

We would like to thank all three referees for their effort and their thoughtful comments. We have included our responses to all three reviewers in this supplement followed by an annotated version of the manuscript. Reviewers' comments are in *italics*, followed by our response to each comment. Changes to the manuscript are in red font within each response and in the annotated manuscript. Line and page numbers denoted our responses refer to the annotated manuscript included here.

Anonymous Referee #1

Received and published: 30 May 2018

General comments

Birks et al. present a technical paper describing a portable ozone calibrator developed by 2B Technologies. The paper is very well written and covers all the technical aspects for qualifying this equipment as an EPA Level 4 transfer. The interest of this equipment is to be easily portable, with low weight and low power consumption. The authors present clearly the technical layout and specifications of the instrument, with all figures being very clear and well presented. Based on theory and experimental tests, the authors prove that the instrument operation is free of pressure dependence or water vapour interference. I recommend the publication of this paper with only minor corrections.

Specific comments

1. For "Air In", the instrument use a chemical scrubber (Line 150 and Figure 2) to remove O3 and NOx. The authors should specify the composition of this scrubber. A related question is the capacity of this scrubber to remove potential atmospheric interferences (as VOC) in highly polluted areas.

We have clarified the details concerning the scrubber in response to both this comment and a similar comment by Referee #3. The scrubber is made of Carulite (a combination of copper and manganese oxides) which catalytically both destroys ozone and oxidizes NO to NO₂. We have changed the manuscript (page, 5, lines 152-154) to read: "...and a chemical scrubber to remove ozone and NO (which can react relatively rapidly with the ozone produced). The scrubber consists of Carulite, which catalytically destroys ozone and oxidizes NO to NO₂. NO₂ is not removed. Air then enters the photolysis chamber containing a low-pressure mercury lamp...". This scrubber is catalytic for both ozone destruction and NO oxidation, so that it has nearly limitless capacity. Further comments concerning possible VOC interferences are addressed in Specific Comment 1 from Referee #3.

2. Table 2 should specify the robustness of the instrument to be used as EPA transfer (estimation of how often it must be calibrated through a higher level EPA transfer).

We have added an entry into Table 2 for the Recommended Calibration time along with an accompanying footnote description: "The recommended calibration time is the maximum time between validation of the Ozone Calibration Source with an independent EPA-certified standard."

3. RH sensor HIH8000 is installed in the flow path upstream the cell. Its layout in the tubing should be slightly described. Its response time should be specified, to prove that potential rapid variations of RH will be included in the lamp intensity process for constant O₃ production.

We have changed the text (page 12, lines 357-361) to read: ,

“...a humidity sensor (Honeywell, HIH8000) was installed in the flow path **via a tee with the sensor head protruding into the main flow** immediately upstream of the photolysis cell...” to describe how the sensor was mounted within the instrument. We have changed the next sentence to read: “The sensor provides simultaneous measurements **of** relative humidity (RH) and temperature **with a response time of ~ 10 seconds** so that mixing ratios...”

It should be noted that the inlet scrubber tends to act as a temporary reservoir for humidity, thus dampening any rapid changes in water vapor concentration.

Technical corrections

Line 334: the mathematic formula should use slightly bigger characters police, in order to be more readable.

We have increased the size of the equations in the text; however, we expect that this will be altered to comply with the journal standards if the manuscript is accepted for final publication.

Anonymous Referee #2

Received and published: 8 June 2018

The authors present a portable ozone calibration source that can serve as a transfer standard for the calibration of ozone monitors, e.g. those deployed in air quality monitoring stations (fulfils the requirements of a U.S. EPA level 4 transfer standard). The manuscript is very clear and well written and actually, it is complete and includes a thorough and interesting discussion about the effect of humidity on the generated O₃ mixing ratio. In fact, I did not find any errors or things that should be changed or corrected. Nevertheless, I'm reluctant in recommending the manuscript for publication in AMT, because it is a description (although very detailed and correct) of a commercial instrument. A good part of the information in the manuscript is already available on the 2B website within the product description of the Model 306 Ozone Calibration Source (<https://www.twobtech.com/model-306-ozone-cal-source.html>) and the operation manual that can be downloaded from the website (Figures 2, 3, 4 and Table 2 of the manuscript). I therefore think that the manuscript does not provide sufficient novel information to justify publication in a research journal like AMT. However, this is rather a political than a scientific or technical question and the decision should be taken by the Editor. Regarding content, the manuscript is fine.

We respect Referee #2 opinion and certainly realize that some of the data presented here is also contained on our website and manuals; however we do feel that the manuscript goes into greater depth on the basic chemistry involved in our Ozone Calibrator to show why it is pressure independent and has only a very small (and correctable) humidity dependence. We also feel that the manuscript provides the general scientific community a good overview into how ozone measurements are validated across large monitoring networks and what is required for an instrument or calibration unit to be certified within these networks.

Anonymous Referee #3

Received and published: 10 June 2018

The manuscript describes a portable ozone calibration source to be easily used at field stations. The O₃ production is based on oxygen photolysis at 184.9 nm using a mercury lamp. Stable O₃ concentration are achieved by controlling the residence time in the photolysis chamber and by monitoring the lamp intensity at its emission wavelength at 253.7 nm. No zero air source is required and implications for the uncertainties are discussed. The authors have proven its capability to be suitable as an ozone calibration source under the tested conditions. I recommend publication after addressing following comments.

General Comments:

The manuscript is well written and describes the device's concept including uncertainty analysis and experimental verification. Critical for the produced O₃ mixing ratio are i.e. the lamp intensity and the phototube which need further information. How stable is the phototube and the O₃ calibration source over time? A discussion about the dependency of O₃ production on the lamp line widths, characteristic for the lamp used, should be included in the manuscript. The O₂ absorption around 184.9 nm has fine spectra and therefore the absorption is highly dependent on the line widths of the lamp (e.g. Lanzendorf et al., Geophysical Research Letters, Vol. 24, no. 23, p. 3037-3038, 1997; Hofzumahaus et al., Geophysical Research Letters, Vol. 24, no. 23, p. 3039-3040, 1997; Ceasy et al., Geophysical Research Letters, Vol. 27, no. 11, p. 1651-1654, 2000).

The stability of the detector is addressed in Specific Comment #3 below. Referee #3 is correct that the spectral overlap between the lamp emission lines and the fine structure of the O₂ Schumann-Runge bands is critical to the linearity and stability of the Ozone Calibrator. It is essential to maintain a constant lamp/photolysis cell temperature (40 ± 1 °C) since both the O₂ absorption cross section and line broadening of the Hg emission lines (primarily Doppler broadening) are sensitive to temperature. It is of key importance that the lamp temperature not change appreciably as its intensity is changed. If this occurred to a significant extent, it would result in a nonlinear ozone output due to a changing spectral overlap. Since the measured output is quite linear with lamp intensity, this suggests minimal change in the line broadening of the 184.9 nm Hg line in our Calibrator. We have included the following discussion concerning this on page 7 at line 205: *Past work has shown that the “effective” absorption cross section of O₂ using a Hg lamp at 184.9 nm varies with O₂ concentration (Creasey et al., 2000; Cantrell et al., 1997). This has been shown to be due to poor overlap between the Hg lamp emission lines and the highly structured O₂ absorption in the Schumann-Runge bands (Lanzendorf et al., 1997). Both the O₂ absorption lines and the broadening of the Hg emission lines are sensitive to temperature and, therefore, controlling the photolysis cell temperature at 40 °C (± 1 °C) is critical to maintaining constant spectral overlap. A changing spectral overlap could result from self-heating within the Hg lamp as the intensity is increased and result in nonlinear ozone production. However, the high degree of linearity observed (Fig. 4) suggests that the lamp temperature (thus the spectral overlap) remains constant over the range of lamp intensities employed.*

A varying spectral overlap may also play a role in the long-term stability as the lamp emission degrades over time. However we have found that the long-term calibration appears to be more sensitive to contamination of the windows which slowly attenuates the 253.7 nm light used to control the lamp intensity. That is why we recommend validating the output of the Ozone Calibrator at least annually with an independent standard and we have included this recommendation in Table 2 at the suggestion of Referee #1.

Specific Comments:

1. Page 5, line 150: *As no zero air gas is used ambient air is scrubbed for O3, NO and NO2. Please provide information what kind of scrubber is used and what its efficiencies are for O3 and NOx. In city environment with more than hundred ppb NOx, residual NOx could have a non-negligible effect on the produced ozone. In VOC rich environments, such as forested regions, the produced ozone has the potential to react with remaining ambient VOCs. Additionally, absorption of the UV light by VOCs could occur. Please estimate the uncertainty for your produced ozone concentration due to VOC reactions and absorption.*

We have clarified the details concerning the scrubber in response to both this comment and a similar comment by Referee #1. The scrubber is made of Carulite (a combination of copper and manganese oxides) which catalytically both destroys ozone and oxidizes NO to NO₂. We have changed the manuscript (page, 5, lines 152-154) to read:

“...and a chemical scrubber to remove ozone and NO (which can react relatively rapidly with the ozone produced). The scrubber consists of Carulite, which catalytically destroys ozone and oxidizes NO to NO₂. NO₂ is not removed. Air then enters the photolysis chamber containing a low-pressure mercury lamp...”.

We also agree with Referee #3 that trace gases (primarily NO₂ and VOCs) could potentially interfere with ozone generated by either chemical reactions or light absorption. To address this we have changed the subtitle of Section 3.3 (beginning on page 9, line 272) to: “**Effect of Trace Gases and Water Vapor on the Ozone Output Mixing Ratio**” and have added the following two paragraphs:

Trace gases that are not removed by the inlet scrubber can affect the ozone output in two ways: (1) direct chemical reaction with the ozone produced or (2) by light absorption that can affect either the overall light intensity (reducing O₂ photolysis) or producing reactive photoproducts. NO₂ and volatile organic compounds (VOCs) are of primary concern (water vapor is a special case and considered separately below). Chemical loss of ozone in the photolysis cell is limited by the short residence time ($\tau_{res} \sim 0.06$ s); however, one must also consider the transit time to an analyzer which is to be calibrated. For a typical transit time of ~ 1 s (1 m length of 4 mm i.d. tubing and an analyzer flow rate of 1 L min⁻¹) and assuming an NO₂ or VOC concentration of 500 ppb (extremely polluted urban area), a rate coefficient of $> 1 \times 10^{-15}$ cm³ molec⁻¹ s⁻¹ is required to remove 1% of the ozone produced. Rate coefficients for NO₂ and relatively stable VOCs (atmospheric lifetime > 3 hr) with ozone are typically more than an order of magnitude smaller (Burkholder et al.,

2015, Finlayson-Pitts and Pitts, 2000). There are VOCs that are much more reactive with ozone (most notably terpenoid compounds in forested areas), but due to this high reactivity, their ambient concentrations are rarely above 1 or 2 ppb (e.g., Yee et al., 2018). Furthermore, these reactive VOCs have been shown to be effectively removed by MnO₂-type scrubbers (Pollmann et al., 2005).

Photolysis of NO₂ and possible VOCs cannot compete with O₂ photolysis due to overwhelming concentration difference. Even though aromatic VOCs typically have large absorption cross sections at 184.9 nm ($\sim 10^{-16}$ cm² molec⁻¹, Keller-Rudek et al., 2013), a mixing ratio of 200 ppb results in a VOC photolysis rate ($= I\sigma_{\text{VOC}}[\text{VOC}]$) that is only 1% of the O₂ photolysis rate (Eq (4)). Therefore, the presence of trace VOCs and NO₂ are not large enough to either affect the light intensity or generate substantial amounts of photoproducts that could impact the ozone concentration produced.

2. *Page 5, line 153: The performance of the phototube is one of the critical devices in the setup. Please state, what kind of phototube is used. What is its long term stability?*

The detector is a solid state silicon photodiode. This is already described in the text and we have included the make/model (Hamamatsu, S12742-254) in the existing description on page 4, line 156.

We have also included a sentence and reference about the long-term stability of silicon photodiodes at page 6, line 158: “Solid-state silicon photodiodes are known to maintain their original sensitivity longer than any other photodetector and, as such, are used as NIST transfer standards (Ryer, 1998). This translates to long-term stability in the ozone output of the Ozone Calibrator.”

3. *Page 6, Line 165: What is the accuracy of the regulated flow?*

The mass flow meter is the Model 4121 made by TSI. It has a stated accuracy of $\pm 2\%$ which is verified by comparison with a NIST traceable flow standard (Bios Defender Model 530) in our laboratory. In line 168 (page 6), where we give the make/model number of the flow meter, we have added the stated accuracy.

4. *Page 6, line 167: Please clarify what is meant by scaling the voltage of the photodiode.*

We apologize for the uncertainty, the phrase “voltage of the photodiode” is unclear. We have changed this to read (page 6, line 173): “In addition to controlling the volumetric flow rate the target photodiode signal (corresponding to the target output ozone) is scaled to the instantaneously measured volumetric flow rate in order to compensate for flow rate fluctuations, (e.g., higher flow rates require higher target photodiode signals). ...”

5. *Page 7, line 202: The measured precision is a combination of the precision of the O3 calibration source and the O3 monitor. The authors state that the measured precision of the O3 monitor at zero ozone is 2.1 ppb and the regression of the combined precision of O3 monitor and O3 calibration source has an intercept of 1.8 ppb. However, it is*

unclear, how a constant offset in the precision can be attributed to the O₃ monitor alone.

At an ozone mixing ratio of zero – there is no contribution to the precision from the O₃ calibration source (the lamp is turned off). Thus the O₃ monitor is responsible for the total uncertainty in this situation. However, Referee #3 is correct that the increase in precision with O₃ mixing ratio is a combination of both the calibrator and O₃ monitor and cannot be separated. We only noted the intercept in the plot of precision vs. [O₃] to show that it was nearly the same as that measured in the absence of ozone (1.8 ppb vs. 2.1 ppb). Assuming that the increase in precision was due solely to the Calibrator output gives the estimated 0.4% precision reported; however this is actually more of an upper limit. We have changed the text at page 7, line 218 to read: “Thus, **assuming this increase is due solely to the Ozone Calibrator (and not the Model 202 monitor)**, the precision of the ozone output is about 0.4% of the target concentration (e.g., ±0.4 ppb at 100 ppb O₃ and ±4 ppb at 1,000 ppb O₃).”

6. Page 8, Line 229: What is the uncertainty using this approximation?

The calculation in the preceding two sentences (page 8, lines 241-247) indicates that assuming optically thin conditions only results in about a 1.2% attenuation of the light. This was erroneously reported at 0.13% and we have corrected this. Therefore, the approximation in Eq. (4) is good to within 1.2%. We have also corrected the text to reflect that the photolysis occurs at 40°C (and not 298 K as was previously written).

7. Page 8, Line 236: The obtained O₃ mixing ratio is a function of O₃ production and O₃ loss. In equation (5) the time dependent loss terms, e.g. O₃ photolysis (184.9 nm, 253.7 nm), have to be considered.

Ozone photolysis is unimportant since it produces oxygen atoms (either directly or via quenching of excited state O(¹D) by nitrogen and oxygen) that primarily recombine with O₂ reforming ozone. The only loss terms that can be important involve reactions of O(¹D) atoms (from ozone photolysis) that are not quenched to ground state oxygen atoms (O(³P)). This primarily will occur due to the presence of water vapor and is discussed in Section 3.3 and shown to have a minimal effect on the ozone produced.

8. Page 9, line 272: The authors have estimated the effect of water on the flow meter reading and its absorption for one special case to be 0.5%. Is this the maximum deviation which can occur?

Yes – the case examined pertains to conditions of 100% RH at 40°C (described in the preceding paragraph – page 10, lines 298-300), which is a likely maximum water vapor concentration in ambient air.

9. Page 16, Table 2: The author stated a lower precision and accuracy than described in the paper to account for potential variability among individual instruments. How were these numbers derived? What is the reason for this variability?

As noted in the comment above – it is nearly impossible to separate the precision and accuracy of the Ozone Calibrator to that of the ozone monitor that is used for standardization. The specifications given in Table 2 are chosen to encompass observed uncertainties observed in our typical ozone monitors.

Technical Comments:

1. *Page 1, line 22: Not consistent: Later in the manuscript response time was stated to be < 30 s.*

We have changed to text to read “30 sec” – consistent with later mentions.

2. *Page 3, Line 69: "Because ozone is an unstable gas, easily decomposing to molecular oxygen, calibrations ..." Please add that ozone is not stable in gas cylinders, e.g. "Because ozone is an unstable gas, easily decomposing to molecular oxygen in gas cylinders, calibrations ..."*

We have changed the text as suggested.

3. *Page 6, line 174: Please specify the type and material of the three-way solenoid valve.*

The valve is from Parker Hannifin and is actually a custom part number – we have included the description: “A three-way solenoid valve (Parker-Hannifin, nickel plated V2 miniature valve) is installed...”

4. *Page 8, Line 223: "... and the oxygen concentration (cO2) in air at a temperature of 298 K ..." Please change to: "... and the oxygen concentration (cO2) in dry air at a temperature of 298 K ..."*

We have changed the text as suggested.

5. *Page 8, Line 223: Please use SI units.*

We have included the pressure in kPa as well as atm.

6. *Page 8, Line 245: Please add the range in which the flow can be maintained.*

The flow is maintained to within 1% (30 cm³ min⁻¹ for a 3.0 L min⁻¹ flow rate). We have included this in the initial description of the instrument on page 6, line 171: “...and regulates the volumetric flow rate to be 3.0 L min⁻¹ ($\pm 1\%$) by means of pulse-width modulation of the power supplied to the pump.”

7. *Page 8, line 250: Please quantify indistinguishable.*

We have changed the text to read: “The output ozone mixing ratios are at these two altitudes are indistinguishable (within 2%), as predicted by theory.”

8. *Page 11, line 321: Please quantify "sufficiently accurate".*

Monteith and Unsworth (2008) state that saturation vapor pressures calculated via Eq (16) are within “1 Pa of the exact values” up to 35°C. Note that the humidity measurement is made at near-ambient temperature and prior to the gas entering the heated photolysis cell. We have added this accuracy quote in the text on page 12, line 364.

9. *Page 11, line 337: Please specify type and material of the three-way valve.*

We have included the manufacturer and product number of the valve. The valve was made of stainless steel, but the material choice for this valve is less critical because this three-way valve only contacts dry zero-grade air in the experiment described.

Portable Ozone Calibration Source Independent of Changes in Temperature, Pressure and Humidity for Research and Regulatory Applications

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5 A. Ennis

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10 **Abstract:**

A highly portable ozone (O_3) calibration source that can serve as a U.S. EPA Level 4 transfer standard for the calibration of ozone analyzers is described and evaluated with respect to analytical figures of merit and effects of ambient pressure and humidity. Reproducible mixing ratios of ozone are produced by the
15 photolysis of oxygen in O_3 -scrubbed ambient air by UV light at 184.9 nm light from a low pressure mercury lamp. By maintaining a constant volumetric flow rate (thus constant residence time within the photolysis chamber), the mixing ratio produced is independent of both pressure and temperature and can be varied by varying the lamp intensity. Pulse width modulation of the lamp with feedback from a photodiode monitoring the 253.7-nm emission line is used to maintain target ozone mixing ratios in the
20 range 30-1,000 ppb. In order to provide a constant ratio of intensities at 253.7 and 184.9 nm, the photolysis chamber containing the lamp is regulated at a temperature of 40 °C. The resulting O_3 calibrator has a response time for step changes in output ozone mixing ratio of ~~20-30~~ s and precision (σ_p) of 0.4% of the output mixing ratio for 10-s measurements (e.g., $\sigma_p = \pm 0.4$ ppb for 100 ppb of O_3). Ambient humidity was found to affect the output mixing ratio of ozone primarily by dilution of the
25 oxygen precursor. This potential humidity interference could be up to a few percent in extreme cases but is effectively removed by varying the lamp intensity to compensate for the reduced oxygen concentration based on feedback from a humidity sensor.

1 Introduction

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Ozone (O₃) is a key constituent throughout the atmosphere. In the lower atmosphere, it is a secondary air pollutant formed by the interaction of sunlight with primary pollutants consisting of oxides of nitrogen, carbon monoxide and volatile organic compounds (e.g., Haagen-Smit, 1952; Birks, 1998; Sillman, 1999). Because of its adverse health effects, ozone is one of six Criteria Pollutants designated by the U.S. Environmental Protection Agency (U.S.-EPA, 2018). Although ground-level ambient ozone levels have improved over the past few decades, many regions in the U.S. are still out of compliance with the National Ambient Air Quality Standard (NAAQS) for ozone, and monitoring of ozone at hundreds of State and Local Air Monitoring Sites (SLAMS) is mandated by the EPA.

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In the stratosphere ozone is continuously formed in the photolysis of oxygen by UV light having wavelengths less than 242 nm. The ozone produced absorbs UV light, protecting the Earth from harmful UV-B radiation in the wavelength range 280-320 nm. Monitoring of the protective ozone layer is done by use of ground-based spectroscopic methods (Gotz, et al., 1934; Stone et al., 2015) along with balloon-launched ozonesondes (Komhyr, 1969), occasional aircraft measurements, and satellites.

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Ozone has also long been used industrially for treatment of drinking water (Guinvarch, 1959; Lebout, 1959; Peleg, 1976; Rice, 1996), and there is a rapidly growing number of other applications involving food processing, deodorization, sanitization and sterilization (e.g., Jordan and Carlson, 1913; Kim, 1999; Karaca and Velioglu, 2007). As a result, ozone measurements are required for monitoring industrial processes and insuring the health and safety of workers.

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All of these areas of study require monitoring of ozone levels in either air or water. Although there are numerous methods for measuring ozone, the UV absorbance technique at the 253.7-nm emission line of a low pressure mercury lamp is now almost universally used. Absorbance has the advantage of being an “absolute” method (in theory relying only on the optical pathlength and absorption cross section of the analyte); however, UV photometers used to measure ozone do still require periodic calibration. Since environmental ozone-monitoring applications often require relatively long-term, continuous measurements, systematic errors can arise due to drift of electrical components (e.g., A/D converters, temperature and pressure sensors) or degradation of instrument components such as the sampling pump or O₃ scrubber. Errors due to incomplete flushing of the detection cell between analyte and reference measurements of light intensity can result from reduced pumping efficiency. Incomplete scrubbing of ozone during the reference light intensity measurement, as well as adsorption/desorption of UV-absorbing species such as aromatic VOCs and elemental mercury from the ozone scrubber (Spicer et al., 2010; Turnipseed et al, 2017), and the effects of changing humidity levels

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on light transmission through the detection cell (Wilson and Birks, 2006) can all affect the photometer's linearity and offset. Ozone instruments based on other techniques such as electrochemical ozonesondes (Komhyr, 1969) or solid-phase or gas-phase chemiluminescence (Regener, 1964; Güsten et al., 1992) also are known to be sensitive to many variables that can induce systematic errors and often require even more frequent calibration checks. As a result, periodic calibrations of ozone monitors of all types are required, and a portable calibrator is highly desirable, especially for instruments deployed in remote locations.

Because ozone is an unstable gas, easily decomposing to molecular oxygen in gas cylinders, calibrations require generating ozone at known concentrations at the site of the ozone monitor to be calibrated. This is done almost universally by use of an ozone calibration source in which ozone is generated by photolysis of O₂ at 184.9 nm using a low pressure mercury lamp. Most commonly, the calibrator dries the ambient air or uses dry air from a compressed gas cylinder to eliminate biases due to water vapor and incorporates an ozone photometer that continuously measures the ozone produced. The target output mixing ratio of ozone is then controlled in a feedback loop that regulates the lamp intensity. Such calibrators are relatively large, heavy and have high power requirements. A more portable instrument such as the one described here can regulate ozone output mixing ratios solely based on feedback from measurements of the lamp intensity and does not require dry air or a built-in photometer.

For regulatory purposes, ozone measurements must be traceable to a fundamental reference standard. In the U.S., the EPA originally prescribed a wet chemical technique for ozone calibrations based on the spectrophotometric analysis of iodine generated by O₃ in a neutral potassium iodide solution (NBKI method) that itself was referenced to an arsenious oxide primary standard (Beard et al., 1977). That method was replaced in 1979 with direct absorbance in the gas phase, now using an accepted value for the absorption cross section for O₃ at 253.7 nm of $1.15 \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1}$ (Burkholder et al., 2015). The U.S. and many other nations are members of the Convention of Meter, which makes use of the International Bureau of Weights and Measures (BIPM) Standard Reference Photometer #27 as the world's ozone reference standard (Paur et al., 2003). Each member state of the Convention of the Meter has one laboratory designated to provide traceability to that country. For the U.S. that laboratory is the National Institute for Standards and Technology (NIST). Standard Reference Photometers (SRPs) are maintained by both NIST and the EPA. The calibrations of regulatory ozone monitors in the U.S. are traceable to these Level 1 SRPs via transfer standards, as detailed in Fig. 1. This figure also shows how EPA-maintained SRPs trace back through the NIST Standard Reference

95 Photometer #0 (SRP#0) to the world standard, SRP #27. Once every two years, the NIST SRP #2 is
calibrated against the NIST SRP #0. The EPA Office of Research and Development Metrology maintains
EPA SRP #1 and #7, and these are verified against the NIST SRP #2 once each year. Verification requires
that a linear regression of the photometer ozone output plotted against the NIST SRP have a slope of
1.00±0.01 and intercept of ±1 ppb; i.e., 1% agreement. Upon verification, EPA SRP #7 is sent to the
different EPA regions for verification of their respective SRPs. As further verification, EPA SRP #7 is
100 occasionally compared to EPA SRP #1.

Transfer standards are defined as “a transportable device or apparatus which, together with
associated operation procedures, is capable of accurately reproducing pollutant concentration
standards or produce accurate assays of pollutant concentrations which are quantitatively related to a
higher level and more authoritative standard” (U.S.-EPA, 2013). Thus, a transfer standard for ozone can
105 be either an ozone source or an ozone analyzer. The EPA accepts up to four levels of ozone transfer
standards for calibration of an ozone monitoring site or field ozone analyzer, as shown in Fig. 1. Also, as
illustrated in this figure, the uncertainty increases with each level of transfer standard. Typically, a Level
2 “uncompromised standard” is maintained in the laboratory where conditions of use may be carefully
controlled. This transfer standard is used to calibrate Level 3 transfer standards that encounter frequent
110 use and potentially rough treatment in the field. The Level 3 transfer standards may be returned on a
frequent basis for verification by the Level 2 standard. Level 4 standards, calibrated against Level 3
standards, also are allowed. Often, level 3 and 4 standards are more portable and designed to be more
rugged and/or less sensitive to environmental conditions than higher level transfer standards. They may
be used for calibrating instruments deployed in remote locations, for example.

115 An EPA Level 2 transfer standard must include both an ozone generation device and an analyzer.
A Level 3 transfer standard can be a combination of an ozone generator and analyzer or only an
analyzer. A Level 4 transfer standard can be an ozone analyzer or only an ozone generation device.
Thus, the ozone calibration source described here qualifies as a Level 4 transfer standard. Levels 2-4
Transfer Standards must undergo a “6x6” verification in which six calibration curves, each consisting of
120 six approximately equally spaced ozone concentrations in a range including 0 and 90% (±5%) of the
upper range of the reference standard, is 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.

125 Here we describe a portable, low-cost ozone calibrator that meets the specifications as an EPA
Level 4 transfer standard. The calibrator is low power, requiring only 18 watts of power, and does not

require the inlet air to be dried. It is independent of both temperature and pressure and corrections due to humidity are easily incorporated. Therefore, it can provide accurate and precise ozone mixing ratios for calibration of field analyzers or can be used as a reliable ozone source in laboratory experiments.

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2 Experimental

The 2B Technologies Model 306 Ozone Calibration Source™ described here makes use of a low pressure mercury (Hg) lamp to photolyze oxygen in ambient air to produce known mixing ratios of ozone. The vacuum UV lines at 184.9 nm are absorbed by O₂ to produce oxygen atoms. The oxygen atoms rapidly attach to O₂ to form ozone molecules according to the same mechanism that is responsible for the presence of Earth's protective ozone layer:

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where $h\nu$ symbolizes a photon of light and M is any molecule (e.g., N₂, O₂, Ar). Absorption of one photon of 184.9-nm light by O₂ results in the formation of two ozone molecules. The concentration of ozone produced in a flowing stream of air depends on the intensity of the photolysis lamp, the concentration of oxygen (determined by pressure, temperature and its mixing ratio in air), and the residence time in the photolysis cell (determined by volumetric flow rate and cell volume). As will be discussed below, pressure and temperature affect the concentration of the ozone produced (e.g., molec cm⁻³), but do not affect the output mixing ratio (e.g., ppb). Thus, by holding the volumetric flow rate constant, it is possible to produce a flow of air containing a constant mixing ratio of ozone that can be varied most conveniently by changing and controlling the lamp intensity.

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Figure 2 is a schematic diagram of the 2B Technologies Model 306 Ozone Calibration Source. Ambient air is forced by an air pump through a particulate filter, a mass flow meter, and a chemical scrubber to remove ozone and ~~NO_x (=NO (which can react relatively rapidly with the ozone produced) + NO₂).~~ The scrubber consists of Carulite, which catalytically destroys ozone and oxidizes NO to NO₂. NO₂ is not removed. before entering Air then enters the photolysis chamber containing a low-pressure mercury lamp (BHK, #81-1025-51) where absorption of 184.9-nm photons by oxygen produces ozone. The lamp intensity at 253.7 nm is monitored by a photodiode (Hamamatsu, S12742-254) having a built-in interference filter centered at 254 nm and is controlled by the microprocessor in a feedback loop to

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maintain a target output ozone mixing ratio. Solid-state silicon photodiodes are known to maintain their original sensitivity longer than any other photodetector and, as such, are used as NIST transfer standards (Ryer, 1998). This translates to long-term stability in the ozone output of the Ozone Calibrator. Note that the lamp emission at 253.7 nm, which is not absorbed by oxygen to make ozone, is monitored instead of the 184.9 nm line. This is because the window that separates the photodiode from the photolysis chamber is much more susceptible to changes in transmission due to deposition of UV-absorbing materials at 184.9 nm than at 253.7 nm. In order to maintain a constant ratio of emission intensities of the Hg lamp at 184.9 and 253.7 nm, the photolysis chamber temperature is regulated at 40 °C by means of a temperature sensor and heating cartridge. Pressure within the gas stream is measured but not controlled. The residence time (~ 0.06 s) is held constant by ensuring a constant volumetric flow rate using a mass flow meter (TSI Instruments, Model 40404041, accuracy of ± 2%) converted to volumetric flow using the measured temperature and pressure of the photolysis cell. -A microprocessor reads the output of the mass flowmeter, temperature and pressure of the photolysis chamber, and regulates the volumetric flow rate to be 3.0 L min⁻¹ (± 1%) by means of pulse-width modulation of the power supplied to the pump. In addition to controlling the volumetric flow rate the target photodiode voltage signal (corresponding to the target output ozone) is scaled to the instantaneously measured volumetric flow rate in order to compensate for flow rate fluctuations, (e.g., higher flow rates require higher target photodiode voltage signals).

Air containing ozone exits the photolysis cell through an overflow tee, where excess air that is not drawn by the ozone monitor being calibrated is exhausted through an internal ozone scrubber. The output of the ozone calibration source may be attached directly to any ozone monitor (providing that its sampling rate is less than 3.0 L min⁻¹); excess ozone flow is diverted through the ozone scrubber internal to the calibrator, and any perturbation in total flow rate is automatically adjusted by the microprocessor using feedback from the mass flow meter. A three-way solenoid valve (Parker, nickel-plated V2 miniature valve) is installed just before the exit of the calibrator that allows the ozone calibration source to be plumbed in-line with the sampling inlet to an ozone monitor, so that the monitor can sample either ambient air or the output of the calibrator. The output of the ozone source is calibrated using a reference ozone monitor with traceability to NIST, and slope and offset calibration parameters are determined from linear regression and applied to the target photodiode voltages to achieve target ozone mixing ratios.

3 Results and Discussion

190 **3.1 Linearity, Reproducibility and Precision of Output Concentration**

195 An example of stepwise outputs of a Model 306 Ozone Calibration Source is provided in Fig. 3. The target output ozone mixing ratio was varied in the range of 0 to 1,000 in steps of 0, 50, 100, 200, 400, 600, 800 and 1,000 ppb. This was followed by a series of decreasing steps back to 0 ppb. A second set of stepwise increases and decreases in target ozone concentrations followed. Each step concentration was maintained for ~5 minutes (30 measurements). Output ozone concentrations were measured and logged every 10 s by a 2B Technologies Model 202 Ozone Monitor, a U.S. EPA Federal Equivalent Method (FEM). Note that the response time to achieve a new target concentration is 3 or fewer data points (< 30 s). The response of the calibration source is actually faster considering that it is convolved with the Model 202 Ozone Monitor which outputs the average of the most recent two 10-s measurements. Figure 4 is a plot of average measured ozone concentration vs target concentration for the data of Fig. 3. Linear regression lines are drawn for the two stepwise increases and two stepwise decreases in target ozone concentration. The data points and four regression lines overlap so well that they cannot be distinguished on the graph. The equations for the linear regression lines have slopes that agree to better than $\pm 1\%$, and the standard deviation of the four intercepts is 1.3 ppb. The coefficients of determination (R^2) are all 0.9999 or 1.0000. Past work has shown that the “effective” absorption cross section of O_2 using a Hg lamp at 184.9 nm varies with O_2 concentration (Creasey et al., 2000; Cantrell et al., 1997). This has been shown to be due to poor overlap between the Hg lamp emission lines and the highly structured O_2 absorption in the Schumann-Runge bands (Lanzendorf et al., 1997). Both the O_2 absorption lines and the broadening of the Hg emission lines are sensitive to temperature and, therefore, controlling the photolysis cell temperature at $40\text{ }^\circ\text{C} (\pm 1\text{ }^\circ\text{C})$ is critical to maintaining constant spectral overlap. A changing spectral overlap could result from self-heating within the Hg lamp as the intensity is increased and result in nonlinear ozone production. However, the high degree of linearity observed (Fig. 4) suggests that the lamp temperature (thus the spectral overlap) remains constant over the range of lamp intensities employed.

215 The precisions ($1\sigma_p$) of the measured output ozone mixing ratios vary from 2.1 ppb at 0 ppb ozone (i.e., the measurement precision of the Model 202 ozone monitor) to 6.2 ppb at 1,000 ppb ozone. A plot of precision vs ozone concentration (data not shown) gives a straight line with intercept of 1.8 ppb, slope of 0.0042 ppb/ppb O_3 and R^2 of 0.9586. Thus, assuming this increase is due solely to the Ozone Calibrator (and not the Model 202 monitor), the precision of the ozone output is about 0.4% of the target concentration (e.g., ± 0.4 ppb at 100 ppb O_3 and ± 4 ppb at 1,000 ppb O_3).

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In order to verify the ability of the Model 306 Ozone Calibration Source to qualify as a US EPA Level 4 Transfer Standard (US EPA, 2013), we carried out a “6x6” calibration in which we measured the output of the ozone calibration source at six different target ozone concentrations (50, 100, 150, 200, 250, and 300 ppb) in addition to a zero ozone measurement on six consecutive days. The ozone output mixing ratios were measured using a 2B Technologies Model 205 FEM ozone monitor. As can be seen in Table 1, the instrument easily met the requirements (given in Table 3-1 of US EPA, 2010) of a Level 4 standard with a measured relative standard deviation (RSD) of 0.26% for the slopes of the regression plots vs. the requirement of $\leq 3.7\%$ and a measured standard deviation of 0.33 ppb of the intercepts vs. the requirement of ≤ 1.5 ppb. Values for the coefficient of determination (R^2) were in the range of 0.9998 to 1.0000 with an average of 0.9999 for the six calibration plots.

Other specifications of that are of interest for portability (such as the size, weight and power requirements) are given in Table 2.

3.2 Effect of Pressure on the Ozone Output Mixing Ratio

As described earlier, the target mixing ratio output of the ozone calibration source is achieved by varying the photolysis lamp intensity and maintaining a constant volumetric flow rate. Pressure within the gas stream is measured to correct the mass flow measurements, but not controlled, since the goal is to produce a constant mixing ratio (mole fraction) of ozone rather than a constant concentration. The absorption cross section (σ_{O_2}) for O_2 at the 184.9 nm Hg line is still poorly known due to significant fine structure in the spectrum but is approximately $1 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ (Yoshino et al., 1997; Creasey et al., 2000), and the oxygen concentration (c_{O_2}) in dry air at a temperature of 298 K and pressure of 1 atm (101.325 kPa) is $5.249 \times 10^{18} \text{ molec cm}^{-3}$. The average path length (l) of the ozone calibration source was designed to be $\sim 0.25 \text{ cm}$, making the absorbance ($\sigma_{O_2}l$) optically thin with a single path absorbance of $\sim 1.3 \times 10^{-23}$; i.e., only 0.1312% of the 184.9-nm light emitted by the lamp is absorbed by oxygen. Under optically thin conditions, the ozone production rate (P_{O_3}) within the photolysis chamber is given by

$$P_{O_3} = 2I\sigma_{O_2}c_{O_2} = 2I\sigma_{O_2}(0.2095c_{air}) \quad (4)$$

where I is the lamp intensity ($\text{photons cm}^{-2} \text{ s}^{-1}$) at 184.9 nm, and c_{O_2} is the concentration of oxygen molecules (molec cm^{-3}), which make up 20.95% of dry air. The factor of 2 accounts for the production of

two ozone molecules for every oxygen molecule photolyzed. The output mixing ratio of ozone (fraction of air molecules that are ozone), X_{O_3} , in ppb is then given by

$$X_{O_3}(\text{ppb}) = \frac{(P_{O_3}, \frac{\text{molec}}{\text{cm}^3 \text{ s}})(\tau_{\text{cell}}, \text{ s})}{(c_{\text{air}}, \frac{\text{molec}}{\text{cm}^3})} \times 10^9 = \frac{2I\sigma_{O_2}(0.2095)V}{F} \times 10^9 \quad (5)$$

where τ_{cell} is the residence time of the photolysis cell, which is equal to the cell volume (V) divided by the volumetric flow rate, F , and P_{O_3} is given by equation 4. Note that the total molecular concentration of air in the denominator of equation 5 cancels with the air concentration in the numerator, so the ozone mixing ratio output is independent of molecular concentration and therefore independent of chamber pressure and temperature (although chamber temperature is controlled for a separate reason described in Section 2). The only parameters that affect the ozone output mixing ratio are the lamp intensity and volumetric flow rate. As mentioned before, the volumetric flow rate is computed from the measured mass flow rate, temperature, and pressure, and is maintained at 3 L min^{-1} .

In order to test for the predicted independence of ambient pressure, the output of a calibrated Model 306 Ozone Calibration Source was measured at six programmed ozone concentrations (0, 100, 200, 300, 400, and 500 ppb) in Boulder, Colorado (5,430 ft, 1,655 m altitude; $P \cong 0.82 \text{ atm}$) and at Fritz Peak (9,020 ft, 2,749 m altitude; $P \cong 0.71 \text{ atm}$) in the mountains west of Boulder. The results are shown in Fig. 5. The output ozone mixing ratios are at these two altitudes are indistinguishable (within 2%), as predicted by theory.

3.3 Effect of Trace Gases and Water Vapor on the Ozone Output Mixing Ratio

Trace gases that are not removed by the inlet scrubber can affect the ozone output in two ways: (1) direct chemical reaction with the ozone produced or (2) by light absorption that can affect either the overall light intensity (reducing O_2 photolysis) or producing reactive photoproducts. NO_2 and volatile organic compounds (VOCs) are of primary concern (water vapor is a special case and considered separately below). Chemical loss of ozone in the photolysis cell is limited by the short residence time ($\tau_{\text{res}} \sim 0.06 \text{ s}$); however, one must also consider the transit time to an analyzer which is to be calibrated. For a typical transit time of $\sim 1 \text{ s}$ (1 m length of 4 mm i.d. tubing and an analyzer flow rate of 1 L min^{-1}) and assuming an NO_2 or VOC concentration of 500 ppb (extremely polluted urban area), a rate coefficient of $> 1 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ is required to remove 1% of the ozone produced. Rate coefficients for NO_2 and relatively stable VOCs (atmospheric lifetime $> 3 \text{ hr}$) with ozone are typically

285 more than an order of magnitude smaller (Burkholder et al., 2015, Finlayson-Pitts and Pitts, 2000).
There are VOCs that are much more reactive with ozone (most notably terpenoid compounds in
forested areas), but due to this high reactivity, their ambient concentrations are rarely above 1 or 2 ppb
(e.g., Yee et al., 2018). Furthermore, these reactive VOCs have been shown to be effectively removed by
MnO₂-type scrubbers (Pollmann et al., 2005).

290 Photolysis of NO₂ and possible VOCs cannot compete with O₂ photolysis due to
overwhelming concentration difference. Even though aromatic VOCs typically have large
absorption cross sections at 184.9 nm ($\sim 10^{-16}$ cm² molec⁻¹, Keller-Rudek et al., 2013), a mixing
ratio of 200 ppb results in a VOC photolysis rate ($= I\sigma_{\text{VOC}}[\text{VOC}]$) that is only 1% of the O₂
photolysis rate (Eq (4)). Therefore, the presence of trace VOCs and NO₂ are not large enough to
either affect the light intensity or generate substantial amounts of photoproducts that could
impact the ozone concentration produced.

295 Due to its high ambient concentration, ~~Water-water~~ vapor is unique and could potentially affect
the output ozone concentration in several ways. The first is simply by dilution. As the relative humidity
increases, the partial pressure and therefore molecular concentration of O₂ decreases, resulting in a
reduced production rate of ozone. The water vapor mixing ratio in the atmosphere is typically ~2% by
volume but could be as high as 7.3% (100% RH at 40 °C), resulting in a 7.3% reduction in ozone output in
300 highly humid air if the ozone calibration source were originally calibrated in dry air.

Another way that water vapor can reduce the output ozone mixing ratio is by attenuating the
lamp intensity through absorbance. The absorption cross section for H₂O at 184.9 nm is 7.14×10^{-20} cm²
molec⁻¹ (Cantrell et al., 1997). In the extreme case mentioned above of a water vapor mixing ratio of
7.3% ([H₂O] = 1.8×10^{18} molec cm⁻³), the average fraction of 184.9-nm light absorbed by water vapor at
305 atmospheric pressure and 40° C integrated over the 0.25 cm path length is 1.6%. An offsetting factor is
that the mass flow controller is 15.4% more sensitive to water vapor ($C_p = 33.59$ J K⁻¹ mol⁻¹) than to air
($C_p = 29.10$ J K⁻¹ mol⁻¹) due to its higher heat capacity (NIST, 2018). Increasing the water vapor mixing
ratio results in a positive error in the measured flow rate, with the result that the air pump is slowed
down in the feedback loop to maintain a constant apparent flow rate and the residence time in the
310 photolysis cell is increased. For a 7.3% increase in water vapor, this effect results in a 1.1% increase in
ozone output. Thus, these two factors – the attenuation of 184.9-nm light by water vapor and the
reduced flow rate due to change in heat capacity of the sample air – offset one another to within ~0.5%
in expected ozone output.

Yet another way that humidity could affect ozone production is through secondary
315 photochemical reactions. The photochemistry of water vapor is rather complicated, especially in the
presence of ozone. HO_x radicals (OH and HO₂) are produced directly by photolysis of water vapor,



and indirectly in the reaction of O(¹D₂) with water vapor. O(¹D₂) is produced in the photolysis of ozone
320 at the principal mercury line of 253.7 nm where ozone has a strong absorption,



Although most of the O(¹D₂) is quenched by oxygen and nitrogen in the air stream, a small fraction can
react with water, producing OH,



325 Hydroxyl radicals participate in a well-known, yet relatively slow, catalytic cycle for ozone destruction
(Bates and Nicolet, 1950):



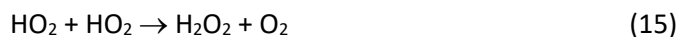
But the concentration of hydroxyl radicals that build up inside the photolysis chamber is limited by its
self-reaction, which actually produces ozone,



335 and by the very fast chain termination reaction of OH and HO₂:



Reaction (14) limits the importance of the self-reaction of HO₂,



which also serves to remove HO₂. Subsequent photolysis of the H₂O₂ product could regenerate OH, but
340 this was found to have no significant effect on the output mixing ratio of ozone in the model calculations
discussed below, likely due to the low amounts of H₂O₂ produced.

The photochemistry within the photolysis chamber was modeled using current
recommendations for the absorption cross sections and reaction rate constants of relevant reactions
summarized in Table 3. Light intensity at 184.9 nm was adjusted in the model to produce desired output
345 mixing ratios of ozone in the range 0-1,000 ppb in the absence of water vapor. Model results for a

target output concentration of 100 ppb ozone are summarized in Fig. 6. In the extreme case of a temperature of 40 °C and 100% RH (water mixing ratio of 7.3%), the ozone output mixing ratio increases by 0.9% (0.9 ppb) due to production of O atoms in the OH self-reaction, reaction 13. For more typical conditions of 25 °C and 50% RH, the increase in ozone production is only 0.2% for a target mixing ratio of 100 ppb. For a target of 1,000 ppb, the percentage increase in ozone production is slightly smaller, being only 0.06% (0.6 ppb) at 40 °C and 100% RH. Under these conditions the catalytic ozone destruction cycle of reactions 9 and 10 begin to offset ozone production in the OH self-reaction. Under more typical conditions of 25 °C and 50% RH, the increase in ozone concentration is modeled to be less than 0.01% (less than 0.1 ppb) for a target of 1,000 ppb ozone.

Based on the analysis given above, the only significant effect of water vapor (> 1%) on the output of the ozone calibration source is the dilution of oxygen in the inlet air. In order to correct for the dilution effect, a humidity sensor (Honeywell, HIH8000) was installed in the flow path via a tee with the sensor head protruding into the main flow immediately upstream of the photolysis cell, and feedback from that sensor was used to adjust the lamp intensity to compensate for dilution of oxygen by water vapor. The sensor provides simultaneous measurements of relative humidity (RH) and temperature with a response time of ~ 10 seconds so that mixing ratios of water vapor may be calculated. Several empirical equations have been developed to fit the vapor pressure of water as a function of RH and temperature. The Magnus-Tetens equation (Tetons, 1930; Montieith and Unsworth, 2008) is sufficiently accurate (within 1 Pa up to T = 35°C, Montieith and Unsworth, 2008) while being simple:

$$P_{H_2O}(mbar) = 6.1078 \exp\left(\frac{17.27 \cdot T(^{\circ}C)}{T(^{\circ}C) + 237.3}\right) \quad (16)$$

The mixing ratio of water is then given by:

$$X_{H_2O} = \frac{P_{H_2O}(mbar)}{P(total)} \times \%RH/100 \quad (17)$$

Water dilutes the oxygen in the photolysis chamber and therefore reduces the output of the ozone source by the same factor. In order to compensate, we may increase the lamp target intensity by a factor of $1/(1 - X_{H_2O})$, and the overall factor we need to multiply the target lamp intensity by is:

$$\frac{1}{\left[1 - \frac{6.1078}{P_{Total}} \exp\left(\frac{17.27 * T(^{\circ}C)}{T(^{\circ}C) + 237.3}\right) \frac{\%RH}{100}\right]} \quad (18)$$

380 In order to test this algorithm, we measured the output of a 2B Technologies Model 306 Ozone Calibration Source with and without water vapor added. A three-way valve directed a volumetric flow rate of 3 L min⁻¹ of dry zero air (US Welding) from a compressed gas cylinder to either bypass or pass through a Nafion® tube immersed in a temperature-controlled water bath to provide either dry air or humidified air to the inlet of the Model 306. The output of the ozone calibration source was sampled by a 2B Technologies Model 211 Ozone Monitor, which because of its gas-phase-scrubber technology and

 385 internal DewLine™ (Nafion® tube) to equilibrate humidity levels of ozone scrubbed and unscrubbed air, has no significant sensitivity to water vapor. Experiments were performed with and without lamp intensity adjustment controlled by the instrument firmware to correct the presence of water vapor. Figure 7a shows the calibration curves obtained for ozone in the range 0-200 ppb at 0% RH (bypass) and an average of 82% RH (water vapor added via Nafion® tube) under ambient conditions of 875 mbar

 390 pressure and temperature of 23.6 °C and with no lamp intensity adjustment for humidity. The slope of the regression line in the presence of humidity is 2.8% lower than that for dry air, which agrees extremely well with the mixing ratio of water calculated to be 2.7%. Figure 7b shows the calibration curves obtained for zero air and for humid air (90% RH at 23.8 °C, 3.2% water vapor) where the calibrator lamp intensity is corrected for the dilution due to humidity. As seen in the figure, the slopes

 395 are now within 0.1% of each other (0.9929 for dry air and 0.9917 for humid air, i.e., no statistical difference).

4 Conclusions

400 The 2B Technologies Model 306 Ozone Calibration Source is capable of producing ozone in ozone-scrubbed ambient air with accuracy and precision better than 1 ppb in the range 30-100 ppb ozone or 1% in the range 100-1,000 ppb. The volumetric flow rate of 3 L min⁻¹ allows calibration of virtually any ozone monitor via sampling from a built-in overflow tee. The instrument is made independent of ambient pressure and temperature by feedback control of the air pump to produce a constant volumetric flow rate through the photolysis chamber. Regulation of the photolysis chamber

 405 temperature, typically at 40 °C, assures a constant ratio of lamp intensities at 184.9 nm (used to photolyze O₂) and 253.7 nm (monitored for feedback control of the lamp intensity). The effect of

ambient humidity on ozone production is primarily that of dilution of the O₂ photochemical precursor. This dilution effect is completely eliminated by means of feedback control of the photolysis source intensity based on real time measurements of humidity. Photochemical reactions involving HO_x species due to the presence of water vapor only contribute to ozone production by a small amount (< 1% at 40 °C and 100% RH). The ozone calibration source described here is low power (~ 18 W) and highly portable, weighing only 2.6 kg and requiring no compressed or dry gas sources. Yet it still meets the requirements of an EPA Level 4 transfer standard that can be used in the calibration of compliance-monitoring ozone monitors.

5 References

Bates, D.R., and Nicolet, M.: The photochemistry of atmospheric water vapor, *J. Geophys. Res.*, 55, 301–307, 1950.

Beard, M.E., Margeson, J.H., and Ellis, E.C.: Evaluation of 1 percent neutral buffered potassium iodide solution for calibration of ozone monitors, Report No. EPA-600/4-77-005, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977.

Birks, J.W.: Oxidant formation in the troposphere. In *Perspectives in Environmental Chemistry*, D. L. Macalady, Oxford University Press, pp. 233–256, 1998.

Burkholder, J.B., Sander, S.P., Abbatt, J., 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 No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 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, 1997.

[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, HO2 and RO2 radicals, *Geophys. Res. Lett.*, 27, 1651-1654, 2000.](#)

[Finlayson-Pitts, B.J. and Pitts, J.N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications, Academic Press, San Diego, 2000.](#)

Gotz, F., Meetham, A.R., and Dobson, G.B.: The vertical distribution of ozone in the atmosphere, *Proc. Roy. Soc. London Ser. A*, 145, 416–446, 1934.

Guinvarch, P.: Three years of ozone sterilization of water in Paris, in *Ozone Chemistry and Technology*, *Adv. Chem.*, Vol. 21., American Chemical Society, 416–429, 1959.

Güsten, H., Heinrich, G., Schmidt, R.W.H., Schurath, U.: A novel ozone sensor for direct eddy flux measurements, *Journal of Atmospheric Chemistry* 14, 73–84, 1992.

- 450 Haagen-Smit, A.J.: Chemistry and physiology of Los Angeles smog, *Industrial and Engineering Chemistry*, 44, 1342–1346, 1952.
- 455 Hudson, R. D., and Mahle, S. H.: Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere. *J. Geophys. Res.*, 77, 2902–2914, 1972.
- Jordan, E.O. and Carlson: A.J., Ozone: Its bactericidal, physiologic and deodorizing action, *JAMA*, 61, 1007–1012, 1913.
- 460 Kim, J.-G., Yousef, A.E., Dave, S., Application of ozone for enhancing the microbiological safety and quality of foods: a review, *Journal of Food Protection*, 62, 1071–1087, 1999.
- Komhyr, W.D.: Electrochemical concentration cells for gas analysis, *Ann. Geophys.* 25, 203–210, 1969.
- 465 [Keller-Rudek, H., Moortgat, G. K., Sander, R., and Sörensen, R.: The MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest, *Earth Syst. Sci. Data*, 5, 365–373, 2013.](#)
- 470 [Lanzendorf, E.J., Hanisco, T.F., Donahue, N.M., and Wennberg, P.O.: Comment on: “The measurement of tropospheric OH radicals by laser-induced fluorescence spectroscopy during the POPCORN field campaign” by Hofzumahaus et al and “Intercomparison of tropospheric OH radical measurements by multiple folder long-path laser absorption and laser-induced fluorescence” by Brauers et al., *Geophys Res. Lettr.*, 24, 3037-3038, 1997.](#)
- 475 Lebout, H.K: Fifty years of ozonation at Nice, *Advances in Chemistry*, Vol. 21, Ozone Chemistry and Technology, pp 450–452, American Chemical Society, 1959.
- Monteith, J.L., and Unsworth, M.H. *Principles of Environmental Physics*. Third Ed. AP, Amsterdam, 2008.
- 480 NIST, National Institute of Standards and Technology, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, <http://webbook.nist.gov>, Visited 2 April 2018.
- 485 Paur, R. J., Bass, A.M., Norris, J.E., and Buckley, T.J.: Standard reference photometer for the assay of ozone in calibration atmospheres, *NISTIR 6369*, Natl. Inst. of Stand. and Technol., Gaithersburg, Maryland, 2003.
- 490 Peleg, M.: The chemistry of ozone in the treatment of water, *Water Research* 10, 361–365, 1976.
- [Pollmann, J., Ortega, J., and Helmig, D.: Analysis of Atmospheric Sesquiterpenes: Sampling losses and mitigation of ozone interference, *Environ. Sci. Technol.*, 39, 9620-9629, 2005.](#)
- 495 Regener, V.H.: Measurement of ozone with the chemiluminescent method, *J. Geophys. Res.*, 69, 3795–3800, 1964.
- Rice, R.: Applications of ozone for industrial wastewater treatment – a review, *Ozone: Science and Engineering*, 18, 477–515, 1996.

Ryer, Alexander. ILT Light Measurement Handbook. Newburyport: International Light, 1998.
<http://www.intl-lighttech.com/services/ilt-light-measurement-handbook> (accessed 26 June 2018).

- 500 Sillman, S.: The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments, *Atmospheric Environment*, 33, 1821–1845, 1999.
- Spicer, C.W., Joseph, D.W., and Ollison, W.M.: A re-examination of ambient air ozone monitor interferences, *J. Air Waste Manage. Assoc.*, 60, 1353-1364, 2010.
- 505 Stone, K., Tully, M.B., Rhodes, S.K., and Shofield, R.: A new Dobson Umkehr ozone profile retrieval method optimizing information content and resolution, *Atmospheric Measurement Techniques*, 8, 1043–1053, 2015.
- 510 Tetens, O.: Über einige meteorologische Begriffe. *Z. Geophys* 6, 207-309, 1930.
- Turnipseed, A., Andersen, P.C., Williford, C.J., and Birks, J.W.: Use of a heated graphite scrubber as a means of reducing interferences in UV-absorbance measurements of atmospheric ozone, *Atmos. Meas. Tech.* 10, 2253–2269, 2017.
- 515 U.S.-EPA: Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone, Ozone Transfer Guidance Document 10/2013, Publication No. EPA-454/B-13-004, Office of Air Quality Planning Standards, Air Quality Assessment Division, Research Triangle Park, North Carolina, October 2013.
<https://www3.epa.gov/ttn/amtic/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf>, Visited April 2, 2018.
- 520 U.S.-EPA: Criteria Air Pollutants, <https://www.epa.gov/criteria-air-pollutants>, Visited 2 February 2018.
- 525 Wilson, K.L. and Birks, J.W.: Mechanism and elimination of a water vapor interference in the measurement of ozone by UV absorbance, *Environmental Science and Technology*, 40, 6361–6367, 2006.
- 530 Yee, L.D., Isaacman-VanWertz, G., Wernis, R.A., Meng, M., Rivera, V., Kreisberg, N.M., Hering, S.V., Bering, M.S., Glasius, M., Upshur, M.A., Be, A.G., Thomson, R.J., Geiger, F.M., Offenber, J.H., Lewandowski, M., Kourtchev, I., Kalberer, M., de Sa, S., Martin, S.T., Alexander, M.L., Palm, B.B., Hu, W., Campuzano-Jost, P., Day, D.A., Jimenez, J.L., Liu, Y., McKinney, K.A., Artaxo, P., Viegas, J., Manzi, A., Oliverira, M.B., de Souza, R., Machado, L.A.T., Longo, K., and Goldstein, A.H.: Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry season, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-191>.

Table 1. Results of a US EPA “6x6” calibration of the Model 306 Ozone Calibration Source.

Day	Slope	Offset, ppb	R²
1	1.0031	0.37	0.9998
2	1.0032	-0.22	0.9998
3	1.0054	-0.05	0.9999
4	1.0088	-0.47	0.9999
5	1.0072	0.29	0.9999
6	1.0021	0.21	1.0000
Average	1.0050	0.02	0.9999
Std. Dev.	0.0026	0.33	0.0001

Table 2. Analytical and Physical Specifications for Ozone Calibration Source

Method of Ozone Production	UV Photolysis of O ₂ at 184.9 nm
Output Concentration Range	0 ppb and 30 to 1,000 ppb
Precision and Accuracy of Output	Greater of 2 ppb or 2% of ozone concentration ¹
Response Time for Change in Ozone Output Concentration	30 s to reach 95% of concentration change
Output Flow Rate	3.0 Liter min ⁻¹ volumetric
Power Requirements	12 V dc or 120/240 V ac, 18 watt
Size	3.5 x 8.5 x 11 in (9 x 21 x 29 cm)
Weight	5.6 lb (2.6 kg)
<u>Recommended Calibration time²</u>	<u>Once a year</u>

¹The 2B Technologies specification for precision and accuracy of the Model 306 Ozone Calibration Source given here is larger than found in this work and accounts for potential variability among individual instruments.

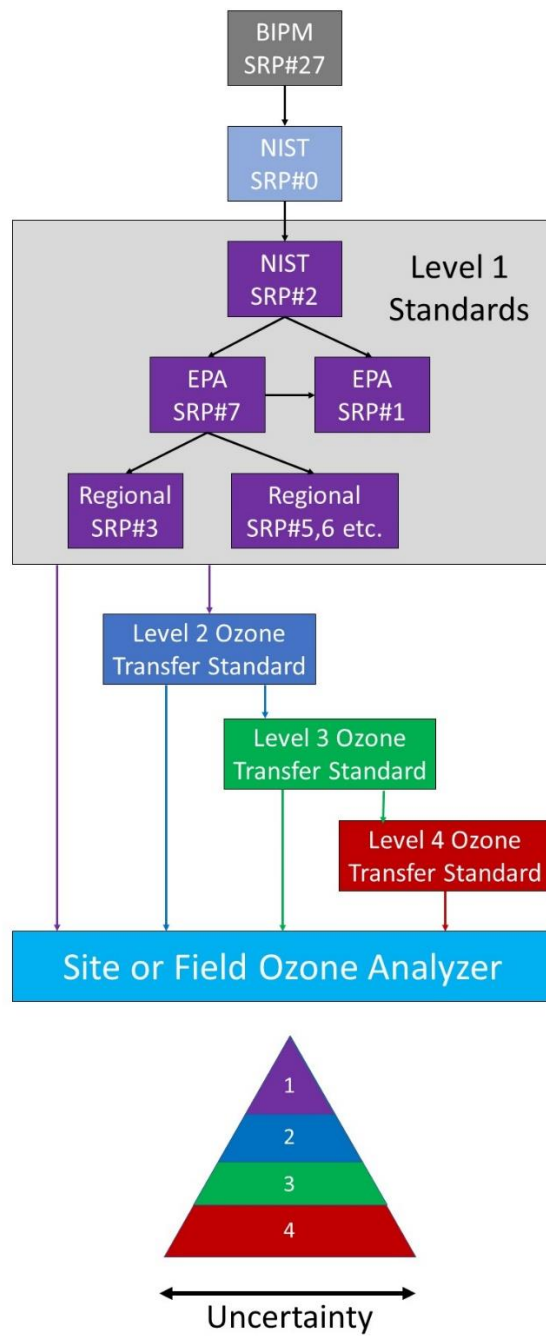
²The recommended calibration time is the maximum time between validation of the Ozone Calibration Source with an independent EPA-certified standard.

550 Table 3. Thermal and photochemical reactions used in modeling the effects of water vapor on the output of the ozone calibration source at 40 °C and 1 atm. Units are cm² molec⁻¹ for absorption cross sections, cm³ molec⁻¹ s⁻¹ for second order reactions and cm⁶ molec⁻² s⁻¹ for third order reactions.

Reaction	Rate Coefficient or Absorption Cross Section	Reference
O ₂ + hv (184.9 nm) → 2 O → 2 O ₃	1.0 x 10 ⁻²⁰	Yoshino et al, 1992 Creasey et al., 2000
H ₂ O + hv (184.9 nm) → OH + H → OH + HO ₂	7.14 x 10 ⁻²⁰	Cantrell et al., 1997
O ₃ + hv (253.7 nm) → O ₂ + O(¹ D ₂)	1.15 x 10 ⁻¹⁷	Burkholder et al., 2015
OH + HO ₂ → H ₂ O + O ₂	1.01 x 10 ⁻¹⁰	Burkholder et al., 2015
OH + O ₃ → HO ₂ + O ₂	8.45 x 10 ⁻¹⁴	Burkholder et al., 2015
HO ₂ + O ₃ → OH + 2 O ₂	2.09 x 10 ⁻¹⁵	Burkholder et al., 2015
OH + OH → H ₂ O + O → H ₂ O + O ₃	1.8 x 10 ⁻¹²	Burkholder et al., 2015
OH + OH (+M) → H ₂ O ₂ (+M)	1.59 x 10 ⁻¹¹	Burkholder et al., 2015
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	1.30 x 10 ⁻¹²	Burkholder et al., 2015
HO ₂ + HO ₂ + M → H ₂ O ₂ + O ₂	3.96 x 10 ⁻³²	Burkholder et al., 2015
O(¹ D ₂) + O ₂ → O + O ₂ → O ₃ + O ₂	3.93 x 10 ⁻¹¹	Burkholder et al., 2015
O(¹ D ₂) + N ₂ → O + N ₂ → O ₃ + N ₂	3.05 x 10 ⁻¹¹	Burkholder et al., 2015
O(¹ D ₂) + H ₂ O → 2 OH	1.97 x 10 ⁻¹⁰	Burkholder et al., 2015

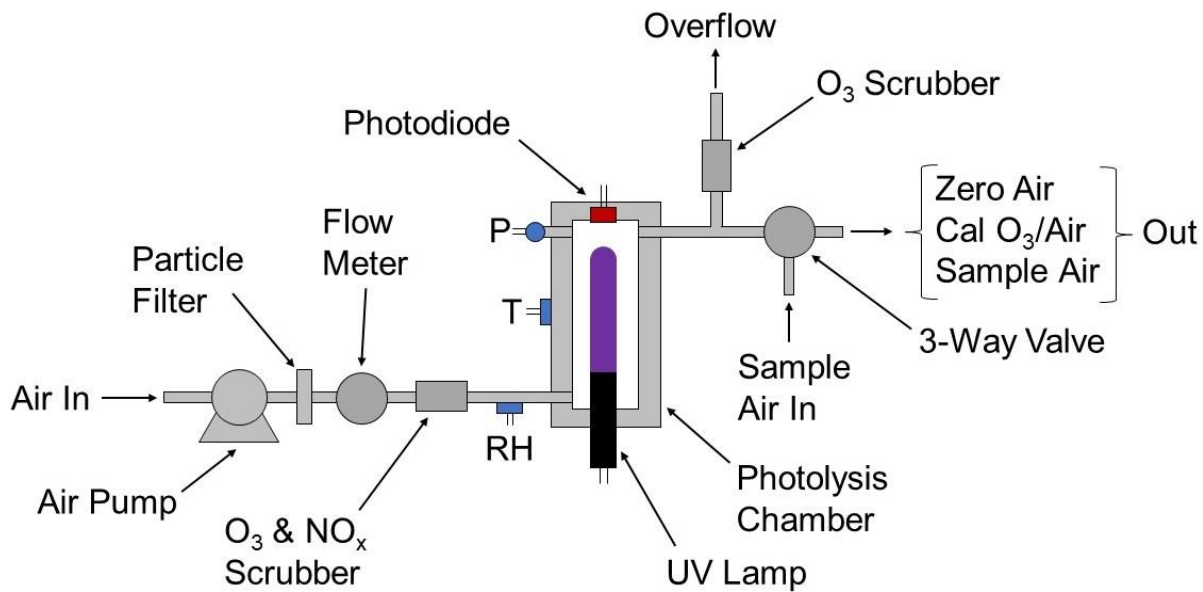
555 Note: Ground state hydrogen and oxygen atoms are assumed to instantaneously attach to O₂ under the photolysis conditions. Photolysis of the H₂O₂ product at both 184.9 nm and 253.7 nm is an insignificant source of OH compared to the photolysis of water and reaction of O(¹D₂) with water. Photolysis of O₃ at 184.9 nm is only ~5% of that at 253.7 nm, and the quantum yield for O(¹D₂) production is only about 50% of that at 253.7 nm and is ignored in the model.

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Figure 1. U.S. EPA ozone transfer standard traceability.



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Figure 2. Schematic diagram of the 2B Technologies Model 306 Ozone Calibration Source.

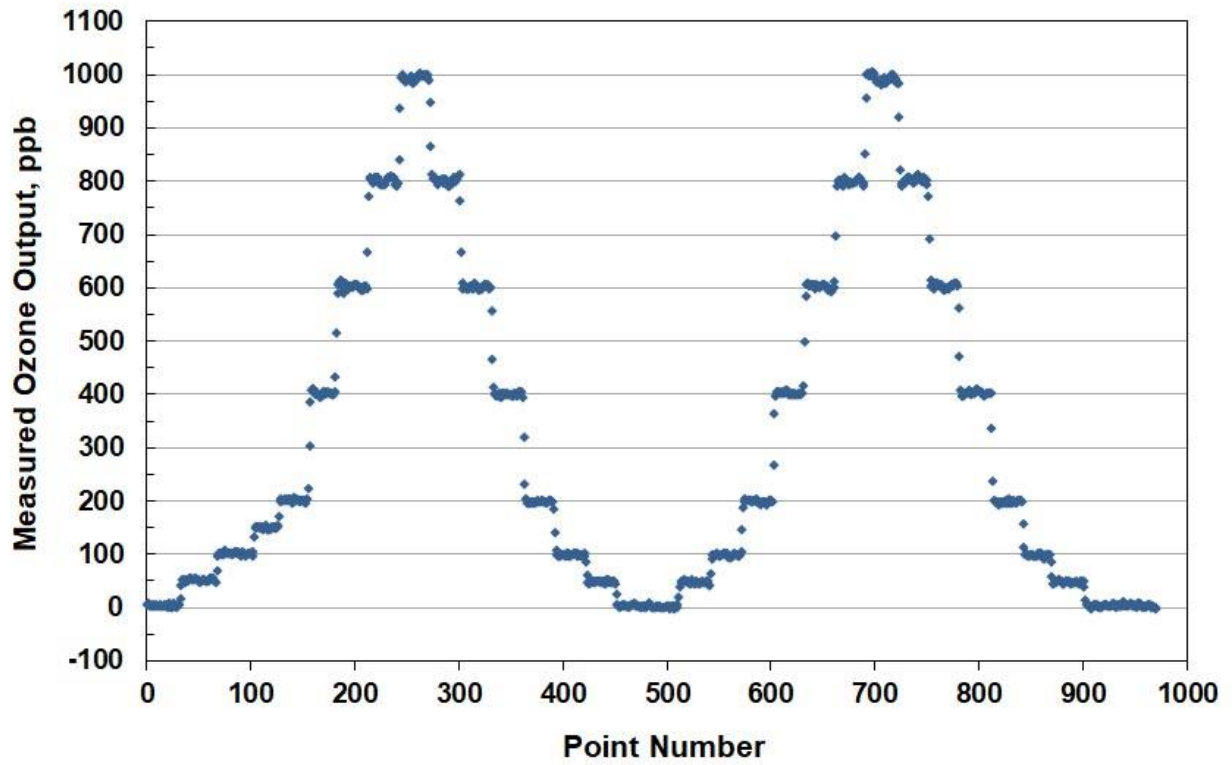


Figure 3. Measured Output of a Model 306 Ozone Calibration Source where the ozone mixing ratio was systematically varied in steps of 50 and 200 ppb (30 points = 5 minutes), as described in the text.

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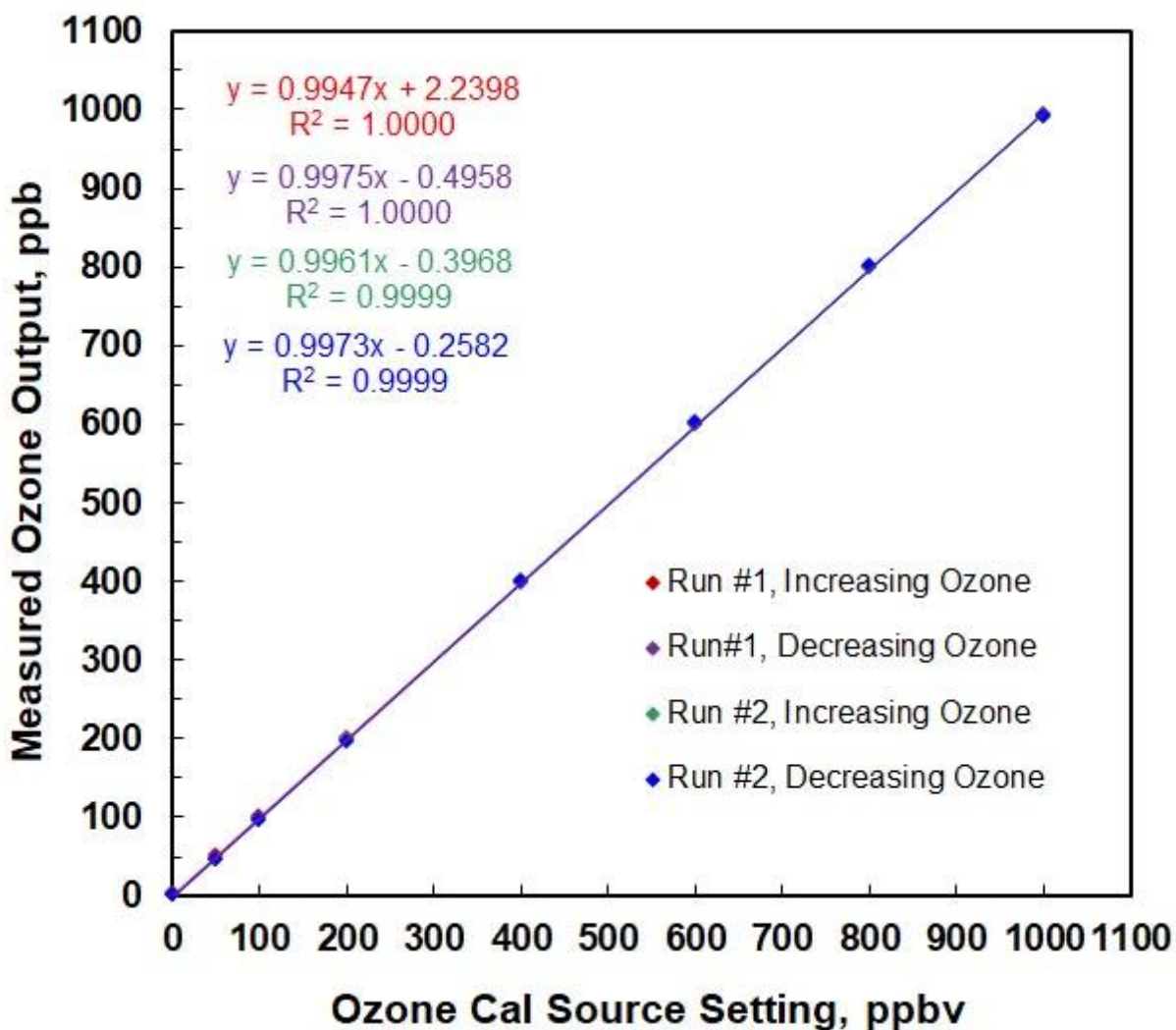


Figure 4. Linear regression for the measured outputs of a Model 306 Ozone Calibration Source of Fig. 3. Note the excellent agreement among the four data sets of increasing and decreasing ozone output concentration. Note that the four regression lines are indistinguishable.

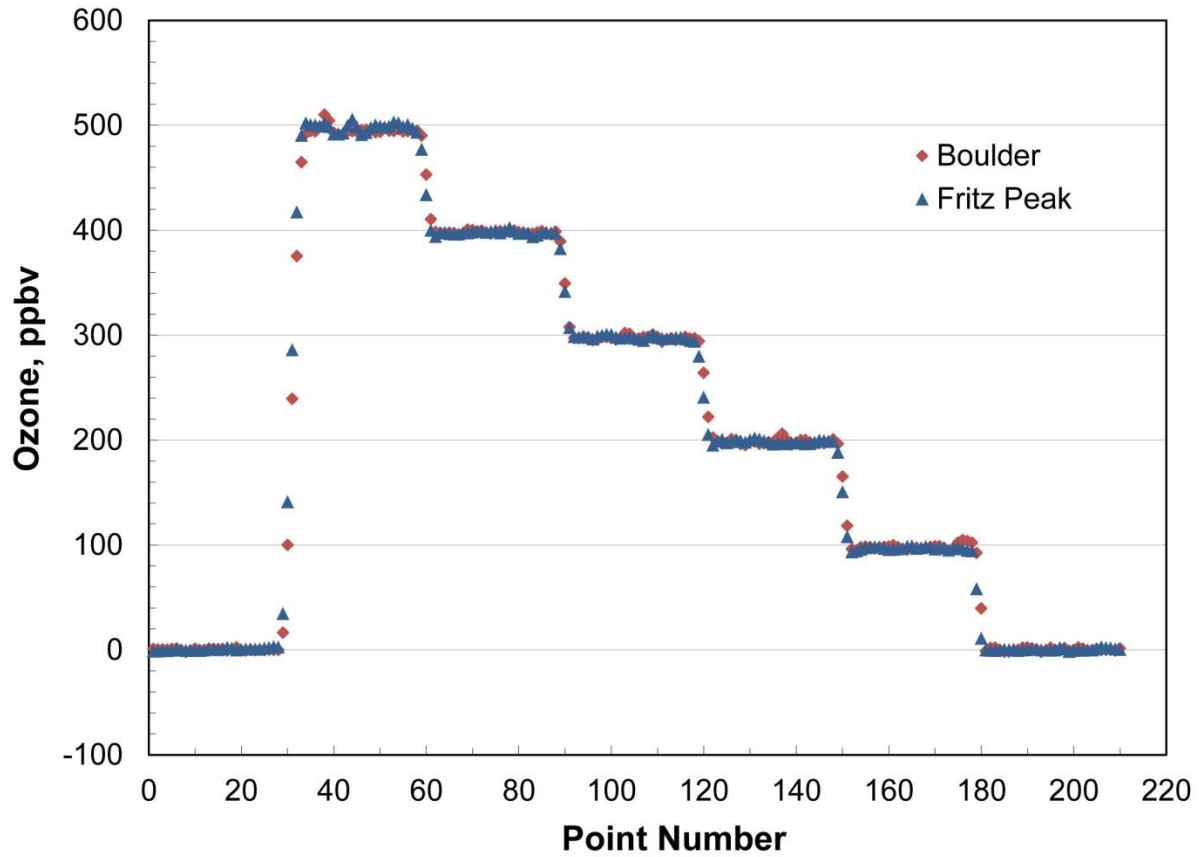


Figure 5. Comparison of ozone output mixing ratios in Boulder, Colorado (5430 ft, 1,655 m altitude) and Fritz Peak (9020 ft, 2749 m altitude) as measured by a 2B Model 202 Ozone Monitor (30 points = 5 minutes).

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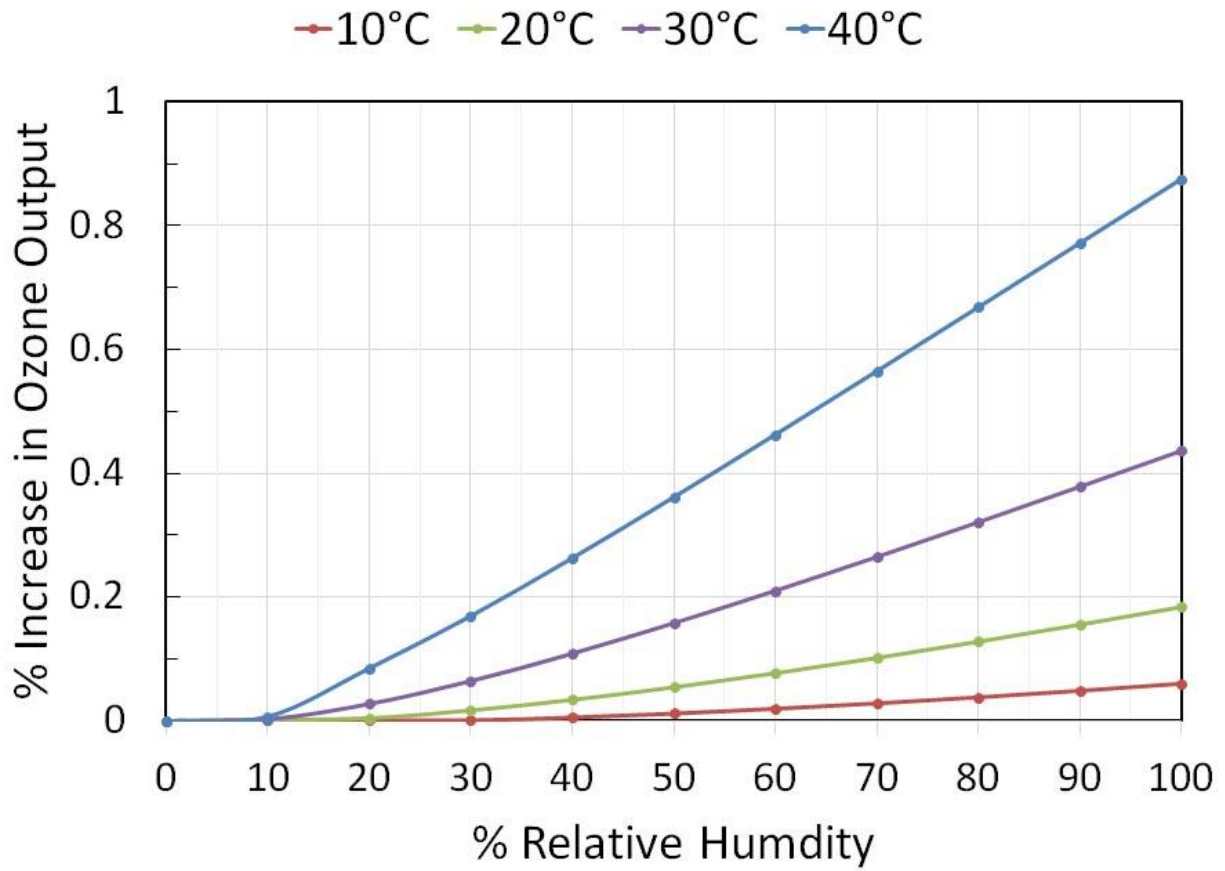
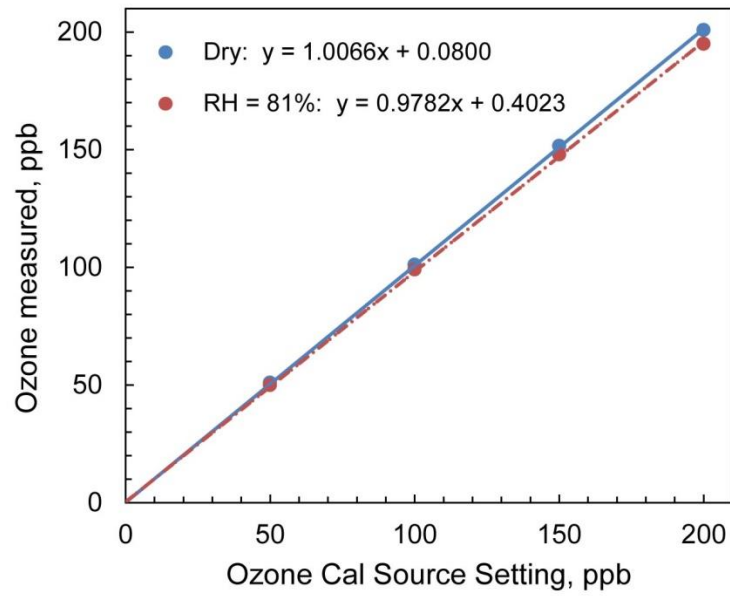


Figure 6. Calculated percent increases in the ozone mixing ratio output (for a target of 100 ppb of O₃) from the ozone calibration source due to photochemical reactions as a function of temperature and relative humidity.

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(a) No Correction for Humidity



(b) Humidity Correction Applied

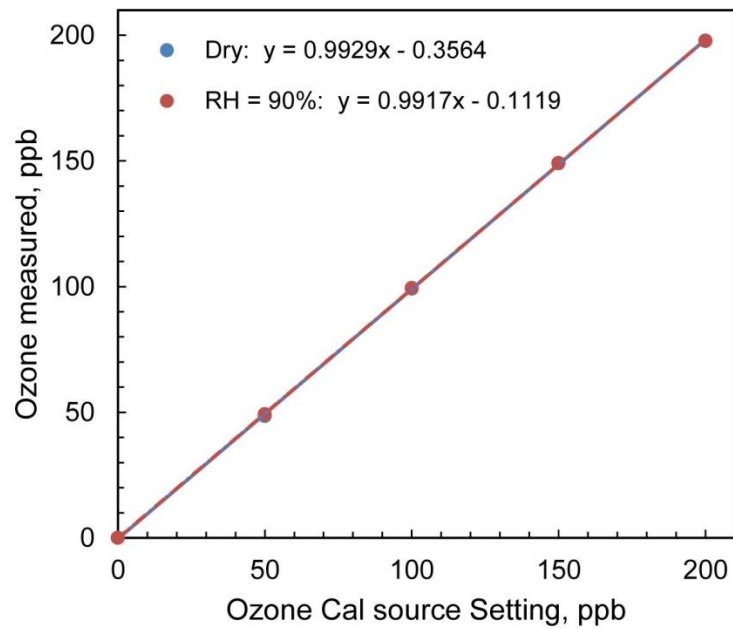


Figure 7. Comparison of the output of the Model 306 ozone calibrator for dry and humid air for (a) no
595 firmware corrections for humidity and (b) firmware corrections applied based on in-line humidity
measurements.