

Standard Operating Procedures
Sulfur Dioxide (SO₂) Monitoring
in Ambient Air by
Ultraviolet (UV) Fluorescence
Spectroscopy

Air Quality Division

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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 sulfur dioxide (SO₂) 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 SO₂ monitoring data in accordance with federal regulations and EPA quality assurance/quality control (QA/QC) requirements. This document is specific to SO₂ monitoring programs which use *Ultraviolet Fluorescence Spectroscopy* 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 SO₂ 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 SO₂ monitoring performed by DEC or other local air pollution control agencies such as for multi-pollutant NCORE monitoring sites; and
- the SOP document for SO₂ 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 make and model of the SO₂ 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 SO₂ 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.

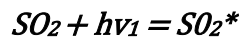
3. SUMMARY OF METHOD

While there are a number of technologies used in the measurement of ambient air concentrations of SO₂, the method employing ultraviolet (UV) fluorescence has been in use since the mid-1970s and has become the industry standard for EPA SO₂ ambient air monitoring. For the purpose of this SOP, the procedures described are applicable specifically to *UV fluorescence instruments*.

3.1 Analytical Technique

The quantitative measurement of SO₂ using this method is based on the characteristic fluorescence released by the SO₂ molecule when it is radiated by ultraviolet light ($h\nu_1$) at a frequency of 214 nanometers. The SO₂ molecule absorb the light which raises the molecule to a higher energy state (SO_2^*). As the molecule decays back to its normal ground state energy it fluoresces giving off a characteristic ultraviolet light ($h\nu_2$) at 330 nm. The decay radiation is passed through a bandwidth filter and into a photomultiplier tube (PMT) that converts the signal into a voltage that is directly proportional to the SO₂ concentration. The chemical reactions are shown in **Equation 1**.

Equation 1 SO₂ reaction resulting from exposure to UV light at 190-230 nm



Where:

SO₂ = sulfur dioxide molecule at a ground energy state

$h\nu_1$ = incidence UV light at ~ 214 nm

SO₂* = sulfur dioxide molecule at an excited energy state

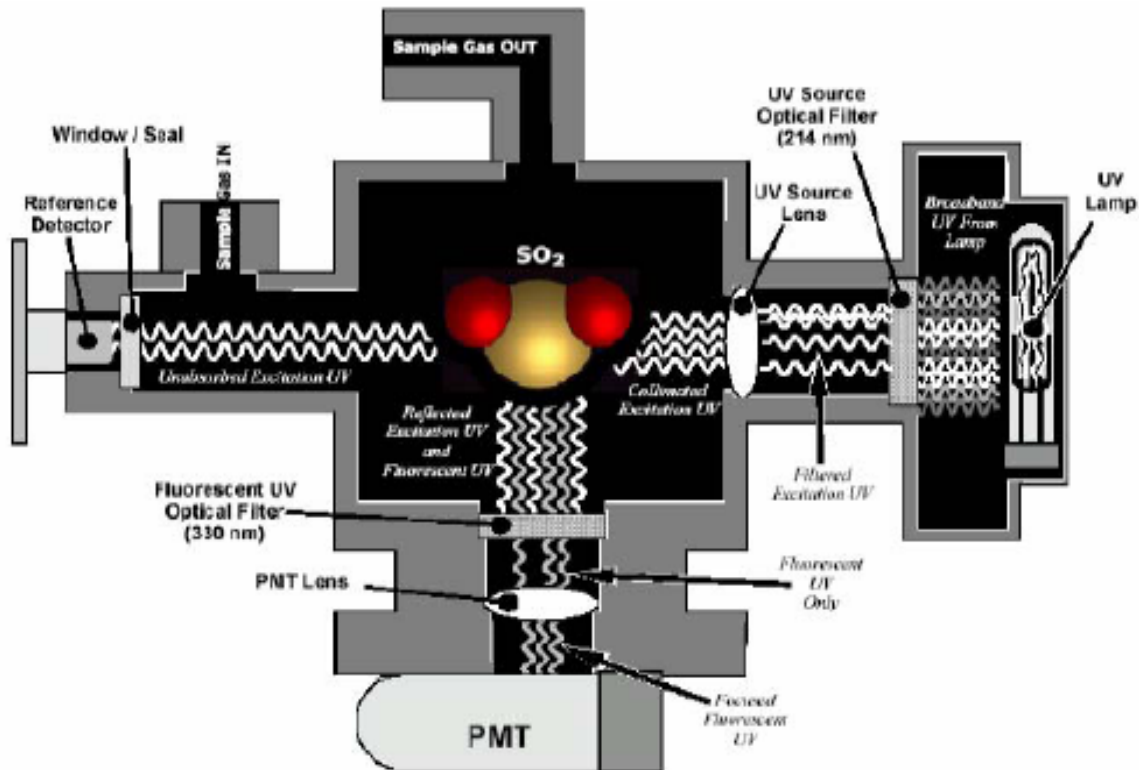
$h\nu_2$ = fluoresced UV light emitted at ~ 330 nm as the sulfur dioxide molecule decays back to the ground energy state.

For modern SO₂ analyzers, this chemical event is initiated, reacted, and detected as sample air is drawn through an optical bench. The optical bench consists of a reaction chamber with: an associated UV source lamp, a lamp reference detector and electronics controls to provide the incidence UV radiation at a regulated intensity, a thermo-electrically cooled photomultiplier tube (PMT) to detect the decay radiation and produce a signal proportional to the SO₂ concentration, and optical windows with condensing lens to focus the radiation and optical bandpass filters to selectively transmit the desired UV frequencies.



Figure 1 presents a schematic illustration of an optical bench for a typical UV fluorescence SO₂ instrument.

Figure 1 Schematic illustration of the optical chamber of the typical UV Fluorescence SO₂ analyzer. (Illustration courtesy of the EPA TAD for NCore Multi-pollutant Monitoring Network¹)



The sample flow through the optical bench is actuated by a downstream vacuum pump, controlled by flow orifices and monitored for temperature and pressure to provide for a volumetric correction of concentrations to EPA standard conditions of 25° C and 760 mm Hg. The analyzer is micro-processor based for signal processing, data acquisition and communications. Prior to the optical bench, hydrocarbons are removed from the sample flow to avoid a primary analytical interference.

¹ Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, EPA-454/R-05-003, September 2005, Section 3, Page 3 of 31.



3.2 Interferences

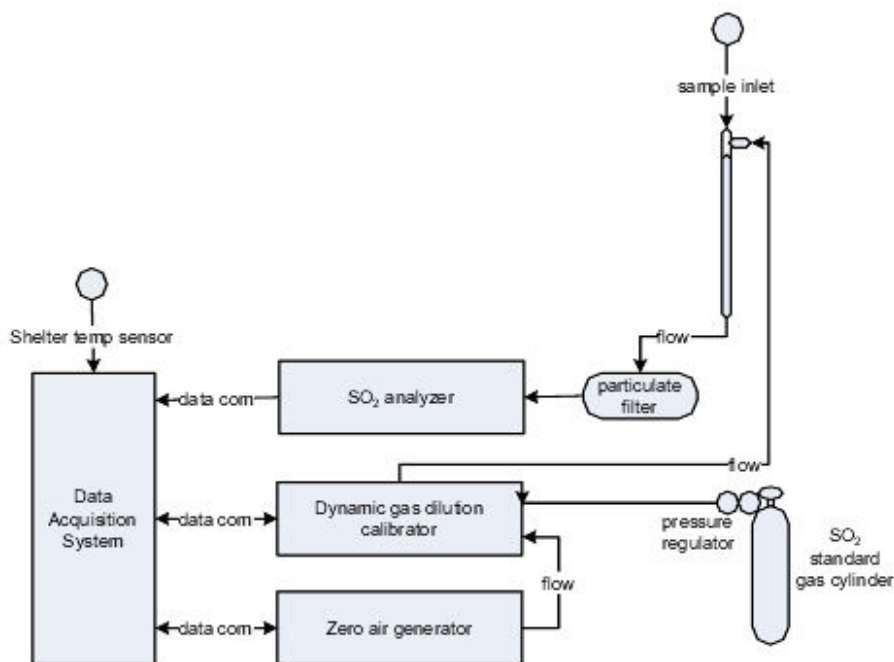
Direct analytical interference for SO₂ UV fluorescence spectroscopy results from other gases present in the sample gas that fluoresce in a similar manner as SO₂. The primary interference is from hydrocarbons, particularly poly-nuclear aromatics (PNA) such as xylene and naphthalene. These interfering gases are removed up stream of the optical bench using a selective membrane permeation device known as a “hydrocarbon kicker.” Nitric Oxide (NO) also fluoresces in a similar spectral range as SO₂. This interference is rejected by using a frequency specific bandpass optical filter that only allows the UV decay radiation for SO₂ to pass into the PMT while blocking the decay radiation from NO. Ozone (O₃) absorbs UV radiation and, therefore, can offset SO₂ concentration by absorbing decay radiation in the reaction chamber. This interference is diminished to an insignificant level by maintaining a short path length between the reaction chamber and the PMT. Third body quenching is the decay of the excited SO₂ molecule to a lower energy state through kinetic energy losses i.e., by collision with a gaseous molecule that results in heat loss rather than an emission of a photon. At ambient concentration levels quenching does not represent a significant offset.

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 2 presents a typical basic configuration of SO₂ monitoring system components.

Figure 2 Typical equipment configuration of an SO₂ monitoring system





Specific information regarding site selection, monitoring shelter and equipment specifications, and data measurement quality objectives are provided in the *Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program*.²

3.4 Health and Safety Precautions

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

1. Properly exhaust any gas output from the SO₂ 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.
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 VERSUS QUALITY ASSURANCE

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 end product (i.e., the resulting pollutant data), 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

² 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



function because it is to ensure strict adherence by site operators to a system or process intended to assure data quality. Another example of a QA document is the *Quality Assurance Project Plan (QAPP) for State of Alaska Air Monitoring & Quality Assurance Program*³. This document sets the data quality objectives for the ADEC statewide monitoring system.

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, SO₂ Data Validation Template*⁴. A copy of the SO₂ data validation template 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*”⁵. For an SO₂ 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;
- 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 SO₂ Data Validation template 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-

³ 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

⁴ EPA Quality Assurance Handbook for Air Pollution Measurements, Volume II, Ambient Air Monitoring Program, EPA-454/B-13-003, May 2013. <https://www3.epa.gov/ttnamti1/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf>

⁵ American National Standard Quality Systems for Environmental Data and Technology Programs ANSI/ASQ E4 <http://www.asq.org/>



point verification of a SO₂ 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 SO₂ analyzers with a selected measurement range of 0 to 500 parts per billion (ppb) would be calibrated at concentrations of 400 ppb, 300 ppb, 200 ppb, 100 ppb, and zero air. However, the primary SO₂ NAAQS is established at a 1-hour average of 75 ppb. For the State of Alaska, most SO₂ concentrations will be recorded at less than 50 ppb. 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 scenario might be to reduce the instrument measurement scale to 0 to 300 ppb with calibration points performed at 240 ppb, 180 ppb, 120 ppb, and 60 ppb. 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.



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 53.⁶ The dynamic calibration system, 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*.⁷ All reference gas standards shall be certified in accordance with the *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards*.⁸

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.

In addition to the main system components, an inventory of manufacturer recommended spare parts shall be ordered and maintained throughout the project.

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

⁶ 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>

⁷ 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>

⁸ EPA Traceability Protocol for Assay and Certification of Gaseous Standards, EPA 600/R-012/533, May 2012,
[Document Display](#) | [NSCEP](#) | [US EPA](#)



replacement of filters and chemical scrubber media. Comparison testing to a certified zero air cylinder is strongly encouraged upon startup and annually thereafter.

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:



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- site visits & 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,
- file records for all equipment certifications and standards 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 loss 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 SO₂ Analyzer

The calibration performed on a continuous SO₂ analyzer shall consist of a multi-point calibration, in which the analyzer is challenged with ultra-pure zero air and at least four up-scale points of known reference gas concentration to assess the analyzer response over the selected measurement range. An initial adjusted multi-point calibration ensures the instrument is performing accurately and establishes a beginning benchmark or bracket that documents the



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instrument meets QC performance criteria. Calibration of the SO₂ analyzer must be performed “in situ” (in place) at the permanent monitoring site. Calibrations should be performed with the reference gas introduced directly to the back of the instrument as to negate any systematic bias that may be introduced from the sample flow system.

Calibration may be performed by any of the following three optional methods:

- a calibration using a dynamic dilution calibration system to precisely blend ultra-pure zero air with a certified reference gas from a single high-pressure cylinder to produce multiple concentrations of SO₂;
- a manual calibration using a direct connection to the analyzer from a series of individual gas cylinders each containing certified reference gases of known concentration. The series of reference gas cylinders shall include a cylinder of ultra-pure zero air and, at least, four individual SO₂ reference gas cylinders each with a different certified concentration; or
- a calibration using a dynamic dilution calibration system to precisely blend ultra-pure zero air with a reference gas generated from a certified SO₂ permeation device to produce multiple concentrations of SO₂.

The procedural principle is the same for all three calibration options. The only difference is how the test atmospheres are blended or delivered to the analyzer. The first option is the most common method used and is described below.

[6.1.1 Calibration procedures using a dynamic dilution calibration system blending zero air and a certified reference gas cylinder](#)

1. Access the SO₂ calibration data sheet or MS Excel spreadsheet and record all the preliminary information for dates, models, serial numbers, etc. Assure that the zero air supply, dynamic calibration system, and certified reference gas cylinder are properly connected and operating pressures set in accordance with the manufacturer’s operating manual. Attach calibration tubing directly from the back of the calibration system output manifold to the sample port on the rear of the analyzer and initiate the flow of zero air.

IMPORTANT NOTE: *During any calibration procedure care shall be taken to not over pressurize the analyzer sample flow system. Excess flow generated from the calibration system must be vented to an atmospheric dump and exhausted outside the monitoring shelter.*

2. Allow sufficient time for the analyzer to respond and the output signal to stabilize. In accordance with the instrument operating manual adjust the analyzer controls until the output response is stabilized at 0 ppb. The values on the analyzer visual display and the DAS should be the same. If not, make appropriate electronic adjustments in accordance with the instrument operating manual.
3. Reset the calibration system to produce a reference gas at a concentration of approximately 80 percent of the selected operating range of the instrument (e.g., 240 ppb on a 0-300 ppb operating range). Calculation of the diluted reference gas



concentration is typically performed automatically by the micro-processor based calibration device. The mathematical calculation is shown in **Equation 2**.

Equation 2 Calculation of the SO₂ reference gas concentration at the calibrator output manifold

$$[SO_2]_{out} = (F_{SO_2} \times [SO_2]_{std}) / (F_{SO_2} + F_D)$$

Where:

[SO₂]_{out} = concentration of the SO₂ reference gas at the calibrator output in ppb

F_{SO₂} = flow rate of the SO₂ certified reference gas from the cylinder in standard cubic centimeters (sccm)

[SO₂]_{std} = concentration of the certified SO₂ reference gas from pressurized cylinder in ppb

F_D = flow rate of the diluent gas (zero air) in sccm

4. Allow sufficient time for the analyzer to respond and the output signal to stabilize. In accordance with the instrument operating manual adjust the analyzer output to match the reference gas concentration. The analyzer visual display value and the DAS value should be the same. If not, make appropriate electronic adjustments in accordance with the instrument operating manual.

IMPORTANT NOTE: *If significant adjustments to the instrument electronics were needed to set the zero and upscale 80 percent calibration concentration, the operator may want to repeat steps 1 – 4 to fine tune the analyzer response.*

5. Once both the zero and upper range calibration adjustments are completed, record the calibration factors from the analyzer's visual display on the calibration data sheet. **Without further adjustment**, recheck the analyzer response to zero air. Allow sufficient time for the analyzer response to stabilize and record the average response from the DAS.

IMPORTANT NOTE: *DEC recommends a minimum period of **at least 15 minutes** at each calibration point. Allow about 10 minutes for the analyzer to respond and stabilize, then record the next five (or more) 1-minute values to calculate an average value.*

7. Recheck the analyzer response to a reference gas at 80 % of the selected operating range of the instrument and record and calculate the average response from the DAS.
8. In successive steps, check the analyzer response to at least three more reference gas concentrations evenly spaced over the selected operating range of the instrument or (as discussed in Section 4.2) within an appropriate range of concentrations expected to be observed. Additional concentrations may be included if deemed necessary. Record and



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calculate the average analyzer response from the DAS for each reference concentration point.

9. With the data collected for the zero air and four up-scale points, plot and perform a least squares regression analysis comparing the reference gas concentrations ([SO₂]_{OUT}) on the x-axis to the actual analyzer responses from the DAS on the y-axis. Generate a best-fit calibration line using **Equation 3**.

IMPORTANT NOTE: *The SO₂ calibration MS Excel spreadsheet should be available from the on-site server. The following equations will be automatically calculated as the spreadsheet is populated with the calibration results.*

Equation 3. Least squares regression equation for calculation of best-fit calibration 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

10. The linear regression will provide a slope (m) and a y-axis intercept as shown by **Equation 3**.
11. For each upscale point re-calculate the analyzer response (y) using the best-fit calibration expression from **Equation 3**.
12. Using **Equation 4**, for each point calculate and record the percent difference between the actual analyzer response recorded during steps 6 and 7 and the calculated best-fit analyzer responses determined from **Equation 3**.

Equation 4. Calculation of percent difference for calibration results

$$d_i = \left[\frac{\text{actual average analyzer response} - \text{calculated best fit analyzer response}}{\text{calculated best fit analyzer response}} \right] * 100$$

13. The Operational QC acceptance criteria for “Verification/Calibration” as shown in the SO₂ Validation Template (May 2013) in **Appendix A** is a percent difference of “All points within ±2 percent of the calibration range best-fit straight line.”
14. An example SO₂ calibration data sheet and spreadsheet with example results is shown in **Figure 2**.
15. Provide any relevant notes on the data sheet related to the calibration e.g., initial calibration, or calibration following diagnostics and replacement of sample pump, or routine 6-month multi-point verification. In addition to the calibration data sheet, note the date with start and end time of the calibration in the station logbook and the DAS electronic log for data documentation.

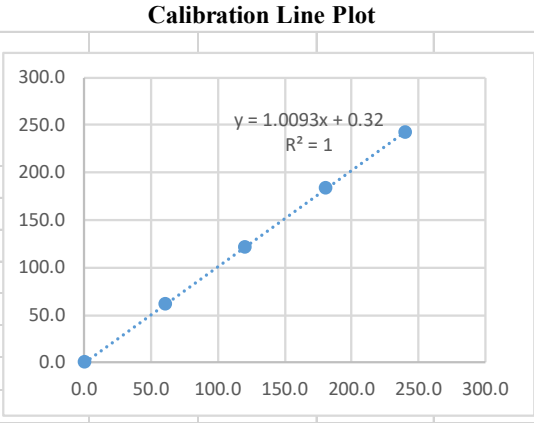


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Figure 3 Example SO₂ calibration data sheet with example results

SO ₂ Calibration Data Sheet					
Station	Eagle Fire Hall		Date	10/3/2013	
Street Address	1st Avenue		Calibrator Manufacturer	Envionics	
City	Eagle Alaska		Model No.	6103	
Calibrated by	Bob Morgan		Serial No.	4499	
Monitoring Agency	ADEC		Last Flow Calibration Date	9/10/2013	
Inst. Manufacturer	TEI				
Model No.	43i SO ₂ Ambient Air Quality Analyzer				
Serial No.	410005569				
SO ₂ Reference Gas Standard					
Gas Vendor Name	Scott-Marren		Cylinder Serial No.	CC154946	
Concentration [SO ₂] _{STD}	51.9	ppm	Cylinder Pressure	psi	1800
	51900.0	ppb	Certification Date	8/30/2013	
			Expiration Date	8/31/2021	
Instrument Calibration Factors					
Instrument Background	As Found	As Left	Calibration Coefficients	As Found	As Left
SO ₂	0.0	2.0	SO ₂	1.000	1.052
SO ₂ Calibration and Linearity Checks				Calibration Line Plot	
Caibration Points	[SO ₂] _{OUT}	SO ₂ Analyzer Response	SO ₂ Analyzer Response from y=mx+b	Percent Difference d _i	
units	ppb	ppb	ppb	%	
Zero Air	0.0	0.2	0.3	na	
80% URL	240.0	242.0	242.6	1.1	
1	180.0	183.0	182.0	1.1	
2	120.0	121.0	121.4	1.2	
3	60.0	61.0	60.9	1.5	
SO ₂ Linear Regression		m =	b =	r ² =	
y=mx+b		1.0093	0.3200	1.0000	
<p>Notes: Initial setup and installation, allowed for 18-hour warm-up and stablization period. Performed an initial calibration. All calibration results within QC acceptance criteria. Commenced data collection at 14:00 10/03/2013. Bob Morgan/ADEC</p>					





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 4** presents an example spreadsheet for the operational checks. It is recommended that these status checks be documented during every site visit or at least weekly. The form may be completed digitally via MS Excel or on a paper copy with files appropriately archived in the data record.

6.2.1 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 SO₂ Data Validation Template shown in **Appendix A**. The monitoring shelter or the room housing the analyzer must contain a sensor to continuously record room temperature to $\pm 1^{\circ}$ 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 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.

6.2.2 Sample System Inspection

The sample system inspection is performed to assess and prevent any bias to the measurements resulting from foreign materials, moisture, or damage. 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; and
- 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.



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Figure 4 SO₂ Monitoring Program Operational Checklist

SO ₂ Monitoring Program - Operational Data Record							
Operational Item	Acceptable Operating Limits or Description	Date	Date	Date	Date	Date	Date
Site Operator or Technician	Initials						
Date	yyyy/mm/dd						
Time of Checks (AST)	hh:mm						
Shelter or Room Temperatures							
Current Temperature °C	(15 to 30 °C)						
Max Temperature °C in last 24 hrs	≤ 30 °C						
Min Temperature °C in last 24 hrs	≥ 15 °C						
Variability in last 24 hrs	SD ≤ 2° C						
Electrical Surge Protection or UPS	Yes or No						
Sample Sytem Inspection							
Sample Inlet open & debris free	Yes or No						
Sample manifold open & debris free	Yes or No						
Sample tubing open & debris free	Yes or No						
Any indication of moisture	Yes or No						
Exhaust tubing open & debris free	Yes or No						
Exhaust exterior open & debris free	Yes or No						
Calibration Gas Cylinder Inspection							
Is Cylinder safely secured to wall?	Yes or No						
Certified SO ₂ Concentration	ppm						
Gas Cylinder Serial No.	#####						
Cylinder Valve and Line Valve	Open						
Tank Pressure psig	200-2000 psig						
Line Pressure psig	25 ± 2 psig						
Zero Air Generator							
Power On	On						
Output Pressure psig	20 to 25 psig						
Pressure Tank Moisture Drain	Operational Yes or No						
Date of Last Reagent Change & Maintenance	yyyy/mm/dd						
MultiGas Calibrator							
Power On	On						
Program Mode	Flow/Conc/Auto						
Display Date & Time (AST, 24-hr clock)	yyyy/mm/dd hh:mm						
Date of Last Flow Calibration	yyyy/mm/dd						
SO ₂ Analyzer							
Power On, Display up, in Sample Mode, & Operating	On with Run Display illuminated (v)						
Current SO ₂ Concentration	SO ₂ PPB #.#						
Comparison of Analyzer to DAS ppb	##/## ± 0.5 ppb						
Current Time (AST, 24-hr clock)	hh:mm						
Alarm Status (Is the Alarm Icon active?)	Yes or No						
(If in alarm status)	Identify Alarm						
Date of Monthly Particulate Filter Changeout	yyyy/mo/dd						
On-Site Data Acquisition System (DAS) & Communications							
Data Logger Power On	Power Switch On (in the up position)(v)						
Display Up and Software Functional	Yes or No						
Date and Time (±1 min NIST AK Std Time)	Yes or No						
DAS/Analyzer Communicating	Yes or No						
Modem/Router Power (On & Functional)	Yes or No						
External Communication (Internet Access)	Yes or No						
If any irregularities are noted in the above readings, provide a full explanation and any corrective actions take in the station logbook.							



6.2.3 Gas Cylinder Inspection

The cylinder gas inspection is to assure the cylinder is safe, appropriately certified and properly delivered to the dynamic gas dilution calibration system. The operational items include:

- the cylinder is safely secured to the wall or other unmovable structure;
- the certified gas concentration;
- the gas vendor's cylinder serial number;
- the gas cylinder valve and line valve are open and functional;
- the tank pressure is within 200 to 2000 psig; and
- the line pressure from the stainless-steel 2-stage pressure regulator is properly set to the calibrator specifications.

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 Multi-gas Calibrator Checks

The on-site multi-gas calibrator blends known concentrations of reference gas and ultra-pure zero air to perform routine QC calibrations and performance verifications of the SO₂ analyzer. The microprocessor-based calibrator consists of at least two mass flow controllers, solenoid valves, a mixer chamber, and sensors for pressure and temperature to correct the volumetric flow rates to standard conditions. (The calibrator may include a third mass flow controller to perform serial dilutions to blend trace-level gas concentrations.) EPA operational QC criteria requires the calibrator mass flow controllers and auxiliary systems to be calibrated semi-annually. Note and record the following operational items:

- power is on, display up, and ready for operation;
- program mode (concentration, flow, or auto);
- display date and time within ± 1 minute of NIST-AST; and
- date of last mass flow controller calibrations.

6.2.6 Analyzer Status Checks

Status checks performed on the SO₂ analyzer will vary among instrument manufacturers but in general they will include:

- power on, the display up, in sample mode, and operating;
- record the current SO₂ concentration in ppb;



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- compare the analyzer display concentration to the DAS display concentration (within ± 0.5 ppb);
- record current date and time (± 1 minute of AST);
- if the current display concentration matches the DAS concentration within;
- 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 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.

6.2.7 Data Acquisition System (DAS) Checks

Whether the DAS is a stand-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:

- the power is on;
- the display is up and software is operational;
- the current date and time is correct and synonymous (within ± 1 minute) with AST;
- the DAS is communicating with analyzer and all other auxiliary instrumentation showing all the configured monitoring channels with instantaneous readings;
- the modem and/or router is powered and functional; and
- confirm external communication with accessibility to the internet.

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 SO₂. 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 SO₂ 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 commonly 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 SO₂ analyzer first with zero air and then with an up-scale SO₂ concentration typically set at 80 percent of the measurement



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range. These checks may be performed manually or through an automated program function of the analyzer, calibration system 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 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 multi-gas calibrator. 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, typically 10-15 minutes. Once stabilized, a five minute average is calculated from the DAS to determine the analyzer response for zero air.
2. Upon completion of the zero air check, the span check is initiated by actuating the multi-gas calibrator (either manually or automatically) to generate an SO₂ 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 recorded from the DAS.

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 SO₂ concentrations which would be measured in ambient air at the monitoring site. 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 after the analyzer response stabilizes. The 5-min avg 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 SO₂ from the sample system. For SO₂ 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 SO₂ 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 SO₂ concentrations. 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 analyses completed using the “SO₂ Calibration Data Sheet” spreadsheet shown in **Figure 3**.

6.3.4 Calculation of Performance Verification Results

The results of the zero air checks are calculated by subtracting the analyzer response from zero as shown below in **Equation 5**.

Equation 5. Calculation of Zero Drift

$$\text{Zero Drift} = 0.0 \text{ (ppb)} - \text{analyzer response to ultra-pure zero air (ppb)}$$

Where:

Zero Drift (ppb)

Analyzer Responses in ppb as recorded from the DAS (ppb)

Zero Air (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

$$\text{Percentage difference (di)} = [(Analyzer - [SO_2]out)/[SO_2]out] \times 100$$

Where:

di = percent difference (%)

Analyzer Responses = analyzer concentration as recorded from the DAS (ppb)

[SO₂]out = Known SO₂ Concentration as determined from the dilution calculation of certified reference gas with zero air (See Equation 2).

The results of a multi-point verification are to be recorded and calculated using the Multi-Point Calibration Data Sheet shown in **Figure 3** and as discussed in section 6.1.1.

6.3.5 Performance Verification QC Limits

The SO₂ Data Validation Template 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” for zero drift as presented in the EPA QA Handbook as revised in 2013⁹ is ± 1.5 ppb; however, EPA revised these criteria in a memorandum from Lewis Weinstock, Office of Air Quality Planning and Standards (OAQPS) on June 3, 2014.¹⁰ The revised zero drift acceptance criteria is now ±3 ppb over a 24-hour period or ±5 ppb over a 14-day period. Deviation beyond these critical QC limits is grounds for data invalidation.

The “Operational Criteria” QC acceptance criteria for multi-point verifications are the same as discussed in section 6.1.1.

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 may be invalidated or at a minimum flagged with a qualifier code. For the threshold conditions highlighted in yellow indicating the data are

⁹ *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program*, EPA-454/B-13-003, may 2013. <https://www3.epa.gov/ttnamti1/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf>

¹⁰ Memorandum, “Revision to the Zero Drift Acceptance Criteria in the QA Handbook” Lewis Weinstock, Office of Air Quality Planning and Standards, June 3, 2013. <https://www3.epa.gov/ttn/amtic/files/policy/zerodriftmemo6314.pdf>



still within 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 $< \pm 2$ 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 may be required.

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 SO₂ 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	
± 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.
Sample system leak check	Monthly with filter change or following any disassembly of the sample system components
Verify analyzer sample flow rate with a certified flow rate standard device, if tolerances exceed manufacturer specifications, inspect and as necessary replace flow capillary and O-rings.	Annually or as indicated by electronic diagnostics
Inspect and clean optical filters and/or condensing lens in the optical bench and O-rings.	As indicated by electronic diagnostics
Assess UV flash lamp function, adjust or replace as needed.	As indicated by electronic diagnostics
Inspect and clean the instrument cooling fan and assess function of the fan, adjust or replace as needed.	Monthly or as needed
Assess function of reference and sample flow solenoids, adjust or replace as needed.	As indicated by electronic diagnostics
FEM Detention for instrument noise, performed in accordance with definitions and procedures in 40 CFR 53.26(b)	Typically DEC accepts the manufacturer's specifications for instrument noise.
FEM Detention evaluation for lower detectable level (LDL) performed in accordance with definitions and procedures in 40 CFR 53.26(b)	Typically DEC accepts the manufacturer's specifications for LDL.
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
Replace scrubber reagents	Annually or an indicated by diagnostics.



Dynamic Dilution Multi-Gas Calibrator Maintenance	
Verify mass flow controller with a certified flow rate standard device, repair and recalibrate if tolerances exceed manufacturers specification	Annually or as indicated by diagnostics
Following annual flow rate verification, inspect flow components O-rings, tubing connectors, and mixing chamber for condition issues. Repair or replace as necessary.	Annually or as indicated by diagnostics
System leak check	Annually or following any disassembly of system components or as indicated by diagnostics.
Inspect and clean the instrument cooling fan and assess function of the fan, clean or replace as needed.	Monthly or as needed

7. QUALITY ASSURANCE

7.1 Qualification, Verification and Re-verification

All transfer standards used to assure traceability to EPA or NIST standard reference materials or devices shall be certified, verified, and re-verified in accordance with the *EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program*, EPA-454/B-13-003, May 2013.

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** SO₂ Data Validation Template, 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**. These 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 SO₂ monitoring system with a zero air concentration and at least three upscale SO₂ concentrations. The SO₂ audit concentrations shall be 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 SO₂ Data Validation Template shown in **Appendix A** requires that QA performance audits be conducted at least once per year. If the results of the QA performance audit are outside the “Operational Criteria”



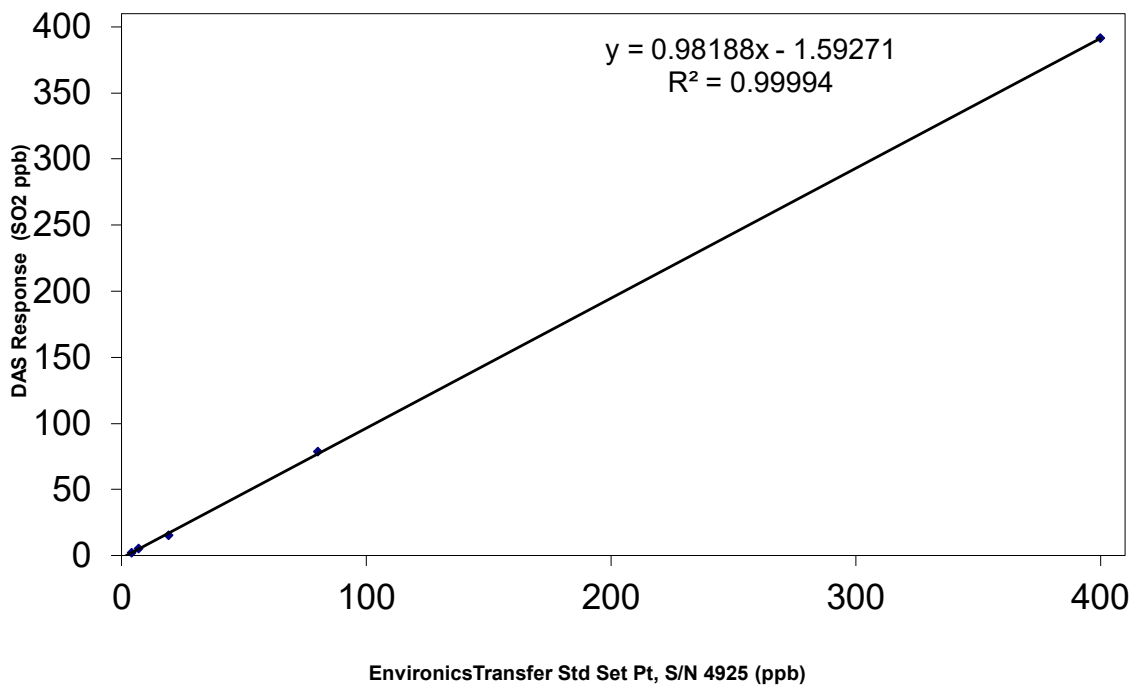
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presented in **Appendix A**, corrective action shall be taken. An example audit report is presented in **Figure 5**.

Figure 5 Example SO₂ QA Performance Evaluation Report

SO₂ monitor Audit						
Site: NCore 809 Pioneer Rd, Fairbanks AK				Calibration: 4-Nov-15		
Date: January 14, 2016 7:45 -11:00 AST				Last QC check: 9-Jan-16		
Monitor: Thermo Sci 43i SO ₂ analyzer, S/N CM08130058 (Range 0-500 ppb)				Time:		
Audit Device: EnviroNics 6103 Transfer Std/Gas Phase Titrator, S/N 4925				audit 8:45:58		
Type of Audit: Through sample manifold				instrument 8:46:00		
				das 8:46:24		
Audit Standard Set Pt (ppb)	DAS SO ₂ value 5-min avg (ppb)	Time (AST)	DAS - Audit (ppb)	Abs (DAS-Audit) Audit*100	Mean Abs % Δ	0-Air Flow (cc/min)
0	-0.3	8:15	-0.3		20.7	4993
400	391.0	8:35	-9.0	2.3		2129
80	78.2	8:50	-1.8	2.3		2181
19	15.3	9:13	-3.7	19.5		4988
7	5.1	9:30	-1.9	27.1		8989
4	1.9	9:46	-2.1	52.5		8991
0	-2.2	10:02				8994
0	-0.1	10:20				2196





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 SO₂ Validation Data Template of **Appendix A**, a technical systems audit is required once every three years for a SLAM site or once for a PSD site. 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 15.3 will be applied.

8. DATA REVIEW, VALIDATION AND REPORTING

To assure the SO₂ 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 SO₂ analyzer produces an electronic signal equivalent to the measured SO₂ 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 average concentrations. Depending on system capability, the on-site DAS may act as a server transmitting the data to a base computer or database server. Data management software on the database server may be programmed to provide routine reporting and editing functions. This may include a near real-time data 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 and database server. The secondary system acts as a data backup system and provides for routine QC data comparisons to check for communication errors.

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 database 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 SO₂ concentrations to alert the AMQA program manager if hourly or 3-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) database or for a PSD data submission to DEC. This procedure is typically the responsibility of the site operator or data manager who is knowledgeable of the day to day data collection effort. It is typically performed on a monthly basis.

The procedure begins by compiling 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 are also required for periods during QC checks and calibrations;
- 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. A tabular view allows the reviewer to observe specific data values. A comparison of hourly values shall be performed comparing the data record from the 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, periods 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 SO₂ Data Validation Template 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 precise despite QC results. For example, failed QC verification checks for zero/span/precision were due to a problem with the on-site calibration system 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 and QA Officer. In either case, an explanation for the action must be included in the data record. Invalidation 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 credible evidence. All data and related records used in the development of the final validated data set submitted to the EPA AQS database 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 DEC'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 the EPA AQS database.

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 SO₂ 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. The data submitted for each valid hour includes the 1-hour average and the twelve 5-minute averages. 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 not required to be reported to AQS but 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 SO₂ 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 3-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) Technical Assistance Document (TAD) *For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network*, EPA-454/R 05-003, September 2005.
- 2) Title 40 CFR Part 50, Appendix A-1, *Reference Measurement Principle and Calibration Procedure for Measurement of Sulfur Dioxide in the Atmosphere (Ultraviolet Fluorescence Method.)*
- 3) Title 40 CFR Part 53, *Ambient Air Monitoring Reference and Equivalent Methods, Subparts A and B*
- 4) Title 40 CFR Part 58, *Ambient Air Quality Surveillance, Subparts A, B, C, Appendices A, C, D, and F*
- 5) EPA *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II, EPA-454/B-13-003, May 2013.
- 6) EPA *Traceability Protocol for Assay and Certification of Gaseous Standards*, EPA 600/R-012/533, May 2012.
- 7) ADEC *Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program*, February 23, 2010.
- 8) Thermo Electron Corporation, *Model 43i-TLE Instruction Manual Pulsed Fluorescence SO₂ Analyzer*, January 2008
- 9) Environics, Inc. *Model 6103 Multi-Gas Calibrator, User's Guide and Technical Service Manual*, Revision 5 March, 2007
- 10) EPA Memorandum, "*Revision to the Zero Drift Acceptance Criteria in the QA Handbook*" Lewis Weinstock, Office of Air Quality Planning and Standards, June 3, 2013.



10. DEFINITIONS OF ACRONYMS & SYMBOLS

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
AQS	“Air Quality System” is the database which contains ambient air pollution data collected by the EPA, state, local, and tribal air pollution control agencies.
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 SO ₂ 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 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



NCORE	an EPA program to establish a national multi pollutant monitoring network that integrates several advanced measurement systems for particles, precursor pollutant gases, and meteorology
NIST	government abbreviation for the “National Institute of Standards and Technology”
OAQPS	EPA “Office of Air Quality Planning and Standards”
ppb	chemical abbreviation for a unit of chemical concentrations expressed as “parts per billion” (Note, because SO ₂ 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 SO ₂ 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”
SO ₂	chemical abbreviation for sulfur dioxide
SOP	common abbreviation for “Standard Operating Procedure”
SPMS	EPA abbreviation for “Special Purpose Monitoring Station”
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
SO₂ Data Validation Template

1) Requirement (SO ₂)	2) Frequency	3) Acceptance Criteria	Information /Action
CRITICAL CRITERIA- SO₂			
<i>One Point QC Check Single analyzer</i>	<i>1/2 weeks</i>	$\leq +10\%$ (percent difference)	1) and 2) 40 CFR Part 58 App A Sec 3.2 3) Recommendation based on DQO in 40 CFR Part 58 App A Sec 2.3.1.2 QC Check Conc. range 0.01 - 0.10 ppm Relative to routine concentrations
Zero/span check	1/2 weeks	Zero drift $< + 3$ ppb over 24 hours* Zero drift $\leq \pm 5$ ppb over 14 days* Span drift $< + 10$	1 and 2) QA Handbook Volume 2 Section 12.3 3) Recommendation and related to DQO
OPERATIONAL CRITERIA- SO₂			
<i>Shelter Temperature Range</i>	<i>Daily (hourly values)</i>	<i>20 to 30° C. (Hourly avg.) or per manufacturers specifications if designated to a wider temperature range</i>	<i>1, 2 and 3) QA Handbook Volume 2 Section 7.2.2 Generally the 20-30° C range will apply but the most restrictive operable range of the instruments in the shelter may also be used as guidance. FRM/FEM list found on AMTIC provides temp. range for given instrument, .FRM/FEM monitor testing is required at 20°-30° C range per 40 CFR Part 53.32</i>
<i>Shelter Temperature Control</i>	<i>Daily (hourly values)</i>	$< + 2^{\circ}$ C SD over 24 hours	1, 2 and 3) QA Handbook Volume 2 Section 7.2.2
<i>Shelter Temperature Device Check</i>	<i>1/6 mo</i>	$+ 2^{\circ}$ C of standard	1, 2 and 3) QA Handbook Volume 2 Section 7.2.2
<i>Annual Performance Evaluation Single Analyzer</i>	<i>Every site 1/year 25 % of sites quarterly</i>	<i>Percent difference of audit levels 3-10 $< +15\%$ Audit levels 1&2 $+ 1.5$ ppb difference or $+15\%$</i>	<i>1 and 2) 40 CFR Part 58 App A sec 3.2.2 3) Recommendation - 3 audit concentrations not including zero. AMTIC guidance 2/17/2011 http://www.epa.gov/ttn/amtic/cpreldoc.html</i>
<i>Federal Audits (NPAP)</i>	<i>1/year at selected sites 20% of sites audited</i>	<i>Audit levels 1&2 $+ 1.5$ ppb difference all other levels percent difference $+ 15\%$</i>	<i>1) 40 CFR Part 58 App A sec 2.4 2) NPAP adequacy requirements on AMTIC 3) NPAP QAPP/SOP</i>
<i>Verification/Calibration</i>	<i>Upon receipt/adjustment/repair/ installation/moving 1/6 months if manual zero/span performed biweekly 1/year if continuous zero/span performed daily</i>	<i>All points within $+ 2\%$ of calibration range of best-fit straight line</i>	<i>1) 40 CFR Part 50 App A-1 Section 4 2 and 3) Recommendation Multi-point calibration (0 and 4 upscale points)</i>
<i>Gaseous Standards</i>	<i>All gas cylinders</i>	<i>NIST Traceable (e.g., EPA Protocol Gas)</i>	<i>1) 40 CFR Part 50 App A-1 Section 4.1.6.1 2) NA Green book 3) 40 CFR Part 50 App F Section 1.3.1 Producers must participate in Ambient Air Protocol Gas Verification Program 40 CFR Part 58 App A sec 2.6.1</i>
<i>Zero Air/ Zero Air Check</i>	<i>1/year</i>	<i>Concentrations below LDL < 0.1 ppm aromatic hydrocarbons</i>	<i>1) 40 CFR Part 50 App A-1 Section 4.1.6.2 2) Recommendation</i>

<i>1) Requirement (SO2)</i>	<i>2) Frequency</i>	<i>3) Acceptance Criteria</i>	<i>Information /Action</i>
			3) Recommendation and 40 CFR Part 50 App A-1 Section 4.1.6.2
<i>Gas Dilution Systems</i>	<i>1/year or after failure of 1 point QC check or performance evaluation</i>	<i>Accuracy + 2 %</i>	1) 40 CFR Part 50 App A-1sec 4.1.2 2) Recommendation 3) 40 CFR Part 50 App A-1 sec 4.1.2
<i>Detection (FEM/FRMs)</i>			
<i>Noise</i>	<i>NA</i>	<i>0.001 ppm (standard range) 0.0005 ppm (lower range)</i>	1) 40 CFR Part 53.23 (b) (definition & procedure) 2) NA 3) 40 CFR Part 53.20 Table B-1
<i>Lower detectable level</i>	<i>1/year</i>	<i>0.002 ppm (standard range) 0.001 ppm (lower range)</i>	1) 40 CFR Part 53.23 (c) (definition & procedure) 2) Recommendation 3) 40 CFR Part 53.20 Table B-1
SYSTEMATIC CRITERIA- SO₂			
<i>Sampler/Monitor</i>	<i>NA</i>	<i>Meets requirements listed in FRM/FEM designation</i>	1) 40 CFR Part 58 App C Section 2.1 2) NA 3) 40 CFR Part 53 & FRM/FEM method list
<i>Standard Reporting Units</i>	<i>All data</i>	<i>ppb (final units in AQS)</i>	1, 2 and 3) 40 CFR Part 50 App T Sec 2 (c)
<i>Rounding convention for data reported to AQS</i>	<i>All data</i>	<i>1 place after decimal with digits to right truncated</i>	1, 2 and 3) 40 CFR Part 50 App T Sec 2 (c)
<i>Completeness</i>	<i>1 hour standard</i>	<i>Hour – 75% of hour Day- 75% hourly Conc Quarter- 75% complete days Years- 4 complete quarters 5-min value reported only for valid hours</i>	1, 2 and 3) 40 CFR Part 50 App T Section 3 (b), (c) More details in CFR on acceptable completeness. 5-min values or 5-min max value only reported for the valid portion of the hour reported. If the hour is incomplete no 5-min or 5-min max reported.
<i>Sample Residence Time Verification</i>	<i>1/year</i>	<i>< 20 seconds</i>	1) 40 CFR Part 58 App E, section 9 (c) 2) Recommendation 3) 40 CFR Part 58 App E, section 9 (c)
<i>Sample Probe, Inlet, Sampling train</i>	<i>All sites</i>	<i>Borosilicate glass (e.g., Pyrex®) or Teflon®</i>	1, 2 and 3) 40 CFR Part 58 App E sec 9 (a) FEP and PFA have been accepted as equivalent material to Teflon. Replacement or cleaning is suggested as 1/year and more frequent if pollutant load or contamination dictate
<i>Siting</i>	<i>1/year</i>	<i>Meets siting criteria or waiver documented</i>	1) 40 CFR Part 58 App E, sections 2-5 2) Recommendation 3) 40 CFR Part 58 App E, sections 2-5
<i>Precision(using 1-point QC checks)</i>	<i>Calculated annually and as appropriate for design value estimates</i>	<i>90% CL CV < 10%</i>	1) 40 CFR Part 58 App A sec 2.3.1.6 & 3.2.1 2) 40 CFR Part 58 App A sec 4 (b) 3) 40 CFR Part 58 App A sec 4.1.2
<i>Bias (using 1-point QC checks)</i>	<i>Calculated annually and as appropriate for design value estimates</i>	<i>95% CL < + 10%</i>	1) 40 CFR Part 58 App A sec 2.3.1.6 & 3.2.1 2) 40 CFR Part 58 App A sec 4 (b) 3) 40 CFR Part 58 App A sec 4.1.3
<i>Annual PE Primary QA Organization (PQAO) Evaluation</i>	<i>1/year</i>	<i>95% of audit percent differences fall within the one point QC check 95% probability intervals at PQAO level of aggregation</i>	1) 40 CFR Part 58 App A Section 3.2.2 2) Recommendation 3) 40 CFR Part 58 App A sec 4.1.4 and 4.1.5