

Monitoring Parameter: Ammonia (NH₃)	Title: Standard Operating Procedure for the Continuous Measurement of Ambient NH₃ DRAFT
Revision No: Draft Revision Date: 09 April, 2018	Reference No: SOP-08 Parent Document: Part B1 – B.C. Field Sampling Manual
<p>1. Introduction and Scope</p> <p>This Standard Operating Procedure (SOP) provides operating guidelines and instructions for the continuous ambient monitoring of Ammonia (NH₃) within the jurisdiction of British Columbia (B.C.).</p> <p>This SOP forms part of the B.C. Field Sampling Manual (BCFSM). Part B - Air and Air Emissions Testing, of the BCFSM provides additional information on Air Quality Monitoring that must be used in conjunction with the information provided in this SOP. Installation and maintenance of NH₃ analyzers within the provincial jurisdiction of B.C. should be carried out with consideration to Part B of the B.C. Field Sampling Manual, the analyzer manufacturer’s manual, and this document.</p>	
<p>2. Document Control</p> <p>This Standard Operating Procedure is a controlled document. Document control provides a measure of assurance that the specifications and guidance it provides are based on current information that has been reviewed by a qualified reviewer/s. Controlled documents are reviewed within a five year life cycle. Please ensure that the revision date listed in the header of this document does not exceed five years.</p> <p>This SOP and the B.C. Field Sampling Manual are available at: www2.gov.bc.ca.</p>	
<p>3. Principle of the Measurement Method</p> <p>Chemiluminescence</p> <p>The principle detection and quantification method deployed for ambient concentrations of NH₃ is chemiluminescence. NH₃ measurement is based on the same principle deployed for nitrogen dioxide (NO₂) measurement. A photomultiplier tube is used to measure the light (<i>hν</i>) emitted by the chemical reaction of nitric oxide (NO) and ozone (O₃).</p> $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$ <p>This method involves two measurement processes. The first process measures the total amount of nitrogen in the ambient air sample, which includes the nitrogen within NH₃, NO₂, and NO. The second process measures the amount of NO and NO₂ (collectively referred to as NO_x). The concentration of NH₃ is then calculated as the difference between the two measurements.</p> <p><u>First Process – Total Nitrogen Measurement</u></p> <p>In the first process, the total nitrogen concentration is determined by passing an ambient air sample through a high temperature (approximately 750 °C) chamber which converts both NH₃ and NO₂ to NO. In a subsequent reaction chamber the converted NO molecules and original NO molecules present in the air sample react with O₃. When exposed to O₃, the converted NO molecules and original NO molecules are readily oxidized to NO₂ in a 1:1 relationship as shown in the equation above. As excited NO₂ decays</p>	

to a lower energy state it releases infrared light with an intensity that is linearly proportional to the amount of NO. The infrared light emitted during this chemical reaction is measured using a photomultiplier tube. The infrared light measurement is used to determine the concentration of total nitrogen.

Second Process – NO_x Measurement

In the second process, the concentration of NO_x (which includes NO and NO₂) is determined by passing the ambient air sample through a molybdenum catalysis oven that is heated to approximately 325 °C, which converts NO₂ to NO. The lower converter temperature prevents the catalytic conversion of NH₃ to NO conducted in the first process. In a subsequent reaction chamber the converted NO molecules and original NO molecules present in the air sample react with O₃. The light emitted during this chemical reaction is measured using a photomultiplier tube. The infrared light measurement is used to determine the concentration of NO_x.

Use of Outputs from Processes 1 and 2 to Calculate NH₃

The concentration of NH₃ is determined by the difference of total Nitrogen and NO_x as follows:

$$NH_3 = \text{total Nitrogen (catalyst converted } NH_3, \text{ and } NO_x) - NO_x$$

A more detailed discussion of the NH₃ measurement principle is typically provided within the manufacturer's operation manual.

4. Interferences

Nitrogen based compounds

The presence of nitrogen based compounds in ambient air may interfere with NH₃ measurement using this method. These compounds are known to erroneously increase analyzer response as they can undergo chemical reactions within the catalysis oven or reaction chamber resulting in an inaccurate analyzer response. Some of the nitrogen based compounds known to interfere with NH₃ measurement include nitrites and nitrates.

H₂O

Water and high levels of carbon dioxide (>0.5 %) have the potential to interfere with measurements. Analyzers situated in areas of high humidity should use a gas dryer to reduce moisture in the sample. The gas dryer should be positioned in the sample line upstream of the analyzer.

Particulate Matter

Particulate matter in ambient air is known to reduce analyzer response by absorbing and scattering light. Interference by particulate matter can be minimized by placing a particle filter at the sample inlet (for analyzers that do not have an internal filter). The particle filter must have a 5 micron pore size and be made of an inert material such as Teflon.

5. Precision and Accuracy

Air contaminant concentration measurements are affected by an instrument's precision and accuracy.

The precision of a measurement is generally considered to be the 'repeatability of the measurement'. This can be confirmed through zero and span checks, and calibrations.

The accuracy of the sensor is generally considered to be a measure of the 'deviation from true'. The accuracy of the sensor can be checked by performing analyzer calibrations against a certified standard gas mixture (see Sections 11 and 12). Accuracy can also be evaluated through periodic span checks.

6. Recommended Equipment and Apparatus

The following are common commercially available NH₃ analyzers suitable for use within the provincial jurisdiction of B.C.:

- Thermo Environmental Instruments (TEI) Model 17i Ammonia Analyzer
- Thermo Scientific Model 17i Ammonia Analyzer
- Teledyne API Model T201 Ammonia Analyzer

This equipment list does not necessarily exclude the use of other commercially available NH₃ analyzers, and analyzers recognized by United States (US) Environmental Protection Agency's (EPA) Environmental Federal Reference and Equivalent Methods. It is recommended however that you consult with the B.C. Ministry of Environment and Climate Change Strategy (ENV) if you intend to deploy an NH₃ analyzer not listed above. Regardless of the equipment deployed, all analyzers should meet the specifications described within this document.

7. Measurement Range and Sensitivity

Typical commercially available NH₃ analyzers can operate at user selectable ranges between 0 and 20000 parts per billion (ppb); for B.C. ENV monitoring purposes analyzers should be set to a range of 0 ppb to 5000 ppb.

Detection limits are determined by instrument type, but are generally around 1 ppb.

8. Site Requirements

Monitoring site specifications should be developed to ensure that the data generated from the site satisfies the requirements of intended or established monitoring objectives. It is recommended that monitoring site requirements be established in consultation with the B.C. ENV to ensure that siting requirements are commensurate with monitoring objectives.

As a preliminary guideline site selection should consider and address: monitoring objectives, representativeness of the region, interference from the surrounding area, and zone type (residential, commercial, industrial) of the monitoring location.

Refer to Section XX of the BCFSM for further information on site selection.

9. Installation Requirements

Follow analyzer specific installation requirements provided in the analyzer manufacturer's manual. Installation should also conform to the following:

- The monitoring station's sampling inlet and manifold shall meet the requirements of the most recent version of the National Air Pollution Surveillance (NAPS) Program's *Monitoring and Quality Assurance/Quality Control Guidelines* Section 8.2 and Section 8.3.
- The ¼ inch diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness.

- A Teflon particulate filter meeting the manufacturer’s pore size specifications must be placed in the sampling line upstream of the analyzer, unless the analyzer is equipped with a similar internal filter. The filter holder should be constructed of an inert material (e.g. Teflon, stainless steel).
- To reduce the risk of moisture entering the analyzer it is recommended that horizontally mounted manifolds be oriented with the ports facing upwards (with the exception of manifolds such as the “ARB style” which must be mounted vertically); ensure any water traps are oriented vertically.
- A data acquisition system (‘DAS’ of ‘data logger’) should be connected to the analyzer to record or download the measurement data from the analyzer. If an analog data logger is used, it must be set to match the voltage range of the analyzer, typically at 1V or 10V full scale. It must be ensured that the analog output matches the digital output displayed on the analyzer. The data logger must also record and monitor any alarm conditions of the analyzer.
- The analyzer must be placed in a weather resistant enclosure that is vented, heated and cooled to maintain a stable temperature preferably in the range of 20 °C and 30 °C but must ultimately be capable of maintaining the operating range specified by the manufacturer. Enclosure temperatures should not deviate by more than 2 °C over a one hour period.
- Remove any sources of solvents and volatile hydrocarbons from the vicinity of the station.
- A permeation dryer should be placed in the sampling line upstream of the analyzer.

10. Operational Requirements

The following activities should be performed by the operator of a continuous automated NH₃ analyzer.

Action	Time/Frequency	Description	Record Keeping
Analyzer Range Set Up	After installation.	As per manufacturers operation manual. Monitoring range should be 0 ppb to 5000 ppb.	Record in logbook, see example station installation record (BCFSM Appendix XX)
Multipoint Verification	<ul style="list-style-type: none"> • After installation (or relocation) following a 24 h to 72 h warm up period; • After analyzer repairs/maintenance that may affect performance of the instrument; • When zero check exceeds ± 0.1 ppm; • When span drift is $\geq \pm 10\%$ of reference value; • For new analyzers, after the first 3 months of operation; • Bi-annually if span checks are conducted daily – or when any threshold above is reached (whichever happens first); 	As per Section 12 of this SOP.	Record in logbook, see example gas calibration activity record (BCFSM, Appendix XX)

	<ul style="list-style-type: none"> Quarterly if span checks are conducted less than daily – or when any threshold above is reached (whichever happens first). 			
Zero and Span Verification	Daily preferred, weekly minimum	As per manufacturers operation manual.	Record in logbook, see example routine maintenance record (BCFSM, Appendix XX)	
Verify Operational Parameters	Each monitor station visit	As per manufacturers operation manual		
Inlet Filter Change	Inspect monthly, change as required	As per manufacturers operation manual. A filter change can affect flow and pressure so a verification or full calibration is required.		
Analyzer Maintenance	As recommended by manufacturer or as required	As per manufacturers operation manual.	Record in logbook	
Sample Path Inspection (Probe to Analyzer)	Each monitor station visit	Where necessary replace with new lines, tighten loose connections, clean manifold if required. Any alteration to the sample pathway should be accompanied by verification or full calibration.	Record in logbook	

11. Zero and Span Checks

Zero and span checks are required to verify analyzer performance between calibrations. These checks should be performed in accordance with Section XX of the BCFSM.

12. Calibration

Calibration should be performed in accordance with Section XX of the BCFSM and the manufacturer's manual. Certain specifics of the NH₃ analyzer calibration are as follows:

A 3-stage calibration is required, which is unique to NH₃ analyzers. The first stage is typical of other continuous gas analyzer types and involves serial dilution of a NO standard to verify analyzer NO and NO_x response.

In the second stage the NO₂ response is verified by gas phase titration. Two levels of ozone are generated and calibrated in the gas phase titration to verify the linearity of the analyzer. This involves titrating the NO standard used in the first stage with a known concentration of ozone. The introduced ozone converts the equivalent amount of NO into NO₂, which is converted back into NO by the analyzer's converter oven and read as NO_x. As the NO and NO_x channels were calibrated and verified in the first stage, the analyzer's response to the remaining NO, not converted by ozone, can be accepted as accurate. Comparison of the introduced ozone concentration with the analyzer's NO_x and NO response therefore allows for a determination of converter efficiency, and verification of the NO₂ channel.

In the third stage, a known concentration of NH₃ is used to verify the catalytic conversion process of the analyzer. Similar to the second stage of calibration, four different levels of NH₃ are generated to verify the linearity of the analyzer.

13. References

Alberta Environment (AENV) 2011. *Standard Operating Procedure for NH₃ Analyzers*. AENV Air Monitoring and Audit Centre.

Greater Vancouver Regional District (GVRD) 2006. *Measurement of Ammonia (NH₃) using Chemiluminescence Ambient Air Monitoring Program Methods*. Air Quality Policy and Management Division.

Thermo Fisher Scientific 2014. *Model 17i Instruction Manual Chemiluminescence NH₃ Analyzer*.

United States (US) Environmental Protection Agency (EPA) 2013. *QA handbook for Air Pollution Measurement Systems Volume II Ambient Air Quality Monitoring Program*. US EPA Office of Air Quality Planning and Standards Air Quality Assessment Division.

Wood Buffalo Environment Association 2013. *Procedures for Operating Continuous Ammonia (NH₃) Analyzers*.

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Approval