

Knowing Your Limits or... How to Develop and Maintain a True Analytical MDL for Particulate Matter Emissions

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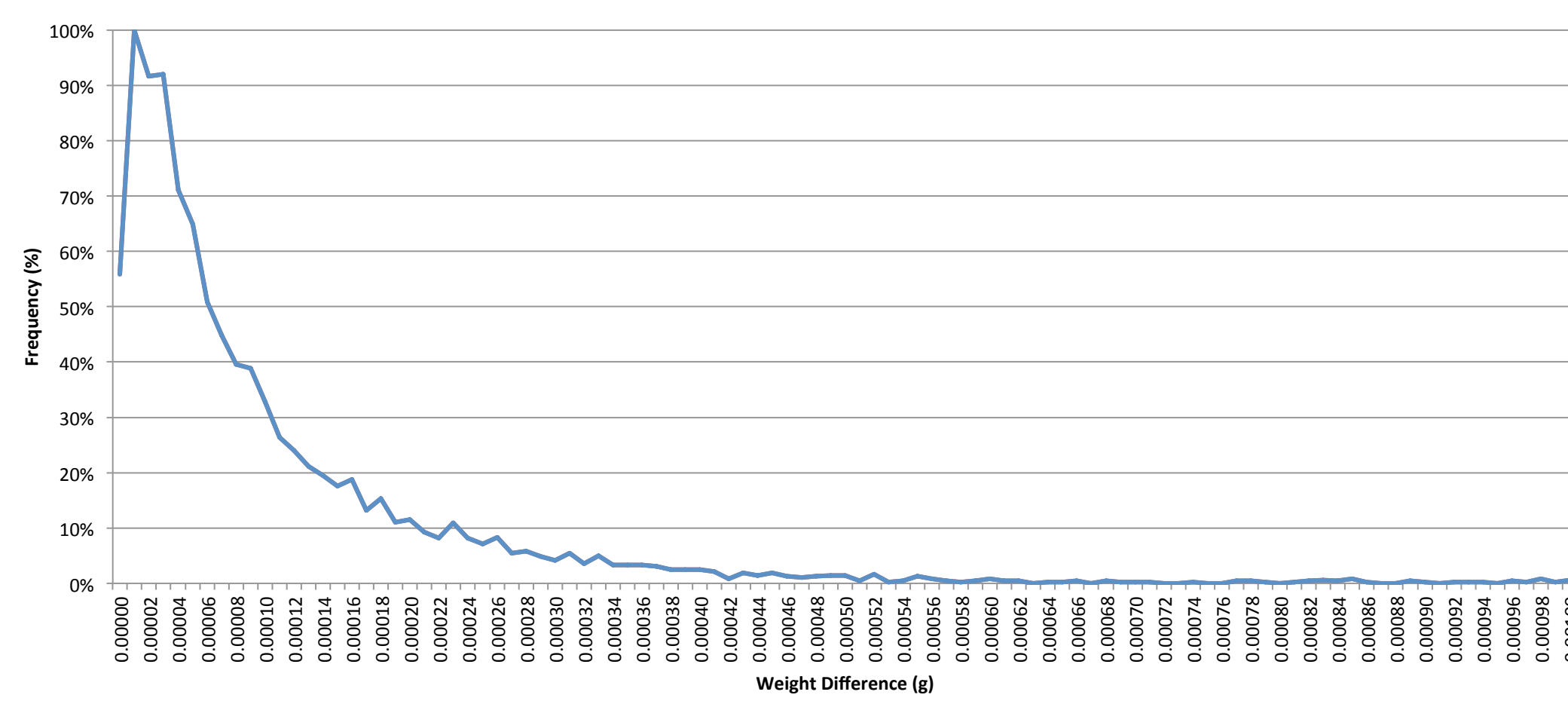
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The Gravimetric MDL

In this poster presentation, CleanAir shows that the media choice affects the analytical MDL for gravimetric methods such as EPA Method 5, 201A, and 202. Using a modified method based on 40 CFR 136 Appendix B, we have developed a procedure for approximation of the analytical MDL.

MDL Depends on Media Choice

- Some use the manufacturer's reported LOQ for 5-place balances.
- The graph below shows the frequency of weight differences for blank media used in common methods including quartz filters and Teflon beakers.



- The graph shows the "background noise" of tared media is high at 0.1 mg.
- Better estimation: 0.27 mg level, and becomes better around the 0.50 mg level (sound familiar?)

Weight Value (g)	Frequency (%)
0.00009	39%
0.00010	33%
0.00011	26%
0.00012	24%
0.00027	5%
0.00028	6%
0.00049	1%
0.00050	1%
0.00051	0%

It's been a while, remind me about 40 CFR 136 Appendix B

- Definition and procedure for the determination of the method detection limit.
- MDL: Minimum concentration to be measured with 99% confidence that the analyte concentration is greater than zero.
- Estimate MDL based on blank replicate study
- Prepare method blanks and spike standard approximately 1-5x the estimated MDL
- Calculate the standard deviation, repeat until the calculated MDL is in the correct range.

Determining the Proper MDL

Perform blank study to determine initial spike level

At least 7 samples

Create mixture that will evaporate to leave spike level amount with an aliquot that can be accurately repeated

Use an inorganic salt (ie Sodium Chloride)

Typical aliquot choice is 5mL

Perform spike study at determined initial spike level

At least 7 samples at the same concentration

Calculate the MDL from the spike study data

Calculate the sample standard deviation

Multiply by the student-t value based on amount analyzed in spike study

Use all significant digits

Determine if spike study passes QA requirements – repeat procedure until all true

Is the spike level higher than the MDL?

Is the spike level less than 10 times the MDL?

Is the average recovery between 90 and 110%?

Results of Early CleanAir MDL Studies

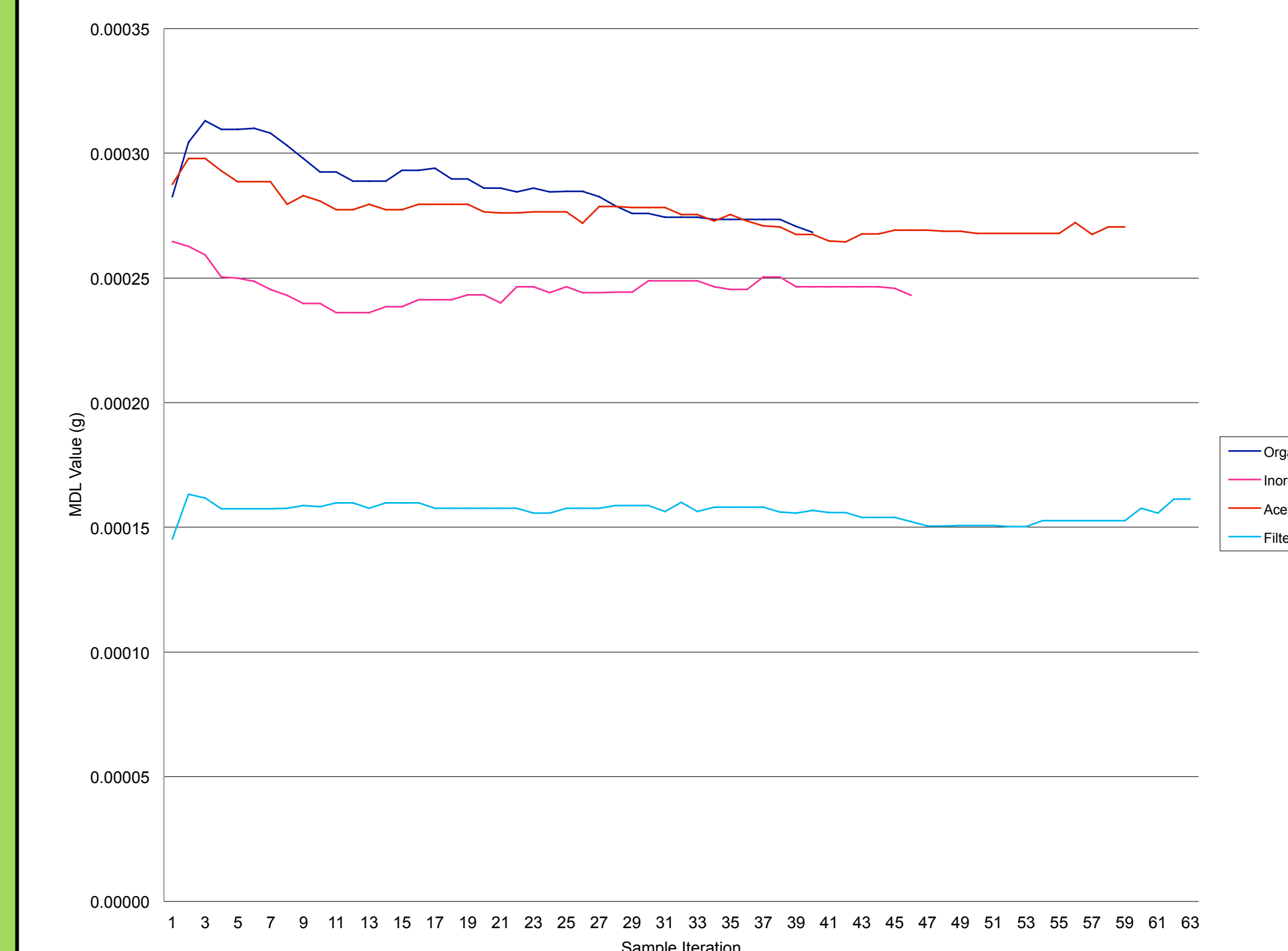
- The table gives data of media choice study performed annually.

Media Type	Year	MDL (mg)
Glass Beaker	2006	0.65
	2007	1.06
	2008	1.11
Teflon Beaker	2009 (Q1-2)	1.02
	2009 (Q3-4)	0.56
	2006	0.42
Filter: Glass Fiber	2007	0.30
	2008	0.32
	2009 (Q1-2)	0.27
	2009 (Q3-4)	0.27
	2009 (Q3-4)	0.27

- Early findings suggests that MDL for fractions was 1.0 mg, filter MDL was 0.50 mg
- No appreciable difference observed between glass and Teflon beakers
- The above data is consistent with US EPA Method 5I. (1 mg MDL; 3 mg PQL)

Using CleanAir's Proprietary Weighing Methods – Current Values

- The graph shows the MDL for different media/fraction choices over a 1 year period.



- Current findings suggest that the MDL for liquid fractions is 0.3 mg.
- Current findings suggest that the MDL for filter fractions is 0.15 mg.

Preliminary Study of Different Blank Media

- Data Table shows preliminary blank media study over a year period during 2012.

Media Type	N	Average (g)	Standard Deviation (g)	MDL _{est} (mg)
Filter: Quartz Fiber ¹	335	0.33721	0.00101	2.01
Filter: Quartz Fiber ²	176	0.48287	0.00036	0.72
Filter: Glass Fiber	241	0.35618	0.00007	0.14
Filter: Alundum Thimble	66	42.28109	0.00256	5.13
Aluminum Dish	203	2.07645	0.00005	0.10
Glass Beaker	167	107.44660	0.00049	0.97

- 1, 2 - Two Quartz fiber filters from different manufacturers
- Difference between Quartz and Glass fiber media. It is believed that Quartz is prone to static electricity issues.

Reasons Why Gravimetric MDL's Matter

- Low level particulate emissions (i.e. total particulate catches less than 50 mg) are becoming increasing commonplace.
- Knowing laboratory MDL's could reduce field testing times when running at clean sources (0.01 lb/10⁶ Btu).
- Reported data is compromised when MDL is misrepresented.
- A properly derived MDL should be reported along with emissions data so the end user knows the uncertainties and limitations associated with the laboratory data.
- Analytical MDL studies should be performed at least monthly

Future Investigations

- Are there better media available that will allow for lower MDLs?
- Are there better methods of preparing media to lower MDLs?
- Does the ambient temperature and humidity affect MDLs?