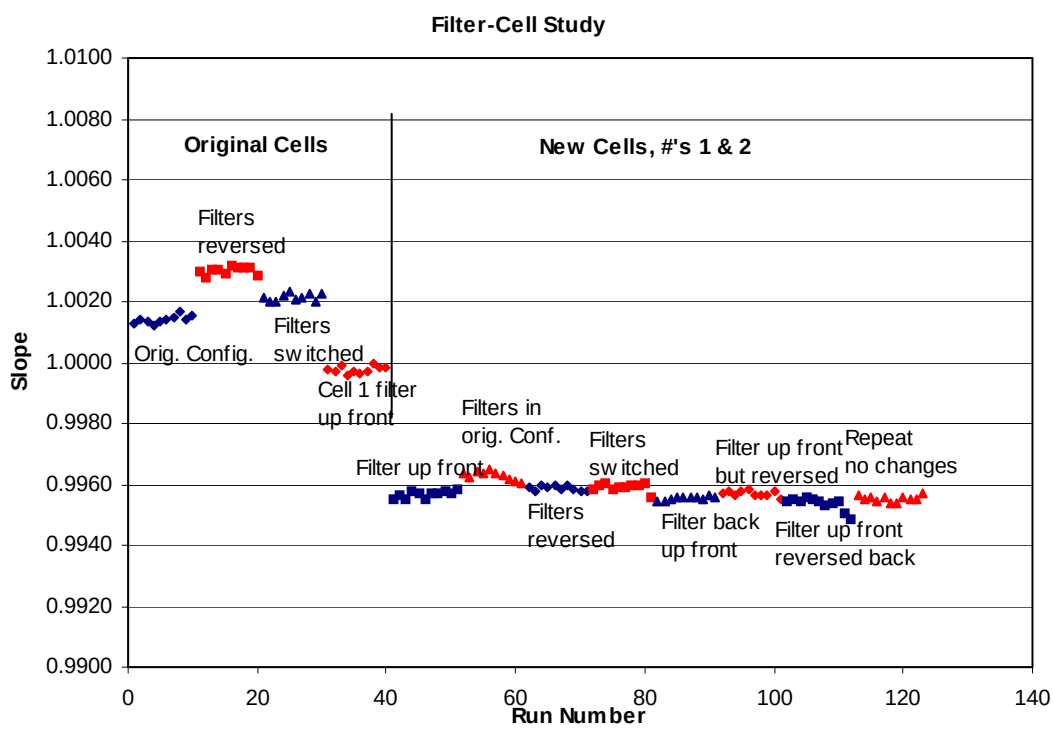
Improving Measurements with NIST's Ozone Reference Standard

The concentration of ozone in the atmosphere continues to be an important global issue both scientifically and politically. Stratospheric ozone protects the Earth from harmful ultraviolet radiation, while tropospheric ozone is a major health concern and contributes to global climate change as a greenhouse gas. The NIST Standard Reference Photometer (SRP), developed jointly with the U.S. Environmental Protection Agency (EPA), has provided an infrastructure for the calibration and traceability of ozone measurements within the U.S. since 1983, and it serves as the highest-level ozone reference standard in the U.S. NIST has provided SRPs to 19 laboratories in 16 countries including several SRPs to the International Bureau of Weights and Measures (BIPM) to serve as an ozone reference standard under the International Committee of Weights and Measures (CIPM).

J.E. Norris and F.R. Guenther (Div. 839)

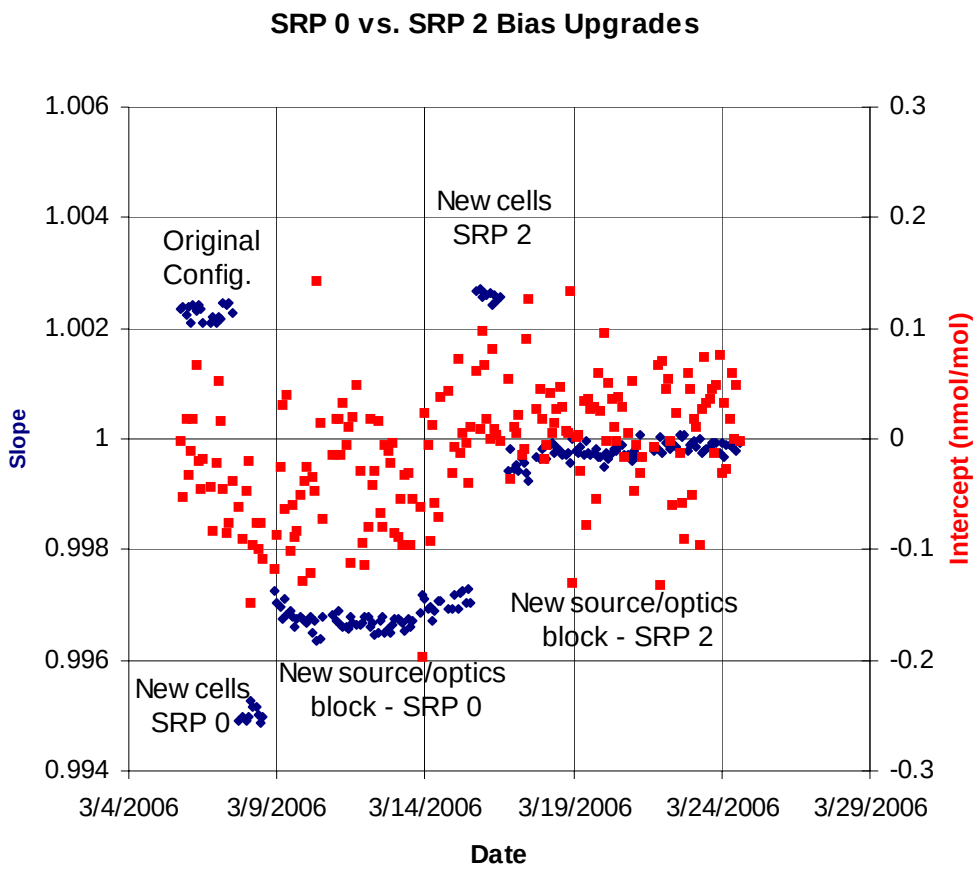
Ozone measurements in the US and many other countries are traceable to the NIST Standard Reference Photometer (SRP). The International Bureau of Weights and Measures (BIPM) and 16 other countries have adopted the SRP as their ozone reference standard. In 2005 the BIPM and NIST completed an in-depth study of systematic biases in the Standard Reference Photometer (SRP) that revealed a temperature measurement bias causing an underestimate of ozone mole fractions by 0.4 %, and an optical measurement bias causing an overestimate of ozone mole fractions by 0.5 %. This resulted in a total estimated measurement bias of 0.1 %. Because all SRPs are essentially identical, these measurement biases exist on all units by varying amounts dependent upon instrument settings, cell window alignment, and laboratory conditions. NIST investigated and developed instrument modifications to reduce or eliminate these biases.

A re-designed source/optics block reduces the temperature gradient through the absorption cells to less than 0.2 °C by thermally isolating the heated-source lamp block. This change and the repositioning of the temperature probe to better monitor the average temperature of the absorption cells has greatly reduce the temperature bias. New absorption cells have been developed with each cell having optically sealed windows positioned at 3° angles. Additionally, collimation of light from the source lamp has been improved to reduce divergence. These design changes help eliminate internal reflections between cell windows and make o-rings to seal the windows to the cell, a potential source of leaks, unnecessary. Two sets of these new cells were tested on one of NIST's two SRPs, SRP 0, with various optical filters and physical positioning to examine the effects on the measurement slope of SRP 0. The results, shown in ***Figure 1***, indicate the effect on the measurement slope due to various positions of the optical filters with the original absorption cells and with the newly designed 3° angled window absorption cells. With the original cells, a maximum 0.16 % change in the slope was seen by changing the position and orientation of the filters, fol-



lowed by a 0.17 % change from the original filter configuration, to a single filter positioned before the cells. The new cells minimize this effect to a maximum of 0.08 % change in the slope regardless of the filter configuration/orientation. The total optical path-length bias measured on SRP 0 during this study was 0.57 %.

Major Accomplishments: During the past year, NIST has developed an upgrade for the SRP that minimizes the temperature gradient and optical path-length biases and has upgraded NIST's two SRPs, SRP 0 and SRP 2. The results of comparisons between these two SRPs are shown in ***Figure 2.*** The upgrades show improved agreement due to the variations in the respective biases. All SRPs worldwide are expected to be upgraded within the next two years, and overall measurement agreement, currently 0.7 %, is expected to improve.

Impact: Worldwide interest in the NIST SRP to serve as a high-level national reference standard for ozone measurement and traceability has continued. Proper maintenance and measurement comparability of all SRPs has a direct effect on global ozone measurements within the troposphere.

Future Plans: In 2007 NIST will participate in a CCQM key comparison on ozone measurements at ambient levels. Plans for several countries' SRP upgrades are already scheduled to take place in 2007, before their participation in the CCQM key comparison. Changes in the ozone mole fraction measurement in an upgraded SRP will be clearly quantified and documented. Also, when an SRP is returned to NIST for upgrade or maintenance, NIST can provide a direct comparison to NIST's primary SRP and submit the data to the BIPM for inclusion in the key comparison.