5 ± 0.9	6.2

^a Concentration difference measured relative to when [O₃] = 0 (no ozone produced).^b From a model of second-order kinetics of the reaction chamber chemistry at 830 mbar.

tion of NO₂ (ΔNO₂/O₃ generated). Here, the O₃ generated is the original set point of the ozone generator on the GPT calibrator. Complete conversion results in -ΔNO=ΔNO₂=O₃ set point (and thus -ΔNO/O₃ set point=ΔNO₂/O₃ set point=1). Figure 12 displays the results graphically by plotting the measured ΔNO/O₃ and ΔNO₂/O₃ (as percentages) vs. the initial NO set point of the GPT calibrator. A second *x* axis is included, indicating the initial NO mixing ratio present in the reaction zone (RZ), which can be used as a reference to Fig. 1. The only difference between the modeled profiles in Fig. 12 and those from Fig. 1 is that here the model was run under the experimentally observed temperatures and pressures. Our measured results agree quite well with modeling of the chemistry. Complete consumption (> 98 %) of the ozone was observed at NO set points above 200 ppb (~ 6 ppm in the RZ) at the lowest temperature (273 K). At room temperature, this level drops to near 100 ppb (~ 3 ppm in RZ) within the errors of the measurements. Note that at the lowest initial NO and O₃ (NO set point 50, O₃ set point 25) where there is measurable residual ozone (~ 4–5 ppb), ΔNO₂ is still equivalent to -ΔNO as expected from the stoichiometry of Reaction (R3). However, the percent error is considerably larger (~ 15 %) due to the smaller concentration changes and the measurement precision of the Model 405 NO₂/NO/NO_x analyzer. It also bears reiterating at this point that it is critical to maintain at least a factor of 2 greater NO to drive the NO/O₃ reaction to completion. Currently the operating firmware of the Model 714 does not allow [NO]/[O₃] < 2. Under these conditions, a general recommendation is that an NO set point of ≥ 200 ppb ensures complete ozone consumption.

5 Conclusions

In the present study we have described two different portable calibration devices that can be used to calibrate air quality monitors. The first uses the photolysis of nitrous oxide to reproducibly generate known concentrations of NO (commercially available as the 2B Technologies Model 408 NO Calibration Source). The second combines this NO generator with a photolytic ozone generator (by the photolysis of air), resulting in a single instrument capable of delivering calibrated mixing ratios of either NO, NO₂, or O₃ (the 2B Technologies Model 714 NO₂/NO/O₃ Calibration Source). The chemistry underlying the generation of each reactant was discussed, and experimental results verified modeling predictions of the chemical systems involved.

Since only a small amount of N₂O is required, an 8 or 16 g cartridge can be utilized as the source gas in either calibrator, thereby eliminating the need for larger (and more expensive) gas calibration mixtures. This makes for the high degree of portability that is often necessary for the calibration of field-based analyzers that cannot easily be removed from service. Furthermore, we have shown that both the Model 408 and 714 produce calibrated mixing ratios that are independent of environmental variables such as temperature, pressure, and humidity. This is also an advantage when operating in field situations in which these variables are not controlled.

Both the NO and NO₂/NO/O₃ calibration systems are initially compared to NIST-traceable calibration standards (either NIST SRM gas mixtures or NIST-traceable ozone generators and/or photometers) to establish the relationship between photolytic lamp intensity and output mixing ratios of NO, NO₂, and O₃. Once this is known, variation of the photolytic lamp intensities can reproducibly generate known concentrations of these reactants. The photolytic calibration systems were shown to deliver output mixing ratios that were

well within the guidelines required by the U.S. EPA to serve as transfer calibration standards for these important pollutants both in terms of accuracy and precision. Therefore, these calibrators can facilitate the calibration of analyzers at field locations where maintaining the high degree of accuracy and precision required by air quality compliance monitoring is challenging.

Data availability. Experimental data presented here are available upon request to the authors (johnb@twobtech.com).

Author contributions. JWB, AAT, PCA, CJW contributed design and engineering of the calibrators described here. JWB, AAT, PCA, CJW, SS and BC were involved in experimental testing and JWB, AAT and CAE were involved in the manuscript preparation.

Competing interests. JWB, AAT, PCA, CJW, SS, BC, and CAE are employed by 2B Technologies, the manufacturer of the Model 408 NO Calibration Source™ and the Model 714 NO₂/NO/O₃ Calibration Source™ described in this paper.

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