



Title: Standard Operating Procedure for Hydrogen Sulphide (H₂S) and Total Reduced Sulphur (TRS) detectors		
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1. INTRODUCTION AND SCOPE

To obtain timely data for the purpose of air quality assessment, air quality trend reporting and to meet the requirements for inclusion of the data in provincial and national air quality databases, a continuous method of monitoring Hydrogen Sulphide (H₂S) and Total Reduced Sulphur (TRS) concentrations in ambient air is used. Both parameters are included in this procedure due to their similarities. 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 H₂S/TRS. Commercially available H₂S/TRS analyzers are used in the method.

This method is applicable to the measurement of H₂S/TRS concentrations in ambient air in the range of 1.0 parts per billion (ppb) to 100.0 parts per billion (ppb) and over.

This method adheres to the requirements of the current Air Monitoring Directive (AMD)1989 by Alberta Environment. 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

Currently H₂S/TRS is measured using chemical conversion to reduce the H₂S and TRS molecules to sulphur dioxide (SO₂) using high temperature. The converted SO₂ molecules are then analyzed using current SO₂ analyzers. The main difference in operation of H₂S/TRS vs. SO₂ analyzers, besides the converter, is that the range for H₂S/TRS is usually lower than SO₂. Below are the descriptions of the differences between the two types of compounds (or analysis techniques).

H₂S

H₂S molecules will be oxidized to SO₂ in the presence of Oxygen and heat. This is accomplished by diverting the sample flow, after a scrubber to remove hydrocarbons, through a H₂S converter, a stainless steel body heated to at least 320 degrees centigrade. Prior to the converter, the sample flow passes through a scrubber to remove all SO₂, and allow only the H₂S molecules to pass through to enter the H₂S converter. The H₂S molecules are then converted to SO₂ as illustrated in the following equation.

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Specifically;



The converted SO₂ molecules then return to the standard SO₂ analyzer for detection and are reported as H₂S.

TRS

Total reduced Sulphur compounds include a variety of airborne compounds that contain Sulphur. Some of the common ones found in Alberta are; Carbonyl Sulphide (COS), Carbon Disulphide (CS₂) and Methyl Mercaptan (CH₃SH). Similar to H₂S, TRS molecules will be oxidized to SO₂ in the presence of Oxygen and heat. The difference between H₂S and TRS in this regard is that the TRS conversion requires a higher temperature. This is accomplished by, again, diverting the sample flow, after the scrubber for removal of hydrocarbons, then through a TRS converter, a Quartz tube heated to at least 800 degrees centigrade. Prior to the converter, the sample flow must pass through a scrubber to remove all SO₂, and allow only the TRS molecules to pass through to enter the TRS converter. The TRS molecules are then converted to SO₂ as illustrated in the following equation.

Specifically;



The converted SO₂ molecules then return to the standard SO₂ analyzer for detection and are reported as TRS.

3. PRINCIPLE OF THE METHOD

The H₂S/TRS 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 100 ppb.

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The detection limit of the analyzer is specified by the manufacturer. Generally it is at the 0.5 ppb level.

4. EQUIPMENT AND APPARATUS

The following are available commercial analyzers configured specifically for the measurement of H₂S and TRS, are suitable for used in this method and are currently in use in the AENV network: Some installations only use a standard SO₂ analyzer with an H₂S or TRS converter added to the system.

- Teledyne – Advanced Pollution Instrumentation (API), Inc Model 101E (H₂S); Model 102E (TRS), API Model 101/101A (H₂S), Model 102/102A (TRS) Analyzers
- Thermo Environmental Instruments (TEI) Models 45A, 45C & 450i H₂S Analyzers with converter model numbers 340 for H₂S and CDN 101 for TRS

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

5. INTERFERENCES

As SO₂ analyzers are used in this method, the same interferences are observed as for SO₂. At concentration levels normally encountered in urban ambient air, gaseous hydrocarbon compounds fluoresce at the same wavelength as SO₂. These hydrocarbon compounds are removed from the sample stream using the following process. The sample air flows through a scrubber for removal of hydrocarbons prior to entering the SO₂ scrubber and the heated converter and then enters the analyzer. This removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO₂ molecules pass through the scrubber for removal of hydrocarbons unaffected.

Particulate matter present in the measurement cell can inhibit analyzer response by absorbing H₂S/TRS molecules, thereby not allowing them to fluoresce. This problem is normally eliminated by using a particle filter of 2.0 micron pore size made of inert material, such as Teflon, before the sample inlet of the instrument.

6. PRECISION AND ACCURACY

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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 spans 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 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.

7. SITE REQUIREMENTS

Site location for H₂S/TRS monitoring should be determined according to the intended application of the monitoring data. In Alberta, H₂S and TRS is monitored for compliance purposes relating to the Oil & Gas industry, and to monitor these compounds in relation to health effects or nuisance odours. Detailed requirements for selection of sites for monitoring ambient H₂S/TRS can be found in the siting criteria section in the 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. This tubing is also used to connect the SO₂ analyzer to the heated converter. These lines should be kept as short as possible to keep residence time of the sample flow to a minimum.

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- 8.2 A Teflon particulate filter Zeflour™ or equivalent with PTFE membrane and support 2.0µm pore size 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.
- 8.6 Refer to setup and setup instructions table for H₂S & TRS analyzers for information on selecting settings for AENV operations.
- 8.7 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.

9. OPERATIONAL REQUIREMENTS

The following activities must be performed when operating a continuous automated UV fluorescent H₂S/TRS 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 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 H₂S for

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the span cycle. H₂S gas is used for both H₂S and TRS analyzers. These two sources are typically provided by internal systems. Zero is typically provided by pulling air through a canister filled with activated charcoal, and span by pulling air from a temperature controlled permeation device after the charcoal cannister. The span can also be provided using a cylinder of H₂S diluted with zero air to the appropriate range. This cycle is normally controlled by the data acquisition system in the station, as it also flags the collected data as calibration and not sample data. The data system is programmed to close contacts that are connected to the zero and span control 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.

9.2 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 an instrument checklist.

9.3 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 H₂S/TRS 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 H₂S/TRS analyzer are found in section 10 of this document.

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9.6 Analyzer Audit

H₂S/TRS 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 H₂S/TRS analyzers is similar to calibration of other continuous ambient air analyzers. This procedure is found in SOP 11 "SOP for Dilution Calibrations", involves generating a known amount of H₂S for both the H₂S and TRS analyzers, which is introduced to the analyzer to verify its performance. There are certain specifics to the H₂S/TRS calibration that are identified in this section.

- 10.1 Calibration Equipment – H₂S/TRS analyzers can be calibrated using either the dilution or permeation method.
- 10.2 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% full scale) and a coefficient of correlation (CC) >0.998.
- 10.3 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.
- 10.4 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.

11. APPLICABLE DOCUMENTS

- **EM-010a** Teledyne – Advanced Pollution Instrumentation (API), Inc Model 101E (H₂S); Model 102E (TRS), API Model 101/101A (H₂S), Model 102/102A (TRS) Analyzer Operating Manual
- **EM-010b** Thermo Environmental Instruments (TEI) Models 45A, 45C & 45i H₂S Analyzer Operating Manual
- **SOP# 11** Dilution Calibrations

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12. LITERATURE REFERENCES

None

13. REVISION HISTORY

Revision 1.0 January 19, 2011: Add reference to dilution calibrations SOP.

14. APPROVAL

Approved by: Harry Benders
Title: Air Monitoring Manager

Date: January 19, 2011