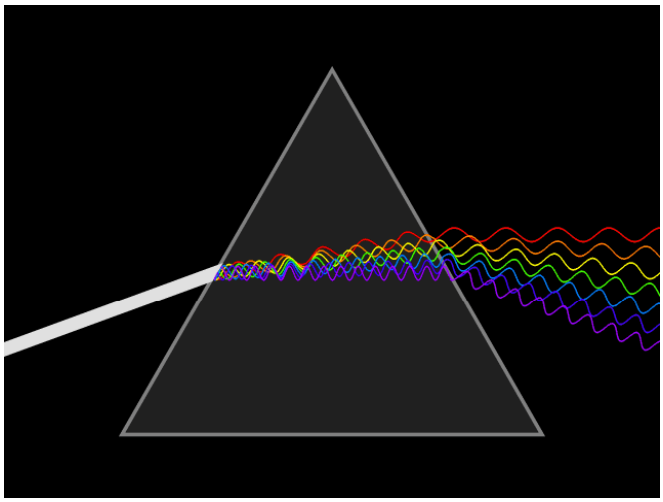
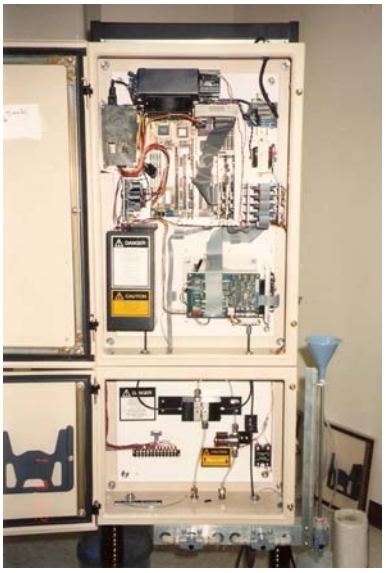
Online Analysis for BNR/ENR Process Monitoring and Control

Bruce Stevens – SE Regional Manager

Physics - Dark Side of the Moon



NASA research and development grants



ChemScan.com

SKYLAB + Lunar Colonization

ChemScan.com

AppliedSpectrometry Associates, Inc.

The Three Wise Men ….. started a business

2010 YEAR WINNER

Applied Spectrometry Associates Inc.

LOCATION: 2325 Parklawn Dr., Waukesha

WEB SITE: www.chemscan.com

YEAR FOUNDED: 1995

PRODUCT OR SERVICE OFFERED: Automatic chemical analysis systems for water and wastewater.

PROJECTED 2006 REVENUE: $2.1 million

LEADERSHIP TEAM: Bernie Beemster, president; Scott Kahle, treasurer; Bruce Reynolds, secretary.

TARGET CLIENTELE: Municipal and industrial water and wastewater treatment plants.

BUSINESS ORGANIZATION MEMBERSHIPS: Metropolitan Milwaukee Association of Commerce, American Water Works Association, Water Environment Federation, Instrument Society of America.

WHAT HAS FUELED YOUR COMPANY'S GROWTH? Dedication to product reliability and customer service.

DO YOU PLAN CHANGES IN YOUR COMPANY IN THE UPCOMING MONTHS? Yes.

WHO ARE THE BUSINESS PEOPLE, LOCAL OR NATIONALLY, WHOM YOU ADMIRE? AND WHAT TRAITS DO THOSE PEOPLE EXHIBIT THAT MAKES YOU ADMIRE THEM? The founders have been influenced by the leaders of several local companies for whom they worked including Nate Zelazo at Astronautics, Donn Dresselhuys at Autotrol and Harry Quadracci at Quad/Graphics. These leaders not only developed substantial businesses, but also helped to develop a generation of future business leaders in Milwaukee.

WHAT IS THE OUTLOOK FOR THE BUSINESS CONDITIONS OF YOUR INDUSTRY OVER THE NEXT SEVERAL MONTHS? State and local government budgets seem to be improving, with more infrastructure projects moving forward and numerous new projects under design. Many of our projects are related to treatment plant construction or improvements and are located in high growth areas of the country. Demand for public facilities in these high growth locations do not seem to be adversely affected by price adjustments in the housing market. Demand is ultimately driven by local population growth, economic activity and employment growth.

Scott Kahle, Bernie Beemster & Bruce Reynolds

EPCOT begin a new era in WWTFs

Reedy Creek Improvement District (RCID)

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

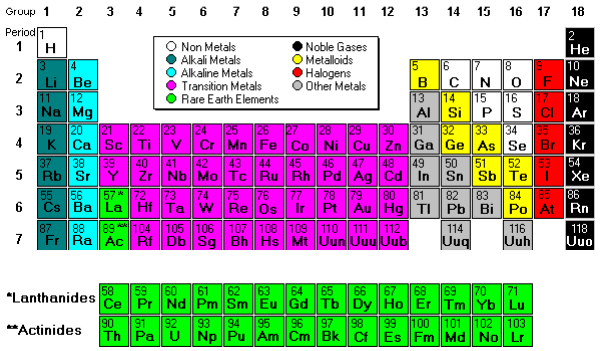
Parameters, Sample Points and Cost of Installation

- Many factors to consider depending on your water characteristics and process equipment
- Where to test
- What to test
- How often to test
- How much to operate and maintain
- How much does it cost to install

"If You Want to Control Process Chemistry, Measure Process Chemistry"

- If a plant has nitrogen and/or phosphorus discharge limits then why measure anything other than nitrogen and phosphorus for process control ?
- Surrogate parameters such as Dissolved Oxygen, ORP , Hardness and Respirometry do not provide any direct information about nutrient levels.
- If your pH is low, you can't nitrify…. If it's high in alkalinity you're OK
- And if there's excess ammonia, you will probably find nitrites in the disinfection system causing high chlorine consumption.

Chemistry



ChemScan.com

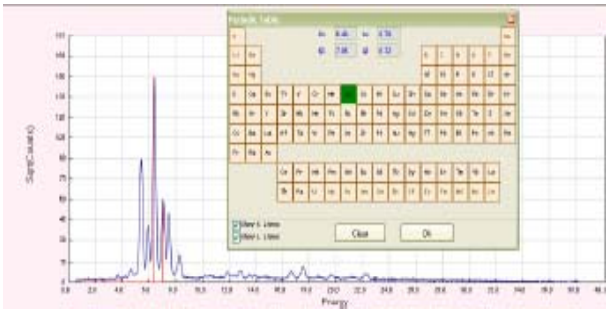
On-line Process Monitoring Requirements

- Analysis of multiple nutrients
- Monitoring of multiple sample points
- Fast response to concentration change
- Tolerance for background chemistry change
- Minimal sample conditioning
- Automatic operation
- Low maintenance

Analyzers and Analysis Systems

- Analyzer products available for specific functions or for general purpose applications
- General purpose analyzer products can be configured to perform specific tasks
  - Analysis of specific nutrient parameters (nitrite, nitrate, ammonia, ortho-phosphorous, others by ChemScan)
  - Multiple incoming sample lines (nutrient profile)
- Accessory items can be used to configure central analysis systems (analyzer + sample extraction + sample conditioning + data communication)

Electromagnetic Spectrum

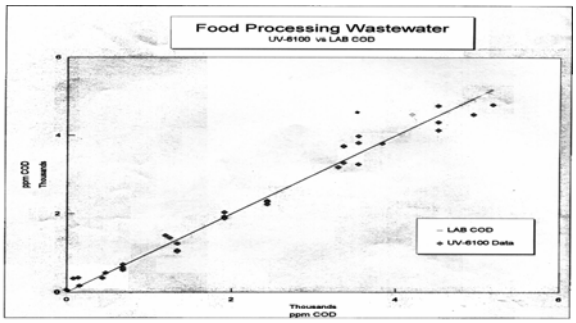


Measurement Methodologies

- Oxidation Reduction Potential
- Amperometric
- Colorimetric
- Voltametry
- Chemical Digestion
- Flame Spectrometry

- UV / VIS Spectroscopy
- NIR Spctroscopy
- Titrimetric
- Nuclear Magnetic Resonance
- GC/MS
- Atomic Absorption Spectrometry
- RAMAN

Control, Correlations and Reporting



Energy Optimization

- Anaerobic Digestion is the new power source along with bacterial fuel cells
- Optimized aeration treatment and reduction of carbon footprint is desirable these days

AnaSense®

Alkalinity & VFAs

On-line Monitoring & Control

For water and wastewater facilities

AnaSense® on-line VFA analyzer

Carmel, CA

Littleton – Englewood, CO

Clearwater, FL pilot

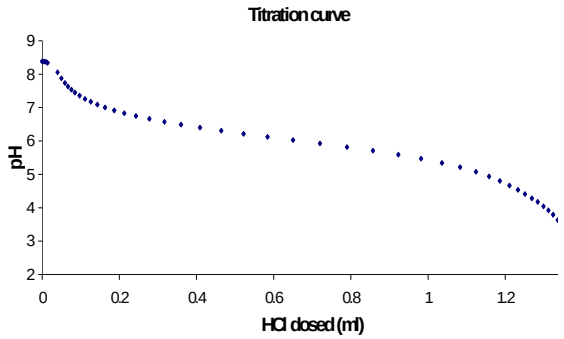
AnaSense® Measured Parameters

1. Volatile Fatty Acids (VFA) = Acetic acid + propionic acid + butyric acid + ...
2. Bicarbonate: HCO_3^- (buffering compound)
3. Alkalinity: Measure for resistance to pH changes
   - Partial alkalinity
   - Total alkalinity

New. ..... Ammonia has been added recently

AnaSense® Working Principle

Sample is titrated with hydrochloric acid in range of pH 7 and 3. VFA, Bicarbonate and alkalinity are calculated from the titration data.



ChemScan.com

Analysis methods of the AnaSense®

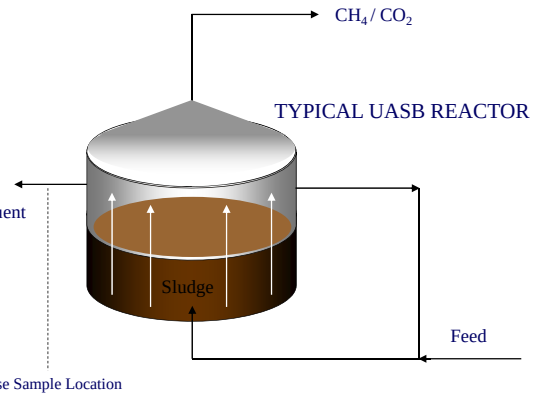
- **Partial Alkalinity** of the sample is determined by titration from the original pH to a pH of 5.75.
- **Total Alkalinity** of the sample is determined by titration from the original pH to a pH of 4.3.
- The acid required to titrate a sample from pH 5.0 to 4.0 can be considered proportional to the content of **VFA** in the sample. (Stripping or not is application dependent)
- The **Bicarbonate** concentration is calculated from the TA concentration, compensated for the VFA concentration.
- Optional: The NaOH required to titrate a sample from pH 8.74 to 9.74 can be considered proportional to the content of A**mmonia** in the sample. (After stripping and determination of VFA)

ChemScan.com

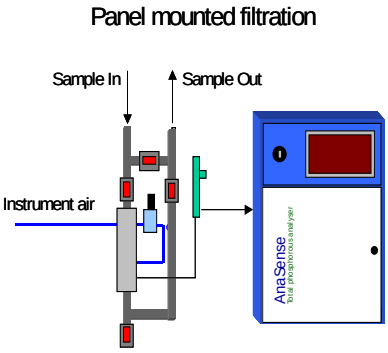
Applications for AnaSense®
alkalinity adjustment in WTPs & BNR plants

- high rate anaerobic reactor systems for:
  - Breweries and beverage industry
  - Distilleries and fermentation industry (also sugar refineries, …)
  - Food Industry (also potato starch processing, …)
  - Pulp and paper (recycling, etc.)
- Other applications include:
  - treatment of chemical and petrochemical industry effluents
  - textile industry wastewater
  - landfill leachate

AnaSense® Implementation UASB/EGSB
(Low Solid Concentration)

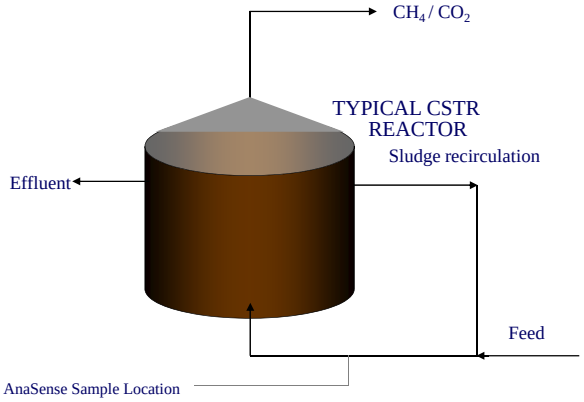


AnaSense® Implementation UASB/EGSB (Low Solid Concentration)



***ModuSize®** self-cleaning filtration system*

AnaSense® Implementation CSTR/SLUDGE FERMENTORS (High Solid Concentration)

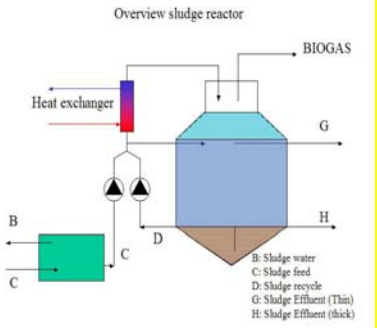


AnaSense® Implementation CSTR/SLUDGE FERMENTORS (High Solid Concentration)

EZ-Dilute® *filtration system*

ChemScan.com

Picture of a typical egg-shaped sludge reactor



Picture of a typical CSTR reactor

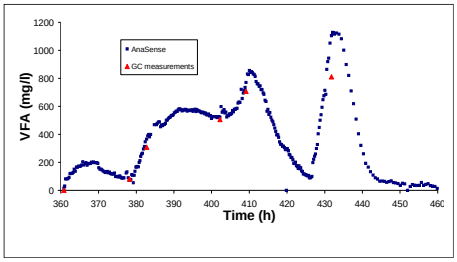
ChemScan.com

AnaSense® versus Lab methods

FIGURE: Validation of the **AnaSense®** results (VFA) with comparison to off-line gas chromatography (GC) results*

Note:

Testing done on a laboratory scale UASB reactor. GC results were recalculated in mol/l and converted in mg/l. A systematic deviation of 15 % compared to the GC reference results is present.



Raw water cycles forward - We check for pH & alkalinity …… then settle, nitrify and clarify !

Onto ammonia conversion and BNR

Alkalinity varies widely depending on geography but you need a bunch of it for nitrification … so measure it and adjust it to raise pH, etc, etc

Bacterial Groupings and Genetics

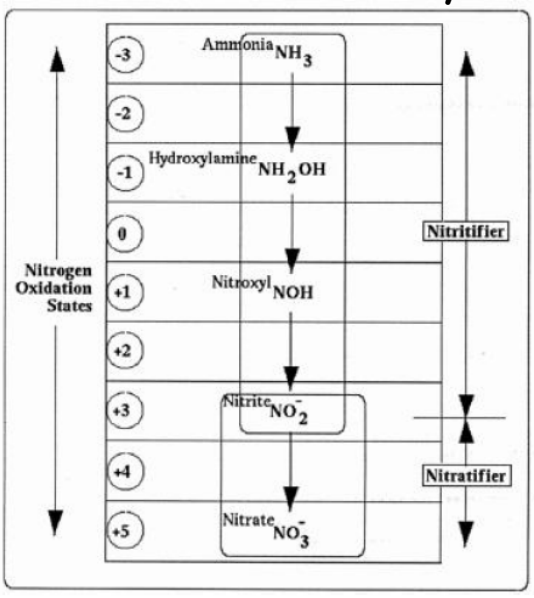
The nitrifying bacterial clan includes two distinctly different subsets, based on their consumption of either ammonia or nitrite. Table 1 provides a breakdown of these affiliated bacterial genus and species members, covering a total of eight separate nitrifying bacteria, including: five species of ammonia-oxidizers (often called `*nitritifiers*'), and three nitrite-oxidizers ( `*nitratifiers*').

TABLE 1. Taxonomy of Nitrifying Bacteria

Taxonomic Group	Preferred Environs: Fresh Water	Saline Water	Soil and Mud	Motility Potential: Motile	Non-Motile
Nitritifiers					
Nitrosomonas europaea	*		*	*	*
Nitrospira briensis	*		*	*	*
Nitrosococcus nitrosus			*	*	*
Nitrosococcus oceanus		*		*	*
Nitrosolobus multiformis	*			*	
Nitratifiers					
Nitrobacter winogradsky	*	*	*	possibly in continuous culture	*
Nitrospina gracilis		*		*	
Nitrococcus mobilis		*		*	

ChemScan.com AppliedSpectrometry Associates, Inc. © 2005 ASA, Inc.

Metabolic Pathways



ChemScan.com AppliedSpectrometry Associates, Inc. © 2005 ASA, Inc.

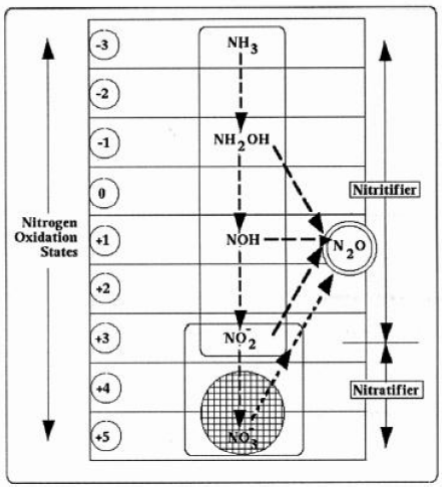
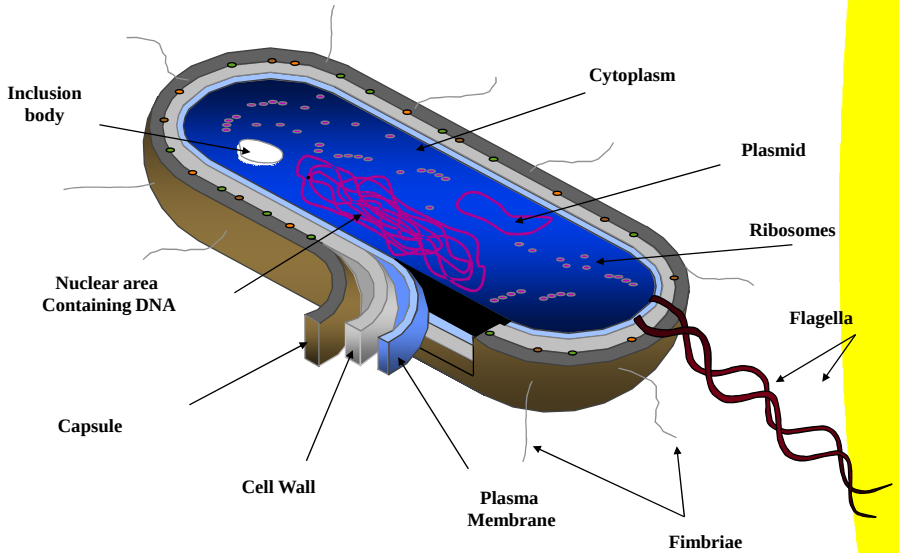
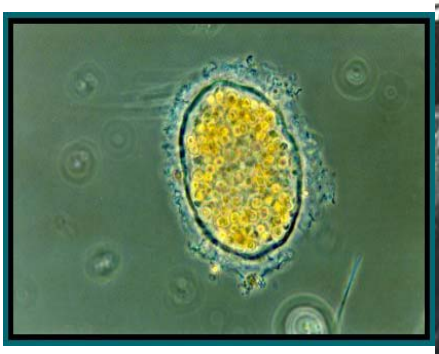


Figure 2. Nitrifier `Denitrification' Pathway

Having only discovered this denitrification capability within the last few years, our awareness and understanding of the nitrifier's denitrification capability is frankly tenuous. At this point, it appears that nitrifier denitrification often falls short of complete nitrate or nitrite reduction to dinitrogen gas. Instead, their `denitrification' behavior seemingly generates a gaseous nitrous oxide product, which in turn might well represent an important contributor to the greenhouse phenomenon.



Designer Bugs are coming soon



ChemScan.com

AppliedSpectrometry Associates, Inc.

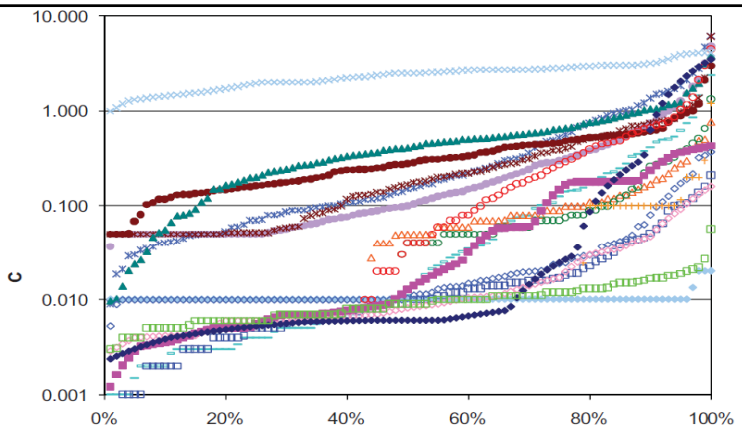


Figure 1. Occurrence of Nitrite in the Final Effluent Streams of 18 Wastewater Treatment Plants

c.

Reduction of Nitrite & Nitrate:

The nitrate reducing bacteria are facultative anaerobic heterotophs.

Therefore, an organic carbon source is required.

For the following equations methanol has been used as the carbon source.

First Energy Reaction:

$6\ NO^-_3 + 2\ CH_3OH \Rightarrow 6\ NO^-_2 + 2\ CO_2 + 4\ H_2O$

nitrate methanol nitrite

Second Energy Reaction:

$6\ NO^-_2 + 3\ CH_3OH \Rightarrow 3\ N_2 + 3\ CO_2 + 3\ H_2O + 6\ OH^-$

nitrite methanol nitrogen gas

ChemScan.com

Optical Colorometric Probes

Insitu probe using - 2 wavelengths

Sc100 Controller – 2 probe capability

ChemScan.com

Several Vendors of colorimetric probes

1. **Provides NOX i.e. NO3 + NO2**
2. **Slow Response time – display is running average of last 30 minutes.**
3. **No true analytical Zero – zero mechanism is inside and never sees the sample.**
4. **Potential Source of error**
5. **Robustness & Service**
   - **Optical window and wiper mechanism are sources of leakage – Annual service required**

Mixed liquor samples need filtration

- **Sample preparation**
  - **Filter Probe sc100 (single sample)**
  - **Filtrax (dual sample)**

Filter Probe sc

Filtrax Sample Filtration System

Wet chemistry analyzers

PO4 analyzer Model with a separate the sc1000 Controller

ChemScan.com

- **Technology – Colorimetric – Molybdovanadate**
- **Range – Low 0.5 – 20 mg/l O-PO4-P**
  Medium 1 – 100 mg/l O-PO4-P
  High 10 – 1,000 mg/l O-PO4-P

- **System Components**
  Analyzer
  sc1000 (Required for outputs & Filtrax)
  Consists of Output module & Interface module
  Filtrax (sample preparation)

ChemScan.com

Amtax (NH3)

Same platform as the Phosphax

ChemScan.com

Is it a lab instrument or online sensor ?

ChemScan.com

AppliedSpectrometry Associates, Inc.

Analyzers with probes that have wet chemistry

- NH4
  - 0 – 20 mg/l & 0 – 100 NH4-N
  - Indophenol Blue
- O-PO4
  - 0 – 6 & 0 – 15 mg/l
  - Molybdenum Blue

- **Costs to operate - keep these in mind**

- Reagent Container - $500 – Replace 5 times per year
  - Consists of Reagents, Standards & Waste bag
- Membrane - $100 – Replace 5 times per year
  - Atmosphere sensitive. Destroyed in 30 minutes exposure
- Annual maintenance – minimum of $3,000.00

ChemScan.com

Wet chemistry
tiny tubes and tight spaces

ChemScan.com

AppliedSpectrometry Associates, Inc.

Blue or yellow method
Colorimetric or spectrometric

TresCon® OP 210

- Yellow method
- Continuous background compensation
- Continuous/Discontinuous operation selectable

On-line orthophosphate measurement

- Control or feedback control of chemical phosphate precipitation, e.g. precipitating agent addition with simultaneous precipitation
- Monitoring biological phosphate elimination
- Measuring the phosphate pollution in natural waters
- Monitoring the phosphate concentration in the drinking water

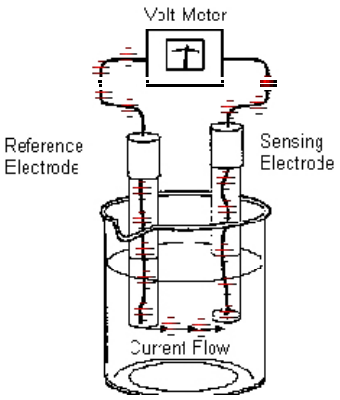
Measuring Principle

The PO_4 module uses the vanadate/molybdate method (yellow method) for determining the orthophosphate content. A reagent reacts with phosphate in the sample to color the sample solution yellow. The intensity of this color is recorded photometrically and evaluated as a measure of the phosphate content.

Amperometric and Gas Sensing Electrodes

- **Technology –– GSE (Colorimetric)**
  - **Similar to ISE. Gas permeates a membrance & reacts with a pH buffer. Color is proportional to concentration**
- **Range – Low 0.5 – 20 mg/l NH3-N**
  Medium 1 – 100 mg/l NH3-N
  High 10 – 1,000 mg/l NH3-N
- **System Components**
  Analyzer sc1000 (Required for outputs & Filtrax)
  Consists of Output module & Interface module
  Filtrax (sample preparation)

ISE probe with internal reference electrodes



ChemScan.com

AppliedSpectrometry Associates, Inc.

How many do you need at your plant for NH3, NO3, NO2

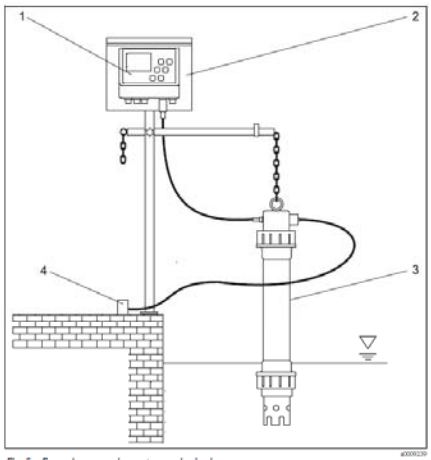


Fig. 5: Example: measuring system on basin rim
1 CAM40 transmitter
2 Upright post with weather protection cover
3 CAS40 sensor
4 Compressed air supply (cleaning)

Don't forget to run, conduit for power

and a separate tube for SCADA DATA

and a compressed air line for cleaning

X ??? Sample points

ChemScan.com

AppliedSpectrometry Associates, Inc.

Probes in a box - optional

8232 Ammonia Monitor

The monitor uses an ammonia gas sensing probe to measure free dissolved ammonia gas. An alkali reagent is used to pre-treat the sample and raise its pH, converting the ammonium ions in solution into dissolved ammonia gas, ensuring a total ammonia measurement is possible.

Application:

- Intake protection for potable water treatment
- Pollution monitoring of rivers
- Monitoring nitrification stage of sewage treatment
- Power plant – ammonia dosed boilers
- Industrial effluent monitoring

Components most ISE systems require

- **Transmitter**
- **Mounting bracket - special hoist (Weight is 5-20 lbs)**
- **Power supply**
- **Universal Signal Converter (USC) – Connect up to 15 transmitters**
- **Membrane Cartridge**
- **Carrier Solution**
- **Calibration Solution**
- **Service Partnership Plan**
- **“friends don’t let friends buy without it”**

ISE & GSE Probe O&M

Article by Thermo Fisher Scientific

Gayle Gleischauf – Applications Manager

Recommendations for Optimizing Performance

Follow Recommended Manufacturer Storage and Maintenance Procedures

published in The Georgia Operator
- Summer 2010

Solutions

- Check to make sure you use the appropriate solute with the specific probe to avoid membrane issues
- Check the Expiration Date
- Check the Fill solution to make sure it's apropos
- Check the NISS Nitrate Interference Suppressor Solution and Ionic Strength Adjustor to apply for each specific probe type
- Is the Ratio correct
- Is it added to both the samples and the standards ?
- Is the storage solution

Storage and Conditioning

- Is the electrode stored correctly
- Does it have the right solution
- Has it been stored for the correct amount of time
- Can it be reconditioned if issues arise with the membrane

Maintenance

- Nitrate and ammonia membranes work best when regularly cleaned or replaced
- Don’t wrinkle the membrane when installing it
- Fill the solution behind the membrane sufficiently and replace it regularly
- Ensure that the nitrate electrode junction is flowing adequately

Testing Conditions

- Stir the standards and samples at a uniform rate to ensure
- Rinse the electrodes with DI water between measurements
- Shake/Blot sensor dry+ allow samples stds to reach room temp
- Check for bubbles on membrane and tap it to release surface tension

Troubleshooting

- Diagnose error with electrode operation slope and drift check
- Prepare DI , add ISA, record mV @1,2,3 min
- Add 10 ml of std and re-record after stable all 3 readings
- Calculate slpe and drift from numerical results and plot
- If out of range perform corrective action per chart
- Make sure temperatures are stable and don’t mix cold DI into reagent solution and expect consistent results

San Jose - Independent studies

Table 4. Ammonia meters results in the mixed liquor.

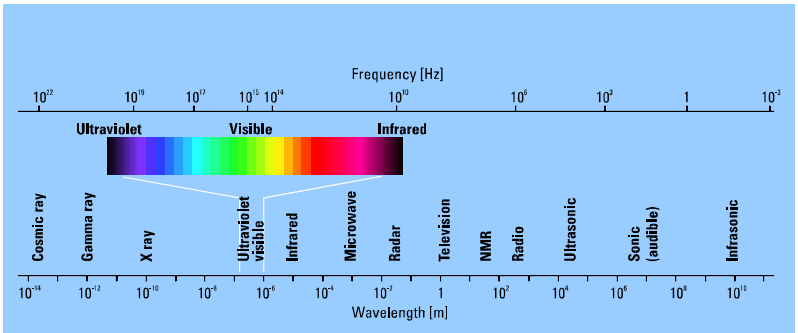
Brand - Sensor		WTW - Varion®Plus 700 IQ				Hach - NH4Dsc	
Location		1	2	3	4	1	2
Nber of samples		44	9	8	12	12	40
Av. Conc. (1) (mg/L)	Lab.	7.0 (±1.5)	4.7 (±1.5)	1.9 (±0.8)	0.2 (±0.1)	20.2 (±2.7)	5.9 (±2.0)
	Meter	7.3 (±1.5)	4.5 (±1.5)	1.9 (±0.9)	0.4 (±0.1)	20.9 (±6.9)	7.6 (±3.6)
Difference (2)		-0.29 mg/L -5.0%	0.20 mg/L 3.2%	-0.02 mg/L -5.0%	0.23 mg/L 53.1%	-0.65 mg/L -2.4%	-1.66 mg/L -55.7%
Conclusion		Recom.	Recom.	Recom.	Not Recom.	Not Recom.	Not Recom.

(1) Concentration in terms of NH_4-N - Standard deviation is specified in bracket.
(2) Difference (mg/L) is between laboratory measurements and meter readings (mg/L). Difference (%) is the ratio between the difference (mg/L) and the laboratory measurements. Av. Conc. = Average Concentration.

When the NH_4 concentration is below 1.9(±0.8) mgNH_4-N/L (Location 4), discrepancy of 53% (0.23 mg/L) was observed. The meter is not accurate enough to detect precisely low ammonia concentration (**Figure 7-d**); the limit of this on-line meter was reached.

The WTW ammonia meter based on ISE measuring principle is only recommended for application with NH_4 concentration in the mixed liquor above 2 mg/L.

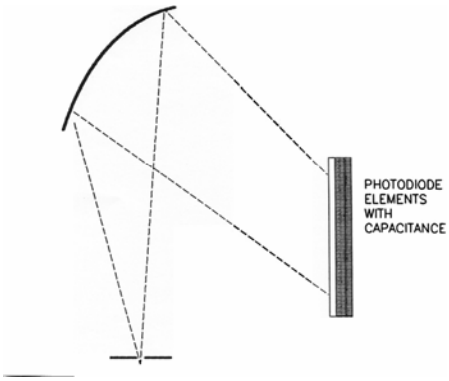
The Electromagnetic Spectrum



$E = h\nu$ $\nu = c / \lambda$

What is Spectroscopy?

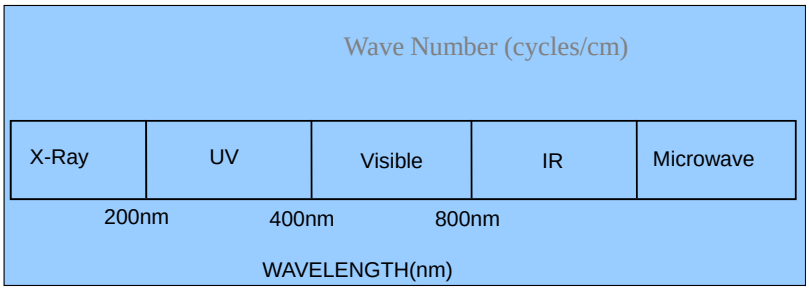
- The study of molecular structure and dynamics through the absorption, emission and scattering of light.



ChemScan.com

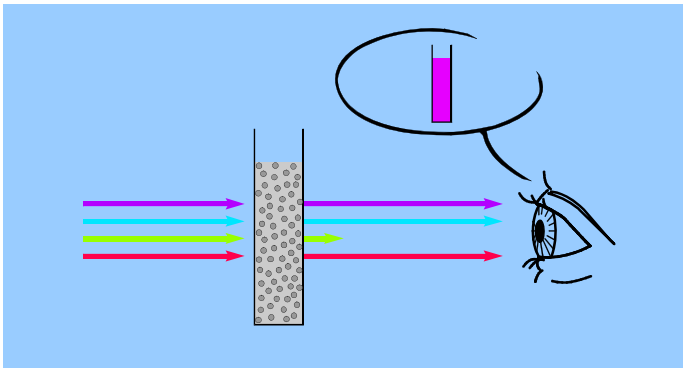
Spectroscopy

Spectral Distribution of Radiant Energy



ChemScan.com

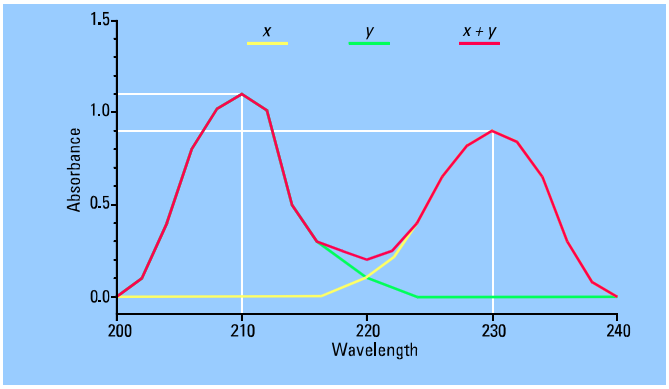
Transmission and Color



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

ChemScan.com

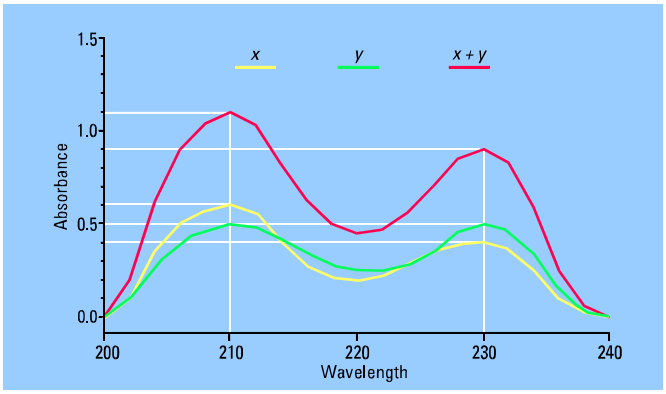
Two-Component Mixture



Example of a two-component mixture with little spectral overlap

ChemScan.com

Two-Component Mixture



Example of a two-component mixture with significant spectral overlap

ChemScan.com

Interferences require wide spectrum analysis

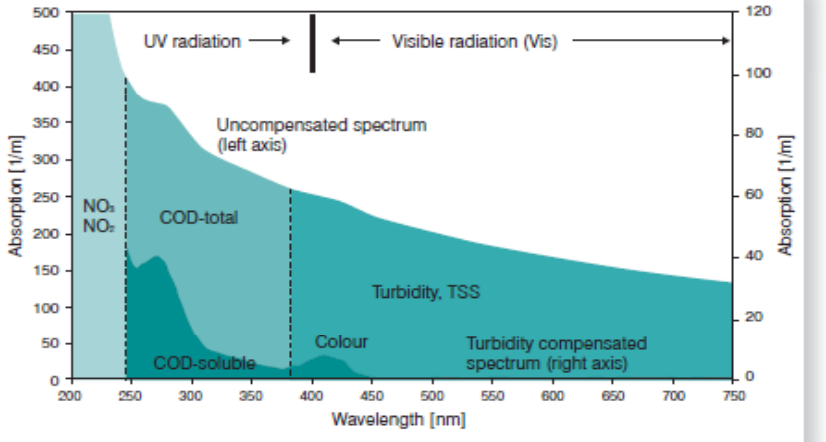
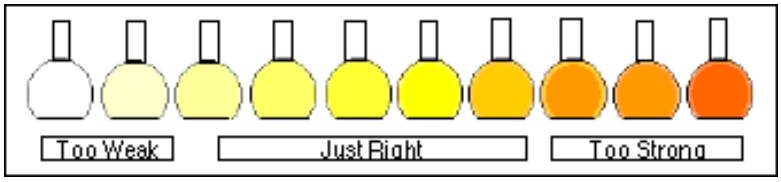


Figure 2. UV-Vis spectrum, and examples of parameters derived out of this spectrum together with their characteristic absorbance profiles

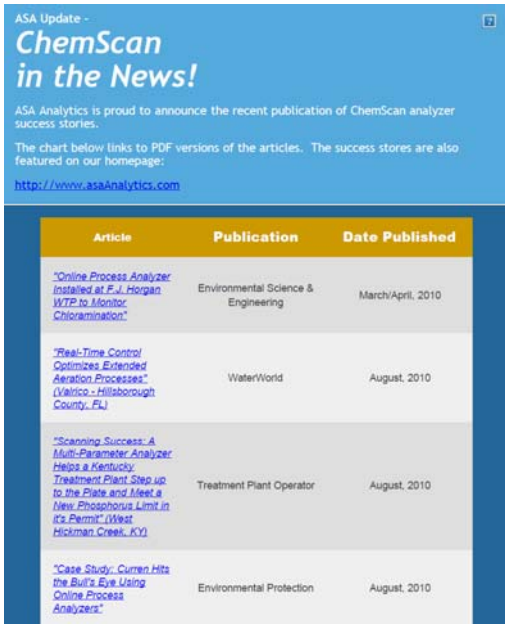
ChemScan.com

AppliedSpectrometry Associates, Inc.



- 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.
- Bernie & Scott did most of the original field work
- Tampa was the first breakthrough on denites limited by phosphorous and was basis for TetraPace™ strategy

www.asaAnalytics.com


ASA Update -

ChemScan in the News!

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

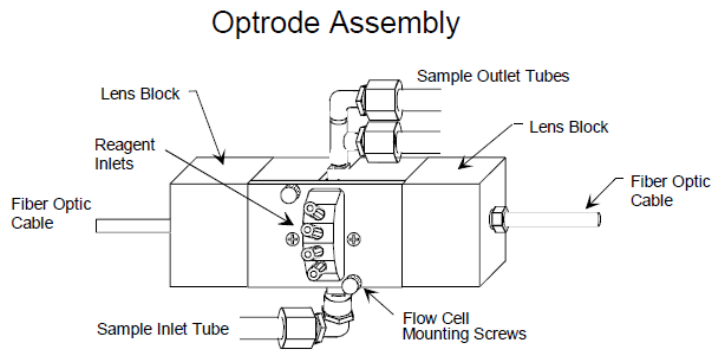
The chart below links to PDF versions of the articles. The success stores are also featured on our homepage:

http://www.asaAnalytics.com

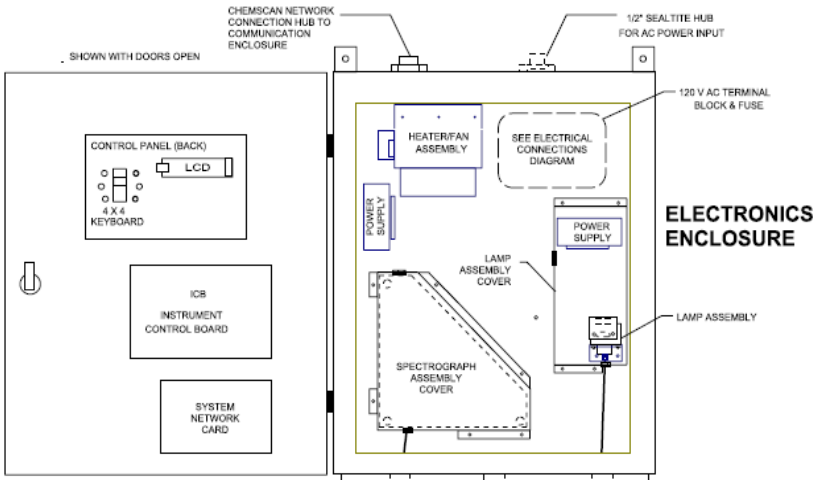
Article	Publication	Date Published
"Online Process Analyzer Installed at F.J. Horgan WTP to Monitor Chloramination"	Environmental Science & Engineering	March/April, 2010
"Real-Time Control Optimizes Extended Aeration Processes" (Valrico - Hillsborough County, FL)	WaterWorld	August, 2010
"Scanning Success: 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

AppliedSpectrometry Associates, Inc.

We extend that platform into a working instrument



How we measure it and control the analysis of liquid samples



Demonstrated Results & Accuracy

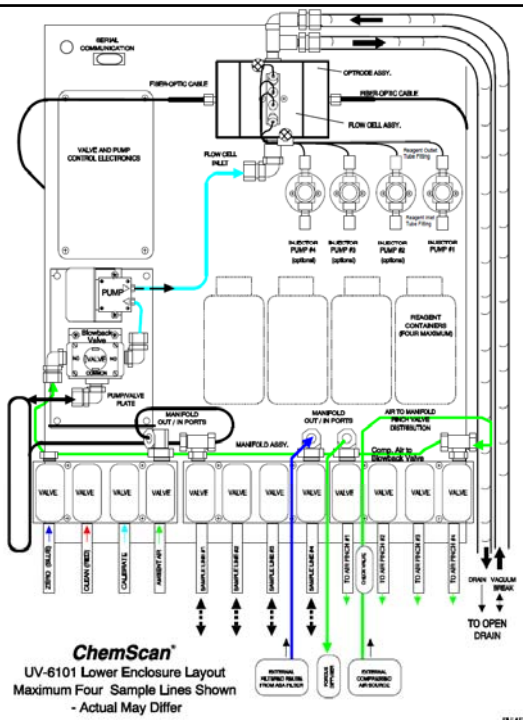
Optimized Performance

Standardized Components

Long Life Cycle

Upgradable for Future Process Modifications

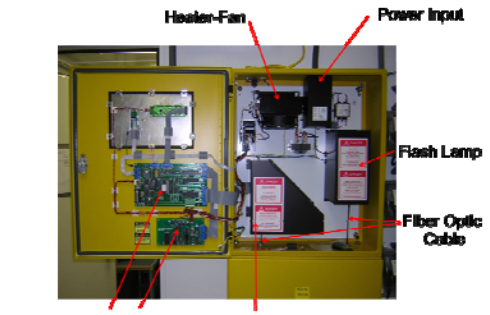
Hand Made in USA



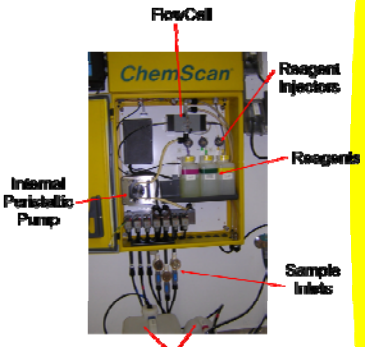
ChemScan®
UV-6101 Lower Enclosure Layout
Maximum Four Sample Lines Shown
- Actual May Differ

ChemScan.com

UV-6101 Analyzer



Analyzer Upper Enclosure



Analyzer Lower Enclosure

ChemScan.com

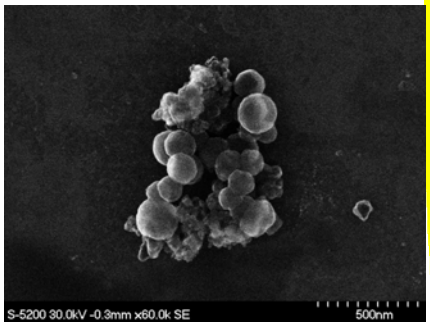
AppliedSpectrometry Associates, Inc.

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.

ChemScan Sample Options

- Wastewater Application Classifications:
  - **Pre Secondary Clarifier**
  - **Post Secondary Clarifier**



Low Solids = No Sample Filters

- All ChemScan Analyzers are Designed to Operate After Sec. Clarifier Without Need for Filtration

  (<150 mg/L TSS and < 60 NTU)

  - **Large Internal Sample Tubing (1/4 inch ID)**
  - **Non clogging, No carryover, Internal Manifold**
  - **Internal Peristaltic or Diaphragm Pump**
- Application Examples:
  - De-nitrification (UV-3150)
  - Effluent Nutrient Analysis (UV-4100 or 6101)
  - Dechlorination (UV-2150/DC)
  - UV Disinfection (UV-0254/T)

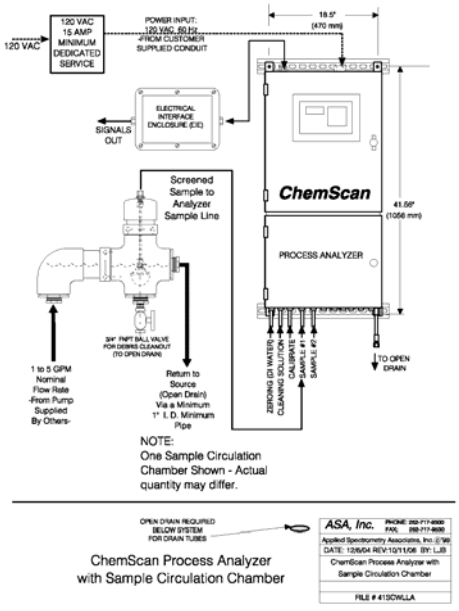
Post Secondary Clarifier Sample Locations

- Direct Inlet of Sample to Analyzer
  - If Analyzer is located at or near process
    - Use Analyzer internal pump (<50 feet)
  - If Analyzer is remote or if there are long distances between samples
    - Use tee connection to external by-pass line, fed by 5 gpm sample pump

ENR Pilot Analyzer Configuration Example: Hagerstown MD

- UV-6101 with 3 Sample Lines
- Parameters: NO2-N, NO3-N, NH3-N, PO4-P and UV-254 %T on each sample line (total of 15 data points)
- Analysis time per sample line: ~9 min.
- Data Communication: MODBUS RTU

Sample Conditioning if algae is present



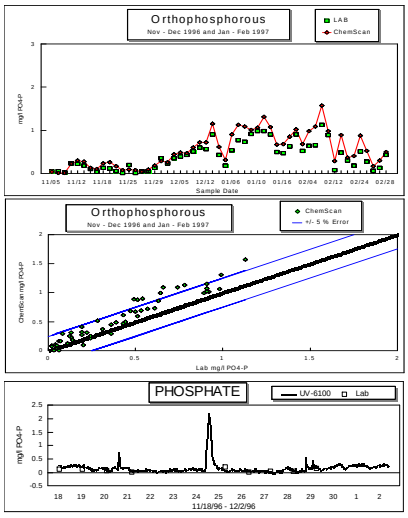
Post Secondary Clarifier Examples

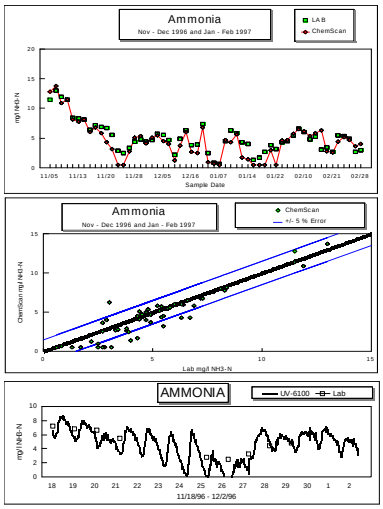
- City of Largo FL – Denitrification Methanol Feed Control 2 Sample Points NO3-N
- City of Tampa FL – HF Curran AWWTP – Denitrification Methanol Feed Control in Continuous Operation Since 1995
- City of Calgary AB - Six Analyzers, 12 Sample Points NO3, NH3, PO4 and TSS on Each Sample

Case Study: Bonnybrook WWTP Calgary ,Alberta

Orthophosphate Four Month Average Error 3.0 %

Ammonia Four Month Average Error 3.0 %





ChemScan System Accessories

- Sample Sequencer – Control up to 8 nodes
  - Central sample pump with individual **motor valve** control
  - Individual **sample pumps** with **check valves**
- Sample Filters - for mixed liquor + primary effluent
  - Central **Cross Flow UF Membrane Filters** (for use with sequencer systems)
  - Dedicated "**Cyclic" Filters** (controlled directly by a general purpose analyzer)
    - Dedicated immersed filter cartridges or
    - Dedicated flow through filter assembly
    - New Membrane Weed in Beta tests now

Pre-Secondary Clarifier Option I

- At-Tank Analysis Systems (< 75 ft)
  - **In-Situ Cyclic Filter (Porous Polyethylene 10-60 microns)**

Examples:

City of Largo (UV-6101, 3 Samples, NO2-N, NO3-N, NH3-N, PO4-P)

Hilliard FL - SBR (UV-4100, 2 Samples, NO2-N, NO3-N, NH3-N, PO4-P)

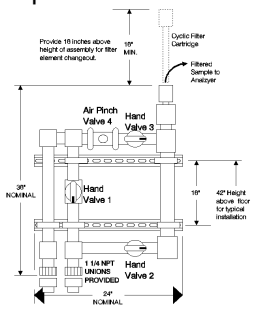
At-Tank Analysis System

(75 ft or less from analyzer + 10 ft lift)

Pre-Secondary Clarifier Option II

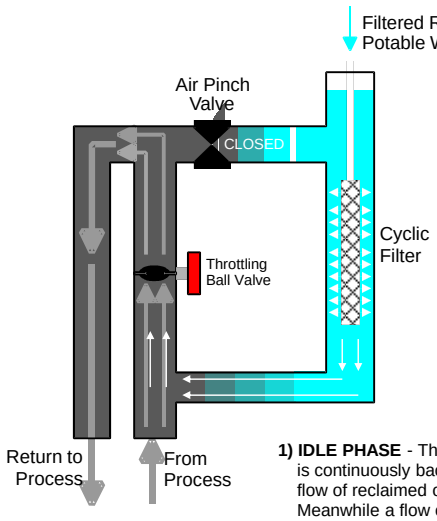
- Remote Process Samples (> 75 ft)
  - **Flow-Through Cyclic Filters, 1.5" sample lines 5 GPM**

New Development that combines the Benefits of Cyclic Filter with Long Distances Between Samples



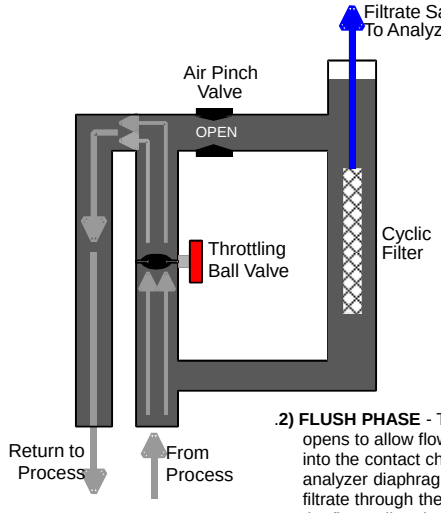
Flow Thru Cyclic Design

Flow Through Cyclic 1



1) IDLE PHASE - The Cyclic Filter is continuously backflushed with a flow of reclaimed or potable water. Meanwhile a flow of sample from process is circulated through the idle chamber but does not contact the filter.

Flow Through Cyclic 2

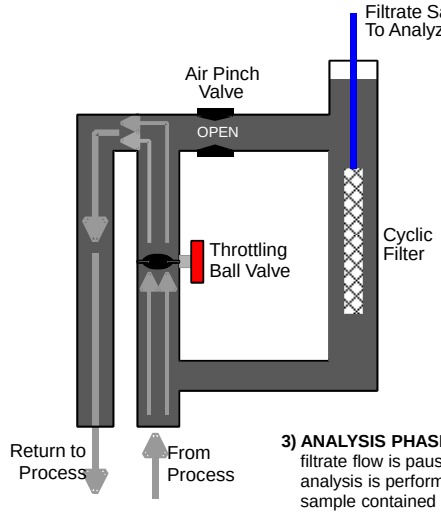


.2) FLUSH PHASE - The pinch valve opens to allow flow of the sample into the contact chamber, while the analyzer diaphragm pump draws filtrate through the analyzer to flush the flow cell and provide fresh sample for analysis.

ChemScan.com

Applied*Spectrometry*
Associates, Inc.

Flow Through Cyclic 3

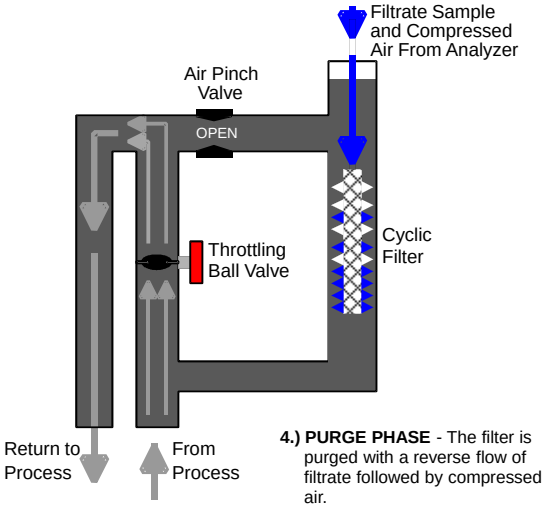


3) ANALYSIS PHASE - The filtrate flow is paused while the analysis is performed on the filtrate sample contained within the flow cell.

ChemScan.com

Applied*Spectrometry*
Associates, Inc.

Flow Through Cyclic 4



4.) PURGE PHASE - The filter is purged with a reverse flow of filtrate followed by compressed air.

ChemScan Process Installations

Well over 500 in the US after many years

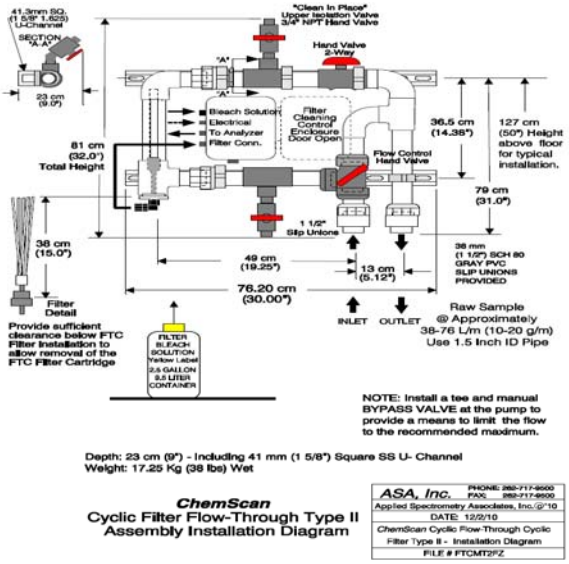
Close to 2000 sample points working daily

Originally worked on effluent monitoring and now have many mixed liquor and high solids sampling analyzers but …… R&D continues

New membranes are now available due to polymer chemistry and advanced water treatment requirements …..

Out of the weeds comes a new option for some WWTFs with high alkalinity and long sludge age / EPS and biofilm issues

Cyclic Weed Beta testing



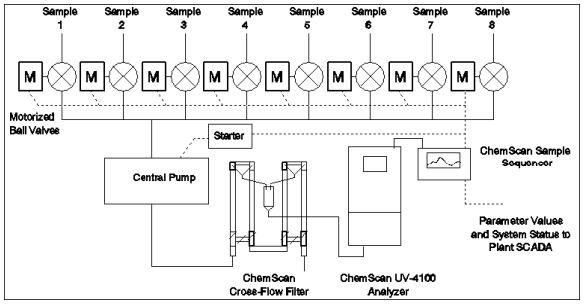
Weed details

Pre-Secondary Clarifier Option III

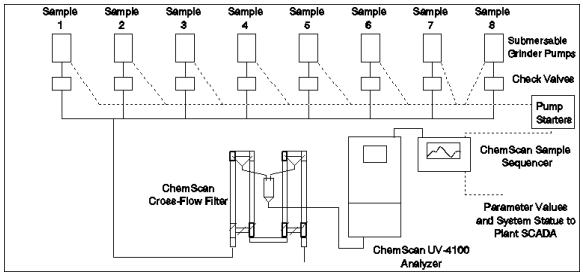
- Central Analysis System with Sample Sequencer, Cross Flow Filter and UV-4100 Analyzer
  - Up to 8 Sample Locations
  - 4 Parameters Per Sample (32 Total Data Points)
  - Low Maintenance (1 Hour / Week)
  - Over 10 years of Proven Reliability
  - High volume flush (30 GPM, 3 ft/sec)

Central Analysis Configuration Options

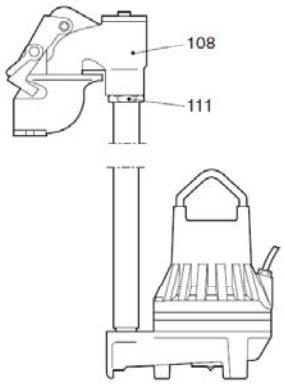
Option 1: 8 Motorized Ball Valves And Central Pump

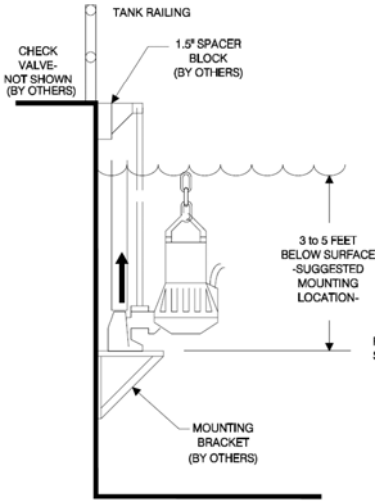


Option 2: 8 Submersible Pumps With Check Valves



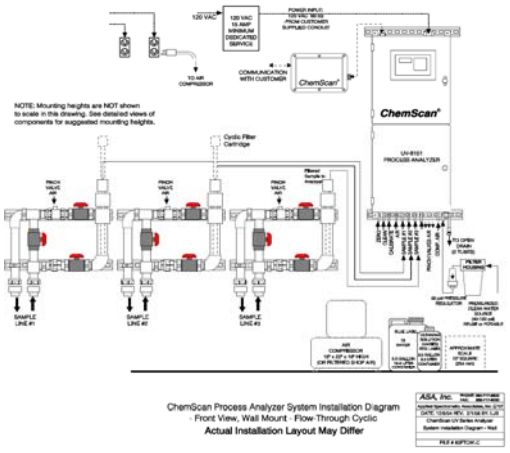
Sample pumping systems





Sequencer and Cross Flow Filter plus Accumulator

Tallahassee, FL ENR – Hazen & Sawyer



Dual Train Control w one central analyzer and valving to alternate between basins

Comparison with In-Situ Systems

ChemScan	In-Situ
• One analyzer system to operate & maintain	• Many instruments to operate & maintain
• No special skill needs	• High O&M skill level
• Central maintenance	• At tank maintenance
• Low ownership cost for complete system	• Ownership cost 2X-3X central system
• Needs sample header plus valves and pumps	• Needs individual power and data connections

Tallahassee - Cost Comparison

- Cost per data point is lowest of ANY other alternative system.
  - Central Analysis Systems are $80,000 to $120,000 incl shelters and sample pumps
  - Individual analyzers at $15,000 each:
    - 32 In-Situ data points = $480,000
    - **24 In-Situ data points = $360,000**
    - 12 In-Situ data points = $180,000

ChemScan Maintenance

- Weekly
  - Check Consumables
- Monthly (<1 hour)
  - Replenish Reagents, Fill Zero Std and Cleaner
  - Replace Pump Tube (quarterly for pressurized)
  - Verify Calibration with Grab Samples (optional)
- Every 2 Years
  - Change Battery
- Every 5 Years
  - Change UV Flash Lamp

Installation

- Installation Costs
  - 3-4 HP pumps are included in the system price
    - Submersible grinder pump (Flygt) is standard
  - Installation includes:
    - Pump platform and guide rails
    - Pump power 230/460V and motor starters or starter panel
    - Pump control signal wire, local on/off switch
    - 2 inch PVC sample pipes and brackets
    - Check valves at drop legs
    - Central analyzer and controller power and data lines
  - Estimate is $25,000 to $50,000 for Central Systems

Central Analysis Examples

- **RDO/Lamb Weston** – SBR Processing Food Waste
  Used to Control Blower Speed, Continuously Since 1996
- **Lexington KY AWWTP** - 8 Sample Points, NO2, NO3, NH3 and PO4, Hourly Plant Profile from Primary Eff. to Final
- **City of Orlando FL**, Conserv I and II , Iron Bridge
  3 AWWTP Plants, 6 Analyzer Systems, 35 Process Sample Points, NO2,NO3,NH3 and PO4

Specialty Analyzers

ChemScan® UV-2150/DC
CHLORINATION-DECHLORINATION ANALYZER

ChemScan® UV-2150/N
WASTEWATER AMMONIA AND NITRATE

ChemScan® UV-3150
PROCESS ANALYZERS

ChemScan® UV-2150/S
CHLORAMINATION ANALYZER

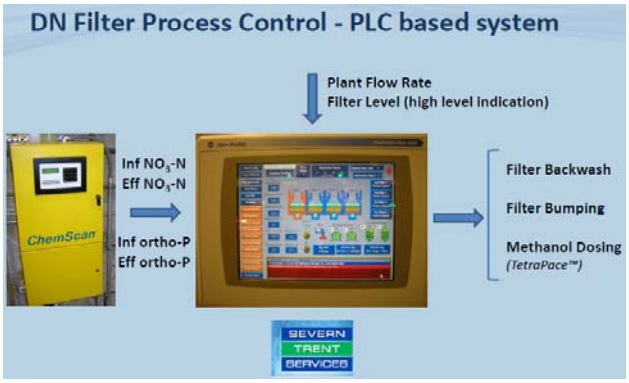
Denite & Ion Exchange Filters

- **Cheshire, CT WWTF** – Kruger Upflow Denite Filter 2 sample points
- **Augusta County Service Authority** – Stuart's Draft, VA WRF Tetra Downflow
- **York River WRF** – HRSD , VA (STS)
- **HL Mooney WWTF** – Lorton, VA (STS)
- **Baltimore, MD** - Back River WWTF
- Oldsmar, FL WWTF – Leopold Downflow
- Indian Head , MD WRF – Blue Water Process
- Salisbury, MD WWTF – Parkson Denites

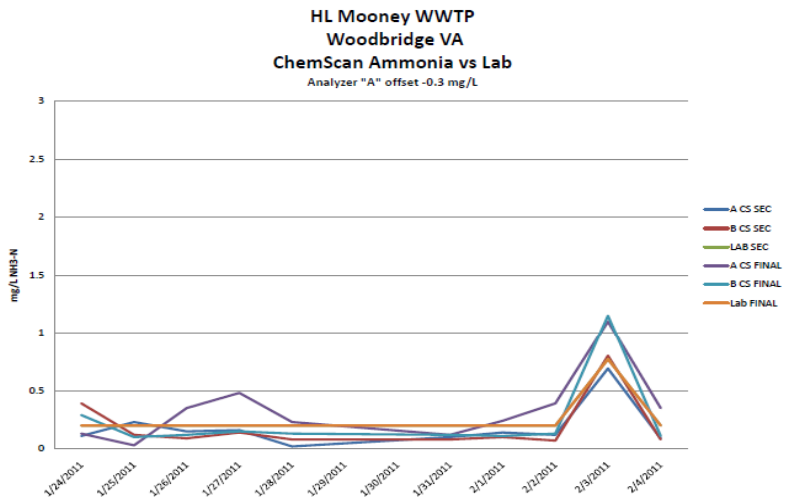
Tonka , H&T, Roberts and other filter arrays for nitrate, arsenic, iron, manganese & TOC

Augusta County Service Authority– Fisherville, Middle River and Stuart's Draft WWTFs for BNR process and Denitrification control

PWCSA - HL Mooney WWTF
10 old + 14 new = 24 Denite Filters



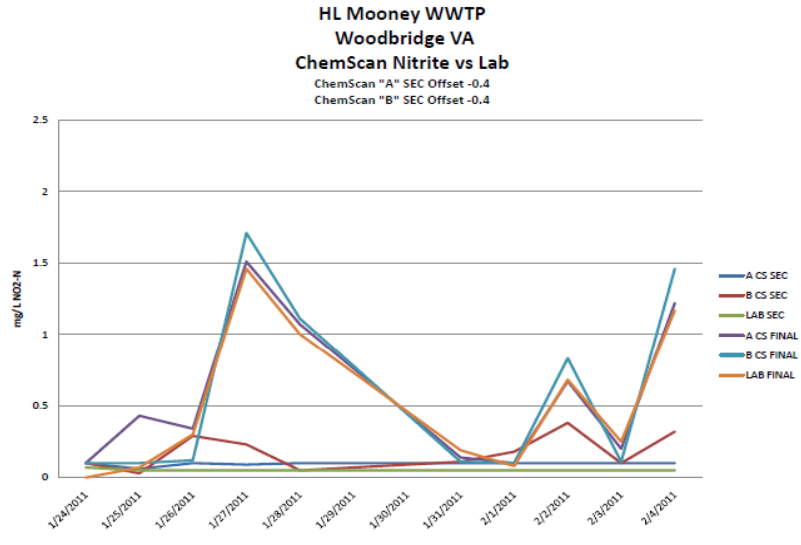
Spectral Comparisons - Ammonia



ChemScan.com

AppliedSpectrometry Associates, Inc.

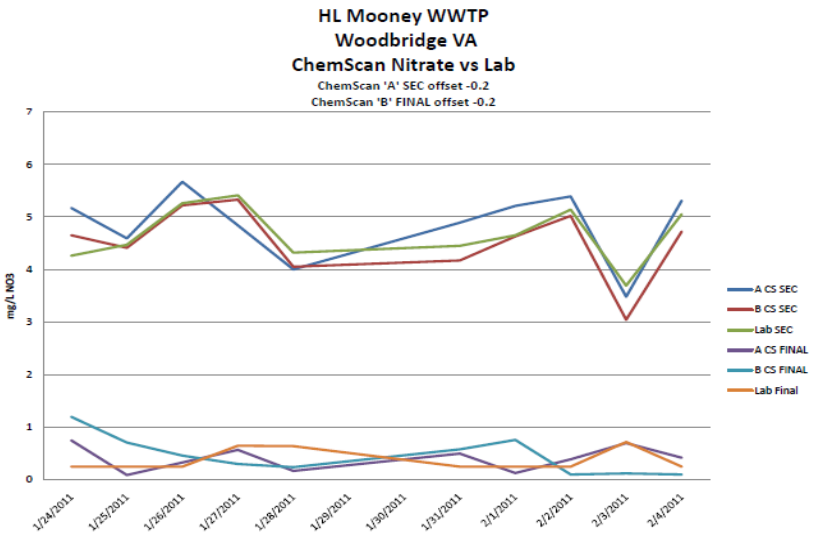
Spectral Comparisons - Nitrite



ChemScan.com

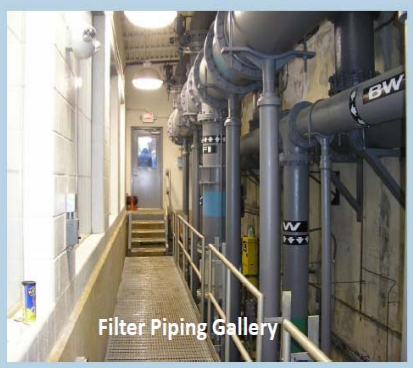
AppliedSpectrometry Associates, Inc.

Spectral Comparisons - Nitrate

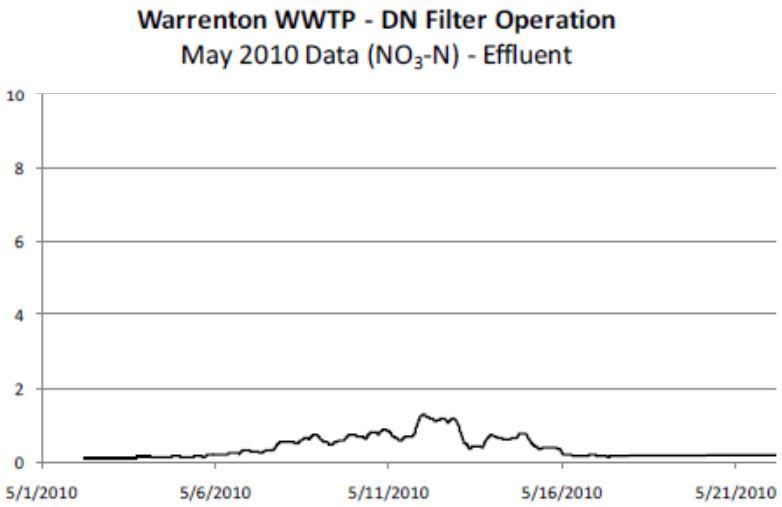


Warrenton, VA Recently Upgraded

Construction of Nutrient Removal Facilities



ChemScan control on Denites

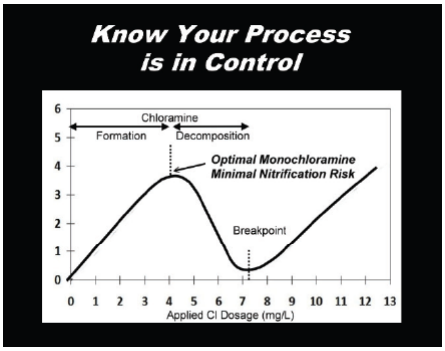


AppliedSpectrometr

ChemScan.com *© 2005 ASA, Inc.*

Charleston, SC – Hanahan WTP

Peak Point Chloramination using 4 parameters to optimize monochloramine formation and minimize chemical consumption



Recent studies - Beware of NDMA formation in secondary effluent

ChemScan.com *© 2005 ASA, Inc.*

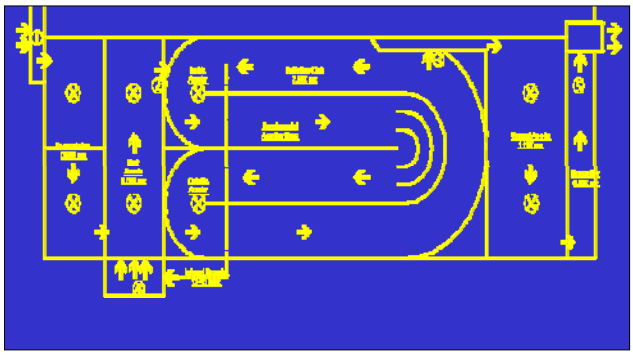
Valrico WRF - Hillsborough County , FL
Aeration Process Control for BNR Optimization

Case Study

5 Stage BarDenPho BNR Process

Monitoring system installed as part of plant upgrade

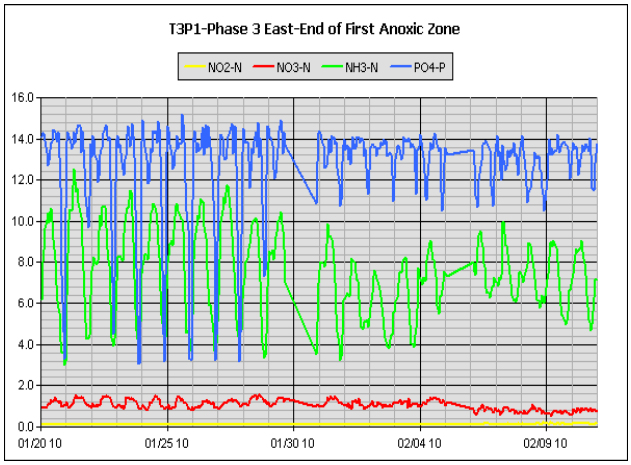
- One analyzer system measuring NH3-N NO3-N NO2-N and PO4-P
- One Sample Sequencer, Eight submersible pumps



BardenPho Sample 1 Anoxic Zone

Phosphate Release, Nitrate Consumption

- High NH3
- High PO4
- Low NO3
- Low NO2



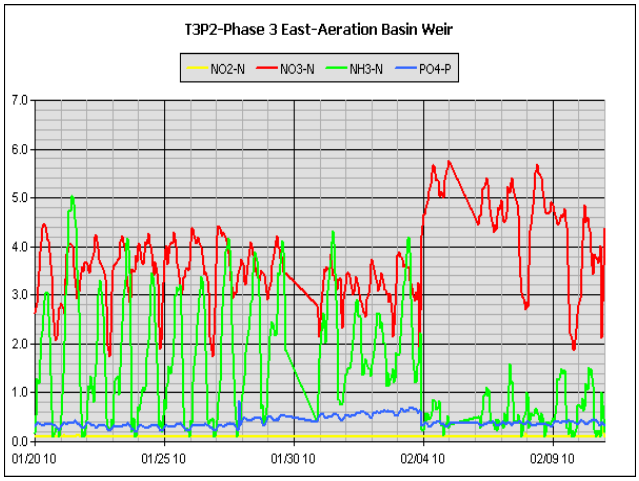
ChemScan.com

*Applied*Spectrometry Associates, Inc.

BardenPho Sample 2 Aeration Basin

Luxury Phosphate Uptake, Ammonia Converted to Nitrate

- Mid Level NH3
- Mid Level NO3
- Low PO4
- Low NO2



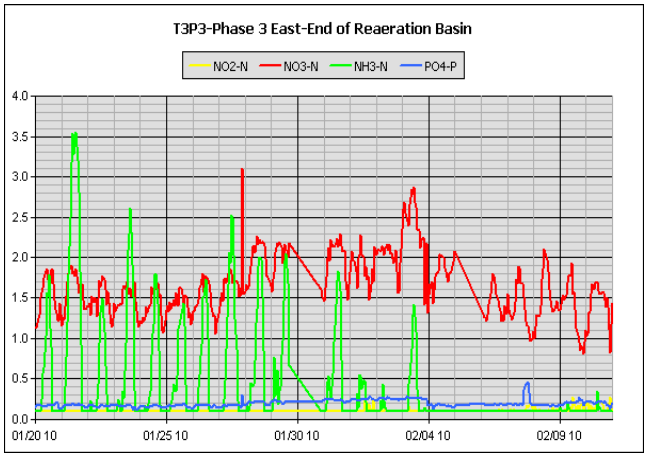
ChemScan.com

*Applied*Spectrometry Associates, Inc.

BardenPho Sample 3 Aeration Basin

Reaeration to Polish Ammonia, Phosphate

- Low NH3
- Low NO3
- Low PO4
- Low NO2



Benefits Realized

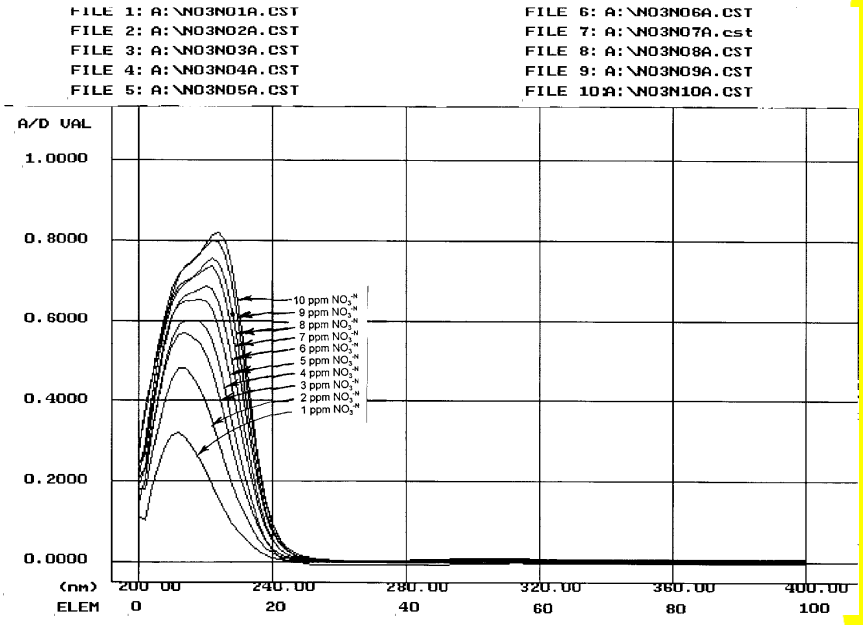
(From Plant Representative's Presentation)

- Rerate permit from 24 to 40 mgd
- Improved effluent quality – more flow with the same or less total pounds of nutrients
- >$30-70 million capital savings
- >$250k per month operating cost reduction
- 40% reduction in effluent nutrients
- 30+% reduction in solids production!
- "Could not have accomplished this without ChemScan Sequencer System"

ChemScan Nitrate Installation

Sycuan CA. Casino WTP - Ion Exchange Denitrification
Nitrate on Three Samples

ChemScan.com

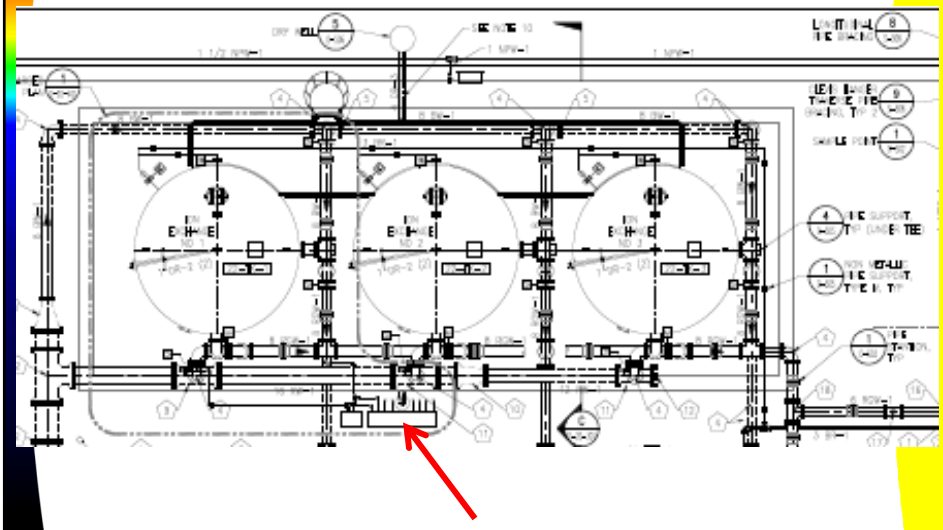


ChemScan.com

ChemScan Nitrate Installation

Avondale AZ.
Nitrate Well Blending - Three Sample Points

IX Filter breakthrough analysis



And now - the mini series….
Coming soon to a theatre near you

Mini UV-0254 Analyzer

- UV Disinfection - Independent Measurement of UV%T or Absorbance for UV Dosage Control at – 254 nM only
- Photodiode receptors and light generators to reduce size and expense of instrument
- Field Calibration for UV Absorbing Organics
- Same Proven Sample Handling as Large ChemScan Analyzers

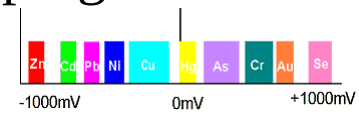
ISO 9001 sira UKAS QUALITY MANAGEMENT

cogent environmental

OVA Series On-line Heavy Metal Analysers

ChemScan.com

Stripping Voltametry



- This method was first described in the 1920s. JAROSLAV HEYROVSKY won the Nobel Prize for chemistry in 1959 for developing it. It is therefore older than Atomic Absorbtion (AAS) or ICP (Induced Coupled Plasma) Spectroscopy
- The original methods used liquid Mercury as the electrode. These devices are called Hanging Mercury Drop devices (HMD).
- Instead of liquid mercury as the electrode, this device uses a glassy carbon electrode that is plated with a very thin film of Mercury. (Mercury Thin Film Electrode, MTFE)

ChemScan.com

Applied Stripping Voltametry – ASV

- ASV is an analytical technique that specifically detects heavy metals such as Arsenic, Cadmium, Lead, Mercury and others.
- ASV essentially works by electroplating certain metals in solution onto an electrode. This concentrates the metal. The metals on the electrode are then sequentially stripped off, which generates a current that can be measured.
- The current (milliamps) is proportional to the amount of metal being stripped off. The potential (voltage in millivolts) at which the metal is stripped off is characteristic for each metal. This means the metal can be identified as well as quantified.

ChemScan.com

- Online monitoring of heavy metals in water, river water, wastewater and industrial effluent.
- Real time results
- Configurable to customer requirements
- Pre-treatment options consist of acid/UV digest for elimination of potential interferences
- Easy to use – trained chemists are not required
- Applications include: As, Hg, Cr, Zn, Cd, Pb, Cu, Ni, Tl
- Quick and accurate analysis
- Excellent correlation with the standard laboratory methods (+/- 10%)

ChemScan.com

Typical Limits of Detection for PDV and OVA monitors

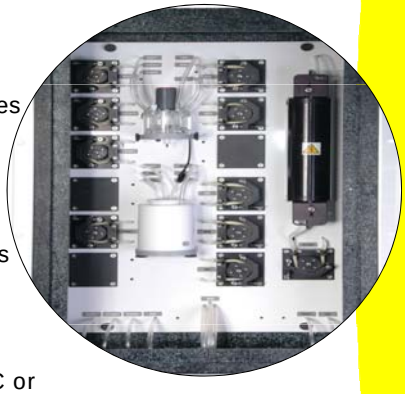
Metal	Metal Name	PDV(Portable analyser)	OVA(on-line analyser)
Ag	Silver	2µg/l	5µg/l
As	Arsenic	0.5µg/l	2µg/l
Au	Gold	5µg/l	5µg/l
Cd	Cadmium	0.5µg/l	0.5µg/l
Co	Cobalt	5µg/l	5µg/l
Cr	Chromium	5µg/l	5µg/l
Cu	Copper	1µg/l	1µg/l
Fe	Iron	5µg/l	10µg/l
Hg	Mercury	0.1µg/l	0.5µg/l
Mn	Manganese	2µg/l	5µg/l
Ni	Nickel	0.2µg/l	0.5µg/l
Pb	Lead	0.5µg/l	1µg/l
Pd	Palladium	5µg/l	1µg/l
Sb	Antimony	1µg/l	1µg/l
Se	Selenium	20µg/l	20µg/l
Sn	Tin	5µg/l	5µg/l
Te	Tellurium	5µg/l	5µg/l
Tl	Thallium	5µg/l	5µg/l
U	Uranium	5µg/l	5µg/l

Note: Detection limits vary with sample type. Typical values are shown.
Methods are available for the determination of metals using voltammetry from USEPA, NIOSH, ASTM, DIN, AOAC and ISO.

ChemScan.com

OVA7000

- High degree of ingress protection (IP65)
- Thermally insulated enclosure temperature range 0 – 60^0 C.
- Separate optional reagent enclosure
- Standard low voltage (12/24V DC) operation for remote sites using supplies from renewable resources.
- AC operation as option
- Standard telemetry TCP/IP, Modbus, Ethernet connection, USB port
- Telemetry options include LAN, wireless LAN and wireless broadband.
- Optional local display.
- Optional back-up power supply.
- All parameters adjustable via laptop PC or remotely making analyser tamper free!



ChemScan.com

BENEFITS (both models)

- Real time results for real time decisions on release of effluent or wastewater discharge
- Improves efficiency of treatment processes for heavy metals
- Low access cost – self financing based on savings in process chemicals with return on investment in as little as 3-6 months
- Process compatible – easily integrated into standard processing systems.
- Added protection against costly environmental agency fines to ensure company reputation is maintained
- Provides an early warning system for rises in metal levels to protect against accidental discharges over consent limits
- Financial savings from reduce man hours in laboratory
- Permanent results archive – for inspection purposes

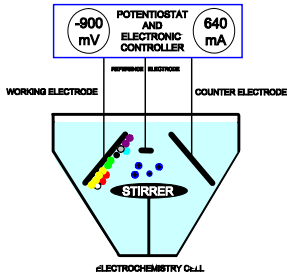
BENEFITS (additional to 7000)

- Reduction in power requirement, 55Watt for DC operation for sites where power supplies are from renewable resources (Solar cells, wind etc)
- Increased IP rating and thermal insulation provides better environmental protection when operating in remote locations. No additional heating of enclosure.
- Variety of protocols ensures compatibility with existing telemetry systems.

Anodic Stripping Voltammetry (ASV)

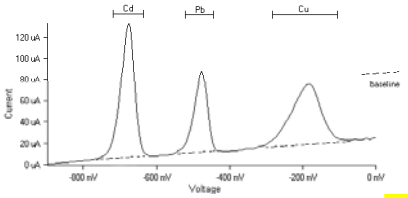
The ASV analysis is in 2 parts:-

1. Plating: concentrates the metal onto the working electrode by reducing the metal ions in solution to the metal.
2. Stripping: Ramps the potential at the working electrode in a positive direction at a fixed rate. This oxidises each metal off the electrode in sequence



The potential of the peak identifies the metal.

The current produced is proportional to the metal concentration on the electrode hence the concentration in the sample itself.



ChemScan.com

Concentration peaks for same metal

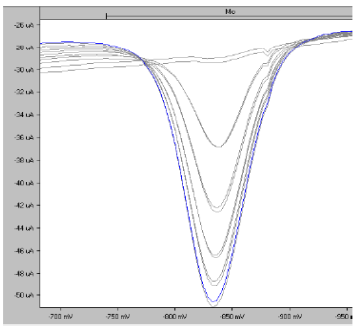


Figure 1. Standard addition of Mo with 20, 40, 60, 80 and 100ppb Additions. The Voltammagram shown is the raw output with the inverted peak

ChemScan.com

METHOD APPROVALS

The methods supported by the OVA5000 are certified by the US EPA and other agencies. Approved methods are listed below:

- European Commission Reference Method for Cd and Pb. Article 2 Section 2 90/515/EEC
- US EPA Method 7472 Mercury in aqueous sample and extracts
- US EPA Method 7063 Arsenic and Selenium in sediment samples
- US EPA Method 7198: Hexavalent Chromium in water
- US EPA Method 1001: Lead in drinking water by ASV
- ASTM Method D3557-95: Cadmium in Water
- ASTM Method D3559-95: Lead in Water
- DIN 38 406, part 16, Zn, Cd, Pb, Cu, Tl, Ni, Co in water samples
- AOAC Method 982.23: Cadmium and Lead in Food (not for fats and oils) (1988)
- AOAC Method 974.13: Lead in Evaporated Milk (1976)
- AOAC Method 979.17: lead in evaporated milk and fruit juice
- AOAC method 986.15: Arsenic, cadmium, lead, selenium and zinc in human and pet foods
- NIOSH Method 7701: Lead by ultrasound & ASV
- Method 3130: Metals by anodic stripping voltammetry (proposed by American Public Health Association, American Water Works Association and the water environment federation, 1995

ChemScan.com

ASV vs. Traditional Techniques

- **ASV does not require the following for operation**:
  - ultra pure gases to produce a flame.
  - fume extraction system.
  - started and stabilised for several hours before attempting an analysis.
  - cooling water supply (ICP)
  - regular replacement of expensive lamps or optical systems
  - A suitably trained chemist
- This indicates more economical analysis with considerable financial savings
- **ASV produces real time results**:
  - Decisions can be taken immediately before accidental discharges over consent limits occur
  - Improves efficiency of treatment processes for heavy metals allowing companies to calculate exact dose requires whilst providing significant financial savings
  - Can be incorporated into standard processing systems which allow remote 24 hours monitoring even while staff are off site

ChemScan.com

Typical OVA5000 Installations

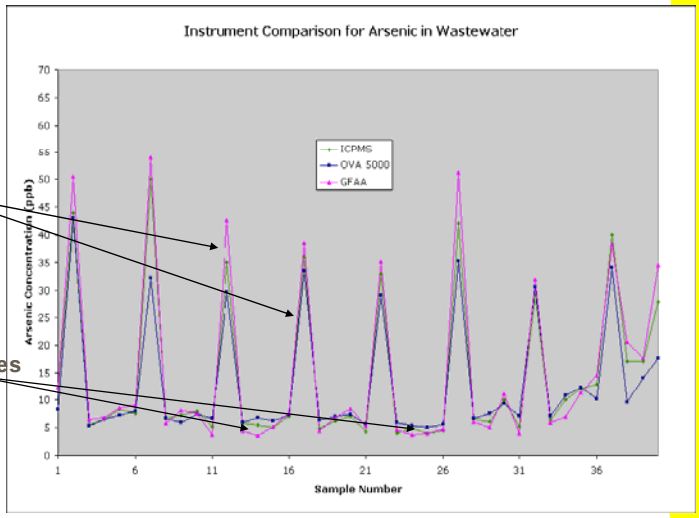
- USEPA “superfund” project site, Vineland, New Jersey, USA.
- River Monitoring Projects – Ministry of Environment, South Korea and Saarland University, Germany.
- Zinc & Lead Smelter Effluent Monitoring – Australia & UK
- Water Treatment works – United Utilities UK
- Electronics Factory Effluent Monitoring – FreeScale, Malaysia.
- Drinking Water Plant – Cheon An City Water, South Korea .
- Laboratory Effluent Monitoring – Ajou University, South Korea.
- US Military Base Effluent Monitoring. Pyeung Teak City Water, South Korea
- State Environmental Protection Agency (China) – Water intake protection 9 units

ChemScan.com

Continuous As monitoring – results of 60 day trial

Spiked Effluent Samples

Effluent Samples



ChemScan.com

RESULTS

OVA5000 was the only instrument to complete the 60 day trial with no failures

- At high concentrations OVA5000 showed a negative bias and the GFAA a high bias compared to the reference ICPMS
- At low concentrations (<10ppb) the OVA5000 showed a correlation coefficient closer to ICPMS result than the GFAA
- Following the evaluation the OVA5000 was subsequently purchased by Sevenson Environmental Services and will be involved in the cleanup operation for the next 30 years
- Connected to plant control system so that arsenic levels in discharge are monitored 24/7
- Effluent proactively controlled to minimize chance of accidental release in to surrounding area
- Offsite operators can begin corrective action if levels in effluent approaches critical level before on call personal arrive on site outside of normal working hours
- Significant cost savings by closing the laboratory at weekends
- Increased protection to local people and environmental health

UPDATE JUNE 2010 – Unit still operating within specification after over 4 years

ChemScan.com

CTM™

Continuous Toxicity Monitor

Automatic, real-time, on-line monitoring device detecting toxic chemicals in water

MODERNWATER

ChemScan.com

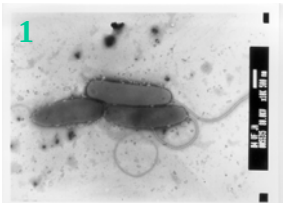
Bacterial Bioluminescence: *Vibrio*

Vibrio fischeri - bacteria sourced from deep sea fish, can be planktonic or symbiotic

Bacteria emit light when healthy, light output reduces **rapidly** on contact with toxins

'Inhibition' = the light goes out

Indicator for human toxicity : 'Biosensor' for monitoring chemical toxicity in water



ChemScan.com

139

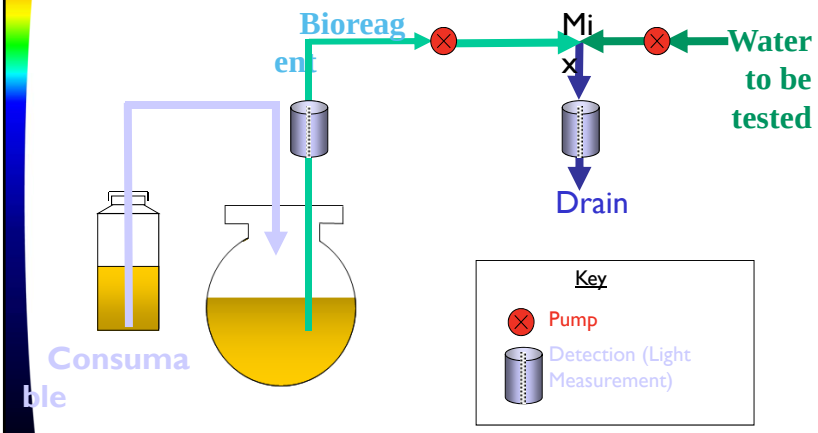
Biosensors in toxicity monitoring

- Lab test since 1980's
- Online toxicity monitor - new opportunities
  - Regulatory and legislative change driving new markets
  - Post 9/11 early warning systems required
- Various on-line analysers developed but reliable long-term automatic operation and rapid detection remain elusive
- Cymtox CTM™ Continuous Toxicity Monitor
  - True early warning system – modern day 'canary in a coal mine'

ChemScan.com

140

Toxicity Testing Diagram



ChemScan.com

141

CTM™ - The Product

- Fully automatic instrument
  - Self calibration and cleaning
- Continuous culturing and detection
  - Detection in 2 minutes
  - Reliable and reproducible
- Detects presence of toxic substances
  - stop/check/go
- 28 days continuous operation
  - Consumable replaced mon
  - ~ 2 hour service per month
- Operating Temp. 1-30 °C
  - Operation >30 C in climate controlled enclosure
- Bacteria compliant with ISO 11348

ChemScan.com

142

Levels of detection

Toxin	Concentration (ppm)	Detection Level	
		2 min	7 min
DMSO	10,000	1	2
Mercury Chloride	0.1	2	4
Potassium Cyanide	2.5	3	2
Glyphosate	0.5	3	3
Atrazine	0.1	3	3
Phenol	20	3	3
Zinc Sulphate	5	3	4
Sodium Nitrite	0.1	3	4
Sodium Arsenite	0.1	3	5
Toluene	0.1	4	3
Malathion	0.1	4	4
Potassium Dichromate	0.1	4	4
Chromium (IV) Oxide	25	5	2

1 : No detection
2 : <10% inhibition
3 : 10-25% inhibition
4: 25-50% inhibition
5: >50% inhibition.

143

Market and legislative drivers

Security/ Security of Supply
- Accidental and deliberate contamination
- Water intake protection - US presidential directive
- Distribution monitoring/ terrorist targets

Environmental
- EU Water Framework Directive – biological health
- Pollution
- Wastewater recycling

Economics
- Cost of monitoring/ manpower
- Asset Protection – WWTP and WTP

144

Requirements for early warning

- US/UK Authorities' wish list
  - Detect broad range of contaminants
  - Reproducible response
  - Minimal false alarms
  - Detect continuously and in real time
  - Automatic
  - Low down time
  - Require a minimal level of skill or training
- CTM™ delivers on all these requirements!

145

ChemScan.com

Where is it used?

146

ChemScan.com

HydroGuard Product Profile

Any Combination of Measurements in a Single Unit!

- ✓ **Free Chlorine (using DPD)**
- ✓ **Total Chlorine (using DPD)**
- ✓ **Free Chlorine (using amperometrics)**
- ✓ **Redox (ORP)**
- ✓ **PH**
- ✓ **Temperature**
- ✓ **Turbidity**
- ✓ **Conductivity**
- ✓ **Flow**

Combination Analyzer systems

AppliedSpectrometry Associates, Inc.

Technology (HydroGuard)

- Colorimetric Calibration free chlorine analyzers
- Patents Pending:
  - ARM™ – Active Regent Mixer
  - ASC™ - Automatic Self Cleaning
- Internal Architecture of Bus Configuration
  - Modular Design allowing for simple customization and field upgrades
- Multi parameter system
  - Up to 8 parameters
  - Free and Total chlorine in one unit

ChemScan.com

HG-702/302 Analyzer and Controller

Chlorine Testing – Free and/or Total

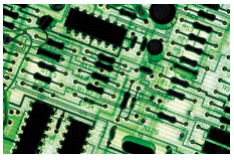
- Most accurate, consistent readings (+/- 5%)
- Consume VERY little reagents (~0.03mL/sample)
- Self zero before each reading
- Self-Cleaning Photocell
- Measurement : 0.00-10 ppm
- Measurement Interval: 2 to 10 minutes

ChemScan.com

Electronics

- IP-65 Rated Enclosures (NEMA 4 equivalent)
- Electronics - SMT Technology
- Separate boards for simple, fast & cost effective maintenance
- Removable terminal blocks for fast connections
- Minimum down-time for maintenance and repairs

Click for Demo



ChemScan.com

Control Relays

6 Independent Relays for Equipment Control

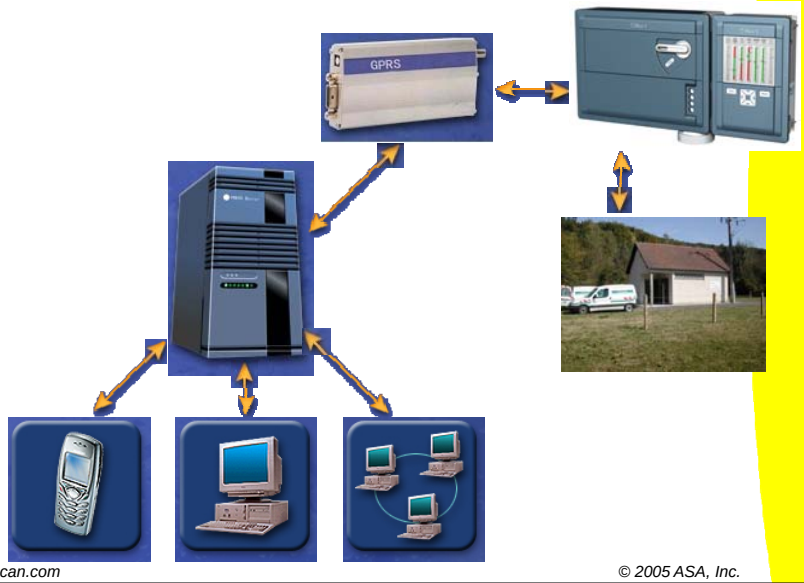
R1 – Main chlorine – on/off or proportional
R2 – Secondary chlorine – on/off only
R3 – pH – acid or base dosing
R4 – NTU – Turbidity
R5 – Alarm – Activates external alarm
R6 – Temperature – operates heater or chiller

Note: Relay functionality may be modified through change in software. Above is for standard software version.

Communication Options

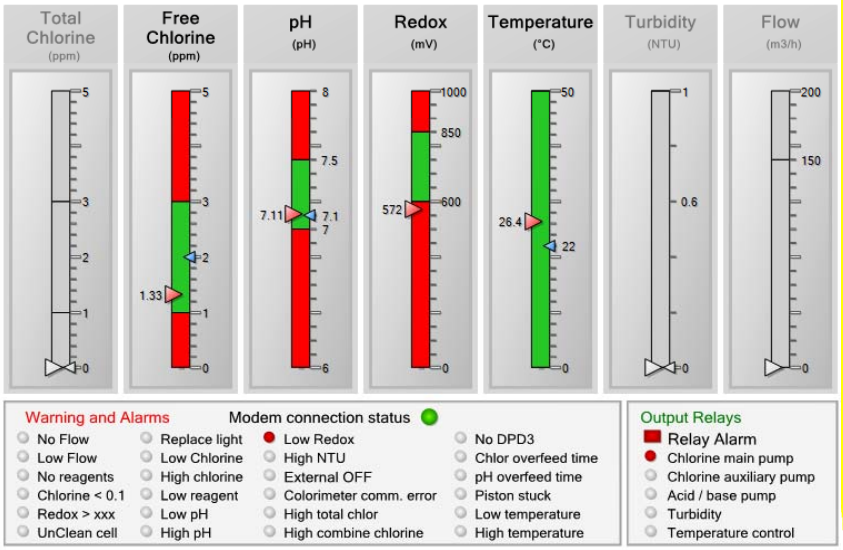
- 4 to 20mA Outputs
  - 2 to 8 channels for any measured variable
  - Dry contacts for non-measurement alarms
- HydroSoft
  - Fixed connection to local computer
  - Multiple Analyzers connected to a computer with only 2 wires
- Wireless
  - Completely Web-based wireless management
  - Real-time information and alerts
  - No phone or internet connection required on site

Internet Connectivity



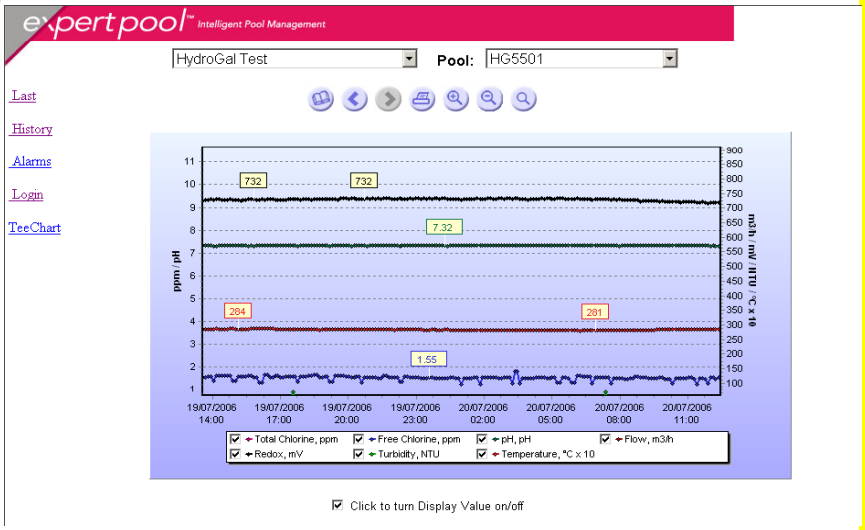
ChemScan.com

Wireless Communication – Real Time



ChemScan.com

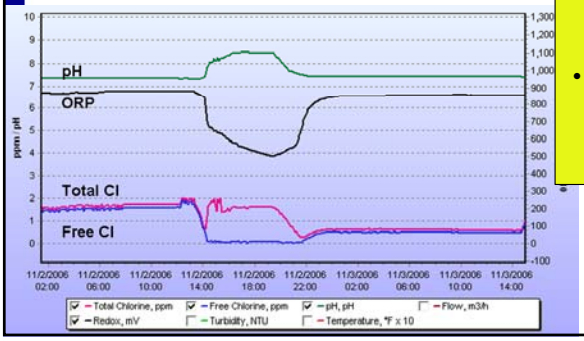
Wireless Communication - History



ChemScan.com

Case study: drinking water installation in the US

- **Site: Single tower/booster station for small town**
  - Receives water 1x per day from nearest city water station
  - Replaced TC amp system (capital controls) with Blue I FC, TC, pH, ORP, and temp (operating with system for several years)
- **Drop in Free Cl during filling process**
- **Also drop in ORP and increase in pH**



- **Through Blue I investigation, an overdose of Ammonia was diagnosed!**
- **Not a new problem, but first time they could see and track it!**