



# **Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone**

Technical Assistance Document

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Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone

Technical Assistance Document

Office of Air Quality Planning and Standards  
Air Quality Assessment Division  
Research Triangle Park, NC

## **Disclaimer**

EPA does not endorse any product or manufacturer. Any references to commercial products or trade names in this document are factual statements regarding types of instruments currently in use.

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## Preface

### **Intent of Document**

This Technical Assistance Document (TAD) defines, specifies, and formalizes the verification procedures of NIST-traceable O<sub>3</sub> transfer standards used for the calibrations (40 CFR Part 50 Appendix D) and Measurement Quality Checks (40 CFR Part 58 Appendix A) of O<sub>3</sub> analyzers. This document identifies what is necessary to establish and maintain the traceability of O<sub>3</sub> measurements within a monitoring network. All O<sub>3</sub> transfer standards must meet these verification requirements. This document updates and replaces the 2013 document entitled “Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone”<sup>1</sup> and the 1979 document entitled “Technical Assistance Document for the Calibration of Ambient Ozone Monitors”<sup>2</sup>. This document removes methods no longer in use and updates and standardizes definitions and procedures. This revision also updates the formatting consistent with other Quality Assurance documents published by the US Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Additional guidance and interpretation are available through the contacts listed below or through any EPA office. EPA strongly encourages those who are implementing O<sub>3</sub> traceability programs to request assistance in planning and implementation.

With this TAD, EPA is detailing its O<sub>3</sub> traceability scheme and more specifically defining the requirements for establishing and maintaining the traceability of O<sub>3</sub> measurements within a monitoring network.

### **Document Review and Distribution**

The information in this document was developed by the members of the Ozone Traceability Workgroup. The workgroup membership consists of all the Level 1 (Standard Reference Photometers) O<sub>3</sub> standard operators in the United States. Therefore, membership includes EPA OAQPS, EPA Office of Research and Development (ORD), ten EPA Regional Offices, the California Air Resources Board (CARB) and the National Institute of Standards and Technology (NIST). This document has been subjected to a peer review by EPA and the ambient air monitoring community nationwide; and has been distributed by OAQPS Quality Assurance staff to promote consistency across EPA in establishing and maintaining O<sub>3</sub> traceability within an O<sub>3</sub> monitoring network. This TAD may be viewed on the Internet and downloaded from the EPA’s Ambient Monitoring Technology Information Center (AMTIC) Homepage<sup>3</sup>.

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<sup>1</sup> Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone. EPA-454/B-13-004 U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, October, 2013. <http://www3.epa.gov/ttn/amtic/qapollutant.html>

<sup>2</sup> Paur, R.J. and F.F. McElroy. Technical Assistance Document for the Calibration of Ambient Ozone Monitors. EPA-600/4-79-057. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, September, 1979. <http://www.epa.gov/ttn/amtic/cpreldoc.htm>

<sup>3</sup> <https://www.epa.gov/amtic>

Recommendations for improvement or revisions are always welcome. Comments should be sent to the Regional Ozone Traceability Workgroup contact identified in the Acknowledgements Section. The Ozone Traceability Workgroup will meet periodically to discuss any pertinent issues and proposed changes.

## Acknowledgements

This document is the product of the combined efforts of the Ozone Traceability Workgroup. Workgroup membership for purposes of this revision include individuals implementing the Level 1 Standard Reference Photometer program from the EPA Office of Air Quality Planning and Standards, EPA Office of Research and Development, EPA Regional Offices, the California Air Resources Board and NIST. The following individuals are acknowledged for their contributions.

Gregory Noah, EPA OAQPS

Joann Rice, EPA OAQPS

Trisha Curran, EPA OAQPS

**\*Scott Moore, EPA ORD**

Timothy Sharac, EPA OAR CAMD

**\*Chris St. Germain, EPA Region 1**

**\*Avraham Teitz, EPA Region 2**

Mustafa Mustafa, EPA Region 2

Loretta Hyden, EPA Region 3

Kia Long, EPA Region 3

Verena Joerger, EPA Region 3

Mike Crowe, EPA Region 4

**\*Keith Harris, EPA Region 4**

Adam Zachary, EPA Region 4

Richard Guillot, EPA Region 4

Justin Coughlin, EPA Region 5

**\*Scott Hamilton, EPA Region 5**

Michael Compher, EPA Region 5

Carrie Cummings, EPA Region 5

**\*Clarence Jackson, EPA Region 6**

Thien Bui, EPA Region 7

**\*James Regehr, EPA Region 7**

Michael Davis, EPA Region 7

**\*Joshua Rickard, EPA Region 8**

Mathew Plate, EPA Region 9

Roseanne Sakamoto, Region 9

Anna Mebust, EPA Region 9

Bilal Qazzaz, EPA Region 9

**\*Barbara Bates, EPA Region 9**

Chris Hall, EPA Region 10

Ranjit Bhullar, CARB

**\*Louise Sorensen, CARB**

**\*James Norris, NIST**

Bob Lordo, Battelle

Cheryl Triplett, Battelle

Ian MacGregor, Battelle

**\*All Level 1 Standard Reference Photometer contacts are in bold.**

## Glossary of Terms

**Acceptance testing** - Acceptance testing is testing that ensures and documents that an overall system is operating properly and as designed

**Adjustment** – A change made to the measurement device (transfer standard or O<sub>3</sub> monitor) resulting in a new internal calibration factor.

**Annual** – Means 365 days.

**Annual Performance Evaluations (APE)** – The measurement quality check that is required in 40 CFR Part 58 Appendix A § 3.1.2.

**Application** – The designation of a specific transfer standard as either a bench or field standard at a specific point in time.

**As-found** – This term is used to describe data recorded prior to any adjustment being made or if an adjustment has not been made the conditions of a device upon receipt.

**As-left** - This term is used to describe data recorded after an adjustment has been made or if an adjustment has not been made the conditions of a device when all services have been completed.

**Bench standard** - A transfer standard that remains stationary. Stationary means the transfer standard is placed at one location for the entire verification period (i.e., placed at one monitoring site and used for remote checks or placed in a laboratory to conduct verifications).

**Best practice** – A procedure that is accepted as being the most correct.

**Calibration** - The comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustment. Calibration of an ambient air monitoring analyzer adjusts the analytical response of the analyzer to more closely agree with a measurement standard of higher accuracy. A calibration is always followed by a verification.

**Calibration scale** - The term used to indicate the concentration range that the O<sub>3</sub> instrument is calibrated over.

**Candidate transfer standard** – A transfer standard that has met all qualification and acceptance testing and is in a verification process.

**Concentration points** – Refers to the pollutant concentration run during a verification cycle.

**Conditioning** – This term is used to describe the process of flowing an ozonated sample through a component of the transfer standard and ancillary equipment.

**Cycle (verification cycle)** – This term refers to the collective comparison of standard concentrations of at least 6 concentration points and a zero.

**Field standard** – A transfer standard that is transported to field sites for use. Transported means that a transfer standard is moved from location to location for use (i.e., to conduct one-point

quality control checks or annual performance evaluations). If a transfer standard is not placed at one location as a bench standard, it is a Field standard.

**Indicated concentration** – The raw concentration that is reported from the front panel, calibrated analog voltage output, digital output or other data reporting mechanism from a device.

**Internal calibration factors** – A term used to describe the number assigned within a transfer standard referencing a mathematical correction of the output concentration internal to the transfer standard computer. Internal calibration factors are sometimes termed coefficient, slope, background or offset. This terminology is vendor specific.

**Level 1** – EPA’s network of Standard Reference Photometers (SRP).

**Level 2** – Any transfer standard that is verified against a Level 1 SRP.

**Level 3** – Any transfer standard that is verified against a Level 2 transfer standard.

**Major repair** – A broad term that describes a repair that is completed to a component of an O<sub>3</sub> instrument that has a direct effect on the measurement.

**Measurement Quality Check** – A one-point quality control check or annual performance evaluation as specified in 40 CFR Part 58 Appendix A.

**Minor repair** - A broad term that describes a repair that is completed to a component of a O<sub>3</sub> transfer standard that does not have a direct effect on the measurement.

**Monitoring organization (MO)** – This term will be used to identify any tribal, state or local organization that is implementing an ambient air monitoring program, especially if they are using the data for comparison to the National Ambient Air Quality Standards (NAAQS).

**One-Point Quality Control Check (QC Check)** – The measurement quality check that is required in 40 CFR Part 58 Appendix A § 3.1.1.

**O<sub>3</sub> Generator** – This term is broadly used as a description of a device that creates an O<sub>3</sub> sample. A typical O<sub>3</sub> generator consists of a temperature-controlled chamber where a stable flow of zero air is pushed across a UV lamp to output ozone concentrations. The amount of ozone generated can be changed by varying the UV lamp intensity, or zero air flow rate.

**QA Handbook** - *QA Handbook for Air Pollution Measurement Systems, Volume II Ambient Air Quality Monitoring Program (EPA-454/B-17-001)*, commonly known as the “QA Handbook”. The most recent version of this document is available on the AMTIC home page.<sup>4</sup>

**Qualification testing** - Initial testing of an overall device design to determine reliability over a range of variables.

**Quality Assurance Project Plan (QAPP)** - A tool required by regulation for project managers and planners to document the type and quality of data needed for environmental decisions and to describe the methods for collecting and assessing those data. See *EPA Requirements for Quality*

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<sup>4</sup> <https://www3.epa.gov/ttn/amtic/qalist.html>

*Assurance Project Plans for Environmental Data Operations (EPA QA/R5)* for more information.<sup>5</sup>

**Reverification** – A verification of a transfer standard that occurs after a verification and when all acceptance testing passes at a prescribed frequency.

**Standard concentration** – The concentration used when conducting calibrations, measurement quality checks or verifications. This concentration is derived from using Equation 10 in Appendix A and/or using the indicated O<sub>3</sub> concentration of the transfer standard. The method will depend upon the traceability scheme.

**Standard Operating Procedure (SOP)** - SOPs are written documents that detail the method for an operation, analysis, or action with thoroughly prescribed techniques and steps, and are officially approved as the method for performing certain routine or repetitive tasks. See the QA Handbook and *Guidance for the Preparation of Standard Operating Procedures EPA QA/G-6*.<sup>6</sup>

**Transfer Standard** – A transportable device or apparatus which, together with associated operational procedures, is capable of accurately reproducing pollutant concentration standards or of producing accurate assays of pollutant concentrations which are quantitatively related to an authoritative standard. In this document this term will be used to describe field and bench O<sub>3</sub> transfer standards.

**Validation template** –The validation template is a table consisting of three criteria: critical, operational, and systematic criteria, where each criterion has a different degree of implication about the quality of the data. This table will list the requirements for collecting valid O<sub>3</sub> data. See QA Handbook Appendix D.

**Verification** – The process used to relate a candidate transfer standard output to a standard of higher authority.

**Verification range** – This term is used to describe the extent of concentrations where a verification is valid. The concentration range is defined by the area between zero and the highest concentration point in the verification.

**Warm-up time** – This term is used to describe the amount of time it takes for an instrument to meet all operational parameters in the instrument manual.

**Zero-air** – This term is meant to describe the air used to generate a test atmosphere and the air used to provide a reference measurement for the assay of the sample. 40 CFR Part 50 Appendix D § 4.4.1 defines Zero-air as follows: “The zero air must be free of contaminants which would cause a detectable response from the O<sub>3</sub> analyzer, and it must be free of NO, C<sub>2</sub>H<sub>4</sub>, and other species which react with O<sub>3</sub>.” The NIST Specifications for the Standard Reference Instrument Series 6008, Ozone Standard Reference Photometer defines zero-air as “...clean, dry air.

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<sup>5</sup> <https://www.epa.gov/quality/epa-qar-5-epa-requirements-quality-assurance-project-plans>

<sup>6</sup> <https://www.epa.gov/quality/guidance-preparing-standard-operating-procedures-epa-qag-6-march-2001>

Preferably, zero-air containing no significant impurities, having less than 1 ppm (parts per million) total hydrocarbons by volume, and containing 20 - 21% oxygen.”

## 1.0 Introduction

### 1.1 The Importance of O<sub>3</sub> Measurement Traceability

Monitor calibrations and measurement quality checks require the generation and assay of known O<sub>3</sub> concentrations from transfer standards that meet the specifications in this TAD. Gaseous O<sub>3</sub> standards cannot be stored for any practical length of time due to the reactivity and instability of the gas. Therefore, traceable O<sub>3</sub> concentrations must be generated and “verified” locally. Devices are commercially available which meet this need. However, these devices must be calibrated and verified against more authoritative standards prior to being used as a standard themselves. These standards are called “transfer standards”. A transfer standard is defined as a device or apparatus which, together with associated operational procedures, is capable of accurately reproducing traceable pollutant concentrations or of producing traceable assays of pollutant concentrations which are quantitatively related to a higher level and more authoritative standard. The transfer standard’s purpose is to transfer the traceability of a pollutant standard to a remote point where it is used to verify or calibrate an air monitoring analyzer. The specific procedures practiced define the resultant measurements’ traceability and have a direct effect on the measured O<sub>3</sub> concentrations.

### 1.2 Code of Federal Regulations (CFR) Requirement<sup>7</sup>

EPA’s Data Quality Objective (DQO) for O<sub>3</sub> is stated in 40 CFR Part 58 Appendix A § 2.3.1.2:

*Measurement Uncertainty for Automated O<sub>3</sub> Methods.* The goal for acceptable measurement uncertainty is defined for precision as an upper 90 percent confidence limit for the CV of 7 percent and for bias as an upper 95 percent confidence limit for the absolute bias of 7 percent.

40 CFR Part 58 Appendix A § 2.6.2 provides that “Test concentrations for O<sub>3</sub> must be obtained in accordance with the ultraviolet photometric calibration procedure specified in appendix D to Part 50 of this chapter and by means of a certified *NIST-traceable O<sub>3</sub> transfer standard*” (emphasis added). Additionally, 40 CFR Part 50 Appendix D § 4.2 provides that “Transfer standards must meet the requirements and specifications set forth in Reference 12” (reference 12 is the 2013 version of this document). This document provides updated specifications and best practices for organizations using O<sub>3</sub> transfer standards for NAAQS comparison to demonstrate NIST traceability.

### 1.3 Summary of Photometric Technique

The UV photometric technique requires a stable O<sub>3</sub> generator, a UV photometer, and a source of clean, dry, pollutant-free air. A flowing (dynamic) system is set up in which clean air is passed through the O<sub>3</sub> generator at a constant flow rate and discharged into a multiport manifold. The

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<sup>7</sup> <https://www.ecfr.gov/>



O<sub>3</sub> concentration in the manifold is assayed by the photometer and is available for calibration of O<sub>3</sub> monitors or verification of transfer standards. The air flow and/or the O<sub>3</sub> generator can be adjusted to provide the approximate O<sub>3</sub> concentration desired. The UV photometer is then used to measure the UV absorption of the generated concentration at a wavelength of 254 nm according to 40 CFR Part 50, Appendix D § 4.3.1. This transmittance measurement, together with the well-established absorption coefficient of O<sub>3</sub> at that wavelength and various instrument parameters, is used to calculate the O<sub>3</sub> concentration by means of the Beer-Lambert absorption law. The accuracy of the photometer and adherence to standard operating procedures is critically important to this technique. Many commercially available instruments have been designated as Federal Equivalent Methods (FEM)<sup>8</sup> and are therefore approved, under the stated conditions, to be used for the measurement of O<sub>3</sub> in ambient air and subsequent comparison to the NAAQS. The FEM designation only applies to analyzers used for this purpose and does not apply to transfer standards. The methodology and specifications for O<sub>3</sub> transfer standards are in this TAD.

#### **1.4 O<sub>3</sub> Technical Assistance Document History**

The original analytical procedure prescribed by the EPA for verifying local O<sub>3</sub> concentrations was a wet chemical technique based on spectrophotometric analysis of iodine generated by O<sub>3</sub> in neutral buffered potassium iodide (NBKI) and referenced to an arsenious oxide primary standard. EPA amended these regulations by replacing the NBKI technique with more effective technique based on absorption of ultraviolet (UV) radiation and referenced to the well-established absorption coefficient of O<sub>3</sub> at a wavelength of 254 nm.

On February 8, 1979 (Federal Register, 44:8221-8233), the EPA amended 40 CFR Part 50, Appendix D to prescribe a calibration procedure for the calibration of reference methods for measuring O<sub>3</sub> in the atmosphere. The procedure is based on the use of UV photometry as the authoritative standard for O<sub>3</sub> and allows the use of transfer standards for the calibration of ambient O<sub>3</sub> monitors, provided such transfer standards are adequately referenced to a UV O<sub>3</sub> standard of higher authority (level) and traceability.

To support the implementation of the new UV transfer standard technique, EPA published two TADs in September 1979. The first TAD was entitled *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone (EPA-600/4-79-056)* with revisions occurring in 2010 (EPA-454/B-10-001) and 2013 (EPA-454/B-13-004). The second TAD was entitled *Technical Assistance Document for the Calibration of Ambient Ozone Monitors (EPA-600/4-79-057)*. While the principles in EPA-600/4-79-056 (and revisions) and EPA-600/4-79-057 remain

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<sup>8</sup> <https://www.epa.gov/amtic/air-monitoring-methods-criteria-pollutants>. Federal equivalent method (FEM) is defined in 40 CFR 58.1 to mean “a method for measuring the concentration of an air pollutant in the ambient air that has been designated as an equivalent method in accordance with part 53 of this chapter; it does not include a method for which an equivalent method designation has been canceled in accordance with § 53.11 or § 53.16.”

correct, many of the procedures in those documents are outdated. Therefore, EPA-600/4-79-056 (and revisions) and EPA-600/4-79-057 are being superseded by this document.

### **1.5 Document Organization**

This document focuses on providing practical information and procedures for establishing and maintaining the traceability of O<sub>3</sub> measurements within a monitoring network. This revision also aims to align the document’s formatting with other QA documents published by OAQPS.

The major part of the document is devoted to the specifications and practical procedures necessary to establish and maintain NIST traceable O<sub>3</sub> transfer standards. The beginning sections provide background and overarching information about traceability and the later sections provide the technical details needed to successfully implement a traceability program. **Section 4.0 gives the O<sub>3</sub> Transfer Standard Requirements and Specifications Table** which is an easy to read table of requirements. This table also provides quick references to sections within the TAD and outside references. Diagrams and flowcharts have been inserted where appropriate to illustrate complicated processes. Section 6.0 lists operational considerations as practical information to be used when working with all O<sub>3</sub> transfer standards. Appendix A provides all equations and example calculations.

### **1.6 Summary of Major Changes from the *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone (2013)***

This document supersedes the 2013 version of *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone (EPA-454/B-13-004)*. The following table is a concise list of the major changes in this TAD. This table does not encompass all changes.

***Table 1-1 List of Major Changes from the Previous Version***

<b>2013 Version (EPA-454/B-13-004)</b>	<b>2023 Version (EPA-454/B-22-003)</b>
Transfer standard nomenclature was ambiguous to application and distance from Level 1 (i.e., all Level 2 were labelled “bench standards”)	Transfer standard nomenclature is clarified and based on application (bench standard or field standard) and distance from Level 1
Reverification frequency was based on distance from SRP	Reverification frequency is based on application (bench versus field)
Levels had differing acceptance criteria	Levels 2 and 3 have the same acceptance criteria
Relative Standard Deviation was used as a measure of transfer standard verification and reverification cycles stability	<sup>1</sup> Standard Deviation is used for verification cycles stability. Change from previous regression slope and intercept are used for reverification stability.
Six Cycles were required for verifications and cycles had to be on different days	<sup>1</sup> Three stable cycles are required for verification and can be conducted on same day

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January 2023*

<b>2013 Version (EPA-454/B-13-004)</b>	<b>2023 Version (EPA-454/B-22-003)</b>
Allowed generator-only devices to be used as O <sub>3</sub> transfer standards	Does not allow generator-only devices to be used as O <sub>3</sub> transfer standards
Level 4 transfer standards were allowed	Level 4 transfer standards are strongly discouraged and are allowed only if additional requirements are met
Did not include best practices	Includes hands-on operational best practices for working with O <sub>3</sub> transfer standards

<sup>1</sup>Appendix D of this TAD provides descriptions and EPA’s rationale for these changes and other verification and reverification requirements.

This TAD, Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone EPA-454/B-22-003, clarifies what is needed to establish and maintain the traceability of O<sub>3</sub> measurements within a monitoring network and, in some cases, provides flexibilities that were not available in the previous version. It supersedes EPA-600/4-79-056 (and revisions) and EPA-600/4-79-057. The Quality Assurance Handbook for Air Pollution Measurement Systems Volume II<sup>9</sup> provides additional information regarding regulatory monitoring for O<sub>3</sub>. Where provisions in this technical assistance document have changed (i.e. calling for 3 cycles instead of the traditional “6X6”) or are clarified, implementation will occur over a phase in period of not more than 2 years from the time this document becomes final.

### **1.7 Use of the Terms Must and Should**

In order to distinguish requirements from provisions that are recommended or a best practice, the following terms will be used with consistency.

**must-** when the element is required because it is necessary to establish and maintain the traceability of O<sub>3</sub> measurements

**should-** when the element is recommended or is a best practice. This term is used when extensive experience in monitoring provides a recommended procedure that would help establish or improve the quality of data or a procedure. The process that includes the term is not required but if not followed, an alternate procedure should be developed that meets the intent of the procedure. In order to distinguish provisions that are necessary to establish and maintain the traceability of O<sub>3</sub> measurements from those that are recommended or a best practice, the following terms will be used with consistency.

## **2.0 EPA’s O<sub>3</sub> Traceability Scheme**

### **2.1 Description of EPA’s O<sub>3</sub> Traceability Scheme**

NIST traceable O<sub>3</sub> transfer standards are required to conduct calibrations and measurement quality checks of O<sub>3</sub> analyzers used to collect data for NAAQS comparison. Gaseous O<sub>3</sub> standards cannot be stored for any practical length of time due to the reactivity and instability of

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<sup>9</sup> <https://www3.epa.gov/ttn/amtic/qalist.html>

the gas. Therefore, O<sub>3</sub> concentrations 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 a measurement result whereby the result can be related to a stated reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty”. EPA broadly uses the NIST “7 Essential Elements of Traceability” as described in Appendix C of this TAD as a guide to establish and maintain NIST traceability of O<sub>3</sub> measurements.

EPA’s traceability scheme is carefully designed so that O<sub>3</sub> data collected while following the procedures in this TAD meet the DQO.

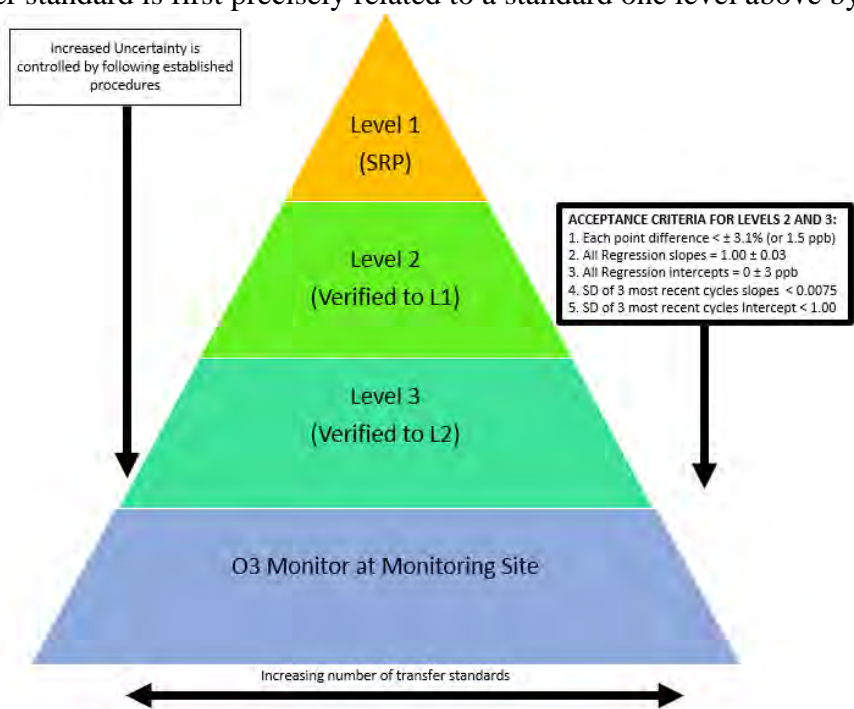
Figure 2-1 illustrates EPA’s transfer standard hierarchy for O<sub>3</sub> measurements. The family of SRPs are defined as Level 1 transfer standards. Beyond the SRPs, all levels of standards are numbered (starting with Level 2) based on its “distance in the traceability chain” from a verification against a Level 1 standard.

For Levels 2 and 3, the transfer standard is first precisely related to a standard one level above by careful comparison as described in this TAD.

Traceability is established by generating known concentrations of O<sub>3</sub> and concurrently assaying these with a verified transfer standard of higher authority. These data are used to establish a linear regression relationship between the candidate transfer standard and the standard one level above it in the hierarchy.

Provided the acceptance criteria (listed in Table 4-1 below) are met, the candidate transfer standard becomes a

verified transfer standard one level below the level of its predecessor. An unbroken chain of calibrations is established by either adjusting the internal calibration factors prior to the verification of the transfer standard being verified, and/or by using Equation 10 of Appendix A to mathematically calculate the standard concentration from the verified device when subsequently used. This process appropriately relates the new transfer standard indicated concentration to its predecessor.

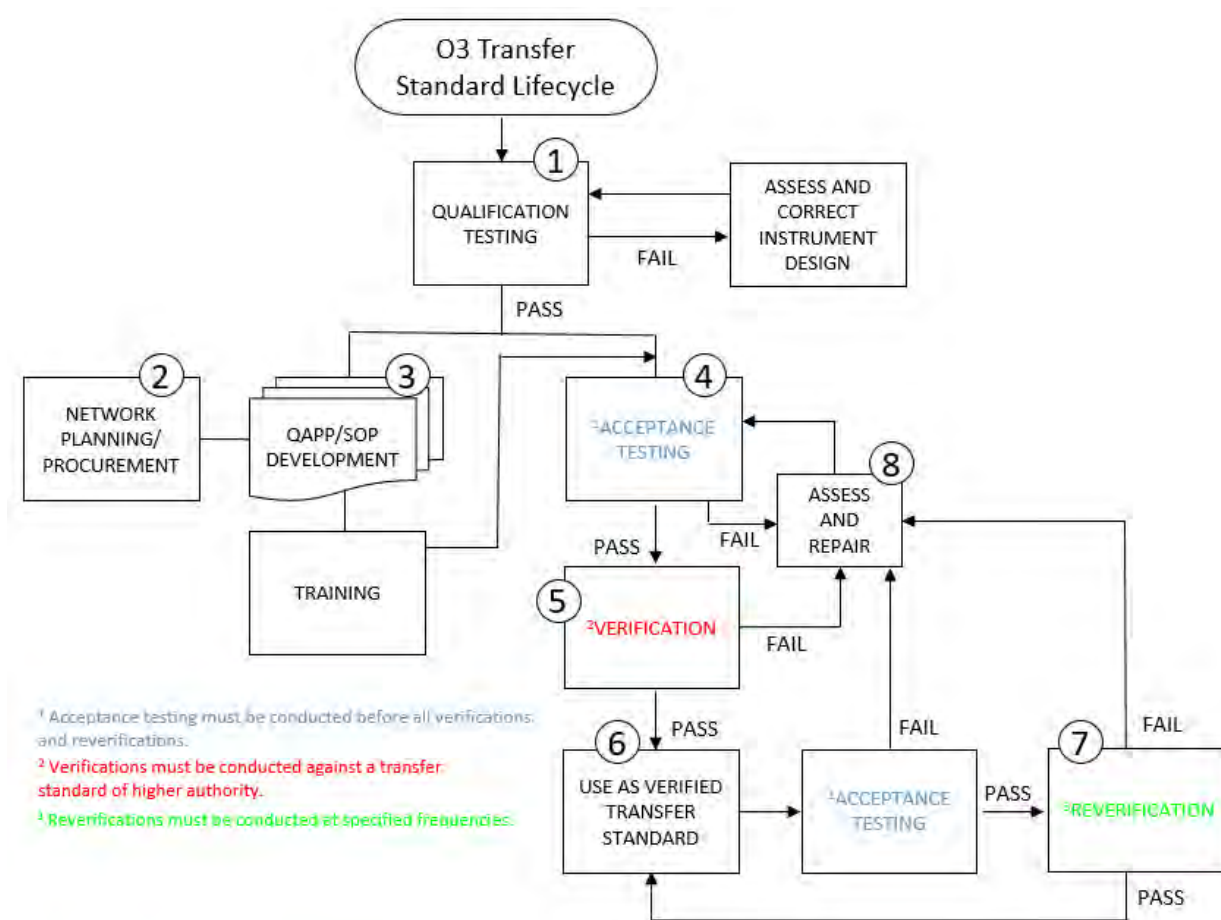


**Figure 2-1 EPA Transfer Standard Hierarchy**

After a passing verification, the transfer standard may then be used to conduct calibrations or measurement quality checks. Transfer standards that do not meet the acceptance criteria in Table 4-1 cannot be used until corrective action is taken and a passing verification is completed.

Reverifications of all transfer standards must be conducted at specified intervals. O<sub>3</sub> transfer standards are complex systems consisting of devices that generate and assay O<sub>3</sub> concentrations. Consequently, their verification and use must be in accordance with these prescribed procedures. This re-comparison serves to ensure that transfer standards are maintaining functionality and traceability. Table 4-1 also provides a summary of the verification and reverification frequencies.

## 2.2 Lifecycle of O<sub>3</sub> Transfer Standards



**Figure 2-2 O<sub>3</sub> Transfer Standard Lifecycle Flowchart**

Successful implementation of an O<sub>3</sub> traceability program will require significant understanding of the procedures involved. The following illustration is meant to assist the user with a visual representation of the general steps involved in maintaining a current verification of an O<sub>3</sub> transfer standard. Figure 2-2 illustrates the typical lifecycle of an O<sub>3</sub> transfer standard.

- ① – Beginning in the top of Figure 2-2, an O<sub>3</sub> transfer standard must undergo qualification testing either at the vendor or at the monitoring organization (MO). If the vendor has previously completed suitable qualification testing and can provide that documentation to the user, it is not necessary for the MO to also conduct the qualification testing since qualification testing is a test of the design of the instrumentation and configuration. Details of the qualification testing process can be found in Section 4.2.1 and in Appendix E.
- ② – The MO should review all specifications and ensure that an adequate transfer standard is chosen that meets the needs of the monitoring objective.
- ③ – After qualified devices are chosen, the MO must develop a suitable QAPP and SOP to document and describe how they will implement this TAD.
- ④ – Acceptance testing is the first step in the verification or reverification process. Acceptance testing ensures the transfer standard is operating as designed. Section 4.2.2 discusses acceptance testing and Appendix B contains an example worksheet which may be used to document acceptance testing. If the acceptance testing fails, the user must determine the cause and correct the problem before attempting the acceptance test again. This may include sending the device back to the manufacturer for repair. The user must successfully complete acceptance testing prior to instrument verification or reverification.
- ⑤ – After successful completion of the acceptance testing, a verification must be conducted against a standard of higher authority. All transfer standards must be verified and reverified according to Table 4-1. Section 5.0 gives general steps for the verification.
- ⑥ – A successfully verified transfer standard may be used within its' verification frequency. Users are strongly encouraged to conduct other checks to ensure that the transfer standards have not drifted. Section 6.2 describes several check methods.
- ⑦ – The transfer standard must undergo acceptance testing and reverification according to the frequencies in Table 4-1.
- ⑧ – The transfer standard must be assessed and repaired if any acceptance testing, verification or reverification fails.

As mentioned above, for an O<sub>3</sub> transfer standard to meet EPA's traceability scheme the criteria in Table 4-1 must be met and documented. If at any time an O<sub>3</sub> transfer standard does not meet the criteria in Table 4-1 or if the verification period has expired, the instrument is no longer a valid transfer standard and cannot be used for O<sub>3</sub> monitoring calibrations or measurement quality checks. EPA's traceability scheme does allow flexibility for expired transfer standards to undergo a reverification if all the criteria in Table 4-1 are met (see Section 2.7) but a transfer standard may not be used if it has exceeded its verification frequency.

### **2.3 Level 1 Transfer Standard Scheme**

All Level 1 transfer standards within EPA's O<sub>3</sub> traceability scheme are SRPs and are bound by the procedures for the EPA's SRP program. Level 1 transfer standards must only be used in a

laboratory setting with adequate environmental conditions (Section 6.20) and only be used to verify or reverify lower level transfer standards. The only exception is when a Level 1 SRP is used to conduct a comparison against an equal Level 1 SRP to provide verification.

All SRPs are designed and built by NIST according to the design specifications in NISTIR 6963 (Paur et al., 2003). Several upgrades have occurred through the years improving the original design (Norris et al., 2013, 2004).

These publications and NIST's continuous testing of the SRPs as designed concludes that "data from the entire SRP network have indicated that the SRP is a reliable and repeatable ozone standard calibration instrument. Intercomparisons conducted annually over more than two decades have shown the SRPs to be in agreement to better than 0.5% over the concentration range 100 ppbv to 1000 ppbv and  $\pm 1$  ppbv over the concentration range of 0 ppbv to 100 ppbv. This network has met the needs of the user community responsible for ozone calibration by providing local access to authoritative standards" (Paur et al., 2003).

Figure 2-3 represents the family of Level 1 SRPs. Traceability of NIST's Level 1 SRPs and EPA's Level 1 SRPs is achieved by demonstrating traceability to the BIPM.QM-K1<sup>10</sup>. The BIPM.QM-K1 is the International key comparison for O<sub>3</sub> reference standards. Participants of the BIPM.QM-K1 are National Metrology Institutes (NMIs) or Designated Institutes (Dis) of Member States of the Convention of the Meter. A DI is an Institute within a country that has been designated by their NMI as the O<sub>3</sub> reference laboratory for that country. NIST is the NMI for the United States of America. An NMI or DI maintains the O<sub>3</sub> standard for their Country and serves as the traceability link for all O<sub>3</sub> measurements within that Country. Each NMI or DI must have an approved quality system and stated Calibration and Measurement Capabilities (CMC) for O<sub>3</sub>. Participation in the BIPM.QM-K1 is then required on specific intervals to show proof of their CMC claims.

Bureau International des Poids et Mesures (BIPM)<sup>11</sup> and NIST both maintain several Level 1 SRPs. Currently, BIPM SRP #27 serves as the reference standard for the BIPM.QM-K1. BIPM SRP #28 is always operated concurrently with BIPM SRP #27 as a check of BIPM SRP #27 during all key comparison measurements. These SRP's purpose can change over time if new SRPs are utilized or other circumstances warrant a change. The results of all participants of the BIPM.QM-K1 are available on the BIPM website in the Key Comparison Database (KCDB)<sup>12</sup>. Successful participation in the BIPM.QM-K1 key comparison is accomplished by demonstrating agreement to the reference instrument within the stated uncertainties. The acceptance limits of an EPA Level 1 SRP must be  $(1.00 \pm 0.01$  slope and  $0.0 \pm 1$  nmol/mol (ppbv) intercept).

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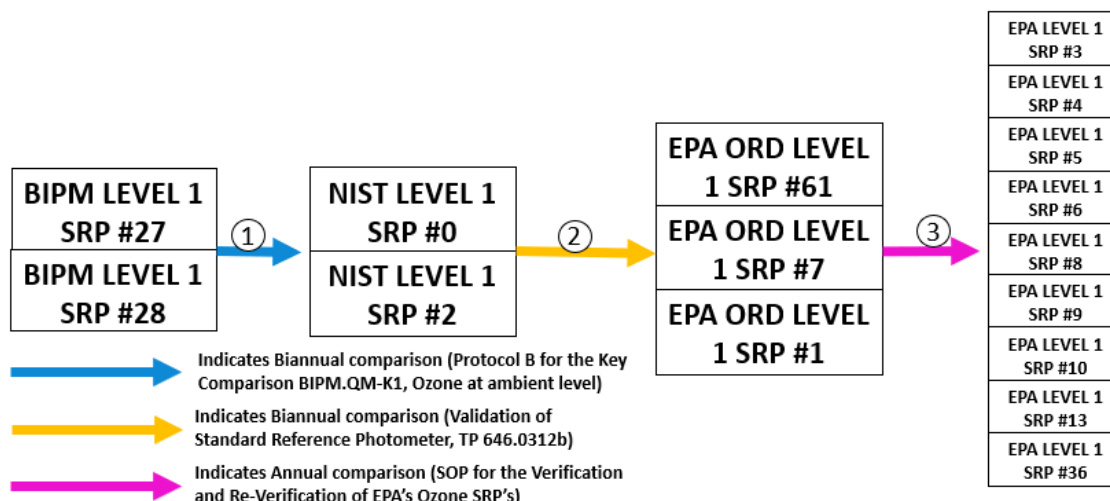
<sup>10</sup> <https://www.bipm.org/en/bipm/chemistry/gas-metrology/ozone/ozone-comparisons.html>

<sup>11</sup> <https://www.bipm.org/>

<sup>12</sup> <https://www.bipm.org/kcdb/>



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① – NIST participates in the BIPM.QM-K1, ozone at ambient level.

*Figure 2-3 Standard Reference Photometers*

② – Within EPA, the ORD Metrology laboratory maintains EPA SRP #1, #7 and #61. EPA ORD sends at least one of these SRPs to NIST for verification biannually. Additional comparisons are made between SRP #1, SRP #7 and SRP #61 as needed throughout the year.

③ – The ORD Level 1 SRP is used to conduct an annual verification against the EPA Regional SRP's.

In 2020, a total of 64 SRPs exist worldwide. Table 2-1 shows a listing of all SRPs that support the NAAQS monitoring network within the US.

*Table 2-1 List of Standard Reference Photometers in the US*

SRP #	Completion Date	Location	Organization
0	August 1985	Gaithersburg, MD	NIST (backup/traveling)
1	February 1983	RTP, NC	EPA ORD
2	February 1983	Gaithersburg, MD	NIST (National Standard)
3	August 1983	Edison, NJ	EPA Region 2
4	September 1983	Sacramento, CA	California ARB
5	March 1985	Houston, TX	EPA Region 6
6	March 1985	Chicago, IL	EPA Region 5
7	January 1986	RTP, NC	EPA OAQPS
8	February 1986	Golden, CO	EPA Region 8
9	May 1987	Chelmsford, MA	EPA Region 1
10	November 1987	Athens, GA	EPA Region 4
13	January 1989	Kansas City, KS	EPA Region 7
36	August 2004	San Francisco, CA	EPA Region 9
61	December 2017	RTP, NC	EPA ORD/OAQPS



## **2.4 Defining the Terms Level 2 and Level 3 Transfer Standard**

The function of Level 2 and Level 3 transfer standards is to duplicate and distribute O<sub>3</sub> atmospheres traceable to a Level 1 SRP with a stated uncertainty. Measurement uncertainty increases with the distance from the first standard in the traceability hierarchy. In traditional terminology, Level 2 transfer standards were termed “primary standards” and Level 3 transfer standards were termed “calibrator”, “field standard” or “transfer standard” (in either case the device that is taken to air monitoring sites). The level number (1, 2 or 3) describes the devices distance from the first standard in the traceability hierarchy whereas the terms “primary standard” or “calibrator” is ambiguous to that important and meaningful fact. Therefore, EPA is now exclusively using the terms “Level 1”, “Level 2” or “Level 3” in order to give these terms more meaningful definitions.

## **2.5 Defining the Terms Bench and Field Transfer Standard**

**Bench standards** are transfer standards that remain stationary. Stationary means the transfer standard is placed at one location for the entire verification period (i.e., placed at one monitoring site and used for remote checks or placed in a laboratory to conduct verifications). To ensure proper functioning of the bench standard, the area where bench standards are operated should be free of dust, maintain regulated humidity (Section 6.20), have a stable power supply, and suitably ventilated. Bench standards are only transported when it must be verified or if repairs or maintenance is necessary.

**Field standards** are transfer standards that are transported to field sites for use. If a transfer standard is not placed at one location as a bench standard, it is a field standard. For example, calibrators designated to perform annual performance evaluations (APE) are field standards because they must travel from site to site to conduct audits. Field standards should always be handled with care to prevent damage.

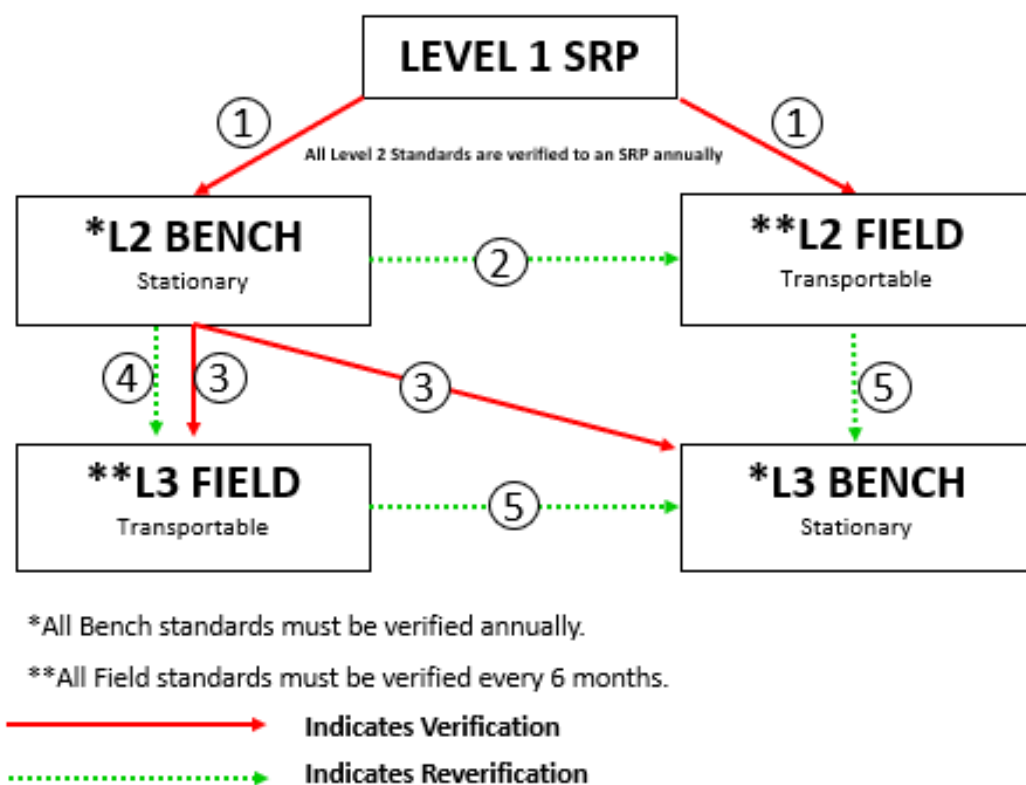
A Level 2 or 3 transfer standard’s application may be either as a bench or field standard. All Level 1 SRPs must function as bench standards. A bench standard may become a field standard at any time; however, the standard would require more frequent reverifications as a result. A field standard **cannot** become a bench standard until it is appropriately verified. For example, consider a standard which is verified against a Level 1 SRP and then designated as a Level 2 bench standard used to conduct Level 3 verifications or Level 2 reverifications. Anytime during its verification period, this Level 2 bench standard may be re-designated as a Level 2 field standard and transported to monitoring sites to conduct work (i.e., calibrations or measurement quality checks). However, if this happens, the standard **cannot** be re-designated back to a Level 2 bench standard until it is verified against a Level 1 SRP.

## **2.6 Bench versus Field Transfer Standard Verification Frequency**

In previous versions of this TAD, EPA stated verification frequencies that were based on the distance the device was from the Level 1. Generally, the further away from the Level 1 the more verifications were required to maintain traceability. Level 2 verifications were required

annually, and Level 3 verifications were required every 6 months. In this revision, EPA uses the application (bench or field standard) of the transfer standard as a means of determining verification frequencies. Field standards are more likely to experience drift due to vibrations and other impacts from repeated transport; therefore, field standards should be verified and checked more frequently. Bench standards will experience less of the impacts related to transport and will be much less likely to experience performance shifts; therefore, bench standards require less frequent checks.

Figure 2-4 shows the verification frequencies and traceability hierarchy EPA has defined for the bench and field standards. Table 4-1 provides a complete listing of O<sub>3</sub> transfer standard verification frequencies and requirements. It should be noted that this diagram shows the verification and reverification frequencies for all possible combinations of bench and field transfer standards. Two Level 2 and Level 3 transfer standards (one bench and one field) are not required. See Section 2.8 for details on traceability schemes. Bench standards require an annual verification frequency and field standards require a 6-month verification frequency as described below.



*Figure 2-4 Verification Frequencies for Bench and Field Transfer Standards*

- ① – All Level 2 transfer standards must be initially verified against a Level 1 SRP, then verified annually or upon failure of a reverification, each time against a Level 1 SRP.
- ② – Level 2 field standards must be reverified against a standard of equal or higher authority (Level 2 bench standard or Level 1 SRP) every 6 months.

- ③ – All Level 3 transfer standards must be initially verified against a Level 2 bench standard.
- ④ – Level 3 field standards must be reverified against a Level 2 bench standard every 6 months.
- ⑤ – Level 3 bench standards must be reverified against a standard of equal or higher authority (Level 2 bench standard or Level 2 or 3 field standard) annually.

Users are cautioned that drift can occur in O<sub>3</sub> transfer standards. Calibrating an O<sub>3</sub> monitor with a transfer standard that has unknowingly drifted can cause systemic data loss in a monitoring network. Therefore, EPA strongly recommends that additional checks be implemented to determine whether drift has occurred in the transfer standard. Section 6.2 provides additional checks recommended by EPA to guard against data loss.

**A verification timeframe begins on the day the verification is completed and not the day the transfer standard is put into service.** This includes both newly verified transfer standards as well as reverifications. For example, if a transfer standard is verified on January 1, is placed on the equipment shelf and not used until May 1 then the reverification timeframe begins on January 1 and not May 1. This also applies to all field standards. If a bench standard is re-designated as a field standard, then a 6-month reverification is required (i.e., 6 months from the time the bench standard was verified).

## **2.7 Lapses in Verification Frequency**

A transfer standard may not be used after the reverification frequency time period has been exceeded. For example, if a Level 3 field transfer standard was verified on January 1 of a given year, it may not be used after July 1 of that same year. The intent of defining frequencies for reverifications is to ensure that drift has not occurred in the measurement system and therefore ensure that drift is not passed down through the traceability hierarchy to the monitor reporting the ambient O<sub>3</sub> concentration. Frequent checks provide assurances that the system is operating as designed and that the stated output is correct. It is important to consistently conduct checks at these defined frequencies. However, EPA recognizes that solely because a transfer standard has exceeded its verification frequency this in and of itself does not warrant a new verification (all three cycles). A transfer standard that has narrowly exceeded its verification time period (i.e., by 30 days) may be reverified if all acceptance testing criteria are met and the device is operating normally. The reverification data must be reviewed against the acceptance criteria and especially against the previous verification data to be certain only acceptable drift has occurred in the measurement system. This process must be fully documented in the QAPP and SOP.

## **2.8 Level 2 and 3 Transfer Standard Scheme**

The primary function of Levels 2 and 3 transfer standards is to duplicate and distribute traceable concentration standards to O<sub>3</sub> monitoring sites where traceability to a Level 1 transfer standard is required. Traceability is required for all O<sub>3</sub> monitors that compare their data to the NAAQS. Depending on the size and complexity of the MO, various levels and numbers of transfer standards are needed; and many different scenarios will be acceptable. A small MO with only

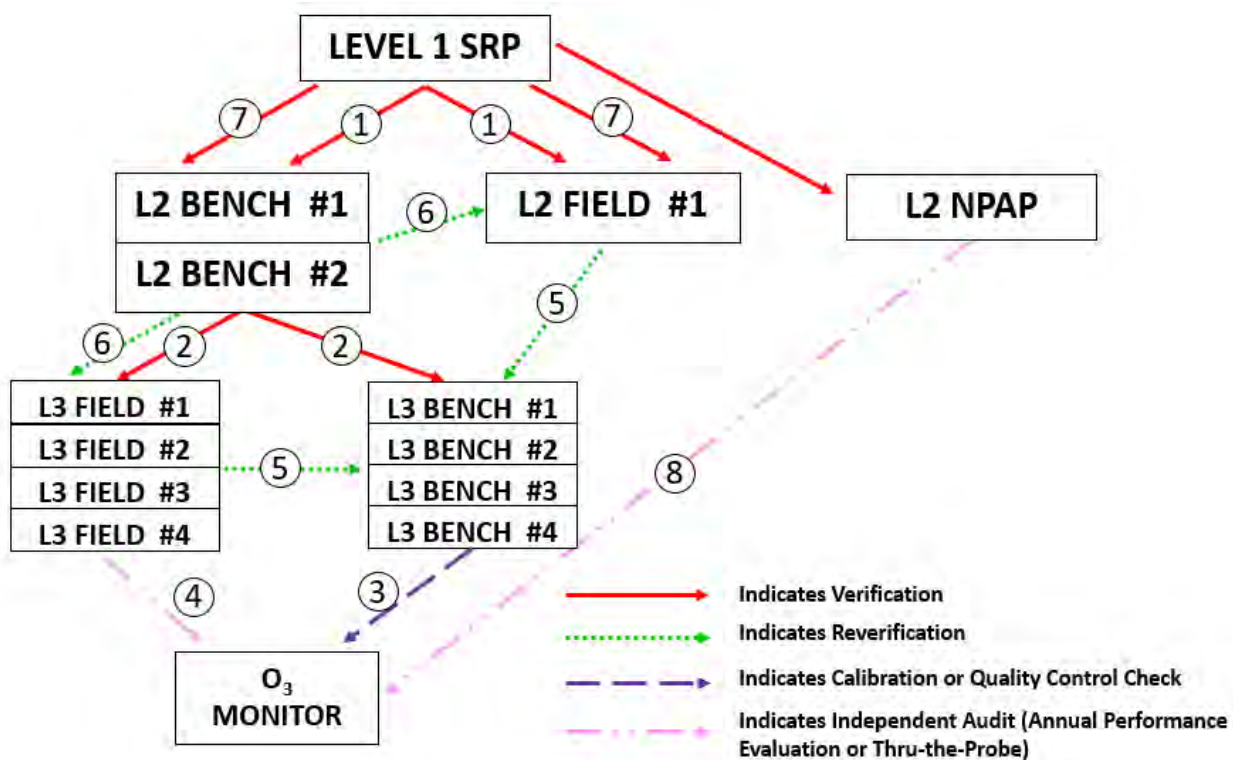
one or two sites may be able to position a Level 2 transfer standard at each site. This arrangement will not be practical for a large monitoring network since each Level 2 transfer standard requires an annual verification against a Level 1 SRP. Larger networks might benefit from bringing two or more Level 2 transfer standards for an annual verification against an SRP.

Three of the most common schemes are described below. The quantity and type of transfer standards needed at Levels 2 and 3 will depend on many factors. **Many variations will be acceptable. Each MO must assess their situation and determine an appropriate traceability scheme.** EPA strongly encourages those who are implementing O<sub>3</sub> traceability programs to request assistance in planning and implementation.<sup>13</sup>

**The circled numbers in the figures correspond to the circled numbers in the descriptions for each step in the traceability scheme.**

### 2.8.1 Scheme #1 – Use of Level 3 Bench Standard and Level 2 Field Standard

Figure 2-5 shows a simplified roadmap to illustrate the verification and reverification pathways for Levels 2 and 3 transfer standards in this scheme. This figure shows an example with four



*Figure 2-5- Traceability Scheme #1: Use of Level 3 Bench Standard and Level 2 Field Standard*

Level 3 bench standards and four Level 3 field standards, where the Level 3 bench standards are positioned at specific monitoring sites and used primarily to perform O<sub>3</sub> monitor calibrations

<sup>13</sup> For further assistance in planning your transfer standard scheme, contact your Regional EPA office.

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and/or quality control (QC) checks (40 CFR Part 58 Appendix A § 3.1.1), and the Level 3 field standards are used to perform APEs of O<sub>3</sub> monitors according to 40 CFR Part 58 Appendix A § 3.1.2. One advantage of this scheme is that the Level 3 bench standard can remain at a monitoring site and is not required to be “swapped out” with a newly reverified Level 3 transfer standard every 6 months. The Level 3 bench standard is reverified at the monitoring site until it fails to meet the acceptance criteria. One disadvantage of this scheme is that, due to the infrequent checks against the Level 2 bench standard, vigilance should be used to ensure drift has not occurred in the transfer standard chain. EPA strongly recommends that additional checks be implemented to determine if drift has occurred. Section 6.2 provides additional checks recommended by EPA to guard against data loss.

① – All Level 2 transfer standards are verified against a Level 1 SRP annually (typically 2-3 Level 2 transfer standards are verified). One of the Level 2 transfer standards is designated as a Level 2 field standard and the remaining Level 2 standard(s) is designated strictly as a Level 2 bench standard and not moved from the laboratory.

② – A Level 2 bench standard(s) is used to verify numerous Level 3 transfer standards. Each verified Level 3 transfer standard is designated as either a bench or field standard. Frequent intercomparison between the Level 2 standards is strongly recommended.

③ – Level 3 bench standards are deployed to specific monitoring sites and used in a stationary application to conduct O<sub>3</sub> monitor calibrations and/or quality control (QC) checks on O<sub>3</sub> monitors. It is also appropriate to conduct O<sub>3</sub> monitor calibrations with a Level 2 field standard at the monitoring site.

④ – Level 3 field standards are used to conduct APEs of O<sub>3</sub> monitors. The Level 3 transfer standard used to conduct calibrations and QC checks must be different than the transfer standard used to conduct the APE.

⑤ – Level 3 bench standards are reverified against Level 2 bench, Level 2 field or Level 3 field standard annually (at the monitoring site or at the Level 2 bench standard location). EPA strongly recommends that additional checks be implemented to ensure that drift has not occurred in the transfer standard.

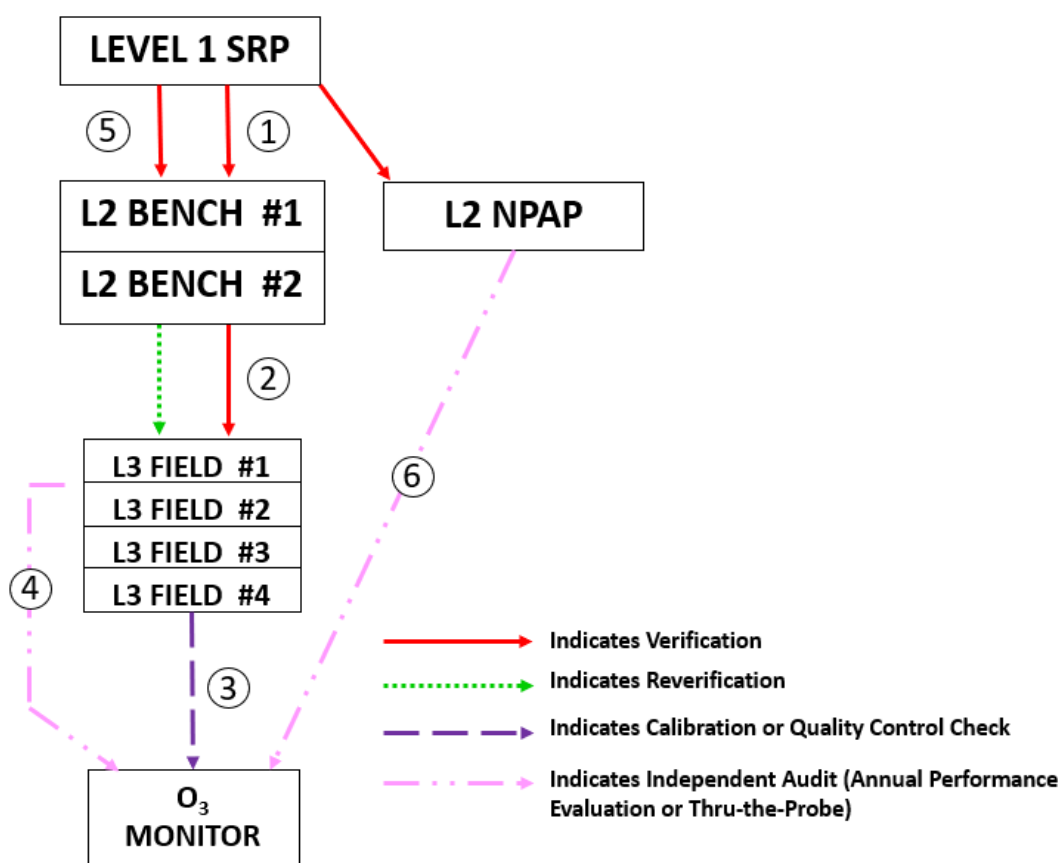
⑥ – Level 2 field standards and Level 3 field standards are reverified against Level 2 bench standards every 6 months. EPA strongly recommends that additional checks be implemented to determine if drift has occurred in the transfer standard.

⑦ - All Level 2 transfer standards are reverified against a Level 1 SRP annually (typically 2-3 Level 2 transfer standards are verified).

⑧ - National Performance Audit Program (NPAP) audits are conducted according to 40 CFR Part 58 Appendix A § 3.1.3.

### 2.8.2 Scheme #2 – Use of Level 3 Field Standard without Level 3 Bench Standard

Figure 2-6 shows a simplified roadmap to illustrate the verification and reverification pathway for Levels 2 and 3 transfer standards in this scheme. Note that all Level 2 standards are designated as bench standards. One advantage of this scheme is that the Level 3 field standards must be brought back to the laboratory hosting the Level 2 bench standard for a direct comparison, thereby adding additional assurance that drift has not occurred in the transfer standard. One disadvantage of this scheme is that Level 3 field standards are transported from site to site which subjects transfer standards to shock, vibration and temperature extremes which can cause measurement drift. EPA strongly recommends that additional checks be implemented to ensure that drift has not occurred. Section 6.2 identifies additional checks recommended by EPA to guard against data loss.



*Figure 2-6 Traceability Scheme #2: Use of Level 3 Field Standard without Level 3 Bench Standard*

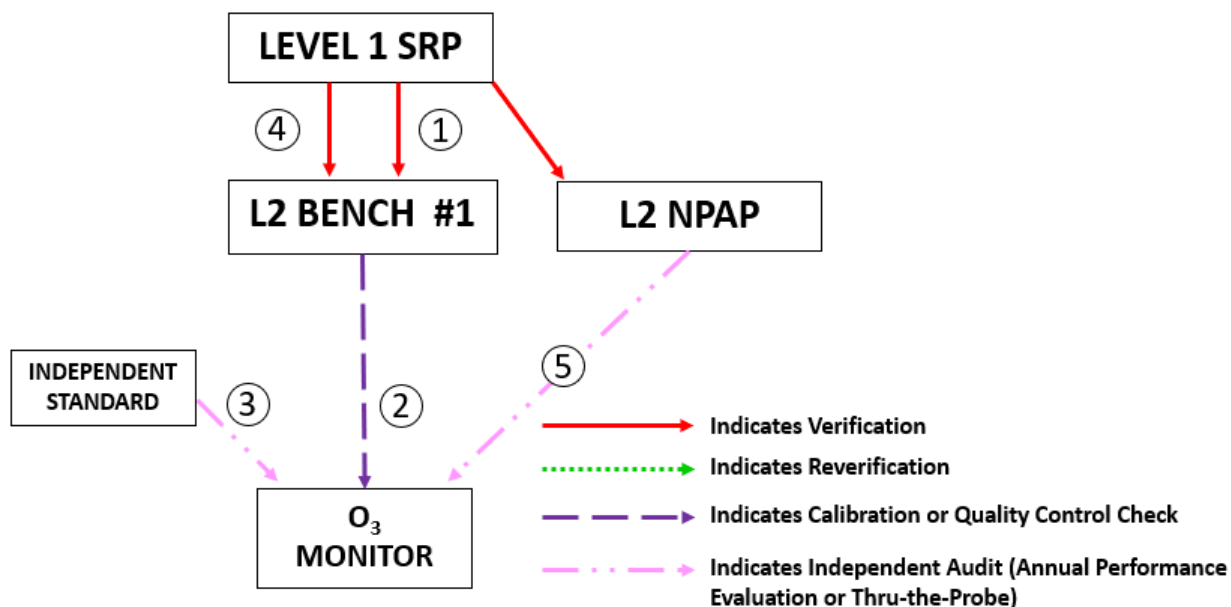
① – All Level 2 transfer standards are verified against a Level 1 SRP annually (typically 2-3 Level 2 transfer standards are verified).

② – The Level 2 bench standard(s) is used to conduct verifications and reverifications of Level 3 field standards.

- ③ – Level 3 field standards are used to conduct O<sub>3</sub> monitor calibrations and/or QC checks (40 CFR Part 58 Appendix A § 3.1.1) on O<sub>3</sub> monitors.
- ④ – Level 3 field standards are used to conduct APEs of O<sub>3</sub> monitors according to 40 CFR Part 58 Appendix A § 3.1.2. The Level 3 transfer standard used to conduct calibrations and QC checks must be different than the transfer standard used to conduct the APE.
- ⑤ – All Level 2 transfer standards are reverified against a Level 1 SRP annually (typically 2-3 Level 2 transfer standards are verified).
- ⑥ - National Performance Audit Program (NPAP) audits are conducted according to 40 CFR Part 58 Appendix A § 3.1.3.

### 2.8.3 Scheme #3 – Use of Level 2 Bench Standard only

Figure 2-7 shows a simplified roadmap to illustrate the verification and reverification pathway for Level 2 transfer standards in this scheme. Here, the single Level 2 bench standard is located at a monitoring site. One advantage of this scheme is that the Level 2 transfer standard is used to directly calibrate the O<sub>3</sub> monitor at the monitoring site, which means the reported O<sub>3</sub> concentration is one level closer to the Level 1 SRP than in Schemes #1 and #2. One major disadvantage of this scheme is that, due to the infrequent checks of the Level 2 bench standard, and the isolation of that standard at the monitoring site (no additional checks from independent transfer standards) vigilance must be used to ensure drift has not occurred in the transfer standard chain. Another disadvantage is that access to a Level 1 SRP is limited and it might not be practical to provide Level 2 field standards at each monitoring site. EPA strongly recommends



*Figure 2-7 Traceability Scheme #3: Use of Level 2 Bench Standard only*

that additional checks be implemented to ensure that drift has not occurred. Section 6.2 provides additional checks recommended by EPA to guard against data loss.

- ① – All Level 2 transfer standards are verified against a Level 1 SRP annually. The number of Level 2 transfer standards depends on the number of monitoring sites.
- ② – The Level 2 bench standard(s) is placed at the monitoring site and used to conduct calibrations or QC checks (40 CFR Part 58 Appendix A § 3.1.1) on O<sub>3</sub> monitors.
- ③ – An independent transfer standard is used to conduct APEs according to 40 CFR Part 58 Appendix A § 3.1.2.
- ④ – All Level 2 transfer standards are reverified against a Level 1 SRP annually (typically 2-3 Level 2 transfer standards are verified).
- ⑤ - National Performance Audit Program (NPAP) audits are conducted according to 40 CFR Part 58 Appendix A § 3.1.3.

## **2.9 Quality Documentation**

Quality system requirements are discussed in EPA documents CIO 2105.0 (formerly EPA Order 5360.1 A2)<sup>14</sup>, *EPA QA/R-2, EPA Requirements for Quality Management Plans*<sup>15</sup>, and *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans*<sup>16</sup>. Traceability and transfer standards must be supported by trained operators and documented procedures. For a claim of traceability to be made, all users of all Levels of O<sub>3</sub> transfer standards must incorporate all relevant information into their Quality Assurance Project Plan (QAPP) and Standard Operating Procedures (SOP). QAPPs and SOPs must provide enough detail to describe their specific traceability scheme with adequate detail and should follow the guidelines in the *QA Handbook for Air Pollution Measurement Systems, Volume II Ambient Air Quality Monitoring Program (EPA-454/B-17-001)*, commonly known as the “QA Handbook”.<sup>17</sup>

This TAD provides best practice procedures while also allowing flexibility for Mos to implement traceability of O<sub>3</sub> measurements according to their specific situation. In any case, it is the MO’s responsibility to ensure that their quality system is documented, accurate, and implemented. EPA Regions and Mos using O<sub>3</sub> transfer standards should incorporate procedures consistent with those outlined in this document into their quality system documentation.

## **2.10 Training**

Training is a required element of an air monitoring QAPP, which includes training plans for technical staff. Minimum training requirements should be developed, completed and documented so that users understand the equipment and procedures. Training should include

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<sup>14</sup> <https://www.epa.gov/sites/production/files/2013-10/documents/21050.pdf>

<sup>15</sup> <https://www.epa.gov/quality/epa-qar-2-epa-requirements-quality-management-plans>

<sup>16</sup> <https://www.epa.gov/quality/epa-qar-5-epa-requirements-quality-assurance-project-plans>

<sup>17</sup> <https://www3.epa.gov/ttn/amtic/qalist.html>



reviewing the QAPP, SOP, relevant instrument manual(s) and hands-on training or shadowing with an experienced technician. Mos should incorporate this training in a comprehensive plan for all personnel involved in O<sub>3</sub> monitoring work. Training may also be available from vendors and can be negotiated when making purchases of commercially available equipment.

### **3.0 Types of O<sub>3</sub> Devices**

#### **3.1 Devices with Photometers**

All O<sub>3</sub> transfer standards must meet the specifications in 40 CFR Part 50 Appendix D § 4.3 and Table 4-1 of this TAD. Users should contact their Regional EPA office prior to putting into service any device that is not specifically designed by the manufacturer as an O<sub>3</sub> transfer standard.

#### **3.2 Generator-Only devices**

Many commercially available O<sub>3</sub> analyzers can be purchased with an internal zero-air scrubber, O<sub>3</sub> generator and a valve that can be used to introduce a zero and O<sub>3</sub> test atmosphere to the photometer at a preprogrammed time. This is commonly referred to as an internal O<sub>3</sub> generator, internal ozonator or internal zero/span option in an O<sub>3</sub> monitor. These devices do not contain an independently verified photometer and cannot be used to conduct measurement quality checks (required by 40 CFR Part 58 Appendix A) or calibrations. The appropriate use for a generator-only device is to conduct automated zero/span checks (usually at midnight each night). Information from these devices should be charted and used to assess the relative stability of the photometer and the general trend of the responses. This data should be used as a diagnostic check to inform the user whether an action limit is breached thereby triggering an evaluation and possible recalibration of the monitor prior to the point of data loss.

The user should set up the nightly check to run automatically and graph the results in a control chart. The user should then frequently review the general trend of the percent differences. Once an action limit (a typical action limit is 50% of the acceptance criteria) is reached, the user should take corrective action. It is also possible to use a data logger or other system to automatically make this determination and send warnings to alert the MO of a breach in action limits.

### **4.0 Verification and Reverification Requirements for O<sub>3</sub> Transfer Standards**

#### **4.1 O<sub>3</sub> Transfer Standard Requirements and Specifications Table**

The following table provides a summary of the requirements for O<sub>3</sub> transfer standards. The last column also identifies the section or appendix of this document where specific requirements can be found and provides citations to additional documents that provide additional relevant information. A candidate transfer standard must pass all the requirements below before being used for O<sub>3</sub> measurement activities.

*Transfer Standards for the Calibration of Air Monitoring Analyzers for Ozone,  
January 2023*

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Reference/Additional Information</b>
<b>Level 1 (SRP to SRP Comparison)<sup>1</sup></b>			
<b>Qualification</b>	Not Applicable	Not Applicable	(Norris et al., 2013, 2004; Paur et al., 2003; Viallon et al., 2006)
<b>Acceptance Testing (Pre-Verification SRP QC checks for temperature and pressure circuits)</b>	Prior to Level 1 reverification Prior to use for Level 2 verification	All acceptance criteria are found in SRP/SOP-1	SRP/SOP-1 Section 9.5.2, 9/18/2015
<b>Stability Monitor</b>	Prior to each use	All acceptance criteria are found in SRP/SOP-1	SRP/SOP-1 Section 9.5.2.10, 9/18/2015
<b>Verification (involves 6 cycles)</b>	Upon receipt and upon major repair	Regression slope = $1.00 \pm 0.01$ Regressions intercept $< \pm 1$ ppb	SRP/SOP-1 (9/18/2015), Section 1.3 SRP/SOP-1 (9/18/2015), Section 9.7.20
<b>All Level 2 and 3 Transfer Standards<sup>2,3</sup></b>			
<b>Qualification</b>	<u>Commercial devices</u> – conducted at vendor <u>Non-commercial devices</u> – 1 time prior to acceptance testing	Repeatability within $\pm 4\%$ or 4 ppb from its indicated value (whichever is greater)	Section 4.2.1 Appendix E Qualification testing conducted by the manufacturer if commercial device.
<b>Acceptance Testing</b>	Upon receipt (new), following repair, or prior to conducting Verifications or Reverifications	Per manufacturer specifications	Section 4.2.2 Appendix B provides a generic Acceptance Testing worksheet Users should also consult the Manufacturer Manual
<b>Verification (involves 3 cycles<sup>4</sup>)</b>	Upon receipt (new), adjustment, or major repair. All Level 2 transfer standards must be verified annually against a Level 1 SRP	Each point difference $< \pm 3.1\%$ (or $\pm 1.5$ ppb for concentration points below 50 ppb) All Regression slopes = $1.00 \pm 0.03$ All Regression intercepts = $0 \pm 3$ ppb Standard Deviation of the 3 Slopes $< \pm 0.0075$ Standard Deviation of the 3 intercepts $< \pm 1.00$ ppb	Section 4.4.1 Appendix A provides example calculations and equations.
<b>Level 3 Bench Transfer Standard<sup>5</sup></b>			
<b>Reverification (involves 1 cycle<sup>4</sup>)</b>	Annually	Each point difference $< \pm 3.1\%$ (or $\pm 1.5$ ppb for concentration points below 50 ppb) Regression slope of reverification cycle must be within $\pm 0.015$ of most recent verification slope Regression intercept of reverification cycle must be within $\pm 1.5$ ppb of most recent verification intercept	Section 4.4.2 Appendix A provides example calculations and equations.
<b>Levels 2 and 3 Field Transfer Standards<sup>6</sup></b>			
<b>Reverification (involves 1 cycle<sup>4</sup>)</b>	Every 6 months	Same as Level 3 Bench Transfer Standard Reverification (above)	Same as Level 3 Bench Transfer Standard Reverification (above)

*Table 4-1 Specifications for O<sub>3</sub> Transfer Standards*

## *Transfer Standards for the Calibration of Air Monitoring Analyzers for Ozone, January 2023*

<sup>1</sup>Level 1 SRP requirements are outside the scope of this document. Please see the Standard Operating Procedure for the Verification and Re-Verification of EPA's O<sub>3</sub> Standard Reference Photometers for more details.

<sup>2</sup>Level 2 Transfer standard verification services are only available through the Standard Reference Photometer Program. Contact the Regional EPA office for scheduling. Small agencies may be able to avoid the cost of Level 2 standard equipment by obtaining access to Level 2 standards through EPA Regional Offices, State agencies, or other cooperating agencies. Some commercial laboratories may also provide O<sub>3</sub> transfer standard verification services.

<sup>3</sup>Acceptance criteria and verification frequencies listed are **minimum requirements**. Organizations should review their procedures and assess their technical expertise with O<sub>3</sub> transfer standards and determine if more stringent criteria should be used (i.e., more frequent verifications) to meet EPA's DQO for O<sub>3</sub>. Contact the EPA Regional Office for assistance in designing and implementing a O<sub>3</sub> traceability scheme.

<sup>4</sup>A cycle consists of at least 6 concentrations and zero. Verification points must be chosen according to Section 6.3.

<sup>5</sup>A Level 3 bench reverification may be conducted against any equal or higher level transfer standard. Additional checks and data reviews are strongly recommended (See Section 6.2).

<sup>6</sup>Level 2 and Level 3 field standards must be reverified against a Level 2 bench standard at least every 6 months. All Level 2 transfer standards must be verified annually against a Level 1 SRP.

### **4.2 Requirements for all Levels**

As described in Section 2.2, the general process for maintaining a verified transfer standard is qualification, acceptance testing, verification and reverification. Qualification and acceptance testing ensure the device is properly designed and that it is operating as designed. Verification and reverification testing are used to relate the candidate standard output to another verified transfer standard in the hierarchy by concurrently generating and assaying various O<sub>3</sub> concentrations.

#### **4.2.1 Qualification Testing Requirements**

Qualification is initial testing of an overall device design to determine reliability over a range of variables. Before a device design can be used as a transfer standard, it must be tested and shown to have adequate performance and reliability. The design must be repeatable over reasonable periods of time and over the range of conditions encountered during lab and/or field use and during transport. Qualification of a transfer standard design may require a series of initial tests to determine reliability.

All O<sub>3</sub> transfer standards must meet the general requirements for qualification. The transfer standard output should not vary by more than  $\pm 4\%$  or  $\pm 4$  ppb (whichever is greater) from its indicated value over a stated range of any of the conditions to which it might be sensitive. All devices used as a transfer standard must complete adequate qualification testing according to Appendix E and the results must be documented.

For most commercially available devices, qualification testing is completed at the vendor during the design phase of manufacturing and with a representative sample of devices. It is important that as Mos plan purchases of new generation transfer standards, they consult with the manufacturers on the processes used to qualify the instruments. It is the user's responsibility to ensure that qualification testing has been completed for each commercially available device purchased. Even if design qualifications have been completed at the vendor, there can be value in conducting qualification testing for newly acquired instruments. This can help ensure the

instruments will perform under various field conditions that might not be observed during a traditional verification process.

#### **4.2.2 Acceptance Testing Requirements**

Acceptance testing is testing that ensures and documents that an overall system is operating properly and as designed. Acceptance testing must be completed after a new transfer standard is received from the manufacturer, prior to verification or reverification of a transfer standard, when a transfer standard is shipped, or when a device requires repair. For new instruments or instruments undergoing repair, EPA recommends that the instruments be operated over several days to ensure that the device is field-ready following any such repair.

Acceptance testing should not be confused with qualification testing (Section 4.2.1) in that it is primarily an examination of the components in the device. Diagnostics data are readily available from the device's front panel and should be reviewed and documented frequently. Acceptance testing should be completed using vigilance but is not meant to be a time-consuming part of the verification process. However, if any component in the acceptance testing is outside the manufacturers recommendation then those components must be corrected prior to verification. An example acceptance test data worksheet is provided in Appendix B.

It is the transfer standard owners responsibility to ensure all acceptance testing and preventive maintenance is completed and to provide that documentation as part of the verification process.

Elements of a proper acceptance test should include:

1. Documentation of testing date, time, operator, instrument make/model/serial number (SN);
2. Documentation ensuring routine maintenance required by the instrument manual has been performed;
3. Direct comparison of sensors impacting the measurement (i.e., sample pressure, sample temperature, analog outputs) if recommended by the instrument manual or if sensor adjustment is required;
4. Documentation of diagnostic parameters in the instruments' menu system and comparison to the manufacturer's specification (i.e., sample pressure, sample temperature, flow);
5. Review and verify that all acceptance test data are within acceptable limits.

#### **4.3 Level 1 Requirements**

Level 1 requirements are not addressed in this TAD. Level 1 transfer standards are addressed in the most recent version of EPA's SRP/SOP<sup>18</sup> and NIST's Gas Sensing Metrology Group Quality Manual (QM-III-646.03), following TP 646.0312b (Validation of Standard Reference Photometer).

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<sup>18</sup> [https://www3.epa.gov/ttnamti1/files/ambient/qaqc/SRP\\_SOP%20R1%209\\_18\\_15.pdf](https://www3.epa.gov/ttnamti1/files/ambient/qaqc/SRP_SOP%20R1%209_18_15.pdf)

#### **4.4 Level 2 and 3 Verification and Reverification Requirements**

Verification and reverification procedures must be developed consistent with the specifications outlined in this TAD. All Level 2 and Level 3 transfer standards require a verification against a Level 1 SRP or a Level 2 bench standard, respectively. The transfer standard of higher authority must have a current verification and all verifications and reverifications must be conducted by a qualified technician. Adjustments to the candidate transfer standards' internal calibration factors must be made prior to verification. Internal calibration factors must be tracked. No adjustments are allowed prior to a reverification.

Each testing cycle which constitutes a verification or reverification of a Level 2 or Level 3 transfer standard will be accomplished by generating and simultaneously assaying varying concentrations of O<sub>3</sub> in the range that the device will be used. A linear regression analysis is conducted using the indicated concentrations of the candidate transfer standard and the standard concentrations of the transfer standard of higher authority. Care must be taken when reviewing candidate transfer standard verification and reverification data to ensure that active and excessive drift is not occurring.

An example verification dataset and calculations can be found in Appendix A.

##### **4.4.1 Verification Requirements**

**Verifications** must be conducted at the frequency stated in Table 4-1. The following is a list of the **verification** requirements for Levels 2 and 3 transfer standards.

1. A **verification** consists of a minimum of three (3) stable testing cycles, each cycle consisting of a zero and at least six (6) upscale concentration points. Concentration points must be chosen according to Section 6.3. The following must hold within and across these testing cycles (equation numbers refer to Appendix A):
  - a. Each point difference must be  $< \pm 3.1\%$  (Equation 1) or  $\pm 1.5$  ppb for concentration points below 50 ppb (Equation 2).
  - b. All Regression Slopes must be  $1.00 \pm 0.03$  (Equation 4).
  - c. All Regression Intercepts must be  $0 \pm 3$  ppb (Equation 4).
  - d. Standard Deviation of the 3 Slopes must be  $< \pm 0.0075$  (Equation 8).
  - e. Standard Deviation of the 3 Intercepts must be  $< \pm 1.00$  ppb (Equation 9).

##### **4.4.2 Reverification Requirements**

**Reverifications** must be conducted at the frequency stated in Table 4-1. The following is a list of the **reverification** requirements for Levels 2 and 3 transfer standards.

1. A **reverification** consists of a minimum of one (1) stable testing cycle consisting of a zero and at least six (6) upscale concentration points. Concentration points must be chosen according to Section 6.3. The following must hold for this testing cycle (equation numbers refer to Appendix A):
  - a. Each point difference must be  $< \pm 3.1\%$  (Equation 1) or  $\pm 1.5$  ppb for concentration points below 50 ppb (Equation 2).

- b. All Regression Slopes must be  $1.00 \pm 0.03$  (Equation 4).
- c. All Regression Intercepts must be  $0 \pm 3$  ppb (Equation 4).
- d. Regression Slope of reverification cycle must be within  $\pm 0.015$  of most recent verification slope
- e. Regression Intercept of reverification cycle must be within  $\pm 1.5$  ppb of most recent verification intercept

#### **4.5 Level 4 Verification and Reverification Requirements**

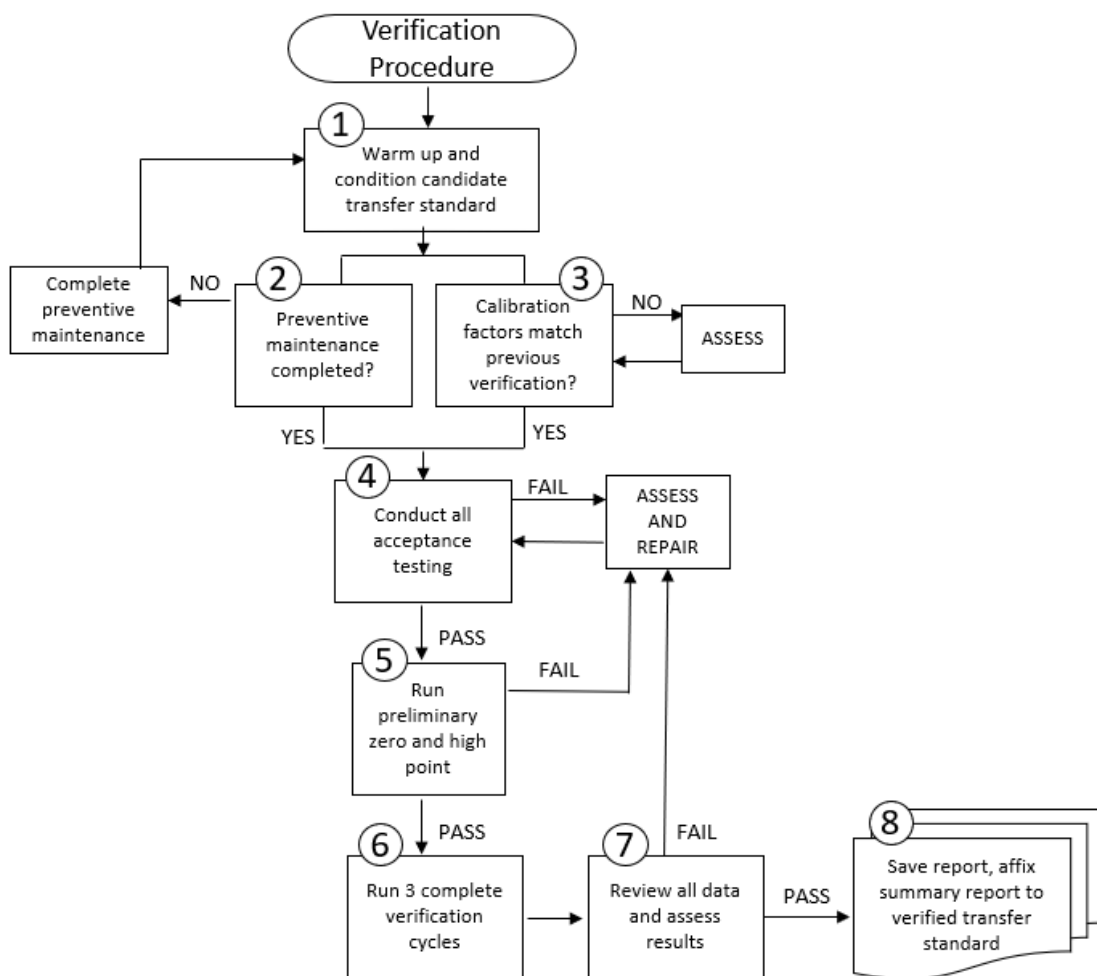
Level 4 transfer standards (for which a verified Level 3 standard would serve as the transfer standard of higher authority) are strongly discouraged. However, in the rare instance when a Level 4 is the only option for establishing traceability, the MO should work with the EPA Regional office for assistance in developing acceptance criteria and procedures that are adequate to meet the EPA's DQO for O<sub>3</sub> and overall minimize uncertainty. At a minimum, Level 4 transfer standards must be reverified at least quarterly. All other minimum requirements for Level 4 transfer standards must be at least as stringent as the Level 3 transfer standard criteria listed in Table 4-1. To guard against systemic data loss, more frequent reverifications or other cross checks must be completed when using Level 4 transfer standards. Section 6.2 provides additional checks recommended by EPA to guard against systemic data loss.

### **5.0 Verification and Reverification Procedure for O<sub>3</sub> Transfer Standards**

#### **5.1 Verification Procedure**

Figure 5-1 gives a generalized flow chart and step-by-step procedure meant to assist the user in acquiring an overall understanding of the verification process for development of their specific SOPs. Users must develop detailed SOPs that are inclusive of all steps and describes their traceability scheme consistent with this TAD.

**The circled numbers in the flowchart correspond to the circled numbers in the verification steps.**



**Figure 5-1 Verification Procedure Flowchart**

① – Place the candidate transfer standard as near as possible to the standard of higher authority to minimize the length of line used – preferably within one (1) meter. Lines must be properly conditioned according to Section 6.15. Warm-up and condition the candidate transfer standard. Ensure the transfer standards are not sampling room air.

Steps 2 and 3 can be conducted while the device is warming up.

② –Review all preventive maintenance documentation from the candidate transfer standard.

③ – Review the previous verification data, verification history, as-left internal calibration factors from the previous verification, and the current internal calibration factors. If the internal calibration factors have changed, determine why they have changed and if the transfer standard has been used subsequently. Changing the internal calibration factors in a transfer standard voids the previous verification.

- ④ – After adequate warm-up, complete all acceptance testing. Document and review all acceptance testing data to ensure that the candidate transfer standard is operating within the manufacturer’s specifications.
- ⑤ – Run a preliminary zero and a preliminary high point. Any stable source of ozone may be used to generate the test concentrations. The high point should be the highest point in the verification (See Section 6.3). Compare the results against established action limits. If an action limit is exceeded, then assess and correct the problem. This could include repair, additional maintenance or adjusting the internal calibration factors. Ensure all parameters are within the manufacturer’s recommendations. If repair or adjustments are made, conduct acceptance testing (Section 4.2.2).
- ⑥ – Run at least three (3) complete cycles consisting of six (6) concentration points (additional concentration points are preferred) and a zero. See Section 6.3 for information on how to chose verification points.
- ⑦ – After the appropriate number of cycles have been completed, review the data and verify they meet all requirements in Table 4-1. All equations, an example verification dataset, and calculations can be found in Appendix A. If any of the requirements are not met, assess the problem and begin the verification process from the beginning.
- ⑧ – Ensure all documentation is complete and all records are saved to the appropriate data storage system. The MO may place a summary report on the verified transfer standard which states at a minimum: the date of the verification, the date of verification expiration, name of person conducting the verification, make/model/SN, current internal calibration factors, dates/slopes/intercepts of the original verification cycles, the average slope and the average intercept. If Equation 10 in Appendix A is used in the traceability scheme, then the user should also state the current equation to be used for calculating the standard concentration when subsequently used. A summary report should be placed on the top of the transfer standard.

## **5.2 Reverification Procedure**

Figure 5-2 gives a generalized flow chart and step-by-step procedure meant to assist the user in acquiring an overall understanding of the reverification process for development of their specific SOPs. The reverification procedure differs from the verification procedure in that only one (1) cycle is required if all acceptance criteria are met. **If at any time during the reverification process the criteria in Table 4-1 are not met, the candidate transfer standard must be assessed and if warranted undergo a new verification according to Section 5.1.**



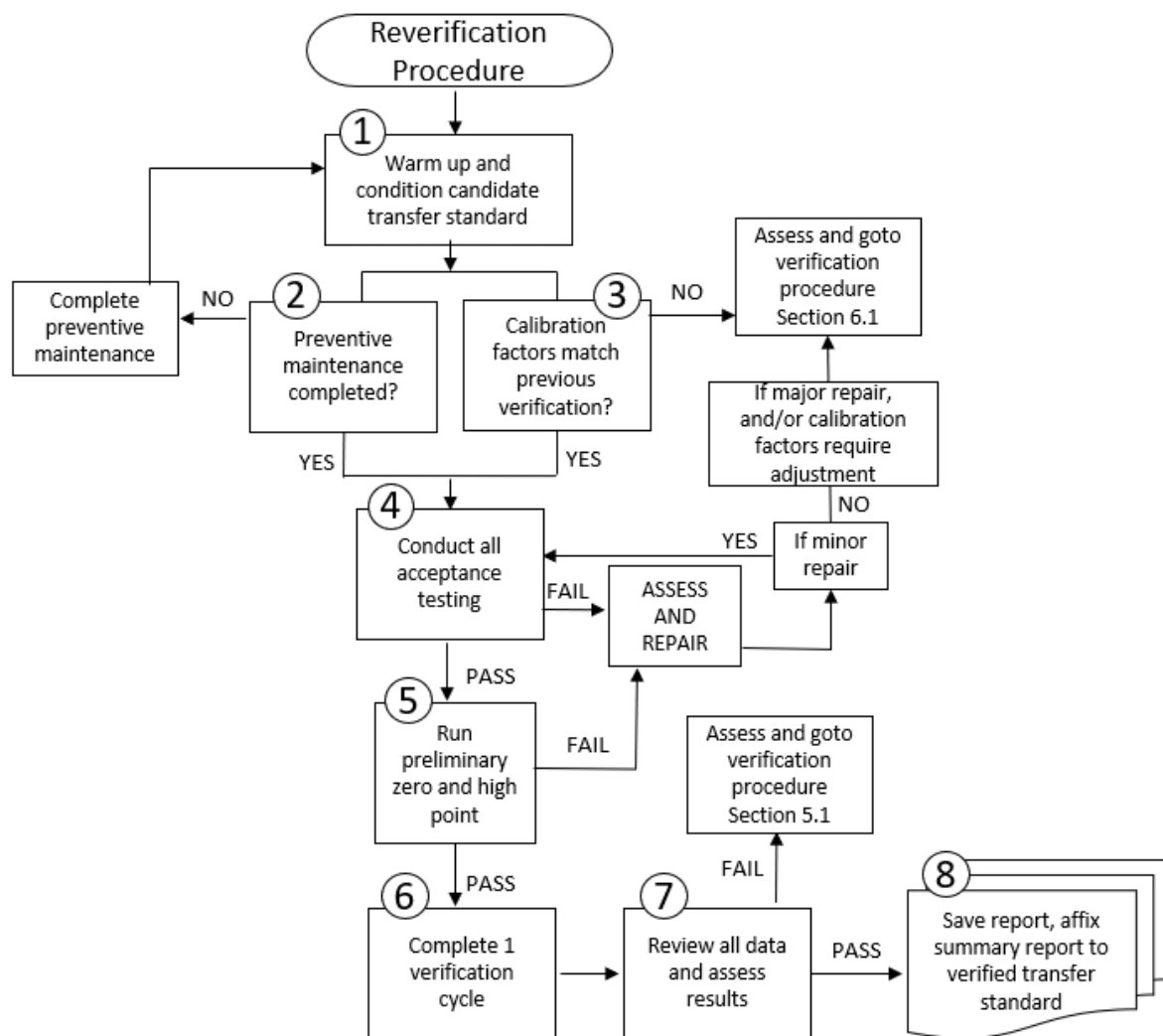


Figure 5-2 Reverification Procedure Flowchart

- ① – Place the candidate transfer standard as near as possible to minimize the length of line used - preferably within one (1) meter. Lines must be properly conditioned according to Section 6.15. Warm-up and condition the candidate transfer standard. Ensure the transfer standards are not sampling room air.
- ② – Review all preventive maintenance documentation from the candidate transfer standard.
- ③ – Review the verification data, verification history, as-left internal calibration factors from the verification, and the current internal calibration factors. If the internal calibration factors have changed, determine why they have changed and if the transfer standard has been used subsequently. Changing the internal calibration factors in a transfer standard voids the previous verification and the candidate transfer standard must undergo a new verification according to Section 5.1.

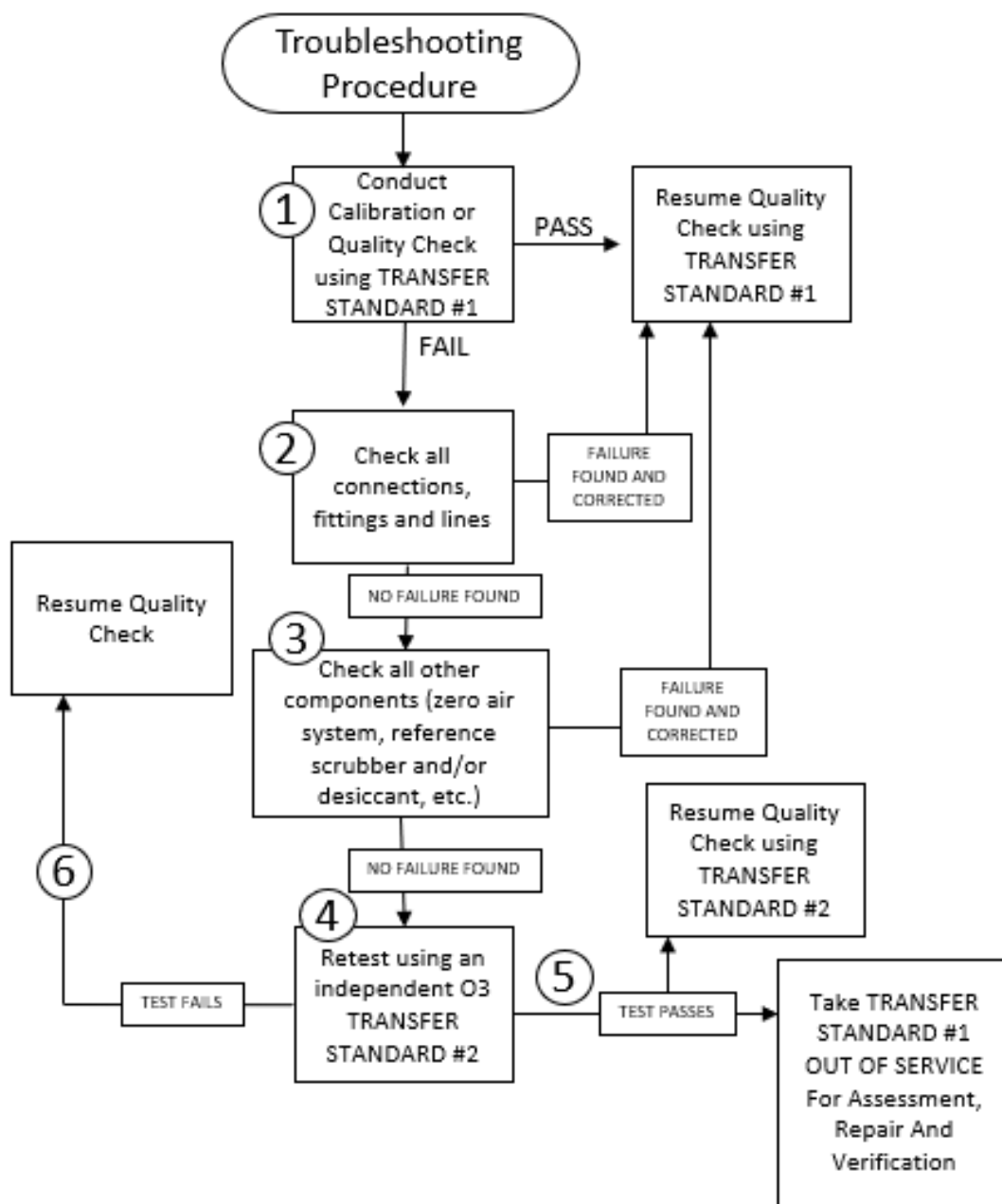
- ④ – After adequate warm-up, complete all acceptance testing. Document and review all acceptance testing data to ensure that the candidate transfer standard is operating within the manufacturer’s specifications.
- ⑤ – Run a preliminary zero and a preliminary high point. Any stable source of ozone may be used to generate the test concentrations. The high point should be the highest point in the verification. Compare the results against established action limits. If an action limit is exceeded, then assess and correct the problem. This could include a major or minor repair, additional maintenance and/or adjusting the internal calibration factors. Ensure all parameters are within the manufacturer’s recommendations. If minor repairs are needed, conduct acceptance testing and rerun the preliminary points. If major repairs are needed or the internal calibration factors are adjusted, then the candidate transfer standard must undergo a new verification according to Section 5.1.
- ⑥ – Run one (1) cycle consisting of a minimum of six (6) concentration points (additional concentration points are preferred) and a zero.
- ⑦ – After the cycle is completed, review the data and verify they meet all requirements in Table 4-1. All equations, an example verification dataset and calculations can be found in Appendix A. If any of the requirements are not met, a new verification must be completed. Assess the problem and begin the verification process according to Section 5.1.
- ⑧ – Ensure all documentation is complete and all records are saved to the appropriate data storage system. The MO may place a summary report on the verified transfer standard which states at a minimum: the date of the verification, the date of verification expiration, name of person conducting the verification, make/model/SN, current internal calibration factors, dates/slopes/intercepts of the original verification cycles, the average slope and the average intercept. If Equation 10 in Appendix A is used in the traceability scheme, then the user should also state the current equation to be used for calculating the standard concentration when subsequently used. A summary report should be placed on the top of the transfer standard.

## **6.0 Operational Considerations of O<sub>3</sub> Transfer Standards**

### **6.1 How to Troubleshoot a Verification, Calibration, or Measurement Quality Check Exceeding an Action Limit or Acceptance Criteria**

When using a verified transfer standard to conduct a verification, calibration or measurement quality check and the check is exceeding an action limit or the stated acceptance criteria it is not acceptable to automatically assume the transfer standard is correct and conduct a calibration of the O<sub>3</sub> analyzer. The user should implement a systematic approach to determine what device is causing the failure and further investigate to determine what component of the device is causing the failure. When a transfer standard is found to be causing a failure, it must be assessed, repaired and verified.

Figure 6-1 provides a suggested approach to assess a failing check. This same approach can be used for verifications, and reverification as well as calibration, and other measurement quality checks of O<sub>3</sub> analyzers.



**Figure 6-1 Troubleshooting Flowchart**

① – The user sets up and properly warms up verified transfer standard #1 at the site. The user allows the indicated concentrations to stabilize. If the percent difference is within the action limit or acceptance criterion, for the procedure the user should resume the check.

- ② – If the results exceed the action limits, the user should recheck all connections, fittings and lines. If a failure is found, the user should correct the problem and resume the test.
- ③ – If no failure is found, the user should recheck all other components such as the zero-air system, and/or desiccant, etc. If a failure is found, the user should correct the problem and resume the test.
- ④ – If no failure is found, the user should retest the analyzer with an independent verified transfer standard (transfer standard #2).
- ⑤ – If the concentrations do not exceed the action limits or acceptance criteria the user should resume the test with transfer standard #2. The user must ensure this transfer standard is appropriate for the type of work being conducted. For example, the transfer standard used for the APE must not be used for the calibration or routine QC checks. Transfer standard #1 must be taken out of service for assessment, repair and verification.
- ⑥ – If transfer standard #2 shows the same results as transfer standard #1, then the user should resume the measurement quality check.

## **6.2 Additional Checks to Guard Against Systemic Data Loss**

Users are cautioned that drift can occur in O<sub>3</sub> transfer standards and calibrating an O<sub>3</sub> monitor with a transfer standard that has unknowingly drifted can cause systemic data loss in a monitoring network. EPA recommends implementing a system of checks for early identification of drift. All available information should be reviewed at least daily to detect measurement system drift. The following are examples of additional checks that should be considered.

**Establishing Action Limits** - An action limit is a percentage of the minimum and maximum values of the defined acceptance criteria. Corrective measures should be taken as soon as values less than the lower action limit and higher than the upper action limit are exceeded. Action limits can initially be set to approximately 50% of the acceptance criteria, however, this may vary depending on the stability of the performance of the parameter being monitored or other factors. Action limits should ultimately be set statistically based on historical data. One approach is to set statistical action limits at plus or minus two standard deviations of the mean, or at approximately 95% certainty. Where statistical action limits are outside of acceptance criteria, corrective actions may be required.

EPA recommends that action limits be set and documented in QAPPs and SOPs. Setting action limits and making the needed correction(s) to the measurement system when action limits are exceeded will minimize the occurrences of exceeding acceptance criteria in transfer standards.

**Conduct More Frequent Reverifications** – Table 4-1 lists the minimum reverification requirements. EPA strongly recommends that additional verifications or spot checks be conducted.

**Conduct Additional Checks of Transfer Standards at Monitoring Sites** – There are many simple ways to conduct additional checks of transfer standards. A simple check can be as easy

as quickly introducing a zero/span atmosphere into the transfer standard to assess the system. If a MO is employing traceability Scheme #1 (Section 2.8.1 - using level 3 bench standards at monitoring sites), additional reverifications can easily be conducted of the transfer standard at the monitoring site using an independent transfer standard. For example, if an APE is being conducted at an O<sub>3</sub> monitoring site, the independent transfer standard used for the APE could supply a sample to both the O<sub>3</sub> analyzer and the Level 3 bench standard simultaneously.

**“Buddy Site” Analysis** – Buddy sites are O<sub>3</sub> monitoring sites that are relatively close to each other, known to have similar hourly concentrations and known to behave similarly under differing environmental conditions. The buddy site check is a subjective test and must never be used to judge data validity. This check is strictly a high-level visual review of a monitoring system’s functionality, including the transfer standards used for calibrations. For example, if two monitoring sites are known to have similar peak concentrations or are known to rise and fall at the same rate and at the same time each day, time series graphs could easily be made of the buddy sites. The graphs could be transposed on one another and used to make a visual determination about whether the buddy sites O<sub>3</sub> analyzers are operating properly. If the graphs do not line up as expected, then an investigation should occur immediately.

Many data logging systems can be programmed to conduct this analysis automatically. The user can set buddy site parameters within the data logger and when the specified parameters are exceeded the data logger can notify the user via email or even text messaging.

**Review Data from Nightly Checks** – These data can be used to determine if the measuring system (including the transfer standards) is operating properly or if additional investigation of the measurement system is warranted. Users can program data loggers or other controls to automatically run nightly O<sub>3</sub> checks. These checks may be the “official” QC check conducted with a verified O<sub>3</sub> transfer standard or may be conducted using the integrated zero span option within the O<sub>3</sub> analyzer. As stated in Section 3.2, the only appropriate use of the integrated zero/span option within the O<sub>3</sub> analyzer is to conduct automated zero/span checks (usually at midnight each night). This data should only be used as a diagnostic check to inform the user whether an action limit is breached, thereby triggering an investigation and possible recalibration of the monitor prior to the point of data loss.

The user should set up the nightly check to run automatically and graph the results in a control chart. The user should review the data and the general trend of the percent differences daily. Once an action limit is reached, the user should conduct an assessment and take corrective action. It is also possible to use a data logger or other system to automatically make this determination and send warnings to alert the MO of a breach in action limits.

**Review APE and Thru-the-Probe (TTP) Results** – APE and TTP audits are conducted using independent transfer standards. TTP audits are conducted using Level 2 field standards verified quarterly. This provides a unique opportunity for the user to see if the overall traceability scheme is functioning within the limits of this TAD. While an independent audit may show failing results for many reasons, it is a good indicator of the overall accuracy of the O<sub>3</sub> analyzer and the transfer standard used for calibration. If the audit results are well within the action limit

or acceptance criteria, then this indicates that the overall monitoring system (including traceability scheme) is functioning as designed. Results should also be compared to the other measurement quality checks conducted at the site to assess whether bias exists with the transfer standard used for calibration.

**Conduct Intercomparison with Neighboring MO** - Transfer standards can be used conveniently to inter-compare among various agencies to assure accuracy and confidence within the traceability scheme. For example, a MO could conduct ‘across state line’ comparisons in joining NAAQS nonattainment areas to assess the accuracy of measurements. This could be informative in areas where different legs of the traceability chain are adjacent geographically but share a nonattainment area. For example, if one State MO conducts annual Level 2 verifications with EPA Region 5 under SRP SN 6 and an adjacent State MO conducts annual Level 2 verifications under a different SRP, both organizations are equidistant from Level 1 and are under a different Level 1. A successful intercomparison adds reassurances to each MO that measurements were being conducted correctly and that their existing traceability schemes are functioning as designed.

### **6.3 Determining the Calibration Scale and the Verification Points**

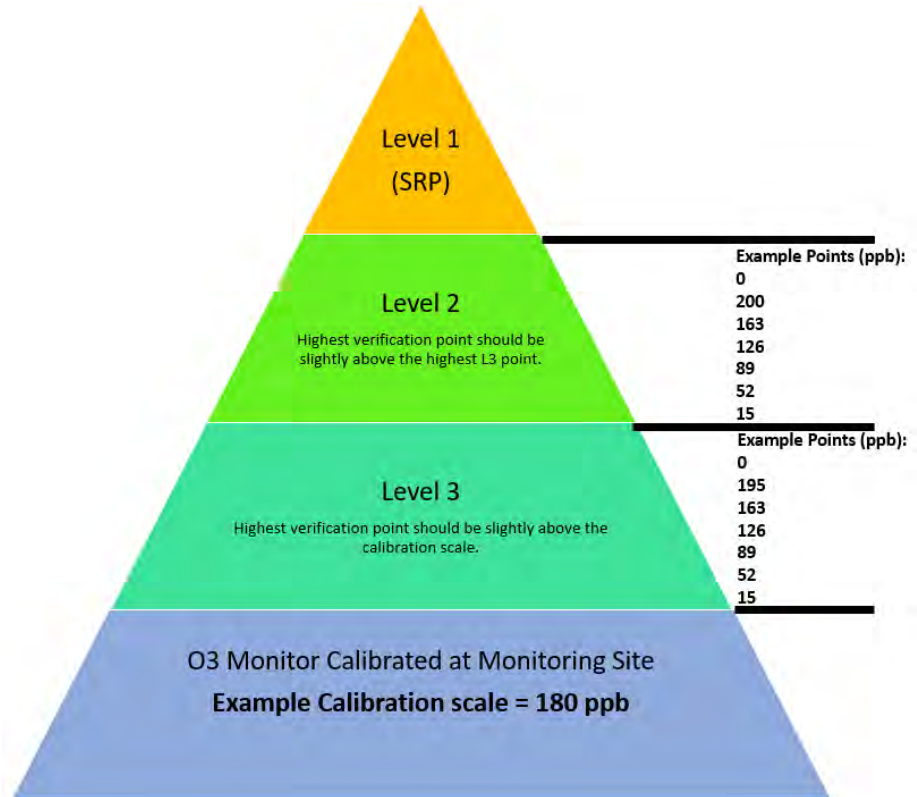
**Calibration Scale** – The first step in determining what concentration points to run during a verification is to determine a calibration scale that is low enough to encompass all possible measurements expected and not so high that most of the measurements are on the low end of the calibration scale. Generally, photometers in most O<sub>3</sub> transfer standards are calibrated by adjusting the zero and span. In the past, O<sub>3</sub> monitors used for regulatory ambient air monitoring were set to an upper range limit (URL) of 500 ppb. The calibration scale was based on the selected URL and span adjustments were made at 80% of the URL (typically 400 ppb). Modern FEM O<sub>3</sub> photometers allow for more flexibility when selecting a calibration scale and the typical high O<sub>3</sub> concentrations measured are many times below 400 ppb. Therefore, a calibration scale should be selected that covers the expected measured values and the NAAQS for O<sub>3</sub>, plus additional room for potential anomalous high ambient O<sub>3</sub> concentrations. The calibration scale concept is fully described in the QA Handbook. The following procedure should be used to determine a calibration scale:

1. Take the previous 3 years of 1-hour values. Determine the highest value.
2. Multiply the highest value by 1.5 to establish the calibration scale. If this value is below the NAAQS, use 1.5 times the controlling NAAQS.

For example, if the 3-year high concentration (1-minute average values are preferred) within a MO is 120 ppb, 1-minute measurements greater than 180 ppb (180 ppb is 1.5 times the highest value) are not likely; therefore, a calibration scale of 180 ppb should safely encompass all potential ambient O<sub>3</sub> measurements.

**Verification Points** - A transfer standard must be verified over the concentration range it will be used with the required number of concentration points (a minimum of 6 concentration points plus a zero) approximately evenly spaced between zero and the selected calibration scale. Additional points may be used (e.g., a point at the NAAQS). Although it is not a requirement to precisely evenly space points, they must not be closely grouped together. For example, it would not be acceptable to assay verification points of 200, 180, 170, 160, 150, 15, 0. It would be acceptable to assay points evenly spaced such as 200, 163, 126, 89, 52, 15, 0.

Users could also add a 70 ppb point to represent the NAAQS concentration or other concentrations. Any concentration point assayed by a verified transfer standard must be equal to or less than the highest point used during its verification. Therefore, it is imperative to choose an appropriate calibration scale for the O<sub>3</sub> monitoring network prior to conducting verification work since this will determine the high point in any subsequent O<sub>3</sub> monitor calibration.



For example, Figure 6-2 shows suggested points for a monitor calibration scale of 180 ppb. The highest point run during the Level 2 transfer standard verification could then be 200 ppb and the highest point run during the Level 3 transfer standard verification could then be 195 ppb. The Level 3 transfer standard would then have a verification range of 0-195 ppb and must not be used at concentrations greater than 195 ppb.

#### **6.4 Warm-up Time and Stability of Indicated Concentration**

Transfer standards must be properly warmed up and be able to provide a stable output prior to use. Operators should consult the manufacturer’s instrument manual for specific recommendations. Warm-up times will vary depending on how or if the transfer standard was transported. Temperature plays a key role in how long it takes for a transfer standard to warm-up and stabilize. Colder temperatures will have longer warm-up times. A minimum warm-up and stabilization time should be no less than 30 minutes but could be much higher (i.e., overnight).

The user should set minimum criteria for warm-up times and objective criteria for output stability and document these in the QAPP and SOP. At a minimum, EPA recommends that an operator wait 5 additional minutes after the analyzer has begun to measure consistent, instantaneous concentrations that show minimal variability and no discernible slope. In general, the longer the operator waits to take a reading, the better the results. Additional information may be found in the QA Handbook.

## **6.5 Timing and Frequency of Verifications and Reverifications**

Significant planning must be considered when determining the verification and reverification schedules. MOs should always have verified transfer standards at Levels 2 and/or 3, and therefore MOs should map out an ideal annual schedule to follow each year for when the Level 2s are verified and subsequently when the Level 3s are verified. For areas where O<sub>3</sub> monitors are operating seasonally (i.e., March to October) Level 2 transfer standards should be completed by January to give plenty of time for Level 3 transfer standards to be verified prior to conducting calibrations at monitoring sites. For areas in which O<sub>3</sub> monitors operate year round, it is important to ensure verified transfer standards are continuously available at Level 2 and 3. EPA recommends scheduling the Level 2 verification well in advance so that the service may be completed without delay. EPA recommends that a tracking sheet or other mechanism be employed to plan and conduct verifications so that verifications do not lapse. Under no circumstances can a O<sub>3</sub> transfer standard be used after the verification has lapsed; however, Section 2.7 does allow for flexibility in conducting reverifications on transfer standards that have lapsed. The traceability process must be fully documented in the QAPP and SOP.

## **6.6 Protecting Transfer Standards Against Damage**

Transfer standards are highly sensitive electronic devices and depending on their designation (bench versus field) may be frequently moved from one location to another location. Extreme care must be taken to minimize damages to the devices, especially in the case of devices that are regularly transported to field locations and used in routine air monitoring. Users should use great care when placing devices on tables or lab benches by gently placing the devices and not setting them down in a rough or carefree manner.

Transport can subject transfer standards to shock, vibration, temperature extremes and static charge which can cause measurement drift. To minimize these conditions, transfer standards should be properly padded while in transport and extreme temperatures should be avoided. Proper padding may also be added to the inside of the chassis to ensure electric cards remain seated. Care should also be taken to protect the transfer standards from static charges. Always place a reminder sticker on the device if padding is used inside the chassis so that the user remembers to remove this prior to turning the instrument on. Proper placement in the vehicle and care when placing the equipment is also necessary to protect the integrity of the transfer standard. Equipment should be strapped down if it is at risk for sliding around in the vehicle. Furthermore, EPA recommends that padded cases be used for transport and that transfer standards not be left in a vehicle in the hot sun or cold temperatures. EPA recommends that if



shipping is required, a specialized padded case or the original box and packing material (in good condition) be used and that **checks be conducted prior to and after shipping.**

Every transfer standard must be traceable to a Level 2 bench standard. A Level 2 bench standard is maintained at a fixed location except when taken to be verified against an SRP. When kept under laboratory conditions, the integrity of the Level 2 bench standard can be preserved. Under the controlled conditions at the fixed location, variability in the Level 2 bench standard will be reduced, providing better accuracy and uniformity among all O<sub>3</sub> analyzers in the network. If doubt arises with the proper functionality of a transfer standard (e.g. due to rough treatment in the field) it can be brought back in for reverification to the Level 2 bench standard.

### **6.7 Maintaining Backup Verified Transfer Standards**

EPA recommends that MOs always have access to back up transfer standards at each level. This is especially true for Level 2s. A Level 2 transfer standard must be transported to one of only 10 locations in the US to be verified against a Level 1 (SRP); this can be very time consuming and is dependent upon the availability of the SRP operator and the MO travel budget. If a Level 2 transfer standard unexpectedly fails in the middle of O<sub>3</sub> season, it may be impossible to repair and verify it before it is needed. This can result in the MO not having the needed Level 3 transfer standards necessary to seamlessly conduct calibrations or other quality work at their monitoring sites.

### **6.8 Preventive Maintenance**

Preventive maintenance must be conducted consistently to be an effective way to minimize malfunctions and downtime. All commercially available devices have manuals that describe preventive maintenance items and frequencies. At a minimum the as-found and as-left conditions of all diagnostics should be observed and documented for all preventive maintenance activities. Assaying ozone test concentrations can also be helpful as an as-found test especially for transfer standards exhibiting abnormal performance. Acceptance testing should also be conducted following preventive maintenance. EPA recommends that transfer standard owners complete and document all preventive maintenance according to the instrument manual as part of and prior to normal verifications or reverifications. Laboratories providing O<sub>3</sub> transfer standard verification services should review documentation showing that preventive maintenance has been completed. Verification services may be refused if this documentation is not presented and current.

### **6.9 Transfer Standard Repairs**

O<sub>3</sub> transfer standards will likely experience damage or malfunction requiring assessment, repair and verification. Major repairs are likely to require the device to be verified. Minor repairs or preventive maintenance are not likely to require the device to be verified. The MO should always follow the manufacturers' recommendations when making repairs. Acceptance testing must always be conducted following any repair.

An as-found test and as-left test should also be conducted to objectify what action to take following a repair (e.g., take no action, conduct verification or conduct reverification). This process should be clearly defined in the QAPP and SOP and a standard form should be used to document what happened. In general, if readings return to normal after acceptance testing, the instrument verification may still be valid. In any case, EPA strongly recommends that a MO have a well-defined and documented approach to repairs and verification. The following table lists some examples of major and minor repairs.

***Table 6-1 List of Common Major and Minor Repairs for O<sub>3</sub> Transfer Standards***

<b>Major Repair (requires verification)</b>	<b>Minor Repair</b>
Detector or Optical Bench malfunction/replacement	Preventive Maintenance as described in the instrument manual
Optical Bench Lamp Replacement	Pump Replacement, rebuilding or other flow related repairs
Photometer tube replacement	Any O <sub>3</sub> generator component
Pressure sensor replacement or recalibration	UV Bench Lamp Adjustment
Temperature sensor replacement or recalibration	Display, Keypad or related boards
Detector or related board replacement	Minor Leak Repair (i.e., tighten a fitting or worn teflon line)
Major Leak repair (i.e., reseal a solenoid valve)	Fuse Replacement
Motherboard Replacement	Fan Replacement
	Optical Bench Temperature Calibration
	All input/output board replacement

## **6.10 Spare Parts Inventory**

The purpose of a spare parts inventory is to minimize downtime when equipment failures occur. For organizations that own many transfer standards EPA recommends that spare parts be on hand for needed repairs. It is not uncommon for transfer standards to require troubleshooting and repair. A listing of spare parts is always available in the equipment manual. Spare parts may be purchased as part of a larger equipment procurement. Users can develop an inventory based on anticipated needs for the spare parts. Preventive maintenance items such as pump rebuild kits, UV lamps, etc. should always be on hand for periodic maintenance or repairs. Other items such as electronics boards, detectors, power supplies, etc. should be available, but may be needed less frequently. Therefore, the user should have less of these on hand or at a minimum have a method to receive these parts quickly. An appropriate spare parts inventory should be kept up-to-date and replenished when parts are used.

## **6.11 Zero-air Supply**

Contamination, humidity, pressure or other problems with zero-air can be a common source of measurement error in O<sub>3</sub> transfer standards. 40 CFR Part 50 Appendix D § 4.4.1 defines zero-air as follows: “The zero-air must be free of contaminants which would cause a detectable response from the O<sub>3</sub> analyzer, and it should be free of NO, C<sub>2</sub>H<sub>4</sub>, and other species which react with O<sub>3</sub>”.

Within a transfer standard, zero-air is pushed through an O<sub>3</sub> generator to generate a test atmosphere. Zero-air is also used to provide a reference measurement for the assay of the sample. The same zero-air source must be used for each component and for both the candidate transfer standard and the standard of higher authority during a verification. Many configurations are acceptable; however, users are cautioned that zero-air must be introduced to the O<sub>3</sub> transfer standard according to the manufacturer’s recommendation using a method that does not alter the zero-air or the pressures within the UV measurement cycles. EPA recommends viewing the photometer sample pressure during the measurement cycle to determine if a change in pressure is occurring when the valve alternates between the reference and sample cycle.

Many adequate zero-air systems are commercially available and should be utilized. Users should utilize oil free air compressors in zero-air systems. It is also acceptable to build a zero-air system using a pump, pressure regulator, silica gel, activated charcoal and molecular sieves. In either case, the zero-air systems must be properly maintained and tested in accordance with the manufacturer's specifications and/or the MO's QAPP or SOP. All maintenance activities must be documented. The QA Handbook provides additional information on adequate zero-air and zero-air testing.

## **6.12 Excess Flow**

There are different ways to set up a flowing system to conduct verifications of O<sub>3</sub> transfer standards. A typical O<sub>3</sub> transfer standard system consists of an O<sub>3</sub> generation device supplied with metered zero-air, a manifold to allow for multiple devices to measure the generator output, and a verified photometer to measure the generated O<sub>3</sub>. Many of these devices are preassembled and commercially available. Each commercially available device will have specifications for zero-air pressure, photometer flow and excess flow in the instrument manual. Operators must follow these specifications as they are the design criteria for the instrument. For all devices, the O<sub>3</sub> generator must have a stable flow and provide enough flow to supply both the candidate transfer standard and the verified transfer standard so they do not pull in room air. Users must be aware of the total output flow of the generator and total photometer flows in both instruments.

## **6.13 Protecting Internal Components of Transfer Standards**

Transfer standards should never be allowed to sample room air unfiltered from room dust or other contaminants. It is best practice to only allow a transfer standard to pull air from a suitable source of zero-air. A particulate filter may be added to the inlet of the transfer standard or the photometer pump can be turned off to protect internal components.

#### **6.14 Acceptable Materials**

Borosilicate glass, FEP Teflon® or their equivalent must be the only material in the sampling train that can be in contact with an ozonated sample while using an O<sub>3</sub> transfer standard. Other materials such as stainless steel or brass may be used in the zero-air system or with any downstream component of the measurement system.

#### **6.15 Line Conditioning and Line Length**

O<sub>3</sub> is a highly reactive gas. An atmosphere of O<sub>3</sub> will be greatly impacted by an improperly conditioned or dirty measurement system. All teflon lines and surfaces in contact with an ozonated sample can scavenge O<sub>3</sub> especially in the presence of dust or debris and must be properly conditioned prior to use. The user should run an ozonated sample (i.e., run the highest O<sub>3</sub> concentration in the traceability scheme) through the transfer standard and any lines used to adequately condition the system. After conditioning, the transfer standard should be run ensuring that all components (lines, fittings, etc.) that will be in contact with the ozonated sample are in line. In other words, the conditioning and testing should be conducted using the same configurations as is used during verifications, calibrations or other measurement quality checks. If O<sub>3</sub> scavenging is still occurring, then the lines should be reconditioned or replaced as necessary.

The measurement system being conditioned should be vented to an exhaust hood or charcoal column so that high concentrations of O<sub>3</sub> are not being exhausted into the laboratory and inhaled by the operator. The length of line used during a verification will have a direct impact on the time it takes each O<sub>3</sub> point to stabilize during a verification and can also impact the stability of the O<sub>3</sub> readings. The length of teflon line used to deliver test atmospheres to candidate transfer standards should be kept to a minimum (i.e., less than 1 meter if possible). EPA recommends that the same set of lines be used for all verifications. The lines should be capped, labelled and kept free from dust or other debris or chemicals when not in use. Operators should have a few sets of lines which are properly conditioned, labelled and stored in a dedicated location. Having multiple sets of known good lines can also aide in troubleshooting.

#### **6.16 Acceptable Testing Devices**

All testing devices used in the acceptance testing and qualification testing must be NIST traceable. These devices include at least temperature, pressure and digital multimeters. Each device should be recertified annually or according to other guidance and be clearly labelled stating, at a minimum, the certification expiration date and entity who conducted the certification. A certification certificate must be filed and stored according to data storage and recordkeeping procedures. EPA recommends that 2 devices be available for each measurement needed and that these devices be certified on alternating schedules so that the user can have a secondary spot check of the measurement. (see GMP 13-2018 Section 1.1.1 NOTE 4)

### **6.17 Data Handling and Documentation**

It is paramount to the transfer standards traceability that a data handling process be in place. All data relevant to the qualification, acceptance testing, verification and reverification must be organized so that information can be accessed in the future. Each transfer standard should have a file which includes all historical information for the device. A file naming convention and file folder structure should be maintained and documented. A summary sheet should be developed and affixed to the transfer standard so that the user can easily see that the device is within verification limits and see when the current verification expires. This will not be the official verification report but will be used to quickly reference the verification summary.

This process must be documented according to a formal records management policy. The QA Handbook provides further information on records management.

### **6.18 Use of Standard Forms and Logbooks**

Developing a consistent technique for documenting information in a logbook and archiving this information is very important. Standard forms should be developed which allow for consistent and thorough documentation of the conditions at the time of use of the transfer standard and the results of the work completed. Standardized forms for maintenance/repairs, acceptance testing, verifications, calibrations and other routine work are needed to provide this documentation. A proper paper or electronic logbook may also be used. The QA Handbook provides more information about logbooks and documentation.

### **6.19 Work Area Cleanliness and Organization**

Good laboratory practices dictate that work areas should be kept clean and organized and it is important to maintain a dust and contaminant-free environment in the laboratory or air monitoring sites where transfer standards are being used. Benches and other surfaces should be wiped down frequently to minimize the potential for contamination of the photometer cell or other critical components in the device. All candidate transfer standards should be checked for excessive dust or other problems inside the chassis of the instrument. Users should keep in mind that the O<sub>3</sub> measurement principle (photometry) is based on absorption of UV light and that O<sub>3</sub> is a highly reactive molecule. Even the smallest amount of dust or other contaminant (Hg, hydrocarbons, bug sprays, perfumes, etc.) will cause large variations in measurements. Laboratory cleaning and organizing should be part of a regular preventive maintenance program.

Labs that handle large numbers of transfer standards should have an area designated for receiving, an area designated for transfer standards in the verification process, and an area where transfer standards are completed and ready to pick up. Signage should be placed to clearly delineate one area from another.

## **6.20 Laboratory Conditions (Temperature, Relative Humidity)**

All transfer standards must be operated within the operating temperature range specified in the instrument manual. Swings in temperature or humidity will impact the operation of transfer standards; therefore, the verification laboratory conditions should be kept relatively constant to within approximately 20-30 degrees C. A certified temperature and relative humidity device can be installed and observed by the user to ensure these conditions are met. Most laboratory air handling systems will control the conditions to within acceptable limits provided the systems are not malfunctioning. In locations where more extreme temperature or humidity shifts are possible, it may be necessary to have additional air handling systems in place and the operator may need to take additional actions to ensure the laboratory conditions are acceptable. EPA recommends that the user document the current lab conditions or otherwise record the laboratory conditions continuously as part of the verification.

## **6.21 Use of Data Loggers or other Automation Software to Run Verifications**

When conducting O<sub>3</sub> verifications it is necessary to generate and assay different concentration points and record the concentrations of the candidate transfer standard and the transfer standard of higher authority. In past years, this required an operator to be in front of these devices while a verification was occurring and manually write down data and change settings to complete a verification. Many different options are available today. MOs can easily set up calibration routines in data loggers or other laboratory software systems to automatically run through the concentration points and record the resultant data. Simple computer programs can also be written to automatically control the O<sub>3</sub> generator and record the data. In either case, the MO will need to have a written procedure and pay close attention to the resultant data. The advantage to the automation is that a person can go do other work while O<sub>3</sub> transfer standards are being verified and multiple verifications can be conducted simultaneously. After the verification cycle completes, the operator can review the data and set up a new verification. Verifications could also be started at the end of a day and allowed to run overnight.

## **6.22 Tools**

A quality tool set is required to conduct O<sub>3</sub> verification work. The most commonly needed tools are a 9/16-inch wrench (a full set is recommended), adjustable pliers or channel locks, line cutters or wire cutters, LED flashlight, magnifying glass, and utility knife. However, many other tools may be needed to conduct this work. A full laboratory tool set is recommended including a vise, soldering equipment, full drill set, and other tools needed for unforeseen repairs or for completing electrical or pneumatic connections.

## **6.23 Safety**

The user must be aware that they are working with electricity and a harmful gas (O<sub>3</sub>). Therefore, any organization conducting this work must have adequate safety training in place. The user

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must also read all manufacturers' safety warnings and follow all laboratory safety requirements (i.e., properly vented exhaust lines, safety glasses, etc).

### **Additional References**

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# Appendix A Equations and Example Calculations

This appendix shows an example verification and reverification for a Level 3 transfer standard (“candidate standard”). Verification example data and calculations are presented first, followed by reverification. EPA recommends using a spreadsheet or other automated data entry system containing embedded equations that perform the calculations automatically. EPA also recommends that all users of this TAD understand how to manually conduct the calculations.

All **verifications** of transfer standards must be completed according to Section 5.0 and Table 4-1. A verification consists of three (3) testing cycles (performed independently) in which the candidate standard’s measurements are compared to those of the bench standard (i.e., , the “standard of higher authority”). **Table A-1** provides an example of verification data for a Level 3 candidate transfer standard used in a monitoring network having a calibration scale of 180 ppb, along with the corresponding data from the Level 2 bench standard. For both standards, measurements were taken at each of eight (8) concentrations (“points”) distributed along the workable range of concentrations.

**Table A-1. Example Verification Data (ppb)**

Conc. Test Point (j)	Cycle 1 (i=1)		Cycle 2 (i=2)		Cycle 3 (i=3)	
	Level 2 Bench Standard (x <sub>1j</sub> )	Level 3 Candidate Transfer Standard (y <sub>1j</sub> )	Level 2 Bench Standard (x <sub>2j</sub> )	Level 3 Candidate Transfer Standard (y <sub>2j</sub> )	Level 2 Bench Standard (x <sub>3j</sub> )	Level 3 Candidate Transfer Standard (y <sub>3j</sub> )
1	0.2	-0.1	0.2	0.0	0.0	0.3
2	200.0	200.9	199.5	201.1	200.1	201.4
3	163.0	163.7	162.6	163.9	163.3	164.3
4	126.0	126.5	126.4	127.3	126.2	127.0
5	89.0	89.3	88.9	89.5	89.5	90.0
6	70.0	70.3	69.9	70.3	70.3	70.7
7	52.0	52.2	51.9	52.2	52.2	52.5
8	15.0	15.0	14.9	14.8	15.0	15.0

Note: Bench standard = standard of higher authority.

The subsections which follow reference a series of equations for statistics that assess the success or failure of a given verification or reverification test, along with the acceptance criteria used to determine success based on each statistic. Each calculation is illustrated using the above example data from Table A-1.

## A1. Per Point Percent Difference (% Diff) in Measured Concentration

**For each test point within a cycle corresponding to a concentration above 50 ppb** (i.e., for  $j=2$  through 7 in Table A-1), the percent difference (% Diff) in measurements between the candidate transfer standard and the standard of higher authority is calculated using Equation 1:

**Equation 1 - Percent difference (% Diff) in measured concentration at the  $j^{\text{th}}$  concentration point within the  $i^{\text{th}}$  cycle**

$$\%Diff_{ij} = \{(y_{ij} - x_{ij}) \div x_{ij}\} \times 100\%$$

where:  $(x_{ij})$  = Measured concentration from the standard of higher authority.

$(y_{ij})$  = Measured concentration from the candidate transfer standard.

At each concentration test point above 50 ppb, the calculated value of  $\%Diff_{ij}$  must be **within  $\pm 3.1\%$**  to be considered acceptable. If this criterion fails at any of these test points, the test cycle's data are disregarded and the cycle is repeated.

To illustrate this calculation, consider the reported data at the highest concentration point in cycle #1 (i.e.,  $i=1, j=2$ ) within Table A-1. Here,

$$\begin{aligned}\%Diff_{12} &= \{(200.9 - 200.0) \div 200.0\} \times 100\% \\ &= 0.45\%.\end{aligned}$$

This value falls within the acceptance criterion of  $\pm 3.1\%$ .

## A2. Per Point Absolute Difference (AbsDiff) in Measured Concentration

**For each test point within a cycle corresponding to a concentration at or below 50 ppb** (i.e., for  $j=1$  and  $j=8$  in Table A-1), the absolute difference (AbsDiff) in measurements between the candidate transfer standard and the standard of higher authority is calculated using Equation 2. Using the same notation as for Equation 1 above:

**Equation 2 - Absolute difference (AbsDiff) in measured concentration at the  $j^{\text{th}}$  concentration point within the  $i^{\text{th}}$  cycle**

$$AbsDiff_{ij} = y_{ij} - x_{ij}$$

At each test point at or below 50 ppb, the calculated value of  $AbsDiff_{ij}$  must be **within  $\pm 1.5$  ppb** to be considered acceptable. If this criterion fails at any of these test points, the test cycle's data are disregarded and the cycle is repeated.

To illustrate this calculation, consider the reported data at the lowest concentration point in cycle 2 (i.e.,  $i=2, j=8$ ) in Table A-1. Here,

$$\begin{aligned} Abs\ Dif_{28} &= 14.8 - 14.9 \\ &= -0.1\ ppb \end{aligned}$$

This value falls within the acceptance criterion of  $\pm 1.5$  ppb.

### A3. Least Squares Linear Regression Analysis (Slope and Intercept Estimation)

**For each cycle within a verification test (and for a reverification test cycle)**, an ordinary least squares linear regression line is fitted to data from all concentration test points to predict the measurement from the candidate transfer standard as a simple linear function of the measurement from the standard of higher authority. If subscript  $i$  refers to the cycle ( $i = 1, 2, 3$ ), the following notation is used:

$(n_i)$  = Number of concentration test points in the  $i^{\text{th}}$  cycle with data reported ( $n_i=8$  in Table A-1 for each cycle).

$(x_{ij})$  = Measurement from the standard of higher authority for the  $j^{\text{th}}$  concentration in the  $i^{\text{th}}$  cycle ( $j=1, \dots, n_i$ ).

$(y_{ij})$  = Measurement from the candidate transfer standard for the  $j^{\text{th}}$  concentration in the  $i^{\text{th}}$  cycle ( $j=1, \dots, n_i$ ).

$(\epsilon_{ij})$  = Absolute difference between  $y_{ij}$  and the value predicted by the regression model ( $\hat{y}_{ij}$ ), for the  $j^{\text{th}}$  concentration in the  $i^{\text{th}}$  cycle ( $j=1, \dots, n_i$ ), also known as “residuals.”

$(\mu_i)$  = Intercept of the linear regression line for the  $i^{\text{th}}$  cycle (needs to be estimated).

$(\beta_i)$  = Slope of the linear regression line for the  $i^{\text{th}}$  cycle (needs to be estimated).

$(\bar{X}_i)$  = Arithmetic mean of values  $x_{ij}$  ( $j=1, \dots, n_i$ ) within the  $i^{\text{th}}$  cycle (see Equations 5 and 6 for arithmetic mean formula).

$(\bar{Y}_i)$  = Arithmetic mean of values  $y_{ij}$  ( $j=1, \dots, n_i$ ) within the  $i^{\text{th}}$  cycle (see Equations 5 and 6 for arithmetic mean formula).

$(m_i)$  = The estimated intercept of the best fit line for the  $i^{\text{th}}$  cycle (using the cycle measurements  $x_{ij}$  and  $y_{ij}$ ).

$(b_i)$  = The estimated slope of the best fit line for the  $i^{\text{th}}$  cycle (using the cycle measurements  $x_{ij}$  and  $y_{ij}$ ).

**Equation 3 – Linear regression model for the  $i^{\text{th}}$  cycle ( $i = 1,2,3$ )**

$$\boxed{y_{ij} = \beta_i + \mu_i x_{ij} + \epsilon_{ij}} \quad (j=1, \dots, n_i)$$

**Equation 4 - Least squares estimates for slope and intercept for the  $i^{\text{th}}$  cycle ( $i = 1,2,3$ )**

$$\text{Slope estimate (unitless): } m_i = \frac{\sum_{j=1}^{n_i} (x_{ij} - \bar{X}_i)(y_{ij} - \bar{Y}_i)}{\sum_{j=1}^{n_i} (x_{ij} - \bar{X}_i)^2}$$

$$\text{Intercept estimate (ppb): } b_i = \bar{Y}_i - m_i \bar{X}_i$$

**Equation 5 – Predicted concentration reported by the candidate transfer standard according to the fitted line within the  $i^{\text{th}}$  cycle ( $i = 1,2,3$ )**

$$\hat{y}_{ij} = b_i + m_i x_{ij} \quad (j=1, \dots, n_i)$$

For a given test cycle, the acceptance criteria for the fitted regression line (Equations 4 and 5) are as follows:

- The value of the slope estimate  $m_i$  (Equation 4) must fall within  $1.00 \pm 0.03$  (i.e., , within  $\pm 3\%$  of 1.00).
- The value of the intercept estimate  $b_i$  (Equation 4) must fall within  $0.00 \pm 3$  ppb.

If either of these two criteria fails for a given test cycle, the test cycle’s data are disregarded and the cycle is repeated.

Using the data from Table A-1, the fitted regression line for each of the three example test cycles has slope and intercept estimates listed in Table A-2. Each of these estimates achieves its respective acceptance criterion.

**Table A-2. Slope and Intercept Estimates for Each Fitted Regression Line (one line per cycle) in the Example Verification Data**

Cycle ( $i$ )	Slope ( $m_i$ )	Intercept ( $b_i$ )
1	1.0053	-0.1518
2	1.0091	-0.2136
3	1.0058	0.0511

#### A4. Average slope ( $\bar{m}$ )

Across the three cycles of a verification test for the candidate transfer standard, the arithmetic average of the estimated slopes from the three cycles is calculated. Using notation from Section A3, the average slope is calculated as follows:

**Equation 6 - Average slope ( $\bar{m}$ ) for a verification test**

$$\bar{m} = \frac{1}{3} \sum_{i=1}^3 m_i$$

Using the slope estimates from Table A-2, the average slope for the example verification data is calculated as

$$\begin{aligned}\bar{m} &= (1.0053 + 1.0091 + 1.0058) \div 3 \\ &= 1.0068.\end{aligned}$$

**A5. Average intercept ( $\bar{b}$ )**

**Across the three cycles of a verification test** for the candidate transfer standard, the arithmetic average of the estimated intercepts from the three cycles is calculated. Using notation from Section A3, the average intercept is calculated as follows:

**Equation 7 - Average intercept ( $\bar{b}$ ) for a verification test**

$$\bar{b} = \frac{1}{3} \sum_{i=1}^3 b_i$$

Using the intercept estimates from Table A-2,

$$\begin{aligned}\bar{b} &= \{(-0.1518) + (-0.2136) + (0.0511)\} \div 3 \\ &= -0.1048.\end{aligned}$$

**A6. Stability Estimate for the Slopes Within a Verification Test (Standard Deviation --  $SD_m$ )**

**Across the three (3) cycles of a verification test** for the candidate transfer standard, the standard deviation of the estimated slopes from the three (3) fitted regression lines is calculated as follows (using notation from Section A3):

**Equation 8 - Standard deviation of the three slopes within a verification test ( $SD_m$ )**

$$SD_m = \sqrt{\frac{1}{3} \left( \sum_{i=1}^3 (m_i - \bar{m})^2 \right)}$$

The calculated value of  $SD_m$  must be below **0.0075**; otherwise, the entire verification test must be repeated.

Using the slope estimates from Table A-2 and the value of  $\bar{m}$  from Section A.4, the standard deviation of the slopes calculated from the example verification data is calculated as

$$\begin{aligned}SD_m &= \sqrt{[(1.0053 - 1.0068)^2 + (1.0091 - 1.0068)^2 + (1.0058 - 1.0068)^2] \div 3} \\ &= \sqrt{[(0.00000205 + 0.00000551 + 0.00000084] \div 3} = 0.00167\end{aligned}$$

This value falls below 0.0075 and thus achieves the acceptance criterion.

**A7. Stability Estimate for the Intercepts Within a Verification Test (Standard Deviation --  $SD_b$ )**

Across the three (3) cycles of a verification test for the candidate transfer standard, the standard deviation of the estimated intercepts from the three (3) fitted regression lines is calculated as follows (using notation from Section A3):

**Equation 9 - Standard Deviation of the three intercepts within a verification test ( $SD_b$ )**

$$SD_b = \sqrt{\frac{1}{3} \left( \sum_{i=1}^3 (b_i - \bar{b})^2 \right)}$$

The calculated value of  $SD_b$  must be below **1.00**; otherwise, the entire verification test must be repeated.

Using the intercept estimates from Table A-2 and the value of  $\bar{b}$  from Section A.5, the standard deviation of the intercepts calculated from the example verification data is calculated as

$$\begin{aligned} SD_b &= \sqrt{[((-0.1518) - (-0.1048))^2 + ((-0.2136) - (-0.1048))^2 + (0.0511 - (-0.1048))^2] \div 3} \\ &= \sqrt{[(0.00221 + 0.01184 + 0.02429) \div 3} = 0.11306 \end{aligned}$$

This value falls below 1.00 and thus achieves the acceptance criterion.

**A8. Standard Concentration for the Candidate Transfer Standard**

For the candidate transfer standard, the method to determine the value of its standard concentration at each concentration point within a test cycle depends upon how the unbroken chain of calibrations is maintained for meeting NIST traceability (Section 2.1). Users must determine and document their chosen method of maintaining the unbroken chain of calibrations.

The three options for the method to determine the standard concentration are as follows:

**Option #1:** The internal calibration factors for the transfer standard's photometer are adjusted via a calibration which is based on the standard concentration of the higher authority transfer standard.

**Option #2:** The internal calibration factors for the transfer standard's photometer are set to one (for the span) and zero (for the zero), a least squares linear regression line (Equation 3) is fitted to the data, and the slope and intercept estimates of this fitted line (Equation 4) are noted. Equation 10 is then used to calculate the standard concentration when the transfer standard is subsequently employed.

**Option #3:** A combination of Options #1 and #2.

The selected method must be consistent throughout the traceability chain and with the procedures in this TAD, and it must be well documented in the QAPP and SOP.

If either Option #2 or Option #3 is implemented, the standard concentration at a given concentration point within the test cycle is calculated as follows:

**Equation 10 - Standard Concentration (ppb) at a given concentration point**

$$\text{Standard } O_3 \text{ Conc} = \frac{1}{m} (\text{Indicated } O_3 \text{ Conc} - b)$$

where: (***m***) = The slope of the test cycle's fitted least squares regression line, as determined by Equation 4.

(***b***) = The intercept of the test cycle's fitted least squares regression line (ppb), as determined by Equation 4.

(***Indicated  $O_3$  Conc***) = The concentration value (ppb) reported by the candidate transfer standard at the given concentration point, either from its front panel, calibrated analog voltage output, digital output, or some other data reporting mechanism.

To illustrate this calculation, consider the second concentration point within cycle #1 in the verification example within Table A-1. Here, the candidate transfer standard reported a concentration of 200.9 ppb. Then considering the slope and intercept estimates for this cycle which are given in Table A-2, the standard concentration would be:

$$\begin{aligned} \text{Standard } O_3 \text{ Conc} &= \frac{1}{1.0053} \{200.9 - (-0.1518)\} \\ &= 200.0 \text{ ppb} \end{aligned}$$

### **A9. Reverification Testing and Acceptance Criteria**

All **reverification tests** for a given transfer standard must be completed according to Section 5.2 and Table 4-1. A reverification test involves performing a single testing cycle. The linear regression model specified in Equation 3 above is fitted to the data produced upon executing this testing cycle.

Use the following steps to determine whether or not a reverification test is successful:

1. Use the data collected during the reverification test cycle to calculate the following:
  - a. Percent difference (***% Diff***) in measured concentration, calculated at each tested concentration point above 50 ppb (Equation 1).
  - b. Absolute difference (***AbsDiff***) in measured concentration, calculated at each tested concentration point at or below 50 ppb (Equation 2).

- c. Least squares estimates for the slope ( $m$ ) and intercept ( $b$ ) of the cycle's fitted regression line (Equation 4).
2. Compare each of the calculated values in #1 against the following acceptance criteria to determine if the acceptance criteria are achieved:
  - a. For a given testing concentration point above 50 ppb, the calculated value of  $\%Diff$  must be **within  $\pm 3.1\%$**  to be considered acceptable.
  - b. For a given testing concentration point at or below 50 ppb, the calculated value of  $AbsDiff_{ij}$  must be **within  $\pm 1.5$  ppb** to be considered acceptable.
  - c. The calculated value of  $m$  must fall **within  $\pm 0.015$**  of the candidate transfer standard's calculated mean slope from the most recent successful verification test (Equation 6) to be considered acceptable.
  - d. The calculated value of  $b$  must fall **within  $\pm 1.5$  ppb** of the candidate transfer standard's calculated mean intercept from the most recent successful verification test (Equation 6) to be considered acceptable.
3. If all acceptance criteria are achieved for the given reverification test cycle (i.e., either #2a or #2b is achieved across all concentration testing points, AND #2c and #2d are achieved for the fitted regression line), then for the given candidate transfer standard,
  - a. Classify the reverification test as having successfully passed.
  - b. Using Equation 10 (and if either Option #2 or #3 above is used), use the updated slope and intercept estimates (from #1c) to calculate the standard concentration when the transfer standard is subsequently used.
4. If one or more instances are noted where acceptance criteria in #2 were not achieved in the reverification test, then the candidate transfer standard should be assessed for problems and, upon resolving any problems, must undergo and pass a full three-cycle verification test (Section 5.1) before it can be used again.



# Appendix B Example Acceptance Testing Data Sheet<sup>19</sup>

<b>Ozone Transfer Standard Acceptance Testing</b>			
1. Complete acceptance testing after proper warm up and while sampling zero air.			
2. Compare all readings to the manufacturers recommendation's.			
3. Readings not meeting the manufacturers recommendation must be corrected prior to conducting verification.			
Operator:			
Organization:			
Instrument Make:			
Instrument Model:			
Instrument SN:			
Date Preventive Maintenance Performed:			
Transfer Standard Role:			
<b>PARAMETERS</b>	<b>Prior to Transport</b>	<b>As Found</b>	<b>As Left</b>
DATE			
TIME			
LAB TEMPERATURE			
LAB STANDARD PRESSURE			
SLOPE (CALIBRATION FACTOR)			
ZERO (CALIBRATION FACTOR)			
SAMPLE PRESSURE			
SAMPLE TEMPERATURE			
CELL #1 INTENSITY			
CELL #2 INTENSITY (if dual cell)			
PHOTOMETER FLOW			
PHOTOMETER LAMP TEMP			
BOX TEMP			
-Additional Parameters, Add Here-			
-Additional Parameters, Add Here-			
-Additional Parameters, Add Here-			
<b>COMMENTS (note all testing parameters that do not meet the manufacturers specifications)</b>			

<sup>19</sup> This form is available at: <https://www.epa.gov/amtic>

# Appendix C Utilizing NIST 7 Essential Elements of Traceability

NIST has developed a document entitled *Good Measurement Practice for Ensuring Metrological Traceability* (GMP 13)<sup>20</sup>. The stated purpose of this document is to “enable compliance with essential elements of Metrological Traceability”. **It is the transfer standard provider’s responsibility to develop procedures and other quality documentation to support their claim of traceability and to ensure that the transfer standard is used appropriately. This TAD provides specific procedures for transfer standard providers and users to follow to meet the claim of traceability for their O<sub>3</sub> measurements.** EPA recommends that all organizations become familiar with the concepts in GMP 13. EPA’s O<sub>3</sub> traceability scheme meets the NIST GMP 13 guidance and “7 Essential Elements” as described below.

## C1. Realization of SI Units

EPA follows the *Guide for the Use of the International Systems of Units* (SI)<sup>21</sup>. While part per million (ppm) and part per billion (ppb) generally are not acceptable SI units, the SI does allow for exceptions per the note in Section 7.10.3 of the SI guide. To avoid confusion among users of this TAD and because the CFR uses ppm and ppb to express the value of quantity (rather than nmol/mol), EPA uses ppm and ppb as the value of quantity for O<sub>3</sub> concentrations in this TAD. Thus, EPA regards ppm and ppb as acceptable units for use in all documentation of EPA’s traceability scheme (Thompson and Taylor, 2008).

## C2. Unbroken Chain of Calibrations

EPA’s O<sub>3</sub> transfer standards transfer traceability from higher authority to lower authority by comparing the NIST Level 1 SRP O<sub>3</sub> standard to EPA Level 1 SRPs, Level 1 to Level 2, and Level 2 to Level 3. Measurements from the NIST Level 1 SRP are linked to the BIPM (i.e., the International Bureau of Weights and Measurements) through participation in the Protocol for the Key Comparison BIPM.QM-K1, Ozone at ambient level<sup>22</sup>. The NIST Level 1 SRP is compared to the BIPM SRP biannually. The NIST Level 1 SRP linked to the BIPM is considered the highest authority standard in the United States. The EPA Office of Research and Development (ORD) Level 1 SRP is compared to the NIST Level 1 SRP annually. EPA Regional Level 1 SRP’s are compared to the EPA ORD Level 1 SRP annually. Level 2 transfer standards are compared to the EPA Regional (or ORD) Level 1 SRP annually. Level 3 transfer standards are compared to Level 2 transfer standards either annually or semiannually (depending on use). A hierarchy diagram and detailed description of EPA’s traceability scheme can be found in Section 2.0.

Beyond the Level 1 SRP, traceability is transferred by comparing the standard concentration of the higher authority transfer standard versus the indicated concentration of the lower authority transfer standard (candidate transfer standard) at various concentrations (at least 6 different

<sup>20</sup> <https://www.nist.gov/system/files/documents/2019/06/21/gmp-13-ensuring-traceability-20190621.pdf>

<sup>21</sup> <https://physics.nist.gov/cuu/pdf/sp811.pdf>

<sup>22</sup> [https://www.bipm.org/utis/en/pdf/BIPM.QM-K1\\_protocol.pdf](https://www.bipm.org/utis/en/pdf/BIPM.QM-K1_protocol.pdf)

concentrations and a zero are required). The unbroken chain of calibrations is established by one of three options:

- 1) The candidate transfer standard photometer internal calibration factors are adjusted by means of a calibration based on the standard concentration of the higher authority transfer standard;
- 2) The candidate transfer standard internal calibration factors are set to one (for the span) and zero (for the zero), a least squares linear regression is calculated, and Equation 10 of Appendix A is used to calculate the standard concentration when the transfer standard is subsequently employed; or
- 3) A combination of options 1 and 2.

The method used should be consistent throughout the traceability chain and must be consistent with the procedures in this TAD and be well documented in the QAPP and SOP.

### **C3. Documented Calibration Program**

All work encompassing traceability of O<sub>3</sub> measurements must be documented in a QAPP and SOP. Each step in the EPA O<sub>3</sub> traceability scheme is completed at defined frequencies. Table 4-1 of this document outlines the required verification intervals and acceptance criteria for each level of transfer standards. Other devices used in EPA's traceability scheme (i.e., pressure, temperature, and voltmeter) are also required to be verified on a regular basis. These devices and frequencies are stated in this document.

### **C4. Documented Measurement Uncertainty**

All Level 1 SRPs are designed and built by NIST to meet the specifications in Standard Reference Photometer for the Assay of Ozone in Calibration Atmospheres, NISTIR 6369.<sup>23</sup> (Paur et al., 2003) The design specification includes an uncertainty budget for the measurement components. All SRPs used within the EPA's O<sub>3</sub> traceability scheme are designed and run identically and therefore the uncertainty is considered to be identical throughout the SRP network. NIST has conducted subsequent studies to test the design specifications and has made several improvements throughout EPA's SRP network which were also rigorously tested and documented. (Norris et al., 2013, 2004; Viallon et al., 2006)

#### **Implementing the O<sub>3</sub> Uncertainty Budget into the SRP Network**

1. NIST Level 1 SRP comparison to ORD Level 1 SRP – NIST provides a report stating the estimated expanded uncertainties of the SRP O<sub>3</sub> concentration defined by the following equation:

$$u(x) = \sqrt{(0.28)^2 + (1.1 \times 10^{-2}x)^2} \text{ nmol/mol}$$

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<sup>23</sup> <https://www.nist.gov/publications/standard-reference-photometer-assay-ozone-calibration-atmospheres>

2. ORD Level 1 SRP comparison to EPA Level 1 SRP – ORD incorporates the uncertainty budget received from NIST into their Verification Reports for the SRP comparisons. For each of the SRPs, the report includes the Expanded Uncertainty. The report includes the uncertainty at the highest concentration, the lowest concentration and the uncertainty at 70 nm/mol (ppbv). The report will also include the formula to be used in calculating the expanded uncertainty.

#### **C5. Documented Measurement Procedure**

EPA has written procedures and guidance for all aspects of O<sub>3</sub> monitoring and requires transfer standard users conducting regulatory O<sub>3</sub> monitoring to have proper written QAPPs, SOPs, validation methods and follow good laboratory practices and equipment handling for providing verification results with accurate and traceable values with appropriate uncertainties.

A certificate and report must be provided to the transfer standard owner after verification detailing the verification results. Users should review the NIST SOP 1<sup>24</sup>, *Recommended Standard Operating Procedure for Calibration Certificate Program*. This procedure should be followed to the extent practical.

#### **C6. Accredited Technical Competence**

Anyone performing work within the EPA traceability scheme must provide proof of technical competence by meeting minimum training requirements. Training records and plans must be documented showing initial and ongoing training. Inter- and intra- laboratory comparisons and outside accreditation should also be considered.

#### **C7. Measurement Assurance**

EPA incorporates measurement control steps to ensure the validity of the O<sub>3</sub> verification process. The procedures and measurands are defined throughout this TAD. EPA recommends that all laboratories verifying O<sub>3</sub> transfer standards:

1. Maintain a transfer standard designated as a check standard for generating control charts to ensure the standard of higher authority is in control;
2. Conduct additional redundant checks and verifications;
3. Conduct comparisons by sending a transfer standard to other branches in the traceability chain to ensure consistency among operators;
4. Conduct frequent reviews of existing QC data collected at monitoring sites;
5. Develop a corrective action plan for when transfer standards are not within established parameters.

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<sup>24</sup> <https://www.nist.gov/system/files/documents/2019/05/13/sop-1-calibration-certificate-preparation-20190506.pdf>

# Appendix D Rationale and Testing Methodology for O<sub>3</sub> Verification and Reverification Acceptance Criteria

## **D1.Introduction**

In revising the 2013 version of *Transfer Standards for the Calibration of Air Monitoring Analyzers for O<sub>3</sub>*, EPA examined every step in the transfer standard verification and reverification process and examined the acceptance criteria used in each process. EPA was interested in determining if these processes or acceptance criteria needed to be updated. This appendix provides a general overview and a plain language description of EPA's approach when reviewing and changing verification/reverification processes and acceptance criteria.

## **D2.Overview of Verification and Reverification Procedure**

Upon receipt of a new candidate transfer standard, and then following any adjustment or major repair of the device, the device is subjected to formal verification testing. In verification testing, the candidate transfer standard's reported measurements are compared to those generated by a standard of higher authority at the same concentration test point. A verification test consists of a minimum of three stable test cycles, each consisting of at least six concentration points distributed across the range of O<sub>3</sub> concentrations expected to be encountered during normal use, as well as 0 ppb. These concentration points should be as evenly spaced as possible across the range and could also include the NAAQS value of 70 ppb. Once a transfer standard has been successfully verified, reverifications are required at a set frequency depending upon their use.

## **D3.Could the minimum number of test cycles within a verification test be reduced from six to three?**

EPA performed a statistical analysis to determine whether a statistically significant difference in the outcome would occur if the number of cycles in a verification test was reduced from six to three. When performing this analysis on Level 3 verification test data when data for only either the first 3 or last 3 cycles were considered, no significant differences in the intercepts or slopes were observed among cycles at a 0.05 level. Thus, EPA determined that the minimum number of test cycles could be reduced from six to three.

## **D4.Acceptance criteria for individual measures at specific test concentration points.**

Within each concentration test point within a test cycle, the measurements taken by the candidate transfer standard are paired with the measurements taken by the standard of higher authority. The two measurements within a sampling pair are first assessed to ensure they do not differ significantly from each other. The measurements within a pair must not differ by more than the following thresholds:

- 3.1%, for concentration points above 50 ppb. (Here, the difference between the two paired measurements is divided by the measurement for the standard of higher authority and expressed as a percentage. The sign of the difference is ignored.)

- 1.5 ppb in absolute value, for concentration points at or below 50 ppb. (Here, only the difference between the two paired measurements is considered, and the sign of the difference is ignored.)

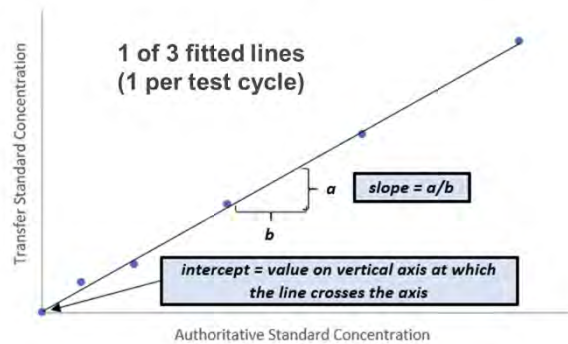
These acceptance criteria were determined in earlier versions of the TAD.

If any concentration test point fails its appropriate acceptance criterion, data from that test cycle are discarded and the test cycle is repeated.

**D5. Acceptance criteria for cycle-specific values of the slope and intercept estimates within a verification test.**

Once the acceptance criteria for individual measurement pairs have been achieved within a given test cycle, a straight line is fitted to the paired measurements across all tested concentration points within the cycle (using “least squares regression”) to predict the measurement from the candidate transfer standard given the measurement from the standard of higher authority. (Thus, the amount of data used to determine a cycle’s straight-line relationship corresponds to the number of concentration points, including 0 ppb, in the given test cycle.) The fitted straight line is defined by its estimated intercept and slope:

- The intercept (in ppb) corresponds to the measurement value for the candidate transfer standard which the line predicts when the measurement for the standard of higher authority equals 0 ppb.
  - For each of the three test cycles, the intercept estimate must fall between -3 ppb and +3 ppb.
- The slope (which is unitless) corresponds to the predicted change in the candidate transfer standard’s measurement value that occurs for each 1.0 ppb increase in the standard of higher authority’s measurement value.
  - For each of the three test cycles, the slope estimate must fall between 0.97 and 1.03.



These acceptance criteria were determined in earlier versions of the TAD.

If either the slope estimate or the intercept estimate within a given test cycle falls outside of its respective acceptance criterion, then the results for the candidate transfer standard do not sufficiently agree (or coincide) with the results for the standard of higher authority for that cycle, and therefore the results are discarded and the cycle must be repeated.

**D6. Could the three test cycles within a verification test be performed on the same day, or must they be performed on different days?**

EPA performed a statistical analysis to assess whether the three test cycles within a verification test should continue to be performed on different (consecutive) days, or if they could be

performed on the same day. Performing test cycles on the same day could lead to resource savings as the time needed to invest in performing a full verification test would be reduced, and the daily set-up for testing would be reduced from three days to one day. In this statistical analysis, EPA wished to assess, for a typical transfer standard, how variability (in the slopes and intercepts of the fitted lines) among cycles performed on a single day compared to the variability across cycles performed on different days. The results of the statistical analysis suggested that the variability in the intercept and slope estimates, calculated across cycles, tended not to differ significantly if those cycles were performed within the same day or performed on different days. (In this analysis, six cycles were assumed within a verification test, rather than three.) Having each cycle performed on the same day was not expected to result in a much higher or lower likelihood of exceeding acceptance criteria compared to performing one cycle per day. Thus, within a verification test, EPA decided to permit the three test cycles to be performed within the same day, as long as conditions were in place to minimize the extent to which the outcomes from one cycle would influence the outcomes from another cycle.

#### **D7. Acceptance criteria for the standard deviation of the slope and intercept estimates across cycles within a verification test.**

Once the acceptance criteria for the three intercept estimates and the three slope estimates are achieved within a verification test, the stability of these estimates across the three cycles was confirmed. A “standard deviation” was used as the measure of stability in these estimates. The standard deviation is a measure of how spread out the estimates are, and in particular, the extent to which they tend to deviate from their mean value.

The direction given earlier in this document is that all three cycles of a verification test can be performed within a single day. Therefore, the acceptance criteria for the standard deviation of the three slope estimates and the standard deviation of the three intercept estimates were derived using historic test data for those verification tests in which the three test cycles occurred within the same day, and the first of the three cycles was the first cycle tested on that day. These data were made available from the EPA Regions for select Levels 2 and 3 transfer standards. Note that it is assumed that this set of available data well represent the full set of all possible outcomes from the single-day verification of Levels 2 and 3 transfer standards.

The acceptance criteria on the standard deviations of the slopes and intercepts took the form of a threshold value (one for the slope estimates, and one for the intercept estimates) against which the standard deviations were compared. If a standard deviation exceeded its threshold, then the standard deviation was deemed too large, and thus the estimates were not adequately stable across the three test cycles. The statistical analysis which EPA used to derive the acceptance thresholds needed to accurately portray the distribution of standard deviations in the slope and intercept estimates (especially the part of the distribution representing large values). Because the available data to inform this distribution was quite limited, EPA applied a statistical simulation procedure to the available data when generating the distribution and deriving the acceptance threshold from it. This simulation required two confidence levels to be selected:

- A confidence level on the upper bound on the standard deviation within a verification test. (That is, the level of confidence at which we are willing to assume that the likelihood of the true standard deviation being below a specified value for a typical verification test.) EPA picked this confidence level to be 90%.
- A confidence level on the upper bound on the standard deviation across multiple verification tests. (That is, the level of confidence at which we are willing to assume that the likelihood of the true standard deviation of the test-specific mean estimate across cycles being below a specified value across the verification tests.) EPA picked this confidence level to be 95%.

Based on these settings, the statistical analyses yielded acceptance thresholds of 0.0075 for the standard deviation of slope estimates, and 1.00 for the standard deviation of intercept estimates. If for a given verification test, the standard deviation of either the slope estimates or the intercept estimates exceed its respective threshold, then the outcomes are not considered stable among the test's three cycles, and the verification test must be repeated on the given candidate transfer standard.

#### **D8. Acceptance criteria for reverification testing).**

Initially, EPA considered an approach for determining acceptance criteria for reverification testing which involved obtaining data from the standard's last three test cycles that passed all acceptance criteria and using the data to calculate "95% prediction intervals" on the slope and the intercept of the anticipated regression line for a future (reverification) testing cycle applied to that standard (hence use of the term "prediction"). The estimated slope and intercept of the reverification's test cycle needed to fall within their respective prediction intervals (for the same standard) to achieve the acceptance criteria for reverification. In testing this approach on example verification and reverification data, however, the prediction intervals were very narrow for standards having high repeatability. Therefore, this approach led to concerns that it would declare highly reliable standards as failing their reverification tests with high likelihood. This failure could also be caused by the small nominal drift in measurements that normally occurs over the elapsed time.

To avoid the ramifications caused by these concerns, EPA rejected this initial approach and took a different approach for determining acceptance criteria for reverifications. The adopted approach utilizes data from the candidate transfer standard's most recent successful verification test – note that this may be different from the sampler's three most recent successful test cycles, as some may have been reverification cycles done on different days. Recall that verification testing involves performing three independent test cycles, each performed on the same day. As given by Equations 8 and 9 of Appendix A, the standard deviation of the three slope estimates ( $SD_m$ ) and the three intercept estimates ( $SD_b$ ), respectively, are calculated from the three fitted regression lines generated within a verification test. For a series of historic verification tests performed across a set of multiple transfer standards, EPA characterized the distributions of the standard deviations (for both  $SD_m$  and  $SD_b$ ) calculated within these tests. Of particular interest were the medians and 95<sup>th</sup> percentiles of these two distributions. From these relationships and



from other data investigations, the following two acceptance criteria were established for the estimated slope and intercept of the reverification test cycle data:

- The slope of the regression line fitted to the reverification cycle data must be within  $\pm 0.015$  of the value of the mean slope ( $\bar{m}$  in Equation 6 in Appendix A) associated with the most recent successful verification test.
- The intercept of the regression line fitted to the reverification cycle data must be within  $\pm 1.5$  ppb of the value of the mean intercept ( $\bar{b}$  in Equation 7 in Appendix A) associated with the most recent successful verification test.

Note that these acceptance criteria for reverifications are one-half (50%) of the acceptance criteria for the mean slope and mean intercept from the verification test, as specified in Table 4-1, Section 4.4.1, and Section D.5. These acceptance criteria take into account the naturally occurring drift in measurements that occurs over time.

## Appendix E Qualification Process

*(reprinted from “Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone, 2013”. Information on O3 generators deleted)*

The first step in establishing the authority of a candidate transfer standard is to prove that it qualifies for use as a transfer standard. In other words, can the output (either an actual O<sub>3</sub> concentration or a concentration assay, depending on the type) of the candidate transfer standard be trusted under the changing conditions of use that might be encountered in field use.

Qualifying new instruments can help ensure the instruments will perform under various field conditions that might not get observed during a traditional verification processes described in Section 4 of this document.

The primary requirement of a transfer standard is repeatability – repeatability under the stress of variable conditions that may change between verification and use. A candidate transfer standard is qualified by proving that it is repeatable over an appropriate range for each variable likely to change between the time and place of verification and the time and place of use. According to the specifications in Section 3, the repeatability must be within  $\pm 4\%$  or  $\pm 4$  ppb, whichever is greater, for each condition or variable that may change between the point of verification and the point of use.

Selecting the conditions that are likely to vary and that may affect the repeatability of the device or procedure is largely a matter of intelligent, informed, judgment. To a large extent, the variables will depend on the nature of the device or procedure; for some candidate transfer standards, the variables to be considered may be quite numerous. It is the user’s responsibility to determine all of the conditions to be considered in the demonstration of repeatability before a candidate transfer standard can be considered qualified for use as a transfer standard. Common conditions likely to affect a wide variety of types of transfer standards include such items as ambient temperature, line voltage, barometric pressure, elapsed time, physical shock, etc. These variables are discussed individually later in this section. Conditions not likely to affect the transfer standard can usually be eliminated from consideration. The user must, however, be constantly alert for the unusual situation where an unexpected condition may significantly affect the repeatability of a transfer standard.

Note that a transfer standard does not necessarily need to be constant with respect to these variables, only repeatable or predictable. While it is certainly desirable that a device or procedure be insensitive to any given variable, it may still qualify as a transfer standard if it is repeatable. For example, it may be difficult to find or design a generation-type transfer standard device that is insensitive to barometric pressure. However, if it is repeatable with respect to barometric pressure, the relationship can be quantitatively defined by a curve or table. At the time of use, the local barometric pressure must be measured, and the curve or table used to “correct” the transfer standard’s indicated output. This technique is acceptable for one or perhaps two variables. But beyond two variables, the difficulties of determining and specifying

the relationship to the variables may become impractical. Fortunately, sensitivity to most variables can be reasonably controlled.

Demonstration of repeatability for a candidate transfer standard normally requires testing for each condition that could or may affect it. Typical tests for common conditions are discussed below. Again, intelligent judgment is required to determine what conditions to test and the extent of testing required to qualify the device or procedure. For commercially available transfer standard devices, some or all the testing may be carried out by the manufacturer, thereby reducing the burden on the user. In some cases, it may be possible to judiciously substitute design rationale for actual testing. For example, a device whose power supply is designed to be highly regulated electronically may not require specific line voltage tests. However, such situations should be viewed with considerable skepticism.

The preceding discussion brings up the further question of whether candidate transfer standards must be tested individually or whether they can be qualified by type, model, or agency. The units of commercially produced transfer standard devices are designed and manufactured to be identical and should therefore have very similar characteristics. The manufacturer could carry out the necessary qualification tests on representative samples, sparing the user the burden of testing each unit or the cost of paying the manufacturer to test each unit individually. Under this concept, it would certainly be appropriate to require the manufacturer to guarantee that each unit meets appropriate performance specifications. However, the user should assume a skeptical attitude, in view of manufacturing tolerances and possible defective components, and carry out at least some minimal tests to verify that each unit is acceptable.

In the case of unique devices assembled by users, testing for all pertinent conditions which could or might affect the device are normally required.

## **QUALIFICATION TESTS**

Some of the more common conditions likely to be encountered or to change while using transfer standards and that may often affect the repeatability of the device or procedure are discussed below. Also discussed are ways or approaches to test for sensitivity to the condition. As noted previously, the exact conditions or variables that must be considered depend on the specific nature of the device or procedure. The user (or manufacturer, etc.) should determine the conditions for each case on an intelligent judgmental basis derived from a complete understanding of the operation of the device or procedure and supported by appropriate rationale.

Once the conditions to be considered have been determined, the objective of the qualification tests is either a or b:

- a) to demonstrate that the candidate transfer standard's output is not affected by more than  $\pm 4\%$  or  $\pm 4$  ppb (whichever is greater) by the condition over a range likely to be encountered during use of the device or procedure;
- b) to demonstrate that the candidate transfer standard's output is repeatable within  $\pm 4\%$  or  $\pm 4$  ppb (whichever is greater) as the variable is changed over a range likely to be encountered during use, and to quantify the relationship between the output and the variable.

## Temperature

Changes in ambient temperature are likely to occur from place to place and from one time to another. Temperature changes are very likely to affect almost all types of transfer standards unless appropriate means are used to avoid adverse effects. Temperature affects transfer standards in many ways: changes in the action of components, changes in chemical reactions or rates of reaction, volume changes of gases, electronic drift, variable warm-up time, etc. The most important effects may well be (1) changes in the output of generation devices, (2) changes in the sensitivity of O<sub>3</sub> analyzer-type systems, and (3) changes in the volume of air flows which must be measured accurately.

Temperature effects can be minimized in several ways. Since shelters for ambient air monitoring are normally maintained at about 20 – 30° C (with some flexibility for fluctuations) all transfer standards should be proven to be repeatable within this range. Transfer standard devices may be made insensitive to temperature changes by design, such as thermostatic regulation of sensitive components or of the entire device, or by temperature compensation.

Temperature effects on air flow measurement can be minimized by the use of mass flowmeters, which do not measure volume, or by the regulation of gas temperatures. In another approach, ordinary ideal-gas-law corrections could be made manually to adjust to measured volumetric flowrates. However, when using orifice control or measurement devices such as critical orifices and rotameters, be sure to use an appropriate correction formula.

Testing a candidate transfer standard for sensitivity to temperature is facilitated by the use of a controlled temperature chamber. However, successful temperature tests can be carried out in many ordinary laboratories where the temperature can be manually controlled by adjusting thermostats, blocking air vents or outlets, opening doors or windows, or using supplemental heaters or air conditioners. A reasonable temperature range would be 20 to 30°C (68 to 86°F). Broader temperature ranges could be used if appropriate.

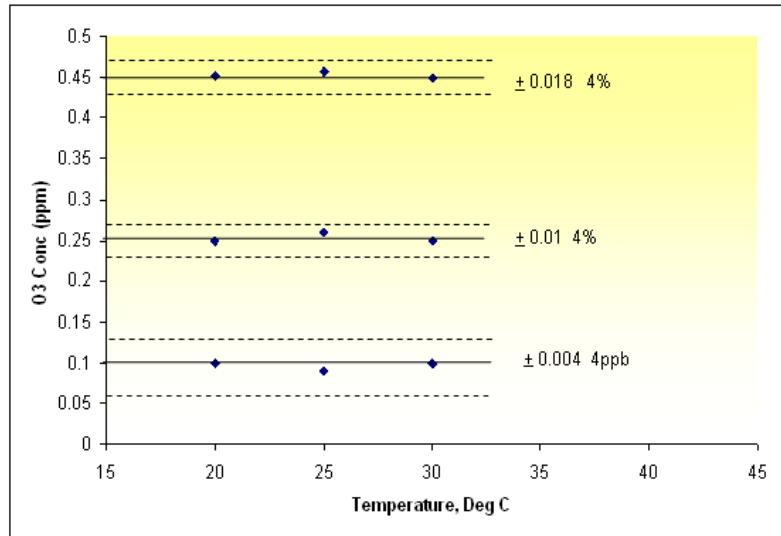
The candidate transfer standard is tested by comparing its output to a stable concentration reference. This reference should ideally be a UV analyzer system at least one level above the level of the transfer standard. It would be best to locate the reference outside of the variable temperature test area. The candidate transfer standard should be tested at a minimum of 3 different points over the temperature range, including the extremes, and at a minimum of 3

different concentrations. Be sure to allow sufficient time for the device or any instruments or equipment associated with the transfer standard to equilibrate (min time period or until reading stabilized) each time the temperature is changed. The test results should be plotted in a fashion similar to the example shown in Figure B.1.

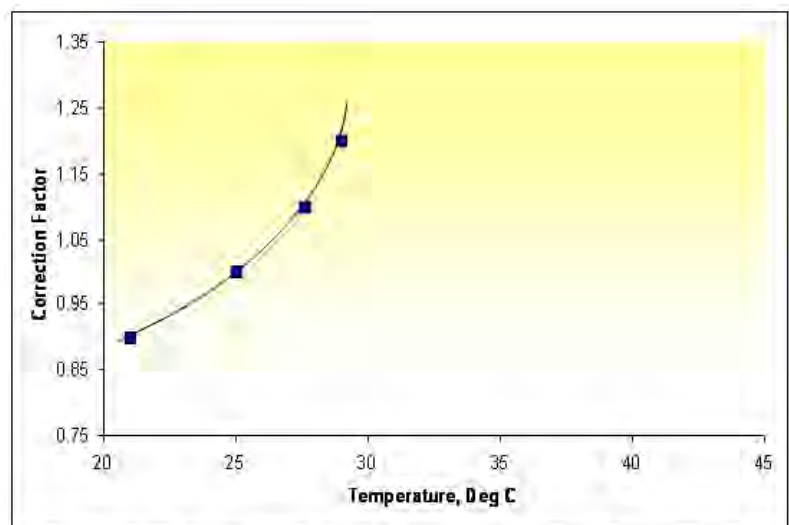
If the candidate transfer standard has a significant temperature dependence, additional test points at various concentrations and temperatures should be taken to define the relationship between output and temperature accurately. Furthermore, if the candidate turns out to have a dependence on more than one condition or variable, tests must be carried out over the range of both variables simultaneously to determine any interdependence between the two variables. Once the test data are acquired, they should be analyzed to determine if some general formula or curve can be derived (either analytically or empirically) to predict the correct O<sub>3</sub> concentration at any temperature in the range (see Figure B.2). The correction formula or curve must be accurate within  $\pm 4\%$  or  $\pm 4$  ppb, whichever is greater. If two or more variables are involved, a family of curves may be required; unless the relationship is rather simple, this situation may prove impractical in actual use.

### Line Voltage

Line voltage is very likely to vary from place to place and from one time to another. Good electrical or electronic design of the transfer standard should avoid sensitivity to line voltage variations, but poorly designed equipment can easily be affected. In addition, line voltage sensitivity may appear only as long-time thermal drift, a rather subtle effect.



**Figure B.1** Example of temperature qualification test results showing no dependence on temperature.



**Figure B.2** Example of a temperature dependence quantitatively defined correction factor.

Aside from adequate design, line voltage effects can be minimized by the addition of an outboard line voltage regulator. However, such devices may distort the line voltage waveform, thereby adversely affecting some types of equipment. If such regulators are used, it is important that the same regulator is used during both verification and use of the transfer standard. Restriction of the transfer standard to a line voltage range in which the effects are insignificant is another alternative, but that would require monitoring the voltage during use and may preclude use at some sites.

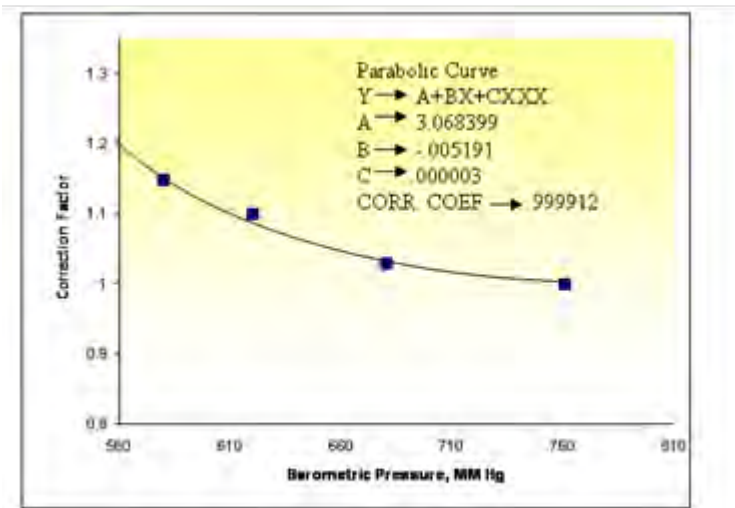
Testing for line voltage sensitivity can be carried out along the same lines as described for temperature testing. The line voltage can be varied by means of a variable voltage transformer (“Variac”) and measured by an accurate ac voltmeter. Do not use electronic “dimmer” controls which operate on a delayed-conduction principle, as such devices cause drastic waveform distortion.

A line voltage range of 105 to 125 volts should adequately cover the vast majority of line voltages available in the U.S. If the transfer standard is used when powered by a small power generator, it should be checked for frequency dependence.

### **Barometric Pressure/Altitude**

Since O<sub>3</sub> concentrations are gaseous in nature, all transfer standards will probably have some basic or inherent sensitivity to change in barometric pressure. Unfortunately, it is rather difficult to minimize barometric pressure effects by design. Air pressures can be regulated mechanically against an absolute reference, but most such schemes are not practical when working with O<sub>3</sub> concentrations because of restrictions to inert materials such as glass or Teflon. At a constant altitude, normal day-to-day variation in barometric pressure is only a few percent. If the use of the transfer standard can be restricted to altitudes within a hundred meters of the verification altitude, it may be acceptable to neglect the barometric effect entirely. However, if the use of a transfer standard is necessary at altitudes significantly different than the calibration altitude, then pressure effects cannot generally be ignored.

Although not readily preventable, pressure effects are likely to be repeatable. As a result, barometric pressure may be the variable most likely to be handled by the defined-relationship approach discussed previously in connection with temperature effects. The technique is very similar to the technique used to determine a temperature relationship; hopefully, a unique quantitative relationship will result, such as that illustrated in Figure B.3. Remember that in any work with O<sub>3</sub> concentrations at altitudes significantly above sea level, the



**Figure B.3 Example of a defined barometric pressure dependence**

concentration units must be clearly understood. The volume ratio concentration units must be clearly understood. The volume ratio concentration units (ppm, ppb, etc.) are independent of pressure, while density units such as  $\mu\text{g}/\text{m}^3$  are related to pressure. (However, the  $\mu\text{g}/\text{m}^3$  unit defined and used by EPA is “corrected” to 1.01 kPa (760 mm Hg) and 25°C and is therefore related to ppm by a constant.)

Testing with respect to barometric pressure may be difficult. The use of a variable pressure chamber is the best approach, but few laboratories have access to such facilities. It is conceivable that various pressures could be obtained in a manifold setup, but construction of such an apparatus is difficult and of questionable validity. The use of a mobile laboratory vehicle which can be driven to various altitudes to conduct tests may offer the most feasible solution. Some types of transfer standards may not require pressure tests because their pressure sensitivity is well known. Some analyzer-type devices are clearly related directly to gas density, where a simple ideal-gas-law correction can be applied. Pressure tests are not needed for these types. For commercially-produced devices, the manufacturer would be expected to carry out the necessary qualification tests and to offer the devices as type-approved, at least with respect to pressure effects.

As a final note of encouragement, automatic compensation for barometric pressure is rapidly becoming economically feasible for some types of O<sub>3</sub> transfer standards by the incorporation of microprocessor technology. At least two manufacturers have used this approach in commercially available instruments.

### **Elapsed Time**

As the elapsed time between verification and use increases, the confidence in the repeatability decreases. As a result, periodic reverification is needed. Some types of O<sub>3</sub> generation devices have a definite loss of output (decay) with time. This decay is usually associated with use-time or on-time rather than total elapsed time. Since the decay rate tends to be quantifiable, it can be

accommodated with the defined-relationship mechanism discussed in connection with temperature effects: the transfer standard is equipped with an hours meter or another time measuring device and a series of tests over a sufficient time period can then be used to determine the decay rate. During use, a correction to the output is applied based on the number of hours of on-time since the last verification.

Another approach is to recertify such a transfer standard often enough so that the error due to decay never exceeds the  $\pm 4\%$  or  $\pm 4$  ppb specification.

### **Variability**

The adequacy of the relationship between a transfer standard and a authoritative reference O<sub>3</sub> standard is dependent on the variability of the transfer standard. Variability reduces confidence in transfer standards. A high degree of variability may be cause for disqualifying a device or procedure for use as a transfer standard, or for selecting one with lower variability. Although the verification procedure in Section 4 includes a test for variability, more extensive tests for variability may be necessary to qualify a transfer standard because the verification test is for variability in the slope of the verification relationship and not for individual point variability. Furthermore, variability may be due to changes in conditions not encountered during verification.

Many different types of transfer standards may have excessive variability for a variety of reasons. Qualification variability testing is perhaps most needed to test for the effect of a variety of non-specific or non-quantitative variables that cannot be tested individually. Whenever increased variability can be assigned to a specific cause, corrective actions or restrictions can be and should be applied to reduce the variability.

The variability test should be carried out on a single-point basis. A series of at least 6 single-point comparisons should be made between the candidate transfer standard and a UV reference at each of at least two fixed concentrations – one low concentration (less than 0.1 ppm) and one high concentration (over 80% of the upper range limit). These comparisons should be made over a variety of conditions and situations and over a number of days. For each concentration, verify that all O<sub>3</sub> concentration measurements determined by the UV reference standard are very nearly equal. Then calculate the average of the 6 (or more) concentrations indicated by the transfer standard, using the following equation:

$$\text{Ave} = \frac{1}{n} \sum_{i=1}^n y_i$$

Where: n = number of comparisons

$y_i$  = O<sub>3</sub> concentration indicated by the transfer standard

Determine the difference between each concentration indicated by the transfer standard and the average concentration ( $y_i - \text{Ave}$ ). Each difference must be less than  $\pm 5\%$  of the average (for concentrations over 0.1 ppm) or less than  $\pm 5$  ppb (for concentrations less than 0.1 ppm).



For this test, the acceptable limits are  $\pm 5\%$  or  $\pm 5$  ppb rather than  $\pm 4\%$  or  $\pm 4$  ppb, because the test is for general variability, which may derive from a number of non-identifiable causes. Under these circumstances slightly wider limits than those allowed for the other qualification tests are acceptable.

One technique that can reduce variability and improve accuracy is repetition and averaging. For example, the variability of assay procedures can be reduced by assaying each concentration several times and averaging the results. Of course, if this technique is used, it becomes a necessary part of the transfer standard procedure and must be carried out each time the transfer standard is used and certified.

### **Relocation**

A transfer standard obviously needs to maintain repeatability after being moved and possibly encountering mechanical shocks, jolts, and stress. Any electrical or thermal stress incident to turning the device or equipment on and off frequently is also of concern, as is consideration of orientation or set-up factors.

Tests for these conditions, while perhaps not particularly quantitative, should include actually moving the candidate device or equipment to different locations and comparing the output each time it is returned. Tests could also include mild shock or drop tests, or tests for any set-up factors which can be specifically identified, e.g., physical orientation, removal of covers, any set-up variations. Any cause-and-effect-relationship discovered should be investigated completely. The tests may be conveniently combined or included with those discussed previously for variability.

### **Operator Adjustments**

Those transfer standard devices whose output is to be related to an operator adjustment should be tested for repeatability with respect to the adjustment. Mechanical adjustments might need to be tested for play, backlash, hysteresis, slippage, and resolution. Other types of adjustments may require tests for analogous aspects. If possible, specific tests should be used. For example, approaching a given setting from both above and below the setting might be appropriate for testing play or hysteresis. If specific tests cannot be designed, then simple repeatability tests at several different settings should be carried out.

### **Malfunctions**

The usefulness of a transfer standard is dependent on the degree of confidence that can be put on its ability to reproduce O<sub>3</sub> standards. While any device is subject to occasional malfunctions, frequent malfunctions would certainly compromise the purpose of a transfer standard. Of particular concern are non-obvious type malfunctions that can cause a significant error of which the operator is unaware. While no specific tests for malfunctions are normally used, the tests described above for the other conditions need to be repeated periodically to check for non-obvious malfunctions. After a malfunction has been corrected, the transfer standard must be recertified.

**Other Conditions**

Any other condition that might affect a candidate device or procedure or that might cause change between the point of verification and the point of use should be tested.