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WBEA – Standard Operating Procedure			
SOP Title		Procedure for operating continuous Hydrogen Sulphide and Total Reduced Sulphur analyzers	
SOP Number		WBEA SOP-ANA-002 H ₂ S/TRS	
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Introduction and Background

This document is intended to be used as a reference for use in the calibration, maintenance and operation of continuous Hydrogen Sulphide and Total Reduced Sulphur analyzers in ambient air. This procedure is intended to be used in conjunction with the manufacturer's operations manual.

This SOP adheres to the requirements of the current Air Monitoring Directive (AMD) finalized by Alberta Environment in 1989. 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 WBEA network. Information used to write this procedure was also taken from sources identified in the reference section.

Principle of the Method

Currently Hydrogen Sulfide (H₂S) and Total Reduced Sulphur (TRS) are measured by the reduction of H₂S and TRS molecules to SO₂ using high temperature in the presence of ambient levels of oxygen. The converted SO₂ molecules are then analyzed using the same analytical technique as SO₂ analyzers. (Refer to WBEA-SOP-ANA-001- SO₂ for procedures on SO₂ Analyzers). As H₂S and TRS are found in much lower concentrations in ambient air, these analyzers are set to a much lower range.

H₂S

H₂S molecules will be oxidized to SO₂ in the presence of Oxygen and heat. Sample flow to an H₂S analyzer initially passes through a SO_x scrubber to remove any SO_x compounds in the sample stream. It then travels through an H₂S converter heated to at least 320 degrees centigrade, which converts the H₂S molecules to SO₂ as illustrated in the following equation. The H₂S converter is typically contained within a modified SO₂ analyzer to monitor specifically for H₂S.

Specifically;



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

TRS

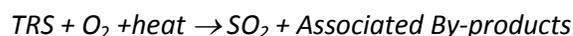
Total reduced Sulphur compounds include a variety of airborne compounds that contain Sulphur. Some of the common ones found in Alberta are; Carbonyl Sulphide (COS), Carbon Disulphide (CS₂) and Methyl

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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 higher temperature converter is always a separate converter from the SO₂ analyzer. Sample flow to a TRS analyzer initially passes through a SO_x scrubber to remove any SO_x compounds in the sample stream. It then travels through a TRS converter heated to at least 800 degrees centigrade, which converts the TRS molecules to SO₂ as illustrated in the following equation.

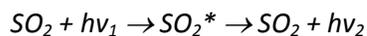
Specifically;



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

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;



* = *Excited State*

hv_1 = *Exposure Light @ Excitation Wavelength*

hv_2 = *Emitted Light @ Emission Wavelength*

The light emitted by the decaying SO₂ 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 SO₂ voltage response which can be scaled into appropriate units.

Measurement Range and Sensitivity

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 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 H₂S/TRS analyzers in the network is approximately at the 0.5 ppb level. The health of the analyzer is important as poor health = higher noise = higher LDL.

Equipment and Apparatus

H₂S & TRS analyzers used in the WBEA network include:

- Thermo Environmental Instruments – model 45C & 450i pulsed fluorescent H₂S analyzer
- Thermo Environmental Instruments – model 43C & 43i-TLE pulsed fluorescent SO₂ analyzer (configured for TRS monitoring)
- CD Nova Inc. – model CDN-101 TRS thermal TRS converter
- Teledyne API – model T-101 fluorescent H₂S analyzer
- Teledyne API – model T-102 fluorescent TRS analyzer

All 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

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 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 SO₂ molecules pass through the hydrocarbon scrubber unaffected.

Particulate matter present in the measurement cell can inhibit analyzer response by absorbing SO₂ 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.

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It should also be noted that some SO₂ scrubbers can absorb H₂S if the zero air being used is extremely dry. This will decrease response as well as prolong response time, for this reason, Zero Air cylinders should not be used and powerful drier units on zero air generators should be by passed.

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 H₂S/TRS 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 H₂S/TRS 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. This tubing is also used to connect the SO₂ analyzer to the heated converter. These lines should be kept as short as possible, and no longer than 10 meters to keep residence time of the sample volume to a minimum.
- 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.

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- 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 the range and sensitivity section of this document. 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 H₂S/TRS is 0 to 100 ppb. This is done as soon as the analyzer is powered up after installation. Refer to the operations manual for instructions on this procedure.
- 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.
- Converter Optimization – after the analyzer has been installed, the converter temperature must be optimized. This process should be completed annually. This task involves the following steps:
 - Have the analyzer running and all connections made
 - Connect the calibration gas source using a calibrator capable of generating selected concentrations
 - Generate a concentration of H₂S at 80% of full scale and wait for the analyzer response to stabilize
 - Increase the converter temperature at increments of 5 degrees, and wait for stable response between each change. The response will start to drop once the optimum temperature has been passed.
 - Decrease the converter temperature at increments of 5 degrees, and wait for stable response between each change. The response will start to drop once the optimum temperature has been passed.
 - The median temperature between these two points is where the converter should be operated

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- Converter Efficiency test – after the analyzer has been installed, the converter temperature must be tested to verify near total conversion of H₂S/TRS to SO₂ is occurring. This process should be completed annually. This task involves the following steps:
 - Have the analyzer running and all connections made
 - Connect the calibration gas source using a calibrator capable of generating selected concentrations; for this initial portion a source gas of SO₂ will be utilized
 - Create a loop bypassing both the SO_x scrubber and converter
 - Generate a concentration of SO₂ at 80% of full scale and wait for the analyzer response to stabilize
 - Adjust the reading to the calculated concentration of the calibration point of SO₂
 - Re-connect the SO_x scrubber and the converter back in-line; continue to maintain the SO₂ point for a short while to verify the removal of SO₂ molecules from the sample stream and prove of the efficiency of the SO_x scrubber. The response of the analyzer should be zero.
 - Modify the calibration point and generate a concentration of H₂S at 80% of full scale and wait for the analyzer response to stabilize
 - Verify the response is within 5% of expected value; in the event of loss of efficiency the converter will require troubleshooting or replacement (see equipment manual for details)

Operating Parameters and Instrument Configuration

The following activities must be performed when operating a continuous automated UV fluorescent SO₂ analyzer in the WBEA network. 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 SO₂ 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

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

Calibration Equipment – H₂S/TRS analyzers are calibrated using the dilution method. Please see WBEA SOP-OPS-002 Dilution Calibration 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.

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- The SO₂ scrubber must be challenged on a monthly basis by introducing SO₂ only to the analyzer for a 20 minute period. If the scrubber is working properly, the analyzer response should be zero for the 20 minute period. If a response is observed greater than 2 ppb, replace the scrubber. This point should be introduced immediately after the as found span point.
- 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 correlation coefficient 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. No point can be out by more than 5% from the calculated concentration.
- 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.
- A recorded trace of the instrument, response over time is required to demonstrate stability and accuracy.

Data Collection and Management

The analog output of the H₂S/TRS analyzers are typically wired to the analog input channels of the station Campbell's Scientific CR3000 Datalogger. This data recorded at 5 minute intervals and is then polled remotely via cellular modem. Alternatively the data can be polled digitally via the serial or Ethernet port, and can be accompanied by the diagnostic or meta-data information.

Reference Documents

- Teledyne – Advanced Pollution Instrumentation (API), Inc Model T-101 (H₂S); Model T-102 (TRS) Analyzer Operation Manual
- Thermo Environmental Instruments (TEI) Models 45C & 450i H₂S Analyzer Operation Manual
- Thermo Environmental Instruments (TEI) Models 43C & 43i-TLE Analyzer Operation Manual
- CD Nova Models CDN-101 Thermal Converter Operating Manual
- Alberta Environment - Alberta Monitoring Directive (1989)