

Standard Operating Procedures Ozone (O₃) Monitoring in Ambient Air by Ultraviolet Absorption Spectrophotometry

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Disclaimer

Any mention of equipment manufacturers, instrument or equipment model numbers, commercial vendors or suppliers does not represent an endorsement by the State of Alaska or the Department of Environmental Conservation.



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1. PURPOSE AND SCOPE

This document shall establish standard operating procedures (SOP) for the collection, review, processing, and reporting of ozone (O₃) ambient air quality monitoring data, either collected by the Alaska Department of Environmental Conservation (DEC) or subject to a regulatory review by DEC.

2. APPLICABILITY

This document provides the basic procedures to collect ambient air quality O₃ monitoring data in accordance with federal regulations and EPA quality assurance/quality control (QA/QC) requirements. This document is specific to O₃ monitoring programs which use *ultraviolet absorption photometry* as the measurement technology. This document is generic in that it does not address site specific issues.

This document shall serve as:

- the SOP document for all O₃ monitoring performed by DEC or other local air pollution control agencies to determine compliance with the National Ambient Air Quality Standards (NAAQS), that is all state and local air monitoring station (SLAMS) networks;
- the SOP document for all trace-level O₃ monitoring performed by DEC or other local air pollution control agencies such as for multi-pollutant NCORE monitoring sites; and
- the SOP document for O₃ special purpose monitoring station (SPMS) performed by DEC or other local air pollution control agencies.

This document may serve as:

- a generic template for industry, monitoring contractors, or other community based monitoring programs in the development of a site-specific SOP.

Please note that each industry, monitoring contractor, or community organization tasked with the installation, operation, and reporting of regulatory monitoring data is strongly encouraged to develop a comprehensive site-specific SOP document. While this SOP provides generic operating procedures to ensure compliance with monitoring regulations and EPA guidance, a site-specific SOP should integrate these procedures with detailed information regarding the makes and models of the O₃ analyzer, calibration system, and data acquisition system, as well as specific information regarding monitoring site location, shelter specifications, and siting requirements. It is incumbent upon the preparer to incorporate the most current updates to federal regulations, EPA requirements, or new equipment technologies.

This SOP document, at the date of issuance, represents the latest information on CO monitoring in regards to federal regulations as published in *Title 40 of the Code of Federal Regulations*



(Parts 50, 52, 53, and 58) and EPA requirements as listed in the *EPA Quality Assurance Handbook for Air Pollution Measurements, Volume II, Ambient Air Monitoring Program, May 2013*.

3. SUMMARY OF METHOD

For the purposes of this SOP manual all O₃ measurements are to be performed based on the analytical technique known as *ultraviolet absorption spectrophotometry*.

3.1 Analytical Technique

Most continuous ozone analyzers designated by the EPA as equivalent methods use the basic principle of Beer-Lambert Absorption Law to measure ozone in ambient air. The Beer-Lambert equation defines how light of a specific wavelength is absorbed by a particular gas molecule over a specific distance at a given temperature and pressure. An analyzer which measures ozone using the Beer-Lambert Law is referred to as a photometer. **Equation 1** presents the mathematical expression for the Beer-Lambert Law.

Equation 1. Equation of the Beer-Lambert Law of light absorption as it applies to spectrophotometry

$$\frac{I}{I_0} = e^{(-axC)}$$

Where:

I = light intensity after absorption by absorbing species

*I*₀ = light intensity before absorption by the absorbing species

e = base of the natural logarithm

a = absorption coefficient for the absorbing species

x = path length between light source and detector

C = concentration of the absorbing gas as ppb at standard temperature and pressure (STP)

To solve the equation for *C*, the concentration of the absorbing gas, is rearranged algebraically as shown in **Equation 2**.

Equation 2. Algebraic rearrangement of the Beer-Lambert Law to solve for concentration

$$C = \ln(I_0/I) \times (10^{-9}/\alpha x) \times (T/273^\circ K) \times (760 \text{ mm Hg}/P)$$

Where:

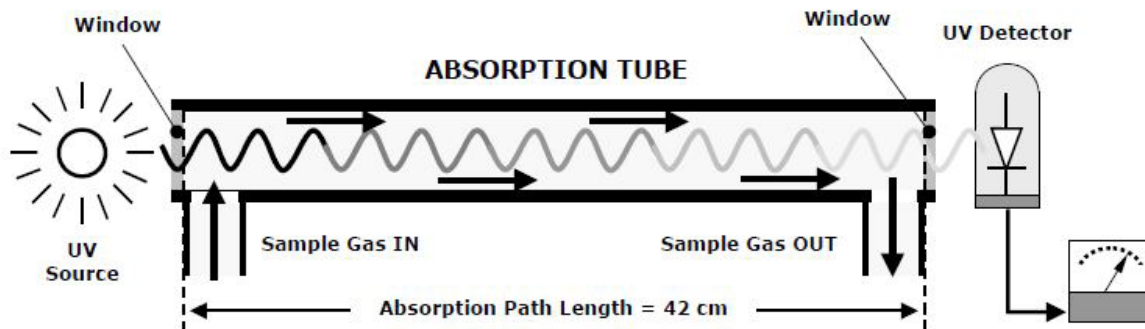
T = temperature as degrees Kelvin

P = pressure as millimeters of Hg

Ambient air is drawn into the analyzer by a vacuum pump into an absorption tube or sample cell of known path length. At one end of the sample cell is a source lamp and optical filter, which emits an ultraviolet (UV) light at a wavelength of 254 nanometers (nm). **Figure 1** show a simple diagram of the absorption tube with the UV light source and the UV detector.



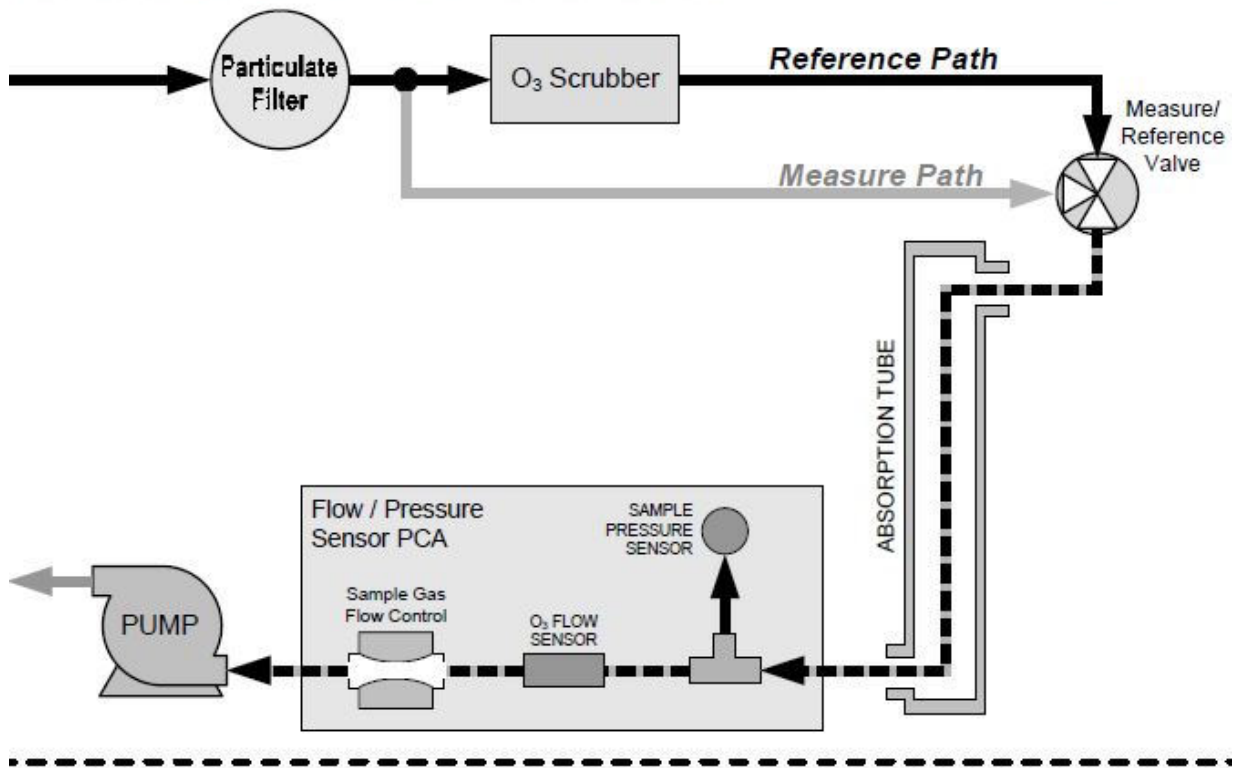
Figure 1. Diagram of O₃ Absorption Path (Courtesy of Teledyne/API)



The UV light is directed through the sample cell to expose the sample gas to the light. As the light passes through the air within the sample cell, energy is absorbed by the ozone molecules in the sample air. A detector at the other end of the sample cell measures the intensity of the light and outputs a signal to the analyzer's microprocessor where the value is stored in electronic memory. The microprocessor controlled analyzer then switches the flow drawing air into the sample cell which has been chemically scrubbed of all ozone. This ozone-free air is known as zero gas. The light intensity is measured during the zero gas cycle and the output is stored in electronic memory. The zero gas serves as a reference which is compared to the sample air. The ozone concentration is electronically calculated using the ratio of light intensity measured for the sample gas to the light intensity measured for the zero gas combined with the known path length, and the absorption coefficient for ozone in air at standard conditions. The analyzer also measures the pressure and the temperature of the sample gas to correct the volumetric concentration. The concentration value is reported to the user via a front panel display and as an electronic output signal recorded by the site data acquisition system. A secondary data acquisition system may be provided by the analyzer electronic memory. **Figure 2** shows a typical diagram of an O₃ analyzer with the reference/measurement gas cycle.



Figure 2. Typical O₃ analyzer flow diagram with reference/measurement gas cycles (Courtesy of Teledyne/API)



3.2 Interferences

Ozone is a strong oxidizing agent and thus a highly reactive gas. Ozone measurements are subject to interferences from a number of other gases including sulfur dioxide (SO₂), nitric oxide (NO), nitrogen dioxide (NO₂), water vapor (H₂O), aromatic hydrocarbons (such as meta-xylene), and mercury vapor. Modern O₃ analyzers use an O₃ scrubbing agent that is specifically designed to remove only O₃ from the zero gas flow during the reference cycle leaving the concentration of any interfering gases chemically inactive. Therefore, any variation in UV light intensities detected during the measurement cycle and the reference cycle would be cancelled out by the signal comparison and only the presences of O₃ would be detected. This technique is effective for SO₂, NO, NO₂, and H₂O; however, the presences of meta-xylene or mercury vapor may still represent a significant interferential effect.

Because O₃ is highly reactive, great care must be taken to maintain the sample gas inlet, manifold and all tubing in a clean and dry manner. Frequent inspection and maintenance is essential to prevent the scrubbing of ambient O₃ within the sample system.

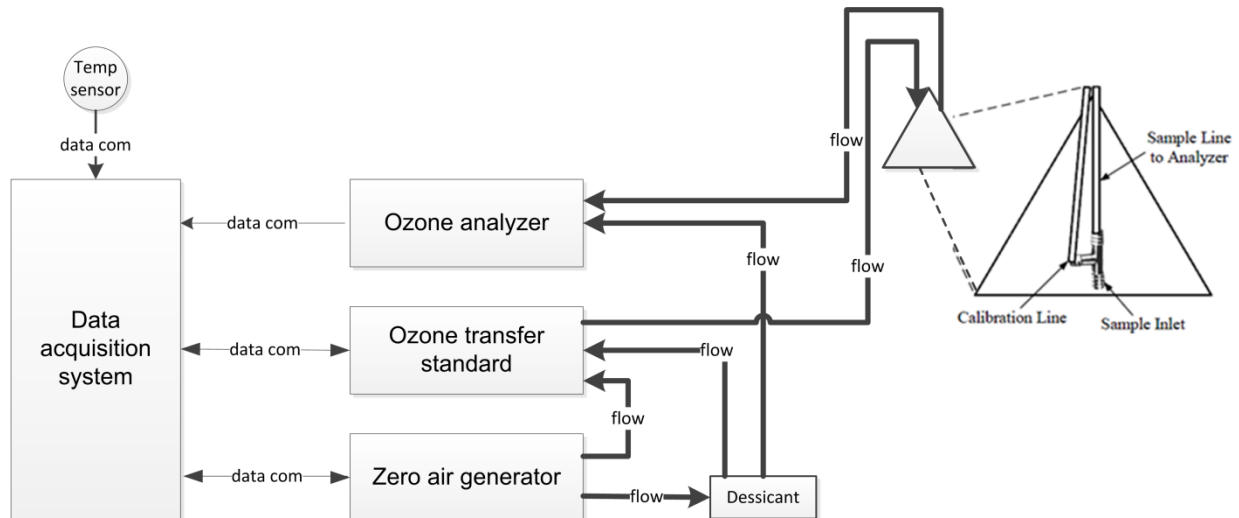


3.3 Basic Monitoring System Configuration

An air monitoring station contains instruments and equipment linked together to form a functional system that will sample, measure, calibrate, record, and store ambient air data.

Figure 3 presents a typical basic configuration of O₃ monitoring system components.

Figure 3. Typical configuration of O₃ monitoring system components



Specific information regarding site selection, monitoring shelter and equipment specifications, data measurement quality objectives are provided in the *Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program*.¹

3.4 Health and Safety Precautions

The following basic precautions should be taken while working with ozone instrumentation and equipment:

1. Properly exhaust any gas output from the ozone analyzer and any excess gas generated from the calibration system to the outside of the monitoring shelter.
2. Assure that all electrical power connections for the monitoring instrumentation and auxiliary equipment are properly grounded with a 3-wire plug.
3. All exterior power circuits must include a ground-fault interrupter.
4. When working on, troubleshooting, or repairing any electrical instrumentation or equipment the technician should remove any jewelry (rings, necklaces or chains) or other personal items which could conduct electricity and result in electrical shock or damage to equipment.

¹ Quality Assurance Project Plan for the State of Alaska Air Monitoring and Quality Assurance Program, DEC February 23, 2010: http://dec.alaska.gov/air/doc/ADEC_AMQA_QAPP_23FEB-final.pdf



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5. Before beginning any repair of electrical instrumentation or equipment (unless otherwise indicated by the equipment service manual), the power shall be turned off and the power cord disconnected.
6. When working on electronic instrumentation and components, the use of an anti-static wristband or floor mat is highly recommended. Properly grounded, these devices will reduce the risk of a static electric discharge which could result in an electrical shock and damage to sensitive electronic components.

The instruments should be placed on a stable bench surface or in an instrument rack with at least 4 inches clearance in the back and 1 inch clearance for the sides, above and below. They must not be placed against heaters or air conditioners. Other routine safety practices shall be observed for the monitoring shelter: the fire extinguisher shall be routinely inspected and serviced; the shelter shall be organized and free of clutter for ease of entry and exit; the electrical service panel shall have unencumbered access; and all walking surfaces, platforms, and ladders shall be maintained to avoid slip and fall hazards.

4. QUALITY CONTROL

Care must be taken not to equate Quality Control (QC) with Quality Assurance (QA). Though the two are very similar, there are some basic differences: QC is concerned with the product, while QA is process or system oriented. Hence, QC is a subset of QA. As an example, preparation of this standard operating procedure is a QA function because it is to ensure strict adherence by site operators to a system or process intended to assure data quality. Routine analyzer calibrations, data verifications, and status checks are QC functions because these checks are on-going technical assessments of the product, i.e., the data. Most of the procedures described in this document are QC procedures. Acceptance criteria for routine QC checks are presented in *EPA Quality Assurance Handbook for Air Pollution Measurements, Volume II, Ambient Air Monitoring Program, May 2013, Appendix D, Ozone Data Validation Table*. As a reference, a copy of the Ozone validation table is presented in **Appendix A** of this document.

4.1 Calibration versus Verification

Calibration is defined as: “*the comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustment*”². For an O₃ monitoring program, an adjusted calibration of the analyzer shall be performed:

- upon initial installation and prior to commencing data collection;
- following physical relocation;
- after any repairs or service that might affect its calibration;

² American National Standard Quality Systems for Environmental Data and Technology Programs ANSI/ASQ E4 <http://www.asq.org/>



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- following an interruption in operation of more than a few days;
- upon any indication of analyzer malfunction or change in calibration; and,
- at some routine interval as required by QC criteria and the QAPP.

The same principle would be true for calibration of any other system measurement devices. See the Ozone Data Validation table in **Appendix A** for specific calibration frequency requirements.

Where a “*calibration*” is associated with an adjustment, a “*verification*” check is a standard comparison to assess on-going data quality and is performed ***without correction***. Verification checks are typically QC procedures performed on a prescribed routine schedule or when some event would necessitate a data assessment. Examples would be: a routine six-month multi-point verification of an O₃ analyzer performed to assess data accuracy and linearity; or single point QC checks for zero/span/precision after a prolonged power outage at a station.

IMPORTANT NOTE: *To properly assess data quality over time, there shall be an initial calibration followed by routine verifications. For the purposes of data review and validation, this establishes the data quality from the beginning of the period with a traceable standard to the time of the verification check where the data quality are again assessed with a traceable standard. This is often referred to as “bracketing the data.” Whenever a measurement device fails a QC performance check or the device becomes inoperable, the data are invalidated from that time the analyzer or system component is repaired and data validity assured back to the last verification check or calibration which passed QC criteria. Unless the measurement device has totally failed, a verification check shall be performed before any adjustment or repair.*

Other common jargon used for verification and calibration procedures are “*As Found*” and “*As Left*.” “*As Found*” would be a verification check to assess data quality without correction. “*As Left*” would refer to the data quality once an adjustment had been successfully made and instrument returned to acceptable performance criteria. As with verification and calibration, “*As Found*” and “*As Left*” relate to bracketing a set of data for the purpose of review and validation.

4.2 Full Scale versus Calibration Scale

Many previous EPA documents and some CFR reference methods refer to calibration at “full scale,” which was interpreted as a multi-point calibration that would be performed over the entire measurement range of the instrument using five evenly spaced points from 80 percent of full scale down to zero. For example, most O₃ analyzers with a selected measurement range of 0 to 0.500 ppm would be calibrated at concentrations of 0.400 ppm, 0.300 ppm, 0.200 ppm, 0.100 ppm, and zero air. However, the primary O₃ NAAQS is established at an 8-hour average of 0.075 ppm. For the State of Alaska, most O₃ concentrations will be recorded at less than



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0.050 ppm. The analyzer response to the above calibration concentrations do not provide much information regarding the stability and accuracy within the range of observed measurements. The EPA suggests monitoring organizations calibrate using points that are more applicable to observed measurements while maintaining a measurement range to assess concentrations above the NAAQS. For example, a more applicable calibration scenarios might be to reduce the instrument measurement scale from 0 to 0.500 ppm to 0 to 0.300 ppm with calibration points performed at 0.240 ppm, 0.180 ppm, 0.120 ppm, and 0.060 ppm. To adapt to this change in focus, the EPA is now using the term “*calibration scale*” to refer to the concentration range used to calibrate or verify a monitoring instrument.

Important Note: *The State of Alaska air monitoring program is currently using a selectable ozone measurement range of 0.000 to 0.300 ppm at all State and Local Air Monitoring Site (SLAMS) locations.*

5. STARTUP PROCEDURES

5.1 Equipment Acquisition, Inspection, and Testing

Prior to startup of any monitoring program all system components will need to be acquired, thoroughly inspected, tested, and the monitoring personnel thoroughly trained. In the case of a gas analyzer, the instrument must be designated as a federal equivalent method (FEM) in accordance with 40 CFR 53.³ The calibration system, ozone transfer standards, zero air generator, and data acquisition system (DAS) must be capable of meeting the specifications as discussed in EPA *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Programs*.⁴ In addition to the main system components, an inventory of manufacturer recommended spare parts shall be ordered and maintained throughout the project.

Each component instrument or device must be thoroughly inspected. New instruments should be carefully unpacked and inspected for damage resulting from shipping. Previously used instruments and devices shall have maintenance logs reviewed to assess time in service, compliance with scheduled maintenance, previous system problems, and parts replacement. All used equipment shall have maintenance and parts replaced as determined appropriate by the inspection.

³ Title 40 of the Code of Federal Regulations, Part 53, Ambient Air Monitoring Reference and Equivalent Methods <http://www.epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf>

⁴ USEPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program, EPA-454/B-13-003, May 2013
<http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf>



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Each instrument or device must be prepared and bench tested prior to start up. This is to ensure that the instrument or device is fully functional, operating within technical specifications, and traceable to the National Institute of Standards and Technology (NIST.)

For calibration systems this will involve leak testing and calibrating mass flow controllers to ensure the accuracy of all flow measurements with traceability to NIST. It will also include initial programming of micro-processor based calibration systems to configure the concentration of standard gases, manual and automated gas blending functionality, event scheduling, and telemetry for data communication.

For zero air generators this will involve leak testing, compression pump testing, functionality of pressure relief valves and moisture drain valves, functionality of heated catalysts, and replacement of filters and chemical scrubber media. Comparison testing to a certified zero air cylinder is strongly encouraged.

The DAS unit's initial programming must be completed to configure all signal input channels and to ensure all calculations for converting electrical (or digital) signals to appropriate engineering units. All signal inputs must be assessed to ensure accurate data transfer from the analyzer and other devices to data memory. The DAS shall also be checked to assess data communications between the monitoring site and base computers or database servers.

Step by step procedures to complete the above tasks will be presented in detail by the manufacturer's operational and service manuals for each specific instrument and device.

5.2 Installation Procedures

Once all monitoring components have been tested for proper functionality, and all standards traceability established, on-site installation can begin.

The analyzer, calibration system, zero air generator, and DAS may be mounted in standard 19-inch instrument racks or bench mounted. In either case, ease of accessibility for power, sample flow, and data connections, as well as access for equipment maintenance is an essential consideration. Sample flow connections shall be as short as practical to meet sample residence time. Compressed gas cylinders must be thoroughly secured in accordance with applicable safety regulations. The room or shelter temperature sensor must be located to provide representative data for the monitoring system environment and certified as traceable to NIST. Accessory equipment such as computers, keyboards, display screens, printers/scanners, and working surfaces should be organized and secured. Storage space for station records, equipment manuals, standard operating procedures, consumable supplies, and spare parts must also be made available.

At initial startup all system components shall be powered up and allowed a sufficient warm-up and shelter temperature equilibration. Most individual instrument manufacturers will state a



warm-up period of at least an hour. Better results are achieved by an equilibration period of at least several hours, overnight is optimum.

5.3 Data Documentation & Recordkeeping Procedures

The collection of valid, representative air quality data is dependent on good recordkeeping procedures. These procedures must be in place prior to the commencement of data collection.

A general station log must be kept in which the site operator will record any event, circumstance, or condition that affects or has the potential to affect data quality. Additional records will include:

- weekly site visit & operational checklists;
- shelter maintenance logs for routine cleaning, repairs, and equipment change outs;
- individual system component repair and maintenance logs (i.e. for the monitoring system analyzer, calibrator, and zero air generator); and,
- a file record for all equipment certifications and standard traceability.

Notes shall be clear and concise but sufficiently thorough to provide an understandable explanation to a third-party responsible for reviewing, validating, and reporting monitoring results. Relevant information must include:

- date and time (in local standard time);
- name of the person recording the log entry and, if applicable, the name of other persons involved in on-site activities;
- if appropriate, system component identification of manufacturer (make), model number, serial number and, where applicable, certification date of traceable standards; and
- specific notes relating to the procedure, event, circumstance or condition and the effect on data quality.

In past days, all these records were kept and recorded in logbooks or on paper checklists, which in many cases may still be appropriate. However, modern DAS systems and software packages have a variety of options for keeping these types of records in an electronic format. Precautions shall be taken to provide secure data backup in a format that (as much as possible) protects against data losses and record alteration.

5.4 Operator Training

It is essential to the success of any air monitoring program that all personnel involved with on-site operations be qualified and thoroughly trained in all aspects of system components and support equipment operation **and** have a thorough understanding of the data validation process, the QAPP and this SOP manual.



IMPORTANT NOTE: Do not underestimate the significant time investment required on the part of the site operator(s) and a senior level instructor to achieve an adequate level of competence.

6. OPERATIONAL PROCEDURES

6.1 Calibration Procedures for the Ozone Analyzer

Unlike other gaseous monitoring systems for sulfur dioxide (SO₂), nitrogen oxides (NO_x), and carbon monoxide (CO), certified concentrations of O₃ are not available in gas cylinders because O₃ is too reactive and will not remain stable over extended periods of time. For O₃ monitoring, the O₃ gases used to challenge the analyzer during calibrations and other QC verification checks are generated and verified on-site using a certified ozone transfer standard.

These calibrations may be performed in a manual or automated mode depending on the capabilities of the analyzer, ozone calibration system, and data acquisition system. Many modern monitoring systems have the capability to conduct remote-controlled calibrations and diagnostics through the data acquisition system. The required frequency for these calibrations and the required QC acceptance criteria are presented in **Appendix A**.

6.1.1 Ozone Transfer Standards

The accepted calibration technique to assure the collection of EPA quality data from ozone photometers requires the use of an ozone transfer standard. The ozone photometer used to measure the ozone concentration in ambient air is referenced to an ozone transfer standard which has been certified for accuracy and stability (repeatability). The ozone transfer standard is a device that consists of a stable ozone generator and/or a UV photometer, and a source of clean, dry, pollutant-free air (zero air). A dynamic flow system is set up in which clean air is passed through the ozone generator at a constant flow rate and discharged into a manifold. The ozone concentration at the manifold is assayed by the photometer and the gas of known concentration is made available for calibration of the on-site ozone analyzer. An ozone transfer standard is certified as stable and accurate through an EPA protocol explained in technical assistance document, *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*.⁵ The technical assistance document provides the scheduled procedures required to establish the authority of the ozone transfer standards through qualification, verification, and periodic re-verification. The EPA established ranking of authority for ozone reference standards as Level 1, 2, 3, and 4. The traceability is established by referencing the on-site ozone transfer standard (Level 3) to an ozone transfer standard of higher authority (Level 2) maintained at the DEC air quality laboratory or another authorized service facility with an

⁵ EPA Technical Assistance Document (TAD) “*Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*,” EPA 454/B-13-004, October 2013.

<http://www.epa.gov/ttnamti1/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf>



ozone transfer standard traceable to a (Level 1) standard reference photometer (SRP). The DEC Level 2 ozone transfer standard is compared to the Level 1 SRP at the State of California Air Resources Board (CARB) metrology laboratory in Sacramento on an annual basis. The ranking of authority for the State of Alaska ozone transfer standards is described below.

Level 1

Standard Reference Photometers

International Bureau of Weights & Measures (BIPM), Paris, FR
National Institute of Standards & Technology (NIST) Gaithersburg MD
EPA Research & Development Laboratory, Research Triangle Park, NC
EPA Regional Office 1-9, Air Laboratories
California Air Resources Board (CARB), Sacramento CA

(Established in a fixed laboratory environment, recertified to BIPM SRP every two years by comparison to a transportable SRP)

Level 2 Ozone Transfer Standards

State of Alaska Reference Photometers (located in Anchorage & Juneau)
Reference Photometers for other Monitoring Organizations

(Distinguished from Level 1 SRP in that Level 2 standards are transported for re-verification to a regional SRP on an annual basis)

Level 3 Ozone Transfer Standards

On-site or Transportable Calibration Systems or Auditing Systems
Reference Photometers or Ozone Generators

(Required re-verification to a Level 2 Ozone Transfer Standard every six months performing a 6-point comparison over 6 days)

Level 4 ozone transfer standards are working standard which require more frequent recertification and are generally not used by DEC. For specific procedures to qualify and recertify the ozone transfer standards at the various levels, see the EPA technical assistance document, *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*.⁶ The QC acceptance criteria for qualification and recertification are presented in **Appendix A**.

6.1.2 Multi-Point Calibrations

The initial multi-point calibration is performed on the ozone analyzer to assure that the instrument responds accurately over the chosen operating range. The measurement range for most modern ozone analyzers is programmable but typically is set to 0.000 to 0.500 parts per million on a volumetric basis (ppmv) or the equivalent 0 to 500 parts per billion on a volumetric basis (ppbv). As discussed in section 4.2, lower measurement ranges may be selected if monitoring for trace levels. For example the State of Alaska uses a measurement range of 0.000 to 0.300 ppm. The ozone transfer standard is programmable to generate ozone

⁶ EPA Technical Assistance Document (TAD) “*Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*,” EPA 454/B-13-004, October 2013.

<http://www.epa.gov/ttnamti1/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf>



concentrations at selected concentration values for five calibration points. Typically the concentrations would be established at the following percentages of the measurement range:

- An initial zero
- 80 to 90 percent of full range
- ~60 percent of full range
- ~40 percent of full range
- <20 percent of full range (usually 18 to 20 percent)

Important Note: *Calibrations are typically performed through a direct connection between the ozone transfer standard and the ozone analyzer.*

After a sufficient equipment warm-up period, the initial adjusted calibration begins with the following steps:

1. From the site server access an MS-Excel spreadsheet “*Ozone Multi-Point Verification and Calibration Data Sheet.*” An example is shown in **Figure 4**. Complete the initial entries for site location, dates, instrumentation, and ozone transfer standard recording all applicable model numbers and serial numbers, and the most recent certification dates. Record the ozone analyzer “As Found” calibration factors for instrument background and calibration coefficient.

Note: The “*Ozone Multi-Point Verification and Calibration Data Sheet*” spreadsheet is set up to calculate data from a multi-point verification followed by an adjust calibration. In the case of an initial calibration only the lower portion of the form “Post-Calibration Results” would be completed.

2. To begin the ozone transfer standard is programmed to direct zero gas into the ozone analyzer. This will be the first calibration point. Once the zero gas flow from the transfer standard has stabilized and the analyzer response is stabilized, the ozone analyzer is adjusted so that the output signal to the DAS and the displayed concentration on the analyzer is equivalent to the concentration displayed by the ozone transfer standard (in this case zero.) Once a stable final zero response has been established, the concentration is recorded in the spreadsheet.

Important Note: *The analyzer response as recorded by the DAS is the primary data record and should be used to document the final concentration values for all calibration points. An analyzer response is typically determined over a 15-minute period with an average calculated from the last five-minutes.*

3. For the second point, the ozone transfer standard is programmed to generate an up-scale concentration at about 80 to 90 percent of the upper measurement range. Once the output of the ozone transfer standard is stabilized and the ozone analyzer response is



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stabilized, the ozone analyzer output is adjusted to match the ozone concentration of the transfer standard. Record the analyzer response from the DAS.

4. Although not required, when performing an adjusted calibration, it is recommended that the next step is to recheck the analyzer response to zero air. Adjust if necessary. Then recheck the analyzer response at the upper scale 80-90 percent concentration and adjust if necessary.
5. Once the ozone analyzer response to zero gas and the upper scale concentration is complete and the analyzer response is within ± 1 ppb at the zero point and ± 2 percent of up- scale concentration, repeat step 2 for the 60 percent concentration point, the 40 percent concentration point, and the 20 percent concentration point. **No further adjustments** are made to the ozone analyzer response at these calibration points. *Note: Additional calibration points below the 20 percent calibration point may be necessary if monitoring for trace levels.*
6. Upon completion, the results of the analyzer response are recorded into the spreadsheet for the zero air and each of the 4 up-scale concentrations. The spreadsheet will perform a least squares (linear) regression analysis comparing the analyzer response to the known concentration $[O_3]_{out}$ at each of the five points. The linear regression will provide a slope and y-intercept of the best-fit line representing the calibration data as shown in **Equation 3**. The spreadsheet will calculate a new analyzer response for each the five points based on the best-line equation.

Equation 3 Least squares regression equation representing the calibration data as a best-fit line.

$$y = mx + b$$

Where:

y = the analyzer response as calculated from the best-fit equation

x = the reference gas concentration

m = the slope of the best-fit line

b = the y-axis intercept of the best-fit line

7. The percent difference is calculated comparing the analyzer response from the best-fit line to the known O_3 concentration from the transfer standard $[O_3]_{out}$ for each up-scale point using **Equation 4**. Record the calibration results in the station log book. The Operational QC acceptance criteria presented in **Appendix A** calculated as percentage difference be within $\pm 2\%$ for each point, the linearity as indicated by slope (m) from **Equation 3** is to be within $\pm 5\%$ (i.e. within a range of 0.95-1.05).



Figure 4 Example “Ozone Multi-Point Verification and Calibration Data Sheet” spreadsheet.

Ozone Multi-Point Verification & Calibration Data Sheet					
Station	Palmer		Date	6/26/2015	
Street Address	South Gulkana Street		Ozone Transfer Standard Manuf	EnviroNics	
City	Palmer Alaska		Model No.	6103	
Performed by	Bob Morgan		Serial No.	4621	
			Date of Last Certification	5/6/2015	
Inst. Manufacturer	Teledyne API				
Model No.	400E		Zero Air Supply Manufacturer	Teledyne API	
Serial No.	2128		Model No.	701	
Meas. Range	0-300 ppb		Serial No.		
Pre-Calibration Multi-Point Verification Results					
Instrument Background	As Found	As Left	Calibration Coefficients	As Found	As Left
O ₃ (zero setting)	-3.9	not adjusted	O ₃ (slope setting)	1.011	not adjusted
The unadjusted multi-point verification checks were within QC acceptance criteria. Each up-scale concentration check was within a percent difference of ± 2% and overall linearity calculated a slope of the Best-Fit line was within 0.95 to 1.05. The error for the zero air point as calculated by the y-intercept was within ± 1.5 ppb.					
O ₃ Verification and Linearity Checks			Best Fit Line Values (x) vs Analyzer Response (y) Plot		
Caibration Points	[O ₃] _{OUT}	O ₃ Analyzer Response	O ₃ Analyzer Response from Best-Fit Line y=mx+b	Percent Difference d _i (Best-fit vs Analyzer Response)	
units	ppb	ppb	ppb	%	
Zero Air	0.0	-1.0	na	na	
80% URL	240.0	234.1	234.0	0.05	
1	120.0	116.4	116.5	-0.09	
2	60.0	57.3	57.8	-0.81	
3	30.0	28.9	28.4	1.76	
O ₃ Linear Regression		Slope m=	y-intcpt b =	correl r=	
		0.9733	0.9790	-0.97	1.0000
QC Acceptance Criteria - All pts within ±2% of cal. Range of best-fit line, Linearity < 5% (m = 0.95 to 1.05)					
Post-Calibration Multi-Point Calibration Results					
Instrument Background	As Found	As Left	Calibration Coefficients	As Found	As Left
O ₃ (zero setting)	-3.9	-4.8	O ₃ (slope setting)	1.011	1.032
Post Calibration Verification passed all QC acceptance criteria.					
O ₃ Calibration and Linearity Checks			Best Fit Line Values (x) vs Analyzer Response (y) Plot		
Caibration Points	[O ₃] _{OUT}	O ₃ Analyzer Response	O ₃ Analyzer Response from Best-Fit Line y=mx+b	Percent Difference d _i (Best-fit vs Analyzer Response)	
units	ppb	ppb	ppb	%	
Zero Air	0.0	0.3	na	na	
80% URL	240.0	239.9	240.0	-0.04	
1	120.0	120.3	120.1	0.20	
2	60.0	60.2	60.1	0.17	
3	30.0	29.7	30.1	-1.38	
O ₃ Linear Regression		Slope m=	y-intcpt b =	correl r=	
		1.0002	0.9994	0.13	1.0000
QC Acceptance Criteria - All pts within ±2% of cal. Range of best-fit line, Linearity < 5% (m = 0.95 to 1.05)					
pass QC		fail QC			



Equation 4. Calculation of Percent Difference

$$\text{Percent Difference (di)} = \frac{\text{Analyzer Response (O3 ppb)} - \text{Known Ozone Concentration ([O3]out in ppb)}}{\text{Known Ozone Concentration ([O3]out in ppb)}} \times 100$$

Where:

di = percent difference (%)

Analyzer Responses as calculated from the best-fit line (ppb)

Known Ozone Concentration as determined from the certified ozone transfer standard (ppb) (often abbreviated as [O₃]_{out}).

8. If the calibration results are not within QC requirement, troubleshoot the problem, make necessary corrections, and re-calibrate the analyzer.

Once the ozone analyzer has been successfully calibrated and meet the applicable QC requirements in **Appendix A**, record the “As Left” calibration factors for instrument background and calibration coefficient. Maintain a copy of the spreadsheet and the DAS 1-minute data for calibration period to be saved for data archival.

6.2 Routine Operational Checks

Routinely scheduled operational checks are essential for evaluating and documenting the on-going quality of the data. These QC checks range from physical inspections of the shelter and sample system to status checks of the various instruments and auxiliary equipment components. **Figure 5** presents an example spreadsheet for the operational checks. It is recommended that these status checks be documented during every site visit. The form may be completed digitally via MS Excel or on a paper copy with files appropriately saved for data archival.

6.2.1 Data Acquisition System (DAS) Checks

Whether the DAS is a standard alone data logger or a computer/server record the manufacturer, model number, and serial number along with the current software and version. Note the following items:

- that the display is up and functional;
- that the current date and time is correct and synonymous (within ± 1 minute) with Alaska Standard Time (AST); and,
- that data from all the configured monitoring channels are showing instantaneous readings.

6.2.2 Shelter Temperature

Maintaining a stable shelter temperature is a factor in preventing calibration drift in monitoring instrumentation and is listed as an operational QC criteria listed in the Ozone Validation Table shown in **Appendix A**. The monitoring shelter or the room housing the analyzer must contain a sensor to continuous record room temperature to ± 1° C. Note the following items: current temperature; daily maximum temperature, daily minimum temperature, and the daily variation in room temperature as standard deviation over the daily 24-hour period. If the daily criteria



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Figure 5 Ozone Monitoring Program Operational Checklist

Station Name								
Station Location								
Date of Operational Checks	YYYY/MO/DD							
Time of arrival on-site (AST)	HR:MN							
Technician Name	Initials							
Operational Checks								
On-Site Data Acquisition System (DAS)								
Computer or Server ID	Make/Model #							
	Serial #							
DAS Software ID	Name & Version							
Power on & display up	Yes or No							
Current date & time within ± 1 min of NIST AST	± 1 min NIST Clock (In AK Std Time)							
Data displays visible for monitoring channels	Yes or No							
Shelter or Room Temperatures								
Current Temperature °C	(15 to 30 °C)							
Daily Max Temperature °C	≤ 30 °C							
Daily Min Temperature °C	≥ 15 °C							
Variability of Daily Temperature	Std Dev of ± 2° C							
Sample System Inspection								
Sample Inlet/Manifold/Tubing open & debris free	Yes or No							
Any indication of moisture	Yes or No							
Exhaust manifold and exterior exit open & debris free	Yes or No							
Zero Air Generator								
Instrument ID	Make/Model #							
	Serial #							
Power On	On							
Output pressure psig	20 to 25 psig							
Pressure tank moisture drain operational	Yes or No							
Date of last scrubber reagent change	YYY/MM/DD							
On-Site Level 3 Ozone Transfer Standard								
Instrument ID	Make/Model #							
	Serial #							
Power On	On							
Program Mode	Flow/Conc/Auto							
Auto Cal Program Schedule	1 MO 00:00 PROG 1							
Current date & time within ± 1 min of NIST AST	Yes or No							
Date of last certification to Level 2 Ozone Transfer Std.	YYYY/MM/DD							
Certified within last 6-months	Yes or No							
Ozone Analyzer								
Instrument ID	Make/Model #							
	Serial #							
Power On	On with Run Display illuminated (v)							
Analyzer fault indicated	Yes or No							
Warning Message	Specify warning							
Current O ₃ display concentration	O3 ppb (###.#)							
Does the O ₃ display conc match the DAS conc within ± 0.5 ppb?	Yes or No							
Date of last calibration	YYYY/MM/DD							
Date of last change of in-line sample filter	YYYY/MO/DD							
Power & Signal Protection								
Surge Protector	Indicators Light On(v)							
Uninterruptable Power Supply (UPS)	Indicators Light On(v)							
Off-site Departure Time	AST							
If any irregularities are noted in the above readings, provide a full explanation and any corrective actions taken in the station logbook.								



are exceeded make a note in the station log to flag data with a QC operational deviation. Take appropriate corrective action to stabilize room temperature.

6.2.3 Sample System Inspection

The sample system consists of:

- a. sample inlet;
- b. (if applicable) a sampling manifold with moisture trap and blower motor;
- c. All gas connections and solenoid valves associated with the calibration system;
- d. all sample tubing within the sample flow system to the analyzer; and
- e. exhaust manifold

The site operator should conduct a visual inspection of the above components during each site visit. Inspection items should include:

- f. breakage, crimps, constriction of flow or discoloration in any of the tubing;
- g. moisture, particulates or foreign matter deposition inside the sample manifold or tubing;
- h. tight, secure connections to prevent leaks;
- i. exhaust manifold flow is unrestricted to the exterior of the shelter.

Any irregularities noted from the above inspections will require immediate corrective action and documented in the station log.

6.2.4 Zero Air Generator Checks

The zero air generator must be checked to insure the unit is on, the display indicates functionality, the output pressure is within acceptable limits and the moisture drain is operating and not blocked. The last change of scrubber media must be recorded and assessed for scheduled replacement.

6.2.5 On-Site Ozone Transfer Standard Checks

The on-site ozone transfer standard generates known concentrations of ozone to calibrate and perform routine QC performance verifications on the ozone analyzer. On-site ozone transfer standards are typically certified as Level 3 devices (see section 6.1.1) and require recertification at the start and completion of every ozone season or, for continuous monitoring programs, every 6 months. Note and record the following operational items:

- instrument manufacturer, model and serial number;
- power is on and display up;
- program mode (concentration, flow, or auto);
- program schedule for automated functions;
- current date and time within ± 1 of AST;
- date of last certification to a higher level standard; and,
- that a certification was performed within the last 6-months.



6.2.6 Analyzer Status Checks

Status checks performed on the ozone analyzer will vary among instrument manufacturers but in general they will include:

- power on and the display up;
- if the analyzer indicate a fault or alarm condition;
- if so, identify the specific condition or warning message;
- record the current ozone concentration;
- current date and time (± 1 minute of AST);
- if the current display concentration matches the DAS concentration within ± 0.5 ppb;
- date of the last multi-point calibration or verification; and,
- date of the last sample filter change.

The site operator must conduct a visual inspection of the sample system particulate filter on a regular basis to assess local dust conditions and determine the frequency of necessary filter changes. Any particulate matter accumulation that discolors of the filter material shall prompt a replacement. At a minimum, the particulate filter should be replaced on a monthly basis. A system leak check is to be performed following each change.

6.3 Routine QC Performance Verification Checks

Upon completion of installation, startup and initial calibration, the monitoring system will generate and store 1-minute data values representing the ambient air concentration of ozone. From this starting point, routine procedures must be performed to assure the on-going quality of the data. The primary quality control (QC) procedures used to verify analyzer performance and data quality are referred to as Zero/Span Checks. These checks assess data accuracy at the low and high ends of the analyzer measurement range. Another QC check is performed to verify data accuracy near the range of ozone concentrations normally measured in ambient air. In the EPA QA Handbook, Volume II, this procedure is referred to as a “One Point QC Check, Single Analyzer,” more frequently referred to as a “precision check.”

6.3.1 Zero/Span Checks

Zero/span checks are to assess data quality and on-going analyzer performance, and are also performed for system diagnostics. This is done by challenging the ozone analyzer first with zero air and then with an up-scale ozone concentration typically set at 80 percent of the measurement range. These checks may be performed manually or through an automated program function of the analyzer, ozone transfer standard and the DAS.

Important Note: *Zero air and calibration gas generated for these checks are introduced to the sample system near the sample probe inlet. In addition to analyzer performance, this allows for an assessment of system bias resulting from the exposure of the calibration gases to the sample system. The required minimum frequency to perform zero/span and precision checks as shown*



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in *Appendix A* is once every two weeks; however, DEC “**highly**” recommends that zero/span and precision check be performed more frequently.

1. The zero check begins with the calibration system generating zero air through the transfer standard. Manual or solenoid valves are actuated to feed the zero air into the sample system for a period of time until the analyzer response stabilizes. The stabilization period of time will depend on the manufacturer’s specification for instrument response. Once stabilized, a five minute average is typically calculated to determine the analyzer response for zero air.
2. Upon completion of the zero air check, the span check is initiated by actuating the transfer standard (either manually or automatically) to generate an ozone calibration gas concentration at 80 percent of the analyzer measurement range. The check is allowed to proceed for a specified period allowing the analyzer response to stabilize. A five minute average for the analyzer response to span gas is then calculated recorded.

6.3.2 Precision Checks

This one-point QC check is performed to assess data accuracy and repeatability within a measurement range more typical of ozone concentration which would be measured in ambient air. The EPA requires that this QC check be performed within a concentration range of 0.010 ppm to 0.100 ppm. The EPA also requires that this one-point QC check be performed at least once every two weeks. (DEC “**highly**” recommends that precision checks be performed more frequently.)

1. Precision checks are typically performed following zero/span checks. Upon completion of the zero/span checks the transfer standard is prompted (either manually or by programmed function) to generate a calibration gas concentration within the range of 0.010 to 0.100 ppm. For consistency in the required statistical analysis of the precision data, once selected this concentration should remain the same for on-going checks. The check is allowed to proceed for a specified period allowing the analyzer response to stabilize. The analyzer response is then recorded by the DAS.
2. At the final conclusion of the Zero/Span/Precision checks, the transfer standard is prompted (either manually or by programmed function) to generate zero air. The purpose of introducing zero air is to purge any residual ozone from the sample system. For ozone monitoring, the zero air purge should proceed for a period of at least five minutes before returning to sample status.

6.3.3 Routine Multi-Point Verifications

EPA requires that analyzer performance across the entire measurement range of the instrument be routinely verified. As shown in Ozone Data Validation Table in **Appendix A**, a multi-point verification is to be performed every six month if zero/span and precision check are conducted biweekly. If zero/span and precision checks are conducted continuously on a daily basis, the multi-point verification need only be conducted once per year. As with the initial calibration the multi-point verification would consist of determinations for zero air and four up-scale ozone concentration. The difference being that for a verification, the analyzer response for each



concentration is recorded “As Found” without any adjustments made to the instrument. Typically the concentrations would be established at the following percentages of the measurement range:

- Zero air
- 80 to 90 percent of full range
- ~60 percent of full range
- ~40 percent of full range
- <20 percent of full range (usually 18 to 20 percent)

Important Note: Unlike a calibration, the zero air and up-scale gases used during a multi-point verification are introduced to the sample system near to the sample inlet to assess system bias as well as analyzer performance.

The results of the multi-point verification are to be recorded and statistical analysis completed using the “Ozone Multi-Point Verification and Calibration Data Sheet” spreadsheet shown in Figure 4.

6.3.4 Calculation of Performance Verification Results

The results of the zero air checks are calculated as percentage difference as shown below in **Equation 5**.

Equation 5. Calculation of Percent Difference for Zero Air Checks

$$\text{Percent Difference (di)} = \frac{\text{Analyzer Response (ppb)} - \text{Known Ozone Concentration (ppb)}}{\text{Full Scale Concentration (ppb)}} \times 100$$

Where:

di = percent difference (%)

Analyzer Responses as actual concentration recorded from the DAS (ppb)

Known Ozone Concentration as determined from the certified ozone transfer standard (ppb)

Full-Scale concentration of the analyzer measurement range (ppb)

The results for the span and precision checks are calculated as percentage difference as shown in **Equation 6**.

Equation 6. Calculation of Percent Difference for Span and Precision Checks

$$\text{Percent Difference (di)} = \frac{\text{Analyzer Response (O}_3 \text{ ppb)} - \text{Known Ozone Concentration ([O}_3\text{]out in ppb)}}{\text{Known Ozone Concentration [O}_3\text{]out(ppb)}} \times 100$$

Where:

di = percent difference (%)

Analyzer Responses as actual concentration recorded from the DAS (ppb)

Known Ozone Concentration as determined from the certified ozone transfer standard (ppb)(often abbreviated as [O₃]_{out}).

The results of a multi-point verification are to be recorded and calculated using the Multi-Point Verification and Calibration Data Sheet shown in **Figure 4** and as discussed in section 6.1.2.



6.3.5 Performance Verification QC Limits

The Ozone Data Validation Table shown in Appendix A present the “Critical Criteria” for a One-Point QC Check, Single Analyzer (the precision point) as ± 10 percent. The same criteria is used for span drift. The “Critical Criteria” zero drift is ± 2 percent of full scale. Deviation beyond these critical QC limits is grounds for data invalidation.

***Important Note:** These “Critical Criteria” are different from current federal QC requirements. Federal regulations as prescribed in Title 40 Code of Federal Regulations, Part 58 have critical criteria for zero drift as ± 1.5 ppb and span drift as percentage difference for the both the span and precision points at ± 7 percent. The State of Alaska requested extended QC requirements to accommodate shelter temperature issues for monitoring shelter located in Alaska’s sub-Arctic and Arctic environments. This waiver was accepted through approval by Region 10 of the DEC air monitoring QAPP⁷.*

The “Operational Criteria” QC acceptance criteria for Multi-point verifications are the same as discussed in section 6.1.2.

6.4 Corrective Actions

To achieve data quality objectives, the site operator and other monitoring staff must respond whenever equipment status checks deviate from operational norms or performance QC verification results approach or fail acceptance criteria. To avoid data invalidation and to optimize data capture, DEC has established specific thresholds when corrective action is warranted. **Table 1** presents the DEC protocol for corrective action thresholds.

If the action thresholds were exceeded, an initial assessment must be made to determine the extent of the corrective action required. For the threshold conditions highlighted in pink indicating exceedance of QC critical criteria, data shall be invalidated or at a minimum flagged with a qualifier code. For the threshold conditions highlighted in yellow indicating the data is still with QC acceptance criteria but requires attention, the corrective action may be less stringent. This may be a matter of performing simple maintenance (e.g. replacing a particulate filter or repairing a leak in the sample system) and may not require an adjustment to the analyzer. For minor zero drift ± 2 ppb, the site operator may adjust the analyzer zero background setting without a calibration. If the calibration drift at the span or precision point exceeds ± 4 percent, further assessment and a recalibration is required.

⁷ Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program, February 23, 2010. http://dec.alaska.gov/air/doc/ADEC_AMQA_QAPP_23FEB10-final.pdf



Following any corrective actions a zero/span/precision check or a full calibration shall be performed to bracket data quality going forward. All corrective actions shall be thoroughly documented in the station logbook and/or the DAS electronic log.

Table 1 Corrective Action Thresholds for the Ozone Analyzer

Zero Drift as percentage difference (d_i) or as absolute difference (ppb)	Description of Corrective Action		Calibration Drift as percentage difference (d_i)
> + 2% of full scale	Invalidate data and recalibrate		> +10 %
> + 2 ppb	Zero Drift	Calibration Drift	> +4 %
	Assess and adjust zero background if needed	Assess and recalibrate if needed	
\pm 2 ppb	No corrective action required		0 to 4%
< - 2 ppb	Zero Drift	Calibration Drift	< -4 %
	Assess and adjust zero background if needed	Assess and recalibrate if needed	
< - 2 % of full scale	Invalidate data and recalibrate		< - 10 %

6.5 Preventative Maintenance

Maintenance procedures or activities that prevent equipment failures, costly repairs, and subsequent data losses need to be performed on a routine basis. **Table 2** is an example preventative maintenance schedule. Site specific SOPs should incorporate specific maintenance schedules for individual equipment components base on their service manuals. These activities should be performed in accordance with service manual recommendations or more often if status and performance verifications indicate the need.

Table 2 Example Preventive Maintenance Schedule

Analyzer Preventative Maintenance	
Maintenance Activity	Scheduled Frequency
Inspect the in-line Teflon filter for particulate deposition and discoloration.	Monthly change recommended or more frequently if needed.



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Sample system leak check	Monthly with filter change or following any disassembly of the sample system components
Assess function of the internal sample pump.	Annual inspection, replace pump diaphragm kit as needed.
Verify analyzer sample flow rate with a certified flow rate standard device, repair and recalibrate if tolerances exceed manufacturers specification	Annually
Inspect and clean reference/sample photometer tubes, check O-rings, and windows.	Annually
Assess UV photometer lamp function, adjust or replace as needed.	As indicated by electronic diagnostics
Assess function of reference ozone scrubber, adjust or replace as needed.	As indicated by service diagnostics
Assess function of reference and sample flow solenoids, adjust or replace as needed.	As indicated by service diagnostics
FEM Detention for instrument noise, performed in accordance with definitions and procedures in 40 CFR 53.26(b)	Annually
FEM Detention evaluation for lower detectable level (LDL) performed in accordance with definitions and procedures in 40 CFR 53.26(b)	Annually
Zero Air Generator Preventative Maintenance	
Assess function of the zero air generator by comparing the analyzer response in ppb between the on-site zero air generator and NIST certified ultra-pure zero air cylinder gas. Recommended maintenance if the comparison differential exceeds the lower detectable level (LDL) of the analyzer.	Annually
Assess the function of the zero air generator dryer by testing the output with a certified digital hydrometer. Maintenance recommended if the dew point of the output zero air exceeds manufacturer's specifications.	Semi-annually
Assess the function of the zero air compressor pump. Rebuild or replace if recommended pressure test exceeds manufacturers specifications.	Annually
Ozone Transfer Standard Preventative Maintenance	
Recertify the on-site Level 3 ozone transfer standard generator to the DEC Level 2 ozone transfer standard. Perform diagnostics, repairs, recalibration and recertification if the testing fails EPA QC criteria.	Semi-annually
Verify mass flow controller with a certified flow rate standard device, repair and recalibrate if tolerances exceed manufacturers specification	Annually



Inspect and clean reference photometer tubes, check O-rings, and windows. Repair or replace parts as needed.	Annually
Assess UV reference photometer lamp function, adjust or replace as needed.	As indicated by electronic diagnostics
Assess UV ozone generator lamp function, adjust or replace as needed	As indicated by electronic diagnostics
Recertify the DEC Level 2 ozone transfer standard to another Level 2 ozone transfer standard of higher authority maintained or recognized by the EPA. (The Level 2 ozone transfer standard typically used for recertification of units on the West Coast is maintained by the California Air Resources Board (CARB) in their Sacramento air monitoring laboratory.)	Annually

7. QUALITY ASSURANCE

7.1 Qualification, Verification and Re-verification

All ozone transfer standards used to assure traceability to EPA or NIST standard reference photometers shall be certified, verified, and re-verified in accordance with the EPA technical assistance document (TAD), *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*, EPA-454/b-10-001, November 2010.

7.2 Data Quality Indicators

Data Quality Indicators are qualitative and quantitative methods used to determine if the Data Quality Objectives of the DEC air program are being satisfied. It is the responsibility of the station operator to take corrective action if the Measurement Quality Objectives are not being met. Quantitative data quality indicators are results from the zero/span/precision QC checks. If QC results are outside of the “Critical Criteria” presented in **Appendix A Ozone Data Validation Table**, immediate corrective action shall be taken. Qualitative data indicators are analyzer status and function checks that indicate analyzer function is outside the “Operational & Systematic Criteria presented in **Appendix A**. This will also require immediate attention to further assess the condition and take corrective action, if warranted.

7.3 Performance Audits

Quality Assurance performance audits shall be conducted utilizing the procedures and calculations specified in 40 CFR 58, Appendix A, "Quality Assurance Requirements for SLAMS, SPM and PSD Monitoring." The audit shall challenge the ozone monitoring system with a zero air concentration and at least three upscale ozone concentrations. The ozone audit concentrations shall selected in accordance with the USEPA Memorandum of November 10, 2010, *Use of Expanded List of Audit Levels for Annual Performance Evaluation for SO₂, NO₂, O₃, and CO as described in 40 CFR 58, Appendix A, Section 3.2.2*. The Ozone Data Validation Table shown in **Appendix A** requires that QA performance audits be conducted at least once per year. It is recommended to conduct a QA performance audit near the beginning and end of the ozone monitoring season or twice per year if monitoring year round. If the results of the

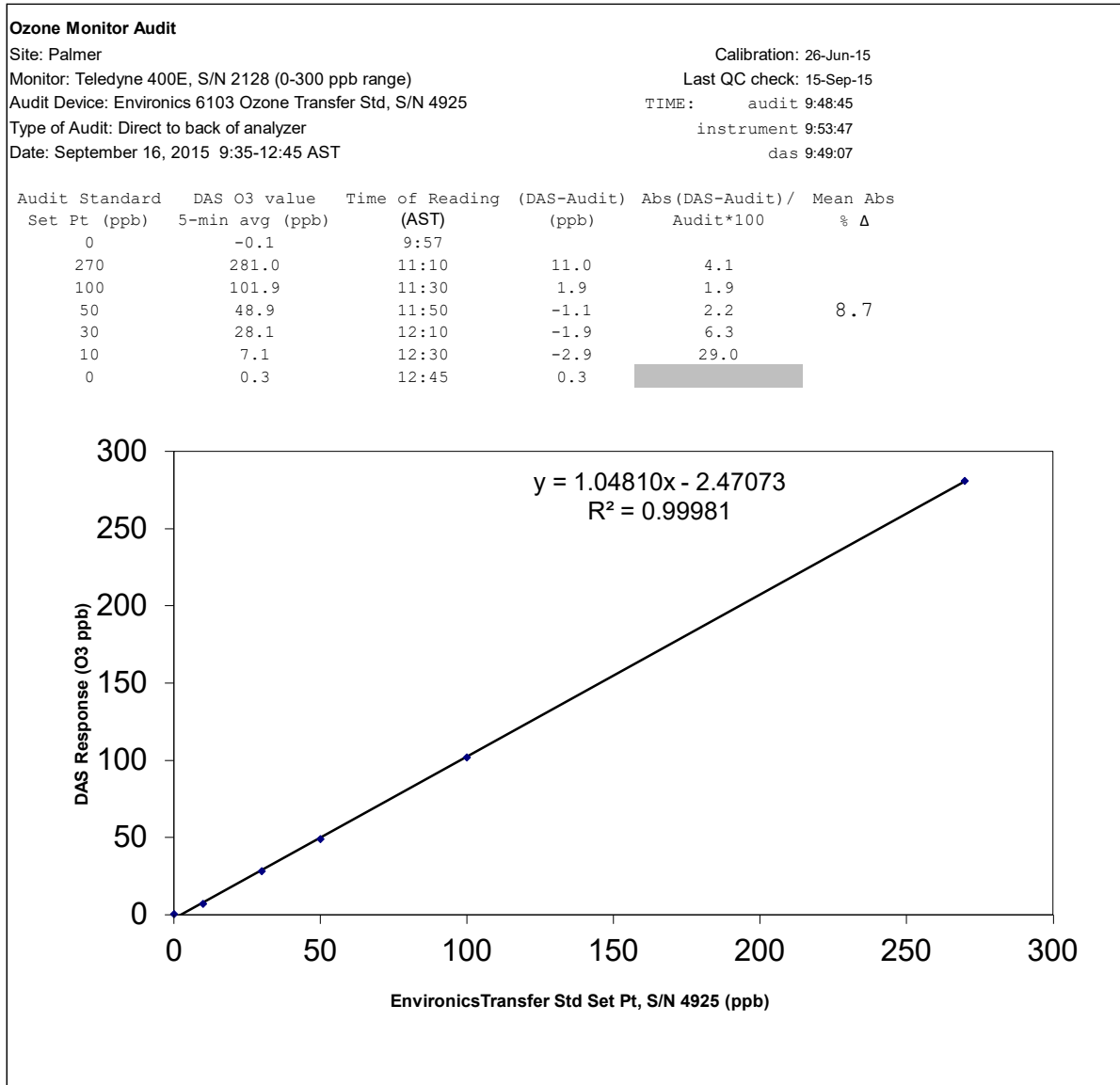


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QA performance audit are outside the “Critical Criteria” presented in **Appendix A**, corrective action shall be taken. An example audit report is presented in **Figure 6**.

Figure 6 Example Ozone QA Performance Evaluation Report





7.4 Technical System Audits

The systems audit is an on-site review and inspection of the entire ambient air monitoring program to assess its compliance with established regulations governing the collection, analysis, validation, and reporting of ambient air quality data. Although not addressed in the Ozone Validation Data Table of **Appendix A**, a technical systems audit is required once every three years. To provide uniformity in the evaluation, the criteria and procedures specified in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Section 2.0.11 will be applied.

8. DATA REVIEW, VALIDATION AND REPORTING

To assure the ozone monitoring data are meeting EPA required data quality objectives (DQO), a strict protocol shall be followed for:

- Data Acquisition
- Daily Review
- Level 1 Data Review, Editing and Data Archival
- Level 2 Data Review and Validation
- Data Submission to EPA AQS
- Annual Summary Reports

8.1 Data Acquisition

The ozone analyzer produces an electronic signal equivalent to the measured ozone concentration. This signal is transmitted to the primary DAS where the data are electronically translated, stored as 1-minute average concentrations and then calculated into 1-hour, and/or 8-hour average concentrations. Depending on system capability, the on-site DAS may act as a server transmitting the data to a base computer or data base server providing near real-time data for presentation to a Web-based air quality index (AQI) reporting system. In addition to the primary DAS data record, concentration data are also recorded to a secondary DAS, which is typically an on-board data logger within the analyzer. This analyzer internal data logger is independent of the primary DAS, serving as a backup system and for routine QC data comparisons.

8.2 Daily Review

To assure on-going data quality and avoid unnecessary data losses, a cursory review of the monitoring data should be performed every business day. The operator or designated data manager will access the data from the DAS using the system's base computer or from the data base server. The data will be reviewed for continuous function and determine if the data are characteristic of normal monitoring trends including typical diurnal and seasonal fluctuations. The most recent QC checks will be reviewed to assess data quality. This combined review is to determine if corrective action is required.



In terms of public health protection and for preparation of air quality alerts, the site operator or data manager shall also track daily ozone concentrations to alert the AMQA program manager if hourly or 8-hour concentrations approach or exceed the NAAQS standards.

8.3 Level 1 Data Review, Editing, and Data Archiving

8.3.1 Data Review

The level 1 review is a detailed review to assess data validity, edit out any erroneous data and prepare the data record for reporting to the EPA Air Quality System (AQS) data base. This procedure is typically the responsible of the site operator or data manager who is knowledgeable of the day to day data collection effort and is typically performed on a monthly basis.

The procedure begins by compilation of all data and information required to assess and validate the data. This information shall include:

- raw data records from the primary DAS data management software, typically 1-hour average concentrations but 1-minute concentrations may be required for detailed assessments and diagnostics;
- raw data records from the secondary data logger, typically 1-hour average concentrations (these data files are obtained by direct download from the analyzer) ;
- records of all QC verifications for zero/span/precision checks, multi-point verifications, and calibrations;
- operational checklists, station logbook notes, maintenance logs, and/or electronic logs of all monitoring events for the reporting period; and
- the most recent results of any QA performance audits.

Once all the information is compiled the reviewer shall examine the data to determine if the data meets data quality objectives. Most data management software systems will allow the reviewer to examine the data in both a tabular view and a graphic view. A graphic examination of the data allows the reviewer to look for trends indicating suspect data or gaps indicating instrumental malfunctions. The tabular allows the reviewer to observe specific data values. A comparison of hourly values shall be performed comparing the data record from primary DAS to the secondary data logger. This will indicate any data storage or communication errors. As the reviewer examines the data over the reporting period, the reviewer shall consult QC results, operational checklists, and station or electronic logs to identify and determine the cause of any periods of missing data, period of data that require invalidation, or data that are valid but require a qualifying explanation. Once identified the reviewer shall develop a written chronology documenting all events which affect data quality.

8.3.2 Data Editing



Once the detailed raw data review is complete, the site operator or data manager shall use the data management software to edit the data record. When the site operator or data manager begins the editing process, the data management software will create a new data file copying the raw data into an edited data folder.

Important Note: EPA data management practices requires that an original unedited “Raw Data” file be maintained for data archives.

The site operator or data manager shall edit the data record according to the findings of the review. The decision to validate or invalidate data shall be in accordance with the “Critical,” “Operational,” and “Systematic” criteria presented in the Ozone Data Validation Table presented in **Appendix A**.

Typically data which fail to meet critical QC criteria are invalidated unless a technical explanation shows the analyzer data were accurate and precision despite QC results. For example, failed QC verification checks for zero/span/precision were due to a problem with the on-site ozone transfer standard and following repairs, the next QC verifications showed the analyzer to still be functioning properly and providing accurate data.

Data collected during periods when there are deviations from “Operational” or “Systematic” criteria may or may not warrant invalidation. The invalidation will depend upon the affect to data quality and shall be a judgement call for the editor. In either case, an explanation for the action must be included in the data record. Invalidations shall be flagged with an EPA AQS null data code. The other data shall be flagged with an EPA AQS data qualifier code. Guidance on AQS null codes and qualifier codes is available from the EPA website <https://www.epa.gov/aqs>. Most data management software systems will allow for editing notes. These explanations shall also be noted in the data chronology.

8.3.3 Data Archiving

Ambient air quality monitoring data used to demonstrate compliance with NAAQS or PSD regulations are legally considered as creditable evidence. All data and related records used in the development of the final validated data set submitted to the EPA AQS data base shall be maintained in a data archive system. These records shall include:

- copies of all station logbook, maintenance logs, operational or status checklists;
- the results of all QC checks and any QA performance audits performed during the reporting period;
- a comparison of the DAS primary data source to a secondary data source which is typically a direct download data from the analyzer,
- all spreadsheets used for data and QC calculations
- the raw data file as recorded by the primary DAS;



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- an edited data file annotated with AQS data null and qualifier codes with an explanation of missing, suspect, and invalidated data; and
- monitoring data chronology developed during the data review and editing process.

These records shall be maintained in accordance with the Department’s records retention policy.

8.4 Level 2 Data Review and Validation

Once the data has been compiled, edited, and annotated with the appropriate AQS null codes and qualifier codes, the preliminary report should be submitted to a colleague for a peer review. The second level review shall be conducted by a qualified air monitoring specialist independent of the site’s day to day monitoring operations. The air monitoring specialist shall provide a thorough review of the raw data, edited data and all the supporting documentation to confirm that the data is accurate and complete. The reviewer shall examine the data record, all QC/QA results, and the data chronology to confirm that the periods of missing, invalidated or qualified data were correctly assessed. The reviewer shall also review all archived data records to determine if the documentation is complete. Any errors or deficiencies will be noted and compiled, then returned to the site operator or data manager for correction. The data set is to be corrected and resubmitted to the senior reviewer. Once the senior reviewer is satisfied that the data set is accurate and complete, the senior reviewer, using the data management software, will validate the data set. The data management software will create new “Validated Data” set which is available for the system administrator to upload to EPA AQS data base.

***Important Note:** Most data management software programs will have a hierarchical authorization protocol to allow specific users to make changes to the data at each stage of data processing. The programs must also maintain a data trail of all editing activities as part of the evidentiary documentation.*

8.5 Data Submission to EPA AQS

The validated ozone data set will typically be reported to the EPA’s AQS database on a quarterly (or more frequent) basis if generated by a SLAM, NCore or SPM station. PSD monitoring programs are not required to report monitoring data to AQS. Quarterly or monthly reports will be submitted within a time period specified by the database manager (preferably the end of the month following the month in which the data were collected), but absolutely no later than two and half months following the end of the respective quarter. Independent projects performed in support of a PSD permit application are typically submitted to DEC at the conclusion of the 1-year monitoring period.



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8.6 Annual Summary Reports

As public outreach the AMQA program will prepare an annual summary report of all monitoring sites. If applicable the finalized ozone data will be included in the annual report. The report shall present:

- the description, location and the monitoring objectives for the site;
- a comparison of ambient air concentrations determined by the monitor program to the 1-hour and 8-hour NAAQS and the calculated design value for the site; and
- any applicable trend analysis related to meteorological or climatological conditions and/or source attribution.



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9. REFERENCES

- 1) Title 40 CFR Part 50, Appendix D *Measurement Principle and Calibration Procedure for Measurement of Ozone in the Atmosphere*.
- 2) Title 40 CFR Part 53, *Ambient Air Monitoring Reference and Equivalent Methods, Subparts A and B*
- 3) Title 40 CFR Part 58, *Ambient Air Quality Surveillance, Subparts A, B, C, Appendices A, C, D, and F*
- 4) EPA *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, EPA-454/B-08-003, December 2008
- 5) EPA technical assistance document (TAD), *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone*, EPA-454/B-13-004, October, 2013
- 6) *Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program*, February 23, 2010.
- 7) Teledyne Advanced Pollution Instrumentation, *Technical Manual Model 400E Ozone Analyzer, Rev E*, June 2009
- 8) Thermo Electron Corporation, *Model 49i Instruction Manual UV Photometric O3 Analyzer*, November 2006
- 9) Environics, Inc. *Model 6103 Ozone Transfer Standard and Multi-Gas Calibrator, User's Guide and Technical Manual*, Revision 5 March, 2007
- 10) Washington State Department of Ecology, Air Quality Program, *Ozone Monitoring Procedure*. 2008.
- 11) Sonoma Technology Inc. *Standard operating procedure for routine operation of the API model 400A ozone analyzer for continuous gas concentrations of ozone in CRPAQS*, February, 2000.



10. DEFINITIONS OF SYMBOLS & ACRONYMS

AMQA	Air Monitoring & Quality Assurance program within the Alaska Department of Environmental Conservation, Air Quality Division
AST	common abbreviation for “Alaska Standard Time,” the EPA requires all air monitoring activities be conducted and the data recorded in accordance with local standard time traceable to US Official Time provided by NIST and the US Naval Observatory
CL	statistical abbreviation for “confidence limit”
CV	statistical abbreviation for “coefficient of variation”
CFR	government abbreviation for “Code of Federal Regulation,” which is used to reference federal regulations for example, 40 CFR 58 is the reference for Title 40, Code of Federal Regulations, Part 58.
° C	chemical abbreviation for a unit of temperature expressed as “degrees Celsius”
DAS	common abbreviation for “data acquisition system,” which for the purposes of this manual, represents a computer-based system that records and stores electronic signals from the ozone analyzer, and provides programmed functions to perform automated quality control checks
DEC	government abbreviation for “Alaska Department of Environmental Conservation”
DQO	government abbreviation for “data quality objectives”
LED	electronic abbreviation for “light emitting diode”
LDL	chemical abbreviation for “Lower Detectable Limit” used when discussing instrumental analysis
MFC	instrumental abbreviation for “Mass Flow Controller,” an electronic device used in gas analyzers and calibration instruments use to detect and precisely control the flow of gas (either pollutant gas and/or zero air) through a monitoring system
mm Hg	chemical abbreviation for a unit of pressure expressed as “millimeters of mercury”
NAAQS	government abbreviation for “National Ambient Air Quality Standards,” which are air quality standards established in regulation under 40 CFR 50 to protect human health and the environment



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NCORE	an EPA program to establish a national multi pollutant monitoring network that integrates several advanced measurement systems for particles, pollutant gases and meteorology
NIST	government abbreviation for the “National Institute of Standards and Technology”
O ₃	chemical abbreviation for “ozone”
ppb	chemical abbreviation for a unit of chemical concentrations expressed as “parts per billion” (Note, because ozone is measured as a gas at ambient conditions, for purposes of this document, parts per billion are expressed on a volumetric basis, ppbv)
ppm	chemical abbreviation for a unit of chemical concentration expressed as “parts per million” (Note, because ozone is measured as a gas at ambient conditions, for purposes of this document, parts per million are expressed on a volumetric basis, ppmv)
PQAO	EPA abbreviation for “principal quality assurance organization”
PSD	government abbreviation for “Prevention of Significant Deterioration,” which is federal regulations under 40 CFR 52 promulgated to protect existing ambient air quality through the permitting process. If a facility’s emissions trigger these regulations, an assessment of ambient air quality is required through pollutant dispersion modeling and/or ambient air quality and meteorological monitoring
QA	common abbreviation for “quality assurance”
QAPP	EPA abbreviation for “Quality Assurance Project Plan”
QC	common abbreviation for “quality control”
RSD	statistical abbreviation for “relative standard deviation”
SD	statistical abbreviation for “standard deviation”
SLAMS	EPA abbreviation for “State and Local Air Monitoring Station”
SOP	common abbreviation for “Standard Operating Procedure”
SPMS	EPA abbreviation for “Special Purpose Monitoring Station”
SRP	EPA abbreviation for “standard reference photometer”
Std. Dev.	statistical abbreviation for “standard deviation”



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- STP chemical abbreviation for “standard temperature and pressure” (Note: the EPA, when requiring a correction to a standard temperature and pressure, uses 25 ° C and 760 mm Hg)
- TAD EPA abbreviation for “Technical Assistance Document”
- USEPA government abbreviation for “United States Environmental Protection Agency,” often shortened to “EPA”



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Appendix A
Ozone Data Validation Table

Requirement	Frequency	Acceptance Criteria	Information/Action
CRITICAL CRITERIA - Ozone			
One-Point QC Check Single Analyzer	1/2 weeks	$\leq \pm 10\%$ (percent difference)	0.010 - 0.100 ppm, Relative to routine concentrations, DEC Air Monitoring Quality Assurance Project Plan (QAPP) ⁸
Zero / Span Checks	1 /2 weeks	Zero drift $\leq \pm 2$ of full scale, Span drift $\leq \pm 10\%$	DEC Air Monitoring Quality Assurance Project Plan (QAPP) ⁹
OPERATIONAL CRITERIA - Ozone			
Shelter Temperature			
Temperature Range	Daily (hourly values)	15 to 30° C (hourly avg.)	DEC Air Monitoring Quality Assurance Project Plan (QAPP) ¹⁰
Temperature Control	Daily (hourly values)	$\leq \pm 2^\circ$ C SD over 24 hours	
Temperature Device Check	2 / year	$\leq \pm 2^\circ$ C of standard	
Precision (using 1-point QC Checks)	Calculated annually and as appropriate for design value estimates	90% CL CV $\leq \pm 7\%$	90% Confidence Limit of coefficient of variation, 40CFR58, App A, Sec 4.1.2

⁸The ozone critical acceptance criterion for precision drift is established in regulation as $\leq 7\%$. However, DEC argued for a critical acceptance criterion of $\leq 10\%$ to accommodate temperature issues for monitoring shelters located in Alaska's Arctic and sub-Arctic environments. EPA Region 10 waived the $\leq 7\%$ requirement through approval of the DEC air monitoring program QAPP.

⁹The ozone critical acceptance criterion for span drift is established in regulation as $\leq 7\%$. However, DEC argued for a critical acceptance criterion of $\leq 10\%$ to accommodate temperature issues for monitoring shelters located in Alaska's Arctic and sub-Arctic environments. EPA Region 10 waived the $\leq 7\%$ requirement through approval of the DEC air monitoring program QAPP.

¹⁰ The ozone operational acceptance criteria for shelter temperature are established in regulation as 20 to 30° C as an hourly average. DEC argued for a operational criterion of 15 to 30° C to accommodate temperature issues for monitoring shelters located in Alaska's Arctic and sub-Arctic environments. EPA Region 10 waived the 20 to 30° C requirement through approval of the DEC air monitoring program QAPP.

Requirement	Frequency	Acceptance Criteria	Information/Action
Bias (using 1-point QC Checks)	Calculated annually and as appropriate for design value estimates	95% CL $CV \leq \pm 7\%$	95% Confidence Limit of coefficient of variation, 40CFR58, App A, Sec 4.1.3
Annual Performance Evaluation			
Single Analyzer	Every site 1 / year 25% of sites quarterly	Percent difference of each audit level $\leq 15\%$	3 consecutive audit concentrations not including zero, 40CFR58, App A, Sec 3.2.2
Primary QA Organization (PQAO)	annually	95% of audit percent difference fall within the one-point QC check 95% probability internals at PQAO level of aggregation	40CFR58, App A, Sec 4.1.4
Federal Audits (NPAP)	1 / year at selected sites 20% of sites audited	Mean absolute difference $\leq 10\%$	40CFR58, App A, Sec 2.4
State Audits	1 / year	State Requirements	
Verification/Calibration	Upon receipt/adjustment/repair/installation/moving 1 / 6 months if manual zero/span performed biweekly, 1 / year if continuous zero/span performed daily	All points within $\pm 2\%$ of full scale of best fit straight line, Linearity error $< 5\%$	Multi-point calibration (zero air and four upscale points) 40CFR50, App D, Sec 5.2.3
Zero Air		Concentration below LDL	
Gaseous Standards		NIST Traceable (e.g. EPA Protocol Gas)	40CFR58, App A, Sec 2.6.1
Zero Air Check	1 / year	Concentration below LDL	
Regional Standard Reference Photometer (SRP) (Level 1 Standard)			
Verification	1 / year	Regression slopes - 1.00 ± 0.01 and intercept ± 1 ppb	Usually at a Regional Office and compared against the traveling EPA SRP

Requirement	Frequency	Acceptance Criteria	Information/Action
Ozone Level 2 Transfer Standard			
Qualification	Upon receipt of transfer standard	$\pm 4\%$ or 4 ppb (whichever is greater)	Transfer Standard Doc EPA-454/B-13-004, App B
verification (6 x 6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-13-004, Sec 4.1
Verification/re-verification to SRP Minimum 6 upscale points 7 replicates	After qualification and upon receipt/adjustment/repair, 1 / year	Each individual point difference $\leq \pm 3\%$	Level 2 standard usually transported to Region's SRP for comparison
(If recertified via a transfer standard)	1 / year	Regression slopes - 1.00 ± 0.03 and two intercepts are 0 ± 3 ppb	
Ozone Transfer Standards Levels 3 and Greater			
Qualification	Upon receipt of transfer standard	$\pm 4\%$ or 4 ppb (whichever is greater)	Transfer Standard Doc EPA-454/B-13-004, App B
verification (6 x 6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-13-004, Sec 4.1
Re-verification to Level 2 Standard	Beginning and end of O3 season, or 1 / 6 months whichever less	New slope = ± 0.05 of previous and RSD of six slopes 3.7%. Std. Dev. Of 6 intercepts 1.5	Transfer Standard Doc EPA-454/B-13-004, Sec 4.2
SYSTEMATIC CRITERIA - Ozone			
Standard Reporting Units	All data	ppm (final units in AQS)	
Completeness (seasonal)	Daily	75% of hourly average for the 8-hour period	8-Hour Average
Sample Residence Time		< 20 seconds	
Sample Probe, Inlet, Sampling train		Borosilicate glass(e.g. Pyrex) or Teflon	40CFR Part 58, App E