## 1.0   Introduction

The H_2S measurement process is similar to the SO_2 process in that they both use an SO_2 analyzer. The difference being is that H_2S process requires an SO_2 scrubber and an in line converter prior to the analyzer. The following is a step by step explanation of the process once the air leaves the station sample manifold and travels to the converter, then the analyzer:

- Ambient air sample enters the converter
- Sample gas goes through an SO_2 scrubber where any SO_2 is removed from the sample gas
- Sample gas goes to goes glass conversion chamber heated to approximately 350 degrees Celsius
- Any H_2S entering the glass conversion chamber is converted to SO_2
- sample gas then exits the converter and goes to the SO_2 analyzer
- the SO_2 reading on the analyzer is equivalent to the H_2S in the sample gas on a 1:1 ratio

The detection principle for the UV fluorescence SO_2 analyzer is based on the principle that SO_2 molecules absorbing 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;
$$SO_2 + hv_1 \rightarrow SO_2{}^* \rightarrow SO_2 + hv_2$$
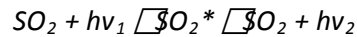
$*$ =   *Excited State*
hv_1 =   *Exposure Light @ Excitation Wavelength*
hv_2 =   *Emitted Light @ Emission Wavelength*

2.0   Applicability and Use

- To obtain timely data for the purpose of air quality assessment

- air quality trend reporting
- meet the requirements for inclusion of data in provincial and national air quality databases
- A continuous method of monitoring hydrogen sulphide concentrations in ambient air

This method is capable of measurement updates at a rate of once every minute. This method captures and records H_2S readings every minute, and one minute readings are compiled in to one hour averages.

2.1   Range

This method is applicable to the measurement of H_2S concentrations in ambient air in the range of 100 parts per billion.

This method adheres to the requirements of the current Air Monitoring Directive (AMD) drafted by Alberta Environment in 1989. In some cases the limits and specifications exceed the requirements of the current AMD and subsequent amendments. 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.

3.0   Additional References

- Alberta Air Monitoring Directive 1989

- 2006 Amendment to the 1989 Alberta Air Monitoring Directive

4.0   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 and monthly calibration checks.

The accuracy of the analyzer 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 team and the use of transfer standards from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily and monthly calibration checks.

The accuracy and precision of the analyzer are specified by the manufacturer in the instrument manual.

4.1   Reporting Detection Limits

The sulphur dioxide analyzers used in this method are commercially available models. The measurement range, depending on the manufacturer make and model, is highly variable. The typical range selection used in Alberta for ambient air monitoring is 0 to 0.1 ppm.

Data generated from these analyzers are reported to the nearest 0.001ppm

5.0   Setup and Operation

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 diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness. These lines should be kept as short as possible to keep residence time of the sample flow to a minimum.

- A particulate filter, made of material that does not absorb hydrogen sulphide, with a pore size of no larger than 5.0µm must be placed in the sampling line before the sample enters the analyzer. The filter is to be located as close as possible to the manifold inlet. The holder for the filter will be made of Teflon or stainless steel.

- A data acquisition system will be connected to the analyzer to record the signal output from the analyzer. For connection to record analog voltage signals, the system will be set to match the voltage range of the analyzer output. Generally this is 10V full scale.

- The monitoring station temperature will be controlled within the range of 20 to 25°C. It is important to note that the analyzer will operate properly at any temperature within this range; however, stability of the station temperature will yield more representative data.

- The monthly multi-point calibration gas is introduced to analyzer upstream the sample filter. The sample inlet filter is changed before the calibration is performed.

- Necessary channels must be put into "Maintenance" before calibration/maintenance starts.

6.0   Calibration Procedure

Below is the procedure used to calibrate the analyzer for the monthly multi-point calibration.

The total flow of any calibration point generated by the calibrator must be at minimum, a factor of 2.5 greater than the flow demand of the analyzer. All calibrations require the sample line from the calibrator to the analyzer have a positive pressure bypass in order to deliver gas to the analyzer at the pressure required by the analyzer.

Prior to commencement of the calibration, a scrubber test is to be performed to verify the scrubber is removing SO_2 from the sample gas. Any detectable SO_2 break through indicates the scrubber material is saturated and must be replaced immediately.

a.   Initiate flow of a zero-air gas to the analyzer. Record the "Diluent and Cal Gas" flow rates.
b.   After the monitor reading has stabilized for 20 minutes, record the resultant unadjusted zero reading as "as found zero".
c.   The operator will then adjust the zero unless the "as found zero" is not 0.00.
d.   After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted zero reading as "adjusted zero".
e.   Initiate a flow of a known gas between 50% and 80% of the full scale to the analyzer. Record the "Diluent Flow Rate" and "Cal Gas Flow Rate". Determine the Calculated concentration (CC) (refer to 8.1-a).
f.   After the monitor reading has stabilized for 20 minutes, record the resultant unadjusted reading as "as found high". Calculate the correction factor (CF) (refer to 8.1-b).

The analyzer will then be adjusted in accordance with the analyzer manufacturers procedures to give a correction factor as close to 1.000 as possible.

If CF is outside +/-15%, an explanation must be given along with corrective actions followed by re-calibration the analyzer (repeat 6.0).

g.   After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted reading as "adjusted high". Calculate and record. Calculate the correction factor (CF). (refer to 8.1b). Correction factor must be as close to 1.000 as possible.

h.   Initiate a flow of a known gas between 25% and 40% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). Correction factor must be 0.95 to 1.05.

i.   Initiate a flow of a known gas between 10% and 20% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). Correction factor must be 0.95 to 1.05.

j.   Initiate flow of a zero-air gas through the analyzer. After the monitor reading has stabilized 20 minutes, record the resultant instrument reading. If the resultant instrument reading is outside of +/-3% of the analyzer full scale, the calibration is to be repeated. (repeat 6.0).

k.   Initiate the analyzer auto zero/span sequence and record the resultant instrument readings for each, and record the new expected value, and input this value in to the logger.

l.   Calculate the average correction factor and record.

m.   Calculate the percent change from the previous calibration (PD) (refer to 8.1-c). Percent change must be < 15%.

7.0   Quality Control Requirements

Below are the requirements for the daily zero and span to ensure proper analyzer operation.

Slope	**0.85 to 1.15**
Intercept	**< 3 % of full scale**
Correlation Coefficient	**>0.995**
Percent Change	**< 15%**

If any of the above criteria are not met, the analyzer is considered to be non-linear. Determination as to why the calibration was not successful followed by repair and re-calibration must be made immediately. The calibration records must document why the initial calibration was not successful.

8.0 Data Calculation and Reporting

8.1 Calculations

a. Calculated Concentration (C.C.)

$$C.C. = \frac{(\text{Source Gas Flow Rate} \times \text{Cal Gas concentration})}{(\text{Source Gas Flow rate} + \text{Dilution Air Flow Rate})} \times 1000$$

Unit: ppm or ppb

b. Correction Factor (C.F.)

$$C.F. = \frac{\text{Calculated concentration}}{\text{Indicated Concentration}}$$

Unit: None

c. Percent Different (P.D.)

$$P.D. = \frac{\text{C.F. after adj. span previous month - C.F. before span adj. currentmonth})}{\text{C.F. before span adj. current month}} \times 100$$

Unit:%

8.2 Reporting

All internal operating parameters of the analyzer are to be entered in the calibration spreadsheet. The station log book is to be updated with:

- Date of the calibration
- Any irregularities during the calibration along with an explanation

- Analyzer change out along with an explanation why

Field service reports will track:

- Date of the calibration
- Consumables required
- Maintenance performed
- Time required
- Calibration anomalies and explanation