EPA United States
Environmental Protection
Agency

Transfer Standards For Calibration of Air Monitoring Analyzers for Ozone

Technical Assistance Document

October 2013

EPA-454/B-13-004
October 2013

Transfer Standards For The Calibration of Ambient Air Monitoring Analyzers For Ozone

Technical Assistance Document

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Research Triangle Park, North Carolina 27711

DISCLAIMER

FOREWORD

This Technical Assistance Document defines, specifies, and formalizes the verification of ozone transfer standards for calibrating ambient ozone analyzers. The procedures and guidance in this document provide monitoring agencies additional flexibility and specific benefits in designing and implementing an effective quality assurance program for their ambient ozone monitoring. This document replaces the 1979 document by the same title (EPA-600/4-79-056). Ultraviolet (UV) photometry has replaced most of the methods described in the 1979 document. This document removes methods no longer in use and updates definitions and procedures as needed.

The original analytical procedure prescribed by the U.S. Environmental Protection Agency (EPA) (under Title 40, Code of Federal Regulations (CFR), Part 50, Appendix D) for certifying local primary O_3 concentrations had been a wet chemical technique based on spectrophotometric analysis of iodine generated by O_3 in neutral buffered potassium iodide (NBKI) and referenced to an arsenious oxide primary standard. EPA has amended these regulations by replacing the NBKI technique with a better technique based on absorption of UV radiation and referenced to the well-established absorption coefficient of O_3 at a wavelength of 254 nm (EPA 1979).

The UV technique requires a stable O_3 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_3 generator at a constant flow rate and discharged into a multiport manifold. The O_3 concentration in the manifold is assayed by the photometer and is available for calibration of O_3 analyzers or verification of transfer standards. To verify some types of transfer standards, some modifications to this system may be required (see Section 3). After the air flow rate is adjusted, the O_3 generator is adjusted to provide the approximate O_3 concentration desired. The UV photometer is then used to measure the UV absorption of the generated concentration at a wavelength of 254 nm. This transmittance measurement, together with the well-established absorption coefficient of O_3 at that wavelength and various instrument parameters, is used to calculate the O_3 concentration by means of the Beer-Lambert absorption law. The accuracy of the photometer is critically important to this technique; however, certain commercial and laboratory photometers have been shown to be adequate to the task.

In 2013, EPA identified some language in the 2010 document that needed revision. The 2010 document included the following sentences in Section 3 and in Appendix B:

“ Only transfer standards that have met the requirements established in 40 CFR Part 50 Appendix D and are either an approved Federal Reference Method (FRM) or Federal Equivalent (FEM) should be used in ambient air monitoring and as such, should meet the qualification requirements described in this Appendix”

Since the guidance allow the transfer standard to be generation device and a analyzer, just a analyzer, or just a generation device, there will be cases where the transfer standards will not be FRM/FEM devices. Therefore, this wording in Section 3 and Appendix B was removed, and additional minor edits were made to this version

PREFACE

Ultraviolet (UV) photometry is currently the most accepted technique for assaying ozone calibration atmospheres in the sub-ppm concentration range to obtain primary ozone standards. Accordingly, the U.S. Environmental Protection Agency has adopted UV photometry as the prescribed procedure for the calibration of reference methods to measure ozone in the atmosphere.

The ozone calibration procedure specifically allows the use of transfer standards for calibrating ambient ozone monitors. Such transfer standards, however, must be suitably referenced to a UV standard of higher authority and traceability.

The U.S. Environmental Protection Agency believes that the use of ozone transfer standards can provide monitoring agencies with a number of worthwhile advantages. However, their use entails a considerable degree of technical expertise in selecting, qualifying, verifying, using, and maintaining the transfer standards. This document offers users technical guidance in these areas.

For the experienced user, this document will help to formalize and standardize the qualification, verification, and use of transfer standards. For the less experienced user, it should serve as a learning aid and an information source.

The accurate, long-term measurement of ozone concentrations in ambient air is not an easy task. Error processes are relentless; the infiltration and magnitude of errors must constantly be held to a minimum to realize quality data. Hopefully, attention to the information and guidance given in this document will help toward that end.

Comments or criticism from readers and users are welcome; any changes resulting from such comments will also be included in any subsequent revision or supplement.

ABSTRACT

On February 8, 1979 (Federal Register, 44:8221-8233), the U.S. Environmental Protection Agency amended Appendix D of Title 40, Code of Federal Regulations (CFR), Part 50, to prescribe a calibration procedure for the calibration of reference methods for measuring ozone in the atmosphere. The procedure is based on the use of ultraviolet (UV) photometry as the authoritative standard for ozone and allows the use of transfer standards for the calibration of ambient ozone monitors, provided such transfer standards are adequately referenced to a UV ozone standard of higher authority (level) and traceability.

This document is intended as a reference aid to help users select ozone transfer standards and reference them to a higher level UV standard. It first describes the theory of traceability, defines ozone transfer standards and then discusses their purpose and role in calibrating ambient ozone analyzers. The various advantages and disadvantages of ozone transfer standards are pointed out to help users determine whether to use a transfer standard or the UV procedure directly. Different types of ozone transfer standards are described, including analytical instruments and ozone generation devices.

The major part of the document is devoted to the procedures necessary to establish the authority of ozone transfer standards: qualification, verification, and periodic reverification. Qualification consists of demonstrating that a candidate transfer standard is sufficiently stable (repeatable) to be useful as a transfer standard. Repeatability is necessary over a range of variables such as temperature, line voltage, barometric pressure, elapsed time, operator adjustments, or other conditions, any of which may be encountered during use of the transfer standard. Tests and possible compensation techniques for several such common variables are provided. Detailed verification procedures are also provided together with the quantitative verification acceptance criteria. Finally, the periodic procedure and specifications necessary to maintain continuous verification of the transfer standard are given.

For convenience, the UV primary ozone standard procedure from 40 CFR Part 50 is reproduced in Appendix A. Other appendices give more specific guidance for the qualification and verification of several common and practical types of transfer standards like ozone generators and ozone analyzers.

This document replaces the 1979 document by the same title (EPA-600/4-79-056). Ultraviolet (UV) photometry has replaced most of the methods described in the 1979 document. This document removes methods no longer in use and updates definitions and procedures as needed.

CONTENTS

FIGURES

TABLES

ACKNOWLEDGMENTS

This Guidance was the product of the combined efforts of the EPA Office of Air Quality Planning and Standards, the Office of Research and Development, the EPA Regional Offices, and the State, Tribal and Local monitoring organizations. The development and review of the material found in this document was accomplished through the activities of the Ozone Traceability Workgroup. The following individuals are acknowledged for their contributions.

State, Tribal and Local Organizations

Anna Kelley, Brian Spreadborough, Ceresa Stewart, David Malorin, Don Gourley, Donald Hammond, Donovan Rafferty, Jeff Wasson, Lynn Geter, Melinda Ronca-Battista, Michael Tolocka, Paul Nichols, Rachael Townsend, Randy Dillard, Rayna Broadway, Robert Russell, Stan Paulsel, Stephanie McCarthy, Yousaf Hameed

EPA Regions

Region	
1	Chris St. Germane
4	Greg Noah, Mike Crowe, Louie Pounds
5	Scott Hamilton
6	John Lay
7	Thien Bui, James Regehr
8	Michael Copeland, Joe Delwiche
9	Mathew Plate

EPA Office of Research and Development – Air Pollution Prevention and Control Division

Paul Groff, Scott Moore

EPA Office of Chemical Safety and Pollution Prevention-Chemical Control Division

Brian Lee

Office of Air Quality Planning and Standards-Air Quality Assessment Division

Lewis Weinstock , Mark Shanis, Dennis Mikel, Dennis Crumpler

SECTION 1

TRACEABILITY AND THE USE OF TRANSFER STANDARDS

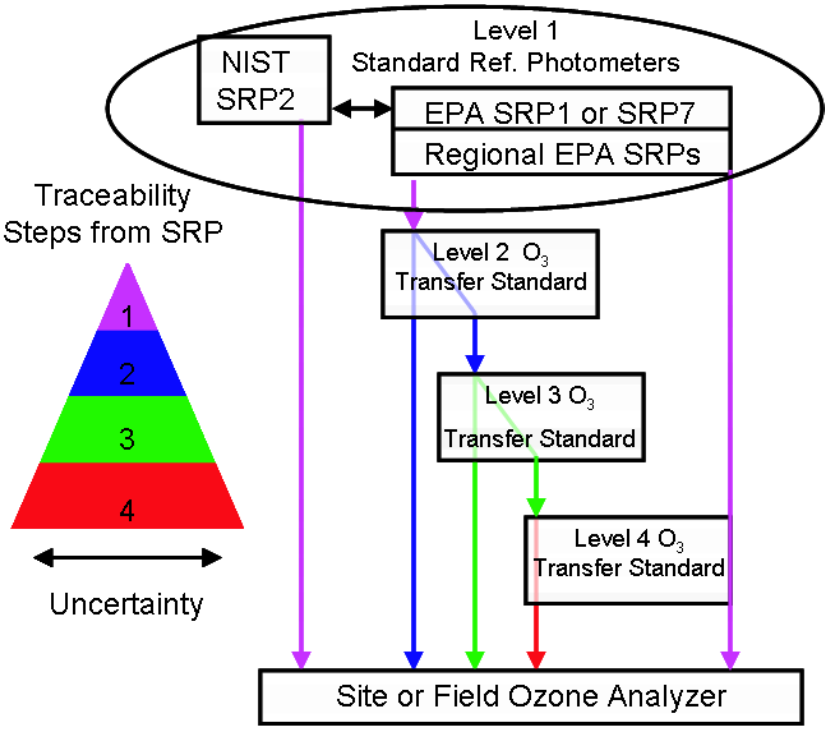

Figure 1.1. Ambient air ozone traceability scheme

In ambient air monitoring applications, precise ozone concentrations called standards are required for the calibration of ozone analyzers. Gaseous ozone standards cannot be stored for any practical length of time due to the reactivity and instability of the gas. Therefore, ozone 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" [1] (ISO).

A claim of traceability requires three elements:

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

Figure 1.1 represents the scheme that will be employed to ensure that the use of ozone transfer standards are applied in a manner that will ensure a specified level of measurement uncertainty and traceability. **Measurement uncertainty** describes a region about an observed value of a physical quantity which is likely to enclose the true value of that quantity. Measurement uncertainty is related with both the systematic and random error of a measurement, and depends on both the bias and precision of the measurement instrument. At each measurement phase (e.g., levels in Fig. 1.1) errors can occur, that in most cases, are additive. The goal of this guidance is to:

---

[1] International Standards Organization (ISO)- International Vocabulary of Basic Terms in Metrology

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

This process is considered performance based. Monitoring organizations that keep measurements well within acceptance limits may be able to extend traceability to more levels (if needed). Transfer standards with considerably more variability may not be able to extend traceability to additional levels. As a general rule of thumb, monitoring organizations should always seek to minimize the use of additional levels of transfer standards.

A **transfer standard** is defined as 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 a higher level and more authoritative standard. The transfer standard's purpose is to transfer the authority of a Level 1 pollutant standard to a remote point where it is used to verify or calibrate an air monitoring analyzer.

Transfer standards may be used for many different purposes. In this document, however, the discussion of transfer standards for ozone (O_3) applies to the family of standards that are used beyond standard reference photometers or Level 1 standards. EPA is attempting to reduce the number of common terms that were used in the past such as: primary standard, local primary standard, transfer standards and working standards that sometimes have been the cause of confusion. This document will identify the family of standard reference photometers (SRPs) as Level 1 standards. Beyond the SRPs, all standards will be considered transfer standards and will be numbered (starting with 2) based on its "distance in the traceability chain" from a verification against a Level 1 standard.

THE FAMILY OF LEVEL 1 STANDARDS- STANDARD REFERENCE PHOTOMETERS (SRPs)

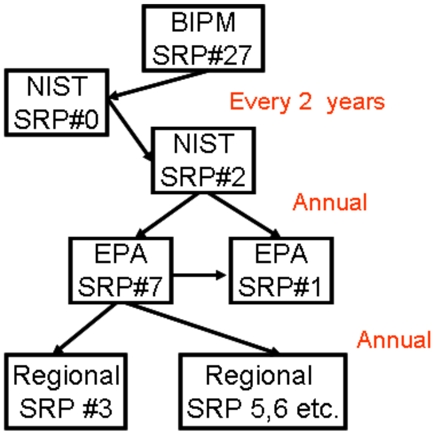

Figure 1.2 Family of Level 1 SRPs

Figure 1.2 represents the family of Level 1 standard reference photometers. Ideally, only one Level 1 (often termed reference standard) exists for each entity to be measured. The International Bureau of Weights and Measures (BIPM)[2] maintains an SRP (#27) as the World's ozone reference standard. All EPA SRPs are now traceable to SRP #27. Each member state of the Convention of the Meter[3] has one laboratory designated to provide traceability to its country. NIST represents that laboratory for the United States. Every 2 years, NIST compares the designated U.S. National ozone reference standard (SRP #2) to SRP #27 indirectly using SRP #0. For ozone, NIST has developed a number of identical SRPs

---

[2] http://www.bipm.org/en/scientific/chem/gas_metrology/ozone_comparisons.html
[3] http://www.speedylook.com/Convention_of_the_Meter.html

(numbered sequentially in order of date assembled) that it distributes to other countries and organizations as well as EPA. Within EPA, the EPA Office of Research and Development Metrology laboratory maintains EPA SRP #1 and #7. Each year it sends both SRPs to NIST for verification. The verification is deemed acceptable when the relationship of SRP #7 or #1 vs. SRP #2 is 1.00 ± 0.01 (slope) and an intercept of 0.0 ± 1 nmol/mol (ppbv). This relates to a bias of 1%. Upon acceptable verification, SRP # 7 is then sent to the EPA Regions to verify the SRPs operated in the Region and used for the ambient air program. Acceptance limits for this verification are basically the same as that for #7 and #1. At some frequency throughout the year, SRP#7 is compared to SRP #1 to ensure it maintains an acceptable level of data comparability. Based on this process, all transfer standards are traceable to BIPM #27.

THE FAMILY OF TRANSFER STANDARDS

The primary functions of a transfer standard are to duplicate and distribute concentration standards to places where comparability to a Level 1 standard is required. The limited number and expense of SRPs makes them impractical for use as transfer standards. Depending on the size and complexity of monitoring organizations, various levels of transfer standards are needed. Small monitoring organizations may be able to provide Level 2 transfer standards to each monitoring site. Large monitoring organizations may bring one Level 2 standard for verification against an SRP and then station this standard at a lab location. In previous guidance documents this Level 2 standard was called the primary standard or the local primary standard because it acted as the reference standard for the monitoring organization. The monitoring organization would then bring one or more Level 3 transfer standards to the Level 2 standard for verification. These Level 3 standards then are compared against the Level 4 standards that are used at the site for routine QC (span checks and one point QC checks) and for calibrating the ozone analyzer. In other cases, where QC standards are not at the monitoring sites, the Level 3 transfer standards may be used to perform the routine bi-weekly QC checks. There are other permutations that may occur with the implementation of these transfer standards.

With each additional level, the number of standards available is multiplied. Each standard is traceable through a chain of “higher” standards to the Level 1 standard. However, as Figure 1.1 indicates, each lower standard in the chain must assume a somewhat greater uncertainty and less authority than the preceding standard. At some point the uncertainty may be beyond acceptable limits.

Level 2 Standards—

As mentioned above, depending on the size of monitoring organizations Level -2 standards can be a monitoring organization’s stationary reference standard or can travel to monitoring sites for verifying and calibrating monitoring instruments. In either case, the Level-2 standard is distinguished as the standard that is transported to a regional SRP for comparison once a year. The SRP comparison is accomplished by comparing a minimum of 7 replicate values of a zero point and a minimum of 6 upscale audit concentrations points. This 7 replicate 6 upscale concentration test is considered a cycle. At a minimum, the SRP comparison will consist of three cycles (approximately 1 hour per cycle). For an acceptable comparison, the average slopes of the 7 replicates for each audit point must be within ± 3% for all three cycles and ± 3ppb at the 0 intercept. There is a separate standard operating procedure (SOP)[4] for this comparison so it is not discussed in any detail in this guidance document. Table 3-1, which summarizes the transfer standard acceptance criteria, includes this comparison as a "verification/reverification to the SRP" and should not be misconstrued as an "initial 6x6 verification". A new Level 2 standard or one that was adjusted or repaired would also be expected to undergo an initial 6x6 verification with an SRP. Using a Level 2 Standard to perform a 6X6 verification of another Level 2 Standard is discouraged. More details of the 6x6 verification are discussed in Section 4.

HOW TRANSFER STANDARDS ARE USED

In use, a transfer standard is first precisely related to a standard at least 1 level above by careful comparison. Then it is transported to the site of the analyzer to be calibrated and used to calibrate the analyzer (if necessary). For some types of transfer standards used in air monitoring, and particularly for O_3 transfer standards, it is highly desirable to recompare the transfer standard to the standard one level above following its return from field use; this recomparison serves as a supplemental check on reliability.

While this concept is relatively simple, the actual use of transfer standards for O_3 is not so simple. Because of the nature of O_3, transfer standards must be capable of accurately reproducing standard concentrations in a flowing system. Ozone transfer standards are complex systems consisting of devices or equipment that generate or assay O_3 concentrations. Consequently, their verification and use must be in accordance with prescribed procedures that are specialized to each specific type of transfer standard. Section 2 describes several different types of O_3 transfer standards and provides general information on the use of each.

Due to the complexity of O_3 transfer standards, there is always some uncertainty in their reliability. Therefore, a major part of the use of an O_3 transfer standard is the need to qualify it, i.e., to determine and prove that it has adequate stability (repeatability) and reliability under conditions of use. General procedures for determining repeatability prior to use, and for assuring reasonable reliability during use are presented in Appendix B.

ADVANTAGES OF OZONE TRANSFER STANDARDS

As noted earlier, since the use of a Level 1 standard is not feasible for field use, the availability of O_3 transfer standards provides an alternative: the Level 2 transfer standard can be used at a fixed location to certify one

---

[4] http://www.epa.gov/ttn/amtic/srpqa.html. Not posted as of this draft since SOP is being updated.

or more O_3 transfer standards which can then be transported to the various field sites and used to calibrate the O_3 analyzers. Some possible advantages from using transfer standards are described below.

Singularity - By using transfer standards, all O_3 analyzer calibrations in a network can be related to a single UV photometer. All measurements in the network are then directly related to a single common standard (Level 2), which can be verified by intercomparison with other UV standards (see below) more easily and more frequently than multiple UV photometers could be. Concern about variations or discrepancies among multiple UV standards is then eliminated.

Level 2 Standard Uncompromised - The use of transfer standards of Level 3 and greater allows the Level 2 standard equipment and procedures to be used at a fixed laboratory location where the conditions of use can be carefully controlled. Neither the equipment nor procedures need to be compromised for field use, and there is no risk of damage to sensitive equipment during transport. Under the controlled conditions and fixed location, variability in the generated authoritative standard will be reduced, providing better accuracy and uniformity among all O_3 analyzers in the network. If doubt arises in the quality of the Level 3 standard due to rough treatment in the field, it can be brought back in for reverification to the Level 2 standard. However, as stated earlier, some smaller monitoring organizations with a small number of ozone sites may have the opportunity to use only Level 2 transfer standards and maintain there traceability at some acceptable frequency with a Level 1 standard.

Economy- Transfer standards (level 3 or greater) may be less expensive than the equipment required for the Level 2 standard . The variety of types of transfer standards offer an agency flexibility in selecting transfer standards based on its available budget, equipment, and expertise. Spare or otherwise idle O_3 analyzers may possibly be converted to transfer standards at little cost, or equipment previously used for O_3 calibrations may be qualified for continued use. Small agencies may even be able to avoid the cost of Level 2 standard equipment by obtaining access to Level 2 standards through Regional Offices, State agencies, or other cooperating agencies. There is also the possibility of purchasing periodic transfer standard verification services from commercial laboratories.

Practicality and Convenience -Transfer standards (level 3 or greater) are generally more rugged and portable than Level 2 standard equipment. They can be designed to be more adaptable to a variety of applications and to be insensitive to various field or transportation conditions, i.e., they can be optimized for field use. They may be easier to use, require less operator training, and be less subject to operator error during use. Multiple transfer standards can be used simultaneously at different locations. Also, transfer standards are often more flexible or adaptable to calibration of various types or models of O_3 analyzers.

Intercomparison - Transfer standards can be used conveniently to intercompare among various Tribal, State and Local, and Federal agencies to assure accuracy and confidence.

DISADVANTAGES OF OZONE TRANSFER STANDARDS

The use of transfer standards is not without some disadvantages. Since a choice is available between using or not using transfer standards, the disadvantages must be weighed carefully against the advantages to determine whether their use is appropriate or cost-effective. Some of the more important disadvantages are described below.

Qualification -Before a device or procedure can be used as a transfer standard, it must be tested and shown to have adequate performance and reliability. It must be repeatable over reasonable periods of time and over the range of conditions encountered during field use and during transport. Qualification of a transfer standard may require a series of initial tests to determine reliability. This problem is addressed in more detail in Appendix B.

Verification of Accuracy/Reliability -Most transfer standards for O_3 involve complex apparatus or procedures or both. As a result, there is always some possibility of error, malfunction, drift, or some other cause for loss of repeatability. In addition, transfer standards have no authority until they are related or verified to a standard at least one level above it by critical comparison. Moreover, they must be reverified periodically to retain their verification. See Section 3, Table 3-1, for the recommended time frames. The time and effort necessary to verify/reverify depends on the type or nature of the transfer standard, and may vary considerably from one type to another.

SECTION 2

TYPES OF TRANSFER STANDARDS FOR OZONE

Several different types of devices or techniques can be considered for use as transfer standards for O_3. They can be loosely grouped into two general categories: ozone analyzers/photometer[5] instruments and generation devices. Within these categories are a variety of techniques and devices that may differ in precision, reliability, portability, economy, and convenience. No single technique or device is necessarily best for all situations. An agency should select an appropriate type of transfer standard based on a complete evaluation of its situation with respect to available funds, available personnel and expertise, equipment on hand, location and distance to field sites, modes of transportation used, number and calibration frequency of analyzers to be calibrated or spanned, etc.

A discussion of the two categories follows, together with examples of some techniques and devices which are currently available and have been used as transfer standards for O_3. Any device or technique to be used must first qualify as an acceptable O_3 transfer standard by demonstrating adequate repeatability (see Appendix B). Then, the transfer standard must be verified by relating it to a standard of higher authority. Sections 3 and 4 provide detailed information on the actual tests and procedures used to qualify, verify, and establish the reliability and accuracy of O_3 transfer standards. Some of the tests are dependent on the level of standard.

OZONE ANALYZERS

Transfer standards which fall into this category employ an instrumental technique to assay stable, flowing O_3 concentrations. The analyzer must be capable of measuring O_3 concentrations adequately over the concentration range of interest, using a well-defined chemical or physical property of O_3. Almost any commercial O_3 analyzer designed for ambient air monitoring, or any other O_3 analyzer that can measure O_3 concentrations suitably in the appropriate concentration range can be used as a transfer standard.

The 1979 version of this document (EPA-600/4-79-056) described two types of analytical instruments: UV analyzers and chemiluminescence analyzers. Due to the ease of use of UV analyzers, chemiluminescence analyzers are not in use and will not be discussed in this document.

As with all O_3 transfer standards, it must be related to a Level 1 standard once it has been qualified. This process is accomplished by simply allowing the transfer standard to sample a portion of the higher level standard O_3 concentration obtained by the prescribed UV technique (see Section 3). Most ozone analyzers provide a measurement of O_3 over a range of concentrations. The entire analytical range

---

[5] Various documents and guidance may use the term photometer and analyzer synonymously. This document will use the term analyzer throughout its sections.

can be verified by comparing the response of the instrument to a series of different O_3 concentrations over the range. (See “Verification” in Section 4.) The verification relationship between the transfer standard and the higher level O_3 standard is then expressed mathematically and by a continuous plot of average instrument response versus higher level standard O_3 concentration, as shown in Figure 4.3.

When an analyzer is used as a transfer standard to calibrate an O_3 monitor at a field site, some additional means must be provided to generate the O_3 concentrations: usually, a UV O_3 generator, an air pump, and an ambient air scrubber to provide clean zero air. The O_3 generator must produce very stable concentrations of O_3 (preferably less than ± 2% change per hour).

There are many UV analyzers in the ambient concentration range commercially available and many contain not only analyzers but also a self-contained O_3 generator that can serve as a transfer standard. They are fairly simple to set up and operate, and are more tolerant of intermittent operation. Although not designed specifically for portability, the UV analyzers may be transported readily and relatively safely if given careful handling; the UV optical systems in these transfer standards, however, must not, be subjected to rough handling. The warm-up and stabilization time of the UV analyzers is normally less than an hour. They are likely to be sensitive to temperature and barometric pressure changes and may require corrections for those parameters. Line voltage sensitivity should also be checked carefully.

It is debatable whether or not the clean air and O_3 generator components should be considered a part of the transfer standard. Ideally, an O_3 transfer standard should be self-contained such that it can completely reproduce O_3 standards. To be self-contained, the O_3 generation components must be an integral part of the transfer standard. An added advantage of this concept is that the O_3 generation components can be inspected, tested, and serviced whenever the analytical instrument is recertified. On the other hand, the authority of the transfer standard is clearly contained in the verification of the analyzer. The O_3 generation components could thus be considered incidental to the use of the transfer standard. Some advantages may therefore be obtained by equipping each field site with its own O_3 generation system – which might also double as a zero-and-span system – and transporting only the analyzer from site to site.

When used as a transfer standard, a UV analyzer may appear to function very much the same as the Level 1 standard (SRP) in the O_3 procedure described in Appendix A. It is therefore easy to confuse the two. The distinction between the two is important and should be clearly understood. When a Level 1 standard is used to generate O_3 concentrations, it must meet all of the specifications prescribed in Appendix A, and the concentration measurements are referenced to the absorption coefficient of O_3. In contrast, an O_3 analyzer used as a transfer standard can only certify an O_3 concentration by previous comparison to a standard of higher authority, reference to the O_3 absorption coefficient is used only indirectly, although it may serve as an internal check of the transfer standard’s reliability (see Section 4). If an analyzer is used as a transfer standard it should be designated as a federal equivalent method. These designations can be found on the AMTIC Website[6]

GENERATION DEVICES

Transfer standards in this category are simply devices that generate accurate O_3 concentrations without having any capability to assay the generated concentration output. The accuracy of these devices depends entirely on their inherent generation stability and reproducibility under changing conditions of use. The most common example of a generation device is the UV (photolytic) O_3 generator. Other types of O_3 generators capable of generating reproducible O_3 concentrations in the appropriate range may also be suitable.

Ozone generator transfer standards consist of an air pump, a device to provide zero air, a flow control system, a means to generate O_3 within the flowing zero air stream, and an output manifold at which the O_3 concentration standard is available for calibration or spanning of field O_3 analyzers. The pump and air scrubber components could be considered ancillary to the O_3 generator system, but ideally these components should be included as integral to the system, since the quality of the zero air and the flow regulation are important to the accuracy of the generation system. If possible, the generation system should be completely self-contained.

Most generation devices have the ability to adjust the O_3 output concentration over a considerable range for convenient calibration of field O_3 analyzers. This adjustment normally has a digital readout, dial or scale associated with it that can be related to a higher authority O_3 standard by a relationship as shown in Figure 4.2. In some generation systems, the output concentration is varied by changing the flow rate, which produces a curved (nonlinear) relationship to the higher authority O_3 standard unless the concentration is plotted versus the reciprocal of the flowrate. Fixed or discretely adjustable O_3 generators produce only one or a few fixed O_3 concentrations that may have to be diluted at the field location to calibrate an O_3 analyzer.

In concept, it would seem that generation devices are well suited as transfer standards for O_3. They are often of relatively simple design, easy to use, moderate in cost, fairly rugged, commercially available, and relatively immune to operator error. In practice, the devices fall somewhat short of the ideal. As noted above, the devices may have no assay capability and depend entirely on their own inherent stability. Consequently, their sensitivity to changing conditions from verification lab to field site and their stability with time must be checked carefully and frequently. Mechanical and electrical integrity and flow

---

[6] http://www.epa.gov/ttn/amtic/criteria.html

stability are also important. Since most generation devices are sensitive to pressure changes (altitude) and often to temperature, corrections for these variables may be necessary. A warm-up period is normally required before the generation device has a stable, repeatable output. Read the manufacturers recommendation and consider local conditions (temperature during transport to monitoring site) on the amount of time necessary for warm-up. With some devices, a restabilization period may be required after each adjustment of the output concentration.

Generation devices are likely to have lamps, glassware, and various electronic components that require reasonably careful handling. Those devices that require dilution of a fixed O_3 concentration must have suitable apparatus and flowmeters to effect accurate dilution, putting an extra burden of accuracy on the operator. Since the generation devices provide their own O_3 output concentrations, a slightly modified procedure is necessary to certify them against a higher authority O_3 standard.

RECOMMENDATIONS ON USE OF SPECIFIC TYPES OF TRANSFER STANDARD DEVICES

Due to the advances in ozone monitoring technology, many of the newer transfer standards include both generators and analyzers. Therefore, it is strongly suggested that:

- Level-2 standards and/or standards used in the verification of other transfer standards include both a generation device and a analyzer.
- Level-3 standards be, at a minimum, an analyzer. The level 3 standard can be a analyzer and generator but should not be just a generator.
- Level-4 and greater can be an ozone analyzer or an ozone generation device.

SECTION 3

SUMMARY SPECIFICATIONS FOR OZONE TRANSFER STANDARDS

As noted in previous chapters, the primary purpose of an O_3 transfer standard is to transfer the accuracy of an O_3 concentration standard of higher authority from one place and time to another. Because a transfer standard has initially (by definition) no authority of its own, its authority must first be established. The essence of establishing the authority of the transfer standard is to establish a high probability or confidence that O_3 concentration standards obtained by means of the transfer standard, under a variety of operational conditions, are very nearly as accurate as the authoritative O_3 standard. This confidence is established first by determining that the transfer standard has adequate reproducibility to **qualify** it as a useful transfer standard, then by **verifying** the transfer standard by relating it to a higher level UV standard, and finally by periodically **reverifying** its accuracy and stability.

This section will first provide a summary description of the specifications for the ozone transfer standards and then provide details on the qualification, verification and re-verification steps. Table 3-1 at the end of this section provide a summary of the specifications.

SUMMARY SPECIFICATIONS

1. **Apparatus** -An O_3 transfer standard should include all basic equipment, materials, and supplies (but not necessarily incidental items) required to carry out its function.

2. **Documentation** -The following comprehensive documentation of an O_3 transfer standard is required:

    2.1. A complete listing and description of all equipment, materials, and supplies necessary or incidental to the use of the transfer standard;

    2.2. A complete and detailed operational procedure for using the transfer standard, including all operational steps, specifications, quality control checks, etc.;

    2.3. Test data, rationale, evidence, and other information indicating that the transfer standard meets the qualification requirements given below;

    2.4. The current verification relationship information (slope and intercept) as described in step 4.6 and applicable to current use of the transfer standard, together with any corrections or restrictions in the operating conditions (temperature, line voltage, barometric pressure, etc.); and

    2.5. A logbook including a complete chronological record of all verification and reverification data, as described under "Verification" and "Reverification" above, as well as all O_3 analyzer calibrations carried out with the transfer standard.

3. **Qualification** —(Details in Appendix B) An O_3 transfer standard must meet the general requirements for qualification; the transfer standard output should not vary by more than ± 4% or ± 4 ppb (whichever is greater) from its indicated value over a stated range of any of the conditions to which it might be sensitive. Qualification was an important step in the initial 1979 guidance since few UV transfer standards were available and monitoring organizations may have been developing these devices internally. It is important that as monitoring organizations plan purchases of new generation transfer standards they consult with the manufacturers on the processes used to qualify the instruments. However, qualifying new instruments can help ensure the instruments will perform under various field conditions that might not get observed during a traditional certification processes described in Section 4 of this document.

4. **Verification**- –(Details in Section 4) Prior to use, an O_3 transfer standard must be verified by establishing a quantitative verification relationship between the transfer standard and the higher level O_3 concentrations obtained by the UV calibration procedure as specified in Appendix D of 40 CFR, Part 50 (EPA 1979). The verification procedure follows:
    4.1 The verification relationship shall consist of the average of 6 individual comparisons of the transfer standard to the authoritative UV O_3 standard system. Each comparison must be carried out on a different day.
    4.2 Each comparison shall consist of at least 6 comparison points at concentrations evenly spaced over the concentration range of the transfer standard, including 0 and 90% (± 5%) of the upper range limit. For the 6 or more comparison points of each comparison, compute the slope and intercept by the least squares linear regression of the transfer standard output (either a generated O_3 concentration or a concentration assay) and the UV authoritative O_3 standard.
    4.3 For the 6 comparisons, compute the average slope ($\overline{\mathrm{m}}$):

$$\overline{\mathrm{m}} = \frac{1}{6}\sum_{i=1}^{6} \mathrm{m}_i \qquad \text{(Eq. 1)}$$

and the average intercept ($\bar{\mathrm{I}}$):

$$\bar{\mathrm{I}} = \frac{1}{6}\sum_{i=1}^{6} \mathrm{I}_i \qquad \text{(Eq. 2)}$$

where m_i and I_i are the individual slopes and intercepts, respectively, of each comparison regression.

4.4 Compute the relative standard deviation of the 6 slopes, (s_m):

$$s_m = \frac{100}{\overline{m}}\sqrt{\frac{1}{5}\left[\sum_{i=1}^{6}(m_i)^2 - \frac{1}{6}\left(\sum_{i=1}^{6} m_i\right)^2\right]}\% \qquad \text{(Eq. 3)}$$

and the standard deviation S_I defined in Equation 4 below for the 6 intercepts:

$$s_I = \sqrt{\frac{1}{5}\left[\sum_{i=1}^{6}(I_i)^2 - \frac{1}{6}(\sum_{i=1}^{6} I_i)^2\right]} \qquad \text{(Eq. 4)}$$

4.5 The value of S_m must be $\leq$ 3.7%, and S_I must be $\leq$ 1.5 (ppb).

4.6 If the transfer standard meets the specifications of 4.5, compute the verification relationship as:

$$\text{Std. } O_3 \text{ conc.} = \frac{1}{\overline{m}} (\text{Indicated } O_3 \text{ conc.} - \overline{I}) \qquad \text{(Eq. 5)}$$

5 **Reverification**[5]—(Details in Section 4) To maintain continuous verification, an O_3 transfer standard must be reverified as follows. In general, O_3 transfer standards should be reverified at the beginning and end of the ozone season or at least every 6 month.

5.1 At the time of reverification, carry out a comparison of the transfer standard to the UV primary standard as prescribed in step 4.2.

5.2 The slope of the new comparison must be within the interval $\overline{m} \pm 0.05\overline{m}$.

5.3 If the transfer standard meets the specification in 5.2, compute a new $\overline{m}$ and a new $\overline{I}$ as prescribed in step 4.3 using the 6 most recent comparisons (running averages).

5.4 Compute a new s_m and S_I as prescribed in step 4.4 using the 6 most recent comparisons.

5.5 If the new s_m and S_I meet the specifications given in 4.5 compute a new verification relationship as prescribed in step 4.6 using the updated $\overline{m}$ and $\overline{I}$.

5.6 If the transfer standard fails any of the reverification specifications, it loses its verification. Reverification then requires repeating all the initial verification steps (steps 4.1 – 4.6).

NOTE- This document does not cover the procedures and requirements of the annual Level-2 standard comparison to the EPA SRPs[6]. Table 3-1 lists acceptance criteria for the comparison.

---

[5] Reverifications are normally considered for Level 3 and 4 standards since a level 2 is usually considered a monitoring organizations "bench standard" while levels 3 and 4 standards are transported to the field.

[6] http://www.epa.gov/ttn/amtic/srpqa.html. Not posted as of this draft since SOP is being updated.

COMPARING LEVEL 3 AND GREATER TRANSFER STANDARDS TO A LEVEL 2 OZONE STANDARD

Basic to the qualification and verification of any O_3 transfer standard is the need to compare the output (either a concentration assay or an O_3 concentration) of the transfer standard to an O_3 standard of higher authority (i.e., the reference standard), so that relationships such as shown in Figures 4.2 and 4.3 can be determined. Exactly how such a comparison is carried out depends on whether the transfer standard is of the assay-type or the O_3-generation type.

Assay-Type Transfer Standards

For transfer standards which provide an assay of an externally generated O_3 concentration, the transfer standard is simply connected to the output manifold shown in Figures 1 and 2 of Appendix A. Make sure that the UV calibration apparatus can supply sufficient flow for both reference and transfer standard photometers. The output of the transfer standard is an indicated concentration (Fig 3.1), which can be compared directly to the primary (reference) standard concentration obtained from the UV calibration system.

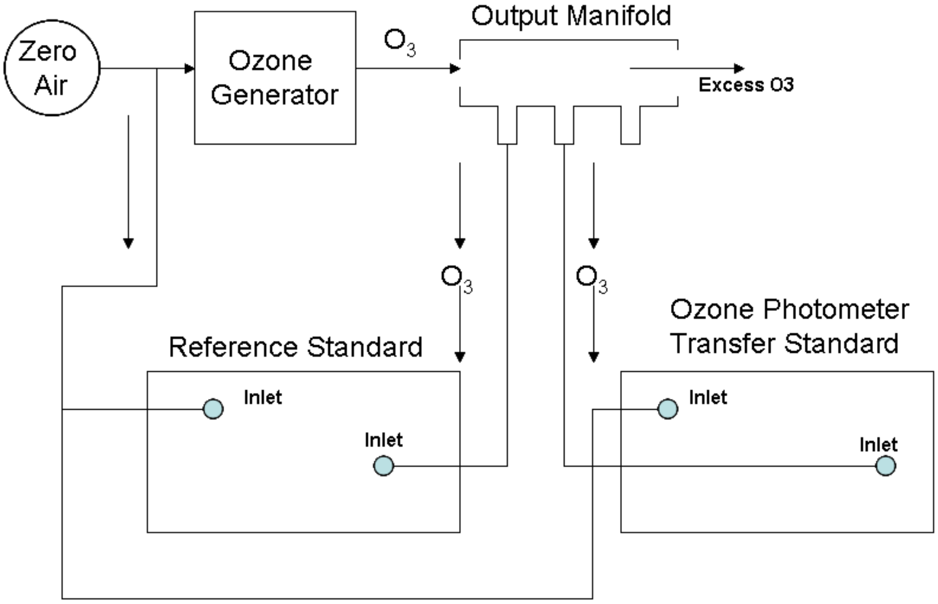

Figure 3.1 Typical sample comparison set-up of an O_3 reference standard to a assay type transfer standard

Ozone-Generation Type Transfer Standards

In comparing a generation-type transfer standard to a UV primary O_3 standard, it obviously cannot be simply connected to the output manifold shown in Figures 1 and 2 of Appendix A; some alternate procedure is necessary. Described below is a procedure that may be used to compare a generation-type transfer standard to a UV primary O_3 standard.

Other procedures are not necessarily precluded, but due concern for accuracy should be exercised. In designing or selecting a transfer standard, preference should be given to transfer standard configurations that allow direct comparison with the photometer, as described in the procedure below. Thus, a transfer standard should have an air supply capable of providing sufficient zero air for the photometer reference cycle without adversely affecting the generated O_3 atmospheres.

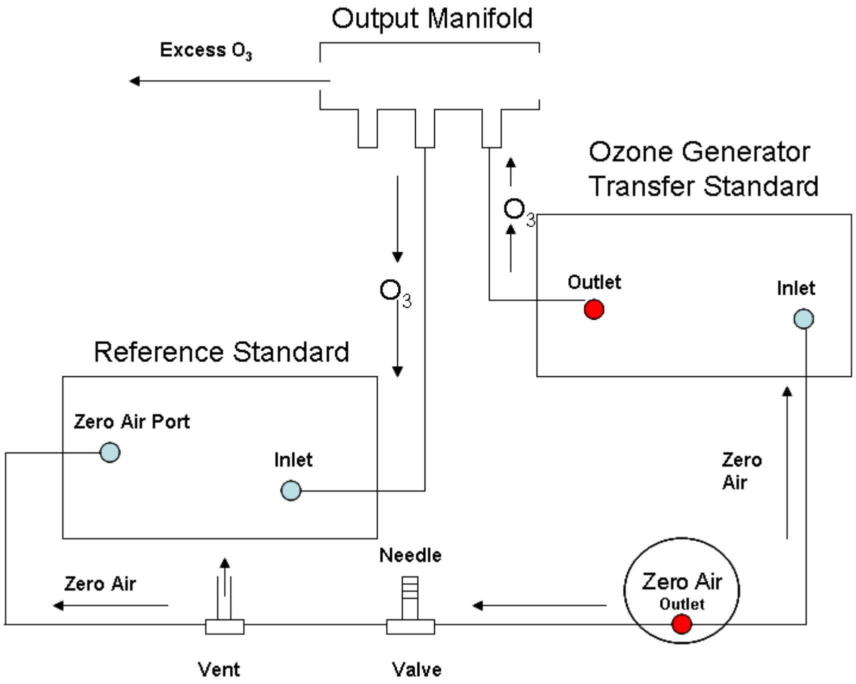

Figure 3.2 Sample comparison set-up of an O3 generation-type transfer standard to a UV reference standard (Procedure 1).

Procedure 1: Assay by Ultraviolet –

The UV procedure for obtaining primary O_3 standards (described in Section 2 and Appendix A) is basically an analytical technique using a UV photometer. The photometer (reference standard) can be used to assay the output concentration of a generation-type transfer standard. To do this, the photometer must be disconnected from its own O_3 generation and output system and connected to the transfer standard output (see Figure 3.2). Care must be exercised to disturb the UV photometer as little as possible from its normal configuration, and to ensure that the output flow of the transfer standard exceeds the flow demand of the UV photometer.

A significant problem arises with this procedure, however. In order to accurately measure I_O for the transmittance (I/ I_O) measurement, the UV photometer must be able to sample zero air from the same source as that used for the generation of the O_3 concentrations (see Appendix A). If the zero air supply of the transfer standard is capable of providing sufficient additional zero air for the photometer, it may be tapped and connected to the two-way valve as shown in Figure 3.2. Care must be exercised in the process to ensure that the transfer standard is not adversely affected.

Table 3-1 Summary Specifications for the Family of Ozone Standards.

Requirement	Frequency	Acceptance Criteria	Information /Action
Regional Standard Reference Photometer (SRP) (Level 1 Standard)			
Verification	1/year	Regression slope = 1.00 ± 0.01 and intercept <± 1 ppb	Usually at a Regional Office and compared against the traveling EPA SRP
Ozone Level 2 Transfer Standard			
Qualification	Upon receipt of transfer standard	±4% or ±4 ppb (whichever greater)	Transfer Standard Doc EPA-454/B-10-001 App B
Verification (6x6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-10-001 Section 4.1
Verification/ reverification to SRP Min- 6 upscale points 7 replicates	After qualification and upon receipt/adjustment/repair 1/year	Each individual point difference ≤ ± 3%	Level 2 standard usually transported to EPA Region's SRP for comparison
(if recertified via a transfer standard)[1/]	1/year	Regression slopes = 1.00 ± 0.03 and two intercepts are 0 ± 3 ppb	
Ozone Transfer Standards Levels 3 and Greater			
Qualification	Upon receipt of transfer standard	± 4% or ±4 ppb (whichever greater)	Transfer Standard Doc EPA EPA-454/B-10-001 App B
Verification (6x6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-10-001 Section 4.1
Reverification to Level 2 standard if transfer standard includes an analyzer (photometer)	Beginning and end of O3 season or 1/6 months whichever less	New slope = ± 0.05 of previous and RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-10-001 Section 4.2
Reverification to Level 2 standard if transfer standard is **only a generator** [2/]	Beginning, each quarter and end of O3 season	New slope = ± 0.05 of previous and RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-10-001 Section 4.2

[1/] Some monitoring organizations have implemented a practice where they send a transfer standard for verification against the Regional SRP rather than the "laboratory bench standard" or the standard the monitoring organization may consider its standard of highest authority. Once the transfer standard is verified against the SRP it's transported back to the monitoring organization where it is immediately compared to the laboratory bench standard. If one reviews Figure 1.1 it becomes evident that using this process in essence makes what the monitoring organization considers its standard of highest authority a level 3 transfer standard. Although it is realized that the practice has been used to "protect" the laboratory bench standard from damage during transport to the Regional SRP, the practice of verifying the monitoring organizations standard of highest authority via a transfer standard is discouraged.

[2/] Since this section includes level 4 transfer standards that may be just generators, more frequent reverification (i.e., quarterly) may be necessary on these standards to ensure stability.

SECTION 4
VERIFICATION & REVERIFICATION PROCESS

The accuracy of a transfer standard is established by (1) relating the output to an O_3 standard of higher authority (level) and (2) demonstrating that the repeatability of the transfer standard is within the limits specified in Section 3.

After a transfer standard has been shown to meet the qualification requirements discussed earlier in this document, the transfer standard must be certified before it can be used. The prescribed formal verification procedure and specifications are set forth in Section 3, but are explained in more detail below. Refer to Section 3 while reading the explanations; the verification procedure step numbers correspond.

4.1 PROCEDURE FOR INITIAL (6x6) VERIFICATION

4.1.1. Verification requires the averaging of 6 comparisons between the transfer standard and a higher level UV O_3 standard. Each comparison must cover the full range of O_3 concentrations and is to be carried out on a different day to a primary standard.

4.1.2. Each comparison must consist of 6 or more individual comparison points, including 0 and 90% (± 5%) of the upper range limit of the transfer standard. The other points must be approximately evenly spaced between these points. For each comparison, the slope and intercept is computed by a least squares linear regression. The result should be similar to the example shown in Figure 4.1. Table 4-1 provides the data set that went into the points derived in Figure 4.1. Most analyzer-type transfer standards will be linear and the linear regression can be calculated directly. However, for non-linear transfer standards or generation-type transfer standards where the output is related to a control setting or an adjustable parameter, a preliminary calibration relationship such as shown in Figure 4.2 is required. Note that the curve shown in Figure 4.2 may have a considerable zero offset and may be nonlinear. This preliminary calibration should also include any necessary correction formulas for defined variables determined during qualification. A smooth curve fitting the points in Figure 4.2 should be drawn or calculated. There are no specific requirements on the form, number of points, linearity, or frequency of repetition for this preliminary calibration. However, excessive inaccuracy in this relationship will show up as variability in the verification comparison and may cause failure of the verification specifications. During the verification comparisons, the preliminary calibration relationship (see Figure 4.2) is used to obtain the indicated O_3 concentration used in the linear regression calculations of Figure 4.1. (Note that Figure 4.1 should be linear even though Figure 4.2 is nonlinear.)

4.1.3. When 6 comparisons as shown in Figure 4.1 have been completed, compute the average slope ($\overline{m}$) from the 6 individual slopes (m_i), and the average intercept ($\bar{I}$) from the 6 individual intercepts, (I_i).

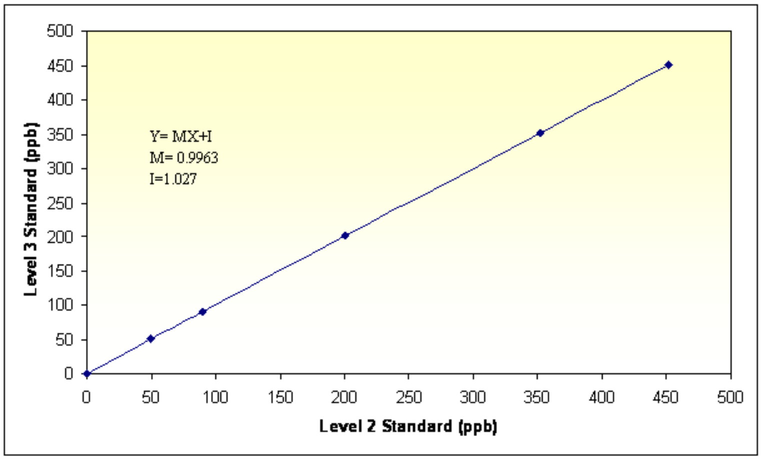

Figure 4.1 Example of a comparison (regression slope and intercept) of Level 3 transfer standard to a Level 2 standard

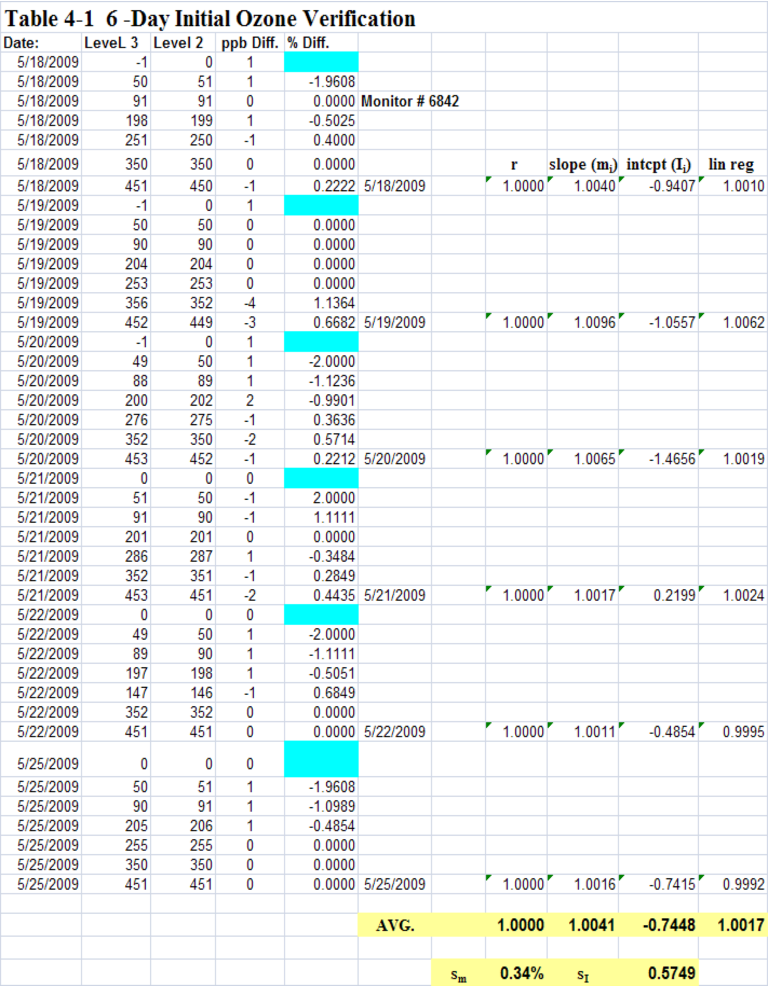

Table 4-1 6 -Day Initial Ozone Verification

Date:	LeveL 3	Level 2	ppb Diff.	% Diff.			r	slope (m_i)	intcpt (I_i)	lin reg
5/18/2009	-1	0	1							
5/18/2009	50	51	1	-1.9608						
5/18/2009	91	91	0	0.0000	Monitor # 6842					
5/18/2009	198	199	1	-0.5025						
5/18/2009	251	250	-1	0.4000						
5/18/2009	350	350	0	0.0000						
5/18/2009	451	450	-1	0.2222	5/18/2009		1.0000	1.0040	-0.9407	1.0010
5/19/2009	-1	0	1							
5/19/2009	50	50	0	0.0000						
5/19/2009	90	90	0	0.0000						
5/19/2009	204	204	0	0.0000						
5/19/2009	253	253	0	0.0000						
5/19/2009	356	352	-4	1.1364						
5/19/2009	452	449	-3	0.6682	5/19/2009		1.0000	1.0096	-1.0557	1.0062
5/20/2009	-1	0	1							
5/20/2009	49	50	1	-2.0000						
5/20/2009	88	89	1	-1.1236						
5/20/2009	200	202	2	-0.9901						
5/20/2009	276	275	-1	0.3636						
5/20/2009	352	350	-2	0.5714						
5/20/2009	453	452	-1	0.2212	5/20/2009		1.0000	1.0065	-1.4656	1.0019
5/21/2009	0	0	0							
5/21/2009	51	50	-1	2.0000						
5/21/2009	91	90	-1	1.1111						
5/21/2009	201	201	0	0.0000						
5/21/2009	286	287	1	-0.3484						
5/21/2009	352	351	-1	0.2849						
5/21/2009	453	451	-2	0.4435	5/21/2009		1.0000	1.0017	0.2199	1.0024
5/22/2009	0	0	0							
5/22/2009	49	50	1	-2.0000						
5/22/2009	89	90	1	-1.1111						
5/22/2009	197	198	1	-0.5051						
5/22/2009	147	146	-1	0.6849						
5/22/2009	352	352	0	0.0000						
5/22/2009	451	451	0	0.0000	5/22/2009		1.0000	1.0011	-0.4854	0.9995
5/25/2009	0	0	0							
5/25/2009	50	51	1	-1.9608						
5/25/2009	90	91	1	-1.0989						
5/25/2009	205	206	1	-0.4854						
5/25/2009	255	255	0	0.0000						
5/25/2009	350	350	0	0.0000						
5/25/2009	451	451	0	0.0000	5/25/2009		1.0000	1.0016	-0.7415	0.9992
					AVG.		**1.0000**	**1.0041**	**-0.7448**	**1.0017**
						s_m	**0.34%**	s_I	**0.5749**	

4.1.4. Compute the relative standard deviation (s_m) of the 6 slopes (m_i) and the standard deviation (s_I) for the 6 intercepts (I_i) defined by equations 3 and 4 in Section 3.

4.1.5. Compare s_m to the 3.7% specification, and compare s_I to the 1.5 (ppb) specification. In the example in Table 4-1, both s_m (0.34%) and s_I (0.57 ppb) were acceptable. If either of these specifications is exceeded, it indicates that the transfer standard has too much variability and corrective action must be taken to reduce the variability before the transfer standard may be certified. (Excessive variability in the UV authoritative standard is possible, although it is much less likely.)

4.1.6. If the specifications are met, the verification relationship for the transfer standard consists of the average slope ($\overline{m}$) and the average intercept ($\overline{I}$) and can be plotted as shown in Figure 4.3. Note that the qualification restrictions must also be included with the verification relationship and should be shown on a plot of the verification relationship as illustrated in Figure 4.3. When the transfer standard is subsequently used, the standard O_3 concentration is calculated from Equation 5.

Transfer Standards Having a Defined Dependence on Some Variable

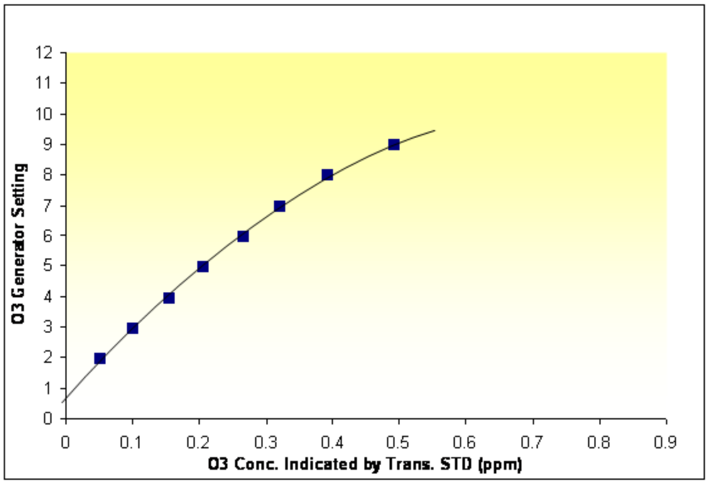

Figure 4.2 Example of a preliminary calibration relationship for an adjustable O_3 device

Verification of transfer standards having a defined dependence on a variable such as barometric pressure or temperature is complicated somewhat by the need to take the variable into account. During verification, the variable must be measured accurately, ideally with the same measuring instrument that will be used during subsequent utilization of the transfer standard. A correction for effect of the variable must then be included, via the preliminary calibration, during the verification comparisons. The final verification relationship must also clearly identify the applicable calibration and correction associated with the transfer standard.

If the effect of the variable is limited to the measurement of gaseous flow rates, the appropriate corrections should be applied to the flowrates during the verification comparisons, and an ordinary comparison similar to Figures 4.1 or 4.2 will result. Where a simple linear dependence on a variable exists, a suitable reference level should be defined (e.g., 1.01 kPa (760 mm Hg) for barometric pressure); then the appropriate mathematical correction (formula) to correct the output from the reference level to any other level within a reasonable range should be specified. An inverse correction is applied to the transfer standard output during establishment of the preliminary calibration (see Figure 4.2) to normalize the output to the reference level. The preliminary calibration relationship is then plotted with the normalized data.

Other approaches can also be used. For example, if the linearity of the transfer standard is not affected by the variable, then the verification relationship can include a “correction factor” relationship as illustrated in Figures B.2 and B.3 of Appendix B. Such a correction factor relationship can be determined either by changing the variable during the preliminary calibrations or by calculation based on data obtained during qualification tests.

Use

After verification, when the transfer standard is used to reproduce O_3 standards, the verification relationship (such as illustrated in Figure 4.3) is used to determine the certified O_3 concentration from the concentration indicated by assay or variable setting. In using transfer standards, it is good practice to try to minimize any change in variables even though the transfer standard may be insensitive to them.

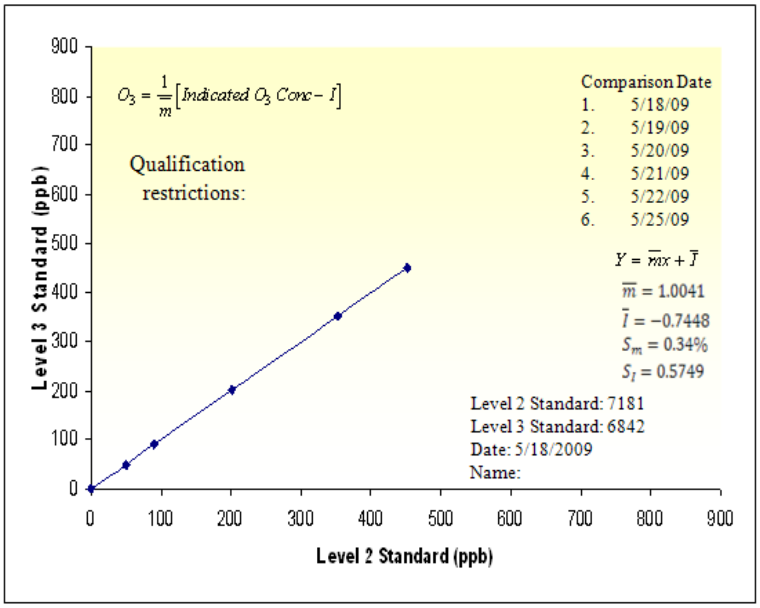

Figure 4.3 Example of a transfer standard certification relationship (average of 6 comparisons, Table 4-1)

This insensitivity is particularly true of transfer standards where there are numerous variables that may not have been included in qualification tests. Special effort should be made to use the same standards, reagents, apparatus, technique, etc., to the greatest possible extent during verification and use. Of course, for any transfer standard which has a defined relationship to some variable, that variable must be accurately measured and the output of the transfer standard must be corrected accordingly.

4.2 PROCEDURE FOR REVERIFICATION

While the principle accuracy of a transfer standard is established during verification, the confidence in that accuracy is maintained by continual reverification to demonstrate stability. The objective is to show, to the greatest extent possible, that the transfer standard did not change significantly between verification and use. However, if the UV authoritative standard is located in a laboratory, the reverification process may always take place under nearly identical conditions (temperature, line voltage, barometric pressure, etc.). Therefore, occasional repetition of the qualification tests discussed in Appendix B may be an important and indispensable supplement to reverification.

Procedure

A verified transfer standard of Level 3 and greater must be reverified at the beginning and end of the ozone season or at least every six months whichever is less. A transfer standard which loses its verification may cause the loss of ambient O_3 measurements made with ambient monitors that were calibrated with the transfer standard. Consequently, a more frequent reverification schedule will reduce the magnitude and risk of any such loss. If a transfer standard in only a generation device (no photometer) it is strongly suggested that more frequent reverifications (i.e., quarterly) occur. More frequent reverification may also provide better accuracy, particularly for transfer standards that show slow but steady change (drift) over long periods of time.

4.2.1 The first step in the reverification procedure is to carry out one comparison (not a complete 6x6) of 6 or more individual comparison points, including 0 and 90% (± 5%) of the upper range limit of the transfer standard to an authoritative standard as specified in step 4.1.2 (see also Figure 4.1).

4.2.2 To maintain verification, the linear regression slope of the new comparison (m) must be within ± 5% of the average slope of the current verification relationship ($\overline{m}$) (i.e., the average slope of the last 6 comparisons). Thus, m must be within the interval $0.95\,\overline{m} \le \overline{m} \le 1.05\,\overline{m}$. A convenient way to monitor the performance of a transfer standard is to plot each new slope as shown in Figure 4.4.

4.2.3 If the new slope is within the ± 5% specification, then a new average slope ($\overline{m}$) and a new average intercept ($\overline{I}$) are calculated using the new comparison and the 5 most recent previous comparisons. Thus $\overline{m}$ and $\overline{I}$ are running or moving averages always based on the 6 most recent comparisons. The new $\overline{m}$ and the new ± 5% limits can also be plotted on the chart shown in Figure 4.4.

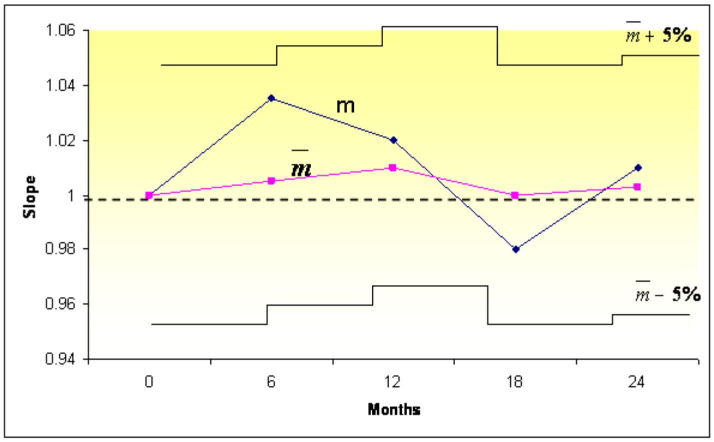

Figure 4.4 Example of a chart showing recertification slope data for a transfer standard

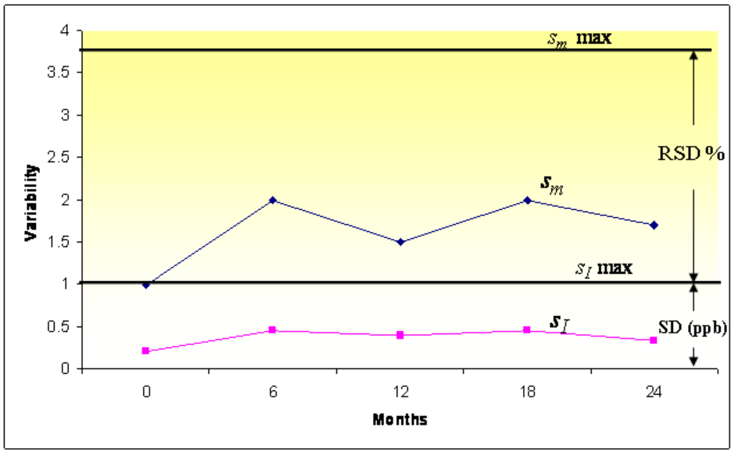

Figure 4.5 Example of a chart showing recertification variability of slope and intercept for a transfer standard

4.2.4 New values for the relative standard deviation of the slopes (s_m) and the quantity (s_I) are calculated based on the new comparison and the 5 most recent previous comparisons. The formulas are equation 3 and 4 in Section 3. These parameters can also be monitored with a chart format similar to Figure 4.5.

4.2.5 The new s_m and s_I must again meet the respective 3.7% and 1.5 SD specifications given in step 4.1.5. If all specifications are met, then a new verification relationship (based on the updated $\overline{m}$ and $\overline{I}$) is established according to step 4.1.6 and illustrated by Figure 4.3.

4.2.6 If a certified transfer standard fails to meet one of the reverification specifications, it loses its verification. Reverification then requires 6 new comparisons according to the entire verification procedure starting at step 4.1. This failure could be due to a malfunction, which obviously should be corrected before repeating the verification procedure. If a transfer standard has been repaired or serviced in a way which could affect its output, the complete verification procedure must also be repeated. Another possible cause for failure of the reverification specifications might be a change in the preliminary calibration (Figure 4.2), which should then be re-established before the verification is repeated.

Cross Checks

Frequently, analyzer -type transfer standard is used with an O_3 generator for which a preliminary calibration such as shown in Figure 4.2 is available (even though the O_3 generator is not certified as a transfer standard). In such a case, any large discrepancy between the two could serve as a warning that the transfer standard may need reverification.

Reverification Tests

Normally, the characteristics of a transfer standard would not be expected to change profoundly or suddenly. For example, a transfer standard that is not initially sensitive to line voltage changes is not likely to become so after a period of use. Malfunctions are a major exception: malfunctions in line voltage regulation or temperature regulation, or other variable control components can easily render a transfer standard sensitive to a variable at any time. Furthermore, the malfunction may not be obvious to the operator and could go undetected for some time. Even a reverification may not disclose such a malfunction. In consequence, some of the qualification tests described earlier should be repeated on some periodic basis. Such tests may be more cursory than the original tests, but are nevertheless important. Other techniques include warning lights or operation indicators on components that are critical to regulatory functions and that might otherwise provide no indication of malfunction. A user should always be somewhat skeptical that a transfer standard is operating properly.

APPENDIX A
ULTRAVIOLET PHOTOMETRIC PROCEDURE FOR PRIMARY OZONE STANDARDS[1]

NOTE: No changes have been made to this Appendix since it reflects what is currently in 40 CFR Part 50 Appendix D

CALIBRATION PROCEDURE

1. Principle. The calibration procedure is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O_3 at 254 nm, (2) the optical path length (ℓ) through the sample, (3) the transmittance of the sample at a wavelength of 254 nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_O, where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample and I_O is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_O. The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha C \ell}$$

(eq. 1)

where:

α = absorption coefficient of O_3 at 254 nm = 308 ± 4 $atm^{-1}\ cm^{-1}$ at 0°C and 760 torr. (1, 2, 3, 4, 5, 6, 7)

C = O_3 concentration in atmospheres

ℓ = optical path length in cm

In practice, a stable O_3 generator is used to produce O_3 concentrations over the required range. Each O_3 concentration is determined from the measurement of the transmittance (I/I_O) of the sample at 254 nm with a photometer of path length ℓ and calculated from the equation,

---

[1] Extracted from the Code of Federal Regulations, Title 40, Part 50, Appendix D, as amended February 8, 1979 (Federal Register, 44:8221-8233).

$$c(\text{atm}) = -\frac{1}{\alpha\ell}\left(\ln\frac{I}{I_0}\right) \tag{2a}$$

or,

$$c(\text{ppm}) = -\frac{10^6}{\alpha\ell}\left(\ln\frac{I}{I_0}\right) \tag{2b}$$

The calculated O_3 concentrations must be corrected for O_3 losses which may occur in the photometer and for the temperature and pressure of the sample.

2. Applicability. This procedure is applicable to the calibration of ambient air O_3 analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 8.

3. Apparatus. A complete UV calibration system consists of an ozone generator, an output port or manifold, a photometer, an appropriate source of zero air, and other components as necessary. The configuration must provide a stable ozone concentration at the system output and allow the photometer to accurately assay the output concentration to the precision specified for the photometer (3.1). Figure 1 shows a commonly used configuration and serves to illustrate the calibration procedure which follows. Other configurations may require appropriate variations in the procedural steps. All connections between components in the calibration system downstream of the O_3 generator should be of glass, Teflon, or other relatively inert material. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 9. For verification of transfer standards which provide their own source of O_3, the transfer standard may replace the O_3 generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

3.1 UV photometer. The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 1. It must be capable of measuring the transmittance, I/I_O, at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O_3 is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O_3 from contact with cell walls and gas handling components. See Reference 9 for additional information.

3.2 Air flow controllers. Devices capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

3.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

3.4 Output manifold. The output manifold should be constructed of glass, Teflon, or other relatively inert material, and should be of sufficient diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

3.5 Two-way valve. Manual or automatic valve, or other means to switch the photometer flow between zero air and the O_3 concentration.

3.6 Temperature indicator. Accurate to ±1°C.

3.7 Barometer or pressure indicator. Accurate to ±2 torr.

4. Reagents.

4.1 Zero air. The zero air must be free of contaminants which would cause a detectable response from the O_3 analyzer, and it should be free of NO, C_2H_4, and other species which react with O_3. A procedure for generating suitable zero air is given in Reference 9. As shown in Figure 1, the zero air supplied to the photometer cell for the I_O reference measurement must be a derived from the same source as the zero air used for generation of the ozone concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of ozone, see Reference 8 for guidance on meeting this requirement.

5. Procedure.

5.1 General operation. The calibration photometer must be dedicated exclusively to use as a calibration standard. It should always be used with clean, filtered calibration gases, and never used for ambient air sampling. Consideration should be given to locating the calibration photometer in a clean laboratory where it can be stationary, protected from physical shock, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

5.2 Preparation. Proper operation of the photometer is of critical importance to the accuracy of this procedure. The following steps will help to verify proper operation. The steps are not necessarily required prior to each use of the photometer. Upon initial operation of the photometer, these steps should be carried out frequently, with all quantitative results or indications recorded in a chronological record either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer is established, the frequency of these steps may be reduced consistent with the documented stability of the photometer.

5.2.1 Instruction manual: Carry out all set-up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

5.2.2 System check: Check the photometer system for integrity, leaks, cleanliness, proper flowrates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

5.2.3 Linearity: Verify that the photometer manufacturer has adequately established that the linearity error of the photometer is less than 3%, or test the linearity by dilution as follows: Generate and assay an O_3 concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and reassay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows:

$$E = \frac{A_1 - A_2 / R}{A_1} \times 100\%$$

(3)

where: E = linearity error, percent

A_1 = assay of the original concentration

A_2 = assay of the diluted concentration

R = dilution ratio = flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 9.

5.2.4 Intercomparison: When possible, the photometer should be occasionally intercompared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 Ozone losses: Some portion of the O_3 may be lost upon contact with the photometer cell walls and gas handling components. The magnitude of this loss must be determined and used to correct the calculated O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 Assay of O_3 concentrations.

5.3.1 Allow the photometer system to warm-up and stabilize.

5.3.2 Verify that the flowrate through the photometer absorption cell, F_p, allows the cell to be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

5.3.3 Insure that the flowrate into the output manifold is at least 1 liter/min greater than the total flowrate required by the photometer and any other flow demand connected to the manifold.

5.3.4 Insure that the flowrate of zero air, F_Z, is at least 1 liter/min greater than the flowrate required by the photometer.

5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then F_Z. The two photometer readings must be equal ($I = I_o$).

NOTE: In some commercially available photometers, the operation of the two-way valve and various other operations in section 5.3 may be carried out automatically by the photometer.

5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of I_o.

5.3.8 Actuate the two-way valve to allow the photometer to sample the ozone concentration until the absorption cell is thoroughly flushed and record the stable measured value of I.

5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 9 for guidance.)

5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(-\frac{1}{\alpha\ell}\ln\frac{I}{I_0}\right)\left(\frac{T}{273}\right)\left(\frac{760}{P}\right)\left(\frac{10^6}{L}\right) \quad (4)$$

where: $[O_3]_{OUT}$ = O_3 concentration, ppm

α = absorption coefficient of O_3 at 254 nm = 308 atm^{-1} cm^{-1} at 0°C and 760 torr

ℓ = optical path length, cm

T = sample temperature, K

P = sample pressure, torr

L = correction factor for O_3 losses from 5.2.5 = (1-fraction O_3 lost)

NOTE: Some commercial photometers may automatically evaluate all or part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For "automatic" photometers which evaluate the first term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O_3 concentration standards as necessary by repeating steps 5.3.6 to 5.3.10 or by Option 1.

5.4 Verification of transfer standards. A transfer standard is certified by relating the output of the transfer standard to one or more ozone standards as determined according to section 5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 8 for guidance.

5.5 Calibration of ozone analyzers. Ozone analyzers are calibrated as follows, using ozone standards obtained directly according to section 5.3 or by means of a certified transfer standard.

5.5.1 Allow sufficient time for the O_3 analyzer and the photometer or transfer standard to warm-up and stabilize.

5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

5.5.3 Generate an O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

5.5.4 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response}\,(\%\text{scale}) = \left(\frac{[O_3]_{OUT}}{URL} \times 100 \right) + Z \tag{5}$$

where: URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.5.2 to 5.5.4.

5.5.5 Generate several other O_3 concentration standards (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 concentration and the corresponding analyzer response.

5.5.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.5.7 Option 1: The various O_3 concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O_3 concentration generated in steps 5.3.6 and 5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system may be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT}\left(\frac{F_0}{F_0 + F_D}\right) \tag{6}$$

where: $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm
F_O = flowrate through the O_3 generator, liter/min
F_D = diluent air flowrate, liter/min

REFERENCES FOR APPENDIX A

1. E.C.Y. Inn and Y. Tanaka, "Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions". *J. Opt. Soc. Am.,* 43,870 (1953).

2. A.G. Hearn, "Absorption of Ozone in the Ultraviolet and Visible Regions of the Spectrum", *Proc. Phys. Soc.* (London), 78,932 (1961).

3. W.B. DeMore and O. Raper, "Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon", *J. Phys. Chem.,* 68,412 (1964).

4. M. Griggs, "Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions", *J. Chem. Phys.,* 49,857 (1968).

5. K.H. Becker, U. Schurath, and H. Seitz, "Ozone Olefin Reactions in the Gas Phase. 1. Rate Constants and Activation Energies", *Int'l.* J. *Chem. Kinetics,* VI,725 (1974).

6. M.A.A. Clyne and J.A. Coxom. "Kinetic Studies of Oxy-Halogen Radical Systems", *Proc. Roy. Soc.,* A3O3,207 (1968).

7. J.W. Simons, R.J. Paur, H.A. Webster, and E.J. Bair, "Ozone Ultraviolet Photolysis. VI. The Ultraviolet Spectrum", *J. Chem. Phys.,* 59, 1203 (1973).

8. "Transfer standards for Calibration of Ambient Air Monitoring Analyzers for Ozone", EPA publication available from EPA, Department E (MD-77), Research Triangle Park, North Carolina 27711.

9. "Technical Assistance Document for the Calibration of Ambient Ozone Monitors", EPA publication available from EPA, Department E (MD-77), Research Triangle Park, North Carolina 27711.

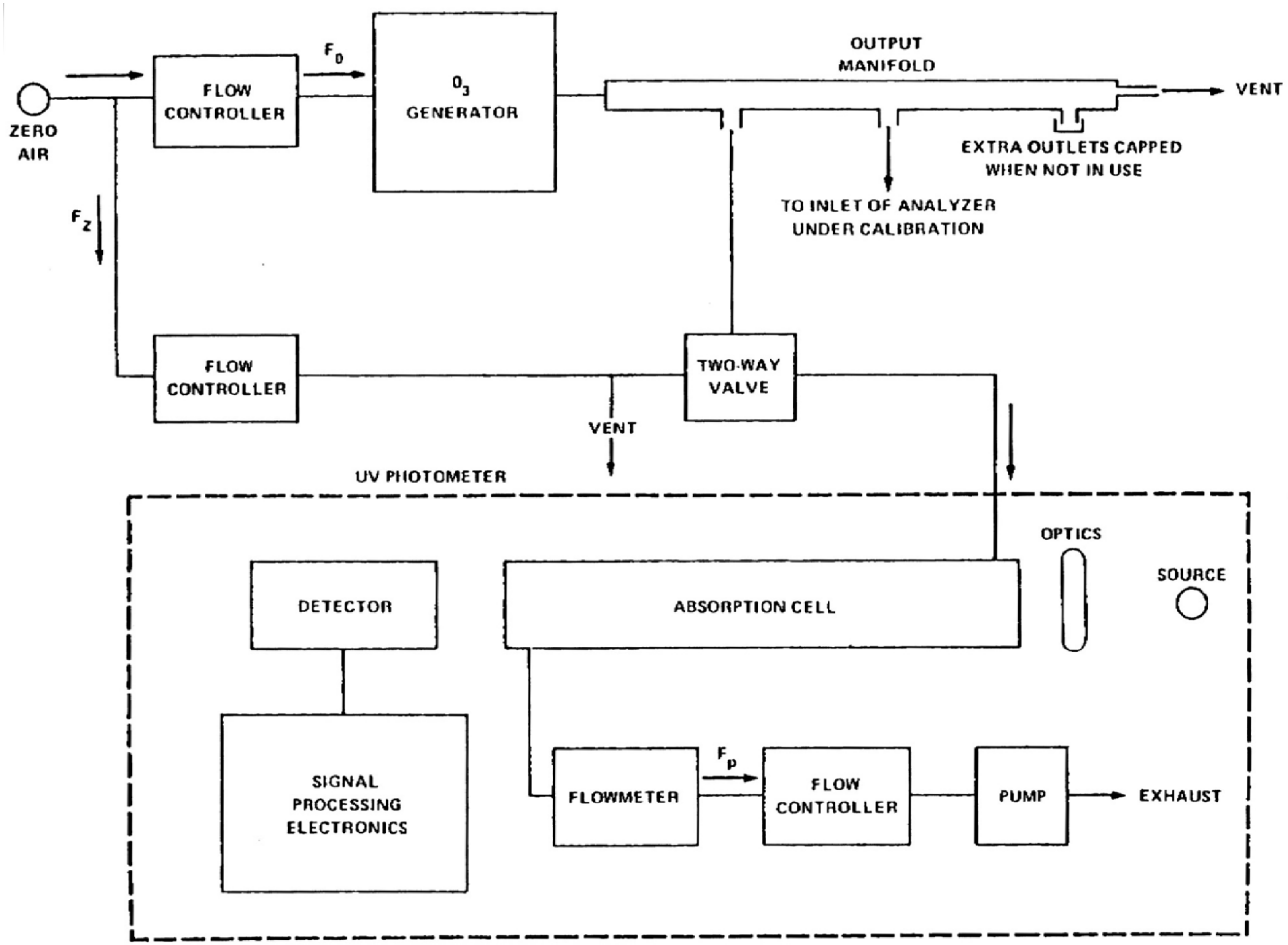

Figure 1. Schematic diagram of a typical UV photometric calibration system.

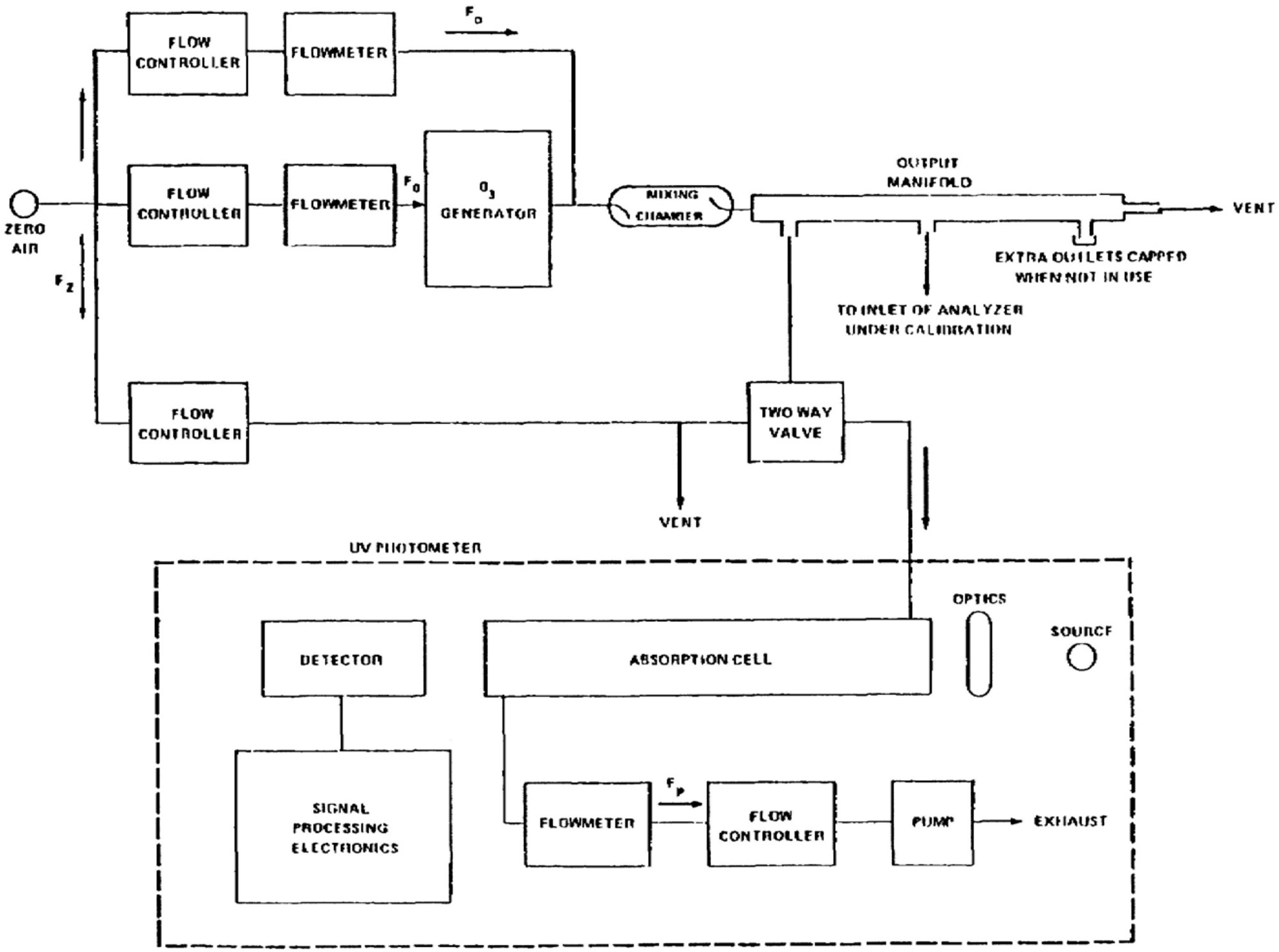

Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).

APPENDIX B
QUALIFICATION PROCESS

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_3 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 ± 4% or ± 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 of 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. Specific recommendations for the common O_3 generators, and O_3 analyzer transfer standards are provided in the appropriate Appendices.

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 ± 4% or ± 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 ± 4% or ± 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_3 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^o 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.

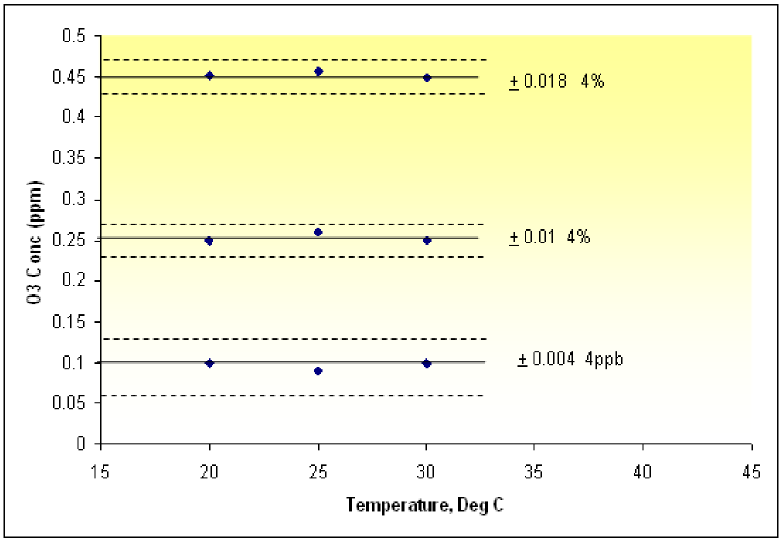

Figure B.1 **Example of temperature qualification test results showing no dependence on temperature.**

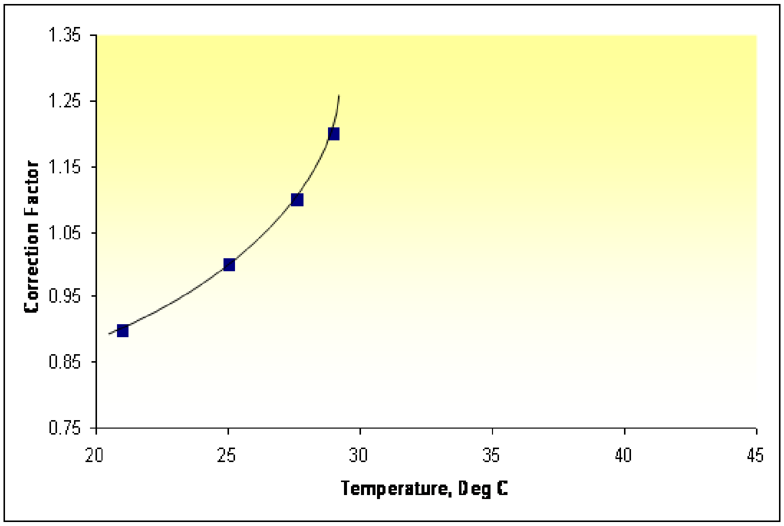

Figure B.2 **Example of a temperature dependence quantitatively defined correction factor.**

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_3 concentration at any temperature in the range (see Figure B.2). The correction formula or curve must be accurate within ± 4% or ± 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.

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_3 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_3 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_3 concentrations at altitudes significantly above sea level, the 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 µg/m^3 are related to pressure. (However, the µg/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.)

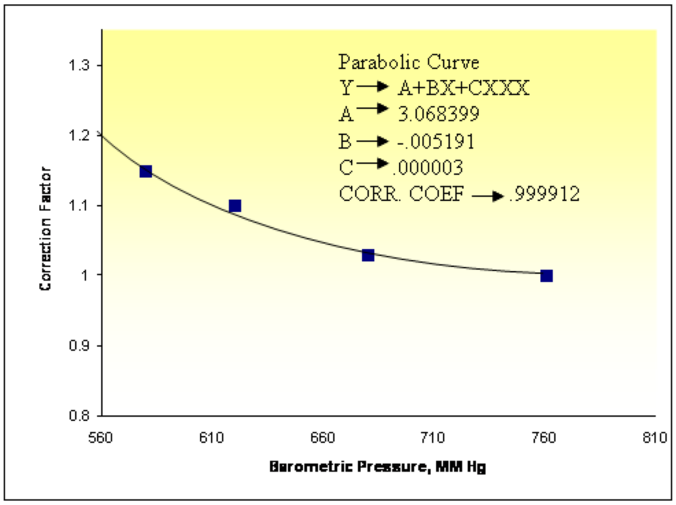

Figure B.3 Example of a defined barometric pressure dependence

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_3 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_3 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 ± 4% or ± 4 ppb specification.

Variability

The adequacy of the relationship between a transfer standard and a authoritative reference O_3 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_3 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:

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

Where: n = number of comparisons

y_i = O_3 concentration indicated by the transfer standard

Determine the difference between each concentration indicated by the transfer standard and the average concentration (y_i − Ave). Each difference must be less than ± 5% of the average (for concentrations over 0.1 ppm) or less than ± 5 ppb (for concentrations less than 0.1 ppm).

For this test, the acceptable limits are ± 5% or ± 5 ppb rather than ± 4% or ± 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 (such as an adjustable O_3 generator) 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_3 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.

Page intentionally left blank

APPENDIX C

VERIFICATION OF AN OZONE GENERATOR AS A TRANSFER STANDARD

Following the specifications in Section 3 and the guidance in Section 4, this appendix attempts to provide more specific instructions for verifying an O_3 generator as a transfer standard.

This appendix assumes that the O_3 generator is of the common UV lamp type. The generator has a means to adjust the O_3 concentration over a convenient range without changing the flowrate, but the device has no means to assay the output O_3 concentration.

PRELIMINARY REQUIREMENTS

The first requirement is a source of zero air. A means of reasonable flow regulation for the zero air is also needed, since the concentration of O_3 generated by the UV lamp varies with flow. Some commercial O_3 generation systems may include some or all of the required zero air source and flow components. Otherwise, the zero air subsystem must be provided by the user. Scrubbed ambient air is preferable to cylinder zero air as the latter may vary in oxygen content or impurity level from one cylinder to another. Decide whether or not the zero air subsystem is to be an integral part of the transfer standard. If not, the flow regulation and flow monitoring components at least should be integral. Be aware that differences in zero air from one zero air system to another may affect the repeatability of the O_3 generator.

The O_3 generator also needs an output manifold which meets the requirements specified in Appendix A. The manifold may be as simple as a tee where one of the legs serves as a vent.

Access to a UV calibration system as described in Appendix A is required for verification of the transfer standard and is also recommended for the qualification tests. Review the O_3 procedure for comparing the output of an O_3-generation-type transfer standard to a UV authoritative reference O_3 standard (see Section 3). Review any operation information or instructions provided by the manufacturer of the O_3 generator to become familiar with its operation.

Review the documentation requirements specified in Section 3 and complete item 2.1.

QUALIFICATION

The next step is to qualify the transfer standard by demonstrating that it is repeatable to within the qualification specifications given in Section 3 (± 4% or 4 ppb, whichever is greater). The variables likely to affect an O_3 generator are the same as those discussed generally below. Refer to Appendix B for additional guidance on each of the qualification tests.

Before starting qualification tests, first prepare a tentative preliminary calibration relationship as shown in Figure 4.2, where the O_3 output concentration is related to the O_3 adjustment setting. Although you may want to prepare a more complete preliminary calibration relationship after qualification, this tentative relationship is necessary to carry out the qualification tests. Prepare the relationship as shown in Figure 4.2 by plotting the transfer standard's output concentration as measured by the UV reference system at various O_3 settings. Note the temperature, barometric pressure, line voltage, and other pertinent conditions. During the qualification tests, use this preliminary relationship to determine each "indicated output" from the transfer standard for a given setting of the concentration adjustment (i.e., sleeve setting or current setting).

QUALIFICATION TESTS

Temperature

If possible, select an O_3 generator which has temperature regulation, preferably one which has a temperature indicator or other warning device to indicate whether the temperature regulator is working properly. Keep in mind that such systems will require a warm-up period before the temperature stabilizes.

Select a temperature range over which the O_3 generator is to be qualified. Temperatures from 20 to 30°C (68 to 86°F) might be appropriate, or possibly 15 to 30°C (59 to 86°F). To show how the indicated output of the generator varies as the temperature changes, test the generator over this temperature range at several O_3 concentrations as suggested by Figure B.1. Be sure (1) that the proper temperature and pressure corrections are made to the UV standard, (2) that the O_3 generator is allowed to equilibrate each time the temperature is changed, and (3) that the O_3 setting is repeated precisely for each different temperature. If the manufacturer has tested the O_3 generator (or one like it), only enough tests are needed to show that the generator is operating properly and meets the specifications.

If the O_3 generator's actual output concentration does not vary more than ± 4% over the entire temperature range, then it is qualified over that temperature range. If it does not meet those specifications, the following options are available:

a) determine if the generator has a malfunction or inadequacy, attempt to correct it, and then retest it;
b) reduce the temperature range to a range over which the generator does meet the specifications (this may inconveniently restrict the subsequent use of the generator); or
c) attempt to determine, either analytically or empirically, the temperature-output relationship such as illustrated in Figure B.2. When this relationship is used to calculate a "corrected" indicated output, the

O_3 generator should meet the specifications. If so, this correction formula becomes a necessary and integral part of the transfer standard and must be included with the preliminary calibration relationship (see Figure 4.2) and ultimately with the verification relationship (see Figure 4.3).

Line Voltage

Line voltage tests are conducted in a fashion analogous to the temperature tests, substituting line voltage variation for temperature variation. A range of 105 to 125 volts should be appropriate. A well designed O_3 generator should show little or no sensitivity to line voltages over this range. If the generator does not meet the specifications, you have the same three options as with temperature, plus a fourth option of adding an external voltage regulator.

Barometric Pressure/Altitude

Virtually all UV O_3 generators are sensitive to pressure changes unless they are specifically designed to compensate for pressure effects. If use of the O_3 generator can be restricted to altitudes within a range of about 100 meters (300 feet), the range of pressure variations is only about 2 or 3% (about 1% for altitude variations and about 1 to 2% for normal barometric pressure changes). Under these conditions an uncompensated O_3 generator operating at ambient pressure can be expected to meet the qualification specifications. Pressure changes could then be ignored and no tests would be necessary.

Where a larger altitude range is needed (or for applications requiring more accuracy), the O_3 generator's sensitivity to pressure changes must be compensated, either by design or by defining the pressure-output relationship and developing a correction formula (see Figure B.3).

Testing for pressure sensitivity is most practically carried out by moving both the O_3 generator and the UV standard system to various altitudes. In doing this, be sure (1) that the proper temperature and pressure corrections are made to the UV standard, (2) that the O_3 setting is repeated precisely for each new pressure, and (3) that other variables (temperature, line voltage, etc.) are controlled so that they do not affect the generator. From the test data, determine an appropriate correction formula and include it with the preliminary calibration relationship and then ultimately with the verification relationship.

Elapsed Time

The output of a UV O_3 generator is likely to decrease somewhat with usage time. Comparisons with a UV reference over a period of time are necessary to determine the rate of decay. Then, either the transfer standard can be recertified often enough so that it stays within specifications between verifications, or a correction factor based on elapsed time can be determined and used with the preliminary calibration relationship.

Variability

General variability (variability other than that associated with a specific known variable) is not likely to be a problem with an O_3 generator unless it is very poorly designed. If any of the other qualification tests show variability not strongly correlated with a specific variable, then a test for general variability would be needed. If the generator meets the specifications for the other tests, no specific test for general variability is required.

Relocation

Relocation tests help to establish the ruggedness of the O_3 generator. During the course of the elapsed-time or other tests, move the O_3 generator about as it might be moved during subsequent use to see if any malfunctions, variability, or other dependability problems are observed that might make use of the generator questionable or inconvenient.

Operator Adjustments

Test the O_3 generator for repeatability of O_3 concentration setting. Check each of several settings repeatedly, approaching sometimes from a higher setting and sometimes from a lower setting. Intersperse the various settings. Note if a stabilization period is required for each new setting, or if any other observable peculiarities are evident. A well-designed O_3 generator is not likely to fail this test, but the information obtained will help to achieve better precision.

Malfunctions

There is no special test for malfunctions. During other tests, be observant for any malfunctions that occur or other characteristic weaknesses in the generator that could cause unreliability. Understand the design and operation of the generator so that you can be alert to non-obvious types of malfunctions such as failure of temperature, line voltage, flow or other regulation mechanisms.

Other Conditions

The tests described above should cover the performance variables for most common UV-type O_3 generators. However, new types of generators or unusual generator designs may require additional special tests.

VERIFICATION

Before conducting the verification tests, decide whether a new preliminary calibration relationship (see Figure 4.2) should be prepared.

A new preliminary calibration relationship is advisable if:

a) the transfer standard needs one or more correction formulas for defined-relationship variables;
b) the original relationship was rough, inaccurate, or incomplete;
c) the original relationship indicates output concentrations more than 30% different than the UV standard; or
d) the qualification tests provided other information to suggest that a new relationship should be prepared.

If a new preliminary calibration relationship is needed, prepare it carefully and accurately, including enough points to define it precisely over the entire operating range. Ozone generators that are non-linear or have appreciable variability need additional comparisons to define the relationship precisely. If any correction formulas are needed, clearly specify the conditions at the time the preliminary calibration relationship is established, and be sure that the specified correction formula is accurate. If necessary, various qualification tests should be repeated to verify that the corrections are accurate. Note or clarify any special operating instructions, operating restrictions, limits, or other pertinent information.

When the preliminary calibration relationship has been prepared, proceed to verify the transfer standard as specified in Section 4. It is very important to complete the documentation requirements specified in Section 3.

USE

In using the O_3 generator as a transfer standard, review the guidance in Section 2. Reverify the transfer standard as required by Section 4. Consider occasional cross checks of the transfer standard to other O_3 standards, and occasionally repeat the qualification tests to be sure the transfer standard is maintaining adequate reliability.

This page intentionally left blank.

APPENDIX D

VERIFICATION OF AN OZONE ANALYZER AS A TRANSFER STANDARD

Following the specifications in Section 3 and the guidance in Section 4, this appendix attempts to provide more specific instructions for verifying an O_3 analyzer as a transfer standard.

The analyzer does not have to be a UV-type analyzer; any type of O_3 analyzer may be considered for use as a transfer standard. However, UV-type analyzers may be more readily portable or have other practical advantages over other types of O_3 analyzers.

An analyzer used as a transfer standard should receive special treatment consistent with its authoritative status; careful handling and storage, frequent maintenance and service and operation by a fully competent operator. In particular, the analyzer should not be used for ambient monitoring between uses as a transfer standard, as dust or dirt buildup in the cell and other operational degradation may occur. Where it is necessary to use an analyzer that has had previous service as an ambient monitor, the analyzer should be thoroughly cleaned and reconditioned prior to verification as a transfer standard.

PRELIMINARY REQUIREMENTS

First, a stable source of O_3 to be assayed by the analyzer/transfer standard, and an attendant source of zero air for the O_3 generator are required. Some analyzers have internal or associated O_3 generators that may be used; otherwise, an O_3 generator/zero air system must be provided by the user. In addition, some means of reasonable flow regulation for the zero air is usually needed, since the concentration of O_3 generated by most O_3 generators varies with flow. Decide whether or not the O_3 generation/zero air system is to be an integral part of the transfer standard. If not, arrangements must be made for an adequate O_3 generator/zero air supply at each site where the transfer standard will be used.

The O_3 generator will also need an output manifold meeting the requirements specified in paragraph 3.4 of Appendix A. The manifold may be as simple as a tee where one of the legs serves as a vent.

Access to a UV calibration system as described in Appendix A is required for verification of the transfer standard and is also recommended for the qualification tests. Comparing the output (indicated concentration) of the O_3 analyzer to the UV authoritative reference O_3 standard is easy, as the analyzer is simply connected to the output manifold of the UV authoritative O_3 standard.

Review any operation information or instructions provided by the manufacturer of the O_3 analyzer to become familiar with its operation. Review the documentation requirements specified Section 3 and complete item 2.1.

QUALIFICATION

The next step is to qualify the standard by demonstrating that it is repeatable to within the specifications given in Section 3 (± 4% or ± 4 ppb, whichever is greater). The variables likely to affect an O_3 analyzer are normally the same as those discussed generally in Appendix B and more specifically below. Refer to Appendix B for additional guidance on each of the qualification tests.

Generally, a preliminary calibration relationship (as shown in Figure 4.2) is not necessary for O_3 analyzers, as most analyzers are linear and provide a direct output indication of concentration. The zero and span of the analyzer should be adjusted for approximate calibration (with respect to the UV standard) over the desired concentration range. The final “calibration” of the analyzer is the verification relationship.

An output-indicating device such as a chart recorder or digital meter is a helpful accessory. But, if such an output indicator is used, it should be permanently associated with the transfer standard analyzer and employed during qualification, verification, and use of the analyzer as a transfer standard.

QUALIFICATION TESTS

Temperature

If possible, select an O_3 analyzer that has good temperature regulation (or compensation), preferably one with a temperature indicator or other warning device to indicate whether the temperature regulator is working properly. Keep in mind that temperature regulation systems require a warm-up period before the temperature stabilizes.

Select a temperature range over which the O_3 analyzer is to be qualified. Temperatures of 20 to 30°C (68 to 86°F) might be appropriate, or possibly 15 to 30°C (59 to 86°F). Test the O_3 analyzer over this temperature range at several O_3 concentrations as suggested by Figure B.1 to depict how the indicated output of the analyzer varies as the temperature changes. Be sure (1) that the proper temperature and pressure corrections are made to the UV standard, (2) that the O_3 analyzer is allowed to equilibrate each time the temperature is changed, and (3) that the O_3 analyzer’s span is not adjusted between each different temperature (adjustment of other parameters to nominal values is permitted). If the manufacturer has tested the O_3 analyzer (or one like it), only enough tests are needed to show that the analyzer is operating properly and meets the specifications.

If the O_3 analyzer's indicated concentration does not vary more than ± 4% or ± 4 ppb over the entire temperature range, then it is qualified over that temperature range. If it does not meet those specifications, the following options are available:

a) determine that the analyzer has a malfunction or inadequacy, attempt to correct it, and then retest it;
b) reduce the temperature range to a range over which the analyzer does meet the specifications (this may inconveniently restrict the subsequent use of the analyzer); or
c) attempt to determine, either analytically or empirically, the temperature-output relationship such as illustrated in Figure B.2. When this relationship is used to calculate a "corrected" indicated output reading, the analyzer should meet the specifications. If so, this correction formula becomes a necessary and integral part of the transfer standard and must be included with the ultimate verification relationship (see Figure 4.3).

Line Voltage

Line voltage tests are conducted in a fashion analogous to the temperature tests, substituting line voltage variation for temperature variation. A range of 105 to 125 volts should be appropriate. A well-designed O_3 analyzer should show little or no sensitivity to line voltage changes over this range. If the analyzer does not meet the specifications, the same three options as with temperature are available, plus a fourth option of adding an external voltage regulator.

Barometric Pressure/Altitude

An O_3 analyzer is likely to be sensitive to pressure changes unless it is specifically designed to compensate for pressure effects. If the use of the transfer standard can be restricted to altitudes within a range of about 100 meters (300 feet), the range of pressure variations is only about 2 or 3% (about 1% for altitude variations and about 1 to 2% for normal barometric pressure changes). Under these conditions an uncompensated O_3 analyzer which operates at ambient pressure could be expected to meet the qualification specifications. However, the analyzer should be tested over a normal range of barometric pressure to be sure. Test the analyzer on various days when the barometric pressure is different and plot the results as shown in Figure B.1.

Where a larger altitude range is needed (or for applications requiring more accuracy) the O_3 analyzer's sensitivity to pressure changes may have to be compensated, either by design or by defining the pressure-output relationship and developing a correction formula (see Figure B.3).

Testing for pressure sensitivity is most practically carried out by moving both the O_3 analyzer and the UV standard system to various altitudes. In doing this, be sure (1) that the proper temperature and pressure corrections are made to the UV standard, (2) that the O_3 analyzer is not adjusted between each different pressure, and (3) that other variables (temperature, line voltage, etc.) are controlled so that they do not affect the analyzer. From the test data, determine an appropriate correction formula and include it with the verification relationship.

Elapsed Time

Ozone analyzers operated exclusively as transfer standards are not likely to change much with elapsed time. The specified reverification frequency should be sufficient to compensate for any long-term response changes in the analyzer.

Variability

General variability (variability other than that associated with a specific known variable) is not likely to be a problem with an O_3 analyzer unless it is very poorly designed. If any of the other qualification tests show variability not strongly correlated with a specific variable, then a test for general variability would be needed. Otherwise, if the analyzer meets the specifications for the other tests, no specific test for general variability is required.

Relocation

Relocation tests help to establish the ruggedness of the O_3 analyzer. During the course of the barometric pressure or other tests, move the transfer standard about as it might be moved during subsequent use to see if any malfunctions, variability, or other problems are observed that might make use of the analyzer questionable or inconvenient. Make sure that the zero, span, and other adjustments can be locked so they don’t change when the analyzer is moved.

Operator Adjustments

Test the analyzer for repeatability with respect to any operator settings such as flow or gas pressure. Note if a stabilization period is required after an adjustment. Note any other observable peculiarities. A well-designed O_3 analyzer is not likely to fail this test, but the information obtained will help to achieve better precision.

Malfunctions

There is no special test for malfunctions. During other tests, be observant for any malfunctions that occur or other characteristic weaknesses in the analyzer that could cause unreliability. Understand the design and operation of the analyzer so that you can be alert to non-obvious types of malfunctions such as failure of temperature, line voltage, flow or other regulation mechanisms.

Other Conditions

The tests described above should cover the performance variables for most common types of O_3 analyzers. However, new types of analyzers or unusual analyzer designs may require additional special tests.

VERIFICATION

Before conducting the verification tests, make any zero, span, or other adjustments to the analyzer as necessary so that the analyzer readings are close to the O_3 concentrations obtained from the UV reference standard.

When the adjustments are complete, lock the adjustments, record their values, and proceed to verify the transfer standard as specified in Section 4. If any correction formulas are needed, use them during the verification procedure and clearly specify the conditions at the time of the verification relationship. Be sure that the specified correction formulas are accurate. Note any special operating instructions, operating restrictions, limits, or other pertinent information. It is very important to complete the documentation requirements specified in Section 4.

USE

In using the O_3 analyzer as a transfer standard, review the guidance under “Use” in Section 4. Make any zero, flow, or other adjustments except span adjustment to the values recorded at the time of verification. Reverify the transfer standard as required by Section 4. Consider occasional cross checks of the transfer standard to other O_3 standards, and occasionally repeat the qualification tests to be sure the transfer standard is maintaining adequate reliability.

This page intentionally left blank.

APPENDIX E

GLOSSARY

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 [1]

set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system and the corresponding values realized by standards [2]

Certification

refers to the qualification processes used to determine if a product has passed performance and quality assurance tests stipulated in regulations and nationally accredited test standards, or that it complies with a set of minimum performance criteria designed to ensure acceptability for the products intended use. (see conformity assessment)

the procedure by which written assurance is given that a product or service conforms to a standard or specification [3]

Notes

Certification verifies that a particular product meets a given level of quality or safety, providing the user with explicit or implicit information about the characteristics and/or performance of the product. [3]

Comparability

property of measurement results enabling them to be compared because they are metrologically traceable to the same stated metrological reference

Conformity assessment

is defined in ISO/IEC(1) Guide 2: 1996 as: "any activity concerned with determining directly or indirectly that relevant requirements are fulfilled." Conformity assessment procedures provide a means of ensuring that the products, services, or systems produced or operated have the required characteristics, and that these characteristics are consistent from product to product, service to service, or system to system. Conformity assessment includes: sampling and testing; inspection; certification (of both products and personnel); and quality and environmental system assessment and registration

Standard Reference Photometer (SRP)

Stationary photometers maintained and operated by EPA. They are referenced directly to the NIST primary photometer. Due to the longer UV paths, the SRPs are more accurate and stable than other photometric devices.

Measurement uncertainty

describes a region about an observed value of a physical quantity which is likely to enclose the true value of that quantity

Qualification

process demonstrating that a transfer standard is sufficiently stable (repeatable) to be used as a transfer standard. For ozone transfer standards acceptance is ± 4% or ± 4 ppb whichever is greater, for each condition or variable that may change between point of certification and point of use

Repeatability [2]

property of a measuring system to provide closely similar indications for replicated measurements of the same quantity under repeatability conditions

Standard [2]

embodiment of the definition of a given quantity, with stated value and measurement uncertainty, used as a reference

national standard [2]

measurement standard designated as a national stated metrological reference

primary standard [2]

measurement standard whose quantity value and measurement uncertainty are established without relation to another measurement standard for a quantity of the same kind

NOTES
1. This definition implies that the establishment of a primary measurement standard has to refer to the definition of any unit concerned, particularly an SI unit
2. The first measurement standard of a calibration hierarchy is always a primary measurement standard.

reference standard [2]

standard, generally having the highest metrological quality available at a given location or in a given organization, from which measurements made there are derived

secondary standard [2]

measurement standard whose quantity value and measurement uncertainty are assigned through calibration against, or comparison with, a primary measurement standard for a quantity of the same kind

NOTES
1. The relation may be obtained directly between the primary measurement standard and the secondary measurement standard, or involve an intermediate measuring system
2. calibrated by the primary standard and assigning a measurement result to the secondary standard
3. A measurement standard having its quantity value assigned by a ratio primary measurement procedure is a secondary measurement standard.

transfer standard

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

transfer device [2]

measurement device used as an intermediary to compare measurement standards

Traceability

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 (ISO). A claim of traceability requires three elements:

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

NOTES

1. the unbroken chain of comparisons is called a traceability chain [2].
2. Institutes should maintain as direct a path as possible between their laboratory standards and NIST

Traceability chain [2]

chain of alternating measuring systems with associated measurement procedures and measurement standards, from a measurement result to a stated metrological reference

NOTE

A metrological traceability chain is defined through a calibration hierarchy from the measurement result to the stated metrological reference

Verification [1] [2]

confirmation by examination and provision of objective evidence that specified requirements have been fulfilled.

NOTES

1. comparison made without calibration
2. Verification should not be confused with calibration of a measuring system, or *vice versa*.

Verification of the accuracy of a transfer standard is established by (1) relating the output to a O_3 standard of higher authority (level) and (2) demonstrating that the repeatability of the transfer standard is within the limits

Validation [1] [2]

Confirmation through examination of a given item and provision of objective evidence that it fulfills the requirements for a stated intended use

References

[1]American National Standard Quality Systems for Environmental Data and Technology Programs ANSI /ASQ E4 http://www.asq.org/

[2] ISO Publications, International vocabulary of basic and general terms in metrology, Revision of 1993 edition The abbreviation of this title is VIM http://www.iso.org/iso/pressrelease.htm?refid=Ref1106

[3] National Institute of Standards and technology, The ABC's Of Certification Activities In The United States NBSIR 88-3821 July 1988 **http://ts.nist.gov/standards/information/cerprime.cfm**

United States
Environmental Protection
Agency

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

Publication No. EPA-454/B-13-004
October, 2013