1. Introduction and Scope

Continuous ambient air analyzers require multipoint calibrations on a routine monthly basis and after any major maintenance are completed. This procedure describes the dilution method used to generate multiple concentrations of gasses to introduce to the continuous analyzers to calibrate their responses. This method is to be used in conjunction with the calibrator's operations manual.

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 versions 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.

LIST OF ABBREVIATIONS / ACRONYMS

AENV	Alberta Environment
AMD	Air Monitoring Directive
DAS	Data Acquisition system a.k.a. datalogger
GPT	Gas Phase Titration
CCM	Cubic Centimeters per Minute
MFC	Mass Flow Controller
OGC	Output Gas Concentration
PPM	Parts Per Million
SCCM	Standard Cubic Centimeters per Minute
SLPM	Standard Liters per Minute
SS	Stainless Steel
NIST	National Institute of Standards and Technologies
NMI	Nederlands Meetinstituut

2. Principle of the Method

The principle of this method utilizes mass flow controllers (MFC) to regulate the flow of one or more separate source gasses, dilution flow and the Ozone generator and combines the flows to generate a known concentration of gas.

The dilution gas source is typically zero air and is usually provided by a zero air system consisting of a compressor, air dryer and a scrubbing system for removal of all compounds found in ambient air. A cylinder of Zero Air can also be used.

The source gas is provided by a cylinder with an analyzed amount of the compound of interest with a balance of Nitrogen gas or air.

Each of these flows is controlled separately with individual mass flow controllers (MFCs). The controlled flows then exit the MFCs and are combined in a mixing chamber to generate a homogeneous gas mixture that exits the calibrator to introduce to the analyzer being calibrated. The dilution calibrator can have an ozone generator installed for the gas phase titration (GPT) portion of a NO_2 calibration. The ozone generator is typically a mercury lamp that emits UV light to form ozone. See figure 1 for flow path.

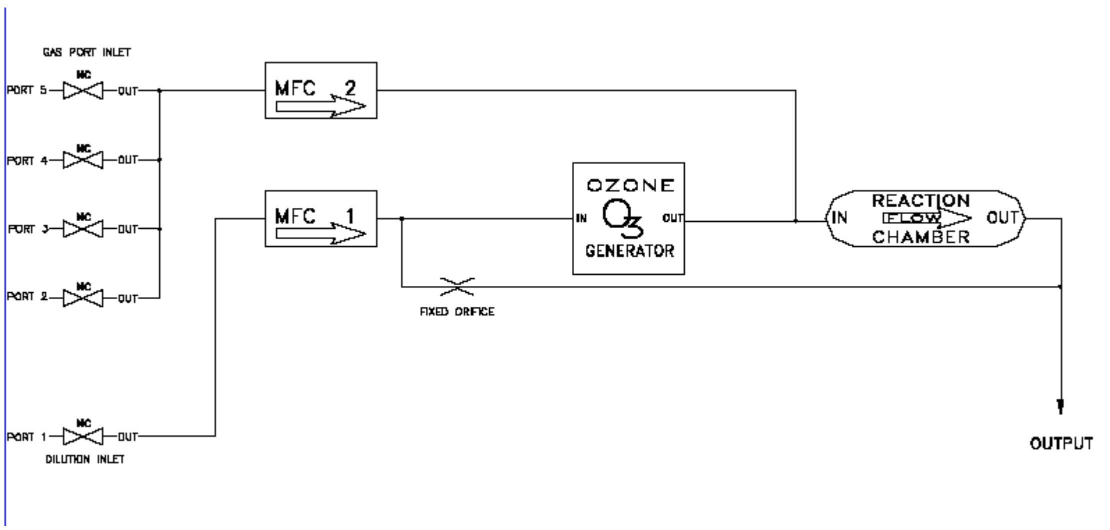

Figure 1 – Typical flow path

3. Measurement Range and Sensitivity

The typical dilution calibrator utilizes MFCs to control the gas flows, and the ozone generator flow described in section 2. These three components of the calibrator govern the range and sensitivity of the calibrator. Table 1 indicates the range and sensitivity for all three components.

Component	Range	Sensitivity (accuracy)	Repeatability
MFC - Dilution	0 – 10 SLPM or 0 – 5 SLPM	± 1.0% of full scale	± 0.15%
MFC(s) - Gas	0 – 100 SCCM or 0 – 50 SCCM	± 1.0% of full scale	± 0.15%
O_3 generator	0.05 – 1.0 PPM	±2.0% of set point or ±3 ppb @ 4 SLPM	N/A

Table 1.

4. EQUIPMENT AND APPARATUS

The following equipment list is required to set up and complete a dilution calibration on an ambient air analyzer:

- Dasibi Multi Gas Dilution Calibrator model 5008 or
- R&R Environmental Devices model MFC201 or
- Sabio Instruments models - 4010 and 2010
- Zero Air Generator models – API 701, Perma Pure ZAG, AENV shop built
- Stainless Steel two stage regulator and proper cylinder gas adapter (CGA)
- Teflon tubing with appropriate stainless steel fittings. Note: tubing must be free of kinks, cracks, dirt, moisture or other foreign material or defects
- Source Gas Cylinder - Certified transfer standards or NIST / NMI standards
- Flow measurement device (Bios) with valid certificate

5. INTERFERENCES

Interferences with the operation of a dilution calibrator are typically the two listed below.

- Moisture can consume source gas molecules if allowed to enter the system. This is prevented by ensuring the zero air generator is functioning properly.
- Ambient temperature and pressure swings can affect the OGC of the calibrator.

However, it must be considered that when changing calibration gases, residue of one gas may interfere with the next gas used. A good practice to reduce the possibility of these types of interferences is to flush the calibrator thoroughly with zero air after the completion of each multipoint calibration.

6. Precision and Accuracy

The measurement precision is generally considered to be the "repeatability of the measurement". Precision in the context of the dilution calibrators relates to the repeatability of the mass flow controllers accuracy. Although all flows are measured for each point in a calibration, the accuracy of the MFCs are confirmed by conducting MFC calibrations annually. See section 10.0 in this document for information on these procedures.

The accuracy is generally considered to be the "deviation from true". This means how close it is to what it should be. Again, all flows are measured for each flow change in a calibration but the accuracy of the MFCs is confirmed through annual MFC calibrations. Refer to the sections identified above for further information on calibration procedures.

7. Site Requirements

All calibration equipment must be set up inside a temperature controlled structure to avoid influence of temperature drift and effects of the weather, i.e. rain, wind, dust, temperature, etc. The calibrator should be set up so that the controls and display are easily accessible as changes need to be made throughout the calibration and flows need to be measured.

The source gas must be at ambient shelter temperature and the cylinder's regulator needs to be purged prior to connecting the Teflon lines to the calibrator.

8. Installation Requirements

All the installation and set up requirements are specified by the manufacturer in the installation procedures of the manual and by AENV for proper calibration of continuous ambient air monitoring equipment. The set up of the calibration system is done at the station where the monitoring is taking place.

NOTE: Calibration equipment including gas cylinders and regulators must be at room temperature before commencing a calibration. When any part of the system has been stored in a vehicle for an extended period such as overnight, a considerable warm-up time must be allowed for this, as much as 24 hours.

Follow the steps below for proper set up of the calibration system.

8.1 Turn the calibrator on and allow it to warm up sufficiently so all components and systems are up to operating temperature and stabilized. Normally 30 minutes should suffice. If equipment has been stored in a cold vehicle in winter warm up and stabilization could take as much as 24 hours.

NOTE: For analyzer calibrations in the Audit Lab and on the MAML omit step 8.1.1

8.1.1 Prior to disconnecting the analyzer's sample line from the sample manifold, the DAS collecting data from that analyzer requires the "Low Input" value in the DAS must be set to 0.0000 (zero). The data channels applicable to the analyzer being calibrated must be flagged for calibration. Consult the manual for the data logger for the menu selections and steps to accomplish this.

NOTE: For ESC loggers the "Low Input" value must be set to zero before setting the calibration flag.

8.2 The dilution calibrator needs to be set up in a location where the controls and display are easily accessible. The zero air generator should be set up nearby. Connect the zero air generator output using ¼ inch outside diameter Teflon tubing to the dilution air "in" port of the calibrator and power on the zero air generator.

For calibration of hydrocarbon analyzers, a high temperature oxidizer for removal of hydrocarbons must be connected and up to operating temperature.

8.3 Purge the source gas cylinder regulator then connect the source gas cylinder to the source gas in port of the calibrator using the following steps:

8.3.1 Connect the 1/8 inch outside diameter Teflon tubing from the cylinder regulator to a vacuum pump. The main cylinder valve must be closed.

8.3.2 With the regulator outlet valve closed, turn on the vacuum pump.

8.3.3 Open the outlet valve of the regulator and allow the vacuum pump to evacuate the regulator for at least 5 minutes.

8.3.4 Close the regulator outlet valve and slowly open the main cylinder valve to fill the regulator, and then close the main valve again.

8.3.5 Repeat steps 8.4.3 & 8.4.4 a minimum of three times to completely flush the regulator with the source gas.

8.3.6 Open the main cylinder valve and with the regulator full of source gas, ensure the outlet valve is closed and turn off the vacuum pump.

8.3.7 Disconnect the line from the vacuum pump and connect to the source gas "in" port of the calibrator. There may be multiple ports for source gas on the calibrator, so connect to the one configured for the gas being used. Consult the calibrator operations manual for more information on configuring these ports.

8.3.8 Open the outlet valve on the regulator to allow source gas flow to the calibrator. Purge the line before tightening to remove air trapped in the line. Then tighten the fitting.

8.4 Connections need to be made at atmospheric pressure from the calibrator output to the analyzer via the sample inlet filter (filter element is to be changed prior to connecting calibration line). This is accomplished by venting either through a calibrator vent port or a SS tee fitting in the sample line from the calibrator to the sample inlet filter, dependent on calibrator configuration and/or preference. The procedure for venting through the sample line is accomplished using the following steps:

8.4.1 Connect a length of ¼ inch outside diameter Teflon tubing from the calibrator output to a SS tee fitting.

8.4.2 Connect a short piece (6" in length) of ¼ inch outside diameter Teflon tubing on the side of the SS fitting to be used as the vent line.

8.4.3 Connect another length of ¼ inch outside diameter Teflon tubing to the last side of the tee. This length is then connected to the analyzer sample filter holder or to the analyzer sample "in" port of the analyzer if the analyzer has an internal filter.

8.4.4 Plug the corresponding sample line connected to the sample manifold to ensure the integrity of the sampling of the other analyzers using the manifold

The dilution calibration system is now set up and ready to perform the required steps to calibrate the analyzer.

9. Operational Requirements

Once the calibration system is set up and ready to begin, the following steps are completed to perform a multipoint calibration on a continuous ambient analyzer. These steps conform to the requirements set out in the AMD.

Described below are the various stages in the calibration and are referred to as “points”. A point is a calibration setting that is held for at least 20 minutes of stable response from the analyzer.

NOTE: For analyzer calibrations in the Audit Lab and on the MAML the concentration for the point is determined by the average of a minimum of 10 minutes of stable response on the analyzer and demonstrated on the electronic chart recorder or data acquisition system.

NOTE: At the air monitoring station the concentration for the point is determined by the average of at least 20 minutes of stable 1 minute averages from the DAS.

All activities and observations carried out during the multipoint calibration must be documented on a multipoint calibration form, and in the station logbook, and/or electronic logbook. This allows other operators to access a history of the calibrations if the regular technician is not available. The following documentation must be available to the operators on site: operational and maintenance manual(s), relevant quality system documents and station site documentation.

9.1 Calibrator Operation

Most calibrators have two operational modes; concentration and manual modes.

In manual mode, the user determines the desired flows to generate the target concentrations. These flows are manually entered and the calibrator achieves the target flow rates to generate the desired concentrations. This is the method most commonly used

In concentration mode, typically a default dilution flow rate (zero air) and the concentration of the source gas cylinder is entered. With this information, the calibrator can calculate required source flows to generate desired concentrations. Using this mode, the desired concentrations are then entered to achieve the desired points.

Either method is acceptable; however, all flows must be measured and recorded on the calibration form regardless of the mode used.

9.2 Zero Point

NOTE: Checking the station automatic daily zero source or internal zero is not an AMD guideline requirement.

The first calibrator point is the zero point.

This is accomplished by setting the dilution calibrator to generate zero air. In most cases the dilution flow is set to <u>5.0 SLPM</u>. Total dilution flow must be at least 2.5 times the sample flow of the analyzer being calibrated. The analyzer should demonstrate a zero output response on the analyzer and DAS, and this point should be held for at least 20 minutes of stable readings. After 15 minutes of stable readings, the analyzer time constant if applicable, must be adjusted to the highest available value (i.e. Thermo analyzers is 300 seconds) and ran for the remaining 5 minutes Record the response (initial concentration) on the calibration form as an average over the 20 minute period.

The analyzer needs to be adjusted if the zero output response is not actually at zero. An adjustment must be made to achieve an output of or very near to zero on the analyzer and on the DAS.

If no adjustment is required, record the initial concentration also as the final concentration on the calibration form and return the time constant back to the original value (i.e. 120 seconds). Proceed to the first upscale point.

If an adjustment is made at the zero point, record the response after adjustment (final concentration) on the calibration form as an average over a 20 minute period of stable readings. When the 20 minutes of stability have been demonstrated, return the time constant back to the original value (i.e. 120 seconds).

Disconnect the calibrator output tubing and measure the zero flow.

9.3 First Upscale Point

The second point is the first upscale point.

Set the dilution calibrator to generate an OGC of 50%-800% of the analyzers full scale.

NOTE: The calibration forms to be used by the AENV Air Monitoring group include an automatic calculation in the margin for the limits as per the AMD for each upscale calibration point based on the analyzer full scale. Set the OGC within these limits for each upscale point.

This point is used to reference the response of the analyzer "as found" and as the only upscale point in the calibration at which adjustments can be made.

Set the calibrator gas flow, using the source gas cylinder concentration, and the set dilution flow rate, to achieve the desired concentration. Then measure the flows of both MFCs and record the values on the calibration form. The SGF is measured first then the DF and SGF are measured together.

This is done using the following equation:

OGC = (SGC x SGF) / (DF + SGF)

Where:

OGC = output gas concentration (PPM)

SGC = source gas concentration (PPM)

DF = dilution (zero) air flow in (SCCM)

SGF = source gas flow in (SCCM)

Reconnect the calibrator output tubing.

The analyzer and DAS should respond at or near the desired concentration, and this point should be held for at least 20 minutes of stable of analyzer DAS readings. After 15 minutes of stable readings, the analyzer time constant if applicable, must be adjusted to the highest available value (i.e. Thermo analyzers is 300 seconds) and ran for the remaining 5 minutes Record the response (initial concentration) on the calibration form as an average over a 20 minute period of stable readings. This response is used as the as found point of the calibration.

The analyzer has to be adjusted if the response is not equal to the calculated OGC.

If no adjustment is required, record the initial concentration on the calibration form also as the final concentration return the time constant back to the original value (i.e. 120 seconds).

If an adjustment has been made at this point record the response after adjustment (final concentration) on the calibration form as an average over a 20 minute period of stable readings. When the 20 minutes of stability have been demonstrated, return the time constant back to the original value (i.e. 120 seconds).

9.4 Second Upscale Point

The next point is the second upscale point.

This is accomplished by setting the dilution calibrator to generate an OGC of 25%-40% of the analyzers full scale. This is done using the equation in 9.2. Record the analyzer DAS response on the calibration form as an average over the 20 minute period of stable readings

At the end of this point disconnect the calibrator output tubing and measure the flows for the second point. Keep the flow meter connected to measure flows for the third upscale point.

9.5 Third Upscale Point

The next point is the third upscale point.

This is accomplished by setting the dilution calibrator to generate an OGC of 10%-20% of the analyzers full scale. This is done using the equation in 9.2. Measure and record the flows on the calibration form and reconnect the calibrator output tubing. Record the analyzer DAS response on the calibration form as an average over the 20 minute period of stable readings.

9.6 Final Calibrator Zero

The calibrator is then set to deliver zero air once again. Demonstrate 20 minutes of stable readings and proceed to next step. No requirement to record final zero on calibration sheet or make any further analyzer adjustments.

NOTE: Due to long residence time of ammonia gas in analyzer and calibration systems, a stable response in this step for ammonia calibrations may take considerably longer than 20 minutes. If so it is acceptable to limit this step to 20 minutes total time.

9.7 Auto Zero and Auto Span Points

NOTE: This step is not used for analyzers in the Audit Lab.

NOTE: For analyzers on the MAML the Zero/Span cycle is triggered manually from the instrument front panel for the duration of at least 10 minutes of stable readings displayed on the analyzer.

Unless continuing on to step 9.8 for NO2 analyzers, the complete daily zero and span cycle for the analyzer must be initiated through the DAS. This diverts the flow from the analyzer sample inlet to pull gas from the internal zero and span sources.

These points are to be run for the duration of a normal Daily Zero/Span Check.

The observed zero response at the DAS should be approximately zero. The observed span response should be at or near to the last recorded expected span value.

Note the zero and span values captured by the DAS from this Auto Zero/Span cycle and record these values in the DAS as the expected values for subsequent Daily Zero/Span checks.

9.8 Gas Phase Titration (GPT) - NO_2 Calibration

When calibrating a continuous NO_2 analyzer a GPT must be completed in addition to the dilution portion of the calibration.

NOTE: The NO decrease values from the GPT portion of the NO_2 calibration can be used to determine the expected concentrations for an O3 analyzer calibration. The O3 analyzer full scale is typically 50% of the NO_2 full scale, therefore this calibration is conducted at lower percentages of full scale than would be used in a normal calibrations.

The GPT involves adding (titrating) ozone to the high point of the NO gas calibration. Ozone reacts with the NO to form NO_2, thereby reducing the response observed on the NO channel and increasing the response observed on the NO_2 channel of the analyzer.

The NO decrease (expected values of NO_2) is calculated using only the NO channel response.

The NO decrease is calculated using the following description:

$NO_i - NO_f$ = NO (decrease)

WHERE

NO_i = NO concentration before introduction of O3

NO_f = NO concentration after introduction of O3

The NO_2 increase (change in NO_2 concentration) is calculated using only the NO_2 channel response at the DAS.

The NO_2 increase is calculated using the following description:

$NO_{2i} - NO_{2f} = NO_2$ (increase)

WHERE

$NO_{2i} = NO_2$ concentration before introduction of O3

$NO_{2f} = NO_2$ concentration after introduction of O3

The GPT (NO_2) portion of the calibration is completed after the dilution portion (NO /NO_x) calibration has been completed. Follow the steps below to complete the GPT portion of the NO_2 calibration.

9.8.1 To start the GPT, set the calibrator to duplicate the high point of NO gas calibration. These values provide the baseline (reference) readings for the NO_2 calibration (NOi, NO_xi and NO_2i). Run this point to obtain 20 minutes of stable readings. Record the analyzer DAS response for NO, NO_x and NO_2 (indicated reference concentrations) on the calibration form as an average over the 20 minute period of stable readings.

9.8.2 First Upscale NO_2 Point

Add an amount of Ozone to the mixture that is 60% - 70% of the high point concentration of NO as per the AMD. Typically a value close to 400 ppb is used. This value could then be used on a subsequent ozone analyzer calibration.

The calibration forms to be used by the AENV Air Monitoring group include an automatic calculation in the margin for the limits as per the AMD for each upscale calibration point based on the analyzer full scale. Set the ozone so that each upscale point in the NO_2 calibration is within these limits.

For the NO_2 calibration with the first GPT point entered, the NO channel response should decrease, the NO_2 channel response should increase, and the NO_x channel should stay the same.

Run this point to obtain 20 minutes of stable readings. Record the analyzer response for NO, NO_x and NO_2 (indicated concentrations) on the calibration form as an average over a 20 minute period of stable and determine the NO decrease and NO_2 increase.

If an adjustment of the NO_2 portion of this analyzer is required, adjust the time constant to the highest value (i.e. Thermo analyzer is 300 seconds) after 15 minutes. Let it run for the remaining 5 minutes and adjust the NO_2 channel in the analyzer to equal the NO decrease observed.

NOTE: Make sure to take into account any NO_2 that is present during the reference point before calculating the actual NO_2 increase.

Record the analyzer response (final concentration) on the calibration form as an average over the 20 minute period of stable readings. Return the time constant back to the original value (i.e. 120 seconds).

9.8.3 Second Upscale NO_2 Point

Add an amount of Ozone to the mixture that is approximately 30% to 40% of the high point concentration of NO.

Run this point to obtain 20 minutes of stable readings. Record the analyzer response for NO, NOx and NO_2 (indicated concentrations) on the calibration form as an average over a 20 minute period of stable readings and determine the NO decrease and NO_2 increase.

9.8.4 Third Upscale NO_2 Point

Add an amount of Ozone to the mixture that is approximately 10% to 15% of the high point concentration of NO.

Run this point to obtain 20 minutes of stable readings. Record the analyzer response for NO, NO_x and NO_2 (indicated concentrations) on the calibration form as an average over the 20 minute period of stable readings and determine the NO decrease and NO_2 increase.

9.8.5 Calibrator Zero

Return the calibrator to deliver calibrator zero air and demonstrate 20 minutes of stable readings. Then follow 9.7 for internal zero and span requirements.

10. CALIBRATION

Calibration of a dilution calibrator involves measuring and adjusting (if required) the flows generated by the mass flow controllers. This procedure is completed as required depending on repairs or problems. Multipoint flow calibrations are conducted on the dilution calibrators to verify precision, accuracy and linearity of the flow controllers.

10.1 Calibration Equipment

Flow calibrations on the mass flow controllers of dilution calibrators are completed using a primary flow meter. The DHI MOLBOX primary flow calibrator or BIOS flow meter with a date-current calibration certificate are used for this purpose.

10.2 Flow Calibration Procedures

Procedures specific to the calibrator used can be found in the calibrator's operations manual.

10.3 Calibrator Maintenance

Preventative maintenance tasks should be completed on the calibrator 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. This is recorded in the instrument log that accompanies each instrument.

11. Applicable Documents

- Alberta Environment Air Monitoring Directive 1989
- **EM-011a** Dasibi Multi Gas Dilution Calibrator operations manual
- **EM-029a** R&R Environmental Devices model MFC201 operations manual
- **EM-012a** Sabio 4010 operations manual
- **EM-012c** Sabio 2010 operations manual
- **Molbox** operator manual

12. Literature References

None

13. Revision History

Revision 1.0 May 21, 2010 – procedural changes incorporated

Revision 1.1 January 21, 2011 – procedural changes incorporated

14. Approval

Approved by: **Harry Benders** **Date:** **March 21, 2010**

Title: **Air Monitoring Manager**