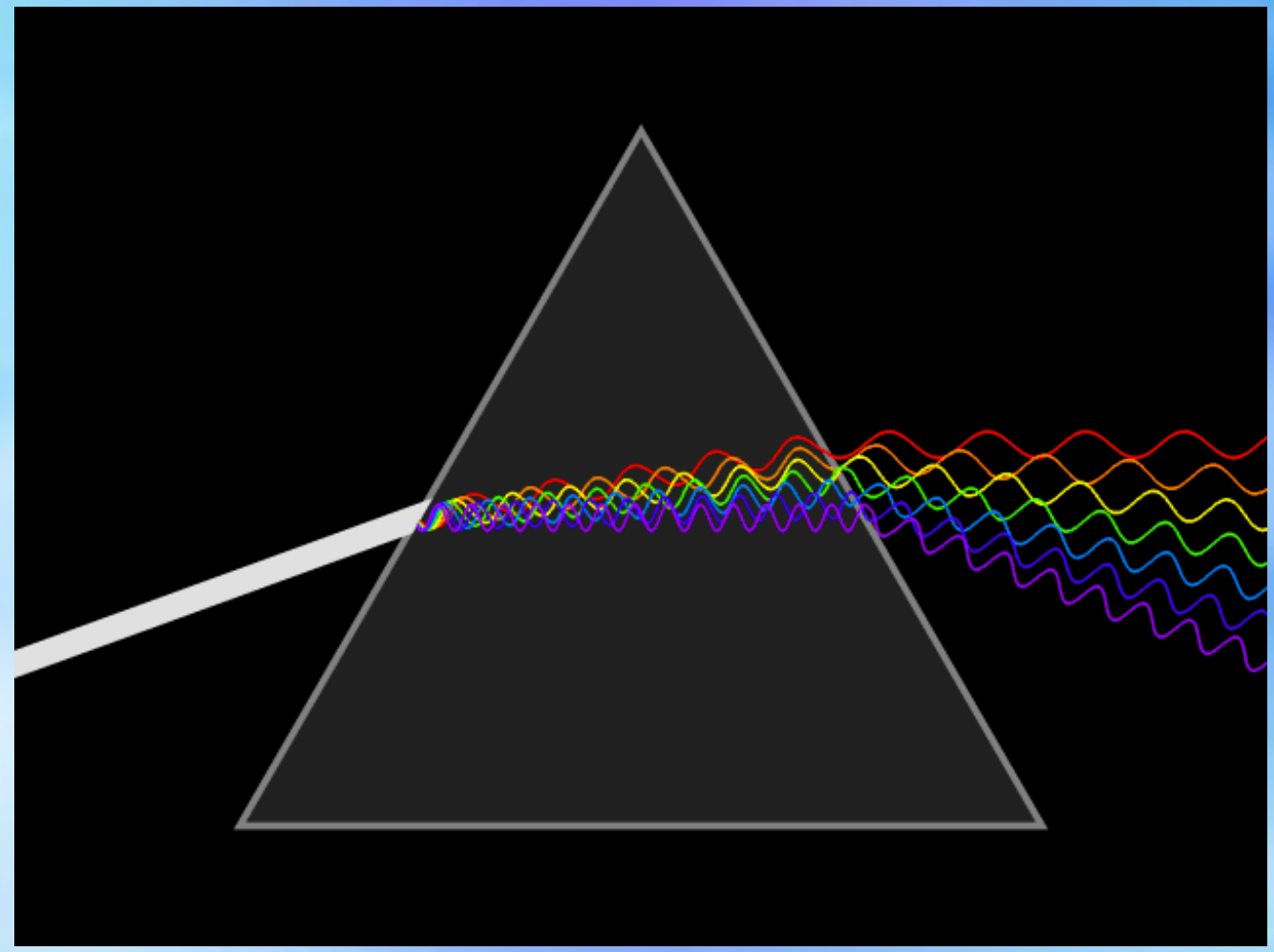
Is the H2O on the Dark Side of the Moon …. chloraminated?



Bruce Stevens – Eastern Regional Manager

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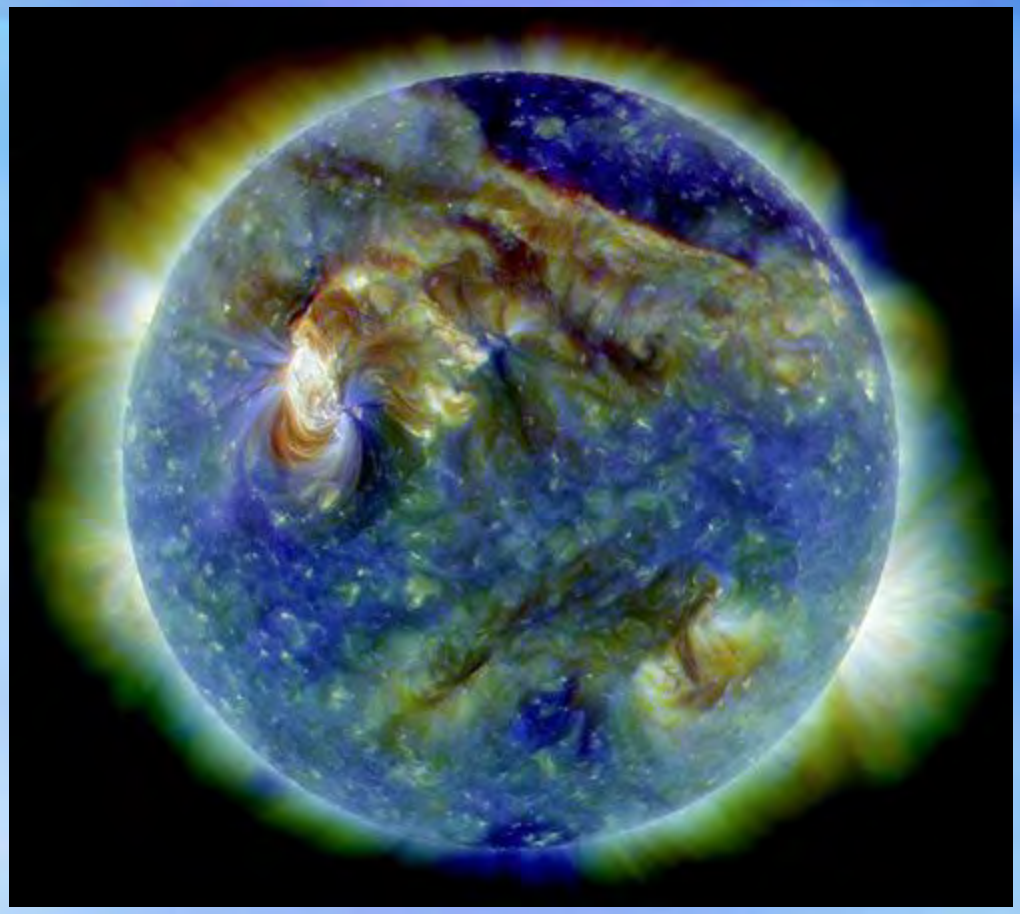
Stellar Origins



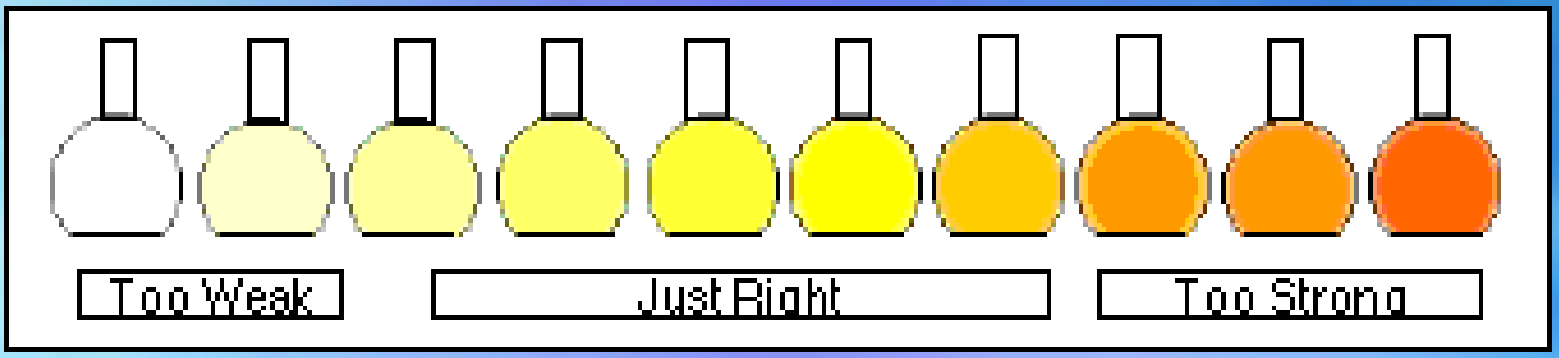
P is formed by fusion of 2 oxygen atoms in large stars

….. as are a few other elements

EPCOT begin a new era

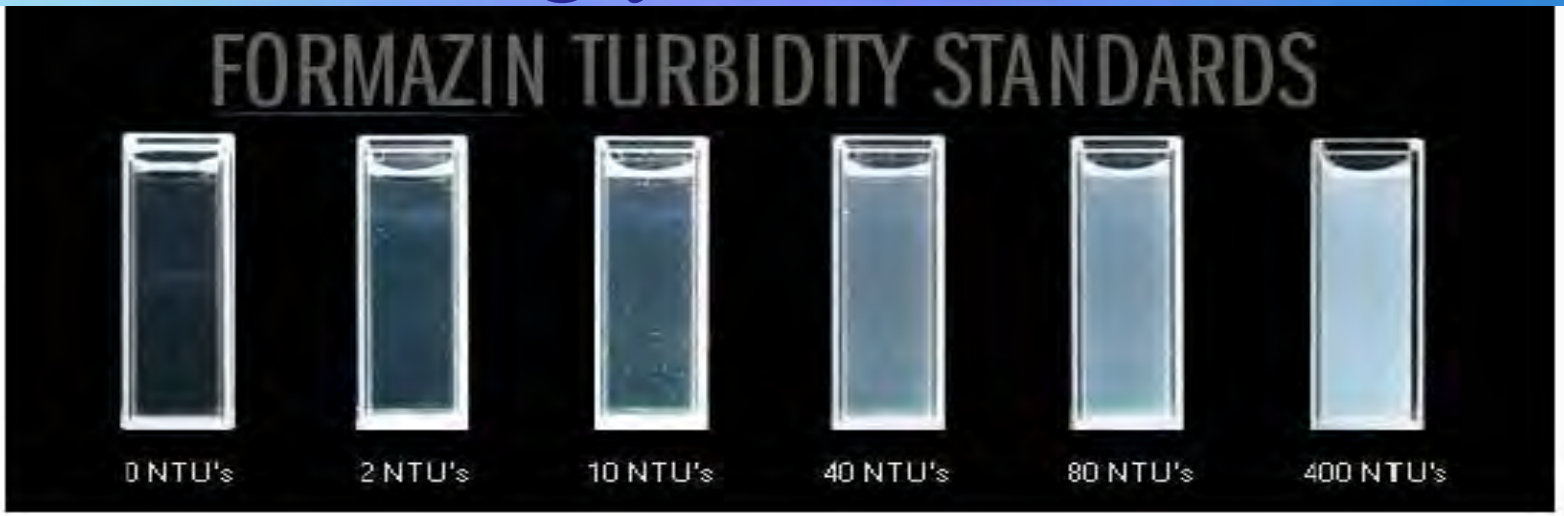
Reedy Creek Improvement District (RCID)

Manages water, waste water and **reclaimed** water for the Disney resorts - ChemScan has assisted them since 1994 in operations



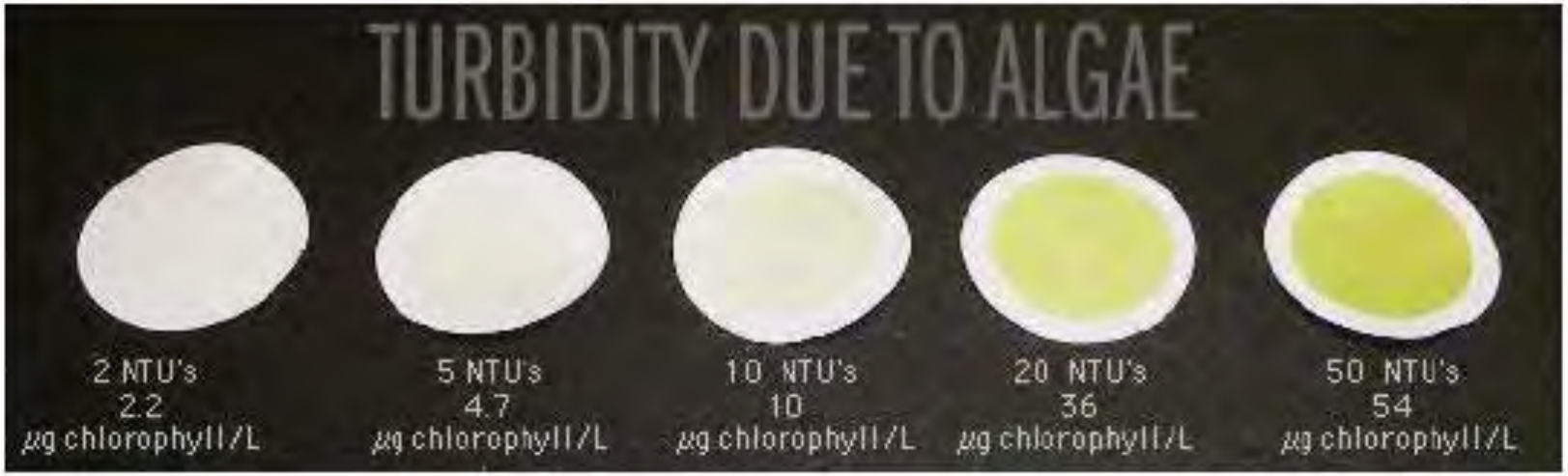
- Every instrument has a useful range for a particular analyte.
- Often, you must determine that range experimentally.
- It’s done by making a dilution set of known concentrations.
- These dilutions are used to make a working curve.
- Standard additions are also used to calibrate analyzers
- Some things can be seen but other times you can’t

Monitoring your Surface WTPs



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

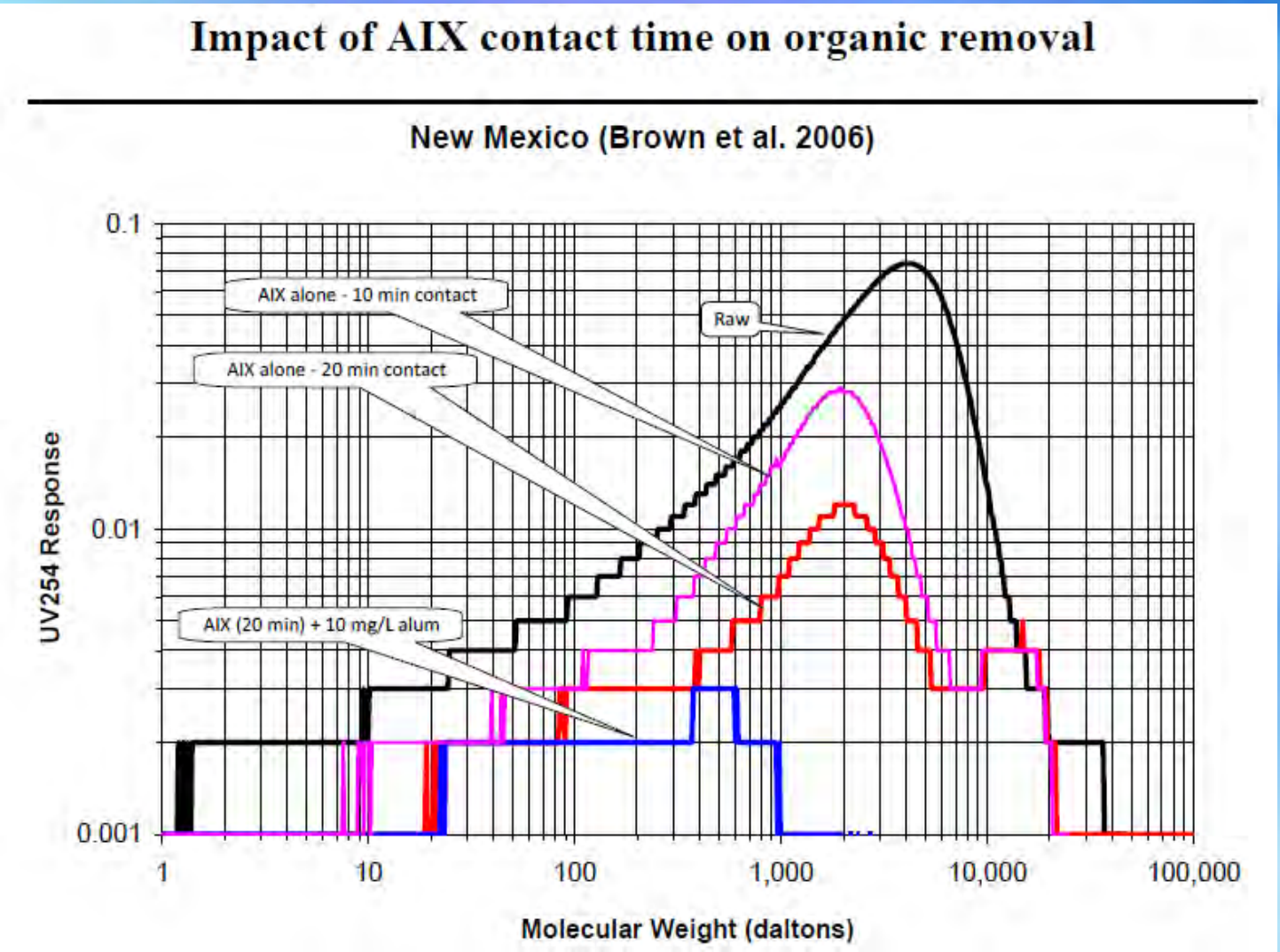


The experiment: Filter equal volumes of water from mid-lake and nearshore at Lake Independence through fine-mesh filters.

UV254 ,Turbs & TSS

- Experience has shown that sometimes turbs don'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 conductiviy, alkalinity ,pH, ORP , chlorides, or other surrogates for GCMS ??

Recent NOM studies by WR Foundation



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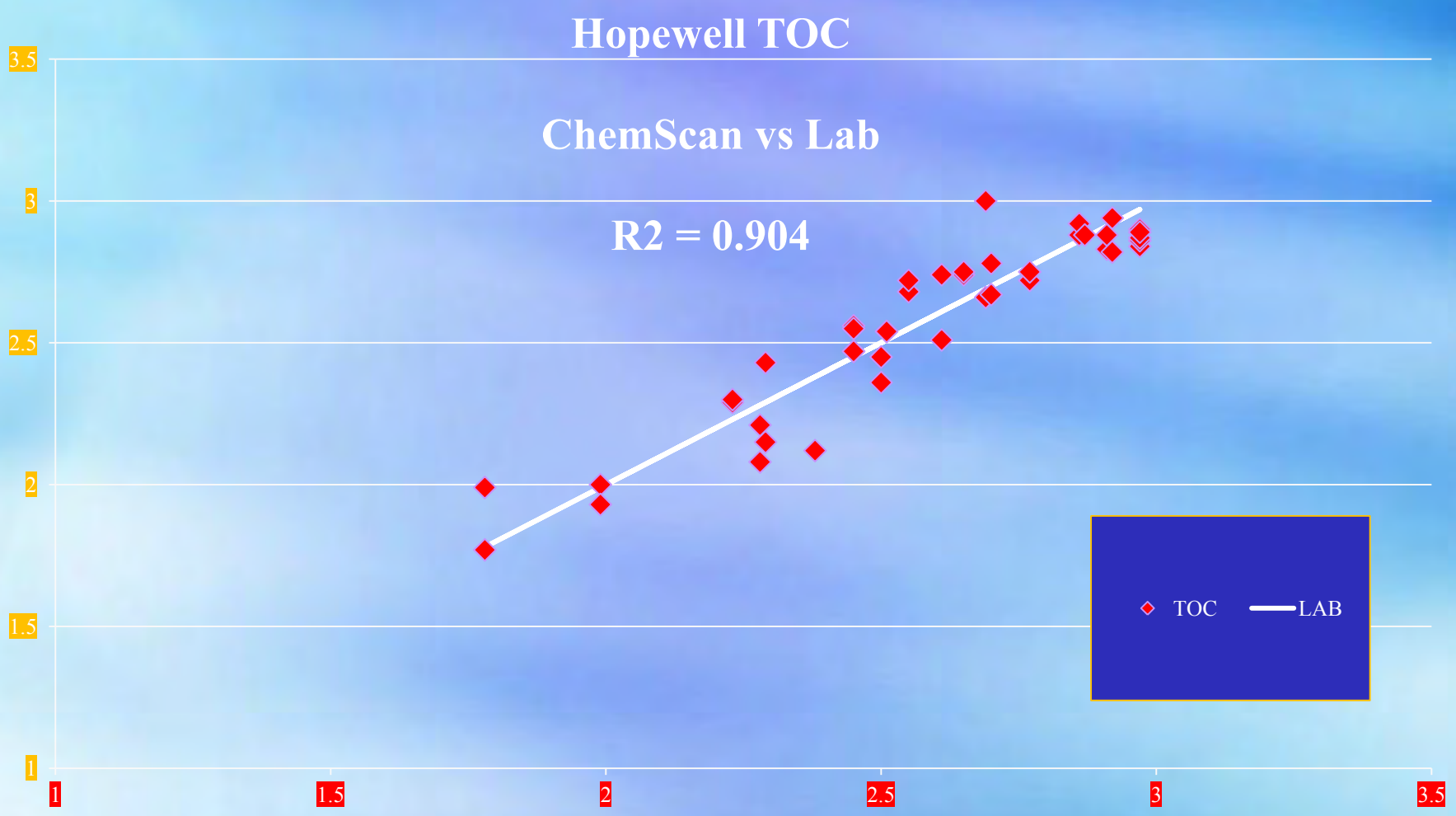
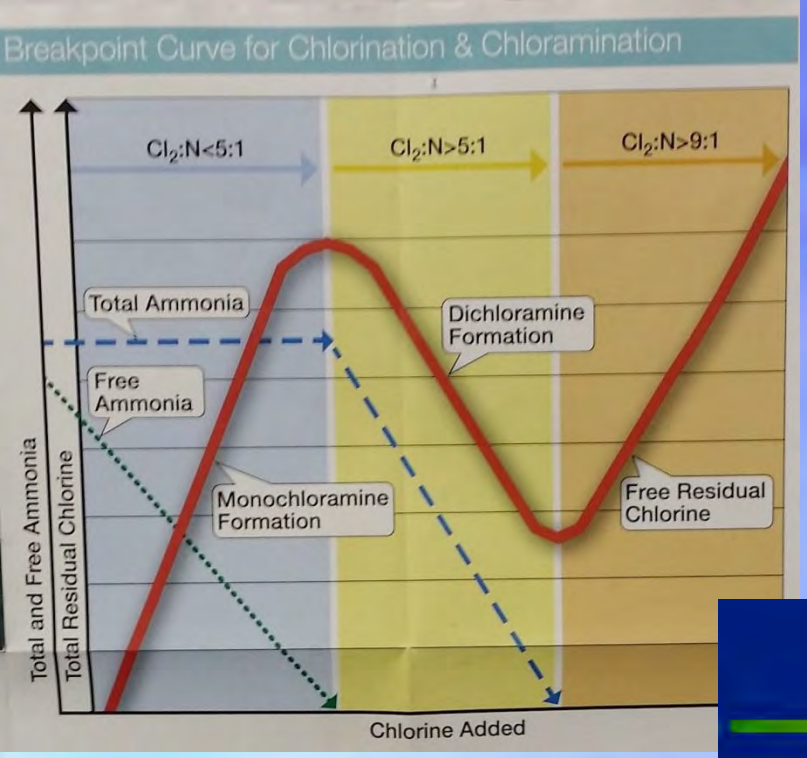
River Water - TOC correlation

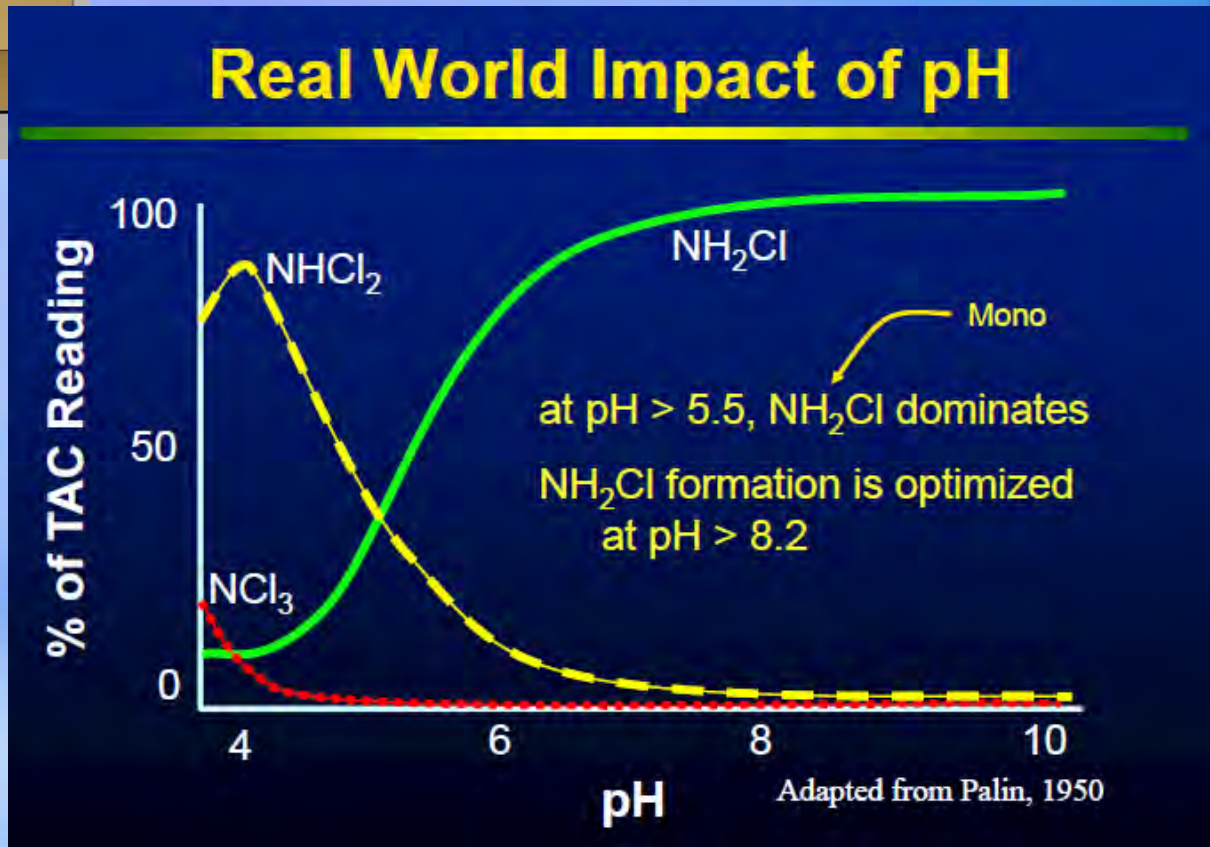


Photometric, Amperometric or Spectrometric

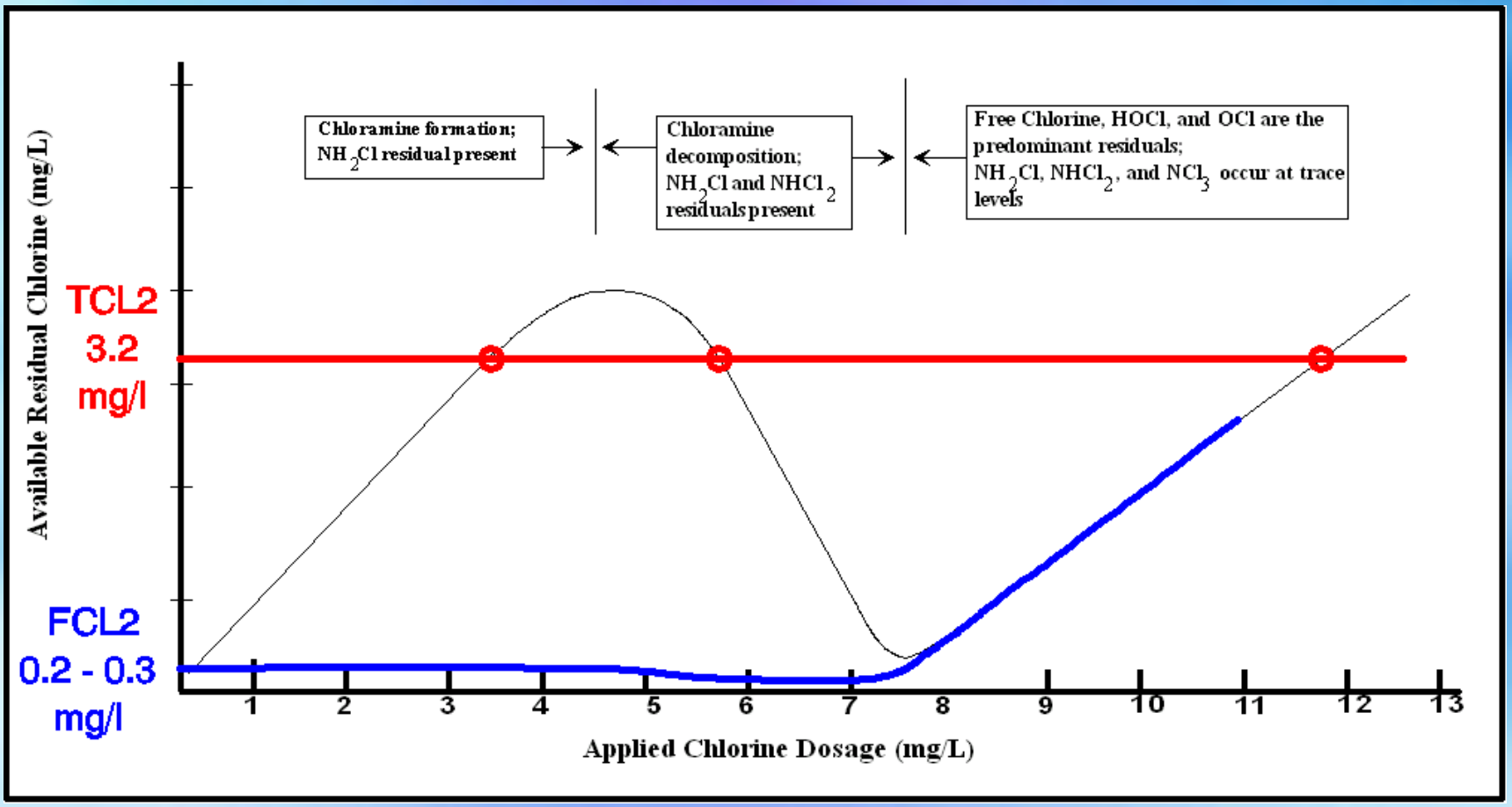
chemistry graphics

(courtesy of Hach and TX CEQ)





Breakpoint as Measured by Free and Total Chlorine Analyzers



- 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 Cl_2 : NH_3-N Ratio (less Free NH3)
- Periodic Chlorine Shocks
- Higher Turnover in Reservoirs
- System Flushing
- Monitoring at Strategic Locations

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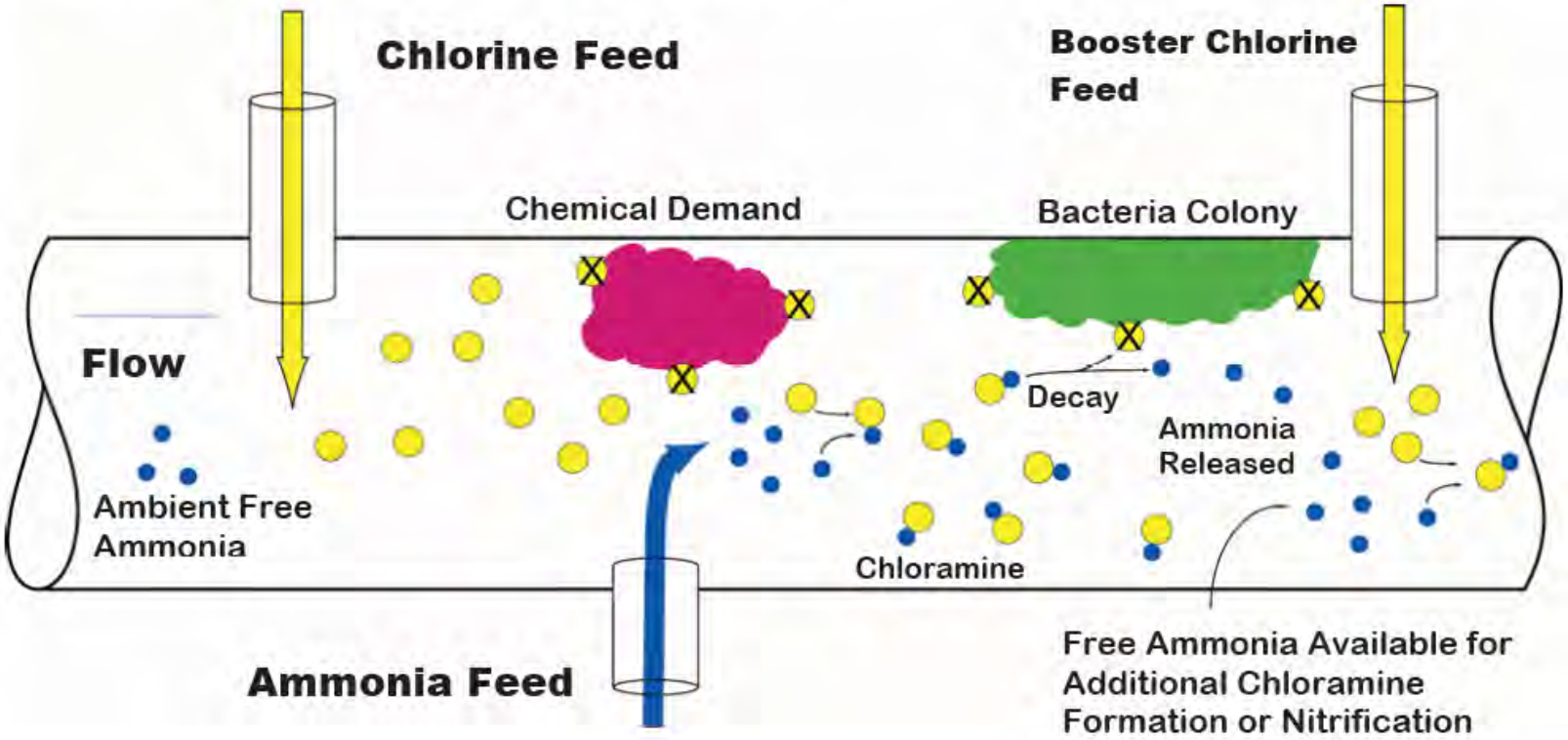
Freese + Nichols
Texas Water ppt 2010

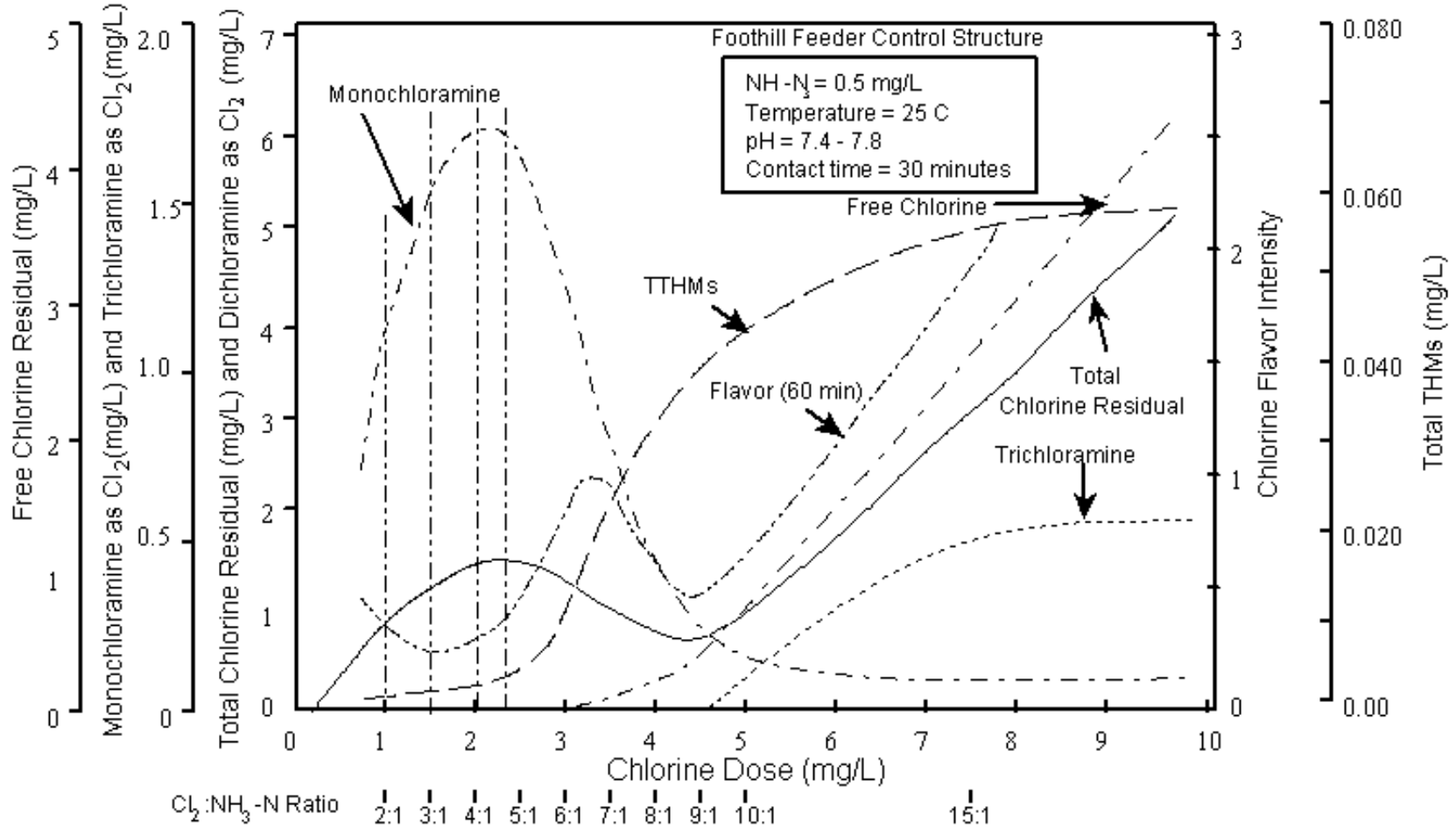
Figure 2 – Chloramine Formation and Decay



City of Milwaukee, WI

Side by Side with Hach APA-6000
Chloramination Monitoring at Two Sample Points
One ChemScan replaces entire wall of equipment

Cl_2:N Ratio Effects on THM and Flavor



Source: Barrett 1985

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

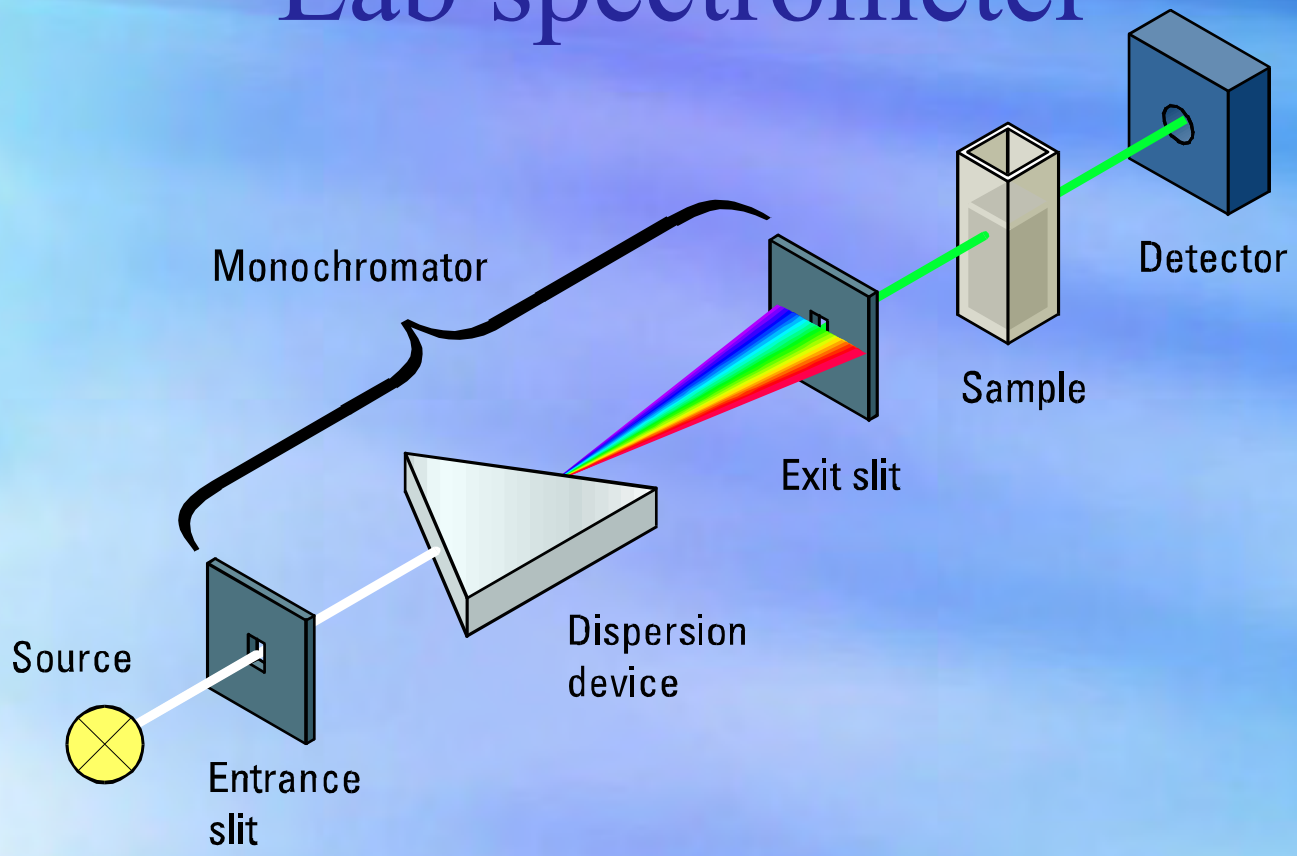
Brominated organic compounds

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

No.	Reaction
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$
11	$HOCl + Br^- \rightarrow HOBr + Cl^-$
12	$HOBr + NH_2Cl \rightarrow NHClBr + H_2O$
13	$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+$
14	$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^-$
15	$NH_3Br^+ \leftrightarrow NH_2Br + H^+$
16	$NH_3Br^+ + NH_2Cl \rightarrow NHClBr + NH_4^+$
17	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$
18	$NH_2Br + NH_2Br \leftrightarrow NHBr_2 + NH_3$
19	$NH_2Br + NHBr_2 \rightarrow$ Products
20	$NHBr_2 + NHBr_2 + H_2O \rightarrow$ Products
21	$2NHClBr + H_20 \rightarrow N_2 + HOBr + 2HCl + HBr$

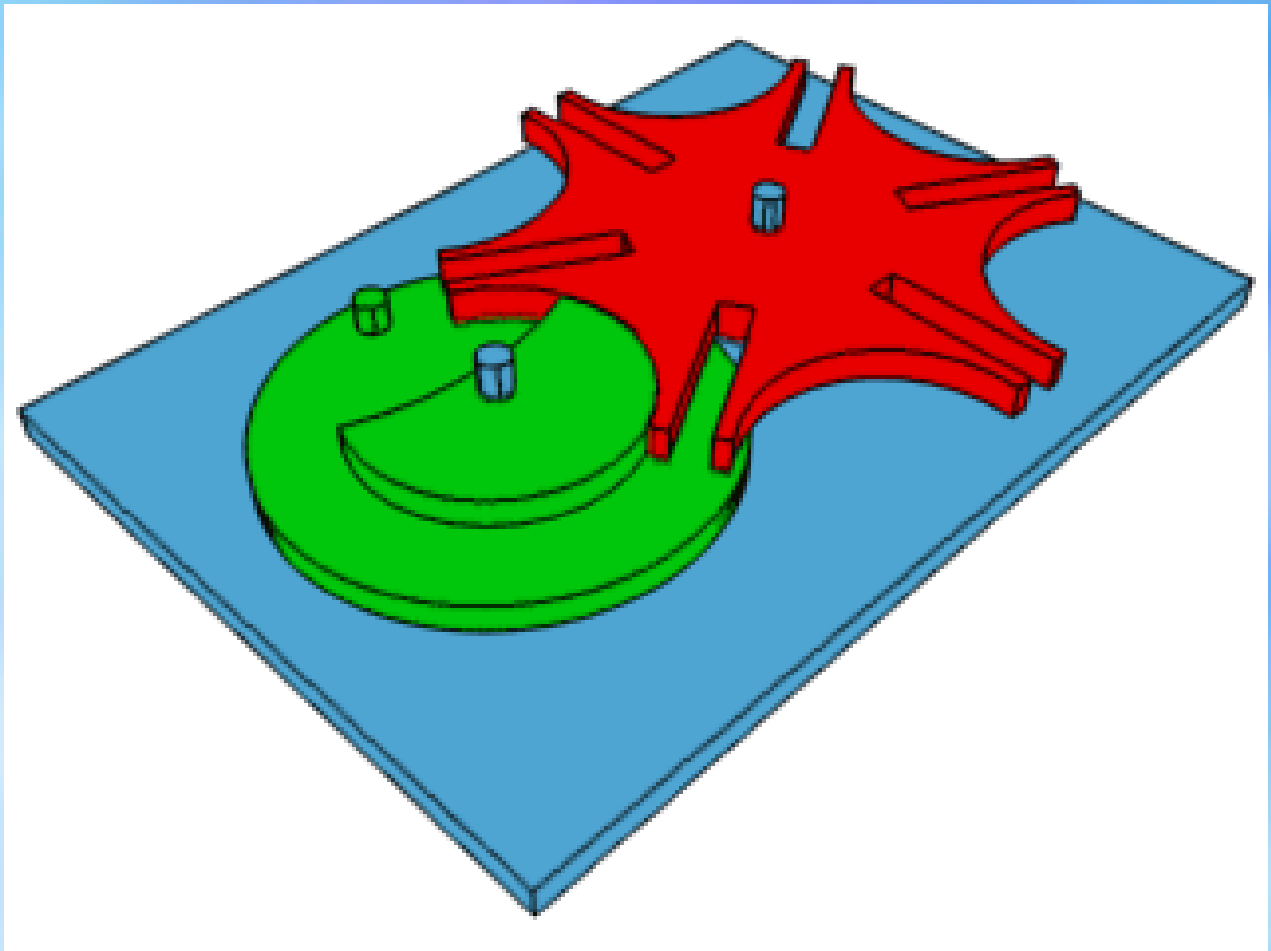
Courtesy Dr. Gregory Popr - Carollo

Lab spectrometer



Automation is Applied

Sampling is Simplified



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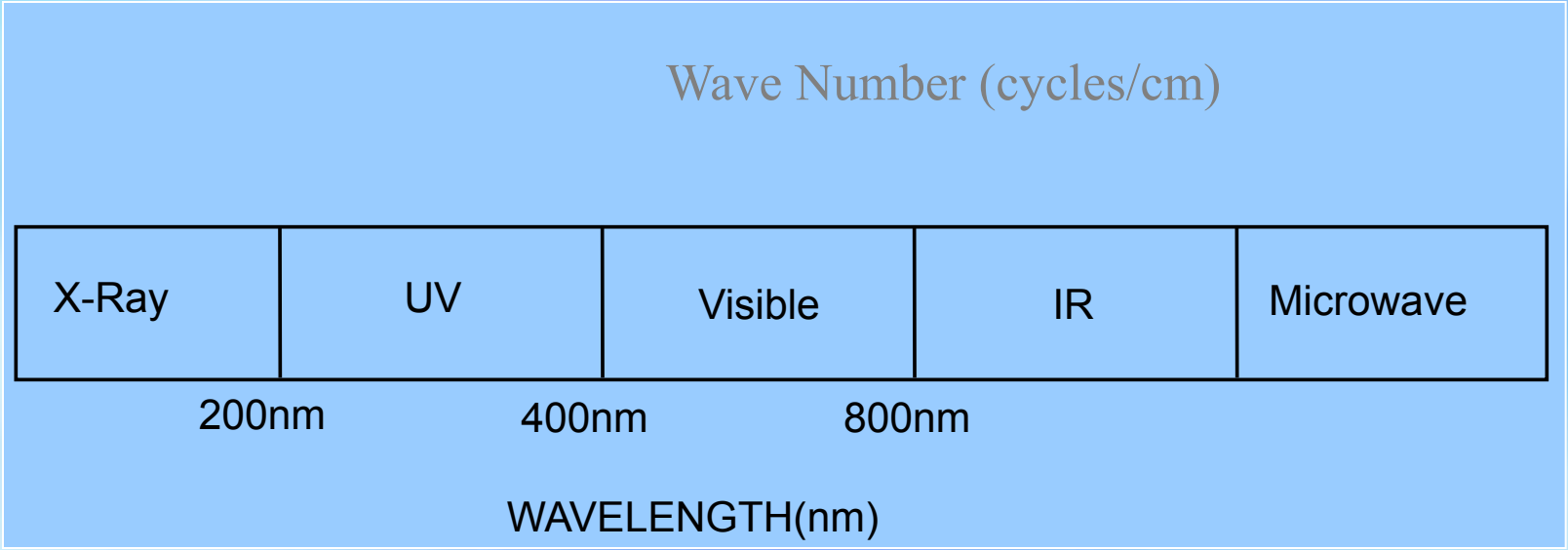
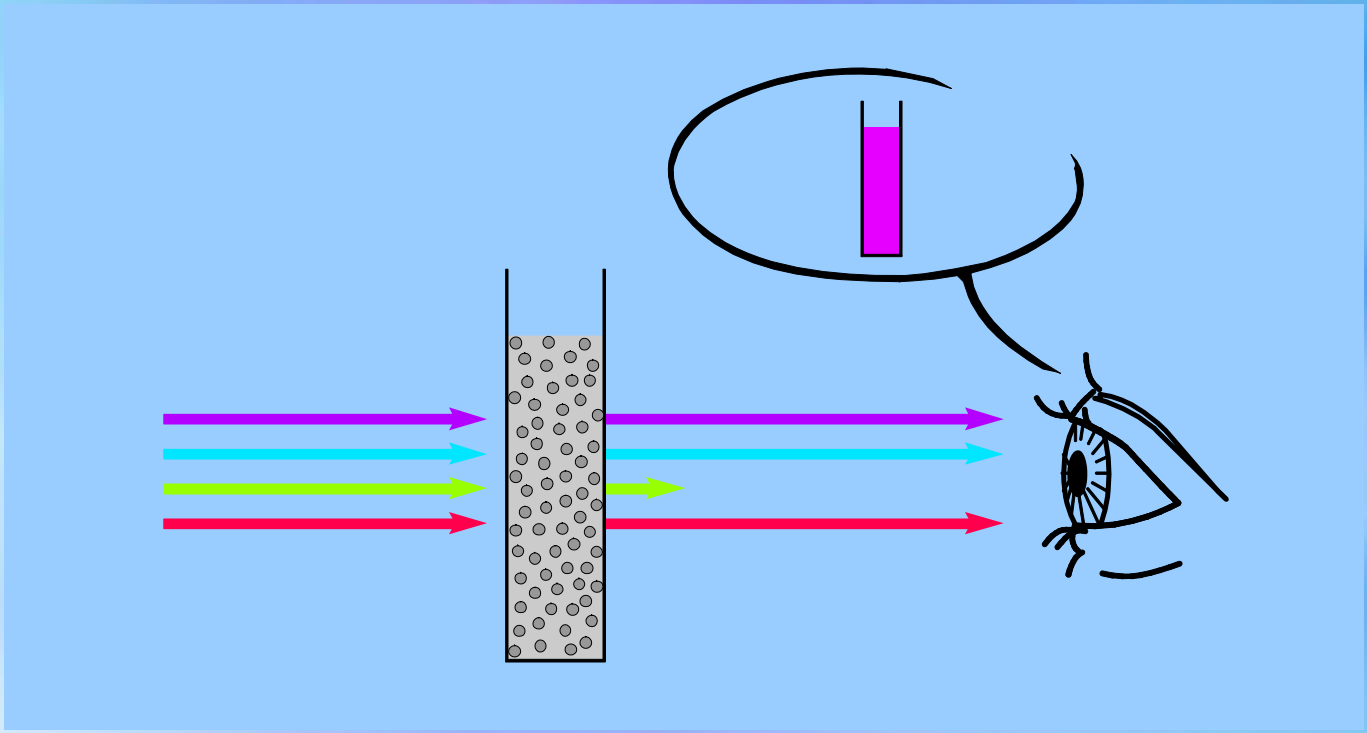
Spectroscopy

Spectral Distribution of Radiant Energy



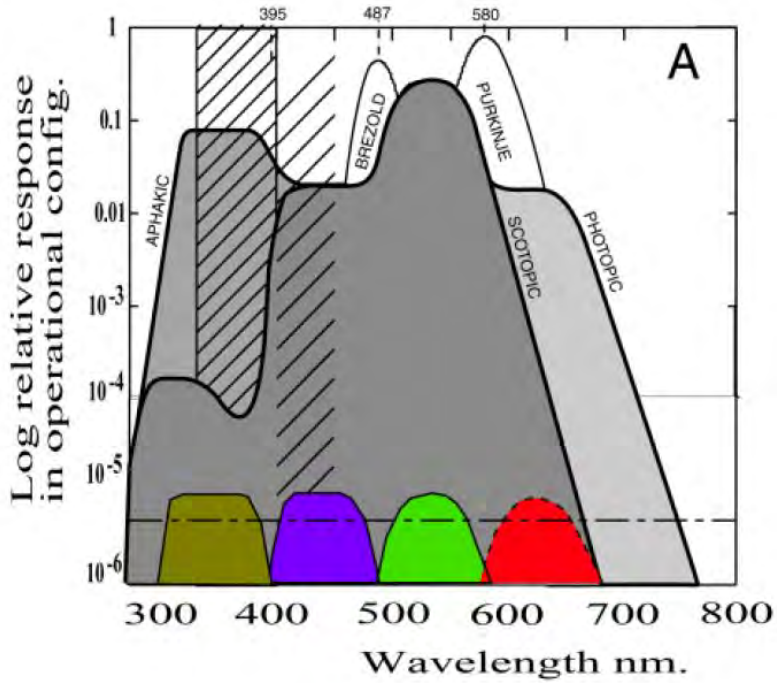
Transmission and Color

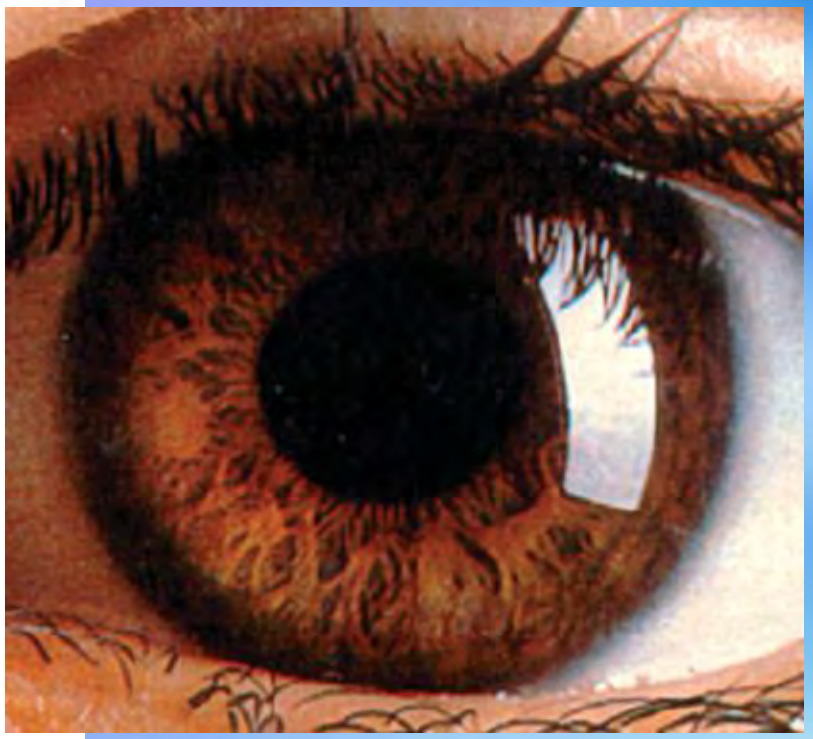


The human eye sees the complementary color to that which is absorbed

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]

Classic Monitoring Device

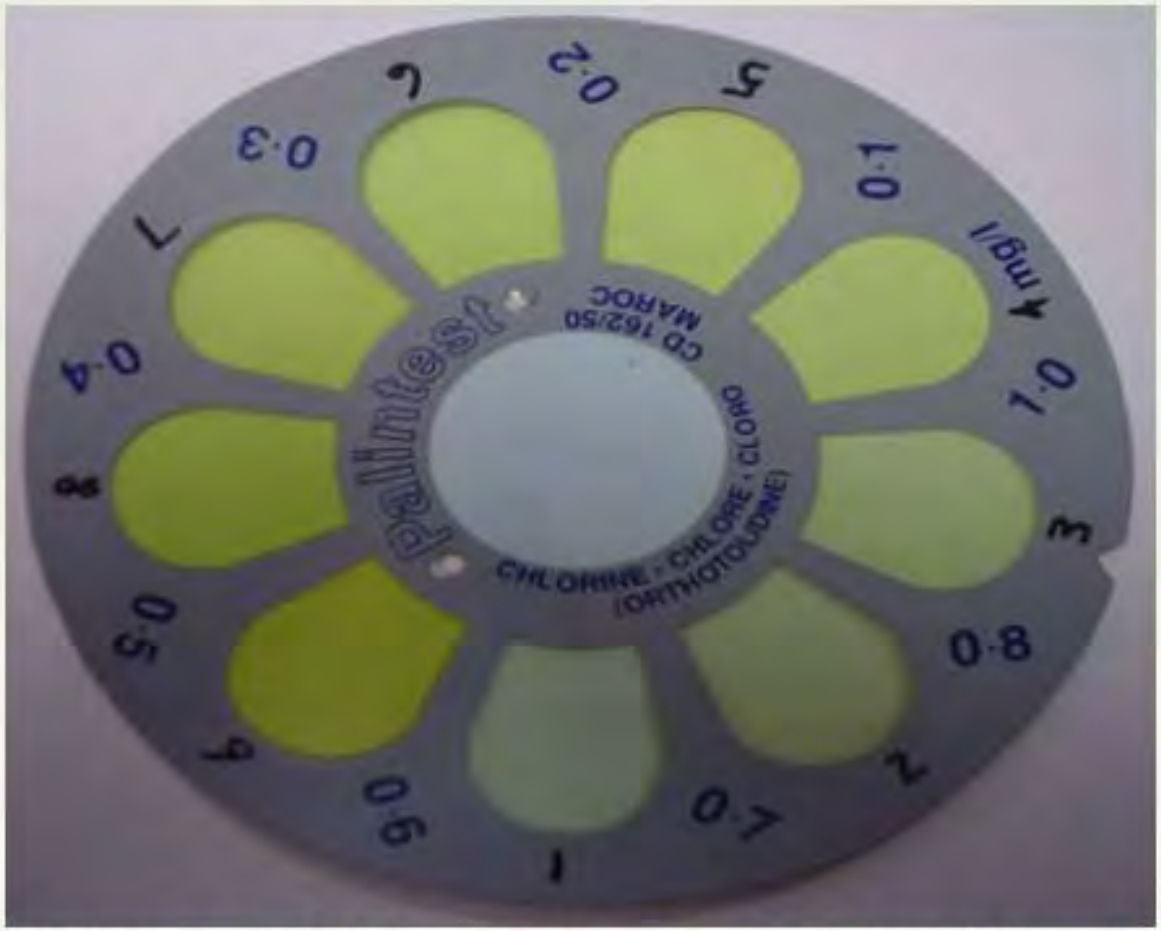


Figure 1. Chlorine Content Color Wheel

Spectrometers are better

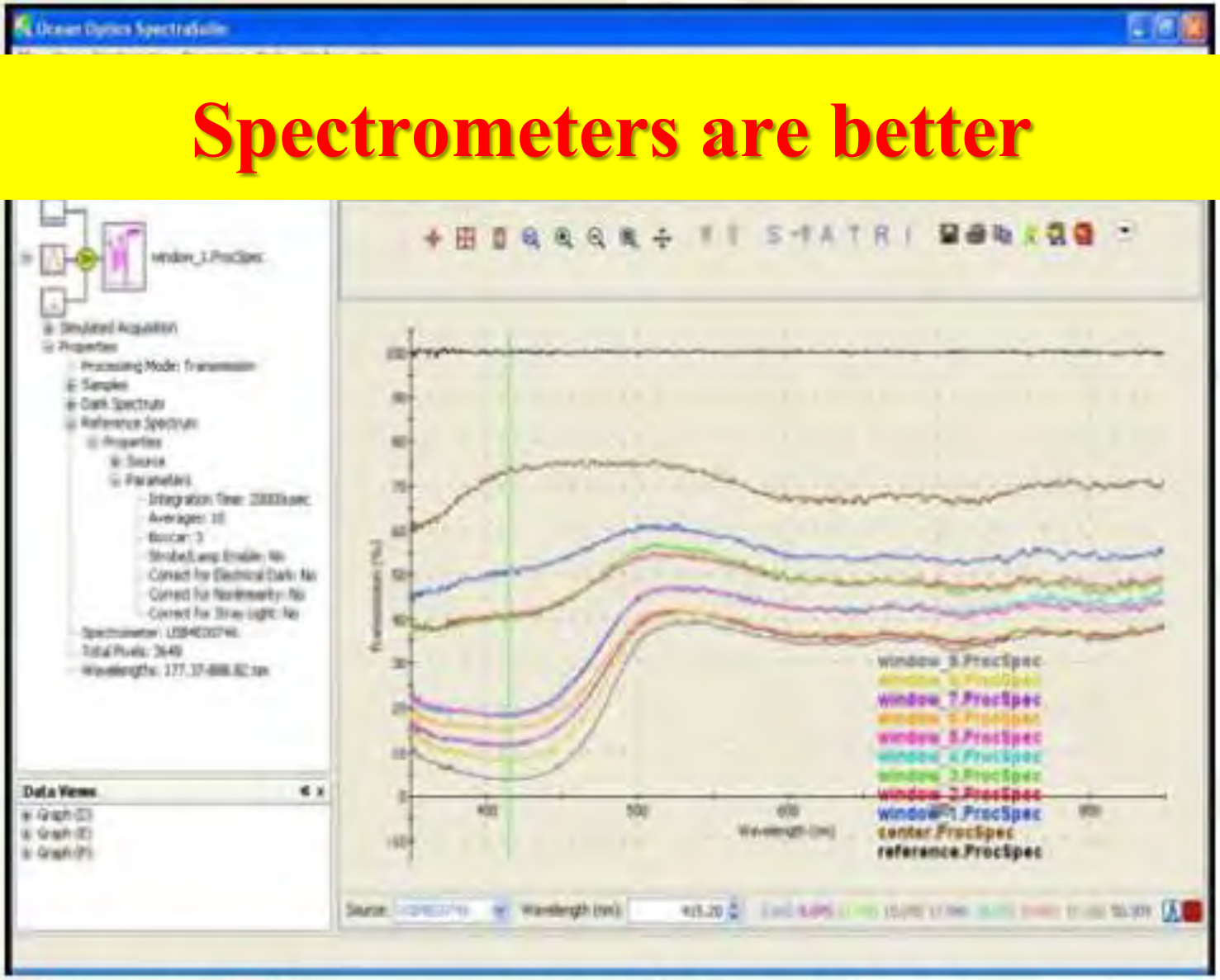
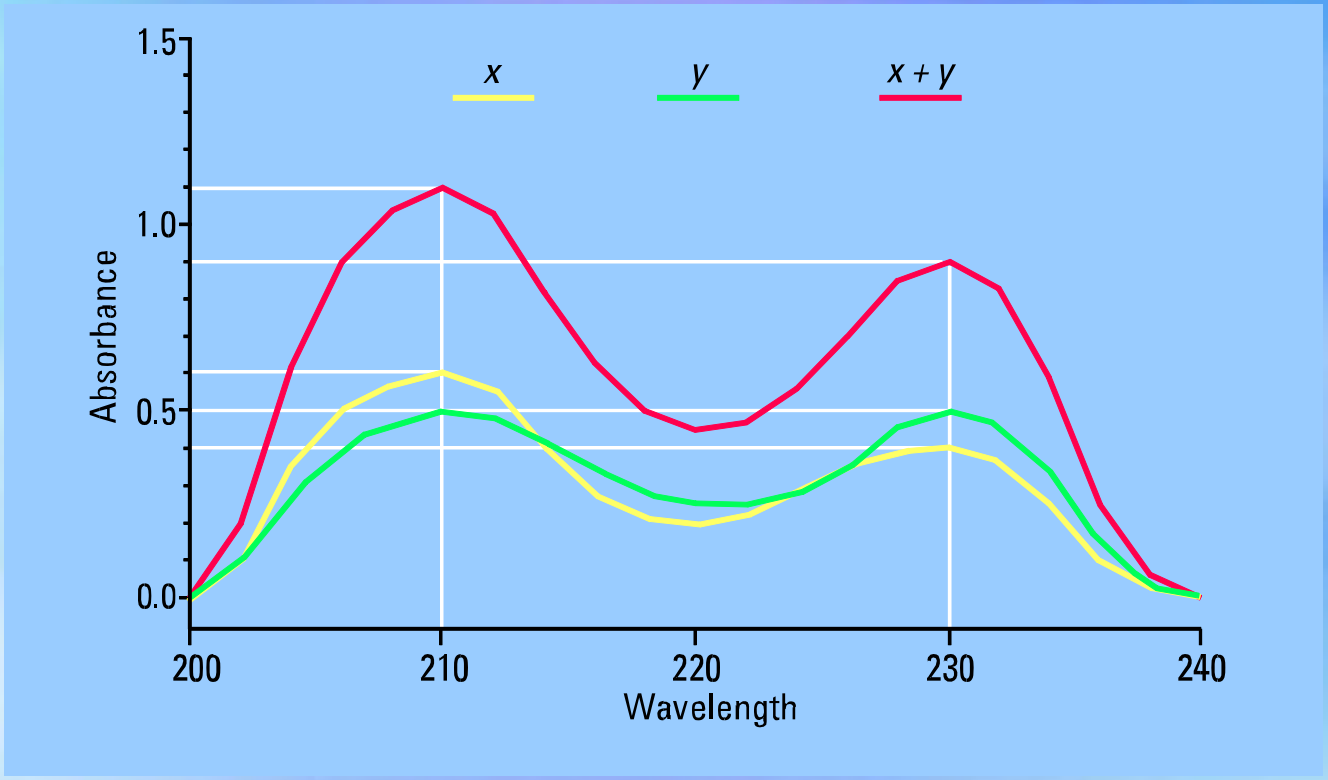


Figure 7. Transmission data with no sample in optical path as reference

Two-Component Mixture



Example of a two-component mixture with significant spectral overlap

Chemometrics

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

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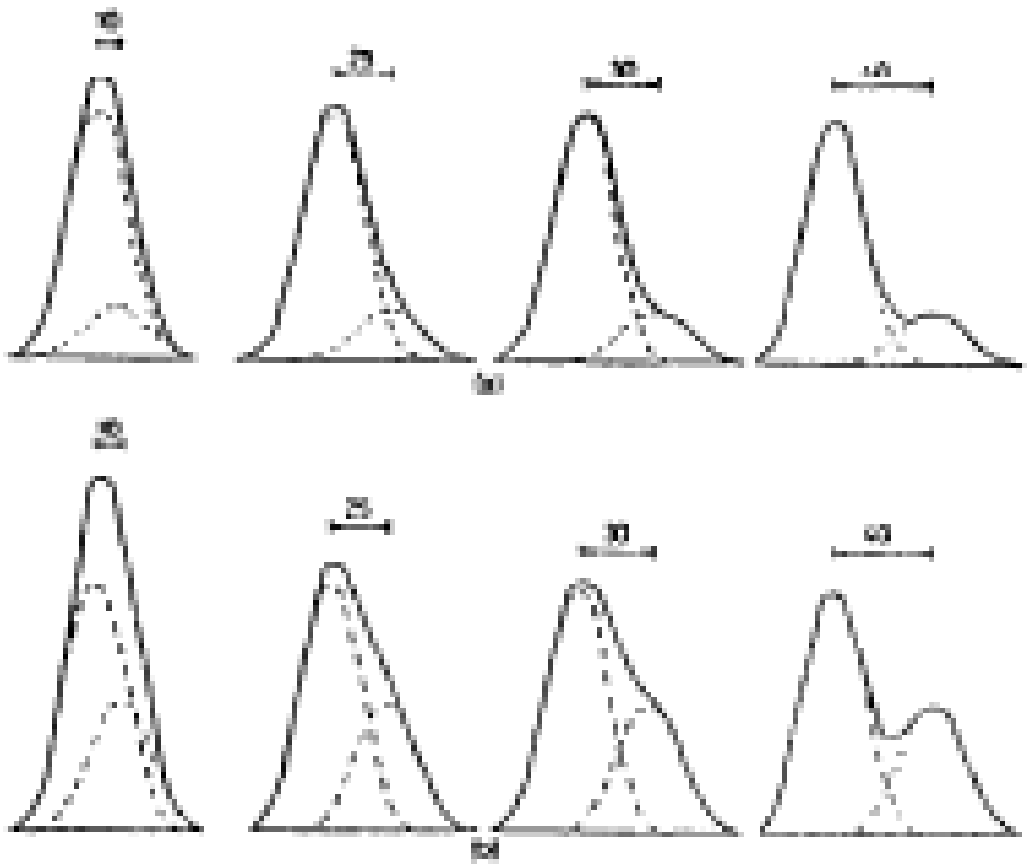
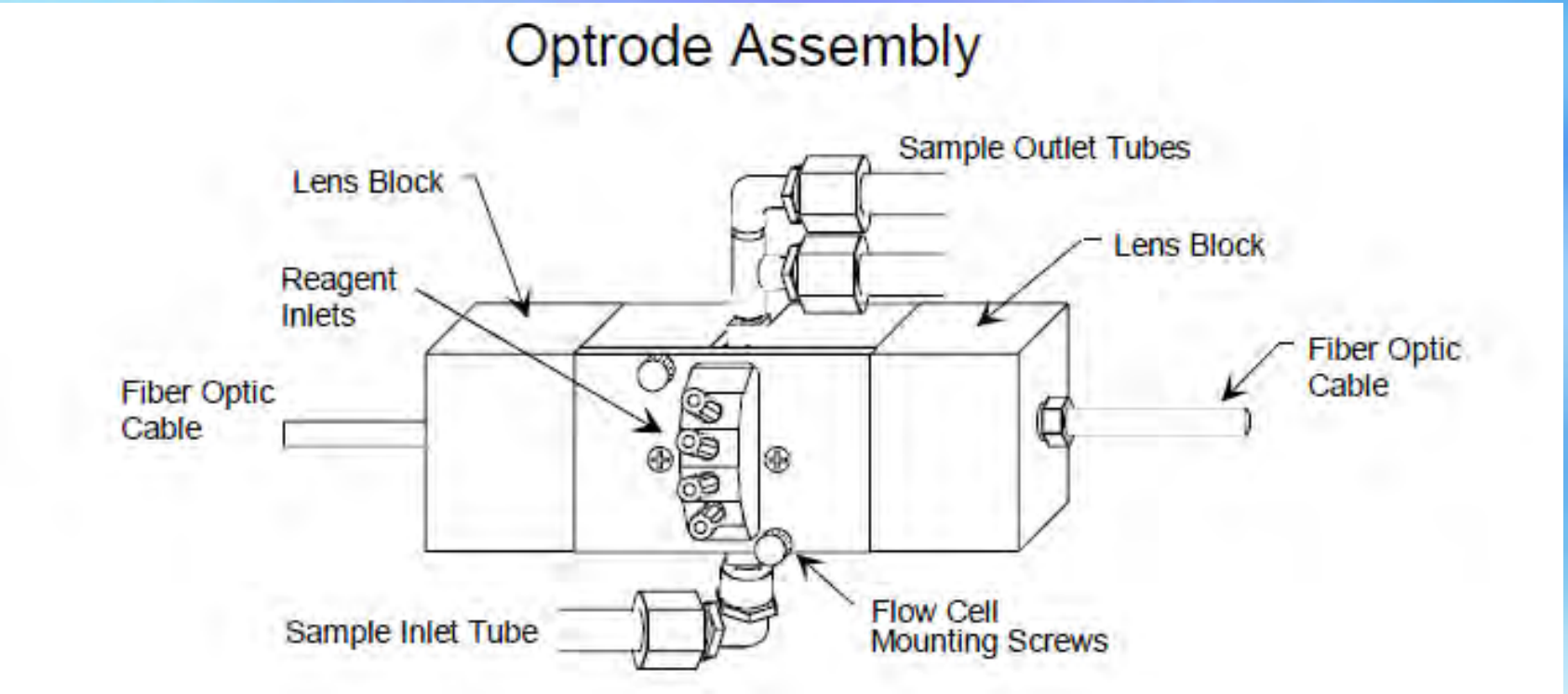
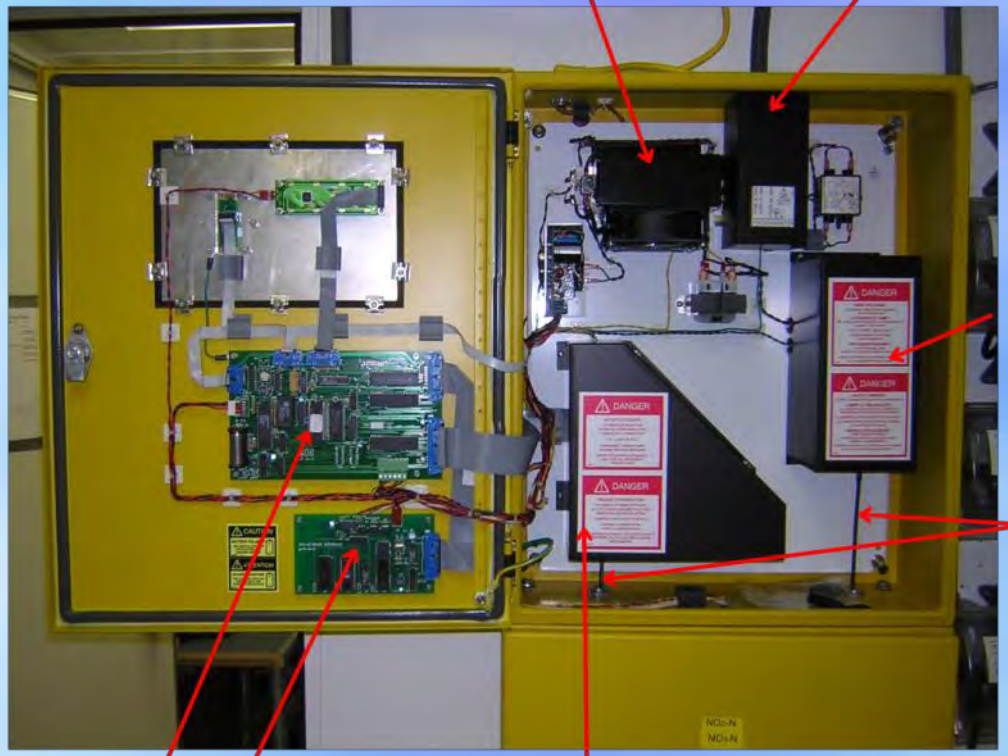
Pattern Recognition Software



We extend that platform into a working instrument



UV-6101 Analyzer
Upper Electonics Enclosure



AppliedSpectrometry Associates, Inc.

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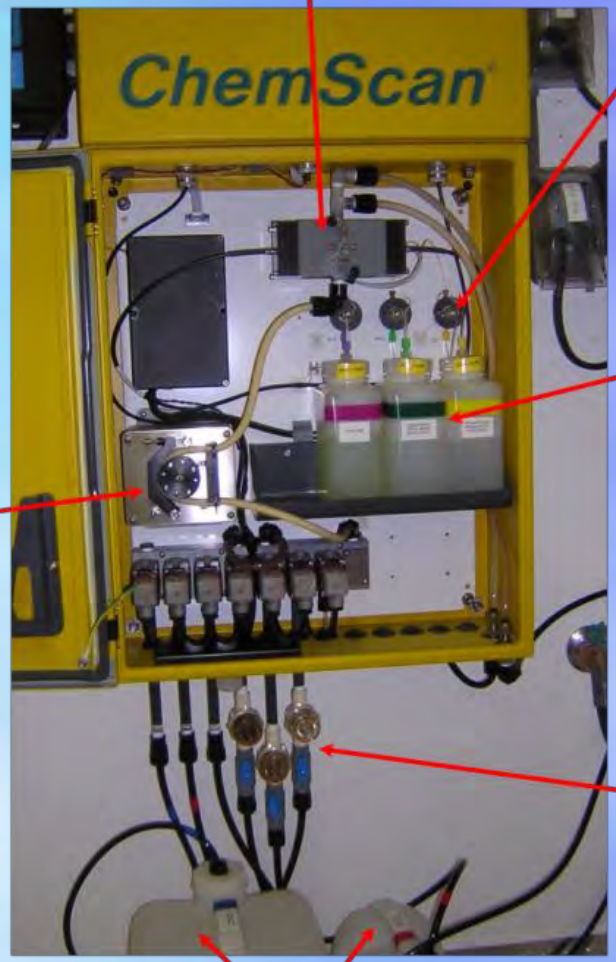
An Online Lab Grade Wide Band Spectrometer

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



FlowCell

Reagent Injectors

Reagents

Internal Peristaltic Pump

Sample Inlets

Zeroing and Cleaning Solution Containers

UV-VIS Analyzer

Lower Enclosure

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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

asa ANALYTICS

Houston, TX Metro MUDs

Consecutive System Chloramination Control
Twenty Seven (27) Analyzers

Monochloramine, Total Chlorine, Free Ammonia and Total Ammonia

Demonstrated Results & Accuracy

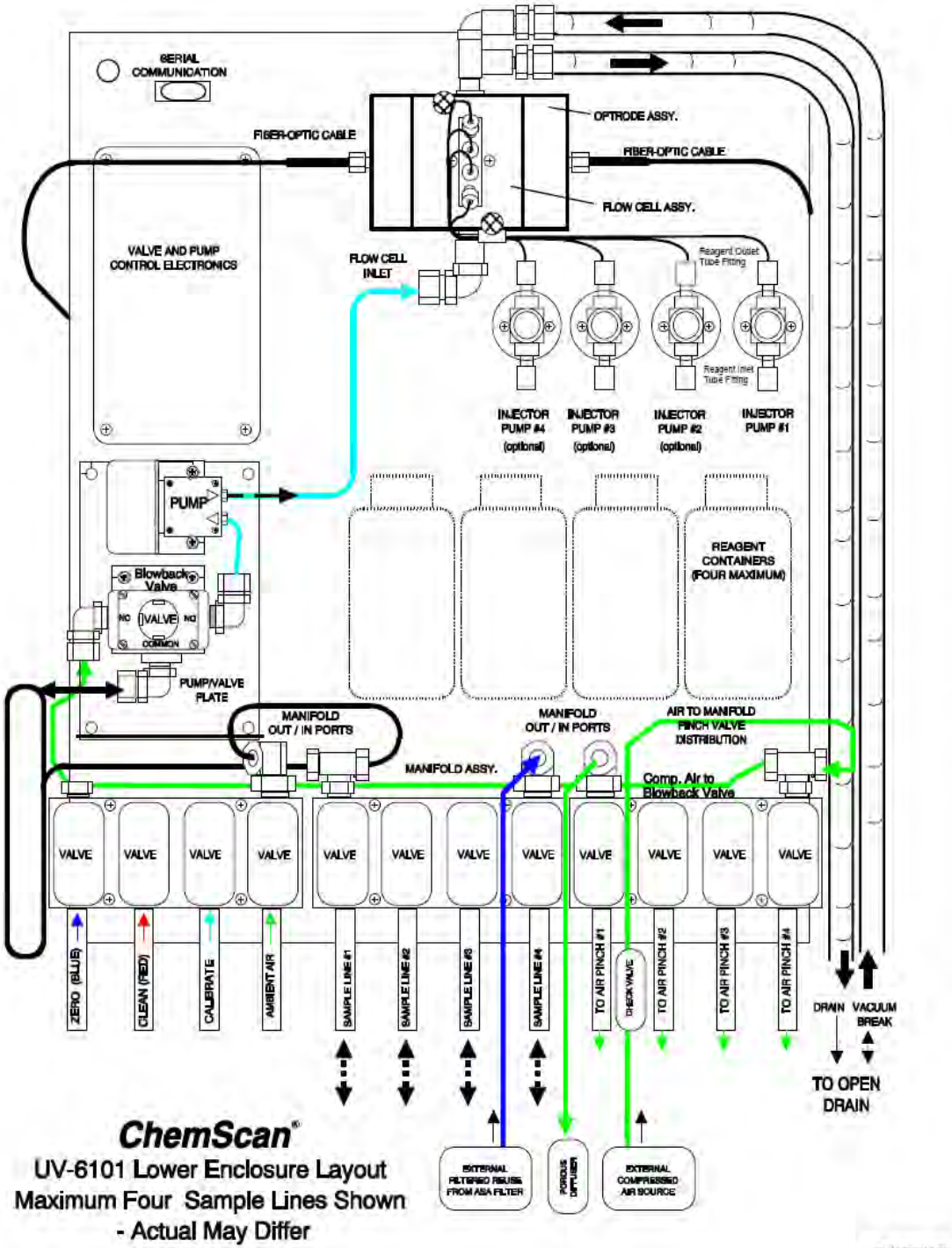
Optimized Performance

Standardized Components

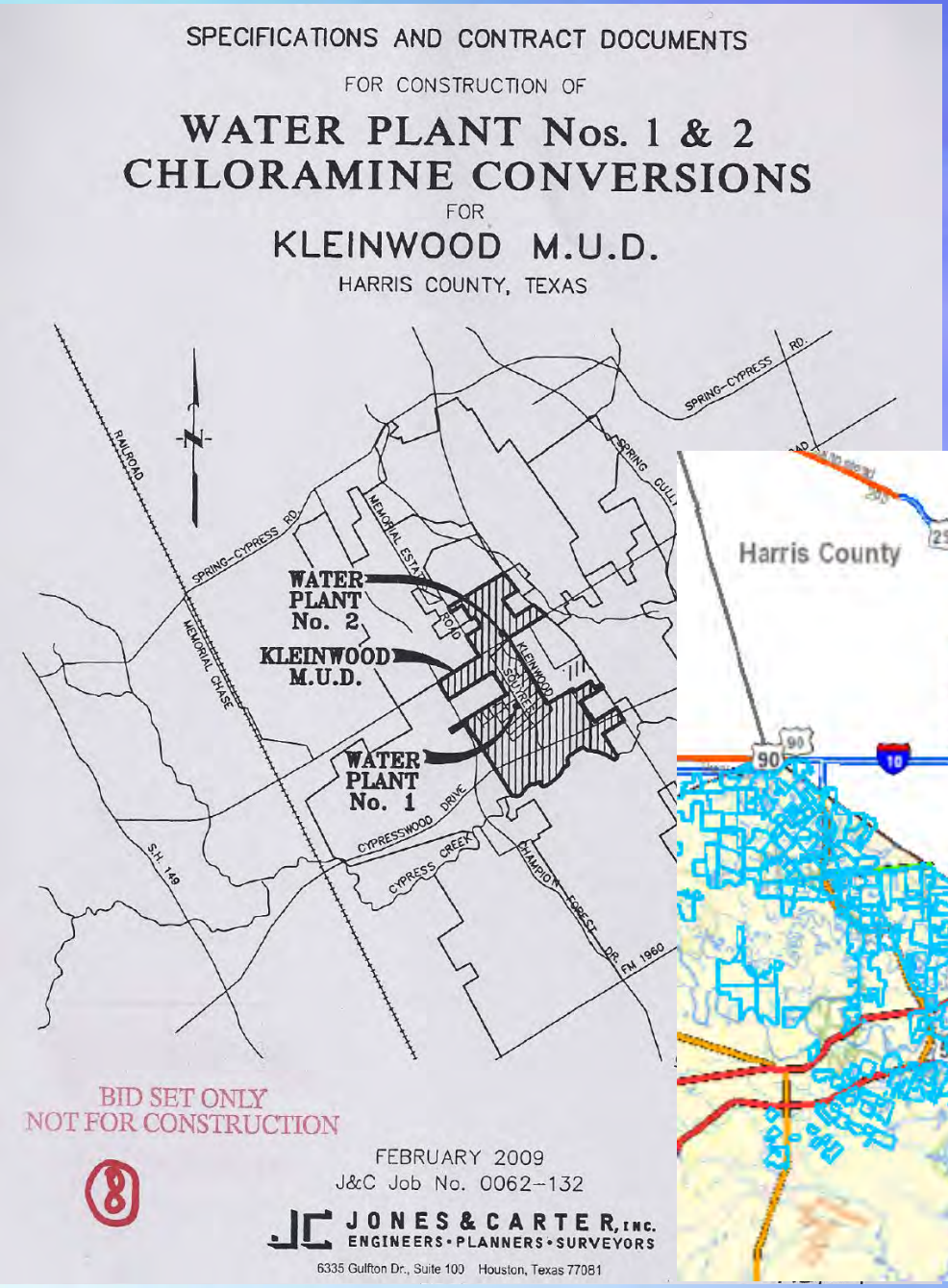
Long Life Cycle

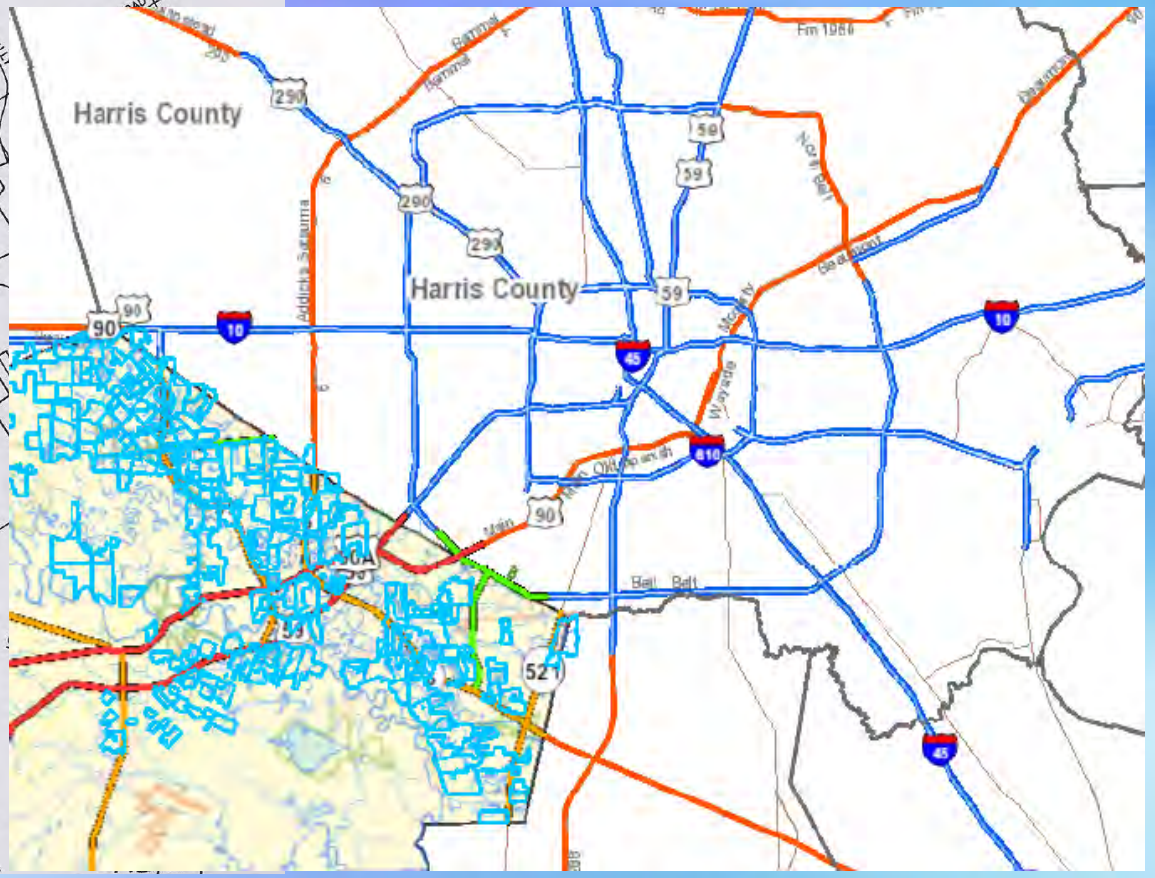
Upgradable for Future Process Modifications

Hand Made in USA

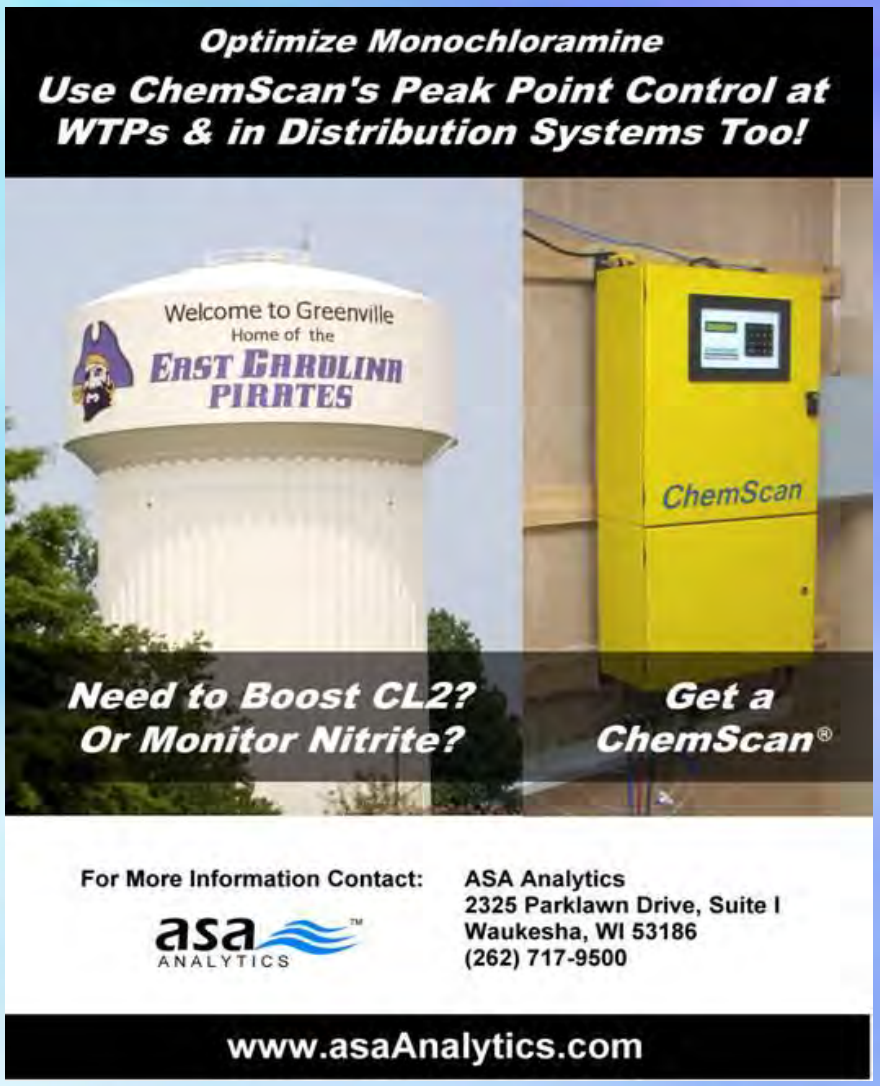


Typical 2 sample lines before and after water transfer from Houston WTPs





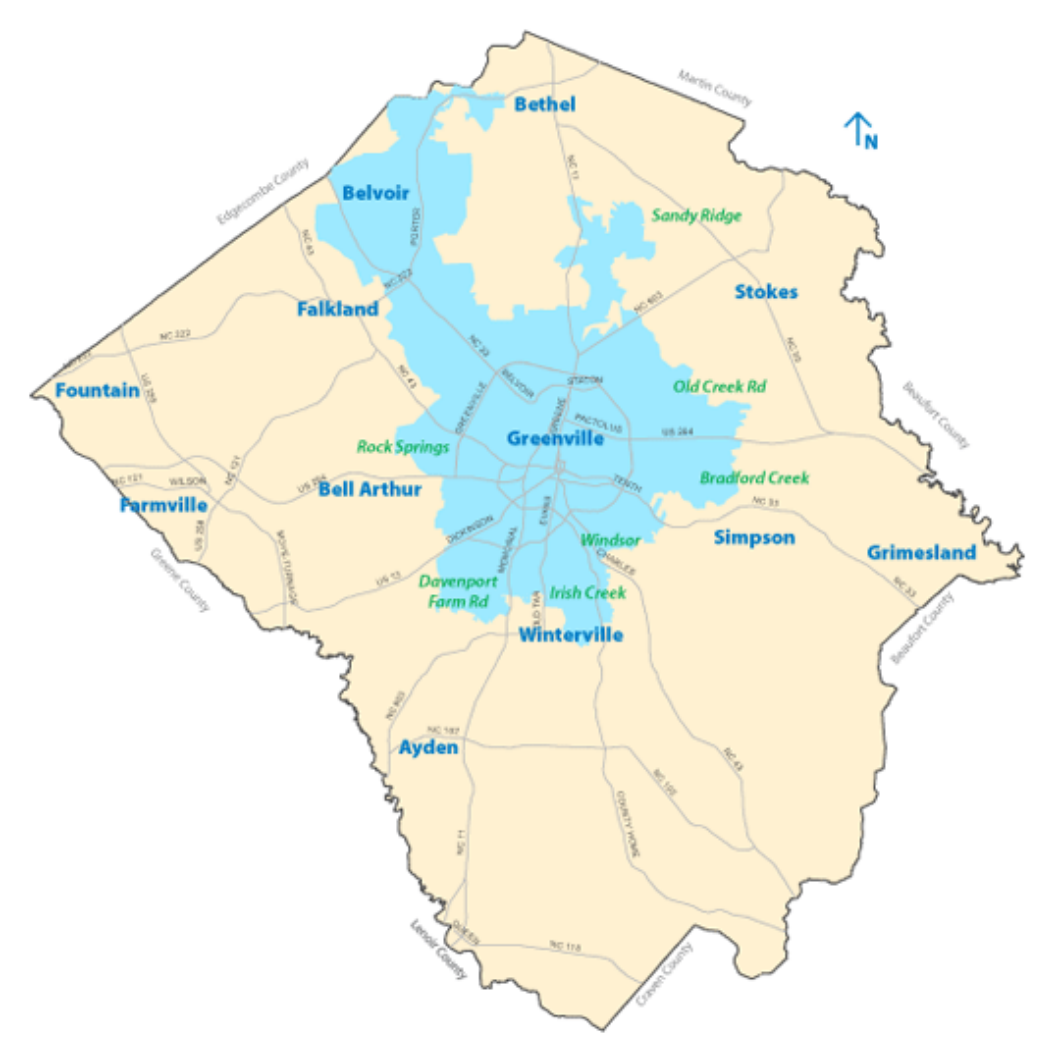
Tank & Distribution Control



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

asa ANALYTICS

Greenville Utilities Commission



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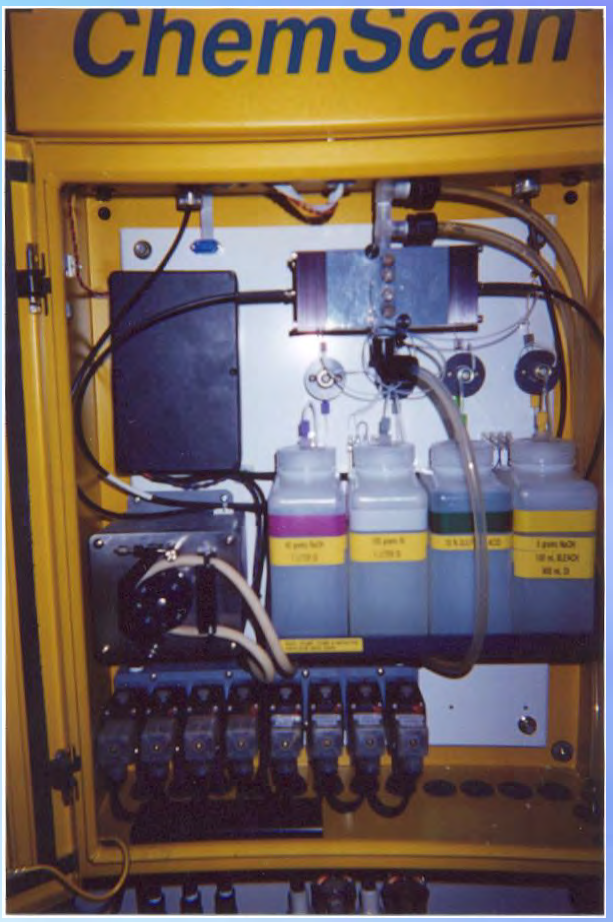
Regional Distribution and Best Tasting Rural Water Contest 2012

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.

asa ANALYTICS

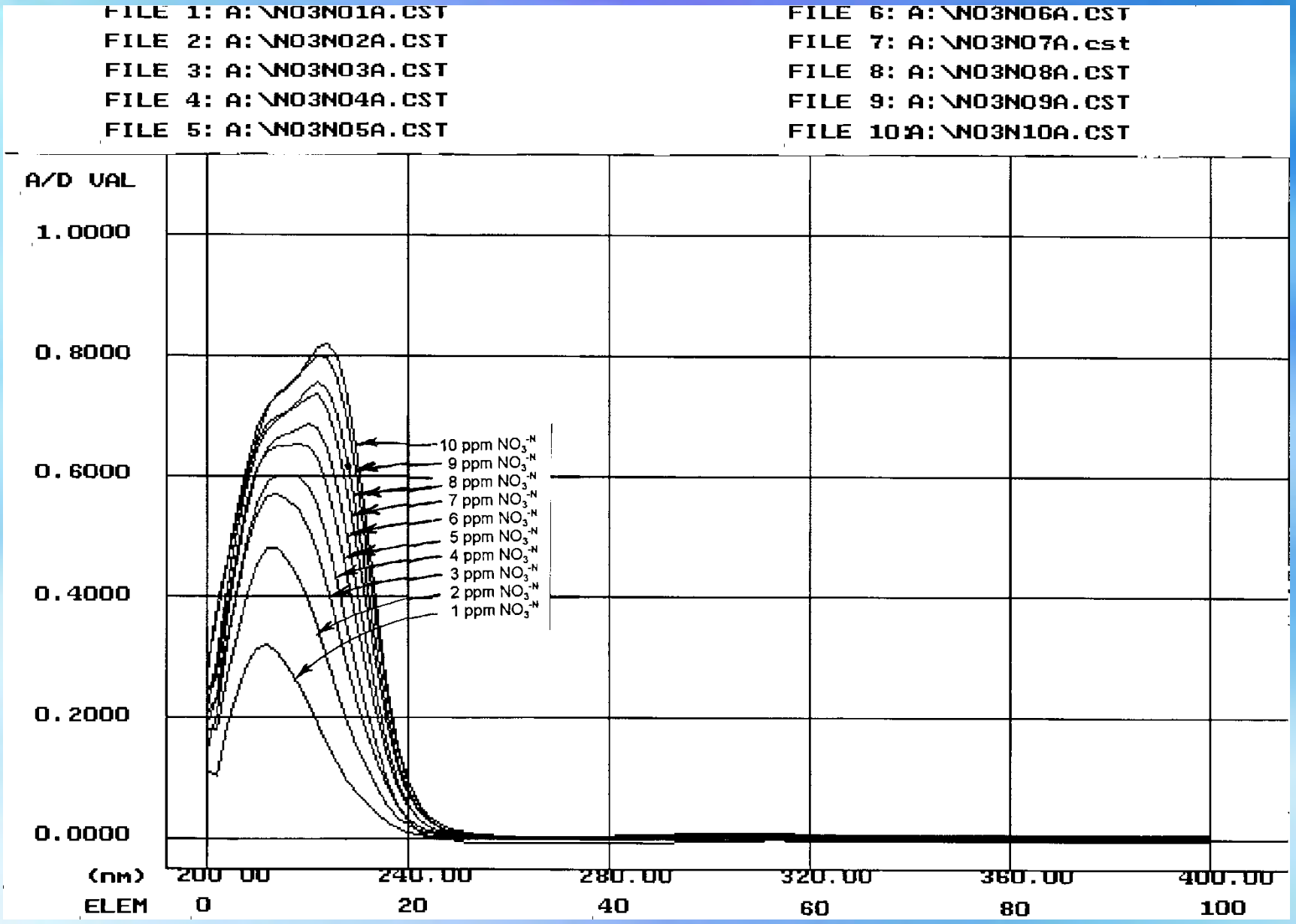
Chloramine Plus

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

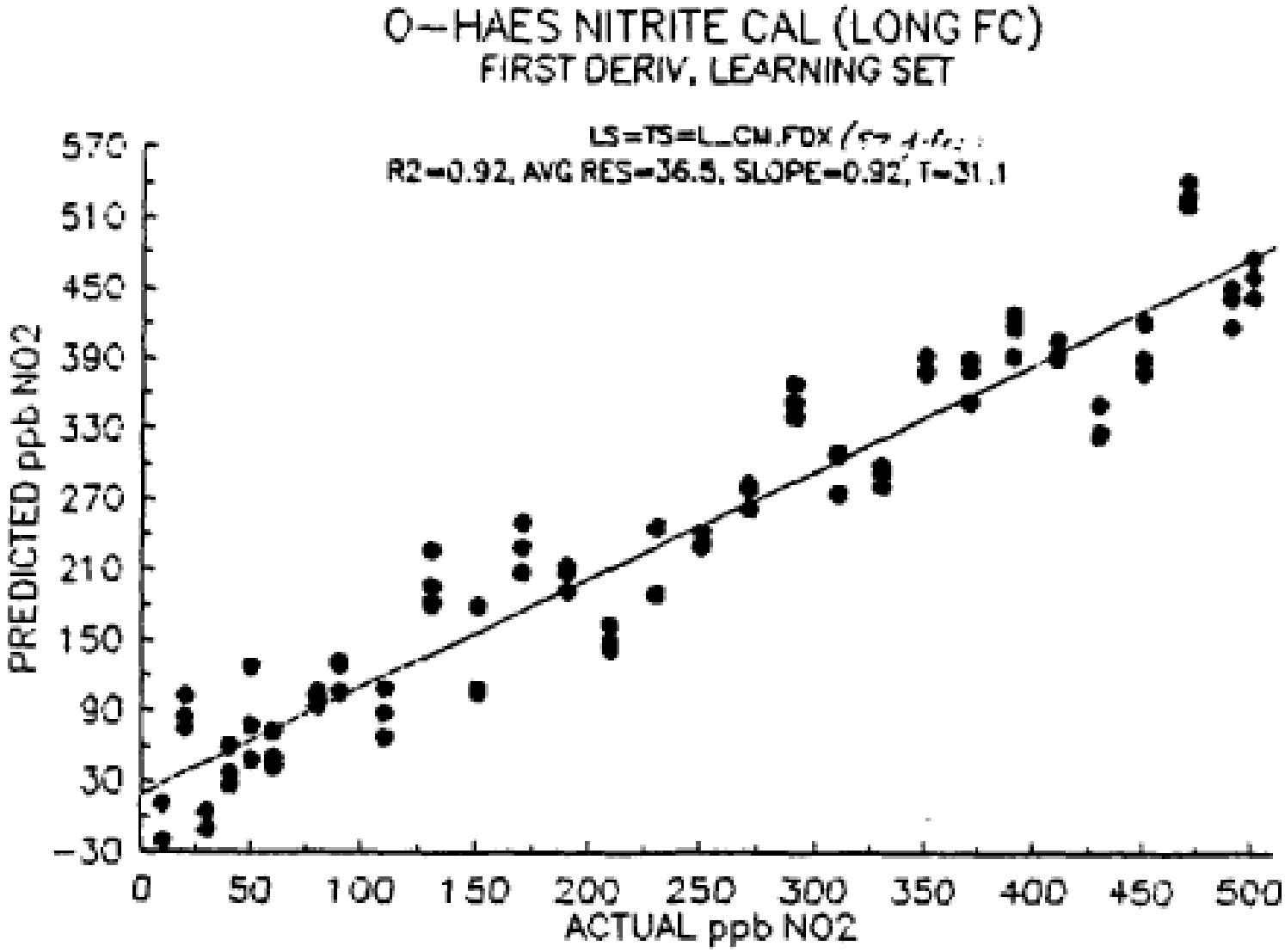


Free Ammonia
Total Ammonia
Mono-chloramine
Total Chlorine
Nitrite
Iron and
Manganese

NO3 Calibration curves



NO2 Calibration Set

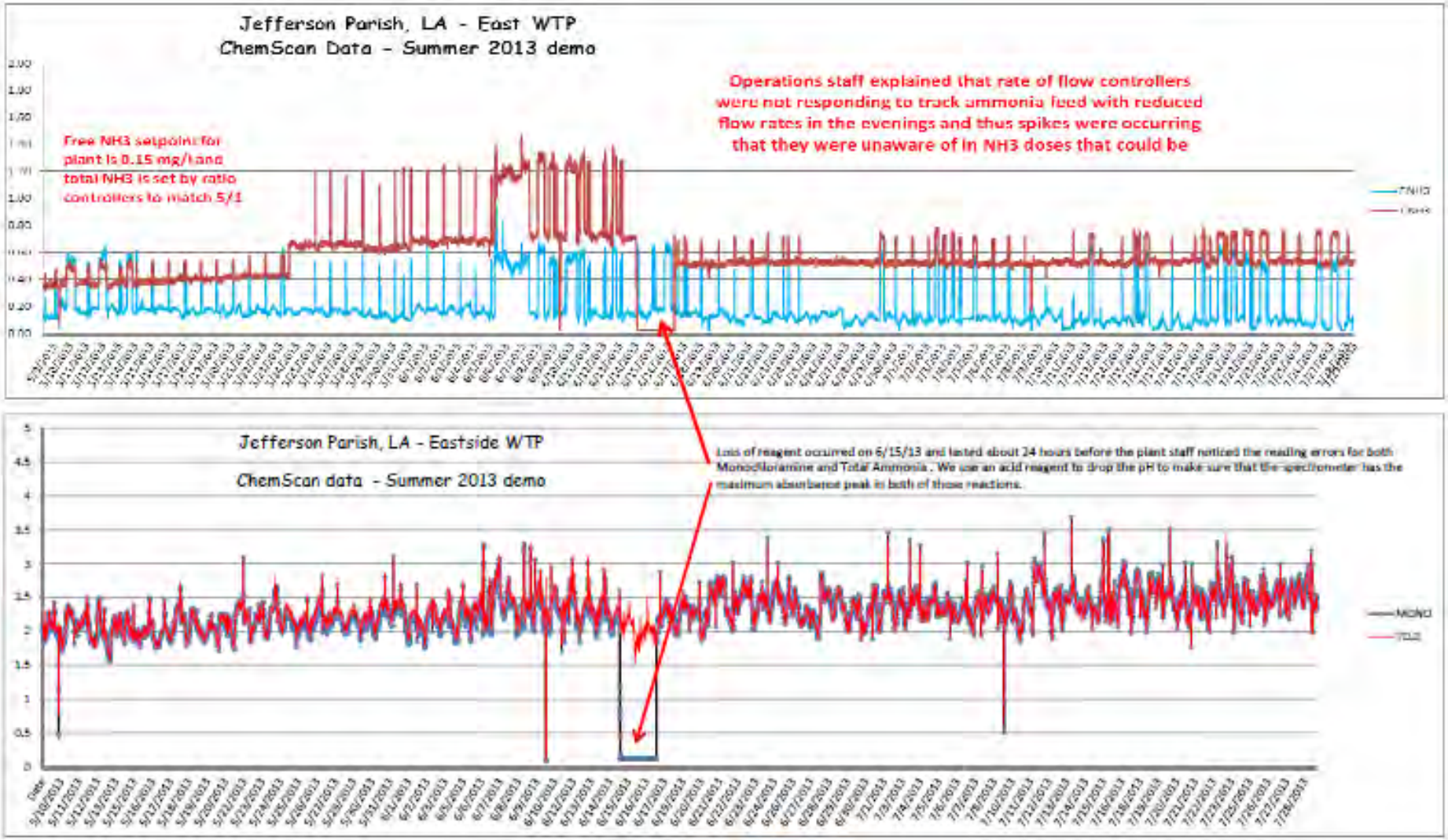


Jefferson Parish, LA demo test

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



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Disinfection Residual Maintenance In Toronto

- 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

TORONTO Water

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

TORONTO Water

asa ANALYTICS

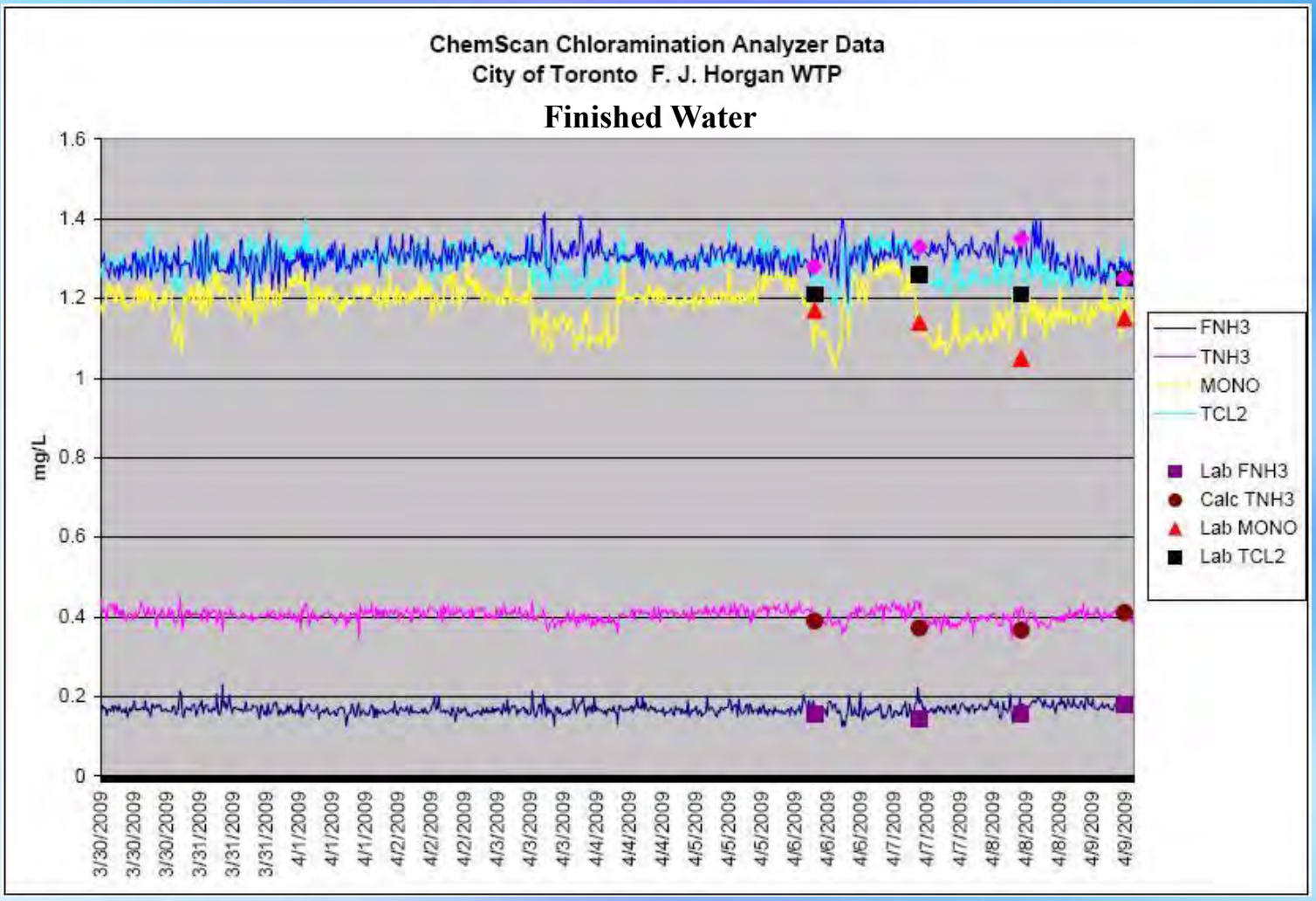
Pilot Scale Testing - Anecdotes

- 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

TORONTO Water

asa ANALYTICS

Full Scale Implementation of ChemScan



TORONTO Water

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

TORONTO Water asa ANALYTICS

Best Tasting Water Contest Winner

AB JEWELL AND MOHAWK
WATER TREATMENT PLANTS
CHLORAMINES MODIFICATION

ATTENDANCE AT PRE-BID CONFERENCE IS MANDATORY

PREPARED BY:
CH2MHILL
401 S. BOSTON, SUITE 330
TULSA, OK 74103
918-583-3057 OFFICE
918-584-5826 FAX
MURRY FLEMING, P.E.

CITY OF TULSA OKLAHOMA

CITY OF Tulsa
A New Kind of *Energy*™

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Conversion from Free CL2 to Combined Chlorine (NH2CL)

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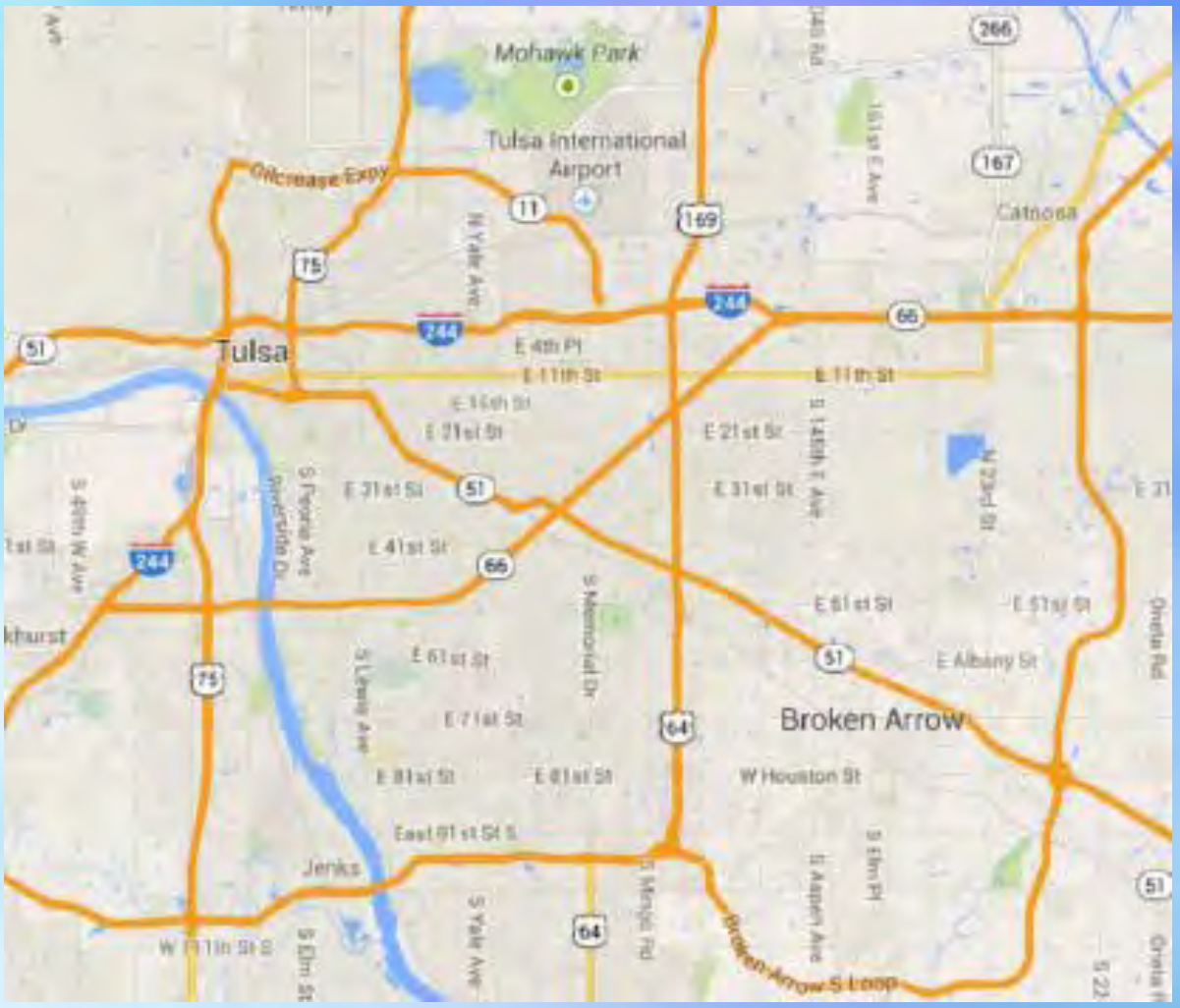
AB Jewell and Mohawk WTPs
90 MGD + 100 MGD respectively

ANALYTICS

System Wide Conversion after 6 months of PR and Preparation

asa ANALYTICS

Conversion and Flushing older water gone in 5 days



186 sq miles of pipes to flush

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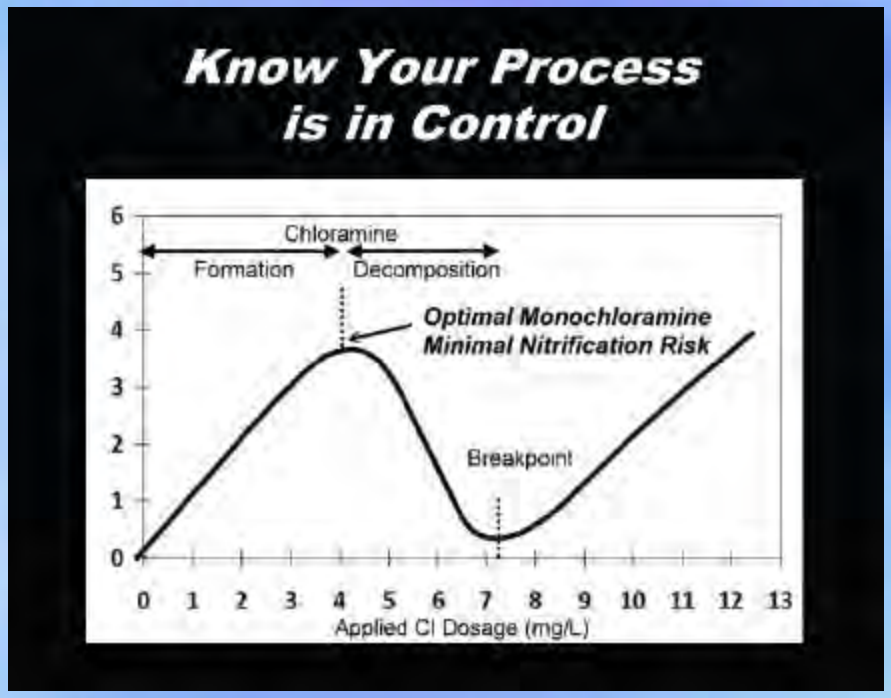
Charleston, SC – Hanahan WTP

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

ASA Update -

ChemScan in the News!

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 stores are also featured on our homepage:

http://www.asaAnalytics.com

www.asaAnalytics.com

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

ChemScan Publications

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

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