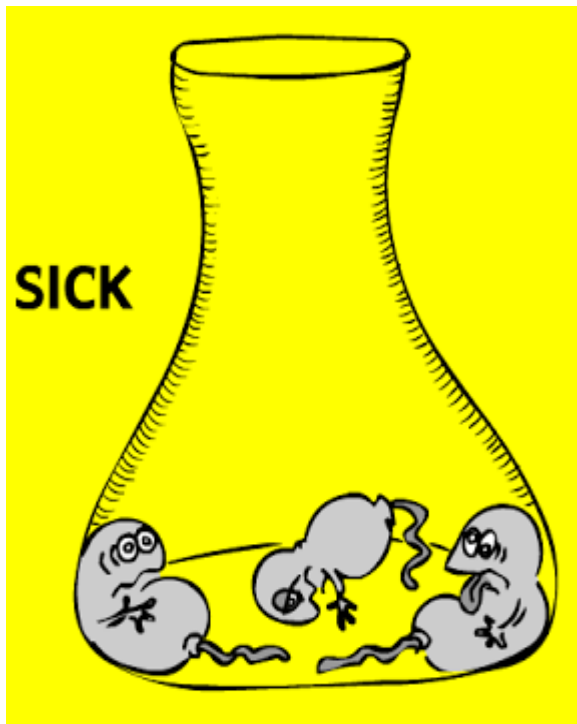


Disinfectants/Disinfection Byproducts – Rules and Requirements

US Environmental Protection Agency
Office of Groundwater and Drinking Water
Technical Support Center
Cincinnati, Ohio

Disinfection



One of the most important steps in protecting public health involves adding disinfectants to finished water to inactivate pathogenic microbes.



Disinfection Byproducts:



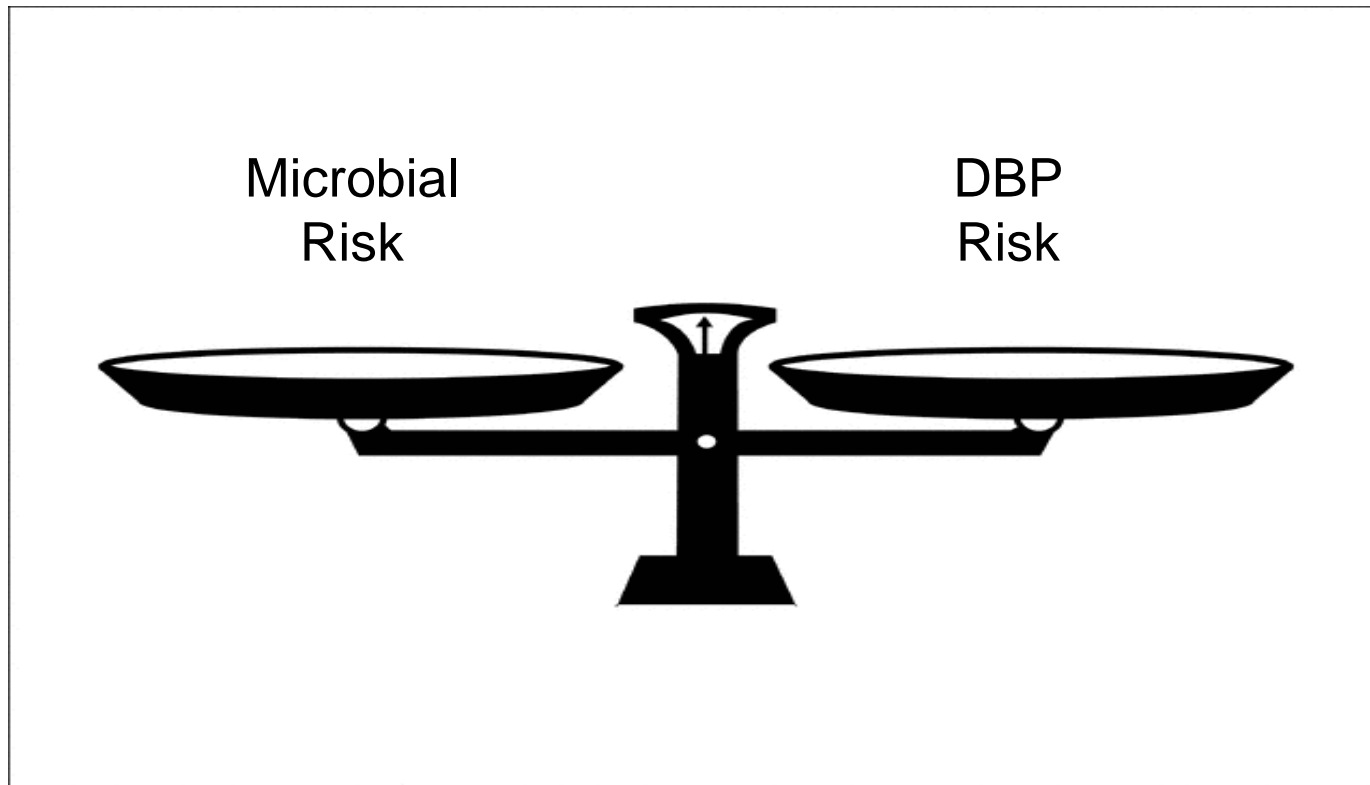
HAAs



Chlorite

Bromate

The Balancing Act





History Lesson – D/DBP 101

- 1989 – Surface Water Treatment Rule (SWTR) [40 CFR Subpart H]
 - Upside:
 - Increased use of disinfectants in surface water systems
 - Established a minimum residual disinfectant level at the entry to the distribution system (0.2 mg/L) [40 CFR 141.72(a)(3) and 141.72(b)(2)]
 - Downside:
 - Increased use of disinfectants increased exposure to disinfection byproducts



- 1992
 - EPA began a Regulatory Negotiation process to develop the Disinfectants/Disinfection Byproducts Rule. Negotiation committee included representatives from:
 - Public utilities
 - State and local agencies
 - Environmental and consumer groups
 - Data gaps
 - DBP health effects
 - DBP and microbial occurrence
 - Treatment





Regulatory Negotiation Committee recommended development of three rules:

- Information Collection Rule
- Two-staged regulation for disinfection byproducts
- “Interim” Enhanced Surface Water Treatment Rule (IESWTR)



- 1996 – Information Collection Rule (ICR)
 - 18-month monitoring period (1997-1998)
 - Monitor for various bacteria, viruses and protozoa in source waters
 - Monitor influent water quality parameters (e.g., organic matter)
 - Monitor for disinfectants and disinfection byproducts
 - Conduct treatment studies



- 1996 – Amendments to the Safe Drinking Water Act
 - Congress affirmed the phased microbiology/D-DBP rulemaking strategy
 - SDWA 1412(b)(2)(C) specifies promulgation of an Interim Enhanced Surface Water Treatment Rule, a Final Enhanced Surface Water Treatment Rule, a Stage 1 Disinfectants and Disinfection Byproducts Rule, and a Stage 2 Disinfectants and Disinfection Byproducts Rule.
 - Schedule established for promulgating rules



- 1998 Final - Stage 1 D/DBP Rule and IESWTR
 - D/DBP Rule
 - Maximum Residual Disinfectant Levels (MRDLs):
 - Chlorine (4 mg/L)
 - Chloramines (4 mg/L)
 - Chlorine Dioxide (0.8 mg/L)
 - Set MCLGs/MCLs for total trihalomethanes (TTHMs), haloacetic acids (HAA5), chlorite, bromate
 - TTHMs (MCL, 80 µg/L)
 - HAA5 (MCL, 60 µg/L)
 - Chlorite (MCL, 1000 µg/L)
 - Bromate (MCL, 10 µg/L)
 - MCL compliance for TTHMs, HAA5 and bromate based on a RAA that averages all samples collected within the distribution system over a one-year period



- 1998 – Stage 1 D/DBP & IESWTR (Cont.)
 - Bromate monitoring only required for systems disinfecting with ozone; chlorite monitoring only required for systems disinfecting with chlorine dioxide
 - Reduce precursor compounds (TOC)
 - Develop 2nd stage of DBP regulations when more health effects & water quality monitoring data become available
- “Interim” Enhanced Surface Water Treatment Rule (1998) – Large water systems
 - 2002 – LT1 ESWTR extends *Cryptosporidium* protection to small systems



- 2006 – Stage 2 D/DBP Rule and LT2 ESWTR
 - MRDLs and MCLs unchanged
 - Targets sites within distribution system with highest DBP levels
 - MCL compliance for TTHMs and HAA5 based on a locational running annual average (LRAA) not a distribution system-wide RAA
 - Established regulatory Minimum Reporting Limits (MRLs) for compliance reporting on CCRs
 - LT2 ESWTR
 - Monitoring source waters for *Cryptosporidium* to determine treatment



Laboratory Certification Considerations

- DBPs
 - MCL compliance samples must be analyzed in certified laboratories
- Disinfectants (residual and MRDLs), water quality parameters, daily chlorite operational control analyses
 - Must use approved methods, but the analyses can be performed by ‘a party approved by EPA or the State’ (i.e., certified laboratory analysis is not required)



Approved Methods for Disinfection By-Products



Approved Methods for Monitoring Disinfection Byproducts - TTHMs 40 CFR 141.131(b)(1) & Appendix A to Subpart C of Part 141				
Methodology	EPA Method	Standard Methods	Standard Methods Online	ASTM
P&T/GC/EICD & PID	502.2 (rev. 2.1)			
P&T/GC/MS	524.2 (rev. 4.1), 524.3, 524.4			
LLE/GC/ECD	551.1			

Approved Methods for Monitoring Disinfection Byproducts – HAA5 40 CFR 141.131(b)(1) & Appendix A to Subpart C of Part 141				
Contaminant/Methodology	EPA Method	Standard Methods	Standard Methods Online	ASTM
LLE (diazomethane)/GC/ECD		6251 B (19 th -22 nd)	6251 B-94,-07	
SPE (acidic MeOH)/GC/ECD	552.1			
LLE (acidic MeOH)/GC/ECD	552.2, 552.3			
IC/ESI/MS/MS	557			



Approved Methods for Monitoring Disinfection Byproducts – Bromate 40 CFR 141.131(b)(1) & Appendix A to Subpart C of Part 141				
Methodology	EPA Method	Standard Methods	Standard Methods Online	ASTM
IC/Conductivity	300.1			D6581-00; -08 A,B
2-D IC/Conductivity	302.0			
IC/Post-Column Reaction	317.0 (rev. 2.0), 326.0			
IC/ICP-MS	321.8			
IC/ESI/MS/MS	557			
Approved Methods for Monitoring Disinfection Byproducts – Chlorite 40 CFR 141.131(b)(1) & Appendix A to Subpart C of Part 141				
Methodology	EPA Method	Standard Methods	Standard Methods Online	ASTM
Monthly Compliance Monitoring:				
IC/Conductivity	300.0 (rev. 2.1); 300.1			D6581-00; -08 A,B
IC/Post-Column Reaction	317.0 (rev. 2.0), 326.0			
Daily Monitoring:				
IC/Conductivity	300.0 (rev. 2.1); 300.1			D6581-00; -08 A,B
IC/Post-Column Reaction	317.0 (rev. 2.0), 326.0			
Spectrophotometric	327.0 (rev. 1.1)			
Amperometric Titration		4500-ClO ₂ E (19 th -22 nd)	4500-ClO ₂ E-00	



Chlorite – Monthly and Daily Monitoring

- Monthly MCL Compliance
 - 3-sample set collected within distribution system
 - Must be analyzed at a certified laboratory
 - Ion chromatography must be used (40 CFR 141.131(b)(1), footnote 8)
- Daily operational control check
 - Sample collected daily at entrance to distribution system
 - Does not have to be analyzed at a certified laboratory
 - Not for compliance – can trigger monthly distribution system monitoring



Bromate

- Stage 2 D/DBP Rule
 - Bromate MCL compliance based on RAA for samples collected at the entrance to the distribution system
 - Significant change relative to Stage 1 Rule for reduced monitoring
 - Stage 1 Rule: reduced monitoring based on raw water bromide concentration ($\text{Br}^- < 50 \mu\text{g/L}$)
 - Stage 2 Rule: more sensitive bromate methods available. Reduced monitoring based on RAA with bromate $< 2.5 \mu\text{g/L}$



DBP MRLs (40 CFR 141.131(b)(2)(iv))

Disinfection Byproduct	Minimum Reporting Level (MRL, µg/L)	MRL Check Std. Allowable Concentrations (µg/L) ($\pm 110\%$)	For Samples at $\leq 5 \times$ MRL, MRL Ck. Std. must meet $\pm 50\%$ criterion
TTHM:			
Chloroform	1.0	0.9-1.1	5.0
Bromodichloromethane	1.0	0.9-1.1	5.0
Dibromochloromethane	1.0	0.9-1.1	5.0
Bromoform	1.0	0.9-1.1	5.0
HAA5:			
Monochloroacetic Acid (MCAA)	2.0	1.8-2.2	10
Dichloroacetic Acid (DCAA)	1.0	0.9-1.1	5.0
Trichloroacetic Acid (TCAA)	1.0	0.9-1.1	5.0
Monobromoacetic Acid (MBAA)	1.0	0.9-1.1	5.0
Dibromoacetic Acid (DBAA)	1.0	0.9-1.1	5.0
Chlorite	20	18-22	100
Bromate	5.0 or 1.0	(4.5-5.5) or (0.9-1.1)	25 or 5.0

Calibration curve **must** encompass the MRL level.

The lab **must** analyze a MRL check standard with a concentration $\pm 110\%$ of the MRL with **each batch of samples**.

The MRL check standard concentration **must** be within $\pm 50\%$ of the expected value if any field samples in the batch has a concentration $< 5X$ the regulatory MRL.



DBP MRL Requirement and “Old” Methods

- Stage 2 D/DBP Rule promulgated in 2006
- Many approved methods pre-date the regulation (and even the ICR): 502.2; 524.2; 551.1; 300.1; 552.1; 552.2; 321.8
 - These methods do not mention a MRL check
- MRL check is a regulatory requirement!
 - Regulation trumps method



Approved Methods for Disinfectant Residuals



- SWTR established minimum level entering distribution system (0.2 mg/L)
- Stage 1 D/DBP Rule established maximum levels
 - Chlorine/Chloramines (4.0 mg/L)
 - Chlorine Dioxide (0.8 mg/L)
- Sampling
 - Chlorine/Chloramines: at the same points in the distribution system and at the same time as total coliform samples
 - Chlorine Dioxide: daily samples at the entrance to the distribution system
- 40 CFR 141.131(c)(3): “A party approved by EPA or the State must measure residual disinfectant concentration.”
 - Must use approved methods



Disinfectant Residuals (40 CFR 141.131(c)(1)) – Approved Methods

Methodology	Standard Methods (19 th -22 nd except as noted)	Standard Methods Online	ASTM	EPA	Other	Residual Measured			
						Free Cl ₂	Com-bined Cl ₂	Total Cl ₂	ClO ₂
Amperometric Titration	4500-Cl D	4500-Cl D-00	D 1253-86, (96), -03, -08			X	X	X	
Low-Level Amperometric Titration	4500-Cl E	4500-Cl E-00						X	
DPD Ferrous Titration	4500-Cl F	4500-Cl F-00				X	X	X	
DPD Colorimetric	4500-Cl G	4500-Cl G-00			Hach 10260	X	X	X	
Syringaldehyde (FACTS)	4500-Cl H	4500-Cl H-00				X			
Iodometric Electrode	4500-Cl I	450-Cl I-00						X	
Amperometric Sensor					ChloroSense	X		X	
Online Cl ₂ Analyzer				334.0		X		X	
Chlorine Dioxide Methods									
DPD	4500-ClO ₂ D (19 th - 20 th only)								X
Amperometric Method II	4500-ClO ₂ E	4500-ClO ₂ E-00							X
Amperometric Sensor					ChlordioX Plus				X
Lissamine Green Spectrophotometric				327.0					X



- Palintest ChloroSense and ChlordioX Plus
 - Portable field instruments that use disposable amperometric sensors
 - ChloroSense approved for free/total chlorine
 - ChlordioX Plus approved for chlorine dioxide (and daily chlorite checks)
 - Factory-set calibrations verified by calibration check stds.
- Hach 10260
 - Automated DPD analysis using prefilled cuvettes containing DPD reagents and an internal photometer
 - Factory-set calibrations verified by calibration check stds.



- EPA Method 334.0
 - Establishes procedure and required QC for using online chlorine analyzers to monitor free/total chlorine levels at a drinking water sampling point
 - Collect grab samples near online analyzer. Analyze grab samples using an approved reference method (e.g., DPD or amperometric titration) to verify calibration and accuracy of the online analyzer
 - 14-day IDC required for online analyzer to verify performance before being put into service for compliance monitoring
 - Minimum weekly online analyzer calibration verification check with a grab sample



Water Quality Parameters



- Water quality parameters (40 CFR 141.131(d)) are not regulated (i.e., no promulgated MCLs)
- “A party approved by EPA or the State” must measure the parameters using approved methods
- Parameters include:
 - Alkalinity. Source water alkalinity is factored into the required percent reduction of TOC. Approved methods at 40 CFR 141.23(k)(1)
 - Bromide. Bromate is produced from ozonation of bromide-containing source waters. Stage 1 Rule reduced bromate monitoring based on source water bromide levels. Changed under Stage 2 Rule (effective April 2009).



- Total Organic Carbon (TOC). Natural organic matter in source water. TOC is combined dissolved organic carbon (DOC) + particulate organic carbon. Primary source of TTHMs and HAA5.
- Dissolved Organic Carbon (DOC). Organic matter that can pass through a filter (0.45 μm).
- UV at 254 nm. Common wavelength for dissolved organic halogens (THMs, solvents, pesticides, PCBs, chlorinated aromatics) and aquatic humic substances (humic and fulvic acids).



- SUVA. Calculated by dividing UV at 254 nm by DOC. Normalizing UV absorbance for DOC provides a measure of aromatic content; aromatic compounds are more amenable to removal by coagulation treatment.
- pH. Factors into treatment requirements for removal of DBP precursors. Approved methods at 40 CFR 141.23(k)(1)
- Magnesium. Hardness indicator. Factors into treatment requirements for removal of DBP precursors. Approved methods at 40 CFR 141.23(k)(1)



Methodology	Standard Methods (19 th – 22 nd except as noted)	Standard Methods Online	ASTM	EPA	Other
Alkalinity					
Titrimetric	2320 B	2320 B-97	D 1067 B-97, -02, -06, -11		USGS I-1030-85
Bromide					
IC/Conductivity			D 6581-00, -08 A,B	300.0, 300.1	
IC/Post-Column Reaction				317.0 (rev. 2.0), 326.0	
Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)					
High Temperature Combustion	5310 B	5310 B-00		415.3 (rev. 1.1), 415.3 (rev. 1.2)	
Persulfate/Oxidation	5310 C	5310 C-00		415.3 (rev. 1.1), 415.3 (rev. 1.2)	
Wet Oxidation	5310 D	5310 D-00		415.3 (rev. 1.1), 415.3 (rev. 1.2)	



Methodology	Standard Methods (19 th – 22 nd except as noted)	Standard Methods Online	ASTM	EPA	Other
UV at 254 nm					
Spectrometry	5910 B	5910 B-00, -11		415.3 (rev. 1.1), 415.3 (rev. 1.2)	
pH					
Electrometric	4500-H ⁺ B	4500-H ⁺ B-00	D 1293-95, -99, -12	150.1, 150.2	
Magnesium					
Atomic Absorption	3111 B	3111 B-99	D 511 B-93, -03, -09		
ICP	3120 B	3120 B-99		200.7	
Complexation	3500-Mg B (19 th ed. only: 3500-Mg E)	3500-Mg B-97	D 511 A-93, -03, -09		
Ion Chromatography			D 6919-03, -09		
Atomic Emission				200.5 (rev. 4.2)	



Summary

- Disinfectant/Disinfection Byproduct rules have evolved coincident with micro rules for over 25 years
 - Optimize microbial protection through disinfection
 - Minimize public exposure to health risks associated with disinfection byproducts
- Stage 1 Rule promulgated to take moderate action to balance risks
 - Pending ICR/Health Effects data
- Stage 2 Rule builds upon Stage 1 Rule by targeting highest risk systems
 - Identify sites with highest levels of DBPs



Summary

- Analysis of DBPs must be performed in a certified laboratory
- Stage 2 Rule established MRL requirements
 - Every sample batch analyzed must contain a MRL check standard
 - Older approved methods do not specify the MRL check
- Analysis of disinfectant residuals and water quality parameters can be performed by 'a party approved by EPA or the State'