Journal of the Air & Waste Management Association
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uawm20

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Accepted author version posted online: 21 Feb 2013.Version of record first published: 20 Apr 2013.

TECHNICAL PAPER

Temperature measurement and optical path-length bias improvement modifications to National Institute of Standards and Technology ozone reference standards

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Ambient ozone measurements in the United States and many other countries are traceable to a National Institute of Standards and Technology Standard Reference Photometer (NIST SRP). The NIST SRP serves as the highest level ozone reference standard in the United States, with NIST SRPs located at NIST and at many U.S. Environmental Protection Agency (EPA) laboratories. The International Bureau of Weights and Measures (BIPM) maintains a NIST SRP as the reference standard for international measurement comparability through the International Committee of Weights and Measures (CIPM). In total, there are currently NIST SRPs located in 20 countries for use as an ozone reference standard. A detailed examination of the NIST SRP by the BIPM and NIST has revealed a temperature gradient and optical path-length bias inherent in all NIST SRPs. A temperature gradient along the absorption cells causes incorrect temperature measurements by as much as 2 °C. Additionally, the temperature probe used for temperature measurements was found to inaccurately measure the temperature of the sample gas due to a self-heating effect. Multiple internal reflections within the absorption cells produce an actual path length longer than the measured fixed length used in the calculations for ozone mole fractions. Reflections from optical filters located at the exit of the absorption cells add to this effect. Because all NIST SRPs are essentially identical, the temperature and path-length biases exist on all units by varying amounts dependent upon instrument settings, laboratory conditions, and absorption cell window alignment. This paper will discuss the cause of, and physical modifications for, reducing these measurement biases in NIST SRPs. Results from actual NIST SRP bias upgrades quantifying the effects of these measurement biases on ozone measurements are summarized.

Implications: NIST SRPs are maintained in laboratories around the world underpinning ozone measurement calibration and traceability within and between countries. The work described in this paper quantifies and shows the reduction of instrument biases in NIST SRPs improving their overall agreement. This improved agreement in all NIST SRPs provides a more stable baseline for ozone measurements worldwide.

Introduction

Ambient ozone measurements in the United States are traceable to a National Institute of Standards and Technology Standard Reference Photometer (NIST SRP) (Paur et al., 2003) that serves as the highest level ozone reference standard to state, local, and tribal regulatory agencies for calibration of network photometers used for compliance purposes. Such regular audits currently provide reliable measures of field monitor precision and bias in response to challenges of ozone in zero air, although not of sample matrix effects arising from ambient humidity and interfering species (Spicer et al., 2010). The NIST SRP was developed in the early 1980s and has served as the NIST reference standard for ozone measurements and calibration since 1983. Since that time, NIST has produced 43 identical NIST SRPs that have been deployed around the United States in U.S. Environmental Protection Agency (EPA) laboratories, and in national metrology institutes and environmental protection laboratories around the world. Since the beginning of this program, the aim was to make all NIST SRPs identical in every way to avoid variations in the actual measurement of ozone. Because various commercial components used in the NIST SRP have become obsolete, periodic upgrades have been necessary. When component changes occurred to a NIST-owned NIST SRP, an attempt is made to change all NIST SRPs in the same way. Due to several obsolete electronic components, in the late 1990s a major upgrade (Norris et al., 2004) of the NIST SRPs began and a few years later all but one NIST SRP had

Journal of the Air & Waste Management Association, 63(5):565–574, 2013. ISSN: 1096-2247 print
DOI: 10.1080/10962247.2013.773951

been upgraded with a new electronics module, a new detector module, a new sampling manifold, and a new version of control software.

In 2000, NIST and the International Bureau of Weights and Measures (BIPM) began a collaboration to transfer the capabilities of NIST's ozone standards program to the BIPM and establish worldwide ozone measurement comparability through the International Committee for Weights and Measures (CIPM) framework. Following some initial training during delivery of two NIST SRPs and detailed training during construction of two more NIST SRPs at NIST, the BIPM constructed a NIST SRP at their facility to be used for research. A detailed investigation (Viallon et al., 2006) of the NIST SRP conducted by the BIPM and NIST (hereafter referred to as the "bias study") revealed a temperature gradient along the optical pathway of approximately 2-3 °C causing an estimated measurement bias of −0.4%. This temperature gradient was found to be caused by the thermal transfer of heat from the source lamp block, which is heated and temperature controlled between 50 and 60 °C. The source lamp block is maintained at a constant temperature well above ambient to provide a more stable source of ultraviolet (UV) light used in the measurement. The original NIST SRP source block, made entirely from aluminum, contained a cartridge heater, a temperature sensor, the UV source lamp, an aperture, and a collimating lens all contained in one unit. This source block was attached to a shutter cover with a 3.2 mm (1/8 inch) piece of cork, and the shutter cover was attached directly to the beam splitter/mirror block, where the absorption cells were also attached on the opposing side. The thermal transfer is made through these components as well as the optical rail in which the beam splitter/mirror block is mounted. This effect was exacerbated by a cover mounted to the optical rail over the source block and shutter cover. This source cover was not used in all NIST SRPs and is not used in the new source/optics block design. Heat from the source block was transferred to the gas in the absorption cells and the gas cooled as it traveled through the cells. The actual gas temperature measurement is made after the gas exits the cells, in a nylon manifold mounted under the optical rail, causing an incorrect temperature measurement. Figure 1 shows the details of the original NIST SRP optical bench design and the temperature gradient transferring heat to the gas in the cells.

In addition to the temperature gradient effect, the bias study (Viallon et al., 2006) revealed the temperature probe used in all NIST SRPs contains a self-heating effect with an estimated bias of 0.3 °C. The NIST SRP temperature probe is a 100 Ω platinum resistance sensor with a 5 mA current flow that produces 25 mW of power dissipation. A change was made to the NIST SRP control software allowing the temperature measurement to be offset by any amount. Independent calibration of the temperature probe can be performed by each NIST SRP owner and the correction can be entered into the NIST SRP control program to provide the correct temperature measurement in the calculation of ozone concentration. The manufacturer of the NIST SRP temperature measurement components has recently developed a prototype electronic circuit that will use a much lower current flow through the resistance sensor, significantly reducing the power dissipation of the temperature sensor. This design will be researched in the near future to determine the benefit of incorporating the prototype sensor on the NIST SRP.

Additionally, the bias study (Viallon et al., 2006) found that multiple reflections of light exist between the quartz absorption cell windows that have an inherent 4% reflectivity and are situated parallel to one another. A pair of 10 nm band pass optical filters (Corion G-10-254-F; now Newport 10MLF10–254; Franklin, MA) mounted at the exit of each absorption cell provided additional reflections of approximately 15% back into each cell, increasing the amount of internal reflections. Portions of this reflected light eventually make it to the detectors, causing the actual path length to be longer than the measured path length used in the calculation of ozone mole fractions. A schematic of this optical path-length bias is shown in Figure 2. The bias study (Viallon et al., 2006) estimated a relative bias of +0.5% for this optical path-length effect.

To handle the temperature gradient bias, the BIPM initially installed a custom-made Peltier cooling device to their NIST SRP beam splitter/mirror blocks. This allows the temperature at the front end of the cells to be maintained within 0.1 °C of the measured temperature at the exit of the cells, thus significantly reducing the temperature gradient. To handle the optical cell length bias, a 0.5% correction was added to the cell length of their NIST SRPs, along with an increased uncertainty. These BIPM-owned NIST SRPs were recently used in the 2007-2008 round of the official international key comparison (BIPM.

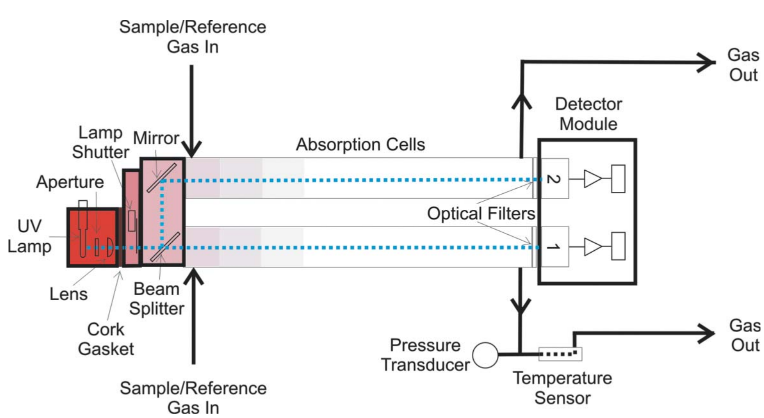


Figure 1. Original NIST SRP optical bench configuration (color figure available online).

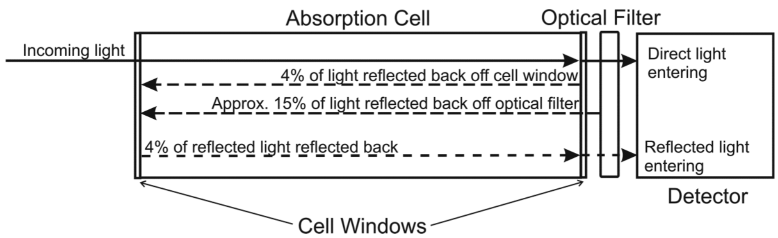


Figure 2. Internal NIST SRP absorption cell reflectivity.

QM-K1, ozone at ambient level). After some discussion as to the feasibility of implementing these custom Peltier cooling devices on all existing NIST SRPs, NIST decided to take a different approach to reduce the measurement biases in all NIST SRPs. The work done to develop and implement the NIST SRP bias upgrade is the basis of this paper.

Methods

Temperature gradient measurements

In order to measure the temperature gradient and its effect on ozone measurements made by a NIST SRP, a system was set up to independently measure the gas temperature entering and exiting one absorption cell of NIST SRP 0, while performing measurement comparisons between NIST SRP 0 and NIST SRP 2. The temperature measurements were made using the same platinum resistance sensor (STOLABs PL-103; Stow Laboratories, Hudson, MA) and manifold configuration used in the NIST SRP. A Teflon manifold with Teflon fittings was placed in line just before the gas enters cell 1, and a nylon manifold with nylon fittings was placed in line just after the same gas exits cell 1. The temperature probes inserted in each manifold are Teflon-coated, as received from STOLABs. Two additional temperature probes were placed on the optical bench between the absorption cells at each end of the cells to monitor the temperature along the optical bench. Each temperature probe was connected to a STOLAB 924PL electronic circuit board that provides an analog signal corresponding to the temperature at the probe. The analog signals are read and recorded by the NIST SRP control program during the comparison measurements. Prior to the beginning of the measurements, each temperature channel was calibrated using a STOLAB PL-30C calibrator at 0 and 30 °C. Because the goal of this system was to measure a difference in temperature, the temperature probe heating effect was ignored in these measurements.

In order to show the agreement among NIST SRPs, they are regularly compared with each other in sets of measurements. In this study, all comparison runs consisted of 10 ozone concentration levels up to approximately 900 nmol/mol performed in random order, with a zero point (no ozone present) at the beginning and end of each comparison run. The results are determined by simple linear regression providing a measurement slope and intercept for each independent comparison run. A series of measurement comparisons between NIST SRP 0 and NIST SRP 2 were performed with no changes made to NIST SRP 2 while maintained with a source block temperature of 60 °C. Because NIST SRP source block temperatures are generally maintained between 50 and 60 °C, measurements were done with the NIST SRP 0 source block temperature set at 50 °C with the source cover on and then off, followed by 60 °C with the source cover on and then off. Then a series of measurements with a different source block design and thermal insulation techniques to minimize the temperature gradient were performed. A maximum temperature gradient of 1.11 °C was found at a source block setting of 60 °C with the source cover in place. This maximum temperature gradient was reduced to 0.09 °C using 19 mm (0.75 inch) extruded polystyrene insulation with a Bakelite mounting plate and a split source block showing a change in the slope of 0.38%. Table 1 shows a summary of these measurements.

Table 1. Summary of initial temperature gradient measurements

Source Block Configuration	Source Block Temp. (°C)	No. of Runs	Avg. Mole Fraction (nmol mol)	Avg. Slope	Avg. Intercept (nmol mol)	Avg. ΔT, Cell 1 (°C)	ΔT, Optical Bench (°C)	Avg. Lab. Temp. (°C)	Avg. Lab. Pressure, (kPa)
Cover on	50	10	900.9	1.00101	−0.064	0.65	2.48	21.7	100.63
Cover off	50	10	928.0	1.00205	−0.060	0.42	1.62	21.6	99.92
Cover on	50	10	914.6	0.99979	−0.061	1.11	3.71	21.4	100.18
Cover off	60	10	930.5	1.00159	−0.017	0.61	2.24	21.5	100.17
0.75” ext. poly.*	60	10	929.6	1.00262	−0.002	0.27	1.25	21.6	99.90
0.75” ext. poly.*	50	10	928.7	1.00302	−0.011	0.18	0.90	21.6	99.27
0.75” ext poly./ plate**	60	19	927.9	1.00364	−0.045	0.09	0.63	21.6	99.37

Notes: $\Delta T =$ change in temperature. *Extruded polystyrene insulation. **Extruded polystyrene insulation and Bakelite mounting plate.

Source/optics block design

After the initial temperature gradient measurements and several discussions with staff from the NIST Building Environment and Fabrication Technology divisions (Zarr and Strawbridge, private communications), a final source/optics block design was developed. The new source/optics block consists of three independent sections separated by 3.2 mm (1/8 inch) cork gaskets. The first section is made from aluminum and contains the heater, temperature sensor, UV lamp, and beam aperture. The second section is a large spacer made of Bakelite, and the third section, also made from aluminum, contains the collimating lens and a single optical filter. The sections are attached to each other through independent mounting holes using machine screws, eliminating any direct metal-to-metal connections. The entire source/optics block is attached to a new shutter cover made from Bakelite separated by a third 3.2 mm (1/8 inch) cork gasket. The four mounting screws and the cork gasket allow for some adjustment of the light beam down the cells. The new source/optics block and shutter cover mounts on the beam splitter/mirror block in the same way as the original design. Figure 3 shows the new source/optics block design in detail. The new design is longer in length, allowing the heated source block portion to extend past the end of the optical rail, further minimizing transfer of heat to the optical rail and thus heat to the absorption cells. Measurements at NIST during installation of the first new source block on NIST SRP 0 resulted in a temperature gradient decrease from an average of 0.78 °C to an average of 0.17 °C. Figure 4 shows these data along with laboratory temperature data during the bias upgrade process of NIST SRP

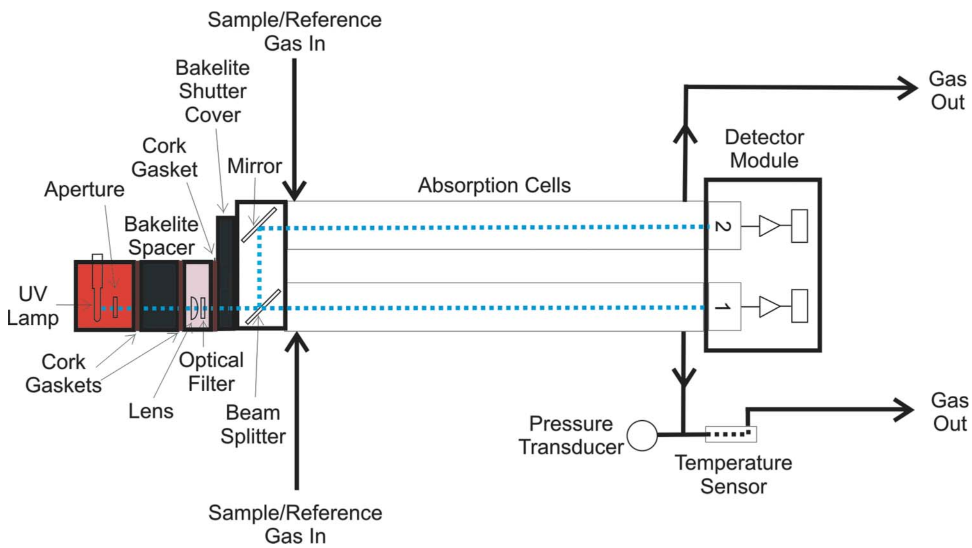


Figure 3. New NIST SRP optical bench configuration (color figure available online).

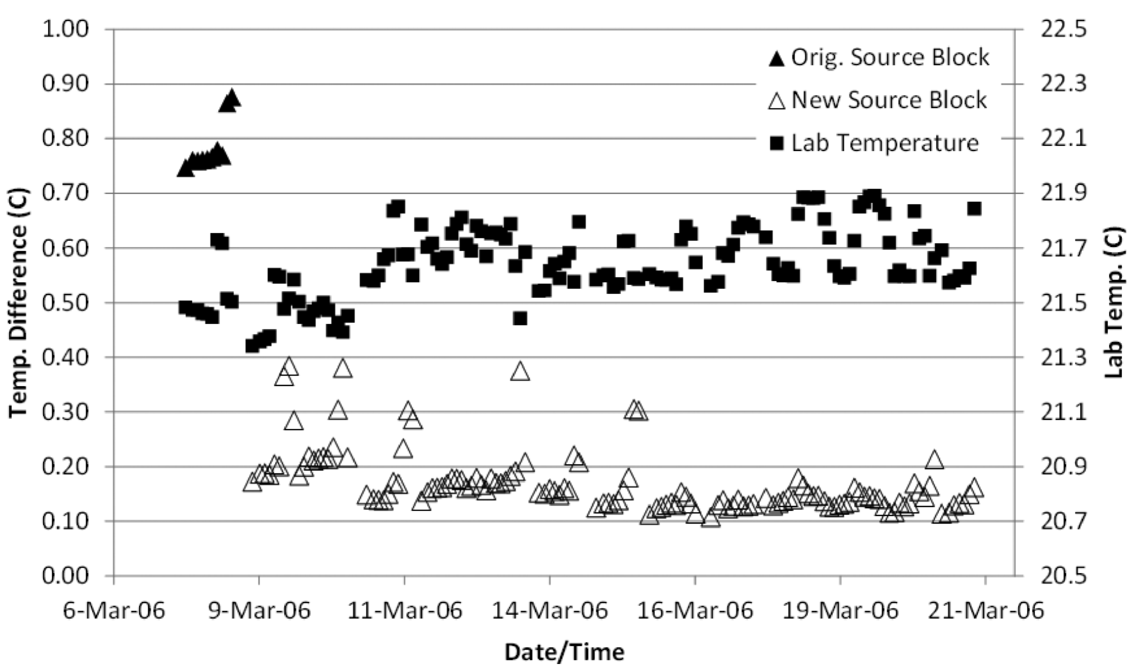


Figure 4. Initial temperature gradient measurements with new source block on NIST SRP 0.

0 and NIST SRP 2. It has also been found that the orientation of the SRP optical bench in the laboratory can have an effect, as temperature gradients generally exist in all laboratories. It is recommended that the optical bench be oriented parallel to the air inlet flow in the laboratory.

During the development of the new source block design, it was found that the focal length of the collimating lens was incorrect. The image produced from the source block before entering the beam splitter and mirror assembly at approximately 0.5 m was a blurry oval image about 150 mm × 100 mm. However, the image seen by the detectors after passing through the beam splitter and mirror was a cylindrical image of about 50 mm in diameter. The new source block design incorporates the proper focal length and produces a perfect concentric image with a much stronger intensity. The amount of divergence is then dependent on the aperture size. Aperture sizes were tested from the original SRP size of 3.2 mm down to 0.3 mm to measure the divergence and signal intensity. In order to maintain the approximate scaler count rate as before, given the same lamp intensity, a 2 mm aperture was chosen. The 2 mm aperture size was a safe choice, as it was clear that a smaller size could be used but would reduce source lamp life. More research is planned to determine if an appropriately sized aperture can be used to keep the divergence smaller than the internal diameter of the cells (13.5 mm). This will be dependent on lamp intensity, light absorption from the optical filter, sensitivity of the detectors, and the counting period of the signal. The 2 mm aperture produces a divergence of approximately 40 mm at a distance of 1 m measured from the front edge of the source/optics block, and approximately 34 mm when connected to the beam splitter/mirror block and measured at the cell end plate where the detector is mounted when in operation.

Absorption cell design

The original NIST SRP absorption cells were made with 15 mm internal diameter (ID) commercial fittings with an O-ring seal to a Teflon end connector that housed the cell window using another O-ring seal. The cells and O-ring seals were forced together with an adjustable bracket between Teflon washers, allowing some variation in the cell length, which is measured once the cells are in place. The alignment of the cell windows was dependent on how tight the connection was made and the precision of the machined Teflon cell end connectors and washers. NIST had already developed a set of prototype cells made of quartz with optically sealed windows to eliminate the Teflon end connector/O-ring seal design. The Korean Research Institute of Standards and Science (KRISS) (Woo, 2003) developed an ozone reference standard that is based upon the NIST SRP design. Realizing this internal reflection problem, KRISS designed the Teflon cell end connectors so that each cell window was at a 3° angle. This same design was implemented in the bias study (Viallon et al., 2006). The final NIST cell design incorporates the same 3°-angled cell window design without the use of Teflon or O-rings. The new NIST SRP absorption cells are made with 13.5 mm ID, 19 mm outer diameter (OD) quartz tubing and with 9.5 mm (3/8 inch) OD inlet and outlet ports. The ends of the cells are ground and polished at approximately 3° angles; 1.6 mm (1/16 inch) quartz windows are then optically sealed to the cell ends. The cells are made such that the angles are parallel to each other so the cell length is the same at any portion of the cell. The cells are mounted in the NIST SRP using custom Teflon end connectors, and Teflon fittings are used to connect the gas lines. The cell length for the first five sets of the new design was measured using a large caliper; subsequently all cells have been measured with a coordinate measurement machine maintained in the NIST inspection shop with an estimated accuracy of ±0.0076 mm (±0.0003 inch). A typical set of new absorption cells have an average optical length of 89.660 ± 0.004 cm.

Ozone measurements were performed with two independent absorption cells of the new design on NIST SRP 0 during comparison with NIST SRP 2. The measurements were performed with the optical filters placed in various configurations on NIST SRP 0, first with the original cells, followed by two sets of the new 3°-angled window cells. In the first set of measurements (set A), the optical filters were arranged in SRP 0's original configuration. The second set of measurements (set B) was with the two rear-mounted optical filters rotated 180° to the opposite side. Because the opposite side of each filter has a higher reflectance, more light was reflected back into the cells, causing an increase in the slope of 0.16%. In the third set of measurements (set C), the filters were rotated back to their original sides, but now switched from cell 1 to cell 2 and vice versa. The results were expected to be the same as set A, but the slope was 0.07% higher than the original set A data. In the fourth set of measurements (set D), both rear-mounted optical filters were removed from the cell end plate and only the cell 1 filter was placed into the source block between the aperture and the collimating lens, which is situated in front of the absorption cells. This removed any light reflection from the filters back into the cells and gave a 0.17% decrease in the slope from the original set of measurements (set A). Next, a set of new absorption cells (cells 1 and 2) made with 3°-angled optically sealed windows were installed into SRP 0 and the measurement set (set D) configuration was repeated. The results showed a shift in the slope of 0.57% from the original set of measurements (set A). This change in slope was similar to the bias study (Viallon et al., 2006) results of 0.50%. Measurements in the configurations A, B, C, and D were repeated, showing little or no change in the slope. Set E was added, which is similar to set D but with the filter rotated 180°, and no change was observed. Set D was then repeated twice because there was a drop off in the slope on the last two comparison runs of the first set. Finally, cells 1 and 2 were replaced in NIST SRP 0 with another set (cells 3 and 4) made with 3°-angled optically sealed windows and measurements of set D were repeated, with no measurable change. The results, which show changes in the slope of NIST SRP 0 versus NIST SRP 2 in each filter configuration using the original cells, and essentially no change in the slope with either of the new design cells installed in NIST SRP 0, can be seen in Figure 5. These measurements indicate that the newly designed cells having 3°-angled cell windows eliminates internal reflections caused by parallel cell windows and optical filter reflections.

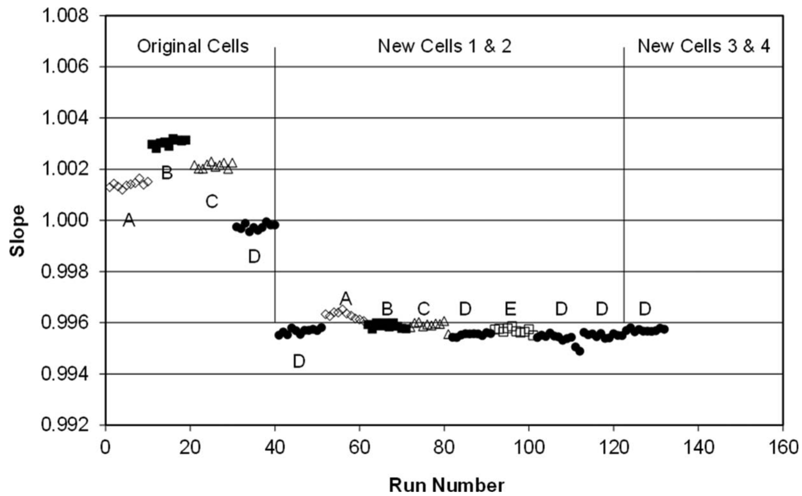
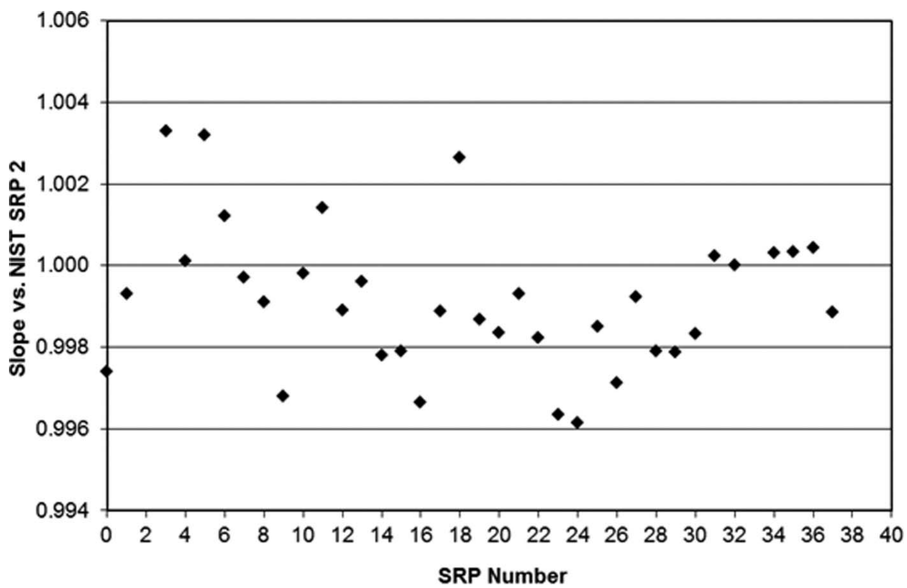


Figure 5. Change in slope resulting from filter configuration and new cells.

Results

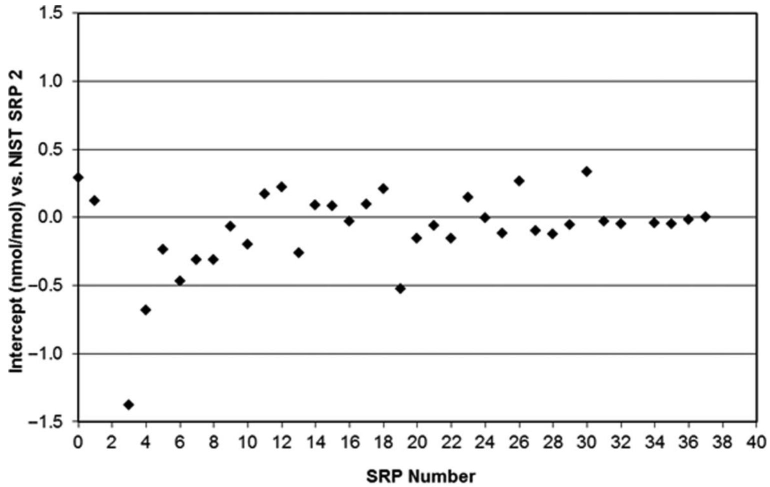
Original NIST SRP comparisons

Upon completion of any new NIST SRP, comparisons against NIST SRP 2 are done as the official validation. The comparisons have been done in several different sampling configurations through the years (Norris et al., 2004). A full NIST SRP comparison consists of multiple ozone concentration levels up to approximately 1 μmol/mol performed in a random order, with a zero point (no ozone present) at the beginning and end of each comparison run. The results are determined by simple linear regression providing a measurement slope and intercept. For comparison with the measurements done in this paper, Figure 6



	Results
Average Slope	0.99916
Standard Deviation	0.00176
Maximum	1.00330
Minimum	0.99613
Difference	0.00717 = 0.72 %

Figure 6. Slopes of initial comparisons of new SRPs versus NIST SRP 2.



	Results (nmol/mol)
Average Intercept:	−0.095
Standard Deviation:	0.314
Maximum:	0.335
Minimum:	−1.38
Difference:	1.72

Figure 7. Intercepts of initial comparisons of new SRPs versus NIST SRP 2.

(slope) and Figure 7 (intercept) are provided to show all original comparison results against NIST SRP 2 before the bias upgrade was implemented on any NIST SRP.

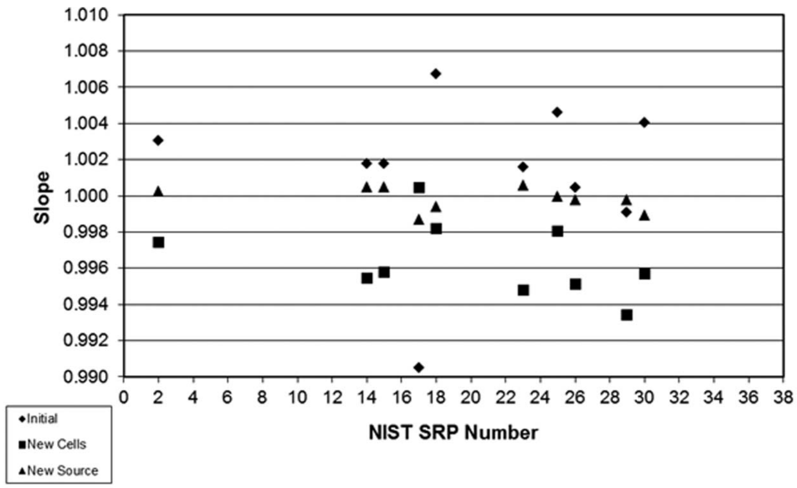
NIST SRP bias upgrade comparisons

Since the development of the NIST SRP bias upgrade, 24 of the 38 NIST SRPs built with the original source block and absorption cells have been upgraded. During the process of each NIST SRP bias upgrade, comparison measurements took place before any changes were made as a baseline reference, after the new 3°-angled window absorption cells were installed to quantify the path-length bias, and after the new source/optics block was installed to quantify the temperature gradient bias. It should be noted that quantification of any bias due to divergence of the light beam down the cells was not determined. Although believed to be a small effect, additional research is planned to determine the magnitude of this bias. Until this can be quantified, an uncertainty component of 0.52 cm has been added to the path-length uncertainty and included in the overall NIST SRP uncertainty budget. Of all bias upgrades, 15 of the 24 completed so far have been done by comparison with either NIST SRP 2 or NIST SRP 0. Figure 8 shows the average slopes obtained during comparisons of the 10 upgraded NIST SRPs with NIST SRP 0, including NIST SRP 2. All of these bias upgrades took place in the laboratory of the specific NIST SRP owner, except that of NIST SRP 2, which was done in the NIST laboratory. The results in Figure 9 show the average slopes obtained during comparisons of the five additional upgraded NIST SRPs directly with NIST SRP 2 in the NIST laboratory. Because the upgrades done outside of NIST by comparison with NIST SRP 0 include data relating NIST SRP 0 versus NIST SRP 2, these data have been corrected back to NIST SRP 2 as well. Table 2 shows the change in slope from each step of the upgrade process for the 15 NIST SRPs upgraded by NIST and compared with either NIST SRP 0 or NIST SRP 2. These results show an average change in the slope of −0.70% due to the path-length bias correction (new cells) and an average change in slope of 0.36% due to the temperature gradient bias correction (new source/optics block).

The BIPM, which maintains NIST SRP 27 as the international ozone reference standard, has performed bias upgrades of six NIST SRPs including NIST SRP 27. The data obtained from this work were by comparison with NIST SRP 27 except for the bias upgrade of NIST SRP 27, which was compared with NIST SRP 28. The EPA has performed bias upgrades to 4 of its 11 NIST SRPs. The results of these additional bias upgrades will not be presented in this paper, but will follow in subsequent reports.

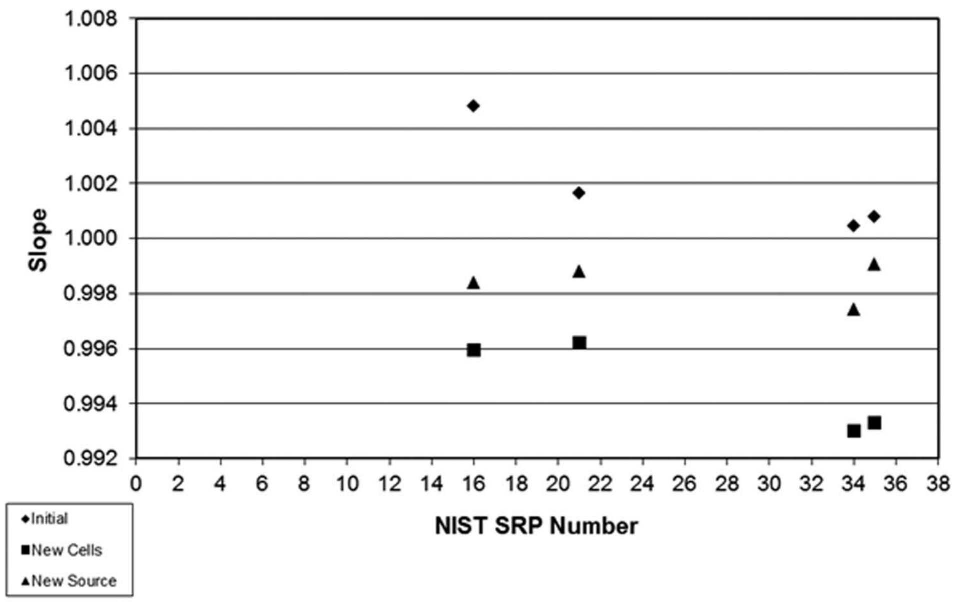
Summary

From the data in Table 2 of the 15 bias upgrades reported here, the change in slope due to the new absorption cells to minimize the optical path-length bias shows an average change of −0.70%. The lowest change of 0.53% was close to the estimated value of 0.5% from the bias study (Viallon et al., 2006), but the highest change of 1.00% was much higher than expected. This spread in results of 0.47% is most likely due to variations in the parallelism of the original cell windows, with the most perfectly parallel windows providing the largest change in slope, as well as variations in the reflectivity of the optical filters, which were originally located at the end of the absorption cells. The new source/optics block, which minimizes the temperature gradient bias, shows an average change in slope of 0.36%, which is close to the bias study (Viallon et al., 2006) estimate of 0.4%. The



	Initial	New cells	New Source (Final)
Average Slope:	1.00327	0.99634	1.00010
Standard Deviation:	0.00312	0.00188	0.00068
Maximum:	1.00963	0.99954	1.00132
Minimum:	0.99908	0.99341	0.99892
Difference:	0.01055 = 1.1 %	0.00613 = 0.61 %	0.00240 = 0.24 %

Figure 8. Slopes of bias upgrade comparisons of NIST SRPs versus NIST SRP 0.



	Initial	New cells	New Source (Final)
Average Slope:	1.00193	0.99462	0.99844
Standard Deviation:	0.00199	0.00169	0.00071
Maximum:	1.00482	0.99620	0.99906
Minimum:	1.00047	0.99301	0.99745
Difference:	0.00435 = 0.44 %	0.00319 = 0.32 %	0.00161 = 0.16 %

Figure 9. Slopes of bias upgrade comparisons of NIST SRPs versus NIST SRP 2.

spread in results of 0.52% is due to several factors: the source lamp block temperature setting, the ambient temperature in the laboratory during the measurements, whether or not the source block cover was installed, and finally in one case a heating device was added along the cells to minimize the temperature gradient.

The results of all original NIST SRP comparisons with NIST SRP 2 (Figures 6 and 7) show an average slope of 0.99916 ± 0.00176, with a spread from maximum slope to minimum slope (difference) of 0.72%. The final comparison data from the 10 bias upgrades against NIST SRP 0 (Figure 8) show an

Table 2. Summary of change in slope during bias upgrades

SRP No.	Date	% Change in Slope New Cells	% Change in Slope New Source	Total % Net Change in Slope
0	March 5–24. 2006	−0.72	0.17	−0.55
2	March 5–24. 2006	−0.55	0.31	−0.24
21	May 16–August 22. 2006	−0.54	0.26	−0.28
17	August 6–10. 2007	−1.00	0.18	−0.82
26	September 10–19. 2007	−0.53	0.46	−0.07
18	September 12–24. 2007	−0.85	0.12	−0.73
23	September 13–21. 2007	−0.68	0.58	−0.10
15	September 17–20. 2007	−0.60	0.45	−0.15
14	September 13–30. 2007	−0.63	0.50	−0.13
29	October 29–November 2. 2007	−0.57	0.64	0.07
25	November 19–23. 2007	−0.65	0.20	−0.46
16	December 6–12. 2007	−0.86	0.25	−0.61
34	March 11–April 6. 2008	−0.72	0.44	−0.28
35	March 17–21. 2008	−0.75	0.54	−0.21
30	April 14–18. 2008	−0.84	0.29	−0.55
	Average:	−0.70	0.36	−0.34
	Standard deviation:	0.14	0.17	0.26
	Maximum:	−0.53	0.64	0.07
	Minimum:	−1.00	0.12	−0.82
	Difference:	0.47	0.52	0.89

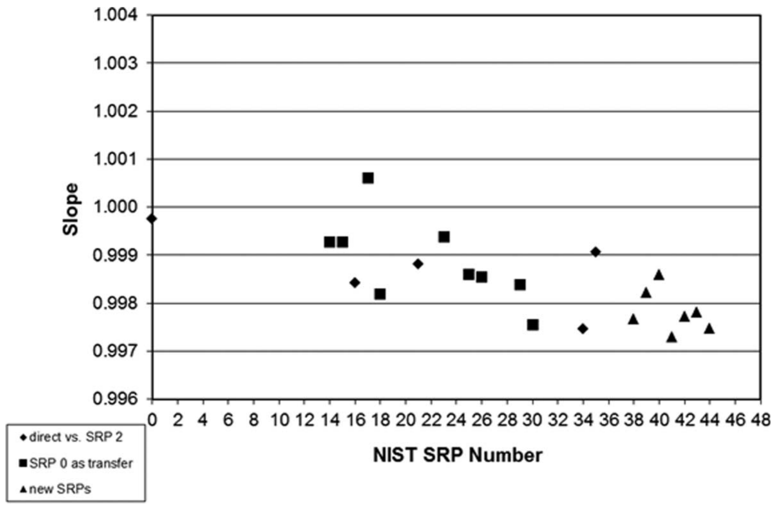
average slope of 1.00010 ± 0.00068, with a difference of 0.24%. Additionally, the final comparison data from the four bias upgrades against NIST SRP 2 (Figure 9, which excludes NIST SRP 0) show an average slope of 0.99844 ± 0.00071, with a difference of 0.16%. NIST SRP 0 is excluded from this data set because NIST SRP 2 had not been upgraded during the NIST SRP 0 bias upgrade. Using the before and after comparison data of NIST SRP 0 versus NIST SRP 2 to correct all data back to NIST SRP 2 as the reference, the combined average slope for 14 bias-upgraded NIST SRPs is 0.99849 ± 0.00085, with a difference of 0.33%. This reduction in the difference from highest to lowest slope versus NIST SRP 2 shows that the bias upgrades have improved the overall measurement agreement of all NIST SRPs. Figure 10 shows these slopes and the slopes from new NIST SRPs built with the bias upgrade.

An improvement in the agreement of NIST SRPs versus NIST SRP 2 either bias upgraded or with the bias upgrade when built has been demonstrated. This confirms the presence of the temperature gradient and optical path-length biases in the previous NIST SRP configuration. The data also indicate that the estimated relative bias of −0.4% for the temperature gradient and the estimated relative bias +0.5% for the optical path-length bias from the bias study (Viallon et al., 2006) are not found in all SRPs. The data show an average optical path-length bias of +0.70%, and an average temperature gradient bias of −0.36%, with an overall average change in the measurement slope of −0.34%.

Conclusion

This study has shown the original NIST SRP design to have a temperature gradient of 1.1 °C when operated in the NIST laboratory, corresponding to an ozone mole fraction bias of 0.39%. This is in good agreement with the results found in the bias study (Viallon et al., 2006). The ability to reduce the temperature gradient from 1.1 °C down to below 0.2 °C was also demonstrated using a redesigned source/optics lamp block with different mounting components. Additionally, the optical path-length bias found in the bias study (Viallon et al., 2006) was found to exist in all NIST SRPs. Use of a modified design for the optical cell incorporating 3°-tilted windows has removed this bias. The known divergence of light down the optical cells was not addressed in this work and additional research is planned to quantify this effect. The 15 NIST SRPs upgraded in this work have shown improved overall agreement. These instruments along with all newly constructed NIST SRPs will be monitored to see if this improvement is maintained.

The worldwide interest in the NIST SRP to serve as a high-level reference standard for ozone measurement and traceability has been consistent and is expected to continue. Proper maintenance and measurement comparability of all NIST SRPs have a direct effect on global ozone measurements within the troposphere.



	Final Results
Average Slope:	0.99849
Standard Deviation:	0.00085
Maximum:	1.00061
Minimum:	0.99729
Difference:	0.00332 = 0.33%

Figure 10. Average slopes of all bias-upgraded NIST SRP comparisons versus NIST SRP 2.

Disclaimer

Certain commercial products or materials identified in this paper are given to adequately discuss the work performed. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Acknowledgment

The authors would like to acknowledge the assistance of Dr. Robert Zarr of the NIST Building Environment Division for guidance on thermal isolation and Mr. Dana Strawbridge of the NIST Fabrication Technology Division for assistance on the machining design of the source/optics block described in this paper. Additionally, the authors would like to acknowledge Mr. Jeffrey Anderson and Mr. John Fuller of the NIST Fabrication Technology Division for assistance in the development and production of the 3°-angled window absorption cells described in this paper.

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