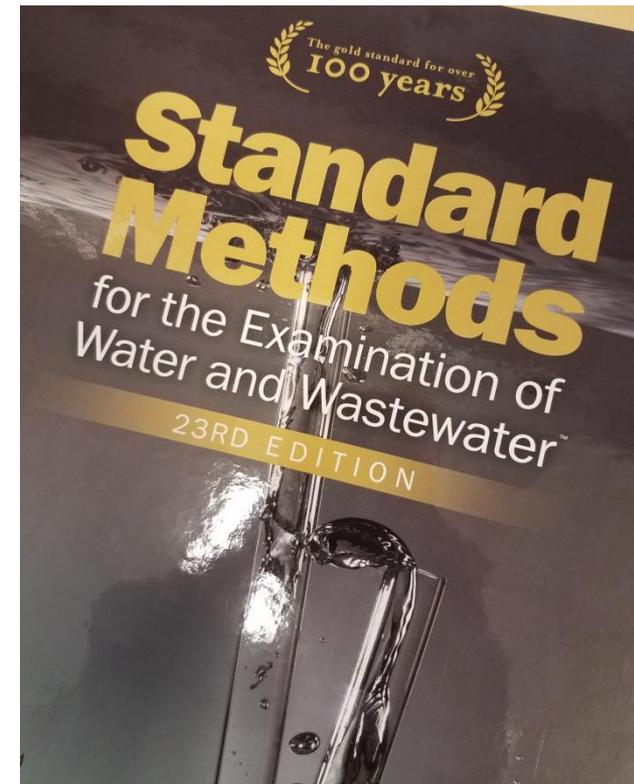




Andy Eaton, PhD, BCES
Technical Director
Joint Editorial Board-Chair

The Standard Methods Validation Process – Responding To Requests For Including New Methods



Standard Methods Axioms



- Most of the methods are “tried and true” and either turned into EPA methods or came from EPA methods.
 - **That does not mean however that all the “validation data” are present.**
- There are “new” methods that do get added to Standard Methods and we have to have guidelines for determining that those methods are acceptable.

Two Types of New Additions



- **Newer or different technologies designed to provide equivalent results to existing methods in the book.**
 - **Nitrate**
 - **TOC**

- **New analytes altogether**
 - **PPCPs**

Modifications to Existing Methods



- Even if a method has been in the book for “generations”, it doesn’t mean there are not errors that can creep in (or were there to begin with) or suggestions for improvements.
- Modifications must still be demonstrated to be effective, and from time to time the data in the method may need to be revisited (**e.g. low level amperometric method for chlorine – 4500CI-E**)

What About New Methods Being Proposed – Particularly by Vendors



- **Standard Methods is not intended to be a backdoor way for manufacturers to gain credibility for new instruments.**
- **Thus many years ago we developed some general guidelines for evaluation of new methods/semi-proprietary techniques.**

Basic Criteria for New Methods – Especially Relevant for Vendors



- The proposed method must have appeared in a peer-reviewed journal (not to include conference proceedings) **or** be based upon peer-reviewed technology.
- The proposed method must provide **comparative data with an approved method** if there is a current method for the parameter(s) of the subject method.

Basic Criteria for New Methods – Especially Relevant for Vendors



- The proposed method must **include data on accuracy and precision** that conform to the current descriptions in Part 1000 and/or the appropriate x020 Section of *Standard Methods*.
- The proposed method must contain **acceptable quality assurance/quality control procedures** that conform as above.

Basic Criteria for New Methods – Especially Relevant for Vendors



- Approval by other standards developing organizations (SDOs) **does not constitute grounds for inclusion** in *Standard Methods*, but may be considered by the Joint Editorial Board (JEB) as an acceptable alternative to publication in peer reviewed literature.
- Any method submitted for inclusion in *Standard Methods* must **first be reviewed and approved by the Joint Task Group (JTG)** for that section, and then approved by the **Part Coordinator and the JEB** per current *Standard Methods* procedures.

Basic Criteria for New Methods – Especially Relevant for Vendors



- The representative of a commercial manufacturer who has submitted a method for consideration **may serve on the JTG, but not as the chair**; said JTG must have a majority of members that are not employees of the submitting company.
- *Standard Methods* does **not typically endorse or adopt methods that use proprietary chemicals or devices for which technical knowledge** regarding safety, health, technical basis for performance and similar information **is not known.**

Basic Criteria for New Methods – Especially Relevant for Vendors



- **Proprietary methods may be considered for unique applications**, at the discretion of the JEB, if they fill a necessary demand in some specific application, such as rapid field methods, inline or instream testing, or high priority pollutants for which otherwise satisfactory methods are not available.

Applying These Criteria to Different Methods



Criterion	6810	5310E-inprocess	4500CL-E
analytes	PPCPs	TOC	chlorine residual
type	new	equivalent	legacy method
peer reviewed method	<input checked="" type="checkbox"/>	TBD	<input checked="" type="checkbox"/>
peer reviewed technology	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
comparative data	<input checked="" type="checkbox"/>	TBD	??
P&A data as per 020 sections	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	??
contains QA/QC	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Approved by others already?	WaterRF	no	<input checked="" type="checkbox"/>
JTG/PC/JEB approval	<input checked="" type="checkbox"/>	TBD	<input checked="" type="checkbox"/>
no manufacturer as chair	<input checked="" type="checkbox"/>	member	<input checked="" type="checkbox"/>
proprietary?	No	Yes	No
Urgent need?	Yes	No	Yes

What are the Issues with Each of These Methods?



6810-PPCPs	5310E – TOC Supercritical oxidation	4500-CL-E Amperometric Titration
22nd edition new method; multi lab validation; LCMRL determinations	manufacturer new method; study plan reviewed by JEB/PC	Question about reliability of MDL in method; need to re-evaluate



- Method evaluated as part of WaterRF project 4167. Round robin study of PPCPs
- After determining that this was one of the better performing methods in multiple aqueous matrices, there was a multi-lab evaluation of LCMRL and IDOC
- Method written in SM format.
- Sent out to ballot, and received no negatives.
- All back up validation information is in 4167 report.

5310E – TOC by Supercritical Water Oxidation – in process



- **GE developed instrument**
- **Prepared study plan for review by SM JEB/PC**
- **Several iterations of study plan to make it more relevant for the “audience”.**
- **Includes comparison with existing SM method (5310B).**
- **Final report to be submitted to SM for review**
- **Study in process**
- **Outline of study plan follows**

5310E Study Plan- Method Comparison



	SCWO (Sievers InnovOx)	High-Temp Combustion (5310B) (Shimadzu L-Series)
Modes of Operation	NPOC, TOC, TC, IC	NPOC, TOC, TC, IC
Concentration Range	0.5 – 50,000 mg/L	4µg/L – 30,000 mg/L
Matrix Types	Wastewater, drinking water, seawater	Wastewater, drinking water, seawater
Detection	Non-dispersive Infrared Radiation (NDIR)	Non-dispersive Infrared Radiation (NDIR)
Inorganic Carbon (IC) Removal	Sparging after sample acidification	Sparging after sample acidification
Oxidation	Sample and reagents (acid & oxidizer) are heated and pressurized in a reactor to 375°C and 3200 psi such that water reaches its critical point. The properties of supercritical water combined with the presence of the oxidizer reagent allow for efficient oxidation of organics to carbon dioxide.	Acidified sample is sent to a heated combustion chamber (680°C) containing an oxidative catalyst such as platinum. Organic molecules are oxidized to carbon dioxide.

Study Plan for 5310E



- **Introduction**
- **Method summary**
- **Instrument settings details**
- **Single lab validation**
 - **Precision and bias**
 - **Analysis of unknown samples**
 - **determination of method ruggedness by varying settings**
- **Direct Comparison with 5310B**
- **Collaborative testing**

Large Suite of Matrices and Types of TOC



Matrix Types	Compounds	Standard Additions (mg/L)
Reagent water	KHP	0
Seawater/brine ¹	Sucrose	1
Wastewater ²	Acetic acid	5
Municipal Water ³	Urea	10
	Nicotinic acid	100
	Pyridine	500 ⁴
	SDBS	
	2-propanol	
	Octoxynol-9	
	Acetonitrile	
	<i>n</i> -butanol	
	Leucine	
	Tartaric acid	
	1,10-phenanthroline	
	1-glutonic acid	

Comparison Between Methods (5310E and 5310B)



- **5 aliquots/5 replicates/ multiple matrices as below. Enough for statistical evaluation**

Matrix Type	Compound	Spike addition
Reagent Water	KHP	0
Seawater/brine	Sucrose	1
Wastewater		5
Muni water		10
		100

Collaborative Testing Is Also Extensive



- **Similar to single lab study, but**
 - **4 participating labs**
 - **2 analysts per lab**
 - **5 replicates per sample**

Matrix Types	Compounds	Standard Additions (mg/L)
Reagent water	KHP	0
Seawater/brine ¹	Sucrose	1
Wastewater ²		5
Municipal Water ³		10
		100
		500 ⁴

5310E Will Ultimately be a Well Validated Method



- **More initial testing than most of the methods that are in Standard Methods**
- **But there was still a lot of back and forth on the study plan.**



- **The method has a 10 ppb detection level listed, but it is such an old method that the validation data are difficult to track down, but ostensibly came from Hach originally.**
- **Labs using the method in NJ are unable to get down to a 10 ppb MDL, but changing that to 20 ppb (achievable) is a technical change, so we need data.**
- **NJ will have multiple labs do MDL determinations and submit to SM for review.**

So What Else Are We Doing?



- We are revisiting sections 1030 and 1040 to try to develop some more standardized validation guidelines. **(Thanks William Lipps for spearheading that....)**
- This will help differentiate between the different scenarios, particularly when it comes to approving methods for potential use in compliance monitoring **(remember that compliance monitoring is not the only thing that Standard Methods is used for).**

Conclusions



- **One size does not fit all when it comes to method validation for Standard Methods.**
- **Having a large number of legacy methods can be challenging.**
- **The newer a method, the more likely it is to have some pretty good validation.**
- **The Standard Methods balloting system also helps to identify issues (after the fact).**

Any Questions?



Andy Eaton
andyeaton@eurofinsus.com
626.386.1125

Eurofins Eaton Analytical, Inc.
www.eurofinsus.com

