Atmospheric
Measurement
Techniques
Discussions

Portable Calibrator for NO Based on Photolysis of N₂O and a Combined NO₂/NO/O₃ Source for Field Calibrations of Air Pollution Monitors

5   John W. Birks, Andrew A. Turnipseed, Peter C. Andersen, Craig J. Williford, Stanley Strunk, Brian Carpenter and Christine A. Ennis

2B Technologies, 2100 Central Ave., Boulder, CO 80301 USA

Correspondence to: John Birks (johnb@twobtech.com)

10

Abstract. A highly portable calibration source of nitric oxide (NO) based on 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 0-1,000 ppb with a precision and accuracy of better than the greater of 3 ppb or 3 % of

15   the target NO mixing ratio over a wide range of environmental conditions of ambient temperature (8.5-35.0 °C), pressure (745-1,015 mbar corresponding to 2.7-0.0 km elevation) and relative humidity (0-100 % RH). Combination of the NO calibration source with a previously described ozone calibration source based on 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

20   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 1,000, 500, and 1,000 ppb, respectively. This portable calibrator may serve as a convenient transfer standard for field calibrations of ozone and NOₓ air pollution monitors.

25

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 photochemical interactions between NOₓ (NO + NO₂) and organic

30   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," and 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 as well as

Atmospheric
Measurement
Techniques
Open Access

EGU

Discussions

35   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 treatment of adult pulmonary
arterial hypertension (Abman, 2013) and for persistent pulmonary hypertension in hypoxic term and near-

40   term newborns ("blue babies") (Clark et al., 2000). During this inhalation therapy, the concentration of NO
(typically 20 parts per million) must be continuously monitored during administration, and, very
importantly, the concentration of its toxic impurity NO_2 must also be continuously monitored and kept
below 3 parts-per-million by volume or ppm (preferably much lower due to the acute NO_2 toxicity).

In all these applications, accurate monitoring of NO, NO_2 and O_3 not only requires stable, robust

45   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 frequency 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

50   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 NO, NO_2 (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

55   for NO as well as the NO_2 conversion efficiency.

Calibration of monitors for NO is typically achieved by 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 part-per-billion by volume (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

60   gas such as nitrogen. This is because NO is thermodynamically unstable with respect to disproportionation
to form N_2O and NO_2 according to the equilibrium (Burkholder et al., 2015):

$$3 \, NO \rightleftharpoons N_2O + NO_2 \qquad \Delta H_{298}^o = \text{-157.6 kJ/mol} \qquad (1)$$
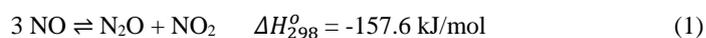
Although extremely slow in the gas phase, this reaction may be catalyzed on the interior walls of
compressed gas cylinders. The walls may be treated to slow the reaction, but the treatment is not always

65   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 (O_2) in the diluent gas can react to
oxidize NO to NO_2 according to the reaction (Atkinson et al., 2004):

Atmospheric
Measurement
Techniques
Discussions

$$2\,NO + O_2 \rightarrow\ 2\,NO_2 \quad k_2 = 2 \times 10^{-38}\ cm^6\ molec^{-2}\ s^{-1}\ at\ 298\ K \tag{2}$$
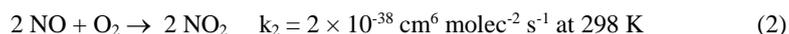
Because of reaction 2, compressed gas standards for NO cannot be made with air as the diluent. This is a
70   disadvantage since it is desirable to calibrate NO instruments using the same diluent gas as the gas being
analyzed, which most commonly is air. Nitric oxide standards are much more stable at high concentrations;
thus, it is common to prepare gas standards at a high ppm level in an unreactive diluent gas such as N_2 and
then dynamically dilute that standard with air prior to entering the analytical instrument being calibrated.
Even at high ppm levels, NIST-certified NO gas standards are typically only certified for 1-2 years.
75   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 flow meters,
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 a
80   NO_2 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 dynamic multipoint
calibration of NO_2 analyzers based on chemiluminescence (Ellis, 1975; U.S.-EPA, 1983): one based on a
permeation tube source of NO_2 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),
85   the difficulty of producing stable and reproducible NO_2 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/N_2 gas standard traceable to a NIST Standard Reference
Material (SRM) with NO_x-free air. The instrument is then calibrated for NO_2 by addition of varying
90   concentrations of ozone to an excess of NO. The 1:1 stoichiometric conversion of NO to NO_2 via the
reaction of NO with O_3 (Burkholder et al., 2015),

$$NO + O_3 \rightarrow\ NO_2 + O_2 \qquad k_3 = 1.9 \times 10^{-14}\ cm^3\ molec^{-1}\ s^{-1}\ at\ 298\ K \tag{3},$$

forms the basis of the calibration. Ozone concentrations are generated by photolysis of O_2 (typically from
air) and added to an excess of NO while allowing for sufficient mixing time so that reaction 3 goes to
95   completion. Nitrogen dioxide is calibrated based on the increase in NO_2 signal ($NO_x – NO$ in CL analyzers)
relative to the decrease in the NO signal (U.S.-EPA 2002). NO_2 formed should equal the NO consumed if
the NO_2 conversion efficiency to NO of the analyzer to be calibrated is unity. Incomplete conversion yields
$[NO_2]_{formed} < [NO]_{consumed}$, such that using the GPT reaction as a calibration incorporates a measure of the
conversion efficiency for analyzers where NO is monitored (i.e., CL analyzers). However, as with the case

100   above concerning NO, a portable means of NO_2 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 NO_2 based on variations of UV absorption (e.g., cavity ringdown and cavity-attenuated phase-shift spectroscopy) have become available (Paldus and Kachanov, 2006; Kebabian et al., 2005; Kebabian et al., 2008). However, many of these do 105   not measure NO. Therefore, for NO_2-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 NO_2. Note that the standard GPT calibration procedures can still be applied to methods that directly measure NO_2 and then indirectly measure NO (the opposite of the chemiluminescence technique) - such as in the long-path folded tubular photometer (FTP) developed in our 110   group that measures direct NO_2 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 N_2O (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 115   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 O_3 Calibration Source™ (described in Birks et al., 2018b) to produce a GPT NO_2 calibrator (the Model 714 NO_2/NO/O_3 Calibration Source™). Here we evaluate the feasibility of using this instrument as a portable transfer standard for NO_2 without the requirements of having a certified gas 120   standard and accurately calibrated mass flow controllers, thus increasing the portability of the transfer standard. Finally, we show that combining the O_3 calibrator and the NO calibrator into one instrument enables the user to perform robust calibrations for all 3 gases (NO_2, NO and O_3) using just one highly portable instrument suitable for laboratory or field applications.

2.   Theory of operation

125   *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 (N_2O) to produce NO. The vacuum UV emission lines of mercury near 184.9 nm are absorbed by N_2O to produce electronically excited oxygen atoms, O (^{1}D),

130 $$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad\qquad (4)$$

Atmospheric
Measurement
Techniques
Discussions
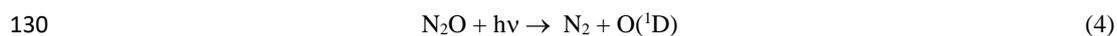
where hv symbolizes a photon of light. These highly energetic oxygen atoms react with N_2O with a near collisional reaction rate coefficient (k = 1.3×10^{-10} cm^3 molec^{-1} s^{-1}) to form three different sets of products

$$O(^1D) + N_2O \quad \rightarrow \quad 2\ NO \qquad \phi = 0.61 \pm 0.03 \qquad (5a)$$
$$\rightarrow \quad N_2 + O_2 \qquad \phi = 0.39 \pm 0.03 \qquad (5b)$$
135
$$\rightarrow \quad N_2O + O(^3P) \quad \phi < 0.01 \qquad (5c)$$
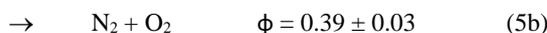
with the branching ratios (φ) shown (Burkholder et al., 2015). Since reaction 5a produces 2 NO molecules, the overall quantum yield for NO production is approximately 1.22. The NO calibration source is similar in design to our ozone calibrator (Birks et al., 2018b), as both make use of the 184.9-nm line of a low-pressure mercury lamp. An important fundamental difference is that the 184.9-nm absorption cross section for N_2O is approximately 14 times larger than that of O_2. The absorption cross section, σ, of N_2O at the
140   184.9-nm mercury emission line is ~1.4×10^{-19} cm^2 molec^{-1} (Creasey et al., 2000; Cantrell et al., 1997) compared to ~ 1×10^{-20} cm^2 molec^{-1} for O_2 (Yoshino et al., 1992, Creasey et al., 2000). Also, O_2 is only 21 % of the air that passes through the photolysis chamber in the ozone calibrator, while N_2O is supplied to the photolysis chamber by a source that is > 99 % N_2O. The result is that the N_2O gas absorbs the 185-
145   nm light ~70 times stronger than does O_2 in air. At 298 K and 1 atm, the molecular concentration, c, is 2.46 $\times 10^{19}$ 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/(σc), 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 (molecules cm^{-3} s^{-1}) depends almost entirely on the lamp intensity and is independent of flow rate (i.e., residence time in the photolysis
150   cell). The NO/N_2O 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 N_2O 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 NO_2 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
155   combine with NO via the reaction:

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (6)$$

(where M is a third body, most likely N_2O in this case). $O(^3P)$ atoms can arise from several possible sources. Nishida et al. (2004) report a quantum yield for $O(^3P)$ from N_2O photolysis of 0.005 ± 0.002 (i.e., NO_2/NO = 0.005/1.22 ~ 0.4 %). Quenching of $O(^1D)$ to $O(^3P)$ by N_2O (reaction 5c) likely contributes up to another
160   0.8 % (Vranckx et al., 2008 report a limit of φ $_{5c}$ < 0.01 at 298K). Oxygen (O_2), which is a typical N_2O impurity, can also photolyze to produce two $O(^3P)$ atoms. Even NO itself could be photolyzed at 184.9 nm (σ ~ 3×10^{-18} cm^2 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.

2.2 Ozone calibration

Our 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 our Model 306 Ozone Calibration Source™ (2B Technologies, Boulder, Colorado), a low-pressure mercury lamp produces calibrated concentrations of ozone by photolysis of oxygen in air:

$$O_2 + h\nu \rightarrow 2\,O \tag{7}$$

$$(O + O_2 + M \rightarrow O_3) \times 2 \tag{8}$$

$$\text{Net: } 3\,O_2 + h\nu \rightarrow 2\,O_3$$
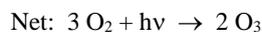
A key difference compared to the NO photolytic source described above (Section 2.1) is that for a 1-cm path length (and at 1 atm and 25 °C), the O_2 absorption in air is nearly optically thin (~ 5 % light absorbed). For an optically thin system, the mixing ratio of ozone produced depends linearly on 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 (Section 2.3) is that the flow rate through the photolysis cell is much lower (~ 50 cm^3 min^{-1} as opposed to 3000 cm^3 min^{-1}). This leads to longer residence times and higher ozone concentrations within the photolysis cell before subsequent dilution downstream. The minor repercussions associated with this modification are discussed in Section 4.

2.3 NO₂ 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. Calibrated concentrations of NO and O_3 are produced as described above. Calibration

Atmospheric
Measurement
Techniques
Open Access
Discussions

EGU

195 of NO_2 is accomplished via the gas phase titration (GPT) technique (reaction 3), 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 $[NO]_{consumed} = [NO_2]_{produced}$. A key difference in the Model 714 from the two individual calibrators is that reaction (3) must be carried out at high concentrations (ppm level) to drive reaction (3) to completion; therefore the NO and O_3 reagents are mixed

200 before subsequent dilution. Modeling the second-order kinetics of reaction (3) (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 seconds. 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 (3) to go to completion because one measures the consumption

205 of NO relative to the production of NO_2. However, residual ozone complicates the calibration protocol as reaction (3) 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 NO_2-only analyzers, it is critical to have > 99 % conversion as the NO_2 signal produced may be correlated to the loss of ozone (which is assumed to be at the calibrated target

210 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.
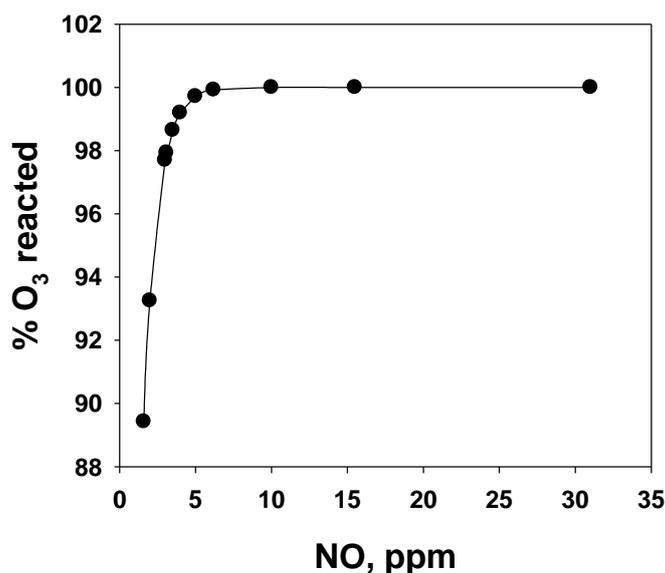

Figure 1. A plot of the percent of O_3 consumed vs. initial NO concentration for the conditions of $[NO] = 2 \times [O_3]$ and a total reaction time of 4 seconds.

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, NO_2 can react with the excess ozone to produce

215   NO_3,

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad\qquad (9)$$

and NO_3 can subsequently form N_2O_5 rapidly via (Bertram et al., 2012):

$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \qquad\qquad (10f, 10r).$$

Reaction (9) is ~600 times slower than reaction (3) ($k_9 = 3.22 \times 10^{-17}$ cm^3 $molec^{-1}$ s^{-1} at 298 K, Burkholder

220   et al., 2015), but can proceed to a small extent at ppm levels of NO_2 and O_3. At room temperature and NO_2 concentrations greater than about 25 ppb, reaction (10) favors N_2O_5 formation and proceeds relatively rapidly (k_{10} ~ 1.4×10^{-12} cm^3 $molec^{-2}$ s^{-1}, Burkholder et al., 2015), thus resulting in a net loss of 2 NO_2 molecules. In typical CL analyzers that use heated molybdenum to convert NO_2 to NO, N_2O_5 production is not observable, since the heated catalyst will thermally decompose N_2O_5 rapidly (reaction 10r), followed

225   by reduction of both NO_2 and NO_3 to NO – thus, not affecting the observed $[NO]_{consumed} = [NO_2]_{produced}$. However, in the case of photolytic NO converters and the long-path FTP method mentioned in the previous section, the formation of N_2O_5 would cause an underestimate in the calibration (i.e., $[NO]_{consumed} >$ $[NO_2]_{produced}$). For photolytic converters, there would be no way to elucidate the error as the lower observed NO_2 would likely be incorporated into an incorrect conversion efficiency.

230   **3.   Experimental**

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 to produce the diluent air stream. The air flow rate is measured by a mass flow meter and is controlled by use of restrictors (not shown) and a needle valve that

235   vents part of the flow. The needle valve is adjusted to produce diluent air at a total output volumetric flow rate of ~3 L min^{-1}. In the most portable configuration of the instrument, nitrous oxide is supplied by a cartridge containing either 8 or 16 grams of liquid N_2O with a headspace pressure of ~50 atmospheres 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

240   to prevent over pressurization. The valve on the cracker/regulator provides a coarse adjustment of the N_2O flow rate. A voltage sensitive orifice (VSO) valve is then used to provide fine control of the N_2O flow rate to 60 ± 1 cm^3 min^{-1} in a feedback loop. Pressure within the gas stream is measured but not controlled. The N_2O then passes through an aluminum photolysis cell (volume ~ 6 cm^3) where a small fraction of the N_2O

Atmospheric
Measurement
Techniques
Discussions

Open Access

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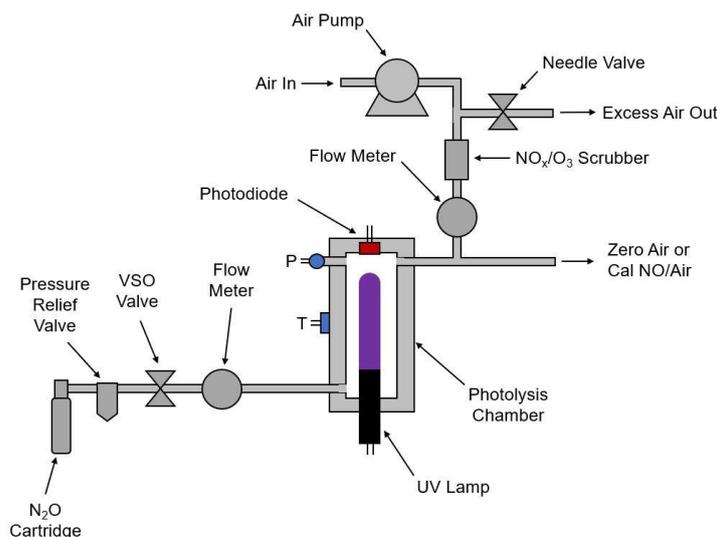
Figure 2. Schematic diagram of the 2B Technologies Model 408 Nitric Oxide Calibration Source.

is converted to NO (and $N_2 + O_2$) by a low-pressure mercury discharge lamp. As discussed above, because

245   the system is optically thick (essentially every photon is absorbed), the NO production rate (molecules s^{-1}) is independent of photolysis cell pressure and N_2O flow rate, the production rate depending only on the lamp intensity. Since nearly all of the 184.9 nm light is absorbed by the N_2O in the cell, the lamp intensity at the 253.7 nm mercury line is monitored by a 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

250   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. The NO/N_2O stream exiting the photolysis chamber is diluted into the ~3 L min^{-1} flow of NO_x-scrubbed air to produce the desired output concentration of NO in air. The photodiode voltage (i.e., a measurement of lamp intensity) is calibrated against the output NO concentration as measured by a NO analyzer that has been recently calibrated using

255   a NIST-SRM NO gas standard/dilution system. Note that 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.

Nitrous oxide can be supplied to the instrument either by means of N_2O cartridges (commercially available and often used as whipped-cream chargers) as shown in Fig. 2, or by connection to a lecture bottle

260   or gas cylinder containing N_2O. The cartridge holder and cracker allow use of either 8- or 16-g cartridges containing liquid N_2O and will supply a gas flow of N_2O of 60 cm^3 min^{-1} for approximately 1.2 or 2.5 hours,

respectively. Alternatively, a lecture bottle or tank of N_2O may be used, allowing continuous operation of 1.5 days for a lecture bottle containing 227 g or 174 days for a QA cylinder containing 27 kg of N_2O.

3.2 *Combined NO2, NO and O3 Calibration Source*

265   A portable calibrated source of NO_2 can be achieved by combining the NO photolytic calibration source (described in Section 2.1 and 3.1) with the photolytic ozone calibration source (described in Section 2.2 and in Birks et al., 2018b). This is commercially available as the 2B Technologies Model 714 $NO_2/NO/O_3$ Calibration Source™, which is capable of providing calibrated mixing ratios of NO_2, NO or O_3. A schematic diagram of the Model 714 $NO_2/NO/O_3$ Calibration Source is shown in Fig. 3. The

270   instrument produces O_3 by photolysis of oxygen in air, NO by the photolysis of N_2O, and NO_2 by gas phase titration (GPT) of known concentrations of O_3 in an excess of NO.
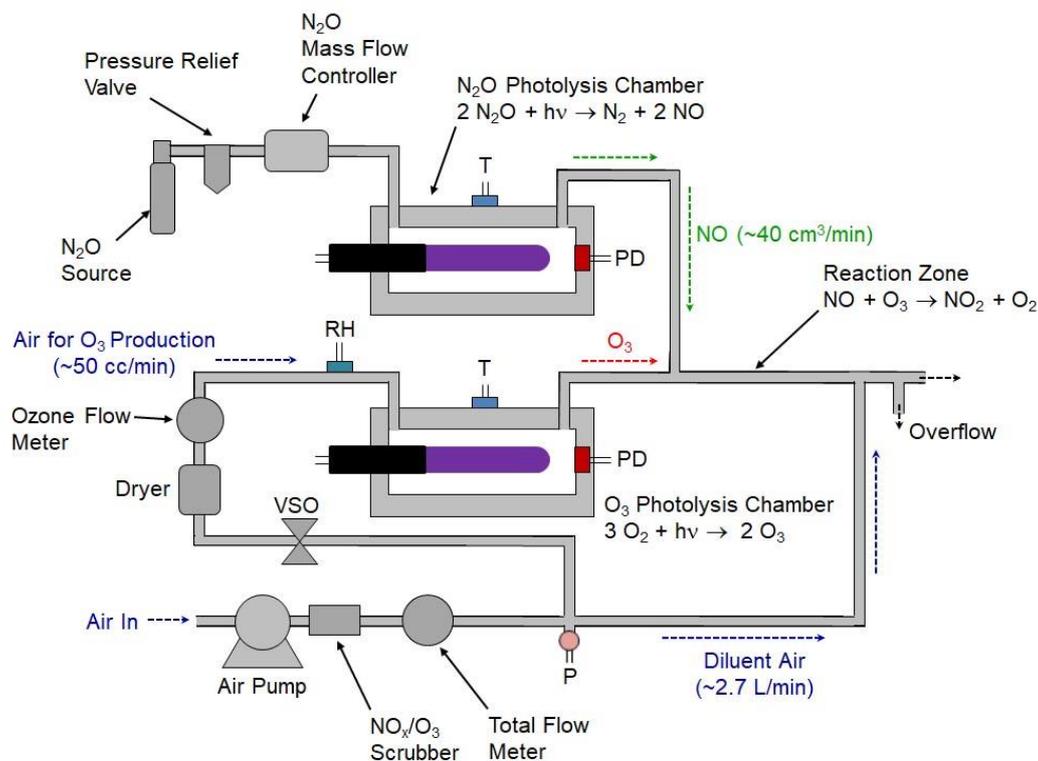

Figure 3. Schematic diagram of the 2B Technologies Model 714 $NO_2/NO/O_3$ Calibration Source.

An air pump pushes ambient air through an O_3/NO_x scrubber; thereafter the flow is split using a restrictor to send a volumetric flow of ~50 cm^3 min^{-1} through an ozone photolysis chamber, with the bulk of the flow, ~2.7 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 flow meter, through the photolysis chamber. For production of NO, a pressurized source of N_2O passes through a mass flow controller and into a NO photolysis chamber at a volumetric flow rate of ~40 cm^3 min^{-1}. Flows through the O_3 and NO photolysis chambers join at a tee prior to entering a reaction zone having a volume of 6.5 cm^3 consisting of 20.3 cm of 6.4-mm i.d. Teflon tubing. When the instrument is in "NO_2" mode (making O_3 and an excess of NO), the O_3 is quantitatively converted to NO_2 during the ~4.3-s residence time. The high concentration O_3, NO or NO/NO_2 mixture is diluted by a factor of ~30-54 (the larger being in the absence of the N_2O flow for outputting only O_3) with O_3/NO_2-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 N_2O flow is turned off when only ozone is being output to conserve N_2O usage. To produce known mixing ratios of NO_2, calibrated amounts of O_3 (corrected for the slight dilution by N_2O) are produced in the range 0-500 ppb with the NO output set at least twice the output ozone (e.g, 1,000 ppb of NO is required for 500 ppb of O_3 to be converted to NO_2). Note that these are the concentrations exiting the calibrator as opposed to the much higher concentrations found within the reaction zone.

3.3   Validation as a suitable transfer standard

As described in Section 1, the U.S.-EPA sets out procedural guidelines for calibration of monitors used for regulatory monitoring of ambient O_3 and NO_2 (U.S.-EPA, 2002; U.S.-EPA, 2013). Since most NO_2 monitors actually monitor NO (CL analyzers), their guidelines also describe 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 NO_2 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 a either a NIST-SRM gas mixture or a gas mixture that is somehow traceable to a NIST-SRM (as with the photolytic NO_2 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 NO_2 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

305   concentrations in a range including 0 and 90 % ($\pm$ 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 6 intercepts cannot exceed 1.5 ppb.

    The "6 $\times$ 6" verification requires an analyzer whose calibration is traceable to a NIST standard.

310   For the measurements presented here, we have used either a 2B Technologies Model 205 or 202 ozone monitor as a reference photometer for O_3, and a 2B Technologies Model 400 (for NO only) or a Model 405 (NO and NO_2) as reference analyzers 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 our currently accredited ozone calibrator (Thermo Scientific Model 49i-PS). The

315   Model 405 also is designated as an FEM for NO_2 (EQNA-0217-243), and it and the Model 400 were calibrated using a Teledyne-API Model 700 Dynamic Dilution Calibrator using a NIST-traceable NO gas mixture (Scott Specialty or Airgas). Furthermore, the ozone photometer (used to measure the ozone for the GPT reaction) within the Model 700 was also calibrated against our NIST-traceable Thermo Scientific ozone standard.

320   Because a goal of the calibration sources is their use in field calibrations of analyzers, we also need 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

325   calibrators. However, this assumes that the N_2O 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 we point out below, mass flow meters depend on molecular composition and will not be perfectly accurate when the water vapor mixing ratio changes. We have previously described similar tests of the ozone calibrator (Birks et al., 2018b), and here we carry out additional environmental tests of the NO

330   calibration source. Furthermore, temperature certainly affects the GPT chemistry (reaction 3) and can place limitations on the usable concentration ranges – typically at low concentrations where reaction (3) 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.

335

Atmospheric
Measurement
Techniques
Discussions

Open Access

EGU

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
340   portable NO calibrator have been limited primarily because users need an instrument that also calibrates
for NO_2 measurements. The photolytic NO generator described here has since been used in the 2B
Technologies Model 211 Scrubberless Ozone Monitor, where NO serves as a gas-phase scrubber, and, more
recently, the Model 714 NO_2/NO/O_3 Calibration Source. The NO generator is identical in all three
instruments – the only differences being the N_2O flow rates used and the degree of dilution. Since, as we
345   discussed in Section 2.1, 1 atm of N_2O is optically thick at 184.9 nm, the flow rate of N_2O 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 N_2O through the chamber produces the same
number of molecules of NO per second as a high flow rate. The effect of changing the N_2O flow rate is
only to change the total flow into which the NO produced is diluted, which is small since the N_2O flow rate
350   is only 1-2 % of the total flow. Optical opacity was verified experimentally by using the NO calibration
source in a Model 714 and varying the N_2O flow rate through the photolysis chamber from 5 to 50 cm^3
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 NO
concentration produced on the flow rate of N_2O within the measured uncertainties. Due to this invariance

Table 1. NO mixing ratios measured from a Model 714 NO_2/NO/O_3 Calibration Source as a function of
the N_2O flow rate.

N_2O flow rate cm^3 min^{-1}	NO mixing ratio[a] ppb ($\pm$ 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

[a]NO measured using a Model 405 NO/NO_2/NO_x monitor.

Atmospheric
Measurement
Techniques
Discussions

355   with N_2O flow, this flow rate is often set based on the balance between N_2O 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 cm^3 min^{-1}) serves to conserve N_2O usage. However, in both the NO calibrators (the Model 408 and

360   714), higher flow rates (40-60 cm^3 min^{-1}) are used to allow for more rapid concentration changes (< 1 minute).

    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 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

365   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 Lpm. There was no measurable difference in the NO mixing ratios (< ± 2 % or 4 ppb, data not shown).

370

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 hours is shown in Fig. 4. The NO calibrator was

375   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 minutes at each concentration. As can be seen the rise (or fall) time between steps is on the order of 1 to 1.5 minutes (samples are every 10 sec) before stable NO outputs are established. Precisions (1σ) averaged 2.6 ppb at non-zero 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

380   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 one standard deviation, with the exception of the 250 ppb level where 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

385   over the entire usable time period of an 8-gram N_2O cartridge (~ 160 min) for a setpoint 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 NO_2/NO/NO_x Monitor. There is a slight

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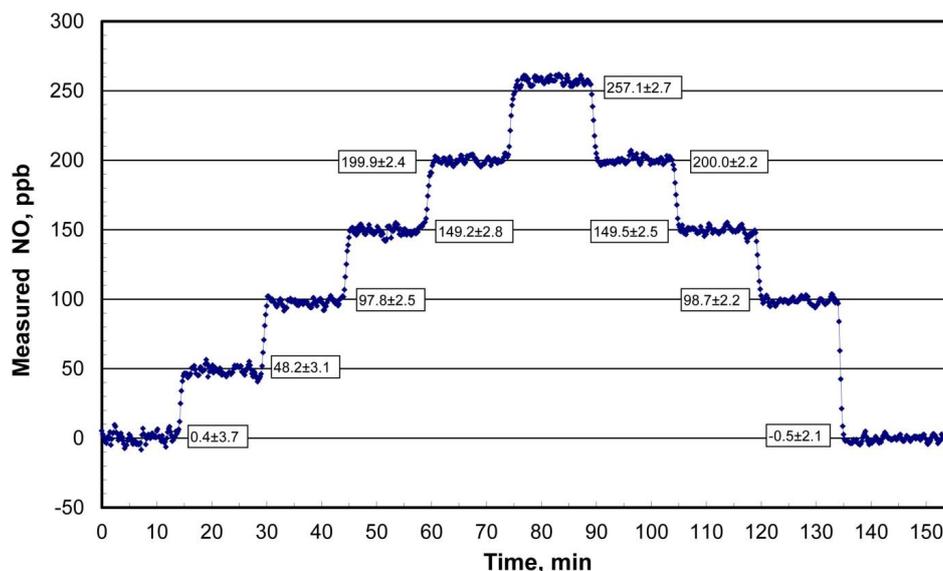
Figure 4. Measured output from Model 408 NO Calibration Source for programmed NO mixing ratios of 0, 50, 100, 150, 200, 250, 200, 150, 100, and 0 ppb and time steps of 15 minutes. Average concentrations after the 1-min step changes are shown along with standard deviations.

increase in the measured NO (4.4 ppb/hr) with a total NO increase of ~ 12 ppb (1.5 % of the 800 ppb setpoint) over the lifetime of the N_2O cartridge. A similar experiment at a setpoint of 200 ppb (data not
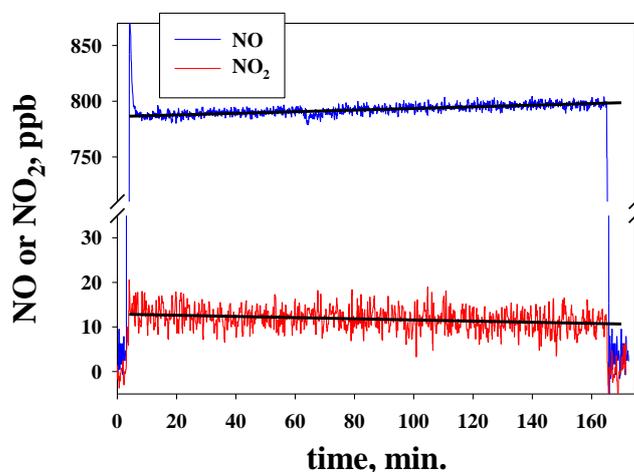

Figure 5. NO and NO_2 output by the NO Calibration Source over the time to use an entire 8-gram N_2O cartridge. The NO setpoint was 800 ppb. Lines drawn are linear fits to data between 15 and 165 minutes.

Atmospheric
Measurement
Techniques
Discussions

390   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 setpoint of 800 ppb) over

the same 2.7-hour 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-gram cartridge. This would be expected to be very

395   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-hour time span needed for conducting calibrations regardless of the

N_2O source.

NO$_2$ showed a corresponding decrease of -0.8 ppb/hr (total of 2.2 ppb) over the course of depleting

the 8-gram N_2O cartridge (see Fig. 5). This small decrease is within the measurement precision of our NO_2

400   analyzer. No decrease in NO_2 could be detected at lower NO setpoints (e.g., 200 ppb) or when using a

larger cylinder. Therefore, the NO_2 produced at a given NO setpoint is essentially constant over a several

hours and would have minimal effect (< 1 %) on NO_2 calibrations described in Section 4.2.

Using the NO calibration source from a Model 714 $NO_2/NO/O_3$ calibrator (S/N = 1014), a "6 × 6"

verification was undertaken to ascertain whether it could be used as a traceable transfer standard for NO.

405   Figure 6 shows the calibration plots obtained over 6 days using a recently calibrated 2B Technologies

Model 405 $NO_2/NO/NO_x$ 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
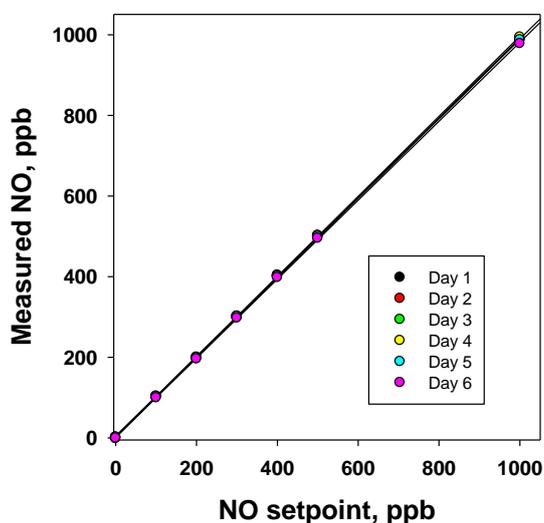

Figure 6. Plots of the NO measured (ppb) from the NO photolysis source of a 2B Technologies
Model 714 $NO_2/NO/O_3$ Calibration Source vs. the NO setpoint on 6 consecutive days.

Table 2. Results from the "6 × 6" validation over six consecutive days for the NO photolysis source in the 2B Technologies Model 714 $NO_2/NO/O_3$ Calibration Source.

NO Setpoint (ppb)	NO measured: Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Average (ppb)	Std. Dev. (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	

coefficients from a linear regression. As can be seen, day-to-day variations are not statistically different from the precision of the measuring analyzer ($\sim \pm 2$ ppb) with the exception of the highest (1000 ppb) point,
410 which has a slightly higher standard deviation (± 5.2 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 successfully meets the
415 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, we made measurements of the output mixing ratio of a Model 408 NO Calibration Source, using a program consisting
420 of steps of 0, 50, 100, 150, and 200 ppb at ambient temperatures of 23.5 °C 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 startup, the

Atmospheric
Measurement
Techniques
Discussions

instrument showed that the photolysis chamber was at 8.5 °C. Results of measurements at the two

425   temperatures are summarized in Table 3. Data at the two temperatures agree very well within the standard

deviations of the measurements.

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

Target NO, ppb	Measured NO, ppb T = 23.5 °C	Measured NO, ppb T = 8.5 °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**

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

430   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. We conclude 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

435   temperatures.

Lack of significant dependence of the NO calibrator of 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, we measured the NO output in Boulder and at

440   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 setpoint (given in the inset panel of Fig. 7) indicate

445   a slightly lower slope (~ 3 %) at the higher elevation site. If there is a slight fall off in output concentration

at high altitudes, it could be explained by the lack of optical thickness within the N_2O photolysis chamber

Atmospheric
Measurement
Techniques
Open Access
Discussions
EGU
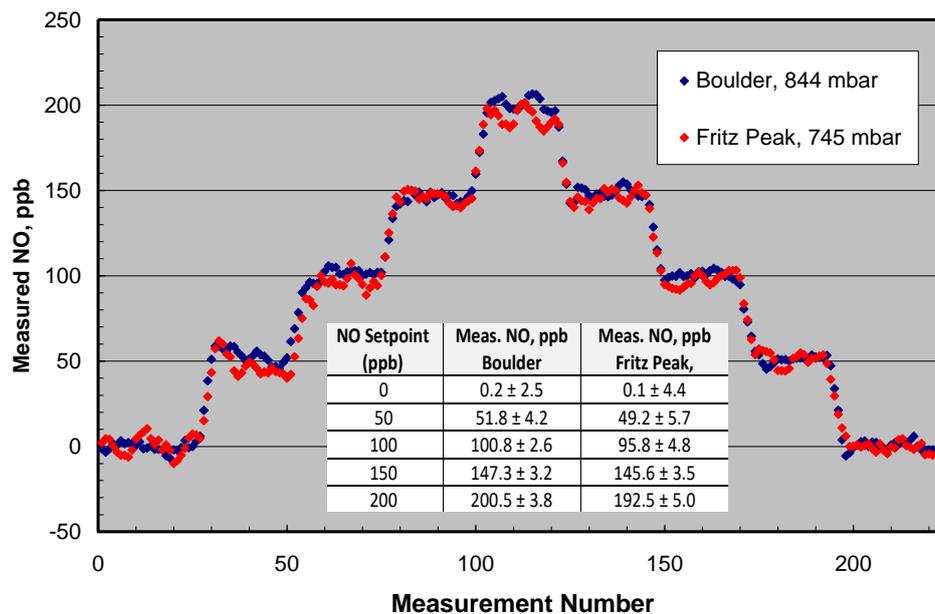
Figure 7. NO measured from the output of a Model 408 NO Calibration Source in Boulder, CO (elevation 1.6 km) and Fritz Peak, CO (elevation 2.7 km). The inset panel gives the averages and standard deviations (1σ) at the different NO setpoints of the calibrator. Measurements were made every 10 seconds.

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.

450   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 flow meter causing small errors in the calculated dilution. Because water has a different heat capacity than air (~ 30 % larger), an airflow saturated with water vapor at 1 atm and 25 °C (saturation vapor pressure = 31.7 mbar, H_2O mole fraction = 3.1 %) has a heat capacity that is about 0.9 %

455   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. We tested the effect of humidity on the NO calibration source output by using a 2B Technologies Model 400 Nitric Oxide Monitor to measure step profiles of 0,

460   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

Atmospheric
Measurement
Techniques
Discussions
Open Access
EGU

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

465   Thermohygrometer inserted in line with the supply air flow. 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 our expectations that any humidity effect is within the statistical uncertainty of the analyzer.
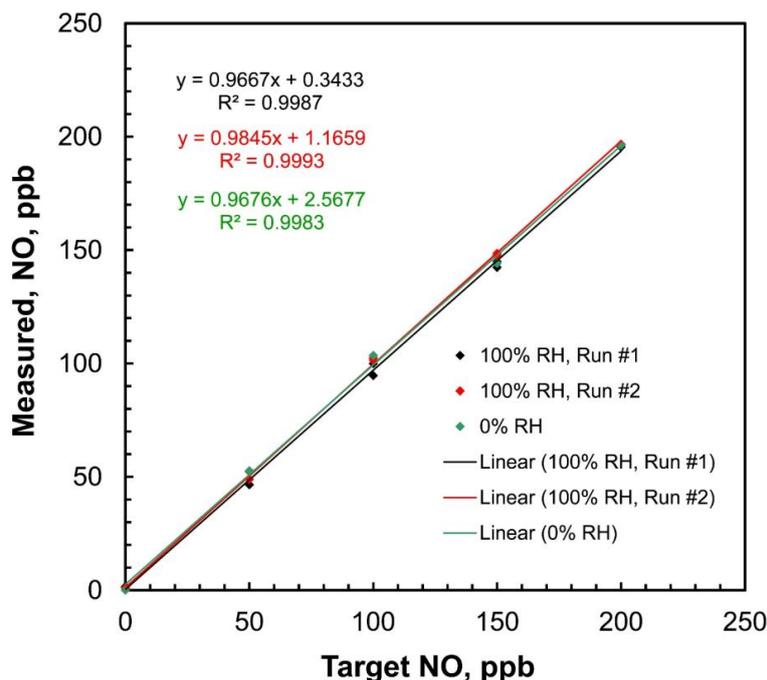

Figure 8. Linear regressions of measured NO concentrations vs. target concentrations of the 2B Technologies Model 408 NO Calibration Source with dilution air containing both 0 and 100 % relative humidity at 23.5 °C.

470   **4.2   *NO$_2$/NO/O$_3$ Calibration Source***

The 2B Technologies Model 714 NO$_2$/NO/O$_3$ Calibration Source is a combination of a Model 306 Ozone Calibration Source and a Model 408 NO Calibration Source (Section 4.1) that allows for generation of calibrated mixing ratios of either O$_3$, NO or NO$_2$ (the latter via the GPT reaction 3). The NO source is identical to the one described in Section 3.1 and 4.1, except the N$_2$O flow rate is typically lowered to around

475   40 cm^3 min^{-1} compared to the earlier Model 408 NO Calibration Source. As noted in Section 3.1, the NO

Atmospheric
Measurement
Techniques
Discussions

Open Access
EGU

output is not affected by the choice of N_2O flow rate due to the optical opacity of the N_2O. The ozone calibration source in the Model 714 does differ from that described previously for our Model 306 (Birks et al., 2018b) in that only a small fraction of the airflow passes through the photolysis cell (only 50 $cm^3 min^{-1}$ as opposed to ~ 3 L min^{-1}). This increases the cell residence time from 0.06 s to ~ 3.6 s, and, consequently,

480   results in production of much higher ozone mixing ratios (up to 15 ppm) exiting the photolysis cell of 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

485   306). A solution to this potential problem will be discussed in the next section.

For the generation of NO_2, the outputs of the NO and O_3 photolysis cells are mixed and allowed to react in a ~6.5 cm^3 Teflon reaction volume. The total flow rate passing through this reactor is 90 $cm^3 min^{-1}$ (40 $cm^3 min^{-1}$ of NO/N_2O and 50 $cm^3 min^{-1}$ of O_3/air) giving a reaction time of 4.3 s. Concentrations within the reaction zone can be calculated by knowing the measured output after dilution (i.e., the setpoint concentration) and the ratio of the reaction zone and dilution flows. With a typical total flow (after dilution)

490   of 2,700 $cm^3 min^{-1}$, initial reaction concentrations are a factor of 30 higher than the setpoint (or output) concentrations. For example, a final output concentration of 200 ppb of NO would give an initial concentration of 6 ppm of NO within the reaction zone.

495   ### 4.2.1   *Water vapor effects and verification of the modified photolytic O_3 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 $NO_2/NO/O_3$ 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

500   the ozone photolysis cell in the $NO_2/NO/O_3$ calibrator described here. Birks et al. (2018a) found that chemical loss of ozone due to OH and HO_2 radicals (generated either by water photolysis at 184.9 nm or by ozone photolysis and subsequent reaction of $O(^1D)$ with H_2O) 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 O_2 precursor by water vapor in the photolysis cell that results in a small of reduction of the ozone

505   generated (up to ~2 %). But the flow rate through the ozone photolysis cell in the $NO_2/NO/O_3$ calibrator is ~60 times slower than in the stand-alone Model 306 (50 $cm^3 min^{-1}$ compared to 3 L min^{-1}). Therefore, the longer residence time generates considerably higher concentrations of ozone, resulting in higher

Atmospheric
Measurement
Techniques
Discussions

Open Access

EGU

concentrations of HO_x (OH and HO_2) radicals when water vapor is present, which, in turn, can catalyze ozone depletion.

510   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 $NO_2/NO/O_3$ 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 lower O_3 setpoints. 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

515   photolysis chamber:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{11}$$

$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \tag{12}$$

$$\text{Net: } 2\,O_3 \rightarrow 3\,O_2$$
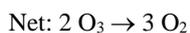
    Experimental results showed that at low RH (RH = 6 – 10 %), the observed decreases in ozone

520   output in the $NO_2/NO/O_3$ 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 6-12 % (34 to 60 ppb). Therefore,

525   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 $NO_2/NO/O_3$ calibrator. An 80 cm^3 silica gel trap (United Filtration, IACH-38-150-80-SG) was added in line to reduce the RH to < 1 % in the O_3-precursor airflow (see Fig. 3). A relative humidity/temperature sensor was also placed just before the ozone photolysis chamber to monitor the RH

530   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 $cm^3\,min^{-1}$, this trap maintained the RH below 2% for more than 24 hours 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/O_3 and dry N_2O/NO, thereby eliminating any possibility of water vapor

535   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 $NO_2/NO/O_3$ calibrator. Ozone concentrations were measured with a 2B Technologies Model 205 Ozone Monitor that had been recently calibrated relative to our primary ozone standard (Section 3.2.3). Calibration plots and results of the linear regressions are shown in Fig. 9. Both

540   the standard deviations in the slopes and intercepts are well within the U.S.-EPA transfer standard

	Slope	Intercept	R^2
Day 1	1.003	0.2	0.9999
Day 2	0.994	0.7	0.9999
Day 3	0.998	0.9	0.9999
Day 4	1.014	-0.1	0.9999
Day 5	1.021	0.5	0.9999
Day 6	1.023	-0.2	0.9999
Avg:	1.009	0.3	
Std.Dev	0.012	0.5	
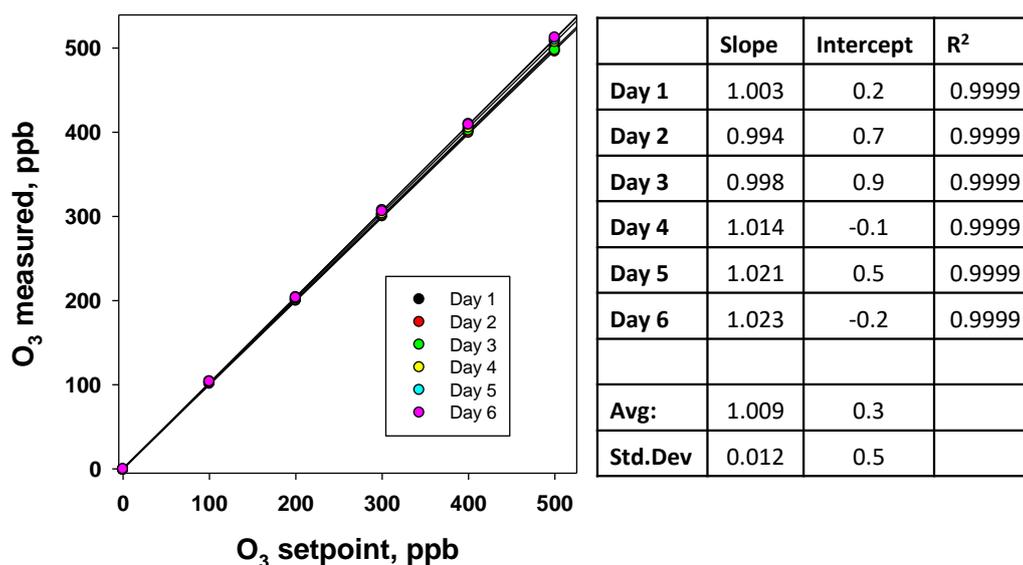
Figure 9. Plots of the O_3 measured vs. the O_3 setpoint in a Model 714 $NO_2/NO/O_3$ calibrator on 6 consecutive days. Regression slopes and intercepts are given in the panel on the right.

requirements ($\sigma_{slope} < 3.7$ %, $\sigma_{intercept} < 1.5$ ppb), thereby confirming that the adaptations made in the O_3 photolysis system for use in the $NO_2/NO/O_3$ calibrator do not adversely impact its use as an O_3 transfer standard.

4.2.2 Precision, accuracy and reproducibility of the NO_2 Calibration Source

545   Figure 10 shows mixing ratios of NO and NO_2 produced by a Model 714 $NO_2/NO/O_3$ calibration source (as measured by a Model 405 $NO_2/NO/NO_x$ Monitor) for an automated sequence of several NO_2 concentrations. The NO setpoint remained constant at 1000 ppb between 5 to 80 minutes during the sequence. Six different ozone concentrations (i.e., equal to the target NO_2 concentrations) were then generated (setpoints = 0, 80, 180, 280, 380, 480 ppb of ozone) each lasting 10 minutes (note, the use of 480

550   ppb instead of 500 ppb allows for visual clarity in the time series graph at the highest concentration). As seen in the figure, NO_2 increases as NO decreases due to its reaction with ozone. The time required to reach a new setpoint is typically < 45 seconds. The measured concentrations averaged over the last 5 minutes of each step are shown in the panel to the right of the figure along with observed precisions (1σ). Note that the precisions for steps 2-8 are nearly the same as those in steps 1 and 9 where no reagent gases were being

555   produced. This suggests that the observed precisions are limited by the measuring analyzer and that the

Atmospheric
Measurement
Techniques
Open Access
Discussions
EGU

	NO	NO$_2$
1	1.0 ± 2.3	0.0 ± 3.3
2	986.4 ± 3.3	9.3 ± 3.2
3	908.6 ± 2.5	88.2 ± 2.4
4	812.7 ± 2.7	185.3 ± 2.5
5	714.5 ± 3.1	284.5 ± 3.0
6	617.8 ± 2.4	379.9 ± 2.9
7	518.6 ± 3.0	478.1 ± 2.5
8	993.4 ± 2.8	5.2 ± 2.0
9	2.5 ± 2.0	-1.3 ± 2.3
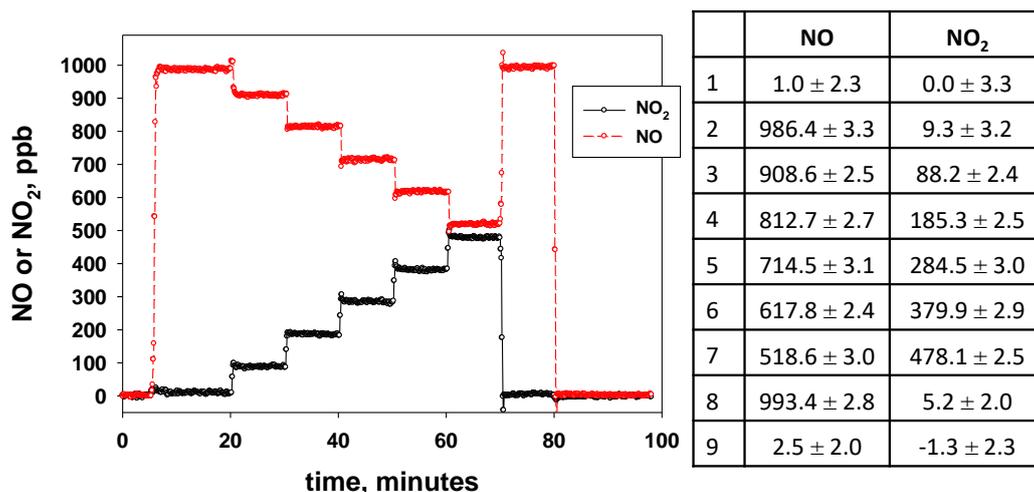
Figure 10. NO and NO$_2$ measured from the output of a Model 714 GPT calibrator. At time = 5 minutes, NO was set to 1000 ppb. At time = 20 minutes, ozone was added and setpoints were varied between 80 and 480 ppb in steps of 100 ppb (this allowed for visual clarity of both NO and NO$_2$ at the highest [O$_3$]). O$_3$ was changed every 10 minutes. Finally, data for [O$_3$] = 0 and [NO] = 0 were repeated for completeness. NO and NO$_2$ were measured using a calibrated 2B Tech Model 405.

actual precisions of the output NO and NO$_2$ concentrations from the calibrator are lower ($\leq \pm 2.8$ ppb for NO, $\leq \pm 2.6$ ppb for NO$_2$, the average precision from Fig. 10 panel).

Also note the small amount of NO$_2$ produced by the NO photolysis source (9.3 ppb, ~ 0.9 % of the NO, see Fig. 10). As discussed in Section 4.2.3, this NO$_2$ is typically small (≤ 2 % of the NO produced), 560 and it is also constant over a given calibration with a set NO concentration. Therefore, a step where NO is present with no accompanying O$_3$ must be included to measure and subtract out this small amount of photolytically produced NO$_2$.

Figure 11 shows the results of a 6×6 verification for NO$_2$ produced by the Model 714 NO$_2$/NO/ O$_3$ calibrator along with the results from the linear regressions. As seen in the figure, plots were extremely 565 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 (O$_3$, NO and NO$_2$) produced in the Model 714 NO$_2$/NO/O$_3$ calibrator pass the statistical tests established for a Level 4 ozone transfer standard.

	Slope	Intercept	R^2
Day 1	0.988	-0.3	0.9999
Day 2	0.993	0.7	0.9999
Day 3	0.994	0.7	0.9999
Day 4	0.996	1.0	0.9999
Day 5	0.997	1.5	0.9999
Day 6	1.000	1.2	0.9999
Avg:	0.995	0.8	
Std.Dev	0.004	0.6	
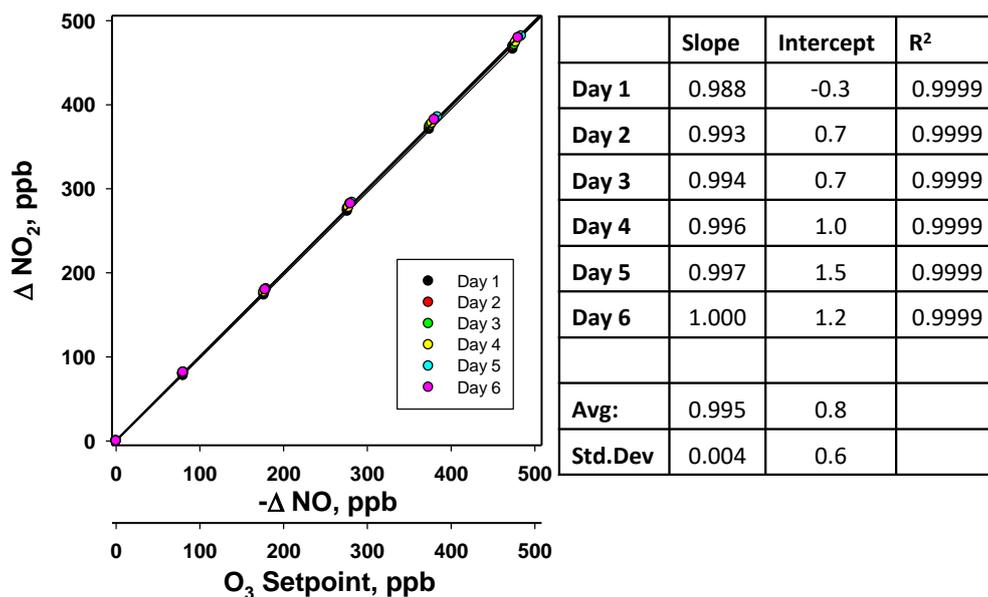
Figure 11. Calibration curves for NO_2 made on 6 consecutive days. $\Delta NO_2 = NO_2 - NO_2(O_3 = 0)$ and $-\Delta NO = NO(O_3 = 0) - NO$ at each ozone setpoint. Slopes, intercepts and correlation coefficients are reported in the panel to the right.

570   *4.2.3 Completeness of reaction and effects of temperature and pressure*

Complete conversion of ozone to NO_2 is not critical if NO is measured as well (then $-\Delta[NO] = \Delta[NO_2]$ and the NO_2 signal can be calibrated relative to NO); however, the conversion efficiency is important in cases where the NO_2 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

575   the chance for undesirable chemistry. Our modeling exercise (see Fig. 1) suggests that we achieve > 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) and 298 K and a reaction time of 4 seconds. We have shown that temperature and pressure do not affect the output mixing ratios from our photolytic sources of ozone and NO; however, these factors can impact the GPT chemistry occurring within the reaction zone. Reaction (3) has a rather

580   substantial activation energy ($E/R = 1,500\,K^{-1}$, Burkholder et al., 2015) resulting in a smaller rate coefficient with decreasing temperature. Lower pressures have the effect of reducing the overall number density of the reactants, which is key to driving reaction (3) to completion. Although our photolytic sources (O_3 and NO) output constant *mixing ratios* with varying pressure, the *number density* (molec cm^{-3}) of ozone and nitric oxide *do vary* with overall pressure changes.

585 We tested this by measuring all three components (O_3, NO and NO_2) for a variety of setpoint concentrations from the calibrator ([NO] varied from 50 to 500 ppb, [O_3] from 24 to 240 ppb) while maintaining [NO] > 2 x [O_3]. Changes in O_3, NO and NO_2 were measured relative to when [O_3] = 0 (i.e., $\Delta NO = NO_{meas} - NO_{O3=0}$). 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 of

590 pressure (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 NO_2 can be quantitated by looking at

595 either the loss of NO (-$\Delta NO/O_3$ generated) or the formation of NO_2 ($\Delta NO_2/O_3$ generated). Here, the O_3 generated is the original setpoint of the ozone generator on the GPT calibrator. Complete conversion results in -$\Delta NO = \Delta NO_2 = O_3$ setpoint (and, thus: -$\Delta NO/O_3$ setpoint = $\Delta NO_2/O_3$ setpoint = 1). Figure 12 displays the results graphically by plotting the measured $\Delta NO/O_3$ and $\Delta NO_2/O_3$ (as percentages) vs. the initial NO setpoint of the GPT calibrator. A second x-axis is included indicating the initial NO mixing ratio present

600 in the reaction zone (RZ), which can be used as 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 setpoints above 200 ppb (~

Table 4. O_3, NO and NO_2 measured at the output of a Model 714 for the NO and O_3 setpoints given in columns 1 and 2. The pressure was 830 mbar. All units are in ppb.

NO setpt.	O_3 setpt. (=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 [O_3] = 0 (no ozone produced)
[b]From a model of 2nd order kinetics of the reaction chamber chemistry at 830 mbar.
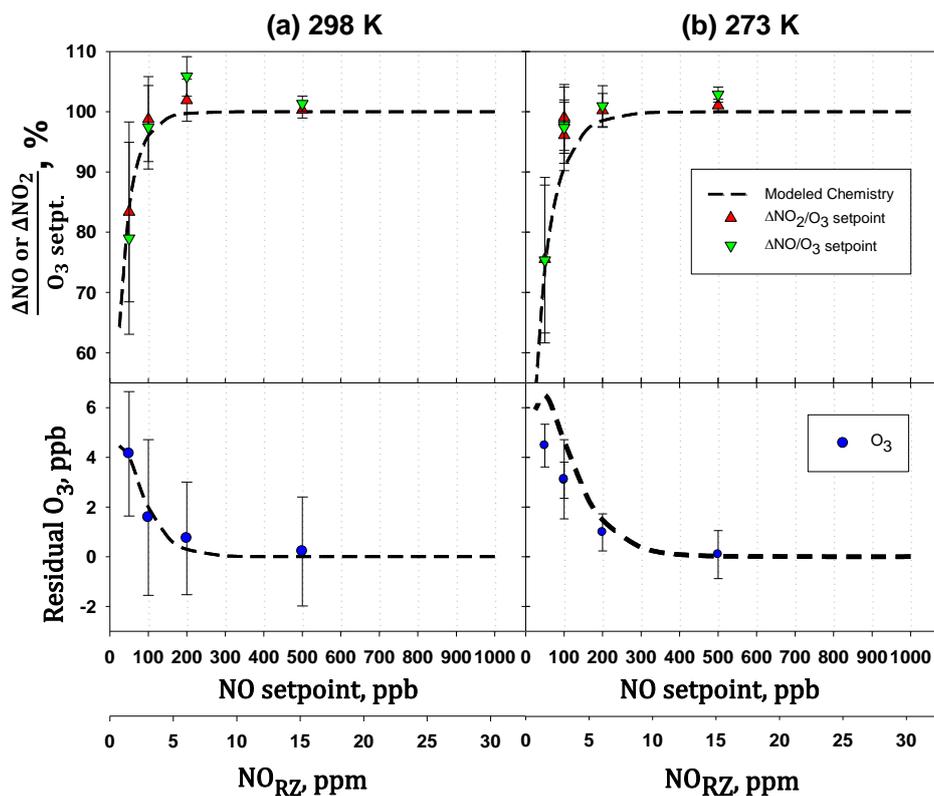
Figure 12. Plots of the amount of NO consumed (ΔNO/O$_3$ setpt) and NO$_2$ formed (ΔNO$_2$/O$_3$ setpt) vs. the NO setpoint. A second x-axis of the NO concentration in the reaction zone (NO$_{RZ}$) is also given as a reference to Fig. 1. Measurements were made with the reaction zone at (a) 298 K and (b) 273 K.

6 ppm in the RZ) at the lowest temperature (273 K). At room temperature, this level drops to near 100 ppb

605 (~ 3 ppm in RZ) within the errors of the measurements. Note that at the lowest initial NO and O$_3$ (NO setpoint = 50, O$_3$ setpoint = 25) where there is measurable residual ozone (~ 4-5 ppb), ΔNO$_2$ is still equivalent to -ΔNO as expected from the stoichiometry of reaction (3). However, the percent error is considerably larger (~ 15 %) due to the smaller concentration changes and the measurement precision of the Model 405 NO$_2$/NO/NO$_x$ analyzer. It also bears reiterating at this point that it is critical to maintain at

610 least a factor of 2 greater NO to drive the NO/O$_3$ reaction to completion. Currently the operating firmware of the Model 714 does not allow [NO]/[O$_3$] < 2. Under these conditions, a general recommendation is that a NO setpoint of ≥ 200 ppb ensures complete ozone consumption.

Atmospheric
Measurement
Techniques
Discussions

5. Conclusions

615   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 photolysis of air) giving a single instrument capable of delivering calibrated mixing ratios of either NO, NO_2 or O_3 (the 2B

620 Technologies Model 714 NO_2/NO/O_3 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 N_2O is required, an 8- or 16-gram cartridge can be utilized as the source gas in either calibrator, thereby eliminating the need for larger (and more expensive) gas calibration

625 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 where these variables are not controlled.

630   Both the NO and NO_2/NO/O_3 calibration systems are initially compared to NIST-traceable calibration standards (either NIST-SRM gas mixtures or NIST-traceable ozone generators/photometers) to establish the relationship between photolytic lamp intensity and output mixing ratios of NO, NO_2 and O_3. 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

635 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.

6. Data availability

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

7. Competing interests

      John Birks, Andrew Turnipseed, Peter Andersen, Craig Williford, Stanley Strunk, Brian Carpenter and Christine Ennis are employed by 2B Technologies, the manufacturer of the Model 408 NO Calibration

645 Source™ and the Model 714 NO_2/NO/O_3 Calibration Source™ described in this paper.

Atmospheric
Measurement
Techniques
Discussions

650

9. References

Abman, S.H.: Inhaled nitric oxide for the treatment of pulmonary arterial hypertension, *Handbook of Experimental Pharmacology*, vol. 218, Springer, Berlin, 257-276, 2013.

655   Andersen, P.C., Williford, C.J. and Birks, J.W.: Method to Produce a Calibration Reagent or Therapeutic Gas by Exposing a Precursor Gas to Ultraviolet Light, U.S. Patent No. US 10,207,927 B2, February 19, 2019, U.S. Patent and Trademark Office, Washington, DC, USA, 2019.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I – gas phase reactions of O_x, HO_x, NO_x and SO_x species, *Atmos. Chem. Phys.*, 4, 1461-1738, 2004.

Bertram, T.H., Cohen, R.C., Thorn III, W.J. and Chou, P.M.: Consistency of ozone and nitrogen oxides standards at tropospherically relevant mixing ratios, *J. Air Waste Manage. Assoc.*, 55, 1473-1479, DOI:10.1080/10473289.2005.10464740, 2005.

Birks, J.W. and Bollinger, M.J.: Method and Apparatus to Detect a Gas by Measuring Ozone Depletion, U.S. Patent No. 7,045,359 B2, May 16, 2006, U.S. Patent and Trademark Office, Washington, DC, USA, 2006.

670

Birks, J.W., Andersen, P.C, Williford, C.J., Turnipseed, A.A., Strunk, S.E., Ennis, C.A. and Mattson, E.: Folded tubular photometer for atmospheric measurements of NO_2 and NO, *Atmos. Meas. Tech.*, 11, 2821-2835, 2018a.

675   Birks, J.W., Williford, C.J., Andersen, P.C., Turnipseed, A.A., Strunk S. and Ennis, C.A.: Portable ozone calibration source independent of changes in temperature, pressure and humidity for research and regulatory applications, *Atmos. Meas. Tech.*, 11, 4797-4807, 2018b.

Burkholder, J.B., Sander, S.P., Abbatt, J.P.D., Barker, J.R., Huie, R.E., Kolb, C.E., Kurylo, M.J., Orkin, V.L., Wilmouth, D.M., and Wine, P.H.: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*, Evaluation Number 18, JPL Publication 15-10, NASA, October 2015.

Cantrell, C.A., Zimmer, A. and Tyndall, G.S.: Absorption cross sections for water vapor from 183 to 193 nm, *Geophys. Res. Lett.*, 24, 2195-2198 DOI: 10.1029/97GL02100, 1997.

685

Chilton, J.E., Timko, R.J. and Chuhta, E.J.: Nitrogen Dioxide Calibration Standards for Portable Monitors, Information Circular 9482, DHHS (NIOSH) Publication No. 2006-104, 2005.

Clark, R.H., Kueser, T.J., Walker, M.W., Southgate, W.M., Huckaby, J.L., Perez, J.A., Roy, B.J., Keszler, M. and Kinsella, J.P.: Low-dose nitric oxide therapy for persistent pulmonary hypertension of the newborn, *N. Engl. J. Med.*, 342, 469-474, 2000.

Creasey, D.J., Heard, D.E. and Lee, J.D.: Absorption cross-section measurements of water vapour and oxygen at 185 nm. Implications for the calibration of field instruments to measure OH, HO_2 and RO_2 radicals, *Geophys. Res. Lett*. 27, 1651-1654, DOI: 10.1029/1999GL011014, 2000.

Demerjian, K.L: A review of national monitoring networks in North America, *Atmos. Environ.*, 34, 1861-1884, 2000.

Ellis, E.C.: Technical Assistance Document for the Chemiluminescent Measurement of Nitrogen Dioxide, Environmental Monitoring Series Report #EPA-600/4-75-003, 1975.

Fontijn, A., Sabadell, A.J. and Ronco, R.J.: Homogeneous chemiluminescent measurement of nitric oxide with ozone. Implications for continuous selective monitoring of gaseous air pollutants*, Anal. Chem.*, 42, 575-579, 1970.

Haagen-Smit, A.J.: Chemistry and physiology of Los Angeles smog, *Ind. Eng. Chem*., 44, 1342-1346, 1952.

Iida, Y., Carnovale, F., Daviel, S. and Brion, C.E.: Absolute oscillator-strengths for photoabsorption and the molecular and dissociative photoionization of nitric oxide, *Chem. Phys*., 105, 211-225, 1986.

Kebabian, P.L, Herndon, S.C. and Freedman, A.: Detection of nitrogen dioxide by cavity attenuated phase shift spectroscopy, *Anal. Chem.*, 77, 724-728, 2005.

Kebabian, P.L, Wood, E.C., Herndon, S.C. and Freedman, A.: A practical alternative to chemiluminescence-based detection of nitrogen dioxide: Cavity attenuated phase shift spectroscopy, *Environ. Sci. Technol.*, 42, 6040–6045, 2008.

Kley, D. and McFarland, M.: Chemiluminescence detector for NO and NO_2, *Atmos. Technol.,* 12, 63-69, 1980.

Nishida, S., Takahashi, K., Matsumi, Y., Taniguchi, N. and Hayashida, S., Formation of $O(^3P)$ atoms in the photolysis of N_2O at 193 nm and $O(^3P)$ + N_2O product channel in the reaction of $O(^1D)$ + N_2O, *J. Phys. Chem. A,* 108, 2451-2456, DOI: 10.1021/jp037034o, 2004.

Paldus, B.A. and Kachanov, A.A.: Spectroscopic Techniques: Cavity-Enhanced Methods, In *Handbook of Atomic, Molecular, and Optical Physics, Part C: Molecules*, edited by G.W.F. Drake, Springer, Berlin, 633-640, 2006.

Ridley, B.A. and Howlett, L.C.: An instrument for nitric oxide measurements in the stratosphere, *Rev. Sci. Instrum.*, 45, 742-746, 1974.

Steffenson, D.M. and Stedman, D.H.: Optimization of the operating parameters of chemiluminescent nitric oxide detectors, *Anal. Chem.*, 46, 1704-1709, 1974.

735

U.S.-EPA: Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence), Quality Assurance Guidance Document 2.3, 58 pp., 2002.

U.S.-EPA: Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone, Technical Assistance

740   Document, Ozone Transfer Standard Guidance Document 10/2013, Publication No. EPA-454/B-13-004, Office of Air Quality Planning and Standards, Air Quality Assessment Division, Research Triangle Park, North Carolina,   68   pp.,   October   2013. https://www3.epa.gov/ttn/amtic/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf, Visited October 10, 2019.

745

U.S.-EPA: Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence). U.S. Environmental Protection Agency. 40 CFR, Part 50, Appendix F, as amended Jan. 20, 1983.

750   U.S.-EPA: NO_2 cylinder guidance for state-local agencies and gas producers, https://www.epa.gov/air-research/no2-cylinder-guidance-state-local-agencies-and-gas-producers, and included pdf links, visited Sept. 5, 2019.

Vranckx, S., Peeters, J. and Carl, S.A.: Absolute rate constant and $O(^3P)$ yield for the $O(^1D) + N_2O$ reaction

755   in the temperature range 227 K to 719 K, *Atmos. Chem. Phys.*, 8, 6261-6272, 2008.

Yoshino, K., Esmond, J.R., Cheung, A.S.C., Freeman, D.E. and Parkinson, W.H.: High resolution absorption cross sections in the transmission window region of the Schumann-Runge bands and Herzberg continuum of O_2, *Planet. Space Sci.*, 40, 185-192, 1992.

760