



CO L O R A D O

**Department of Public
Health & Environment**

Air Pollution Control Division

Technical Services Program

APPENDIX GM15

Standard Operating Procedure for Method Detection Limit (MDL) Determination

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Standard Operating Procedure for Method Detection Limit determination

1 SCOPE AND APPLICABILITY

1.1 Introduction

This standard operating procedure (SOP) document describes the procedures used by members of the Air Pollution Control Division (APCD) to determine the Method Detection Limit (MDL) of analytes sampled at air monitoring sites. The procedures given in this SOP are a supplement to APCD's Quality Assurance Project Plan (QAPP) and the latest information published in the Code of Federal Regulations.

1.2 Method Overview

The MDL determination procedure is based off the Photochemical Assessment Monitoring Stations (PAMS) program's technical assistance document (TAD) (EPA, 2019). This procedure was built upon the 40 CFR Part 136 Appendix B. The MDL method is expanded by taking into account a potential for background contamination to be present in the sample collection process and instrument zero drift. The MDL procedure approximates "the lowest concentration (or amount) of analyte than can be reported with 99% confidence that the actual concentration (or amount) is greater than zero (EPA, 2019). MDL tests are to be performed annually, post annual maintenance and if possible calibration. The measurements, activities performed, and equipment used all are required to be documented in order to reconstruct the MDL determinations if so needed at a later date.

1.3 Format and Purpose

The sequence of topics covered in this MDL determination follows 2007 EPA guidance on preparing standard operating procedures (SOPs) (US EPA, 2007). This method was also written to help understand how and why key procedures are performed.

2 SUMMARY OF METHOD

2.1 MDL Determination

The MDL determination involves measuring minimally seven low concentration "spikes" and minimally seven "blanks" (zeros), over the course of three different, non-consecutive days. This allows the incorporation of temporal variability and instrument performance. A MDL dilution system and gas cylinders are transported to site and set up to deliver test gas through the probe to the gaseous analyzers. The MDL tests are performed one day for on analyte and then alternated with another analyte on the next until the minimum number of samples is measured for all available gaseous analyzers present at the site. Once all low concentration spikes and blanks are analyzed a MDL value is calculated for each respectively. The data and calculations are recorded and saved in a file. A report is generated detailing all the activities, data, and results which is then saved (along with the data files) to the J:\GMM Group\La Casa MDL directory.

3 DEFINITIONS

The CDPHE/APCD/TSP QAPP contains an appendix P2, of acronyms and definitions. Any commonly used shorthand designations for items such as the sponsoring organization, monitoring site, and the geographical area will be defined and included in this SOP or in the QAPP.

4 HEALTH AND SAFETY WARNINGS

Gas Hazards

Gas cylinder certification involves the use of several gases such as, carbon monoxide (CO), sulfur dioxide (SO₂), nitric oxide (NO), etc. CO is a colorless, odorless, and tasteless gas. It is a hazardous compound as it combines with

hemoglobin and reduces the oxygen carrying ability of the blood. SO₂ is a hazardous compound with a sharp irritating odor that causes severe respiratory tract, eye, and skin burns. NO is also a hazardous compound that causes skin and eye irritation, and contains material that can cause target organ damage. NO gas may be fatal if inhaled for a prolonged period or at a high concentration. Gas cylinders balanced with nitrogen also present an asphyxiation hazard.

As several of the source gases are poisonous gases, calibration source tanks and delivery systems, or any other calibration span gas, should be vented to the atmosphere rather than into the laboratory or other sampling area. If this is impossible, limit operator exposure to the gas by getting fresh air every 5 to 10 minutes. The operator must leave the area immediately if he/she experiences lightheadedness, headache or dizziness. Refer to the respective material data safety sheet (MSDS) for more information on hazards and safety.

Electrical Hazards

1. Always use a third ground wire on all instruments.
2. If it is necessary to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltage inside the analyzer. The analyzer has high voltages in certain parts of the circuitry, including a 110 volt AC power supply. Refer to the manufacturer's instruction manual and know the precise locations of these components before working on the instrument.
3. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.
4. Always unplug the analyzer whenever possible when servicing or replacing parts.

5 CAUTIONS

To prevent damage to the equipment, the following precautions should be taken:

1. Keep the interior of the instruments and laboratory clean.
2. Inspect the system regularly for structural integrity.
3. Inspect tubing for cracks and leaks.
4. EPA protocol gases are hazardous materials. Long term exposure can cause problems with motor coordination and mental acuity. It is strongly recommended that all agencies have MSDS at all locations where gas cylinders are stored or used. MSDS are located on the gas room door of the APCD laboratory. MSDS can be obtained from the DOT or from your vendor.

6 INTERFERENCES

Interferences are physical or chemical entities that cause measurements to be higher (positive) or lower (negative) than they would be without the entity. The only interference that would cause a reading to be higher or lower would be due to pneumatic leaks in the calibrator, mis-calibrated or otherwise inaccurate pressure or temperature sensors, impurities present in the source gas cylinders, and/or diluent air source. Interferences of the gas analyzers are the purview of their respective SOPs and manuals.

7 PERSONNEL QUALIFICATIONS

General Personnel Qualifications are discussed in the CDPHE/APCD/TSP QAPP main body.

8 MDL APPARATUS AND MATERIALS

8.1 Assay Equipment

8.1.1 Gaseous Analyzers

See the respective SOPs and operator manuals on the operation and calibration of the gaseous analyzers (NO, SO₂, O₃ and CO) to be used for MDL determination.

8.1.2 Calibrator

The calibrator used to generate test gas concentrations during the calibration check and dilution check must have certified mass flow controllers. See the Standards SOP Appendix QA2 Section 5 and the calibrator operator's manual on the procedures for certifying the calibrator.

8.1.3 Dilution system

The MDL dilution system is composed of a zero air pack and a calibrator with certified MFCs (Figure 1). The test gas cylinders are precisely diluted with zero air to achieve the desired concentration via certified MFCs. The diluted gas concentrations are then sampled by a gaseous analyzer.

8.1.4 Wiring, Tubing and Fittings

Teflon™ and borosilicate glass are inert materials that should be used exclusively throughout the ambient air intake system. It is recommended that Polytetrafluoroethylene (PTFE) or Fluoroethylpropylene (FEP) Teflon™ tubing be used. PTFE or FEP Teflon is the best choice for the connection between an intake manifold and the bulkhead fitting. While not preferred, the use of stainless steel tubing and fittings in the sample train is permissible for standard (not trace level) CO analyzers. Examine the tubing and discard if particulate matter has collected on the tube's interior. All fittings and ferrules should be made of Teflon™ or stainless steel.

8.1.5 Reagents and Standards

The calibrator requires O₃ as a reagent for GPT with NO source gas. Since O₃ is short lived and highly reactive, it is generated internally by the calibrator. All source gas is obtained from cylinders whose contents must be traceable to NIST Standard Reference Material (SRM) gases via EPA Protocol procedures.

8.1.6 Spare Parts and Incidental Supplies

- Laboratory gas analyzer and calibrator manuals
- Teflon™ crush washers for cylinder regulators
- FEP or PTFE tubing

8.2 Calibration Equipment

See the respective gas analyzer and calibrator manuals and SOPs for calibration equipment, reagents, and standards.

9 CALIBRATION

See the respective gas analyzer and calibrator manuals and SOPs for the Calibration procedures.

10 MDL DETERMINATION PROCEDURE

10.1 Introduction

The following section describes how the MDL data are obtained and the calculations used to determine the final MDL value. An overview of the steps to determine the MDL value is given below:

1. MDL dilution system setup at the site (section 10.1.1)
2. Run MDL blanks (MDLb) for each analyte (section 10.1.2)
3. Calculate the MDLb from the seven discrete 20-30 min averaged zeros. (section 10.1.3)
4. Select the MDL spike (MDLsp) concentration (section 10.1.4)
5. Run the MDLsp concentration for each analyte (section 10.1.5)
6. Calculate the MDLsp value (section 10.1.6)
7. Determine the MDL value (section 10.1.7)

The preceding steps must be repeated for each analyte. After MDL procedure is completed for each analyte, data compiled and analyzed, a report is generated with all the findings.

10.1.1 MDL Dilution System Setup

The MDL dilution system is comprised of a high output zero air source, a dilution calibrator with MFCs that will allow for very low concentrations, and gas cylinders. At the site, the dilution system is completely independent from the site equipment. Figure 1, illustrates the proper setup.

1. Install the zero air pack and dilution calibrator and power on
2. Setup remote communications with the site datalogger
3. Purge the regulator (section 10.1.8) and connect the gas cylinders to the calibrator.
4. Plumb the zero air pack to the calibrator
5. Connect a tube from the calibrators output to the tee above the valve on the cal gas manifold for the desired analyte to be tested.

10.1.2 MDLb Run Procedure

At the site:

1. Connect the cal gas line from the MDL calibrator to the tee above the valve on the cal gas manifold of the desired analyte to be tested.
2. Ensure the MDL calibrator and zero air pack are operating
3. Disable the analyte channel on the data logger and start the MDL zero sequence on the MDL calibrator.

4. Ensure the MDL calibrator is operating the sequence and the gaseous analyzer is responding appropriately.
5. Ensure that the response of the instrument is stable after some time. If not attempt to troubleshoot and fix the issue.

10.1.3 Calculate MDL_b

Once there have been a minimum of seven 20-30 minute average zeros over three non-consecutive days, the MDL_b may be calculated. The MDL_b is calculated as follows (EPA, 2019):

1. Calculate the average concentrations of the zero blank measurement concentrations, \bar{x}_b
2. Calculate the standard deviation of the zero blank measurement concentrations, s_b
3. Multiply s_b by the one-sided 99th percentile Student's t value corresponding to the number of blanks analyzed.
4. Calculate the MDL_b as the sum of \bar{x}_b and the product of s_b and the associated Student's t value:

Equation 1. MDL_b

$$MDL_b = \bar{x}_b + s_b * t$$

10.1.4 Selecting the Concentration to find MDL_{sp}

To select the concentration for the MDL_{sp}, the following should be considered (in decreasing order of importance) (EPA, 2019):

1. The concentration at which the instrument response is approximately 3-to-5 times the baseline response or lower limit of detection.
2. Analysis of a suite of zero blanks (i.e. measurements to determine the MDL_b) – calculate the standard deviation of the zero blanks and multiply by 3.
3. Previous acceptable MDL studies and related experience.

This selected concentration will be sampled by the gaseous analyzers in order to calculate the MDL_{sp}. If the MDL dilution system cannot generate a low enough concentration that is selected, then generate as low a concentration as possible given the dilution system's limitations. Operating the calibrator Mass Flow Controllers (MFCs) outside the 10 to 90% full scale is allowed as the stability of the concentration is more important than the absolute accuracy, and will not impact the MDL determination (EPA, 2019).

10.1.5 MDL_{sp} Run Procedure

The MDL_{sp} run procedure is as follows:

At the site:

1. Connect the cal gas line from the MDL calibrator to the tee above the valve on the cal gas manifold of the desired analyte to be tested.
2. Ensure the MDL calibrator and zero air pack are operating
3. On the first day, run the concentration at the desired flows and ensure that the zero air pack maintains pressure. If not increase the zero air pack's pressure, but do not exceed 35psi.
4. Disable the analyte channel on the data logger and start the MDL sequence on the MDL calibrator.
5. Ensure the MDL calibrator is operating the proper sequence and the gaseous analyzer is responding appropriately.
6. Ensure that the response of the instrument is stable after some time. If not attempt to troubleshoot and fix the issue.

10.1.6 Calculate MDL value for analyte

Once there have been a minimum of seven 20-30 minute average spiked measurements over three non-consecutive days, the MDL_{sp} may be calculated. The MDL_{sp} is calculated as follows (EPA, 2019):

1. Calculate the standard deviation of the calculated concentrations for the measurement periods, s_{sp}
2. Calculate the MDL_{sp} by multiplying s_{sp} by the one-sided 99th percentile Student's t value at 99% confidence corresponding to the number of measurement periods analyzed

Equation 2. MDL_{sp}

$$MDL_{sp} = s_{sp} * t$$

3. Compare the MDL_{sp} value to the spike concentration, it should fall in between the MDL_{sp} and 10-fold MDL_{sp}:

Equation 3. MDL_{sp} Range

$$MDL_{sp} < spike\ concentration < 10 * MDL_{sp}$$

4. If not then the MDL_{sp} procedure should be repeated with an adjusted spiking concentration, if possible
 - a. For $MDL_{sp} > spike\ concentration$, the spike level should be increased by 2-to-3 fold
 - b. For $spike\ concentration > 10 * MDL_{sp}$, the spike level should be decreased by 2-to-3 fold

10.1.7 Determine the MDL value

Once the MDL_b and the MDL_{sp} have been calculated, compare the two values. The higher of the two will be reported as the MDL for the analyte.

10.1.8 Regulator Purge Procedure

1. Inspect Teflon washer and replace if necessary.
2. Connect the regulator to the new gas bottle.
3. Purge the regulator and line:
 - a. Ensure regulator valve is closed.
 - b. Using a quick connect with a push stop and connect to the vacuum side of a pump.
 - c. Back off the regulator pressure knob, and close the regulator valve.
 - d. Quickly open the gas bottle valve until the bottle-side pressure gauge reads the bottle psi.
 - e. Quickly close the gas bottle valve.
 - f. Open the regulator valve and the gas line until the regulator gauges go to vacuum.
 - g. Close the regulator valve and the gas line.
 - h. Repeat for a total of three times

11 HANDLING AND PRESERVATION

Refer to the relevant EPA protocol gas MSDS for handling and preservation of compressed gas cylinders.

12 SAMPLE PRESERVATION AND ANALYSIS

EPA protocol gas samples receive no special preparation prior to MDL determination. Therefore a section for sample preservation and analysis in this SOP is not required.

13 TROUBLESHOOTING

13.1 General Factors

Troubleshooting is necessary if a candidate standard fails the certification. Care must be taken to ensure that the assay system is working properly and not causing issues. Some common issues are:

- Regulator and gas line not purged correctly, causing low response.
- Leaks in the analyzer or dilution system.
- Zero air pack pressure dropping too low due to very high dilution flow demands.

13.2 Instrument Troubleshooting

See the respective analyzer and calibrator SOP for additional troubleshooting techniques and information.

14 DATA MANAGEMENT AND RECORDS MANAGEMENT

14.1 Data Management

Data are generated from the analyzer(s) at intervals internally set, ranging from an averaging time of 20 seconds to 5 minutes. The data is collected by the on-site data logger as near-real-time data (often every 3 to 10 seconds) and is aggregated into 1 and 5 -minute averages.

14.2 Records Management

Records of laboratory analyzer multi-point calibration, MFC verifications, and candidate assay data are kept in both electronic and hard-copy formats. These records are kept in the relevant databases and filing locations. The MDL determination activities and results are compiled into a report and kept on the J: Drive along with the data.

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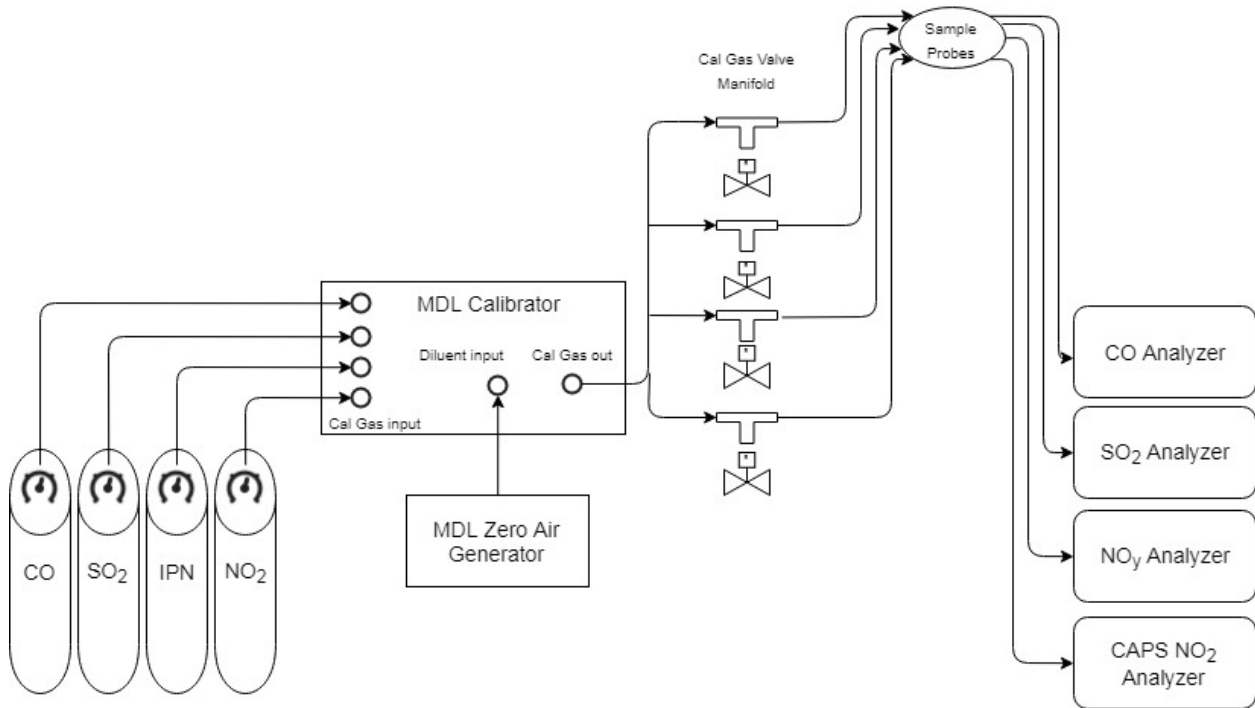


Figure 1. Pneumatic connections for MDL study.

Gas Cylinder Certification Form
 APCD

Assay Results		
Level 1	NO	Nox
Dilution Ratio Lab Standard	#DIV/0!	
Dilution Ratio Candidate	#DIV/0!	
Computed Cylinder Conc:	#DIV/0!	#DIV/0!
Cylinder Conc. % Diff:	#DIV/0!	#DIV/0!
Candidate Certification Pass?	#DIV/0!	#DIV/0!

Level 2	NO	Nox
Dilution Ratio Lab Standard	#DIV/0!	
Dilution Ratio Candidate	#DIV/0!	
Computed Cylinder Conc:	#DIV/0!	#DIV/0!
Cylinder Conc. % Diff:	#DIV/0!	#DIV/0!
Candidate Certification Pass?	#DIV/0!	#DIV/0!

Figure 2 continued. Gas Cylinder Certification Form (page 2)