UTILIZING AN ON-LINE TTTHM ANALYZER TO AID IN COMPLIANCE WITH DBP REGULATIONS

SHARON FILLMANN
OPERATIONS & WATER QUALITY MANAGER

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Disinfection By-Product Formation

Naturally-Occurring Organic Matter (NOM)
e.g.
- Humic Acids
- Fulvic Acids

Chlorine Based Compounds for Microbiological Disinfection
e.g.
- Chlorine
- Hypochlorite
- Chlorine Dioxide

Disinfection By-Products*
e.g.
- Trihalomethanes
- Haloacetic Acids
- Bromate
- Chlorite

Disinfection By-Products*
- Several thousand are known
- More than 500 have been toxicologically reviewed
- Several classes and compounds are regulated in drinking water:
  ◆ Trihalomethanes
  ◆ Haloacetic Acids
Evolution of DBP Regulations

**Evolution of DBPs (THMs) Regulations**

- US-EPA Stage 2 DBPR in force with levels of THMs to 80 µg /L
- US-EPA Stage 1 DBPR proposed levels of 80 µg /L
- WHO published guideline values for THMs
- U.S. EPA regulation to control THMs at 100 µg /L
- 1976
  - NCI published results linking chloroform to cancer
  - NOM Survey reported high THMs in US Chlorinated Drinking water
- 1975
  - NOR Survey reported high THMs in US Chlorinated Drinking water
- 1972
  - Rook reported first THM – Chloroform in chlorinated drinking water
- 1908
  - US First Chlorination, Jersey City, New Jersey, began chlorination of drinking water
  - Chlorine was widely used as a disinfectant of drinking water.
  - Snow used Chlorine to disinfect London’s water supply during now-famous cholera epidemic

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NORS-US National Organics Reconnaissance Survey
NOMS-US National Organic Monitoring Survey
WHO-World Health Organization
NCI- US National Cancer Institute
US-EPA-Environmental Protection Agency
Stage 1 Disinfection By Product Rule

Source: EPA, 40 CFR Parts 9, 141, and 142 National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, p 411
Stage 2 Disinfection By Product Rule

Source: EPA, 40 CFR Parts 9, 141, and 142 National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, p 411
Stage 1 vs. Stage 2 Rule

- Stage 2 sample sites chosen from the highest results of Stage 1 and IDSE sampling.

- Stage 2 compliance based on running annual average per location rather than a system average.

- Specific distribution “hot spots” become compliance risks since compliance calculated as a running annual average per location.
United Water Hummelstown WTP

4 MGD

- ACH
- Chlorine
- KMnO4

Membrane Filtration

- Post Caustic
- H2SO4
DBP Formation and Variables

✓ Disinfectant
  ▪ Type
  ✓ Point of Application
  ✓ Dose
  ✓ Residual
  ❑ Contact Time/Water Age

✓ pH
  ❑ Bromide
  ❑ TOC
    ➢ TOC Removal
  ❑ Temperature
Changes to Reduce DBPs at Hummelstown

- **2010-2011**
  - Optimize Control of Permeate and Entry Point Chlorine
    - Reduce Permeate Residual to 0.1-0.2 ppm
    - By Reducing Pre Cl2 dose
    - Reduce and Be Consistent with Post Cl2 dose/residuals

- **2011**
  - Implement H2SO4 feed (started July 28, 2011)
    - Reduce Permeate pH to 6.8 - 7.2
    - Enhanced Coagulation vs Manganese Removal
    - TOC removal increased by 15% after pH decrease
    - THMs decreased by 20%; HAAs increased by 15%- limited data
    - THMs reduced through membrane, but EP THMs similar to past
    - THM formation reaction quick and not complete through membrane

- **2012**
  - Additional KMnO4 contact time
    - Install additional contact pipe for 20 min contact time
    - Reduce THMs

- **2013**
  - Treatment Anomalies with high pre Cl2 demand from 2012 -2013
  - Partner with PA DEP, SRBC, PA American to set up watershed study
Swatara Creek Treatment Anomalies Observed by Both United Water and PA American

- Aug 20 - Sept 8 2012
- Sept 19 - 22 2012
- Oct 3 - 5 2012
- Oct 19 - 23 2012
- Oct 29 – Nov 1 2012 (Hurricane Sandy)
- Nov 12 – 16 2012
- May 6 – 14 2013
Impacts Observed at UW Hummelstown WTP

- Pre-Cl2 Demand increased from 130 % to 290 %
- Post Cl2 Demand increased from 144 % to 167 %
- Raw Water TOC increased from typical 1.5 - 2 ppm to 5 - 7 ppm
- Finished TOC increased from avg 1.1 - 1.7 ppm to 3 - 4.5 ppm
- Finished TTHMs increased by 3 – 3.5 times
- Finished HAA5s increased by 3 times
- For 5 events, TTHMs estimated by mathematical regression models increased from 19 ppb to 140 ppb
- For 5 events, HAA5s estimated by mathematical regression models increased from 13 ppb to 140 ppb
- For 1 event, Actual finished water TTHMs were 67 and 80 ppb at 2 different labs while the model estimated 90 ppb on Oct 30, 2012
- For 1 event, Actual finished water HAA5s were 149 and 112 ppb at 2 different labs while the model estimated 119 ppb on Oct 30, 2012
Hummelstown EP DBPs per QTR 2008-2014

THMs (ppb)

Higher raw water TOC, 2.8 ppm on 8/9/12

Enhanced coag w/ H2SO4
7/28/11

Why monitor THMs online?

- THM100 enables Real-Time Monitoring of THMs in Drinking Water
- THMs can vary dramatically over time/days and during seasonal events
- Online THM monitoring and trending with online TOC, Turbidity, Chlorine and pH provides snapshot of overall WQ
- Allows for systems to optimize operational and chemical feed systems to minimize THMs
- Systems can test automatically at any location and also bring grab samples from around the plant or system to manually inject for analysis

- Regulatory Benefits
  - Enables Compliance Management – Proactive
  - Minimizes Public Health Hazards from exposure to contaminants
  - Minimizes Potential Regulatory Violations
Standard Method for DBP Analysis

- System collects a water sample
- Physically delivers it to the lab
- A lab technician prepares the sample
- The sample is analyzed on a GC/MS instrument; costs?
- Results are reported to the water system in 10-14 days
- Water system logs data
- Operators make adjustment to the treatment process based on these results?
- How to get operators to use the data as an operational tool?
AMS THM-100 – Another Option

- First commercial in-line instrument for TTHM and CHCl₃ monitoring with manual sampling capability
- Installed at multiple water utilities with excellent correlation to lab results
- Unattended 24/7 results in 1 hour which can immediately be used to modify the process
- Self calibrating – no need for skilled operator intervention at anytime
- 5-200 (in μg/L) range for TTHM and Chloroform
- 2’ (W) x 1.3’ (D) x 5’ (H)
- 100 lbs
Organization of THM-100 System

W – 2.0’ (610mm), D - 1.33’ (406mm)
H – 5.0’ (1,524mm)
Weight – 100lbs (45.3kg)

Electronics Cabinet

Process Cabinet

Chemical Reagents and Standards

www.ams-h2o.com
## THM-100 Principal of Operation

<table>
<thead>
<tr>
<th>Analysis Steps</th>
<th>THM-100 Process Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draw Finished Water Sample</td>
<td>Fill Reservoir (Purge Vessel)</td>
</tr>
<tr>
<td>Extract THMs</td>
<td>Purge Reservoir and Trap THMs</td>
</tr>
<tr>
<td>Concentrate THMs</td>
<td>Desorb Trap and Dissolve THMs into Reagents</td>
</tr>
<tr>
<td>React THMs with Reagents</td>
<td>Initiate the Fujiwara Reaction</td>
</tr>
<tr>
<td>Measure change in Absorbance</td>
<td>Spectrophotometric Detection at 540 nm</td>
</tr>
<tr>
<td>Determine Concentration of the dominant THM and TTHM</td>
<td>Quantitative Determination of dominant THM and TTHM Concentrations</td>
</tr>
<tr>
<td>Report total THM and Chloroform results</td>
<td>Make Results Available on the System and via 4-20 mA and the Ethernet</td>
</tr>
</tbody>
</table>

- All four THMs are converted to the same product when treated with a pyridine derivative in an aqueous base:

\[
\begin{array}{c}
X, X', X'' = Br, Cl \\
\end{array}
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\[
\begin{array}{c}
\text{Fujiwara Product } \quad \lambda_{max} \sim 540 \text{ nm}
\end{array}
\]
Data Reliability: Labs vs. Online (Spiked Samples)

- 5 US-EPA Accredited Labs & 3 THM-100 Monitors
- Sample Water Spiked at TTHM 79.5 µg/L (60% CHCl₃)
1. Optimization of DBP Mitigation Technologies
- Raw Water Blending
- Enhanced Coagulation
- Filtration – MIEX, GAC, Nano filtration
- Disinfectants – Chloramines, Chlorine Dioxide, UV, and Ozone
- Storage – Aeration, Tank mixing

2. Contract compliance and quality control in consecutive systems

3. Compliance monitoring
Real-time TTHM Analysis for Local Water Quality Control and Consecutive System Monitoring
UW Hummelstown WTP on-line TTHM (ppb)

TTHM MCL 80 ppb
Hummelstown THM Measurements
Online vs Three Analytical Labs

CHCl3 Conc - Lab [ALS]
TTHM Conc - Lab [ALS]
TTHM - Lab [Microbac Harrisburg]
TTHM - Lab [Benchmark]
CHCl3 Conc - Online
TTHM Conc - Online
Sporadic Grab-Samples and Lab Analyses May be Inaccurate and Miss THM Events
United Water Take Aways

- Not used during peak seasonal conditions- watershed study
  - Partner with PA American, PA DEP and SRBC

- No grab sample or “bottle injection” option

- No connection with online SCADA for trending

- Online TOC data not trended in SCADA

- TTHM Online Analyzer as an Operational Tool
  - Provides real time changes to TTHM levels
  - Keep it simple
  - The Good, The Bad, The Ugly
  - Maintenance Free