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1 INTRODUCTION

In ambient air monitoring applications, gas concentration standards are required for the calibration and auditing of various ambient gas monitors. Because of the instability of ozone (O_3), the certification of O_3 concentrations as Standard Reference Materials (SRMs) is impossible. Therefore a Standard Reference Photometer (SRP) was developed as a primary standard to validate the linearity of other photometers when challenged with various concentrations of locally generated O_3 gas. This document has been prepared to assist the EPA (U.S. Environmental Protection Agency) operators of the NIST (National Institute of Standards and Technology) Standard Reference Photometer (SRP) in terms of operation, repairs, and verification. Also included is a brief history of the SRP development.

1.1 Ozone Photometers Classified

Ozone photometers (standards) can be classified into two basic groups: stationary and travelling standards. A stationary O_3 standard is an on-site unit that has been dynamically generated and assayed by ultraviolet (UV) photometry in accordance with the procedures prescribed by the U.S. Environmental Protection Agency under Title 40 of the *Code of Federal Regulations*, Part 50, Appendix D (40 CFR Part 50)[1]. An O_3 travelling standard is a transported device or apparatus, which, together with associated operational procedures, is capable of O_3 concentrations and accurately analyzing O_3 concentrations which are quantitatively related to another O_3 photometer.

In ambient air monitoring applications, precise O_3 photometers called transfer standards are required for the calibration of O_3 analyzers. Therefore, an O_3 standard must be generated and "verified" on site. When the monitor to be calibrated is located at a remote monitoring site, it is necessary to use a transfer standard that is traceable to a more authoritative standard. **Traceability** is "the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties"[2] (ISO).

A claim of traceability requires three elements:

1. A declaration of the source of traceability (*e.g.,* NIST),
2. A full description of the traceability chain from the source to the measurement of interest, and
3. An uncertainty claim with supporting data. The responsibility for providing support for an uncertainty claim rests with the entity making the claim (*i.e.,* the provider), but the responsibility for assessing the validity of such a claim rests with the consumer.

Figure 1.1 represents the scheme that will be employed to ensure that the use of O_3 transfer standards is applied in a manner that will ensure a specified level of measurement uncertainty and traceability. As

[1] U.S. Environmental Protection Agency, *Code of Federal Regulations*, Title 40, Part 50, Appendix D, July 1, 2010
[2] International Standards Organization (ISO) – International Vocabulary of Basic Terms in Metrology, JCGM_200_2008.pdf, October 08, 2008

detailed within the Technical Assistance Document (TAD) for *Transfer Standards For Calibration of Air Monitoring Analyzers for Ozone* dated November 2010. [3]

Measurement uncertainty describes a region about an observed value of a physical quantity, which is likely to enclose the true value of that quantity. Measurement uncertainty is related with both the systematic and random error of a measurement, and depends on both the bias and precision of the measurement instrument. At each measurement phase (e.g., levels in Fig. 1.1) errors can occur, that in most cases, are additive. This SOP will also discuss:

- The acceptable amount of measurement uncertainty in O_3 transfer standard, and
- Develop a method to characterize measurement uncertainty through the transfer standard verification process in order to allow the use of transfer standards to an acceptable number of levels.

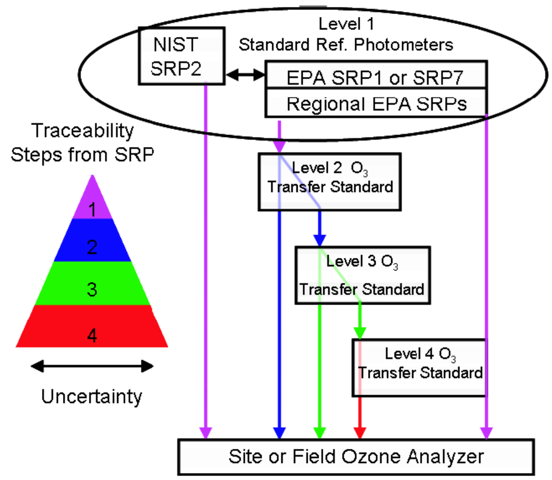

Figure 1.1. Ambient air ozone traceability scheme

1.2 The NAAQS and Health Effects of Ozone

In 2008 the EPA revised the O_3 National Ambient Air Quality Standards (NAAQS) in Regions 1-10 for the purpose of implementing the revised primary and secondary O_3 NAAQS. In March 12, 2008 (73 FR 16436: March 27, 2008) to implement its new primary O_3 standard.[4] This new primary O_3 standard was lowered from 0.08 parts per million by volume (ppm_v) per 8 hours of exposure to a level of 0.075 ppm_v per 8 hours of exposure based on numerous epidemiological studies conducted during the past decade in which many of the health effects associated with O_3 exposure were identified.

O_3 can make it more difficult to breathe deeply and vigorously, cause shortness of breath and pain when taking a deep breath, cause coughing and a sore or scratchy throat, inflame and damage the lung lining, make the lungs more susceptible to infection, aggravate lung disease such as asthma, emphysema, and chronic bronchitis, increase the frequency of asthma attacks, and continue to damage the lungs even when the symptoms have disappeared.[5] Some people are more sensitive to O_3 than others. Sensitive groups include children; people with lung disease, such as asthma, emphysema, or chronic bronchitis; chronically ill people; and older adults. Even healthy adults who are active outdoors can experience O_3's harmful effects.

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[3] U.S. Environmental Protection Agency, *Transfer Standards For Calibration of Air Monitoring Analyzers for Ozone*, Technical Assistance Document, November 2010

[4] National Ambient Air Quality Standards (73 FR 16436: March 27, 2008 implement its new primary O_3 standard

[5] AQI(Air Quality Index), EPA-456/F-09-001,EPA airnow.gov

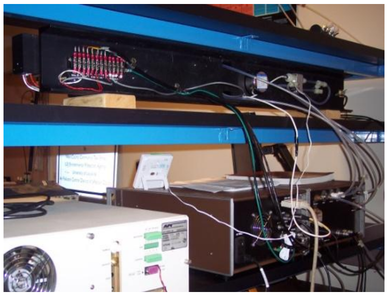
1.3 NIST Standard Reference Photometer (SRP) History

A collaborative effort between NIST and EPA in the development of the original SRPs has become the basis for O_3 measurements globally. The SRP Program began in the early 1980's as collaborative effort between NIST and the EPA to design, construct, certify, and deploy a network of identical O_3 reference instruments. The design specifications called for an instrument with a standard uncertainty of ±2 nmol/mol (ppb_v) in the range of 0 nmol/mol to 100 nmol/mol and ±2% in the range of 100 nmol/mol to 1000 nmol/mol. Since the SRPs have been deployed, beginning in 1983, the performance of all SRP's has exceeded the design specifications. In the US, two (2) SRPs are maintained by NIST, one serving as the NIST standard and the other as a backup/travelling instrument. Eleven (11) additional SRPs are maintained by the EPA at various EPA Regional laboratories across the United States to facilitate requests for local access to authoritative (ie, NIST) reference standards. The current international network of SRPs total nearly fifty (50) worldwide that now includes instruments maintained in at least fifteen (15) countries. The international network is coordinated by the Bureau International des Poids et Mesures (BIPM) in France, which maintains the international responsibility for the comparison of national O_3 standards as the NIST does here in the United States.

Over the past several years, the network of NIST SRPs has undergone significant upgrades in its electronic systems, sampling configuration, and control software. Each SRP consists of a separate optical bench and two instrumentation modules (electronics and pneumatics). The UV photometer consists of a low-pressure mercury discharge lamp, UV filter, UV beam splitter, two absorption cells, and signal-processing electronics. A new electronics module was designed as a plug-compatible replacement for the original unit to simplify upgrading of existing systems in May 2003. Several improvements were made in the overall electronics module design to provide enhanced stability and to simplify operation.

Front view SRP-10 in Region 4

Back view SRP-10 in Region 4



The electronics upgrade also involved a complete redesign of the detector module. The new detector V/f converters are more stable, and three times more sensitive than the previous ones. This provides increased measurement sensitivity through higher resolution scaler counts, a longer source lamp life, a lower noise level, and a smoother output signal.

The most recent upgrade to the SRPs solved a previously existing zero O_3 measurement bias, as well as improved the accuracy of the pressure measurements by using equal length sample and reference lines, effectively balancing the pressure drop through each sample pathway. The new dual manifold sampling configuration is now considered standard on the SRP. New SRPs are produced and delivered using this sampling configuration.

Control Software Upgrade[6]

Since the beginning of the SRP program, control of the instrument was handled in part by computer. Originally, the SRP was controlled by using a Hewlett Packard HP85B computer with a GPIO interface card. This version 1 control software was written using HP Series 80 software. While certain functions of this operation were automated, an operator was required to manually start each concentration measurement and manually change O_3 generator settings. Additionally, an independent computer was required for the operation of each SRP.

In 1992, NIST developed a new SRP control system based on the personal computer (PC). An Industry Standard Architecture (ISA) 24-bit digital input/output (DIO) control card was used to interface the SRP to the PC. Version 2 control software was written using QuickBASIC™ version 4.5. At the request of EPA, it was written to emulate the original software. While some improvements were made, the basic functionality of the SRP control remained the same.

In 1995, NIST developed an automated control system allowing multiple SRPs to be automatically compared to each other using one PC without the presence of an operator. Additionally, analog output signals from commercial O_3 instruments could be read simultaneously by the same PC to provide automated verifications. Version 3 control software was written in the "C" programming language using a front-end graphical interface similar to Windows™. While Windows™ version 3.1 was available during this time, the new version 3 control software was DOS based. When Windows™ 95 began to be used on SRP control computers, SRP operators began to notice problems running the version 3 control software in Windows™ from a DOS shell, and even from DOS several SRP operators continued to have problems. Most of the problems were related to reading the analog output signal from a commercial O_3 instrument and seemed to be PC dependent. Increasing processor speeds of the newer PCs may have contributed to the problems. For these reasons, in 2000 NIST began developing a new software/hardware update for the SRP using Peripheral Component Interconnect (PCI) control cards, and Windows-based VisualBASIC™ software. Use of the version 4 SRP control system began at NIST in November 2001, and became available to all other SRP users in April 2002.

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[6] "Upgrade and Inter-comparison of the U.S. Environmental Protection Agencies Ozone Reference Standards", Paper # 04-A-530-AWMA, June 22, 2004 , James E. Norris, Alan H. Band, Robert J. Bass, and Franklin R. Guenther

Hardware

Use of the ISA bus in PCs has vanished and it became impossible to purchase a PC with ISA expansion slots necessary for the operation of the version 3 software. A fourth generation control program for the SRP has been developed by NIST. New software was required due to the unavailability of new computers with the ISA bus. New computers are now available with the PCI bus only which means that the SRPs must now use new PCI control cards. SRP owners who have the older software operating on older computers do not have to upgrade, however NIST will no longer support the old software. A direct replacement of the ISA multi-function card previously used was not available in a PCI version. The PCI replacement uses a different connector so an additional signal distribution module was designed and produced to handle the new connector used on the PCI card. This allowed continued use of existing SRP control cables. A direct replacement for the 24-bit DIO card for controlling a guest SRP was available for PCI bus operation.

Software

The new software called “SRP Control” was written in VisualBasic™ version 6.0 and operates under the Windows™ NT, 2000, or XP environment. The program works in conjunction with Excel™ 2003 (version -xls) where all data collected from the program are automatically reported to templates, which can be customized to suit the user’s needs. The templates can have additional macros performing specific calculations or operations available in Excel™. The control system is operated using scripts, which call lower-level functions embedded in the program. The user cannot modify the lower-level functions, but the default scripts can be modified or new scripts written, to obtain customized system operations. This allows the user to create custom program control without the possibility of corruption to the basic functions of the SRP. Comparisons to an SRP can be done for up to three guest instruments (Level 2 transfer standards), including multiple guest SRPs. The guest system data input can be via SRP digital interface, serial communication, analog signal, or manual input of O_3 concentrations from the guest instrument display. Internal O_3 generators available on some guest O_3 instrumentation can be operated using serial communication. Calibration methods created for specific instrumentation can be saved and recalled for repeated use, or linked together in series to provide consecutive calibrations with different formats on the same instrument. Network access to the control system providing some control functions is available, but can be difficult to implement with network security systems.

The current version is 4.41 from NIST web site http://www.nist.gov/mml/analytical/gas/SRPpage.cfm

The next version is likely to be a LabView application. It is possible to connect SRP to SRP via USB interface, however, additional hardware would need to be purchased and there is a known Ozone Lamp voltage issue that limits the control of the Ozone Lamp from Zero-100% to Zero-50%.

Proposed Future Upgrades: Low voltage temperature STOWLAB cards to minimize a 0.2 deg C observed temperature bias, four temperature sensors one each on the inlet and outlet of each of the cells, two pressure transducers to measure the pressure from each cell and the LabView Control Software.