WBEA – Standard Operating Procedure

SOP Title	Procedures for operating continuous Ammonia (NH_3) analyzers
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Implementation date	February 19, 2013

Revision History

Revision #	Date	Description	Author

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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 analysis of Ammonia 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 NH_3 analyzers are based on the same principle as NO_2 analyzers in that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO_2 molecules decay to lower energy states.

Specifically;

$$NO + O_3 \rightarrow NO_2 + O_2 + hv$$

Ammonia analyzers typically have three active channels or modes, Total Nitrogen (Nt), Total Oxides of Nitrogen (NO_x) and Nitric Oxide. The NH_3 and NO_2 outputs are calculated from the signal of these channels as follows:

- To measure the NO_x ($NO + NO_2$) concentration, NO_2 is transformed to NO prior to reaching the reaction chamber. This transformation takes place in a molybdenum converter heated to approximately 325^{o}C. Upon reaching the reaction chamber, the converted molecules along with the original NO molecules react with ozone. The resulting signal represents the NO_x reading.
- To measure the Nt ($NO + NO_2 + NH_3$) concentration, both the NO_2 and NH_3 are transformed to NO prior to reaching the reaction chamber. This transformation takes place in a stainless steel converter heated to approximately 750^o C. Upon reaching the reaction chamber, the converted molecules along with the original NO molecules react with ozone. The resulting signal represents the Nt reading.
- The NO_2 concentration is determined by subtracting the signal obtained in the NO mode from the signal obtained in the NO_x mode. $NO_x - NO = NO_2$
- The NH_3 concentration is determined by subtracting the signal obtained in the NOx mode from the signal obtained in the Nt mode. $Nt - NO_x = NH_3$ most models of analyzer output NO_x, NT, and NH_3 concentrations to the front panel display and NO, NO_2, NH_3, and NO_X concentrations to the analog outputs.

Dry air enters the NH_3 analyzer through a permeable membrane dryer system to remove any moisture. This dry air then flows through a flow sensor, and then through a silent discharge ozonator. The ozonator generates the necessary ozone concentration needed for the chemiluminescent reaction. The ozone reacts with the NO in the air sample entering the detector to produce electronically excited NO_2 molecules. A photomultiplier tube (PMT) housed in a thermoelectric cooler detects the NO_2 luminescence.

Measurement Range and Sensitivity

The NH_3 analyzer used in this method is a commercially available model. The measurement range is user selectable at ranges between 0 to 10.0 parts per million by volume (ppm). The typical range selection used in the WBEA network is 0 to 2.5 ppm.

The detection limit of the analyzer is specified by the manufacturer and specific settings applied to the analyzer when placed in the field. This is also 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); generally it is at the 1.0 ppb level. The health of the analyzer is important as poor health = higher noise = higher LDL.

Equipment and Apparatus

NH_3 analyzers used in the WBEA network include:

- Thermo Environmental Instruments – model 17C and 17i series

NH_3 analyzers in use are all EPA approved and AMD compliant monitors. This does not exclude the use of other equipment that has received the USEPA Reference and Equivalent Method designation.

Interferences

At concentration levels normally encountered in urban ambient air, other Nitrogen based compounds will be converted and subsequently detected in the Nt mode of the analyzer. These include the following compounds at the listed temperatures:

- PAN (Peroxyacytyl nitrate) - (375°C - 450°C)
- ethyl nitrate; ethyl nitrite; HONO; HNO_3 - (350°C, 375°C, 450°C)
- methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitrocresol - (450°C)

As the NO_x converter temperature is maintained at 325°C, the influence of these compounds is minimal. For the purposes of this method, NO_x is generally considered to include only NO_2 and NO. The Nt converter operates at a higher temperature, but considering the range of the analyzer, the influence of these compounds is minimal. For the purposes of this method, Nt is generally considered to include only NH_3, NO_2 and NO.

Particulate matter present in the measurement cell can inhibit analyzer response by absorbing NH_3, NO_2 and NO molecules, thereby not allowing them to luminescence. This problem is normally eliminated by using a particle filter of 5.0µm pore size made of inert material, such as Teflon, prior to 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 NH_3 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 NH_3 analyzer. The station is sited according to appendix A-2, Station Site Criteria section of the AMD. Site location for NH_3 monitoring should be determined according to the intended application of the monitoring data.

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. The length of tubing must be kept as short as possible and no longer than 10 meters.
- 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.
- 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. For serial or LAN connection there must be a station router in place and configurations made to the analyzer settings, the router, and the data logger. 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.
- 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 NH_3 is 0 to 2.5 ppm. 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.

Operational and Maintenance Requirements

The following activities must be performed when operating a continuous automated chemiluminescent NH_3 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 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), quality system manual 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 NH_3 and NO_2 for the span cycle. These two sources are typically 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 normally controlled by the DAS 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.

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 recorded digitally via DAS collection or documented on calibration reports.

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.

Annual Tasks

The following are preventative maintenance measures intended to keep analyzer operation optimal. For details refer to the operating manual.

- O-ring fittings at the orifices or capillaries must be replaced as ozone will corrode the rubber and increase the probability of leaks.
- Cleaning the reaction chamber to ensure that HNO_2 dust does not build up a residue that can impede the sensitivity of the PMT.
- Rebuild or replace pump to ensure the analyzer is under a consistent vacuum level.

Semi Annual Tasks

- Replace charcoal scrubber upstream of pump; this will prevent the O3 generated by the NOX analyzer from eating away the seals and depleting the vacuum capacity of the pump. It is ideal to replace this scrubber during pump maintenance (see Annual Tasks).

Multipoint Calibration

Multipoint calibrations are conducted on the NH_3 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, prior to removal, and monthly to comply with Alberta Environment regulations. This procedure is also completed before and after any major maintenance to confirm the precision and accuracy.

Analyzer Audit

NH3 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.

Calibration Requirement

The calibration procedure for NH_3 is unique to the calibration of other continuous ambient air analyzers in that it is a three stage calibration. The first stage is the dilution portion and involves generating a known amount of NO which is introduced to the analyzer to verify its performance. A known amount of NO gas will travel through the analyzer in all three modes to provide the same signal on all active channels. A single high concentration of NO is generated in order to establish as found reaction level. Once the high point has stabilized a controlled amount of Ozone is introduced to the NO high point. This causes the NO to react with the Ozone to form NO_2 which challenges the molybdenum converter to convert the generated NO_2 back to NO to be analyzed. After the second phase is complete it is routine to return to zero before beginning the final phase. The third phase of the calibration involves introducing a known amount of NH_3 to challenge the High Temperature Nt converter to convert the NH_3 back to NO to be analyzed. Three levels of NH_3 are generated in this phase of the calibration to again verify the linearity of the instrument. There are certain specifics to the NH_3 calibration that are identified in this section. The main calibration procedure can be found in WBEA SOP-OPS-002 Dilution Calibration Procedure.

- Calibration Equipment – NH_3 calibrations can be calibrated using the dilution method, or a combination of the dilution method and the permeation method. If a combination of calibrators is used, the permeation calibrator is fitted with an NH_3 certified permeation device for the NH_3 part of the calibration only. A cylinder of NH_3 with the dilution calibrator can also be used for this portion of the calibration. The calibration methods used are sited in the reference above.

- 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.
- 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, ±0.05, and intercept of ±3% full scale and a coefficient of correlation (CC) >0.995.
- 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 NH_3 analyzers is typically wired to the analog input channels of the station Campbell's Scientific CR3000 Micrologger. 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

- Thermo Environmental Instruments (TEI) Model 17C NH3 Analyzer Operating Manual