Title: Standard Operating Procedure for Measurement of Ozone in Ambient Air by Ultraviolet (UV) Photometry		
Procedure No: SOP-022	Revision No: 1.1 January 27, 2011	Page No.: 1 of 8

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 Ozone concentration in ambient air samples 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 concentration of ozone. Commercially available ozone analyzers are used in the method.

This method is applicable to the measurement of ozone concentration 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) 1989 by Alberta Environment. 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 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 method uses the principle of ultra violet (UV) light absorption of the ozone molecule at the wavelength of 254 nm. By knowing the absorption coefficient of ozone, geometry of the measurement cell, and the pressure and temperature of the air sample, the concentration of the ozone in the sample can be determined by the transmittance of UV light through the measurement cell. The quantities are related to the Beer-Lambert Law. (Lodge, 1991).

Ambient air is drawn through the instrument by a pump at the exit end of the flow path. The sample air is scrubbed of ozone by passing through a catalytic converter. This ozone free air sample is passed through the measurement cell and the intensity of the UV light is measured by a stabilized photo detector. The second half of the measurement cycle allows the sample air to pass directly through to the measurement cell without catalytic conversion. The intensity of the UV light will be partially absorbed by the presence of ozone molecules in the sample. By comparing the difference in the UV transmittance of scrubbed and unaltered air the concentration of ozone in the air sample can be quantified.

3. MEASUREMENT RANGE AND SENSITIVITY

The ozone 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 49, 49C 49i 49iPS Ozone 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, gaseous compounds such as nitrogen dioxide, sulphur dioxide and volatile organic compounds (VOC) have negligible effect on the accuracy of the measurement.

Particulate matter present in the measurement cell will interfere with UV absorption measurement by either scattering and or absorption of the instance beam. This problem is normally eliminated by using a particle filter of 2.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

6. PRECISION AND ACCURACY

The measurement precision of the particular model of the analyzer is established by the manufacturer. For analyzers in the AENV network this value is 1.0 ppb.

The accuracy of the analyzer is also dependent on the accuracy of the calibration transfer standard. The transfer standards used in the NAPS network are calibrated against the National Institute of Standards and Technology (NIST) standard reference

photometer (SRP) number 16 maintained at the Environmental Technology Centre (ETC) of Environment Canada. The performance of the SRP is established by means of inter comparison with other SRP's. The transfer standards used in the field have similar performance as the analyzers. The specification used herein for the uncertainty estimates is a precision of 1.0 ppb.

The following table is the estimated uncertainty.

Table 1

Uncertainty Estimate

Source of Error	Ozone (ppb)
Transfer Standard Precision	1.0
Analyzer Precision	1.0
Total Uncertainty	1.4

7. SITE REQUIREMENTS

Site location of the ozone monitoring station should be determined according to the intended application of the monitoring data. Detailed requirements for selection of sites for monitoring ambient ozone for the Canada Wide Standard (CWS) determination can be found in "Guidance Document on Achievement Determination-Canada Wide Standards for Particulate Matter and Ozone[3]" section 3.0. Requirements for the immediate surroundings of the site can be found in the AMD, Appendix A-1 - Standard Site Criteria.

8. INSTALLATION REQUIREMENTS

All the installation requirements as specified by the manufacturer in the installation procedures as well as the general requirements below must 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 An entirely Teflon particulate filter membrane (Pall Scientific Zeflour or equivalent) capable of removing al least 99% of particles of 2.0µm and larger must be placed in the sampling line before the air sample enters the detection cells. The holder for such filter must also be made of Teflon, stainless steel or Delrin.

8.3 A data logger 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.

8.4 Connection of Status line to the data logger should be completed as well to monitor any alarm conditions.

8.5 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.

8.6 Within the vicinity of the station all products containing solvents and other sources of hydrocarbon should be avoided.

9. OPERATIONAL REQUIREMENTS

The following table of activities must be performed when operating a continuous automated UV photometric ozone analyzer in the AENV network. The following documentation must be available to the operators on site: operational and maintenance manual(s), station site documentation.

Table 2

Analyzer Operational Requirements

Action	Time and Frequency	Procedure	Documentation	Action by
Set analyzer and data system range (500 ppb or 1000 ppb)	After installation	As per manufacturer's manual	Entry to log book/instrument setup	Station operator
Zero and span verification	Daily	Automated and controlled internally by the analyzer or externally by the data system	Stored in data system	Data system
Verification of operational test parameters	Weekly	As per manufacturer's manual	Entry to station /instrument checklists	Station operator
Inlet filter change	changed monthly	As per manufacturer's manual	Entry to log book/instrument maintenance sheet	Station operator
Analyzer maintenance	As recommended by manufacturer	As per manufacturer's manual	Entry to log book/instrument maintenance sheet	Station operator
Clean inlet lines	As required	Replacement with new lines	Entry to log book/instrument maintenance sheet	Station operator

Action	Time and Frequency	Procedure	Documentation	Action by
Calibration	After installation or repair and monthly	See section 10.0	Entry to log book; /instrument maintenance sheet report to network manager	Station Operator
Calibration verification	annually	See audit section	Entry to log book; /instrument maintenance sheet report to designated manager	Network auditor

10. CALIBRATION

The calibration procedure for Ozone analyzers is similar to calibration of other continuous ambient air analyzers. This procedure involves generating a known amount of ozone, which is introduced to the analyzer to verify its performance. There are certain specifics to the Ozone calibration that are identified in this section.

10.1 Calibration Equipment – Calibration equipment specific to the Ozone analyzer is GPT is our standard method a transfer standard UV photometer calibrated annually against a local primary standard. Procedures to operate the transfer standard can be found in the Photometer operations manual. A zero air system is used to supply clean air for the calibrator. The system should supply zero air with less than 1.0 ppb of ozone, less than 1.0 ppb of NOx and less than 1.0 ppb of organic compounds.

10.2 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 +/- 3% full scale and a coefficient of correlation (CC) >0.995.

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.

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11. APPLICABLE DOCUMENTS

- **EM-022a** Thermo Environmental Instruments (TEI) Models 49 Ozone Analyzer Operating Manual
- **EM-022b** Thermo Environmental Instruments (TEI) Models 49C Ozone Analyzer Operating Manual
- **EM-022c** Thermo Environmental Instruments (TEI) Models 49i Ozone Analyzer Operating Manual
- **EM-022d** Teledyne-API model 400 O3 analyzer Operating Manual
- **EM-022e** Thermo Environmental Instruments (TEI) Models 49iPS Ozone Primary Standard Analyzer Operating Manual

12. LITERATURE REFERENCES

- Lodge. 1991. "Methods of Air Sampling and Analysis", 3rd edition. *p.422*
- "Technical Assistance Document for the Calibration of Ambient Ozone Monitors". EPA/600/4-79-057, September 1979, United States Environment Protection Agency, Research Triangle Park, NC 27711.
- "Guidance Document on Achievement Determination-Canada Wide Standards for Particulate Matter and Ozone". ISBN: 1-896997-41-4 PN 1330, October 2002, Canadian Council of Ministers of the Environment.
- "Guideline on Ozone Monitoring Site Selection". EPA 454/R-98-002, August 1998, United States Environment Protection Agency, Research Triangle Park, NC 27711.

13. REVISION HISTORY

Revision 1.0

Add reference to 49iPS to Section 4 and 11

Revision 1.1

Section 7 – Added reference to AMD

Section 8 – reword for clarity

Section 9 – formatting

Section 10 – changed criteria to match calibration sheets

Changed “Team Leader” to “Manager”

14. APPROVAL

Harry Benders

Approved by: **Harry Benders** **Date: July 29, 2009**

Title: **Air Monitoring Manager**