



Air Monitoring Directive Chapter 7: Calibration

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1.0 Purpose

This Calibration document forms a part (Chapter 7) of Alberta's Air Monitoring Directive (Alberta Environment and Parks 2016, as amended from time to time) and will hereafter be referred to as the Calibration Chapter. Refer to Chapter 1 (the AMD Introduction) for requirements and definitions that apply to all parts of the AMD, a list of what components constitute the AMD, and details on review of and revisions to the AMD.

The purpose of the Calibration Chapter is to:

- outline the minimum requirements for calibration of continuous ambient air analyzers and meteorological sensors; and
- promote consistent use of air monitoring equipment across the province.

Calibration of an analyzer establishes the quantitative relationship between actual substance concentration input (in ppm, ppb, $\mu\text{g m}^{-3}$, etc.) and the analyzer's response (chart recorder reading, output volts, digital output, etc.). This relationship is used to adjust analyzer response values to corresponding pollutant concentrations. Since the response of most analyzers has a tendency to change somewhat with time (drift), the calibration must be conducted periodically to maintain a high degree of accuracy.

Cal 1-A The person responsible must comply with the requirements in the Calibration Chapter (Chapter 7) of the AMD on or before September 23, 2015 for all continuous ambient air analyzers and meteorological sensors.

Cal 1-B The person responsible shall calibrate each continuous ambient air analyzer and meteorological sensor a) in accordance with the requirements of the Calibration Chapter (Chapter 7) of the AMD and b) as specified in the analyzer's operation or instruction manual.

Cal 1-C Any conflict between the Calibration Chapter (Chapter 7) of the AMD and an analyzer's instruction/operation manual shall be resolved in favour of the Calibration Chapter, unless otherwise authorized in writing by the Director.

1.1 Amendments

August 3, 2016

1. Update to document design/branding.
2. Added guidance below Cal 2-H clarifying that shut down refers to shut down prior to removal of the analyzer from the station or removal of the station as a whole.
3. Cal 2-L was split into two requirements to provide clarity and avoid contradiction with Cal 5-A.

4. Guidance and example calculation added under clause 3-E (c) for ozone calibrations using the Gas Phase Titration method following the NO/NO_x analyzer calibration.
5. Removed reference to Cal 3-H from clauses 3-F and 3-G. Removed bullets a and b from Cal 3-H so that flow measuring instruments need only be "certified at least annually against a NIST primary standard or other authoritative standards such as a traceable bubble flow meter or gas meter".
6. Clarified in clauses Cal 3-G and 5-A that flow measurement must be conducted with a certified flow measuring device.
7. Changed Cal 4-A (d) to "40% to 80% of the analyzer's range", rather than "40 - 80% of the analyzer's upscale point", to encompass new technology.
8. In section 5.1, changed guidance to make it clear that the temperature range given is an example only.
9. Added requirement to calibrate H₂S and TRS analyzers as well as perform SO₂ scrubber checks in Cal 5-A (bullet dd).
10. Guidance added under Cal 5-I, including examples of ozone points, for using calibration results from the GPT portion of a NO/NO₂/NO_x calibration to conduct an ozone analyzer calibration.
11. Amended Cal 10-A to add "are deemed to be invalid" to clarify that not all zero-span drift limit exceedances indicate invalid data.

2.0 General Calibration Requirements

Calibration is used to ensure standardized data will be gathered in the month following the calibration, and act as a reference relative to the previous monthly calibration. The station operator should perform a visual inspection of wind instruments and function checks on each visit to the continuous ambient air monitoring station. Function checks on continuous analyzers should include checking for abnormal performance of instruments such as:

- excessive signal noise;
- unstable baseline;
- positive and/or negative drift;
- spiking;
- long response time;
- incorrect flow/pressure readings;
- warning light indications; and
- pump or power failure.

Corrective action should be taken to restore instrument performance if performance is not up to specifications.

The Audit Chapter of the AMD (Chapter 8) outlines requirements for verifying the accuracy of calibrators on an annual basis as well as other requirements related to audits.

Cal 2-A The person responsible shall conduct calibrations of each analyzer at the field monitoring site where the analyzer operates.

Cal 2-B The person responsible must keep (a) the analyzer to be calibrated and (b) the calibration equipment within the equipment operating temperatures prior to conducting the calibration.

Cal 2-C While conducting any calibration, the person responsible must:
(a) have the analyzer operating in its normal sampling mode; and
(b) sample the test atmosphere through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and through as much of the ambient air inlet system as is practicable.

Cal 2-D The person responsible must conduct the calibration at the analyzer's normal operating range.

Analyzer operating ranges are outlined in Monitoring Chapter (Chapter 4) of the AMD.

Cal 2-E When an analyzer will be used for more than one range, or when an analyzer has auto ranging capability, the person responsible must calibrate the analyzer separately on each applicable range.

- Cal 2-F The person responsible shall:*
- (a) log all data collected during calibration; and*
 - (b) flag the data system during calibration to ensure the data is not reported as valid ambient data.*
- Cal 2-G The person responsible must evacuate any regulator to remove oxygen and other contaminants from the pressure regulator and delivery system:*
- (a) when installed onto a cylinder;*
 - (b) for the first time a regulator is installed on a cylinder and every time the regulator is removed; and*
 - (c) prior to every use.*

The procedure that should be used for evacuating a regulator to remove oxygen and other contaminants from the pressure regulator and delivery system prior to use is outlined in Appendix A.

2.1 Multi Point Calibration Requirements

Multi point calibrations are used to establish or verify the linearity of analyzers.

- Cal 2-H The person responsible shall conduct Multi Point Calibrations:*
- (a) monthly, at a minimum;*
 - (b) within 3 days of initial installation of the analyzer;*
 - (c) before and after repairs and maintenance work if able to perform a calibration;*
 - (d) prior to shut down;*
 - (e) after interruption in operation for more than 4 consecutive days; and*
 - (f) if results indicate analyzer malfunction or change in calibration.*

Shut down refers to shut down prior to removal of the analyzer from the station or removal of the station as a whole.

- Cal 2-I The person responsible shall conduct the Multi Point Calibrations in Cal 2-H to include a zero concentration and a minimum of three test concentrations within the analyzer's operating range.*

Required analyzer operating ranges are outlined in Monitoring Chapter (Chapter 4) of the AMD.

- Cal 2-J In the event that the AMD does not specify an operating range for an analyzer:*
- (a) the highest calibration point must be, at a minimum, two times the short-term Ambient Air Quality Objective, when an Ambient Air Quality Objective exists, unless otherwise authorized in writing by the Director; and*

(b) a minimum of three concentrations shall be spaced equally over the scale range at (i) 10-20%, (ii) 30-40%, and (iii) 60-80% of full scale.

In the absence of an Ambient Air Quality Objective for the compound of interest, a concentration between 60% and 80% of the full scale range of the analyzer under calibration should be used for the highest upscale point.

Cal 2-K When calibrating an analyzer that is non-linear by design, the person responsible must include a minimum of 5 upscale calibration points.

Calibration points for non-linear calibrations (e.g., with GC type analyzers) should be plotted or evaluated statistically as they are obtained so that any irregular points can be investigated or repeated immediately. One of the following methods should be used:

- the analyzer readings are plotted against the respective test concentrations, and the best nonlinear curve to fit the points is determined; or
- least squares regression analysis (with an appropriate transformation of the data for non-linear analyzers).

2.2 Zero and High Point Calibration Adjustment

Cal 2-L For analyzers in routine operation, the person responsible must:
(a) perform as found zero prior to adjusting the zero, and
(b) perform as found span prior to adjusting the span value.

Cal 2-M For zero and high point calibration adjustments, the person responsible must use data that has not been corrected for zero or slope.

Cal 2-N Analyzers that have zero and high concentration adjustment controls shall be adjusted based on the (a) zero and (b) highest test concentrations, respectively, during the routine monthly multi point calibration.

The requirements in Cal 2-N will provide the desired scale range within the analyzer's specifications.

Cal 2-O The person responsible shall use the analyzer's individual zero and high point controls for each channel to adjust the individual channel's outputs.

NO/NO₂/NO_x analyzers may not have individual zero and span controls for each channel. In this case, Cal 2-P applies.

- Cal 2-P The person responsible shall make zero and high point adjustments for NO/NO₂/NO_x analyzers according to the NO/NO₂/NO_x analyzer's operations and instruction manual.*
- Cal 2-Q After the analyzer has been allowed to stabilize on the new zero and high point adjustments, the person responsible must introduce the remaining calibration test concentrations into the analyzer to prove linearity of the analyzer.*
- Cal 2-R The person responsible must use the same device to record final, post-adjusted analyzer response readings and subsequent ambient measurements.*

3.0 Calibration Standards

- Cal 3-A When calibrating an analyzer, the person responsible must use calibration standard gases of the compound the analyzer is designed to analyze.*
- Cal 3-B All calibration standards and measurement devices used by the person responsible must be:*
- (a) certified as traceable to either:*
 - (b) the U.S. National Institute of Standards and Technology (NIST); or*
 - (c) the Dutch Metrology Institute (VSL) primary standard; or*
 - (d) derived from local or working standards (e.g., cylinders of compressed gas or permeation devices).*
- Cal 3-C A working standard, also known as the secondary standard, used by the person responsible shall be certified directly to the Standard Reference Material or Certified Reference Material.*

3.1 Zero Standards

Test concentrations at zero concentration are considered valid standards. Although zero standards are not required to be traceable to a primary standard, care should be exercised to ensure that zero standards are indeed adequately free of all substances likely to cause a detectable response from the analyzer. Zero concentrations can be acquired through zero air generation devices or purchased standards.

3.2 Standards for Ozone

Cal 3-D Test concentrations of ozone used by the person responsible must be traceable to a primary standard UV photometer as described in “US EPA 40 CFR Part 50 Appendix D”.

Procedures for certifying transfer standards for ozone against UV primary standards are provided in Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone (EPA-454/B-10-001, November 2010).

Cal 3-E As mentioned in Section 5.3 Gas Phase Titration of the Calibration Chapter, a previously calibrated NO_x/NO/NO₂ analyzer and a NO in N₂ calibration gas mixture can be used to determine O₃ concentrations provided the following conditions are met:

- (a) the NO_x/NO/NO₂ analyzer used to determine the O₃ concentrations must be located at the same site as the O₃ analyzer that is being calibrated;*
- (b) calibration of the O₃ analyzer using the GPT derived O₃ concentrations from the calibration of the NO₂ channel of the NO_x/NO/NO₂ analyzer must be conducted within 24 hours of the GPT calibration of the NO_x/NO/NO₂ analyzer;*
- (c) if the calibration is not conducted within 24 hours of the GPT calibration, flows must be confirmed with a measurement device that is traceable to a primary standard;*
- (d) the NO in N₂ calibration gas mixture must be certified by a third party as not containing more than 1% NO₂;*
- (e) the calibration system used to generate the test concentrations must use variation of light intensity of a UV-type O₃ generator;*

A photometer controlled and measured system is preferred for ozone generation.

- (f) the total flows used to generate each test concentration of O₃ must be equivalent to the gas and diluent flows associated with the generation of each test concentration during the GPT; and*
- (g) the calculated O₃ concentration must be adjusted in the event that flow changes are observed.*

If ozone generators are used in Gas Phase Titrations or ozone calibrations, the generators should be calibrated regularly against an ozone primary standard (photometer). This is to ensure that variations in lamp power fluctuations are minimized.

As per Cal 3-E (c), ozone calibrations using the Gas Phase Titration method need to be done immediately following the NO/NO_x analyzer calibration. This will ensure no variation in flows or determined ozone concentrations will be seen. If using the Gas Phase Titration method the

next day (within 24 hours) then it is recommended the flows be verified to ensure the accuracy of the ozone concentration. A simple calculation can be used to determine the concentrations:

$$C_2 = \frac{V_1 C_1}{V_2}$$

Where:

C_1 = ozone concentration determined from the previous NO/NO_x calibration

C_2 = new concentration

V_1 = total flow from the previous NO/NO_x calibration

V_2 = total flow as measured for new ozone concentration determination

E.g.,:

$$C_2 = \frac{5020 \text{ sccm} * 0.400 \text{ ppm}}{4998 \text{ sccm}} = 0.402 \text{ ppm}$$

This shows about a 1% change from the previous calibration (within 24 hours).

3.3 Flow Calibration

Flow calibrations should be conducted on field calibration devices, as they can be one of the largest sources of error in a dilution calibration.

Cal 3-F The person responsible shall (a) equip all field standard calibration devices with a mass flow controller or (b) conduct a volumetric flow calibration.

Cal 3-G The person responsible shall conduct flow verification measurements on all field calibration devices, using a certified flow measuring device, at all test concentration points for multi point calibrations.

Cal 3-H The person responsible shall have flow or volume measuring instruments certified at least annually against a NIST primary standard or other authoritative standards such as a traceable bubble flow meter or gas meter.

4.0 Daily Zero-Span Test Procedure

The following daily zero-span test procedure is only adequate for commercial analyzers which have not undergone any modifications that have resulted in a substantial change in the performance characteristics of the analyzer. Instruments should be maintained within calibration specifications to minimize the need for zero adjustments.

To prevent the loss of data from the daily zero-span, the test should be started no earlier than 15 minutes before the hour and end no later than 15 minutes past the hour. As a result, both hours would have at least 45 minutes of data.

- Cal 4-A The person responsible must conduct automated or manual daily zero-span tests in accordance with the following requirements:*
- (a) daily, 23 to 25 hours apart;*
 - (b) daily zero-span test time shall not exceed 1 hour per calendar day for commercial ambient air quality analyzers;*
 - (c) zero and test gases (span gases) that are kept or generated at the monitoring location shall be used;*
 - (d) the test gas concentration shall range between 40% to 80% of the analyzer's range;*
 - (e) a minimum of 10 minutes stability must be achieved for a test gas concentration to be considered a valid response;*
 - (f) for auto range analyzers the daily zero-span test must be conducted on the lowest range;*
 - (g) when deviations of greater than $\pm 10\%$ from the calibration function occur, corrective action pursuant to Cal 10-C must be carried out;*

The zero baseline of the analyzer may be corrected based on the daily zero-span test.

- (h) analyzer sensitivity shall not be corrected based on the daily zero-span test;*
- (i) analyzers with automatic dynamic span adjustment capability shall not have the automatic dynamic span adjustment feature activated;*
- (j) Data Acquisition Systems with automatic dynamic span adjustment capability shall not have the automatic dynamic span adjustment feature activated; and*
- (k) zero and span control charts must be used to monitor the performance of the analyzers.*

There are different ways to construct control charts. An example of a control chart is shown in Appendix B.

5.0 Multi Point Calibration Procedure

Three commonly used types of calibration methods for continuous ambient air analyzers are:

- dilution based on standardized gas cylinders;
- dilution based on certified permeation devices; and
- gas phase titration.

Table 1 provides an overview of acceptable calibration methods used for continuous ambient air analyzers.

Table 1 Acceptable calibration methods

Parameter	Calibration Methods			
	Cylinder Dilution	Permeation Device	Gas Phase Titration	UV Photometer
SO ₂	X	X		
H ₂ S	X	X		
NO	X			
NO ₂			X	
O ₃			X	X
CO	X			
Hydrocarbons	X			
NH ₃	X	X		
Ethylene	X			
TRS	X	X		
BTEX	X			
Styrene	X			

Cal 5-A The person responsible must follow the calibration procedure specified in the equipment manufacturer's manual, as per Cal 1-B, for the analyzer being calibrated, in addition to the following minimum requirements:

- (a) the sample inlet particulate matter filter must be replaced prior to commencing the calibration;*
- (b) all gases shall be introduced upstream from the inlet filter;*
- (c) only raw unadjusted data shall be used for calibration purposes (all previous correction factors, slope/intercept, and coefficients shall be removed from the data acquisition system prior to commencing a calibration);*
- (d) the calibration system must warm up to its operating temperature prior to calibration;*

Normally this requires about 3 hours or longer if the calibrator has been left in cold weather.

- (e) for a permeation system:*
 - (i) the calibrator must be kept operational when moving from location to location; or*
 - (ii) the permeation tube must be allowed to stabilize for a minimum of 24 hours in the permeation chamber prior to use;*

A permeation calibrator can be kept operational using an inverter when it is being moved from location to location. During stabilization, the calibrator should be purged at all times to eliminate

accumulation of permeated gases in the oven chamber. Several commercially available permeation calibrators use a carrier flow to maintain a constant temperature around the tube during transport. In this instance, equilibration is not necessary because the oven temperature is continuously maintained within 0.1°C of the desired permeation temperature.

(f) gas cylinders, including the necessary regulators, must be allowed to warm up to room temperature;

Gas cylinders can take 12 to 24 hours to warm up to room temperature.

(g) when using gas cylinders, the pressure regulator and lines must be purged prior to use to avoid contamination;

The procedure in Appendix A for purging (evacuating) a regulator should be used.

(h) after purging the regulator:

- (i) the same transfer line must be connected to the gas inlet of the calibrator;*
- (ii) the cylinder main valve must be opened slowly;*
- (iii) the regulator outlet pressure must be set as required by the calibrator;*
and
- (iv) the regulator valve must be opened slowly;*
- (i) the output from the calibrator must be at ambient pressure to avoid pressurizing the analyzer;*

The equipment manufacturer's manual should be referred to for acceptable methods to achieve ambient pressure as referred to in Cal 5-A (i).

(j) the flow rate(s) of the calibrator must be checked with a certified flow meter against the operating specifications to achieve the desired concentrations required for the calibration;

(k) flow rates must be corrected to standard temperature and pressure (STP) conditions (760 mm Hg and 25°C);

(l) all functional and operational checks must be conducted prior to the calibration;

(m) the calibration gas must be introduced through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and through as much of the ambient air inlet system as is practicable;

(n) the calibrator total airflow output must be set to provide excess flow at a minimum 2.5 times the intake flow rate of the analyzer;

(o) the calibrator must be set to:

- (i) deliver zero gas; and*
- (ii) measure the flow rate of zero gas, using a certified flow measuring device;*

- (p) *the zero reading of the analyzer must be stabilized and 15 minutes of stable response must be recorded as the “as found response”;*
- (q) *the analyzer must be adjusted to the zero reading, if required, and 15 minutes of stable adjusted response must be (i) obtained and (ii) recorded;*
- (r) *the highest test concentration (60-80% of the operating range) must be introduced into the analyzer. The operator must do the following:*
 - (i) *measure gas flow, using a certified flow measuring device, and total flow to determine the high point concentration;*
 - (ii) *obtain and record stable response for 15 minutes; and*
 - (iii) *record as the “as found response”;*

If the “as found response” of this first calibration point deviates more than $\pm 10\%$ from the expected calibrator response, as per Cal 9-F, corrective action must be taken (repair or maintenance is required).

- (s) *when observing the response, any changes from the previous calibration must be noted;*
- (t) *the high point setting must be adjusted to a 1:1 relationship with the calibration gas concentration;*
- (u) *15 minutes of stable response must be obtained and recorded after adjusting the high point setting;*
- (v) *further span changes must not be conducted after demonstration of 15 minutes of stable response;*
- (w) *after the zero and high point settings are satisfactory, consecutively lower gas concentrations of (i) 30-40% then (ii) 10-20% must be introduced into the analyzer;*
- (x) *gas flow and total flow must be measured, using a certified flow measuring device, at (i) the completion of the mid-point and (ii) the start of the low-point gas concentrations;*
- (y) *15 minutes of stable response must be demonstrated for each test concentration;*
- (z) *the maximum time required to reach a stable response shall not exceed 20 minutes;*
- (aa) *for NH₃, the time required to reach a stable response shall not exceed 45 minutes;*
- (bb) *using the readings obtained, a regression analysis must be performed to obtain the calibration results;*

Refer to Appendix C, Least Square Regression Analysis, for details on establishing regression parameters and the least square calculation procedure.

- (cc) *the daily automated zero-span test cycle shall be used to zero and span the analyzer;*

This serves to re-establish the zero air and the span gas concentration for the required daily zero-span test. The zero and span values obtained from the post calibration zero-span automated run are used as the true reference values to compare the ongoing zero/span checks.

(dd) during multi point calibrations, monthly at a minimum, TRS and H₂S analyzers must be (i) calibrated by use of a permeation device or dilution of bottled gasses traceable to primary standards and (ii) checked for SO₂ scrubber efficiency for possible interference of SO₂; and

Any measureable response to SO₂ is unacceptable.

(ee) the calibration shall be documented as required by Section 11.0 of the Calibration Chapter.

5.1 Dynamic Calibration Using a Permeation Device

A permeation device is a sealed ampule with a permeable membrane to the vapour of the chemical compound it contains. The compound is held in liquid/vapour phase equilibrium inside the ampule.

At a given temperature, the permeation device provides a constant flow of its compound into the carrier gas stream. The permeation rate of the device is highly temperature dependent and for example could require temperature control in the order of $\pm 0.05^{\circ}\text{C}$ at 35°C .

Cal 5-B When conducting a dynamic calibration using a permeation device, the person responsible shall follow the multi point calibration procedure in Cal 5-A.

Appendix D describes how to calculate calibration concentrations to be introduced into an analyzer when conducting a dynamic calibration using a permeation device with fixed permeation rate.

5.2 Dilution Calibration

Dilution calibrations use a calibration gas that is derived from a compressed gas cylinder. The accuracy of the calibration is directly dependent upon the accuracy of flow measurements and corrections applied to those flows.

Cal 5-C The person responsible shall follow the multi point calibration procedure in Cal 5-A when conducting dilution calibrations.

Calculations for determining the concentration of calibration gas after dilution are included in Appendix E.

Descriptions of flow measurement devices (bubble flow meter, mass flow meter, rotameter or orifice with pressure chart) and correction calculations are included in Appendix F.

5.2.1 Hydrocarbons Calibration by Dilution Method

Reactive hydrocarbons are described as non-methane hydrocarbons. The term hydrocarbons is used to include all organic compounds which give response to the Flame Ionization Detector.

Cal 5-D The person responsible must calibrate all total hydrocarbon ambient analyzers with a mixture of methane and propane.

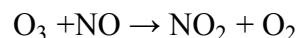
The balance gas in the mixture can be air, nitrogen or another gas that does not cause a detector response.

Cal 5-E When the person responsible calibrates reactive hydrocarbon or total hydrocarbon analyzers, the calibration gases used must be expressed as "methane equivalent".

The calculations for methane equivalent are included in Appendix G.

5.3 Gas Phase Titration

GPT may be used as a method of generating primary standards for nitrogen dioxide and ozone. The reaction which takes place when O₃ is added to NO is:



The reaction relationship is 1:1 in theory, but in practice the perfect stoichiometry is never achieved. However, since the GPT method does yield better than 99% conversion, it is very useful for:

1. calibration of NO – NO_x – NO₂ analyzers;
2. calibration of O₃ analyzers;
3. verification of O₃ generators; and
4. determination of NO₂ – NO converter efficiency.

The calibration system used for GPT is essentially the same as the dilution system outlined in Section 5.2, but incorporates an ozone generator to the dilution side of the flow system. Refer to the equipment manufacturer's manual for details.

The accuracy of the calibration is directly related to the following parameters:

1. quality of dilution zero air;
2. accuracy of compressed NO gas standard;

3. accuracy of flow measurements and stability of flows;
4. stability of the ozone generator and stability of flow through the ozone generator chamber;
5. compatibility of materials used in the construction of the calibration system; and
6. condition of analyzers being calibrated or used as a reference.

All of the above items can significantly affect the accuracy, linearity and repeatability of the calibration.

Calculations for GPT are included in Appendix H.

5.3.1 NO/NO_x Calibration

Cal 5-F When conducting NO/NO_x calibrations, the person responsible shall follow the multi point calibration procedure in Cal 5-A.

5.3.2 NO₂ Calibration

Cal 5-G The person responsible shall use the following steps for all NO₂ calibrations:

- (a) at the end of the NO/NO_x calibration do not run the zero span test;*
- (b) reintroduce the highest NO concentration which was generated in the NO portion of the calibration;*
- (c) let stabilize for 15 minutes;*

The NO and NO_x channels may or may not be at exactly the same level depending on NO₂ impurity in the gas standard.

- (d) the presence of any NO₂ impurity in the NO gas standard must be taken into account in the NO portion of the calibration;*
- (e) do not make adjustments to the analyzer at this stage;*
- (f) introduce ozone such that 60% to 70% of the highest NO concentration used to calibrate the analyzer is converted to NO₂;*

This high point (Cal 5-G (f)) is the first point for calibration of the NO₂ channel.

- (g) adjust the analyzer's NO₂ output, as per the manufacturer's procedure, to the introduced gas concentration once a stable reading is achieved;*
- (h) ozone is then introduced such that 30% to 40% of the NO concentration is converted to NO₂;*

This is the second and mid-point (Cal 5-G (h)) for calibration of the NO₂ channel.

- (i) 15 minutes of stable readings must be demonstrated;*
- (j) do not adjust the analyzer output for this second point;*
- (k) introduce ozone such that 10% to 15% of the NO concentration is converted to NO₂;*

This is the third and low-point (Cal 5-G (k)) for calibration of the NO₂ channel.

- (l) do not adjust the analyzer output for this third point;*
- (m) plot the NO₂ increase versus the NO decrease to produce a calibration curve;*
- (n) the average converter efficiency for the calibration must then be i) calculated and ii) recorded;*
- (o) the average converter efficiency must be between 96 to 104%; and*
- (p) document the calibration as required by Section 11.0 (Calibration Records) of the Calibration Chapter of the AMD.*

Absolute converter efficiency can be determined using electronic factors that are stored in most analyzers. Refer to the analyzer operation manual for further information on determining converter efficiency. For example: Thermo Models 42 and 17 C and i series analyzers store the NO₂ coefficient (NO₂ COEF). TECO model 42 and API 200 A and E series analyzers store the converter efficiency (CE).

Cal 5-H The person responsible must have the analyzer serviced by a qualified technician or by the manufacturer if the converter efficiency falls outside the range (96 to 104%) in Cal 5-G (o).

5.4 Ozone Calibration

5.4.1 Method 1 - Varying Dilution Gas Flow

An ozone analyzer can be calibrated by using a fixed UV generator setting along with a fixed flow through the O₃ generator chamber. The O₃ concentration is then varied by changing the dilution flow.

5.4.2 Method 2 - Varying UV Lamp Power

An ozone calibration may also be conducted using fixed flows and varying the ozone lamp setting. However, some inaccuracy may result due to lamp variation from one calibration to another.

A photometer is a calibrated ozone system that provides a feedback loop to vary the ozone lamp setting to provide a desired ozone concentration. This is typically more accurate than an ozone generator that only varies the lamp setting.

5.4.3 Method 3 - Direct Gas Phase Titration

Calibration results from the GPT portion of a NO/NO₂/NO_x calibration conducted within the previous 24 hours can be used to conduct an ozone analyzer calibration.

- Cal 5-I The person responsible shall use the following steps for all calibrations using Direct Gas Phase Titration:*
- (a) introduce zero gas from the calibrator to the analyzer;*
 - (b) allow sufficient time for the analyzer to stabilize;*
 - (c) record the reading;*
 - (d) adjust if necessary and record any changes;*
 - (e) introduce ozone from the calibrator using the same ozone lamp output setting and flow rate as was used during the high NO₂ point of the recent NO/NO₂/NO_x calibration;*
 - (f) add the flow rate value used for NO calibration gas during the high point of the NO/NO₂/NO_x calibration to the dilution flow rate for the O₃ calibration being conducted;*

This is to ensure that the total flow rate during the O₃ calibration is the same as it was during the GPT portion of the NO/NO₂/NO_x calibration.

- (g) calculate the O₃ concentrations for all O₃ calibration points by subtracting the NO value after the O₃ was introduced from the NO value prior to any O₃ introduction during the recent NO/NO₂/NO_x calibration;*
- (h) allow the analyzer to reach 15 minutes of stable reading;*
- (i) record the analyzer concentration as the "as found" span value;*
- (j) adjust the analyzers response to match the calculated concentration;*
- (k) record the adjusted response as the adjusted high span value;*
- (l) allow 15 minutes of stable readings following adjustment (make no further adjustment to the analyzer);*
- (m) reduce the calibrator ozone lamp output setting to the same value as was used for the mid NO₂ point of the recent NO/NO₂/NO_x calibration (do not change the total dilution flow);*
- (n) wait until 15 minutes of stable readings are observed;*
- (o) record the analyzer concentration as the mid span value;*
- (p) reduce the calibrator ozone lamp output setting to the same value as was used for the low NO₂ calibration point of the recent NO/NO₂/NO_x calibration (do not change the total dilution flow);*
- (q) wait until 15 minutes of stable readings are observed;*
- (r) record the analyzers concentration as the low span value; and*
- (s) using the readings obtained, perform a regression analysis to obtain the calibration results.*

If the person responsible uses the method in Cal 5-I to calibrate an ozone analyzer, determination of what points will be used based on the range of the NO/NO_x analyzer being calibrated have to be considered. This would be for operating ranges of 0.5 to 1.0 ppm full-scale and NO concentrations of 0.800 ppm and/or 0.400 ppm at 5000 sccm total flow.

- For 1.0 ppm full-scale NO/NO_x analyzers, consider 2 upscale high points. Use the 60% - 70% range for the NO₂ calibration high point and add an additional point in the 45% - 55% range to be used for the ozone analyzer upscale high point. Both the mid-point and low-point values are not affected. This would add 4 points to the NO/NO_x GPT calibration instead of the usual 3 points typically used.
- For 1.0 ppm full-scale NO/NO_x analyzers, consider using a value in the 55% range of the ozone high point. This would bring the ozone high point into a working range for ozone analyzer calibration purposes but it would not meet the Gas Phase Titration requirements for doing a NO₂ calibration for the high point only (60% - 70%).
- For 0.5 ppm full-scale NO/NO_x analyzers, consider upscale points of approximately 300 ppb for the high point, 200 ppb for the mid-point, and 100 ppb for the low point. This will ensure these data used for ozone calibration purposes meet the AMD calibration requirements.

6.0 Calibration of Wind Instruments

The Monitoring Chapter of the AMD (Chapter 4) provides minimum performance specifications for wind instruments.

Cal 6-A The person responsible must remove all mechanical wind instruments from the tower at least once a year for:

- (a) mechanical inspection;*
- (b) mechanical alignment;*
- (c) electronic alignment; and*
- (d) calibration.*

When inspecting mechanical wind instruments, bearings and potentiometers should be checked to ensure they are in good working condition. An RPM generator can be used to calibrate wind speed and devices are available to help align the instrument properly. Alternatively, the instrument can be sent for factory calibration.

Cal 6-B The person responsible must have all ultrasonic wind systems:

- (a) electronically inspected once a year; and*
- (b) factory calibrated at a minimum every 2 years.*

When inspecting ultrasonic instruments, ensure that the aviary spikes are in their proper place and not touching the heaters, that heaters are functioning properly, and that wind speed is being registered. More frequent calibrations may be required if the ultrasonic wind head is in a high humidity area or on a mobile monitoring unit.

- Cal 6-C The person responsible shall:*
- (a) note the date of the last calibration on each monthly wind table in monthly reports; and*
 - (b) submit to the Regulator a copy of the wind instrument calibration with the monthly report (for the month in which the calibration was conducted).*

The Reporting Chapter of the AMD (Chapter 9) provides requirements for monthly reports.

Cal 6-D If more than 10% of the monthly operating time of wind instruments is used for calibration, the person responsible must count the time exceeding 10% as down time.

Cal 6-E The person responsible must keep a service record for each wind instrument which contains all work performed to bring the instrument back to original operating conditions.

7.0 Calibration of High Volume Samplers

Cal 7-A The person responsible shall calibrate high volume samplers at least every three months.

Cal 7-B The person responsible shall calibrate high volume samplers:

- (a) in accordance with the method in Cal 7-E; or*
- (b) by other equivalent methods that have been authorized in writing by the Director.*

7.1 Orifice Calibration Unit

Cal 7-C Before calibrating a flow recorder, the person responsible must calibrate the orifice calibration unit against the positive displacement primary standard.

Cal 7-D The person responsible must calibrate the orifice calibration unit in accordance with the following steps:

- (a) attach the orifice calibration unit to the intake end of the positive displacement primary standard;*
- (b) attach a high volume blower unit to the exhaust end of the primary standard;*

- (c) connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit leaving the other end open to the atmosphere;
- (d) vary the operation of the blower unit such that a series of different, but constant airflows, usually six, are obtained for five minutes each;
- (e) record the reading of the differential manometer at each airflow;

The different constant airflows are obtained by placing a series of load plates, one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure at the inlet of the primary standard below atmosphere.

- (f) a correction must be made for the increase in volume caused by the decrease in inlet pressure;
- (g) attach one end of a second differential manometer to the inlet pressure tap of the primary standard leaving the other end of the manometer open to the atmosphere;
- (h) during each of the constant airflow measurements made in Cal 7-D (d), measure the true inlet pressure of the primary standard with this second differential manometer;
- (i) measure the (i) atmospheric pressure and (ii) temperature;
- (j) correct the measured air volume to true air volume as directed in Appendix I of the Calibration Chapter;
- (k) obtain the true airflow rate, Q , as directed in Appendix I of the Calibration Chapter; and
- (l) plot the differential manometer readings of the orifice unit versus Q .

The orifice calibration unit can then be used to calibrate the high volume sampler.

7.2 High Volume Sampler Calibration

- Cal 7-E The person responsible must calibrate high volume samplers in accordance with the following steps:*
- (a) assemble a high volume sampler with a clean filter in place;
 - (b) run for at least five minutes;
 - (c) attach the flow recorder and adjust to obtain a reading of 65% of full scale;
 - (d) seal the adjusting mechanism so that it cannot be changed easily;
 - (e) shut off the motor;
 - (f) remove the filter;
 - (g) attach the orifice calibration unit in its place;
 - (h) operate the high volume sampler at a series of different but constant airflows (usually six, one filter and five load plates);
 - (i) take the readings of the differential manometer from the orifice calibration unit;
 - (j) record the readings of the flow recorder for each flow rate;
 - (k) measure the ambient atmospheric pressure and temperature;

- (l) convert the differential manometer readings to cubic metres per minute (Q);
and
(m) plot flow recorder readings against Q .

Calculations for high volume sampler calibration can be found in Appendix I.

8.0 Calibration of Other Analyzers

Cal 8-A For methods not detailed in the Calibration Chapter (Chapter 7) of the AMD, the person responsible must obtain written authorization from the Director for calibration methodologies before use.

9.0 Calibration Acceptance Limits

Cal 9-A For all calibrations conducted by the person responsible, the results must meet or exceed the calibration acceptance limits/criteria specified in Table 2 and Cal 9-C to Cal 9-J, inclusive.

Cal 9-B In the event that calibration results do not meet the requirements of clauses Cal 9-C to Cal 9-J, the person responsible shall take corrective action as specified under Cal 10-C.

Cal 9-C For each calibration, the person responsible must generate a calibration curve from (a) at least three, non-zero concentrations of the gas being used and (b) a calibration zero air source.

Cal 9-D The person responsible shall use least square regression analysis, for each calibration, to determine compliance with the calibration acceptance limits.

Table 2 Verification check/calibration acceptance criteria

Parameter	Requirement	Calibration Acceptance Criteria
Gaseous Parameters	Zero check	$\leq \pm 3\%$ of full scale
	Span check	$\leq \pm 10\%$
	Multipoint Verification/ Calibration	Within $\pm 10\%$ of the least squares regression slope (0.9 to 1.10) Correlation coefficient ≥ 0.995
Particulate Matter	Flow check, leak check, temperature check and pressure check	Within manufacturer's specific limits
Scalar Wind Direction	Alignment check	$\leq \pm 10^\circ$ from compass observation
All meteorology (except winds)		$\leq 15\%$ from audit reference

The results of the calibration are plotted on a graph as indicated concentrations (analyzer response) (C_i) versus calculated concentrations (C_c). The ratio of C_c/C_i for the highest calibration concentration is defined as the correction factor of the instrument. Similar ratios for other calibration points are compared with the correction factor to check for linearity. The final correlation may be obtained from least square linear regression of C_i on C_c . Please refer to Appendix C (Least Square Regression Analysis) for details on establishing regression parameters and the least square calculation procedure.

Cal 9-E For digital systems, calibration data points used for digital printouts or graphical plots must, at minimum, be based on 1 second averaging to a maximum of 5 minute (300 second) averaging.

The calibration results should be supported by recorder traces (or digital printouts or graphical plots in the case of digital systems) to demonstrate the stability and accuracy of the measurement.

Cal 9-F The first calibration point "as found" must not deviate more than $\pm 10\%$ from the expected calibrator response.

Cal 9-G Deviation from the adjusted slope must be less than or equal to $\pm 5\%$ for any one point.

Cal 9-H The intercept must be within $\pm 3\%$ of the full range of the analyzer.

Cal 9-I The correlation coefficient must be greater than, or equal to, 0.995.

Cal 9-J When conducting a dynamic calibration using a) a permeation device, or b) a dilution calibrator, the person responsible shall maintain accuracy within $\pm 2.5\%$.

10.0 Assessment and Corrective Action

Data flags are used to mark data when calibration results are found to be outside the acceptable limits prescribed in the Calibration Chapter.

Cal 10-A When the zero or span drift limits set out in Section 4.0 of the Calibration Chapter are exceeded and measurements are deemed to be invalid, the person responsible shall flag ambient measurements back to the most recent point in time where such measurements are known to be valid.

Usually this point in time is the previous calibration (or accuracy audit or last good calibration span verification), unless some other point in time can be identified and related to the probable cause of the excessive drift (such as a not allowing enough time for instrument response to stabilize, power failure or malfunction, or malfunctioning of the span equipment).

Cal 10-B The person responsible must flag data collected following an analyzer malfunction or period of non-operation as invalid until the next calibration, unless the unadjusted, “as found”, zero and high point readings at that calibration support data validity.

Cal 10-C When analyzer performance does not meet the Calibration Acceptance Limits as set out in Section 9.0 of the Calibration Chapter, the person responsible must take immediate corrective action to ensure the analyzers are operating within the manufacturer’s specifications and the Calibration Acceptance Limits.

11.0 Calibration Records

Cal 11-A The person responsible shall a) record and b) retain with the analyzer for a minimum of three years, all data and calculations involved in the calibration activities for each analyzer.

Cal 11-B The person responsible must:
(a) record stored electronic factor(s) with the calibration results; and
(b) enter all data relevant to the calibration on the analyzer’s calibration record.

Cal 11-C The person responsible shall program digital systems to update calibration data points at a minimum every 30 seconds.

Cal 11-D The person responsible shall graph calibration data to demonstrate the stability of each measurement point.

Additional requirements for documentation and the maintenance of records are set out in the Quality Chapter (Chapter 5) of the AMD.

11.1 Calibration Reports

Cal 11-E All calibration reports submitted to the Regulator shall include, at a minimum, all of the following:

- (a) identification of analyzer calibrated including:
 - (i) its location;*
 - (ii) date of calibration;*
 - (iii) make/model;*
 - (iv) serial number;*
 - (v) date last calibrated; and*
 - (vi) inlet flow;**
- (b) the calibration method used;*
- (c) calibrator make/model;*
- (d) calibrator serial number;*
- (e) calibration standard certificate expiration date;*
- (f) conditions under which calibration is conducted:
 - (i) temperature; and*
 - (ii) barometric pressure;**
- (g) calibration results including:
 - (i) total flow;*
 - (ii) gas flow;*
 - (iii) expected concentration or calculated concentration;*
 - (iv) actual response as found (zero and high point); and*
 - (v) indicated responses for all calibration points;**
- (h) calculation of correction factor;*
- (i) correction factor(s) from the previous calibration;*
- (j) correction factor(s) from the current calibration;*
- (k) calibration curve;*
- (l) linear regression analysis; and*
- (m) identification of person who conducted the calibration.*

Cal 11-F The person responsible shall keep copies of Calibration reports in Cal 11-E at the continuous ambient air monitoring station.

Refer to Appendix J for an example of a calibration report. Calibration report templates are available on the AMD website

The Reporting Chapter of the AMD (Chapter 9) provides detailed reporting requirements.

Any comments, questions, or suggestions regarding the content of this document may be directed to:

ESRD.AMDFeedback@gov.ab.ca

Air Policy
Alberta Environment and Parks
Main Floor, Oxbridge Place
9820 – 106 Street
Edmonton, Alberta T5K 2J6

Website: AEP.alberta.ca/

Original signed by: _____
Hamid Namsechi, Director
Air Policy
Environment and Parks

Date: August 3, 2016

Appendix A Procedure for Evacuating a Regulator

The following procedure should be used for evacuating (purging) a regulator to remove oxygen and other contaminants from the pressure regulator and delivery system prior to use:

1. Connect the regulator to the cylinder. With the cylinder valve closed, connect a vacuum pump to the outlet on the regulator and start the pump.
2. Open the outlet port, evacuate for a minimum of 5 minutes, then close the evacuation port.
3. Slowly open and close the cylinder valve to charge the regulator.
4. Repeat steps 2 and 3 a minimum of 3 more times to be sure all oxygen or other impurities are removed from the regulator.

Appendix C Least Square Regression Analysis

A regression analysis must be performed on the calibration results to provide a quantitative assessment of the analyzer performance. From this analysis, the response of the analyzer can be corrected to obtain the calibration value. Most calculators/spreadsheets are able to perform this analysis and produce the slope, intercept and coefficient of correlation. The following procedure summarizes the steps involved in this calculation.

It is necessary to define the dependent and independent variables in the analysis. The two variables involved are (i) the true or calculated values used in the calibration or audit of the analyzer (calculated concentration) and (ii) the values indicated by the analyzer (analyzer response). The independent variable can be arbitrarily set as the true value or as the analyzer response value provided it is properly indicated to avoid any misunderstanding when using the resultant equation.

The regression coefficients are calculated by designating the calculated/audit concentration ($\mu\text{g}/\text{m}^3$ or ppm) as the abscissa (x variable) and the analyzer response ($\mu\text{g}/\text{m}^3$ or ppm) as the ordinate (y variable). The resultant equation is in the form of:

$$y = mx + b$$

Where:

y	= analyzer response (indicated concentration)
m	= slope
x	= calculated/audit concentration
b	= the intercept

The slope in this equation (m) gives the amount and direction of the analyzer response deviation from the calibration value. For example a slope of 1.10 indicates that the reading of the analyzer is 10% high whereas a slope of 0.95 indicates that the analyzer reading is 5% low. The intercept (b) is related directly to the zero offset of the analyzer. For example an intercept of 0.05 indicates that the analyzer has a zero offset of +0.05.

To calculate the parameters in the equation, let:

Y_i	= i^{th} reading of the analyzer
X_i	= i^{th} calibration value (true value)
n	= number of calibration points

The calculations are as follows:

Slope m:

$$m = \frac{\sum_1^n X_i Y_i - \sum_1^n X_i \sum_1^n Y_i}{n \sum_1^n X_i^2 - \left(\sum_1^n X_i\right)^2}$$

Intercept b: $b = \bar{y} - m\bar{x}$

Where:

\bar{x} = mean of x

\bar{y} = mean of y

Correlation Coefficient R:

$$R = \frac{n \sum_1^n X_i Y_i - \sum_1^n X_i \sum_1^n Y_i}{\left[\left(n \sum_1^n X_i^2 - \left(\sum_1^n X_i \right)^2 \right) \left(n \sum_1^n Y_i^2 - \left(\sum_1^n Y_i \right)^2 \right) \right]^{1/2}}$$

The slope is the parameter used to assess the accuracy of the analyzer response with respect to the calibration value. The correlation coefficient is an indication of the degree of linearity. The intercept shows the offset of the analyzer response with respect to the calibration zero.

Appendix D Calculation - Dynamic Calibration Using a Permeation Device

Permeation rate in nanograms/minute is calculated using the following expression:

$$P_T = \frac{FC}{K_m}$$

Where:

P_T = permeation rate in nanograms/minute at $T^\circ\text{C}$

F = flow rate in cubic centimetres/minute at STP

C = concentration in ppm (Volume)

K_m = molar constant = $\frac{24.46}{\text{Molecular Weight}}$

Where 24.46 is the ideal gas molar volume in litres at STP.

K_m can also be expressed as:

$$K_m = \frac{1}{\text{molecular density}}$$

Where:

molecular density = $\frac{\text{molecular weight}}{\text{molecular volume}}$

with a known permeation rate:

$$\text{Concentration (ppm)} = \frac{P_T \times K_m}{F}$$

TABLE OF MOLECULAR WEIGHTS AND CONSTANTS AT STP

Gas	Formula	Molecular Weight	K_m
Hydrogen sulphide	H_2S	34.08	0.719
Nitrogen dioxide	NO_2	46.01	0.532
Sulphur dioxide	SO_2	64.07	0.382

Appendix E Dilution Calibration Calculation

In order to determine the concentration of calibration gas after dilution, the following relationship is used:

$$C_F = \frac{F_C \times C_S}{F_t}$$

Where:

C_F = output concentration (ppm)

C_S = concentration of compressed gas being diluted (ppm)

F_C = flow of compressed gas corrected to STP

F_D = flow of zero gas (dilution air) corrected to STP

F_t = total flow ($F_C + F_D$)

Appendix F Flow Measurements and Corrections

Bubble Flow Meter

The bubble flow meter technique is an absolute method of measuring the mass flow of gases. In order to measure mass flow in standard cubic centimeters per minute, the volume flow must be corrected for temperature, atmospheric pressure, and the vapour pressure of water.

Correction is made using the following equation:

$$\text{Mass Flow (standard cc/min)} = \frac{\text{Volume (cc)}}{\text{Time (min)}} \times \frac{(P - P_v)}{760} \times \frac{298}{(273 + T)}$$

Where:

- P = atmospheric pressure (mm of Hg)
- P_v = vapour pressure of water (mm of Hg) at T°C, see table below
- T = temperature of gas (°C)

TABLE OF VAPOUR PRESSURE OF WATER (P_v)

°C	Inches Hg	mm Hg	°C	Inches Hg	mm Hg
15	.50	12.79	24	.88	22.38
16	.54	13.63	25	.94	23.76
17	.57	14.53	26	.99	25.51
18	.61	15.48	27	1.05	26.74
19	.65	16.48	28	1.12	28.35
20	.69	17.54	29	1.18	30.04
21	.73	18.65	30	1.25	31.82
22	.78	19.83	31	1.33	33.70
23	.83	21.07	32	1.40	35.66

Linear Mass Flow Meters

Although linear mass flow meters are generally very stable, it is desirable that calibration checks be performed periodically. The unit should be checked at several points over its full range using a bubble flow meter. Particulates carried into the flow meter by the gas stream will result in inaccuracy, or at worst, clogging of the sensor. Therefore, the best method of ensuring that the flow meter remains stable and accurate is to provide good flow filtration.

Rotameter

In order to measure mass flow using a rotameter, the volumetric flow must be corrected for both temperature and atmospheric pressure. The equation for correction of volumetric to mass flow is:

$$F_{STP} = F_{AMB} \times \frac{P_A}{760} \times \frac{298^{1/2}}{T_A}$$

Where:

F_{STP} = mass flow at STP, which is ambient volumetric flow corrected for temperature and pressure

F_{AMB} = flow, for a given float ball position, as read from the manufacturer's curve

P_A = ambient barometric pressure (mm of Hg)

T_A = ambient temperature (°K)

The rotameter is a moderately accurate, rugged, field portable measuring device. Since air density will affect the accuracy of the unit, it is essential that STP corrections be applied to all flow measurements.

Accuracy is affected by build-up of contaminants on both the walls of the tube and the indicator ball. Therefore, some effort should be made to eliminate particles from the air stream.

Rotameters can be cleaned by running methanol through the unit. Rotameters should be cross-checked using a bubble flow meter or mass flow meter approximately every 6 months.

Capillary and Orifice Systems

Capillary and orifice based calibration systems use a set of flow restrictors and a corresponding set of pressure differential versus flow curves to give a predetermined flow. Because of the high sensitivity to the diameter of the restrictor (proportional to the 4th power), and variances in the repeatability of pressure gauges, accuracy of these systems generally leaves much to be desired. Therefore, flows should be cross-checked more frequently than with other systems. If this system is used to generate a calibration standard, the flow system should be used only to maintain a constant flow. The flow measurement should be done with either a bubble flow meter or a mass flow meter.

Appendix G Methane Equivalent Calculation

Methane equivalent is obtained from the following expression:

$$\text{Methane Equivalent} = \frac{\text{Molecular weight of hydrocarbon gas (in calibration mixture)}}{\text{Molecular weight of methane}}$$

EXAMPLE: Calibration mixture is 1.40 ppm propane (C₃H₈), 5.00 ppm methane (CH₄) with the balance being zero air.

Total hydrocarbon content is:

Methane Equivalent

$$\begin{aligned} &= \left(\frac{\text{molecular weight of C}_3\text{H}_8}{\text{molecular weight of CH}_4} \times 1.40 \text{ ppm} \right) + 5.00 \text{ ppm} \\ &= \left(\frac{(3 \times 12.01) + (8 \times 1.008)}{12.0 + (4 \times 1.008)} \times 1.40 \text{ ppm} \right) + 5.00 \text{ ppm} \\ &= \left(\frac{44.09}{16.04} \times 1.40 \right) + 5.00 \text{ ppm} \\ &= (2.75 \times 1.40) + 5.00 \text{ ppm} \\ &= 3.85 + 5.00 \\ &= 8.85 \text{ ppm} \end{aligned}$$

Appendix H Gas Phase Titration Calculations

For determination of NO concentration:

$$C_F = \frac{F_C \times C_S}{F_t}$$

Where:

C_F = output concentration (ppm)

C_S = NO concentration of compressed gas (ppm)

F_C = NO flow at STP

F_D = dilution flow at STP

F_t = total flow ($F_C + F_D$) at STP

For determination of O₃ concentration:

$$NO_I - NO_{II} = O_3$$

Where:

NO_I = NO concentration before introduction of O₃

NO_{II} = NO concentration after introduction of O₃

For determination of NO₂ concentration when O₃ is known:

$$NO_I - NO_{II} = NO_2$$

or

$$O_3 = NO_2$$

Since the NO_x converter in all analyzers is never 100% efficient, a calculation of converter efficiency must be performed.

$$\text{Converter efficiency} = \frac{\text{NO}_2 \text{ increase} \times 100\%}{\text{NO decrease}}$$

Appendix I High Volume Sampler Calculations

Calibration of Orifice

True Air Volume

Calculate the air volume measured by the positive displacement primary standard:

$$V_a = \frac{(P_a P_m)}{P_a} \times V_m$$

Where:

- V_a = true volume of air at atmospheric temperature, in cubic metres
- P_a = barometric pressure, in millimetres of mercury
- P_m = drop in pressure at inlet to reference orifice, in millimetres of mercury
- V_m = volume measured using the standard orifice, in cubic metres

Conversion factors:

- Inches of mercury x 25.4 = millimetres of mercury
- Inches of water x 73.48×10^{-3} = inches of mercury
- Cubic feet of air x 0.0283 = cubic metres of air

True flow rate

$$Q = \frac{V_a}{T}$$

Where:

- Q = flow rate of air, in cubic metres per minute
- T = duration of sampling, in minutes

Sample Volume

The volume of air sampled is calculated by the following equation:

$$V = QT$$

Where:

- V = air volume sampled, cubic metres
- Q = average sampling rate, cubic metres/minute
- T = sampling time, in minutes

The average sampling rate, Q , is determined from the recorder chart by estimation, if the flow does not vary more than $0.11 \text{ m}^3/\text{min}$ during the sampling period. If the flow rate does vary more

than 0.11 m³/min during the sampling period, read the flow rate from the chart at 2 hour intervals and take the average.

Corrections for Pressure or Temperature

If the pressure or temperature, during calibration of a high volume sampler, is substantially different from the pressure or temperature during orifice calibration, a correction of the flow rate, Q, may be required. If the pressures differ by no more than 15 percent and the temperatures differ by no more than 100 percent, the error in the uncorrected flow rate will not be more than 15 percent. If necessary, obtain the corrected flow rate as directed below.

This correction applies only to orifice meters having a constant overflow coefficient. The coefficient for the calibrating orifice has been shown experimentally to be constant over an operating range of 0.6 to 2.2 cubic metres per minute. Calculate corrected flow rate according to the formula:

$$Q_2 = Q_1 \left[\frac{T_2 P_1}{T_1 P_2} \right]^{1/2}$$

Where:

- Q₂ = corrected flow rate, m³/min
- Q₁ = flow rate during high volume calibration, m³/min
- T₁ = absolute temperature during orifice unit calibration, °K or °R
- P₁ = barometric pressure during orifice unit calibration, mm Hg
- T₂ = absolute temperature during high volume calibration, °K or °R
- P₂ = barometric pressure during high volume calibration, mm Hg

Calculation of Mass Concentration of Suspended Particulates

$$S.P. = \frac{(W_2 - W_1) \times 10^6}{V}$$


Where:

- S.P. = mass concentration of suspended particulates, µg m⁻³
- W₁ = initial weight of filter, grams
- W₂ = final weight of filter, grams
- V = barometric pressure during orifice unit calibration, mm Hg
- 10⁶ = conversion factor from grams to micrograms.

Weights are determined to the nearest 0.1 milligram, airflow rates are determined to the nearest 0.03 cubic metres per minute, times are recorded to the nearest two minutes, and mass concentrations are reported to the nearest microgram per cubic metre.

Appendix J Example of a Calibration Report

Calibration report templates are available on the AMD website.



**CH₄/Non CH₄
Calibration Report Form**

Date: [Click here to enter a date](#)

Location: [Click here to enter text](#) Temperature: °C

Performed by: Name of operator Barometric Pressure: Text

Monitor:

Make/model: Serial number: s/n

Inlet flow (scfm): Inlet flow. Range ppm: CH₄ Range NMHC Range THC Range

Last calibration date: [Click to enter date](#) As found Co/Ci: CH₄ Co/Ci. NMHC Co/Ci. THC Co/Ci.

Before Calibration:

CH₄ Cal Factor: Factor

NMHC Cal Factor: Factor

THC Cal Factor: Factor

Span Value (CH₄/NMHC): Span value

After Calibration:

CH₄ Cal Factor: Factor

NMHC Cal Factor: Factor

THC Cal Factor: Factor

Span Value (CH₄/NMHC): Span value

Calibration Method: Method

Calibrator:

Make/model: Serial number: s/n

Flow Device #: Zero Air ID#: ID number

Gas Cylinder #: Cylinder number

CH₄ Conc (ppm): # CH₄ Equiv (propane only) (ppm): #

Propane Conc (ppm): # Total CH₄ Equiv (ppm): #

Calibration standard certificate expiration date: [Click here to enter a date.](#)

Calibrator Reference Settings:

Flows	Zero	High	Mid	Low
Dilution	#	#	#	#
Gas	#	#	#	#

Calibration:

Calibrator Measured Flows			Calculated Conc. (Co) (ppm)			Indicated Conc. (Ci)						Final Co/Ci		
						CH ₄		NMHC		THC				
Air	Gas	Total	CH ₄	NMHC	THC	Initial	Final	Initial	Final	Initial	Final	CH ₄	NMHC	THC
#	0.00	#	#	0.0000	0.0000	#	#	#	#	#	#	#	#	#
#	#	#	#	#	#	#	#	#	#	#	#	#	#	#
#	#	#	#	#	#	#	#	#	#	#	#	#	#	#
#	#	#	#	#	#	#	#	#	#	#	#	#	#	#

Average Correction Factors (CF) =

Linear Regression Analysis: Y = mx + b (where x = calculated concentration, y = indicated concentration)

	CH ₄	NMHC	THC
Correlation Coefficient:	#	#	#
m (slope):	#	#	#
b (intercept as % of full scale):	#	#	#

Remarks: [Click here to enter text](#)

Next Calibration due by: [Click here to enter a date](#)

June 2014
CH₄/Non CH₄ Calibration Report Form
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