Title: Standard Operating Procedure for Measurement of SO_2 by SO_2 fluorescence		
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1. INTRODUCTION AND SCOPE

To obtain timely data for the purpose of air quality assessment, air quality trend reporting, air quality index reporting and to meet the requirements for inclusion of the data in provincial and national air quality databases, a continuous method of analyzing Sulphur Dioxide (SO_2) concentrations in ambient air is used. This method is capable of measurement updates at a rate of once every five minutes or faster. Readings from instruments of this method enables the calculation of hourly averaged concentrations of SO_2. Commercially available SO_2 analyzers are used in the method.

This method is applicable to the measurement of SO_2 concentrations in ambient air in the range of 1.0 parts per billion (ppb) to 1.0 parts per million (ppm).

This method adheres to the requirements of the current Air Monitoring Directive (AMD) 1989 by Alberta Environment. In some cases the limits and specifications exceed the requirements of the current AMD. It should be considered that the current and any future amendments or drafts of the AMD will be used as the benchmark for requirements and criteria for ambient air monitoring practices conducted in the Province of Alberta. Information used to write this procedure was also taken from sources identified in the reference section.

2. PRINCIPLE OF THE METHOD

The main detection principle for the UV fluorescence SO_2 analyzer is based on the principle that SO_2 molecules absorb ultraviolet (UV) light at the wavelength of 214 nm. The absorbed UV energy excites the outer electrons to the next state. The excited electrons then return to the original state and emit photons at the 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 detected by the photo multiplier tube (PMT) 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 converted to ppb.

Thermo Environmental Instruments (TEI) currently utilizes the pulsed UV fluorescence detection system. The pulsed UV fluorescence source utilizes a UV flashlamp and pulse trigger pack system built in to the lamp socket and power supply. This causes the lamp to "pulse" on and off to derive the "dark current" for baseline reference. Ambient air is drawn into the analyzer through the sample inlet. 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 (214 nm). 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 SO2 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

3. 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 typical range selection used in Alberta is 0 to 500 ppb.

The detection limit of the analyzer is specified by the manufacturer. Generally it is at the 1.0 ppb level.

4. EQUIPMENT AND APPARATUS

The following are available commercial analyzers suitable for used in this method and are currently in use in the AENV network:

- Thermo Environmental Instruments (TEI) Models 43A, 43C & 43i SO_2 Analyzers

This list does not exclude the use of other equipment that has received the USEPA Reference and Equivalent Method designation.

5. 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 2.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

6. 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. See section 9.0 in this document for information on daily calibration checks.

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 transfer standards such as those available from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily span checks and monthly calibrations. Refer to the sections identified above for further information on accuracy relating to calibration and audit procedures.

7. SITE REQUIREMENTS

Site location for SO_2 monitoring should be determined according to the intended application of the monitoring data. Detailed requirements for selection of sites for monitoring ambient SO_2 can be found in “Optimum Site Exposure Criteria for SO_2

Monitoring" EPA-450/3-77-013. Requirements for the immediate surroundings of ambient monitoring sites can be found in Air Monitoring Directive.

8. 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. Considerations for siting requirements can be found in the reference listed in section 7.0 above.

8.1 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.

8.2 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.

8.3 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 (DAS) system should be set to match the voltage range of the analyzer output. Generally this is 1V or 10V full scale.

8.4 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.

8.5 Within the vicinity of the station all products containing solvents and other sources of hydrocarbon must be avoided.

9. OPERATIONAL REQUIREMENTS

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 station logbook, and/or station checklists. This allows other operators 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), and station site documentation.

9.1 Set Up

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. Setup configuration recorded and kept with the instrument.

9.2 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 SO2 for the span cycle. These two sources are typically provided by internal systems. Zero is typically provided by pulling air through an activated charcoal canister, and span by pulling air from a temperature controlled permeation device. This cycle is normally controlled by the data system in the station, as it also flags the collected data as calibration and not sample data. The DAS is programmed to close contacts that are connected to the zero and span contacts on the analyzer. It is recommended to run the zero cycle after the span in order to reduce settling time after the check since zero levels are normally closest to ambient measurements. Refer to the analyzer manual for more information.

9.3 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 on a weekly basis and recorded on a site/instrument checklist (see appendix A).

9.4 Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. This should not occur until the as found points have been completed to rule out any interference. Inlet filters are changed every month before each calibration.

9.4 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 station log book and a record kept with the instrument documentation.

9.5 Multipoint Calibration

Multipoint calibrations are conducted on the SO_2 analyzer to verify precision, accuracy and linearity of the instrument. This procedure must be completed after the analyzer has been installed following at least a 24 hour warm up period, after any repairs or maintenance has taken place which may affect the performance of the instrument and monthly to comply with Alberta Environment regulations. Calibration procedures specific to the SO2 analyzer are found in section 10 of this document.

9.6 Analyzer Audit

SO_2 analyzers operating in Alberta are required to undergo an on-site audit once per year. This audit involves the Alberta Environment Audit Program staff visiting the site with the NIST traceable standards to verify the accuracy and linearity of the instrument.

10. CALIBRATION

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.

10.1 Calibration Equipment – SO_2 calibrations can be calibrated using either the dilution or permeation method

10.2 Referring to the calibration procedure outlined in SOP#11 Dilution Calibrations, calculate the slope and intercept of the 4 data points against the calibrator values using linear regression analysis. The acceptance criteria are slope of 1.0 +/- 0.1 and intercept of +/- 3% of full scale and a coefficient of correlation (CC) of >0.998.

10.3 A zero/span check cycle is run through the DAS following the calibration to verify the span values and to pick up and zero offset.

10.4 The analyzer is adjusted for zero reading and for a reading of 1:1 at the highest scale point in the calibration. Slope and intercept corrections are not performed.

11. APPLICABLE DOCUMENTS

- **EM-021a** Teledyne – Advanced Pollution Instrumentation (API), Inc Model 100E SO_2 Analyzer Operating Manual
- **EM-021b** Teledyne – Advanced Pollution Instrumentation (API), Model 100/100A SO_2 Analyzer Operating Manual
- **EM-021c** Thermo Environmental Instruments (TEI) Models 43A SO_2 Analyzer Operating Manual
- **EM-021d** Thermo Environmental Instruments (TEI) Models 43C SO_2 Analyzer Operating Manual
- **EM-021e** Thermo Environmental Instruments (TEI) Models 43i SO_2 Analyzer Operating Manual

12. LITERATURE REFERENCES

None

13. REVISION HISTORY

Revision 0 (new document)

Revision 1 Grammatical changes, refer to SOP#11 in section 10.2

14. APPROVAL

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Approved by: **Harry Benders** **Date: January 24, 2011**

Title: **Air Monitoring Manager**