

Chapter 3

Continuous Monitoring of Sulfur Dioxide

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1.0 Introduction

It is the intent of this chapter to outline the requirements for the ambient air monitoring of sulfur dioxide (SO₂). This chapter must be followed by all agencies or groups that conduct continuous ambient air SO₂ monitoring within the State of Indiana and submit data to the Air Quality System (AQS) database. This chapter does not replace the analyzer operating manual. Read the analyzer operating manual thoroughly before performing any analyzer calibration, audit, or maintenance. An analyzer operating manual should be available at the monitoring station as a reference guide.

2.0 Probe Siting Criteria

For specific siting requirements for SO₂ monitors and inlet probes, refer to Chapter 1 of this manual and to the Code of Federal Regulations (CFR) 40, Part 58 Appendix E. Listed below are general guidelines:

2.1 Horizontal and Vertical Probe Placement

1. The probe line inlet must be 2-15 meters above ground level.
2. The probe line inlet must be at least 1 meter vertically and horizontally away from any supporting structure and away from dusty or dirty areas.

2.2 Spacing from Obstructions

1. Do not place the probe line inlet near furnace or incinerator flues, or any minor SO₂ source.
2. If on a rooftop, the probe line inlet must be at least 1 meter from supporting structures such as walls and penthouses.
3. The distance between obstacles and the probe line inlet must be at least twice the height that the obstacle protrudes above the inlet.
4. Air flow must be unrestricted in an arc of at least 180° around the probe line inlet, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in that arc.
5. If on the side of a building, the probe line inlet must have 180° clearance and include the predominant winter wind direction.

2.3 Spacing from Trees

Maintain a minimum distance of 10 meters between the inlet probe and the drip line of obstructing trees. The drip line of trees is the point on the ground where water will drip down from the outermost branches of the tree. If possible the inlet probe should be placed at least 20

meters from the drip line of trees because trees and similar vegetation can absorb SO₂.

3.0 Monitoring Methodology

All methods used to monitor SO₂ must be a reference or equivalent method as described in 40 CFR Part 50.1. The method predominately used for continuous SO₂ monitoring within the State of Indiana is the pulsed fluorescence measurement method. For all instrumentation refer to the manufacturer's instruction manual for analyzer-specific requirements and procedures.

3.1 Pulsed Fluorescence Method

The pulsed fluorescence method of measuring ambient levels of SO₂ involves the reaction of SO₂ with ultraviolet (UV) light. Sample air passes through a catalyst that conditions the sample by scrubbing out aromatic hydrocarbons. The air sample is drawn into the sample reaction cell in which the fluorescent measurement takes place. The UV excitation of SO₂ in the air sample creates a fluorescent light output proportional to the SO₂ concentration. A photomultiplier tube (PMT) measures the fluorescent light output. The current output of the PMT is processed by an electrometer amplifier that sends a voltage to the analyzer output terminals. This voltage may be adjusted to correspond to SO₂ concentrations in the reaction cell.

4.0 Calibration Methodology

Dynamic calibration involves introducing gas samples of known concentrations to an analyzer in order to adjust the instrument to a predetermined sensitivity and to derive a calibration relationship. In general, the systems used for calibrating SO₂ analyzers use zero air to dilute a high SO₂ concentration down to the desired concentration. Zero air is air that is dry and free of the pollutant being measured, as well as any contaminants that interfere with the measurement of the pollutant of interest. Pollutants that interfere with SO₂ include hydrogen sulfide (H₂S) and hydrocarbons. Activated charcoal is used to scrub H₂S and SO₂. Also, analyzers contain devices to scrub hydrocarbons out of the air sample.

Always refer to the manufacturer operating manual for analyzer-specific instructions for the calibration of a particular instrument.

4.1 Dilution System

An SO₂ dilution system consists of a cylinder of SO₂ in an oxygen-free gas (e.g., nitrogen), a dilution/blending system, and a source of zero air (see Figure 1). Listed below are specific components of the SO₂ dilution system:

1. A zero air flow controller capable of maintaining and measuring constant air flows within $\pm 2\%$ of the curve flow. The flow controller may be a mass flow controller, rotameter, capillary or pressure regulator (snubber) type. The curve flow refers to the laboratory measured and calibrated flow of the device as compared to a Standard.

2. An SO₂ flow controller made of nonreactive material (e.g., stainless steel or PTFE) and capable of maintaining and measuring constant flows within $\pm 2\%$ of the curve flow. The flow controller may be a mass flow controller, rotameter, capillary, or snubber type.
3. A pressure regulator for the cylinder of the SO₂ gas. The regulator must be made of nonreactive materials and be able to deliver SO₂ at a suitable pressure. Typical delivery pressure of pollutant gas is between 20 and 40 pounds per square inch gauge (psig). Check the operating manual of the system for the specific gas pressure needed. The regulator must have the appropriate cylinder connection fitting to match the gas cylinder.
4. A shutoff valve constructed of a nonreactive material, is used to stop the SO₂ flow when zero air alone is required.
5. A mixing chamber constructed of a nonreactive material and designed to provide thorough mixing of the SO₂ and dilution air.
6. An output manifold (of nonreactive material, e.g., glass or Teflon) to provide a vented sample to the analyzer.
7. A zero (clean) air system which is free of the contaminants of SO₂, H₂S, and hydrocarbons. Zero air must also be moisture free/dry (see Section 4.0).
8. A cylinder of SO₂ gas certified by the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section (IDEM, OAQ, QAS) (see Chapter 6 of this manual, "Certification Methods for Transfer Standards"). The SO₂ cylinder valve fitting must be compatible with the appropriate regulator fitting.

A National Institute of Standards and Technology (NIST) traceable bubble meter or a certified flow measuring device may be used to measure the flows directly, instead of using calibrated flow controllers for the gas and air flows. All flows must be corrected to Standard Reference Conditions (SRC) (see Section 5.1).

4.2 Permeation System

Permeation systems are essentially no longer used in SO₂ monitoring. More information on permeation systems can be found here:

<http://www.epa.gov/ttnamti1/files/ambient/criteria/reference-equivalent-methods-list.pdf>

4.3 Certification Requirements

SO₂ calibration systems that are taken to and from air monitoring sites must be certified by the IDEM/OAQ/QAS at least every six months. Station calibrators require an annual certification on their air/gas flow controllers. Please see Chapter 1 and Chapter 6 for a more detailed explanation of calibration and certification requirements.

For blending systems with mass flow meters/controllers, the certification includes calibrating the flow meters before the SO₂ gas certification.

System recertification must be performed immediately if any of the following conditions occur:

1. Major maintenance on the calibrator or dilution system (e.g., replacing the mass flow meter, replacing interior lines).
2. Any unexplained problems with calibrations or audits that make calibrator output concentrations questionable.
3. Replacement of the certified SO₂ gas cylinder with another certified cylinder (NOTE: the gas cylinders used for the station calibrators are certified with the QA Certification Facility Calibrator and the value is valid for a specific required time frame. See Chapter 6 for specific details).
4. Replacement of the permeation tube.

5.0 Analyzer Calibration Procedures for Manual Systems (non-LEADS)

The calibration procedure outlined below is general. Always refer to the manufacturer operating manual for analyzer-specific procedures. An analyzer operating manual should be available at each monitoring site.

A zero and span (data validation audit) should be conducted before any recalibration. Conduct this audit before any analyzer adjustments. The purpose of the audit is to validate data from the last audit or calibration to the present date (see Section 6.0 for audit procedures).

A multi-point calibration consists of a zero concentration (pollutant free and dry air) and four upscale points, the highest being a concentration above the NAAQS and higher than any routine values one might expect at the site. The other concentrations should be spaced approximately equally over the scale range. This multi-point calibration should be performed at the time of initial installation. A multi-point calibration of an analyzer must be performed if any of the following conditions exist:

1. A six (6) month period has lapsed since the most recent multi-point calibration.
2. An interruption of more than a few days of operation.
3. Any repairs are made which may affect calibration, e.g.
 - a. Replacement of electronic boards
 - b. Replacement of any optics (mirrors)
 - c. Replacement of solenoid switching valves
4. Physical relocation of the analyzer.

5. Any other indication of possible significant inaccuracy of the analyzer.
6. Calibration points are **not** within $\pm 2\%$ of the full range of the analyzer (e.g., if the range is 0.5 ppm, then the measured values must be within ± 0.010 ppm of the standard. Therefore, if the standard concentration introduced into the analyzer is .400 ppm, the measured value must be between .390 and .410 ppm.).

A sample calibration form is provided with this chapter (see Form 1). The form may be modified for use by the user. Users may also use electronic forms such as those written in Microsoft Excel or Microsoft Word.

NOTE: ALL SO₂ ANALYZERS MUST BE ROUTINELY CALIBRATED AT LEAST ONCE EVERY SIX (6) MONTHS.

5.1 SO₂ Calibration Procedure with Dilution System

During the calibration, the analyzer must be operating in its normal sampling mode. The calibration gas must pass through all filters, scrubbers, conditioners, and other components used during the normal ambient sampling mode. All operational adjustments (e.g., sample flow or PMT voltages) to the analyzer should be completed before the calibration.

The following steps should be taken and all relevant information should be recorded on the calibration form.

1. Record the station name and the USEPA Air Quality System identification number (AQS).
2. Identify the person performing the calibration (initials) and record the date of the calibration.
3. Record the analyzer manufacturer name (brand), model number, and serial number.
4. Record the analyzer settings for sample flows and vacuum settings (if applicable).
5. Record the SO₂ calibration system's manufacturer name, model number, and serial number.
6. Record the SO₂ calibration gas cylinder manufacturer, number, the certified concentration, certification date, and cylinder pressure.

NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG (POUNDS PER SQUARE INCH GAUGE). GASES MAY BECOME UNSTABLE AT LOW PRESSURE AND CAUSE CALIBRATION ERRORS.

All calibration and audit cylinders must be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM). See Chapter 6 of this manual for traceability and certification procedures.

7. Record the initial zero and span potentiometer (pot) settings of the analyzer before any adjustments. Analyzer controls will vary with each manufacturer's brand and model. In addition, record any diagnostics performed on the analyzer.

There are analyzers that are microprocessor-controlled and have no potentiometers but will have readings that correspond to the zero and span pot settings. Record these readings. Because calibration adjustments will differ between analyzer models, consult the manufacturer's manual before performing the calibration.

8. Select and record the operating range of the analyzer to be calibrated. The range of the analyzer is sometimes called the Upper Range Limit (URL).

NOTE: SELECT A RANGE FOR WHICH THE ANALYZER HAS BEEN DESIGNATED AS AN USEPA EQUIVALENT METHOD. MOST ANALYZERS ARE CALIBRATED IN THE 0.000 TO 0.500 PPM RANGE. THE OTHER COMMONLY USED RANGE IS 0.000 TO 1.000 PPM. REFER TO THE ANALYZER'S MANUAL FOR DESIGNATED RANGES.

9. Confirm that the analyzer is connected to a recording device such as a data acquisition system (DAS), a strip chart recorder, and/or a digital voltmeter.
10. Adjust the flow of the diluent air (zero air) on the calibrator system so that its total output flow exceeds the total flow demand of the analyzer by at least 25%.

For example: If the analyzer flow demand is 2.00 liters per minute (l/min) then the total output flow from the calibrator should be no less than 2.50 l/min.

The excess flow from the calibrator is necessary to ensure that the analyzer has a sufficient amount of sample flow; otherwise, the analyzer could draw air from other than the desired sample stream.

11. Record the starting time of the calibration on the calibration form.
12. Connect the analyzer "sample in" port to the "sample out" port of the calibrator using a vented nonreactive sample line or manifold.

WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE CALIBRATOR SO THAT EXCESS SAMPLE FLOW CAN BLEED OFF. AN UNVENTED SAMPLE GAS MAY PRESSURIZE AND DAMAGE THE ANALYZER.

13. Allow the analyzer to sample zero air until the SO₂ response stabilizes (usually 10 to 20 minutes). After the response has stabilized, adjust the analyzer zero control to the desired zero offset. Usually the analyzer has an offset of zero. To observe any negative zero drift, the Quality Assurance Section recommends a +5% offset for the chart recorder.

14. Record the stable zero air analyzer response from the data acquisition system, voltmeter and/or strip chart.
15. Attach a stainless steel regulator to the SO₂ gas calibration cylinder. QAS recommends purging gas through the regulator and inlet line for a few seconds before connecting the gas to the calibrator. This is to flush out any impurities that may reside in the gas line. Attach the outlet line from the regulator to the gas inlet line on the calibrator.
16. Adjust the SO₂ flow of the dilution system (or calibrator) to generate a concentration of approximately 80% to 90% of the upper range limit (URL) of the SO₂ channel. This is the span point.

For example: For an analyzer set on a 0.500 ppm range, 90% of the URL would be 0.450 ppm.

17. Calculate the exact SO₂ concentration [SO₂]_{out} (also known as the standard concentration) for the span point using Equation 3-1.

NOTE: THE BRACKETS [] DENOTE A CONCENTRATION (PARTS PER MILLION, ppm) WHILE AN "F" WITH A SUBSCRIPT DENOTES A FLOW.

Equation 3-1

$$[\text{SO}_2]_{\text{out}} = \frac{F_{\text{SO}_2} \times [\text{SO}_2]_{\text{std}}}{F_{\text{SO}_2} + F_d}$$

Where:

[SO ₂] _{out}	=	output concentration of SO ₂ measured in ppm
[SO ₂] _{std}	=	certified concentration of the SO ₂ gas cylinder measured in ppm
F _{SO₂}	=	cylinder flow of the SO ₂ gas measured in cc/min at SRC
F _d	=	flow of the dilution gas (zero air) measured in cc/min at SRC

NOTE: MOST MASS FLOW CONTROLLED CALIBRATORS INDICATE THE DILUTION FLOW (F_d) IN LITERS PER MINUTE (l/min). CONVERT l/min TO cc/min BY MULTIPLYING l/min x 1000 cc/L (cc/min = l/min x 1000).

Example calculation using Equation 3-1:

F _{SO₂}	=	45.0 cc/min
F _d	=	4,955.0 cc/min
[SO ₂] _{std}	=	50.0 ppm
[SO ₂] _{out}	=	$\frac{45.0 \text{ cc/min} \times 50.0 \text{ ppm}}{45.0 \text{ cc/min} + 4,955.0 \text{ cc/min}}$

$$[\text{SO}_2]_{\text{out}} = \frac{2,250.0 \text{ cc/min} \times \text{ppm}}{5,000.0 \text{ cc/min}} = 0.450 \text{ ppm}$$

NOTE: BECAUSE DATA IS REPORTED TO THREE SIGNIFICANT DIGITS, IT IS SUGGESTED THAT THE CONCENTRATION BE ROUNDED TO THE NEAREST THOUSANDTH PPM (.XXX).

18. Record the $[\text{SO}_2]_{\text{out}}$ concentration.
19. The analyzer should sample the generated concentration until the SO_2 response stabilizes (usually 10 to 20 minutes). Adjust the SO_2 span control to obtain the desired recorder response determined by Equation 3-2.

Equation 3-2

Desired Recorder Response (% of scale) =

$$\frac{([\text{SO}_2]_{\text{out}} \times 100)}{\text{URL}} + Z_{\text{SO}_2}$$

Where:

- $[\text{SO}_2]_{\text{out}}$ = output concentration of SO_2 measured in ppm
- URL = upper range limit of the SO_2 analyzer measured in ppm
- Z_{SO_2} = recorder zero response of the SO_2 analyzer measured in percent

Example calculation using Equation 3-2:

$$\text{Desired Recorder Response (\% of scale)} = \frac{(0.450 \text{ ppm} \times 100)}{0.500 \text{ ppm}} + 5.0\% = 95.0\%$$

20. After setting the zero and span pots, run three more evenly spaced concentrations between the zero and span concentrations. **Run these concentrations and record the responses without any further adjustments to the analyzer.**

For example, a typical SO_2 calibration with an URL of 0.500 ppm would consist of the following concentrations (listed in the order that they should be run):

- 0.000 ppm (zero)
- 0.400 to 0.450 ppm (span)
- 0.250 to .300 ppm
- 0.150 to .200 ppm
- 0.080 to 0.100 ppm

Note that the zero should be rerun after a major span adjustment to ensure no drift has occurred.

Additional concentrations may be generated by either increasing the calibration dilution flow (F_d), decreasing the SO_2 cylinder gas flow (F_{SO_2}), or a combination of these two actions.

For each concentration generated, calculate the exact standard SO_2 concentration using Equation 3-1. Record the information on the SO_2 calibration form.

21. Two methods may be used to determine the slope of the analyzer calibration relationship after finishing all of the calibration points.

The more commonly used and recommended method is to set the analyzer's slope to a constant value (e.g., for a 0.500 ppm range, use a 0.500 slope for a 1 volt output). This method allows the same slope to be used for data reduction over the entire network.

Use Equation 3-3 to calculate the observed (or measured) concentration for all upscale analyzer responses. Use Equation 3-4 to calculate the percent difference (% diff.) between the standard and observed concentrations.

The standard concentration is $[SO_2]_{out}$ as calculated from Equation 3-1. The observed concentration is defined by the following equation:

Equation 3-3

$$\text{obsv. conc.} = (\text{resp.} - \text{zero resp.}) \times \text{slope}$$

NOTE: PLEASE MAKE NOTE OF THE FOLLOWING ABBREVIATIONS THAT WILL BE USED THROUGHOUT THIS CHAPTER:

observed concentration = obsv. conc.
standard concentration = std. conc.
analyzer response = resp.
analyzer zero response = zero resp.
percent difference = % diff.

Example calculation:

Where:

resp. = 0.427 V (volt)
zero resp. = 0.007 V
slope = 0.500
obsv. conc. = $(0.427 - 0.007) \times 0.500$
obsv. conc. = 0.210 ppm

Equation 3-4

$$\% \text{ diff} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

Example calculation:

Where:

$$\text{std. conc.} = 0.205 \text{ ppm}$$

$$\text{obsv. conc.} = 0.210 \text{ ppm}$$

$$\% \text{ diff} = \frac{0.210 - 0.205}{0.205} \times 100$$

$$\% \text{ diff.} = 0.0244 \times 100$$

$$\% \text{ diff.} = 2.4\%$$

NOTE: BECAUSE PRECISION AND ACCURACY DATA IS REPORTED TO THE NEAREST TENTH OF A PERCENT, QAS SUGGESTS THAT THE PERCENT DIFFERENCE BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).

An alternate method is to use a calculator or computer program to calculate the slope and intercept of the line-of-best-fit through the calibration points using least-squares linear regression. Include the upscale concentrations and the zero point in the calculation.

This method, while minimizing the total error of the calibration points, requires using a different slope and intercept for each monitor from which data are reduced.

22. All observed and standard concentrations for SO₂ calibrations must agree within ±2% of the range of the analyzer e.g.(0.010 ppm on a 0.5 ppm range, 0.020 ppm on a 1.0 ppm range). If any observed concentration is outside the limits of ±2% of the analyzer's range, then rerun and recalculate that concentration.

Analyzers that cannot routinely meet the calibration limit require maintenance.

23. Run and record any analyzer diagnostic tests. These tests provide baseline data for future troubleshooting procedures.
24. For an on-site calibration, complete the following steps:
- Reconnect the analyzer to the sample line or manifold.
 - Ensure that the analyzer is in the normal sampling mode.
 - Ensure that the analyzer is connected to all data recording devices and that all strip charts have been annotated. All strip charts should be annotated with the following information:

Site name

Parameter

Date

Chart speed
Operation being performed (e.g., calibration)
Calibration starting time
Initials of the person performing the calibration
Standard concentrations of all responses
Initial and final zero
Calibration ending time

- d. Record all pertinent information in the site logbook.
- e. Log off of the DAS.
- f. Post a copy of the calibration at the site or save an electronic copy such that it can be accessed at the site.
- g. It is also recommended that a calibration sticker be attached to the analyzer that contains the following information:

Site Name
AQS Number
Analyzer Serial Number
Slope (SO₂)
Calibration Date
Calibration Performed By
Due Date of Next Calibration

5.2 SO₂ Calibration Procedure with Permeation System

During the calibration, the analyzer must be operating in its normal sampling mode. The calibration gas must pass through all filters, scrubbers, conditioners, and other components used during the normal ambient sampling mode. All operational adjustments (e.g., sample flow or PMT voltages) to the analyzer should be completed before the calibration.

Many calibration procedures used for permeation systems are the same as for dilution systems. Listed below are the primary differences between permeation systems and dilution systems:

1. The standard (known) concentrations are calculated with different formulas.
2. Instead of an SO₂ cylinder, the permeation tube, vial, or wafer supplies the SO₂ for the calibration.
3. Flows are generally controlled by rotameters; therefore, each total flow must be individually measured with an NIST-traceable bubble meter or other type of certified flow device.
4. Permeation tubes must equilibrate to the oven temperature for a minimum of 24 hours before

use. Vials must equilibrate for 48 hours. Higher temperature ovens, > 30°C, may require a longer equilibration period.

Follow the same procedures as outlined in Section 5.1 for a dilution system; disregard references to cylinder setup. Remember to record the certified permeation rate of the permeation tube.

WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE CALIBRATOR SO THAT EXCESS SAMPLE FLOW CAN BLEED OFF. AN UNVENTED SAMPLE GAS MAY PRESSURIZE AND DAMAGE THE ANALYZER.

NOTE: IF USING A PERMEATION SYSTEM, BE SURE THAT THE SYSTEM IS THOROUGHLY WARMED BY CHECKING THE TEMPERATURE ON THE FRONT PANEL METER OR APPROPRIATE INDICATOR.

Calculate the exact SO₂ concentration for the span point. To calculate the concentration of SO₂ generated by a permeation system, it is necessary to measure the total air flow coming out of the system. If a bubble meter is used, correct the measured air flow to Standard Reference Conditions (SRC) (Equation 3-6). Finally, calculate the SO₂ concentration using the corrected air flow and the permeation rate of the tube or vial in use with the system.

Use Equation 3-5 to calculate the total measured air flow, F_t, measured with a bubble meter.

Equation 3-5

$$F_t = \frac{\text{vol(L)} \times 60(\text{sec/min}) \times \text{CF}}{\text{time(sec)}}$$

Where:

vol = the volume standard of gas, measured in liters
time = time for bubble meter to fill with the volume standard of gas, measured in seconds
CF = correction factor applied to the measured flow to convert to Standard Reference Conditions

The correction factor, CF, corrects air flow to Standard Reference Conditions. Standard Reference Conditions (SRC) are 760 millimeters of mercury (mmHg) air pressure and 298 Kelvin (K) air temperature. The correction factor is calculated in Equation 3-6:

Equation 3-6

$$CF = \frac{(P_{amb} - P_{vap}) \times T_{std}}{T_{amb} \times P_{std}}$$

Where:

- P_{amb} = ambient station pressure at the time of flow measurement, measured in mmHg
 P_{vap} = vapor pressure corresponding to the current ambient temperature, measured in mmHg. This can be found on a lookup table (see Table 1).
 T_{std} = Standard Reference Condition temperature of 298 K. See Table 2 for temperature conversions.
 T_{amb} = ambient temperature at the time of flow measurement, measured in Kelvin (K)
 P_{std} = Standard Reference Condition pressure of 760 mmHg

Use Equation 3-7 to calculate the standard concentration of SO₂.

Equation 3-7

$$[SO_2]_{out} = \frac{\text{perm. rate} \times 0.382}{F_t}$$

Where:

- perm. rate = permeation rate of the SO₂ tube or vial, measured in µg/min
 F_t = the total flow measured in l/min and corrected to SRC

The constant 0.382 is based on the molecular weight of SO₂, measured in Liters/gram.

The following example shows the calculation of a concentration with a permeation system.

A permeation system contains an SO₂ permeation tube with a permeation rate of 2.200 µg/min. The air flow is measured with a 1000 cc (1 liter) bubble meter in a time of 7.50 seconds. Ambient temperature is 295 K and ambient pressure is 745 mmHg. The vapor pressure, P_{vap} , is 19.8 mmHg.

Calculate the correction factor with Equation 3-6:

$$CF = \frac{(P_{amb} - P_{vap}) \times T_{std}}{T_{amb} \times P_{std}}$$

$$CF = \frac{(745 - 19.8) \times 298}{295 \times 760}$$

CF = 0.9639

Calculate the air flow with Equation 3-5:

$$F_t = \frac{\text{vol(L)} \times 60(\text{sec/min}) \times \text{CF}}{\text{time(sec)}}$$
$$F_t = \frac{1.0(\text{L}) \times 60(\text{sec/min}) \times 0.9639}{7.50(\text{sec})}$$

$F_t = 7.711 \text{ l/min}$

Calculate the standard or known concentration with Equation 3-7:

$$[\text{SO}_2]_{\text{out}} = \frac{\text{perm. rate} \times 0.382}{F_t}$$
$$[\text{SO}_2]_{\text{out}} = \frac{2.200 \times 0.382}{7.711}$$
$$[\text{SO}_2]_{\text{out}} = 0.109 \text{ ppm}$$

NOTE: BECAUSE DATA IS REPORTED TO THREE SIGNIFICANT DIGITS, IT IS SUGGESTED THAT THE CONCENTRATION BE ROUNDED TO THE NEAREST THOUSANDTH PPM (.XXX).

Record the $[\text{SO}_2]_{\text{out}}$ concentration on the calibration form, along with the ambient temperature and pressure.

The analyzer should sample the generated concentration until the SO_2 response stabilizes (usually 10 to 20 minutes). Adjust the SO_2 span control to obtain the desired recorder response determined by Equation 3-2.

After setting the zero and span pots, determine three evenly spaced concentration between the zero and span concentrations. **Run these concentrations and record the responses without any further adjustments to the analyzer.**

For example, a typical SO_2 calibration with an URL of 0.500 ppm would consist of the following concentrations (listed in order that they should be run):

0.000 ppm (zero)
0.400 to 0.450 ppm (span)
0.250 to .300 ppm

0.150 to .200 ppm
0.080 to 0.100 ppm

Additional concentrations may be generated by adjusting the calibration total flow F_t . For each concentration generated, calculate the exact SO_2 concentration using Equations 3-5, 3-6 and 3-7. Record the information on the SO_2 calibration form.

5.3 Calibration Frequency

To ensure accurate on-site SO_2 measurements, calibrate the analyzer at the time of installation and recalibrate whenever any of the following occur:

1. It has been more than six months since the analyzer's most recent calibration.
2. An interruption of more than a few days of the analyzer's operation.
3. Any major repairs to the analyzer.
4. Physical relocation of the analyzer.
5. Any performance audit failure or excessive zero/span drift by the analyzer (see Chapter 11, Valid Data Requirements, for drift limitations).

6.0 LEADS

The Leading Environmental Analysis and Display System (LEADS) is a data acquisition system used by the State of Indiana's Ambient Monitoring Network. The system pairs an on-site calibrator with the analyzer in order to perform automated calibrations, zero/span checks and one-point quality control checks (precision audit). It also flags invalid data automatically, which aids in the QA/QC procedure.

Daily zero and span checks are ran. These checks are used to catch analyzer drift and to help determine data validation. These quality control measures are intended to further ensure high quality monitoring data and to prevent unnecessary data loss. Once a week a one-point quality control check (precision audit) is done along with the daily zero and span check. Currently, all continuous sulfur dioxied analyzers are routinely audited remotely through the LEADS. The zero, span and precision one-point quality control check are scheduled by the OAQ/AMS/LEADS Administrator and are set to run at midnight. The span concentration is .400 ppm SO_2 and the precision level check is .090 ppm SO_2 . For data validation, the span must be within $\pm 10\%$. The One-Point Quality Control Check must be $\leq \pm 10\%$; if not, determine if maintenance is needed and then run a multi-point calibration.

On-site manual precision audits (8.1) may be conducted by IDEM quality assurance staff on an as needed basis such as:

- LEADS communication malfunction
- Unstable or failing remote audit results

See Chapter 1 of the Quality Assurance Manual for introductory LEADS information.

7.0 SO₂ Analyzer Calibration Procedure

See LEADS Manual Chapters 2, 3, and 4 for Calibration Procedures. See also the following SOPs for API-Teledyne 700 and 703 Operation, Certification, and Calibration: API 700 Cert, API 700 MFC Cal, API 700 Operation, API 703 Cert, and LEADS Calibrator Audit.

8.0 Quality Assurance Audits

Quality assurance audits ensure the validity of the SO₂ data submitted to the national AQS database. Results of these audits are also used to estimate the Precision and Accuracy (P&A) of the monitoring network's data. IDEM/OAQ/QAS submits the statewide P&A to the USEPA every quarter. See Chapter 13, "Data Quality Assessment," of this manual for detailed information on P&A.

8.1 Data Validation and Precision Audits for Manual Systems

Routine audits are performed bi-weekly (every two weeks) to assess the validity and precision of the SO₂ data. The bi-weekly audit consists of challenging the analyzer with two upscale SO₂ concentrations using a certified SO₂ standard gas cylinder and dilution system or permeation system. The audit device must meet the same criteria as that of the system used for the calibration, and it must be certified by the IDEM/OAQ/QAS (see Section 4.0 of this chapter, and Chapter 6 of this manual, "Certification Methods for Transfer Standards").

The first bi-weekly audit point consists of an SO₂ concentration in the 70-90% URL range (e.g., 0.35 ppm to 0.45 ppm for a monitor with a range of 0.500 ppm). This concentration is the span (validation point) and is used to validate data back to the most recent audit or calibration. See Chapter 11, "Valid Data Requirements," in this manual for the details of data validation.

The second bi-weekly audit point consists of an SO₂ concentration in the required range of 0.01 ppm to 0.10 ppm. This second quality control audit point is used to assess the precision of the data based on quarterly calculations.

The system used to calibrate the analyzer may be used to perform the bi-weekly audits on the analyzer. It is suggested, but not required, that the auditor be different from the person who performed the calibration.

A sample audit form is provided with this chapter (see Form 2). The form may be modified for use by the user.

The field audit procedure is as follows:

NOTE: MAKE NO ADJUSTMENTS TO THE ANALYZER BEFORE THE AUDIT

1. Record the station name and the AQS site identification number on the SO₂ audit form.
2. Identify the person performing the audit (initials) and record the audit date.
3. Record the analyzer's operational period (date and time). The operational period is defined as the period of time starting from the last audit or calibration (date and time) to the current audit beginning (date and time).
4. Record the analyzer's manufacturer name, model number, and serial number.
5. Record the analyzer's settings: flows, vacuum, initial and final zero and span potentiometer settings.

NOTE: IT IS GOOD PRACTICE TO INSPECT THE ANALYZER BEFORE THE START OF THE FIELD AUDIT. FOR EXAMPLE, CHECK TO SEE THAT THE ANALYZER IS IN THE NORMAL SAMPLING MODE, THE SAMPLE LINE IS CONNECTED TO THE SAMPLE MANIFOLD OR OUTSIDE SAMPLE LINE, THE ANALYZER IS CONNECTED TO THE DATA RECORDING DEVICE(S), OR ANY OTHER CONDITION THAT COULD AFFECT THE DATA OR THE FIELD AUDIT RESULTS.

6. Record the analyzer's last calibration date. Analyzers must have a multi-point calibration at least once every six months.
7. Record the audit device manufacturer name, model number, and serial number.
8. When using a dilution system, record the SO₂ audit gas cylinder manufacturer, serial number, certified concentration, and certification date. If using a permeation system, record the system manufacturer's name, serial number, permeation rate of the permeation tube, and the serial number of the permeation tube.

NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG. GASES MAY BECOME UNSTABLE AT LOW PRESSURES AND CAUSE AUDIT ERRORS. BE SURE THAT THE AUDIT SYSTEM AND GAS HAVE A CURRENT CERTIFICATION (WITHIN THE LAST 6 MONTHS) BEFORE PROCEEDING.

NOTE: IF USING A PERMEATION SYSTEM, BE SURE THE SYSTEM IS THOROUGHLY WARMED BY CHECKING THE TEMPERATURE ON THE FRONT PANEL METER OR APPROPRIATE INDICATOR.

9. Record the zero and span potentiometer (pot) settings. Analyzer controls will vary with each

manufacturer's brand and model. Also record the results of any diagnostics performed on the analyzer.

Analyzers which are microprocessor-controlled have no potentiometers but will have readings that correspond to the zero and span potentiometer settings. Record these readings.

10. Record the analyzer's primary and secondary recording device. If a digital voltmeter (DVM) is used during the audit, record that on the audit form.
11. Confirm that the analyzer is connected to a recording device (e.g., a data acquisition system (DAS), a strip chart recorder, and/or a digital voltmeter).

NOTE: AMBIENT NETWORK SITES WHICH USE A DATA ACQUISITION SYSTEM (DAS) MAY RECORD THE AUDIT CONCENTRATIONS AS AN EXCEEDANCE; THEREFORE, IT IS IMPORTANT TO LOG ON TO THE DAS SO THAT THOSE VALUES CAN BE FLAGGED.

12. Adjust the flow on the audit device so that its total output flow exceeds the total flow demand of the analyzer by at least 25%.
13. Connect the analyzer's "sample in" port to the "sample out" port of the audit device using a vented nonreactive (e.g., Teflon) sample line or manifold.

NOTE: LOG ON AND ANNOTATE ALL DATA RECORDING DEVICES (E.G., DATA ACQUISITION SYSTEM OR STRIP CHART RECORDER) WITH THE AUDIT STARTING DATE AND TIME.

WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE AUDIT DEVICE SO THAT EXCESS SAMPLE FLOW CAN BLEED OFF. AN UNVENTED SAMPLE GAS MAY PRESSURIZE AND DAMAGE THE ANALYZER.

14. Allow the analyzer to sample zero air until the SO₂ response stabilizes (usually 10 to 20 minutes). Record the analyzer response to zero air on the audit form.
15. If using a cylinder dilution system, attach a stainless steel regulator to the SO₂ cylinder. QAS recommends purging gas through the regulator and inlet line for a few seconds before connecting the gas to the calibrator. This is to flush out any impurities that may reside in the gas line. Attach the gas line to the audit system.
16. For the span (data validation concentration), adjust the SO₂ flow from the audit system to generate a concentration of approximately 80% of the upper range limit (URL) of the SO₂ analyzer.

The span (data validation point) can range between 70% and 90% of the URL of the SO₂

analyzer. Be sure that the validation point does not exceed the highest point of the calibration used to certify the audit equipment. See Section 5.1, #16 for an example calculation.

17. Calculate the exact SO₂ concentration [SO₂]_{out}. See Section 5.1, #17 for dilution system calculations, or Section 5.2.2 for permeation system calculations. Record this concentration on the audit form. Also record the audit setting, gas flow, and total flow.
18. After the analyzer response has stabilized, record the responses on the audit form.
19. Using the analyzer's current calibration slope and zero response with Equation 3-3, convert the analyzer response from the primary recording device (resp.) to a concentration (ppm). Record the concentration as the observed concentration.

NOTE: THE STANDARD CONCENTRATION IS DEFINED AS [SO₂]_{OUT}, WHICH IS CALCULATED FROM EQUATION 3-1. THE OBSERVED CONCENTRATION (OBSV. CONC.) IS DEFINED BY EQUATION 3-3.

20. Calculate and record the percent difference between the standard concentration (std. conc.) and observed concentration (obsv. conc.). See Equation 3-4 to calculate the percent difference.
21. The results of the validation audit will determine one of the following outcomes:
 - a. If the percent difference for the SO₂ validation audit is within ±10%, the collected data is valid.

NOTE: BECAUSE P&A DATA IS REPORTED TO THE NEAREST TENTH OF A PERCENT, QAS SUGGESTS THAT THE PERCENT DIFFERENCE BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).

- b. If the percent difference for the SO₂ validation audit is greater than ±10%, then the network operator must be informed that the analyzer is out of calibration. The data collected since the last audit or calibration may be invalid based on further investigation but a recalibration must be done as soon as possible. The SO₂ quality control (precision) audit should still be performed (Section 6.1, #22).

NOTE: IN THIS CASE, ALTHOUGH THE DATA FOR THE OPERATING PERIOD IS INVALID, IT STILL MAY BE HELPFUL TO CONTINUE THE AUDIT. THE QUALITY CONTROL (PRECISION) AUDIT MAY ASSIST IN DIAGNOSING PROBLEMS WITH THE SYSTEM.

22. For the SO₂ quality control (precision) audit, adjust the SO₂ flow on the audit system to obtain an SO₂ concentration ([SO₂]_{out}) between 0.01 ppm and 0.10 ppm. This is the required range for the precision audit concentration.

The steps involved with the precision audit are the same as for the data validation point. Results of precision point audits are used in quarterly calculations of a monitoring network's precision; however, if the percent difference is greater than $\pm 10\%$, data may be invalid based on further investigation.

23. After the audit is complete (span or accuracy), perform the following:
 - a. Reconnect the analyzer's sample line to the outside sample line or manifold.
 - b. Ensure that the analyzer is in the normal sampling mode and has its normal flow.
 - c. Ensure that the data recording devices are connected to the analyzer and are registering an appropriate response.
 - d. Log off and annotate all data recording devices with the ending time of the audit, the initials of the auditor, and the percent difference results of the validation and precision audits.
 - e. For a strip chart recorder, be sure to indicate the following information on the chart: site name, audit starting and ending time, zero response, upscale responses for standard concentrations, parameter, and the auditor's initials.

Record all applicable information in the site logbook or electronically: include at least the audit date, the initials of the auditor, the type of audit (validation/precision and/or accuracy), and the percent difference results of the validation and precision audits.

8.2 Accuracy Audits

Accuracy audits must be performed on at least 25% of the network analyzers each calendar quarter as per 40 CFR Part 58. At the end of the year, all analyzers must have had an accuracy audit. To ensure accuracy audits are not missed, it is strongly recommended that an accuracy audit be performed on each analyzer once per quarter.

Networks which have four or fewer analyzers must conduct audits so that all analyzers have had an accuracy audit by the end of the year. Accuracy would then be calculated in the 2nd and 4th quarters of the year. Because this is a statistical assessment of the accuracy of the data, it is suggested that accuracy audits be conducted more often than once per quarter (e.g., monthly). This ensures a larger and more representative database for the accuracy calculations.

40 CFR Part 58 requires that a different audit system and gas standard from that was used to calibrate be used to perform the accuracy audit. The auditor should also be different from that of the person who performed the calibration. The analyzer must be collecting valid data in order to conduct an accuracy audit.

To perform accuracy audits, follow the same auditing procedures and calculations used in Section 8.1. Any results more than $\pm 15\%$ can result in data being invalid. Further research such as zero and span analysis may help pinpoint where an issue is and if any data is invalid.

The following SO₂ concentrations must be run for an accuracy audit on an analyzer calibrated to 500 ppm:

- a. 0.0500 ppm to 0.0999 ppm
- b. 0.1500 ppm to 0.2599 ppm
- c. 0.2600 ppm to 0.7999 ppm

*These ranges are referenced from a 2010 USEPA Office of Air Quality Planning and Standards memorandum and are not yet in the CFR. This memo can be found at: <http://www.epa.gov/ttn/airs/airsaqs/memos/Tech%20Memo%20for%20PE%20Audit%20Levels.pdf>

9.0 Data Reduction and Reporting

The primary National Ambient Air Quality Standard (NAAQS) for SO₂ is the 99th percentile of 1-hour daily maximum concentrations averaged over 3 years or a 24-hour average of 75 ppb. The secondary standard is a 3-hour average of 0.5 ppm.

The continuous data submitted to IDEM for entry into the AQS database must be reduced to 24 1-hour averages and 288 five-minute averages per day. This reduction must follow the guidelines and requirements set forth in Chapter 12 of this manual.

Data should be submitted to the IDEM Ambient Monitoring Section by the 30th day after the end of each month. This will allow sufficient time for review before AQS submittal deadlines. The deadline is 60 days after the end of each reporting quarter.

10.0 Routine Station Operation

Scheduled checks are essential to the quality assurance program for verifying the validity of the monitoring system. At least once each week, the network operator should call up the site and confirm normal operation. About every two to three weeks the operator should visit each site to physically determine the operating conditions and perform any routine maintenance.

10.1 Site Checks

All sites should have a bound logbook in which weekly site checks, analyzer checks, and audit information can be recorded. An electronic logbook can be utilized at LEADS enabled sites.

- The average shelter temperature should range from 20 °C to 30 °C (68 °F to 86 °F). A certified thermograph or other temperature-recording device must be installed for continuous monitoring of the site temperature fluctuations as per 40 CFR Part 53.31(1).

The indoor temperature recording device should be checked at least once every six months and be within ± 2 °C of the transfer standard

Data may be invalidated by the IDEM/OAQ/QAS any time the shelter temperature is outside the 15 °C to 33 °C (59 °F to 91.4 °F) temperature range.

- Inspect the sample manifold and blower, exterior and interior sample lines, candy cane, and funnel for cleanliness, leaks, and obstructions. Check that the blower motor is running. Check moisture traps for any accumulated water. Sample line should be changed out on a one to four year cycle, depending on how dirty the site is, condition of the line, and thru the probe audit results
- All data recording devices should be inspected for ink trace or printout legibility, paper supply, and correct time (or time synchronization)

All data recording devices remain on the site's local standard time all year. That is, sites in the Eastern Time Zone remain on Eastern Standard Time all year; whereas, those sites in the Central Time Zone stay on Central Standard Time all year.

- Record all site activities and checks in the site logbook or electronically if LEADS is installed

10.2 Analyzer Checks

- All analyzers require a particulate filter assembly for the sample inlet. Check the analyzer manual for the recommended filter size and type

Change the inlet particulate filter every two to three weeks or more often as needed. A clean filter will minimize the reaction of SO₂ in the sample air with particulate matter on the filter. If needed, flag any data collected during a filter change.

After installing a clean filter, be sure to reassemble the inlet filter holder tightly in order to prevent leaks. Check the assembly for leaks. This can be done by plugging the sample inlet and watching the sample flow indicator, which should drop to zero. If it does not, there is a leak in the filter assembly or in the analyzer and it should be fixed.

- Check analyzer flow rates, vacuum readings, and the zero and span potentiometer settings. Record these in the site logbook. These readings should correspond to those from the last calibration
- Verify that the analyzer is in the normal sampling mode, and that it is connected and providing a signal to the primary and secondary data recording devices. Check that the data recording devices are recording properly

- Some analyzer models have extensive diagnostic testing capability, some of which may need to be conducted weekly. Check the site logbook or electronic log and conduct any indicated tests
- All analyzers must undergo routine maintenance. Each analyzer brand and model has specific requirements and timetables for performing maintenance

A schedule for routine maintenance should be made and followed. Listed below are some items common to most SO₂ analyzers which require regular maintenance:

- Sample pump
- Interior filters/screens (cleaning or replacement)
- Cooling fan (cleaning and lubrication)
- Charcoal scrubber column (replacement)
- Catalyzing agents (replacement)

10.3 Zero/Span Checks

Zero/span checks are recommended daily. The check consists of a zero air check and introduction of an SO₂ concentration that is 70% to 90% of the analyzer's range. Most analyzers that have zero/span options can be set up to cycle automatically through the zero/span check each day. For these analyzers, check the strip chart for the most recent zero and span. During routine site checks, record the last zero and span check in the site logbook. Compare the most recent readings with the logbook entries for any zero or span drift. Dramatic shifts in zero and/or span values may require a recalibration of the analyzer. For analyzers not equipped with a daily zero and span device, perform a zero/span check at least once each week.

If a bi-weekly span (validation audit) exceeds the allowed $\pm 10\%$ percent difference and records of zero/span checks can be supplied to identify when excessive drift began, it may not be necessary to invalidate an entire operational period. Allowable span drift is $\leq +10\%$ and zero drift is $\leq \pm 3.0$ ppb for a 24 hour period and $\leq \pm 5.0$ ppb over a fourteen day period. The QA Section Chief makes the final decision on data validation.

11.0 Preventive Maintenance

All analyzers must have routine preventive maintenance performed to ensure proper operation. Most analyzers have a checklist (from the manufacturer) detailing what items need maintenance and the frequency for this preventive maintenance. An analyzer-specific schedule should be located at each site, and all maintenance should be recorded in the site logbook or electronic logbook. Refer to the manual for a preventive maintenance checklist.

12.0 NCore Trace Level Monitoring

The National Core (NCore) multi-pollutant stations are part of an overall strategy to integrate multiple monitoring networks and measurements, including research grade sites and State and local air monitoring stations (SLAMS). Research grade sites would provide complex, research grade monitoring data for special studies; the proposed amendments do not include requirements for these sites. SLAMS would include sites needed for National Ambient Air Quality Standard comparisons and other data needs of monitoring agencies. The number and placement of SLAMS monitors would vary according to the pollutant, population, and level of air quality problem. The April 2004 draft version of the National Ambient Air Monitoring Strategy presented a taxonomy in which monitoring stations belonged to three levels, called Level 1 (research sites), Level 2 (what are called NCore multi-pollutant sites in this notice), and Level 3 (what have been called SLAMS/NAMS (national air monitoring stations) in the past). The three Levels combined were referred to as the NCore System. We have decided to dispense with the three-level taxonomy because it does not encompass all relevant monitoring efforts. The collection of all ambient air monitoring, including research sites, all types of monitoring by States and Tribes, and all types of ambient monitoring by Federal agencies is referred to as the National Ambient Air Monitoring System (NAAMS). We are retaining the “NCore” label for the multi-pollutant sites in particular, because the term with this meaning has become part of the vocabulary of the State/local monitoring community.

40 CFR 53 and 58 (1-17-06) required that States operate from one to three National Core (NCore) multi-pollutant monitoring sites. Monitors at NCore multi-pollutant sites are required to measure particles (PM_{2.5}, speciated PM_{2.5}, PM_{10-2.5}), O₃, SO₂, CO, nitrogen oxides (NO/NO₂/NO_x), and basic meteorology. Monitors for all the gases except for O₃ are required to be more sensitive than standard Federal Reference Method (FRM)/Federal Equivalent Method (FEM) monitors, so they can accurately report concentrations that are well below the respective NAAQS but that can be important in the formation of O₃ and PM.

40 CFR did not propose specific locations for these sites, but instead USEPA collaborated on site selection with States individually and through multi-state organizations. The objective is that sites be located in broadly representative urban (about 55 sites) and rural (about 20 sites) locations throughout the country to help characterize regional and urban patterns of air pollution. USEPA expect that in many cases States would collocate these new stations with Photochemical Assessment Monitoring Station (PAMS) sites already measuring O₃ precursors and/or National Air Toxic Trends Station (NATTS) sites measuring air toxics.

For sulfur dioxide (SO₂), nitrogen dioxide (NO₂), carbon monoxide (CO), and ozone (O₃), we are proposing to estimate precision and bias on confidence intervals at the site level of data aggregation rather than the primary quality assurance organization. Estimates at the site level can be accomplished with the automated methods for SO₂, NO₂, CO and O₃ because there is sufficient QC information collected at the site level to perform adequate assessments. Since the criteria pollutant data are used for very important decisions (comparison to the NAAQS), providing precision and bias estimates at upper confidence limits would provide a higher probability of making appropriate decisions. The intent of this proposed change is to move

organizations to a “performance-based” quality system. Organizations that demonstrate acceptable performance would be allowed the flexibility to reduce the frequency of certain QC checks. These agencies are expected to shift resources used for these QC checks into higher priority QA work (40 CFR 53 and 58 1-17-06).

USEPA is also proposing several QA program changes to update the existing requirements in 40 CFR Part 58 to reflect current program needs and terminology:

USEPA removed SO₂ and NO₂ manual audit checks. A review of all SLAMS/NAMS/PAMS sites by monitor type revealed that no monitoring organizations are using manual SO₂ or NO₂ methods, nor are any monitoring organizations expected to use these older technologies. Instead of the old manual methods, monitoring sites are using continuous methods to perform these audit checks. USEPA removed the manual method QC checks because the continuous check methods are covered by the current QA procedures.

USEPA changed the concentration ranges for QC checks and annual audit concentrations. The one point QC check concentrations for the gaseous pollutants SO₂, NO₂, O₃ and CO were expanded to include lower concentrations. Lower audit ranges were added to concentration ranges in the annual audit concentrations. Adding or expanding the required range to lower concentration ranges was appropriate due to the lower measured concentrations at many monitoring sites as well as the potential for NCore stations to monitor areas where concentrations are at trace ranges.

Please see Chapters 1 and 13 of this Manual for more information on NCore implementation and procedures.

12.1 NCore Monitoring Methodology for SO₂

Equipment used will be similar to current models, with added modifications to allow for higher sensitivity. Analyzers will still employ pulsed fluorescence method. See Section 3.1 in this chapter for a description of this process.

Requirements for NCore monitoring of SO₂ (include, but are not limited to):

1. Incoming sample air must not be pressurized.
2. Air flow to the sampler from the inlet sample probe must be unrestricted.
3. Air must pass through an H₂S and hydrocarbon scrubber before entering the sampler.
4. Zero air source capable of providing zero air containing concentrations lower than the instrument’s lower detection limit (LDL), at least <40 ppb SO₂.
5. NIST traceable calibration gas ±2% accuracy with nitrogen balance.

13.0 Equations

Equation 3-1

$$[\text{SO}_2]_{\text{out}} = \frac{F_{\text{SO}_2} \times [\text{SO}_2]_{\text{std}}}{F_{\text{SO}_2} + F_d}$$

Equation 3-2

Desired Recorder Response (% of scale) =

$$\frac{[\text{SO}_2]_{\text{out}} \times 100}{\text{URL}} + Z_{\text{SO}_2}$$

Equation 3-3

obsv. conc. = (resp. - zero resp.) x slope

Equation 3-4

$$\% \text{ diff} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

Equation 3-5

$$F_t = \frac{\text{vol(L)} \times 60(\text{sec/min}) \times \text{CF}}{\text{time(sec)}}$$

Equation 3-6

$$\text{CF} = \frac{(P_{\text{amb}} - P_{\text{vap}}) \times T_{\text{std}}}{T_{\text{amb}} \times P_{\text{std}}}$$

Equation 3-7

$$[\text{SO}_2]_{\text{out}} = \frac{\text{perm. rate} \times 0.382}{F_t}$$

14.0 Requirements and Definitions

1. Analyzers must be recalibrated at least once every 6 months. A valid calibration requires a minimum of 4 upscale concentrations plus a zero.
2. A valid calibration requires that any observed and standard concentration agree within $\pm 2\%$ of the range of the analyzer e.g.(0.010 ppm on a 0.5 ppm range, 0.020 ppm on a 1.0 ppm range).
3. SO₂ gas cylinders used with station calibrators must be certified once every four years and for calibrators that are taken to and from site(s) every six months. Permeation devices must be certified by IDEM-OAQ-QAS at least once every six months. Any mass flow meters used with the calibration or auditing device must be certified once every year.
4.
 - a. Zero and Span (data validation) checks are daily and precision audits are weekly on each analyzer by LEADS. For NCORE the zero/span is weekly, same as the precision.
 - b. The span (data validation audit concentration) should be between 70% and 90% of the analyzer's range. The precision audit concentration must be between 0.01 ppm and 0.10 ppm, except for NCORE which is approximately 10 ppb.
5. The percent difference data validation limits for the accuracy audit are:
 - a. $< \pm 7.5\%$ --- The analyzer is in calibration and data is valid.
 - b. $\leq \pm 15\%$ and $\geq \pm 7.5\%$ --- The analyzer is out of calibration but data is valid.
 - c. $> \pm 15\%$ --- The analyzer is out of calibration and data is invalid.
 - d. Audit levels 1&2 allow ± 1.5 ppb difference or $\pm 15\%$.
6. The percent difference for the validation(span) and precision point is $\pm 10\%$.
7. The drift limits are $\leq \pm 3.0$ ppb (24 hr) and $\leq +5.0$ ppb (>24 hr-14 day) for the zero and $\leq \pm 10\%$ for the span.
8. An accuracy audit must be performed on at least 25% of the analyzers in the network for each calendar quarter. For networks with four or fewer analyzers, an accuracy audit must be performed on each analyzer so that by the end of the year all analyzers have received one accuracy audit. Three concentrations must be run in the following ranges:
 - a. 0.0500 ppm to 0.0999 ppm
 - b. 0.1500 ppm to 0.2599 ppm
 - c. 0.2600 ppm to 0.7999 ppm

For NCORE, the accuracy ranges are in the following ranges:

- a. 8 ppb to 19.9 ppb
- b. 20 ppb to 49.9 ppb

c. 50 ppb to 99.9 ppb

Figure 1
SO₂ DILUTION SYSTEM

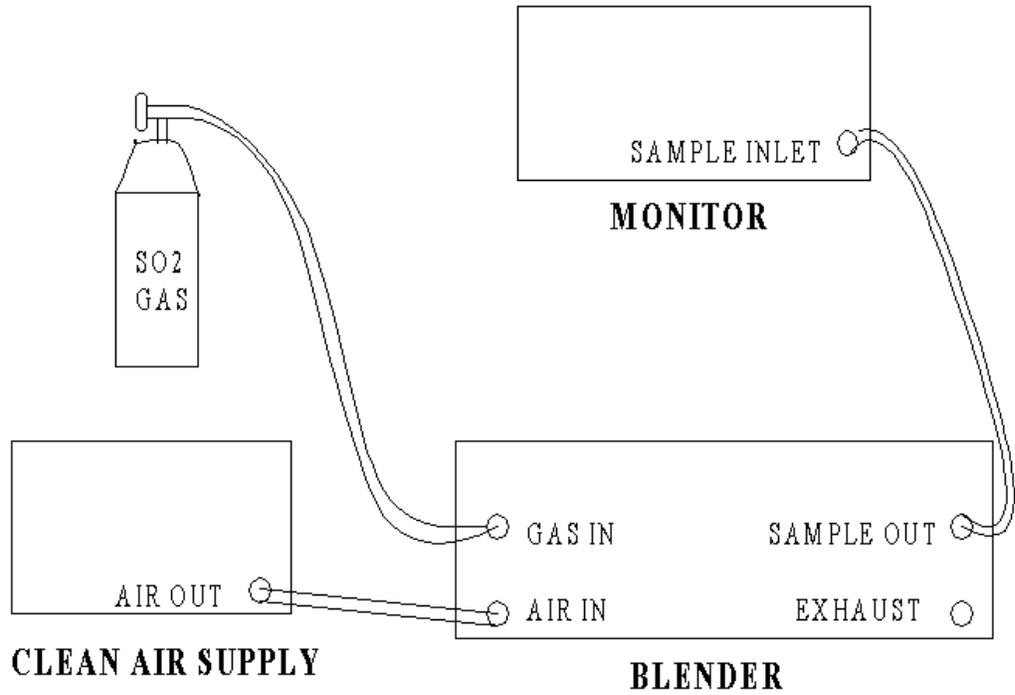
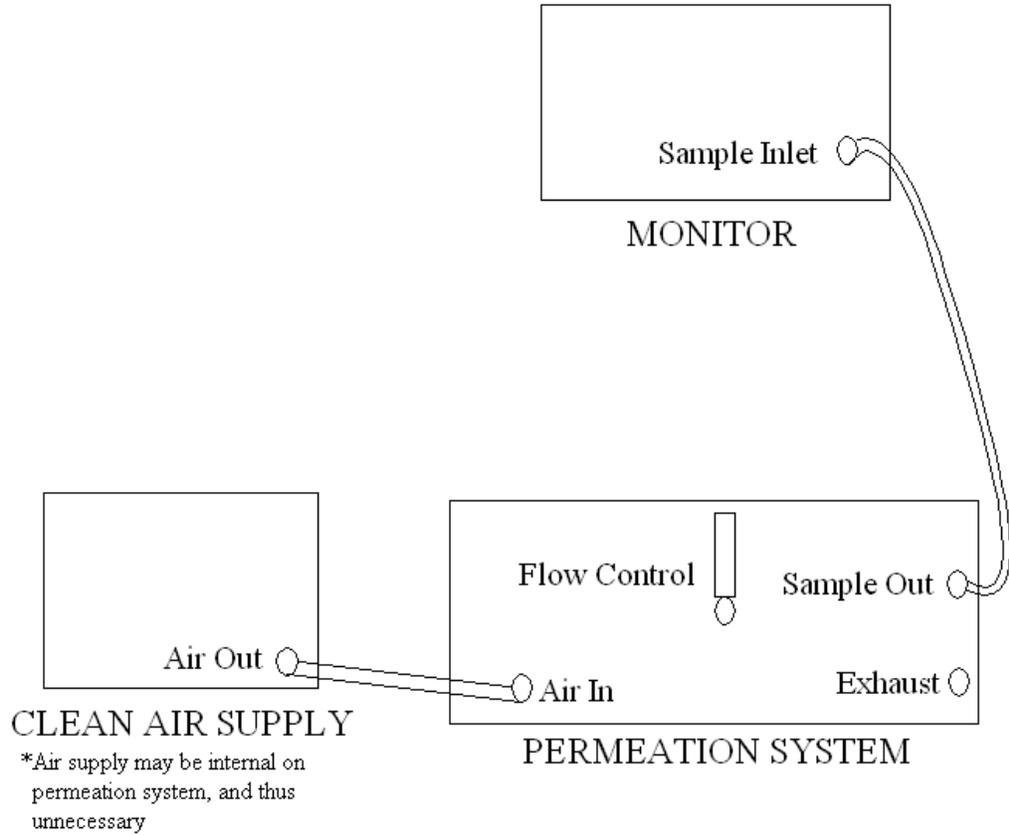


Figure 2
SO₂ PERMEATION SYSTEM



Form 1
Sulfur Dioxide (SO₂) Audit/Calibration

Site: _____ **AQS #:** _____ **Initials:** _____
Date: _____ **Start Time:** _____ **End:** _____

Analyzer Information		
Monitor Brand/Serial #: _____	Initial Zero: _____	
Initial Span: _____ Range: _____	Final Zero: _____	
Final Span: _____		
Cylinder Information		
Brand/Serial #: _____	Slope: _____	
Measured Concentration Formula: _____		
Calibration Information		
Brand/Serial #: _____	Standard Conc. Formula: _____	
Span Response: _____	Zero Response: _____	Certification Date: _____

Calibration Data

Primary Recording Device: _____ Units: _____
Secondary Recording Device: _____ Units: _____

Audit Point

Calibrator Setting	Flow From Standard @ SRC	Total Flow @ SRC	Monitor Response DVM / %	Measured Concentration	Standard Concentration	Percent Difference

Calibration Points

Form 2
Sulfur Dioxide (SO₂) Audit Sheet

Site Name: _____

Date: ___/___/___

AQS#: _____

Auditor: _____

Start Time: _____

End Time: _____

ANALYZER INFORMATION

Serial Number	Brand	Model	Cal. Date	Slope	Intercept

AUDIT DEVICE INFORMATION (if blending)

Serial Number	Brand	Model	Cert. Date	Slope	Intercept

CYLINDER INFORMATION

Serial Number	Brand	Pressure	Cert. Date	Cert. (STD) Concentration

Audit

Analyzer Response Zero: _____

Audit Display Zero: _____

Audit Point or Cylinder #	Analyzer Response	Actual Conc. In PPM	STD Cylinder Conc./ Blender Display in PPM	*Corrected Actual Conc. In PPM	Percent Difference

* Apply a Slope and Intercept to the Actual Concentration to obtain Corrected Actual Concentration

Table 1
Vapor Pressure Values (above water)

Temperature (°C) (K)	Vapor Pressure (mmHg)
15 288	12.8
16 289	13.6
17 290	14.5
18 291	15.5
19 292	16.5
20 293	17.5
21 294	18.6
22 295	19.8
23 296	21.1
24 297	22.4
25 298	23.8
26 299	25.2
27 300	26.7
28 301	28.3
29 302	30.0
30 303	31.8
31 304	33.7
32 305	35.7
33 306	37.7

Table 2
Temperature Conversion Equations

$$\text{Degrees Celsius (}^{\circ}\text{C)} = (\text{Degrees Fahrenheit (}^{\circ}\text{F)} - 32)/1.8$$

$$\text{Kelvin (K)} = \text{Degrees Celsius (}^{\circ}\text{C)} + 273$$