Update on ASTM and Standard Methods method development activities

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SM And ASTM - Voluntary Consensus Standard Development Organizations (SDO)

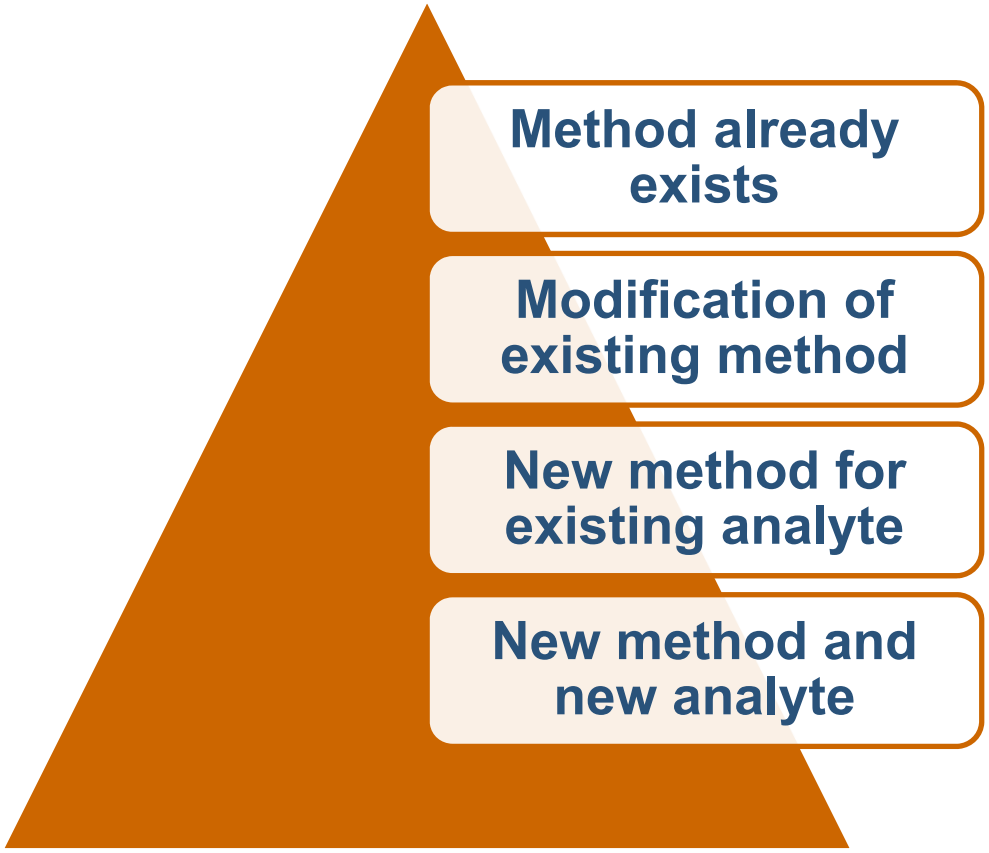
- AKA – VCSB
- Standard Method = A method of known and demonstrated precision issued by a SDO
- Standard Reference Method = A Standard Method with demonstrated accuracy

Reference = John K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, 1987

New Guides To Task Groups To Gather All Information Needed During Method Development

- "In accordance with the National Technology Transfer and Advancement Act (NTTAA), EPA considers Voluntary Consensus Standards Bodies (VCSB), such as Standard Methods and ASTM in regulatory actions when periodically updating the list of approved methods."
- The new Validation Procedures will provide guidelines to method developers as to information EPA needs
- so that ASTM and/or Standard Methods can easily submit new, and updated methods for use in wastewater, drinking water, and RCRA compliance

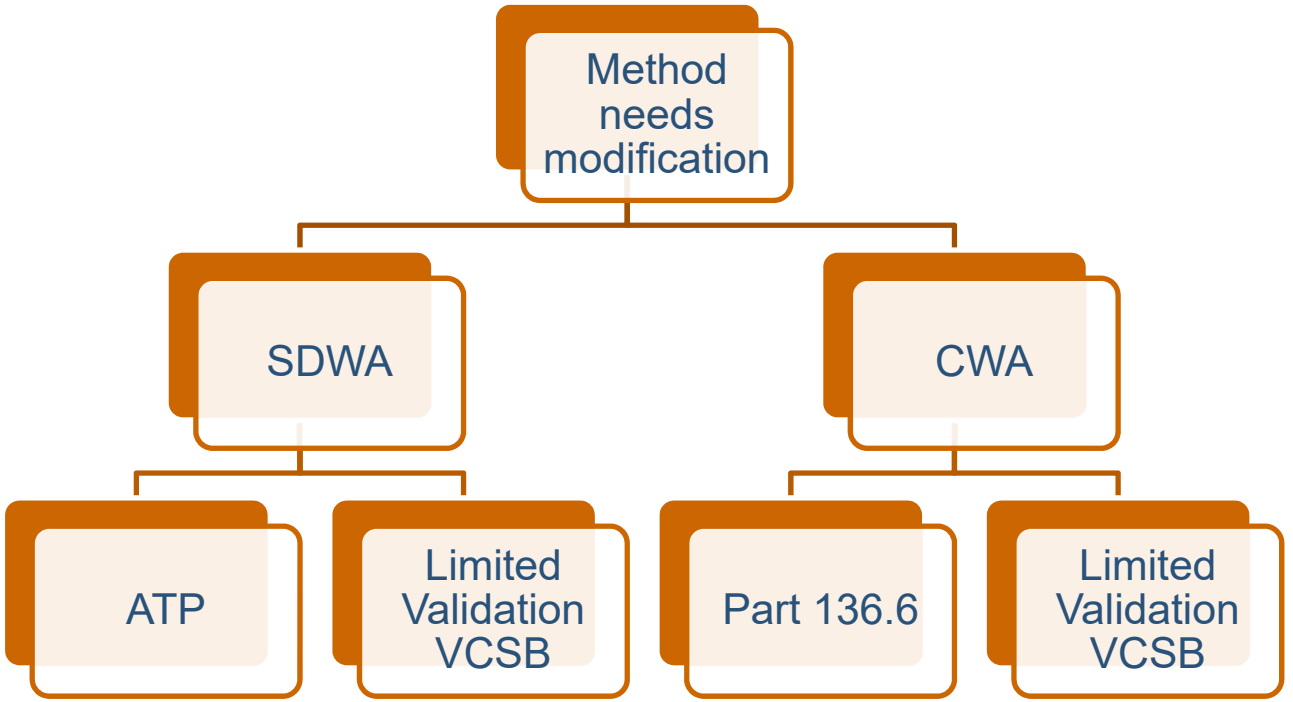
Methods We Develop And / Or "Validate"



Method Already Exists

- This “validation” is what a lab does
  - MDL
  - LCMRL
  - IDAC
  - Spikes
  - Duplicates
- Lab compares performance to criteria in existing method
- This type of method validation is NOT what ASTM or SM does

Modification Of An Existing Method



In lab you can modify a method and keep data on file, at VCSB a technical modification requires new data and balloting, editorial requires balloting.

Red Line, reason for change, and possible two column comparison to EPA

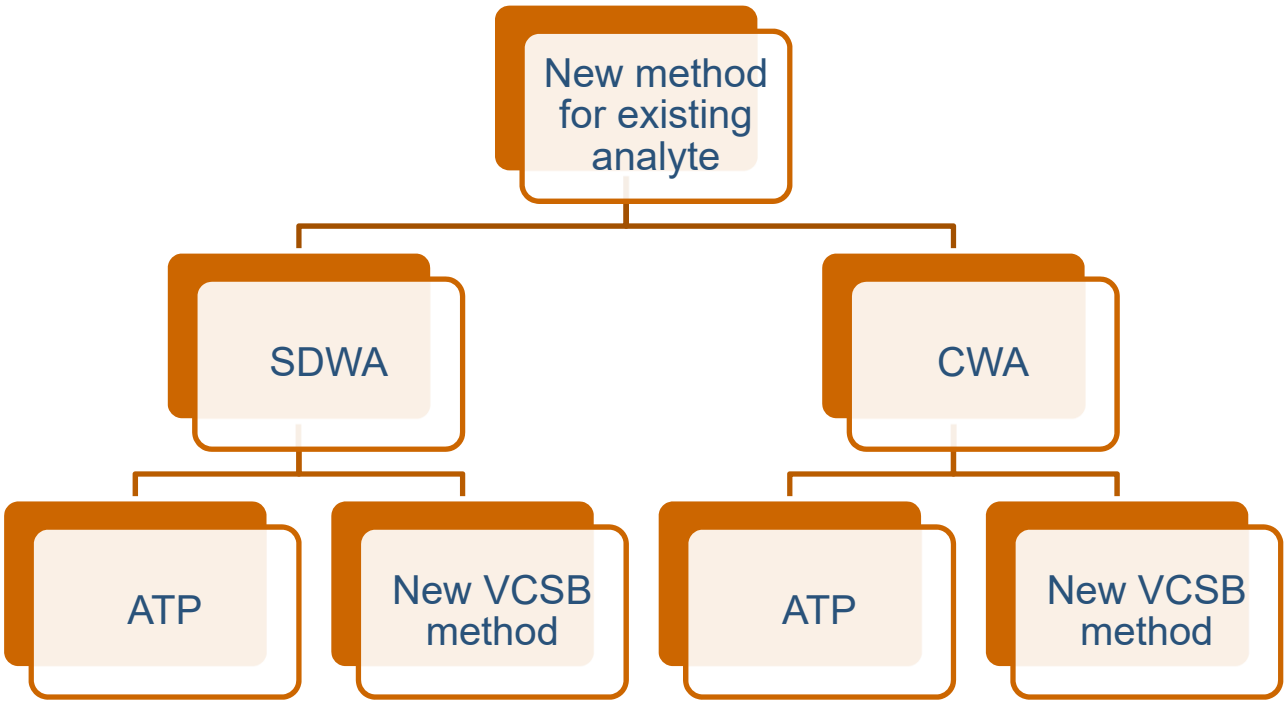
Examples Of Modifying An Existing Consensus Standard

- MDL incorrect, or newer MDL needed
  - Create task group
  - Collect data, verify at several locations over several days
  - Break method, re-verify
  - Modify text, ballot at task group and main committee

- Incorrect reagent recipe
  - Historical data search
  - Editorial → SM can make change, ASTM re-ballot
  - Not editorial → collect data, and re-ballot

- Convert manual method to automated method
  - This is a new method for VCSB

New Method For An Existing Analyte



VCSB require task group, single and multiple lab "validation", balloting. Validation plan and full data package submitted to EPA

Examples Of New Method For Existing Parameter

- There is already a SDWA, CWA, or “RCRA” parameter → new method is:
  - Different extraction / digestion
  - Different determination step
- This requires:
  - Task group
  - Rationale
  - Extensive Single lab study
    - Single operator precision and accuracy
  - Comparison with existing method(s)
  - Ruggedness
  - Multiple laboratory study
    - Reproducibility between labs
  - Validation plan and data package

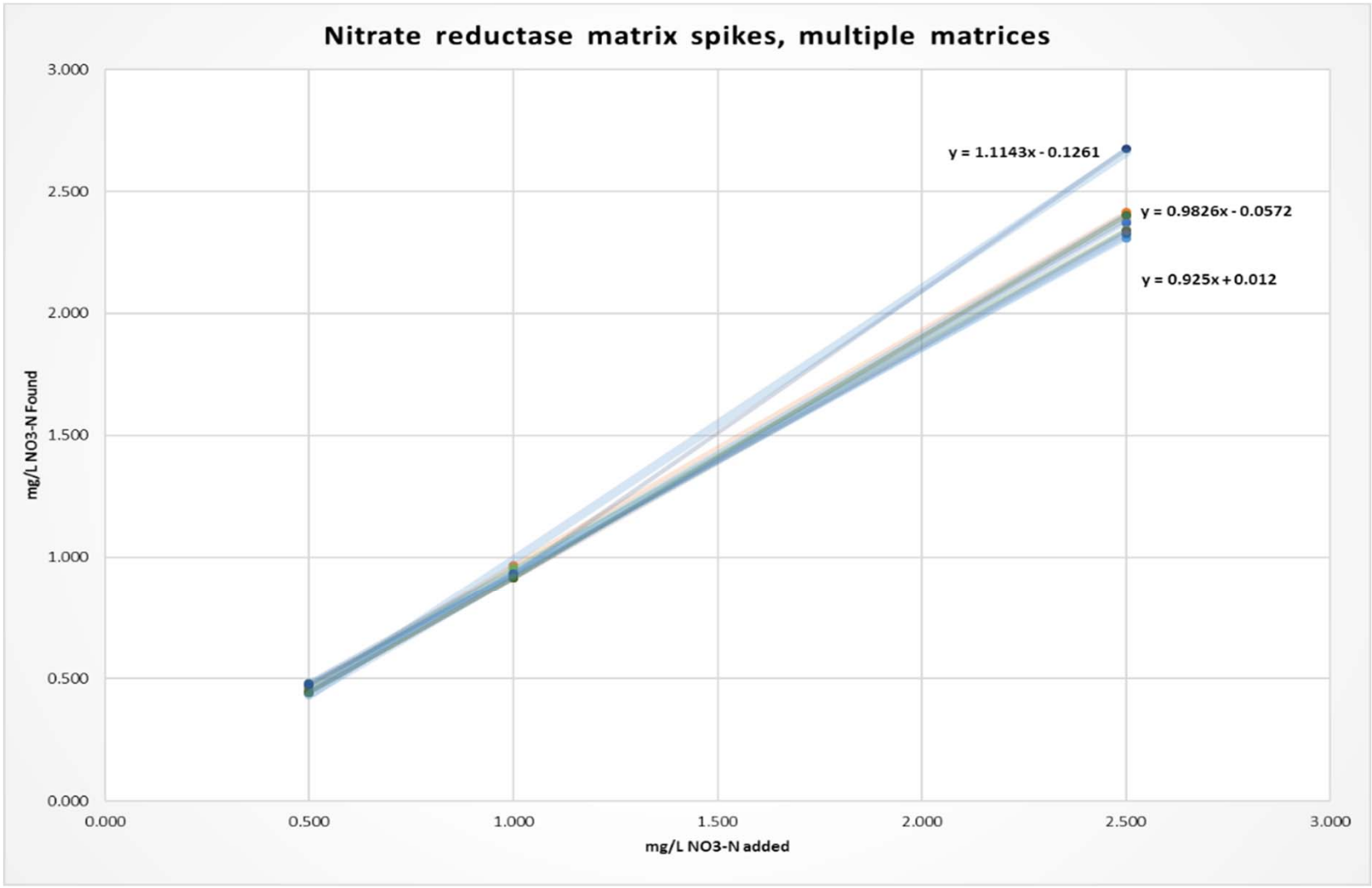
Rationale → Why Do We Need A New Method For An Existing Parameter?

- Lower detection limits
- Better precision
- Better recovery
- Fewer interferences
- Less waste (time, reagents, hazardous waste)
- Fewer chemicals/steps
- Reduce solvent use
- Improve safety

Single Lab Study Of A New Method For An Existing Parameter Establishes:

- Selectivity → prove new method measures what it says it measures
- Calibration/Standardization technique → required curve fitting or standardization protocols
- Reagent recipes, preparation, containers, shelf life (if different)
- Holding time and preservation (if different)
- Quantitation limit and range
- Applicable matrices (if different)
- Comparison to existing method
- MDL, ML, and calibration range
- Repeatability on standard solutions
- Bias using reference materials
  - RM if available
  - Spiked matrices (if possible)
- Ruggedness

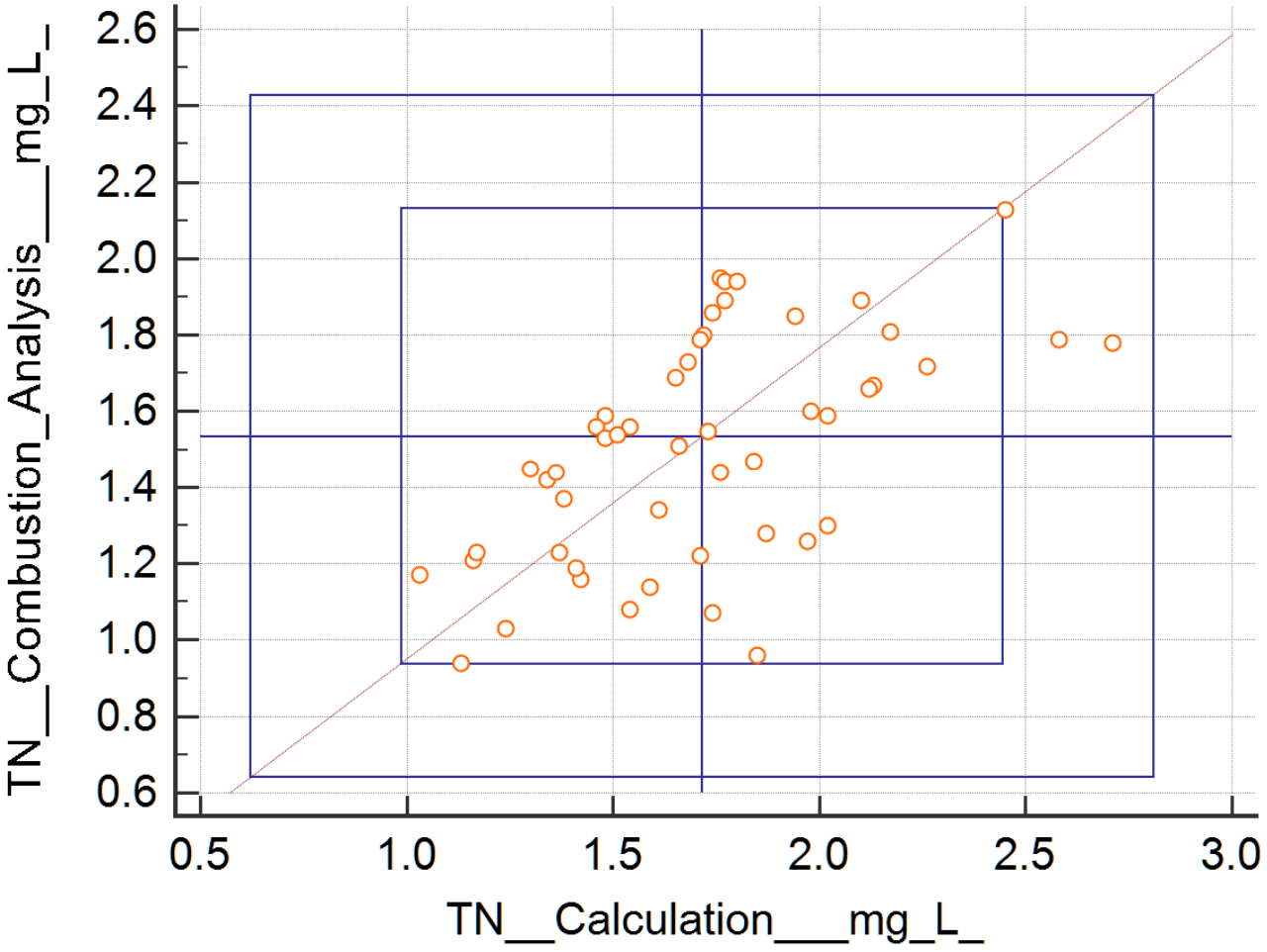
Single Lab Study Of Precision And Bias
Spiking Multiple Matrices At 3 Concentrations



Single Lab Study Comparing Two Methods

Analysis by Cd Reduction (mg NO_3+NO_2-N/L)	Analysis by Reductase (mg NO_3+NO_2-N/L)
0.96	0.94
0.04	0.05
0.32	0.24
0.68	0.68
10.1	11.6
0.75	0.79
2.5	3.11

Single Lab Study Comparing Two Methods Using Youden Plot



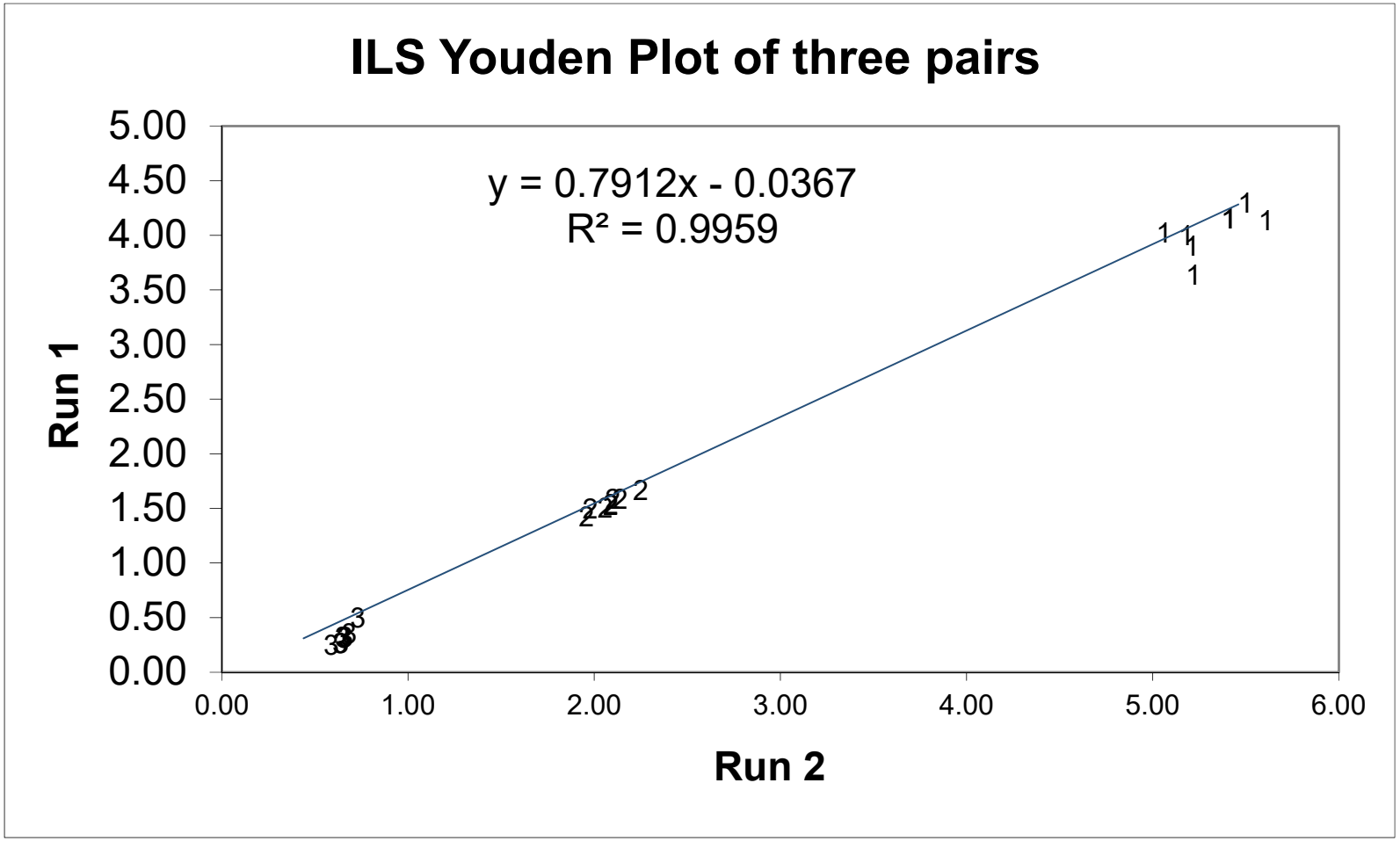
What is ruggedness, and how to test for it?

What steps are so critical that changing them changes the result?

Factor	Nominal	Variation
Portion size	10 ml	25 ml
Evaporation temperature	160 °C	220 °C
Evaporation time	1 hour	30 minutes
Digestion temperature	370 °C	380 °C
Digestion time	15 minutes	1 hour

Once All Other Tests Are Completed You Conduct A Multiple Laboratory Study:

- **Establish reproducibility of method between laboratories**



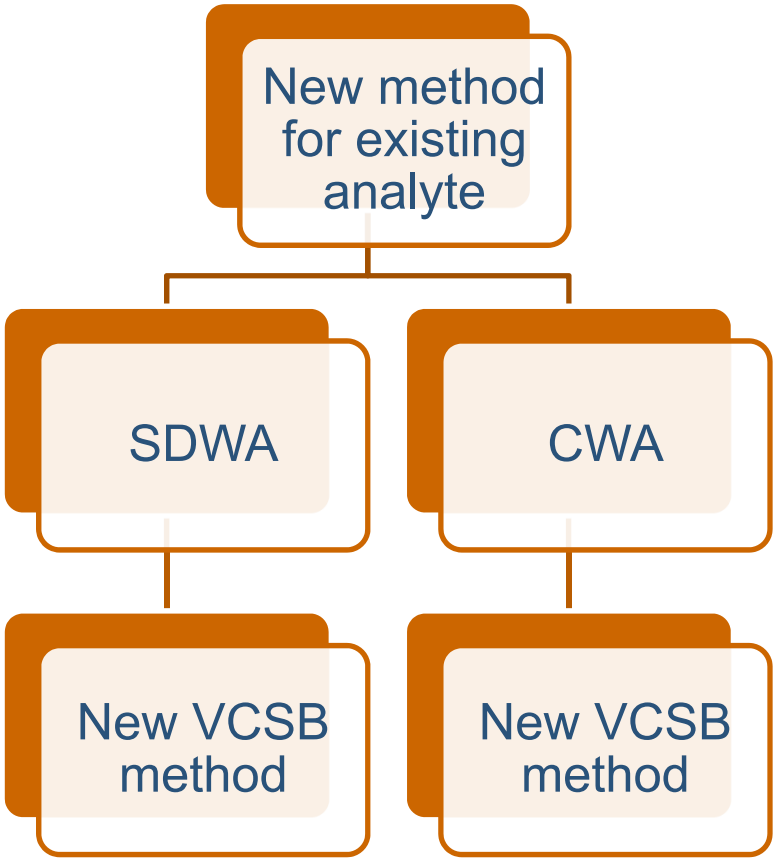
Precision And Bias Report With Youden Pairs:

Number of useable pairs	6	6	6	6	7	7
True Concentration (mg/L)					50.1	40.1
Mean Concentration (mg/L)	3.88	3.31	8.29	9.63	49.8	40.2
% Recovery					99.4	100
Overall Standard Deviation	0.34	0.56	1.19	1.36	4.28	3.18
Overall % RSD	8.78	16.2	14.2	14.0	8.60	7.90
Number of Useable Pairs	6		6		7	
Single Operator Standard Deviation	0.37		0.59		1.32	
Single Operator % RSD	10.2		6.58		2.94	

Precision And Bias Report With Blind Duplicates:

Matrix	5	6	7	8	9	12
Number of useable values	14	12	12	14	12	12
True concentration (mg/L)	5.39	N/A	N/A	21.0	N/A	0.501
Mean Recovery (mg/L)	5.67	1.61	1.68	21.9	3.63	0.808
% Recovery	105	N/A	N/A	104	N/A	161
Overall Standard Deviation, St	0.777	0.265	0.350	2.53	0.374	0.162
Overall Relative Standard Deviation (%)	13.71	16.48	20.99	11.54	10.28	20.02
Single Operator Standard Deviation So	0.549	0.243	0.329	1.156	0.317	0.150
Single Operator Relative Standard Deviation (%)	9.68	15.47	19.75	5.27	8.71	18.59

New Method For A New Analyte



VCSB require task group, single and multiple lab “validation”, balloting. Validation plan and full data package submitted to EPA

Examples Of New Method For Existing Parameter

- There is not a SDWA, CWA, or RCRA parameter → new method is:
  - Maybe reported in literature
  - Maybe a technique used, but not formalized
- This requires:
  - Task group & rationale
  - More extensive Single lab study than previous
    - Single to several lab operator precision and accuracy
  - Extensive evaluation of interferences
  - Lots of “optimization”: operation, extractions, digestions
  - Ruggedness
  - Multiple laboratory study
    - Reproducibility between labs
  - Validation plan and data package

Rationale → Why Do We Need A New Method?

- Is there a demand or need to analyze compound X?
- How will we test for it? Is this the best way?
- How low, or at what concentrations?
- What matrices?
- Who are the stakeholders?
- Do any other countries do this test?

Single Lab Study Of A New Method Establishes:

- Selectivity → prove new method measures what it says it measures
- Calibration/Standardization technique → required curve fitting or standardization protocols
- Reagent recipes, preparation, containers, shelf life
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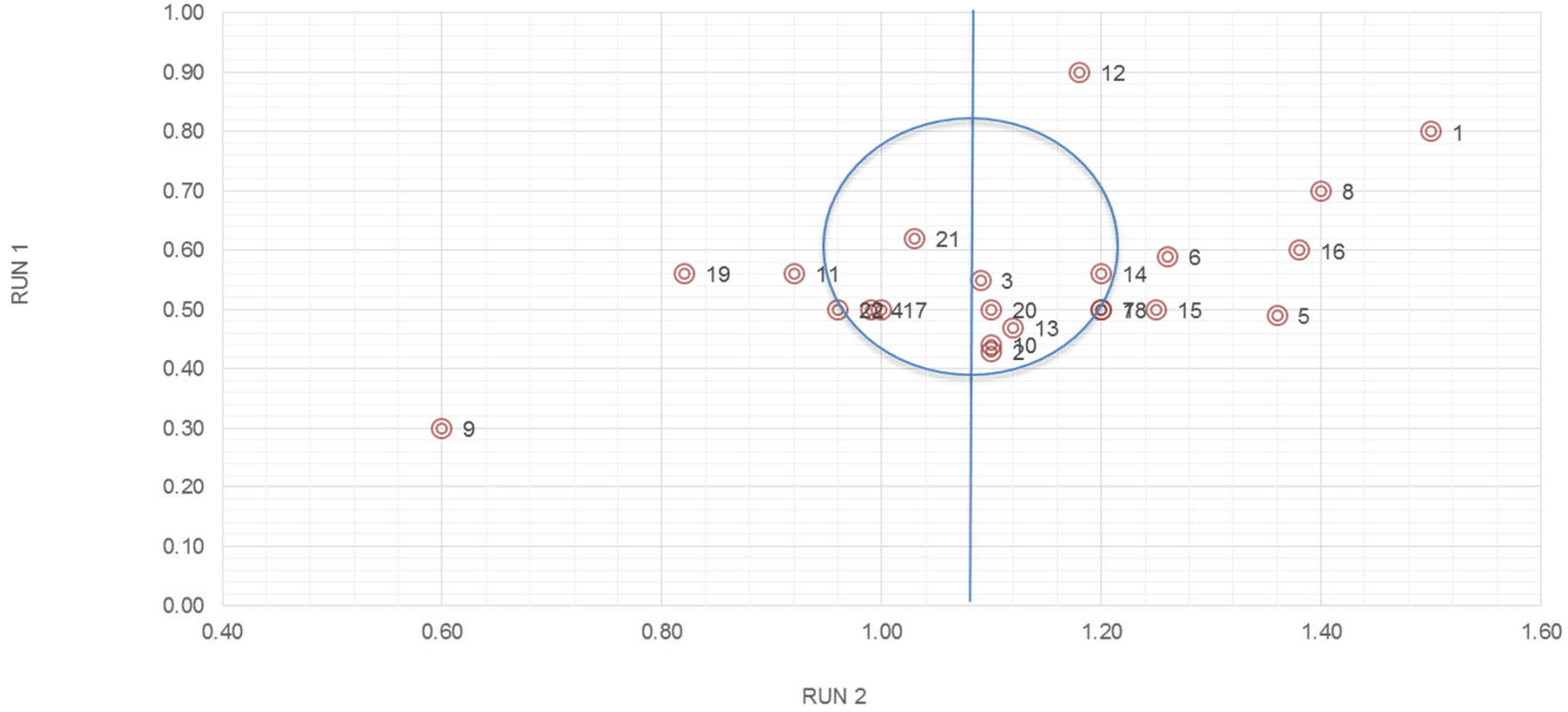
- Quantitation limit and range
- Applicable matrices
- Interferences and mitigation
- MDL, ML, and calibration range
- Repeatability on standard solutions
- Bias using reference materials
  - RM if available
  - Spiked matrices (if possible)
- Ruggedness

Once All Other Tests Are Completed You Conduct A Multiple Laboratory Study:

- **Establish reproducibility or lack of reproducibility between laboratories**



Conclusion:

- Brief overview of approach
- Both SM and ASTM guide in draft form
- Working with EPA to standardize guides
- Guide to create consistency between task groups
- As always, steps vary

Any Questions?

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Thank You!