United States
Environmental Protection
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Research and Development

Environmental Monitoring and Support
Laboratory
Research Triangle Park, NC 27711

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September 1979

Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone

Technical Assistance Document

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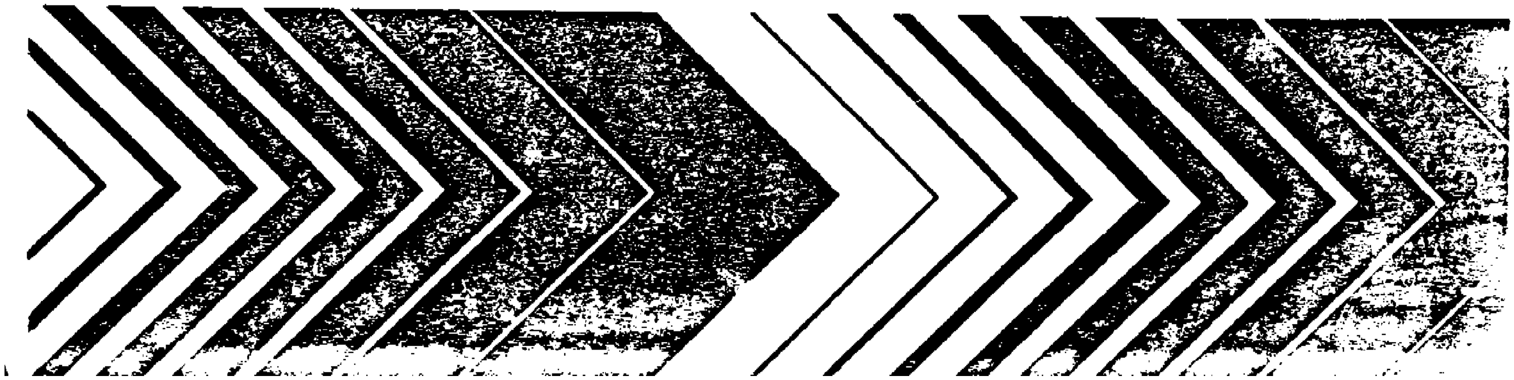

TRANSFER STANDARDS
FOR THE CALIBRATION OF AMBIENT AIR MONITORING ANALYZERS FOR OZONE

Technical Assistance Document

by

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

This Technical Assistance Document defines, specifies, and formalizes the certification 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.

Thomas R. Hauser, Ph.D.
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PREFACE

Ultraviolet (UV) photometry currently appears to be the most accurate 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.

To minimize the immediate impact of the new calibration procedure, as well as to permit flexibility to capitalize on the potential advantages of transfer standards, the new 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 primary ozone standard.

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

For the experienced user, this document will hopefully help to formalize and standardize the qualification, certification, and use of transfer standards. For the less experienced user, it should serve as a learning aid and an information source. The document is quite comprehensive and oriented more toward new users, being primarily a reference document. As it is designed for quick and easy referral, there is some repetition.

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.

I regret that the data represented in the figures are pure fiction. I would have greatly preferred to use figures generated from real data, but such data were not available at the time. When such data become available, a supplement or revision will be considered to include them in the document. 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 new calibration procedure for the calibration of reference methods for measuring ozone in the atmosphere. The new procedure is based on the use of ultraviolet (UV) photometry as a primary standard for ozone. The new calibration procedure specifically allows the use of transfer standards for the calibration of ambient ozone monitors, provided such transfer standards are adequately referenced to a primary UV ozone standard.

This document is intended as a reference aid to help users select ozone transfer standards and reference them to a primary UV standard. It first 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. Several different types of ozone transfer standards are described, including analytical instruments (chemiluminescence and UV analyzers), manual analytical procedures (potassium iodide and gas phase titration procedures), 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, certification, and periodic recertification. 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 certification procedures are also provided together with the quantitative specifications that the transfer standard must meet to achieve certification. Finally, the periodic recertification procedure and recertification specifications necessary to maintain continuous certification 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 certification of several common and practical types of transfer standards — the BAKI manual procedure, two gas phase titration procedures, ozone generators, and ozone analyzers.

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ACKNOWLEDGMENTS

The author wishes to acknowledge the generous and invaluable assistance of Michael Beard, Dr. John Clements, Dr. Richard Paur, Larry Purdue, Jack Puzak, Kenneth Rehme, and the many others who reviewed or otherwise helped in the preparation of this document.

SECTION 1

WHAT IS A TRANSFER STANDARD?

DEFINITION

In ambient air monitoring work, the very low pollutant concentration standards needed to calibrate ambient monitors are often difficult or impossible to contain in a movable form. These concentration standards must therefore be generated in situ in some sort of flowing system. When the monitor to be calibrated is located at a remote monitoring site, it is often more convenient to use a transfer standard rather than a primary standard calibration system. 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 an authoritative master standard.

Transfer standards may be used for many different purposes. In this document, however, the discussion of transfer standards for ozone (O_3) applies only to the final standard used to calibrate an air monitoring analyzer (usually under field conditions).

PURPOSE

The primary functions of a transfer standard are to duplicate and distribute concentration standards to places where comparability to a primary standard is required. Ideally, only one primary standard exists for each entity to be measured. This standard is often maintained by the National Bureau of Standards (NBS). The NBS then makes available a limited number of secondary standards that are carefully compared and certified against the primary standard.

These special transfer standards are known as Standard Reference Materials (SRM). The limited number and expense of SRM's generally make them impractical for the numerous routine applications for standards. The SRM's are normally reserved as local standards and referred to as "local primary standards". These local primary standards are then used to certify local (secondary) transfer standards — often called "working standards" — for routine use. Occasionally, additional intermediate standards are used. With each additional stage, the number of standards available is multiplied. Each standard is traceable through a chain of "higher" standards to the primary standard. However, each lower standard in the chain must assume a somewhat lower accuracy and hence less authority than the preceding standard.

In the less-than-ideal realm of concentration standards for ambient air pollutants, this scheme is complicated by many factors. Not the least of these factors is that available SRM's may be in a form requiring an accurate application technique (e.g., a permeation device must be used in an accurate dilution apparatus to obtain a concentration standard), or that SRM's may not be available at all, as is the case for 0_3. In these situations, the technique or procedure used to generate a local primary standard dynamically becomes critically important. Nevertheless, the function of a transfer standard remains the same: to transfer the authority of a pollutant standard from a locally generated primary standard to a remote point where it is used to calibrate an air monitoring analyzer.

HOW TRANSFER STANDARDS ARE USED

In use, a transfer standard is first precisely related to an SRM or local primary standard by careful comparison. Then it is transported to the site of the analyzer to be calibrated and used to calibrate the analyzer. For some types of transfer standards used in air monitoring, and particularly for 0_3 transfer standards, it is highly desirable to recompare the transfer standard to the local primary standard 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 certification and use must be in accordance with prescribed procedures that are specialized to each specific type of transfer standard. Section 4 describes several different types of O_3 transfer standards and provides general information on the use of each. Sections 5 and 6 provide additional information and specifications on certification of O_3 transfer standards.

Due to the complexity of O_3 transfer standards, there is always some degree of doubt or lack of confidence 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 Section 5. Appendices B, C, D, E, and F contain more specific information on the qualification of several commonly used types of transfer standards for O_3.

SECTION 2

WHY USE AN OZONE TRANSFER STANDARD?

OZONE CONCENTRATION STANDARDS

The reactivity and instability of O_3 precludes the storage of O_3 concentration standards for any practical length of time. It also precludes direct certification of O_3 concentrations as SRM's. Moreover, there is no available SRM which can be readily and directly adapted to the generation of O_3 standards analogous to permeation devices for sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). While an O_3 generating device may someday achieve SRM status, the present situation requires that O_3 standards be generated and certified locally, based on a related chemical or physical primary standard. Dynamic generation of O_3 concentrations is relatively easy with a source of ultraviolet (UV) radiation. But accurately certifying an O_3 concentration as a local primary standard, requires assay of the concentration by a comprehensively specified analytical procedure which must be performed each time a standard is needed.

Until recently, the 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 has 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 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). This new UV technique is described briefly in Section 3 and appears in complete form in Appendix A of this document.

ADVANTAGES OF OZONE TRANSFER STANDARDS

We are assuming here that O_3 concentration standards are needed to calibrate an O_3 analyzer for ambient monitoring. Usually, a number of such analyzers need to be calibrated, and they are located at various field sites separated by appreciable distances. Also, these analyzers presumably require recalibration at periodic intervals. Consequently, a large number of O_3 standards will be required at various times and places. Ozone standards may also be needed to check the span or precision of these analyzers between calibrations.

As noted earlier, primary O_3 standards* must be obtained at the time and place of use by analytically assaying dynamically-generated O_3 concentrations. The primary UV standard procedure could be used at each field site each time an O_3 analyzer required calibration, but the availability of O_3 transfer standards provides an alternative: the primary UV standard procedure can be used at a fixed location to certify one or more O_3 transfer standards which can then be transported to the various field sites and used to calibrate the O_3 analyzers. The choice of whether to use transfer standards or not is up to the monitoring agency, and may depend on a number of factors such as number and location of ambient O_3 analyzers to be calibrated, equipment and expertise available, frequency of calibration, etc. 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

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*From here on, the word "local" has been dropped from "local primary ozone standard". This is largely for convenience, but it also reflects the fact that at present local primary O_3 standards are also absolute primary O_3 standards by default, since no higher O_3 standards are available from NBS.

then directly related to a single common standard†, 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 photometers is then eliminated. If the common UV photometer should ever prove to be significantly inaccurate on some occasion, a single common correction factor could possibly be applied to all network data (provided that historical details of the photometer performance are quantitatively determinate).

Primary Standard Uncompromised

The use of transfer standards allows the primary 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 primary standards will be reduced, providing better accuracy and uniformity among all O_3 analyzers in the network.

Economy

Transfer standards may be less expensive than the equipment required for the primary standard procedure. The variety of types of transfer standards (see Section 4) offer an agency flexibility in selecting transfer standards based on its available budget, equipment, and expertise situation. 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 primary standard equipment by obtaining access to primary standards through Regional Offices, State agencies, or other cooperating agencies. There is

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†Note that the term "standard" is used to refer either to O_3 concentration standards or to the apparatus and procedure used to obtain them.

also the possibility of purchasing periodic transfer standard certification services from commercial laboratories.

Practicality

Transfer standards are generally more rugged and easily portable than primary 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.

Intercomparison

Because of the lack of an NBS SRM for O_3, there is always some doubt as to the accuracy of a locally generated O_3 standard. Transfer standards can be used conveniently to intercompare primary standards among various local, State, and Federal agencies to assure accuracy and confidence.

Convenience

Transfer standards may be more convenient to use than the primary O_3 standard procedure. Multiple transfer standards can be used simultaneously at different locations. The operation of transfer standards may be simpler or more convenient. Commercial transfer standards tend to be more readily available than equipment for the primary O_3 standard procedure. Also, transfer standards are often more flexible or adaptable to calibration of various types or models of O_3 analyzers.

DISADVANTAGES OF OZONE TRANSFER STANDARDS

As might be expected, 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 precisely 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 Section 5.

Certification of Accuracy

Transfer standards have no authority until they are related to a primary standard by critical comparison. Moreover, they must be recompared to the primary standard periodically to retain their certification. The time and effort necessary to certify and recertify a transfer standard against a primary standard depends on the type or nature of the transfer standard, and may vary considerably from one type to another. Sections 5 and 6 address this problem in more detail.

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. Continual tests and checks are necessary to verify and assure the continued accuracy and integrity of the transfer standards. Additional information on quality assurance procedures tailored to the particular type of transfer standard used is contained in Sections 5 and 6.

2. *WHY USE AN OZONE TRANSFER STANDARD?/Disadvantages*

Loss of Accuracy

Use of a transfer standard in lieu of a primary standard will necessarily increase the possible error by some degree. However, an adequate quality assurance procedure will keep the loss of accuracy within reasonable limits.

SECTION 3

PRESCRIBED ULTRAVIOLET PROCEDURE FOR PRIMARY OZONE STANDARDS

The procedure prescribed by EPA regulations for obtaining dynamic primary O_3 concentration standards is specified in Part 50 of Title 40, CFR Appendix D (EPA 1979). This section of the regulation prescribes a new assay technique based on absorption of UV radiation, replacing the previous iodometric technique. The new UV technique is reproduced in Appendix A to this document.

DESCRIPTION

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 certification of transfer standards. (To certify some types of transfer standards, some modifications in this system may be required; see Section 5.) 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. Additional information and guidance on the use of this technique and on selecting a suitable photometer is given in the following sections.

SECTION 4

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 three general categories: analytical instruments, manual analytical procedures, and generation devices. Within these categories are a variety of techniques and devices having widely different degrees of 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 three categories follows, together with examples of some techniques and devices which are currently available and have been used as transfer standards for O_3. Of course, any device or technique to be used must first qualify as an acceptable O_3 transfer standard by demonstrating adequate repeatability. Then, the transfer standard must be certified by relating it to a primary standard. Refer to Sections 5 and 6 for detailed information on the actual tests and procedures used to qualify, certify, and establish the reliability and accuracy of O_3 transfer standards.

ANALYTICAL INSTRUMENTS

Transfer standards which fall into this category employ an instrumental technique to assay stable, flowing O_3 concentrations. The analytical instrument 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. Examples of transfer standards using an instrumental technique would include 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.

As with all O_3 transfer standards, the analytical instrument to be used must be related to a primary standard once it has been qualified. This process is accomplished by simply allowing the analytical instrument to sample or extract, from the output manifold, a portion of the primary standard O_3 concentration obtained by the prescribed UV technique (see Section 3). Most analytical instruments provide a measurement of O_3 over a range of concentrations. The entire analytical range can be certified by comparing the response of the instrument to a series of different O_3 concentrations over the range. (See "Certification" in Sections 5 and 6.) The certification relationship between the analytical instrument and the primary O_3 standard is then expressed mathematically and by a continuous plot of average instrument response versus primary standard O_3 concentration, as shown in Figure 5-8 (pg 5-24).

Alternatively, the analytical instrument can be related to a primary standard at only one or two O_3 concentrations rather than over the entire analytical range, thereby reducing the time required for certification. When subsequently used at a field site, the O_3 concentration must be adjusted until the transfer standard indicates exactly the same response as it did during comparison to the primary standard. Once this identical concentration is obtained, it can be quantitatively diluted with zero air to produce lower concentrations. However, this dilution technique may reduce the accuracy of the field concentrations because of the errors associated with the flow measurements and because of the increased complexity of the field calibration system due to the additional dilution and mixing apparatus.

The analytical instrument itself can only assay existing O_3 concentrations. When 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).

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 certification of the analytical instrument. 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 analytical instrument from site to site.

General information on qualification and certification of analytical instruments is contained in Section 5, and the specifications in Section 6. More specific information for qualifying and certifying an O_3 analyzer as a transfer standard may be found in Appendix F.

Chemiluminescence Analyzers

Chemiluminescence analyzers may be used as transfer standards, but they tend to have several practical disadvantages. Most such analyzers intended for ambient monitoring are designed for continuous operation, and may experience difficulty during intermittent operation. Most require from 1 to 4 hours to warm up and stabilize before highly repeatable performance can be expected. The need for an external supply of ethylene and the potential safety hazards of frequent connection and disconnection of the ethylene source may constitute serious drawbacks. Commonly available commercial analyzers tend to be heavy, not readily portable, and not designed for rapid and frequent start-up and shutdown. Although not particularly delicate, the electronics, photomultiplier, cell assembly, and coolers are not intended to resist the frequent mechanical shocks that might be encountered in transit. Sensitivity to temperature, line voltage, and pressure variations would have to be checked carefully. Also, the cost of chemiluminescence analyzers tends to be quite high.

On the positive side, there is at least one commercially available chemiluminescence O_3 analyzer designed for portable, intermittent operation. It is fairly light weight, battery or line powered, has a self-contained ethylene supply, and claims to have good temperature regulation. Other portable analyzers may be available in the future. Such portable units would alleviate many of the problems mentioned above and could be seriously considered as candidate transfer standards.

Ultraviolet Analyzers

As of this writing, at least one UV analyzer in the ambient concentration range is commercially available. Others are likely in the future. One model includes a self-contained O_3 generator. In general, UV analyzers appear to be better suited for use as transfer standards than chemiluminescence analyzers. The UV units are considerably simpler to set up and operate, do not require ethylene, and are more tolerent of intermittent operation. They are usually self-contained and lighter in weight than the chemiluminescence units. 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 analyzers, 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.

When used as a transfer standard, a UV analyzer may appear to function very much the same as the UV photometer in the O_3 primary standard procedure (see Appendix A). It is therefore easy to confuse the two. The distinction between the two is important and should be clearly understood. When a UV photometer is used to generate primary standard O_3 concentrations, it must meet all of the specifications prescribed in the O_3 primary standard procedure (see 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 primary standard; 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 5).

MANUAL ANALYTICAL PROCEDURES

Transfer standards in this category consist of a combination of laboratory apparatus and a prescribed procedure that is manually executed to assay O_3 concentrations. The procedure 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. Since the apparatus, the execution of the procedure, and possibly even the procedure itself may vary somewhat from user to user, each user must qualify and certify a procedural transfer standard in his own use-situation. Examples of transfer standards using manual analytical procedures include the Boric Acid Potassium Iodide (BAKI) technique, the Gas Phase Titration (GPT) with excess nitrogen oxide (NO) technique, and the GPT with excess O_3 technique. Any other analytical procedure capable of measuring O_3 concentrations adequately in the appropriate concentration range could also be considered a possible transfer standard. Since only O_3 should be present in the atmosphere to be analyzed, interferences are not normally a problem.

At one time, procedures based on the BAKI and GPT techniques were considered candidate procedures for obtaining primary O_3 concentration standards (EPA 1976). A BAKI procedure was even given that status on a temporary basis (EPA 1979). For this reason the two GPT procedures which were previously published by EPA (1976) and the BAKI procedure were all designed to provide measurements of O_3 concentration based on a specified non-O_3 standard. For BAKI, the standard is potassium iodate primary standard, and for GPT the standard is an NO SRM.

When these techniques are used as transfer standards, they are used to transfer the authority of a UV primary standard, though only in a relative sense. The techniques' capability to provide O_3 concentration assays based on an independent standard is not used as a primary part of the transfer standard function. It is important to understand this distinction between the use of these techniques as transfer standards and their use as independent (primary) standards. Except for a temporary exception for BAKI, O_3 monitors in the field must be calibrated by either direct or traceable reference to a primary standard based on UV absorption as specified in the regulations (EPA 1979) and not by reference to one of the independent standards associated with these techniques. Each of the procedures based on BAKI and GPT has now been revised to reflect its use as a transfer standard rather than as a primary standard. These suggested, revised procedures, together with specific guidance on qualification and certification, are included in Appendices B, C. and D.

Once a procedural manual analytical transfer standard has been qualified for use, it is certified. The certification is similar to the certification of an analytical instrument transfer standard: The procedure must be related to the primary standard by direct comparison. Primary O_3 standards over the range of interest are assayed according to the procedure and compared (see Section 5). Then the certification relationship between the analytical procedure and the primary ozone standard is expressed both mathematically and by a continuous plot of the concentrations indicated by the procedure versus the primary ozone concentrations (see Figure 5-8, pg 5-24). Since manual analytical procedures may have considerable variation in response to a fixed O_3 concentration, it may be necessary or advisable to carry out a number of assays on each O_3 concentration to get an accurate certification. In this case, these replicate assays must be specified as a part of the transfer standard procedure and must then be carried out during use of the procedure.

When the procedure is subsequently used at a field site to calibrate an O_3 analyzer, the certification relationship is used to determine the "certified" (standard) O_3 concentration from the concentration indicated by the procedure. Even though the indicated concentration is derived from the procedure's independent standard, the certified concentration to be used for the analyzer calibration must be determined from the certification relationship. Because of the possible variability noted above, it may be advisable to carry out multiple assays on each O_3 concentration at the field site and average them to achieve accurate results.

Boric Acid Potassium Iodide Procedure

Following expiration of the 18-month period, during which time the BAKI procedure is approved for independent certification of primary O_3 concentrations (EPA 1979), this technique may be useful as a transfer standard. Even during the 18-month period the procedure would be more reliable if used as a transfer standard instead of a primary standard. Successful use of the procedure requires thorough familiarization with the procedure and good laboratory technique on the part of the user; careful attention to the procedural instructions is important to control variability. If variability proves to be a problem, multiple samples may be required of each assay concentration.

Nevertheless, use of the BAKI procedure is quite inexpensive and may be advantageous for an agency that has the necessary equipment, is familiar with the procedure or able to train operators, and is willing to spend the time required. The agency, though, must be able to demonstrate acceptable measurement variability. A suggested BAKI procedure incorporating the appropriate restrictions and steps to qualify and certify the procedure as a transfer standard is provided in Appendix B.

As with instrumental transfer standards, the BAKI procedure can only assay existing O_3 concentrations. Hence, an O_3 generator system is needed at the field site to produce O_3 concentrations that are assayed by the procedure and then used to calibrate the O_3 monitor. Whether or not this O_3 generator system should be considered a part of the procedure is discussed briefly above under "Analytical Instruments".

Gas Phase Titration Procedures

There are two separate GPT techniques: in one, an O_3 concentration is titrated with an excess of NO; in the other, an NO concentration is titrated with excess O_3. Suggested procedures and guidance for qualifying, certifying, and using both techniques as transfer standards are presented in Appendices C and D, respectively. As the two procedures are similar they are discussed together here.

Both GPT procedures require the user to be thoroughly familiar with the procedure and the GPT apparatus. Careful attention to the procedural steps and specifications is essential for good results. The need for an NO cylinder standard may affect the portability of the system.

The GPT-NO procedure requires the use of an NO analyzer to measure the titrated NO. This technique is an approved and widely used technique for the calibration of NO_2 analyzers. Many agencies are familiar with the technique, have the required equipment, and may be able to use the same equipment for both NO_2 and O_3 calibrations conveniently at sites which have an NO analyzer.

The excess O_3 GPT procedure does not require the calibrated NO analyzer, and can therefore be used at sites which do not have an NO analyzer. The excess O_3 procedure is somewhat more critical with respect to flow dynamics than the excess NO technique, and particular care should be taken to insure that all procedural specifications are met.

Because of the rather specific flow dynamics requirements of the GPT procedures, and the intimate relationship of the O_3 generator to the GPT system, the O_3 generator is usually considered an integral part of the GPT system and not readily separable. Thus, the GPT procedures, though basically analytical techniques, can assay only those O_3 concentrations generated within the GPT system. The GPT system provides assayed O_3 concentrations convenient for calibrating field O_3 analyzers at an output manifold. Certifying GPT systems is therefore very similar to certifying O_3 generation devices (see Section 5 for details).

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, an air scrubber 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 means to adjust the O_3 output concentration over a considerable range for convenient calibration of field O_3 analyzers. This adjustment normally has a dial or scale associated with it that can be related to primary O_3 standards by a relationship as shown in Figure 5-7 (pg 5-23). In some generation systems, the output concentration is varied by changing the flow rate, which produces a curved (nonlinear) relationship to the primary O_3 standards unless the concentration is plotted versus the reciprocal of 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, but nevertheless warrant serious consideration as transfer standards. 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 certification lab to field site and their stability with time must be checked carefully and frequently (see Section 5). Mechanical and electrical integrity and flow 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 modest but important warm-up period is usual before the generation device has a stable, repeatable output. 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 primary UV O_3 standard (see Section 5).

4. *TYPES OF TRANSFER STANDARDS/Generation Devices*

General information on the qualification and certification of 0_3 generators is contained in Section 5, the specifications in Section 6. More specific information for qualifying and certifying an 0_3 generator as a transfer standard may be found in Appendix E.

SECTION 5

ESTABLISHING THE AUTHORITY OF OZONE TRANSFER STANDARDS

As noted in previous chapters, the primary purpose of an O_3 transfer standard is to transfer the accuracy of a primary O_3 concentration standard 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 primary O_3 standards. This confidence is established first by determining that the transfer standard has adequate reproducibility to qualify it as a useful transfer standard, then by certifying the transfer standard by relating it to a UV primary standard, and finally by periodically recertifying it by reverifying its accuracy and stability.

TRANSFER STANDARD SPECIFICATIONS

Section 6 specifies the formal requirements a transfer standard must meet to be certified for use in calibrating ambient O_3 analyzers. The material in Section 5 explains those requirements more fully, as well as the actual techniques used for qualifying and certifying transfer standards.

COMPARING TRANSFER STANDARDS TO AN ULTRAVIOLET PRIMARY OZONE STANDARD

Basic to the qualification and certification 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 a primary O_3 standard, so that relationships such as shown in Figures 5-7 and 5-8 (pp 5-23 and 5-24) 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 (BAKI, O_3 analyzer), 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 the photometer and the transfer standard. The output of the transfer standard is an indicated concentration, which can be compared directly to the primary standard concentration obtained from the UV calibration system.

Ozone-Generation Type Transfer Standards

Transfer standards that generate O_3 concentrations themselves include O_3 generators and may include those assay procedures which have an integral source of O_3 (such as GPT). 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 are three alternate procedures that may be used to compare a generation-type transfer standard to a UV primary O_3 standard. They are listed in order of preference.

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 first procedure. 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.

Procedure 1: Assay by Ultraviolet--

The UV procedure for obtaining primary O_3 standards (described in Section 3 and Appendix A) is basically an analytical technique using a UV photometer.

The photometer 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 5-1). 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.

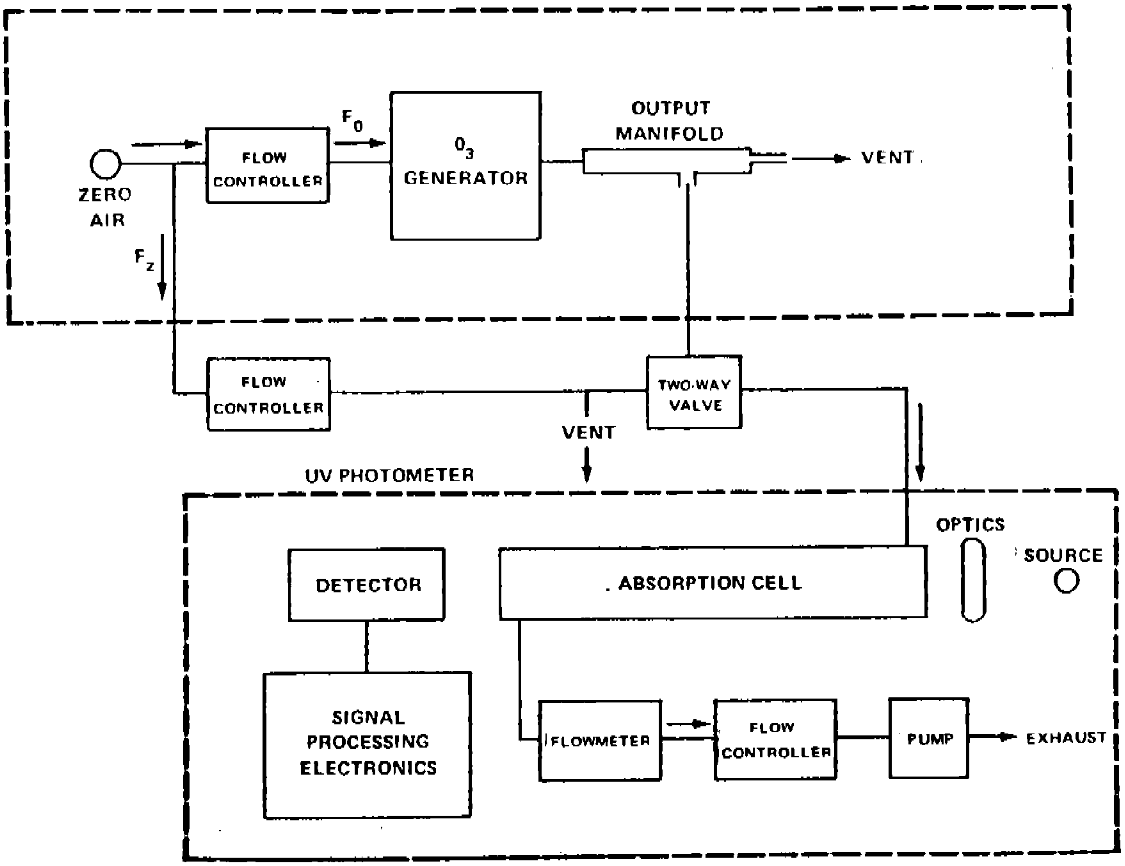

Figure 5-1. Sample comparison set-up of an O_3 generation-type transfer standard to a UV primary standard (Procedure 1).

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 (or GPT system) 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 1 of Appendix A. Care must be exercised in the process to ensure that the transfer standard is not adversely affected. If the zero air supply cannot provide sufficient additional zero air, or cannot be readily tapped, then Procedure 2 or 3 below must be used to compare the transfer standard to the UV primary standard.

Procedure 2: Comparison by Calibrated Ozone Analyzer--

In its normal configuration, the UV primary O_3 standard system produces assayed O_3 concentration standards. Such standards can be used to calibrate an ordinary ambient O_3 analyzer as specified in Appendix A. The calibrated O_3 analyzer is then immediately used to assay the output concentrations of the generation-type transfer standard (see Figure 5-2). In this situation the O_3 analyzer can be used as a temporary or short-term transfer standard without the otherwise required qualification tests described later in this section, since the O_3 analyzer is used immediately after calibration. Accordingly, it is used under the same conditions as those during calibration, and it is not shut down or moved between calibration and use. Nevertheless, it is important that the analyzer be stable between calibration and subsequent use to assay the transfer standard output. The analyzer calibration should therefore be rechecked at several concentrations against the primary standard after the transfer standard is certified. Also, the entire process of calibration, use, and calibration recheck of the O_3 analyzer should be repeated each time a generation-type transfer standard is certified or recertified.

Procedure 3: Comparison by Uncalibrated Ozone Analyzer--

It is possible to avoid the calibration and calibration recheck steps in the previous procedure by using an uncalibrated O_3 analyzer to compare the

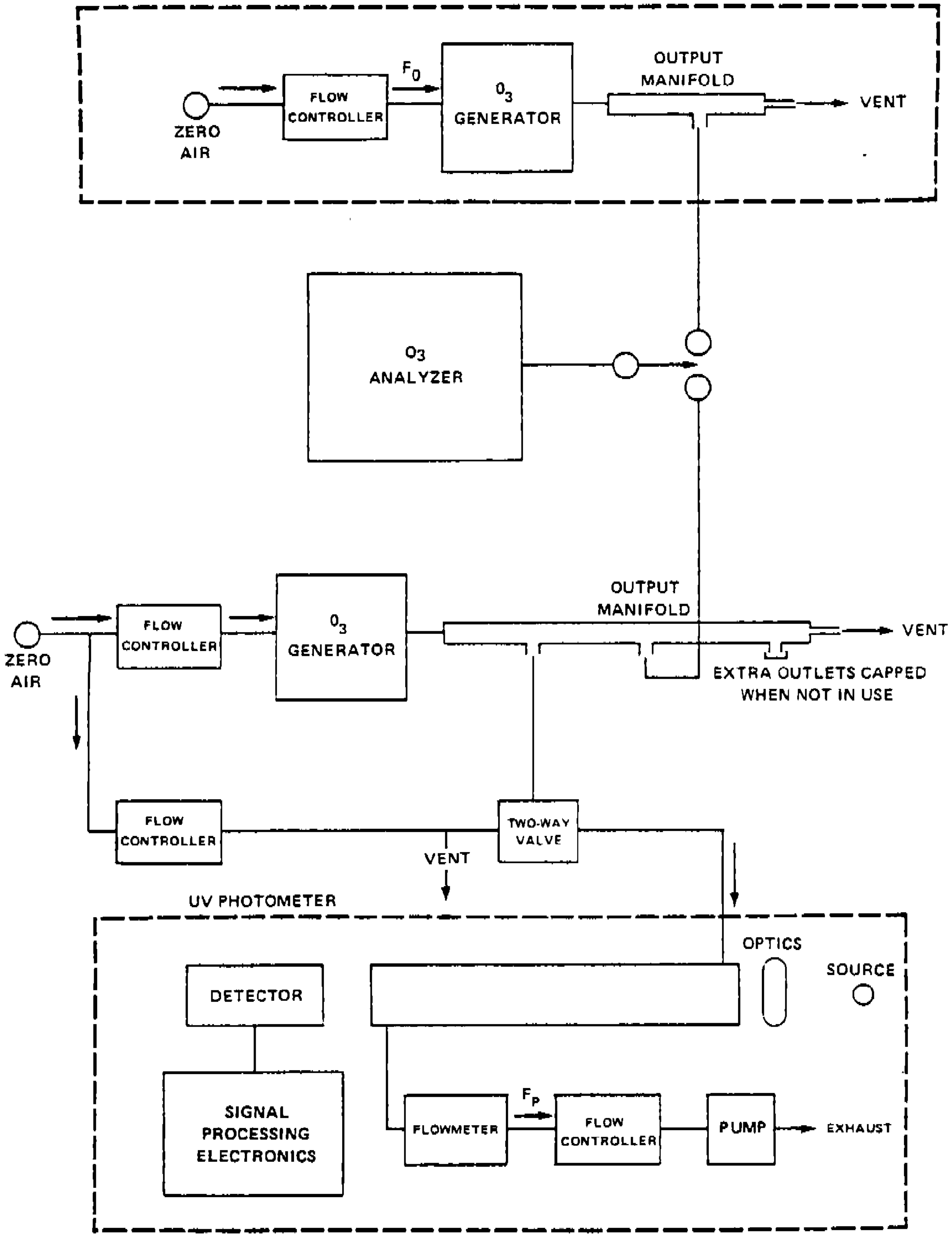

Figure 5-2. Sample comparison set-up of an O_3 generation-type transfer standard to a UV primary standard (Procedures 2 and 3).

transfer standard to a primary standard. The primary O_3 standard, the transfer standard output, or both, are adjusted until each is producing exactly the same output concentration. This equivalence point is determined by switching an uncalibrated O_3 analyzer back and forth between the primary standard and the transfer standard (see Figure 5-2). Of course, the O_3 analyzer must not drift or change its sensitivity during this process, and sufficient time must be allowed for a stable reading on each source. When there is no doubt that the analyzer response is exactly the same for both the primary standard and the transfer standard, the transfer standard output is comparable to the UV primary standard at that concentration. This process must be repeated for each concentration at which the transfer standard is to be compared.

This procedure is of obvious advantage for transfer standards which have only a single or a few fixed outputs. It could also be used to rapidly verify the accuracy of transfer standards between their periodic recertifications.

QUALIFICATION

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. A transfer standard must be assumed unacceptable until it can be conclusively demonstrated to be acceptable.

The primary requirement of a transfer standard is repeatability — repeatability under the stress of variable conditions that may change between certification 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 certification and the time and place of use. According to the specifications in Section 6, the repeatability must be within ± 4% or ± 4 ppb, whichever is greater, for each condition or variable that may change between the point of certification 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 judgement. 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 qualifed 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 <u>repeatable</u> or <u>predictable</u>. 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 with respect to the variable. 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 judgement is required to determine what conditions to test and the extent of testing required to qualify the device or procedure. For qualification of procedural candidates such as BAKI or GPT, testing may be minimal, provided the user is adequately trained, uses good laboratory technique, and uses a specific apparatus and set of supplies (see Appendices B, C, D,). 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 qualifed by type, model, or agency. In the case of procedural candidates such as BAKI and GPT, it seems clear that each user must qualify them in his own laboratory/use situation, since these procedures have a number of potential variables. The procedure should be tested with respect to conditions to which it might be sensitive, such as those discussed below, while attempting to hold all other conditions (source of chemicals, apparatus, laboratory technique, operator, etc.) as constant and uniform as possible throughout the testing process as well as during subsequent certification and use of the procedure.

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 he buys 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 meet 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 judgemental basis derived from a complete understanding of the operation of the device or procedure and supported by appropriate rationale. Specific recommendations for several common transfer standards — BAKI, GPT with excess NO, GPT with excess O_3, O_3 generators, and O_3 analyzers — are given in Appendices B, C, D, E, and F, respectively.

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 assay systems, and (3) changes in the volume of air flows which must be measured accurately.

Temperature effects can be minimized in several ways. The simplest way might be to restrict the use of the transfer standard to a temperature range over which the effects are within the specification. This restriction may be the only practical approach for some candidates, but it may also preclude use of such a transfer standard in too many situations. 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 photometer system as described in Appendix A. The reference could also be another transfer standard known to be very repeatable and, in particular, very insensitive to temperature changes. Still, it would be best to locate the reference outside of the variable temperature test area. The candidate transfer standard should be tested at several different points over the temperature range, including the extremes, and at several different concentrations. Be sure to allow sufficient time for the device or any instruments or equipment associated with the transfer standard to equilibrate each time the temperature is changed. The test results should be plotted in a fashion similar to the example shown in Figure 5-3.

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 5-4). 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.

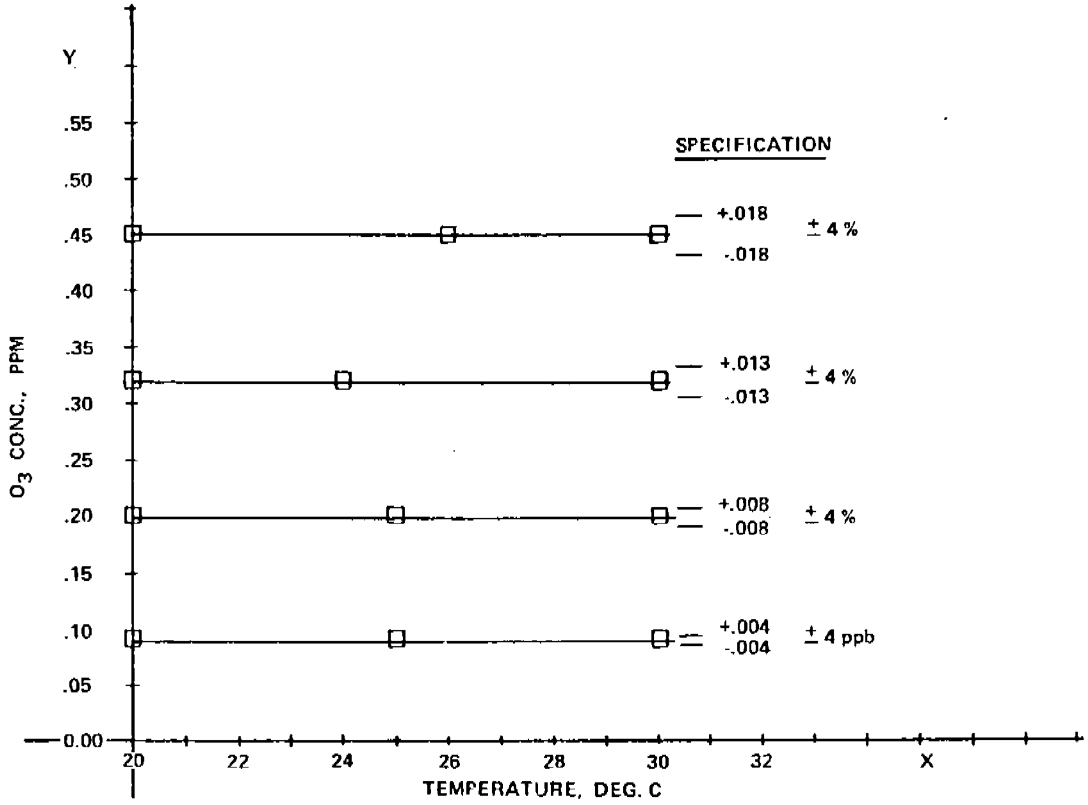

Figure 5-3. Example of temperature qualification test results showing no dependence on temperature.

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

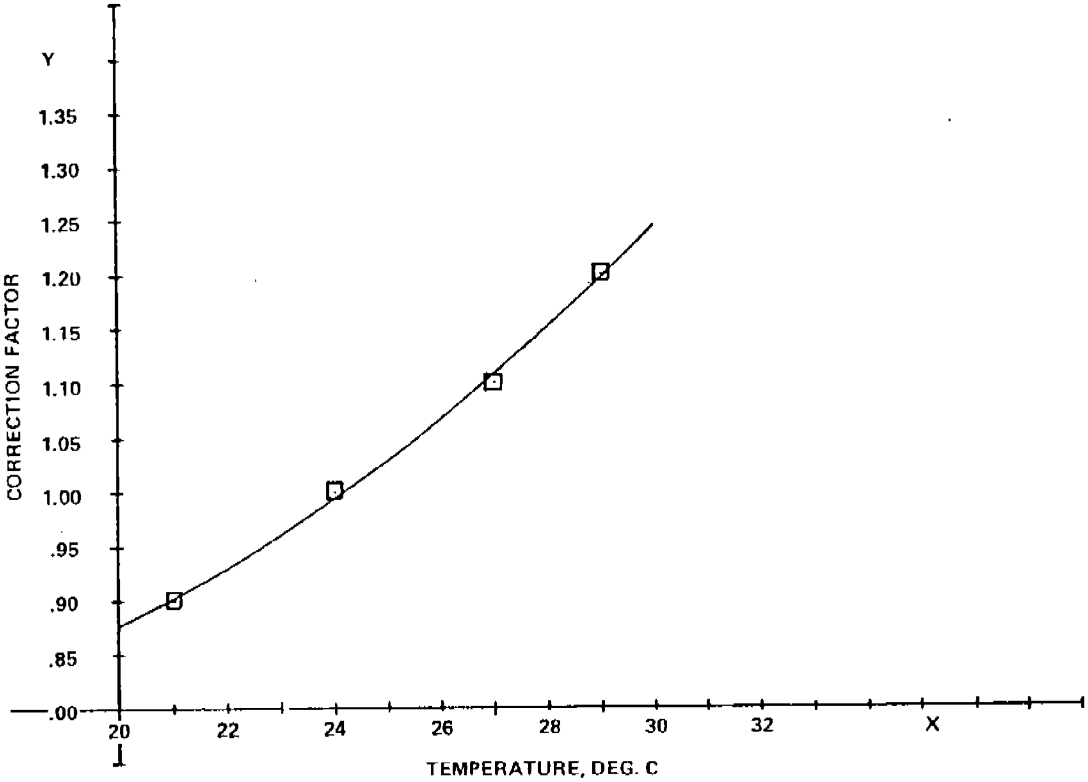

Figure 5-4. Example of a temperature dependence quantitatively defined as a correction factor.

equipment. If such regulators are used, it is important that the same regulator is used during both certification 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. In the case of BAKI and GPT, the effect is limited primarily to the measurement of flowrates, which were discussed briefly under temperature effects and are applicable to barometric pressure changes as well. 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 certification 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 5-5. 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.)

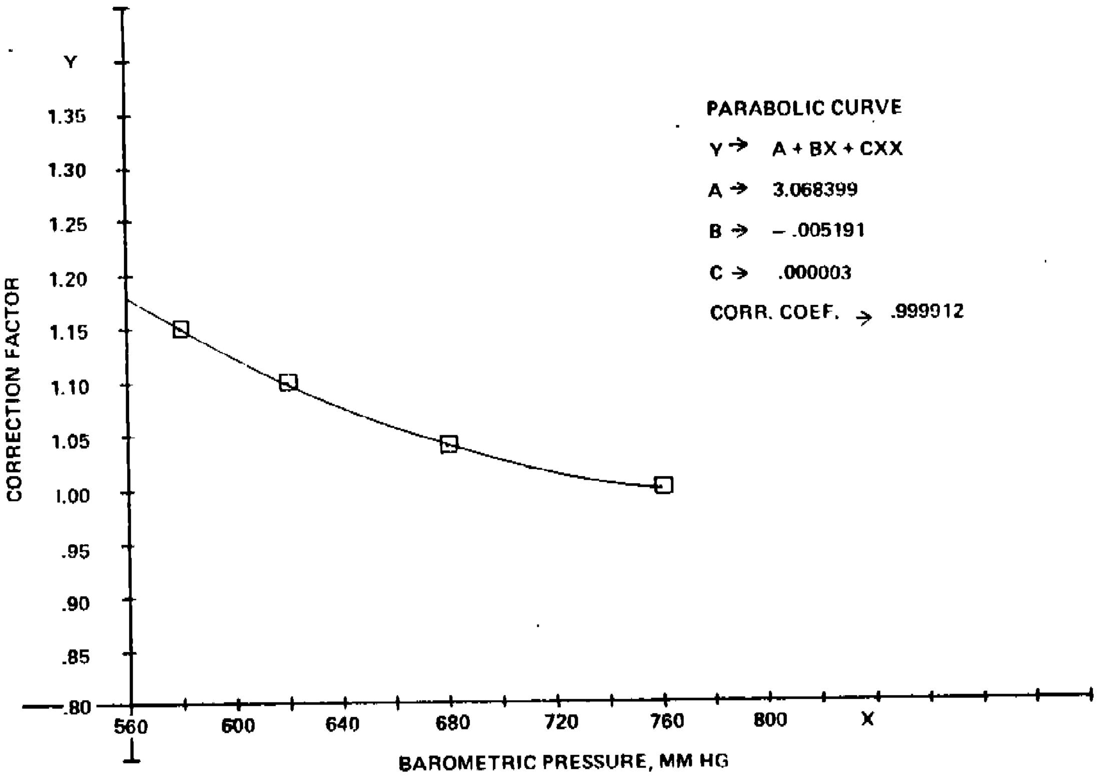

Figure 5-5. Example of a defined barometric pressure dependence.

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. For BAKI and GPT, the flow-measurement problem constitutes the only pressure effect. Some assay-type devices (such as a UV analyzer) 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 certification and use increases, the confidence in the repeatability decreases. As a result, periodic recertification 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 accomodated with the defined-relationship mechanism discussed in connection with temperature effects: the transfer standard is equipped with an hours meter or another me-time 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 certification.

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 preciseness of the relationship between a transfer standard and a primary O_3 standard is dependent on the variability of the transfer standard.

Variability reduces confidence in the accuracy of a certified transfer standard. 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 certification procedure in Section 6 includes a test for variability, more extensive tests for variability may be necessary to qualify a transfer standard because the certification test is for variability in the slope of the certification relationship and not for individual point variability. Furthermore, variability may be due to changes in conditions not encountered during certification.

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. For example, qualification variability tests for BAKI and GPT could include the use of various operators, various sources of chemicals and water, minor variations or substitutions of apparatus and components, etc. These tests might be conveniently combined with tests for the relocation and operator adjustments described below. Whenever increased variability can be assigned to a specific cause, corrective actions or restrictions can be and should be applied to reduce the variability.

Qualification testing for individual-point variability, unlike the certification 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 primary standard are very nearly equal. Then calculate the average of the 6 (or more) concentrations indicated by the transfer standard, using the following equation:

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

where n = number of comparisons

$y_i = O_3$ 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 certification and the point of use should be tested.

CERTIFICATION

The accuracy of a transfer standard is established by (1) relating the output to a primary O_3 standard and (2) demonstrating that the repeatability of the transfer standard is within the limits specified in Section 6.

A good transfer standard is precisely repeatable. Its accuracy, however, is entirely relative and comes strictly by certification to a primary UV O_3 standard. Certification establishes a precise quantitative relationship between the output of the transfer standard and a series of primary O_3 concentrations. The primary O_3 concentrations must be obtained by means of the UV calibration procedure reproduced in Appendix A. Note that the BAKI procedure, which is a temporary alternate to the UV procedure to provide monitoring agencies with a transition period for implementing the new UV procedure, is not approved for certifying transfer standards.

After a transfer standard has been shown to meet the qualification requirements discussed earlier in this section, the transfer standard must be certified before it can be used. The prescribed formal certification procedure and specifications are set forth in Section 6, but are explained in more detail below. Refer to Section 6 while reading the explanations; the certification procedure step numbers correspond.

Procedure for Certification

5.1 Certification requires the averaging of 6 comparisons between the transfer standard and a UV primary O_3 standard system. Each comparison must cover the full range of O_3 concentrations and is to be carried out on a different dard to a primary standard, refer to the portion of this section entitled "Comparing Transfer Standards to an Ultraviolet Primary Ozone Standard".

5.2 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 5-6. Most assay-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 5-7 is required. Note that the curve shown in Figure 5-7 may have a considerable zero offset and may be nonlinear. This preliminary calibration should also include any necessary correction formulas for defined variables. A smooth curve fitting the points in Figure 5-7 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 certification comparison and may cause failure of the certification specifications. During the certification comparisons, the preliminary calibration relationship (see Figure 5-7) is used to obtain the indicated O_3 concentration used in the linear regression calculations of Figure 5-6. (Note that Figure 5-6 should be linear even though Figure 5-7 is nonlinear.)

5.3 When 6 comparisons as shown in Figure 5-6 have been completed compute the average slope ($\bar{m}$) from the 6 individual slopes (m_i), and the average intercept ($\bar{I}$) from the 6 individual intercepts, (I_i).

5.4 Compute the relative standard deviation (s_m) of the 6 slopes (m_i) and the quantity S_I defined by Equation 4 for the 6 intercepts (I_i) using the formulas given.

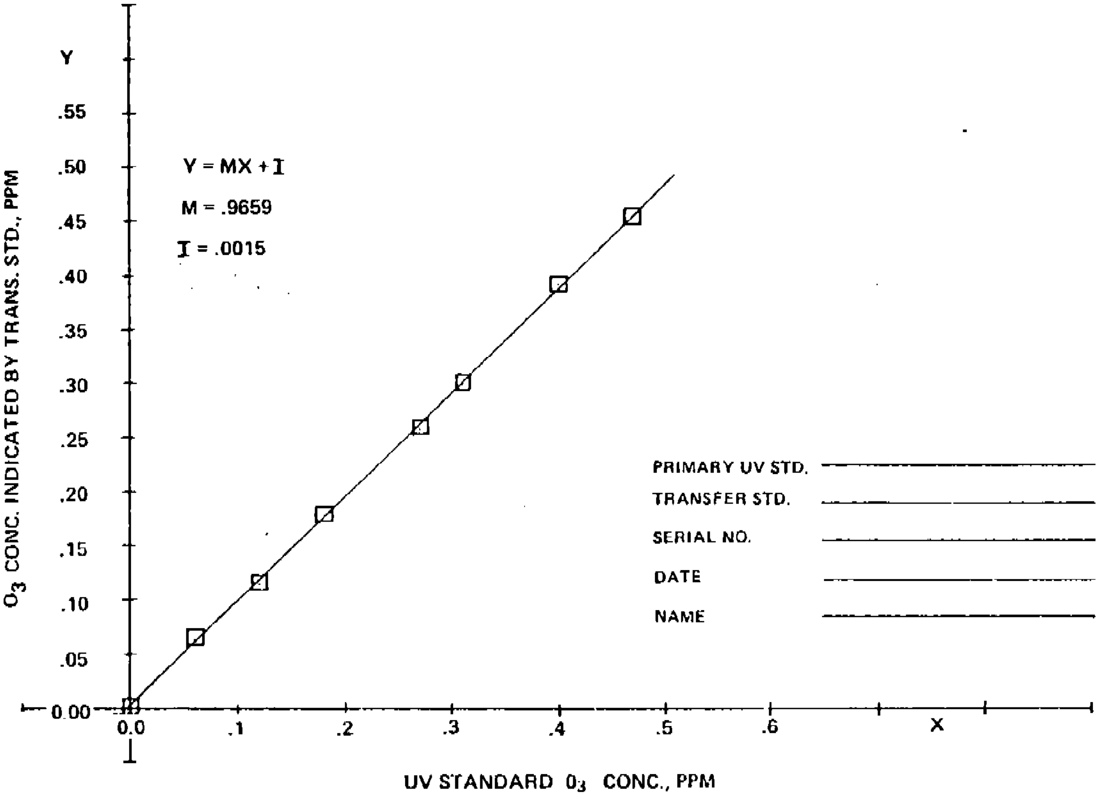

Figure 5-6. Example of a comparison (regression slope and intercept) of a transfer standard to a primary O_3 standard.

5.5 Compare s_m to the 3.7% specification, and compare s_I to the 1.5 specification. 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 primary standard is possible, although it is much less likely.)

5.6 If the specifications are met, the certification relationship for the transfer standard consists of the average slope ($\bar{m}$) and the average intercept ($\bar{I}$) and can be plotted as shown in Figure 5-8. Note that the qualification restrictions must also be included with the certification relationship and

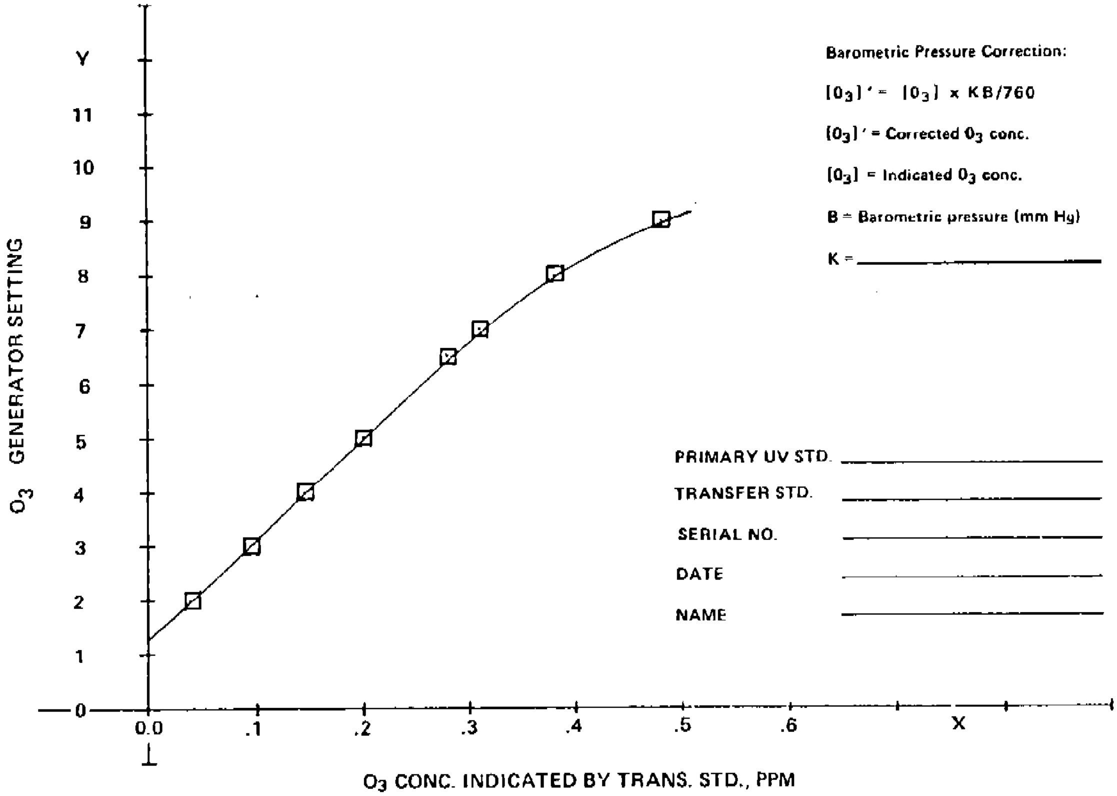

Figure 5-7. Example of a preliminary calibration relationship for an adjustable O_3 device.

should be shown on a plot of the certification relationship as illustrated in Figure 5-8. 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

Certification 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 certification, 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

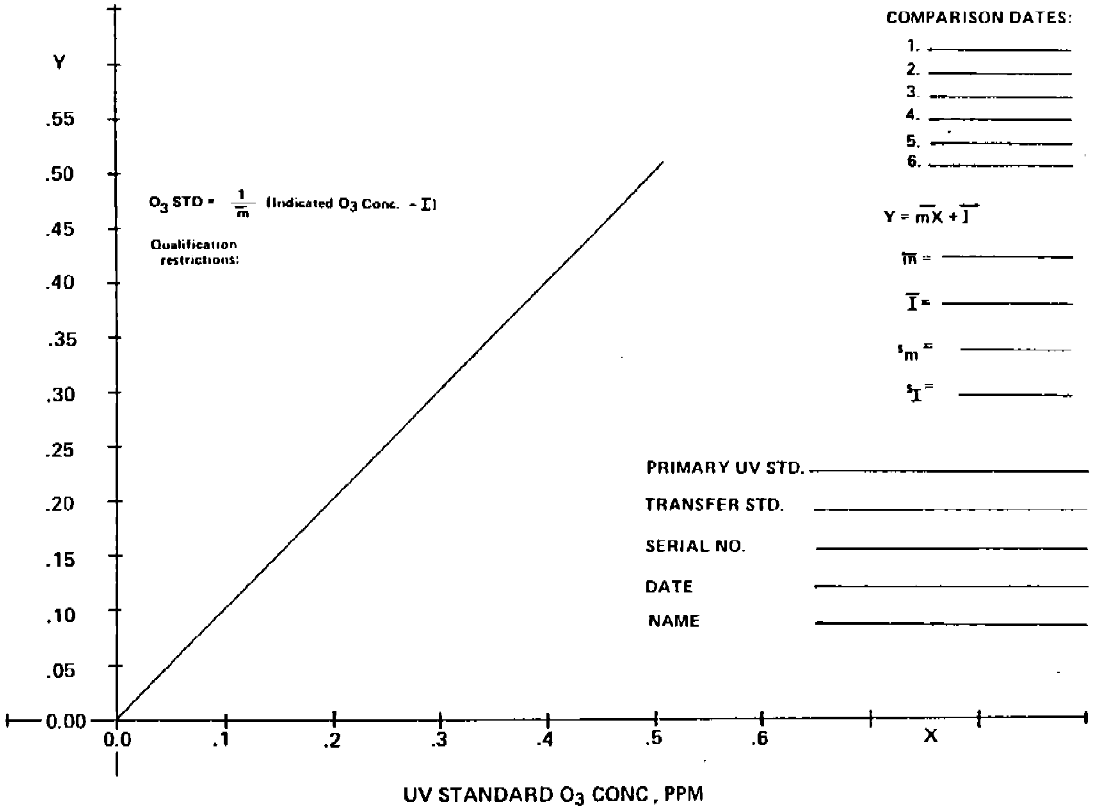

Figure 5-8. Example of a transfer standard certification relationship (average of 6 comparisons).

calibration, during the certification comparisons. The final certification 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 certification comparisons, and an ordinary comparison similar to Figures 5-6 or 5-7 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 5-7) 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 certification relationship can include a "correction factor" relationship as illustrated in Figures 5-4 and 5-5 (pp 5-13 and 5-16). 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. Another technique is to use a preliminary calibration consisting of a family of curves as illustrated by Figure 5-9. Here, interpolation can be used to obtain the indicated 0_3 concentration at values of the variable falling between the lines.

In any case, the technique used must be completely described in writing, verified to make sure it is accurate, and clearly understood by all users of the transfer standard.

Use

After certification, when the transfer standard is used to reproduce 0_3 standards, the certification relationship (such as illustrated in Figure 5-8) is used to determine the certified 0_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. 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 certification and use. Of course, for any transfer standard which has

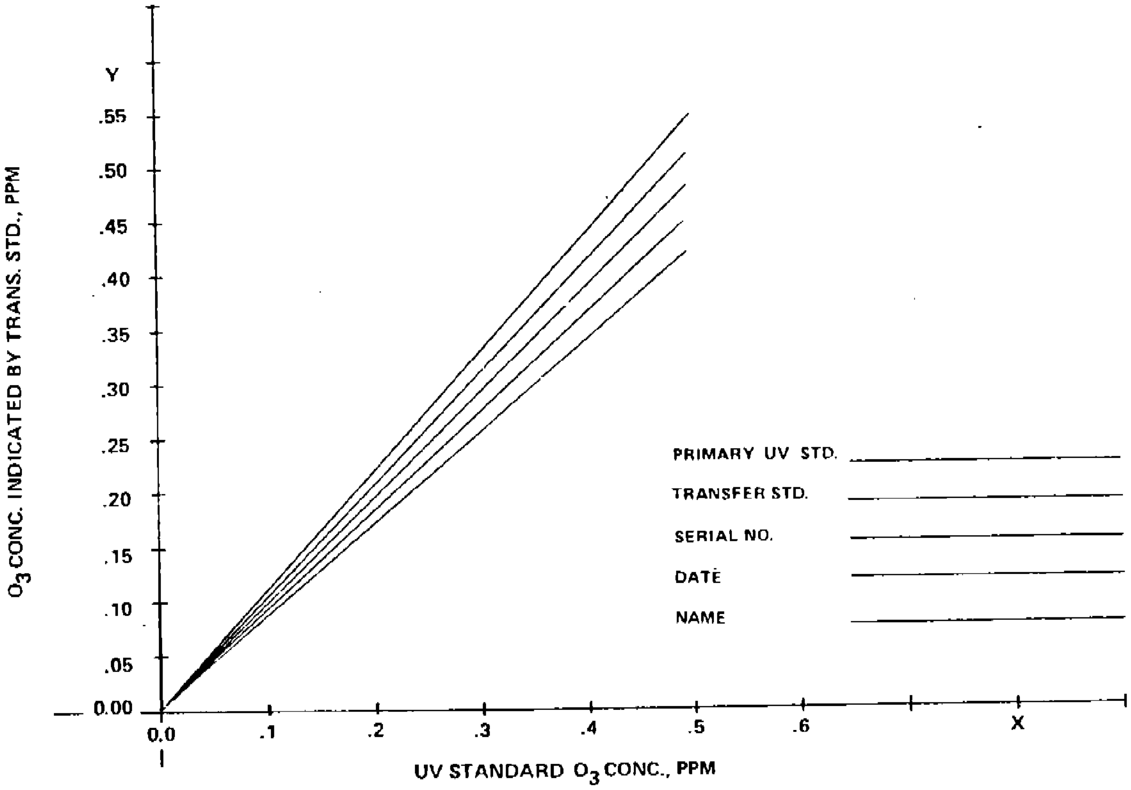

Figure 5-9. A "family" of preliminary calibration curves.

a defined relationship to some variable, that variable must be accurately measured and the output of the transfer standard must be corrected accordingly.

Traceability

Ozone standards obtained from a transfer standard will always be somewhat less accurate than primary O_3 standards because of the inevitable variability in the certification process. Consequently, it is good practice to always certify a transfer standard directly against primary O_3 standards obtained by the UV calibration procedure. Certification of a transfer standard against another transfer standard is discouraged, but could be appropriate for some limited purposes if the variability of both transfer standards is very low. The use of more than one intermediate transfer standard should be avoided.

RECERTIFICATION

While the principle accuracy of a transfer standard is established during certification, 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 certification and use. However, if the UV reference system is located in a laboratory, the recertification process may always take place under nearly identical conditions (temperature, line voltage, barometric pressure, etc.). Therefore, ocasional repetition of the qualification tests discussed earlier in this section is an important and indispensable supplement to recertification, though not specifically required by Section 6.

The procedure and specifications for recertification are prescribed explicitly in Section 6, but are explained in more detail below. Paragraph numbers refer to the corresponding paragraph of the recertification procedures in Section 6.

Procedure for Recertification

A certified transfer standard must be recertified at least twice per calendar quarter to maintain continuous certification. A transfer standard which looses its certification may cause the loss of ambient O_3 measurements made with ambient monitors that were calibrated with the transfer standard. Consequently, more frequent recertification schedule will reduce the magnitude and risk of any such loss. More frequent recertification may also provide better accuracy, particularly for transfer standards that show slow but steady change (drift) over long periods of time.

6.1 The first step in the recertification procedure is to carry out a comparison to a UV primary standard as specified in step 5.2 (see also Figure 5-6, pg 5-22).

6.3 To maintain certification, the linear regression slope of the new comparison (m) must be within ± 5% of the average slope of the current certification relationship ($\bar{m}$) (i.e., the average slope of the last 6 comparisons). Thus, m must be within the interval $.95\ \bar{m} \le m \le 1.05\ \bar{m}$. A convenient way to monitor the performance of a transfer standard is to plot each new slope on a chart format such as shown in Figure 5-10.

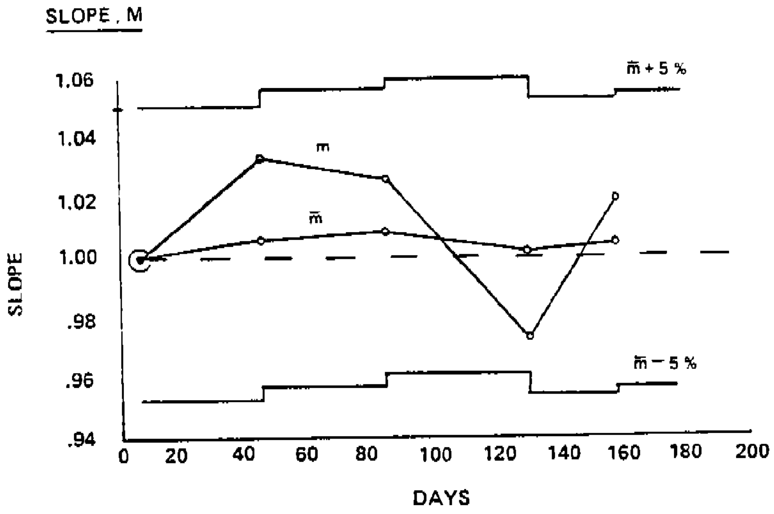

Figure 5-10. Example of a chart showing recertification slope data for a transfer standard.

6.3 If the new slope is within the ± 5% specification, then a new average slope ($\bar{m}$) and a new average intercept ($\bar{I}$) are calculated using the new comparison and the 5 most recent previous comparisons. Thus $\bar{m}$ and $\bar{I}$ are running or moving averages always based on the 6 most recent comparisons. The new $\bar{m}$ and the new ± 5% limits can also be plotted on the chart shown in Figure 5-10.

6.4 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 given in step 5.4. These parameters can also be monitored with a chart format similar to Figure 5-11.

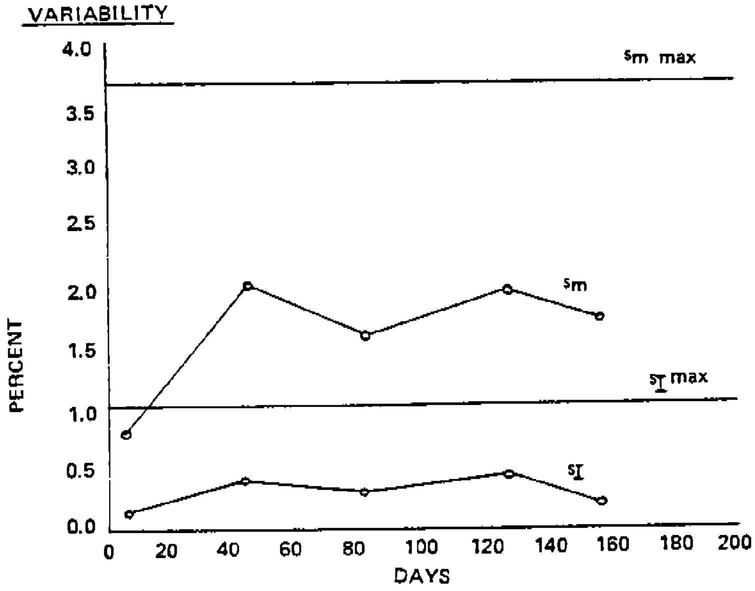

Figure 5-11. Example of a chart showing recertification variability of slope and intercept for a transfer standard.

6.5 The new s_m and s_I must again meet the respective 3.7% and 1.5 specifications given in step 5.5. If all specifications are met, then a new certification relationship (based on the updated $\bar{m}$ and $\bar{I}$) is established according to step 5.6 and illustrated by Figure 5-8 (pg 5-24).

6.6 If a certified transfer standard fails to meet one of the recertification specifications, it looses its certification. Recertification then requires 6 new comparisons according to the entire certification procedure starting at step 5.1. This failure could be due to a malfunction, which obviously should be corrected before repeating the certification procedure. (If a transfer standard has been repaired or serviced in a way which could affect its output, the complete certification procedure must also be repeated.) Another possible cause for failure of the recertification specifications might be a change in the preliminary calibration (Figure 5-7, pg 5-23), which should then be re-established before the certification is repeated.

Cross Checks

Frequently, an assay-type transfer standard is used with an O_3 generator for which a preliminary calibration such as shown in Figure 5-7 (pg 5-23) 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 recertification.

Recertification 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 recertification 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.

SECTION 6

SPECIFICATIONS FOR OZONE TRANSFER STANDARDS

1. DEFINITION

An O_3 transfer standard is a transportable device or apparatus together with associated operational procedures and documentation that is capable of either accurately reproducing O_3 concentration standards or of producing accurate assays of O_3 concentrations that are quantitatively related to an authoritative master standard.

2. 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.

3. DOCUMENTATION

The following comprehensive documentation of an O_3 transfer standard is required:

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

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

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

3.4 The current certification relationship information (slope and intercept) as described in step 5.6 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

3.5 A logbook including a complete chronological record of all certification and recertification data, as described under "Certification" and "Recertification" above, as well as all 0_3 analyzer calibrations carried out with the transfer standard.

4. QUALIFICATION

An 0_3 transfer standard must meet the general requirements for qualification as described in Section 5; 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. Documentation of conformance to this requirement shall be provided as required by step 3.3.

5. CERTIFICATION

Prior to use, an 0_3 transfer standard must be certified by establishing a quantitative certification relationship between the transfer standard and the primary 0_3 concentrations obtained by the UV calibration procedure as specified in Appendix D of 40 CFR, Part 50 (EPA 1979). The certification procedure follows:

5.1 The certification relationship shall consist of the average of 6 individual comparisons of the transfer standard to the primary UV 0_3 standard system. Each comparison must be carried out on a different day.

5.2 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 primary O_3 standards.

5.3 For the 6 comparisons, compute the average slope ($\bar{m}$):

$$\bar{m} = \frac{1}{6} \sum_{i=1}^{6} m_i \qquad \text{(Eq. 1)}$$

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

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

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

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

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

and the quantity S_I defined in Equation 4 for the 6 intercepts:

$$s_I = \frac{100}{\bar{m}} \sqrt{\frac{1}{5} \left[\sum_{i=1}^{6} (I_i)^2 - \frac{1}{6} \left(\sum_{i=1}^{6} l_i \right)^2 \right]} \qquad \text{(Eq. 4)}$$

5.5 The value of s_m must be $\leq 3.7\%$, and S_I must be ≤ 1.5.

5.6 If the transfer standard meets the specifications of 5.5, compute the certification relationship as:

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

6. RECERTIFICATION

To maintain continuous certification, an O_3 transfer standard must be recertified as follows. In general, O_3 transfer standards should be recertified at least twice per calendard quarter; a transfer standard which remains at a fixed monitoring site may be recertified once per quarter if it is sufficiently stable to avoid loss of certification over that time period (see step 6.6).

6.1 At the time of recertification, carry out a comparison of the transfer standard to the UV primary standard as prescribed in step 5.2.

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

6.3 If the transfer standard meets the specification in 6.2, compute a new $\bar{m}$ and a new $\bar{I}$ as prescribed in step 5.3 using the 6 most recent comparisons (running averages).

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

6.5 If the new s_m and s_I meet the specifications given in 5.5 compute a new certification relationship as prescribed in step 5.6 using the updated $\bar{m}$ and $\bar{I}$.

6.6 If the transfer standard fails any of the recertification specifications, it looses its certification. Recertification then requires repeating all the initial certification steps (steps 5.1 — 5.6.)

7. TRANSFER STANDARDS HAVING FEWER THAN FIVE DISCRETE OUTPUTS

Generation-type transfer standards having discrete or fixed outputs that are too few in number to meet the requirements of step 5.2 may be certified as follows:

7.1 If the transfer standard is to be used for calibration, it must incorporate an integral dilution system to provide capability for at least 6 calibration concentrations (including zero). The complete transfer standard system, including the dilution system, should then be certified as specified under subsections 5 and 6 above.

7.2 If the transfer standard is to be used for purposes other than calibration where discrete outputs are acceptable (e.g., audits, span checks), the transfer standard may be certified at each discrete output by substituting single point comparison, d_i, for the slopes m_i, and ignoring all steps pertaining to intercepts. Calculate $\bar{d}$ (Equation 1), $s_{\underline{d}}$ (Equation 3) and substitute them for $\bar{m}$ and s_m, respectively. If s_d is $\leq 3.7\%$, compute the certified discrete output as

$$\text{Std. } O_3 \text{ conc.} = \frac{1}{\bar{d}} (\text{Indicated } O_3 \text{ conc.}) \qquad \text{(Eq. 6)}$$

Recertification is carried out similarly.

REFERENCES

U.S. Environmental Protection Agency. October 6, 1976. Measurement of Photochemical Oxidants in the Atmosphere: Calibration of Reference Methods. Federal Register, 41:44049.

U.S. Environmental Protection Agency. February 8, 1979. Amendments to Title 40, Code of Federal Regulations, Part 50 (Appendix D), Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere. Federal Register, 44:8821.

APPENDIX A

ULTRAVIOLET PHOTOMETRIC PROCEDURE FOR PRIMARY OZONE STANDARDS*

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,

$$\text{Transmittance} = \frac{I}{I_o} = e^{-\alpha C \ell} \qquad (1)$$

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

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

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,

$$c(\text{atm}) = -\frac{1}{\alpha\ell}(\ln I/I_o) \qquad (2a)$$

or,

$$c(\text{ppm}) = -\frac{10^6}{\alpha\ell}(\ln I/I_o) \qquad (2b)$$

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 certification 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 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:

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \qquad (3)$$

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.

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

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 Certification 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:

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

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_0) 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:

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

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

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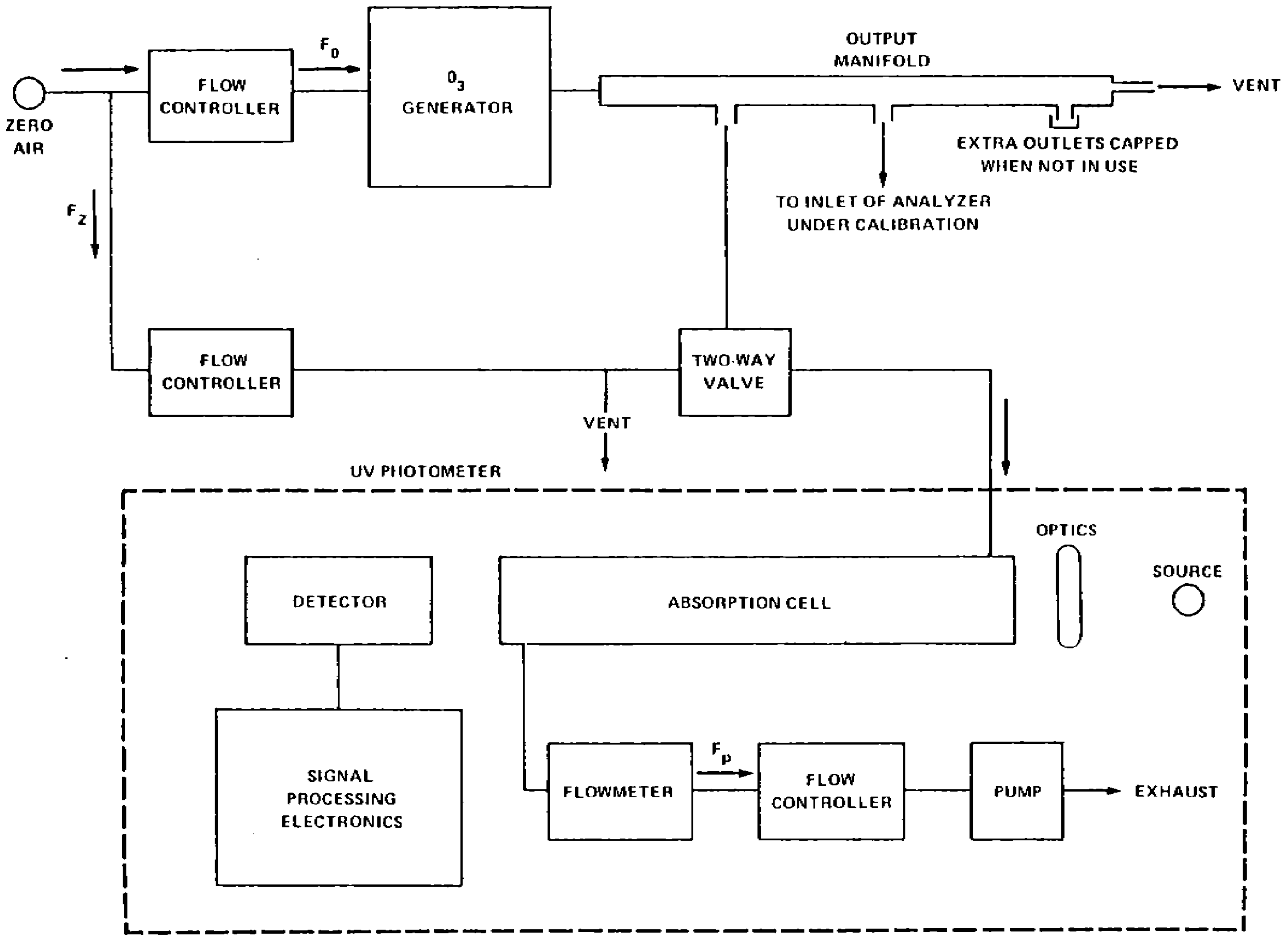

Figure 1. Schematic diagram of a typical UV photometric calibration system.

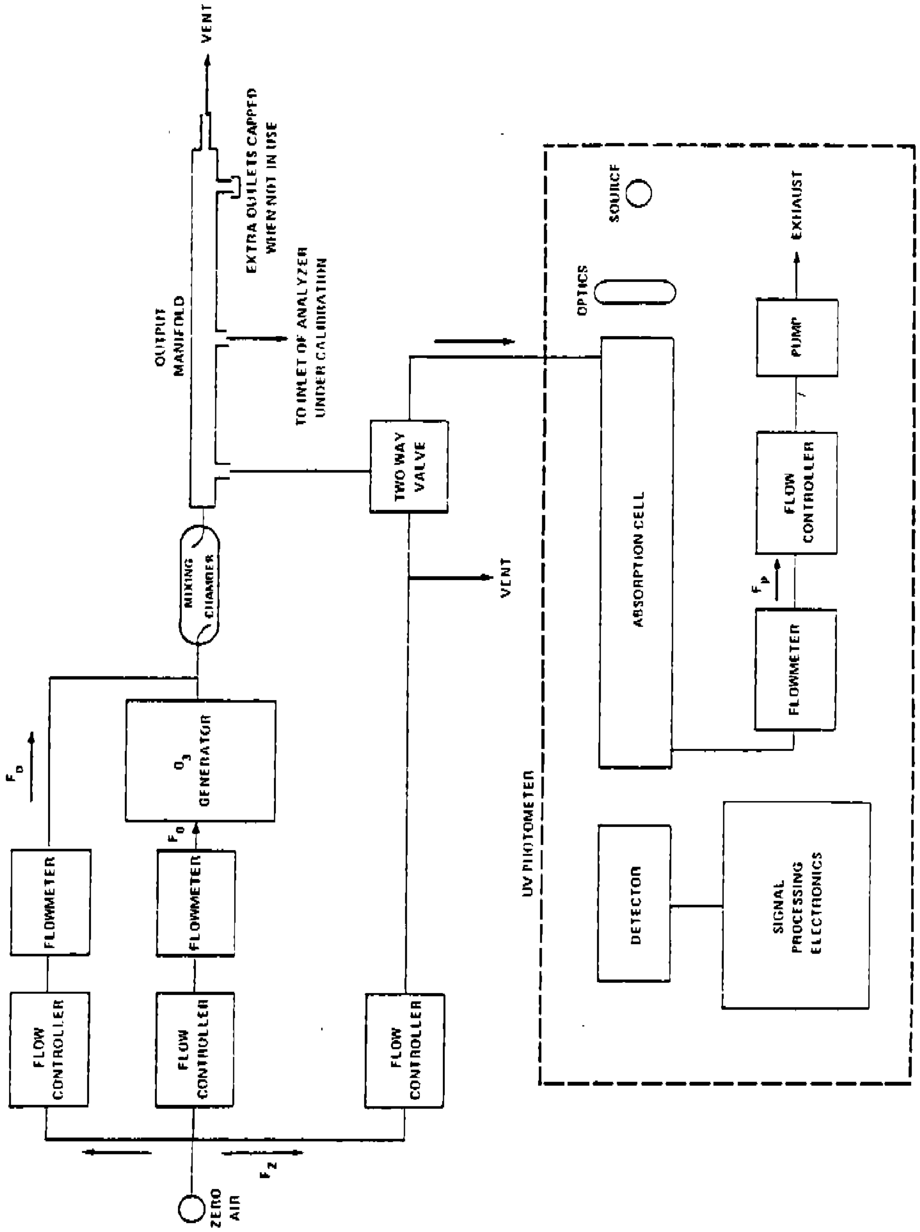

Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).

APPENDIX B

CERTIFICATION OF THE BORIC ACID POTASSIUM IODIDE PROCEDURE AS A TRANSFER STANARD

Following the guidance in Sections 4 and 5 and the specifications in Section 6, this appendix attempts to provide more specific instructions for certifying the Boric Acid Potassium Iodide (BAKI) procedure as a transfer standard. The recommended version of the BAKI procedure appears at the end of this appendix. Because of the extensive and intimate involvement of the user with the procedure, the user-procedure combination must be certified, rather than the procedure itself; each user or user-agency must certify the procedure under its own set of circumstances.

PRELIMINARY REQUIREMENTS

Perhaps the first and surely one of the most important requirements is the skill of the analyst, who must have adequate training in chemical laboratory technique, be thoroughly familiar with the BAKI procedure, and follow the procedure completely and accurately. Some period of practice is often necessary to achieve consistent results. If problems are encountered, the analyst should seek assistance. The success of the method is quite dependent on the skill and ability of the analyst.

The apparatus should be assembled and checked for compliance with specifications, cleanliness, absence of leaks, and proper operation. Once assembled, the apparatus and components should be dedicated exclusively to use as a transfer standard, and the same apparatus (as far as possible) should be used whenever the transfer standard is used or certified. To the greatest extent practical, reagents should be common (i.e., from the same container or lot) throughout the qualification, certification, and use of the procedure as a transfer standard.

An important requirement is a stable source of O_3 to be assayed by the transfer standard procedure, also an attendant source of zero air for the O_3 generator. Since the concentration of O_3 generated by most O_3 generators varies with flow, some means of reasonable flow regulation for the zero air is usually needed. Some helpful guidance for these items may be found in paragraphs 3.3, 3.4, and 4.1 of Reference 3. Decide whether or not the O_3 generation/zero air system is to be an integral part of the transfer standard (see pg 4-2). 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 which meets the requirements of 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 certification of the transfer standard and is also recommended for the qualification tests. Comparing the output (indicated concentration) of the BAKI procedure to the UV primary O_3 standard is easy, as the procedure simply assays the output manifold of the UV primary O_3 standard.

Review any operation information or instructions provided by the manufacturer of the spectrophotometer to become familiar with its operation.

Review the documentation requirements specified in paragraph 3 of Section 6 and complete item 3.1.

QUALIFICATION

The next step is to qualify the procedure by demonstrating that it is repeatable to within the specifications in paragraph 4 of Section 6 (± 4% or ± 4 ppb, whichever is greater). The variables likely to affect the BAKI procedure are similar to those discussed generally in Section 5 and are discussed more specifically below. Refer to Section 5 for additional guidance on each of the qualification tests. A preliminary calibration relationship (as shown in Figure 5-7, pg 5-23) is not necessary for the BAKI procedure, as it is linear and provides a direct output indication of concentration. To minimize potential sources of variability, the apparatus, reagents, supplies, techniques, procedures, and conditions should be kept as constant as possible from qualification to certification to use of the procedure. Therefore, these items should be identified in detail as part of the documentation requirements of paragraph 3 of Section 6.

QUALIFICATION TESTS

Temperature

Over normal ranges of room temperatures, effects of temperature change on the BAKI procedure should be minimal. The most important effect is on the measurement of the air volume sampled. As noted in step 4.5.4.1, this air sample volume must be corrected to reference conditions (25°C and 760 torr). This correction depends on the type of flowmeter used. For a flowmeter which measures actual volume (wet test meter, dry gas meter, bubble meter, etc.) the volume measurement is corrected by using the ideal gas law. Wet volume meters (wet test meters, bubble meter) may require water vapor corrections. Orifice type flowmeters (rotameters, calibrated hypodermic needles) require an orifice correction. Flowmeters which measure mass flow should require no correction. (All flowmeters, of course, require accurate calibration.) If you are unsure of the volume measurement correction, consult the flowmeter instruction manual or other authoritative reference.

Temperature may affect the spectrophotometer slightly but probably not enough to be significant over reasonable room temperatures. The flow controllers and O_3 generator are likely to be affected but any such effect is accounted for in the procedure.

Line Voltage

Any line-powered components, such as the spectrophotometer or flowmeter, could be affected by changes in line voltage. Well-designed equipment will show little or no sensitivity to voltage changes over a range of 105 to 125. Look for voltage regulating capability and voltage sensitivity specifications associated with the equipment. Or, use external line voltage regulators. If there is any doubt about line voltage sensitivity effects, then line voltage tests should be carried out as described in Section 5.

Barometric Pressure/Altitude

The only effect of normal changes in pressure on the BAKI procedure will be in measurement of the sample volume flowrate. (The O_3 generator will likely be affected but, again, the procedure accounts for that.) If 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, the effect could be ignored. However, since the sampled volume must be corrected to standard conditions, the correction for pressure should be included in that correction. As with temperature effects, the pressure correction depends on the type of flowmeter used. Consult the flowmeter manual or other reference to determine the proper correction formula.

Elapsed Time

Normally, elapsed time has no significant effect on the BAKI procedure as long as the apparatus is kept clean and in good working order, and the reagents are prepared fresh as specified. Flowmeters normally require periodic recalibration.

Variability

General variability can sometimes be a problem with BAKI. As noted previously, changes in the apparatus, reagents, supplies, procedure, etc., should be avoided as much as possible to minimize potential variation from those sources. When a component, reagent, or procedure is changed, a recertification comparison should be carried out to see if the variability or the certification relationship is affected. For any significant change which is to be a variable or option (i.e., sometimes used, sometimes not used), then a variability test as described in Section 5 chould be carried out to see if the BAKI procedure still qualifies when the variable is exercised. In this case, judgment is needed to decide whether the change would or might cause additional variability in the procedure.

As an example, consider an agency which wishes to qualify several analysts and several sets of apparatus. Must each analyst be tested, qualified, and certified with each set of apparatus? For more than a very few analysts and sets of apparatus, this becomes impractical. In this case, the agency should insure that each analyst is adequately trained, thoroughly familiar with the procedure, and can make accurate temperature and pressure corrections to the measured flowrates. Then, if each analyst is qualified with at least one set of apparatus, and each apparatus is qualified with at least one analyst, adequate results can reasonably be expected from any analyst-apparatus combination.

Relocation

Relocation tests help to establish the ruggedness of the BAKI apparatus. Move the equipment about as it might be moved during subsequent use to see if any malfunctions, leaks, variability, or other problems are observed which might make use of the procedure questionable or inconvenient. (Make sure that the wavelength and other adjustments on the spectrophotometer can be locked so they don't change when it is moved.) If possible, include relocation in the variability tests to measure the effect of relocation on variability.

Malfunctions

There is no special test for malfunctions. During other tests, be observant for any leaks or malfunctions that occur or other characteristic weaknesses in the apparatus or equipment which could cause unreliability. Understand the design and operation of the components so that you can be alert to nonobvious types of malfunctions.

In summary, the primary qualification tests for most users of the BAKI procedure are variability and relocation tests.

CERTIFICATION

When the BAKI procedure has been shown to meet the qualification requirements, certify the procedure as specified in Section 6. Additional guidance is contained under "Certification" in Section 5. If any volume or flow correction formulas are needed, use them during the certification procedure and clearly specify the conditions at the time of the certification 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 paragraph 3 of Section 6.

USE

In using the BAKI procedure as a transfer standard, review the guidance under "Use" in Section 5. Recertify the transfer standard as required by Section 6 (with further explanation of recertification in Section 5). 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.

RECOMMENDED VERSION OF BORIC ACID POTASSIUM IODIDE TRANSFER STANDARD PROCEDURE

This procedure can be used as a transfer standard for calibration of O_3 analyzers in accordance with the guidance and specifications set forth in Sections 5 and 6.

1. Principle. This procedure(1) is based upon the reaction between ozone (O_3) and potassium iodide (KI) to release iodine (I_2) according to the stoichiometric equation(2):

$$O_3 + 2I^- + 2H^+ \rightarrow I_2 + H_2O + O_2 \qquad \text{(Eq. B-1)}$$

The stoichiometry is such that the amount of I_2 released is equivalent to the amount of O_3 absorbed. Ozone is absorbed in a 0.1 M boric acid (H_3BO_3) solution containing 1% KI, and the I_2 released reacts with excess iodide ion (I^-) to form triiodide ion (I_3^-) which is measured spectrophotometrically at a wavelength of 352 nm. The output of a stable O_3 generator is assayed in this manner, and the generator is immediately used to calibrate the O_3 analyzer. The O_3 generator must be used immediately after calibration and without physical movement, and it is recalibrated prior to each use. Alternatively, the O_3 analyzer may be calibrated by assaying the O_3 concentrations using the prescribed procedure while simultaneously measuring the corresponding O_3 analyzer responses. Ozone concentration standards may also be generated by an optional dilution technique. With this option, the highest O_3 concentration standard is assayed using the prescribed procedure. The additional O_3 concentration standards required are then obtained by dilution.

2. Apparatus. Figures B-1 and B-2 illustrate a typical BAKI O_3 transfer standard system and show the suggested configuration of the components listed below. All connections between components downstream of the O_3 generator should be of glass, Teflon, or other relatively inert material.

2.1 Air flow controller. Device capable of maintaining a constant air flowrate through the O_3 generator within ± 2%.

2.2 Air flowmeter. Calibrated flowmeter capable of measuring and monitoring the air flowrate through the O_3 generator within ± 2%.

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

2.4 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 analyzer connection. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

2.5 Impingers. All glass impingers with the specifications indicated in Figure B-2 are recommended. The impingers may be purchased from most major glassware suppliers. Two impingers connected in series are used to insure complete collection of the sample.

2.6 Air pump and flow controller. Any pump and flow control device capable of maintaining a constant flowrate of 0.4 to 0.6 l/min through the impingers may be used. A critical orifice as described by Lodge et al.(3) is recommended. The orifice should be protected against moisture and particulate matter with a membrane filter or moisture trap containing Drierite, silica gel, or glass wool. The air pump must be capable of maintaining a pressure differential of at least 0.6 to 0.7 atmospheres across the critical orifice. Alternatively, a needle valve could be used with the pump to adjust the flow through the impingers. A flowmeter is then recommended to monitor the flow. The needle valve-flowmeter combination should be protected against moisture and particulate matter with a membrane filter or moisture trap.

2.7 Thermometer. Accurate to ± 1%°C.

2.8 Barometer. Accurate to ± 2 torr.

2.9 Volumetric flasks (Class A). 25, 100, 200, 1000-ml.

2.10 Pipets (Class A). 1, 5, 10, 15, 20, and 25-ml volumetric; 1-ml or 10-ml graduated.

2.11 Spectrophotometer. Capable of measuring absorbance at 352 nm with an absolute accuracy of ± 1% and linear reponse over the range of 0 to 1.0 absorbance units. The photometric accuracy may be checked using optical glass filters which have certified absorbance values at specified wavelengths. Matched 1-cm or 2-cm cells should be used for all absorbance determinations.

3. Reagents.

3.1 Zero air. The zero air must be free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with 1% BAKI. Air meeting this requirement may be obtained by: (1) passing it through silica gel for drying; (2) treating it with O_3 to convert any nitric oxide (NO) to nitrogen dioxide (NO_2); (3) passing it through activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove any NO_2, hydrocarbons, and traces of water vapor; and (4) passing it through a 2-μ filter to remove any particulate matter.

3.2 Boric acid (H_3BO_3). ACS reagent grade.

3.3 Potassium iodide (KI). ACS reagent grade.

3.4 Hydrogen peroxide (H_2O_2). ACS reagent grade, 3 or 30%.

3.5 Potassium iodate (KIO_3). ACS reagent grade, certified 0.1 N.

3.6 Sulfur acid (H_2SO_4). ACS reagent grade, 95 to 98%.

3.7 Distilled water. Used for preparation of all reagents.

3.8 Absorbing reagent. Dissolve 6.2 g of boric acid (H_3BO_3) in approximately 750 ml of distilled water in an amber 1000-ml volumetric flask. The flask may be heated gently to speed dissolution of the H_3BO_3, but the solution must then be cooled to room temperature or below before proceeding with the reagent preparation. (While the H_3BO_3 solution is cooling, prepare the hydrogen peroxide (H_2O_2) solution according to the directions in step 3.9.) When the H_3BO_3 solution has cooled, add 10 g of potassium iodide (KI) to the H_3BO_3 solution and dissolve. Add 1 ml of 0.0021% H_2O_2 solution (see step 3.9) and mix thoroughly. Within 5 minutes after adding the peroxide, dilute to volume with distilled water, mix, and determine the absorbance of this BAKI solution at 352 nm against distilled water as the reference. The pH of the BAKI solution should be 5.1 ± 0.2.

Set the absorbing solution aside for 2 hours and then redetermine the absorbance at 352 nm against distilled water as the reference. If the resultant absorbance from this second determination is at least 0.008 absorbance units/cm greater than the first determination, the absorbing reagent is ready for use. If no increase or an increase of less than 0.008 absorbance units/cm is observed, the KI reagent probably contains an excessive amount of a reducing contaminant and <u>must be discarded</u>. In this event, prepare fresh absorbing reagent using a different number lot of KI. If an unacceptable absorbing reagent results from different lots of KI, test the possibility of contamination in the H_3BO_3 by using a different numbered lot of H_3BO_3.

3.9 Hydrogen peroxide solution (0.0021%). Using a graduated pipet, add 0.7 ml of 30% or 7.0 ml of 3% hydrogen peroxide (H_2O_2) to approximately 200 ml of distilled water in a 500-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. To prepare the 0.0021% solution, pipet 5 ml of the above solution into 50 ml of distilled water in a 100-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. This 0.0021% H_2O_2 solution must be prepared fresh each time a fresh batch of absorbing reagent is prepared. Therefore, the remaining contents of both volumetric flasks should be discarded after treatment of the BAKI absorbing reagent (see step 3.8).

3.10 Standard potassium iodate solution (0.1 N). Use a commercial standard solution of potassium iodate (KIO_3) having a certified normality.

3.11 Sulfuric acid (1 N). Dilute 28 ml of concentration (95 to 98%) sulfuric acid (H_2SO_4) to volume in a 1000-ml volumetric flask.

4. Procedure.

4.1 Assemble an O_3 generation system such as shown in Figure B-1.

4.2 Assemble the KI sampling train such as shown in Figure B-2. All connections between the various components must be leak tight and may be made using grease-free ball joint fittings, heat-shrinkable Teflon tubing or Teflon tube fittings. The connection to the O_3 output manifold should be made using 6 mm (1/4 in.) Teflon tubing not to exceed 1.5 meters in length.

4.3 Calibrate all flowmeters and critical orifices under the conditions of use against a reliable flow or volume standard such as an NBS traceable bubble flowmeter or wet test meter. Correct all volumetric flowrates to 25°C and 760 torr as follows:

$$F_R = F_S \times \frac{P_S - P_{H_2O}}{760} \times \frac{298}{T_S + 273} \qquad \text{(Eq. B-2)}$$

where: F_R = flowrate corrected to reference conditions (25°C and 760 torr), 1/min

F_S = flowrate at sampling conditions, 1/min

P_S = barometric pressure at sampling conditions, torr

P_{H_2O} = vapor pressure of H_2O at T_S, torr, for wet volume standard (for a dry standard, $P_{H_2O} = 0$.)

T_S = temperature at sampling conditions, °C

4.4 Potassium iodide calibration curve.

4.4.1 Prepare iodine standards, fresh when needed, as follows:

4.4.1.1 Accurately pipet 10 ml of 0.1 N standard potassium iodate ($K1O_3$) solution into a 100-ml volumetric flask containing approximately 50 ml of distilled water. Add 1 g of potassium iodide (KI) and 5 ml of 1 N sulfuric acid (H_2SO_4), dilute to volume with distilled water, and mix thoroughly.

4.4.1.2 Immediately before use, pipet 10 ml of the iodine (I_2) solution prepared in step 4.4.1.1 above into a 100-ml volumetric flask and dilute to volume with absorbing reagent. Then further dilute this solution by pipetting 10 ml of it into a 200-ml volumetric flask and diluting it to volume with absorbing reagent.

4.4 1.3 In turn, pipet 5, 10, 15, 20, and 25 ml aliquots of the final I_2 solution prepared in step 4.4.1.2 above into a series of 25-ml volumetric flasks. Dilute each to volume with absorbing reagent and mix thoroughly. To prevent I_2 losses by volatilization, the flasks should remain stoppered until absorbance measurements are made. Absorbance measurements (see step 4.4.2) should be taken within 20 minutes after preparation of the I_2 standards.

4.4.2 Determine the absorbance of each I_2 standard at 352 nm. Also measure the absorbance of a sample of unexposed absorbing reagent. Determine the net absorbance of each I_2 standard as

$$\text{net absorbance} = \begin{pmatrix}\text{sample}\\ \text{absorbance}\end{pmatrix} - \begin{pmatrix}\text{unexposed}\\ \text{reagent}\\ \text{absorbance}\end{pmatrix} \qquad \text{(Eq. B-3)}$$

4.4.3 For each I_2 standard, calculate the net absorbance/cm as:

$$\text{net absorbance/cm} = \frac{\text{net absorbance}}{b} \qquad \text{(Eq. B-4)}$$

where: b = spectrophotometer cell path length, cm

4.4.4 For each I_2 standard, calculate the I_2 concentration in mole/l as:

$$[I_2]_i = N_{KIO_3} \times \frac{1 \text{ eq } I_2}{1 \text{ eq } KIO_3} \times \frac{1 \text{ mole } I_2}{2 \text{ eq } I_2} \times \frac{10}{100} \times \frac{10}{100} \times \frac{10}{200} \times \frac{V_i}{25} \qquad \text{(Eq. B-5a)}$$

where: eq = equivalent

or,

$$[I_2]_i = N_{KIO_3} \times V_i \times 10^{-5} \qquad \text{(Eq. B-5b)}$$

where: $[I_2]_i$ = concentration of each I_2 standard, mole I_2/liter

N_{KIO_3} = normality of KIO_3 (from step 3.10), equivalent/liter

V_i = volume of I_2 solution (from step 4.4.1.3) = 5, 10, 15, 20, or 25 ml

4.4.5 Plot net absorbance/cm (y-axis) versus the mole I_2/l (x-axis) for each I_2 standard and draw the KI calibration curve. Calculate the slope of the curve in liter mole^{-1} cm^{-1} and record as S_c. The value of the slope should be 26,000 ± 780. If the slope is not within this range, and the photometric accuracy of the spectrophotometer meets the specifications given in 2.11, repeat the procedure using freshly prepared I_2 standards. If the slope is still not within the specified range, repeat the procedure using a different lot of certified 0.1 N KIO_3 to prepare the I_2 standards.

NOTE: Preparation of a new KI calibration curve may not be necessary each time the BAKI procedure is used, if adequate repeatability can be established with less frequent KI calibration.

4.5 Calibration of the O_3 generator.

4.5.1 Adjust the air flow through the O_3 generator to the desired flowrate and record as F_0. At all times the air flow through the generator must be greater than the total flow required by the sampling systems, to assure exhaust flow at the vent.

4.5.2 With the O_3 generator off, flush the system with zero air for at least 15 minutes to remove residual O_3. Pipet 10 ml of absorbing reagent into each of 2 impingers and connect them into the sampling train as shown in Figure B-2. Draw air from the output manifold of the O_3 calibration system through the sampling train at 0.4 to 0.6 l/min for 10 minutes. Immediately transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance - unexposed reagent absorbance) of each solution at 352 nm within 3 minutes. Add the net absorbances of the two solutions to obtain the total net absorbance. Calculate the indicated O_3 concentration (system blank) as equivalent O_3 concentration according to 4.5.4. If the system blank is greater than 0.005 ppm O_3, continue flushing the O_3 generation system for an additional 30 minutes and redetermine the system blank. If the system blank is still greater than 0.005 ppm O_3, the zero air probably contains traces of an oxidizing contaminant, and the activated charcoal and molecular sieve (see step 3.1) should be replaced.

4.5.3 Adjust the O_3 generator to generate an O_3 concentration in the range of interest and allow the system to equilibrate for about 15 minutes. The uncalibrated O_3 analyzer to be calibrated can conveniently be used to indicate the stability of the O_3 generator output. When the O_3 generator output has stabilized, pipet 10 ml of absorbing reagent into each impinger. Draw O_3 from the output manifold of the O_3 calibration system through the sampling train at 0.4 to 0.6 l/min. Use a sample time of between 10 and 30 minutes such that a total net absorbance between 0.1 and 1.0 absorbance units is obtained. (At an O_3 concentration of 0.1 ppm and a sampling rate of 0.5 l/min, a total net absorbance of 0.1 absorbance units should be obtained if a sampling time of

20 minutes and 1-cm spectrophotometer cells are used.) Immediately after collection, transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance - unexposed reagent absorbance) of each solution at 352 nm within 3 minutes. Add the net absorbances of the two solutions to obtain the total net absorbance.

4.5.4 Calculation of indicated O_3 concentration.

4.5.4.1 Calculate the total volume of air sampled, corrected to reference conditions of 25°C and 760 torr as

$$V_R = F_R \times t_S \qquad \text{(Eq. B-6)}$$

where: V_R = volume of air sampled, corrected to reference conditions, liter
F_R = sampling flowrate corrected to reference conditions, l/min
t_S = sampling time, min

4.5.4.2 Calculate the I_2 released in moles as

$$\text{mole } I_2 = \frac{\text{total net absorbance} \times 0.01}{S_c \times b} \qquad \text{(Eq. B-7)}$$

where: total net absorbance = sum of net absorbances for the two solutions
0.01 = volume of absorbing reagent in each impinger, liter
S_c = slope of KI calibration curve, liter mole^{-1} cm^{-1}
b = spectrophotometer cell path length, cm

4.5.4.3 Calculate the μl of O_3 absorbed as

$$\mu l\ O_3 = \text{mole } I_2 \times \frac{1 \text{ mole } O_3}{1 \text{ mole } I_2} \times \frac{24.47 \text{ l } O_3}{\text{mole } O_3} \times \frac{10^6\ \mu l\ O_3}{1\ O_3} \qquad \text{(Eq. B-8a)}$$

or,

$$\mu l\ O_3 = \text{mole}\ I_2 \times 24.47 \times 10^6 \qquad \text{(Eq. B-8b)}$$

4.5.4.4 Calculate the indicated O_3 concentration in ppm as

$$[O_3]_{OUT} = \frac{\mu l\ O_3}{V_R} \qquad \text{(Eq. B-9)}$$

4.5.5 Repeat steps 4.5.3 and 4.5.4 at least one more time at the same O_3 generator setting. Average the two (or more) determinations and record the average along with the O_3 generator setting.

4.5.6 Adjust the O_3 generator to obtain other O_3 concentrations over the desired range. Determine each indicated O_3 concentration using the procedure given above. Five or more O_3 concentrations are recommended. Plot the indicated O_3 concentrations versus the corresponding O_3 generator settings and draw the O_3 generator calibration curve.

4.6 Certification as a transfer standard.

4.6.1 Carry out appropriate qualifications tests as discussed earlier in this appendix.

4.6.2 Certify the procedure against a primary O_3 standard as described in Sections 5 and 6 of this report. Prepare a certification relationship curve relating indicated O_3 concentrations to the primary standard O_3 concentrations, similar to Figure 5-8 (pg 5-24) of this document.

4.6.3 Recertify the procedure as appropriate in accordance with Sections 5 and 6 of this report.

4.7 Calibration of the O_3 analyzer.

4.7.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize.

4.7.2 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".

4.7.3 Using the O_3 generator, the same F_0, the O_3 generator calibration curve, and the certification relationship obtained in step 4.6.2, generate a certified O_3 concentration near 80% of the desired upper range limit (URL) of the O_3 analyzer.

4.7.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{CERT}}{URL} \times 100\right) + Z \qquad \text{(Eq. B-10)}$$

where: $[O_3]_{CERT}$ = certified O_3 concentration at the output manifold, ppm
URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the certified O_3 concentration and the O_3 analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 4.6.2 through 4.7.4.

4.7.5 Generate several other O_3 concentrations (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 generator settings (preferably the same settings as used in step 4.5) or by Option 1. For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding certified O_3 concentration from the certification relationship.

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

4.7.7 Option 1: The various O_3 concentrations required in step 4.7.5 may be obtained by dilution of the certified O_3 concentration generated in 4.7.3. With this option, accurate flow measurements are required. The dynamic calibration system must be modified as shown in Figure B-3 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_0) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. The highest O_3 concentration standard required (80% URL) is assayed according to the procedure in step 4.5. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{CERT} = [O_3]_{CERT} \left(\frac{F_0}{F_0 + F_D}\right) \qquad \text{(Eq. B-11)}$$

where: $[O_3]'_{CERT}$ = diluted O_3 concentration, ppm

F_0 = flowrate through the O_3 generator, l/min

F_D = diluent air flowrate, l/min

NOTE: Direct calibration of the O_3 analyzer may also be accomplished by assaying the O_3 concentrations using the procedure in step 4.5 while simultaneously measuring the corresponding O_3 analyzer responses as specified in step 4.7.

References for Appendix B

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2. B.E. Saltzman and N. Gilbert. Iodometric Microdetermination of Organic Oxidants and Ozone. Anal. Chem., 31:1914, 1959.

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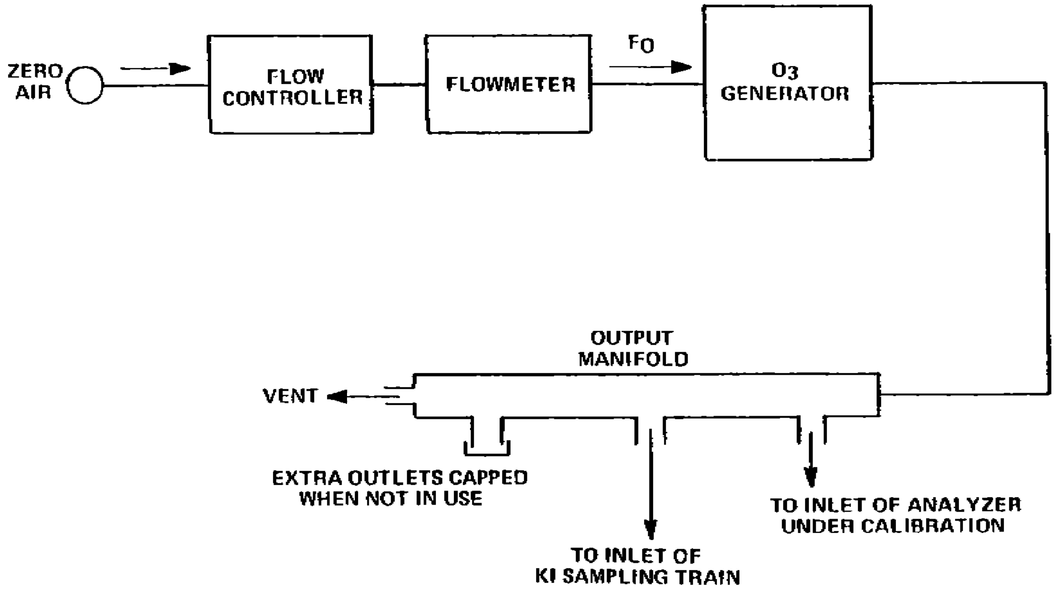

Figure B-1. Schematic diagram of a typical BAKI calibration system.

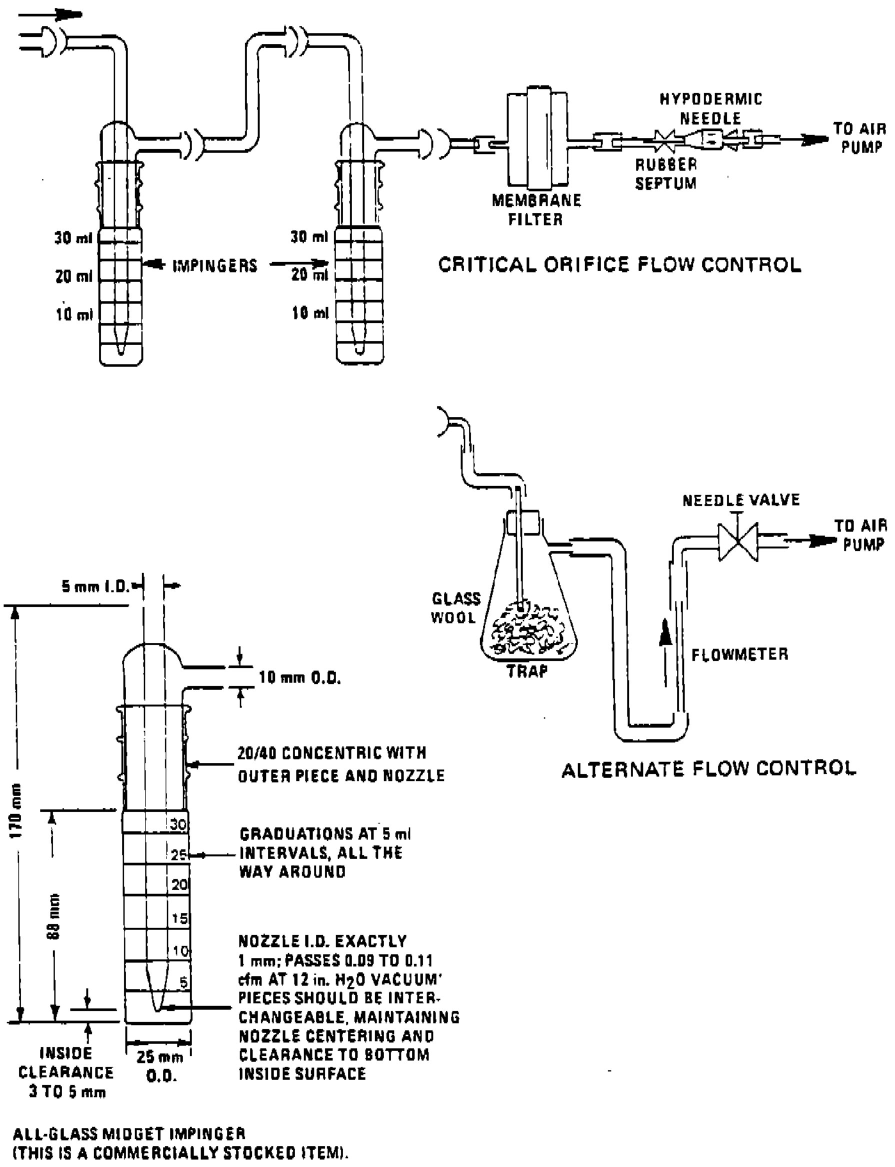

Figure B-2. Components of a KI sampling train.

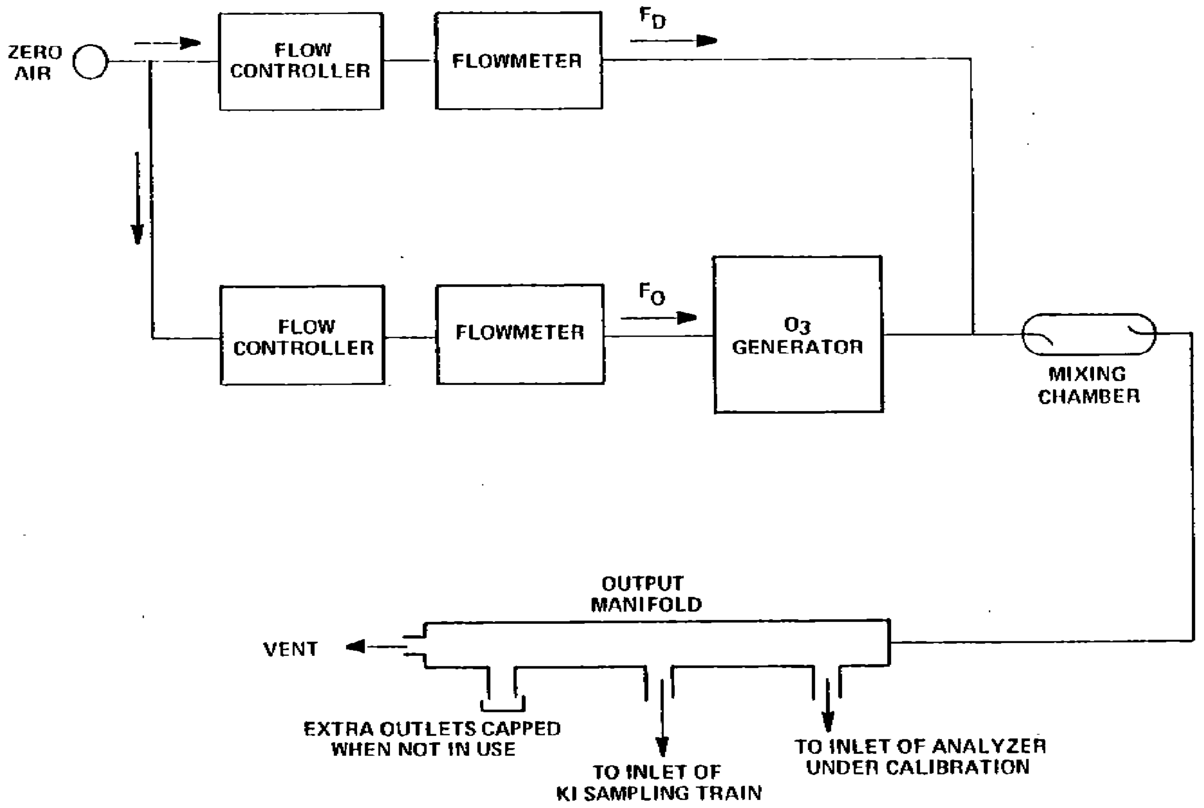

Figure B-3. Schematic diagram of a typical BAKI calibration system (Option 1).

APPENDIX C

CERTIFICATION OF THE GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE PROCEDURE AS A TRANSFER STANDARD

Following the guidance in Sections 4 and 5 and the specifications in Section 6, this appendix attempts to provide more specific instructions for certifying the gas phase titration with excess nitric oxide (GPT-NO) procedure as a transfer standard. The recommended version of the GPT-NO procedure appears at the end of this appendix. Because of the extensive and intimate involvement of the user with the procedure and often with the assembly of the apparatus, the user-procedure combination must be certified, rather than the procedure itself. Hence, each user or user-agency must certify the procedure under its own set of circumstances.

PRELIMINARY REQUIREMENTS

Laboratory tests show that the GPT-NO apparatus and equipment is of critical importance to the success of the GPT-NO procedure. The GPT-NO system must be assembled with great care and attention to the requirements and specifications in the procedure and by an analyst who thoroughly understands the procedure. The assembled system, or a commercially obtained GPT system, should be carefully and completely checked for absence of leaks, compliance with the dynamic specification and other specifications, cleanliness, and proper operation. Once assembled, the apparatus and components should be dedicated exclusively to use as a transfer standard, and the same apparatus (as far as possible) and the same flowrates should be used whenever the transfer standard is used or certified. The NO cylinder standard used should be considered a part of the transfer standard, and the procedure should be recertified whenever a new NO cylinder is needed.

Also important is the skill of the analyst, who must have adequate training in laboratory technique, be thoroughly familiar with the GPT-NO procedure, and able to follow the procedure completely and accurately. Some period of practice is often necessary to achieve consistent results. If problems are encountered, the analyst should seek assistance.

The procedure requires a stable source of O_3 and an attendant source of zero air for the O_3 generator. Since the concentration of O_3 generated by most O_3 generators varies with flow, some means of reasonable flow regulation for the zero air is usually needed. Some helpful guidance for these items may be found in paragraphs 3.3, 3.4, and 4.1 of Reference 2.

The GPT-NO system will also need an output manifold which meets the requirements of step 3.4 of Appendix A. The manifold may be as simple as a TEE where one of the legs serves as a vent. The GPT-NO procedure requires an on-site NO analyzer, but it need not be a part of the transfer standard.

Access to a UV calibration system as described in Appendix A is required for certification of the transfer standard and is also recommended for the qualification tests. Since the O_3 generator is an integral part of the GPT-NO system, compare the output (indicated concentration) of the GPT-NO procedure to the UV primary O_3 standard by using one of the three methods described in Section 5.

Although the NO cylinder standard is not required to be NBS-traceable, use of an NBS-traceable NO standard provides a valuable advantage as a cross check of the accuracy of the transfer standard. A substantial discrepancy between the indicated O_3 concentration based on the traceable NO standard and the UV O_3 standard would indicate a serious problem with one of the systems which must be resolved before the transfer standard can be relied upon.

Review any operation information or instructions provided by the manufacturer of the GPT system, the NO analyzer, and other components to become familiar with their operation.

Review the documentation requirements specified in paragraph 3 of Section 6 and complete item 3.1.

QUALIFICATION

The next step is to qualify the procedure by demonstrating that it is repeatable to within the specifications in paragraph 4 of Section 6 (± 4% or ± 4 ppb, whichever is greater). The variables likely to affect the GPT-NO procedure are similar to those discussed generally in Section 5 and are discussed more specifically below. Refer to Section 3 for additional guidance on each of the qualification tests. A preliminary calibration relationship (as shown in Figure 5-7, pg 5-23 is not necessary for the GPT-NO procedure, as it is linear and provides a direct output of indicated concentration. To minimize potential sources of variability, the apparatus, NO standard, flowrates, techniques, procedures, and conditions should be kept as constant as possible from qualification to certification to use of the procedure. Therefore, these items should be identified in detail as part of the documentation requirements of paragraph 3 of Section 6.

QUALIFICATION TESTS

Temperature

Over normal ranges of room temperatures, effects of temperature change on the GPT-NO procedure should be minimal. The most important effect is on the measurement of the gas volume flow rates. As required by the procedure, gas flow rates must be corrected to reference conditions (25°C and 760 torr). This correction depends on the type of flowmeter used. For a flowmeter which measures actual volume (wet test meter, dry gas meter, bubble meter, etc.), the volume measurement is corrected by using the ideal gas law. Wet volume meters (wet test meters, bubble meters) may require water vapor corrections. Orifice type flowmeters (rotameters, calibrated hypodermic needles) require an orifice correction. Flowmeters which measure mass flow should require no correction. (All flowmeters, of course, require accurate calibration.) If you are unsure of the volume measurement correction, consult the flowmeter instruction manual or other authoritative reference.

The flow controllers and O_3 generator may be affected by temperature changes, but any such effect is accounted for in the procedure.

Line Voltage

Any line-powered components, such as flowmeters could be affected by changes in line voltage. Well designed equipment will show little or no sensitivity to voltage changes over a range of 105 to 125. Look for voltage regulating capability and voltage sensitivity specifications associated with the equipment. Or, use external line voltage regulators. If there is any doubt about line voltage sensitivity effects, then line voltage tests should be carried out as described in Section 5.

Barometric Pressure/Altitude

The only effect of normal changes in pressure on the GPT-NO procedure will be in measurement of the gas volume flowrate. (The O_3 generator will likely be affected but, again, the procedure accounts for that.) If 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% of altitude variations and about 1 to 2% for normal barometric pressure changes). Under these conditions, the effect could be ignored. However, since the flowrates must be corrected to standard conditions, the correction for pressure should be included in that correction. As with temperature effects, the pressure correction depends on the type of flowmeter used. Consult the flowmeter manual or other reference to determine the proper correction formula.

Elapsed Time

Normally, elapsed time has no significant effect on the GPT-NO procedure as long as the apparatus is kept clean and in good working order. Flowmeters normally require periodic recalibration.

Variability

General variability can sometimes be a problem with GPT-NO. As noted previously, changes in the apparatus, NO standard, flowrates, procedure, etc., should be avoided as much as possible to minimize potential variation from those sources. When a component, NO standard, or procedure is changed, a recertification comparison should be carried out to see if the variability or the certification relationship is affected. For any significant change which is to be a variable or option (i.e., sometimes used, sometimes not used), then a variability test as described in Section 5 should be carried out to see if the GPT-NO procedure still qualifies when the variable is exercised. In this case, judgment is needed to decide whether the change would or might cause additional variability in the procedure.

As an example, consider an agency wishing to qualify several analysts and several sets of GPT-NO apparatus. Must each analyst be tested, qualified and certified with each set of apparatus? For more than a very few analysts and sets of apparatus, this becomes impractical. In this case, the agency should insure that each analyst is adequately trained, thoroughly familiar with the procedure, and can make accurate temperature and pressure corrections to the measured flowrates. Then, if each analyst is qualified with at least one set of apparatus, and each apparatus is qualified with at least one analyst, adequate results can reasonably be expected from any analyst-apparatus combination.

Relocation

Relocation tests help to establish the ruggedness of the GPT-NO apparatus. Move the equipment about as it might be moved during subsequent use to see if any malfunctions, leaks, variability, or other problems are observed which might make use of the procedure questionable or inconvenient. If possible, include relocation in the variability tests to measure the effect of relocation on variability.

Malfunctions

There is no special test for malfunctions. During other tests, be observant for any leaks or malfunctions that occur or other characteristic weakness in the apparatus or equipment which could cause unreliability. Understand the design and operation of the components so that you can be alert to non-obvious types of malfunctions.

In summary, the primary qualification tests for most users of the BAKI procedure are variability tests, relocation tests, and verification that each operator can make the proper temperature, pressure, and other corrections to the flow measurement.

CERTIFICATION

When the GPT-NO procedure has been shown to meet the qualification requirements, certify the procedure as specified in Section 6. Additional guidance is contained under "Certification" in Section 5. If any volume or flow correction formulas are needed, use them during the certification procedure and clearly specify the conditions at the time of the certification 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 paragraph 3 of Section 6 .

USE

In using the GPT-NO procedure as a transfer standard, review the guidance under "Use" in Section 5. Recertify the transfer standard as required by Section 6 (with further explanation of recertification in Section 5). 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.

RECOMMENDED VERSION OF GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE TRANSFER STANDARD PROCEDURE

This procedure can be used as a transfer standard for calibration of O_3 analyzers in accordance with the guidance and specifications set forth in Sections 5 and 6.

1. Principle.

1.1 The procedure is based upon the rapid gas phase reaction between nitric oxide (NO) and ozone (O_3) as described by the following equation(1):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(Eq. C-1)}$$

When O_3 is added to excess NO in a dynamic system, the decrease in NO concentration is equivalent to the concentration of O_3 added. The NO is obtained from a standard NO cylinder and O_3 is produced by a stable O_3 generator. A chemiluminescence NO analyzer is used to measure the change in NO concentration. The concentration of O_3 added may be varied to obtain calibration concentrations over the range desired. The dynamic system is designed to produce locally high concentrations of NO and O_3 in the reaction chamber, with subsequent dilution, to insure complete O_3 reaction with relatively small chamber volumes.

1.2 This procedure may be used either to calibrate an O_3 analyzer directly, or (more commonly) to calibrate an O_3 generator which is used immediately after calibration and without physical movement to calibrate the O_3 analyzer. This O_3 generator must be recalibrated prior to each use.

1.3 When this procedure is used directly to calibrate an O_3 analyzer, the O_3 concentration is first established by gas phase titration (GPT), then the NO flow is diverted to allow the O_3 concentration to pass to the output manifold.

2. Apparatus. Figure C-1, a schematic of a typical GPT-NO apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be glass or Teflon. Additional information regarding the assembly of a GPT-NO calibration apparatus is given in Reference 2.

2.1 Air flow controllers. Devices capable of maintaining constant air flow within ± 2%.

2.2 Nitric oxide flow controller. A device capable of maintaining constant NO flow within ± 2%. Component parts in contact with the NO must be of a non-reactive material.

2.3 Air flowmeters. Properly calibrated flowmeters capable of measuring and monitoring air flows within ± 2%.

2.4 Nitric oxide flowmeter. A properly calibrated flowmeter capable of measuring and monitoring NO flows within ± 2%. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.5 Pressure regulator for standard nitric oxide cylinder. This regulator must have non-reactive internal parts and a suitable delivery pressure.

2.6 Ozone generator. Capable of generating stable levels of O_3 over the range and flow rates required (see step 4).

2.7 Reaction chamber. A glass chamber for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) is as specified in step 4. For practical reasons, t_R should be less than 2 minutes.

2.8 Mixing chamber. A glass chamber of proper design to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specifications given in step 4 are met.

2.9 Output manifold. The output manifold should be constructed of glass or Teflon of sufficient diameter to insure a minimum pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.10 Chemiluminescence nitric oxide analyzer. The NO channel of any chemiluminescence NO/NO_2/NO_x analyzer which essentially meets the performance requirements for reference methods for NO_2 (Federal Register, 41:52693, December 1, 1976) may be used; it is used only as a relative indicator and is not considered an integral part of the transfer standard.

3. Reagents.

3.1 Nitric oxide concentration standard. Compressed gas cylinder containing 50 to 100 ppm NO in N_2. Although this NO standard need not be NBS-traceable, a useful cross check of the transfer standard's accuracy is obtained if this NO standard is traceable to an NBS NO Standard Reference Material (SRM 1683 or SRM 1684) or an NO_2 Standard Reference Material (SRM 1629). With a traceable NO standard, the transfer standard's indicated O_3 concentration should agree with the UV standard within - 5% to + 15% (most GPT-NO systems have a positive bias). If it does not, a problem with either the transfer standard or the UV standard is indicated.

3.2 Zero air. Air, free of contaminants which will cause a detectable response on the NO or O_3 analyzer or which might react with either NO or O_3 in the gas phase titration. A procedure for generating zero air is given in Reference 2.

4. Dynamic parameter specifications.

4.1 The residence time (t_R) in the reaction chamber and the gas flows (F_0 and F_{NO}) (see Figure C-1) must be adjusted according to the following relationships:

$$P_R = [NO]_{RC} \times t_R \geq 3.75 \text{ ppm-min} \qquad \text{(Eq. C-2)}$$

$$[NO]_{RC} = [NO]_{STD} \left(\frac{F_{NO}}{F_0 + F_{NO}}\right) \qquad \text{(Eq. C-3)}$$

$$t_R = \frac{V_{RC}}{F_0 + F_{NO}} < 2 \text{ min} \qquad \text{(Eq. C-4)}$$

where: P_R = dynamic specification, determined empirically, to insure complete reaction of the available O_3, ppm-min

$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm

t_R = residence time in the reaction chamber, min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_{NO} = NO flow, scm^3/min

F_0 = O_3 generator air flow, scm^3/min

V_{RC} = volume of the reaction chamber, scm^3

4.2 These parameters may be selected according to the following sequence:

4.2.1 Determine F_T, the total flow required at the output manifold (F_T = analyzer(s) demand plus 10 to 50% excess).

4.2.2 Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately equivalent to 90% of the upper range limit (URL) of the O_3 concentration range to be covered.

4.2.3 Determine F_{NO} as

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} \qquad \text{(Eq. C-5)}$$

4.2.4 Select a convenient or available V_{RC}. Intially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm^3.

4.2.5 Compute F_0 as

$$F_0 = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{3.75}} - F_{NO} \qquad \text{(Eq. C-6)}$$

4.2.6 Compute t_R as

$$t_R = \frac{V_{RC}}{F_0 + F_{NO}} \qquad \text{(Eq. C-7)}$$

Verify that $t_R > 2$ minutes. If not, select a reaction chamber with a smaller V_{RC}.

4.2.7 Compute F_D as

$$F_D = F_T - F_0 - F_{NO} \qquad \text{(Eq. C-8)}$$

where: F_D = diluent air flow, scm^3/min

4.2.8 If F_0 turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_0 and F_D. For a more detailed discussion of these requirements, and other related considerations as well as example calculations, refer to Reference 2.

5. Procedure.

5.1 Assemble a dynamic transfer standard system such as shown in Figure C-1.

5.2 Establish the dynamic parameters as indicated in step 4.

5.3 Insure that all flowmeters are properly calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet test meter traceable to NBS. All volumetric flowrates should be corrected to 25°C and 760 torr.

5.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of the procedure to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in Reference 2.

5.5 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in step 4.2. The total air flow must exceed the total demand of the analyzer(s) or UV certification photometer connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Record F_O, F_D, and F_{NO} used during certification and use approximately the same F_O, F_D, and F_{NO} during field use.

5.6 Calibration of the NO analyzer.

5.6.1 Allow sufficient time for the NO analyzer to warm up and stabilize.

5.6.2 Allow the NO analyzer to sample zero air until a stable NO response is obtained, and make the proper zero adjustments.

5.6.3 Adjust F_{NO} to obtain an NO output concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact concentration is calculated from

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad \text{(Eq. C-9)}$$

where: $[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

Sample this NO concentration until the NO analyzer response has stabilized. Adjust the NO span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \frac{[NO]_{OUT}}{URL} \times 100 \qquad \text{(Eq. C-10)}$$

where: URL = upper range limit of the NO analyzer, ppm

Record the NO concentration and the analyzer response. The NO analyzer should be spanned to the same range as that of the O_3 analyzer to be calibrated. If substantial adjustment of the span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 5.6.2 and 5.6.3.

5.6.4 Generate several additional NO concentrations (at least five are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each NO concentration, calculate the exact NO concentration generated using Equation C-9 and record the analyzer response. Plot the analyzer response versus the calculated NO concentration and draw the NO calibration curve. This plot should be linear. For subsequent calibrations, this curve may be verified with a two-point calibration.

5.7 Calibration of the O_3 generator.

5.7.1 Adjust F_O, F_{NO}, and F_D as determined in step 4.2 and used in step 5.5; generate an NO concentration near 90% of the URL of the NO range. Using the NO analyzer and calibration curve obtained in step 5.6.4, measure and record this NO concentration as $[NO]_{orig}$.

5.7.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in NO concentration equivalent to approximately 80% of the URL. The O_3 concentration must not exceed 90% of the available NO concentration.

5.7.3 Calculate the indicated O_3 concentration as

$$[O_3]_{OUT} = ([NO]_{orig} - [NO]_{rem}) \left(\frac{F_O + F_{NO} + F_D}{F_O + F_D}\right) \qquad \text{(Eq. C-11)}$$

where:
$[O_3]_{OUT}$ = indicated O_3 concentration at the output manifold when $F_{NO} = 0$, ppm
$[NO]_{orig}$ = original NO concentration, ppm
$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

Record $[O_3]_{OUT}$ and the corresponding generator settings.

5.7.4 Adjust the O_3 generator settings to obtain other O_3 concentrations over the desired range, using Equation C-11 to calculate the indicated O_3 concentrations (5 or more O_3 concentrations are recommended.) Plot the indicated O_3 concentrations versus the corresponding O_3 generator settings and draw the O_3 generator calibration curve. Record the O_3 generator settings used during certification, and use approximately the same setting during field use. The O_3

generator calibration curve should replicate fairly closely each time the transfer standard is used; substantial deviations may indicate a problem with the transfer standard.

5.8 Certification as a transfer standard.

5.8.1 Carry out appropriate qualification tests as discussed earlier in this appendix.

5.8.2 Certify the procedure against a primary O_3 standard as described in Sections 5 and 6. Prepare a certification relationship curve relating indicated O_3 concentrations to the primary standard O_3 concentrations, similar to Figure 5-8 on page 5-24.

5.8.3 Recertify the procedure as appropriate in accordance with Sections 5 and 6.

5.9 Calibration of the O_3 analyzer.

5.9.1 Allow sufficient time for the O_3 analyzer to warm up and stabilize.

5.9.2 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".

5.9.3 Using the O_3 generator as calibrated above, generate a certified concentration near 80% of the URL of the O_3 analyzer. F_O, F_D, F_{NO}, and the O_3 generator setting should be as close as possible to their values during certification. Use the O_3 generator calibration curve and the certification relationship curve from step 5.8.2 to establish the certified concentration, $[O_3]_{CERT}$.

5.9.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{CERT}}{URL} \times 100\right) + Z \qquad \text{(Eq. C-12)}$$

where: $[O_3]_{CERT}$ = certified O_3 concentration at the output manifold, ppm

URL = upper range limit of the O_3 analyzer, ppm

Z = recorder response with zero air, % scale

Record the certified O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.8.2 and 5.8.4.

5.9.5 Generate several other O_3 concentrations (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 generator setting (preferably the same settings as used in step 5.7.4). For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding certified O_3 concentration from the certification relationship.

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

OPTIONS: If either of the optional procedures below are elected, the same procedure must be used during qualification, certification, and field use.

5.9.7 Option 1: The various O_3 concentrations required in step 5.9.5 may be obtained by dilution of the certified O_3 concentration generated in step 5.9.3. In this case, F_D is increased to various values to decrease the O_3 output concentration, which is calculated as

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_0 + F_D}{F_0 + F'_D}\right) \qquad \text{(Eq. C-13)}$$

where: $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm
F'_D = the new diluent air flow, scm^3/min

Since only one O_3 generator setting is used, the generator need be calibrated only at that setting. Or, $[O_3]_{OUT}$ may be obtained from Equation C-11 and the certification relationship without actually calibrating the O_3 generator, if the setting is not changed from that used in steps 5.7.2 and 5.7.3. Because F_D must be increased substantially to obtain low O_3 concentrations, the original F_D should be as small as possible (consistent with step 5.5).

5.9.8 Option 2: The O_3 analyzer may be calibrated "directly" by GPT-NO without intermediate calibration of the O_3 generator and without changing F_D. Under this option, the various O_3 concentrations required for calibration in steps 5.9.4 and 5.9.5 are obtained by adjusting the O_3 generator settings. For each such adjustment, the certified O_3 concentration is first established by GPT-NO using Equation C-11 and the certification relationship. Then the NO flow is diverted to allow the O_3 to be delivered to the output manifold and sampled by the O_3 analyzer.

References for Appendix C

1. K.A. Rehme, B.E. Martin, and J.A. Hodgeson. Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide, and Ozone Analyzers by Gas Phase Titration. EPA-R2-73-246, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. March, 1974. pp. 17

2. E.C. Ellis. Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide. EPA-600/4-75-003, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

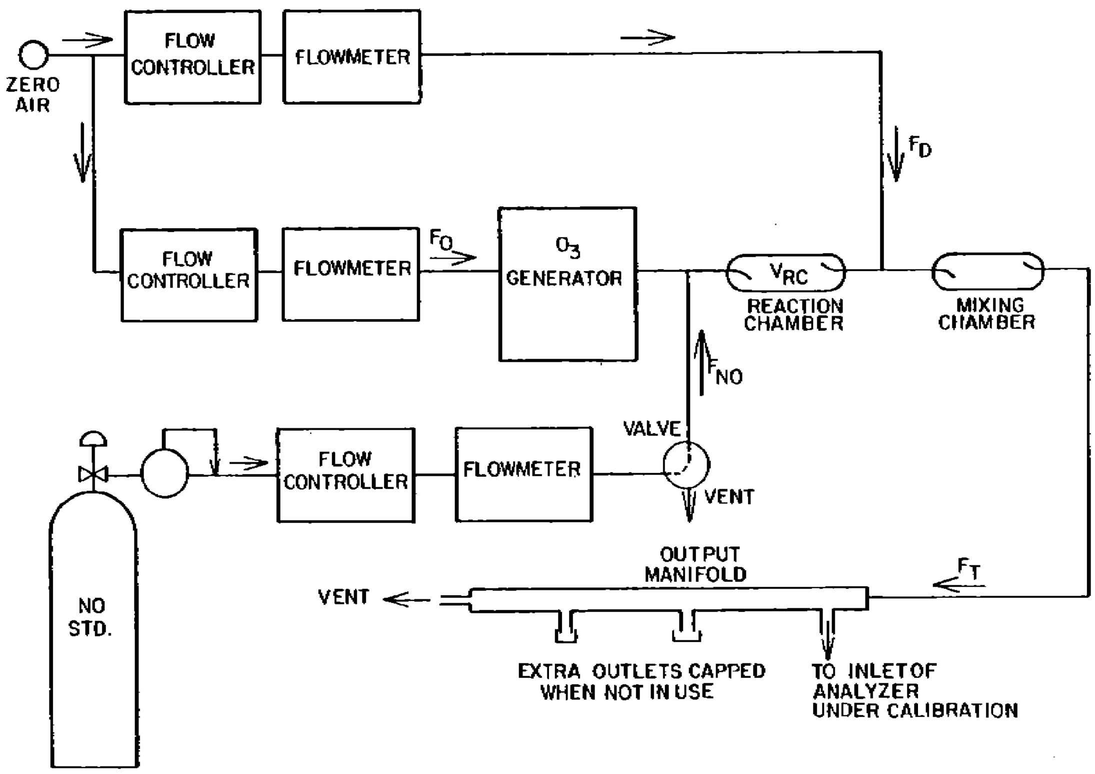

Figure C-1. Schematic diagram of a typical GPT system.

APPENDIX D

CERTIFICATION OF THE GAS PHASE TITRATION WITH EXCESS OZONE PROCEDURE AS A TRANSFER STANDARD

Following the guidance in Sections 4 and 5 and the specifications in Section 6, this appendix attempts to provide more specific instructions for certifying the gas phase titration with excess ozone (GPT-O_3) procedure as a transfer standard. The recommended version of the GPT-O_3 procedure appears at the end of this appendix. Because of the extensive and intimate involvement of the user with the procedure and often with the assembly of the apparatus, the user-procedure combination must be certified, rather than the procedure itself. Hence, each user or user-agency must certify the procedure under its own set of circumstances.

PRELIMINARY REQUIREMENTS

Laboratory tests show that the GPT-O_3 apparatus and equipment is of critical importance to the success of the GPT-O_3 procedure. The GPT-O_3 system must be assembled with great care and attention to the requirements and specifications in the procedure and by an analyst who thoroughly understands the procedure. The assembled system, or a commercially obtained GPT-O_3 system, should be carefully and completely checked for absence of leaks, compliance with specifications, cleanliness, and proper operation. Once assembled, the apparatus and components should be dedicated exclusively to use as a transfer standard, and the same apparatus (as far as possible) should be used whenever the transfer standard is used or certified. The NO cylinder standard used should be NBS-traceable and should be considered a part of the transfer standard; the procedure should be recertified whenever a new NO cylinder is used.

Also important is the skill of the analyst, who must have adequate training in laboratory technique, be thoroughly familiar with the GPT-O_3 procedure, and follow the procedure completely and accurately. Some period of practice is often necessary to achieve consistent results. If problems are encountered, the analyst should seek assistance.

The procedure requires a stable source of O_3 and an attendant source of zero air for the O_3 generator. Since the concentration of O_3 generated by most O_3 generators varies with flow, some means of reasonable flow regulation for the zero air is usually needed. Some helpful guidance for these items may be found in paragraphs 3.3, 3.4, and 4.1 of Reference 2.

The GPT-O_3 system will also need an output manifold which meets the requirements of step 3.4 of Appendix A. The manifold may be as simple as a TEE where one of the legs serves as a vent.

The dynamics of the procedure (various flowrates and residence time of the reaction chamber) are somewhat critical to the procedure and must be optimized to avoid both incomplete reaction of NO as well as secondary reaction of NO_2 with O_3. Initial flowrates are established by theoretical calculations, but the final values must be determined emperically for each system. The flowrates are optimized by measurement to detect residual NO and loss of NO_2, or alternatively by carefully determining the GPT/UV O_3 ratio. In either case, thorough understanding of the GPT reactions and careful measurements are necessary.

Access to a UV calibration system as described in Appendix A is required for certification of the transfer standard and is also recommended for the qualification tests. Since the O_3 generator is an integral part of the GPT-O_3 system, compare the output (indicated concentration) of the GPT-O_3 procedure to the UV primary O_3 standard by using one of the three methods described in Section 5.

Review any operation information or instructions provided by the manufacturer of the GPT-O_3 system components and other components to become familiar with their operation.

Review the documentation requirements specified in paragraph 3 of Section 6 and complete item 3.1.

QUALIFICATION

The next step is to qualify the GPT-O_3 procedure by demonstrating that it is repeatable to within the specifications in paragraph 4 of Section 6 (± 4% or ± 4 ppb, whichever is greater). The variables likely to affect the procedure are similar to those discussed generally in Section 5 and are discussed more specifically below. Refer to Section 5 for additional guidance on each of the qualification tests. A preliminary calibration relationship (as shown in Figure 5-7, pg 5-23 is not necessary for the GPT-O_3 procedure, as it is linear and provides a direct output of indicated concentration. To minimize potential sources of variability, the apparatus, NO standard, techniques, procedures, and conditions should be kept as constant as possible from qualification to certification to use of the procedure. Therefore, these items should be identified in detail as part of the documentation requirements of paragraph 3 of Section 6.

QUALIFICATION TESTS

Temperature

Over normal ranges of room temperatures, effects of temperature change on the GPT-O_3 procedure should be minimal. The most important effect is on the measurement of the gas volume flow rates. As required by the procedure, gas flow rates must be corrected to reference conditions (25°C and 760 torr). This correction depends on the type of flowmeter used. For a flowmeter which measures actual volume (wet test meter, dry gas meter, bubble meter, etc.), the volume measurement is corrected by using the ideal gas law. Wet volume meters (wet test meters, bubble meters) may require water vapor corrections. Orifice type flowmeters (rotameters, calibrated hypodermic needles) require an orifice correction. Flowmeters which measure mass flow should require no correction.

(All flowmeters, of course, require accurate calibration.) If you are unsure of the volume measurement correction, consult the flowmeter instruction manual or other authoritative reference.

The flow controllers and O_3 generator may be affected by temperature changes, but any such effect is accounted for in the procedure.

Line Voltage

Any line-powered components, such as flowmeters, could be affected by changes in line voltage. Well designed equipment will show little or no sensitivity to voltage changes over a range of 105 to 125. Look for voltage regulating capability and voltage sensitivity specifications associated with the equipment. Or, use external line voltage regulators. If there is any doubt about line voltage sensitivity effects, then line voltage tests should be carried out as described in Section 5.

Barometric Pressure/Altitude

The only effect of normal changes in pressure on the GPT-O_3 procedures will be in measurement of the gas volume flowrates. (The O_3 generator will likely be affected but, again, the procedure accounts for that.) If 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, the effect could be ignored. However, since the flowrates must be corrected to standard conditions, the correction for pressure should be included in that correction. As with temperature effects, the pressure correction depends on the type of flowmeter used. Consult the flowmeter manual or other reference to determine the proper correction formula.

Elapsed Time

Normally, elapsed time has no significant effect on the GPT-0_3 procedure as long as the apparatus is kept clean and in good working order. Flowmeters normally require periodic recalibration.

Variability

General variability can sometimes be a problem with GPT-0_3. As noted previously, changes in the apparatus, NO standard, procedure, etc., should be avoided as much as possible to minimize potential variation from those sources. When a component, NO standard, or procedure is changed, a recertification comparison should be carried out to see if the variability or the certification relationship is affected. For any significant change which is to be a variable or option (i.e., sometimes used, sometimes not used), then a variability test as described in Section 5 should be carried out to see if the GPT-0_3 procedure still qualifies when the variable is exercised. In this case, judgment is needed to decide whether the change would or might cause additional variability in the procedure.

As an example, consider an agency wishing to qualify several analysts and several sets of GPT-0_3 apparatus. Must each analyst be tested, qualified and certified with each set of apparatus? For more than a very few analysts and sets of apparatus, this process becomes impractical. In this case, the agency should insure that each analyst is adequately trained, thoroughly familiar with the procedure, and can make accurate temperature and pressure corrections to the measured flowrates. Then, if each analyst is qualified with at least one set of apparatus, and each apparatus is qualified with at least one analyst, adequate results can be reasonably expected from any analyst-apparatus combination.

Relocation

Relocation tests help to establish the ruggedness of the GPT-O_3 apparatus. Move the equipment about as it might be moved during subsequent use to see if any malfunctions, leaks, variability, or other problems are observed which might make use of the procedure questionable or inconvenient. If possible, include relocation in the variability tests to measure the effect of relocation on variability.

Malfunctions

There is no special test for malfunctions. During other tests, be observant for any leaks or malfunctions that occur or other characteristic weakness in the apparatus or equipment which could cause unreliability. Understand the design and operation of the components so that you can be alert to non-obvious types of malfunctions.

In summary, the primary qualification tests for most users of the BAKI procedure are variability tests, relocation tests, and verification that each operator can make the proper temperature, pressure, and other corrections to the flow measurements.

CERTIFICATION

When the GPT-O_3 procedure has been shown to meet the qualification requirements, certify the procedure as specified in Section 6. Additional guidance is contained under "Certification" in Section 5. If any volume or flow correction formulas are needed, use them during the certification procedure and clearly specify the conditions at the time of the certification 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 paragraph 3 of Section 6.

USE

In using the GPT-O_3 procedure as a transfer standard, review the guidance under "Use" in Section 5. Recertify the transfer standard as required by Section 6 (with further explanation of recertification in Section 5). 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.

RECOMMENDED VERSION OF GAS PHASE TITRATION WITH EXCESS OZONE TRANSFER STANDARD PROCEDURE

This procedure can be used as a transfer standard for calibration of O_3 analyzers in accordance with the guidance and specifications set forth in Sections 5 and 6.

1. Principle.

1.1 The procedure is based upon the rapid gas phase reaction between ozone (O_3) and nitric oxide (NO) in accordance with the following equation[(1)]:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(Eq. D-1)}$$

When NO is added to O_3 in a dynamic system, the decrease in O_3 response observed on an uncalibrated O_3 analyzer is equivalent to the concentration of NO added. By measuring this decrease in response and the initial response, the O_3 concentration can be determined. Additional O_3 calibration concentrations are generated by a dilution technique. The GPT system is used under predetermined flow conditions to insure that the reaction of NO is complete and that further reaction of the resultant nitrogen dioxide (NO_2) with residual O_3 is negligible.

2. Apparatus. Figure D-1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections

between components in the calibration system downstream from the O_3 generator should be glass or Teflon. Additional information regarding the assembly of a GPT calibration apparatus is given in Reference 2.

2.1 Air flow controllers. Devices capable of maintaining constant air flow within ± 2%.

2.2 Nitric oxide flow controller. A device capable of maintaining constant NO flow within ± 2%. Component parts in contact with the NO must be of a non-reactive material.

2.3 Air flowmeters. Properly calibrated flowmeters capable of measuring and monitoring air flows within ± 2%.

2.4 Nitric oxide flowmeter. A properly calibrated flowmeter capable of measuring and monitoring NO flows within ± 2%. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.5 Pressure regulator for standard NO cylinder. This regulator must have non-reactive internal parts and a suitable delivery pressure.

2.6 Ozone generator. Capable of generating a stable level of O_3 at the flow rates required (see step 4).

2.7 Reaction chamber. A glass chamber for the quantitative reaction of NO with excess O_3. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) is as specified in step 4.

2.8 Mixing chamber. A glass chamber of proper design to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the other specifications given in step 4 are met.

2.9 Output manifold. The output manifold should be constructed of glass or Teflon of sufficient diameter to insure a minimum pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

3. Reagents.

3.1 Nitric oxide concentration standard. Cylinder containing 50 to 100 ppm NO in N_2. The cylinder should be traceable to an NBS NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). Traceability is important because the $[O_3]_{GPT}/[O_3]_{UV}$ ratio is useful for optimizing the system flowrates (step 4.3) and as a check of the transfer standard's accuracy. The cylinder (working standard) should be recertified on a regular basis as determined by the local quality control program.

3.2 Zero Air. Air, free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with either NO or O_3 in the gas phase titration. A procedure for generating zero air is given in Reference 2.

4. Dynamic parameter specifications.

4.1 Prior to qualification and certification of the apparatus and procedure, the residence time (t_R) in the reaction chamber and the gas flows (F_O and F_{NO}, see Figure D-1) must be optimized. Initially, they should be adjusted according to the following relationships:

$$P_R = [O_3]_{RC} \times t_R = 2.0 \text{ ppm-min} \qquad \text{(Eq. D-2)}$$

$$[O_3]_{RC} = [O_3]_{OUT} \left(\frac{F_T}{F_O + F_{NO}}\right) \qquad \text{(Eq. D-3)}$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \qquad \text{(Eq. D-4)}$$

where: P_R = dynamic specification, determined empirically, to insure complete reaction of NO, ppm-min

$[O_3]_{RC}$ = O_3 concentration (approximate) in the reaction chamber, ppm

t_R = residence time in the reaction chamber, min

$[O_3]_{OUT}$ = 80% URL concentration of O_3 (approximate) at the output manifold, ppm

F_T = total flow at the output manifold, scm^3/min

F_O = O_3 generator air flow, scm^3/min

F_{NO} = NO flow, scm^3/min

V_{RC} = volume of the reaction chamber, scm^3

4.2 These parameters may be selected according to the following sequence:

4.2.1 Determine F_T, the total flow required at the output manifold (F_T = output demand plus 10 to 50% excess).

4.2.2 Determine $[O_3]_{OUT}$ as the 80% URL concentration required at the output manifold.

4.2.3 Determine F_{NO} as

$$F_{NO} = \frac{0.8 \times [O_3]_{OUT} \times F_T}{[NO]_{STD}} \qquad \text{(Eq. D-5)}$$

where: $[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

4.2.4 Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 300 to 1500 scm^3.

4.2.5 Compute F_O as

$$F_O = \sqrt{\frac{[O_3]_{OUT} \times F_T \times V_{RC}}{2.0}} - F_{NO} \qquad \text{(Eq. D-6)}$$

4.2.6 Compute t_R as

$$t_R = \frac{V_{RC}}{F_0 + F_{NO}} \qquad \text{(Eq. D-7)}$$

4.2.7 Compute F_D as

$$F_D = F_T - F_0 - F_{NO} \qquad \text{(Eq. D-8)}$$

where: F_D = diluent air flow, scm^3/min

4.2.8 If F_0 turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_0 and F_D.

4.3 Determine the final system flowrates as follows: Using the GPT-O_3 system and the gas flows determined above, generate an 80% URL O_3 concentration as measured by the primary standard UV photometer. Measure this same O_3 concentration using the GPT-O_3 procedure (steps 5.6.1 through 5.6.6). Calculate the ratio of the two measurements, $[O_3]_{GPT}/[O_3]_{UV}$. For most GPT-O_3 systems, this ratio should be between 0.95 and 1.15 when using a dynamic parameter specification of 2.0 (most GPT-O_3 systems show a positive bias). Ratios greater than 1.05 are indicative of incomplete NO reaction (which can be verified by using an NO analyzer to detect any unreacted NO in the output). Ratios less than 1.05 are indicative of reaction of resultant NO_2 with residual O_3 (excessive residence time). When ratios outside this range are obtained or when a ratio closer to 1.00 is desired, the gas flows must be adjusted and new comparative measurements obtained. This process is most easily accomplished by varying F_0 and F_D while maintaining F_{NO} and F_T constant. Decreasing F_0 should decrease the comparative ratio; likewise, increasing F_0 should increase the ratio. Once an acceptable ratio (0.95 to 1.15) is obtained, record F_0, F_D, and F_{NO}. These flow conditions must then be used during qualification, certification, and subsequent use of the GPT-O_3 procedure as a transfer standard.

NOTE: The $[O_3]_{GPT}/[O_3]_{UV}$ ratio can also be affected by an inaccurate NO cylinder standard, inaccurate flow measurements, leaks, and possibly other factors. Errors from these factors must thus be eliminated before the flows are adjusted based on that ratio. If possible, measurements with an NO/NO_2 analyzer should be used to establish optimum flowrates to avoid both incomplete NO reaction and secondary reaction of NO_2 with O_3.

5. Procedure.

5.1 Assemble a dynamic transfer standard system such as shown in Figure D-1.

5.2 Establish the dynamic flow conditions as indicated in step 4.

5.3 Insure that all flowmeters are properly calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet test meter traceable to NBS. All volumetric flowrates should be corrected to 25°C and 760 torr.

5.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in Reference 2.

5.5 Certification as a transfer standard.

5.5.1 Carry out appropriate qualification tests as discussed earlier in this appendix, using the indicated O_3 concentration ($[O_3]_{OUT}$) from Equation D-10 for qualification tests.

5.5.2 Certify the procedure against a primary O_3 standard as described in Sections 5 and 6. Prepare a certification relationship curve relating indicated O_3 concentrations ($[O_3]_{OUT}$ from Equation D-10, step 5.6.6) to the primary standard O_3 concentrations, similar to Figure 5-7, pg 5-23). Record the gas flows (F_O, F_D, F_{NO}), and the O_3 generator setting required for the 80% URL O_3 concentration.

5.5.3 Recertify the procedure as appropriate in accordance with Sections 5 and 6.

5.6 Calibration of the O_3 analyzer.

5.6.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize. Adjust the diluent air and O_3 generator air flows to the same values as used during certification. To insure that no ambient air is pulled into the manifold vent, the total air flow must exceed the demand of the analyzer under calibration or the UV certification photometer connected to the output manifold. 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".

5.6.2 Adjust the O_3 generator to generate an O_3 concentration of approximately 80% of the URL using the same generator setting as during certification. When the response has stabilized, record the response as I_O. If the analyzer response is offscale, adjust the diluent air flow (F_D) until an on-scale response is obtained and measure the new flow.

5.6.3 Turn the NO flow on and adjust to the same value as used during certification. Provided the O_3 generator output has not changed significantly, the O_3 analyzer response should decrease by 75 to 80% of its original value. When the resultant response has stabilized, record the response as I.

5.6.4 Measure the NO flow and record as F_{NO}.

5.6.5 Calculate the exact NO concentration from

$$[NO] = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad \text{(Eq. D-9)}$$

where: [NO] = diluted NO concentration, ppm

5.6.6 Calculate the indicated O_3 concentration from

$$[O_3]_{OUT} = \frac{I_o - Z}{(I_o - Z)\left(\frac{F_O + F_D}{F_{NO} + F_O + F_D}\right) - (I - Z)} \times [NO] \qquad \text{(Eq. D-10)}$$

where: $[O_3]_{OUT}$ = indicated O_3 concentration, ppm
I_o = original O_3 analyzer response, % chart
I = resultant O_3 analyzer response after addition of NO, % chart
Z = stable zero air response, % chart

5.6.7 Remove the NO flow. The O_3 analyzer response should return to its original value.

5.6.8 Determine the certified O_3 concentration from the certification relationship obtained in step 5.5.2 and adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{CERT}}{URL} \times 100\right) + Z \qquad \text{(Eq. D-11)}$$

where: $[O_3]_{CERT}$ = certified O_3 concentration, ppm
URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale.

If substantial adjustment of the span control (more than ± 15%) is necessary, make the span adjustment and repeat steps 5.6.1 through 5.6.8. If F_D had to be adjusted to give an on-scale O_3 analyzer response, readjust to the initial value prior to repeating these steps. After the final span adjustment, record the certified O_3 concentration and the analyzer response.

5.6.9 Calculate the indicated O_3 concentration produced by the O_3 generator from

$$[O_3]_{GEN} = [O_3]_{OUT} \left(\frac{F_0 + F_D}{F_0}\right) \qquad \text{(Eq. D-12)}$$

where: $[O_3]_{GEN}$ = O_3 concentration produced by the O_3 generator, ppm

5.6.10 Generate several other O_3 concentrations (at least four are suggested) by increasing F_D, the diluent air flow. Calculate the diluted O_3 concentrations from

$$[O_3]'_{OUT} = [O_3]_{GEN} \left(\frac{F_0}{F_0 + F'_D}\right) \qquad \text{(Eq. D-13)}$$

where: $[O_3]'_{OUT}$ = diluted indicated O_3 concentration, ppm
F'_D = the new diluent air flow, scm^3/min

5.6.11 Allow the O_3 analyzer to sample each diluted O_3 concentration until a stable response is obtained. For each concentration, determine the certified O_3 concentration from the certification relationship and record the analyzer response and the corresponding certified O_3 concentration.

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

References for Appendix D

1. K.A. Rehme, B.E. Martin, and J.A. Hodgeson. Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide, and Ozone Analyzers by Gas Phase Titration. EPA-R2-73-246, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. March, 1974. pp. 17

2. E.C. Ellis. Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide. EPA-600/4-75-003. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

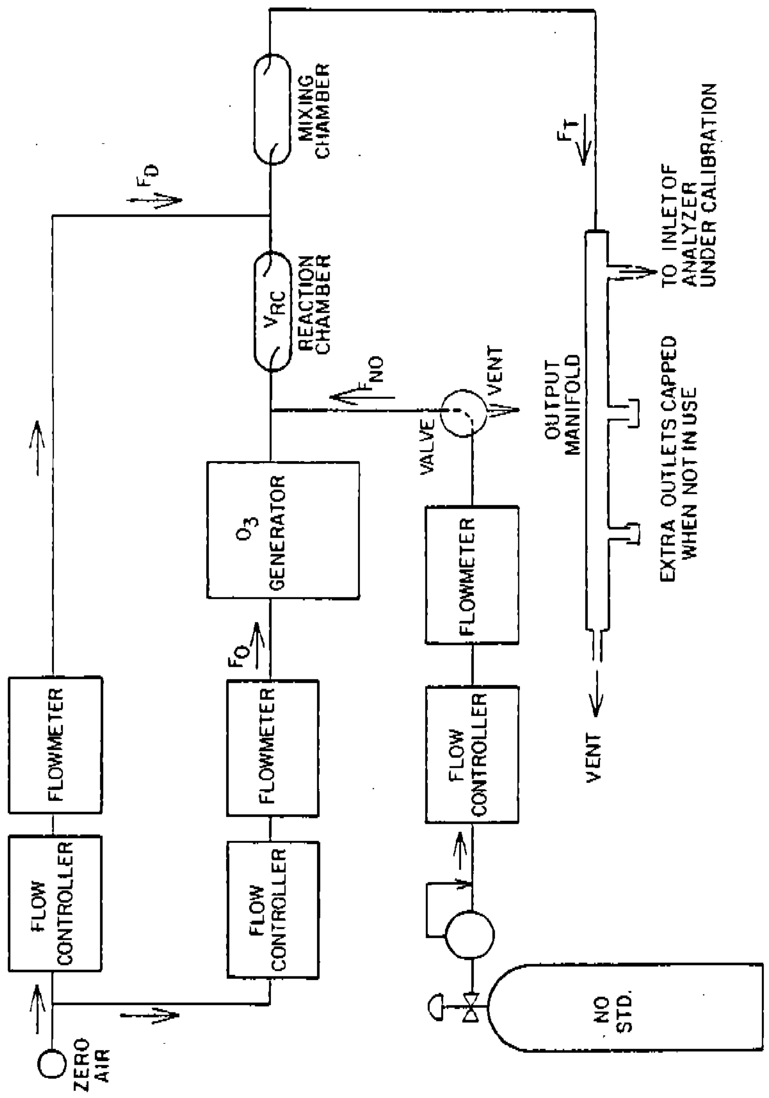

Figure D-1. Schematic diagram of a typical GPT system.

APPENDIX E

CERTIFICATION OF AN OZONE GENERATOR AS A TRANSFER STANDARD

Following the guidance in Sections 4 and 5 and the specifications in Section 6, this appendix attempts to provide more specific instructions for certifying an O_3 generator as a transfer standard.

We will assume, here, that the O_3 generator is of the common UV lamp type. We will also assume that it has a means to adjust the O_3 concentration over a convenient range without changing the flowrate, but that 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. Some helpful guidance may be found in Section 2 of this document. Decide whether or not the zero air subsystem is to be an integral part of the transfer standard (see pg 4-2). 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 paragraph 3.4 of Appendix A. The manifold may be as simple as TEE where one of the legs serves as a vent.

Access to a UV calibration system as described in Appendix A is required for certification of the transfer standard and is also recommended for the qualification tests. Review the O_3 alternate procedures for comparing the output of an O_3-generation-type transfer standard to a UV primary O_3 standard (see Section 5) and decide which procedure to use.

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 paragraph 3 of Section 6 and complete item 3.1.

QUALIFICATION

The next step is to qualify the transfer standard by demonstrating that it is repeatable to within the specifications given in paragraph 4 of Section 6 (± 4% or 4 ppb, whichever is greater). The variables likely to affect an O_3 generator are the same as those discussed generally in Section 5, and specifically below. Refer to Section 5 for additional guidance on each of the qualification tests.

Before starting qualification tests, first prepare a tentative preliminary calibration relationship as shown in Figure 5-7 (pg 5-23), 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 5-7 by plotting the transfer standard's output concentration as measured by the UV reference system at various O_3 settings as discussed in Section 5 under "Comparing Transfer Standards to an Ultraviolet Primary Ozone Standard". 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. Twenty 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 5-3 (pg 5-12). 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 5-4 (pg 5-13. 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 5-7, pg 5-23) and ultimately with the certification relationship (see Figure 5-8, pg 5-24).

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 5-5, pg 5-16).

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 certification 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 certifications, 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

Recolation 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 perculiarities 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.

CERTIFICATION

Before conducting the certification tests, decide whether a new preliminary calibration relationship (see Figure 5-7, pg 5-23) 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 certify the transfer standard as specified in Section 6. Additional guidance is contained under "Certification" in Section 5. It is very important to complete the documentation requirements specified in paragraph 3 of Section 6.

USE

In using the O_3 generator as a transfer standard, review the guidance under "Use" in Section 5. Recertify the transfer standard as required by Section 6 (with further explanation of recertification in Section 5). 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.

APPENDIX F

CERTIFICATION OF AN OZONE ANALYZER AS A TRANSFER STANDARD

Following the guidance in Sections 4 and 5 and the specifications in Section 6, this appendix attempts to provide more specific instructions for certifying 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. We will assume, here, that the analyzer is to be certified over a range of O_3 concentrations, e.g., 0 to 1 ppm.

An analyzer used as a transfer standard should receive special treatment consistent with its authoritative status: careful handling and storage, extra frequent maintenance service and maintenance checks, operation by a fully competent operator, etc. In particular, the analyzer should not be used for ambient monitoring between uses as a transfer standard, as dust or dirt build-up 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 certification 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. Some helpful guidance may be found in Section 2 of this document. Decide whether or not the O_3 generation/zero air system is to be an integral part of the transfer standard (see pg 4-2). 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 certification 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 primary O_3 standard is easy, as the analyzer is simply connected to the output manifold of the UV primary 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 in paragraph 3 of Section 6 and complete item 3.1.

QUALIFICATION

The next step is to qualify the standard by demonstrating that it is repeatable to within the specifications given in Section 6 (± 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 Section 5 and more specifically below. Refer to Section 5 for additional guidance on each of the qualification tests.

Generally, a preliminary calibration relationship (as shown in Figure 5-7 pg 5-23) 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 certification 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, certification, 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. Twenty 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 5-3 (pg 5-12) 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 5-4 (see pg 5-13). 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 certification relationship (see Figure 5-8, pg 5-24).

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 5-3 (pg 5-12).

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 5-5, pg 5-16).

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 certification relationship.

Elapsed Time

Ozone analyzers operated exclusively as transfer standards are not likely to change much with elapsed time. The specified recertification 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.

CERTIFICATION

Before conducting the certification 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 primary standard.

When the adjustments are complete, lock the adjustments, record their values, and proceed to certify the transfer standard as specified in Section 6. Additional guidance is contained under "Certification" in Section 5. If any correction formulas are needed, use them during the certification procedure and clearly specify the conditions at the time of the certification 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 paragraph 3 of Section 6.

USE

In using the O_3 analyzer as a transfer standard, review the guidance under "Use" in Section 5. Make any zero, flow, or other adjustments except span adjustment to the values recorded at the time of certification. Recertify the transfer standard as required by Section 6 (further explanation in Section 5). 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.