

Title: Standard Operating Procedure for Measurement of Oxides of Nitrogen in by Chemiluminescence		
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1. INTRODUCTION AND SCOPE

To obtain timely data for the purpose of air quality assessment, air quality trend reporting, air quality index reporting and to meet the requirements for inclusion of the data in provincial and national air quality databases, a continuous method of analyzing Nitric Oxide (NO), Oxides of Nitrogen (NO_x), and Nitrogen Dioxide (NO₂) 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 NO₂. Commercially available NO₂ analyzers are used in the method.

This method is applicable to the measurement of NO₂ concentrations in ambient air in the range of 1.0 parts per billion (ppb) to 1.0 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

The analyzer is based on the principle that nitric oxide (NO) and ozone (O₃) react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO₂ molecules decay to lower energy states.

Specifically;



The analyzers have two active channels or modes, the NO mode and the NO_x mode. Using the signal data from these two active modes, the NO signal is subtracted from the NO_x signal to give the NO₂ signal. This is accomplished considering the following. Nitrogen dioxide (NO₂) must first be transformed into NO before it can be measured using the chemiluminescent reaction. NO₂ is converted to NO by a molybdenum NO₂-to-NO converter heated to about 325°C. The ambient air is drawn into the NO_x analyzer using an external vacuum pump. The sample flows through a particulate filter, a capillary, and then to the mode solenoid valve. The solenoid valve routes the sample either straight to the reaction chamber (NO mode) or through the NO₂-to-NO converter

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and then to the reaction chamber (NO_x mode). A flow sensor prior to the reaction chamber measures the sample flow.

Dry air enters the NO_x analyzer through either a permeable membrane dryer system or a canister of silica gel 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 ambient air sample to produce electronically excited NO₂ molecules. A photomultiplier tube (PMT) housed in a thermoelectric cooler detects the NO₂ luminescence. The NO and NO_x concentrations calculated in the NO and NO_x modes are stored in memory. The difference between the concentrations are used to calculate the NO₂ concentration. The NO_x analyzer outputs NO, NO₂, and NO_x concentrations to both the front panel display and the analog outputs.

3. MEASUREMENT RANGE AND SENSITIVITY

The NO_x 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 500 ppb.

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) Models 42, 42C & 42i NO_x Analyzers

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 NO_x mode of the analyzer. These include the following compounds at the listed temperatures.

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PAN (375°C, 450°C); ethyl nitrate; ethyl nitrite; HONO; HNO₃ (350°C, 375°C, 450°C); methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitroresol (450°C)

As the 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 NO₂ and NO.

Particulate matter present in the measurement cell can inhibit analyzer response by absorbing NO and NO₂ molecules, thereby not allowing them to luminesce. 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.

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 and monthly calibration checks. 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 team and the use of transfer standards from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily 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 NO_x monitoring should be determined according to the intended application of the monitoring data. Detailed requirements for selection of sites for monitoring ambient NO_x for the Canada Wide Standard (CWS) determination can be found in “Guidance Document on Achievement Determination-Canada Wide Standards for Particulate Matter and Ozone³” section 3.0. Requirements for the immediate surroundings of ambient monitoring sites can be found in the Station Site Criteria section of the AMD.

8. INSTALLATION REQUIREMENTS

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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.
- 8.2 A Teflon particulate filter Zeflour™ or equivalent with PTFE membrane and support of 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.
- 8.3 A data acquisition system 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.
- 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.

9. OPERATIONAL REQUIREMENTS

The following activities must be performed when operating a continuous automated chemiluminescent NO/NOx/NO₂ 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

---THIS DOCUMENT MUST NOT BE PHOTOCOPIED---

Additional copies are available from the Air Monitoring Manager or designate

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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 provided by pulling air through a charcoal canister. The span is provided using a cylinder of NO. This cycle is normally controlled by the data 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 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 checklist (see controlled documents for an example of a station checklist).

9.3 Inlet Filter Change

The sample inlet filter is typically checked 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. If the filter has visible particulate on it, change the filter with a new Teflon filter.

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.

9.5 Multipoint Calibration

Multipoint calibrations are conducted on the NO/NO_x/NO₂ 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. Calibration procedures specific to the NO₂ analyzer are found in section 10 of this document.

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9.6 Analyzer Audit

NO/NO_x/NO₂ analyzers operating in Alberta are required to undergo an on-site audit once per year. This audit involves the Alberta Environment audit team visiting the site with the NIST traceable standards to verify the accuracy and linearity of the instrument.

10. CALIBRATION

The calibration procedure for NO/NO_x/NO₂ analyzers is unique to the calibration of other continuous ambient air analyzers in that it is a two 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 both modes to provide the same signal on both 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 NO₂ which challenges the molybdenum converter to convert the generated NO₂ 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. There are certain specifics to the NO₂ calibration that are identified in this section.

- 10.1 Calibration Equipment – NO₂ calibrations can be calibrated using only the dilution method. The calibrator used must also have the capability of generating stable low level concentrations of Ozone for the GPT portion of the calibration.
- 10.2 Referring to the calibration procedure SOP 11 “SOP for Dilution Calibrators”, 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 $\pm 3\%$ full scale and a coefficient of correlation (CC) > 0.998 . These values are calculated on all three outputs of the NO₂ analyzer to ensure proper operation of the instrument.
- 10.3 The slope and intercept can be used to compensate the output of the analyzer by entering them in to the data system if this is possible. If the data system is not capable of this action, the slope and intercept can be used to compensate the collected data during the data validation process.

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11. APPLICABLE DOCUMENTS

- **EM-037a** Thermo Environmental Instruments (TEI) Model 42 NO/NO_x/NO₂ Analyzer Operating Manual
- **EM-037b** Thermo Environmental Instruments (TEI) Model 42C NO/NO_x/NO₂ Analyzer Operating Manual
- **EM-037c** Thermo Environmental Instruments (TEI) Model 42i NO/NO_x/NO₂ Analyzer Operating Manual

12. LITERATURE REFERENCES

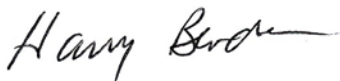
None

13. REVISION HISTORY

Revision 0 (new document)

Revision 1.0 January 17, 2011 Change reference from NO₂ analyzers to NO_x analyzers several places, Change SOP reference section 10.2

14. APPROVAL



Approved by:

Harry Benders

Date: January 17, 2011

Title:

Air Monitoring Manager