Standard Operating Procedures for Sulfur Dioxide (SO_2) Monitoring by Ultraviolet Fluorescence

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PROCEDURE PLAN APPROVAL

Title: Standard Operating Procedures for Sulfur Dioxide (SO_2) 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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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

ppb	part per billion
ppm	parts per million
PQAO	principal quality assurance organization
QA	quality assurance
QC	quality control
PSD	prevention of significant deterioration
sccm	standard cubic centimeter
SLAMS	state and local air monitoring station
SPMS	special purpose monitoring station
SO_2	sulfur dioxide
SOP	standard operating procedure
TAD	technical assistance document
VOC	volatile organic compound
URL	upper range limit
UV	ultraviolet

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 SO_2 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 (SO_2) pollution is a human health and environmental concern. The EPA established a 1-hour primary National Ambient Air Quality Standard (NAAQS) for SO_2 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 SO_2 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 SO_2 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 SO_2 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 (ie., 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 SO_2 should be designed to:

- determine 1-hour, 3-hour, 24-hour (arithmetic average), and annual (arithmetic average) concentrations of SO_2 ambient air for comparison to primary and/or secondary SO_2 NAAQS,

- collect 5-minute data for NCore[1] and SLAMS reporting requirements (40 CFR 58.16) and

- determine representative levels of SO_2 in populated areas with regards to public health protection and public education

1.3 THEORY OF OPERATION: UV FLUORESCENCE METHOD

The SO_2 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. SO_2 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: $$SO_2 + h\nu_1 \rightarrow SO_2^* \rightarrow SO_2 + h\nu_2$$

Where:

$h\nu_1$ = incidence light

$h\nu_2$ = fluoresced light

SO_2^* = SO_2 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 SO_2 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 SO_2-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 SO_2 in the cylinder gas high enough

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[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.

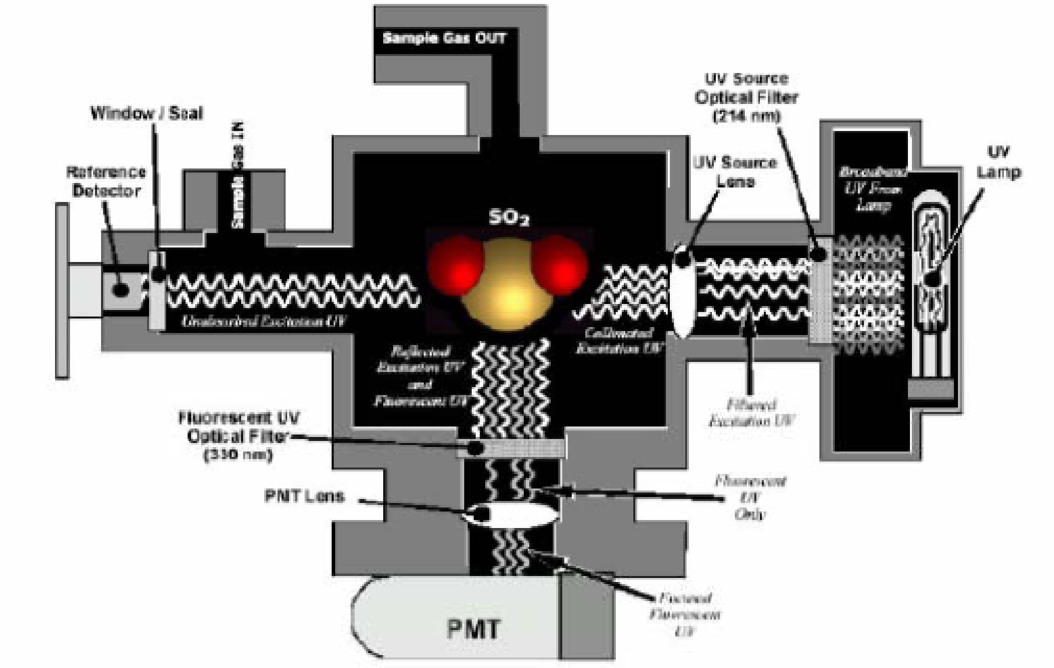


Figure 1: Schematic illustration of the optical chamber of a precursor SO_2 analyzer. (taken from TAD for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network, version 4)

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_2S.

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 SO_2 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 SO_2 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

Scale	Distance from trees to probe or inlet	Height (meters)	Distance from Supporting Structures (meters)		Other Spatial Criteria
			Vertical	Horizontal	
Middle, Neighborhood, Regional	> 10	2 - 15	> 1	> 1	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 SO_2. 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 SO_2 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 ACQUSITION 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 SO_2 cylinder gas or SO_2 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 SO_2 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 SO_2 working standard against NIST-SRM, CRM, or NTRM are found in section 3.3.4, Certification of SO_2 Working Standards.

3.1.1 ZERO AIR

Dry zero air, verified to be free of contaminants that would cause detectable responses in the SO_2 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 (CO_2), approximately 380 ppm CO_2, is maintained in any zero air source used so as to mimic ambient atmospheric air.

3.1.2 SULFUR DIOXIDE (SO_2) CYLINDER GAS

SO_2 Concentration Standard--SO_2 cylinder gas must contain a known concentration of SO_2 in Nitrogen (N_2). SO_2 cylinder calibration gases must be certified traceable to a NIST-SRM, CRM, or NTRM cylinder gas.

3.1.3 SULFUR DIOXIDE (SO_2) PERMEATION DEVICES

SO_2 Concentration Standard--SO_2 permeation device(s) suitable for generating SO_2 concentrations at the required flow rates over the required concentration range. The SO_2 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 SO_2 Gas Cylinder, or

Method B: Calibration by Dynamic Dilution of an SO_2 Permeation Tube.

NOTE: Analyzers used for monitoring SO_2 in the ambient air must be US EPA-designated reference or equivalent method SO_2 analyzers.

3.2.1 CALIBRATION FREQUENCY

To ensure accurate measurements of SO_2 concentrations, calibrate the analyzer at the time of installation. An activity matrix for calibration procedures is presented in table 2. The SO_2 analyzer will require a recalibration whenever one of the following conditions occurs:

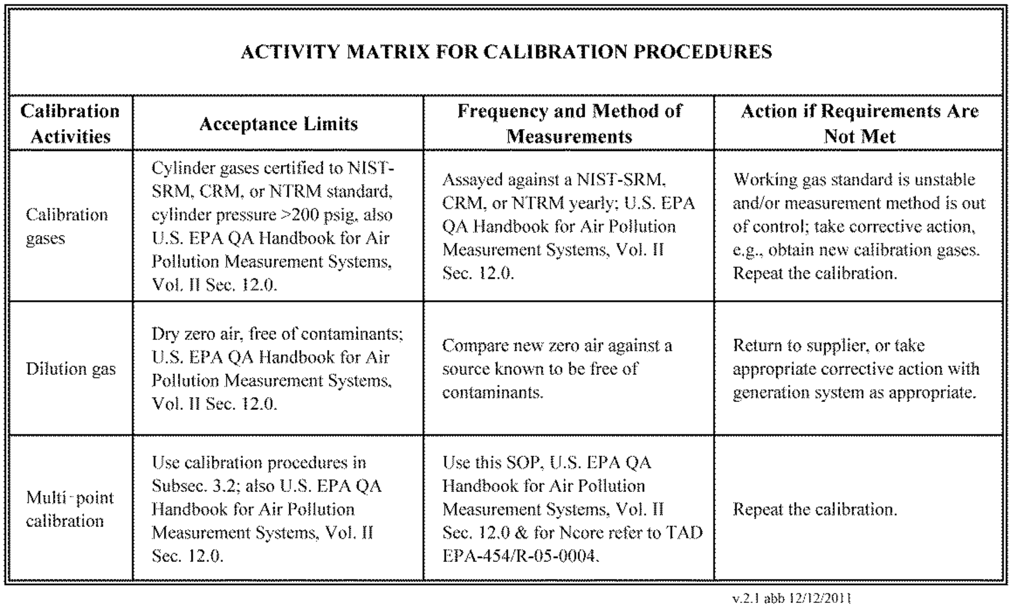
- six months has elapsed since the last calibration;
- major disassembly or replacement of any major component(s) of the SO_2 analyzer and monitoring system;
- the monitor fails a performance audit;
- a level 1 zero/span SO_2 gas check is not within tolerance (15 %) of the corresponding zero/span gas 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 SO_2 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.

Table 2: Activity matrix for calibration procedures



ACTIVITY MATRIX FOR CALIBRATION PROCEDURES

Calibration Activities	Acceptance Limits	Frequency and Method of Measurements	Action if Requirements Are Not Met
Calibration gases	Cylinder gases certified to NIST-SRM, CRM, or NTRM standard, cylinder pressure >200 psig, also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Vol. II Sec. 12.0.	Assayed against a NIST-SRM, CRM, or NTRM yearly; U.S. EPA QA Handbook for Air Pollution Measurement Systems, Vol. II Sec. 12.0.	Working gas standard is unstable and/or measurement method is out of control; take corrective action, e.g., obtain new calibration gases. Repeat the calibration.
Dilution gas	Dry zero air, free of contaminants; U.S. EPA QA Handbook for Air Pollution Measurement Systems, Vol. II Sec. 12.0.	Compare new zero air against a source known to be free of contaminants.	Return to supplier, or take appropriate corrective action with generation system as appropriate.
Multi-point calibration	Use calibration procedures in Subsec. 3.2; also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Vol. II Sec. 12.0.	Use this SOP, U.S. EPA QA Handbook for Air Pollution Measurement Systems, Vol. II Sec. 12.0 & for Ncore refer to TAD EPA-454/R-05-0004.	Repeat the calibration.

v.2.1 abb 12/12/2011

3.2.2 CALIBRATION METHOD A: Dynamic Dilution of a High Concentration SO_2 Gas Cylinder

In this method, a high concentration certified SO_2 in N_2 cylinder is diluted with dry zero air to generate incremental concentrations of SO_2 to calibrate the analyzer's SO_2 responses.

Before using the assembled and/or purchased systems for SO_2 calibrations, your system must:

1. Use an SO_2 standard gas traceable to a NIST-SRM, CRM, or NTRM. This high concentration SO_2 gas cylinder (preferably in the range of 30-50 ppm and the remaining balance N_2) is the primary sulfur dioxide (SO_2) calibration source from which all subsequent SO_2 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 SO_2 concentration that is approximately 80% of the upper range limit (URL) of the SO_2 range to be calibrated;

4. Have a gas calibration system with a mixing chamber capable of diluting the output of the SO_2 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).

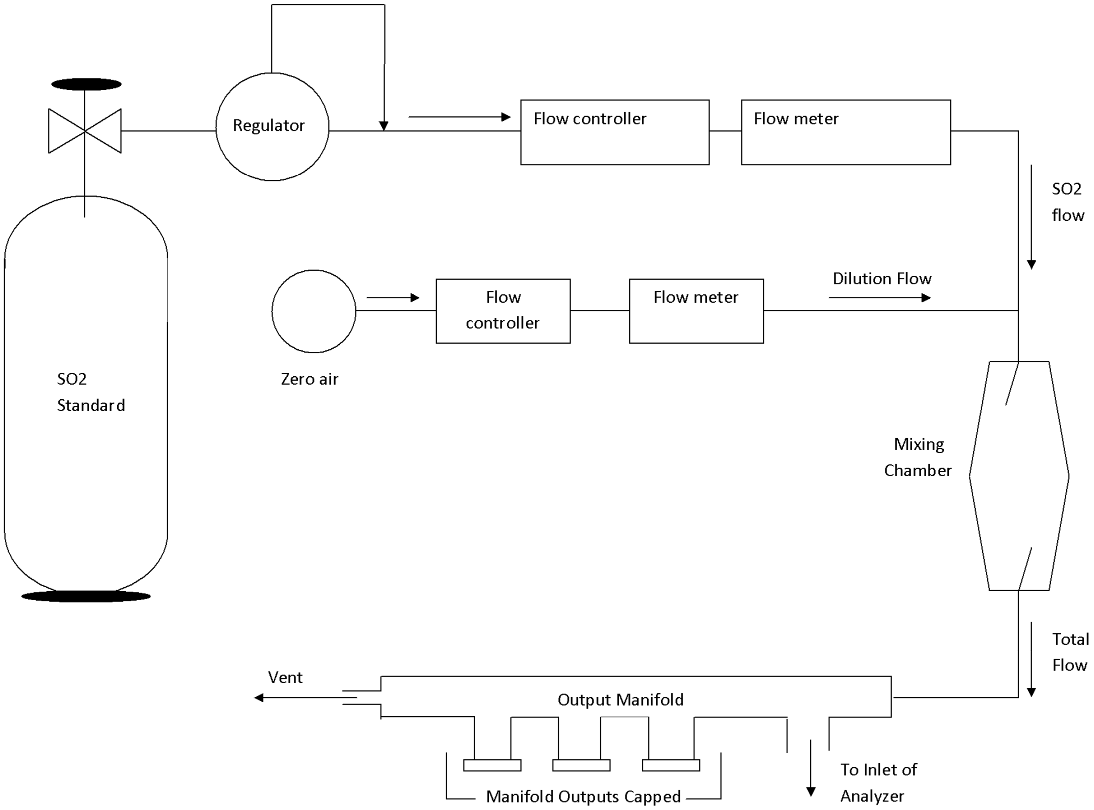


Figure 2: Schematic diagram of a typical gas dilution configuration for SO_2 calibration.

Precautions must be taken to remove O_2 from the SO_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 SO_2 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: i.e., T_{std} = 298^oK (25^oC, 77^oF) and P_{std} = 760mm 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) SO_2 cylinder gas flow (F_{SO2}) by solving equation 2 for F_{SO2}. Adjust F_{SO2} to generate an SO_2 concentration of approximately 80% of the URL of the analyzer. Record F_{SO2} on the 80% URL line (figure 4) or make a note in the DAS and/or logbook as necessary.

Equation 2: $FSO_2 = (FD \times [SO_2]out)/([SO_2]std - [SO_2]out)$

where: $[SO_2]_{out}$ = 80% URL SO_2 gas concentration

$[SO_2]_{std}$ = SO_2 cylinder gas concentration

F_{SO2} = flow rate of SO_2 cylinder gas, sccm

F_D = flow rate of dilution air, sccm;

13. Calculate the exact SO_2 concentration $[SO_2]_{OUT}$ by solving equation 3.

Equation 3: $[SO_2]_{OUT} = F_{SO2} \times [SO_2]_{STD}/(F_{SO2}+F_D)$

Record the $[SO_2]_{OUT}$ 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 SO_2 response has stabilized. Adjust span response for the analyzer SO_2 channel for a balanced output equal to the SO_2 calibration gas.

    If substantial adjustment of the SO_2 span control is necessary, recheck the zero and span adjustment in steps 11 and 14. Record the analyzer's SO_2 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) , SO_2 gas concentrations by decreasing F_{SO2} or increasing F_D. Use equation 1 to calculate F_{SO2} flows Then measure SO_2 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 ≥ 0.995 for the calibration to pass EPA and ADEC criteria.

SO_2 CALIBRATION DATA FORM BY GAS DILUTION (Method A)

1 Station ______________________________

2 Calibrated by ____________________ Date ____________________

3 Analyzer Mfr. ____________________ 4 Calibrator Mfr. ____________________

Model ____________________ Model ____________________

S/N ____________________ S/N ____________________

6 SO_2 Reference Standard ______________________________

Supplier ____________________ Cylinder Number ____________________

Concentration $[SO_2]_{Std}$ ____________________ Cylinder Pressure

Reference to NIST-SRM, CRM, or NTRM ______________________________

By ____________________ Date of Reference ____________________

6 Zero Air Make/Model # ____________________ Serial Number ____________________

7 Flow Rate Calibrator ____________________ Reference Standard

Make/Model # ____________________ Serial Number ____________________

8 Zero Knob Setting ____________________ Span Knob Setting ____________________

9 Temperature ____________________ Barometric Pressure ____________________

Equations Used for SO_2 Calibration

Equation 2: $F_{SO2} = (F_D \times [SO_2]_{OUT})/([SO_2]_{STD} - [SO_2]_{OUT})$

where: F_{SO2} = flow rate of SO_2 standard, sccm

F_D = flow rate of zero air, sccm

Equation 1: $[SO_2]_{OUT} = F_{SO2} \times [SO_2]_{STD}/(F_{SO2} + F_D)$

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)

Calibrations Points SO2	1 F_D, sccm	2 F_{SO2}, sccm	3 $[SO_2]_{OUT}$, ppm	4 SO_2 DAS reading	5 SO_2 recorder reading
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

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Figure 3: Example of data record format for calibration by gas dilution.

3.2.3 CALIBRATION METHOD B: Dynamic Dilution of an SO_2 Permeation Tube

The principle: In a permeation device, an easily liquefiable gas such as SO_2 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 SO_2 analyzer's responses are calibrated with accurately known concentrations of SO_2 that are dynamically produced by diluting the effusion from an SO_2 permeation device, with various flows of clean air to obtain a calibration for SO_2. The SO_2 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 SO_2 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 SO_2 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 SO_2 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 cm^3/min) that is maintained at the same temperature as the permeation device flushes the SO_2 out of the device housing into a mixing chamber where the SO_2 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 SO_2 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 SO_2 permeation device is to be used as the reference standard for calibration, the permeation rate of the device must be traceable to a NIST SO_2 in N_2 cylinder gas standard SRM or SO_2 permeation device SRM. Procedures for certifying the reference standard against NIST-traceable SO_2 in N_2 or SO_2 permeation standards and for inter-comparing SO_2 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 SO_2 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 SO_2 to form an acid mist, thus changing the SO_2 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.

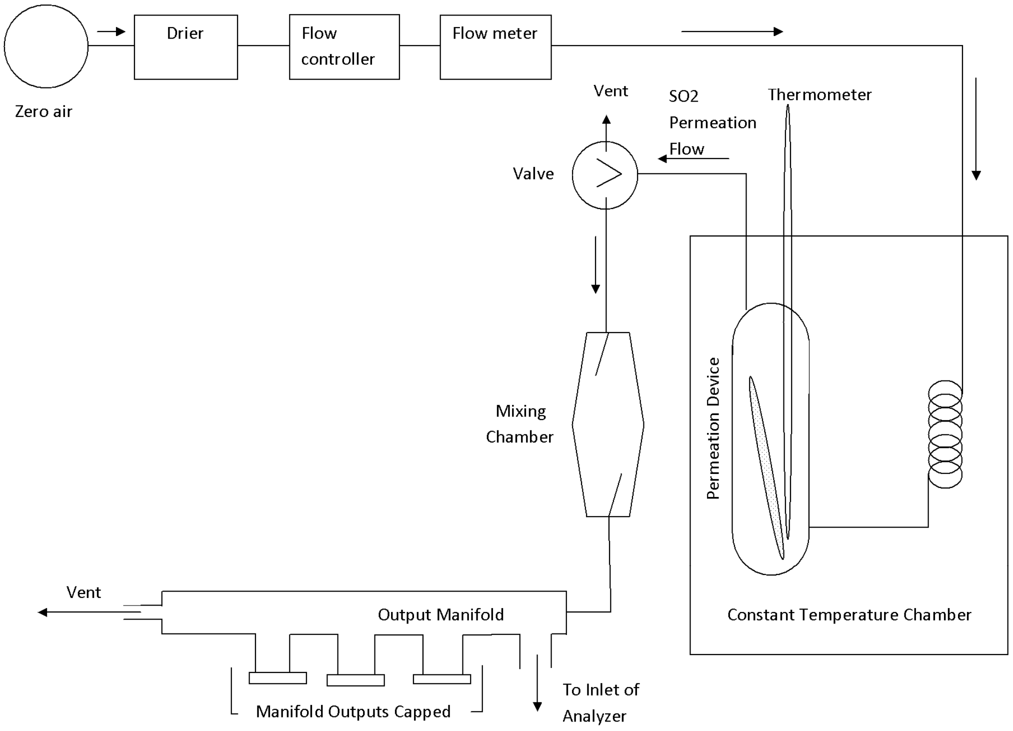


Figure 4: Schematic diagram of a typical dynamic dilution permeation device calibration system.

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: $$[SO_2]_{out} = (P \times K_m)/(F_P + F_D)$$

where: $[SO_2]_{out}$ = diluted SO_2 concentration supplied to the analyzer

P = permeation rate, µg/min

K_m = molar constant for SO_2 = 0.382 (@ 30°C and 760 mmHg)

F_P = air flow across permeation device, sccm

F_D = diluent air flowrate, sccm

Record the 80% URL value in column 3, $[SO_2]_{OUT}$ or in DAS and logbook.

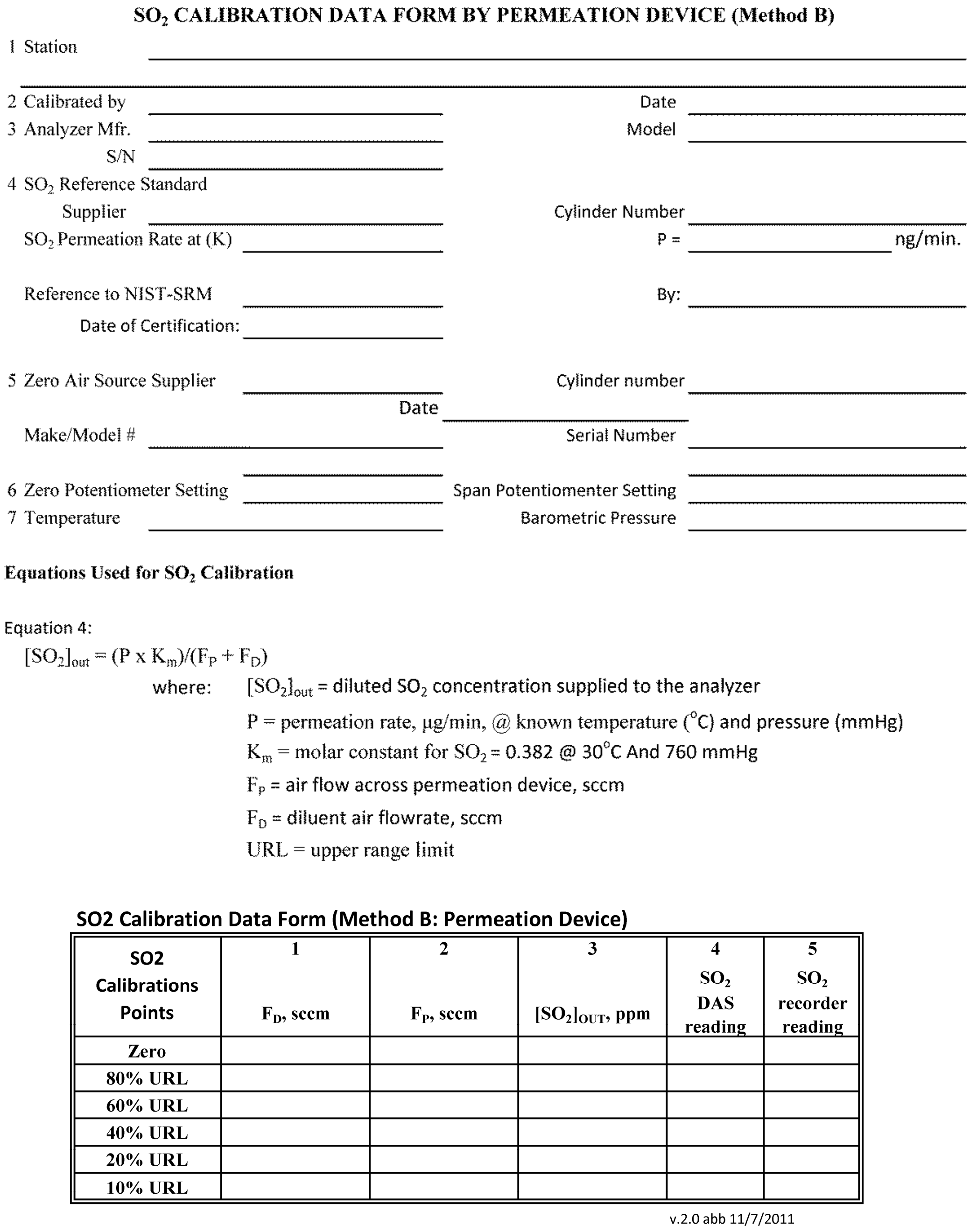
14. Allow the analyzer to sample this 80% URL SO_2 concentration until a stable response is obtained (a response that does not vary by more than ±1% of full scale over a 5-minute time period); then adjust the analyzer's span control to read actual $[SO_2]$ concentration.

    Sample this 80% URL SO_2 concentration until the analyzer's responses have stabilized. Record these values in columns 4 and 5 or in DAS and logbook.

    15. Adjust F_D to generate at least three more evenly-spaced SO_2 gas concentrations. Use equation 4 to calculate F_D flows for these concentrations. Measure F_P and F_D using a NIST-traceable intermediate primary standard. Measure and record the F_P and F_D air stream (in-line) temperature and pressure. Correct the actual measured flows to STP conditions. Record the analyzer's measured $[SO_2]$ response for each concentration. Calculate the SO_2 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 $[SO_2]$ responses against the corresponding SO_2 calibration gas concentrations. Calculate the $[SO_2]$ 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 $\geq$0.995. If not, correct the problem and recalibrate the analyzer. Record each iteration until the correlation coefficient meets required level.



SO_2 CALIBRATION DATA FORM BY PERMEATION DEVICE (Method B)

1 Station ______________________________

2 Calibrated by ____________ Date ____________

3 Analyzer Mfr. ____________ Model ____________

S/N ____________

4 SO_2 Reference Standard

Supplier ____________ Cylinder Number ____________

SO_2 Permeation Rate at (K) ____________ P = ____________ ng/min.

Reference to NIST-SRM ____________ By: ____________

Date of Certification: ____________

5 Zero Air Source Supplier ____________ Cylinder number ____________

Date ____________

Make/Model # ____________ Serial Number ____________

6 Zero Potentiometer Setting ____________ Span Potentiomenter Setting ____________

7 Temperature ____________ Barometric Pressure ____________

Equations Used for SO_2 Calibration

Equation 4:

$[SO_2]_{out} = (P \times K_m)/(F_P + F_D)$

where: $[SO_2]_{out}$ = diluted SO_2 concentration supplied to the analyzer

P = permeation rate, µg/min, @ known temperature (°C) and pressure (mmHg)

K_m = molar constant for SO_2 = 0.382 @ 30°C And 760 mmHg

F_P = air flow across permeation device, sccm

F_D = diluent air flowrate, sccm

URL = upper range limit

SO2 Calibration Data Form (Method B: Permeation Device)

SO2 Calibrations Points	1	2	3	4	5
	F_D, sccm	F_P, sccm	$[SO_2]_{OUT}$, ppm	SO_2 DAS reading	SO_2 recorder reading
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

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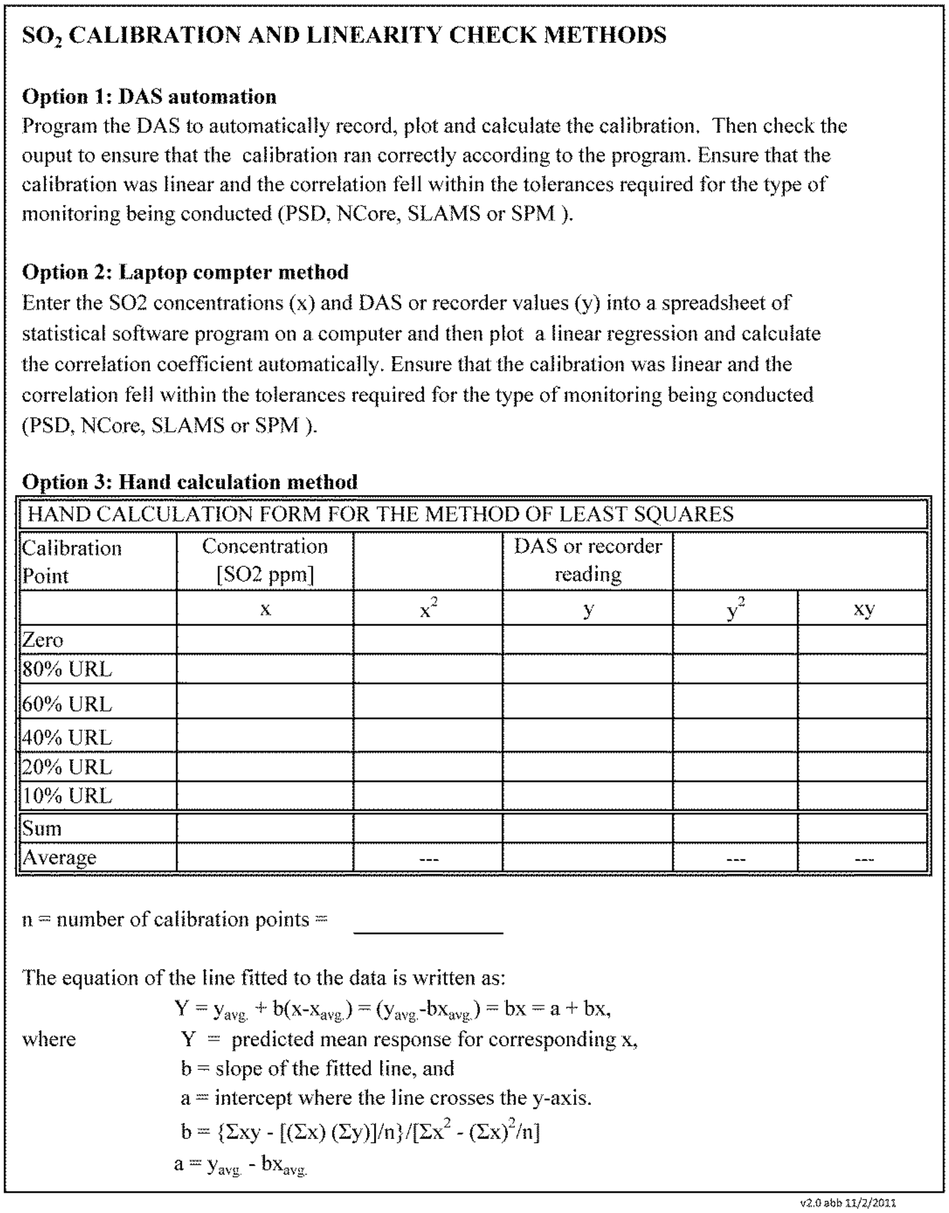
Figure 5: Example data collection format for calibration by permeation device.

3.3.4 SO_2 WORKING STANDARDS

NIST-SRM or CRM SO_2 in N_2 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 SO_2 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.



SO_2 CALIBRATION AND LINEARITY CHECK METHODS

Option 1: DAS automation

Program the DAS to automatically record, plot and calculate the calibration. Then check the ouput 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 compter 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

HAND CALCULATION FORM FOR THE METHOD OF LEAST SQUARES

Calibration Point	Concentration [SO2 ppm]		DAS or recorder reading		
	x	x^2	y	y^2	xy
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					
Sum					
Average		---		---	---

n = number of calibration points = ______________

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

$$Y = y_{avg.} + b(x-x_{avg.}) = (y_{avg.}-bx_{avg.}) = bx = a + bx,$$

where Y = predicted mean response for corresponding x,

b = slope of the fitted line, and

a = intercept where the line crosses the y-axis.

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

$$a = y_{avg.} - bx_{avg.}$$

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Figure 6: SO_2 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 SO_2 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

Shelter/Analyzer Inspection Checklist	
Date	Time onsite
Personnel inspecting	Current shelter temperature
Range of shelter temperature since last inspection	
Condition of particluate filter(s)	
Check diagnostics	Check for errors
Correct settings of:	flow meters regulators temperature control indicators
Verification that analyzer is in sample mode*	
Verification that zero and span potentiometers are locked and set at the proper values	
Verification that DAS is funtioning correctly	
Comments	Time offsite

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

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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 SO_2 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 SO_2 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 (SO_2 Zero/Span Drift Control Limits) summarizes the required quality control actions for the use of zero and span checks to determine SO_2 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 SO_2 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 SO_2 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 SO_2 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

OPERATIONAL ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
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	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.

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SO_2 ANALYZER ZERO/SPAN DRIFT CALIBRATION LIMITS

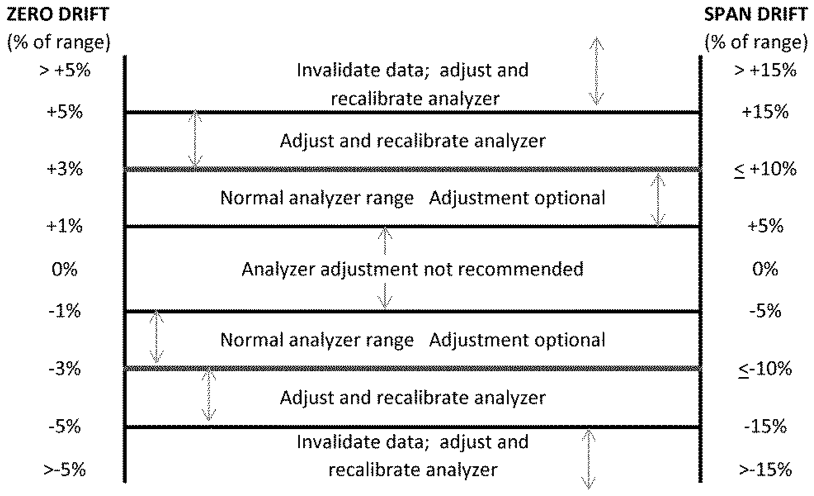

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Figure 7: SO_2 analyzer zero/span drift calibration limits

SO_2 ANALYZER OPERATIONAL CHECKLIST

Site ID ______________ Date ______________
Site Location ______________ Technician ______________
Site Address ______________

1. Inspect thermograph for temperature variations greater than +2°C (4°F). Identify time frame 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: ______________

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

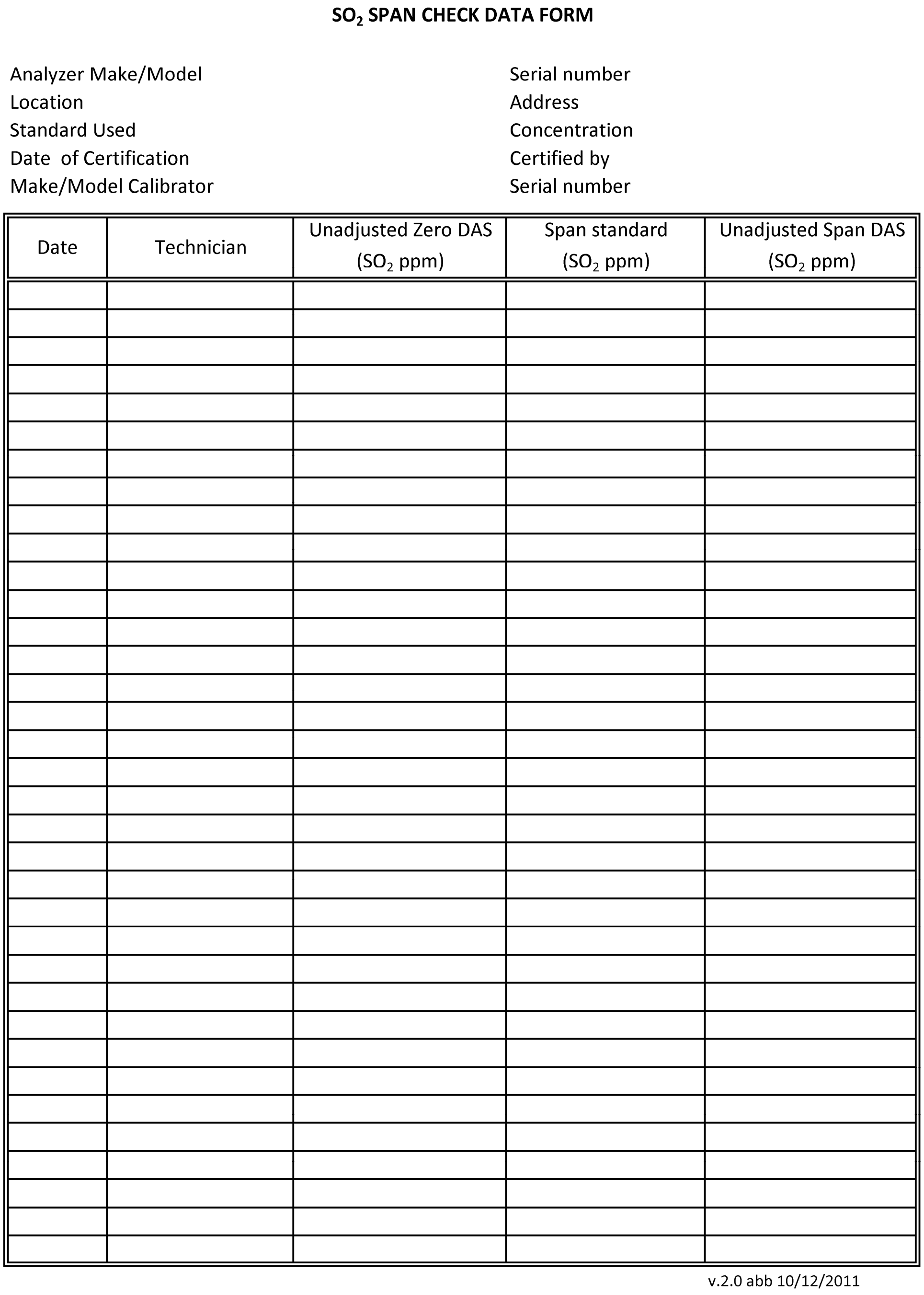
7. Is the unadjusted zero within tolerance? ______________
Comments: ______________

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 SO_2 analyzer operation sheet.



SO_2 SPAN CHECK DATA FORM

Analyzer Make/Model
Serial number
Location
Address
Standard Used
Concentration
Date of Certification
Certified by
Make/Model Calibrator
Serial number

Date	Technician	Unadjusted Zero DAS (SO_2 ppm)	Span standard (SO_2 ppm)	Unadjusted Span DAS (SO_2 ppm)

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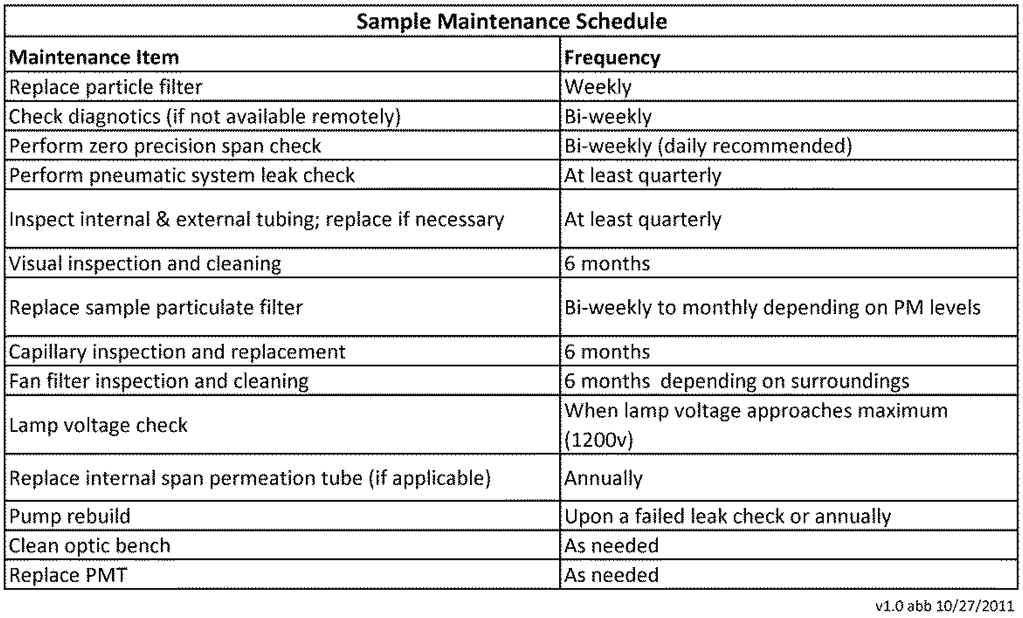
Figure 9: Example SO_2 span check data form.

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



Sample Maintenance Schedule

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

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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 SO_2 calibration curve. Confirm that the zero baseline is correctly set.

6.3 ACCURACY/BIAS

The accuracy of the SO_2 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 reports[2] on the monthly data report described below.

For NCore and SLAMS[3], monthly (or at longest, quarterly[4]) 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;

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[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).

SO_2 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 0-0.5ppm range or for NCore 0.004ppm 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

SO_2 data must be reported to the EPA's Air Quality System (AQS) on a quarterly basis for NCore and SLAM sites. SO_2 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:

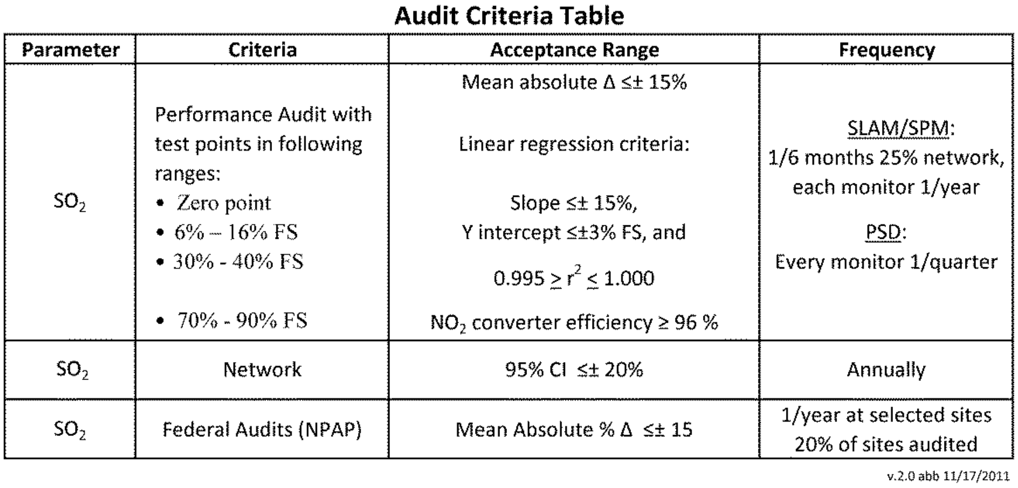
1. All valid or flagged 5-minute, 1-hour, and 24-hour averages (from all channels used to calculate and report SO_2 data);
2. Minimum and maximum 5-minute, 1-hour, and 24-hour averages and other summary statistics for all reported parameters;
3. Data which has exceeded the full scale range of the analyzer 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: SO_2 audit criteria table.



Audit Criteria Table

Parameter	Criteria	Acceptance Range	Frequency
SO_2	Performance Audit with test points in following ranges: • Zero point • 6% – 16% FS • 30% - 40% FS • 70% - 90% FS	Mean absolute Δ ≤± 15% Linear regression criteria: Slope ≤± 15%, Y intercept ≤±3% FS, and $0.995 \geq r^2 \leq 1.000$ NO_2 converter efficiency ≥ 96 %	SLAM/SPM: 1/6 months 25% network, each monitor 1/year PSD: Every monitor 1/quarter
SO_2	Network	95% CI ≤± 20%	Annually
SO_2	Federal Audits (NPAP)	Mean Absolute % Δ ≤± 15	1/year at selected sites 20% of sites audited

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9 REFERENCES

"4.06 Method for the Determination of Sulfur Dioxide (SO_2) 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, 1996.

"AQS Technical Note-NAAQS Reporting Issues for NO2 and SO2 NCore Reporting Issues for NOy and trace-level gases," U.S. EPA, Office of Air Quality Planning and Standards, Research Park Triangle, NC, http://www.epa.gov/ttnamti1/files/NAAQSReportingUpdate11032010.pdf, November 2010.

"Quality Assurance Handbook for Air Pollution Measurements," Volume II, APA-454/R-98-004, U.S. EPA, Research Triangle Park, NC 27711, August 1998.

"Quality Assurance Project Plan for the State of Alaska Air Monitoring & Quality Assurance Program," QAPP, State of Alaska, Department of Environmental Conservation, Division of Air Quality, Air Monitoring and Quality Assurance (AMQA) program, http://www.dec.state.ak.us/air/doc/ADEC_AMQA_QAPP_23FEB10-final.pdf, February 2010.

"Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network," Version 4, EPA-454/R-05-004, U.S. EPA, September 2005.

APPENDIX A: SO_2 CRITICAL CRITERIA VALIDATION

State of Alaska Dept. Environmental Conservation

Division of Air Quality

SO_2 Method Validation Criteria

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 SO_2 methods (FRM/FEM), and
- As a tool for validating SO_2 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. SO_2 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

Parameter	Criteria	Acceptable Range	Frequency	Samples Impacted	40 CFR Reference	EPA QA Guidance/Manual	ADEC AM&QA QAPP
Standard Reporting Units							
SO_2		ppb	Hourly Avg.	All	Part 50.17 & 50.4	Vol 2 MS 2.3, 2.6, 2.9,	
Reporting Intervals							
SO_2		5-minute, 1-hour, 24-hour, Annual PSD & SLAMS/NCore/SPM	Quarterly	All	Part 58.16	Vol II Sec. 14	Section 7 18 AAC 50.010 Alaska Ambient Air
Data Completeness							
SO_2	Valid data capture	≥75 % (≥90% for NCore station)	Hourly	S	Part 58 App A	EPA-450/4-87-007 May 1987	Section 7
	(PSD Quality Monitoring) Valid data capture	≥ 80% hourly data	Quarterly (4 consecutive quarters)	G1			
Equipment							
SO_2	FRM/FEM Analyzer	0 – 500ppb and/or as specified in FRM/FEM designation (or approximately 0-100 ppb trace for NCore)	Purchase	All		http://www.epa.gov/ttn/amtic/criteria.html.	Section 11.5
SO_2	SO_2 Calibration/Audit System	Gas dilution of SO_2 cyl gas with zero air or Dilution of SO_2 permeation device	Purchase	All		Vol II, Section 12	
SO_2	Sample Lines, probes and manifolds	Pyrex® (borosilicate) glass, FEP Teflon® or their equivalent	Purchase	All	Part 58 App. E Sec 9a	Vol II: Sec 7.2 & Appendix F	
SO_2	Pneumatic fittings	Teflon, stainless steel	Purchase	All		Vol II: Sec 7.2 & Appendix F	
SO_2	Gas regulator	Stainless steel, dual stage	Purchase	All			
SO_2	Data Logger/Chart Recorder/Data Acquisition System (DAS)	Collection of continuous data	Purchase	All			
SO_2	24-hr temp recorder	Record continuous temp data	Purchase	All			

State of Alaska Dept. Environmental Conservation

Division of Air Quality

I. SO_2 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

Parameter	Criteria	Acceptable Range	Frequency	Samples Impacted	40 CFR Reference	EPA QA Guidance/Manual	ADEC AM&QA QAPP
Calibration/Verification							
SO_2	Multi-point Calibration SO_2 – via dilution of cylinder gas or permeation device	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	Initial, quarterly thereafter	G1		Vol II: Part 1 Sec 12	Section 16
SO_2	Zero/Span QC Check Zero drift Span drift (80% of Full Scale)	≤ ± 3% of full scale ≤ ± 15% Δ (NCore is < ±10%)	1/ 2 weeks	G1		Vol. II, Sec. 12 & Appendix D	MQO Table, Data Validation Tables Section 16
SO_2	One Point QC Check 10 to 100 ppb	≤ ± 15% Δ (NCore is ≤ ±10%)	1/ 2 weeks	G1	Part 58 Appendix A 3.2.1	Vol. II Appendix D	Section 16

II. SO_2 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

Parameter	Criteria	Acceptance Range	Frequency	Samples Impacted [a]	40 CFR Reference	EPA QA Guidance/Manual	ADEC AM&QA QAPP
Station Design/Siting Criteria							
SO_2	Siting Criteria	Un-obstructed probe inlet See references for specific siting criteria	All	All	Part 58 App E	Vol II: Part 1 Sec 7.2 (with regards to Shelter temperature, see waiver note in Criteria column)	Sections 10 and 11
SO_2	Sample residence time for sample introduced through sample train	Required < 20 seconds from sample inlet to back of analyzer (measured as first upscale response) & recommended < 10 seconds	All	G1			
SO_2	Shelter temperature ***[Note: EPA waiver received for Alaska lowering the acceptable low temperature limit from 20° to 15° C]***	15° – 30°C (hourly average) or instrument must be operated per manufacturer specifications	Daily	All	Part 53.20 (see waiver note in Criteria column)		
	Shelter temperature control	± 2°C SD over 24 hours	Daily (hourly values)	G1			
Detection							
SO_2	Noise/Lower Detection Limit (LDL)	5 ppb/ 10 ppb For NCore see EPA-454/R-05-0003	LDL Check 1/year	All	Part 53.23	For NCore see EPA-454/R-05-0003	
Calibration/QC Check & Audit Standards							
SO_2	Permeation Devices	NIST Traceable	Purchase	G, G1	Part 58 App A	Vol II: Appendix D &/or for NCore see EPA-454/R-05-0003	Section 16
SO_2	Cylinder Gases	EPA Protocol/NIST Traceable, SO_2 in N_2	Purchase	G, G1	Part 58 App A 2.6		
SO_2	Zero Air	Free of any substance that might react and/or interfere with measured parameter Concentrations below parameter/method LDL	Purchase or generate Analyze 1/year	G, G1			
SO_2	Flow standards (for calibrating flow meters and gas dilution/GPT calibrator, etc)	NIST Traceable ± 1 % accuracy, certified over intended range of use	Initial calibration, 1/year thereafter	G, G1		Vol II: Appendix D	
SO_2	Gas Dilution/GPT (Diluent and pollutant flow controllers)	NIST Traceable ± 2 % accuracy, certified over intended range of use against NIST Traceable Flow Standard See other criteria in EPA Reference	1/3 months	G, G1			
QC Checks							

II. SO_2 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

Parameter	**Criteria**	**Acceptance Range**	**Frequency**	**Samples Impacted [a]**	**40 CFR Reference**	**EPA QA Guidance/Manual**	**ADEC AM&QA QAPP**
	Shelter Temp Check Record status of check	15° – 30°C (hourly average) or Instrument must be operated per manufacturer specifications, and ± 2°C SD	1/2 weeks	G1		Vol II: Part 1 Section 7	
SO_2	Sample Train inspection	Free of dirt/debris/moisture	1/2 weeks	G1		Vol II: Part 1 Section 7	
	Analyzer sample flow rates	Within analyzer specs					
SO_2	Data logger hourly values verification against Analyzer stored data or chart recorder hourly values	Within 1 significant digit	7% all data	G1			
Monitor Maintenance							
SO_2	Scheduled maintenance activities	Per manufacturer's recommendations	Per manufacturer's recommendations	G1			
Precision (using 1 point QC Checks)							
SO_2	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	http://www.epa.gov/ttn/amtic/parslist.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
Bias/Accuracy (using 1 point QC Checks)							

II. SO_2 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

Parameter	Criteria	Acceptance Range	Frequency	Samples Impacted [a]	40 CFR Reference	EPA QA Guidance/Manual	ADEC AM&QA QAPP
SO_2	95% confidence Limit of Absolute Bias Estimate	95% CL CV ≤± 15% (For an NCore station CV<±10%)	Annually and as appropriate for design value estimates	G, G1	Part 58 App A section 3.2.1	http://www.epa.gov/ttn/amtic/parslist.html & 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)*	
Annual Performance Evaluation							
SO_2	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 $0.995 \geq r^2 \leq 1.000$ NO_2 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		
SO_2	Network	95% CI ≤± 20%	Annually				
SO_2	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. SO_2 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

Parameter	Criteria	Acceptable Range	Frequency	Samples Impacted [a]	40 CFR Reference	EPA QA Guidance/Manual	ADEC AM&QA QAPP
Data Completeness							
SO_2		≥ 75% NCore, SLAMS, SPM ≥ 80% PSD	quarterly	G1			
Calibration/Verification							
	Clock/timer Verification	≤ ± 1 minute.	1/4 weeks	G1			
Technical Systems Audit							
SO_2	Review of entire field/lab & data reporting process	NCore/SLAMS/SPM networks	1/3 years.	G, G1		Vol II: Appendix D	
		PSD	Within 1 month of start-up and annually thereafter	G, G1			

APPENDIX B: NCORE RECOMENDATION TABLES

TABLE B1: NCORE ANALYZER FEATURES

NCore Analyzer Features: Sulfur Dioxide	
Recommended features for high sensitivity SO2 measurements	
Feature	**Function**
High intensity pulsed UV light source	To provide greater sensitivity
Multiple reflective optical filters	To exclude all light at wavelengths that may cause intereferance
Optical filtering	To maximize rejection of NO molecule fluorescence
Calibration equipment for high sensitivity SO2 measurements	
Feature	**EPA requirement**
MFC calibrator	+/- 2% accuracy and flow rates of MFC channels calibrated using NIST traceable flow standard
Calibration standards	NIST-traceable standards
Zero air	< 0.05 ppb
Primary SO2 standard	Accuracy ≤ 2% & certificate of calibration including uncertainty, concentration & expiration date; NIST-traceable standards recommended but not required

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TABLE B2: NCORE PERFORMANCE CRITERIA

NCore Performance Criteria: Sulfur Dioxide

Recommended method performance criteria

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

Sampling Requirements

Criteria	Acceptable Range	Frequency
Manifold inlet	3 to 15 m above ground level and 1 meter vertical and horizontal from structures	--
Probe position	270° unrestricted airflow (including the dominant wind direction)	--
Probe separation	>20 meters from dripline of trees or structures and twice the distance from obstacle(s) as the height of the obstacle(s)	--
Shelter temperature	15-30°C and Δ T < 5°C in 24-hours	daily
Sample inlet or manifold	FEP or PTFE tubing (1/4 in OD suggested) with a 1 micron Teflon® filter[2] or glass manifold (1 inch suggested) if supplying air to multiple analyzers	Weekly (filter change[1])

[1] Suggested not required

[2] If opting to used FEP or PFTE tubing with a 1-micron filter

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