



<b>Title: Standard Operating Procedure for NH<sub>3</sub> Analyzers</b>		
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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 analyzing Ammonia (NH<sub>3</sub>) concentrations in ambient air is used. 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 NH<sub>3</sub>. Commercially available NH<sub>3</sub> analyzers are used in the method.

This method is applicable to the measurement of NH<sub>3</sub> concentrations in ambient air in the range of 0.01 parts per million (ppm) to 10.0 parts per million (ppm).

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. Information used to write this procedure was also taken from sources identified in the reference section.

## 2. PRINCIPLE OF THE METHOD

Ammonia (NH<sub>3</sub>) detectors are based on the same principle as Nitrogen dioxide (NO<sub>2</sub>) analyzers in that nitric oxide (NO) and ozone (O<sub>3</sub>) react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO<sub>2</sub> molecules decay to lower energy states.

Specifically;



Ammonia analyzers have three active channels or modes, Total Nitrogen (Nt), Total Oxides of Nitrogen (NO<sub>x</sub>) and Nitric Oxide. The NH<sub>3</sub> and NO<sub>2</sub> outputs are calculated from the signal of these channels as follows.

To measure the NO<sub>x</sub> (NO + NO<sub>2</sub>) concentration, NO<sub>2</sub> is transformed to NO prior to reaching the reaction chamber. This transformation takes place in a molybdenum converter heated to approximately 325°C. Upon reaching the reaction chamber, the

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converted molecules along with the original NO molecules react with ozone. The resulting signal represents the NO<sub>x</sub> reading.

To measure the Nt (NO + NO<sub>2</sub> + NH<sub>3</sub>) concentration, both the NO<sub>2</sub> and NH<sub>3</sub> are transformed to NO prior to reaching the reaction chamber. This transformation takes place in a stainless steel converter heated to approximately 750° 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<sub>2</sub> concentration is determined by subtracting the signal obtained in the NO mode from the signal obtained in the NO<sub>x</sub> mode.  $NO_x - NO = NO_2$

The NH<sub>3</sub> concentration is determined by subtracting the signal obtained in the NO<sub>x</sub> mode from the signal obtained in the Nt mode.  $Nt - NO_x = NH_3$  The Model 17C outputs NO, NO<sub>2</sub>, and NH<sub>3</sub> concentrations to the front panel display and NO, NO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>x</sub> concentrations to the analog outputs. See figure 1 for the 17C/17i flow diagram.

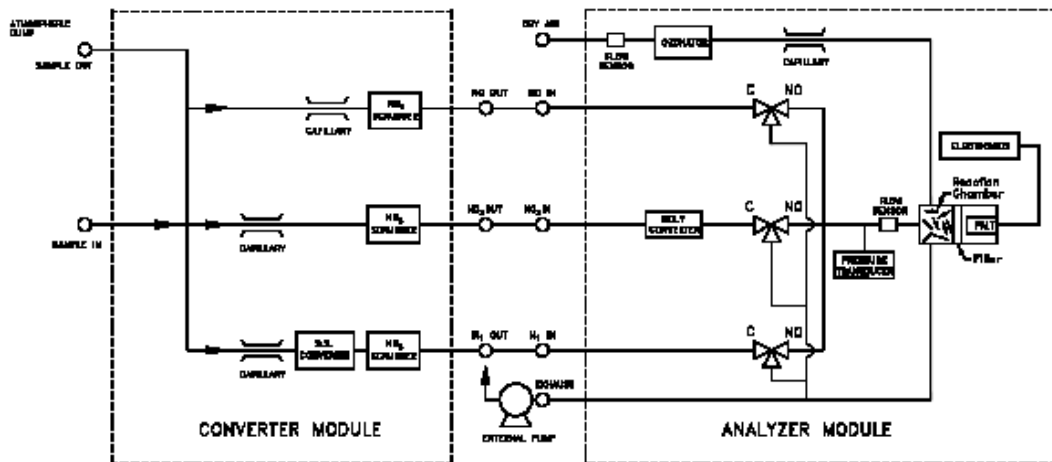


Figure 1 – TEI model 17C/17i flow path

Dry air enters the NH<sub>3</sub> 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<sub>2</sub> molecules. A photomultiplier tube (PMT) housed in a thermoelectric cooler detects the NO<sub>2</sub> luminescence.



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### 3. MEASUREMENT RANGE AND SENSITIVITY

The NH<sub>3</sub> 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 Alberta is 0 to 5.0 ppm.

The detection limit of the analyzer is specified by the manufacturer. Generally it is at the 1.0 ppb level.

### 4. EQUIPMENT AND APPARATUS

The following are available commercial analyzers suitable for used in this method and are currently in use in the AENV network:

- Thermo Environmental Instruments (TEI) Model 17C NH<sub>3</sub> Analyzer
- Thermo Environmental Instruments (TEI) Model 17i NH<sub>3</sub> Analyzer

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

### 5. INTERFERENCES

At concentration levels normally encountered in urban ambient air, other Nitrogen based compounds will be converted and subsequently detected in the Nt and NO<sub>x</sub> modes of the analyzer. These include the following compounds at the listed temperatures.

PAN (375°C, 450°C); ethyl nitrate; ethyl nitrite; HONO; HNO<sub>3</sub> (350°C, 375°C, 450°C); methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitroresol (450°C)

As the NO<sub>x</sub> converter temperature is maintained at 325°C, the influence of these compounds is minimal. For the purposes of this method, NO<sub>x</sub> is generally considered to include only NO<sub>2</sub> 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<sub>3</sub>, NO<sub>2</sub> and NO.

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Particulate matter present in the measurement cell can inhibit analyzer response by absorbing NH<sub>3</sub>, NO<sub>2</sub> and NO molecules, thereby not allowing them to luminesce. This problem is normally eliminated by using a particle filter of 2.0µm pore size made of inert material, such as Teflon, prior to the sample inlet of the instrument.

## 6. 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. 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 NH<sub>3</sub> monitoring should be determined according to the intended application of the monitoring data. Detailed requirements for selection of sites for monitoring ambient NH<sub>3</sub> and for the immediate surroundings of the monitoring site can be found in the Station Site Criteria section of the AMD.

## 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.

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- 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.
- 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 system should be set to match the voltage range of the analyzer output. Generally this is 1V or 10V full scale and is scaled to convert the output signal to the concentration range outlined in section 3. See the DAS operations manual for instructions on configuring these channels
- 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 instructions and setup table for NH<sub>3</sub> analyzer 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 chemiluminescent NH<sub>3</sub> 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), quality system manual and station site documentation.

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### 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 NO for the span cycle. These two sources are typically provided by internal systems. Zero is typically provided by pulling air through an MSA type "N" scrubbing canister and span using cylinders of NO. 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. 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 a site/instrument checklist (see controlled documents for an example of a station checklist).

### 9.3 Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. These test parameters should be monitored on a weekly basis and recorded on a site/instrument checklist (see appendix A).

### 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/or the electronic logbook. This is also recorded in the instrument log that accompanies each instrument.

### 9.5 Multipoint Calibration

Multipoint calibrations are conducted on the NH<sub>3</sub> 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, and monthly to comply with Alberta Environment regulations. This procedure is also completed after any major maintenance to confirm the precision and accuracy after repairs. Calibration procedures specific to the NH<sub>3</sub> analyzer are found in section 10 of this document.

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### 9.6 Analyzer Audit

NH<sub>3</sub> 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 most ammonia analyzers 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. Three concentrations of NO are generated in order to verify the linearity of the analyzer. Once the dilution portion of the calibration is complete, the Gas Phase Titration (GPT) begins. The GPT involves adding controlled amounts of Ozone to the NO flow generated in the dilution portion of the calibration. This causes the NO to react with the Ozone to form NO<sub>2</sub> which challenges the molybdenum converter to convert the generated NO<sub>2</sub> back to NO to be analyzed. Three levels of Ozone are generated in this phase of the calibration to again verify the linearity of the instrument. The third phase of the calibration involves introducing a known amount of NH<sub>3</sub> to challenge the High Temperature Nt converter to convert the generated NH<sub>3</sub> back to NO to be analyzed. Three levels of NH<sub>3</sub> are generated in this phase of the calibration to again verify the linearity of the instrument. There are certain specifics to the NH<sub>3</sub> calibration that are identified in this section.

- 10.1 Calibration Equipment – NH<sub>3</sub> calibrations can be calibrated using the dilution method, or a combination of the dilution method and the permeation method. The dilution calibrator used must also have the capability of generating stable low level concentrations of Ozone for the GPT portion of the calibration. If a combination of calibrators is used, the permeation calibrator is fitted with an NH<sub>3</sub> certified permeation device for the NH<sub>3</sub> part of the calibration only. A cylinder of NH<sub>3</sub> with the dilution calibrator can also be used for this portion of the calibration.
- 10.2 Referring to the calibration procedure in SOP 11 “SOP for Dilution Calibrations”, calculate the slope and intercept of the 4 data points for each phase 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. These values are calculated on all four outputs of the NH<sub>3</sub> analyzer to ensure proper operation of the instrument.

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10.3 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-008a** Thermo Environmental Instruments (TEI) Model 17C NH<sub>3</sub> Analyzer Operating Manual
- **EM-008b** Thermo Environmental Instruments (TEI) Model 17i NH<sub>3</sub> Analyzer Operating Manual
- **SOP11** Dilution Calibrations

#### 12. LITERATURE REFERENCES

None

#### 13. REVISION HISTORY

Revision 0 New document

Revision 1 - Jan 14/09 - Section 4, and 11 add reference to TECO 17i analyzer

Revision 1.1 January 17, 2011, Section 10.2 update SOP reference

#### 14. APPROVAL



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Approved by: **Harry Benders**  
Title: **Air Monitoring Team Leader**

Date: **January 17, 2011**

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