WBEA – Standard Operating Procedure

SOP Title	**Procedures for operating continuous Sulphur Dioxide analyzers**
SOP Number	**WBEA SOP-ANA-001 SO2**
Author	**Gary Cross**
Implementation date	**February 8 2013**

Revision History

Revision #	Date	Description	Author

Table of Contents

Introduction and Background

This document is intended to be used as a reference for use in the calibration, maintenance and operation of continuous Sulphur Dioxide analyzers in ambient air. The proper utilization of this procedure in conjunction with the operators manual will conform to the current Alberta Air Monitoring Directive (AMD) and enable the data to be included in provincial and national air quality data bases

Principle of the Method

The primary detection principle utilized in Sulphur Dioxide analyzers is Ultra Violet (UV) fluorescence. Where a valence electron absorbs UV at a wavelength of 214 nm and enters an excited state. When the electron drops back into its usual state, a photon is emitted at a lower energy wavelength of 390 nm.

Specifically;

$$SO_2 + hv_1 \rightarrow SO_2^* \rightarrow SO_2 + hv_2$$

$*$	=	*Excited State*
hv_1	=	*Exposure Light @ Excitation Wavelength*
hv_2	=	*Emitted Light @ Emission Wavelength*

The light emitted by the decaying SO_2 electrons is filtered and channeled into a photo multiplier tube (PMT) amplified and converted to an electrical signal. The electronics system in the analyzer then conditions the PMT signal in order to output an SO_2 voltage response which can be scaled into appropriate units.

Measurement Range and Sensitivity

The SO_2 analyzers used in this method are commercially available models. The measurement range is user selectable at ranges between 0 to 1000 parts per billion by volume (ppb). The standard range selection used in the WBEA network is 0 to 1000 ppb. Digital data can also be captured from the SO2 analyzer by the datalogging system eliminating the need to scale the data captured. The calibrated values processed by the analyzer are recorded directly in ppb values.

The sensitivity of the analyzer is generally referred to as the detection limit of the analyzer. This is governed by the noise level of the output signal, whether analog or digital. Two times the noise level is generally accepted as the lower detectable limit (LDL) and on most SO2 analyzers in the network is approximately at the 1.0 ppb level. The health of the analyzer is important as poor health = higher noise = higher LDL.

Equipment and Apparatus

SO_2 analyzers used in the WBEA network include:

- Thermo Environmental Instruments – model 43C & 43i pulsed fluorescent analyzer
- Teledyne API – model 100A fluorescent analyzer

Both of these models are EPA designated analyzers and data produced from these instruments is accepted by all agencies.

This does not exclude the use of other equipment that has received the USEPA Reference and Equivalent Method designation, however none are currently used in the WBEA network.

Interferences

At concentration levels normally encountered in urban ambient air, gaseous hydrocarbon compounds fluoresce at the same wavelength as SO_2. These compounds are removed from the sample stream using the following process.

The sample air flows through a scrubber to remove hydrocarbons as it enters the analyzer. This removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO_2 molecules pass through the hydrocarbon scrubber unaffected.

Particulate matter present in the measurement cell can inhibit analyzer response by absorbing SO_2 molecules, thereby not allowing them to fluoresce. This problem is normally eliminated by using a

particle filter of 5.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

Precision and Accuracy

The measurement precision is generally considered to be the "repeatability of the measurement". Precision of the data output by the analyzer is established by the manufacturer, but confirmed during daily span checks and monthly calibrations.

The accuracy of the sensor is generally considered the "deviation from true". This means how close it is to what it should be. The benchmark of "what it should be" is provided by the Alberta Environment Audit Program staff and the use of high quality standards such as available from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily span and monthly calibration checks. Refer to the sections identified above for further information on accuracy relating to calibration and audit procedures.

Site Requirements

All SO_2 analyzers are housed in a temperature controlled ambient air monitoring shelter in a standard instrument rack. Sample air is brought into the shelter using a glass sample inlet system and made available to the SO2 analyzer. The station is sited according to appendix A-2, Station Site Criteria section of the AMD.

Installation Requirements

All the installation requirements are specified by the manufacturer in the installation procedures of the manual. General requirements listed below must also be followed.

- The ¼ inch outside diameter (inside diameter of 3/16 inch or 1/8 inch) connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness.
- A Teflon particulate filter with a pore size of no larger than 5.0µm must be placed in the sampling line before the air sample enters the detection cells and is recommended to be located as close as possible to the inlet manifold. The holder for such filter must also be made of Teflon, stainless steel or delrin.
- A data acquisition system (DAS) should be connected to the analyzer to record or download the signal output from the analyzer. For connection to record analog voltage signals, the system should be set to match the voltage range of the analyzer output. In the WBEA network the standard is 5V full scale and is scaled to convert the output signal to the concentration range outlined in section 3. See the DAS operations manual for instructions on configuring these channels.

- The analyzer has the capability to output specific alarms or a general alarm via a contact closure. These outputs are connected to the digital input section of the DAS. See the DAS operations manual for instructions on configuring these channels
- The monitoring station temperature should be controlled within the range of 15 to 30°C. It is important to note that the analyzer will operate properly at any temperature within this range; however, the stability of the station temperature is most important. Large changes in temperature over short periods of time can affect the precision of the analyzer.
- Within the vicinity of the station all products containing solvents and other sources of hydrocarbon must be avoided.
- Range Set – the typical range used for monitoring SO_2 is 0 to 1000 ppb. This is done as soon as the analyzer is powered up after installation. Refer to the operations manual for instructions on this procedure.

Operating Parameters and Instrument Configuration

The following activities must be performed when operating a continuous automated UV fluorescent SO_2 analyzer in Alberta. All operational activities conducted at any ambient monitoring station, must be documented in the Doc-It system. This allows other staff within WBEA to access a history of the station if the regular technician is not available. The following documentation must be available to the operators on site: operational and maintenance manual(s), quality system documentation and station site documentation.

Daily Requirements

Zero/Span Check – a zero/span cycle is required every day to verify the analyzer's performance. This involves diverting the sample flow of the analyzer so that the analyzer subsequently samples zero air for the zero cycle and air with a known amount of SO_2 for the span cycle. These two sources are provided by the in-situ calibration system. A zero air point of dilution air only is generated through a saved sequence in the calibrator, and span is generated by a saved calibration point in the calibrator, typically the high point of the routine multipoint calibration sequence. This cycle is controlled by the data system in the station, as it also flags the collected data as calibration and not sample data. During the daily zero/span cycle WBEA runs zero for twenty minutes to ensure stability, followed by a twenty minute span. The remaining twenty minutes of the hour is flagged down to allow the analyzer to return to ambient air prior to collecting valid data again. Refer to the analyzer manual for more information.

Analyzer Test Parameters

The analyzer monitors and displays test functions in order for the operator to monitor the performance of specific systems within the analyzer. These test parameters should be monitored during the multipoint calibration process and recorded on the calibration report.

Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. The filter change is completed after the as found points have been completed and before the multipoint calibration is carried out. This is done to establish a reference prior to the removal of the filter.

Analyzer Maintenance

Preventative maintenance tasks should be completed on the analyzer on a periodic basis. These tasks are outlined in the operations manual. A strict regiment of these tasks should be adhered to as they are intended to fix a problem before it happens. Any maintenance must be recorded in the Doc-It system. This is also recorded in the instrument log that accompanies each instrument.

Leak Check

Leak check must be performed annually to ensure the analyzer is functioning and is measuring only sampled air. Refer to analyzer specific operating manual for exact details on how to conduct a proper leak check. For both systems in the WBEA network, the Hydrocarbon Kicker must be bypassed prior to any leak check.

Calibration Requirement

The calibration procedure for SO_2 analyzers is similar to calibration of other continuous ambient air analyzers. This procedure involves generating a known amount of SO_2, which is introduced to the analyzer to verify its performance. There are certain specifics to the SO_2 calibration that are identified in this section.

Calibration Equipment – SO_2 analyzers are calibrated using the dilution method. Please see WBEA SOP-OPS-002 Dilution Calibration Procedure for details on this procedure.

- Three upscale points must be used, spaced approximately 15%, 30% and 60% of full scale as well as minimum of a single zero point from a separate zero air source.
- SO_2 must have at least one point above and one point below 170 ppb.

- Calibration results must be graphed as indicated concentrations (C_i) versus calculated concentrations (C_c) from which the slope of the graph, the intercept and final correction co-efficient are calculated.
- The acceptance criteria are slope of 1.0, ±0.1, and intercept of ±3% full scale and a coefficient of correlation (CC) >0.998.
- A zero/span check cycle is run using the DAS following the calibration to confirm the "as left" zero and span values. These values typically are used as the target values for the daily zero and span until the next calibration is completed.
- A recorded trace of the instrument, response over time (currently the TRMC plot) is required to demonstrate stability and accuracy, and must be included in the calibration report.

Data Collection and Management

The analog output of the SO_2 analyzers is typically wired to the analog input channels of the station Campbell's Scientific CR3000 Datalogger. This data recorded at 5 minute and hourly intervals and is then polled remotely via cellular modem.

Reference Documents

- *MODEL 43C PULSED FLUORESCENCE SO2 ANALYZER*, THERMO ENVIRONMENTAL INSTRUMENTS INC. Franklin MA, 2000, 5-1 – 7-9.
- *MODEL 43i PULSED FLUORESCENCE SO2 ANALYZER*, THERMO ENVIRONMENTAL INSTRUMENTS INC. Franklin MA, 2000, 5-1 – 7-9.
- *MODEL 200A FLUORESCENCE SO2 ANALYZER*, TELEDYNE_API INC. San Diego, CA
- Alberta Monitoring Directive (1989) and Amendments (2006)
- State of California Air Resources Board (CARB) Method Volume II Standard Operating Procedures for Air Quality Monitoring Appendix C dated April 1984