The Method Update Rule Potable vs. Non-Potable Water - What Methods are being reported for Accreditation

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Topics to Cover

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- Background of the EPA's Method Update Rule (MUR)
- Methods & analytes selection process
- Data Gathering
- Data analysis for Water Supply (WS) and Water Pollution (WP) Programs
- Comparison of reporting rates of approved methods between the WS and WP programs
- Comparison of performance of cross over methods between WS and WP programs
- Comparison of concentration ranges between WS and WP programs
- Conclusions

MUR Background Information

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- What is the MUR?
  - The "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures"
  - OR the "MUR"
- MUR Timeline
  - August 2003 & April 2004
    - The proposed method changes were published by EPA for comment
  - July 2006
    - EPA Administer signed the final MUR
  - March 12, 2007 final MUR published

MUR Background Information

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- The MUR updates the list of approved methods allowed to be utilized for the following programs:
  - Analysis of Pollutants under the Clean Water Act (CWA); 40 CFR Part 136
  - Safe Drinking Water Act (SDWA)
    - National Primary Drinking Water Regulations; 40 CFR Part 141.23
    - Secondary Drinking Water Regulations; 40 CFR Part 143

Data Gathering

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- A comparison between these sources was used to determine which analytes and methods resided in both the SDWA and CWA as a starting list of analytes and methods to be examined

- Analytical methods also had to be new methods to either the SDWA and/or the CWA

- The majority of the changes were to the inorganic methods for the SDWA and CWA

Data Gathering

- The following crossover methods were selected:

Program	Analyte Group	Method Description	Number of Analytes
CWA	Metals	EPA 200.8 (ICP-MS)	19 metals
	Metals	EPA 200.9 (SFGTAA)	18 metals
	Mercury	EPA 245.7 (CFAFS)	Mercury specific
	Anions	EPA 300.0 (IC)	8 anions
		EPA 300.1 (IC)	8 anions
	Cyanide	EPA 335.4	Cyanide specific
SDWA	Anions	EPA 300.0	7 anions

Analyte Selection

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- The list of analytes to be examined was further narrowed to include a subset of transition metals, alkali earth metals, and trace metals.

- The criteria for these metals were whether the MUR added new analytical methods to one of the programs and/or they were regulated by the USEPA.

- The list of metals was arsenic, beryllium, chromium, copper, lead, selenium, and zinc.

- The 40 CFR Part 141.23 regulates arsenic, beryllium, mercury, chromium, and selenium and the 40 CFR Part 141.89 regulates copper, and lead.

Analyte Selection (con't)

- A list of anions were selected that crossed between the two programs; chloride, fluoride, sulfate.
- Cyanide was added due to the number of methods changes that were incorporated into the MUR.
- Mercury was added due to it's regulatory standing and the additional methods that the MUR approved.

Crossover Methods by Analyte

- The analytes were each reviewed between the SDWA and CWA to determine specific analytical methods that crossed between the programs for each analyte.

Analyte	Methods
Arsenic	EPA 200.7, EPA 200.8, EPA 200.9 SM3113B, SM3120B
Beryllium	EPA 200.7, EPA 200.8, EPA 200.9, SM3113B, SM3120B
Chromium	EPA 200.7, EPA 200.8, EPA 200.9 SM3113B, SM3120B
Copper	EPA 200.7, EPA 200.8, EPA 200.9, SM3111B, SM3113B, SM3120B
Lead	EPA 200.7, EPA 200.8, EPA 200.9, SM3111B, SM3113B, SM3120B
Selenium	EPA 200.8, EPA 200.9, SM3113B, SM3114B
Zinc	EPA 200.7, EPA 200.8, SM3111B, SM3120B
Mercury	EPA 200.8, EPA 245.1, EPA 245.2, & SM3112B
Cyanide	EPA 335.4, SM4500CN-C,E,F,G
Chloride	EPA 300.0, EPA 300.1, SM4110B, SM4500-Cl B,D
Fluoride	EPA 300.0, EPA 300.1, SM4500-F B, C, D, E, SM4110B
Sulfate	EPA 300.0, EPA 300.1, SM4500-SO4 C, D, SM4110B

Data Gathering

- The implementation of the MUR was in March 2007.
- The data was gathered two years prior to this date and the study data the following year post implementation
- These represented 23 studies prior to the MUR and 11 studies post MUR for both water pollution (WP) and the water supply (WS) proficiency testing studies
- The WP proficiency testing program supports the CWA.
- The WS proficiency testing program supports the SDWA.

Data Gathering

- The data that was extracted included; study identifier, customer identifier, methods description, technology code, assigned value, laboratory reported value, evaluation, and laboratory percent recovery.

- The data collected was divided into four parts; WS pre-MUR implementation, WS post-MUR implementation, WP pre-MUR implementation, and WP post-MUR implementation.

- By breaking the data into these major component parts, we would be able to isolate reporting trends, methods usage, method performance, as well as, make comparisons between the WS and WP programs

Data Analyses

- Once the data was collected the percent mean recovery, percent standard deviation, failure rate and the percent of total reported methods was calculated for each analyte for each of the methods identified.

- The data was first reviewed as analyte groups for the reported methods to determine at this level if there was a difference between the two time frames, pre and post MUR implementation, for each study types, WS and WP.

Data Analyses

- Special consideration was given to Standard Methods since each of the analytes has little different series referencing different technologies.
- The Standard Methods were broken down into the different technologies for data analysis.

Standard Method	Technology	Technology Code
SM 4500 – Cl- B, C & E	Titration/Colorimetric	TITR/Color
SM 4500 – Cl- D	Ion Selective Electrode	ISE
SM 4500 – F- C	Ion Selective Electrode	ISE
SM 4500 – F- D & E	Titration/Colorimetric	TITR/Color
SM 4500 – SO4- C & D	Gravimetric	Grav
SM 4500 – SO4- E	Turbimetric	Turb
SM 4500 – SO4- F	Titration/Colorimetric	TITR/Color

Data Analysis – WS Metals

- WS Total Metals

WS Total Metals			
		Pre MUR WS	Post MUR WS
Analyte Name	**Method**	**Method n%**	**Method n%**
Total Metals	Total EPA 200.7	28.4%	27.4%
Total Metals	Total EPA 200.8	35.2%	41.4%
Total Metals	Total EPA 200.9	9.84%	7.85%
Total Metals	Total Other	9.87%	3.89%
Total Metals	Total SM 3111 B	5.43%	5.12%
Total Metals	Total SM 3113 B	12.7%	11.6%
Total Metals	Total SM 3120 B	0.815%	0.581%

Data Analysis – WS Total Anions

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- WS Total Anions

WS Total Anions			
		Pre MUR WS	**Post MUR WS**
Analyte Name	**Method**	**Method n%**	**Method n%**
Total Anions	Total EPA 300.0	47.7%	58.7%
Total Anions	Total EPA 300.1	1.97%	3.82%
Total Anions	Total Other	13.5%	12.7%
Total Anions	Total SM 4110 B	6.72%	2.75%
Total Anions	Total Grav	1.21%	1.21%
Total Anions	Total ISE	20.1%	2.00%
Total Anions	Total TITR/Color	9.21%	14.7%
Total Anions	Total Turb	3.11%	3.77%

Data Analysis – WS Mercury

- WS Mercury

WS Mercury			
		Pre MUR WS	Post MUR WS
Analyte Name	**Method**	**Method n%**	**Method n%**
Mercury	EPA 200.8	17.90%	22.10%
Mercury	EPA 245.1	57.70%	52.70%
Mercury	EPA 245.2	7.38%	7.91%
Mercury	Other	5.60%	6.50%
Mercury	SM 3112 B	11.50%	10.70%

Data Analysis – WS Cyanide

- WS Cyanide

WS Cyanide			
		Pre MUR WS	Post MUR WS
Analyte Name	**Method**	**Method n%**	**Method n%**
Cyanide	EPA 335.4	30.3%	31.2%
Cyanide	Other	18.9%	18.3%
Cyanide	SM 4500 CN C	3.52%	1.52%
Cyanide	SM 4500 CN E	39.0%	39.8%
Cyanide	SM 4500 CN F	7.92%	8.38%
Cyanide	SM 4500 CN G	0.377%	0.761%

Data Analysis – WP Total Metals

- WP Total Metals

WP Total Metals			
		Pre WP	Post WP
Analyte Name	Method	Method n%	Method n%
Total Metals	Total EPA 200.7	29.2%	27.7%
Total Metals	Total EPA 200.8	19.0%	19.9%
Total Metals	Total EPA 200.9	2.03%	1.88%
Total Metals	Total Other	39.8%	39.1%
Total Metals	Total SM 3111 B	3.10%	3.86%
Total Metals	Total SM 3113 B	4.78%	5.19%
Total Metals	Total SM 3120 B	2.10%	2.28%

Data Analysis – WP Total Anions

- WP Total Anions

WP Total Anions			
		Pre WP	Post WP
Analyte Name	**Method**	**Method n%**	**Method n%**
Total Anions	Total EPA 300.0	40.5%	40.1%
Total Anions	Total EPA 300.1	0.360%	1.17%
Total Anions	Total Other	34.4%	28.6%
Total Anions	Total SM 4110 B	1.72%	2.65%
Total Anions	Total Grav	1.10%	1.07%
Total Anions	Total ISE	6.56%	8.18%
Total Anions	Total TITR/Color	13.3%	16.1%
Total Anions	Total Turb	1.90%	2.01%

Data Analysis – WP Total Mercury

- WP Mercury

WP Mercury			
		Pre WP	Post WP
Analyte Name	**Method**	**Method n%**	**Method n%**
Mercury	EPA 200.8	6.00%	6.19%
Mercury	EPA 245.1	47.7%	43.5%
Mercury	EPA 245.2	6.18%	5.85%
Mercury	Other	33.1%	37.0%
Mercury	SM 3112 B	6.97%	7.42%

Data Analysis – WP Cyanide

- WP Cyanide

WP Cyanide			
		Pre WP	Post WP
Analyte Name	**Method**	**Method n%**	**Method n%**
Cyanide	EPA 335.4	16.6%	21.4%
Cyanide	Other	51.8%	38.9%
Cyanide	SM 4500 CN C	2.94%	2.14%
Cyanide	SM 4500 CN E	26.6%	36.3%
Cyanide	SM 4500 CN F	0.718%	1.14%
Cyanide	SM 4500 CN G	0.287%	0.143%

Analyte Specific Changes

- Metals across the analyte list showed an increase of 5 % to 10% in the usage of EPA 200.8 for WP and WS proficiency testing studies.

- Anion specific changes in participation

WP Analyte Participation Changes				
		Pre MUR	Post MUR	
Analyte Name	**Method**	**Method n%**	**Method n%**	**Delta**
Chloride	SM 4110 B	1.45%	16.6%	15.1%
Chloride	SM 4500 Cl- E	5.73%	22.4%	16.7%
Fluoride	SM 4500 F- C	22.0%	27.6%	5.56%

Data Analysis – Analyte Specific

- The MUR change removing approval for methods for chloride and fluoride are the most likely reason for laboratories to be shifting to these previously approved methods.

- For chloride, the following methods were deleted; EPA 325.1, EPA 325.2, and EPA 325.3.

- For fluoride, the following methods were deleted; EPA 340.1, EPA 340.2, and EPA 340.3.

Comparison WS and WP Programs

- The next step in examining the data is to compare the data gathered for the performance of the methods as to how they relate between the WS and WP programs.

- The WS and WP programs vary in several different ways.
  - The concentration ranges between the two programs are different.
  - The acceptance criteria for the WS study are largely based on fixed percentages found in the 40 CFR Part 141, while the WP acceptance criteria are largely based on regression equation criteria found in the TNI Fields of Proficiency Testing (FOPT).
  - The WS acceptance criteria are based on a ±2 standard deviation or 95% confidence interval, while the WP program is based on a ±3 standard deviation or 99% confidence interval.

WS-WP Concentration Range Comparison

		WP TNI Ranges		WS TNI Ranges		Concentration Overlap	
Analyte	**Units**	**Low**	**High**	**Low**	**High**	**Low**	**High**
Arsenic	µg/L	70	900	5	50	None	
Beryllium	µg/L	8	900	1	10	8	10
Chromium	µg/L	17	1000	10	200	17	200
Copper	µg/L	40	900	50	2000	50	900
Lead	µg/L	70	3000	5	100	70	100
Selenium	µg/L	90	2000	10	100	90	100
Zinc	µg/L	100	2000	400	2500	400	2000
Mercury	µg/L	2	30	0.5	10	10	30
Chloride	mg/L	35	275	5	100	35	100
Fluoride	mg/L	0.3	4	1	8	1	4
Sulfate	mg/L	5	125	5	500	5	125

WS-WP Concentration Range Comparison

- Very few of the analytes listed above have overlapping concentration ranges.
- Where the concentration ranges do overlap it is typically a narrow region of the overall concentration range.
- Makes combining the WS and WP programs difficult given the narrow window in which the ranges are established.

Method Performance by Program

- Focus on examining each of the programs separately and then compare the data collected for method performance based on the percent standard deviation.
- The percent standard deviation is a very good indicator of the variability of the analyses for each of the methods in each of the programs.
- By program compare the expected standard deviation to the calculated percent standard deviation.
- Then perform a comparison between programs of the lowest concentration acceptance criteria to the calculated percent standard deviation.

WP Standard Deviation Comparison

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Analyte Name	Low Concentration	Expected Low Stand Deviation	High Concentration	Expected High Stand Deviation	WP Calculated Stand Deviation
Arsenic	70	7.33%	900	5.42%	11.4%
Beryllium	8	8.84%	900	4.68%	12.0%
Chromium	17	9.02%	1000	4.27%	12.4%
Copper	40	6.06%	900	3.09%	9.66%
Lead	70	7.37%	3000	3.86%	11.9%
Selenium	90	7.34%	2000	6.13%	17.3%
Zinc	100	6.08%	2000	4.71%	11.3%
Mercury	2	13.1%	30	12.4%	17.9%
Chloride	35	5.66%	275	4.37%	8.76%
Fluoride	0.3	17.7%	4	5.22%	10.6%
Sulfate	5	14.0%	125	5.15%	16.9%
Cyanide	0.1	31.2%	1	11.6%	18.0%

WS Standard Deviation Comparison

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Analyte Name	Low Concentration	Expected Low Stand Deviation	High Concentration	Expected High Stand Deviation	WS Calculated Stand Deviation
Arsenic	5	15.0%	50	15.0%	10.6%
Beryllium	1	7.50%	10	7.50%	13.6%
Chromium	10	7.50%	200	7.50%	13.2%
Copper	50	5.00%	2000	5.00%	8.34%
Lead	5	15.0%	100	15.0%	10.6%
Selenium	10	10.0%	100	10.0%	12.3%
Zinc	400	5.00%	2500	5.00%	6.07%
Mercury	0.5	15.0%	10	15.0%	19.5%
Chloride	5	15.2%	100	4.43%	9.56%
Fluoride	1	5.00%	8	5.00%	6.74%
Sulfate	5	17.3%	500	5.55%	7.21%
Cyanide	0.1	12.5%	0.5	12.5%	13.0%

Standard Deviation Comparison between Study Types

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Analyte Name	WS Expected Standard Deviation	Calculated WS Standard Deviation	WP Expected Standard Deviation	Calculated WP Standard Deviation
Arsenic	15.0%	10.6%	7.33%	11.4%
Beryllium	7.50%	13.6%	8.84%	12.0%
Chromium	7.50%	13.2%	9.02%	12.4%
Copper	5.00%	8.34%	6.06%	9.66%
Lead	15.0%	10.6%	7.37%	11.9%
Selenium	10.0%	12.3%	7.34%	17.3%
Zinc	5.00%	6.07%	6.08%	11.3%
Mercury	15.0%	19.5%	13.1%	17.9%
Chloride	15.2%	9.56%	5.66%	8.76%
Fluoride	5.00%	6.74%	17.7%	10.6%
Sulfate	17.3%	7.21%	14.0%	16.9%
Cyanide	12.5%	13.0%	31.2%	18.0%

Standard Deviation Comparison between Study Types

- Analyte differences between study types

Analyte Name	Calculated WS Standard Deviation	Calculated WP Standard Deviation	Delta Between Calculated WS & WP
Selenium	12.3%	17.3%	5.00%
Zinc	6.07%	11.3%	5.23%
Fluoride	6.74%	10.6%	3.86%
Sulfate	7.21%	16.9%	9.69%
Cyanide	13.0%	18.0%	5.00%

Acceptance Criteria Comparison

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- The acceptance criteria between the WS and WP programs vary in regulatory focus.
  - The concern for public health is the basis for determining the WS program concentration ranges and acceptance criteria.
  - The overriding concern for setting action levels for the NPDES program that controls discharge of treated effluent into US waterways is the priority for setting limits for the WP program.

Acceptance Criteria Comparison

- The WP acceptance criteria note the expected standard deviations for the high concentrations are very different than the WS expected standard deviations. This is a combined effect of the regression equation and the concentration range.

- When the lower expected WP concentration standard deviation is comparable to the WS expected standard deviation, they are quite comparable.

Standard Deviation Comparison between Study Types

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- The calculated standard deviations are also quite comparable between the analyte groups, for example the most of the metals standard deviations for WP are comparable to those in the WS metals analyte group.

- This is not to be unexpected considering the percentages of laboratories that reported results were both study types.

- However, with the concentration ranges having little overlap, there are going to be differences in the ability of the instrumentation and analytical capabilities of the methods to quantify at both the low end and high end of a working calibration range.

Laboratory Participation Data

- How many laboratories crossover between study types?

Percentage of Laboratories with Dual Participation

Analyte	Method	% WP Cross	% WS cross
Arsenic	EPA 200.8	60.8%	50.2%
Beryllium	EPA 200.8	60.8%	52.4%
Chromium	EPA 200.8	58.1%	51.1%
Copper	EPA 200.8	54.8%	48.5%
Lead	EPA 200.8	60.5%	51.9%
Mercury	EPA 200.8	66.7%	29.9%
Selenium	EPA 200.8	60.2%	51.7%
Zinc	EPA 200.8	54.6%	52.7%
Cyanide	EPA 335.4	54.5%	66.7%
Chloride	SM 4110 B	27.3%	37.5%
Chloride	SM 4500 Cl E	30.8%	70.6%
Fluoride	EPA 300.0	59.6%	50.5%
Fluoride	SM 4500 F C	53.7%	23.9%
Sulfate	EPA 300.0	55.4%	56.9%

Method Frequency Conclusions

- For both the WS and WP programs there is evidence of changes in the reporting frequency of methods.
- The methods that showed the greatest increase in reporting were EPA 200.8 for all metals analyses, including mercury, and EPA 300.0 for all anions.
- These methods represent advancements in technology and allow efficiencies to be gained in the laboratory performance and improved laboratory accuracy.

Method Frequency Conclusions

- Other methods such as EPA 200.9, SM 3111 B, and the titrimetric/colorimetric methods for anions showed no change between the pre and post MUR timeframe.
- EPA 300.0 and EPA 300.1 were newly approved for the WP program with the publication of the MUR, though their participation rates showed little or no change upon approval.
- The deletion of many of EPA's WP wet chemistry methods caused a shift in the use of Standard Methods, as seen by the increase in the reporting of Standard Methods for chlorine and fluoride methods.

Method Frequency Conclusions

- A large drop in reporting frequency for the ISE methods for anions was also observed, in conjunction with the increase in the reporting of Standard Methods.
- Laboratories are much quicker to adopt methods that are more efficient and are more technologically advanced.
- Regulatory agencies are quicker to recognize the advancements that laboratories are making and the are willing to accredit laboratories for these more efficient and advanced methods.

Method Frequency Conclusions

- Overall, the changes in the MUR had more of a dramatic effect on laboratories reporting methods that were deleted as opposed to laboratories adopting newer methods.

WS - WP Comparison Conclusions

- When comparing the two programs, WP and WS, to determine whether the cross over methods and selected analytes could be combined into a single proficiency testing study several barriers were observed.

- The first barrier was the concentration ranges between the two programs. The data shows that there are very limited instances where the two concentration ranges have enough overlap to be viable for combining the two programs.

WS - WP Comparison Conclusions

- The next barrier that was recognized was that the acceptance criteria are also quite different.
- The acceptance criteria for the WP program are based on ± 3 expected standard deviations.
- The acceptance criteria are based on the on a tighter ± 2 standard deviations.

WS - WP Comparison Conclusions

- Though this may lead to the belief that using the WS limits for a single criteria between the two programs.
- The WS and WP program acceptance criteria are regulatory based on completely separate assumptions.
- The WS limits are public health based for drinking water
- The WP acceptance criteria are focused on NPDES action limits

WS - WP Comparison Conclusions

- The two acceptance requirements serve very different regulatory purposes, one to ensure public health in drinking water for WS and to ensure that waterways are free from pollutants from treated effluent.

- The overall data quality objectives are much different between the two programs.

WS - WP Comparison Conclusions

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- The last barrier is the performance of the methods and instrumentation.
- As the data shows with sulfate, selenium, zinc, and cyanide, there are differences in analytical capability and data quality between the two programs.
- Though few analytes may present a cross over opportunity, the majority of the analytes will have too many significant barriers to over come to be combined into a single proficiency testing program.

WS - WP Comparison Conclusions

- The next steps in evaluating the possible combining of the WS and WP programs into a single proficiency testing program would include further data analysis of all of the analytes listed between the two programs.

- This data set was small and only represents one proficiency testing provider's data. A larger study with data from all of the proficiency testing providers would reflect a more accurate national picture of laboratory performance.

The end

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