# Method Detection Limit (MDL) Development and Standardization

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# Overview

- We're all using

40 CFR APPENDIX B TO PART 136 — DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT— REVISION 1.11

# Method Detection Limit Definition

- "The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte."*

* 40 CFR Appendix B to part 136

# Method Detection Limit Working Definition

- Statistically calculated concentration where you would expect to "qualitatively" identify the target analyte
- Measure of how well you can repeat an analysis
- Function of the ability to prepare identical low concentration samples.

# Practical MDL Determination

- Your MDL is a measure of YOUR laboratory's sensitivity using YOUR chemicals, equipment, and staff.
- If you spike at your MDL concentrations you should find:
  - 50% of the values would fall above the MDL (detected)
  - 50% would fall below (not detected)

# MDL Basics

1. Analytical systems (Instruments)
   - Run on systems that are operating properly
     - Calibration meets criteria
     - Columns in good condition
   - Avoid contaminate carry-over from previous samples
   - Blank samples meet criteria
   - Routine maintenance is complete

# MDL Basics, Continued

2. Calibrating for the MDL procedure
   - MDL studies are typically done at the beginning of a season or new year.
   - Generate a new calibration curve prior to analyzing the MDL samples.
   - Calibrate using the same calibration range used for field samples
   - Verify calibration curve with second source standard

# MDL Basics
# Procedures to Improve the MDL

3. Choosing the proper spike level !
   - Prepare standard 2.5 to 5 times the estimated detection limit. (MDL is a function of the spike concentration!)
   - Analyze at least seven (7) samples at the spike level, calculate the MDL
     - Accept the MDL if the calculated value is less than the spiked value.
     - Reprepare at a lower level and rerun the seven set series if calculated MDL is greater than 5 times the spiked level

**Calculated MDL < Spike Level < 5 x Calculated MDL**

# Procedures to Improve the MDL, Continued

4. Replicate sample preparation
   - Method requires at least 7 replicates – ERG recommends 10
     - Ensures the minimum number (seven) of replicates are met in the event of outliers, which should only include:
       - Obvious analyst error
       - Improper sample preparation
       - Reject entire outlier sample data set
   - Use the correct Student's T value for the number of replicates (n-1 degrees of freedom)

# Procedures to Improve the MDL, Continued

5. Analyzing blanks
   - Analyze at least one method blank to measure background contaminations
   - Minimizing the blank helps control the variation (precision) of the MDL replicate runs
     - With the exception of metals, blank subtraction is not allowed for MDL determination.

# Calculations to Determine MDL

Three important things to remember about calculating MDLs are:

- Use the sample standard deviation,
- Use the correct Student's t-value, and
- Use correct significant figures

# Calculation
# 40 CFR Appendix B part 136

| Number of replicates | Degrees of Freedom (n-1) | $t_{(cn-1,.99)}$ |
|---|---|---|
| 7 | 6 | 3.143 |
| 8 | 7 | 2.998 |
| 9 | 8 | 2.896 |
| 10 | 9 | 2.821 |

## Example

MDL=2.821 ($S_{pooled}$)

where 2.821 is equal to t(10,1-α=.99)

# MDL Verification

- Analyzing a single sample spiked at the MDL concentration
  - If the analytical response is NOT distinguishable from a reagent blank, the calculated MDL is unreasonably low
    - This could happen if you make exact replicate samples and your system is inherently noise free.
    - The MDL study should be repeated at a different concentration. (Higher or Lower?)
  - If the analyte is detected at the presumed MDL, the MDL is defensible and should be reported

# MDL Issues: What Affects Precision

- Background interferences and Blank contamination are variable and raise MDL spike
- Precision of standards preparation equipment (volumetric glassware, gas metering equipment, syringes etc) is variable
- Physically unable to produce a low enough standard to perform MDL study
- Instrument noise
- Others?

# MDL Issues: What Affects TO-15 Precision

- VOC concentrator performance
- Different behavior of polar vs. nonpolar TO-15 compounds
- Variation in canister manufacture, use, or age
- Precision of standards preparation (mass flow controllers, etc)
- Ability to make standards concentration low enough to perform MDL study
- Others?

# Spike Sample Preparation for Canisters (TO-15)

- Static Dilution
  - Spike the canister with a mixture of liquid components prepared in static dilution bottles
- Dynamic Dilution
  - Mix standards and humidified zero air with mass flow controllers and a calibration manifold

Better precision and lower detection possible with dynamic dilution spike preparation.

# MDL Issues: What Affects Carbonyl Precision

- Background and blank contamination: Interferences from DNPH cartridges are variable and raise MDL
- Precision of standards preparation equipment (volumetric glassware, syringes, etc)
- Carbonyl extraction technique
- Others?

# Spike Sample Preparation for Carbonyls (TO-11A)

- Vendor prepared stock solution
- Prequalified cartridge blank Lot
- High quality solvents
- Class A glassware
- Gas tight syringes
- Repeatable spiking technique

# MDL Issues: What Affects Metal Precision

- For determination of Quartz filters that have a high background:
  - Analyze to initially determine which elements have background interferences
    - Spike filters and determine the MDL using standard procedures for elements w/o background
    - Analyze 7-10 non-spiked filters to determine MDL for filters that have high background

# IO-3.5 MDL Example

| Analyte | Average Quartz Filter (ng/strip) |
|---|---|
| Antimony | 6.4 |
| Arsenic | 11.5 |
| Beryllium | 4.1 |
| Cadmium | 23.3 |
| **Chromium** | **408** |
| Cobalt | 6.0 |
| Lead | 77.7 |
| Manganese | 93.3 |
| Mercury | 11.7 |
| **Nickel** | **43.6** |
| Selenium | 10.7 |

# IO-3.5 MDL Example (cont.)

| Analyte | Average Blank Quartz Filter (ng/strip) | Spiked Amount | MDL (ng/strip) |
|---|---|---|---|
| Chromium | 408 | *BLANK* | 76.2 |
| Nickel | 43.6 | *BLANK* | 29.4 |

Analyzed a spike concentration at 25 and 75 ng to verify MDL concentration.

# Summary
# Improving MDLs

- Control variation in spike sample preparation
- Control background as much as possible
- Control instrument performance
- Improve sensitivity of analysis
  - Larger injections
  - Concentrate samples
  - Sensitive detectors (e.g., Full Scan vs. SIM MS)

# MDL Common Sense Check

- Does the spike level exceed 5 times the MDL? If so, the spike level is high.
- Is the MDL higher than the spike level? If so, the spike level is too low.
- Are the replicate recoveries reasonable?

# MDL Final Check

- Does the calculated MDL meet the objectives for your program?

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