

Chapter 5

Sulfur Dioxide Measurement Principles and Calibration Procedures

Introduction

In this chapter, the discussion will begin with the reference and equivalent methods for the measurement of sulfur dioxide (SO₂) in the atmosphere (i.e., measurement principles) and the associated calibration procedures for these methods. Sulfur Dioxide is the only gaseous criteria pollutant for which the reference method is a manual method; requiring separate procedures for sampling and analysis. The equivalent methods for the determination of SO₂ in ambient air are currently the methods of choice since they employ automated continuous instruments.

While the obvious problems of widespread elevated concentrations have been largely solved for some criteria pollutants, problems related to particulate matter (PM), ozone (O₃), and toxic air pollutants remain. It is now clear that even very low air pollution levels can be associated with adverse environmental and human health effects. As a result, the use of highly sensitive commercial air pollutant monitors for the characterization of the precursor gases CO, SO₂, and total reactive oxides of nitrogen (NO_y) in a new national core monitoring network (NCore). The high sensitivity CO and SO₂ analyzers are fundamentally the same as those designated as Federal Reference and Equivalent methods (<http://www.epa.gov/ttn/amtic/criteria.html>), but with Precursor Gas Technical Assistance Document (TAD) modifications to improve sensitivity and accuracy or reduce interferences. The use of such precursor gas analyzers in the NCore network will still allow determination of compliance with the NAAQS, but will provide measurements at much lower detection limits than are achievable by current monitors. The implementation of high sensitivity monitoring for CO, SO₂, and NO_y in the NCore network will require installation of new analyzers at selected sites, and implementation of new monitoring, calibration, and data acquisition procedures. The purpose of Precursor Gas TAD is to provide state, local, and tribal (S/L/T) agencies with guidance on the equipment, procedures, data acquisition, and quality assurance/quality control (QA/QC) efforts needed to properly implement high sensitivity precursor gas monitoring.

A discussion of the sampling and analyzer design considerations for precursor gas monitoring will be provided following the discussion on monitoring with the traditional instruments (based on the USEPA's Equivalent methods).

High sensitivity precursor gas analyzers will increasingly be brought online; however, traditional analyzers will remain part of the NAAQS monitoring network for many years to come.

Pararosaniline Method: Reference Method for the Determination of SO₂ in the Atmosphere

The reference method for the determination of sulfur dioxide in ambient air is a wet-chemical colorimetric process involving spectrophotometric analysis. This method is referred to as the West-Gaeke Method or more commonly as the Pararosaniline Method. This is a manual method requiring the sampling of ambient air for later analysis. A brief description of the Reference Method is presented here to provide the reader with a general understanding of manual sampling for gaseous constituents.

In sampling for SO₂, ambient air is drawn through an absorber containing a solution of potassium tetrachloromercurate (TCM). Any sulfur dioxide present in the ambient air is absorbed in the solution, thereby reacting with the TCM to form a monochlorosulfonatomercurate complex, which is resistant to any further oxidation from strong oxidants which might be present in the air (e.g., ozone, oxides of nitrogen, oxygen). Sampling times are most often 30 minutes, 1 hour, or 24 hours, depending on the results desired, type of sampling, and the expected ambient SO₂ concentrations. Sampling flow rates and subsequent air volumes are dependent on sample time. A typical sampling train used to sample for SO₂ for a 24 hour period is shown in Figure 5-1.

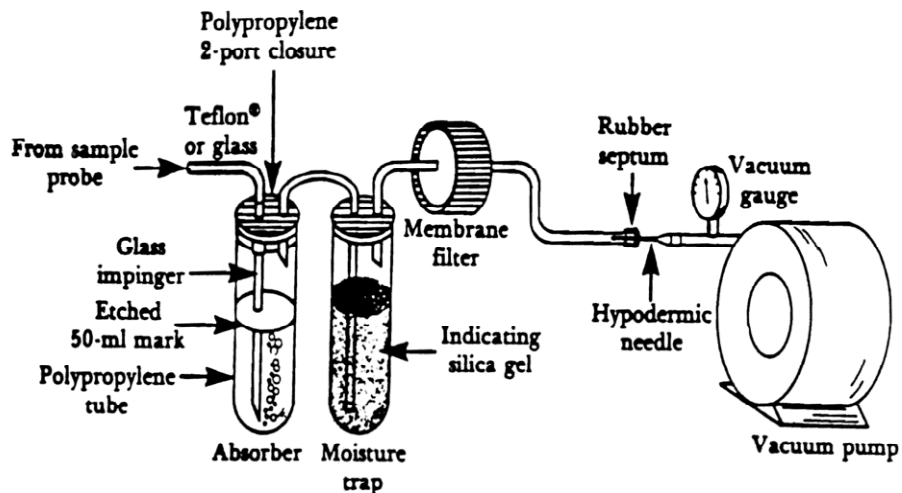


Figure 5-1 Typical 24 hour sampling train

After sampling is completed, the absorbing solution is allowed to set for 20 minutes to allow any ozone in the solution to decompose. The absorbing solution is then treated with sulfamic acid to destroy any nitrite, which results from the absorption of oxides of nitrogen from the sampled atmosphere (Pate et al. 1965). Next, the solution is treated with a 0.2% formaldehyde solution and the pararosaniline. Pararosaniline, formaldehyde, and the bisulfate anion react to form the bright pinkish-colored methyl sulfonic acid. Between 30 and 60 minutes after the addition of pararosaniline, the solution is analyzed spectrophotometrically at 548 nm, and SO₂ concentration is determined from a calibration

curve prepared using sodium sulfite-TCM standardized solutions or an SO₂ permeation tube. Additional information regarding the pararosaniline method can be found 40 CFR 50 Appendix A.

The pararosaniline method is rarely used since the advent of continuous, automated instrumental methods for sulfur dioxide with equivalent accuracy and precision of this wet-chemical reference method. Constant on-line monitoring, real-time data output, greater sensitivity, and the ability to transmit data directly into computerized data acquisition systems and/or remote telemetry systems represent major advantages of instrumental techniques.

UV Fluorescence Spectroscopic Instruments

The Ultraviolet (UV) fluorescence monitoring method for atmospheric SO₂ was developed to improve upon the flame photometric detection (FPD) method for SO₂, which in turn had displaced the pararosaniline wet chemical method for SO₂ measurement. The pararosaniline method remains the U.S. EPA's Reference Method for atmospheric SO₂, but is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as Equivalent Methods by EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity, sensitivity, and the absence of consumables, such as the hydrogen gas needed for the FPD method.

The focus of this chapter will be to discuss the automated UV fluorescence monitoring method as the measurement principle for sulfur dioxide in the atmosphere. Any analyzer that uses the specified measurement principle, meets the prescribed specification, and is calibrated in accordance with the specified calibration procedure may be designated an equivalent method by EPA. The calibration procedure consists of checking the analyzer's response by "challenging" the analyzer with known concentrations of sulfur dioxide.

Detection and Measurement Principle

Fluorescence spectroscopy is the measurement of "fluorescent" light emitted by certain molecules when excited by a radiation source of appropriate energy or wavelength. In this process, the molecule that is excited by the light energy will remain excited for about 10⁻⁸ to 10⁻⁴ seconds. This time period will be sufficient for the molecule to dissipate some of this energy in the form of vibrational and rotational motions. Because some of the original light energy is dissipated in this way, the resultant light energy emitted by the molecule is of lower energy than the original light source. Therefore, the "fluorescent" light observed from the

molecule is of a longer wavelength (shorter frequency). The wavelengths of light which excite a compound and fluoresce from it are individually characteristic of that compound and can be used to both identify and quantify it.

When using fluorescence spectroscopy for quantitative analysis, emission intensity is dependent on the total number of excited molecules and is, therefore, theoretically directly proportional to concentration. This holds true at very low concentrations; however, as concentration increases, absorption by the sample of both primary and secondary light becomes significant, finally resulting in a phenomenon called “concentration quenching”. Quenching is the process which occurs when an excited molecule collides with another molecule before it can release its extra energy as light. The energy is dissipated in the collision and, therefore, the presence of the molecule is not noted by the fluorimeter. Other gases present in a sample can also exhibit varying degrees of quenching. Due to concentration quenching, the linear plot of concentration versus instrumental response may reach a plateau and return toward baseline. When this occurs, dilution of samples is required (APHA).

To assure a measurable difference between the light absorbed and the light fluoresced, a high energy, short wavelength source of light is used in fluorescence spectroscopy instruments. This is best supplied by an ultraviolet (UV) light source.

Chemistry

Fluorescence spectroscopy has been applied to ambient air monitoring for sulfur dioxide. Sulfur dioxide absorbs light in three primary regions:

Region	Wavelength
1	390 nm to 340 nm
2	320 nm to 250 nm
3	230 nm to 190 nm

Regions 1 and 2 tend to exhibit high degrees of quenching with other molecules found in ambient air and are, therefore, not suited to SO₂ monitoring applications. Region 3 is free of quenching by air and most other molecules that would be found in ambient air. It is for this reason that the excitation energy for SO₂ fluorescence comes from Region 3.

Ultraviolet radiation in Region 3 is used to irradiate the sample gas containing SO₂. The high energy ultraviolet light is absorbed by SO₂ and excites it to SO₂^{*} by Equation 5-1:



The ultraviolet light in the system is given by Equations 5-2:

$$(Eq. 5-2) \quad I_a = I_o [1 - \text{Exp}(-a\ell[SO_2])]$$

Where: I_a = irradiating light (ultraviolet)

I_o = incident light intensity

a = absorption coefficient of SO_2

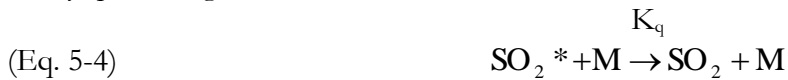
ℓ = length of light path through sample

$[SO_2]$ = sulfur dioxide concentration

The excited SO_2^* can then return to the ground state by fluorescence:



Or by quenching:



where M is the quenching species characteristic of the background air or by dissociation by Equation 5-5:



Using the above equations, an expression can be written representing the fluorescent intensity, available at the detector, from this process:

$$(Eq. 5-6) \quad I_f = \frac{K_f I_o [1 - \text{Exp}(-a\ell[SO_2])]}{K_f + K_d + K_q[M]}$$

Where:

I_f = intensity of the fluorescence

I_o = incident light intensity

a = absorption coefficient of SO_2

ℓ = length of light path through sample

$[SO_2]$ = sulfur dioxide concentration

K_f = rate constant, fluorescence

K_q = rate constant, quenching

K_d = rate constant, dissociation

$[M]$ = concentration of quenching molecules

When the SO_2 concentration is relatively low and the path length of exciting light (ultraviolet) is short, the above expression reduces to:

$$(Eq. 5-7) \quad I_f = \frac{K_f I_o a \ell [SO_2]}{K_f + K_d + K_q[M]}$$

and since K_f , K_d , K_q , $[M]$, I_o , and ℓ are constant, then:

$$\text{(Eq. 5-8)} \quad I_f \propto [\text{SO}_2]$$

the fluorescent signal (I_f) is directly proportional to the SO_2 concentration (Wolfe and Oliver 1975) (Zolner, Cieplinski, and Helm).

Apparatus

Typically, the fluorescent SO_2 analyzer can be conveniently divided into two major components: the analyzer and the electronics. The TECO 43 series analyzer serves the purpose for the following demonstration of a basic fluorescent analyzer. Figure 5-2 is a basic diagram of an SO_2 fluorescence analyzer. Sample gas enters the analyzer via a diaphragm pump and is directed through hydrocarbon “kicker,” which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO_2 molecules pass through the hydrocarbon “kicker” unaffected. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO_2 molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths which excite SO_2 molecules. As the excited SO_2 molecules decay to lower energy states they emit UV light that is proportional to the SO_2 concentration. The bandpass filter allows only the wavelengths emitted by the excited SO_2 molecules to reach the photomultiplier tube (PMT). The PMT detects the UV light emission from the decaying SO_2 molecules. The photodetector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light. The sample, upon exiting the fluorescence chamber, flows through a flow sensor, a capillary, and the shell side of the hydrocarbon “kicker.”

The “Kicker” assembly consists of the membrane tube and Teflon tube. The pump creates the vacuum between the membrane and the Teflon tube causing a differential pressure. Polynuclear Hydrocarbon (PAH) in the sample is removed while passing through membrane tube by this differential pressure.

The electronics section can be further subdivided into two main areas of interest: the ultraviolet light source, and the signal processing electronics. Early in the development of SO_2 fluorescence analyzers it was recognized that a long lived, compact, high energy UV light source would be required before the instrument would be practical for air monitoring. After considerable investigation, it was determined that a pulsed source of ultraviolet light would satisfy the requirements of high irradiation energy, long life, and small size. The original fluorescence analyzer manufactured by the Thermo Electron Corporation was termed a “pulsed-phased fluorescence SO_2 analyzer” due to the use of the pulsed source of light. Newer model fluorescence SO_2 analyzers (Beckman, Monitor Labs) use a continuous source of ultraviolet light. The light from the source is filtered by a bandpass filter to assure that the light entering the fluorescence chamber is 210 nm (remember Region 3) which

allows the most advantageous excitation of sulfur dioxide molecules. Another filter (350-nm bandpass) is used on light exiting the chamber to eliminate interference which can occur within the range of the fluorescence emission spectrum.

The signal processing section is composed of a preamplifier which converts the photovoltaic tube current pulses to voltage pulses. The amplifier then increases the voltage signals to useable levels. The signal is then filtered and routed to a meter display/recorder circuit.

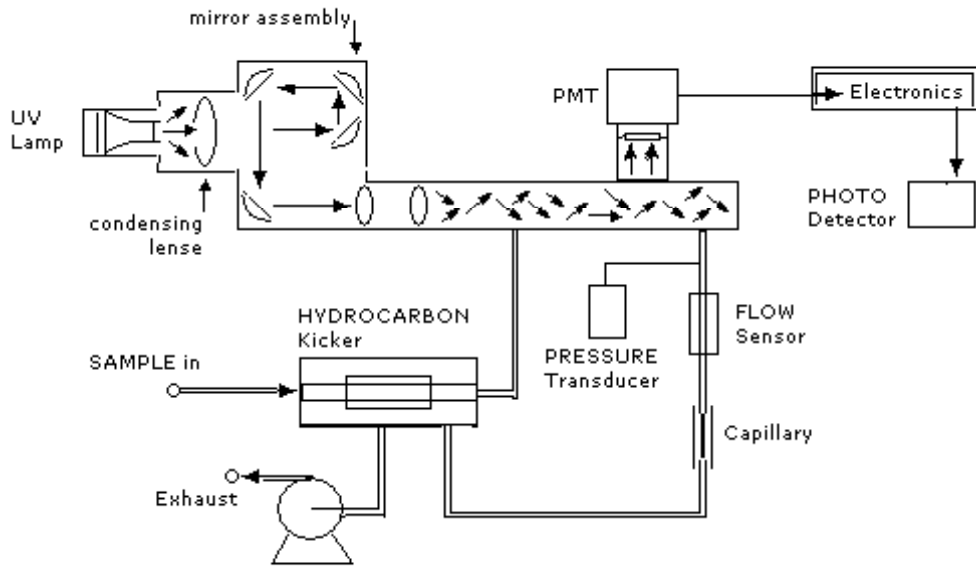


Figure 5-2. Fluorescence SO₂ analyzer. (Source: TECO Model 43C Operating Manual)

Calibration

Calibration of the instrument may be achieved by two methods: a permeation tube system or a dynamic dilution system connected to a cylinder of standardized gas. The permeation method uses the same equipment and setup as shown in Chapter 4 - *Generation of Test Atmospheres*. At least four concentrations of sulfur dioxide within the working range of 10 to 95% full scale and zero air are introduced to the analyzer. The instrument's response is compared to the standards introduced, and the instrument is adjusted to give accurate readings. Frequent (once a day) zero and single point calibration checks (80% full scale) are prudent after the instrument is placed in service. Calibration should be carried out under the same conditions as are found when analyzing ambient concentrations. Refer to the instrument's operation manual for more detailed and specific calibration procedures.

Calculations

Sulfur dioxide analyzers generally read out directly in ppm. Before the direct concentration readout is utilized, it is necessary to calibrate the analyzer using known concentrations of gases. If it is necessary to convert SO₂ concentrations from ppm to milligrams per cubic meter (mg/m³), the following conversion factor can be used:

$$\text{(Eq. 5-9)} \quad \frac{\text{mg SO}_2}{\text{m}^3} = \text{ppmSO}_2 \times 2.61$$

If the analyzer does not readout in ppm, but rather in $\frac{\text{mg SO}_2}{\text{m}^3}$, the following factor can be used to derive the ppm SO₂ concentration:

$$\text{(Eq. 5-10)} \quad \text{ppmSO}_2 = \frac{\text{mg SO}_2}{\text{m}^3} \times 0.388$$

Calibration Procedure

Calibration consists of determining the response of the instrument to various known concentrations of sulfur dioxide generated and preparing calibration curves or tables. Calibration of the instrument may be achieved by two methods: a permeation tube system or a dynamic dilution system connected to a cylinder of standardized gas. Refer to Chapter 4 - *Generation of Test Atmospheres*, for further details regarding dynamic dilution and/or permeation techniques to generate calibration standards. The analyzer is set up in its sampling mode and “zero” gas is introduced via the analyzer’s sampling line. The zero adjustment control is set to give an instrument readout reflecting zero concentration. An SO₂-free (< 0.0005 ppm) air supply is required for the proper calibration and evaluation of the analyzer. There are several methods that are acceptable to generate this zero gas (Chapter 4 - *Generation of Test Atmospheres*).

The next step in calibration is the introduction of the span gas. This gas should have a SO₂ concentration that is approximately 80% of the instrument’s operating range (e.g., 80% of an upper range limit – URL, value of 0.500 ppm is 0.400 ppm). The instrument’s span adjustment control is set so that the instrument’s output reflects the span gas concentration. At least three other concentrations of sulfur dioxide covering the analyzer’s operating range are then introduced to check linearity of response. SO₂ cylinder gases may consist of SO₂ and dry nitrogen if they are to be diluted to at least 100:1 with air when preparing calibration gases. The nominal concentration for a cylinder of SO₂ is 50 ppm. Standard Reference Materials (SRMs) or gaseous standards traceable to SRMs are required for calibrating and auditing ambient air and stationary source pollutant monitoring systems. Refer to the document, EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, for further details regarding EPA Standard Reference Materials (SRMs). If a data

recorder is used with the analyzer, it should be adjusted to reflect the calibration standards. A calibration curve should be prepared for each instrument calibration. The instrument's operating manual should be consulted for additional recommendations concerning calibration.

Frequent (once a day) zero and single point calibration checks (80% full scale) are prudent after the instrument is placed in service. Calibration should be carried out under the same conditions as are found when analyzing ambient concentrations.

Method Characteristics and Capabilities

Advantages

These instruments are well suited to ambient air monitoring in that they have a fairly rapid response time, require no ancillary equipment or reagents, and are relatively insensitive to changes in temperature and flow variations. Fluorescence SO₂ monitors have proven to be reliable and maintenance free for extended periods. Unlike flame photometric analyzers, they are capable of being located in areas where flammable gases would cause a hazard.

Interferences

The principle interferences to the fluorescence technique include water vapor, oxygen, and aromatic hydrocarbons. Water vapor and oxygen act as interferences in that they quench the fluorescence emissions resulting in the instrument reporting a lower than true SO₂ concentration. Interference by water can be alleviated using a drying element on the sample gas. Some manufacturers utilize a permeation dryer (e.g. Nafion dryer) to remove vapor phase moisture (which results in quenching) from the gas stream while leaving the SO₂ molecules unaffected. The dry gas then enters the fluorescence chamber. After the sample air exits the chamber it passes over the outside of the permeation dryer; regaining the moisture removed, and is then passed to the outside air unaltered, thereby keeping it continuously regenerated. More commonly in modern SO₂ instruments, water interference is minimized by selection of the incident wavelength used for measurement.

The effect of oxygen quenching can be minimized by maintaining identical oxygen concentrations in the calibration gases as found in the air sampled.

Certain aromatic hydrocarbons will fluoresce at the same wavelength band as SO₂, thereby giving high results. The most significant of these is a class of hydrocarbons called polynuclear aromatic hydrocarbons (PAH); of which naphthalene is a prominent example. Xylene is another hydrocarbon that can cause interference. These hydrocarbons can be eliminated from the sample gas by use of hydrocarbon "kicker" upstream of the reaction chamber. These devices operate on a selective permeation principle, allowing only hydrocarbon molecules to pass through the tube wall, while allowing SO₂ molecules to pass through unaffected. The driving force for the hydrocarbon removal is the differential partial pressure across the wall. This differential pressure is produced within the instrument by

passing the sample gas through a capillary tube to reduce its pressure and feeding it into the shell side of the hydrocarbon kicker. These devices are non-serviceable. If malfunction is suspected a leak check should be performed based on manufacturer's instructions and the device replaced if it fails the test.

Nitrogen oxide (NO) also fluoresces in a spectral range close to SO₂. Interference from NO is addressed by the presence of the band pass filter, which allows only the wavelengths emitted by the excited SO molecules to reach the PMT.

Range and Sensitivity

Fluorescence SO₂ monitors have a potential range of 0.2 to 250 mg/m³ (0.050 ppm to 100.0 ppm).

Problems, Precautions, Troubleshooting

Fluorescence SO₂ monitors are characteristically dependable, low-maintenance instruments. Some areas where problems do arise are the following:

As mentioned in the section on flame photometric SO₂ analyzers, the photomultiplier tube can degrade and periodically needs replacing. Again, if the pmt is replaced, then "burning in" of the pmt is necessary before the instrument is brought on line again.

A lowering of response in a fluorescence analyzer may indicate that the ultraviolet light source needs replacing. This can be determined by injecting a low level known concentration SO₂ gas and noting if the response is lower than normal. Another cause of lowered response is increased quenching due to moisture or dirt in the fluorescence chamber. This can be alleviated by cleaning the chamber (see instructions in the analyzer's operating manual) and then replacing the permeation dryer, if so equipped. Ensure that an appropriate filter is in place at the sample inlet. The instrument's automated diagnostic system and the operating manual are the best source for aids in troubleshooting and maintenance.

Prior to undertaking extensive troubleshooting procedures, realize that many instrument malfunctions are related to system or subsystem flow leaks.

Quality Assurance

Quality assurance is in important consideration of monitoring. The requirements of a QA program for all types of reference and equivalent methods are contained in the following:

Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1

High Sensitivity SO₂ Analyzer – Precursor Gas Monitoring

Since the high sensitivity SO₂ analyzers deployed at NCore sites are intended to monitor low ambient SO₂ concentrations, it is important that they meet a variety of performance criteria. Many of these performance criteria are more stringent than those for routine SO₂ analyzers; consequently, a number of features are required in the high sensitivity SO₂ analyzers in order to achieve the performance criteria.

The following section describes the recommended performance criteria and the analyzer features that are recommended in order to achieve the performance criteria at the NCore sites.

Recommended Method Performance Criteria

The U.S. EPA has recently assessed the measurement quality objectives needed for high sensitivity precursor gas monitoring in NCore, relative to the long-established statistics stated in 40 CFR 58. In particular, EPA recommends that measurement quality objectives for bias and precision be based on upper confidence limits at the monitoring site level, to provide a higher probability of reaching appropriate conclusions (e.g., in comparisons to NAAQS). The intent of this recommendation is to move S/L/T agencies to a performance-based quality system i.e., allowing organizations that show tight control of precision and bias to reduce the frequency of certain QC checks, and to focus their quality system efforts where most needed.

The U.S. EPA recommends that the high sensitivity SO₂ analyzers that are deployed at NCore sites meet the following method performance criteria. Additional details regarding these criteria can be found in USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, (EPA-454/R-05-003).

Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. Precision is assessed from checks that are performed at least once every two weeks and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity SO₂ analyzers have a 95 percent probability limit for precision of ± 15 percent or less. Calculation of precision starts with the comparison of the known challenge concentration used in the precision checks to the corresponding measured concentrations reported by the analyzer.

Bias

Bias is defined as a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias is assessed from the degree of agreement between a measured value and the true, expected, or accepted value. Analyzer bias is calculated using comparisons of known challenge concentrations to the corresponding measured concentrations reported by the analyzer. The challenge comparisons used to assess bias should be the same as those used to assess precision. It is recommended that high sensitivity SO₂ analyzers have an upper bound for the average bias of ± 15 percent or less.

Representativeness

Representativeness refers to whether the data collected accurately reflect the conditions being measured. It is the data quality indicator most difficult to quantify. Unless the samples are truly representative, the other indicators are meaningless. Representativeness for monitoring of low ambient levels of SO₂ in NCore is different than for routine monitoring, since the objectives of the monitoring are much different. Representativeness can only be assured in terms of the appropriate selection of the sampling site, proper implementation of ambient air sampling, and reasonable coverage of the sampling schedule (i.e., 24 hours per day, 7 days per week, ideally).

Completeness

Completeness is defined as the amount of data collected relative to the total expected amount. Ideally, 100 percent of the expected amount of data would always be collected; in practice, completeness will be less for many reasons, ranging from calibration time and site relocation to power outages and equipment failure. For monitoring of ambient SO₂ concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

Comparability

Comparability is defined as the process of collecting data under conditions that are consistent with those used for other data sets of the same pollutant. The goal is to ensure that instruments purchased and operated by different states and local agencies produce comparable data. To promote comparability, the USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, (EPA-454/R-05-003) describes the recommended characteristics of high sensitivity SO₂ analyzers and the procedures for their installation and use.

Method Detection Limit

The *method detection limit* (MDL) refers to the lowest concentration of a substance that can be reliably determined by a given procedure. The MDL is typically not provided by the vendor. Based on the objectives of the Precursor Gas Program, it is expected that most sites will be measuring pollutant concentrations at lower ranges than the typical SLAMS/NAMS network. Therefore, the ability to quantify concentrations at these lower levels will be very important. The use of a vendors advertised LDL is sufficient to make intelligent purchasing

decisions; however, vendors quantify LDLs under ideal conditions and therefore one might consider this value as the best possible detection that can be achieved.

As these monitors are deployed into monitoring networks, where both environmental conditions, equipment (calibration, dilution devices, sampling lines, gaseous standards) and operator activities can vary, it is important to estimate what pollutant concentrations can truly be detected, above background noise (the potential conditions mentioned above). The site specific MDL establishes an estimate based on the routine operation (and conditions) of that instrument in the network and provides a more meaningful evaluation of data as it is aggregated across the precursor gas network.

It is recommended the MDL for high sensitivity SO₂ analyzers be established prior to putting the analyzers into service, and should be 0.0003 ppm (0.30 ppb) or lower over an averaging time of no more than 5 minutes.

Lower Detectable Limit

The *Lower Detectable Limit (LDL)* is the minimum pollutant concentration that produces a signal of twice the noise level. To estimate the LDL, zero air is sampled and the noise level of the SO₂ readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive range of high sensitivity CO analyzers should be 0.0002 ppm (0.20 ppb) or lower, over an averaging time of no more than 5 minutes.

Linear Range

The *linear range* of each high sensitivity SO₂ analyzer should extend from approximately 0.20 ppb to at least 100 ppb. Users should determine if their range should exceed 100 ppb and adjust accordingly. Note that some high sensitivity SO₂ analyzers can operate simultaneously on a number of ranges, with each range recorded on a separate data logger channel with its own calibration curve. Although requiring slightly more effort to calibrate and maintain, recording of multiple ranges would allow capture of a wide range of SO₂ concentrations.

Zero/Span Drift

Zero drift is defined as the change in response to zero pollutant concentration, over 12- and 24-hour periods of continuous unadjusted operation. Span drift is defined as the percent change in response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation. Zero and span drift specifications should be obtained from the vendor prior to putting a high sensitivity SO₂ analyzer into service. Such SO₂ analyzers should have 12- and 24-hour zero drift less than 0.20 ppb, and should have a span drift of less than ± 1 percent of the full scale measurement range of the analyzer per 24 hours.

NO Rejection Ratio

The NO rejection ratio refers to the effectiveness with which fluorescent emission from nitric oxide (NO) is blocked in a UV fluorescence SO₂ analyzer. This interfering emission

can be greatly reduced by optical filtering of the light reaching the PMT. For high sensitivity SO₂ monitoring in NCore, it is recommended that the NO rejection ratio of the SO₂ analyzer be at least 100 to 1, i.e., 100 ppb of NO must produce a response equivalent to that from no more than 1 ppb of SO₂.

Recommended Features for High Sensitivity SO₂ Measurements

Continuous UV fluorescence SO₂ analyzers are commercially available from a number of vendors. The design of these analyzers is similar among vendors with some slight variations. A schematic diagram of a typical high-sensitivity fluorescence instrument is essentially the same as that of a traditional or routine fluorescence instrument (Figure 5-2). In general, analyzers contain the following systems:

1. *Pneumatic System:* This portion of the analyzer consists of sample probe, sample inlet line, particulate filter, hydrocarbon scrubber/kicker, dryer (if needed), sample cell, flow meter, and pump, all used to bring ambient air from the inlet to the detector.
2. *Analytical System:* This portion of the analyzer consists of the UV source with the associated source filters, lenses, and optics, as well as the light baffles, the detector (photomultiplier tube), and bandpass filters.
3. *Electronic Hardware:* This portion of the analyzer consists of the electronic components that control the analyzer and process the signals. This part of the analyzer generally requires little or no maintenance. If the instrument is operated outside the manufacturer's recommended temperature range, however, individual integrated chips can fail and cause problems with operation, data storage, or retrieval.

In addition to these general systems, the high sensitivity versions of the commercial UV fluorescence SO₂ analyzers typically have the following features that allow them to measure SO₂ at sub-ppb levels:

1. A high intensity pulsed UV light source that provides a greater degree of sensitivity;
2. Multiple reflective optical filters that allow only light at the wavelength causing excitation of the SO₂ molecules to enter the optical chamber, while excluding all light at wavelengths that may cause interference; and,
3. Optical filtering to maximize the rejection of fluorescence from NO molecules.
4. A hydrocarbon "kicker" which removes aromatic hydrocarbons from the sample (by forcing the molecules to permeate through the tube wall), allowing SO₂ molecules to pass through the "kicker" unaffected.

It is recommended that the high sensitivity SO₂ analyzers deployed in NCore employ these features.

Potential Problems and Solutions

This section describes several of the potential problems associated with precursor SO₂ measurements, and discusses the practical solutions to these problems, many of which the SO₂ analyzer vendors have already implemented in their analyzers.

The following sections describe several potential positive and negative sources of interference or bias. In each section recommended procedures to minimize these interferences or sources of bias are described.

Sources of Positive Interference or Bias

Positive interference in precursor SO₂ monitoring can result from other gases in the sample that happen to fluoresce at the same wavelength as SO₂. Perhaps the most prevalent sources of this type of interference are volatile aromatic (e.g., xylenes) and poly-nuclear aromatic (PNA) (e.g., naphthalene) hydrocarbons. Such compounds absorb UV photons and fluoresce in the region of the SO₂ fluorescence. Consequently, any such aromatic hydrocarbons that are in the optical chamber can act as a positive interference. To remove this source of interference, the high sensitivity SO₂ analyzers have hydrocarbon scrubbers or “kickers” to remove these compounds from the sample stream before the sample air enters the optical chamber, as discussed earlier in this chapter regarding traditional, routine analyzers.

Another potential source of positive interference is nitric oxide (NO). NO fluoresces in a spectral region that is close to the SO₂ fluorescence. However, in high sensitivity SO₂ analyzers, the bandpass filter in front of the PMT is designed to prevent NO fluorescence from reaching the PMT and being detected.

Care must be exercised when using multi-component calibration gases containing both NO and SO₂ that the NO rejection ratio of the SO₂ analyzer is sufficient to prevent NO interference.

The most common source of positive bias (as opposed to positive spectral interference) in high sensitivity SO₂ monitoring is stray light reaching the optical chamber. Since SO₂ can be excited by a broad range of UV wavelengths, any stray light with an appropriate wavelength that enters the optical chamber can excite SO₂ in the sample and increase the fluorescence signal. Furthermore, stray light at the wavelength of the SO₂ fluorescence that enters the optical chamber may impinge on the PMT and increase the fluorescence signal. The analyzer manufacturers incorporate several design features to minimize the stray light that enters the chamber. These features include the use of light filters, dark surfaces, and opaque tubing to prevent light from entering the chamber.

Sources of Negative Interference or Bias

Non-radiative deactivation (quenching) of excited SO₂ molecules can occur from collisions with common molecules in air, including nitrogen, oxygen, and water. During collisional quenching, the excited SO₂ molecule transfers energy kinetically allowing the SO₂ molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO₂ fluorescence and results in the underestimation of SO₂ concentration in the air sample.

The concentrations of nitrogen and oxygen are constant in the ambient air, so quenching from those species at a surface site is also constant, but the water vapor content of air can vary. Despite this variability, in routine ambient monitoring the effect of water vapor on SO₂

fluorescence measurements is negligible. Only if high or highly variable water vapor concentrations were a concern (as in source sampling), should it be necessary to dry the sample air using optional equipment available from the analyzer vendors.

Condensation of water vapor in sampling lines must be avoided, as it can absorb SO₂ from the sample air. The simplest approach to avoid condensation is to heat sampling lines to a temperature above the expected dew point, and within a few degrees of the controlled optical bench temperature. An alternative approach would be to maintain all sampling lines at reduced pressure by locating the analyzer's critical orifice at the sample inlet point.

The positive and negative interferences discussed here, in many cases, are common to both the high sensitivity and traditional routine analyzers; however, as a percentage of the measured SO₂ concentration their influence is much greater for the high sensitivity analyzer.

Calibration Equipment

The equipment required for calibration of a high sensitivity SO₂ analyzer includes a MFC calibrator unit, and a source of zero air. The following equipment is recommended for calibration of a high sensitivity SO₂ analyzer.

Calibration Standard and Standard Delivery System

The calibration standards used for the calibration of high sensitivity SO₂ analyzers should be generated by dilution of a commercially-prepared and certified compressed gas SO₂ standard using a MFC calibration unit. That commercially-prepared standard may contain only SO₂ in an inert gas (e.g., N₂), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). However, note the caution regarding potential NO interference in mixed standards containing SO₂ and NO mentioned previously.

It is important when purchasing a MFC calibrator that it meets the 40 CFR 50 requirements of ± 2 percent accuracy, and that the flow rates of both MFC channels are calibrated using a NIST traceable flow standard.

When the analyte concentration in the commercially-prepared standard cylinder is certified by reference to NIST standards, and the MFCs are calibrated to NIST-traceable standards, the resulting working gas concentration is considered to be NIST-traceable.

Refer to Chapter 4 - *Generation of Test Atmospheres*, for more detail regarding the MFC dynamic calibration units and the traceability of calibration standards.

Zero Air Source/Generator

Zero air is required for the calibration of precursor SO₂ instruments. This air must contain no detectable SO₂ (i.e., SO₂ content must be less than the LDL of the SO₂ analyzer) and be free of particulate matter. Suitable zero air may be supplied from compressed gas cylinders

of purified air. However, it may be expensive to maintain a sufficient supply of zero air cylinders to operate a precursor SO₂ analyzer continuously. As an alternative, many commercially available zero air generation systems can supply suitably SO₂-free air.

To ensure that the zero air used is free from contaminants, the SO₂ analyzer should be independently supplied with zero air from different sources. If the analyzer responds differently to the different sources, generally the source with the lowest response is the highest quality source. Confirmation of zero air quality can be achieved using various additional scrubbing traps. For example, ambient air can be scrubbed of SO₂ using a 24 x 7 purged activated carbon. The carbon type used for scrubbing is important; Barnebey & Sutcliffe Corp. (formerly Barnebey-Cheney, Columbus, Ohio, www.bscarbon.com), type GI, has been shown to work well.

As an alternative to using an activated carbon scrubber, a sodium carbonate coated denuder, such as the Sunset Laboratory Model #DN-315 stainless steel concentric denuder, can be used.

Alternatively, a cartridge of soda lime attached to the outlet of the zero air system will last for extended periods (potentially over one year) and maintain SO₂ at less than 0.05 ppb.

Note: For zero-air sources based on removing SO₂ by means of soda lime, charcoal, or a denuder as described above, the inlet air must be outside ambient air rather than instrument shelter air. Contaminant levels inside the shelter may greatly exceed those in outside air. Also to the extent possible, the components of the zero-air system should be free of materials that might outgas hydrocarbons.

Reagents and Standards

Routine operation of high sensitivity SO₂ analyzers requires the use of calibration standards and zero air to conduct periodic calibrations and instrument checks. This section describes the requirements for these gases.

Calibration Standards

The primary SO₂ standards used must be certified, commercially-prepared compressed gas standards, with a certified accuracy of no worse than ± 2 percent. SO₂ gas standards of 10 to 20 ppm are conveniently diluted with a MFC calibrator down to working concentrations of 20 ppb or less. The commercially-prepared standard may contain only SO₂ in an inert gas (e.g., N₂), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). The potential for NO interference must be kept in mind if a standard containing both SO₂ and NO is used for SO₂ calibration. It is critical when placing an SO₂ gas standard into service that the cylinder regulator be fully purged to avoid the effect of trace moisture on the delivered SO₂ concentration.

Evacuating the regulator by means of a vacuum line attached to the regulator outlet, before purging for a few minutes with the cylinder gas, is an effective procedure to dry and condition the regulator.

Every gas standard used in precursor gas monitoring must be accompanied by a certificate of calibration from the vendor stating the concentration of the standard, the uncertainty of that certification, and the expiration date of the certification. Standards traceable to NIST are preferred. Certification documents for all standards must be retained in a common location and reviewed periodically so that standards for which the vendor's certification has expired may be removed from service and replaced.

Zero Air

Zero air used as dilution gas for calibration purposes should have an SO₂ concentration below the LDL of the SO₂ analyzer. Multiple zero air sources should be checked, and soda lime, charcoal, or sodium carbonate scrubbers may be necessary to achieve adequate zero air quality. A canister of soda lime followed by a particle filter on the outlet of the zero air source will remove SO₂ for extended periods. Breakthrough can be tested by temporarily adding a carbonate denuder and observing zero gas readings.

Quality Control

A through quality control program is critical to the collection of high sensitivity SO₂ monitoring data and must be implemented at each NCore site. Components of such a program are described below.

Site Visit Checklists and Remote Diagnostic Checks

To determine whether the SO₂ analyzer is working properly, field operators should conduct routine checks of instrument diagnostics and performance every time they visit the monitoring station. Each agency needs to develop diagnostic or maintenance checklists or electronic spreadsheets to document that all required checks have been made. Such lists and sheets should be useful both for collecting diagnostic information and for assessing the quality of the monitoring data. To the extent possible, diagnostic checks can be done remotely, provided the data acquisition system allows remote access to instrument diagnostic information.

Multipoint Calibrations

A multipoint calibration includes a minimum of four points (three spaced over the expected range and a zero point), generated by the calibration system. Although more points may be preferable, current high sensitivity SO₂ analyzers provide inherently linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the precursor SO₂ analyzer being put into service and at least every six months thereafter. An analyzer should be calibrated (or recalibrated) if any of the following conditions occur:

1. Upon initial installation;

2. The Level 1 span check or precision check difference exceeds 15 percent;
3. After repairs or service is conducted that may affect the calibration;
4. Following physical relocation or an interruption in operation of more than a few days;
5. Upon any indication that the analyzer has malfunctioned or a there has been a change in calibration; or,
6. The measured concentration values during challenges with performance test (audit) samples differ from the certified standard values by ± 15 percent. (Generally this challenge is conducted as a blind audit, such that the site operator is not aware of the gas standard concentrations delivered to the analyzers.)

The analyzers should be calibrated *in-situ* without disturbing the normal sampling inlet system to the degree possible.

Level 1 Zero/Span Checks

Level 1 zero and span calibrations are simplified, two-point calibrations used when adjustments may be made to the analyzer. When no adjustments are made to the analyzer, the Level 1 calibration may also be called a zero/span “check” and must not be confused with a level 2 zero and span check. Level 1 zero and span checks should be conducted nightly if the calibration system and SO₂ analyzers used can be programmed to automatically perform these. They are used to assess if the analyzers are operating properly and to assess if any drift in instrument response has occurred.

The zero/span calibrations are conducted by challenging the analyzer with zero air and a test atmosphere containing SO₂ at a concentration of between 70 percent and 90 percent of the full measurement range in which the analyzer is operating. The challenge gas should be sampled through as much of the sampling inlet system as practical to mimic the actual sampling of ambient air.

The results of the Level 1 zero/span check should be plotted on control charts to graphically illustrate the trends in the response of the analyzer to the challenge gases. The span check should not exceed ± 15 percent and the zero drift should not exceed ± 0.5 percent of full scale. If the measured concentrations fall outside of the control limits, the accuracy of the MFC calibration system should be checked with a NIST-traceable flow standard. If the MFC flow accuracy is confirmed, the data recorded since the last successful Level 1 check should be flagged and the analyzer should be recalibrated using the multipoint calibration procedures as described earlier in this section; in conjunction with the procedures in the instrument’s operating manual.

State-of-the-art calibration equipment now exists that is fully automated. These "new generation" calibration units are fully integrated with computers, mass flow calibrators, and

the associated hardware and software where they can create test atmospheres manually or automatically. For the precursor gas program, it is recommended that the NCore sites have fully automated calibration capability. Below are a number of reasons why this is advantageous:

- By performing the calibrations or checks automatically, agencies no longer spend the manpower needed to perform them.
- Automated calibrations or checks can be triggered internally or by a DAS. Since newer DASs allow remote access; this allows a remote user to challenge the analyzers without actually being present.
- High sensitivity precursor gas analyzers are expected to have more zero and span drift than less sensitive analyzers; therefore, it is important that a zero and Level I check be performed daily.
- New generation DASs can record calibration data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

Precision Checks

At least once every two weeks a precision check should be conducted by challenging the SO₂ analyzer with a known low SO₂ concentration to assess the performance of the analyzer. The precision checks should be conducted by challenging the SO₂ analyzer with a standard gas of known concentration between 10 and 50 ppb. After completion of the precision check, the operator should calculate the percent difference between the measured value and the known standard value. Precision should be calculated quarterly, using the calculated percent differences from the precision checks (For more detail on calculating precision, refer to Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4, EPA-454/R-05-003). For acceptable precision to be maintained it is recommended that the calibration system's gas flows be verified frequently against a NIST flow standard, and adjusted if necessary before making any adjustments to the analyzer.

Preventive Maintenance and Troubleshooting

Long-term operation of continuous high sensitivity precursor gas analyzers requires a preventive maintenance program to avoid instrument down-time and data loss. This section briefly describes several key items that might be included in the preventive maintenance program established for high sensitivity SO₂ analyzers deployed at NCore sites, as well as some of the troubleshooting activities that may be useful in resolving unexpected problems with these analyzers. This discussion is not meant to be exhaustive or comprehensive in detail. More thorough discussions can be found in the analyzer operation manuals, and should be included in SOPs developed for these analyzers. Example SOP's prepared by EPA are included as Appendix B of the Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003).

Preventive Maintenance

Routine preventive maintenance procedures should be in place to prevent down-time and data loss. Management and field operators should jointly develop their preventive maintenance program. A program designed by persons unfamiliar with analyzer operations may include unnecessary items or omit mandatory ones. Several factors linked to shelter and sampling manifold design can contribute to data loss. SO₂ values can be low if the sample probe, manifold, and lines are dirty, cracked, or leaky. The sample probe and manifold should be cleaned at least every six months. Sampling lines should be replaced every two years. Teflon® filters used in the sampling train to remove fine particles may need to be replaced as often as every week, depending on the condition of the filter and the particulate loading around the monitoring site.

Table 5-1 illustrates items that monitoring agencies should include in their preventive maintenance program for high sensitivity SO₂ monitoring.

Item	Schedule
Replace particle filter	Weekly
Replace internal span permeation tube (if applicable)	Annually
Perform pneumatic system leak check	At least quarterly
Inspect internal, external tubing; replace if necessary	At least quarterly
Rebuild or replace pump	Annually
Replace UV lamp	As needed
Clean optic bench	As needed
Replace PMT	As needed

In addition to a schedule, the preventive maintenance plan should also include more detailed task descriptions, such as illustrated below:

- Because the analyzer pneumatic system requires so much preventive maintenance, the tubing, solenoids, and pump should be inspected regularly. Cracked tubing or loose fittings can cause the instrument to analyze room air rather than ambient air and lead to invalid data. A faulty pump can also cause problems with pneumatic systems. When oscillations in the flow rate force the operator to adjust the flow continually, the pump is failing and should be either repaired or replaced. The pump should be rebuilt or replaced when it is unable to maintain a vacuum of at least 25 inches of Hg.
- Check the instrument for vibration. When pumps get old, they sometimes will vibrate more than is normal. If this occurs, it can cause cracks if the tubing is touching another surface.
- Consult the analyzer operations manual for complete details on operation and maintenance.

Troubleshooting

High sensitivity SO₂ analyzers are subject to many factors that can cause inaccurate measurements or down-time. Table 5-2 summarizes common problems seen with high sensitivity SO₂ analyzers, their possible causes, and possible solutions. More specific information can be found in the manufacturer's operations manual.

Table 5-2. Instrument troubleshooting for precursor SO₂ analyzers.

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty optics	Clean optics bench
	PMT failure	Replace PMT
High positive zero drift	Defective bandpass filter	Replace filter
	PMT failure	Replace PMT
No response to span gas	UV source is defective	Replace UV lamp
	UV power supply defective	Replace UV power supply
	PMT failure	Replace PMT
Zero output at ambient levels	Pump failure	Check pump
	UV lamp failure	Replace UV lamp
	UV power supply defective	Replace power supply
	PMT failure	Replace PMT
No flow through analyzer	Pump failure	Replace/ rebuild pump head

When troubleshooting, an operator must constantly be aware of environmental factors that may affect the instruments. Environmental factors can also cause sporadic problems that can be difficult to diagnose. Examples of factors that may affect the performance of the high sensitivity SO₂ analyzers are:

- Variable shelter temperature (fluctuations greater than several degrees);
- Excessive vibration from other equipment;
- Voltage instability (e.g., fluctuations in the 110 VAC line voltage);
- Air conditioning system blowing on the instrument; and,
- Frequent opening of the door of the shelter.

References

NOTE: REFERENCES WERE NOT PROVIDED BY THE AUTHORS OR WERE DELETED FOR THIS CHAPTER (EPA 464, July 1983).

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