2017 US EPA Method Update Rule

Overview and MDL review

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Methods and Detection Limits

- Initial rule proposal February of 2015
- Finally signed August of 2017

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Method Updates

- All acceptable methods from Standard Methods have been updated to the 22nd Edition

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology[58]	EPA[52]	Standard methods	ASTM	USGS/AOAC/other
1. Acidity, as $CaCO_3$, mg/L	Electrometric endpoint or phenolphthalein endpoint		2310 B-2011	D1067-11	I-1020-85.[2]
2. Alkalinity, as $CaCO_3$, mg/L	Electrometric or Colorimetric titration to pH 4.5, Manual		2320 B-2011	D1067-11	973.43,[3] I-1030-85.[2]
	Automatic	310.2 (Rev. 1974)[1]			I-2030-85.[2]

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Standard Methods

- The Standard Methods updates are primarily to reflect updates to the quality control sections.
  - 1020: general QC requirements
  - 2020: 2000 series methods and has a chart indicating required QC
  - 3020: 3000 series methods
  - 4020: 4000 series methods and has a chart indicating required QC
  - 9020: 9000 series methods

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QUALITY ASSURANCE/QUALITY CONTROL (2020)/Quality Control Practices

TABLE 2020:I. METHODS IN PART 2000 INDICATING OR AMENABLE TO INITIAL QUALITY CONTROL

	Section	Bias	Precision	MDL	Operational Range
2120B	Color	–	×	–	–
2120C		–	×	×	–
2120D		–	×	×	–
2120E		–	×	×	–
2120F		–	×	×	–
2130B	Turbidity	–	–	×	–

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QUALITY ASSURANCE/QUALITY CONTROL (2020)/Quality Control Practices

TABLE 2020:II. SUMMARY OF ONGOING QUALITY CONTROL FOR METHODS IN PART 2000

	Section	Calibrate or Standardize	QCS	MB	LFB	Duplicates	LFM
2120B	Color	×	×	–	–	×	–
2120C		×	×	–	–	×	–
2120D		×	×	–	–	×	–
2120E		×	×	–	–	×	–
2120F		×	×	–	–	×	–
2130B	Turbidity	×	×	–	–	–	–

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TABLE 4020:I. MINIMUM QUALITY CONTROL FOR METHODS IN PART 4000

Section	Method Blank	LFB*	LFM† & LFMD‡	Other	Section	Method Blank	LFB*	LFM† & LFMD‡	Other
4110B	×	×	×	1,3	4500-Cl B	×	×	–	2,3
4110C	×	×	×	1,3	4500-Cl C	×	×	–	2,3
4110D	×	×	×	1,3	4500-Cl D	×	×	–	2,3
4140	×	×	×	1,3	4500-Cl F	×	×	–	2,3
					4500-Cl G	×	×	–	2,3
4500-B.B	×	×	×	3	4500-Cl H	×	×	–	2,3
4500-B.C	×	×	×	3	4500-Cl I	×	×	–	2,3
	×								

1. Additional QC guidelines in method.
2. Duplicates of the sample will be run.
3. Refer to 4020B for further QC requirements.
4. Compare to results from Section 4500-CO_2 4500-CO_2.D.
5. Additional QC check with pH standard whose value is bracketed by calibration standards.
6. Zero check with zero oxygen sample.

This table is not comprehensive; refer to the specific method and 4020B for further details.

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TABLE 5020:I. MINIMUM QUALITY CONTROL FOR METHODS IN PART 5000

Section	Analyte	Method Blank	LFB*	LFM† & LFMD‡	Other
5210B	BOD	-	-	-	1,2,3
5210C		-	-	-	1,2,3
5210D		-	-	-	1,2,3
5220B	COD	×	×	×	1,2,3
5220C		×	×	×	1,2,3
5220D		×	×	×	1,2,3

* Laboratory-fortified blank.
† Laboratory-fortified matrix.
‡ Laboratory-fortified matrix duplicate.
§ A sample preparation technique that is normally combined with a subsequent determinative technique
× indicates that a QC type is mandatory for the method.
- indicates that a QC type is not mandatory for the method.
1. Additional QC guidelines in method.
2. Duplicates or LFMD of the sample will be run.
3. Refer to 5020B for further QC requirements.
This table is not comprehensive; refer to the specific method and 5020B for further details.

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Other Methods

- Micro: All Standard Methods have been updated to the 22nd Ed.
- Several US EPA organics methods updated
  - 608 is now 608.3
  - 624 is now 624.1
  - 625 is now 625.1

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Alternate Test Procedures Now Approved

- Colilert-18 has been approved for Fecal Coliform
- HACH 10242: “Simplified Spectrophotometric Measurement of TKN in Water and Wastewater”
- HACH 10206: “Spectrophotometric Measurement of Nitrate in Water and Wastewater”
- ASTM I-2547-11, I-2548-11, and NECi enzymatic reaction for Nitrate/nitrite

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40 CFR 136.3 Corrections

- Typographical errors, technology updates, etc.
  - Whole Effluent Toxicity Acute and Chronic Methods Manuals—clarifications in the definition of terms, consistency corrections among all three manuals.
  - Table II, Required Containers, Preservation Techniques, and Holding Times
    - Sodium thiosulfate concentrations for bacterial tests have been changed from **0.0008%** to **0.008%** sodium thiosulfate

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Corrections and Clarificaitons

- Alternative Test Procedures Section: error in 2012 Method Update Rule appeared to give State permitting authorities the authority to approve ATPs for limited use.
  - This was never the intent
  - Only the Regional ATP Coordinator can approve the limited use of ATPs

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Method Detection Limit Study Updates

- The MDL procedure was updates in three significant ways
  - The procedure now uses method blanks in addition to spikes to determine the MDL
  - The MDL now requires multiple dates worth of data in order to be more representative of the full year
  - The lab can now pool data from multiple instruments to calculate one MDL

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What has changed?

- The definition for one
  - Old: “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.”
  - New: "The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results."

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Initial MDL Study Walkthrough

- Initially it is very similar to the previous MDL procedure
  - Estimate the MDL
    - The average determined concentration plus 3X the standard deviation of a set of blanks
    - 3-5 times the signal to noise ratio
    - The concentration equivalent to three times the standard deviation of replicate instrumental measurements of spiked blanks
    - That region of the calibration where there is a significant change in sensitivity, i.e., a break in the slope of the calibration
    - Instrumental limitations

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Initial MDL Study Walkthrough

- Select a spiking level
- Process a minimum of seven spiked samples and method blanks
  - These must be prepared in at least three separate batches across at least three days
  - May include multiple instruments

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Initial Spike Evaluation and Calculations

- Did the spiked samples provide numerical results?
- Compute the MDL_s

(ii) Compute the MDL_s (the MDL based on spiked samples) as follows:

$$MDL_S = t_{(n-1,\ 1-\alpha=0.99)} S_s$$

where:

MDL_s = the method detection limit based on spiked samples

$t_{(n-1,\ 1-\alpha = 0.99)}$ = the Student's *t*-value appropriate for a single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom. See Addendum Table 1.

S_s = sample standard deviation of the replicate spiked sample analyses.

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Initial Blank MDL

- Three different methods to calculate the initial MDL_b based on results
  - No numerical results?
  - Some numerical results?
  - All results are numerical?

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)} S_b$$

where:

MDL_b = the MDL based on method blanks

$\bar{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = the Student's *t*-value appropriate for the single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom. See Addendum Table 1.

S_b = sample standard deviation of the replicate method blank sample analyses.

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Continuing Data Collection

- Quarterly data collection
  - A minimum of two spiked samples per instrument per quarter in which the method is used
- At least once per year, re-evaluate the spiking level
- If the method is modified in a way that can reasonable expected to change its sensitivity
- If a new instrument is added to a group of instruments whose data are being pooled

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Ongoing Annual Verification

- At least once every 13 months, re-calculate MDL_s and MDL_b from the collected data
- Include data generated within the last 24 months
- Include the initial MDL spiked samples if within the 24 months
- Ideally use all method blank results from the last 24 months

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Ongoing Blank Calculations

- They want you to use 24 months worth of blank data if possible
- The lab has the option of using only the last six months of blank data or the 50 most recent method blanks, whichever is more
- Use the greater of the MDL_s or MDL_b

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FAQs

- Will the number of MDL samples significantly increase?

Comparison of Number of Samples Analyzed in MDL Procedures

Samples Required	Revision 1.11	Revision 2
Spiked samples	7/year	8/year (2/quarter)
Methods blanks (MBs)	0	0 (use routine MBs)

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FAQs

- Is the lab required to recalculate the MDL every quarter?
- Will labs have to analyze more samples for methods that are rarely used?
- If the laboratory does not use a method during a quarter, will the laboratory still need to analyze low-level spiked samples?

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FAQs

- What happens if the laboratory has less than 7 sample spikes when calculating the MDL?
- Could one high blank result drastically elevate the MDL?
- What if a laboratory buys a new instrument and wants to include it in a multi-instrument MDL?
- Why are acceptable calibrations and batch quality control (QC) not mentioned in the Initial MDL procedure?

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FAQs

- Why is so much ongoing data collection necessary, and what additional quality is this practice of ongoing data collection providing?
- If the MDL and ML values change, permit limits may need to be reviewed.

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Questions?

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