Standard Operating Procedures for
Sulfur Dioxide (SO₂) Monitoring by Ultraviolet
Fluorescence

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PROCEDURE PLAN APPROVAL

Title: Standard Operating Procedures for Sulfur Dioxide (SO₂) Monitoring by Ultraviolet Fluorescence

This manual documents the standard operating procedures (SOP) established by the Alaska Department of Environmental Conservation (ADEC), Division of Air Quality for the continuous monitoring of sulfur dioxide in ambient air. This manual for sulfur dioxide monitoring is recommended for approval and commits the ADEC Air Monitoring and Quality Assurance (AMQA) program to follow the procedures detailed in this document.

Approval Signatures

Date: 2/13/2012

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Date: 2/13/2012

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ACKNOWLEDGEMENTS

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DEFINITIONS AND ACRONYMS

°C  degrees Celsius
μg/min micrograms per minute
ADEC Alaska Department of Environmental Conservation
AMQA Air Monitoring and Quality Assurance
CFR Code of Federal Regulations
CRM Certified Reference Material
EPA U.S. Environmental Protection Agency
F_d diluent flow
FEM Federal Equivalent Method
FRM Federal Reference Method
in. Hg inches mercury, pressure
IR infrared
LDL lower detectable limit
MDL method detection limit
mm Hg millimeters mercury, pressure
NAAQS National Ambient Air Quality Standards
NCore National Core Monitoring Network (multi-pollutant)
NIST National Institute of Standards and Testing
NIST-SRM National Institute of Standards and Testing Standard Reference Material
NTRM NIST Traceable Reference Material
PAH polycyclic aromatic hydrocarbons
PEP performance evaluation program
PMT photomultiplier tube
<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ppb</td>
<td>part per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PQAO</td>
<td>principal quality assurance organization</td>
</tr>
<tr>
<td>QA</td>
<td>quality assurance</td>
</tr>
<tr>
<td>QC</td>
<td>quality control</td>
</tr>
<tr>
<td>PSD</td>
<td>prevention of significant deterioration</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeter</td>
</tr>
<tr>
<td>SLAMS</td>
<td>state and local air monitoring station</td>
</tr>
<tr>
<td>SPMS</td>
<td>special purpose monitoring station</td>
</tr>
<tr>
<td>SO₂</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>SOP</td>
<td>standard operating procedure</td>
</tr>
<tr>
<td>TAD</td>
<td>technical assistance document</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compound</td>
</tr>
<tr>
<td>URL</td>
<td>upper range limit</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
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1. INTRODUCTION

This document is intended for people responsible for collecting and processing sulfur dioxide data supported by the Alaska Department of Environmental Conservation (ADEC). It is also intended as a standard operating procedure (SOP) for Prevention of Significant Deterioration (PSD) monitoring for industry in Alaska. The procedures given in this SOP are to be used in conjunction with the monitoring site’s Quality Assurance Project Plan (QAPP), the latest information published in the Code of Federal Regulations, and the Operator’s Manual for the specific analyzer being used. Successful SO₂ data capture should be ensured if all requirements in this document are met or exceeded.

The U.S Environmental Protection Agency (EPA) has determined that sulfur dioxide (SO₂) pollution is a human health and environmental concern. The EPA established a 1-hour primary National Ambient Air Quality Standard (NAAQS) for SO₂ of 75 parts per billion in 2010 and retained the annual (0.03 ppm) and 24-hour (0.14 ppm) standards (both arithmetic averages) that had been in place since 1971. The EPA will address the secondary SO₂ standard by 2012, which is currently a 3-hour standard set to 0.5 ppm.

1.1 PURPOSE AND SCOPE

This document is to assist personnel tasked with operating sulfur dioxide monitoring systems and collecting data that are subject to regulatory review by the ADEC AMQA program. The successful capture of accurate data with minimal loss depends not only on reliable equipment, but also upon procedures designed to assure that EPA and ADEC data quality objectives are achieved.

This document provides information to be used in the development of a sulfur dioxide monitoring project whether the data is to be used for state and local air monitoring (SLAM) to determine attainment with the NAAQS, NCORE trace level concentration monitoring, special purpose monitoring (SPM), or monitoring performed by a stationary source in support of an air quality permit to confirm prevention of significant deterioration (PSD).

Please note that each agency or company tasked with the installation, operation, and reporting of regulatory monitoring data is required to develop standard operating procedures specific to the type of equipment used including the makes and models of the SO₂ analyzer, calibration system and data acquisition system, as well as specific information regarding shelter specifications and siting requirements. Both ultraviolet (UV) fluorescence and flame photometric detection (FPD) methods are acceptable SO₂ monitoring federal equivalent methods (FEM). Most agencies or companies will choose to use an UV fluorescence method instead of a FPD method because of its better linearity sensitivity and lack of consumables (i.e., hydrogen gas). A UV fluorescence monitor is **required** at NCORE sites because of the trace-level concentration requirements for NCORE stations.
1.2 DATA QUALITY OBJECTIVES
Data Quality Objectives (DQOs) are a set of specifications that if they are all met or exceeded will maximize the likelihood of successful acquisition of good quality data that are valid and useful for their intended purpose. They define appropriate types of data and also specify a combination of the EPA’s and the monitoring program’s precision and bias tolerances for measurement errors. Specific monitoring objectives for SO2 should be designed to:

• determine 1-hour, 3-hour, 24-hour (arithmetic average), and annual (arithmetic average) concentrations of SO2 ambient air for comparison to primary and/or secondary SO2 NAAQS,

• collect 5-minute data for NCore¹ and SLAMS reporting requirements (40 CFR 58.16) and

• determine representative levels of SO2 in populated areas with regards to public health protection and public education

1.3 THEORY OF OPERATION: UV FLUORESCENCE METHOD
The SO2 analysis is based on the principle of the characteristic fluorescence released by the sulfur dioxide molecule when it is radiated by ultraviolet light of 190-230 nm. SO2 absorbs light in this region of the spectrum without any quenching by air or most other molecules found in polluted air. The decay radiation is passed through a bandwidth filter and into a photomultiplier tube (PMT) that converts the signal into a voltage that can be directly measured.

Equation 1: \[ \text{SO}_2 + h\nu_1 \rightarrow \text{SO}_2^* \rightarrow \text{SO}_2 + h\nu_2 \]

Where:

\[ h\nu_1 = \text{incidence light} \]

\[ h\nu_2 = \text{fluoresced light} \]

\[ \text{SO}_2^* = \text{SO}_2 \text{ in its excited state} \]

Potential interferences to the fluorescent technique include any species that either quench or exhibit fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO2 at some wavelengths. Where water vapor presents a problem, it can be removed by a dryer within the instrument. In most analyzers, the water interference is minimized by careful selection of the incident radiation wavelength. Difference in oxygen concentrations between the two matrices can become significant if a low-level SO2-in-nitrogen cylinder gas is diluted to prepare a calibration standard. In such a case, the nitrogen in the pollutant flow stream may "dilute" the oxygen in the dilution air stream, significantly decreasing the oxygen concentration. This situation can be avoided by keeping the concentration of SO2 in the cylinder gas high enough.

¹ NCore recommendations are expected to be codified into federal regulation soon (estimated 2012-2013).
that the nitrogen contributed by the pollutant flow stream is insignificant with respect to the total flow volume.

Polycyclic aromatic hydrocarbons (PAH) such as naphthalene exhibit strong fluorescence in the same spectral regions as SO$_2$ and are major interferences. These aromatics must be removed from the sample gas stream by an appropriate scrubber upstream of the reaction chamber, e.g., hydrocarbon “kicker”. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient hydrogen sulfide (which normally does not interfere with the fluorescent technique) into SO$_2$. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H$_2$S.

Nitric oxide (NO) fluoresces in a spectral range close to SO$_2$. Interference from NO is addressed by the presence of the band pass filter which allows only the wavelengths emitted by the excited SO$_2$ molecules to reach the PMT.

The operating range for this method is 0-0.5 ppm or 0-0.1 ppm, depending upon each analyzer's "EPA Designated Reference or Equivalent Method" operating range. The method detection limit is 2% of full scale. The purpose of the monitoring (SLAM, NCore, SPM or PSD) will likely determine the range of the analyzer selected for the monitoring project. **Analyzers used for monitoring SO$_2$ in the ambient air must be US EPA-designated federal reference or federal equivalent method (FRM or FEM) SO$_2$ analyzers.**
1.4 HEALTH AND SAFETY WARNINGS, CAUTIONS
Sulfur dioxide (SO$_2$) is a colorless, nonflammable gas that has a strong suffocating odor. Sulfur dioxide can be detected by taste and odor in ambient air at concentrations as low as 0.3 ppm. Higher levels of SO$_2$ can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. The SO$_2$, or any other calibration span gas, should be vented to the atmosphere rather than into the shelter or other sampling areas. If this is impossible, limit operator exposure to SO$_2$ by getting fresh air every 5 to 10 minutes. The operator must leave the area immediately if he/she experiences light headedness, headache or dizziness.

The following basic precautions should be taken while working with SO$_2$ instrumentation:

1. Operate all monitoring instruments with the available grounding plug (3-wire plug);
2. Exhaust the analyzer safely, especially when calibrating the unit with high SO$_2$ concentrations;
3. When working/troubleshooting/repairing any electrical instrument, the power should usually be turned off and the power line disconnected;
4. Risk of electrical shock or damage to the electronic components should be minimized by wearing an antistatic wristband when working on the PMT and other components requiring high voltages. Be sure to ground the wristband properly;
4. Take normal precautions for shock protection/prevention when working inside of any electrical instrument with the power connected. Remove rings, watches, bracelets and necklaces to prevent electrical burns;
5. Ensure that all high-pressure gas tanks are securely chained or otherwise attached to something solid so that the tanks remain in an upright and secure position at all times.

2 SITE REQUIREMENTS AND INSTALLATION
This section describes the recommended and required initial site selection and installation procedures for placing a SO$_2$ analyzer in a monitoring station. Complete documentation of the site selection and installation should help to avoid later questions about data quality and capture rates.

2.1 SITE SELECTION
Siting criteria differences and similarities between SLAMS and PSD monitoring are discussed in 40 CFR Part 58, Appendix A. The siting criteria for SLAMS and NCore sites are discussed in 40 CFR Part 58, Appendix D. Probe and monitoring path specifications can be found in 40 CFR Part 58, Appendix E. The spatial scales of representativeness used in this SOP (i.e., micro,
middle, neighborhood, urban and regional) are defined and discussed in 40 CFR Part 58, Appendix D. Siting recommendations are contained in this document but refer to 40 CFR and

2.1.1 PROBE PLACEMENT
The height of the SO₂ inlet probe must be 2 to 15 meters above ground. The distance of the inlet probe from any supporting structures must be greater than one meter vertically and horizontally. Airflow must be unrestricted in an arc of at least 270 degrees around the inlet probe, and the predominant wind direction for the season of greatest pollutant concentration must be included in the 270 degree arc. If the probe is located on the side of a building, 180 degrees of clearance is required and the predominant wind direction must again be included in the 180 degree arc. No furnace or incineration flues or other minor sources of SO₂ should be nearby. The separation distance is dependent on the height of the flues, type of waste or fuel burned, and sulfur content of the fuel. Table 1 summarizes the probe installation requirements for SLAM, NCore, SPM and PAM sites. The inlet probe must be located away from obstacles and buildings. The distance between the obstacle(s) and the inlet probe must be at least twice the height that the obstacle protrudes above the inlet probe. Sampling stations that are located closer to obstacles than this criterion allows should not be classified as a neighborhood scale since the measurements from such a station would closely represent middle scale stations. Therefore, stations not meeting this criterion should be classified as middle scale.

Table 1: Probe installation requirements of SLAMS, NCore and PAMS sites

<table>
<thead>
<tr>
<th>Scale</th>
<th>Distance from trees to probe or inlet (meters)</th>
<th>Height (meters)</th>
<th>Distance from Supporting Structures (meters)</th>
<th>Other Spatial Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle, Neighborhood, Regional</td>
<td>&gt; 10</td>
<td>2 - 15</td>
<td>&gt; 1</td>
<td>&gt; 1</td>
</tr>
</tbody>
</table>

Must have an unrestricted air flow of 270° around the inlet probe or 180° if located on the side of a building. (see CFR Part 58, Appendix E).

2.1.2 MONITORING SHELTER
The monitoring shelter's role in quality assurance is to provide security, electrical power and a temperature-controlled environment in which the sampling equipment can operate at optimum performance. The mean shelter temperature should be within 15 to 30°C. Alaska has received an EPA sanctioned exception to the CFR required shelter temperature range because of its extreme cold weather. Daily fluctuations should not exceed ±2°C. A continuous recording thermograph should be installed at the shelter to continuously record daily fluctuations in temperature. Fluctuations greater than ±2°C can cause the electronic components of the
analyzer to drift and thus introduce error to the data. For this reason, excursions outside the specifications should be flagged to indicate questionable data.

In addition to a temperature-controlled environment, it is highly recommended that all power supplied to sensitive monitoring equipment be conditioned. Appropriate selection of a power conditioner for the monitoring area will minimize equipment failure and loss of data.

### 2.3 STATION INSTALLATION

#### 2.3.1 SAMPLE TRAIN MATERIALS

Sampling train (probes, gas lines, manifolds) must be constructed of borosilicate glass, PTFE (Polytetrafluoroethylene) or FEP (Fluoroethylpropylene) Teflon®, or equivalent material, to minimize possible reaction(s) and degradation of SO₂. Stainless steel (s.s.316 or better) is allowed but should be avoided because it is expensive, hard to clean and can develop micro-cracks that are difficult to detect. The use of integrating flasks on the sample manifold is strongly discouraged. Even with nonreactive gas line materials, reactive particulate matter is deposited on sample train walls over time. Therefore, the time it takes the gas to transfer from the probe inlet to the sampling device (residence time) is also critical. Residence time must not exceed 20 seconds and, **if at all possible**, it is recommended that it not exceed 10 seconds.

Sample train specifications are listed below:

- **Sample Probe and Gas Manifold Material**: Borosilicate (Pyrex®) Glass, PTFE or FEP Teflon (or equivalent), stainless steel (s.s.316 or better).

- **Filter Material**: Particulate filter(s), if used, must be borosilicate (Pyrex) glass, PTFE or FEP Teflon®, stainless steel (s.s. 316 or better), or equivalent material.

- **Valve(s) Material**: Borosilicate (Pyrex) glass, PTFE or FEP Teflon, or stainless steel (s.s.316 or better).

- **Gas Lines**: Gas lines, including sample, span, and calibration lines, must be borosilicate (Pyrex) glass, PTFE or FEP Teflon, or stainless steel (s.s.316 or better).

- **Sample Train Gas Residence Time (from test gas introduced at sample inlet to first upscale analyzer response)**: 10 seconds preferred, 20 seconds maximum.

The use of particulate filters on the sample manifold and inlet line is optional but strongly encouraged. Filters reduce the analyzer's susceptibility to interference, malfunction, or damage due to particulates. The user is cautioned, however, that particulate matter concentrated on a filter may cause erroneous SO₂ measurements. For this reason, filters should be changed frequently. In addition, a particulate filter may only be used in the sample line (between the gas manifold and the analyzer). Prior to routine use, it is incumbent on the user/manufacturer to prove that an in-line filter does not bias the reliability of the analyzer to measure actual
concentrations of SO$_2$ in ambient air. These checks must be conducted at calibration, and at periodic intervals thereafter, to test the integrity of the sample introduction system. It is up to the operating agency to design and implement these checks. As with all instrument checks, documentation is a required QA activity.

Gas lines, including sample, span and calibration lines, must be either borosilicate glass, PTFE or FEP Teflon, or stainless steel (s.s.316 or better). Sample lines should be kept as short as possible to reduce sample gas residence time. All fittings must be compatible (e.g., both male and female ends either stainless steel or Teflon). Demonstration of compliance may be physical testing or calculated. The residence time within the sampling line should be minimized to: 1) reduce the possibility of reactive gas interactions and 2) to minimize SO$_2$ adsorption on the surface of the lines.

Further information and requirements regarding probe and manifold materials and designs can be found in the 2008 "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Ambient Air Specific Methods, Section 7.2.1 Design of Probes and Manifolds for Automated Methods." Please note that as of the writing of this document in December 2011, Volume II of the “Quality Assurance Handbook for Air Pollution Measurement Systems” was being revised by EPA and may contain revisions which include recently promulgated NCore site requirements.

2.3.2 EQUIPMENT SETUP
The relevant technical and operations manual(s) should be followed in the setup and connection of the SO$_2$ analyzer, data acquisition system, calibration system and any telemetry necessary for station to operate completely. Calibration systems are detailed in section 3 and diagrammed in figures 2 and 4. Connections to the data acquisition system (DAS) are described in section 2.3.3.

2.3.3 DATA ACQUISITION SYSTEM
All SO$_2$ continuous analyzers should be connected to a data acquisition system (DAS) or data logger. Manufacturer’s operation and technical manuals should be consulted for specific instructions on how to hook up the cables (usually RS232) between the DAS, instrument and any remote access hardware/software used for a site.

3 SAMPLER CALIBRATION
The accuracy and validity of measurement data recorded by air monitoring equipment depends on the quality assurance procedures used. The primary procedure is dynamic calibration, which determines the relationship between the observed and the actual values of the variable being measured.

In dynamic multi-point calibration, an instrument's responses are related to successive gas samples of known concentrations. A minimum of four reference points and a zero point are
recommended to derive the calibration relationship. The "true" value of each SO₂ cylinder gas or SO₂ permeation tube must be traceable to a National Institute of Standards and Technology-
Standard Reference Material (NIST-SRM), Certified Reference Material (CRM), or NIST Traceable Reference Material (NTRM).

3.1 STANDARD REFERENCE MATERIALS
To assure data of desired quality, the SO₂ measurement process must be under defined control limits, and any systematic errors, when combined with random variations in the measurement process, must result in a small level of uncertainty.

Good data quality requires documentation of the quality control checks and performing independent audits of the measurement process. These tasks necessitate maintaining good data recording practices and using materials, instruments, and measurement procedures traceable to reference standards of known quality. To establish traceability, multiple measurements must be made of standard reference materials (primary, secondary, and/or working standards), and process control procedures must be established. More specifically, working calibration standards must be traceable to standards of higher accuracy, such as NIST-SRM, CRM, or NTRM. Procedures for certification of an SO₂ working standard against NIST-SRM, CRM, or NTRM are found in section 3.3.4, Certification of SO₂ Working Standards.

3.1.1 ZERO AIR
Dry zero air, verified to be free of contaminants that would cause detectable responses in the SO₂ analyzer, may be purchased in high-pressure gas cylinders or generated with commercially available clean air systems. Care should be taken to ensure that an ambient concentration of carbon dioxide (CO₂), approximately 380 ppm CO₂, is maintained in any zero air source used so as to mimic ambient atmospheric air.

3.1.2 SULFUR DIOXIDE (SO₂) CYLINDER GAS
SO₂ Concentration Standard--SO₂ cylinder gas must contain a known concentration of SO₂ in Nitrogen (N₂). SO₂ cylinder calibration gases must be certified traceable to a NIST-SRM, CRM, or NTRM cylinder gas.

3.1.3 SULFUR DIOXIDE (SO₂) PERMEATION DEVICES
SO₂ Concentration Standard--SO₂ permeation device(s) suitable for generating SO₂ concentrations at the required flow rates over the required concentration range. The SO₂ permeation devices must be certified traceable to a NIST-SRM, CRM, or NTRM source.

3.2 CALIBRATION PROCEDURES
All calibrations must be done in situ, at the permanent monitoring station, and disturbing the least amount of the normal sampling inlet system. Either of two methods may be used for dynamic multi-point calibration of the analyzer. These are:

Method A: Calibration by Dynamic Dilution of a High Concentration SO₂ Gas Cylinder, or
Method B: Calibration by Dynamic Dilution of an SO2 Permeation Tube.

NOTE: Analyzers used for monitoring SO2 in the ambient air must be US EPA-designated reference or equivalent method SO2 analyzers.

3.2.1 CALIBRATION FREQUENCY
To ensure accurate measurements of SO2 concentrations, calibrate the analyzer at the time of installation. An activity matrix for calibration procedures is presented in table 2. The SO2 analyzer will require a recalibration whenever one of the following conditions occurs:

- six months has elapsed since the last calibration;
- major disassembly or replacement of any major component(s) of the SO2 analyzer and monitoring system;
- the monitor fails a performance audit;
- a level 1 zero/span SO2 gas check is not within tolerance (15%) of the corresponding zero/span gas concentration;

NOTE: If the monitor fails a precision quality control (QC) check, the instrument response should be used only as an indicator of the analyzer's performance (no analyzer adjustment can be taken based solely on an analyzer's response to a precision gas). A level 1 zero/span QC check must be performed immediately thereafter to determine if the analyzer is within calibration tolerance.

- physical relocation of the monitor;
- a significant interruption in analyzer operation; or
- any other indication such as excessive zero or span drift, or malfunction of the SO2 monitoring system is observed.

Following any repairs which might affect the analyzer's calibration, the zero and span should be checked to determine if a calibration is necessary. If the analyzer zero and span drifts do not exceed the calibration limits in figure 7 (located at the end of section 4.2.2), a calibration need not be performed. If either the zero or span drift exceeds its respective calibration limit, investigate the cause of the drift, take corrective action, and recalibrate the analyzer.
3.2.2 CALIBRATION METHOD A: Dynamic Dilution of a High Concentration SO₂ Gas Cylinder

In this method, a high concentration certified SO₂ in N₂ cylinder is diluted with dry zero air to generate incremental concentrations of SO₂ to calibrate the analyzer's SO₂ responses.

Before using the assembled and/or purchased systems for SO₂ calibrations, your system must:

1. Use an SO₂ standard gas traceable to a NIST-SRM, CRM, or NTRM. This high concentration SO₂ gas cylinder (preferably in the range of 30-50 ppm and the remaining balance N₂) is the primary sulfur dioxide (SO₂) calibration source from which all subsequent SO₂ dilutions (calibration standards) are made;

**NOTE:** All regulators used in a calibration system (zero air and standard gases) should have a nonreactive diaphragm and internal parts and be cleaned prior to initial use to remove potential manufacturing residues that may contaminate the calibration system.

2. Have a minimum total flow output that exceeds the analyzer flow demand by at least 10 percent;

3. Be capable of generating an SO₂ concentration that is approximately 80% of the upper range limit (URL) of the SO₂ range to be calibrated;

4. Have a gas calibration system with a mixing chamber capable of diluting the output of the SO₂ cylinder with zero air to the desired concentrations via a system of mass-flow-controllers, and that controls and regulates flow rates to ±1%.
Flow rates must be measured with an accuracy of ±2% of stated flow. All parts of the gas dilution calibrator in contact with the SO$_2$ output must be glass, Teflon (and to a limited amount), s.s.316 or better quality stainless steel;

6. Have dry dilution (zero) air which is free of interferents that would cause a detectable response in the SO$_2$ analyzer. This zero air is used to establish and check the analyzer's zero baseline and to dilute the SO$_2$ gas to the desired calibration point and QC check concentrations. Zero air may be supplied from cylinders or from a clean air generator; and

7. Have an output manifold of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 3 for a schematic diagram of a typical gas dilution calibration system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary primary standard (e.g., soap bubble meter, laminar flow element (LFE), wet test meter.) Correct all volumetric flow rates to 25°C (298 K, 77°F) and 760 mm (29.92 in.) Hg. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual).
Figure 2: Schematic diagram of a typical gas dilution configuration for SO\textsubscript{2} calibration.

Precautions must be taken to remove O\textsubscript{2} from the SO\textsubscript{2} pressure regulator and delivery system prior to the start of calibration. Failure to do so can cause significant errors in calibration. This problem may be minimized by:

a. carefully evacuating the regulator after it has been connected to the cylinder, but before opening the cylinder valve;

b. thoroughly flushing the regulator and delivery system with cylinder gas after opening the cylinder valve; and

c. not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Connect the output cables of the analyzer to the input cables of the strip chart recorder, if applicable, and/or the data acquisition system (DAS). All adjustments to the analyzer should be performed based on the appropriate DAS and/or strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and/or recorder responses.
Prior to calibrating the SO₂ analyzer, verify the accuracy of the DAS and/or recorder with a power supply and a volt meter of known accuracy. At a minimum, 80%, 20%, and 0% of analyzer full scale responses should be verified. Both chart recorder and DAS readouts should be within ±2% full scale volts of the analyzer output.

During the calibration, the analyzer must be operating in its normal sampling mode, and the test atmosphere must pass directly to the sample inlet of the analyzer. Ensure that calibration gases are introduced to the analyzer at atmospheric pressure.

**Note:** During a calibration, the analyzer's response(s) is set to equal the calibration gas concentration. Any external filters, scrubbers, conditioners, etc., may introduce bias to the measurement system. After completing the calibration, conduct a level 1 zero/span quality control check and measure the responses. Reconnect all in-line sample conditioning equipment and repeat the same level 1 zero/span quality control check. The differences between the two measured level 1 zero/span checks should be zero. If not, the in-line conditioners are introducing bias to the measurement system. Because zero and calibration adjustments differ between analyzers, consult the operators manual before calibrating the analyzer.

1. Record pertinent information on a calibration data form (Figure 4) or a logbook including the station name and address, date, shelter temperature, person performing the calibration, analyzer and calibrator make, model and serial numbers, as well as SO₂ cylinder number, supplier, pressure and NIST traceability document;

7. Record the zero and span knob settings after the calibration is complete so that these settings can be used at a later date to determine changes in the instrument performance characteristics;

10. Provide zero air to the input of the calibrator. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the atmospheric dump. For safety concerns, ensure that the atmospheric dump vents outside the monitoring shelter. Measure the diluent air flow using a NIST-traceable intermediate primary standard. Consult the respective manufacturer's standard operating procedures manual for specific directions. Measure and record temperature and pressure of the (in-line) diluent air flow. Correct the actual measured air flow to standard temperature and pressure conditions [STP: \( T_{std} = 298^\circ K \) (25°C, 77°F) and \( P_{std} = 760\text{mm Hg} \) (29.92 in. Hg)]. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). Record the standardized diluent air flow \( (F_D) \) in figure 4 or record the information in the DAS and logbook as needed;
NOTE: When installing an atmospheric dump use as short of a line as possible, and one of
larger diameter to minimize back-pressure.

11. For a minimum of 15 minutes, allow the analyzer to sample zero air until a stable response
is obtained (a response that does not vary by more than ±1% of full scale over a 5 minute
time period). Record the stable zero air response.

NOTE: For a strip chart recorder, offset the analyzer zero to +5% of the strip chart scale. This
facilitates observing negative zero drift. Adjust the analyzer zero control to read zero.

12. Select the operating range of the analyzer (e.g., 0-500 ppb). Determine the 80% upper
range limit (URL) SO₂ cylinder gas flow (FSO₂) by solving equation 2 for FSO₂. Adjust
FSO₂ to generate an SO₂ concentration of approximately 80% of the URL of the analyzer.
Record FSO₂ on the 80% URL line (figure 4) or make a note in the DAS and/or logbook
as necessary.

Equation 2: \( FSO₂ = \frac{(FD \times [SO₂]_{out})}{([SO₂]_{std} - [SO₂]_{out})} \)

where: \([SO₂]_{out} = \) 80% URL SO₂ gas concentration

\([SO₂]_{std} = \) SO₂ cylinder gas concentration

FSO₂ = flow rate of SO₂ cylinder gas, sccm

FD = flow rate of dilution air, sccm;

13. Calculate the exact SO₂ concentration \([SO₂]_{OUT}\) by solving equation 3.

Equation 3: \( [SO₂]_{OUT} = \frac{FSO₂ \times [SO₂]_{STD}}{(FSO₂ + FD)} \)

Record the \([SO₂]_{OUT}\) on the 80% line (figure 4) or make a note in the DAS and/or
logbook as needed;

14. Sample the generated concentration until the SO₂ response has stabilized. Adjust span
response for the analyzer SO₂ channel for a balanced output equal to the SO₂ calibration
gas.

If substantial adjustment of the SO₂ span control is necessary, recheck the zero and span
adjustment in steps 11 and 14. Record the analyzer’s SO₂ response under columns 4 and
5 on the 80% URL line (figure 4) or make a note in DAS and/or logbook as needed;

15. Generate at least three more, for a total of five (zero, and 4 upscale points) , SO₂ gas
concentrations by decreasing FSO₂ or increasing FD. Use equation 1 to calculate FSO₂
flows Then measure SO₂ and diluent flows as described in steps #10 and #12. Correct
all flows to STP conditions. Record the calibration data for each point;
16. Plot the analyzer's SO$_2$ responses against the corresponding SO$_2$ calibration gas concentrations. Determine the best straight line by the method of least squares. This can be done with a programmed calculator or with the calculation data form presented in figure 4 or program the DAS to do the plot and least squares regression; and

17. Calculate the SO$_2$ linear regression calibration curve. Record the slope (m), y intercept (b), and correlation coefficient (r) for the SO$_2$ curve. The correlation coefficient (r) must be $\geq 0.995$ for the calibration to pass EPA and ADEC criteria.

**SO$_2$ CALIBRATION DATA FORM BY GAS DILUTION (Method A)**

<table>
<thead>
<tr>
<th>1 Station</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Calibrated by</td>
<td></td>
</tr>
<tr>
<td>3 Analyzer Mfr.</td>
<td>4 Calibrator Mfr.</td>
</tr>
<tr>
<td>Model</td>
<td>Model</td>
</tr>
<tr>
<td>S/N</td>
<td>S/N</td>
</tr>
</tbody>
</table>

6 SO$_2$ Reference Standard

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Cylinder Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration [SO$<em>2$]$</em>{std}$</td>
<td>Cylinder Pressure</td>
</tr>
<tr>
<td>Reference to NIST-SRM, CRM, or NTRM</td>
<td></td>
</tr>
<tr>
<td>By</td>
<td>Date of Reference</td>
</tr>
</tbody>
</table>

6 Zero Air Make/Model #

<table>
<thead>
<tr>
<th>Serial Number</th>
</tr>
</thead>
</table>

7 Flow Rate Calibration

<table>
<thead>
<tr>
<th>Reference Standard</th>
</tr>
</thead>
</table>

8 Make/Model #

<table>
<thead>
<tr>
<th>Serial Number</th>
</tr>
</thead>
</table>

9 Zero Knob Setting

<table>
<thead>
<tr>
<th>Span Knob Setting</th>
</tr>
</thead>
</table>

9 Temperature

<table>
<thead>
<tr>
<th>Barometric Pressure</th>
</tr>
</thead>
</table>

**Equations Used for SO$_2$ Calibration**

**Equation 2:**

$$F_{SO2} = \left( F_D \times [SO_2]_{OUT} \right) \times \left( [SO_2]_{STD} - [SO_2]_{OUT} \right)$$

where:

- $F_{SO2}$ = flow rate of SO$_2$ standard, scem
- $F_D$ = flow rate of zero air, scem

**Equation 1:**

$$[SO_2]_{OUT} = \frac{F_{SO2} \times [SO_2]_{STD}}{F_{SO2} + F_D}$$

where:

- $[SO_2]_{STD}$ = concentration of the standard
- $[SO_2]_{OUT}$ = concentration at the output manifold undiluted SO$_2$ standard

**SO$_2$ Calibration Data Form (Method A: Gas Dilution)**

<table>
<thead>
<tr>
<th>Calibrations Points SO$_2$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_D$ scem</td>
<td>$F_{SO2}$ scem</td>
<td>$[SO_2]_{OUT}$ ppm</td>
<td>DAS reading</td>
<td>SO$_2$ recorder reading</td>
</tr>
<tr>
<td>Zero</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80% URL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60% URL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% URL</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% URL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% URL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: Example of data record format for calibration by gas dilution.
3.2.3 CALIBRATION METHOD B: Dynamic Dilution of an SO₂ Permeation Tube

The principle: In a permeation device, an easily liquefiable gas such as SO₂ is condensed inside an inert container, all or part of which is constructed from a polymeric material (often Teflon). Gas from the container permeates and passes through the polymer walls at a temperature-dependent rate. The rate of gas effusion (in μg/min) at a constant temperature can be established by gravimetric determination of the weight loss of the permeation device over a known period of time.

In this calibration procedure, the SO₂ analyzer's responses are calibrated with accurately known concentrations of SO₂ that are dynamically produced by diluting the effusion from an SO₂ permeation device, with various flows of clean air to obtain a calibration for SO₂. The SO₂ permeation device used must be certified traceable to a NIST-SRM, CRM, or NTRM source.

Figure 5 depicts a diagram of a typical permeation device calibration system. The system consists of three functional sections:

1. A controlled-temperature section that houses the SO₂ permeation device and is flushed continuously with purified, dry zero air or nitrogen.

2. A regulated source of clean, dry zero air for dilution of the SO₂ effluent from the permeation device.

3. A dilution-mixing, sampling and exhaust system.

Temperature control is crucial for this procedure; a change in temperature of about 0.5°C effects a change in the permeation rate of the device of about four percent. For this reason, it is important that the temperature of the device be maintained at a constant value within ±0.1°C, and that it be closely monitored when the device is in use.

Generally, the SO₂ permeation device is housed in a temperature-controlled glass container that has an entrance and exit port at opposite ends; a glass thermometer accurate to ±0.05°C may be placed beside the device to monitor its temperature. A small fixed zero air or nitrogen flow (about 100 cm³/min) that is maintained at the same temperature as the permeation device flushes the SO₂ out of the device housing into a mixing chamber where the SO₂ is diluted with clean, dry zero air. A valve, e.g., a three-way stopcock, placed at the exit of the device housing, may be used to divert the SO₂ stream to a vent when clean air is required at the manifold for making the necessary zero adjustments to the analyzer.

To maintain the temperature of the permeation device to within ±0.1°C of the desired value, the device and housing may be either placed physically inside a constant temperature chamber, or they can be located externally to the constant temperature chamber with the heat transfer medium circulated around the device housing. The flushing zero air or nitrogen passes through
a heat exchanger, e.g., a coil of copper tubing, contained in the constant temperature chamber before passing over the device to adjust its temperature to that of the device.

Permeation devices are available from commercial sources and from NIST as a Standard Reference Material (SRM). Both NIST and commercial manufacturers provide explicit instructions on the proper use and handling of their devices needed to obtain accurate measurements.

If the SO₂ permeation device is to be used as the reference standard for calibration, the permeation rate of the device must be traceable to a NIST SO₂ in N₂ cylinder gas standard SRM or SO₂ permeation device SRM. Procedures for certifying the reference standard against NIST-traceable SO₂ in N₂ or SO₂ permeation standards and for inter-comparing SO₂ working standards are found in section 3.3.4.

The dynamic permeation tube dilution calibrator is required to dilute the output from the temperature-controlled permeation system to the desired concentration. All parts in contact with the SO₂ output must be glass or Teflon. The system must be capable of controlling and measuring flow rates to within ±2 percent of stated flow. A small portion of this dried zero air (approximately 100 sccm) is used as the flush gas for the permeation device.

In figure 2, the zero air stream is split to allow a small air flow to pass continuously over the permeation device. Alternatively, the flush gas could be supplied from a cylinder of pre-purified dry air or nitrogen. Whatever its source, it is extremely important that the flushing stream be extra dry so that moisture does not condense on the surface of the device. Water condensate could react with the effusing SO₂ to form an acid mist, thus changing the SO₂ concentration. A transparent drying column containing a mixture of molecular sieve (e.g., 6-16 mesh, type 4A) and indicating calcium sulfate (e.g., Drierite®) has been used effectively as a moisture scrubber on the flush gas line.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 2 for a schematic diagram of a typical permeation device calibration system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary or primary standard (e.g., laminar flow element (LFE), or wet test meter). Correct all volumetric flow rates to 298 K (25°C, 77°F) and 760 mm Hg (29.92 in.Hg). Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). For the calibrator, ensure that the permeation chamber temperature indicator is calibrated under conditions of use to a NIST-traceable intermediary or primary standard.
Figure 4: Schematic diagram of a typical dynamic dilution permeation device calibration system.

Connect the recorder and DAS output cables of the analyzer to the input cables of the strip chart recorder and DAS. All adjustments to the analyzer should be performed based on the appropriate DAS and/or strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and recorder responses.

Calibration gases must be introduced directly to the sample inlet port of the analyzer at atmospheric pressure. Dynamic calibration systems based upon SO$_2$ permeation tube dilution systems may be used to calibrate an SO$_2$ analyzer provided they meet the following requirements:

1. Air flow controllers capable of maintaining constant air flows within ±2 percent of the required flow rate;
2. Component parts in contact with SO$_2$ gases of non-reactive and non-adsorbent material (i.e., borosilicate glass, FEP Teflon, or equivalent material);
3. Air flow indicator capable of measuring and monitoring flows with an accuracy of ±2 percent of the measured flow rate. In addition, each flow meter must be calibrated to a NIST-traceable source (i.e., laminar flow element or wet test meter);

4. Constant temperature chamber (constructed of non-reactive and non-adsorbent material) capable of housing the SO$_2$ permeation device(s) and maintaining its temperature to within ±0.1°C;

5. Temperature measuring device capable of measuring and monitoring the temperature of the SO$_2$ permeation chamber with an accuracy of ±0.05°C;

6. Drier and scrubber(s) to remove moisture and contaminants from the permeation device air system. The use of the drier is optional with SO$_2$ permeation devices not sensitive to moisture (refer to the supplier's instructions for use of the permeation device);

7. Valve(s) to divert the SO$_2$ from the permeation device when zero air is required at the manifold. Valve(s) must be constructed of borosilicate glass, Teflon, or other non-reactive material;

8. Mixing chamber, designed to provide thorough mixing of reaction products and diluent air, is constructed of borosilicate glass (preferred) or other non-reactive and non-adsorbent material; and

9. Output manifold constructed of borosilicate glass (preferred), Teflon, or non-reactive and non-adsorbent material. The manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

Follow procedure in Sec. 3.2.2, pg 17.

Determine the 80% upper range limit (URL) dilution gas flow ($F_D$) by solving equation 4 for $F_D$.

13. Calculate the SO$_2$ concentration using equation 4 below:

Equation 4: \[ [\text{SO}_2]_{\text{out}} = \frac{P \times K_m}{(F_p + F_D)} \]

where: $[\text{SO}_2]_{\text{out}} =$ diluted SO$_2$ concentration supplied to the analyzer

$P =$ permeation rate, $\mu$g/min

$K_m =$ molar constant for SO$_2$ = 0.382 (@ 30°C and 760 mmHg)
FP = air flow across permeation device, sccm

FD = diluent air flowrate, sccm

Record the 80% URL value in column 3, [SO₂]_{OUT} or in DAS and logbook.

14. Allow the analyzer to sample this 80% URL SO₂ concentration until a stable response is obtained (a response that does not vary by more than ±1% of full scale over a 5-minute time period); then adjust the analyzer’s span control to read actual [SO₂] concentration.

Sample this 80% URL SO₂ concentration until the analyzer's responses have stabilized. Record these values in columns 4 and 5 or in DAS and logbook.

15. Adjust FD to generate at least three more evenly-spaced SO₂ gas concentrations. Use equation 4 to calculate FD flows for these concentrations. Measure FP and FD using a NIST-traceable intermediate primary standard. Measure and record the FP and FD air stream (in-line) temperature and pressure. Correct the actual measured flows to STP conditions. Record the analyzer's measured [SO₂] response for each concentration. Calculate the SO₂ concentration using equation 4. Record the values in columns 4 and 5 of figure 5 or note in DAS and logbook.

**NOTE:** *An equilibration time of at least fifteen minutes is recommended between concentration changes.*

16. Plot the analyzer's [SO₂] responses against the corresponding SO₂ calibration gas concentrations. Calculate the [SO₂] linear regression calibration curve. Record the slope (m), y intercept (b), and correlation coefficient (r) for each calibration curve. The correlation coefficient for each curve must be ≥0.995. If not, correct the problem and recalibrate the analyzer. Record each iteration until the correlation coefficient meets required level.
3.3.4 SO₂ WORKING STANDARDS

NIST-SRM or CRM SO₂ in N₂ gas cylinders are certified for 6 months at concentrations below 40 ppm and 2 years at concentrations greater than 40 ppm. After 6 months, cylinders with < 40 ppm SO₂ can be sent back to the supplier to be analyzed and, if they pass criteria, will be recertified for use for 2 years. After the certification date has passed, new NIST-traceable gases must be purchased from a qualified vendor.
**SO₂ CALIBRATION AND LINEARITY CHECK METHODS**

**Option 1: DAS automation**
Program the DAS to automatically record, plot and calculate the calibration. Then check the output to ensure that the calibration ran correctly according to the program. Ensure that the calibration was linear and the correlation fell within the tolerances required for the type of monitoring being conducted (PSD, NCore, SLAMS or SPM).

**Option 2: Laptop computer method**
Enter the SO₂ concentrations (X) and DAS or recorder values (Y) into a spreadsheet of statistical software program on a computer and then plot a linear regression and calculate the correlation coefficient automatically. Ensure that the calibration was linear and the correlation fell within the tolerances required for the type of monitoring being conducted (PSD, NCore, SLAMS or SPM).

**Option 3: Hand calculation method**

<table>
<thead>
<tr>
<th>Calibration Point</th>
<th>Concentration [SO₂ ppm]</th>
<th>DAS or recorder reading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>x</th>
<th>x²</th>
<th>y</th>
<th>y²</th>
<th>xy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ n = \text{number of calibration points} \]

The equation of the line fitted to the data is written as:

\[ Y = y_{\text{avg}} + b(x - x_{\text{avg}}) = y_{\text{avg}} - bx_{\text{avg}} \]

where

\[ Y = \text{predicted mean response for corresponding x,} \]

\[ b = \text{slope of the fitted line, and} \]

\[ a = \text{intercept where the line crosses the y-axis.} \]

\[ b = \frac{(\Sigma xy - (\Sigma x)(\Sigma y)/n)}{(\Sigma x^2 - (\Sigma x)^2/n)} \]

\[ a = y_{\text{avg}} - bx_{\text{avg}} \]

---

**Figure 6: SO₂ calibration and linearity check methods.**

4 OPERATIONAL PROCEDURES

Essential to quality assurance (QA) are scheduled quality control (QC) checks for verifying the operational status of the monitoring system. The operator should visit the site at least once every **two** weeks. Every two weeks a Level 1 zero/span QC check must be conducted on the analyzer. Level 1 zero/span checks must be conducted between 70% and 90% of the analyzer's operating measurement range.
NOTE: It is strongly encouraged that an automatic system for the remote-controlled activation and recording of Level 1 zero/span checks be installed so that more frequent (e.g., daily) systematic zero/span checks are conducted.

In addition, an independent precision check at a concentration between 16% and 20% of the SO₂ analyzer's upper range limit (URL) must be carried out at least once every two weeks. Table 3, page 31, lists suggested QC activities for routine operations. To provide for documentation and accountability of activities, it is recommended that a checklist be compiled and then filled out by the field operator as each activity is completed. The completed checklist can then be filed with other site operational information (e.g., calibrations, maintenance, etc.) to provide complete documentation for the site.

4.1 EQUIPMENT

4.1.2 SAMPLE INTRODUCTION SYSTEM

The sample introduction system consists of:

a. intake port;
b. particulate and moisture traps;c. sampling manifold;d. sampling blower; and
e. sampling line to the analyzer.

As part of the QA program, the field operator should inspect the above components on a predetermined schedule for:

a. breakage;b. leaks;c. particulates or foreign matter;d. moisture deposition in sample line or manifold; and
e. sample line connected to sample manifold.

Any component of the sample introduction system that is not within tolerance needs to be cleaned, repaired, or replaced immediately.
4.1.2 ANALYZER INSPECTION

Table 3: Sample checklist for Shelter/Analyzer inspections

<table>
<thead>
<tr>
<th>Shelter/Analyzer Inspection Checklist</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
</tr>
<tr>
<td>Personnel inspecting</td>
</tr>
<tr>
<td>Range of shelter temperature since last inspection</td>
</tr>
<tr>
<td>Condition of particulate filter(s)</td>
</tr>
<tr>
<td>Check diagnostics</td>
</tr>
<tr>
<td>Correct settings of:</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Verification that analyzer is in sample mode*</td>
</tr>
<tr>
<td>Verification that zero and span potentiometers are locked and set at the proper values</td>
</tr>
<tr>
<td>Verification that DAS is functioning correctly</td>
</tr>
<tr>
<td>Comments</td>
</tr>
</tbody>
</table>

*Or the equivalent of sample mode, not in zero or calibrate mode

4.2 QUALITY CONTROL (QC) PERFORMANCE CHECKS

Zero and span checks are required to document that the analyzer meets precision and bias criteria by comparing the response of the instrument to known SO2 concentrations. If an analyzer's response falls outside the prescribed limits, the cause must be determined and corrected. Maintenance of a quality control chart is highly recommended to provide a visual check to determine:

1. if the analyzer is within control conditions; and
2. the trend of the analyzer's bias so corrections can be made to improve control over the SO2 measurement process before an out-of-limits situation occurs.

Standard(s) used for multi-point calibration may be used for conducting zero and span checks. It is essential that the same SO2 gas be used each time a zero/span check is conducted. This provides a means to track the analyzer's reliability to measure the same gas over a long period.

Figure 7 (SO2 Zero/Span Drift Control Limits) summarizes the required quality control actions for the use of zero and span checks to determine SO2 analyzer calibration control.

4.2.1 LEVEL 1 ZERO/Span CHECK

To conduct a level 1 zero/span check, the analyzer should be operating in its normal sampling mode with the test concentrations passing through as much of the inlet and sample conditioning system as is practicable.

No adjustment(s) to the analyzer may be made during the zero and span calibration. Analyzer response readings must be obtained "as is" before any adjustments are made to the analyzer. These unadjusted zero and span readings provide valuable information for:
a. confirming the validity (or invalidating) the measurements obtained immediately preceding the calibration;
b. monitoring the analyzer's calibration drift; and
c. determining the frequency of recalibration.

To conduct a Level 1 zero and span check:

1. Disconnect the analyzer's inlet from the ambient sample probe at the junction of the probe manifold and the sample line, and connect it to the SO2 gas or permeation device dilution calibration system. Ensure that the zero/span gas is delivered to the analyzer at atmospheric pressure. Leave the analyzer in its normal sampling mode;
2. Sample and measure the span test concentration and record the unadjusted, stable ("as is") span response reading on a spreadsheet or log sheet and on an X-S control chart used for recording Level 1 zero/span checks, or confirm that the DAS has done it and record it in the station log book;

**NOTE:** All analyzer response readings must be recorded in the analyzer's normal output units (e.g., millivolts, % of scale, etc.--the same units used for the calibration curve). If these units are concentration units, they should be identified as "indicated" or "uncorrected" to differentiate them from the "actual" concentration units that are used for reporting the reference span gas concentration measurements.

3. Sample and measure the zero test concentration standard and record;
4. Perform analyzer adjustments (flow, pressure, etc.) or analyzer maintenance, if needed;
5. If adjustment of the zero is needed, or if any adjustments have been made to the analyzer, adjust the zero to the desired zero reading. Offsetting the zero reading (e.g., to 5% of scale) may help to observe any negative drift that may occur. Record the adjusted, stable zero reading;
6. Sample and measure the span test concentration. If span adjustment is needed, adjust the span response to the desired value, allowing for any zero offset used in the previous step. Record the final adjusted, stable span reading; and
7. If any adjustments were made to the zero, span, or other parameters, or if analyzer maintenance was carried out, allow the analyzer to restabilize at the new settings, then recheck the zero and span readings. Record the new zero/span settings as well as the actual zero and span readings.

When the response from a span check is outside the control limits, the cause for the extreme drift should be determined and the appropriate corrective action(s) must be taken. Some of the causes for drift are listed below:
a. lack of preventive maintenance;
b. fluctuations in the electrical power supply;
c. fluctuations in flow;
d. changes in zero air source;
e. change in span gas concentration;
f. degradation of photomultiplier tube;
g. electronic and physical components not within manufacturer's specifications; and/or
h. change in environmental temperature control.

For specific and detailed corrective actions to be taken, please consult the manufacturer's instruction/operations manual or technical manual.

4.2.2 PRECISION

For continuous analyzers, a periodic check is used to assess the data for precision. A one-point precision check must be conducted at least once every two weeks on each analyzer at a concentration between 16% and 20% of the analyzer's upper range limit (URL). The analyzer must be operated in its normal sampling mode. The precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The precision check gas standard must be traceable to a NIST-SRM, CRM, or NTRM. The precision check standard should be independent from that used for calibration.

The precision check procedure follows:

1. Connect the analyzer to a calibration system to generate an SO₂ precision gas that has a concentration between 16% and 20% of the analyzer's URL (between 0.08 and 0.10 ppm for a 0.5 ppm URL). Ensure that the precision gas is delivered to the analyzer at atmospheric pressure. The SO₂ precision gas may be generated by either Method A or Method B. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero or span adjustment(s);

2. Allow the analyzer to sample the precision gas until a stable response is obtained (at least 15 minutes); and

3. Record this value: a) on the precision check form (see figure 11 at the end of this section), b) on an X-S quality control chart, c) on a spreadsheet, and d) in the station log book as "unadjusted precision check" or if the precision check is programmed to be run by the DAS, record it a) in the DAS log system and b) in the station log book as "unadjusted precision check" and look at the X-S quality control chart in the DAS.

The difference between the concentration indicated by the analyzer and the actual concentration of the precision check gas is used to assess the precision of the monitoring
data (see EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems; Volume 2.0.8 Calculations to Assess Monitoring Data for Precision and Accuracy for SLAMS and PSD Automated Analyzers and Manual Methods or EPA454/R-05-003 Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCORE Multi-pollutant Monitoring Network, Version 4, Section 3.3).

Use the same control criteria to evaluate acceptable SO$_2$ precision checks as used to evaluate acceptable level 1 span checks (see figure 7).

**SO$_2$ Precision Checks by Dynamic Dilution of an SO$_2$ Cylinder Gas (Method A)**

To conduct SO$_2$ precision checks by gas dilution, follow the procedures used in subsection 3.2.2 (SO$_2$ multi-point calibration by gas dilution). Instead of generating multiple SO$_2$ gas concentrations for a multi-point calibration, generate one level of SO$_2$ between 16% and 20% of analyzer full range (e.g., 0.08 to 0.10ppm for a 0 - 0.5ppm full scale range for SLAMS, PSD or SPM stations).

**SO$_2$ Precision Checks by Dynamic Dilution of an SO$_2$ Permeation Device (Method B)**

To conduct SO$_2$ precision checks by SO$_2$ permeation device method, follow the procedures used in subsection 3.2.3 (SO$_2$ multi-point calibration by dynamic dilution of an SO$_2$ permeation device). Instead of generating multiple SO$_2$ gas concentrations for a multi-point calibration, generate one level of SO$_2$ between 16% and 20% of analyzer full range (e.g., 0.08 to 0.10ppm for a 0-0.5ppm full scale range).
### Table 4: Operational activity matrix

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Acceptance Limits</th>
<th>Frequency and Method of Measurement</th>
<th>Action if Requirements Are Not Met</th>
</tr>
</thead>
</table>
| Shelter Temperature | Mean temperature between 15 to 25°C, daily fluctuations not greater than ±2°C (±4°F) | Edit thermograph chart or check DAS daily for variations greater than ±2°C (±4°F) | 1. Make a note in the DAS &/or logbook  
2. Repair or adjust temperature control system |
| Sample introduction system | No moisture, foreign material, leaks, obstructions; sample line connected to manifold | Weekly visual inspection | Clean, repair or replace as needed |
| Data Acquisition System (DAS) | 1. Check that the DAS connections to the instrument are working correctly  
2. Compare a direct download of the instrument to the DAS data to make sure that it is gathering data correctly | Weekly download and visual inspection | 1. Visually and electronically check that the connection b/w the DAS and instrument is working  
2. Do a direct download of the instrument for the last week and compare at least 10% of the data to the data collected by the DAS. |
| Analyzer operational settings | 1. Flow and regulator indicators at proper settings  
2. Temperature indicators cycling or at proper levels  
3. Analyzer set in sample mode  
4. Zero and span controls locked | Weekly visual inspection | Adjust or repair as needed |
| Analyzer operational check | Zero/span checks within tolerance limits as described in Subsection 4.1 | Level 1 zero/span checks every 2 weeks; Level 2 between Level 1 checks at frequency desired by user | 1. Isolate source of error, and repair  
2. After corrective action, recalibrate analyzer |
| Analyzer precision check | Precision checks within tolerance limits as described in Subsection 4.2 | Every 2 weeks | Precision check criteria not met, conduct level 1 zero/span check to substantiate problem |

#### SO₂ Analyzer Zero/Span Drift Calibration Limits

<table>
<thead>
<tr>
<th>ZERO DRIFT (% of range)</th>
<th>SPAN DRIFT (% of range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; +5%</td>
<td>&gt; +15%</td>
</tr>
<tr>
<td>+5%</td>
<td>+15%</td>
</tr>
<tr>
<td>+3%</td>
<td>≤ +10%</td>
</tr>
<tr>
<td>+1%</td>
<td>+5%</td>
</tr>
<tr>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>-1%</td>
<td>-5%</td>
</tr>
<tr>
<td>-3%</td>
<td>≤-10%</td>
</tr>
<tr>
<td>-5%</td>
<td>-15%</td>
</tr>
<tr>
<td>&gt;-5%</td>
<td>&gt;-15%</td>
</tr>
</tbody>
</table>

Figure 7: SO₂ analyzer zero/span drift calibration limits
SO₂ ANALYZER OPERATIONAL CHECKLIST

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site Location</td>
<td>Technician</td>
</tr>
<tr>
<td>Site Address</td>
<td></td>
</tr>
</tbody>
</table>

1. Inspect thermograph for temperature variations greater than +2°C (4°F). Identify timeframe of any temperature level out of tolerance.
   Comments: 

2. Inspect sample introduction system for moisture, particulate buildup, foreign objects, breakage, leaks.
   Comments: 

3. Is sample line connected to manifold?
   Comments: 

4. Check data acquisition system.
   Comments: 
   Okay? Corrective action taken.

5. Inspect analyzer operational parameters.
   - Sample flow rate
   - Analyzer in sample mode
   - Zero and span potentiometers locked at correct setting
   Comments: 

6. Zero the analyzer.

7. Is the unadjusted zero within tolerance?
   Comments: 

8. Span the analyzer.

9. Is unadjusted span within tolerance?
   Comments: 

10. Enter zero and span values on span check data form.
11. Return to sample mode.
12. Record cylinder pressure of zero and span tanks.
   - Zero air
   - Span air

13. Close valve on zero and span tanks.

**Figure 8: Example SO₂ analyzer operation sheet.**
5 SAMPLER MAINTENANCE

Because preventive maintenance requirements vary from instrument to instrument, the manufacturer's manual should be consulted for a specific analyzer. From these instrument-specific maintenance requirements a suitable preventive maintenance schedule should be
developed for each instrument and a detailed preventive maintenance record kept on site. A general sample maintenance schedule is shown in table 5.

Table 5: Sample maintenance schedule

<table>
<thead>
<tr>
<th>Maintenance Item</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replace particle filter</td>
<td>Weekly</td>
</tr>
<tr>
<td>Check diagnostics (if not available remotely)</td>
<td>Bi-weekly</td>
</tr>
<tr>
<td>Perform zero precision span check</td>
<td>Bi-weekly (daily recommended)</td>
</tr>
<tr>
<td>Perform pneumatic system leak check</td>
<td>At least quarterly</td>
</tr>
<tr>
<td>Inspect internal &amp; external tubing; replace if necessary</td>
<td>At least quarterly</td>
</tr>
<tr>
<td>Visual inspection and cleaning</td>
<td>6 months</td>
</tr>
<tr>
<td>Replace sample particulate filter</td>
<td>Bi-weekly to monthly depending on PM levels</td>
</tr>
<tr>
<td>Capillary inspection and replacement</td>
<td>6 months</td>
</tr>
<tr>
<td>Fan filter inspection and cleaning</td>
<td>6 months depending on surroundings</td>
</tr>
<tr>
<td>Lamp voltage check</td>
<td>When lamp voltage approaches maximum (1200v)</td>
</tr>
<tr>
<td>Replace internal span permeation tube (if applicable)</td>
<td>Annually</td>
</tr>
<tr>
<td>Pump rebuild</td>
<td>Upon a failed leak check or annually</td>
</tr>
<tr>
<td>Clean optic bench</td>
<td>As needed</td>
</tr>
<tr>
<td>Replace PMT</td>
<td>As needed</td>
</tr>
</tbody>
</table>

6 CALCULATIONS AND DATA VALIDATION

6.1 DATA ACQUISITION, PROCESSING, AND REPORTING
Sulfur dioxide data are acquired from analyzers by data acquisition systems (DAS) or direct downloads at the site to a laptop. Processed raw data are forwarded to the agency program or project manager from their station manager(s) or automatically (after review by the operator and perhaps others as necessary) by the DAS. PSD monitoring data should be put through a similarly structured data flow in order to obtain and maintain the best data quality and data capture rates possible.

6.1 SPAN DRIFT CHECK
The first level of data validation should be to accept or reject monitoring data based upon routine periodic analyzer checks. It is recommended that results from the Level 1 zero and span checks be used as the first level of data validation for accepting data. This means that up to two weeks of monitoring data may be invalidated if the span drift for a Level 1 zero and span check is equal to or greater than 15%. For this reason it is strongly recommended that zero and span checks be conducted more frequently than the bi-weekly requirement.
6.2 DATA REDUCTION
Data can be reduced automatically. Automatic data reduction is done by DAS that are programmed at the time of the analyzer's multi-point calibration. Items to note while doing or programming data reduction include:

a. All hours in which a precision check was performed must be manually or automatically averaged to exclude the period precision gas was sampled through the ambient port of the analyzer;

b. The hours in which a zero-span was performed by the operator may have to be edited manually or automatically to exclude the zero span period from the sample average. There must be 45 minutes of sample time to form a valid hourly average. Likewise, there must be 18 valid hours sampled in a 24-hour period beginning a 00:00 and ending at 23:59 to have the day count as a measurement day; and

c. Use the most recent valid SO2 calibration curve. Confirm that the zero baseline is correctly set.

6.3 ACCURACY/BIAS
The accuracy of the SO2 analyzer is assessed by auditing the performance of the analyzer as described in section 7. The audit values and the corresponding analyzer responses are reported. The percentage differences between these values are used to calculate accuracy as described in 40 CFR 58, Appendices A and B.

6.4 DATA REPORTING
It is incumbent upon the local and/or ADEC database manager to decide whether to include any flagged data in ADEC's air monitoring database in the case of SLAMS, SPM or NCore monitoring. If the monitoring is for PSD purposes, it is incumbent on the contractor conducting the site operation to report all of the original (raw) data and the finalized (flagged) data to the project director. It is strongly suggested that contractors and their subcontractors conducting PSD monitoring model their internal data reports2 on the monthly data report described below.

For NCore and SLAMS3, monthly (or at longest, quarterly4) data reports submitted to ADEC must include (but not be limited to) the following QA documentation:

1. All valid or flagged 5-minute, 1-hour, and 24-hour averages;

2. Minimum and maximum 5-minute, 1-hour, and 24-hour averages and other summary statistics;

---

2 PSD monitoring no longer requires submission of monitoring data to the state.
3 40 CFR 58.16(g) only specifies SLAMS monitoring but ADEC assumes that this will be applied to NCore sites also as NCore recommendations are codified into requirements in the near future (2012 or 2013).
4 40 CFR 58.16 (b) requires that ADEC load data by the end of the next quarter (i.e., 1st quarter data, from January, February and March, must be loaded to AQS by June 30th of that year).
3. Data which has exceeded the full scale range of the analyzer shall be flagged and explanation(s) provided;

4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;

5. Details of all maintenance activities and any changes to instrument and standard operating procedures;

6. Results of all pre-calibration checks and unadjusted zero/span checks;

7. Results of all analyzer calibrations;

8. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;

9. Results of all calibration flow checks; and

10. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks.

11. Comparison of different data collection methods used (i.e., DAS and instrument, or instrument and chart recorder).

SO₂ information and hourly averages from data acquisition systems may be polled and processed into AQS format by computer with the appropriate computer software. However, data reduced and reported in this manner must be verified against a 7% direct download from the analyzer. Differences between reported DAS collected/analyzer direct downloaded data must agree within 4% of the analyzer's calibrated full scale range (e.g., 0.02 ppm for a 0-0.5 ppm range or for NCORE 0.004 ppm for a 0-0.1 ppm range). If obvious differences are noted between the two collecting/reporting systems, all data back to the last acceptable Level 1 zero/span check must be examined by both systems. The reason(s) for the difference(s) must be investigated, corrected, and documented. The appropriate sections of collected data that do not meet data validation requirements must be invalidated. Other questionable data should be flagged and reported to the local agency data base manager in the case of SLAMS, SPM or NCORE monitoring or the primary contractor in the case of PSD monitoring.

6.5 DATA SUBMISSION
SO₂ data must be reported to the EPA’s Air Quality System (AQS) on a quarterly basis for NCORE and SLAM sites. SO₂ data from SPM sites may be reported to AQS. Quarterly reports must 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 three months following the end of the respective quarter. Independent projects performed in support of a permit application (i.e. PSD) are not required to submit quarterly reports to ADEC.
Quarterly data reports submitted to the ADEC must include (but not be limited to) the following QA documentation:

1. All valid or flagged 5-minute, 1-hour, and 24-hour averages (from all channels used to calculate and report SO$_2$ data);
2. Minimum and maximum 5-minute, 1-hour, and 24-hour averages and other summary statistics for all reported parameters;
3. Data which has exceeded the full scale range of the analyzer shall be flagged and exceedance(s) justified or nullified and explained;
4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;
5. Details of all maintenance activities and any changes to instrument and standard operating procedures;
6. Results of all pre-calibration checks and unadjusted zero/span checks;
7. Results of all analyzer calibrations;
8. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;
9. Results of all calibration flow checks; and
10. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks; and
11. The original raw data files.

7 PERFORMANCE AUDITS
The performance audit is the responsibility of the agency or group conducting the monitoring program. At any time, ADEC may choose to conduct oversight audits of any monitoring project for which the ADEC is designated the principal quality assurance organization (PQAO).

The performance audit is a quantitative comparison of results between the site SO$_2$ analyzer and an independent audit system brought to the site. It is an independent assessment of the accuracy of data generated by the analyzer. Independence is achieved by having the SO$_2$ audit performed by an auditor trained and experienced in the SO$_2$ method he/she will be auditing. The auditor must be independent of the site operator, and must use audit standards, reference materials, and equipment different from those used to calibrate the analyzer or perform QC checks.
Table 6: SO₂ audit criteria table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptance Range</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Performance Audit with test points in following ranges:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zero point</td>
<td>Mean absolute Δ ≤ 15%</td>
<td>SIAM/SPM: 1/6 months 25% network, each monitor 1/year</td>
</tr>
<tr>
<td></td>
<td>6% – 16% FS</td>
<td>Linear regression criteria:</td>
<td>PSO: Every monitor 1/quarter</td>
</tr>
<tr>
<td></td>
<td>30% - 40% FS</td>
<td>Slope ≤ 15%,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70% - 90% FS</td>
<td>Y intercept ≤ 3% FS, and</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.995 ≥ r² ≤ 1.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₂ converter efficiency ≥ 96 %</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Network</td>
<td>95% CI ≤ 20%</td>
<td>Annually</td>
</tr>
<tr>
<td>SO₂</td>
<td>Federal Audits (NPAP)</td>
<td>Mean Absolute % Δ ≤ 15</td>
<td>1/year at selected sites</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20% of sites audited</td>
</tr>
</tbody>
</table>

9 REFERENCES

“4.06 Method for the Determination of Sulfur Dioxide (SO₂) Monitoring by Ultraviolet Fluorescence,” SOP, State of Alaska, Department of Environmental Conservation Division of Air Quality, Environmental Conservation, Division of Air Quality, Air Monitoring and Quality Assurance (AMQA) program, [http://www.dec.state.ak.us/air/doc/Chapter%204.6%20SO2.PDF](http://www.dec.state.ak.us/air/doc/Chapter%204.6%20SO2.PDF), 1996.


APPENDIX A: SO₂ CRITICAL CRITERIA VALIDATION
The Gaseous validation template is to be used for the following purposes:

- To provide a "look-up" table of all the significant quality control criteria important for the proper implementation of the Federal Reference and/or Equivalent SO₂ methods (FRM/FEM), and
- As a tool for validating SO₂ data.

In order to accomplish both objectives the quality control criteria are organized into the following three classes/tables:

**I. CRITICAL CRITERIA TABLE**

Criteria deemed critical to maintaining the integrity of a sample or group of samples reside in the Critical Criteria Table. Observations that do not meet each and every criterion on the Critical Table should be invalidated unless there are compelling reasons and justifications for not doing so. Basically, the samples for which one or more of these criteria are not met are invalid unless proven otherwise. The cause for not operating in the acceptable range for each violated criteria must be investigated and minimized to reduce the likelihood that additional samples will be invalidated.

**II. OPERATIONAL EVALUATIONS TABLE**

Criteria important for maintaining and evaluating the quality of the data collection system reside in the Operational Evaluations Table. Violation of a criterion or a number of criteria may be cause for invalidation. The decision should consider other quality control information that may or may not indicate the data are acceptable for the parameter being controlled. Therefore, the sample or group of samples for which one or more of these criteria are not met is suspect unless other quality control information demonstrates otherwise. The reason for not meeting the criteria MUST be investigated, mitigated and/or justified.

**III. SYSTEMATIC ISSUES TABLE**

Criteria important for the correct interpretation of the data but do not usually impact the validity of a sample or group of samples reside in the Systematic Issues Table. For example, data quality objectives are included in this table. If data quality objectives are not met, this does not invalidate any samples but it may impact the error rate associated with the attainment/non-attainment decision.
# I. SO2 FRM/FEM CONTINUOUS ANALYZERS CRITICAL CRITERIA

**Samples Impacted:** S- single instrument hourly value, G1-Group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptable Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard Reporting Units</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td></td>
<td>ppb</td>
<td>Hourly Avg.</td>
<td>All</td>
<td>Part 50.17 &amp; 50.4</td>
<td>Vol 2 MS 2.3, 2.6, 2.9,</td>
<td></td>
</tr>
<tr>
<td><strong>Reporting Intervals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td></td>
<td>5-minute, 1-hour, 24-hour, Annual PSD &amp; SLAMS/NCore/SPM</td>
<td>Quarterly</td>
<td>All</td>
<td>Part 58.16</td>
<td>Vol II Sec. 14</td>
<td>18 AAC 50.010 Alaska Ambient Air</td>
</tr>
<tr>
<td><strong>Data Completeness</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>Valid data capture</td>
<td>≥75 % (≥90% for NCore station)</td>
<td>Hourly</td>
<td>S</td>
<td></td>
<td></td>
<td>Section 7</td>
</tr>
<tr>
<td>(PSD Quality Monitoring) Valid data capture</td>
<td></td>
<td>≥ 80% hourly data</td>
<td>Quarterly (4 consecutive quarters)</td>
<td>G1</td>
<td>Part 58 App A</td>
<td>EPA-450/4-87-007 May 1987</td>
<td>Section 7</td>
</tr>
<tr>
<td><strong>Equipment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>FRM/FEM Analyzer</td>
<td>0 – 500ppb and/or as specified in FRM/FEM designation (or approximately 0-100 ppb trace for NCore)</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td><a href="http://www.epa.gov/ttn/amtic/criteria.html">http://www.epa.gov/ttn/amtic/criteria.html</a></td>
<td>Section 11.5</td>
</tr>
<tr>
<td>SO2</td>
<td>SO2 Calibration/Audit System</td>
<td>Gas dilution of SO2 cyl gas with zero air or Dilution of SO2 permeation device</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td>Vol II, Section 12</td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>Sample Lines, probes and manifolds</td>
<td>Pyrex® (borosilicate) glass, FEP Teflon® or their equivalent</td>
<td>Purchase</td>
<td>All</td>
<td>Part 58 App. E Sec 9a</td>
<td>Vol II: Sec 7.2 &amp; Appendix F</td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>Pneumatic fittings</td>
<td>Teflon, stainless steel</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td>Vol II: Sec 7.2 &amp; Appendix F</td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>Gas regulator</td>
<td>Stainless steel, dual stage</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>Data Logger/Chart Recorder/Data Acquisition System (DAS)</td>
<td>Collection of continuous data</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>24-hr temp recorder</td>
<td>Record continuous temp data</td>
<td>Purchase</td>
<td>All</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# I. SO₂ FRM/FEM CONTINUOUS ANALYZERS CRITICAL CRITERIA

Samples Impacted: S-s single instrument hourly value, G1-Group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptable Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SO₂</strong></td>
<td>Multi-point Calibration</td>
<td>5 points including zero with span concentration between 80 – 90% of Analyzer Full Scale response All points within ± 2% of full-scale best fit straight line</td>
<td>Initial, quarterly thereafter</td>
<td>G1</td>
<td>Vol II: Part 1 Sec 12</td>
<td>Section 16</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Zero/Span QC Check</td>
<td>≤ ± 3% of full scale ≤ ± 15% Δ (NCore is &lt; ±10%)</td>
<td>1/2 weeks</td>
<td>G1</td>
<td>Vol. II, Sec. 12 &amp; Appendix D</td>
<td>MQO Table, Data Validation Tables Section 16</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>One Point QC Check</td>
<td>10 to 100 ppb</td>
<td>1/2 weeks</td>
<td>G1</td>
<td>Part 58 Appendix A 3.2.1</td>
<td>Vol. II Appendix D Section 16</td>
<td></td>
</tr>
</tbody>
</table>
## II. SO₂ FRM/FEM CONTINUOUS ANALYZERS OPERATIONAL EVALUATIONS

Samples Impacted: G1-group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network  
CL = confidence limit; SD= standard deviation; CV= coefficient of variation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptance Range</th>
<th>Frequency</th>
<th>Samples Impacted a</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Station Design/Siting Criteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Siting Criteria</td>
<td>Un-obstructed probe inlet</td>
<td>All</td>
<td>All</td>
<td>Part 58 App E</td>
<td>Vol II: Part 1 Sec 7.2 (with regards to Shelter temperature, see waiver note in Criteria column)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>See references for specific siting criteria</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sections 10 and 11</td>
</tr>
<tr>
<td>SO₂</td>
<td>Sample residence time for sample introduced through sample train</td>
<td>Required &lt; 20 seconds from sample inlet to back of analyzer (measured as first upscale response) &amp; recommended &lt; 10 seconds</td>
<td>All</td>
<td>G1</td>
<td></td>
<td>Part 53.20 (see waiver note in Criteria column)</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Shelter temperature [Note: EPA waiver received for Alaska lowering the acceptable low temperature limit from 20°C to 15°C]</td>
<td>15° – 30°C (hourly average) or instrument must be operated per manufacturer specifications</td>
<td>Daily</td>
<td>All</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shelter temperature control</td>
<td>± 2°C SD over 24 hours</td>
<td>Daily (hourly values)</td>
<td>G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Detection</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Noise/Lower Detection Limit (LDL)</td>
<td>5 ppb/ 10 ppb</td>
<td>LDL Check /year</td>
<td>All</td>
<td>Part 53.23</td>
<td>For NCore see EPA-454/R-05-0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>For NCore see EPA-454/R-05-0003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Calibration/QC Check &amp; Audit Standards</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Permeation Devices</td>
<td>NIST Traceable</td>
<td>Purchase</td>
<td>G, G1</td>
<td>Part 58 App A</td>
<td>Vol II: Appendix D &amp;/or for NCore see EPA-454/R-05-0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cylinder Gases</td>
<td>EPA Protocol/NIST Traceable, SO₂ in N₂</td>
<td>Purchase</td>
<td>G, G1</td>
<td></td>
<td></td>
<td>Section 16</td>
</tr>
<tr>
<td>SO₂</td>
<td>Zero Air</td>
<td>Free of any substance that might react and/or interfere with measured parameter Concentrations below parameter/method LDL</td>
<td>Purchase or generate Analyze 1/year</td>
<td>G, G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Flow standards (for calibrating flow meters and gas dilution/GPT calibrator, etc)</td>
<td>NIST Traceable ± 1% accuracy, certified over intended range of use</td>
<td>Initial calibration, 1/year thereafter</td>
<td>G, G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Gas Dilution/GPT (Diluent and pollutant flow controllers)</td>
<td>NIST Traceable ± 2% accuracy, certified over intended range of use against NIST Traceable Flow Standard See other criteria in EPA Reference</td>
<td>1/3 months</td>
<td>G, G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>QC Checks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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February 2012
### II. SO₂ FRM/FEM CONTINUOUS ANALYZERS OPERATIONAL EVALUATIONS

**Samples Impacted:** G1-group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network  
CL = confidence limit; SD= standard deviation; CV= coefficient of variation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptance Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Shelter Temp Check Record status of check</td>
<td>15° – 30°C (hourly average) or Instrument must be operated per manufacturer specifications, and ± 2°C SD</td>
<td>1/2 weeks</td>
<td>G1</td>
<td></td>
<td>Vol II: Part 1 Section 7</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Sample Train inspection</td>
<td>Free of dirt/debris/moisture</td>
<td>1/2 weeks</td>
<td>G1</td>
<td></td>
<td>Vol II: Part 1 Section 7</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Analyzer sample flow rates</td>
<td>Within analyzer specs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Data logger hourly values verification against Analyzer stored data or chart recorder hourly values</td>
<td>Within 1 significant digit</td>
<td>7% all data</td>
<td>G1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Monitor Maintenance**

<table>
<thead>
<tr>
<th>SO₂</th>
<th>Scheduled maintenance activities</th>
<th>Per manufacturer’s recommendations</th>
<th>Per manufacturer’s recommendations</th>
<th>G1</th>
</tr>
</thead>
</table>

**Precision (using 1 point QC Checks)**

| SO₂ | 90% Confidence Limit of coefficient of variation | 95% CL. CV ≤ ±15% (NCore , CV ≤ ±10%) | Annually and as appropriate for design value estimates | G, G1 | 40 CFR Part 58, App A section 3.2.1 | | |

**Bias/Accuracy (using 1 point QC Checks)**

[http://www.epa.gov/ttn/amtic/par lists.html](http://www.epa.gov/ttn/amtic/par lists.html) & for NCore see EPA-454/R-05-0003

Guideline on the Meaning and The Use of Precision and Bias Data Required by 40 CFR Part 58 App A Data Assessment Statistical Calculator (DASC) – The software to assist those in calculating the new precision and bias statistics – MS Excel File Type

Section 7 Table A7  
Section 14 Table B11
### II. SO₂ FRM/FEM CONTINUOUS ANALYZERS OPERATIONAL EVALUATIONS

Samples Impacted: G1-group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network  
CL = confidence limit; SD= standard deviation; CV= coefficient of variation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptance Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>95% confidence Limit of Absolute Bias Estimate</td>
<td>95% CL CV ≤± 15% (For an NCore station CV&lt;±10%)</td>
<td>Annually and as appropriate for design value estimates</td>
<td>G, G1</td>
<td>Part 58 App A section 3.2.1</td>
<td><img src="http://www.epa.gov/ttn/amtic/parslist.html" alt="Link" /> &amp; for NCore EPA-454/R-05-0003 Guideline on the Meaning and The Use of Precision and Bias Data Required by 40 CFR Part 58 App A Data Assessment Statistical Calculator (DASC) – The software to assist those in calculating the new precision and bias statistics – MS Excel File Type)</td>
<td></td>
</tr>
</tbody>
</table>

### Annual Performance Evaluation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptance Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
</table>
| SO₂       | Performance Audit with test points in following ranges:  
- Zero point  
- 6% – 16% FS  
- 30% - 40% FS  
- 70% - 90% FS | Single Analyzer Audited  
Mean absolute Δ ≤± 15%,  
Linear regression criteria:  
Slope ≤ ±15%,  
Y intercept ≤±3% FS, and  
0.995 ≥ r² ≤ 1.000  
NO₂ converter efficiency ≥96% | NCore/SLAMS/SPM  
1/6 months 25% network, each monitor 1/yea  
PSD  
Every monitor 1/quarter | G1 | Part 58 App A section 3.2.2 |
| SO₂ Network | 95% CI ≤± 20% | Annually |
| SO₂ Federal Audits (NPAP) | Mean Absolute % Δ ≤± 15  
1/year at selected sites  
20% of sites audited | G, G1 | Part 58 App A Sec 2.4 | Vol II: App. D |

CL = confidence limit; SD= standard deviation; CV= coefficient of variation
### III. SO₂ FRM/FEM CONTINUOUS ANALYZERS SYSTEMATIC ISSUES

Samples impacted: G1-group of hourly values from 1 instrument, G-group of hourly values from multiple instruments in a network

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Acceptable Range</th>
<th>Frequency</th>
<th>Samples Impacted</th>
<th>40 CFR Reference</th>
<th>EPA QA Guidance/Manual</th>
<th>ADEC AM&amp;QA QAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Completeness</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td>≥ 75% NCore, SLAMS, SPM</td>
<td>quarterly</td>
<td>G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>≥ 80% PSD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calibration/Verification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clock/timer Verification</td>
<td></td>
<td>≤ ± 1 minute.</td>
<td>1/4 weeks</td>
<td>G1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Technical Systems Audit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Review of entire field/lab &amp; data reporting process</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Vol II: Appendix D</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCore/SLAMS/SPM networks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PSD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Within 1 month of start-up and annually thereafter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G, G1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX B: NCORE RECOMENDATION TABLES
### TABLE B1: NCORE ANALYZER FEATURES

**NCore Analyzer Features: Sulfur Dioxide**

#### Recommended features for high sensitivity SO2 measurements

<table>
<thead>
<tr>
<th>Feature</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>High intensity pulsed UV light source</td>
<td>To provide greater sensitivity</td>
</tr>
<tr>
<td>Multiple reflective optical filters</td>
<td>To exclude all light at wavelengths that may cause interference</td>
</tr>
<tr>
<td>Optical filtering</td>
<td>To maximize rejection of NO molecule fluorescence</td>
</tr>
</tbody>
</table>

#### Calibration equipment for high sensitivity SO2 measurements

<table>
<thead>
<tr>
<th>Feature</th>
<th>EPA requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC calibrator</td>
<td>+/-2% accuracy and flow rates of MFC channels calibrated using NIST traceable flow standard</td>
</tr>
<tr>
<td>Calibration standards</td>
<td>NIST-traceable standards</td>
</tr>
<tr>
<td>Zero air</td>
<td>&lt; 0.05 ppb</td>
</tr>
<tr>
<td>Primary SO2 standard</td>
<td>Accuracy ≤2% &amp; certificate of calibration including uncertainty, concentration &amp; expiration date; NIST-traceable standards recommended but not required</td>
</tr>
</tbody>
</table>
### TABLE B2: NCORE PERFORMANCE CRITERIA

**NCore Performance Criteria: Sulfur Dioxide**

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Acceptable Range</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision</td>
<td>95% probability limit for precision of +/- or less</td>
<td>1/2 weeks</td>
</tr>
<tr>
<td>Precision level&lt;sup&gt;1&lt;/sup&gt;</td>
<td>5 - 10 ppb</td>
<td>1/2 weeks</td>
</tr>
<tr>
<td>Mid point span&lt;sup&gt;1&lt;/sup&gt;</td>
<td>50 ppb</td>
<td></td>
</tr>
<tr>
<td>Level 1 span (action tolerance)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>90 ppb</td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>Upper bound of average bias &lt; 10%</td>
<td>yearly</td>
</tr>
<tr>
<td>Completeness</td>
<td>90%</td>
<td>daily, quarterly, annually</td>
</tr>
<tr>
<td>MDL</td>
<td>Standard deviation of seven 20 to 25 1-minute measurement of concentration (1 to 5 times the estimated MDL) &lt; 0.30 over and averaging time of &lt; 5 minutes</td>
<td>7 times over 5 to 14 days</td>
</tr>
<tr>
<td>LDL</td>
<td>&lt; 0.20 ppb over an averaging time of &lt; 5 minutes</td>
<td>--</td>
</tr>
<tr>
<td>Linear Range</td>
<td>0.20 to 100 ppb</td>
<td>--</td>
</tr>
<tr>
<td>Zero Drift</td>
<td>&lt; +/- 0.20 ppb</td>
<td>12- to 24-hour</td>
</tr>
<tr>
<td>Span Drift</td>
<td>&lt; +/- 1%</td>
<td>24-hour</td>
</tr>
<tr>
<td>NO rejection ratio&lt;sup&gt;2&lt;/sup&gt;</td>
<td>&gt; 1:100</td>
<td>--</td>
</tr>
<tr>
<td>Calibration</td>
<td>Minimum 4 point (3 points and zero)</td>
<td>Annually or more often as needed</td>
</tr>
<tr>
<td>Level 1 Zero/Span checks</td>
<td>&lt; +/- 10% drift &lt; +/- 0.5 % of full scale; 90 ppb</td>
<td>1/2 weeks</td>
</tr>
<tr>
<td>Cylinder concentration</td>
<td>10-15 ppm</td>
<td>--</td>
</tr>
</tbody>
</table>

**Sampling Requirements**

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Acceptable Range</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manifold inlet</td>
<td>3 to 15 m above ground level and 1 meter vertical and horizontal from structures</td>
<td>--</td>
</tr>
<tr>
<td>Probe position</td>
<td>270° unrestricted airflow (including the dominant wind direction)</td>
<td>--</td>
</tr>
<tr>
<td>Probe separation</td>
<td>&gt;20 meters from dripline of trees or structures and twice the distance from obstacle(s) as the height of the obstacle(s)</td>
<td>--</td>
</tr>
<tr>
<td>Shelter temperature</td>
<td>15-30°C and Δ T &lt; 5°C in 24-hours</td>
<td>daily</td>
</tr>
<tr>
<td>Sample inlet or manifold</td>
<td>FEP or PTFE tubing (1/4 in OD suggested) with a 1 micron Teflon® filter&lt;sup&gt;3&lt;/sup&gt; or glass manifold (1 inch suggested) if supplying air to multiple analyzers</td>
<td>Weekly (filter change&lt;sup&gt;3&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

<sup>1</sup> Suggested not required  
<sup>2</sup> if opting to used FEP or PTFE tubing with a 1-micron filter  
<sup>3</sup> if using a 1-micron filter