Is the H2O on the Dark Side of the Moon .... chloraminated?

Bruce Stevens – Eastern Regional Manager
P is formed by fusion of 2 oxygen atoms in large stars
..... as are a few other elements
EPCOT begin a new era

Reedy Creek Improvement District (RCID)

Manages water, waste water and **reclaimed** water for the Disney resorts - ChemScan has assisted them since 1994 in operations
• Every instrument has a useful range for a particular analyte.
• Often, you must determine that range experimentally.
• It’s done by making a dilution set of known concentrations.
• These dilutions are used to make a working curve.
• Standard additions are also used to calibrate analyzers.
• Some things can be seen but other times you can’t
In lakes and streams, there are 3 major types of particles: *algae*, detritus (dead organic material), and silt (inorganic, or mineral, *suspended sediment*). The algae grow in the water and the detritus comes from dead algae, higher plants, *zooplankton*, bacteria, fungi, etc. produced within the *water column*, and from watershed vegetation washed in to the water. Sediment comes largely from shoreline erosion and from the resuspension of bottom sediments due to wind mixing.
UV Absorbance, TSS & Turbidity

**TURBIDITY DUE TO ALGAE**

- 2 NTU's: 2.2 µg chlorophyll/L
- 5 NTU's: 4.7 µg chlorophyll/L
- 10 NTU's: 10 µg chlorophyll/L
- 20 NTU's: 36 µg chlorophyll/L
- 50 NTU's: 54 µg chlorophyll/L

**TURBIDITY DUE TO SEDIMENT**

- 2 NTU's: 2.2 mg TSS/L
- 5 NTU's: 6.3 mg TSS/L
- 10 NTU's: 12 mg TSS/L
- 20 NTU's: 24 mg TSS/L
- 50 NTU's: 64 mg TSS/L

The experiment: Filter equal volumes of water from mid-lake and nearshore at Lake Independence through fine-mesh filters.
UV254 , Turbs & TSS

- Experience has shown that sometimes turbidity doesn’t tell you everything… So try TSS or UV
- Sometimes TSS correlates but sometimes color and dissolved organics affect the measurement
- In some cases 1-2 wavelength UV 254 works well but other times it won’t correlate …..
- Will T CL be good enough, or do you really need nitrite and free ammonia to monitor nitrification.
- What about conductivity, alkalinity, pH, ORP, chlorides, or other surrogates for GCMS ??
Recent NOM studies by WR Foundation

Impact of AIX contact time on organic removal

New Mexico (Brown et al. 2006)

UV254 Response

Molecular Weight (daltons)
River Water - TOC correlation

Hopewell TOC

ChemScan vs Lab

R2 = 0.904
Photometric, Amperometric or Spectrometric

Chatham County, NC - 3M tank with Sanford Feed Flow Fill and Draw Cycle

Factory Program Reload on 02/14

Offset applied

Chemical Feed

F NH3
T NH3
Mono
T CL2

Test Kit FNH3
Test Kit Mono
Test Kit TNH3
Test Kit TCL2
chemistry graphics
(courtesy of Hach and TX CEQ)

Real World Impact of pH

- NHCl₂
- NH₂Cl
- NCl₃

at pH > 5.5, NH₂Cl dominates

NH₂Cl formation is optimized at pH > 8.2

Adapted from Palin, 1950
A Total Chlorine result has 3 possible locations on the breakpoint curve.
Free Chlorine reacts with Monochloramine giving a false reading until beyond the Breakpoint.
First Indication of Free Chlorine is AFTER Dichloramine Formation.
Distribution Nitrification Control

- Maintain Higher Chloramine Residual
- Higher Cl₂ : NH₃-N Ratio (less Free NH₃)
- Periodic Chlorine Shocks
- Higher Turnover in Reservoirs
- System Flushing
- Monitoring at Strategic Locations
Figure 2 – Chloramine Formation and Decay

Chlorine Feed

Chemical Demand

Booster Chlorine Feed

Bacteria Colony

Decay

Ammonia Released

Flow

Ambient Free Ammonia

Ammonia Feed

Chloramine

Free Ammonia Available for Additional Chloramine Formation or Nitrification
City of Milwaukee, WI

Side by Side with Hach APA-6000
Chloramination Monitoring at Two Sample Points
One ChemScan replaces entire wall of equipment
Cl₂:N Ratio Effects on THM and Flavor

Figure: Effect of chlorine dose on chloramine species, TTHM, and flavor found by MWD

Source: Barrett 1985
### Brominated organic compounds

**Table 2-7 – Bromide-chloramine reactions of importance in drinking water treatment**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOCl + NH₃ → NH₂Cl + H₂O</td>
</tr>
<tr>
<td>11</td>
<td>HOCl + Br⁻ → HOBr + Cl⁻</td>
</tr>
<tr>
<td>12</td>
<td>HOBr + NH₂Cl → NHClBr + H₂O</td>
</tr>
<tr>
<td>13</td>
<td>NH₂Cl + H⁺ ↔ NH₃Cl⁺</td>
</tr>
<tr>
<td>14</td>
<td>NH₃Cl⁺ + Br⁻ → NH₃Br⁺ + Cl⁻</td>
</tr>
<tr>
<td>15</td>
<td>NH₃Br⁺ ↔ NH₂Br + H⁺</td>
</tr>
<tr>
<td>16</td>
<td>NH₃Br⁺ + NH₂Cl → NHClBr + NH₄⁺</td>
</tr>
<tr>
<td>17</td>
<td>HOBr + NH₃ → NH₂Br + H₂O</td>
</tr>
<tr>
<td>18</td>
<td>NH₂Br + NH₂Br ↔ NHBr₂ + NH₃</td>
</tr>
<tr>
<td>19</td>
<td>NH₂Br + NHBr₂ → Products</td>
</tr>
<tr>
<td>20</td>
<td>NHBr₂ + NHBr₂ + H₂O → Products</td>
</tr>
<tr>
<td>21</td>
<td>2NHClBr + H₂O → N₂ + HOBr + 2HCl + HBr</td>
</tr>
</tbody>
</table>

*Courtesy Dr. Gregory Popr - Carollo*
Lab spectrometer

Diagram showing the components of a lab spectrometer: source, entrance slit, dispersion device, exit slit, sample, monochromator, and detector.
Automation is Applied
Sampling is Simplified
### Spectroscopy

**Spectral Distribution of Radiant Energy**

<table>
<thead>
<tr>
<th>Wave Number (cycles/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray</td>
</tr>
<tr>
<td>UV</td>
</tr>
<tr>
<td>Visible</td>
</tr>
<tr>
<td>IR</td>
</tr>
<tr>
<td>Microwave</td>
</tr>
<tr>
<td>200nm</td>
</tr>
<tr>
<td>400nm</td>
</tr>
<tr>
<td>800nm</td>
</tr>
</tbody>
</table>
Transmission and Color

The human eye sees the complementary color to that which is absorbed
The EYE ..... Color Wheels

It is a little known fact that the human eye has a significant capability in the ultraviolet spectrum. The complete spectral sensitivity of the human eye is shown in the following figure under a variety of conditions.

Variations in spectral response under various conditions [from Section 17.2.2]
Figure 1. Chlorine Content Color Wheel
Spectrometers are better

Figure 7. Transmission data with no sample in optical path as reference
Example of a two-component mixture with significant spectral overlap
3.1.3 Modes of Operation

1. On-line
   - Read samples
   - Calculate, store and display results
   - Output signals

2. Off-line
   - Perform calibration
   - Setup instrument parameters

3.1.4 Analytical Algorithms

1. Multiple variable regression analysis
2. Principal components preprocessing
3. First derivative preprocessing
4. Second derivative preprocessing
5. Principal components rotation preprocessing
Pattern Recognition Software
We extend that platform into a working instrument.
UV-6101 Analyzer
Upper Electronics Enclosure

Heater-Fan  Power Input
Flash Lamp  Fiber Optic Cable
Instrument Control Circuit and Network Communication  Spectrograph
An Online Lab Grade
Wide Band Spectrometer

Capable of handling both reagent assisted and directly read samples

Calibration / Validation Port for grab sample analysis and site specific optimization

Capable of field modification and correlation with lab results to build confidence

Self Zeroing, self cleaning and future process enhancements in time as needed
UV-VIS Analyzer
Lower Enclosure

- FlowCell
- Reagent Injectors
- Reagents
- Sample Inlets
- Internal Peristaltic Pump
- Zeroing and Cleaning Solution Containers
An optical instrument .......... not a control panel

• Light projected from a Xenon flash lamp thru a fiber optic cable to a hand built spectrograph that reads every ..... 2 nanometers across a 260 nM wavelength spectrum

• Expansion, contraction, corrosion, humidity and physical positioning of the instrument affect the performance

• It is not a solid state box that you can place anywhere and in any position that you find convenient.

• Probes and other colorimetric analyzers do not compare
Houston, TX    Metro MUDs

Consecutive System Chloramination Control
Twenty Seven (27) Analyzers

Monochloramine, Total Chlorine, Free Ammonia and Total Ammonia
Demonstrated Results & Accuracy

Optimized Performance

Standardized Components

Long Life Cycle

Upgradable for Future Process Modifications

Hand Made in USA
Typical 2 sample lines before and after water transfer from Houston WTPs
Tank & Distribution Control

- OWASA
- High Point
- Burlington
- Greenville, NC
- Houston, TX
- Pasco County, FL
- Hillsborough County, FL
- Miami Dade Water
- Palm Beach County
- Sarasota, FL

Optimize Monochloramine
Use ChemScan's Peak Point Control at WTPs & in Distribution Systems Too!

Welcome to Greenville
Home of the
EAST CAROLINA PIRATES

Need to Boost CL2? Or Monitor Nitrite?
Get a ChemScan®

For More Information Contact:
ASA Analytics
2325 Parklawn Drive, Suite I
Waukesha, WI 53186
(262) 717-9500

www.asaAnalytics.com
Regional Distribution and Best Tasting Rural Water Contest 2012

Above: The judges this year were Rita Mroczek with Division of Water Quality, Lisa Edwards with Division of Environment and Natural Resources-PWSS, Ava Richardson a professional Water Taster from Wilmington, and Marvin Hutchinson with USDA from the Shelby Office. Left: Greenville Utilities, the winner of the 2012 water taste test.
Chloramine Plus

Oxnard CA - Distribution Water Monitoring
One ChemScan UV-6101 Analyzer is used to detect

Free Ammonia
Total Ammonia
Mono-chloramine
Total Chlorine
Nitrite
Iron and
Manganese
NO3 Calibration curves
NO2 Calibration Set

\[LS=TS=LCM.FDX(\frac{y}{x})\]

- \(R^2 = 0.92\)
- AVG RES = 36.5
- SLOPE = 0.92
- \(T = 31.1\)

**Graph:**
- Predicted ppb NO2 vs. Actual ppb NO2
- Data points plotted
- Linear trend line
- Axes labels:
  - Y-axis: Predicted ppb NO2
  - X-axis: Actual ppb NO2
Jefferson Parish, LA demo test

ChemScan system caught the daily overfeed of Ammonia due to poor valve control and ratio metric feed inadequacies. Time to replace those old valves?

Three hours or so every day after turndown from 60 MGD to 15 MGD, the spike was going out to the system even though the pump feed controllers read proper ratios.
Recent studies confirm ratio control problems
Chloramination is used at all four WTPs in Toronto for maintenance of a secondary disinfectant.

A chloramination process that is carefully monitored and optimized for the production of monochloramine will produce good quality water and maintain the integrity of the distribution system.
Pilot Scale Testing - Results

- Monochloramine values were 0.1 – 0.2 mg/L lower than Total Chlorine – indicating a good chlorine to ammonia ratio

- Free Ammonia was constantly below 0.05 mg/L – indicating very little free ammonia “leak” into the distribution system

- Total Ammonia – Readings for this parameter were quite stable
Pilot Scale Testing - Anecdotes

- During the test, ChemScan recorded an ammonia feed problem at the plant.
- Analyzer indicated ammonia was being underfed.
- Loss of ammonia resulted in a chlorine to ammonia ratio greater than 5:1.
- Free ammonia was constantly at the detection limit of the machine.
- The difference between Total Chlorine and Monochloramine was greater than 0.1 mg/L.
Full Scale Implementation of ChemScan

ChemScan Chloramination Analyzer Data
City of Toronto  F. J. Horgan WTP
Finished Water

- FNH3
- TNH3
- MONO
- TCL2

- Lab FNH3
- Calc TNH3
- Lab MONO
- Lab TCL2

Conclusions

• A chloramination analyzer has helped the plant identify opportunities to optimize chloramination process control

• Analyzer can be used to help detect ammonia feed problems and control nitrification in the distribution system

• Unit has proven to be reliable and cost effective

• Rapid detection of problems
  – Prevents excess production of water that is not chloraminated at optimal levels
Best Tasting Water Contest Winner

AB JEWELL AND MOHAWK
WATER TREATMENT PLANTS
CHLORAMINES MODIFICATION

ATTENDANCE AT PRE-BID CONFERENCE IS MANDATORY

PREPARED BY:
CH2MILL
401 S. BOSTON, SUITE 330
TULSA, OK 74103
918-583-3057 OFFICE
918-584-5826 FAX
MURRY FLEMING, P.E.
Conversion from Free CL2 to Combined Chlorine (NH2CL)
AB Jewell and Mohawk WTPs
90 MGD + 100 MGD respectively
System Wide Conversion after 6 months of PR and Preparation
Conversion and Flushing
older water gone in 5 days

186 sq miles of pipes to flush
Charleston, SC – Hanahan WTP

Peak Point Chloramination using 4 parameters to optimize monochloramine formation and minimize chemical consumption for 11 years +

Broad Spectrum Analyzers for Differential Spectroscopy
Chloramination

East Bay Municipal Utility District (MUD) CA.
Chloramination Control - Fourteen Analyzers
Free Ammonia and UV-254 %T
ChemScan in the News!

ASA Update -

ASA Analytics is proud to announce the recent publication of ChemScan analyzer success stories.

The chart below links to PDF versions of the articles. The success stories are also featured on our homepage:

http://www.asaAnalytics.com

<table>
<thead>
<tr>
<th>Article</th>
<th>Publication</th>
<th>Date Published</th>
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<tr>
<td>&quot;Online Process Analyzer Installed at F.J. Horgan WTP to Monitor Chloramination&quot;</td>
<td>Environmental Science &amp; Engineering</td>
<td>March/April, 2010</td>
</tr>
<tr>
<td>&quot;Real-Time Control Optimizes Extended Aeration Processes&quot; (Valrico - Hillsborough County, FL)</td>
<td>WaterWorld</td>
<td>August, 2010</td>
</tr>
<tr>
<td>&quot;Scanning Success: A Multi-Parameter Analyzer Helps a Kentucky Treatment Plant Step up to the Plate and Meet a New Phosphorus Limit in Its Permit&quot; (West Hickman Creek, KY)</td>
<td>Treatment Plant Operator</td>
<td>August, 2010</td>
</tr>
<tr>
<td>&quot;Case Study: Curren Hits the Bull's Eye Using Online Process Analyzers&quot;</td>
<td>Environmental Protection</td>
<td>August, 2010</td>
</tr>
</tbody>
</table>

www.asaAnalytics.com
• #54 NOM Analysis at Boyle
• #51 NOM Analysis at WSSC
• #127 Specific Absorbance
• #42 Percent Transmittance
• #68 NOM Correlation
• #126 TOC Correlation
• #39 COD Correlation