SHIMADZU
Excellence in science

Positively Changing the World with New Techniques and Improved Laboratory Methods

William Lipps
August 2021
NEMC

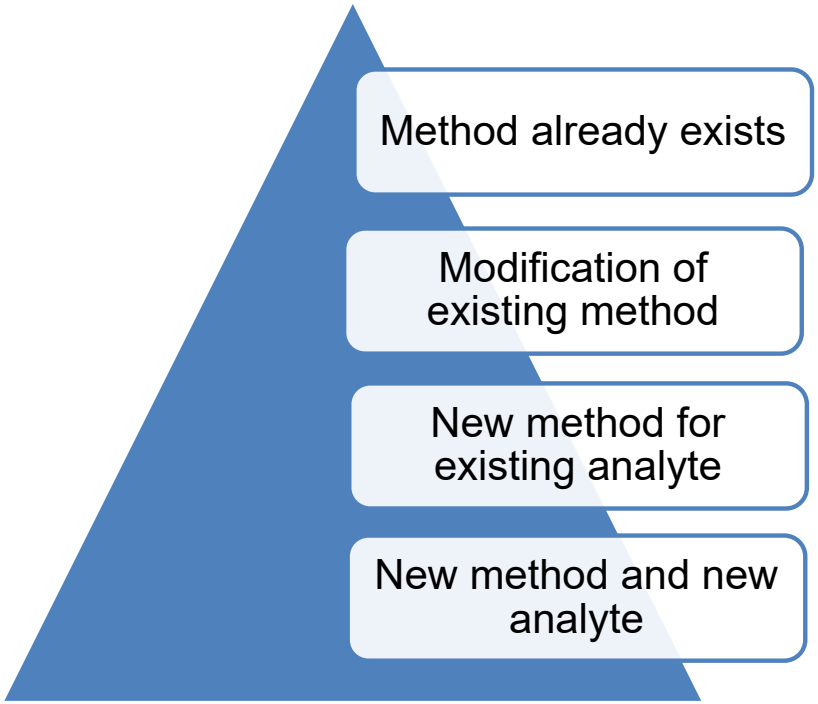
SHIMADZU

Three scenarios that may require a new or improved method

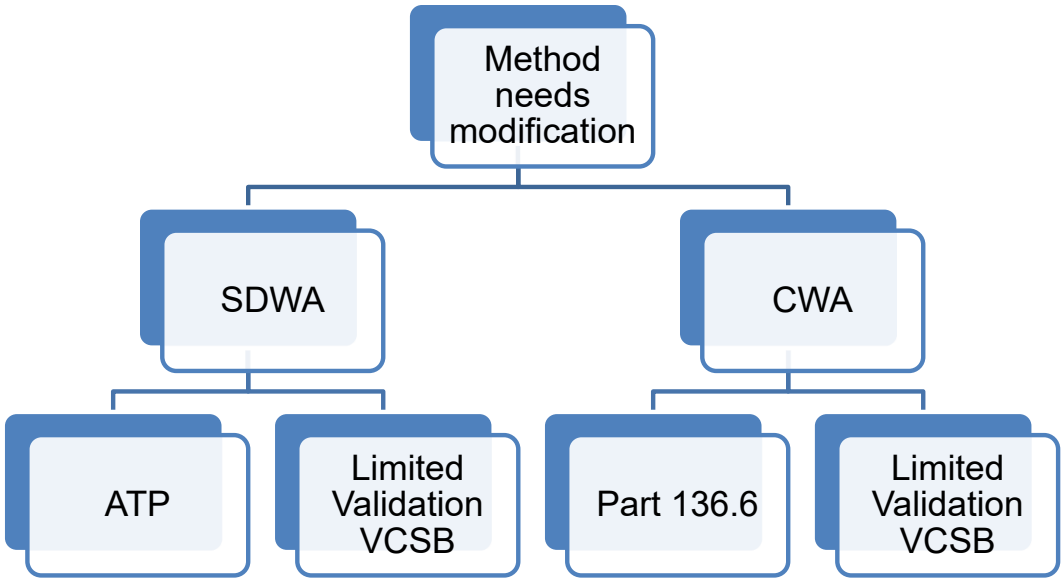
If the method is useful as it is, then do nothing

Easy

Hard



For existing methods, you can do an ATP, or modify it at a VCSB

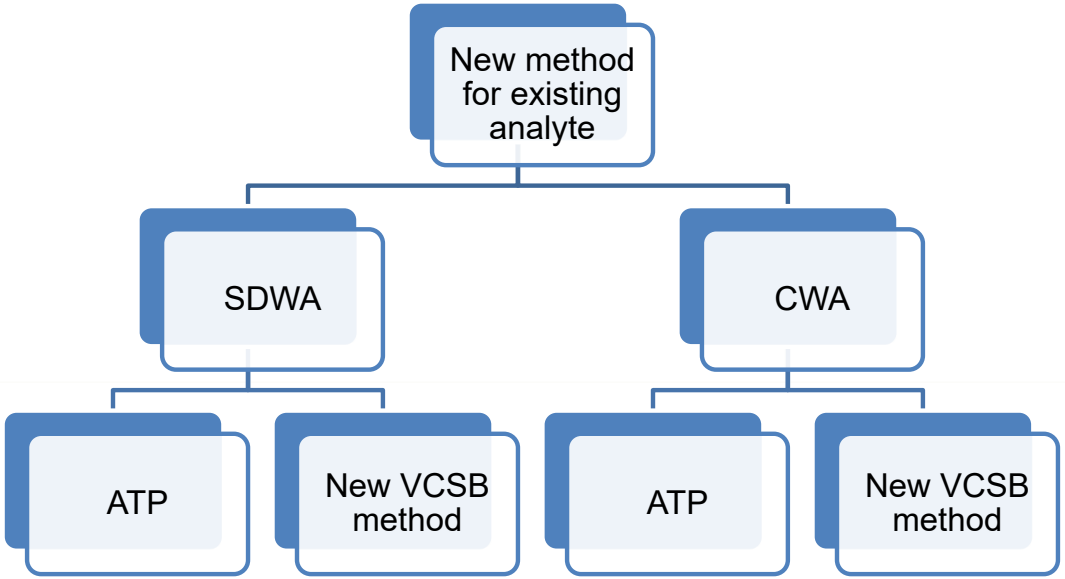


In the lab you can modify a CWA method and keep data on file, at VCSB a technical modification requires new data and balloting.

Red Line, reason for change, and possible two column comparison to EPA
SDWA requires an ATP to modify a method

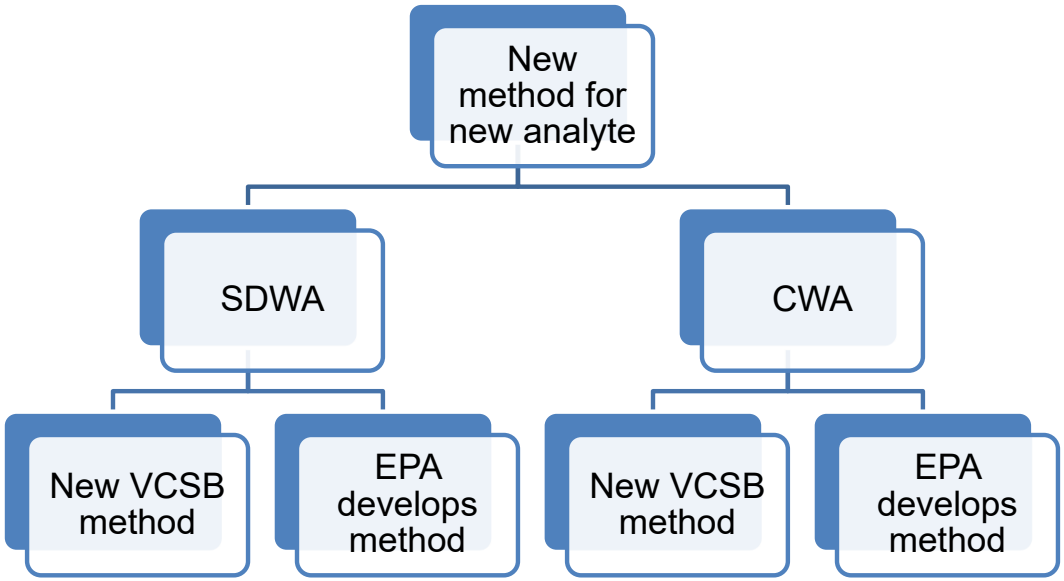
SHIMADZU

For a new method on an EXISTING analyte, with an existing approved method you can do an ATP or new method at a VCSB



SHIMADZU

For a new method with new analytes, you can wait for EPA or do it yourself at a VCSB



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

SHIMADZU

SM and ASTM - voluntary consensus standard development organizations (SDO)

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

Voluntary Consensus Standard Bodies that are Standard Development Organizations (SDOs) develop standard methods that can be approved by EPA for compliance testing.

Standard Method = A method of known and demonstrated precision issued by an SDO

Standard Reference Method = A Standard Method with demonstrated accuracy

SHIMADZU

VCSB Methods are routinely used nationally and worldwide for compliance testing

TABLE IB - LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology [35]	EPA [36]	Standard methods	ASTM	USGS/AOAC/other
1. Acidity, as CaCO3, mg/L	Electrometric endpoint or phenolphthalein endpoint		2310 B-2011	D1067-11	I-1020-85. [2]
2. Alkalinity, as CaCO3, 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]
3. Aluminum - Total, [4] mg/L	Digestion, [4] followed by any of the following:				
	AA direct aspiration [38]		3111 D-2011 or 3111 E-2011		I-3051-85. [2]
	AA furnace		3113 B-2010.		
	STGFAA	200.9, Rev. 2.2 (1994)			
	ICP/AES [39]	200.5, Rev 4.2 (2003); [68] 200.7, Rev. 4.4 (1994)	3120 B-2011	D1976-12	I-4471-97. [50]

"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."

Validation Procedures provide guidelines to method developers to ensure the provide the information EPA needs

ASTM and/or Standard Methods often submit new, and updated methods for use in wastewater, drinking water, and RCRA compliance

SHIMADZU

The validation guidelines for EPA ATP's, new EPA methods, and VCSB's are very similar

- Selectivity
- Calibration/Standardization technique
- 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

SHIMADZU

A VCSB validation differs from a lab validating a method, because usually no method exists

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

SHIMADZU

Examples of modifying an existing consensus standard or EPA method

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 must re-ballot
- Not editorial → create a task group, collect data, and re-ballot

Convert manual method to automated method

- This is a new method for VCSB
- Allowed modification, for a lab, at Part 136.6
- Requires an ATP for SDWA

SHIMADZU

Examples of a new method for an existing parameter

There is already a SDWA, CWA, or "RCRA" parameter/method → new method is required when:	This requires:
• Different extraction / digestion • Different determination step	• Task group at a VSCB or an ATP • Rationale • Validation Plan • Extensive Single lab study • Single operator precision and accuracy • Comparison with existing method(s) • Ruggedness • Multiple laboratory study • Data package

SHIMADZU

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	Increase safety

SHIMADZU

Examples of a new method for a new parameter

There is not a SDWA, CWA, or RCRA parameter or method:

Maybe reported in literature

May be a technique used, but not formalized

This requires:

Task group or EPA Work Group

Rationale

Validation Plan

Extensive Single lab study

Single to several lab operator precision and accuracy

Extensive evaluation of interferences

Lots of “optimization” of instrument operation, extractions, digestions

Ruggedness

Multiple laboratory study

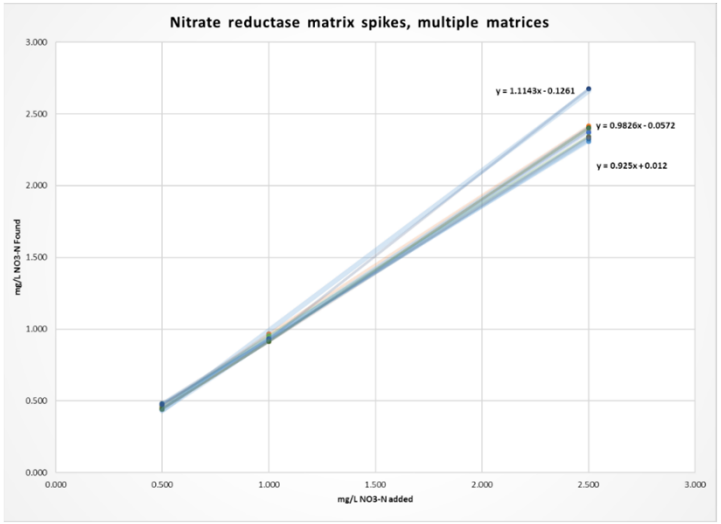
Data package

SHIMADZU

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 precision and bias spiking multiple matrices at three concentrations



Calibration/Standardization technique	Selectivity
Quantitation limit and range	Interferences and repeatability in applicable matrices
MDL, ML,	Repeatability on standard solutions

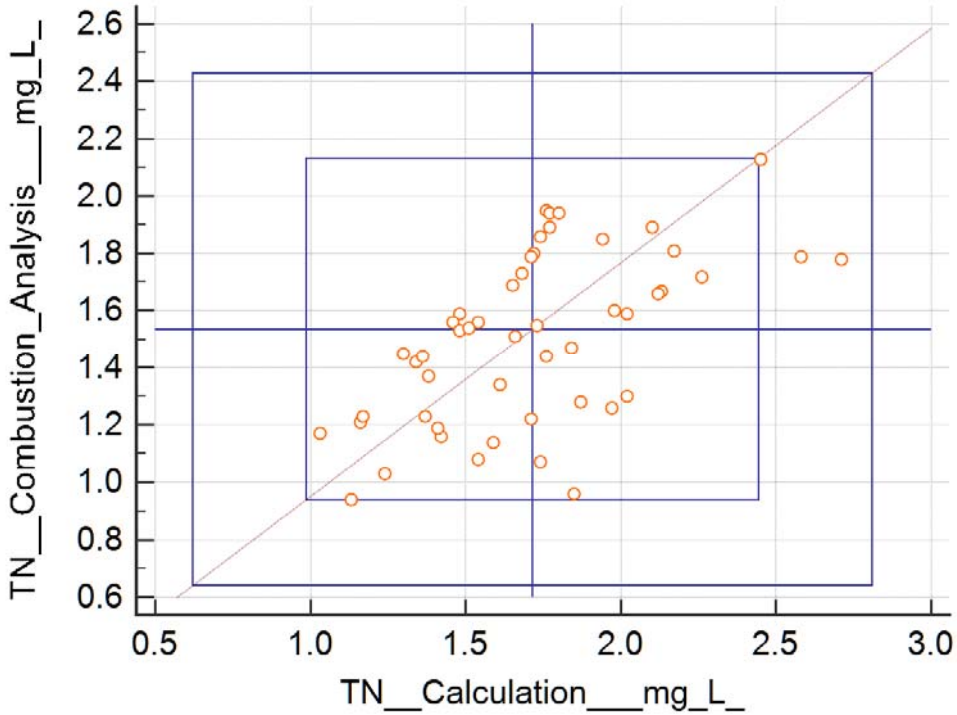
SHIMADZU

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

SHIMADZU

Single lab study comparing two methods using Youden plot



SHIMADZU

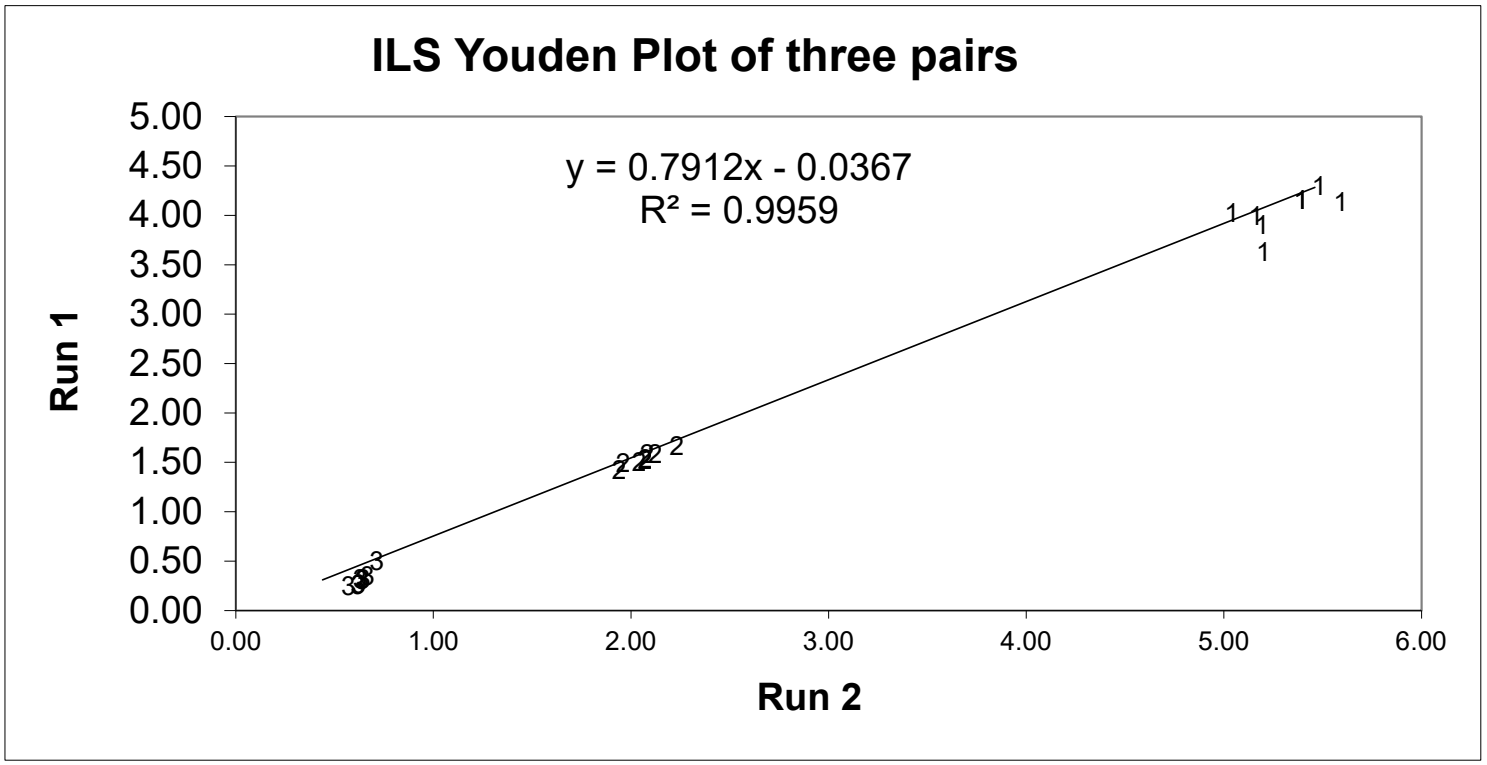
Example of a Ruggedness study for TKN

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

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

SHIMADZU

Once all other tests are completed you conduct a multiple laboratory study:



SHIMADZU

ILS 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**	

SHIMADZU

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

SHIMADZU

Some examples of method ATPs with no VCSB equivalent

4. Ammonia (as N), mg/L	Manual distillation [6] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993)	4500-NH3 B-2011		973.49. [3]
	Nesslerization			D1426-08 (A)	973.49. [3] I-3520-85. [2]
	Titration		4500-NH3 C-2011		
	Electrode		4500-NH3 D-2011 or E-2011	D1426-08 (B)	
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods		4500-NH3 F-2011		See footnote. [60]
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods	350.1, [30] Rev. 2.0 (1993)	4500-NH3 G-2011, 4500-NH3 H-2011		I-4523-85. [2]
	Automated electrode				See footnote. [7]
	Ion Chromatography			D6919-09	
	Automated gas diffusion, followed by conductivity cell analysis				Timberline Ammonia-001. [74]
38. Nitrate (as N), mg/L	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997)	4110 B-2011 or C-2011	D4327-03	993.30. [3]
	CIE/UV		4140 B-2011	D6508-10	D6508, Rev. 2. [54]
	Ion Selective Electrode		4500-NO3− D-2011		
	Colorimetric (Brucine sulfate)	352.1 (Issued 1971) [1]			973.50. [3] 419D [17] p. 28. [9]
	Spectrophotometric (2,6-dimethylphenol)				Hach 10206. [75]
	Nitrate-nitrite N minus Nitrite N (See parameters 39 and 40)				
39. Nitrate-nitrite (as N), mg/L	Cadmium reduction, Manual		4500-NO3− E-2011	D3867-04 (B)	
	Cadmium reduction, Automated	353.2, Rev. 2.0 (1993)	4500-NO3− F-2011	D3867-04 (A)	I-2545-90. [51]
	Automated hydrazine		4500-NO3− H-2011		
	Reduction/Colorimetric				See footnote. [62]
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997)	4110 B-2011 or C-2011	D4327-03	993.30. [3]
	CIE/UV		4140 B-2011	D6508-10	D6508, Rev. 2. [54]
	Enzymatic reduction, followed by automated colorimetric determination				I-2547-11, [72] I-2548-11, [72] N07-0003. [73]
	Spectrophotometric (2,6-dimethylphenol)				Hach 10206. [75]

SHIMADZU

Examples of ATPs with consensus method and EPA equivalents

23. Cyanide - Total, mg/L	Automated UV digestion/distillation and Colorimetry				Kelada-01. [55]
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry			D7511-12	
	Manual distillation with MgCl2, followed by any of the following:	335.4, Rev. 1.0 (1993) [57]	4500-CN– B-2011 and C-2011	D2036-09(A), D7284-13	10-204-00-1-X. [56]
	Flow Injection, gas diffusion amperometry			D2036-09(A) D7284-13	
	Titrimetric		4500-CN– D-2011	D2036-09(A)	p. 22. [9]
	Spectrophotometric, manual		4500-CN– E-2011	D2036-09(A)	I-3300-85. [2]
	Semi-Automated [20]	335.4, Rev. 1.0 (1993) [57]			10-204-00-1-X, [56] I-4302-85. [2]
	Ion Chromatography			D2036-09(A)	
	Ion Selective Electrode		4500-CN– F-2011	D2036-09(A)	
24. Cyanide - Available, mg/L	Cyanide Amenable to Chlorination (CATC); Manual distillation with MgCl2, followed by Titrimetric or Spectrophotometric		4500-CN– G-2011	D2036-09(B)	
	Flow injection and ligand exchange, followed by gas diffusion amperometry [59]			D6888-09	OIA-1677-09. [44]
	Automated Distillation and Colorimetry (no UV digestion)				Kelada-01. [55]
24.A Cyanide - Free, mg/L	Flow Injection, followed by gas diffusion amperometry			D7237-10	OIA-1677-09. [44]
	Manual micro-diffusion and colorimetry			D4282-02	

SHIMADZU

Examples of new modified VCSB methods in process

- ASTM WK59699 Revision of D5673 - 16 Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
- ASTM WK66230 Revision of D3454 - 18 Standard Test Method for Radium-226 in Water
- ASTM WK75659 Revision of D5174 - 07(2013) Standard Test Method for Trace Uranium In Water by Pulsed-Laser Phosphorimetry
- Standard Methods 4500 – pH
- Standard Methods 4500 - Cl

SHIMADZU

Examples of new VCSB methods in process

- WK57556 Total Hardness of Water, Wastewater with Color Using Titration and Optical Spectroscopy as End Point Determination
- WK74312 Bioavailable Aluminum in Water with Suspended Solids
- WK77585 Available Sulfide in Water by Gas Extraction
- WK67788 Identification of Polymer Type and Quantity (Mass) Measurement of Microplastic Particles and Fibers in Waters with High-to-Low Suspended Solids Using Pyrolysis-Gas Chromatography/Mass Spectrometry: Py-GC/MS
- WK57480 Measuring Volatile Organic Compounds (VOCs) in Water utilizing Headspace Analysis with Gas Chromatography and Mass Spectrometry (Headspace GC/MS)
- WK54549 Determination of Pesticides, PCBs, and Polychlorinated Biphenyl Congeners in Aqueous Solution by Tandem GCMSMS
- WK67565 Spectroscopic Identification and Quantification of Microplastic Particles and Fibers in all High and Low Turbidity Water Matrices including Municipal Wastewater Using IR and Raman Spectroscopy.
- WK68866 Determination of Adsorbable Organic Fluorine in Waters and Waste Waters by Adsorption on Activated Carbon followed by Combustion Ion Chromatography
- WK73235 Determination of Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Cosolvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
- WK74011 Determination of Nitrosamines in Non-potable Water by Tandem Liquid Chromatography Mass Spectrometry (LCMSMS)

SHIMADZU

Conclusion:

- Brief overview of ATP and VCSB approach
- Both VCSB and EPA validation approach similar
- VCSB's work with EPA to standardize new or modified methods
- VCSB a way to get new methods with new parameters published

SHIMADZU

Any Questions?

William Lipps
wclipps@shimadzu.com

Shimadzu Scientific Instruments