TNI 2016 Standard: Detection, Quantitation, and Calibration

TCEQ Trade Fair

May 2019

AGENDA

- Implementation of the 2016 Standard
- Part 1: Revised Section 1.5.2 on Limit of Detection (LOD) and Limit of Quantitation (LOQ) and EPA MDL
  - 2:15 – 3:15
- Part 2: Revised Section 1.7 on Calibration
  - 4:00 – 5:00

2016 Standard

- Effective in Texas on January 31, 2020

New and Updated Implementation Resources

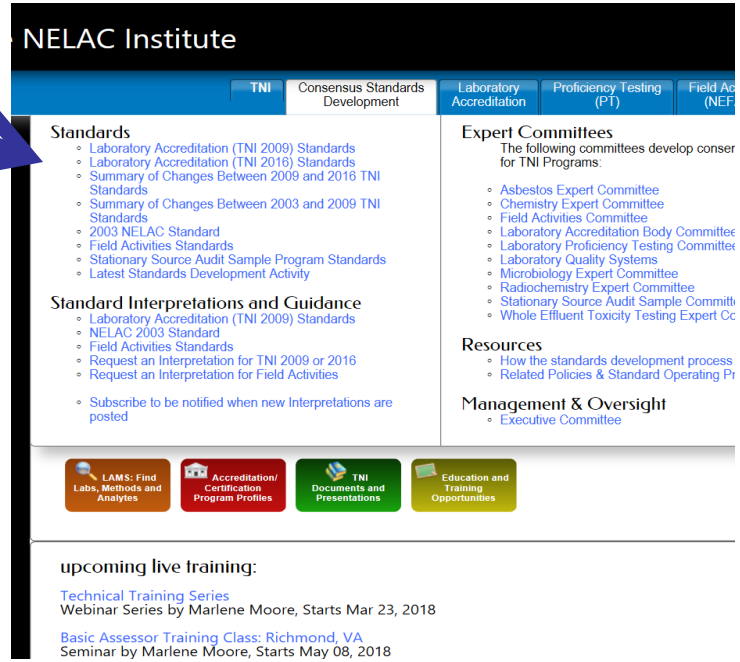
- Three Guidance Documents
- Revised Small Laboratory Handbook
- Revised Quality Manual Template
- 2016 Checklists
- 5 Downloadable Webcasts
- Comparison Document: 2003-2009-2016
- Early Implementation
  - Sections 1.5.2 and 1.7 can be implemented now!
- Review of Standard Interpretations (August 2019)

Webcasts

- Compare 2009 to 2016
  - Proficiency Testing
  - Quality Systems
  - Chemistry
  - Microbiology
  - Radiochemistry

Comparison and Advocacy Documents

- 2003 to 2009
- 2009 to 2016
- 2003 to 2016
- Benefits of the 2016 Standard
- TNI's National Accreditation Standard



Early Adoption

- Many of the changes could be implemented now , e.g.
  - New LOD and LOQ procedures
  - New calibration requirements
- Some may have to wait until the standard is effective, e.g.
  - PTRL reporting
  - Single point calibration for support equipment
- Talk to your AB!

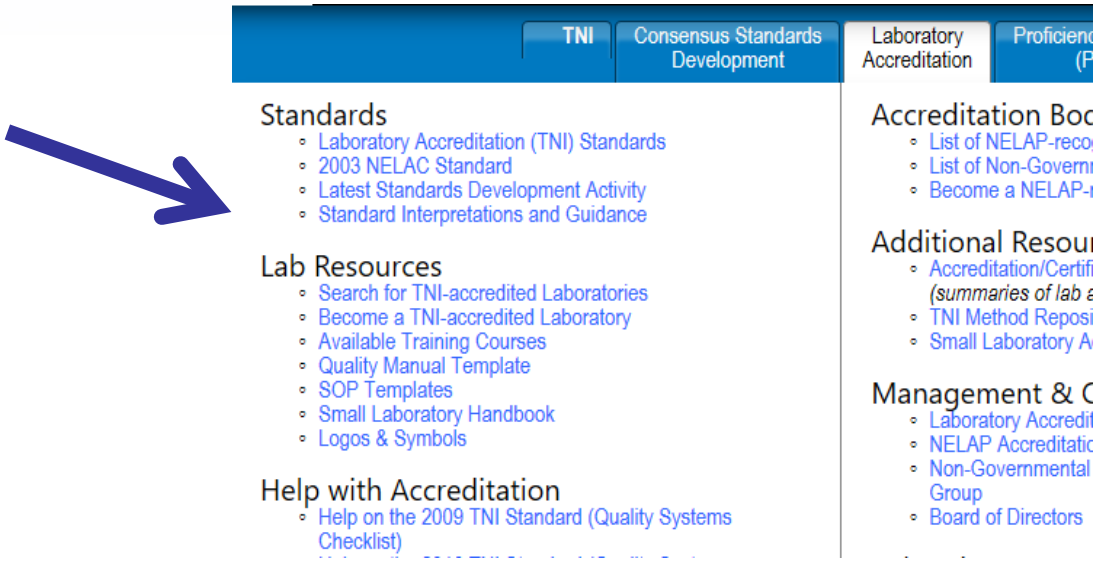
Revised Quality Manual Template

4.4 Review of Contracts

The <Laboratory Director? Client Services Manager? Project Manager? Quality Manager? Technical Managers? Who?> determines if the laboratory has the necessary accreditations, resources, including schedule, equipment, deliverables, and personnel to meet the work request.
<How is the review documented?>
The <Who?> informs the client of the results of the review if it indicates any potential conflict, deficiency, lack of accreditation, or inability of the lab to the complete the work satisfactorily.

New Guidance Documents

- Proficiency Testing Reporting Limit (PTRL)
  - Requires lab to be able to measure to a specified concentration
- Detection and Quantitation
- Instrument Calibration



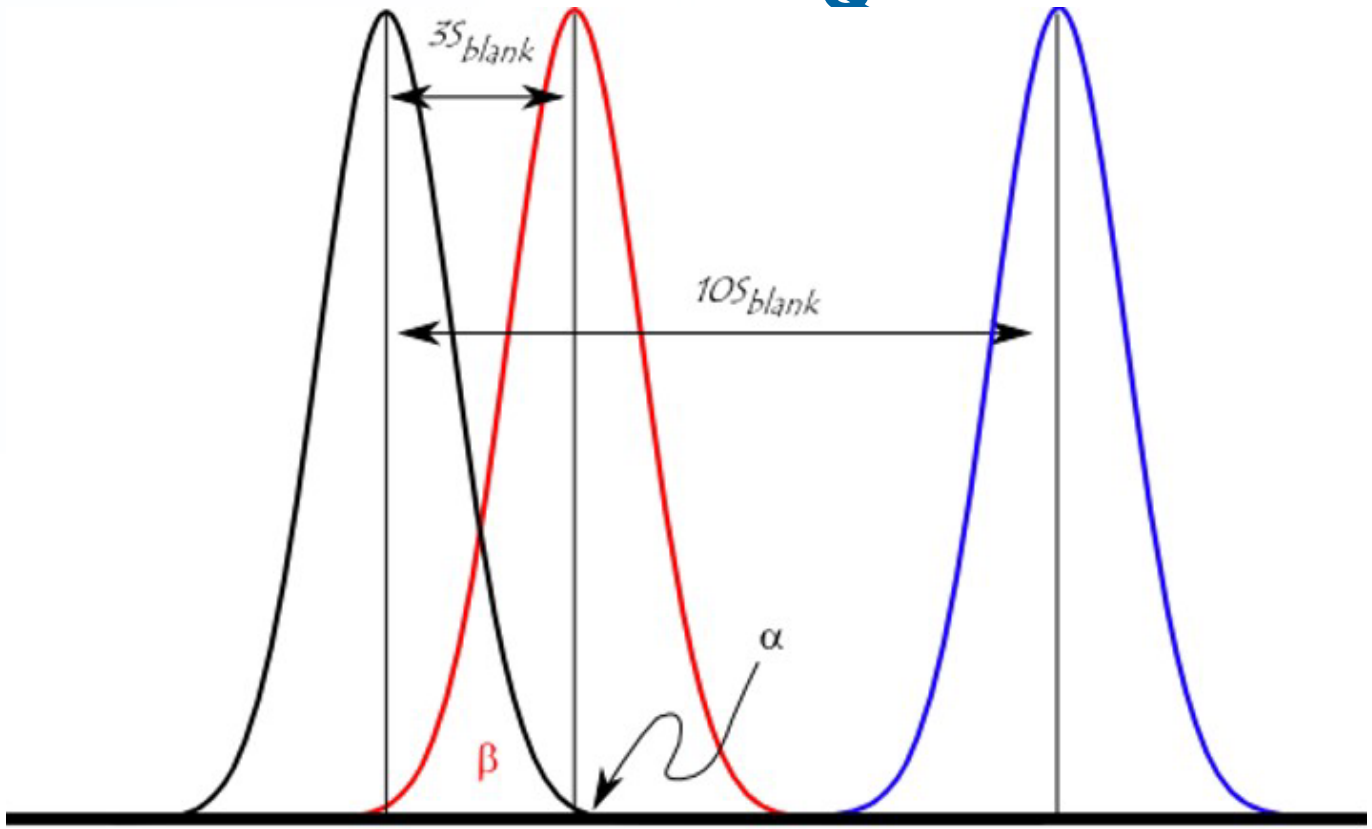
THE NELAC INSTITUTE

TNI Efforts to Bring Science to Detection and Quantitation

MDL / LOD / DL / LOQ

- **EPA MDL:** The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is **distinguishable from method blank** results.
- **TNI LOD:** The minimum result, which can be reliably **discriminated from a blank** with a predetermined confidence level. Also used is Detection Limit.
- **TNI DL:** See Limit of Detection
- **TNI LOQ:** The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified **degree of confidence**.
- **DOD/DOE LOD:** The smallest concentration of a substance **that must be present in a sample in order to be detected** at the DL with 99% confidence.

Currie's Mathematical Relationship of L_C, L_D, and L_Q



Goal of the Chemistry Committee Efforts for LOD/LOQ

- Fix problems with EPA MDL procedure
  - Done; new part 136 procedure finalized by EPA in 2017
- Ensure TNI LOD is aligned with MDL
  - Definitions are comparable
  - Procedures are comparable, but EPA has more details
- Ensure LOD and LOQ are compatible
- Avoid confusion with DOD LOD

Fundamental Elements

- Initial determination using spikes and blanks with two goals
  - Verify LOQ
  - Calculate LOD/MDL
- Periodic verification using spikes and blanks with two goals
  - Verify LOQ
  - Recalculate LOD/MDL

The TNI standard has these as two separate steps, 1.5.2.1 (LOD), and 1.5.2.2 (LOQ), but it is one procedure

Overview of Initial Procedure

Step 1. Select LOQ

Step 2. Analyze 7 blanks and 7 spikes

Step 3. Evaluate results

Step 4. Calculate MDL_s and MDL_b and establish MDL

Step 5. Verify LOQ

Overview of Periodic Verification

Step 1. 2 spikes per instrument per quarter

Step 2. Collect blank data

Step 3. Recalculate MDL annually

Step 4. Verify LOQ

LOD (DL) / MDL

- TNI: Module 4, Section 1.5.2
- EPA: 40 CFR Part 136 (2017 MUR)

Good News

- The revised EPA MDL and TNI LOD are mostly compatible
- If you are compliant with the revised EPA MDL then you are also compliant with the current TNI standard
- If you are compliant with the revised TNI standard then you mostly compliant with the current EPA MDL.
  - The EPA procedure contains more details
  - EPA requires a little bit more
  - TNI does not allow EPA options for blanks
  - TNI has a few issues that need correcting

Fundamentals Stay the Same

- Definition has the same intent
  - What is the lowest result that is qualitatively reliable, i.e., the lowest result that reliably indicates the analyte is in the sample?
- Calculation is unchanged
  - Calculate the DL as Student's t times the standard deviation of results
- Incorporate entire analytical process, including sample preparation

What is Different?

- Requires calculation of a MDL based on blanks (MDL_b) as well as an MDL based on spikes (MDL_s)
- The higher of the two becomes the MDL
- Incorporates longer term variance
- Includes checks for reasonableness
- Works effectively with the LOQ

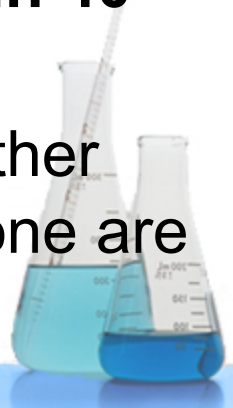
TNI LOD Procedure

2009

- Use any appropriate procedure
- Must used procedure specified by method
- Exceptions, including tests that cannot be spiked
- Not required if not reporting to LOD

2016

- Use any procedure **that contains certain elements**
- Must use procedure specified by mandated method
- Exceptions, except **blanks may be used** as appropriate
- **Required for all tests**
- Note: **MDL procedure in 40 CFR 136 may be used**
- Unstated Note: While other options are possible, none are known to exist



Exceptions

- Not applicable to tests that do not yield blank results, or are impractical
  - e.g., pH, color, odor, temperature, or dissolved oxygen (EPA adds BOD and “many titration methods”)
- Not applicable to tests where spiking solutions are not available.
- EPA: MDL determinations using spiked samples may not be appropriate for all gravimetric methods (e.g., residue or total suspended solids), but an MDL based on method blanks can be determined in such instances.

Initial MDL Required Elements

EPA	TNI
Incorporate entire analytical process	Incorporate entire analytical process
Include data from at least 7 low-level spikes and method blanks analyzed over multiple days	Include data from at least 7 low-level spikes and method blanks analyzed over multiple days
Include criteria for evaluating false positives in blanks	Include criteria for evaluating false positives in blanks
Include criteria for evaluating qualitative identification	Include criteria for evaluating qualitative identification
For wastewater only	Performed in quality system matrix of interest

Additional Requirements

EPA

Estimate MDL using any of several criteria

Calculate MDL_s and MDL_b

Use the larger as the reported MDL

TNI

- No requirements provided

Four Step Procedure

1. Estimate an initial MDL (EPA Only)
2. Determine the initial MDL

Initial

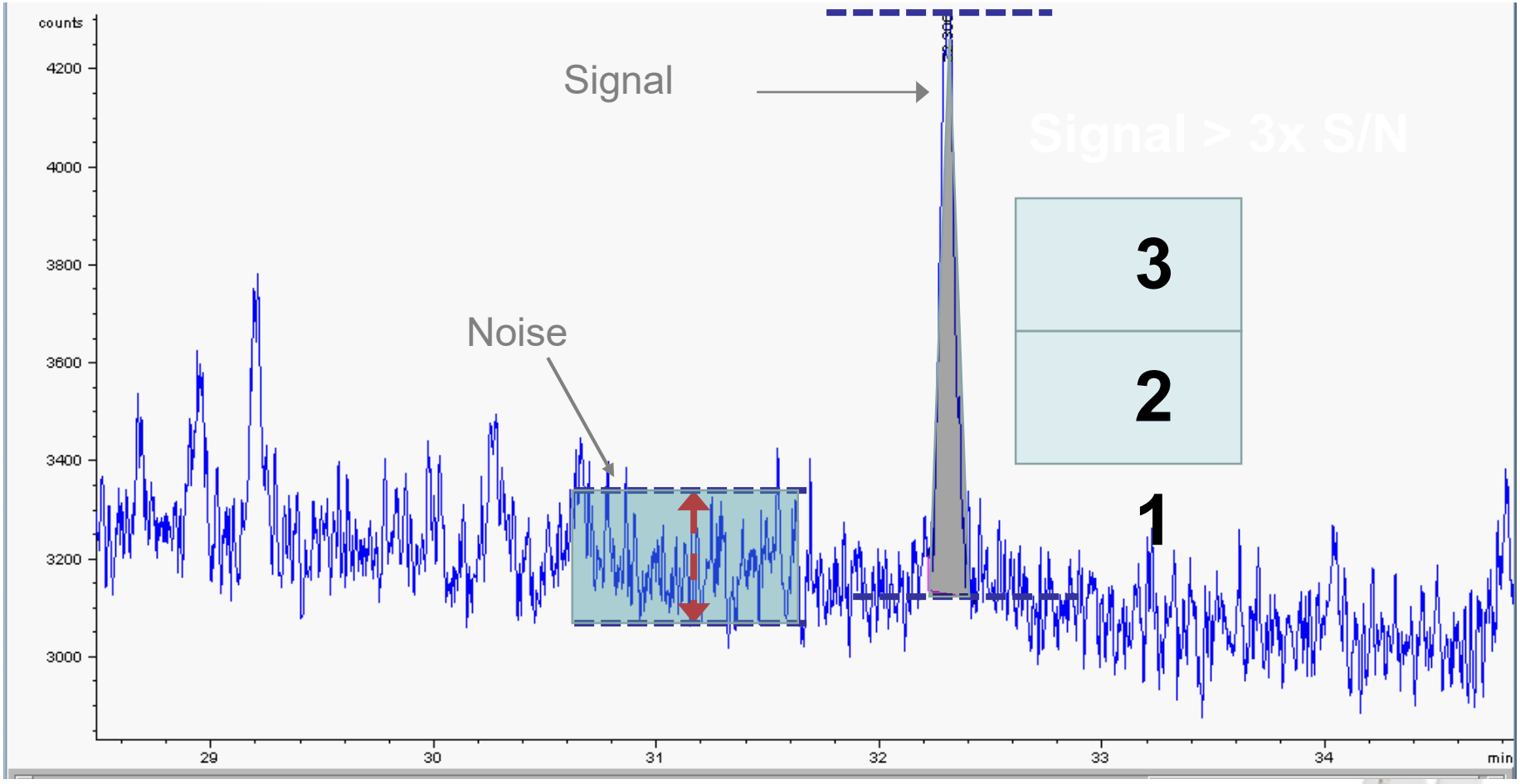
3. Periodic data collection
4. Annual recalculation (EPA Only)

On-going

1. Estimate an Initial MDL (EPA)

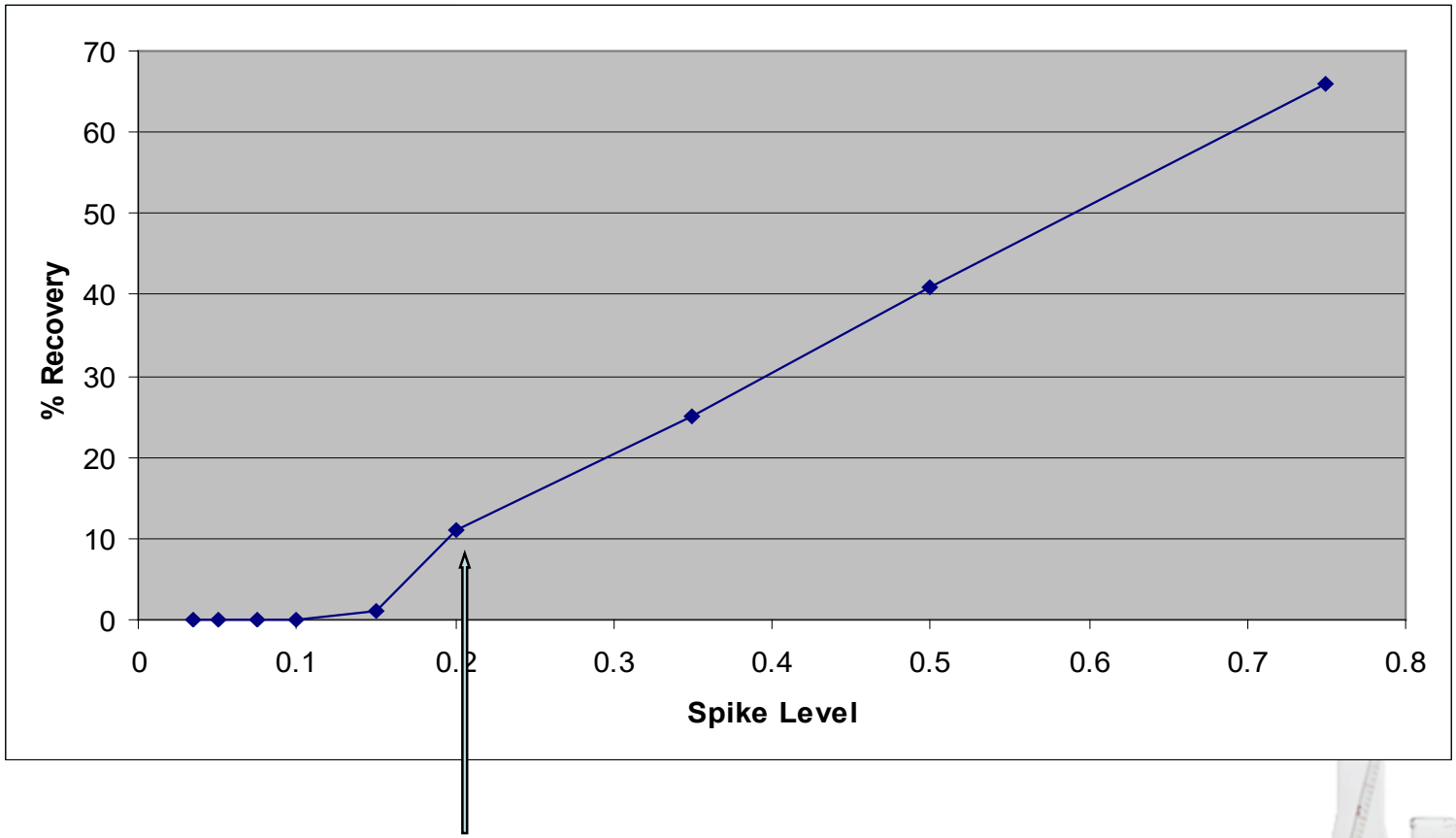
- The mean plus three times the standard deviation of a set of method blanks, **OR**
- The concentration value that corresponds to an instrument signal/noise in the range of 3 to 5, **OR**
- Three times the standard deviation of spiked blanks, **OR**
- That region of the standard curve where there is a significant change in sensitivity, **OR**
- Instrumental limitations, **OR**
- Previously determined MDL.

Defining Signal to Noise



https://www.agilent.com/cs/library/technicaloverviews/Public/5990-7651EN.pdf

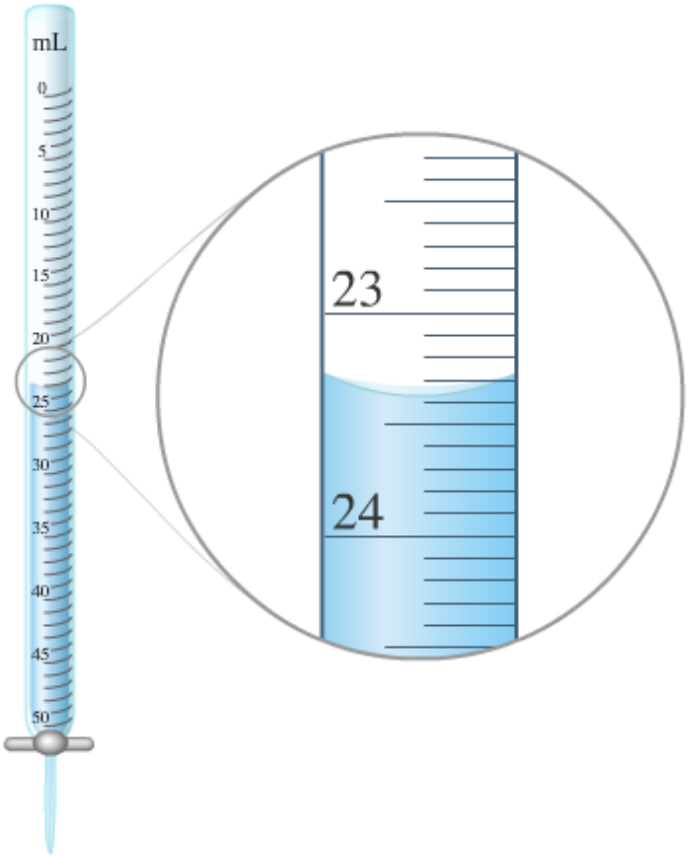
Change in Sensitivity



Region of the curve where there is a significant change in sensitivity

THE NELAC INSTITUTE

Instrument Limitations



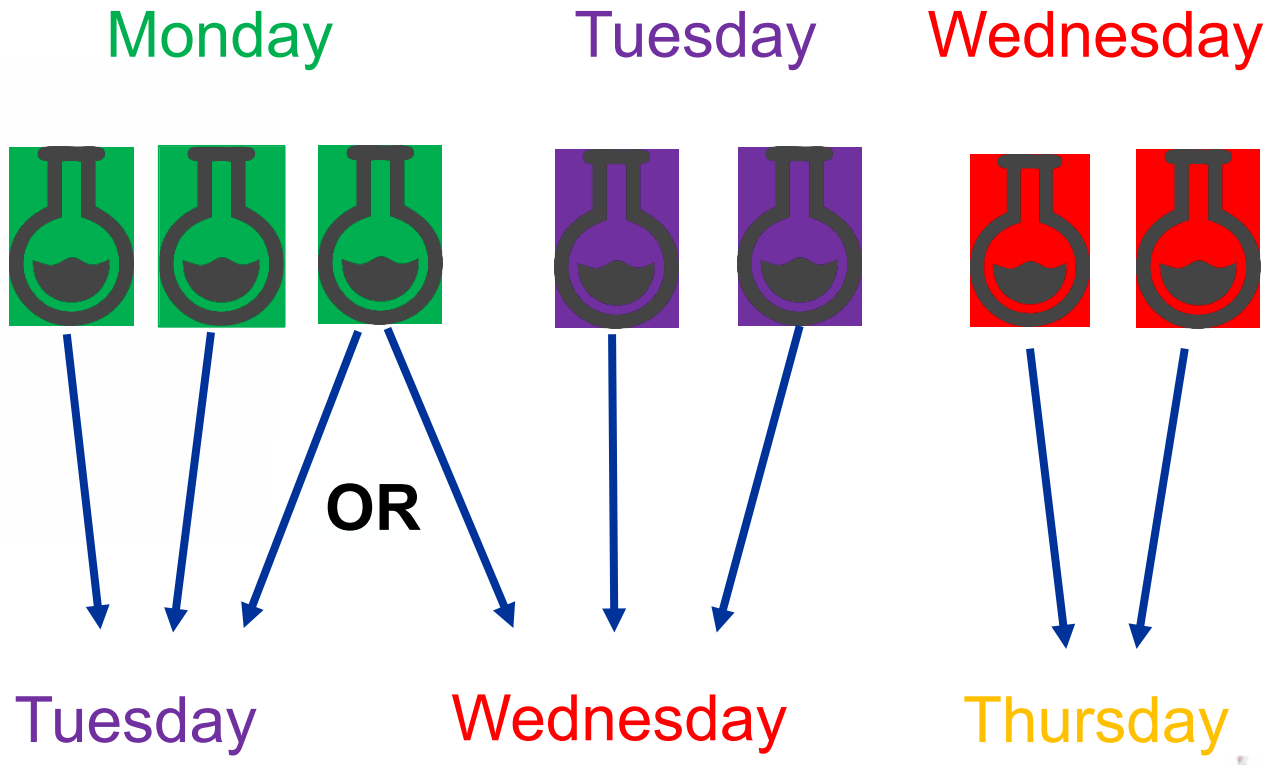
2. Determine the Initial MDL

- Select a spiking level, typically 2 – 10 times the estimated MDL.* (TNI requires spikes to be at or below the LOQ)
- Analyze a minimum of 7 spikes and 7 blanks.
- Include at least three batches on three separate days.
- Existing data may (must) be used if generated within the last 2 years.
- Samples must be distributed across all of the instruments.
- A minimum of two spikes and two blanks on different days for each instrument. (TNI only requires one spike and one blank**)

* Spiking levels in excess of 10 times the estimated detection limit may be required for analytes with poor recovery

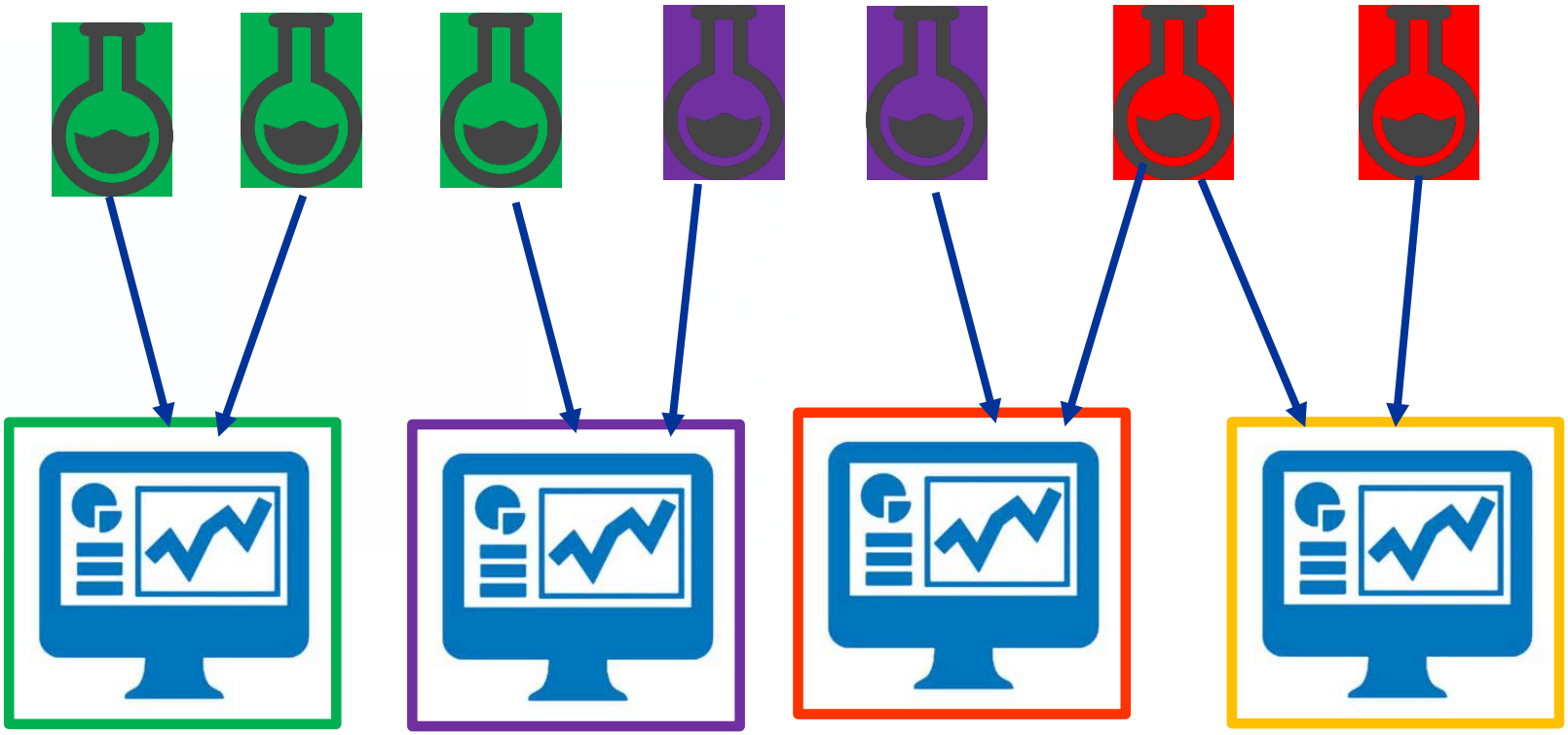
**But LOQ spike requires two.

Example – Single Instrument



Run a method blank with each spike, unless you have the data!

Multiple (4) Instruments



Tuesday
Wednesday

Tuesday
Wednesday

Wednesday
Thursday

Wednesday
Thursday

Run a method blank with each spike, unless you have the data!

2c. Evaluate the Spike Results and Calculate MDL_s

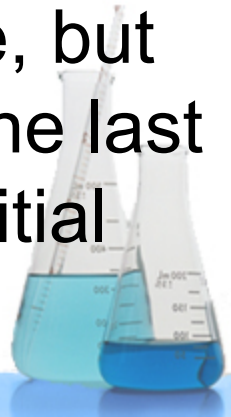
- Statistical outlier removal not allowed, but "documented instances of gross failures" may be excluded as long as 7 spike and 7 blank results are available
- If any result from the spiked samples does not meet the qualitative identification criteria* or does not provide a result greater than zero then repeat the spikes at a higher concentration.
- $MDL_s = tS_s$ of spike results
  - =STDEV(A1:Ax)*t

* A set of rules or guidelines for establishing the identification or presence of an analyte. Qualitative identification does not ensure that quantitative results can be obtained.

There are no recovery requirement for the DL spikes, but TNI requires lab generated limits for the on-going verification of the LOQ.

EPA FAQ: What happens if the laboratory has less than 7 sample spikes when calculating the MDL?

- The minimum number of samples is 7. If the analysis is performed regularly, then there will likely be 16 spiked samples per instrument (2 per quarter over 2 years) and many more blanks.
- If the analysis is performed very rarely, then there may be less than 7. In this case, the laboratory needs to perform a new initial MDL procedure, but can use the samples that are available over the last 2 years to contribute to calculating the new initial MDL.

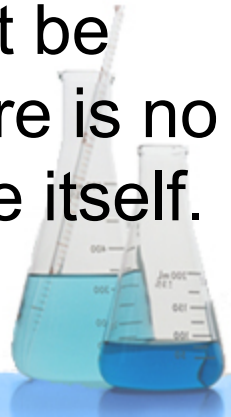


EPA FAQ: Will laboratories have to analyze more samples for methods that are rarely used?

- No, the MDL procedure could potentially require fewer samples for rarely used methods. For example, if a laboratory analyzed 7 batches of samples spread out over a 2-year period then the laboratory would have enough sample spikes and blanks to recalculate the MDL. This would be half of what was normally done year.

EPA FAQ: Why are acceptable calibrations and batch QC not mentioned?

- If the laboratory is performing an initial MDL without client samples, most batch QC is not required.
- The spiked samples are essentially laboratory fortified blanks, and the MS/MSD are not required if there are no client samples.
- Ongoing MDL samples should be analyzed with client samples, so all normal batch QC should be present.
- The methods already specify that calibrations must be completed before performing any analyses, so there is no need to add this requirement to the MDL procedure itself.



2.d Calculate MDL_b

- $MDL_b = X + tS_b$ if all blanks have numerical results*
  - =(STDEV(A1:Ax)*t) + AVERAGE(A1:Ax)
- MDL_b = Not applicable if all results are ND
- MDL_b = Highest blank result if some but not all blanks have numerical results*
- MDL_b = 99th Percentile if >100 results are available
  - =PERCENTILE(A1:Ax,0.99)

* A numerical result includes both positive and negative results, but not results of “ND” (not detected) commonly observed when a peak is not present in chromatographic analysis.

99th Percentile

- For “n” blank results where n>100, sort the blanks in rank order
- Calculate n * 0.99 and select that value

=PERCENTILE(A1:A164, 0.99)

- 159 blank results < 1.5
- 160 = 1.5
- 161 = 1.7
- **162 = 1.9**
- 163 = 5.0
- 164 = 10.0

164 * 0.99 = 162.36

99th percentile = 1.9

Calculate MDL_b - TNI

- 1.5.2.1.3 (e) the DL procedure shall include criteria for and evaluation of false positive rates in routine method blanks;
- NOTE: One option is to follow the United States Environmental Protection Agency Method Detection Limit (MDL) procedure, effective September 27, 2017.

EPA FAQ: Could a high blank drastically elevate the MDL?

- It depends – a method blank can be ignored if it is associated with an instance of gross failure.
- A lab might have over a hundred blanks over a two year period and then can use the 99th percentile option.
- There is also an option to use the most recent 50 blanks or last six months of data, whichever yields the greater number of blanks.

MDL_s - Phosphorous

Batch	Extracted	Analyzed	Sample ID	Instrument	Spike	Result	%R
B7H1623	8/22/17	8/24/17	B7H1623	FIA-02	0.02	0.021	105%
B7H1624	8/22/17	8/24/17	B7H1624	FIA-02	0.02	0.023	115%
B7H1687	8/23/17	8/24/17	B7H1687	FIA-02	0.02	0.02	100%
B7H1827	8/24/17	8/30/17	B7H1827	FIA-02	0.02	0.021	105%
B7H1881	8/24/17	8/30/17	B7H1881	FIA-02	0.02	0.021	105%
B7H2076	8/28/17	9/1/17	B7H2076	FIA-02	0.02	0.021	105%
B7H2086	8/28/17	9/1/17	B7H2086	FIA-02	0.02	0.016	80%

MDL = SD * t (n=7, df=6)
= 0.02* 3.143 = 0.007

MDL_b - Phosphorous

Batch	Extracted	Analyzed	Instrument	Result
B7H1623	8/22/17	8/24/17	FIA-02	-0.003
B7H1624	8/22/17	8/24/17	FIA-02	-0.007
B7H1687	8/23/17	8/24/17	FIA-02	-0.002
B7H1827	8/24/17	8/30/17	FIA-02	0.005
B7H1881	8/24/17	8/30/17	FIA-02	0.006
B7H2076	8/28/17	9/1/17	FIA-02	-0.018
B7H2086	8/28/17	9/1/17	FIA-02	-0.019

MDL = (SD * t) + X (n=7, df=6)

= (0.01 * 3.143) = 0.031+ (-.00543) = 0.026

Phosphorous MDL

MDL_s

Average Result	0.020
StdDev	0.002
Avg Recovery	102%
MDLs	0.007

MDL_b

Mean	-0.00543
StdDev	0.0100
MDLb	**0.026**

Our QA Manager just calculated the phosphorus MDLb from 149 data points and 99th percentile was **0.020.**

Organics – Benzene by 614

Batch	Analyzed	SampleID	Instrument	Analyst	Spike	Result	%R
B7G1395	21-Jul-17	B7G1395	GCMS-08	KED	0.50	0.57	114%
B7G1745	26-Jul-17	B7G1745	GCMS-08	MWS	0.50	0.53	106%
B7F1327	20-Jun-17	B7F1327	GCMS-04	CEM	0.50	0.51	102%
B7F1514	22-Jun-17	B7F1514	GCMS-04	CEM	0.50	0.53	106%
B7F1610	23-Jun-17	B7F1610	GCMS-04	CEM	0.50	0.54	108%
B7E1368	20-May-17	B7E1368	GCMS-06	CEM	0.50	0.48	96%
B7F0843	13-Jun-17	B7F0843	GCMS-06	CEM	0.50	0.54	108%

BTEX By 624

MDL_s

	Benzene	Toluene	Ethyl Benzene	Xylenes
Average Result	0.529	0.514	0.449	1.264
StdDev	0.028	0.045	0.067	0.280
Avg Recovery	106%	102%	90%	84%
MDLs	**0.088**	**0.142**	**0.210**	**0.880**

MDL_b

	Benzene	Toluene	Ethyl Benzene	Xylenes
Numeric Results	ND	ND	ND	ND
Mean	0.00	0.00	0.00	0.00
StdDev	0.00	0.00	0.00	0.00
MDLb	NA	NA	NA	NA

EPA FAQ: If the MDLs change, permit limits may need to be reviewed.

- The new MDL procedure may cause some additional contaminants to have MLs above the permit requirements for a specific analysis. The "Sufficiently Sensitive Method" rule is very clear about what to do in this case; see 40 CFR 122.21(e)(3).
- Additionally, supporting documents are available in the docket: EPA–HQ– OW–2014–0797 (www.regulations.gov)

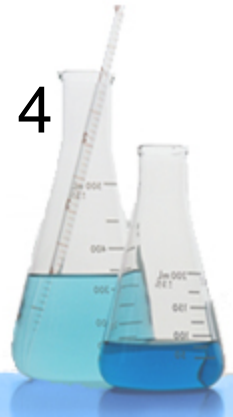
3. Periodic Data Collection

- At least two spikes and two blanks on each instrument per quarter in separate batches (unless no samples are analyzed)
  - TNI: One spike and one blank/quarter
- At least 7 spikes per year (EPA only)
- At least 7 blanks per year (EPA only)

EPA: If more than 5% of the spikes do not return positive numerical results that meet all identification criteria, then the spiking level must be increased and the initial MDL re-determined
TNI: New study required if verification fails (no positive result for spikes or blank results above DL)

The 5 % Rule (One Instrument)

- Must evaluate once per year
- Can use 2 years of data
- 2 years of data
  - Year 1 – 7 spikes from initial + 6 spikes from 3 quarters = 13
    - 5% = 0.65 = 0 failures
  - Year 2 – 7 spikes from initial + 6 spikes from 3 quarters + 8 spikes from 4 quarters = 21
    - 5% = 1.05 = 1 failure allowed
  - Year 3 – 8 spikes from 4 quarters + 8 spikes from 4 quarters = 16
    - 5% = 0.8 = 0 failures allowed



Example – Single Instrument: Every Quarter

Extraction Batch

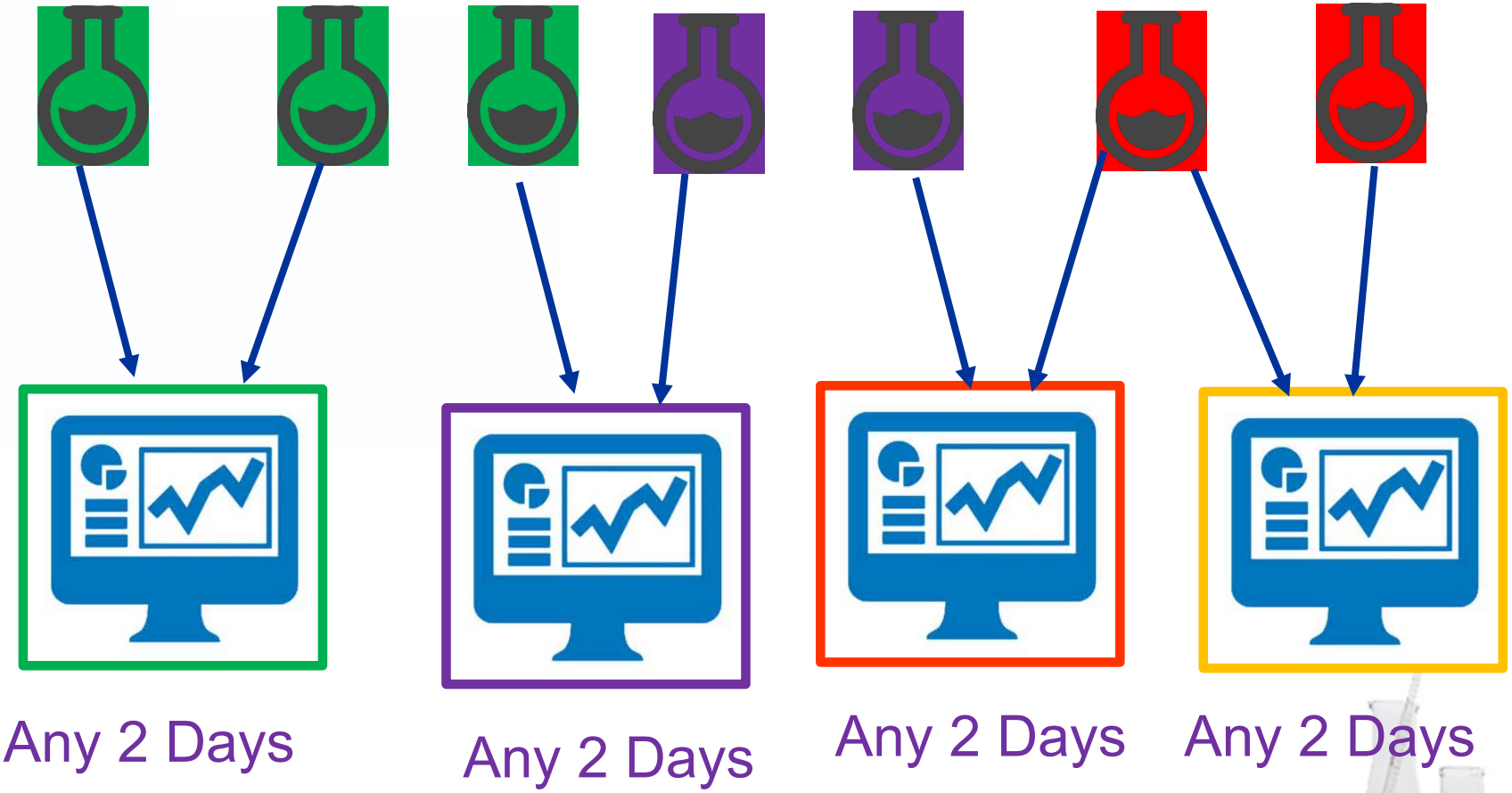
Analysis Batch

Any day

Any other day

Run a method blank with each spike, unless you have the data!

Multiple (4) Instruments: Every Quarter



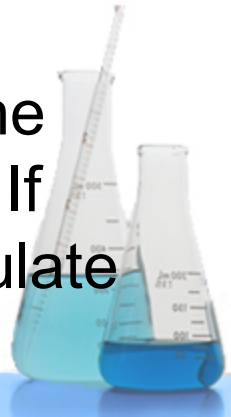
Run a method blank with each spike, unless you have the data!

Additional Requirement 1

- EPA: If the method is altered in a way that can be *reasonably expected* to change its sensitivity, then re-determine the initial MDL, and the restart the ongoing data collection.
- TNI: If the method is altered in a way other than routine maintenance and the change can be expected to elevate the detection limit, then a spike at or below the LOQ concentration and a blank shall be prepared and analyzed. If the spike at the LOQ concentration gives a result meeting qualitative identification criteria above zero, and the blank gives a result below the DL, then the DL is verified. If not, the DL shall be re-determined.

Additional Requirement 2 (EPA)

- If a new instrument is added to a group of instruments, analyze a minimum of two spiked replicates and two method blank replicates on the new instrument.
  - If both method blank results are below the existing MDL, then the existing MDL_b is validated.
- Combine the new spiked sample results with the existing spiked sample results and recalculate the MDL_s.
  - If the recalculated MDL_s is within 0.5 to 2.0 times the existing MDL_s, then the existing MDL_s is validated. If either of these two conditions is not met, then calculate a new MDL.



EPA FAQ: If the laboratory does not use a method during a quarter, will the laboratory still need to analyze low-level spiked samples?

- No, the laboratory needs to analyze at least seven low-level spiked samples and seven method blanks for one instrument in a two-year period (spread over 3 batches), but is also supposed to analyze two spiked samples per quarter in separate batches **any quarter samples are analyzed.**

A Simple Way to Do This

- Analyze a low-level spiked sample with the first two analytical batches every quarter.
- If no samples are analyzed, then there is no need to analyze spiked samples or method blanks.
- If one batch of samples is analyzed during a quarter, then the laboratory should include one low-level spiked sample in that batch.
- If two or more batches of samples are analyzed, the laboratory should include one low-level spiked sample in at least two of those batches.

4. Annual Recalculation (EPA only)

- Every 13 months, recalculate MDL_b and MDL_s from collected blank and spike results.
- Include all data over a two-year period, but exclude any data with failed batch QC or other gross failures.
- Ideally, use all blanks, but **as an option,** you may use 6 months of blanks or the 50 most recent, whichever is greater.

If the verified MDL is within a factor of 0.5 to 2.0 of the existing MDL, and fewer than 3% of the method blank results have numerical results above the existing MDL, then the existing MDL may be left unchanged. Otherwise, adjust the MDL to the new verification MDL.

Annual Recalculation (TNI)

- At least once per year, the laboratory shall tabulate all results of the ongoing verification sample testing. **All data representative of the current operations shall be used**, if generated within the last two (2) years.

EPA FAQ: Is the lab required to recalculate the MDL every quarter?

- No, the MDL is only calculated once a year. MDL spiked samples are now analyzed every quarter in which the method is used, but the calculation is only required to be performed once a year.

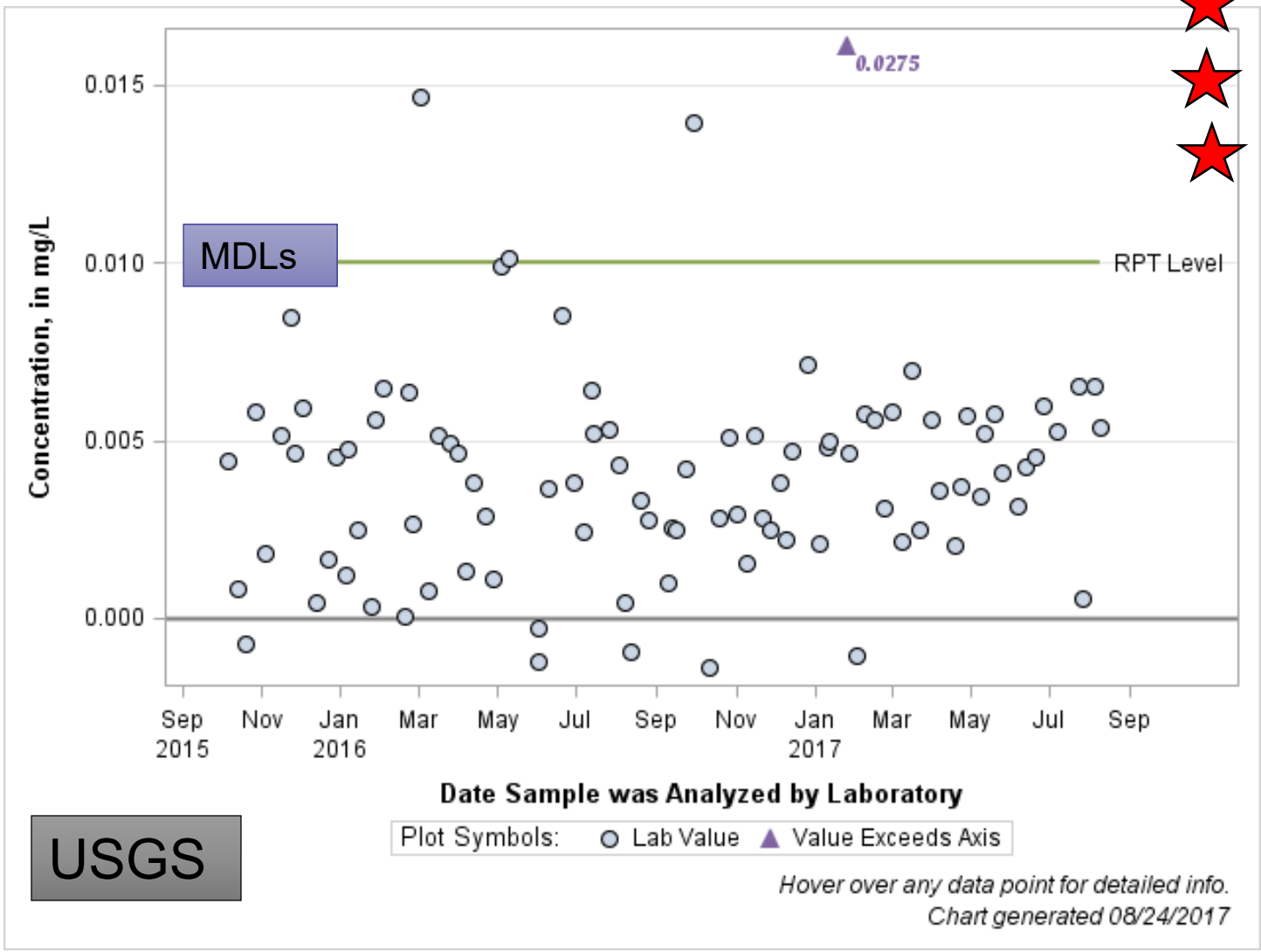
EPA FAQ: Why is so much ongoing data collection necessary, and what additional quality is this providing?

- Ongoing data collection captures instrument drift and the variation in equipment conditions throughout the year.
- Many laboratories currently analyze the MDL aliquots immediately after the instrument is serviced and all consumable instrument parts are new, thus yielding a best-case MDL value.
- Ongoing data collection leads to an MDL that represents what is actually practiced throughout the year.

Let's Verify Some MDLs

- Ammonia
  - MDL_b ($X + tS_b$)
  - MDL_b (99^{th} percentile)
  - MDL_b (last 50) or MDL_b (last six months)
- Acrolein
  - MDL_s

Blank Data - Ammonia



USGS

- 0.016 (99th)
- 0.014 (last 50)
- 0.013 (all data)

4 results > MDLs; MDLs not valid

Acrolein Periodic Spikes, 10 ug/L

R1	R2	R1	R2	R1	R2	R1	R2	SD	MDLs
A	A	B	B	C	C	D	D		
9/1/17	9/2/17	9/2/17	9/2/17	9/3/17	9/4/17	9/4/17	9/4/17		
8.1	8.2	11	12	9.3	9.5	12	11.9	1.3	4.0
12/2/17	12/2/17	12/3/17	12/3/17	12/4/17	12/4/17	12/4/17	12/4/17		
8	8.3	10.5	10.7	8.4	8.7	8.2	8.3		
3/4/18	3/5/18	3/4/18	3/5/18	3/5/18	3/6/18	3/5/18	3/6/18		
8.5	8.7	11.2	11.5	9.5	9.7	9	9.4		
6/4/18	6/5/18	6/4/18	6/5/18	6/5/18	6/6/18	6/5/18	6/6/18		
11	10.8	9	8.8	8.5	8.7	10.6	10.2	1.29	**3.2**

Initial MDL = SD * 2.998 (n=8, df=7)

New MDL = SD * 2.453 (n=32, df=31)

3.2/4.0 = 0.76

MDL is verified and may be changed or not

Documentation

- Data and calculations used, including n, X, *s*
- Dates of preparation and analysis (TNI only)
- Instrument ID (TNI only)
- Sample matrix
- Spike value and recovery
- Analyst name not required. A)

NEW Determine MDL in a Specific Matrix

Analyze the sample. If the response for the native concentration is at a signal-to-noise ratio of approximately 5-20, determine the matrix-specific MDL according to Section 2 but without spiking additional analyte.

10 X Rule is Gone

OLD

If the level of analyte exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Intended to be used to establish MDLs in wastewater matrices where the analyte was present, but incorrectly used to evaluate low-level spikes.

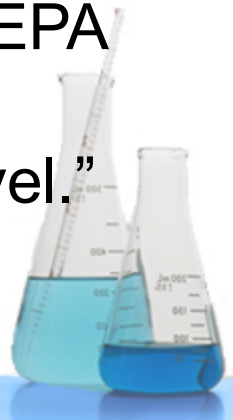
Table 1: Student t Values

- As published, missing many values
- http://www.itl.nist.gov/div898/handbook/eda/section3/eda3672.htm
- Use the values in the 99% column. This particular table shows degrees of freedom, which is the number of replicates minus one. An easy way to check is to look at the student t for 7 (6 degrees of freedom) which is 3.143.

cum. prob	$t_{.50}$	$t_{.75}$	$t_{.80}$	$t_{.85}$	$t_{.90}$	$t_{.95}$	$t_{.975}$	$t_{.99}$	$t_{.995}$	$t_{.999}$	$t_{.9995}$
one-tail	0.50	0.25	0.20	0.15	0.10	0.05	0.025	0.01	0.005	0.001	0.0005
two-tails	1.00	0.50	0.40	0.30	0.20	0.10	0.05	0.02	0.01	0.002	0.001
df											
6	0.000	0.718	0.906	1.134	1.440	1.943	2.447	3.143	3.707	5.208	5.959
7	0.000	0.711	0.896	1.119	1.415	1.895	2.365	2.998	3.499	4.785	5.408
8	0.000	0.706	0.889	1.108	1.397	1.860	2.306	2.896	3.355	4.501	5.041
9	0.000	0.703	0.883	1.100	1.383	1.833	2.262	2.821	3.250	4.297	4.781
10	0.000	0.700	0.879	1.093	1.372	1.812	2.228	2.764	3.169	4.144	4.587

The MDL and ML in EPA

- Minimum level (ML) – The term “minimum level” refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher.
- Minimum levels may be obtained in several ways:
  - they may be published in a method;
  - they may be based on the lowest acceptable calibration point used by a laboratory; or
  - they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3.
- For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level.”



MDLs and Other EPA Programs

- Drinking Water
  - OGWDW Memo (See next few slides)
- RCRA
  - Uses LOQ concept; MDL not required but allowed
- Air
  - Many air methods cite Part 136

OGWDW Memo

- If a laboratory practices good hygiene by keeping their laboratory clean (i.e. sample prep areas, glassware, instrumentation, etc.), the method blanks should never indicate a recurring background as nearly all blank failures would invalidate analytical results.
- MDL specifically cited in Part 141 for some regulated analytes
- Part 136 specifically referenced in some EPA methods, but others reference the original publication
  - It becomes a judgement call. Just be consistent in applying such judgement across the region.
- ***From the standpoint of conducting drinking water analyses, the MDL_b should not be the higher value.*** If it is, that's a sure sign the lab needs to take corrective action

OGWDW Memo (Cont)

- For some drinking water contaminants, qualification for reduced monitoring is based on specified low threshold levels. In order for a laboratory to meet those levels, they will need to optimize *lower* detection levels. Pooling data from multiple instruments will have the net effect of increasing variability, resulting in *higher* calculated MDL values.
- This specification of determining the MDL per method and per instrument precludes the option of determining a multi-instrument MDL for instruments that will be used to analyze drinking water.

An initial demonstration of capability (IDC) must be performed for each method. The IDC includes a determination of MDL. An IDC should be performed for each instrument. It is also recommended that an IDC be performed by each analyst. In addition, it is recommended that the IDC also address the variability introduced if more than one sample preparation technician is used. Precision, accuracy and MDL should be similar for each technician. (DW Cert Manual)

OGWDW Memo Impact

- Written as guidance (“should”)
- Subject to interpretation by states and EPA regions

Implementation

- Start by evaluating existing blank data
  - Establish MDL_b where justified
- You can use existing spike data, if you meet the new requirements
- If not, start collecting spike and blank data (at least 2 per instrument) to supplement your existing dataset

Frequently Asked Questions – Jerry Parr

- > 100 questions organized into 36 subjects, e.g.
  - **3.0 Data Evaluation and Calculation of the Initial MDL**
    - 3.1 Negative Values for Blanks
    - 3.2 Requirement for an MDL Study and Reporting to MDL
    - 3.3 Qualitative Identification Criteria
    - 3.5 Protection from False Negatives
    - 3.6 Validity of the MDL
    - 3.7 MDL for Sample Preparation
    - 3.8 Data Analysis Software
    - 3.9 Student t Numbers
    - 3.10 QC Failures and Outlier Tests

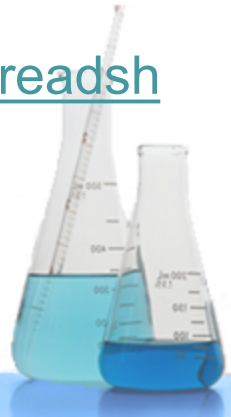
MDL Spreadsheets

- Virginia
  - MDL Procedure Checklist
  - MDL Data Collection Template Example (7 samples)
  - Student's t table with calculator for values >100

https://dgs.virginia.gov/division-of-consolidated-laboratory-services/certification-accreditation/certificationaccreditation-toolbox/

- Wisconsin
  - DNR Spreadsheet to calculate the new LOD

https://dnr.wi.gov/Regulations/labCert/documents/EPA_LOD_Spreadsheet5-17-18.xls



LOD and LOQ in TNI

- Designed to work in harmony
- One study, spike at LOQ
  - Used to verify LOQ
  - Used to calculate LOD
- New Guidance document provides many examples

LOQ – 1.5.2.2

- The laboratory shall **select** an LOQ for each analyte, consistent with the needs of its clients, and greater than the DL. An LOQ is required for each quality system matrix of interest, technology, method, and analyte.
- **Exceptions:** any component or property for which spiking solutions are not available or a quantitation limit is not appropriate, such as pH, color, odor, temperature, dissolved oxygen, or turbidity.

Selecting the LOQ

- Must be at or above the lowest calibration standard
- Must be verified with spikes at or below the selected LOQ
- Tip: Run spikes at low calibration standard, or ½ concentration

LOQ Initial Verification

- 7 spiked blanks at or **below** LOQ
  - 3 batches over 3 days
  - At least 2 spikes per instrument
  - These spikes may also be used for DL
  - May use existing data
- The LOQ must be at or **above** the lowest calibration standard
- The laboratory must establish QC acceptance criteria for the LOQ spikes

This is the same procedure as for the DL but with QC criteria added.

Initial Verification Criteria

- All results are quantitative.
- The mean recovery of each analyte is within the laboratory established accuracy acceptance criteria.
- The LOQ is greater than the established DL and at or above the spiking concentration.
- If the LOQ is less than or equal to the DL, the LOQ shall be raised to greater than the DL.

QC Acceptance Criteria

- Established by the laboratory
- LCS limits may not be appropriate, but could be used
- TNI guidance suggests alternate limits such as 50-150 %, or using 4 standard deviations from LCS, or 10-20 % wider than LCS limits.
- TNI guidance suggest labs could develop acceptance limits after the initial study

On-going Verification

- One spike sample per quarter per instrument
  - This may also be used for DL verification
  - Must meet identification criteria and be above zero
  - Once per year compile the data and create a statement of precision and accuracy

Results of each LOQ verification sample analysis shall be evaluated at the time of the testing and shall meet the qualitative identification criteria and the quantitated result shall be greater than zero.

LOQ - New Section 1.5.2.3

- 1.5.2.3 - If no analysis was performed in a given year, the verification of the DL/LOQ is not required, but a new initial DL/LOQ verification shall be performed prior to analysis of client samples.

TNI Guidance Document

THE NELAC INSTITUTE

TNI V1M4 2016 Standard Update
Guidance on Detection and Quantitation

GUID-3-110-Rev0
January 30, 2019

This document was prepared to provide guidance on the detection and quantitation section (1.5.2) of Module 4 of the 2016 TNI Standard Volume 1, i.e., V1M4. This document does not discuss all sections of V1M4, only those which have changed substantially with the 2016 TNI Standard. This document is not intended to be an official interpretation of the Standard, nor is it to be used in place of the Standard. This document is only intended to help users of the Standard understand the changes and implement them in their laboratory. If there are questions regarding the use and implementation of the Standard, contact the appropriate accreditation body. Standard Interpretation Requests may be made through the TNI website.

https://nelac-institute.org/content/NELAP/interpret.php

Summary

- TNI LOD = EPA MDL (This is the default)
- Other approaches to LOD or LOQ in regulation and/or methods would take precedence
- Procedure for verifying LOQ involves the same set of spikes used for the LOD, reducing the burden on labs and provides assurance that both the LOD and the LOQ are valid

THE NELAC INSTITUTE

Take a Break

THE NELAC INSTITUTE

TNI Efforts to Bring Science to Instrument Calibration

Instrument Calibration for Chemical Testing

ISO/IEC 17025: 5.6.1

- *All equipment used for tests having a significant effect on the accuracy or validity of the result of the test shall be calibrated before being put into service. The laboratory shall have an established program and procedure for the calibration of its equipment.*

Instrument calibration is the fundamental building block for analytical measurements.

Chemistry Committee Goals

Limit any requirements to those where there are clearly demonstrable weakness that may result in inaccurate quantitation.

Must be:

Practical

Cost effective

Auditable

Instrument Calibration

2009

- 1.7.1 Initial Calibration
- 1.7.1.1 Instrument Calibration
  - 10 subsections
- 1.7.1.2 Continuing Calibration
  - 5 subsections

2016

- 1.7.1 Calibration
- 1.7.1.1 Initial Calibration
  - 13 subsections
- 1.7.1.2 Continuing Calibration Verification
  - 6 subsections

1.7.1.1 Initial Calibration

Sections	Updates
a, b, c and d Essential elements	Language changes but similar
e Removal and replacement of calibration standards	Comprehensive changes and additions
f Minimum number of calibration standards	Changes
g, h, i and j Calibration range and requirement for acceptance criteria	Language changes but similar
k Requirement for a measure of relative error	New
l Single point calibrations	Language changes but similar
m Aroclors	New
n ICV	Language changes but similar
o Sensitivity check	New
p Linear range	Language changes but similar

1.7.1.1 (a) – (c): Essential Elements

- Details must be in SOP or test method.
- Raw data records must be retained.
- Must use the most recent valid calibration unless specified by method.
- Calibration standards must be traceable to a national standard when available.

Traceability

- "NIST Traceable" can mean
  - Traceable to a certified reference material
  - Traceable to a NIST weight

Best Practices for Certified Reference Materials
NEMC 2014
http://nemc.us/meeting/2014/nemc-program.php#tpm1_4
Click on Thursday

1.7.1.1.e
Removal and Replacement of Calibration Standards

- Provide language that reflects current industry data integrity practices relating to dropping calibration standard.

Need a Written Procedure

i. Removal of Calibration Standards – Low/High
ii. Removal of Calibration Standards – Interior
iii. Adjust LOQ and range
iv. Minimum number of standards (1.7.1.1(f))
v. Replacement of Calibration Standards
vi. Technically valid reason

Written Procedure

- Procedure must comply with all requirements in 1.7.1.1.e
- Can be in:
  - SOP (test method or non-test method), or
  - Quality Manual
- Recommend incorporate language into Data Integrity program and training (if not already done)

Removal – Low/High

"the action of taking away or abolishing something unwanted"

i. The laboratory may remove individual analyte calibration levels from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted.

- Whether a single analyte curve (e.g., NO_3) or a multi-analyte curve (e.g., VOA) you can remove the lowest and/or highest calibration standard for any individual analyte, and do it multiple times.

Removal of Low Point

Concentration, ug/L	Area	Response Factor
0.05	1097075	21941500
0.5	12858983	25717966
2.5	67621646	27048658
5	1.43E+08	28600000
10	3.02E+08	30200000

With 0.05 standard; RSD = 11.8% FAIL

Without 0.05 standard; RSD = 6.95% PASS

Adjust LOQ/RL and Quantitation Range

- *iii. The laboratory shall adjust the LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.*

- If you drop the lowest calibration standard your LOQ or reporting level goes up. Data reported below lowest calibration standard concentration must be qualified.
- If you drop the highest calibration standard then your quantitation range goes down. Possible more dilutions and or qualified data if reported above quantitation range.

Qualifying Data

- A best practice for avoiding inappropriate practices:
  - Reporting marginal data as perfect
  - Encouraging analysts to “cheat” to pass QC
- Two equally valid approaches:
  - A data “flag” such as “J” = estimated concentration
  - A narrative discussion such as “this result was slightly above the upper calibration range of the standard and the reported result may have increased bias”

Removal - Interior

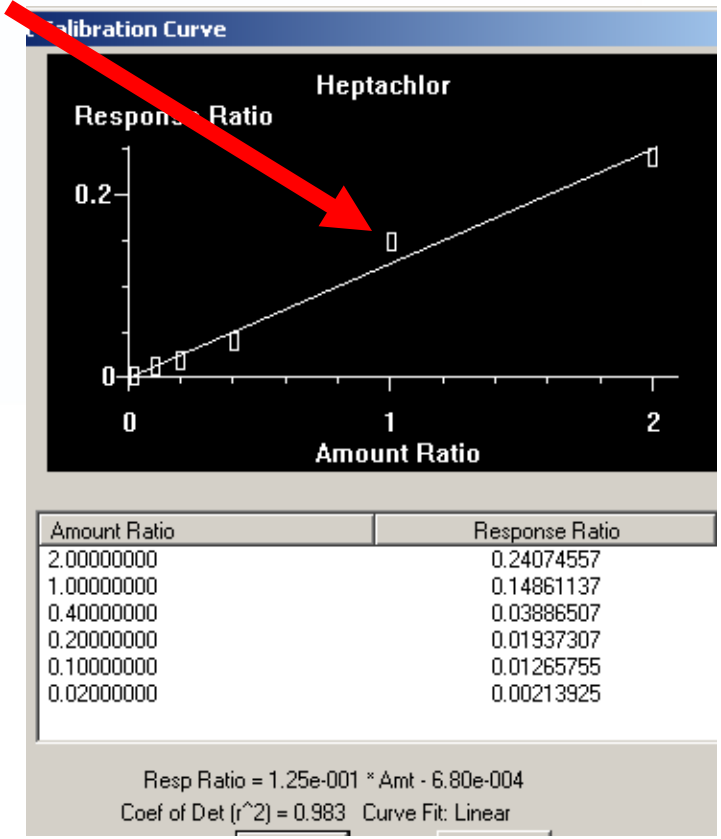
Not Properly Introduced

- *ii. The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument…. A laboratory that chooses to remove a calibration standard from the interior of the calibration shall remove that particular standard calibration level for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.*

- not properly introduced e.g.,"…bent injection needle on an auto-injector that yields very low responses for all the compounds because the injection was not completed…" MICE

Removal of Interior Level To Pass Calibration Criteria

With 1.0 level standard

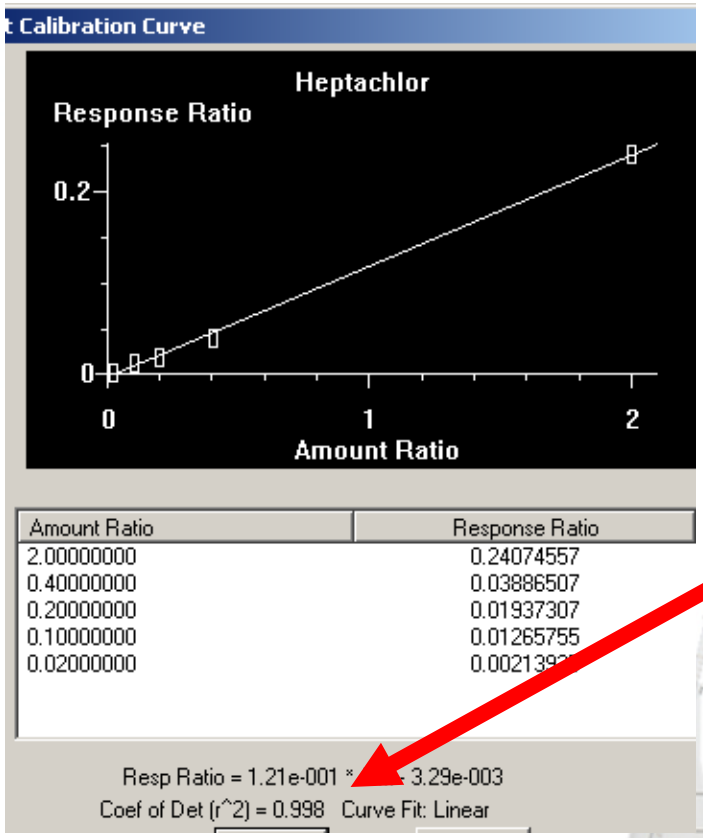


Amount Ratio	Response Ratio
2.00000000	0.24074557
1.00000000	0.14861137
0.40000000	0.03886507
0.20000000	0.01937307
0.10000000	0.01265755
0.02000000	0.00213925

Resp Ratio = 1.25e-001 * Amt - 6.80e-004
Coef of Det (r^2) = 0.983 Curve Fit: Linear

Fails R^2 criteria

Drop 1.0 level standard



Amount Ratio	Response Ratio
2.00000000	0.24074557
0.40000000	0.03886507
0.20000000	0.01937307
0.10000000	0.01265755
0.02000000	0.0021392

Resp Ratio = 1.21e-001 * 3.29e-003
Coef of Det (r^2) = 0.998 Curve Fit: Linear

Passes QC

THE NELAC INSTITU

*RESPONSE FACTOR REPORT GC MS #2

Method Path : C:\MSDchem\1\METHODS\
Method File : 032702.M
Title : method 525
Last Update : Wed Mar 27 14:03:40 2002
Response Via : *INITIAL CALIBRATION

* CALIBRATION FILES
1 =CAL1.D 2 =CAL2.D 3 =CAL3.D 4 =CAL4.D 5 =CAL5.D 6 =CAL6.D

*		COMPOUND	1	2	3	4	5	6	* AVG	%RSD
1)	I	p-Terphenyl-d14	----------ISTD----------							
2)		Acenapthene-d10	----------ISTD----------							
3)		Hexachlorocycl...	0.331		0.267	0.248	0.242	0.226	0.263	15.56
4)		Propachlor	0.623	0.559	0.510	0.462	0.454	0.528	0.523	12.12
5)		Hexachlorobenzene	0.510	0.493	0.501	0.507	0.494	0.546	0.509	3.87
6)	I	Chrysene-d10	----------ISTD----------							
7)		Simazine	0.285	0.277		0.140	0.153	0.113	0.194	42.01
8)		Atrazine	0.418	0.446	0.299	0.292	0.359	0.282	0.349	20.01
9)		Pentachlorophenol	0.202	0.164	0.078	0.040	0.037	0.028	0.092	80.85
10)		Lindane	0.250	0.272	0.208	0.211	0.292	0.256	0.248	13.51
11)		Metribuzin	0.261	0.278	0.176	0.128	0.141	0.101	0.181	40.35
12)		Alachlor	0.209		0.177	0.172	0.209	0.166	0.187	11.18
13)		Heptachlor	0.120		0.097	0.097	0.127	0.107	0.110	12.31
14)		Metalochlor	0.618	0.680	0.504	0.468	0.549	0.489	0.552	14.97
15)		Aldrin	0.122	0.146	0.119	0.125	0.171	0.142	0.137	14.45
16)		Heptachlor Epo...	0.087		0.084	0.089	0.116	0.114	0.098	15.76
17)		Butachlor	0.273	0.286	0.207	0.190	0.200	0.161	0.219	22.48
18)		Nonachlor	0.140		0.128	0.136	0.180	0.153	0.148	13.87
19)		4,4-DDE	0.234	0.257	0.221	0.222	0.285	0.315	0.256	14.84
20)		Dieldrin	0.140	0.150	0.143	0.148	0.190	0.202	0.162	16.49
21)		Endrin	0.042		0.034	0.032	0.039	0.037	0.037	10.53

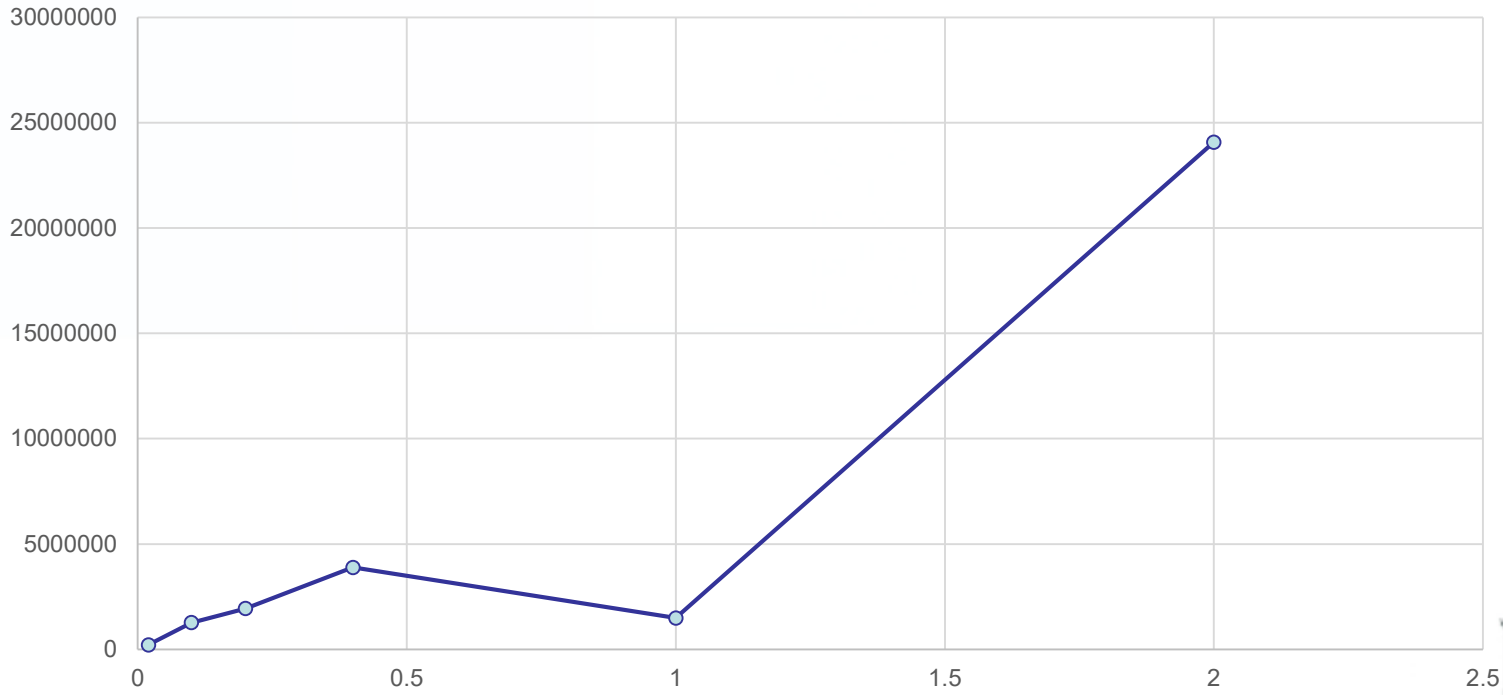
Removal - Interior

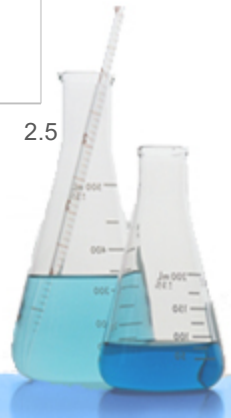
Incorrect

- *ii. The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates …an incorrect standard was analyzed. A laboratory that chooses to remove a calibration standard from the interior of the calibration shall remove that particular standard calibration level for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.*

- incorrect e.g., "…single standard that has gone so bad that the difference is obvious to the naked eye…" MICE

Incorrect Standard





Minimum Number of Standards

iv. The laboratory shall ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for number of initial calibration points as mandated by this standard, the method, or regulatory requirements.

- See section (f)

Replace

"to put something new in the place or position of something"

v. The laboratory may replace a calibration standard provided that

a. the laboratory analyzes the replacement standard within 24 hours of the original calibration standard analysis for that particular calibration level;

b. the laboratory replaces all analytes of the replacement calibration standard if a standard within the interior of the calibration is replaced; and

c. the laboratory limits the replacement of calibration standards to one calibration standard concentration.

The BIG Caveat

- *vi. The laboratory shall document a technically valid reason for either removal or replacement of any interior calibration point.*

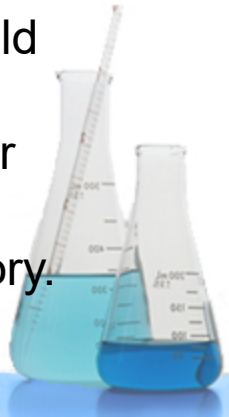
- The intent is to allow a laboratory to provide a sound documented technical reason for the rare instance of removal of a standard from a curve. Only gross technical errors are to be allowed. It is not intended to allow substitution to improve curve fitting.
- You must have a documented valid reason to either remove or replace any interior standard!
- Not to just pass calibration criteria, calibration

1.7.1.1 (f) Minimum Number of Standards

For regression or average response/calibration factor calibrations the minimum number of non-zero calibration standards shall be as specified in the table below.

Type of Calibration Curve	Minimum Number of Calibration Standards[b]
Threshold Testing[a]	1
Average Response	4
Linear Fit	5
Quadratic Fit	6

a - The initial one point calibration shall be at the project specified threshold level.
b - Fewer calibration standards may be used only if equipment firmware or software cannot accommodate the specified number of standards. Documentation detailing that limitation shall be maintained by the laboratory.



Three Degrees of Freedom

Type of Calibration Curve	Minimum number of calibration standards	Degrees of Freedom
Threshold Testing	1	Not Applicable
Average Response	4	3
Linear Fit	5	3
Quadratic Fit	6	3

The degrees of freedom in the equation scientifically justifies the minimum number of calibrants for all curve fitting routines.

1.7.1.1(k) Relative Error

- What is Relative Error?
  - Error measured as a percentage rather than an absolute value
    - If the true value is 20 and the measured result is 22:
      - Absolute Error is 2
      - Relative error is 10%

Examples

Which curve type would you have selected based on "r^2" ???

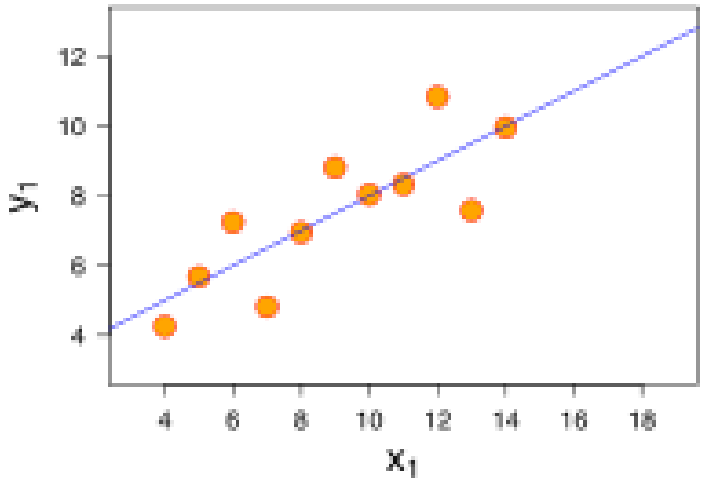
Fluoride Method 300.0		Relative Error		
			Weighted Curves	
Conc.	**Response**	**Linear**	**Linear 1/x**	**Linear $1/X^2$**
0.05	**1497075**			
0.5	**12858983**			
2.5	**67621646**			
5	**1.43E+08**			
10	**3.02E+08**			
	r^2	**0.9994**	**0.9990**	**0.9979**

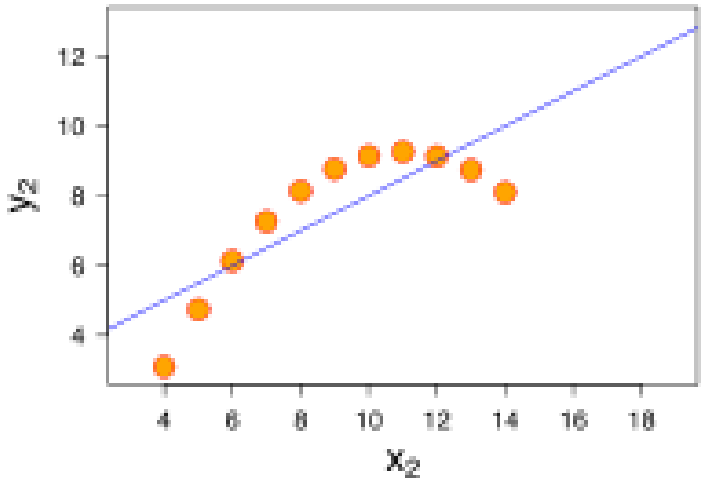
Which Curve Type??

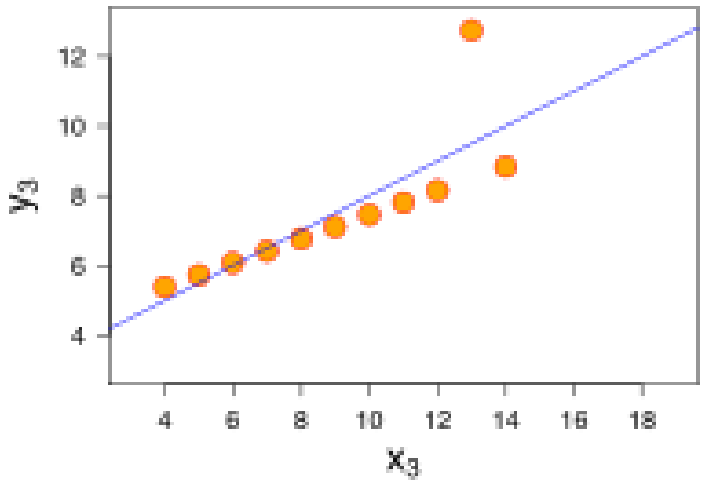
Propachlor Method 8081		Relative Error		
			Weighted Curves	
Conc.	Response	Linear	Linear 1/x	Linear $1/X^2$
5	$2.67X10^6$			
25	$9.99X10^6$			
50	$1.74X10^7$			
125	$3.86C10^8$			
175	$5.21X10^8$			
250	$7.18X10^8$			
500	$1.37X10^9$			
	r2	0.999	0.997	0.991

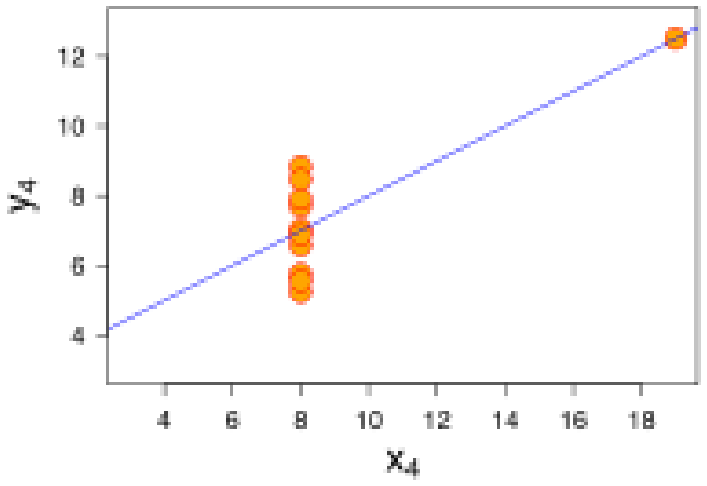
THE NELAC INSTITUTE

Anscombe's Quartet



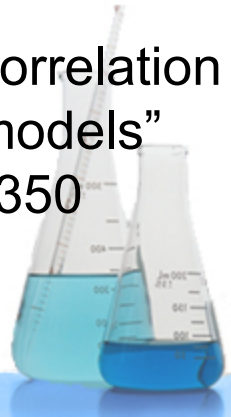






Correlation Coefficient and Calibration

- "Very **common mistakes** in the analytical calibration process are the use of correlation coefficients… *Evaluation of analytical calibration based on least squares linear regression for instrumental Techniques, Francisco Raposo, TrAC 77, Match 2016*
- The correlation coefficient, which is a measure of two random variables, **has no meaning in calibration** because the values x are not random quantities *Guidelines for Calibration in Analytical Chemistry, NIST, 1998*
- "For most applications, and calibration curves in particular, the correlation coefficient must be regarded as **a relic of the past**." Meier and Zund, *Statistical Methods in Analytical Chemistry*, 2000
- "One practice that **should be discouraged** is the use of the correlation coefficient as a means of evaluating goodness of fit of linear models" Van Arendonk and Skogerboe, *Anal. Chem*. 53, 1981, 2349-2350



Why do we need to evaluate relative error in a curve?

- Correlation coefficient does not effectively control relative error, but it will take decades to remove this from EPA methods, if ever
- Without an evaluation of relative error, results especially towards the low end of the calibration can be meaningless

Is Relative Error Currently Used in Environmental Testing?

- Yes:
  - Most methods express CCV (Continuing Calibration Verification) limits as relative error:
    - True value +/- 20%

Relative Error in SW-846

Method 8000D

- Either of the two procedures described in 11.5.4.1 and 11.5.4.2 may be used to determine calibration function acceptability for linear and non-linear curves
- 11.5.4.1 Calculation of the % error
  - *Same as TNI Relative error option but required at all points*
- 11.5.4.2 Calculation of Relative Standard Error
  - *Same as TNI RSE*

Does "may" mean that one or the other can be used, but one must be?

Does "determine calibration function acceptability" mean that if these options are used, then R2 does not need to be determined?

Relative Error in 40 CFR Part 136.6

- As an alternative to using the average response factor, the quality of the calibration may be evaluated using the Relative Standard Error (RSE). The acceptance criterion for the RSE is the same as the acceptance criterion for Relative Standard Deviation (RSD), in the method.
- The RSE may be used as an alternative to correlation coefficients and coefficients of determination for evaluating calibration curves for any of the methods at Part 136. If the method includes a numerical criterion for the RSD, then the same numerical value is used for the RSE.

Relative Error in Drinking Water Methods (e.g., 524.4)

The initial calibration is validated by calculating the concentration of the analytes for each of the analyses used to generate the calibration curve by use of the regression equations. Calibration points that are ≤MRL must calculate to be within +50% of their true value. All other calibration points must calculate to be within +30% of their true value

Same as the TNI Relative error but required at all levels

Note that correlation coefficient is not included in the method

Average Response Factor and Relative Error

j) the laboratory shall use and document a measure of relative error in the calibration.

i. for calibrations evaluated using an average response factor, the determination of the relative standard deviation (RSD) is the measure of the relative error;

If your calibration is evaluated by RSD then no further relative error evaluation is needed

Correlation Coefficient and Relative Error

ii for calibrations evaluated using correlation coefficient or coefficient of determination, the laboratory shall evaluate relative error by either:

a. *measurement of the Relative Error (%RE)*
b. *measurement of the Relative Standard Error (%RSE)*

Option 1: Relative Error

Relative error is calculated using the following equation:

$$\%\ Relative\ Error = \frac{x'_i - x_i}{x_i} \times 100$$

x_i = True value for the calibration standard

x'_i = Measured concentration of the calibration standard

Does that look familiar?

CCV % drift

$$\%\ Drift = \frac{x'_i - x_i}{x_i} \times 100$$

Same formula, but used with an inital calibration standard rather than continuing

Option 1: Relative Error

This calculation shall be performed for two calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level.

The Relative Error at both of these levels must meet the criteria specified in the method. If no criterion for the lowest calibration level is specified in the method, the criterion and the procedure for deriving the criterion shall be specified in the laboratory SOP.

Essentially, measure the error at the low point and mid-point of the calibration using the same calculation as for a CCV

Option 2: Relative Standard Error, RSE

$$\%\ RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

Where

x_i = True value of the calibration level i.

x'_i = Measured concentration of calibration level i.

p = Number of terms in the fitting equation.

(average = 1, linear = 2, quadratic = 3).

n = Number of calibration points.

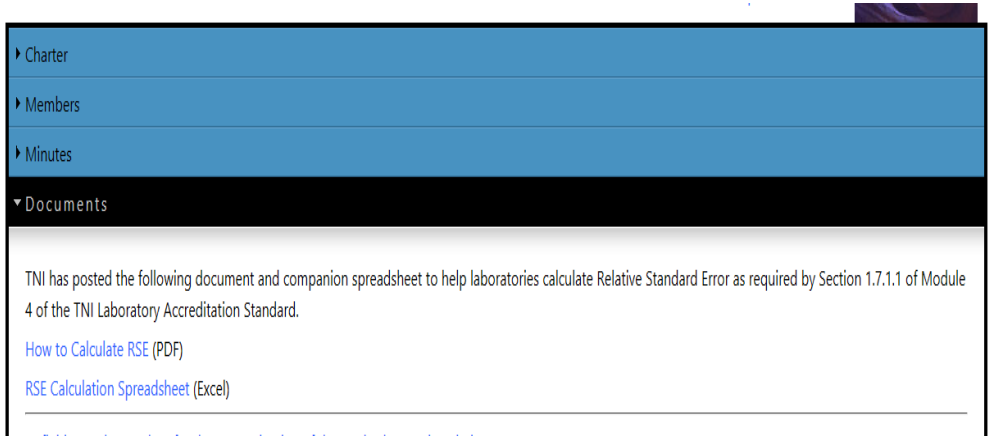
A little complicated but just like RSD for an average curve

- Provides one number to evaluate the curve (like RSD)

Calculation of RSE

1. Compute the difference between the true and measured concentration at each level, divide by the true concentration and square the results.
2. Sum the squares and divide by the number of calibration standards minus the number of terms.
3. Compute the square root and express as a percentage.

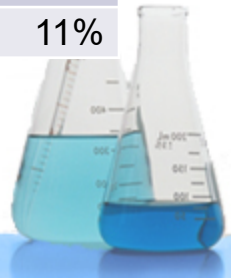
See basic RSE calculator on TNI website
https://nelac-institute.org/committee/chemistry



RSE Calculator

n, Number of points		= B5		
p, Number of terms		= B7		
True Value	Measured Value	((Measured-True)/True)^2	Column C/(n-p)	%RE
=A11	=B11	=POWER((A11-B11)/A11,2)	=D13/(B5-B7)	=(B11-A11)/A11*100
=A12	=B12	=POWER((A12-B12)/A12,2)	=D13/(B5-B7)	=(B12-A12)/A12*100
=A13	=B13	=POWER((A13-B13)/A13,2)	=D13/(B5-B7)	=(B13-A13)/A13*100
=A14	=B14	=POWER((A14-B14)/A14,2)	=D13/(B5-B7)	=(B14-A14)/A14*100
=A14	=B15	=POWER((A15-B15)/A15,2)	=D13/(B5-B7)	=(B15-A15)/A15*100
		Sum	=SUM(E13:E17)	0.012368633
		Square root	=SQRT(E21)	0.1112
		%RSE	=E22*100	11%

Note: For the Number of Terms, use 1 for average response factor, 2 for linear regression and 3 for quadratic.



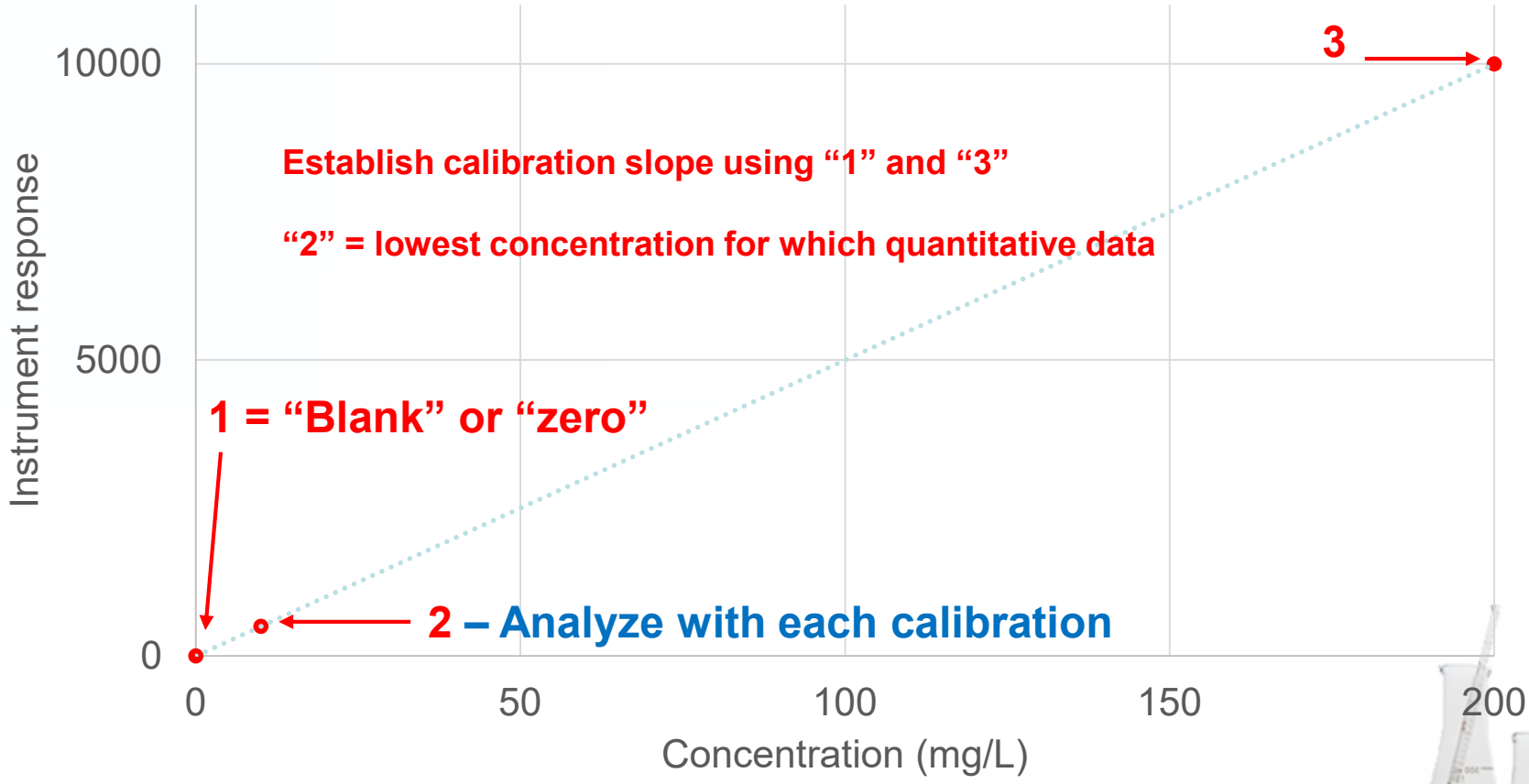
RSE Acceptance Criteria

must meet the criterion specified in the method. If no criterion is specified in the method, the maximum allowable RSE shall be numerically identical to the requirement for RSD in the method. If there is no specification for RSE or RSD in the method, then the RSE shall be specified in the laboratory SOP.

1.7.1.1 (I) Single point calibration and linear range

- Some methods allow calibration with only a blank (or “zero”) and a single calibration standard
  - e.g., ICP technology
- 2016 standard requires
  - Single point used to establish the calibration shall be analyzed at least daily
  - Standard at or below the quantitation limit shall be analyzed with each calibration and shall meet recovery limits

Required at least daily:



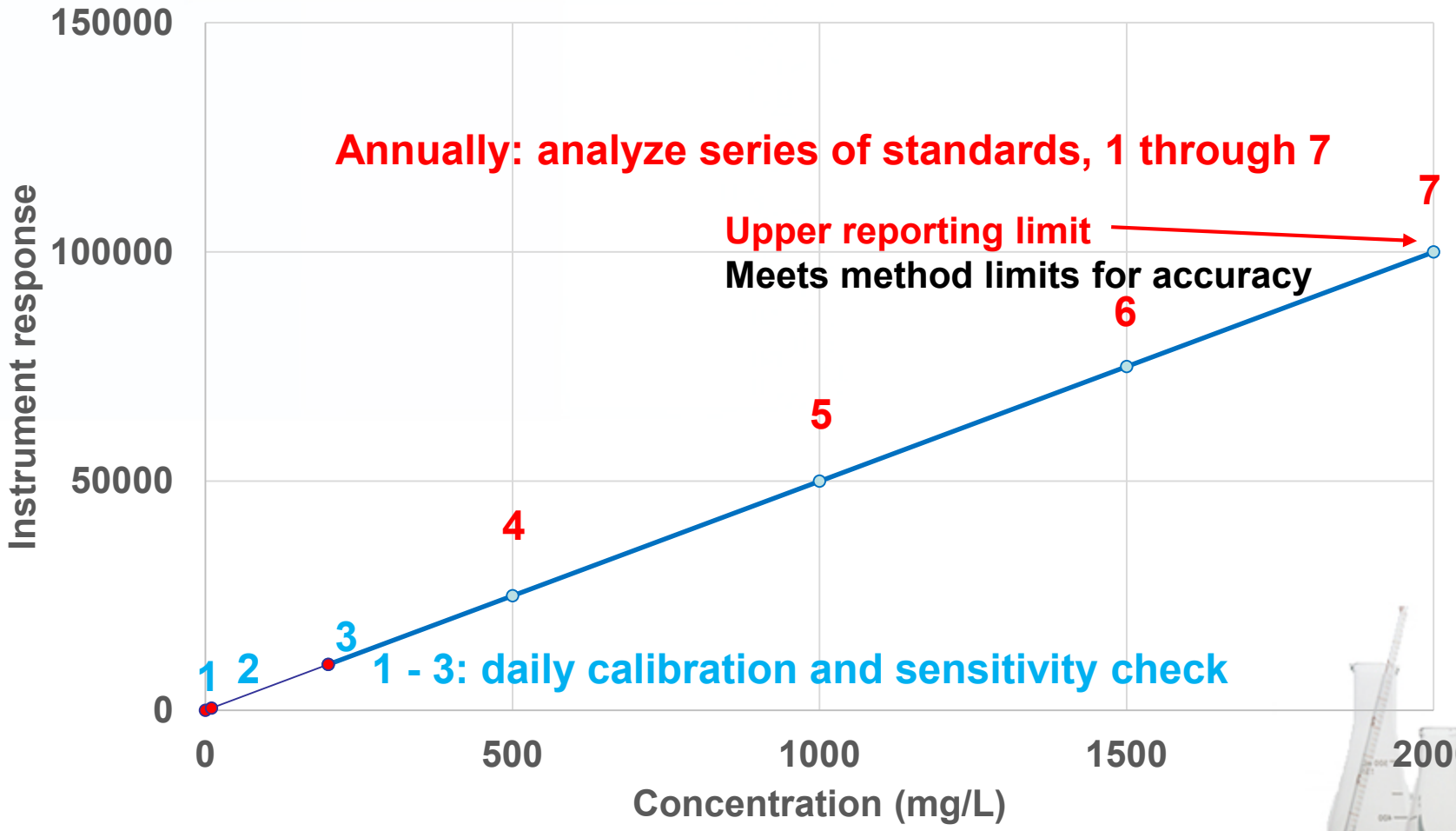
No change from 2009 Standard

1.7.1.1 (p) Reporting

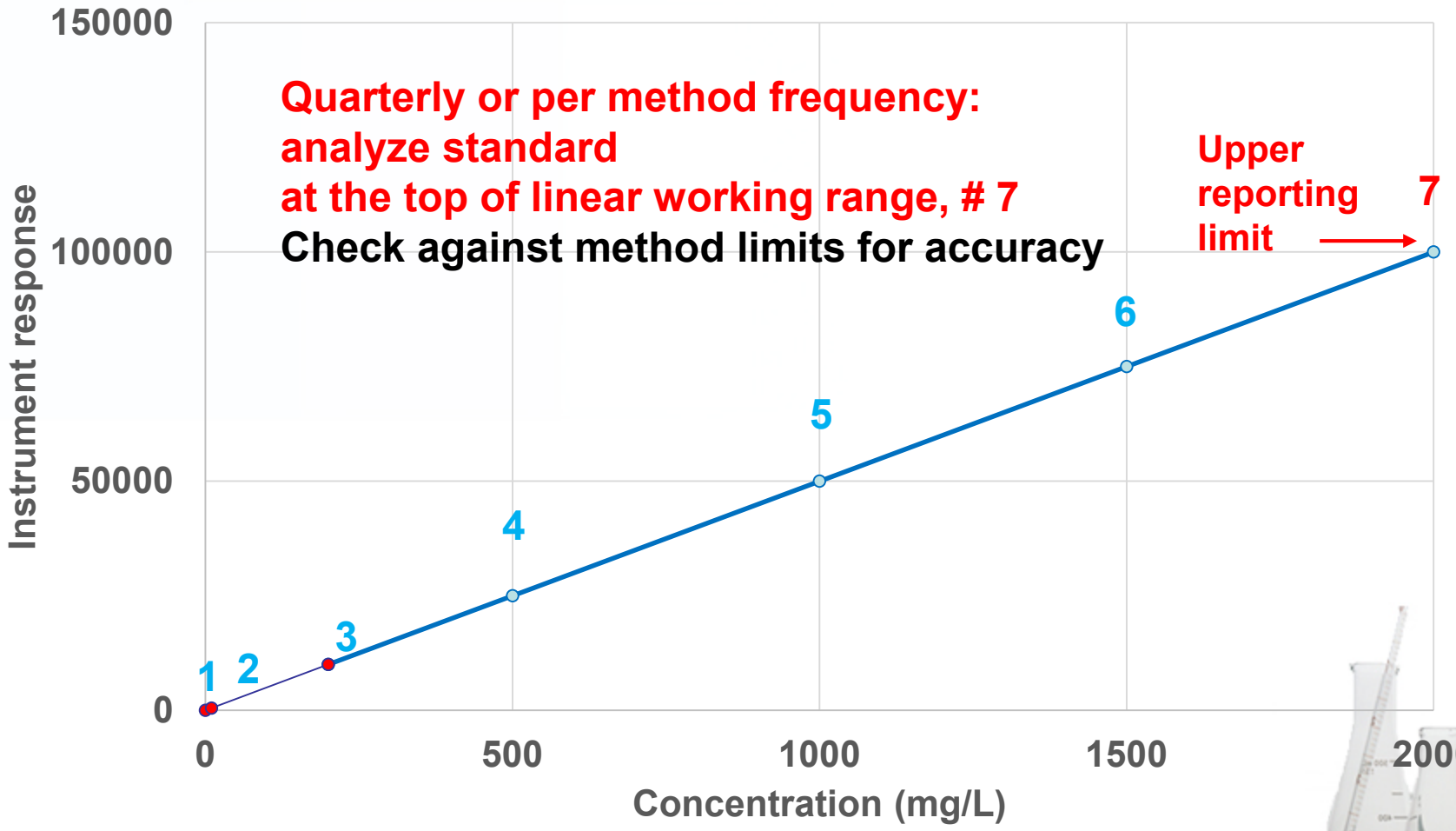
If the method allows, data within the linear range, but above daily calibration may be reported without qualification:

- Establish the linear range using a series of standards annually
- Verify quarterly

Linear Range
Annual Requirement



Linear Range Quarterly Requirement



1.7.1.1 (m)- Aroclors

m. for analysis of Aroclors which use a linear through origin model (or average response factor) the minimum requirement is to perform an initial multi-point calibration for a subset of Aroclors (e.g., a mixture of 1016/1260) and to use a one-point initial calibration to determine the calibration factor and pattern recognition for the remaining Aroclors;

Consistent with method 8082

1.7.1.1 (n): Initial Calibration Verification (ICV)

- ICAL must be verified with second source standard
  - No criteria specified
- Second source = obtained from a different supplier or a separate lot from the same supplier

BENZIDINE? REALLY?
NEMC: 1998
Roy Keith Smith

Purposes of Second Source

1. Qualitative Agreement: Confirm Identity of Compounds in Primary Standard

2. Quantitative Agreement: Confirm Concentrations of Primary Standard Compounds

3. Degradation: Monitor and identify if occurring during analytical sequences

1.7.1.1 (o) Sensitivity Check

o. for those methods where reporting non-detected analytes based on successful completion of a sensitivity check is allowed (similar to threshold testing but only for non-detects) the requirements of this standard shall not prohibit the practice;

Method 8000D
In order to report non-detected analytes that exceed the lower acceptance criteria (e.g., <-20%), a sensitivity verification standard at or below the LLOQ should be analyzed in the analytical batch. The analyte should be detected in the LLOQ standard and meet all of the qualitative identification criteria that the laboratory routinely uses

1.7.1.2 – Continuing Calibration

Sections	Updates
a and b Overview	No change
c CCV level	New
d When CCV is required	Changes and additions
e Raw data	No change
f Acceptance criteria	Changes

1.7.2.1 (c)
CCV Concentration

The concentration shall be equal to or less than half the highest level in the calibration

1.7.2.1 (d) Frequency of the CCV

- At the beginning and end of each analytical batch
  - Ending requirement is waived if internal standard is used and not required by the method. (Same as 2009)
- Additions
  - Second source ICV that passes CCV criteria may be used in place of a CCV
  - LCS that passes CCV criteria may be used in place of a CCV for methods where the calibration goes through the same process as the LCS

1.7.2 (f) Acceptance Criteria

- (i) Obvious cause that impacts only the CCV
- (ii) No obvious cause or impact to other samples
- (iii) Data qualification
  - (a) exceeded high
  - (b) exceeded low

2009 vs 2016

- 2016
  - Requires identifiable cause for CCV failure for second CCV to be acceptable. If cause is not identifiable requires corrective action.
  - Requires only one passing CCV after corrective action.
  - Data may be reported with qualifiers under the special conditions unless prohibited by the client, regulatory program or regulation.
- 2009
  - Does not require identifiable cause for CCV failure before analysis of second CCV
  - Requires two passing CCVs after corrective action
  - States data is fully useable under the special conditions

i. Obvious Cause

*if an **obvious** cause for the calibration verification failure is identified that impacts **only** the calibration verification sample (e.g. a missed autosampler injection), then analysis may proceed if a second calibration verification sample is analyzed immediately and the result is within acceptance criteria.*

Samples analyzed previously shall be considered valid if bracketed by a passing calibration verification sample (refer to 1.7.2(d)).

The cause for the failure of the first calibration verification result shall be documented.

ii. No Obvious cause

if the cause for the calibration verification failure is **not obvious** and/or has the **potential** to have identifiable or has **impacted other samples**, then corrective action shall be performed and documented. Prior to analyzing samples, the laboratory shall demonstrate acceptable performance after corrective action with calibration verification or a new initial calibration shall be performed. Samples analyzed prior to the calibration verification failure shall be **reanalyzed** or the results **qualified** if calibration verification bracketing is required (refer to 1.7.2(d))

1.7.2 (f) ii

- CCV fails and impacts other samples or cause is unknown
  - Just fails
  - Poor Peak shape
  - Poor response
  - Incorrect IS concentration

- Perform Corrective Action
  - Replace Reagent
  - Replace Internal Standard valve
  - Clean needle
  - Replace injection port liner
  - Replace tubing

1.7.2 (f) ii

- Document the corrective action
- Demonstrate acceptable performance with new CCV or recalibration

- Don’t forget samples before a failing CCV will also need to be reanalyzed if bracketing is required, or qualified as listed in the next section.

iii. Data Qualification

Data associated with an unacceptable calibration verification shall be qualified if reported, and shall not be reported if prohibited by the client, a regulatory program or regulation.

Data associated with calibration verifications that fail under the following special conditions shall still be qualified, but may use a different qualifier

- High bias and non-detects
- Low bias and above reg limit/decision level

1.7.2 (f) iii

*a. when the acceptance criteria for the continuing calibration verification are exceeded **high** (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or*

1.7.2 (f) iii

b. when the acceptance criteria for the continuing calibration verification are exceeded ***low*** *(i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.*

1.7.2 (f) iii

- Qualify if CCV is out high and samples are non detect
- Qualify if CCV is out low and samples exceed the maximum regulatory/decision level
- Reanalyze in all other cases

TNI Guidance Document

TNI Guidance on Instrument Calibration

GUID-3-110-Rev0

December 5, 2018

This document was prepared to provide guidance on the instrument calibration section (1.7) the 2016 TNI Standard Volume 1Module4 (V1M4) Quality Systems for Chemical Testing. This document focuses primarily on those parts of section 1.7 which have changed substantially with the 2016 TNI Standard. This document is not intended to be an official interpretation of the Standard, nor is it to be used in place of the standard. This document is only intended to help users of the standard better understand and implement the standard in their laboratory. If there are questions regarding the use and interpretation of the Standard, submit a Standard Interpretation Request (SIR) for an official interpretation using the process on the TNI website. Note: Language quoted from the standard is shown in grey text boxes.

1.0 Introduction

The 2016 Standard contains several significant changes from the 2009 standard, including:

- removal and replacement of calibration points;
- minimum number of standards;
- relative error;
- single point calibration and linear range methods; and
- continuing calibration acceptance criteria.

https://nelac-institute.org/content/NELAP/interpret.php

THE NELAC INSTITUTE

Summary

- Extensive changes to the calibration section mostly designed to prevent inappropriate practices
- Number of standards revised to have a sound statistical basis.
- Relative error section should improve accuracy, especially at the low end of the curve, and eliminate the use of R^2
- Other minor changes

Thank You

TNI Chemistry Committee

2010-2015

Richard Burrows, Chair
TestAmerica Laboratories

Francoise Chauvin
New York City DEP

Anand Mudambi
US EPA OSA

Nancy Grams
Advanced Earth Technologists

Scott Siders
Illinois EPA

Gary Ward
Oregon DOH

Colin Wright
Florida DEP

Dan Dickinson
New York DOH

Brooke Connor
USGS

Tim Fitzpatrick
Florida DEP

Lee Wolf
Columbia Analytical Services

John Phillips
Ford Motor Company

Valerie Slaven

Gale Warren
New York DOH

91 meetings