PNCWA 2012 - Wastewater Influent Monitoring to Minimize Process Upsets

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Wastewater Influent Monitoring

Presenter Information

- BSE in Chemical and Biomolecular Engineering (University of Pennsylvania)
- ~ 3 years at the Philadelphia Water Department as Environmental Engineer
  - On-line instrumentation and data analysis on drinking water side (water security)
- ~ 2.5 at s::can Measuring Systems
  - Product/Application Support, Sales, etc.

Wastewater Influent Monitoring

Company Information

- 1999 – s::can Messtecnik GmbH founded in Vienna, Austria
  - Submersible UV-Vis spectrometer probe
- 2002 – 2006 - Development of full online instrumentation product line
- 2006 – Opened office in the USA under s::can Measuring Systems LLC

Wastewater Influent Monitoring

Overview

- Concepts behind UV-Vis spectroscopy
  - How do we measure?
- What do we measure in wastewater influents?
  - Dissolved Sulfide Monitoring
  - BOD (equivalent) Monitoring
  - Event Detection
- How to use this information? (Greg Land, Kemira)

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Goals

- **Goals of monitoring influent wastewater quality:**
  - **Cost savings**
    - Dose chemicals on a **mass to mass basis** instead of using flow and grab sample results.
      - Feed-forward process control
    - Save costs on lab sampling and analysis by utilizing on-line data.
  - **Improve effluent quality**
    - Finely tune processes using high-frequency data instead of grab or composite samples – **tells whole story!**
    - Detect abnormal wastewater compositions and take corrective actions to protect the plant/process before problems are evident.

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Monitoring techniques

- **Applications discussed today**
- UV-Vis spectroscopy
  - Submersible UV-Vis spectrophotometer
  - Single instrument provides multiple parameters (i.e. BOD, COD, TSS, dissolved H_2S)
  - No consumables or moving parts

- Remote access to data and control feedback using advanced software
  - Industrial PC with web-server front-end
  - I/O versatility for integration
  - Data validation for reliable output to process control systems
  - Wastewater quality alarms for contaminant alerts and identification (future)
  - Remote access capabilities via 3G/4G internal modem or LAN connection

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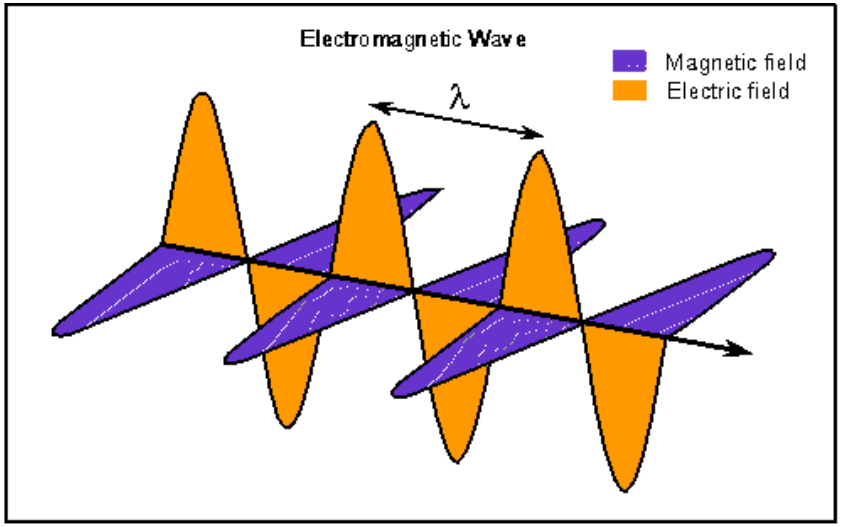
How do we measure - Back to basics

- *Electromagnetic radiation* (EMR) refers to light, x-rays, radio waves, etc. in which electric and magnetic fields vary simultaneously

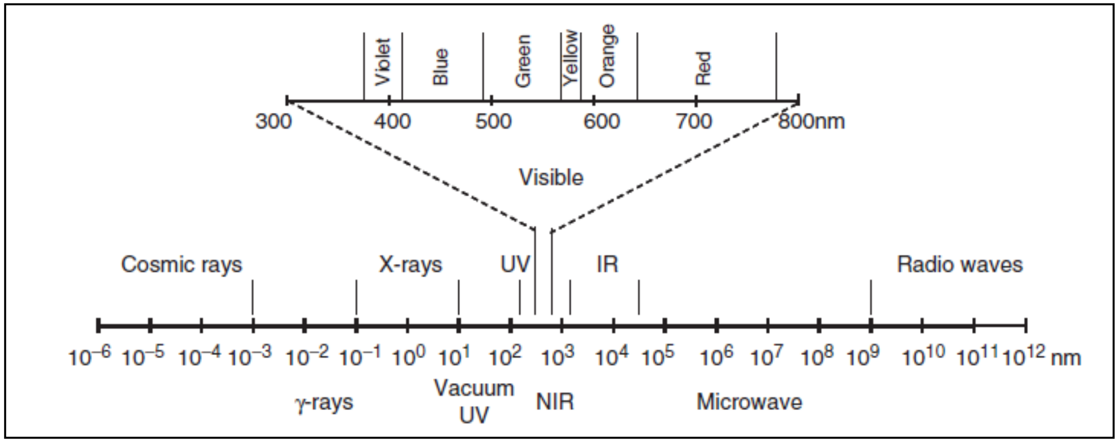


- The relationship between frequency, wavelength, and speed of EMR (constant in vacuum):

$$\nu\lambda = c$$

- The energy of a photon:

$$E = hc/\lambda \; 10 \uparrow 9$$



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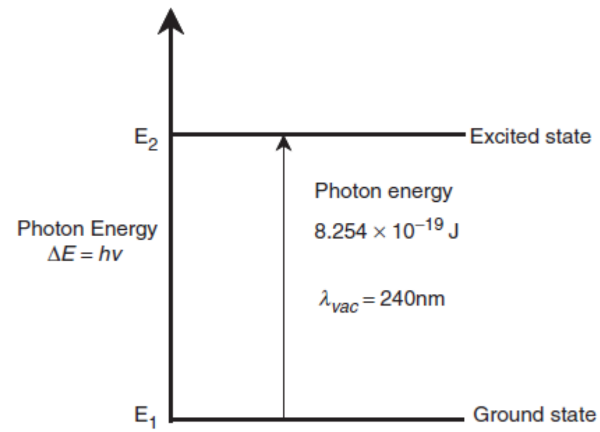
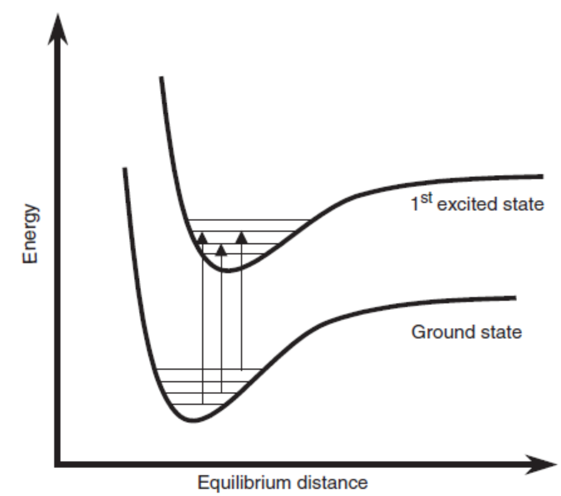
How do we measure - Back to basics

- *Spectroscopy* is the branch of science concerned with the investigation and measurement of spectra produced when matter interacts with, or emits electromagnetic radiation



- UV-Vis spectroscopy measures light absorption due to energy level transitions of electrons
  - Electronic transitions are quantized, meaning they can only occur at specific energies
  - This allows identification and quantification of certain compounds



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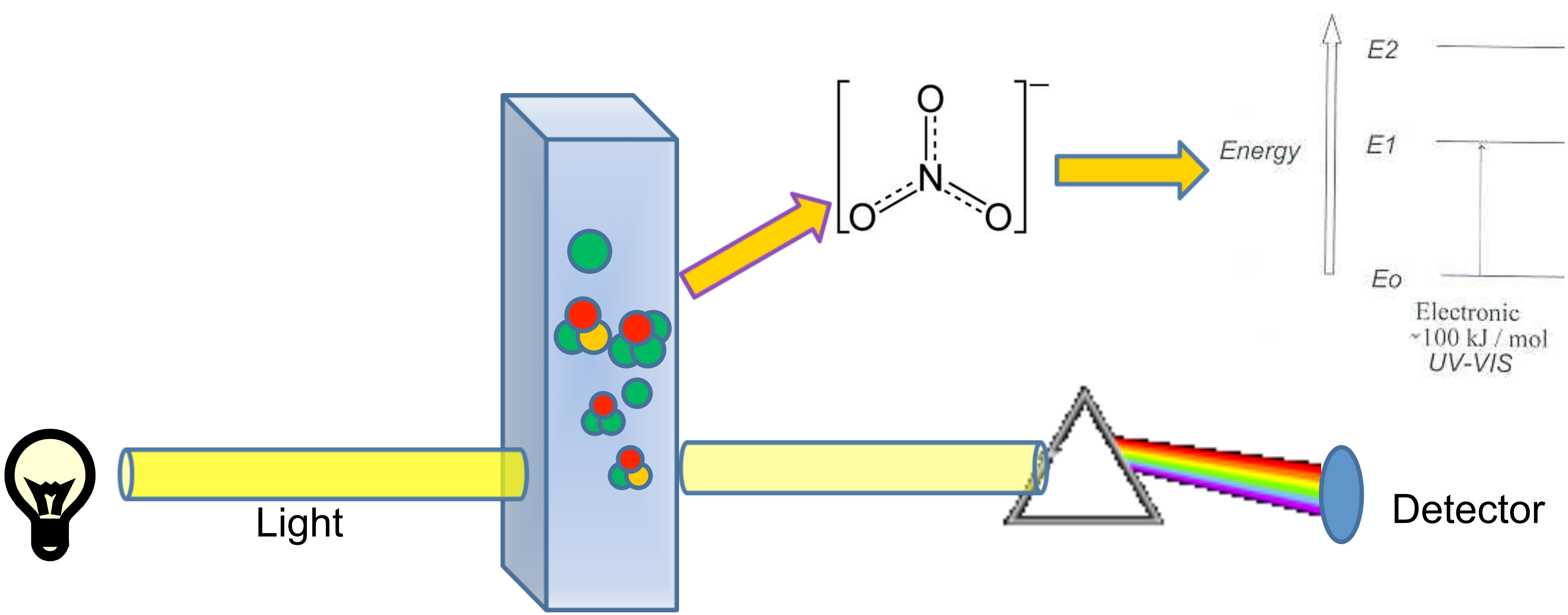
How do we measure? - UV-Vis spectroscopy

- [illegible] (Beer-Lambert Law)



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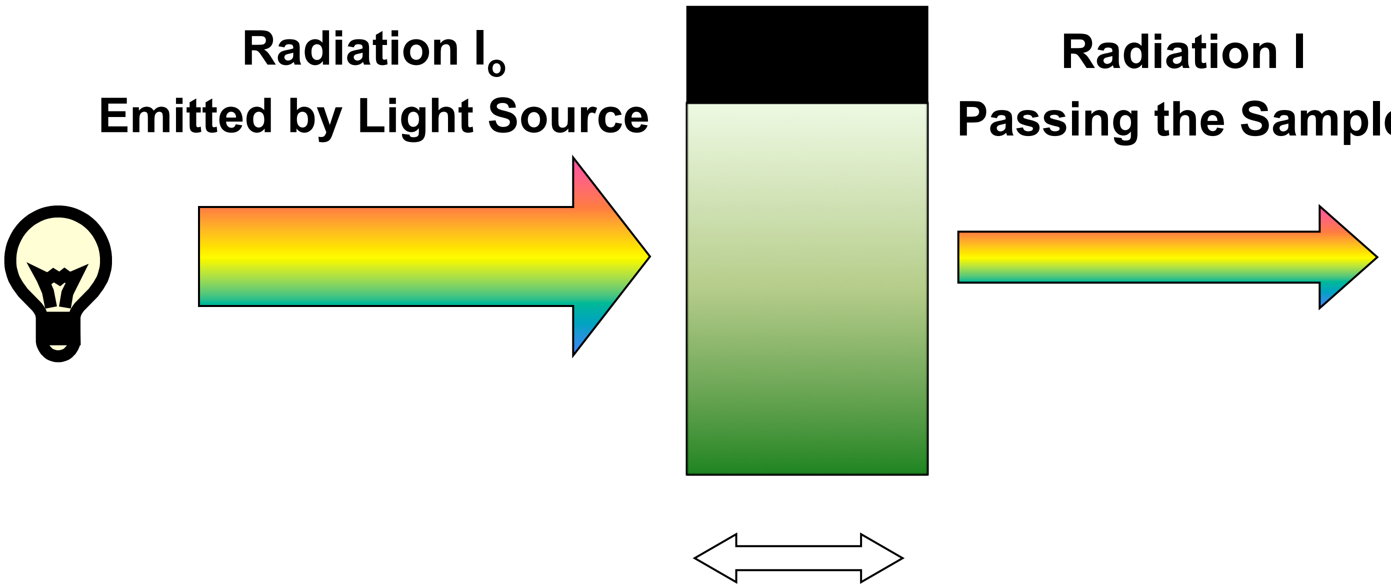
How do we measure - UV-Vis spectroscopy



Optical Pathlength OPL [mm]

ε = Extinction coefficient of solute

C = Concentration of solute

Absorbance A = - log (I/Io) = ε * C * OPL

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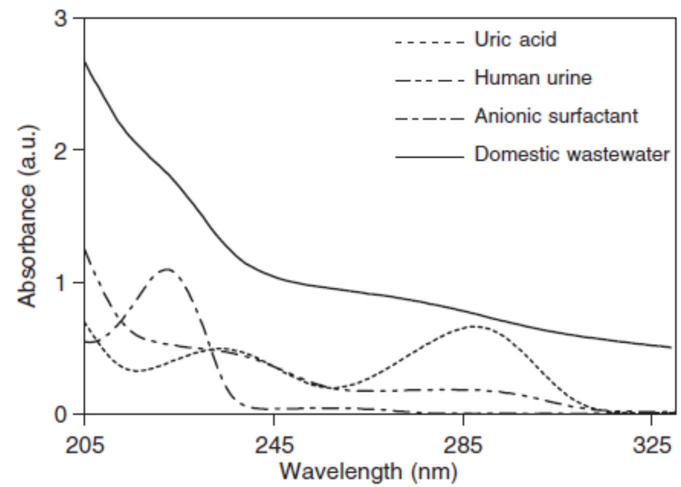
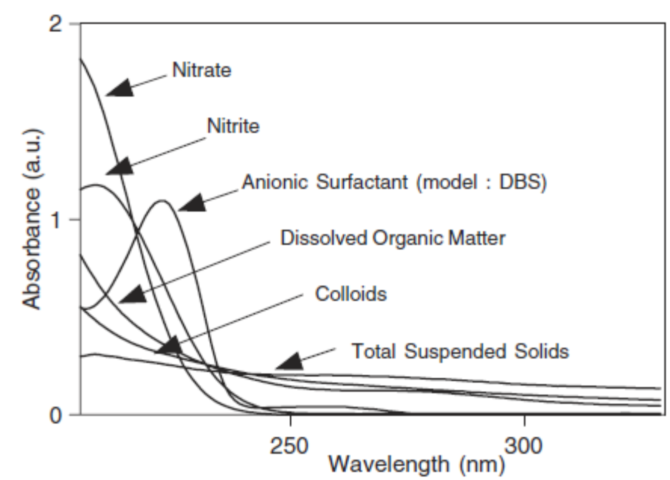
How do we measure - UV-Vis spectroscopy

- Determining the concentration of a single compound such as dissolved sulfide in a clean water is simple.



- A real wastewater matrix is complicated due to many overlapping spectral and light scattering due to suspended solids.

- Fitting algorithms such as partial least squares are used to form algorithms which extract the relevant spectral information for parameter estimation
  - Typical parameters include: COD, BOD5, TSS, Nitrate, etc. for wastewater



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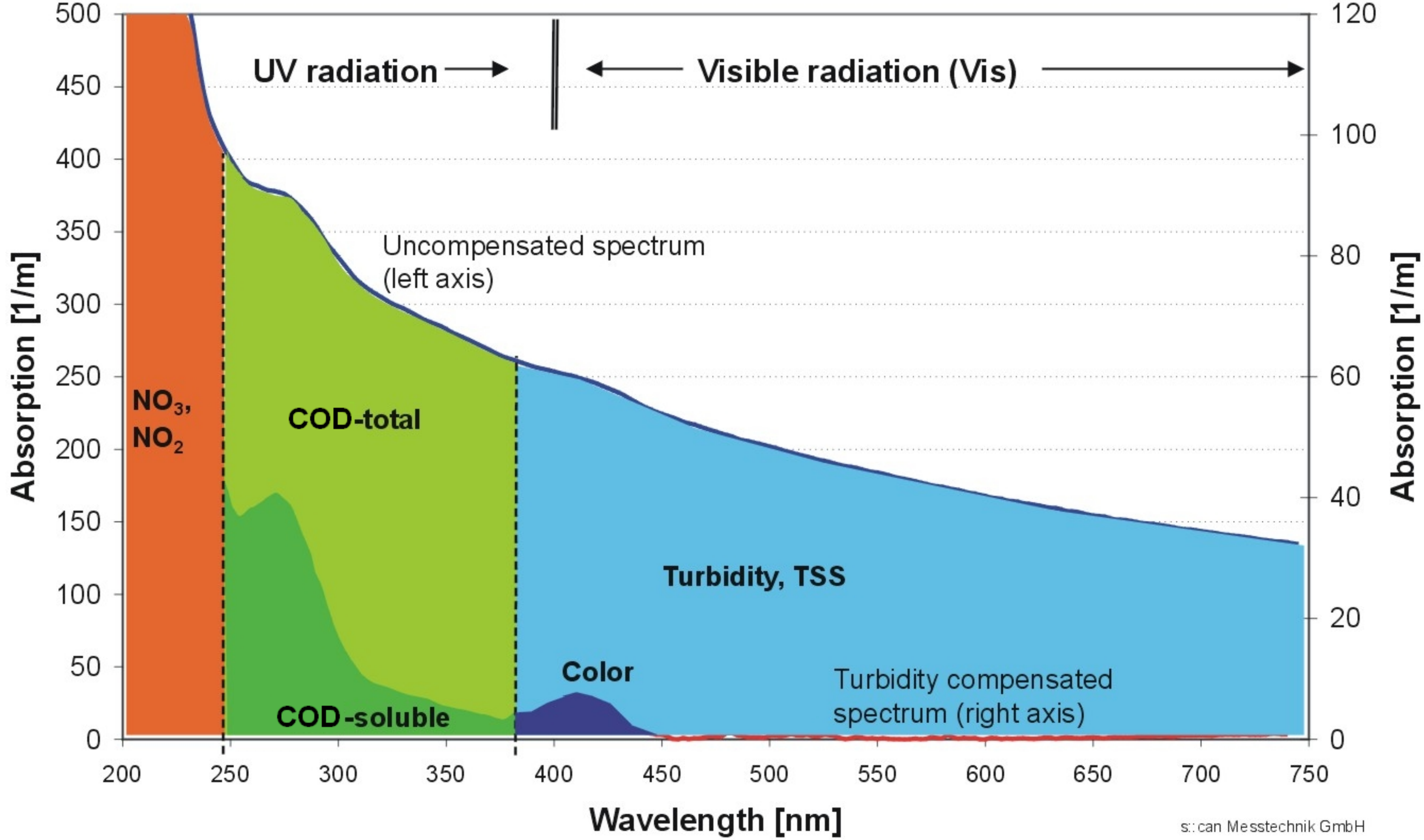
How do we measure - UV-Vis spectroscopy



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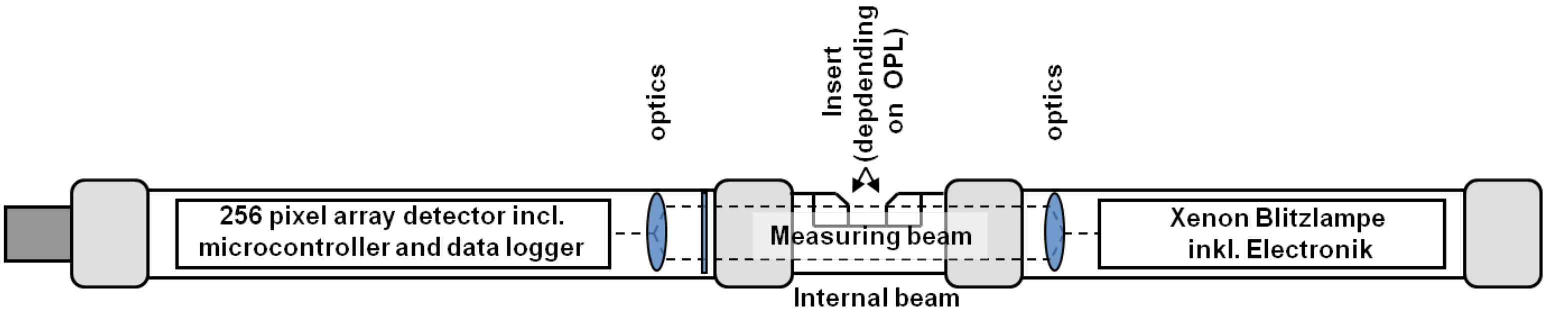
How do we measure - Sensor design



- **How it works:**
  - Xenon flash-lamp is used as the light source
  - Light beam is split and sent through measuring path and internal reference path
    - Measurement of reference path energy accounts for aging of lamp and detector eliminating drift
    - Automatically detects problems with optical components and alerts the user
  - 256-pixel photodiode array detector measures absorption between 200 – 750 nm

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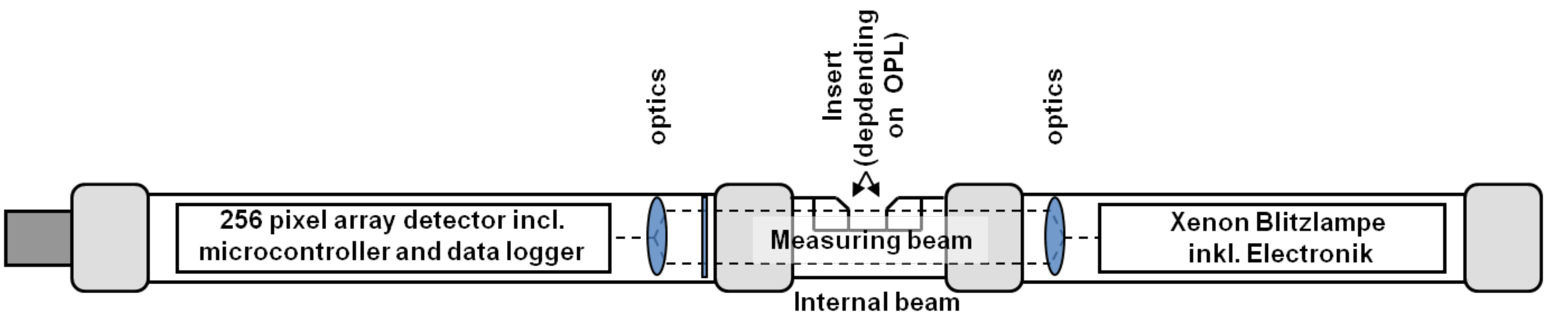
How do we measure - Sensor design



- **Advantages**
  - No need to “recalibrate” the sensor to account for aging
  - No need to return the sensor to manufacturer for routine lamp replacement (typical lamp life-time ~ 10 years)
  - Self-diagnostics for issues with lamp or detector
  - No consumable or replacement parts
  - 3 – 5 year warranty standard
  - Full spectrum allows complete compensation of cross-sensitivities and compound differentiation

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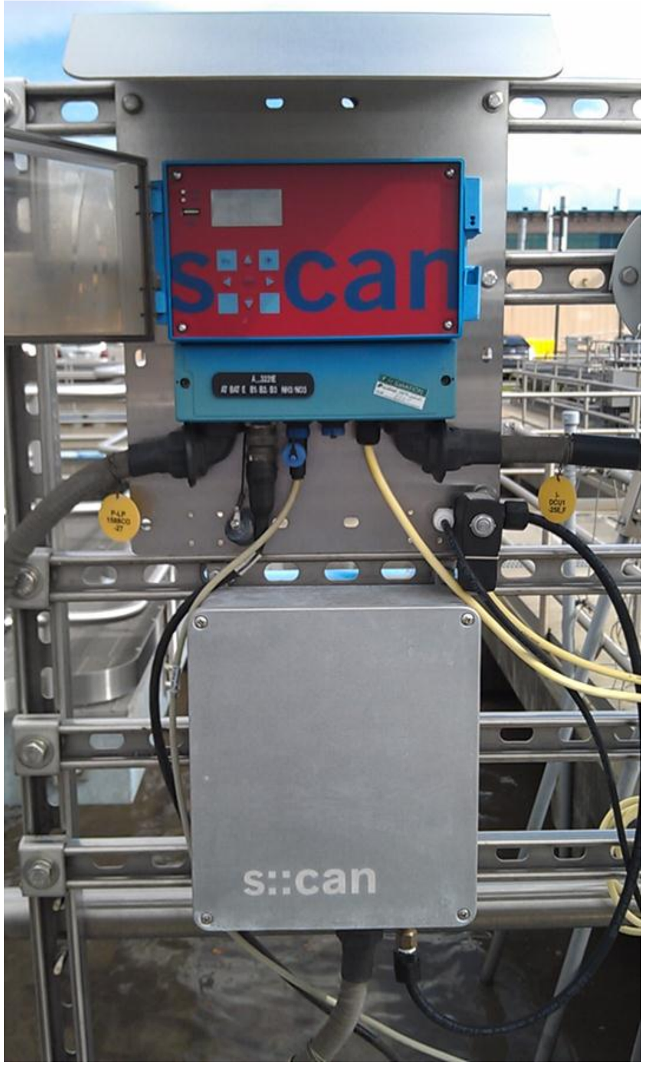
How we measure - Maintenance

- **Air cleaning apparatus:**
  - High pressure (120 psi) air compressor with small footprint
  - 12 VDC solenoid valve (normally closed)
  - Valve can be triggered by relay on controller or directly by the spectrometer probe (i.e. for remote applications)

- **Advantages**
  - High pressure blast acts as a "sand-blaster" to clean the windows with the solids in the process
  - Avoids smearing and inefficient cleaning as seen using wipers
  - Suitable for high fat content applications (i.e. dairy)



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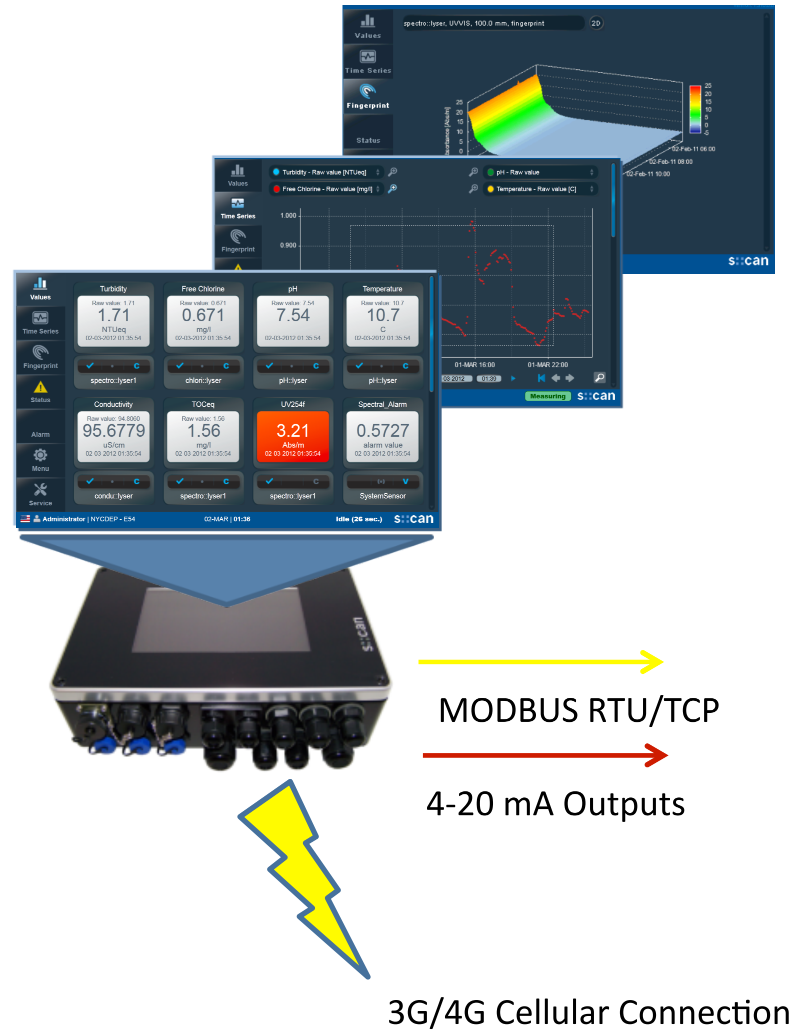
How we measure – Data Storage

- Controller (con::cube) logs data from the sensor
- Can interface with MODBUS RTU/TCP, Profibus, SDI-12, 4-20 mA, etc.
- 3G/4G internal modem for remote connectivity, calibrations, data visualization
- Currently developing PLC-like functionality (i.e. PID control loops)



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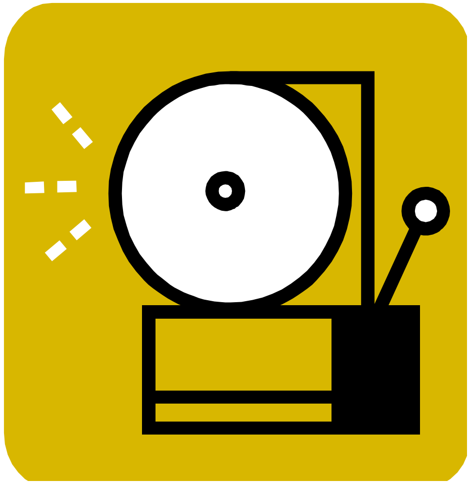
What we measure – Influent Wastewater

- **Alarms for Industrial Contamination**
  - Goals: Detect and identify a wide array of potential industrial contaminants
  - Benefits: Help prevent plant upsets or complete biological losses, identify polluters in collection system
  - Advantages: Minimal maintenance, detects a wide-array of contaminants

- **Dissolved sulfide and BOD**
  - Goals: Dose pre-treatment chemicals on a **mass to mass basis**
  - Benefits: Enhanced Process Control, Chemical Cost Savings,
  - Advantages: Minimal maintenance, accurate measurements, remote access

Wastewater Influent Monitoring (Contaminant Alarms)

- **Problem Description**
  - The wastewater treatment plant in this case is subject to unexpected industrial discharges which can upset the wastewater process
  - Various industries in the area feed into the collection system and could contribute harmful constituents
  - Can different contaminants be identified?



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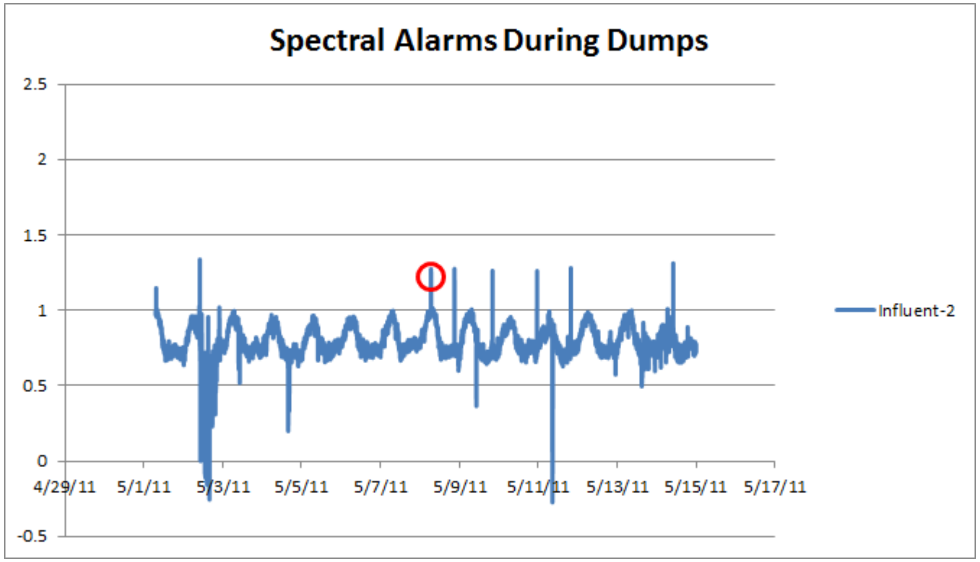
Wastewater Influent Monitoring (Contaminant Alarms)

- **Details**
  - At first, COD set-points from the instrument were investigated to detect contamination.
    - Changes were not significant during contamination
  - Instead, the deviations in the raw spectral fingerprint were used
  - Rich dataset that can detect and differentiate between a **wide** variety of substances



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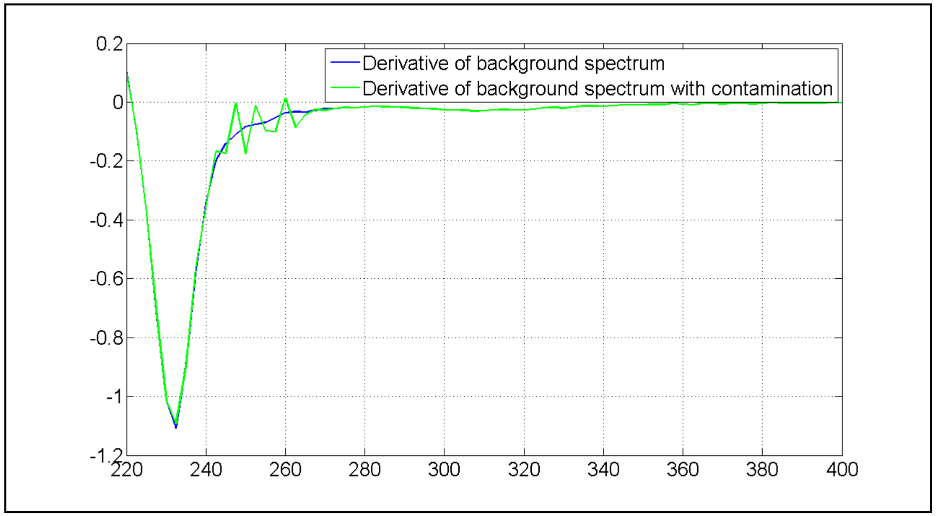
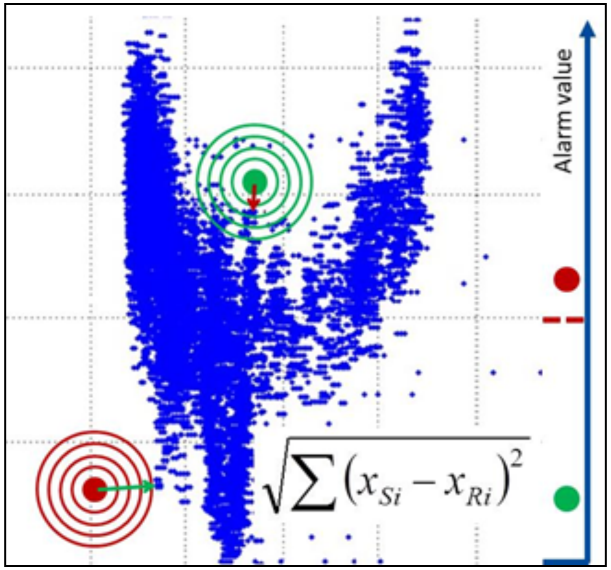
Wastewater Influent Monitoring (Contaminant Alarms)

- **Spectral Alarms**
  - First the data is pre-processed to remove the effects of changes in solids content
  - Then, a training set of *normal* fingerprint data is compiled by the system (automated)
  - New data points are compared to the baseline set and evaluated based on **multivariate distance**





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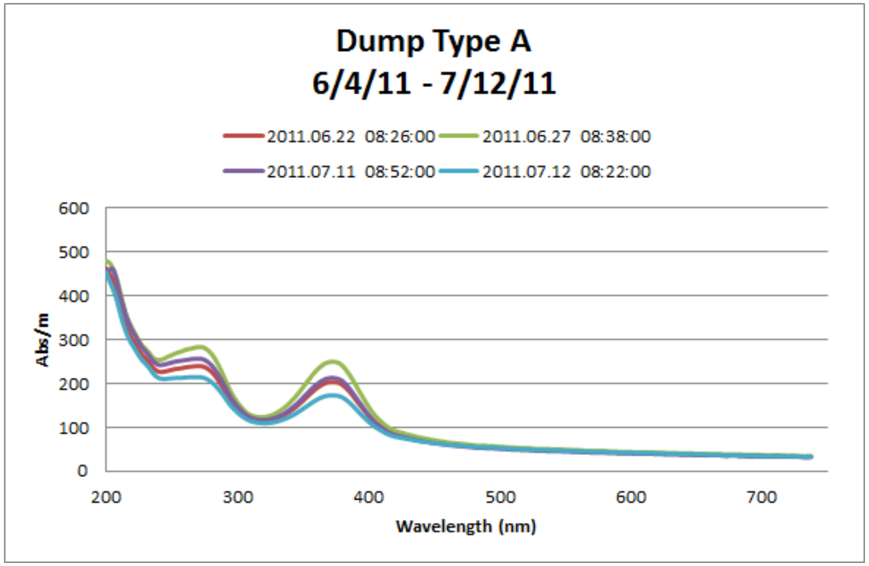
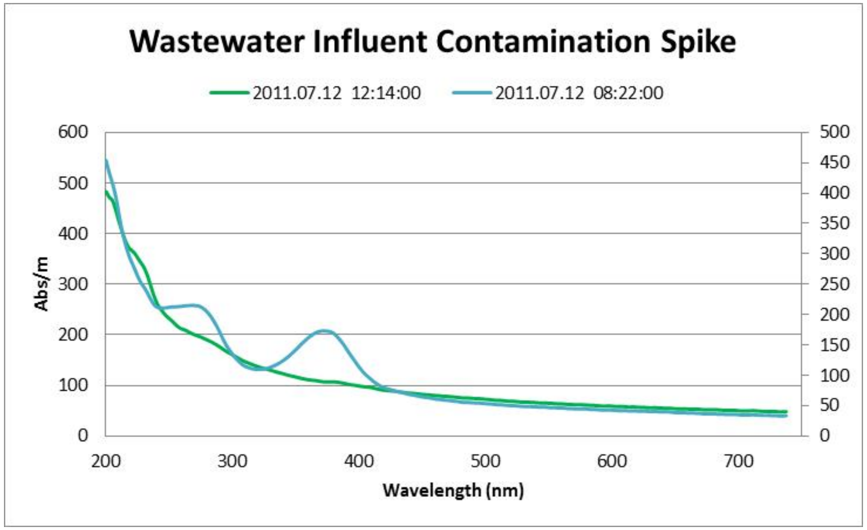
Wastewater Influent Monitoring (Contaminant Alarms)

- **Results**
  - The fingerprint alarms led us to investigate individual spectra
  - In this case, a distinct spectral was noted repeatedly
  - Other abnormal spectra were also identified suggesting multiple dischargers





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Wastewater Influent Monitoring (Contaminant Alarms)

- **Results**
  - Comparison of the abnormal spectra to reference libraries identified the compound as hexavalent chromium
    - This compound is commonly used in metals manufacturing which was one of the industries in the area

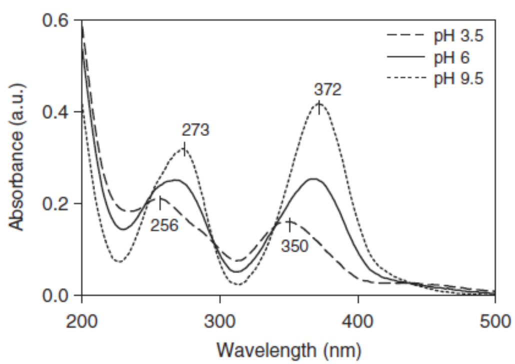
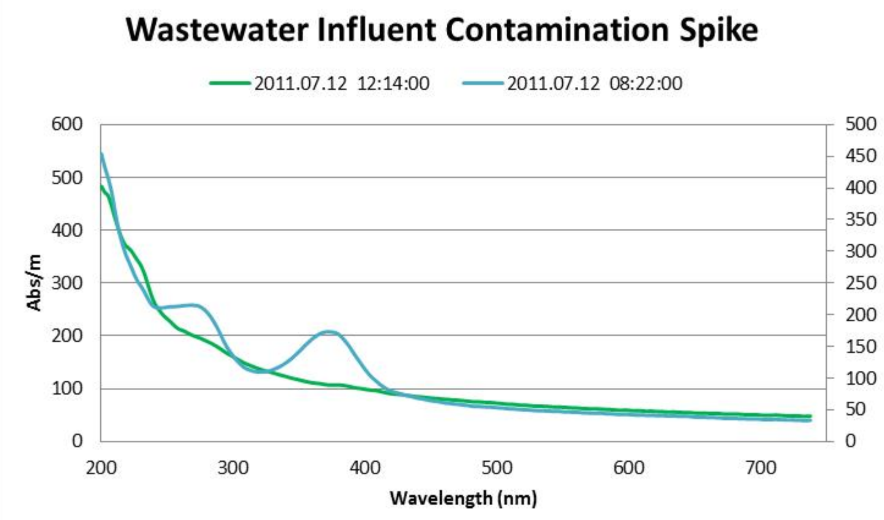


FIGURE 21. *Absorption spectra of a $K_2Cr_2O_7$ solution (1 mg/L of Cr, pathlength 50 mm) for different pH.*



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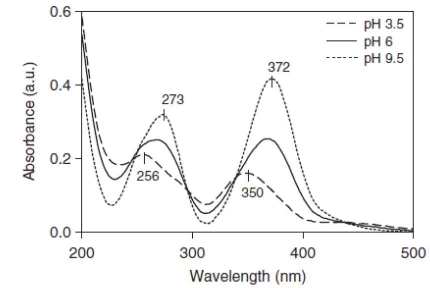
Wastewater Influent Monitoring (Contaminant Alarms)

- **Next Steps**
  - Develop a library of potential contaminants in this customer's area with UV-Vis spectra
  - Automatically search the library for contaminants when an alarm is detected and show possible matches
  - Install sensors in the collection system for COD, H_2S, and alarm monitoring



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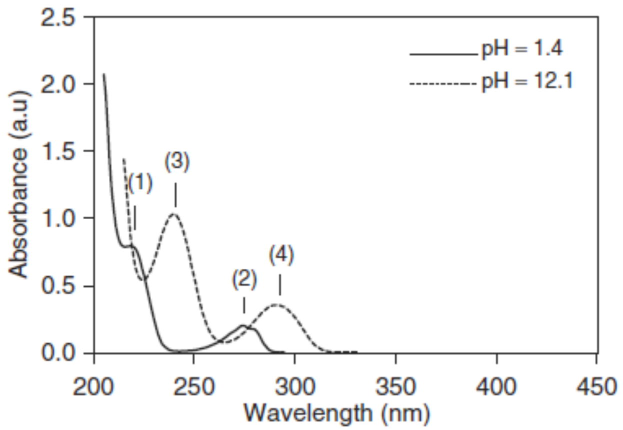

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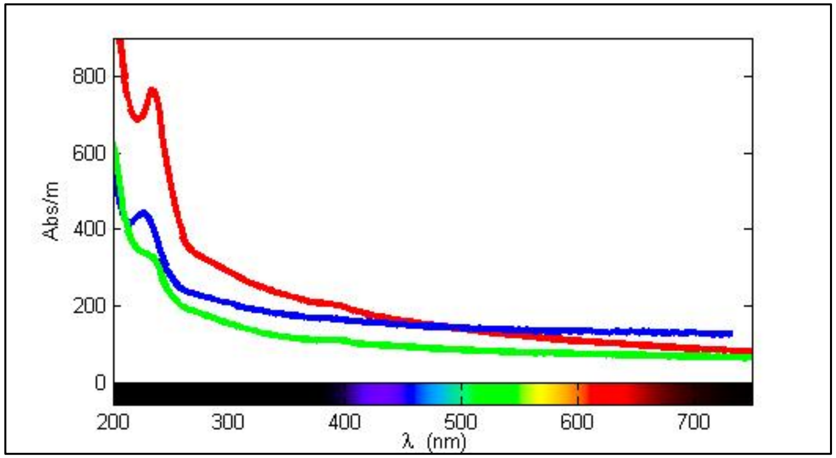
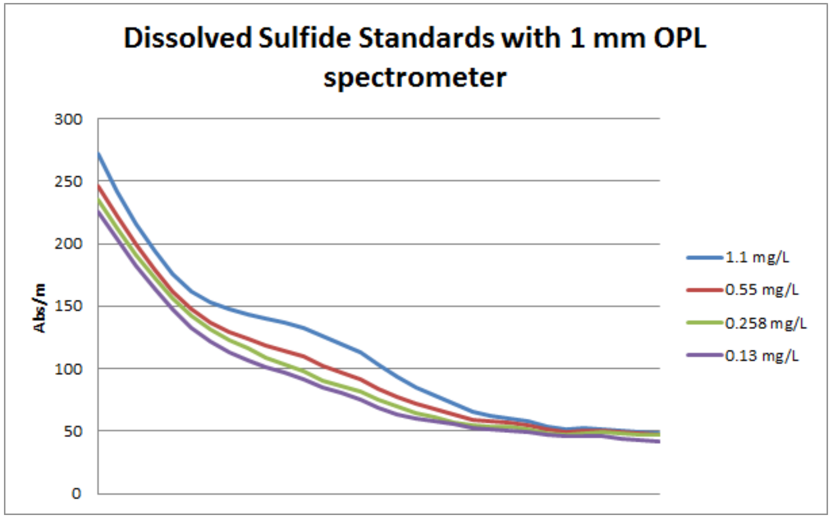
What we measure – Dissolved Sulfide

- **Dissolved Sulfide Measurement**
  - It was discovered that the UV absorption changes were due to dissolved sulfide which absorbs in the UV spectrum
  - Pioneering work for real-time dissolved sulfide monitoring conducted in New Zealand
  - Advanced algorithms were developed to decompose the spectral data and account for cross-sensitivities in real wastewater





Wastewater Influent Monitoring

What we measure – Dissolved Sulfide

- **Details**
  - Hydrogen sulfide exists in a liquid/vapor equilibrium
  - In the aqueous phase, there are three species in equilibrium:
    - $H_2S \leftrightarrow HS^- + H^+$
    - $HS^- \leftrightarrow S^{2-} + H^+$
  - The active species absorbs in the UV spectrum without the use of reagents
    - Cross-sensitivities must be compensated for using advanced algorithms
  - A pH sensor is utilized to compensate for the equilibrium shift between the species of interest

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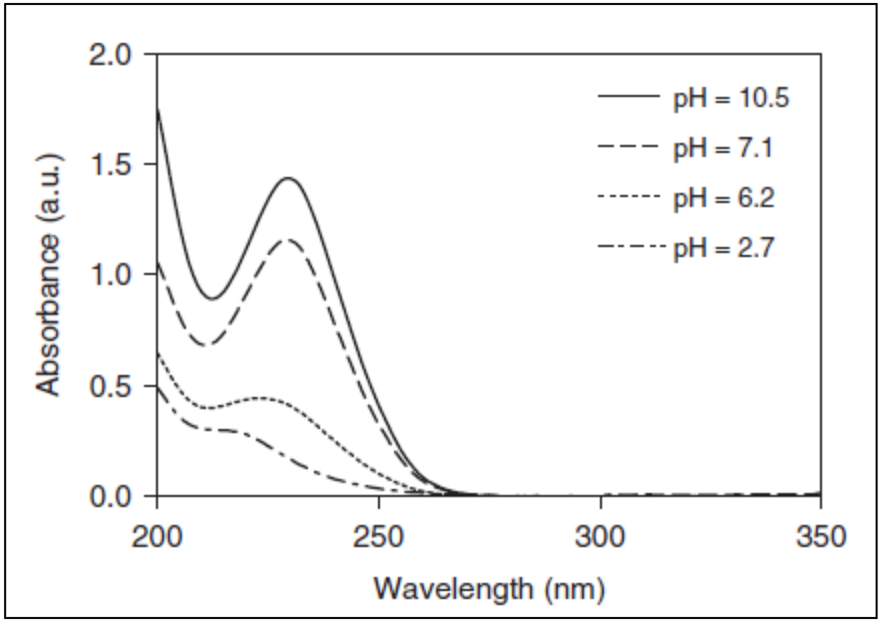
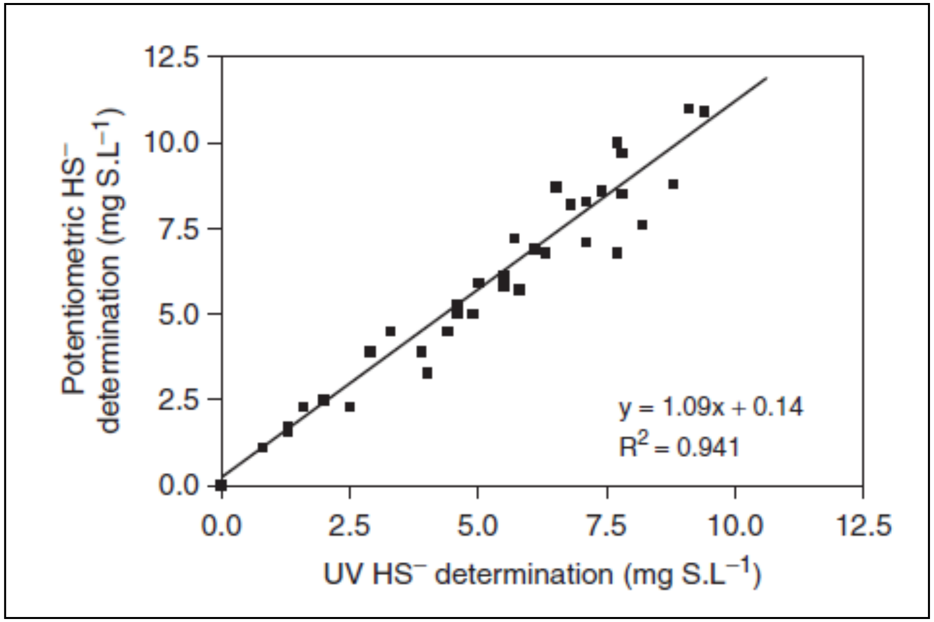
What we measure – Dissolved Sulfide





- UV-Vis spectra and dissolved sulfide UV versus Lab correlations from literature
- Even with a difficult wastewater matrix the dissolved sulfide signal is strong enough for reliable quantification

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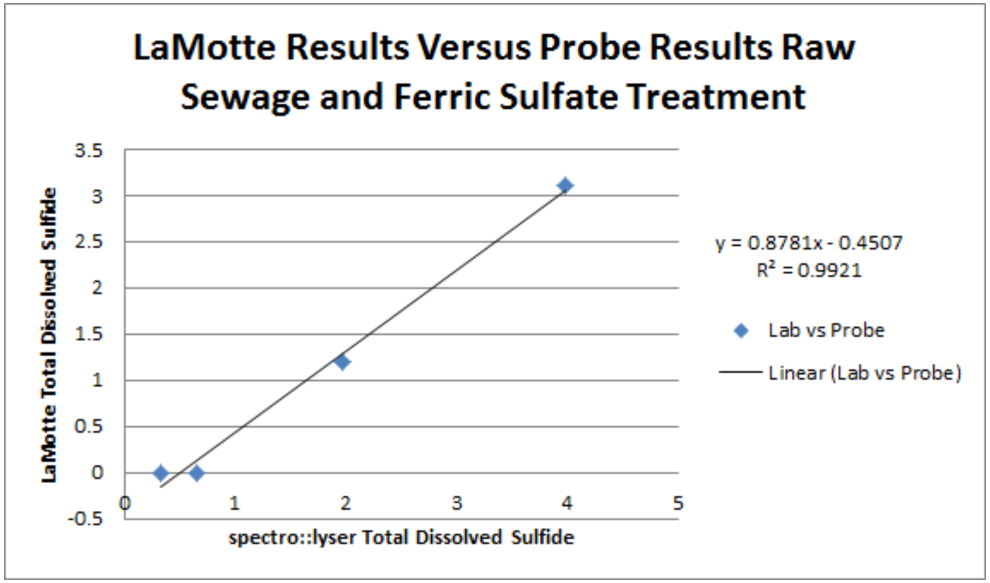
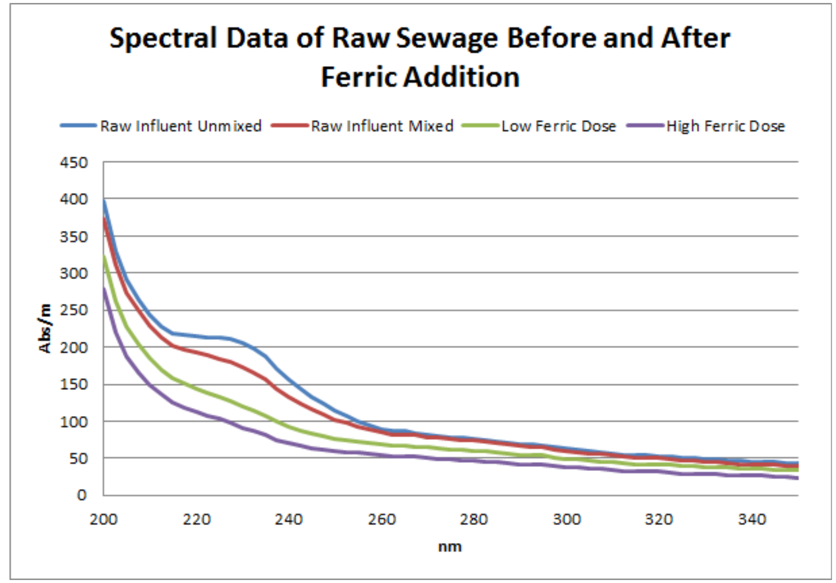
What we measure – Dissolved Sulfide





- Lab testing to validate probe response
- Good agreement with reference test (LaMotte)
- Next step was full-scale installation and validation

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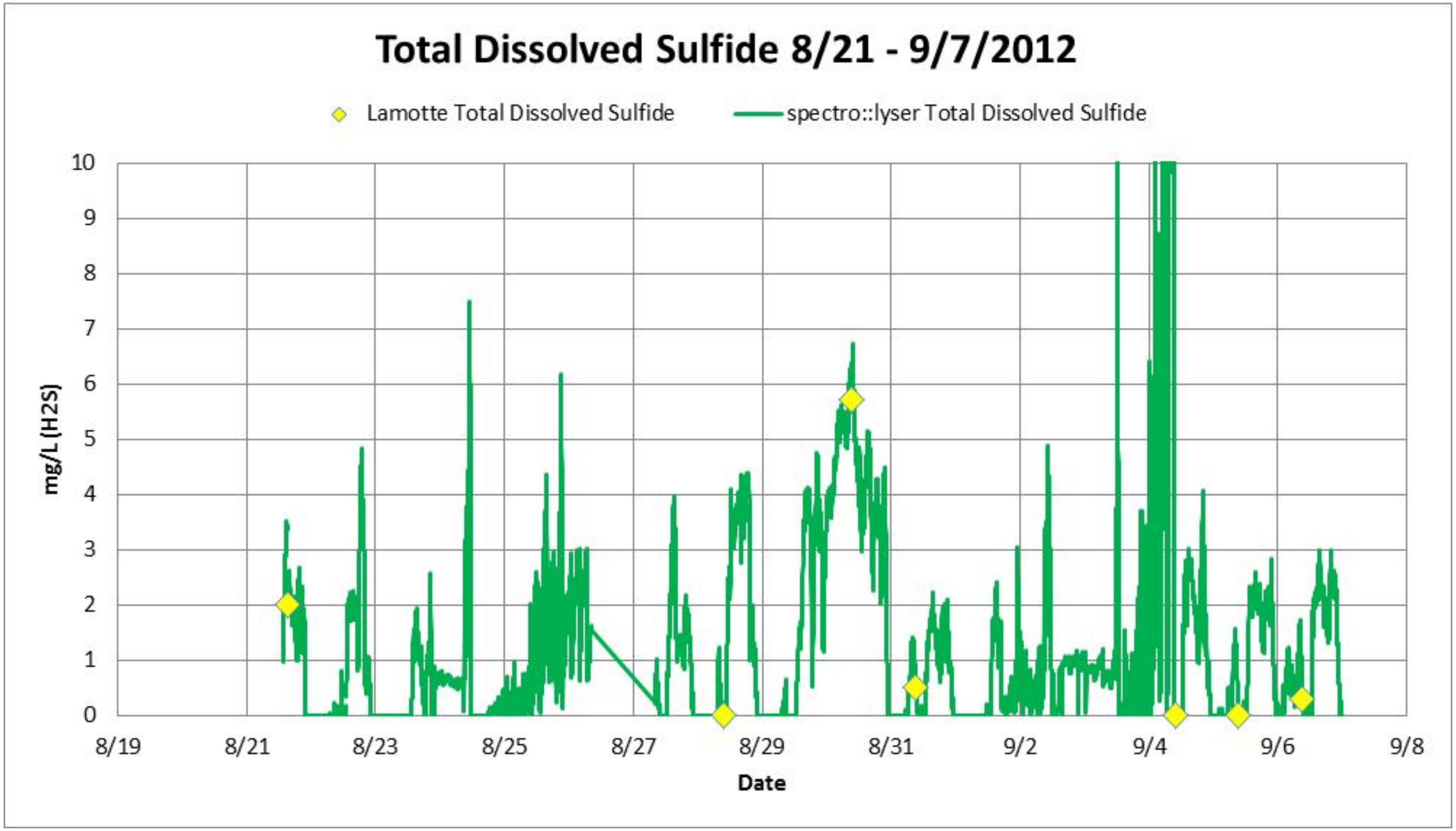
What we measure – Dissolved Sulfide



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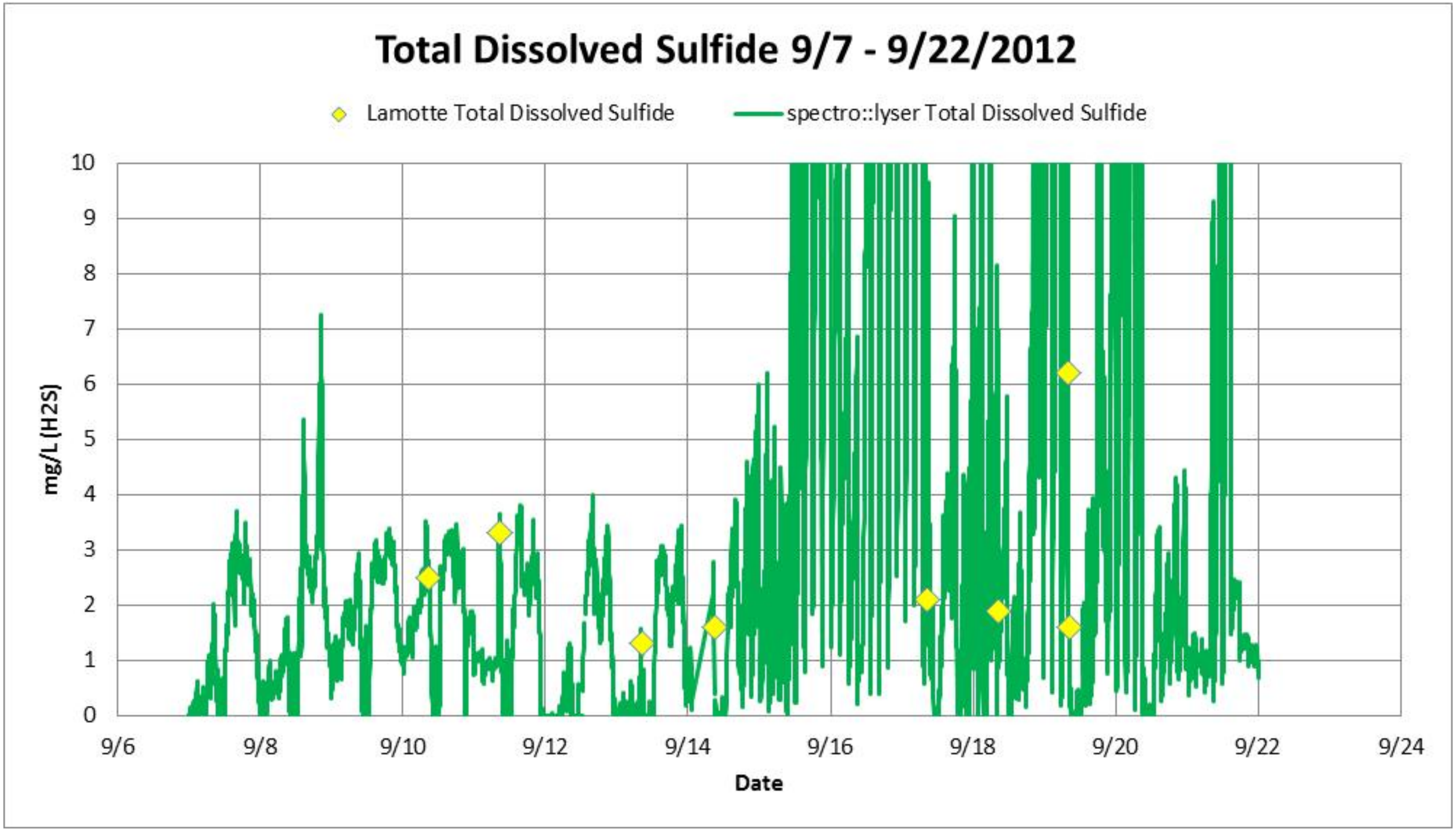
What we measure – Dissolved Sulfide



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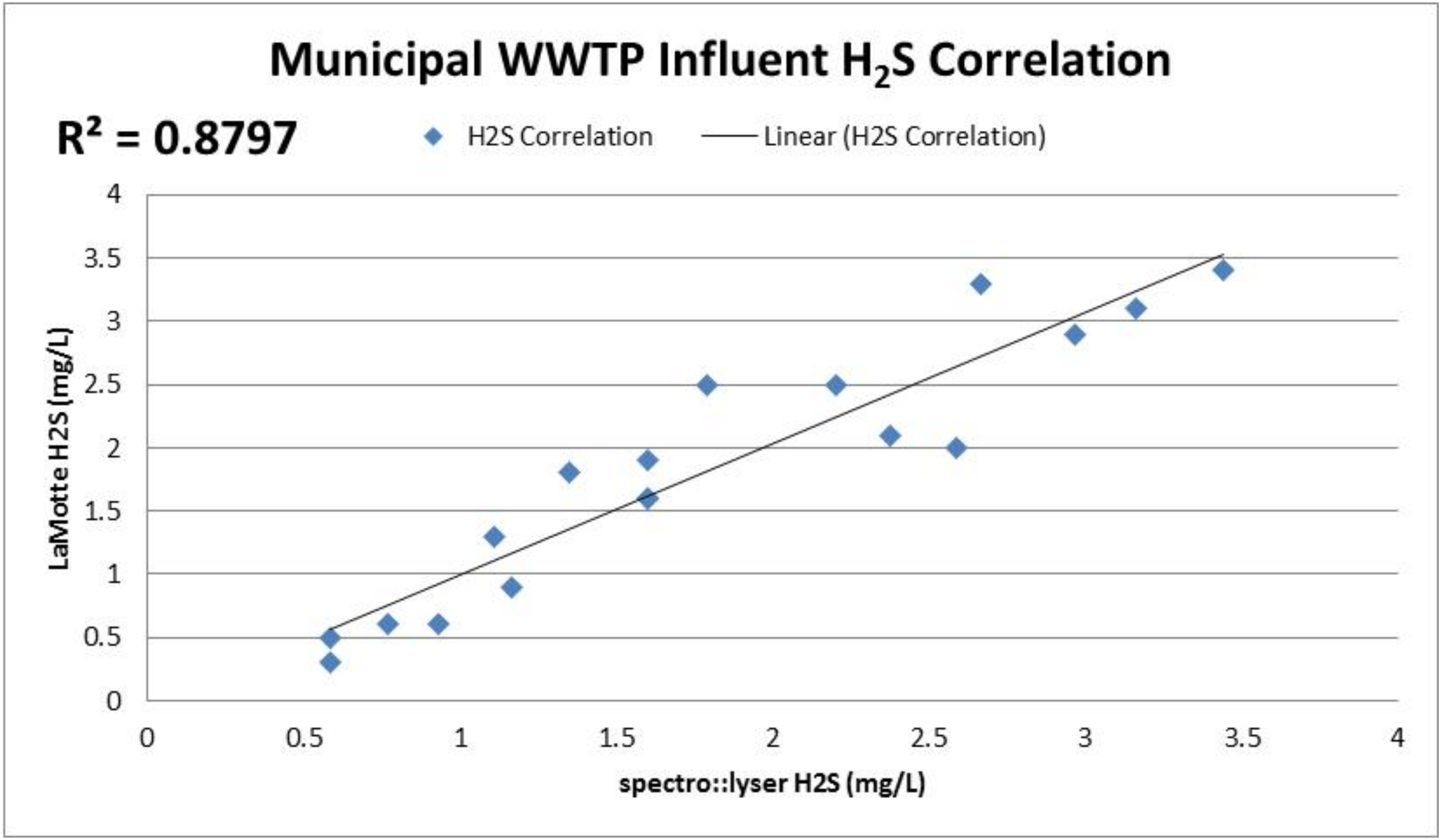
What we measure – Dissolved Sulfide



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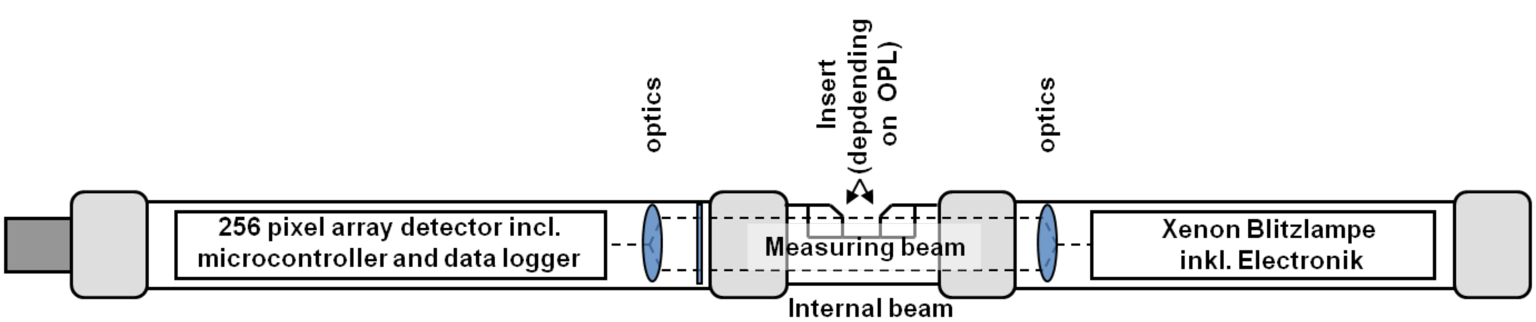
What we measure – BOD

- **BOD Analysis**
  - Lab results require five days making process control difficult
    - This is especially true during transient conditions such as storm events
  - Conventional on-line BOD analyzers require significant maintenance and consumables
  - TSS analyzers can provide some useful information but does not always correlate well with BOD
  - **What about spectroscopy?**



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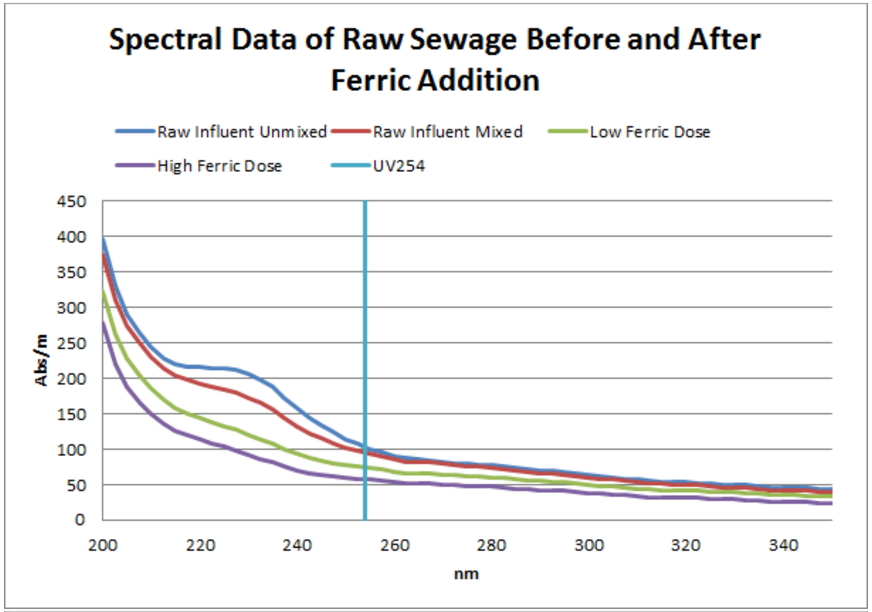
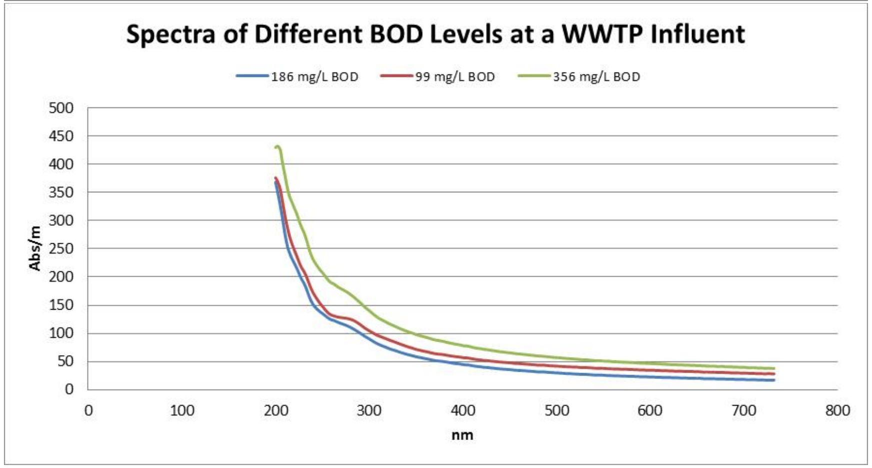
What we measure – BOD

- **On-line BOD Analysis**
  - UV-Vis absorption measures the constituents of BOD and then predicts the actual BOD from algorithms
    - Spectroscopy is **not** simply UV254 which does not work effectively for on-line BOD at WWTP influents
    - Spectroscopy is also much more accurate than simple TSS correlation with BOD





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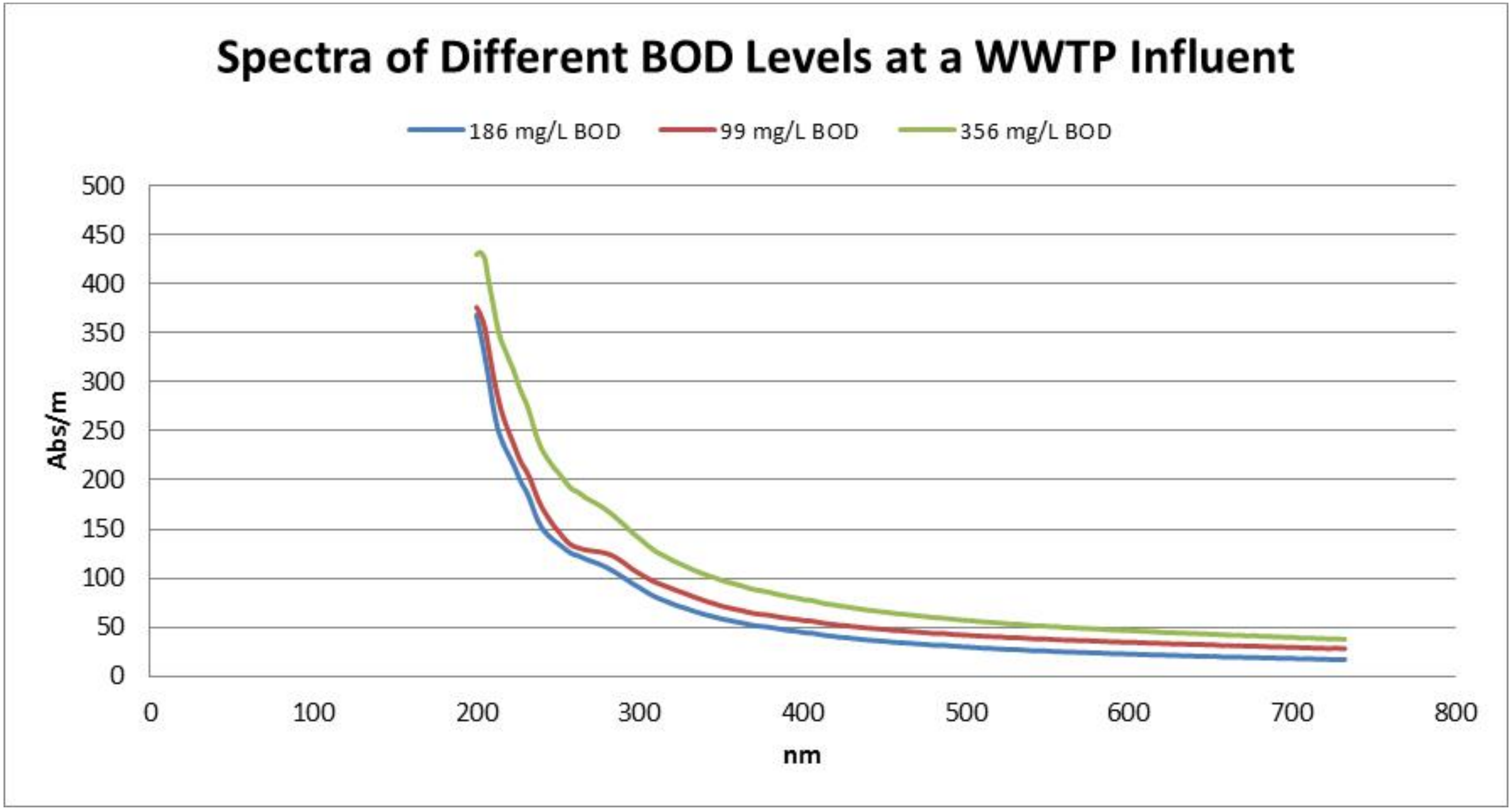
What we measure – BOD



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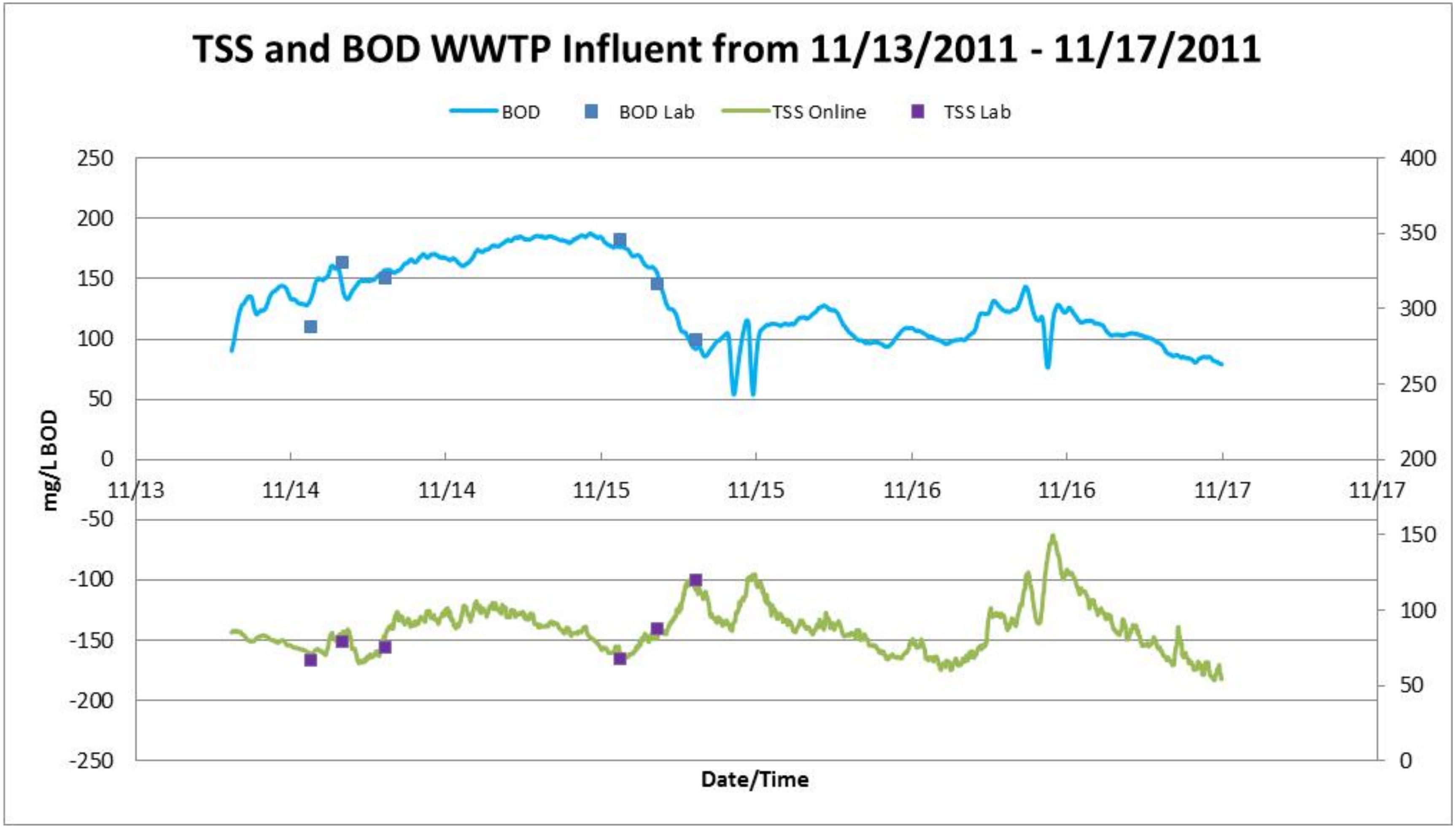
What we measure – BOD



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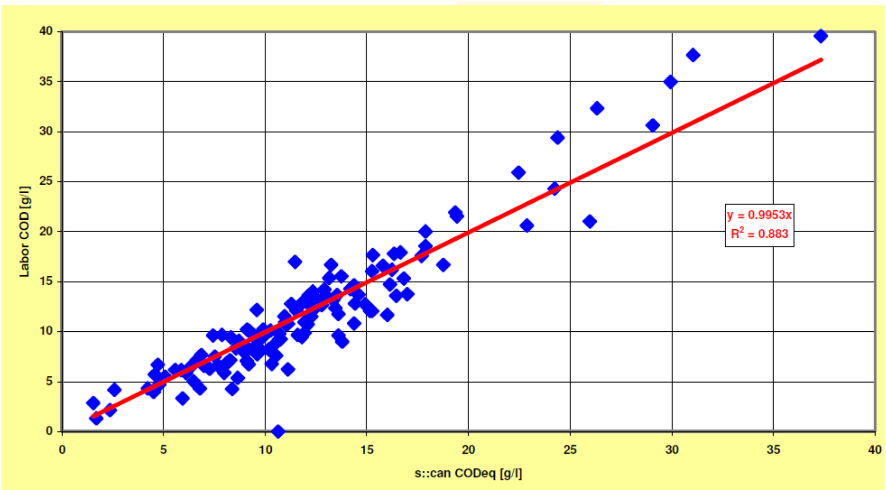
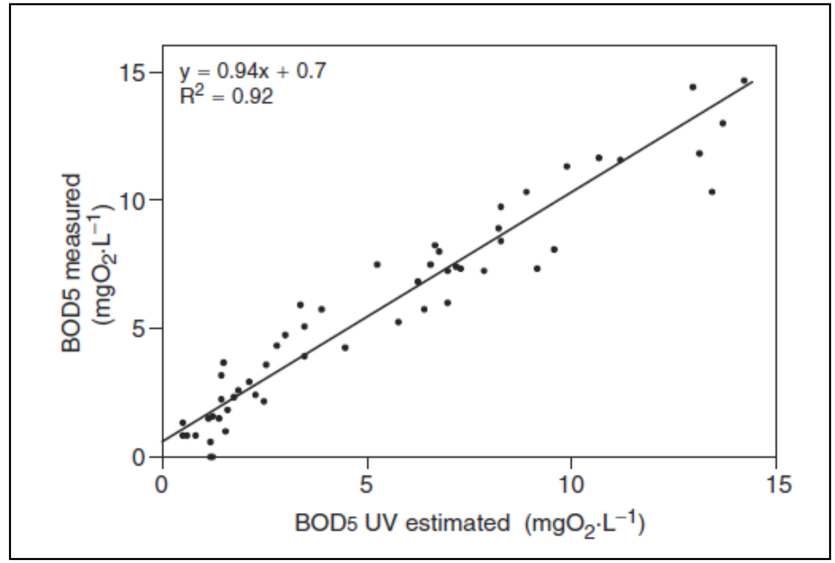
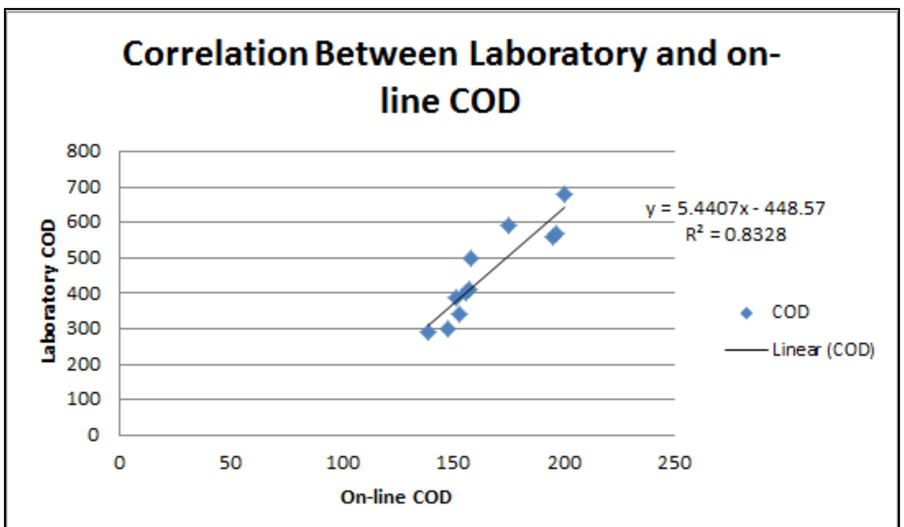
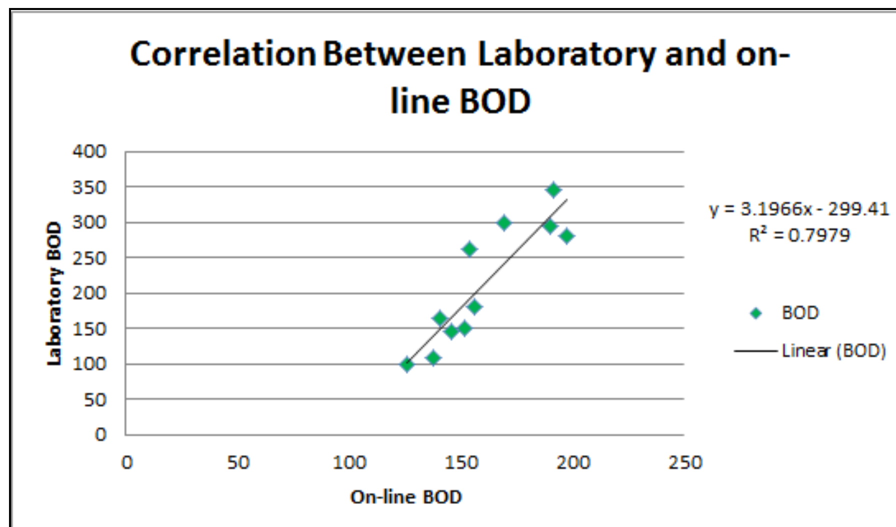
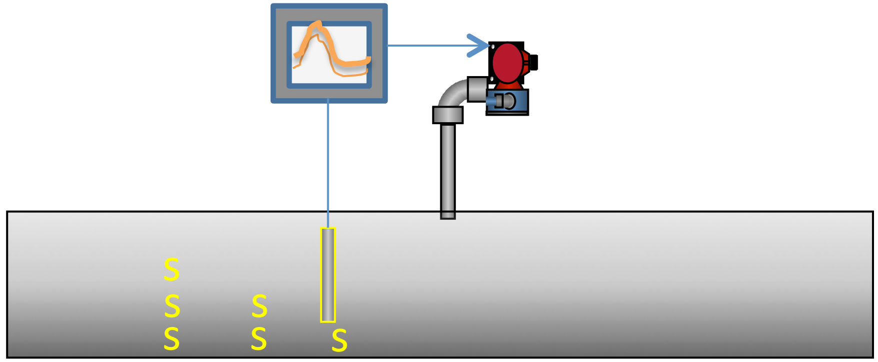
What we measure – BOD and COD











Application Potential

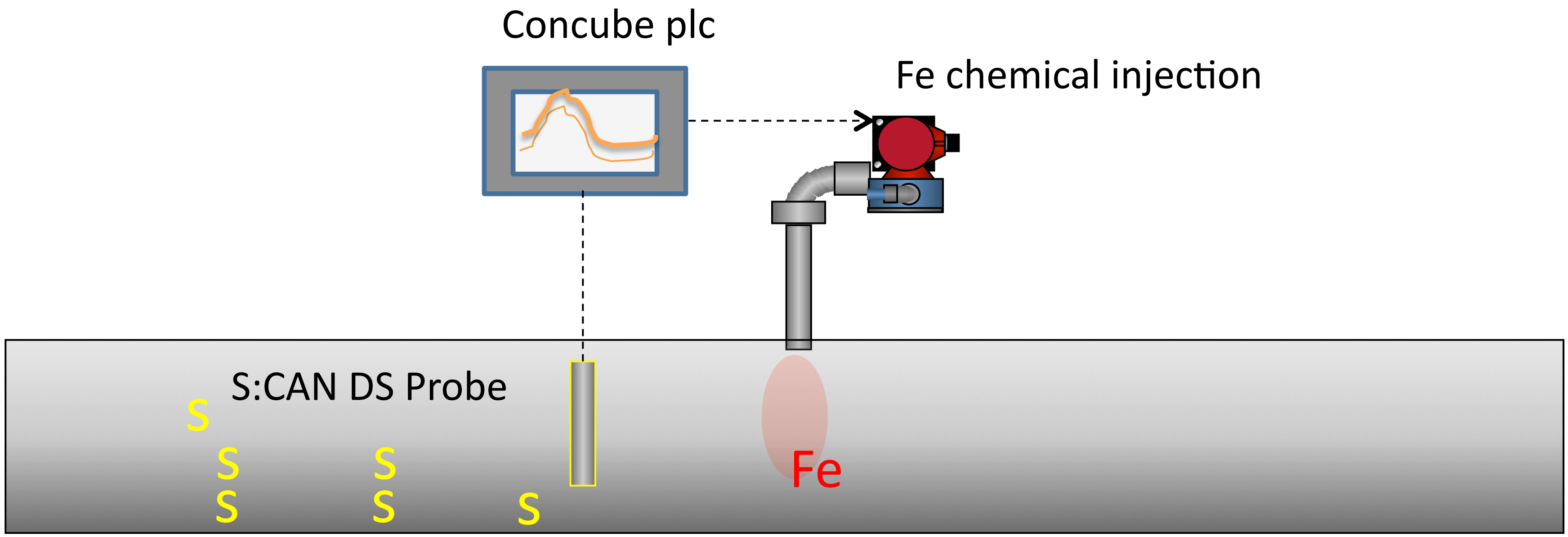
1) DS probe/ Concube Integrated into Odor Control System

2) Illustration of Dosing Mechanics for Mg/L vs Mg/Mg

3) Future

4) What This Means To You

1) DS probe/ Concube Integrated into Odor Control System



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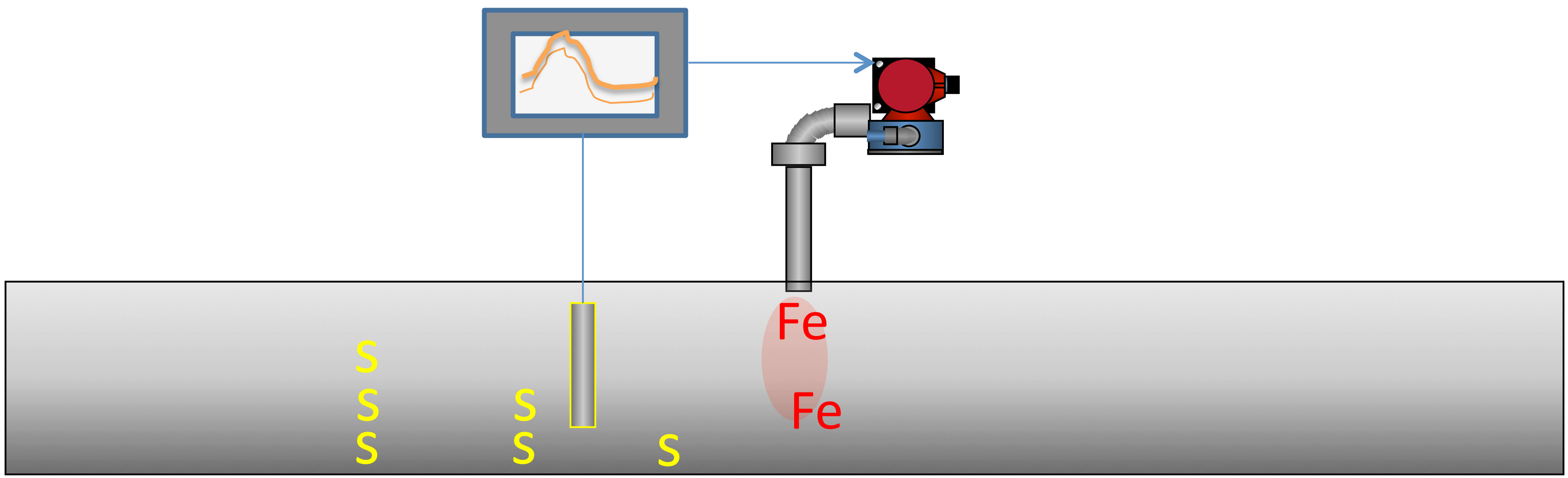

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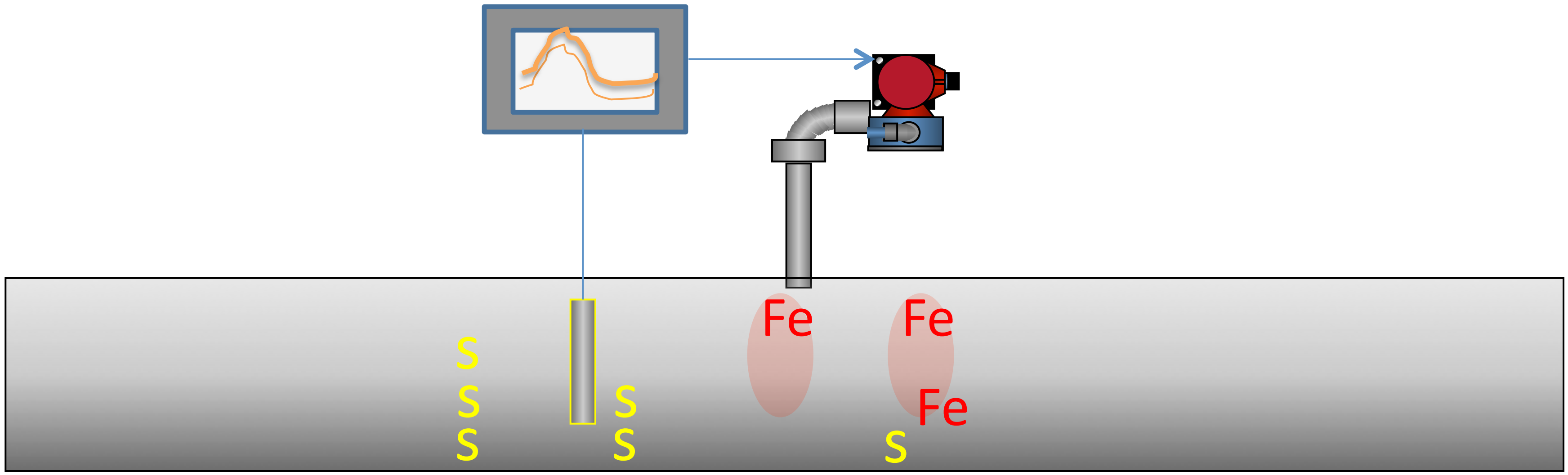

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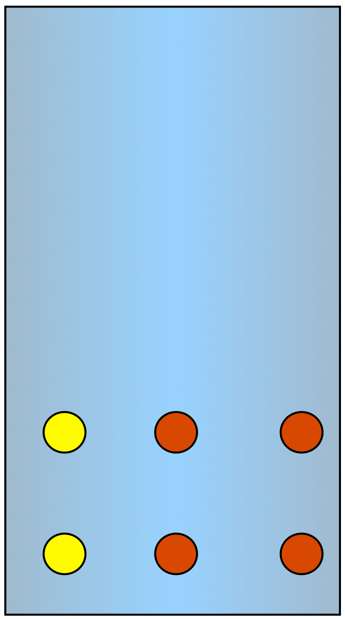
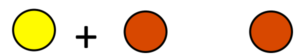
1) Illustration of Dosing Mechanics for Mg/L vs Mg/ Mg



Ideal treatment mass ratio DS-> Fe



= DS target residual

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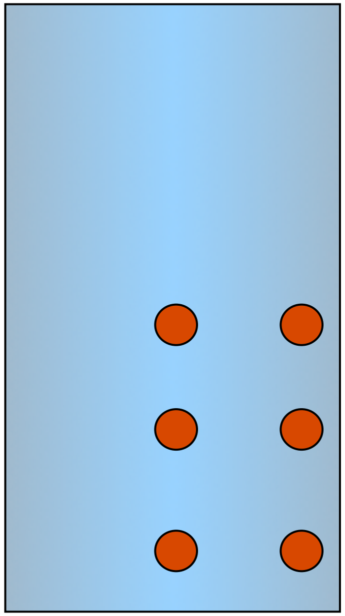
6 mg/L is the field applied dose



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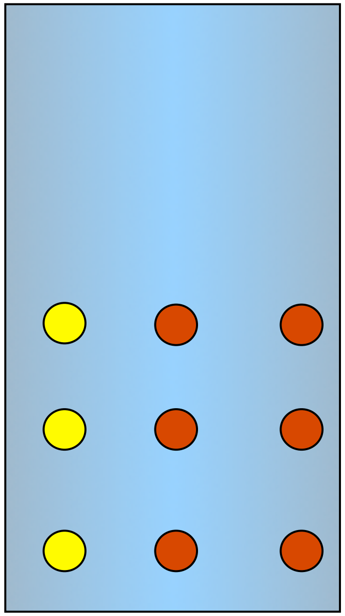

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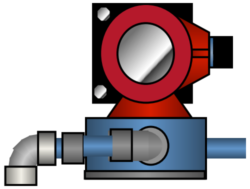

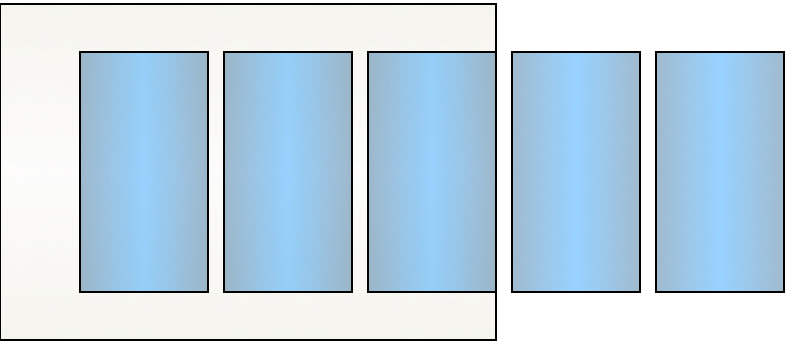

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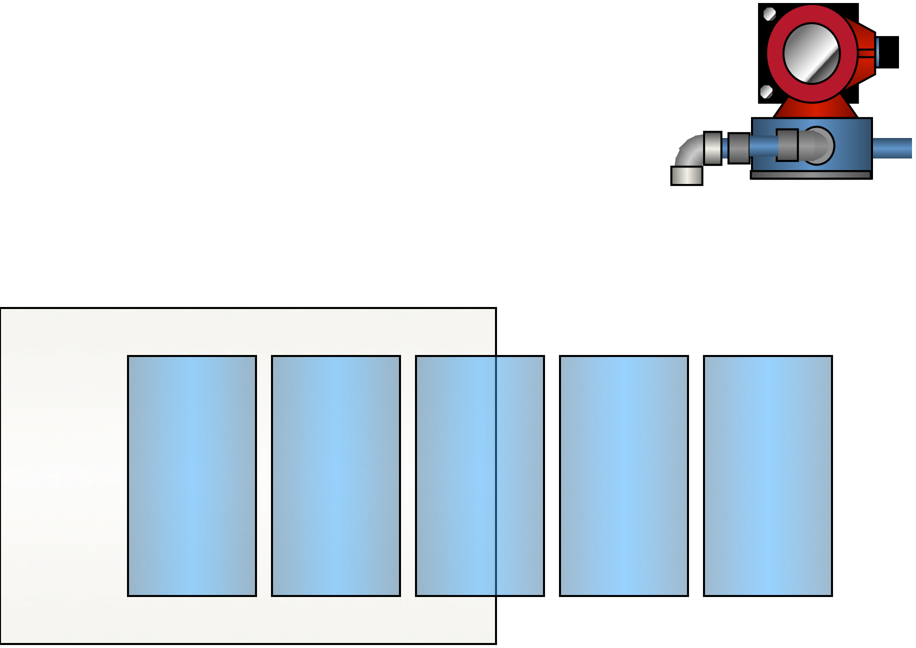

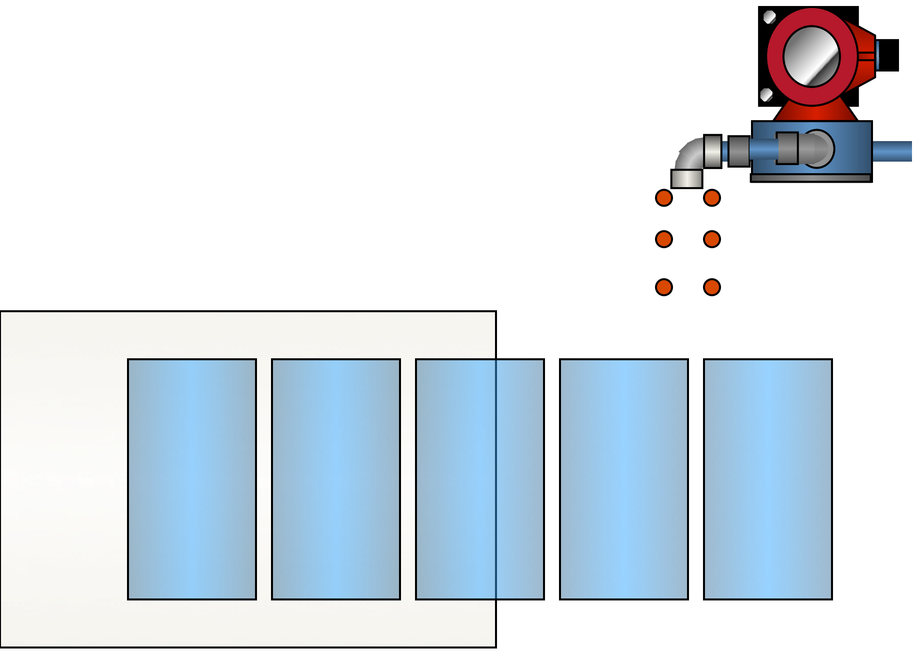

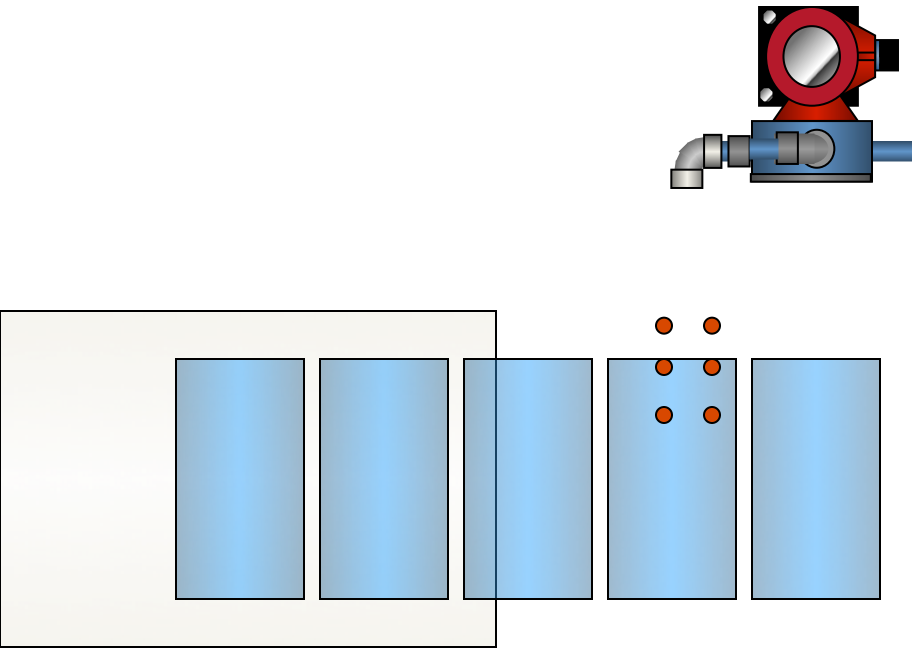

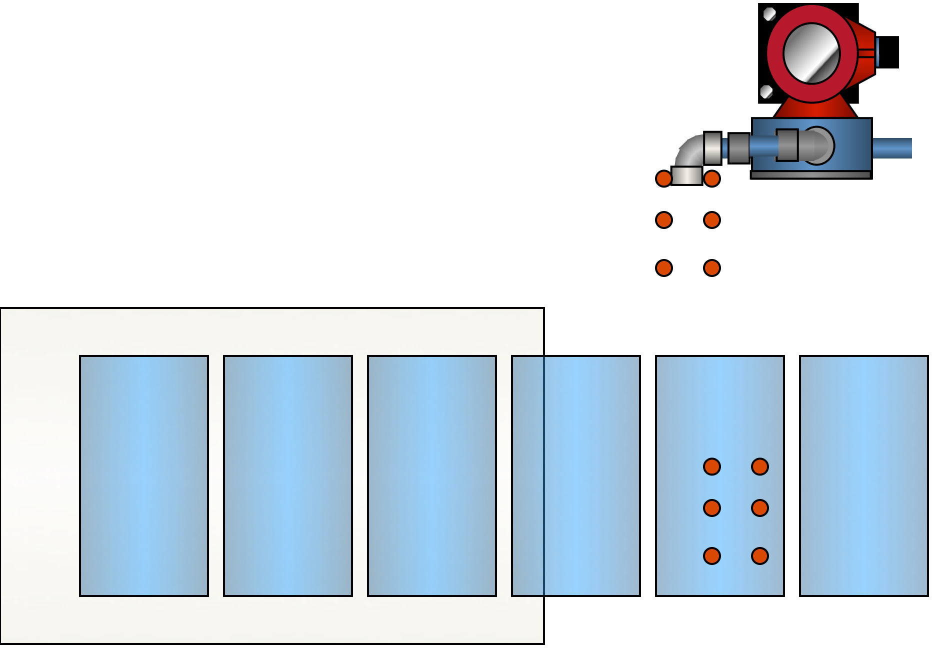

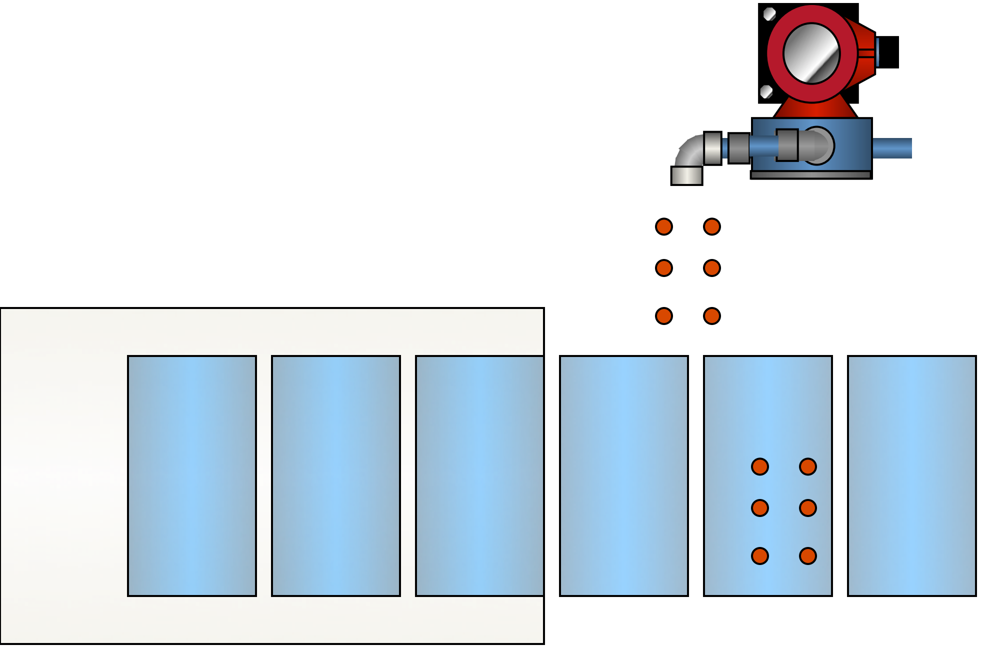

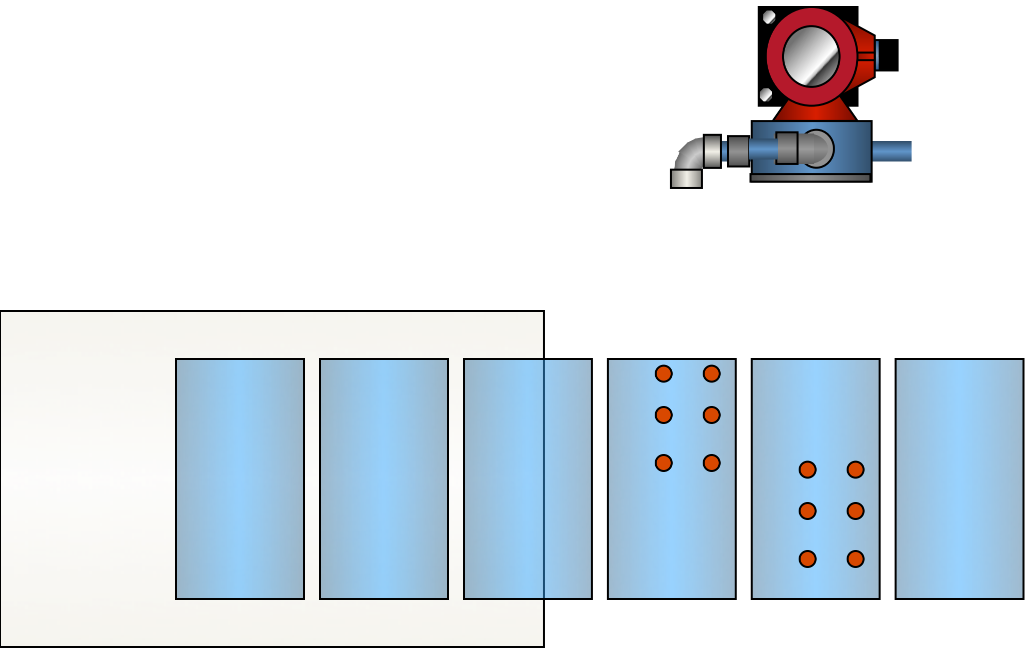

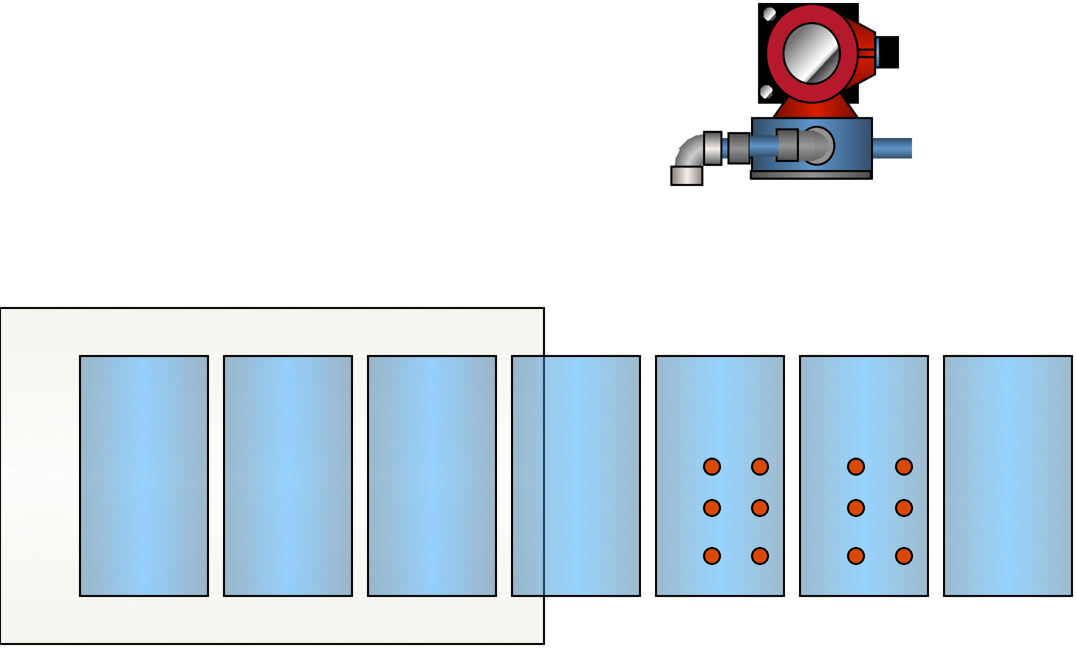

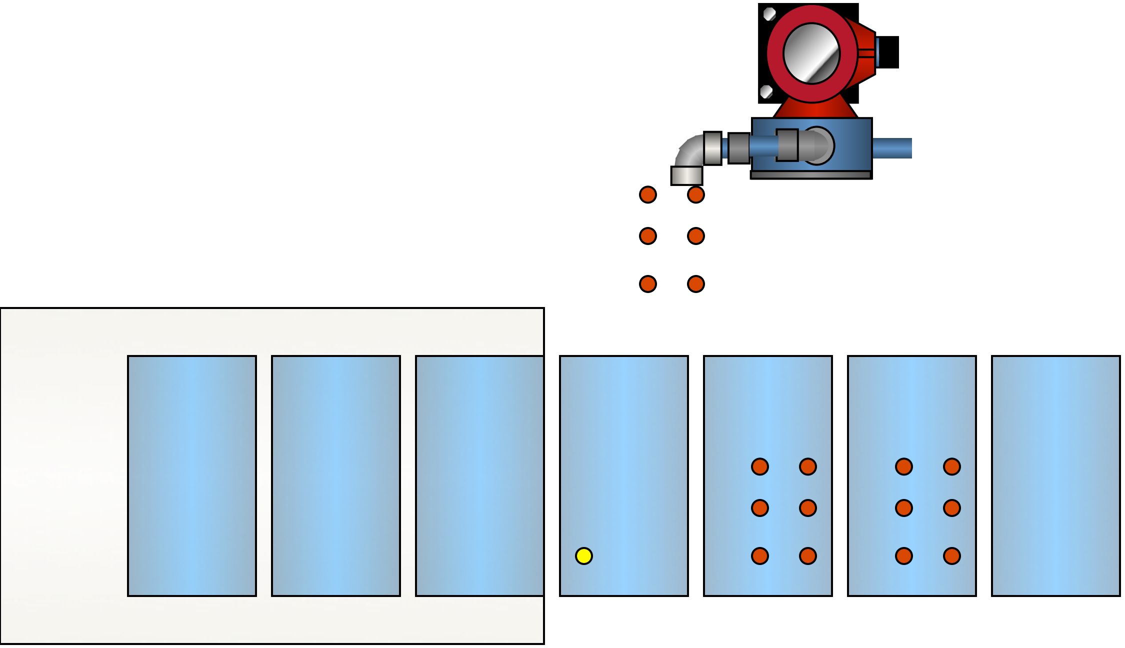

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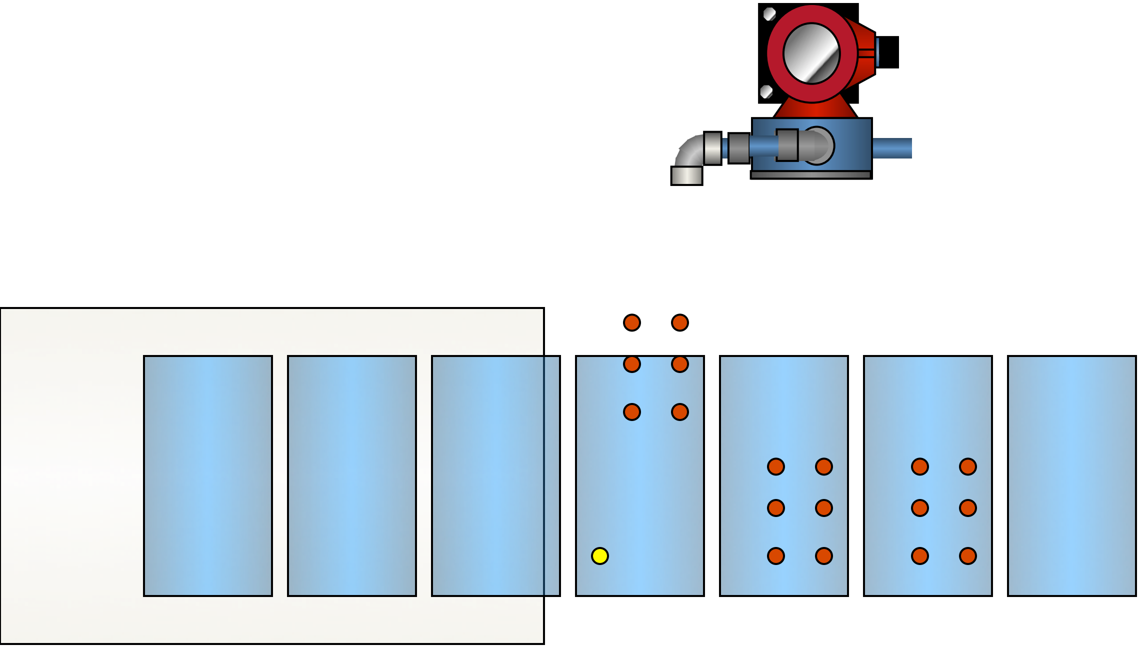

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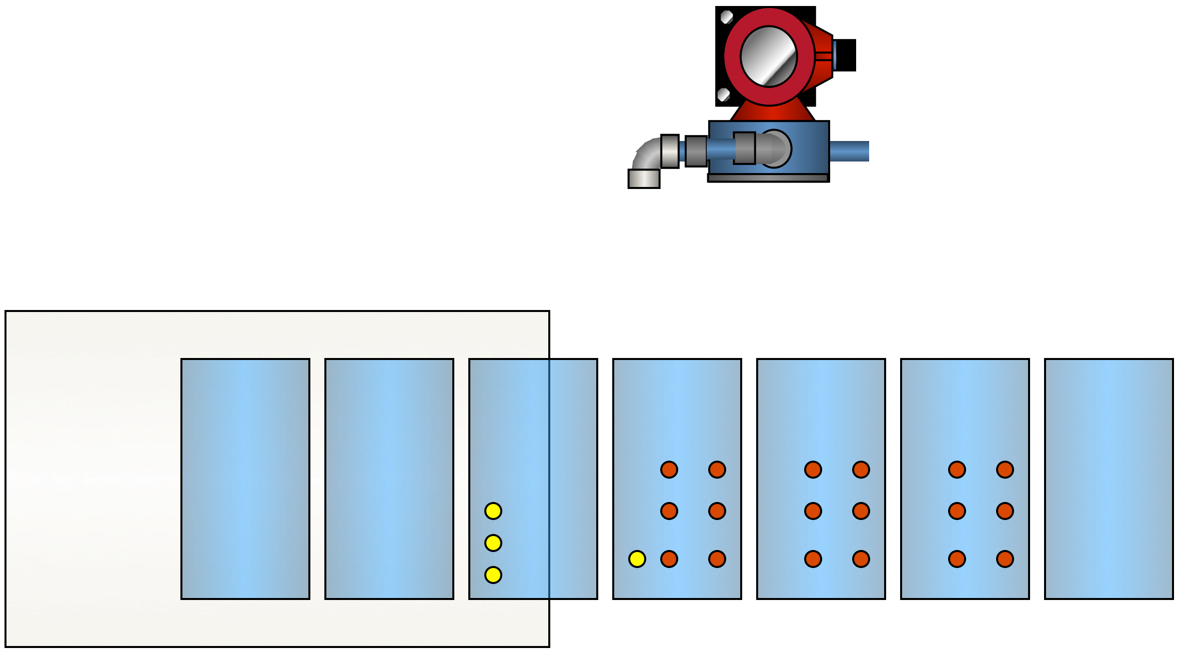

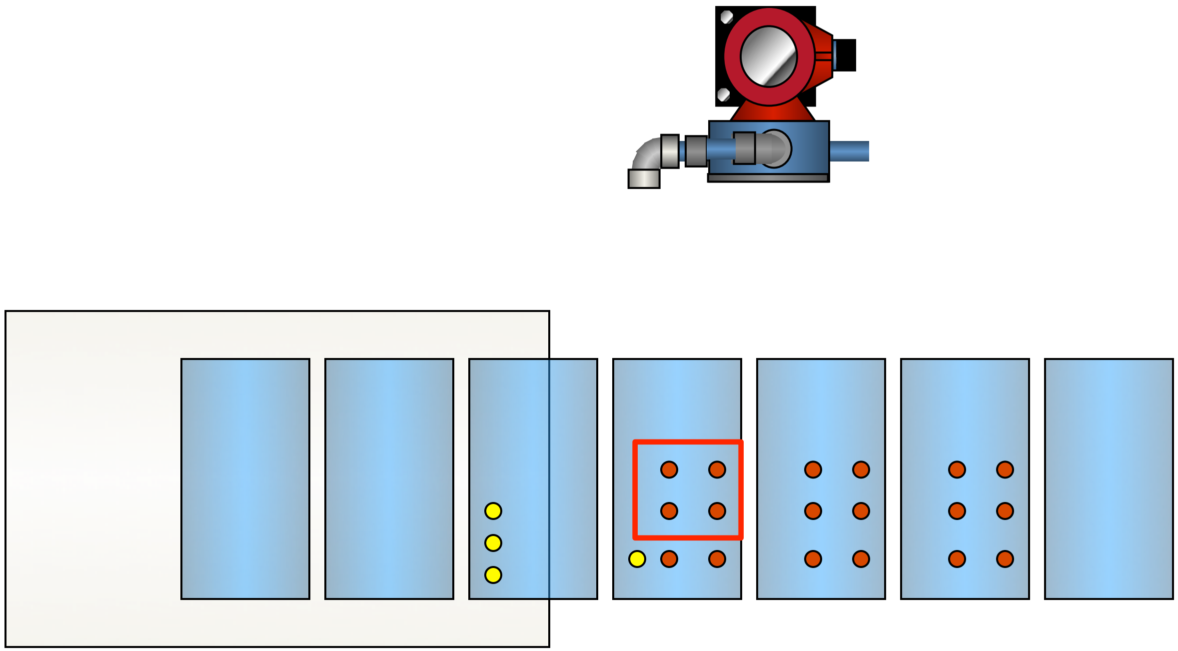

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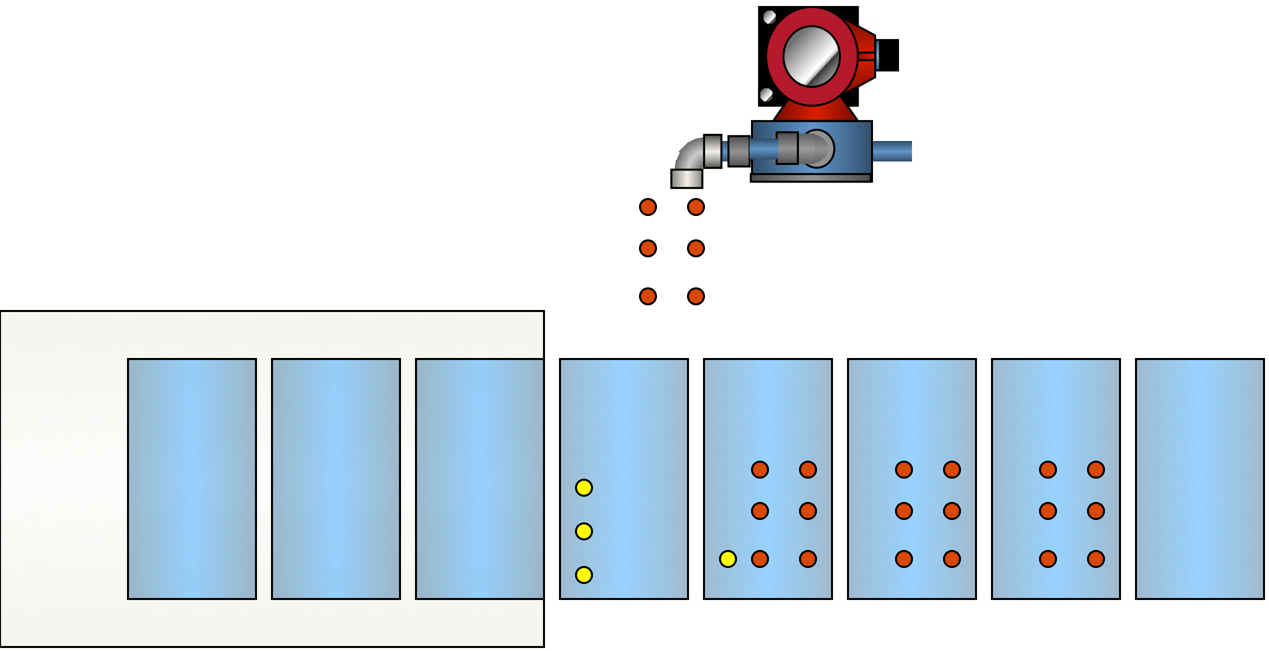

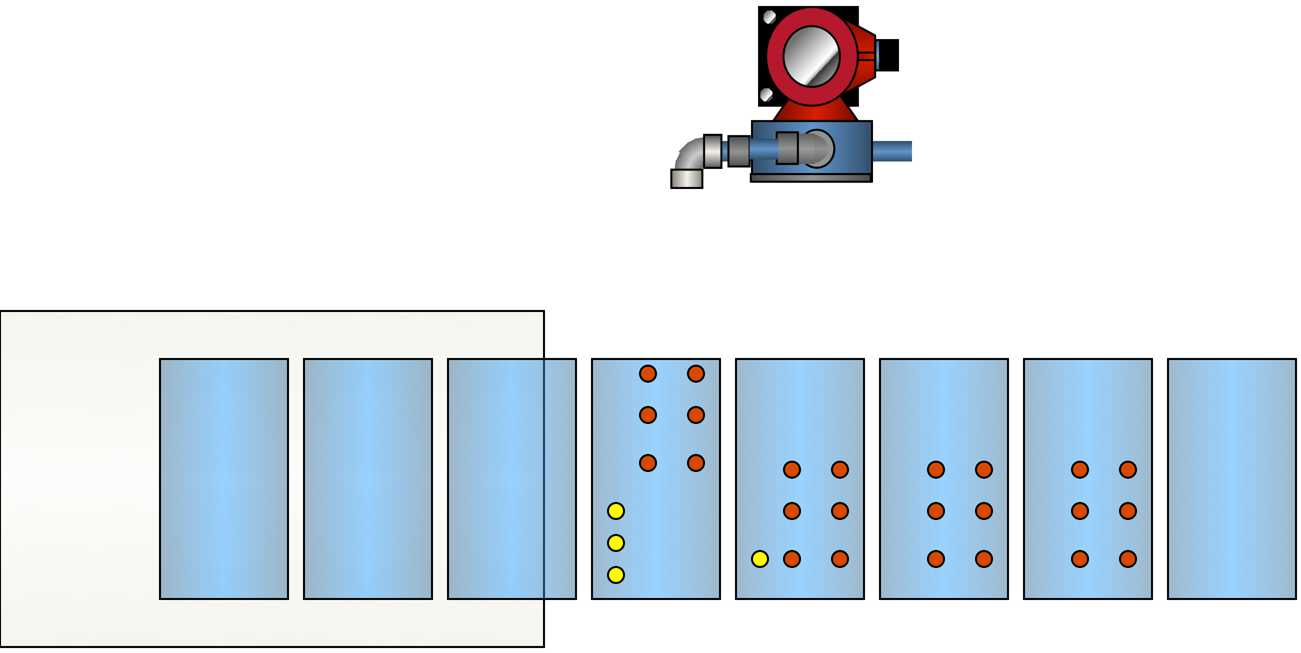

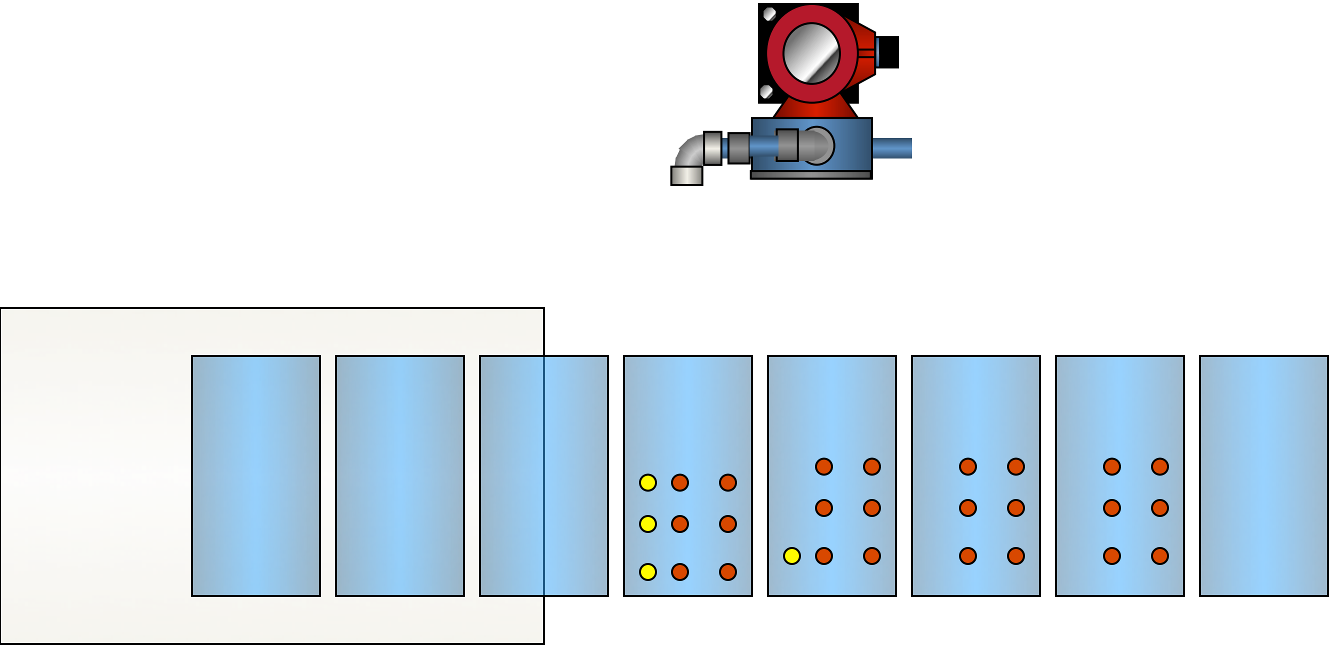

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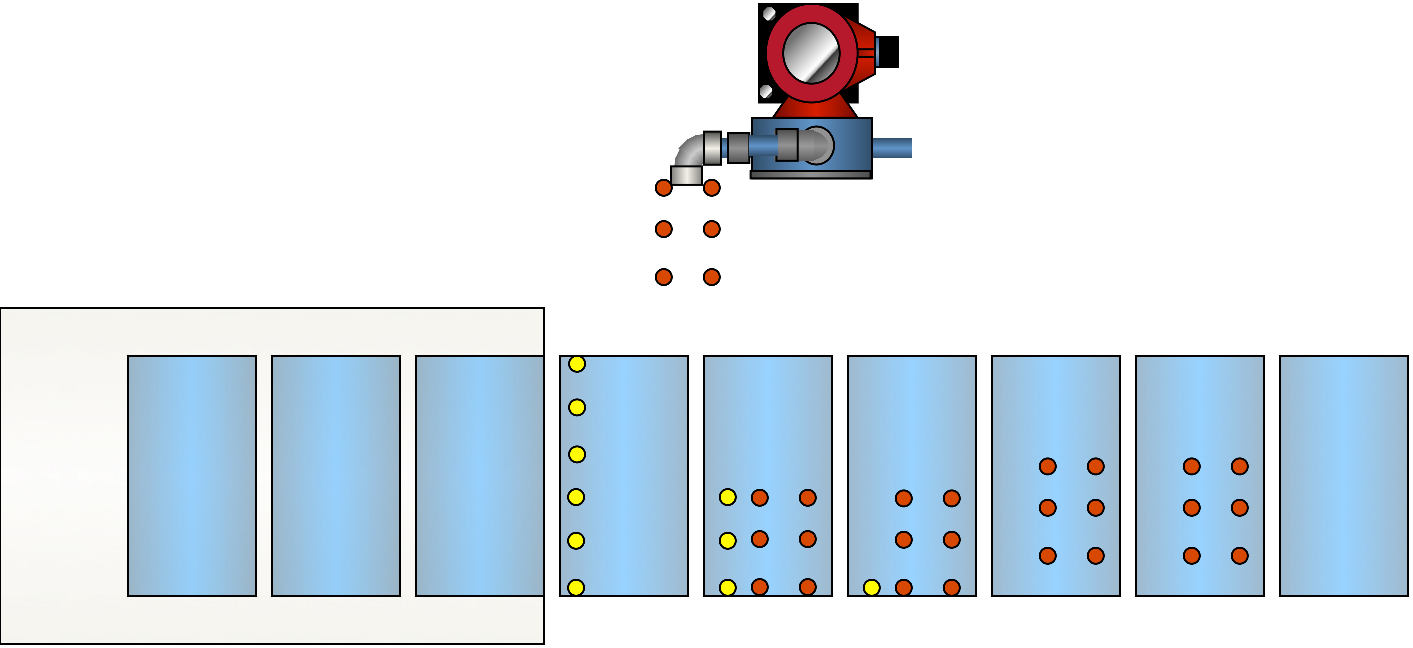

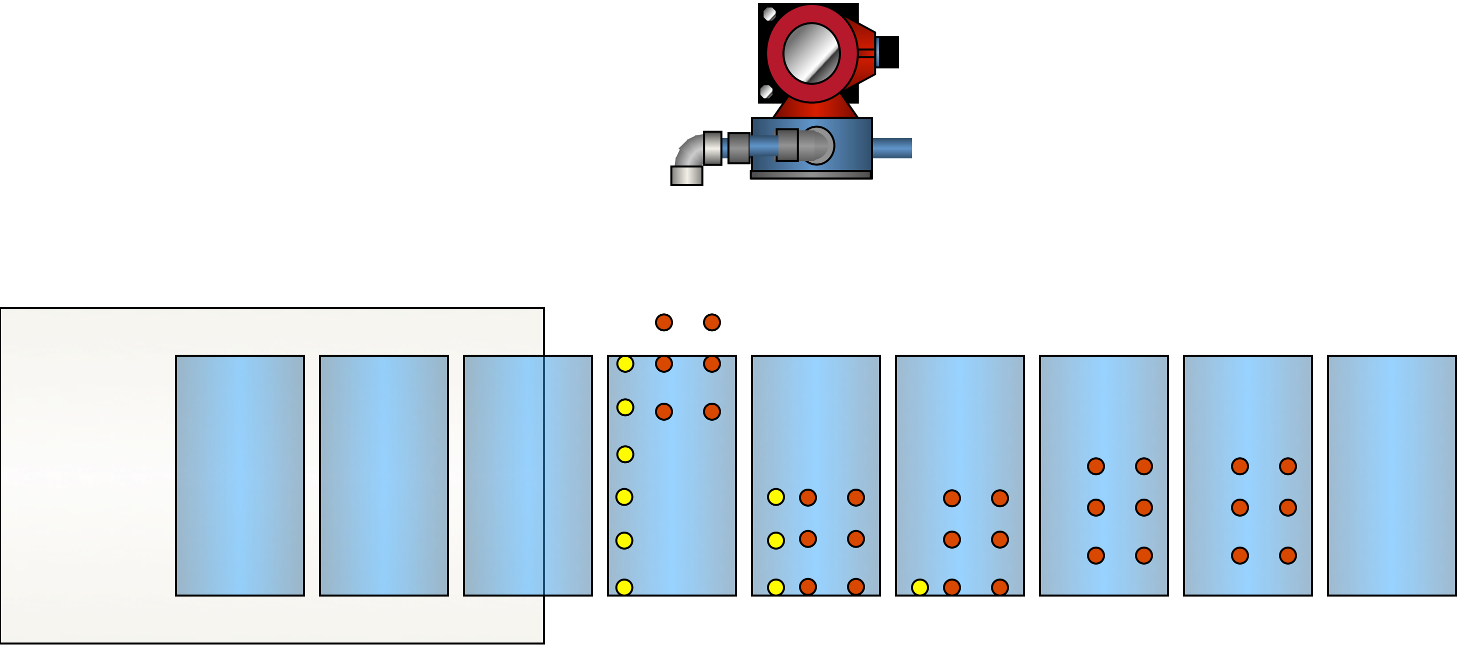

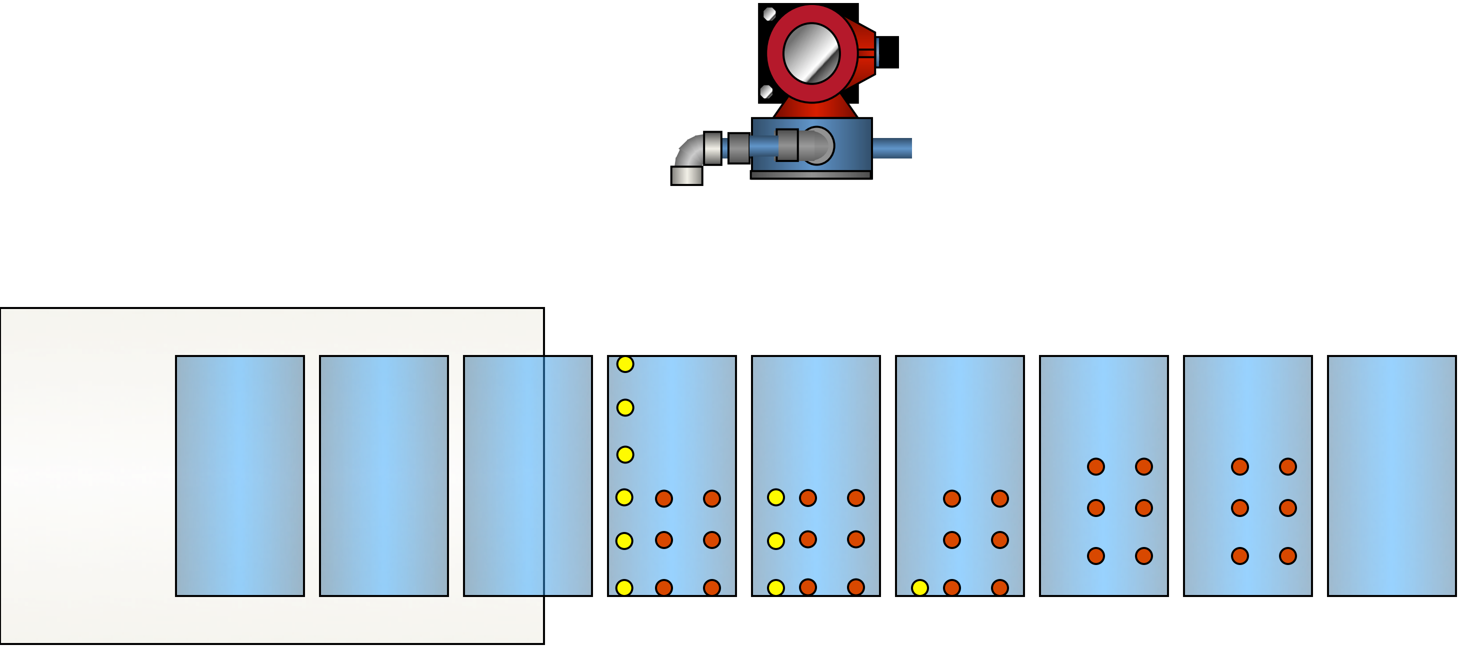

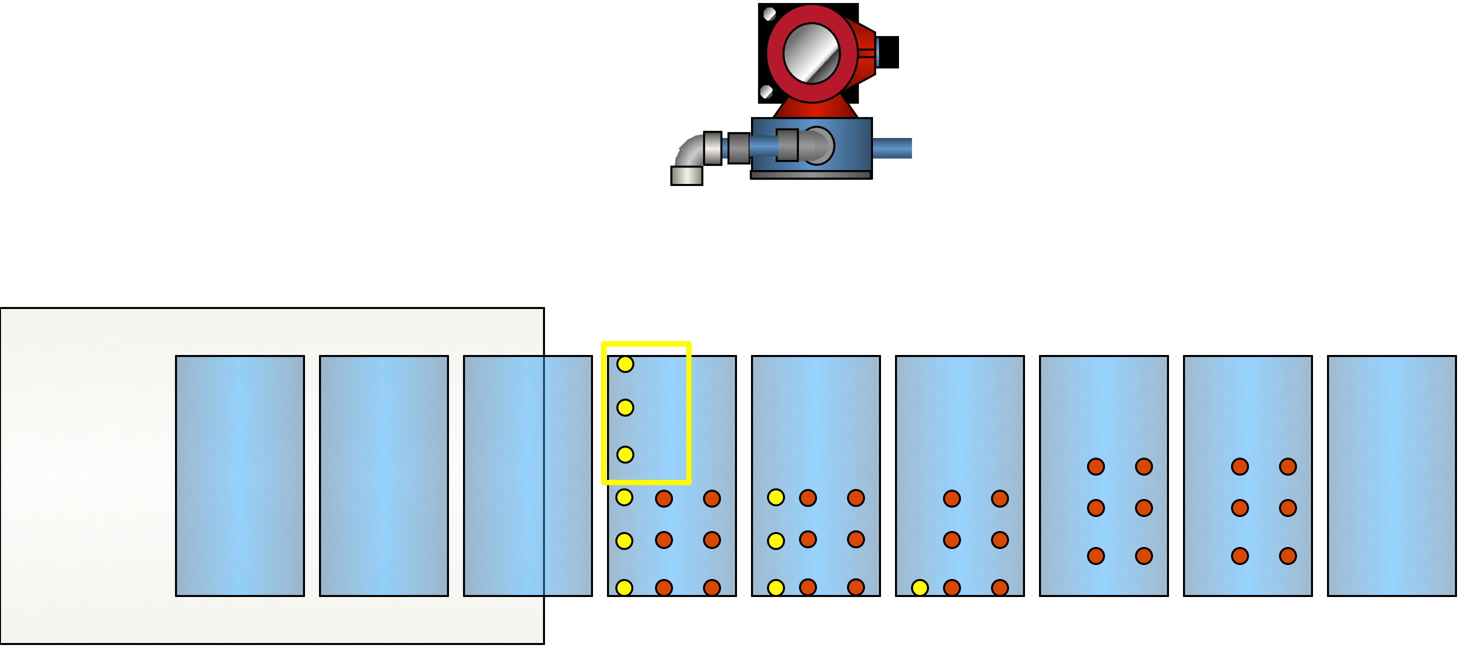

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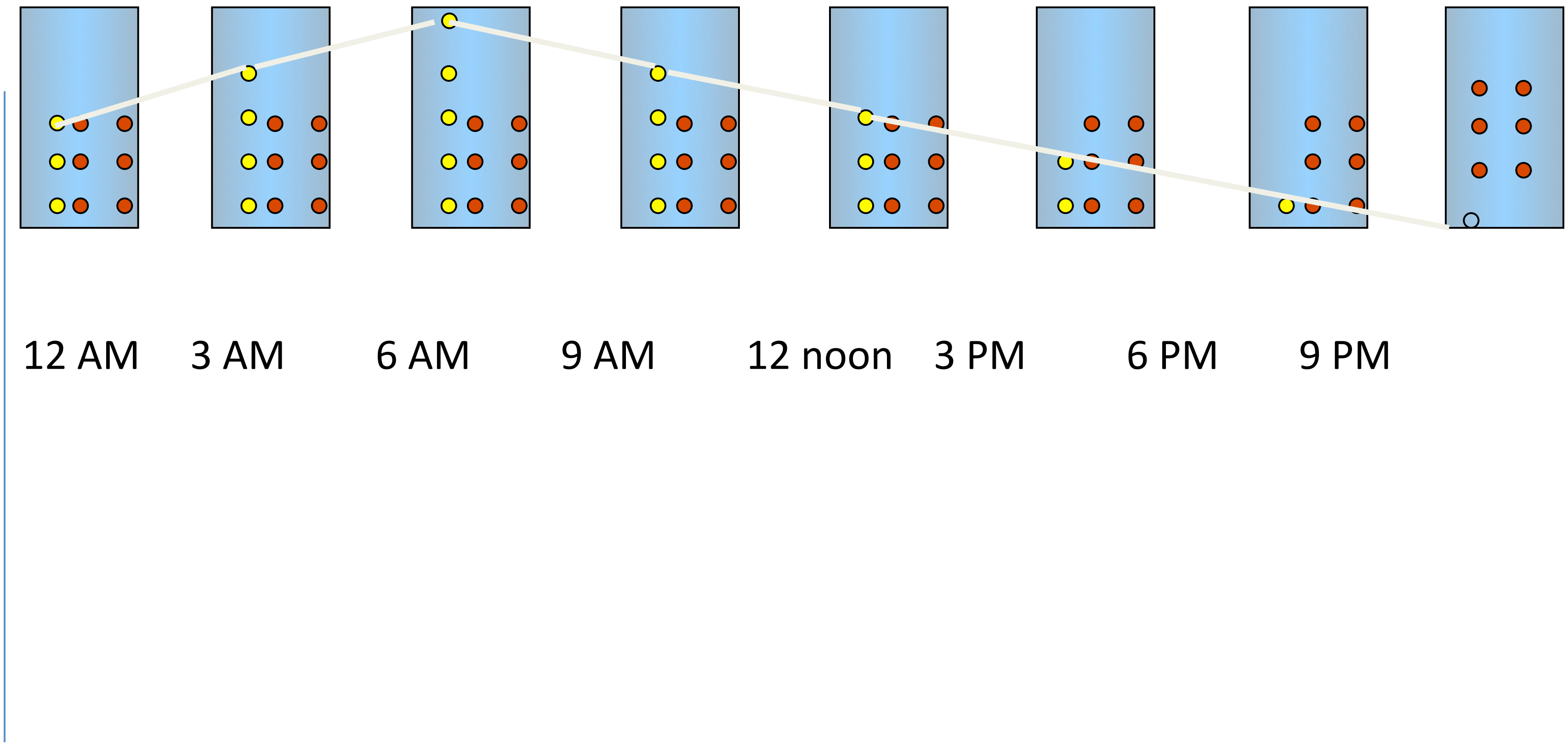

12 AM 3 AM 6 AM 9 AM 12 noon 3 PM 6 PM 9 PM

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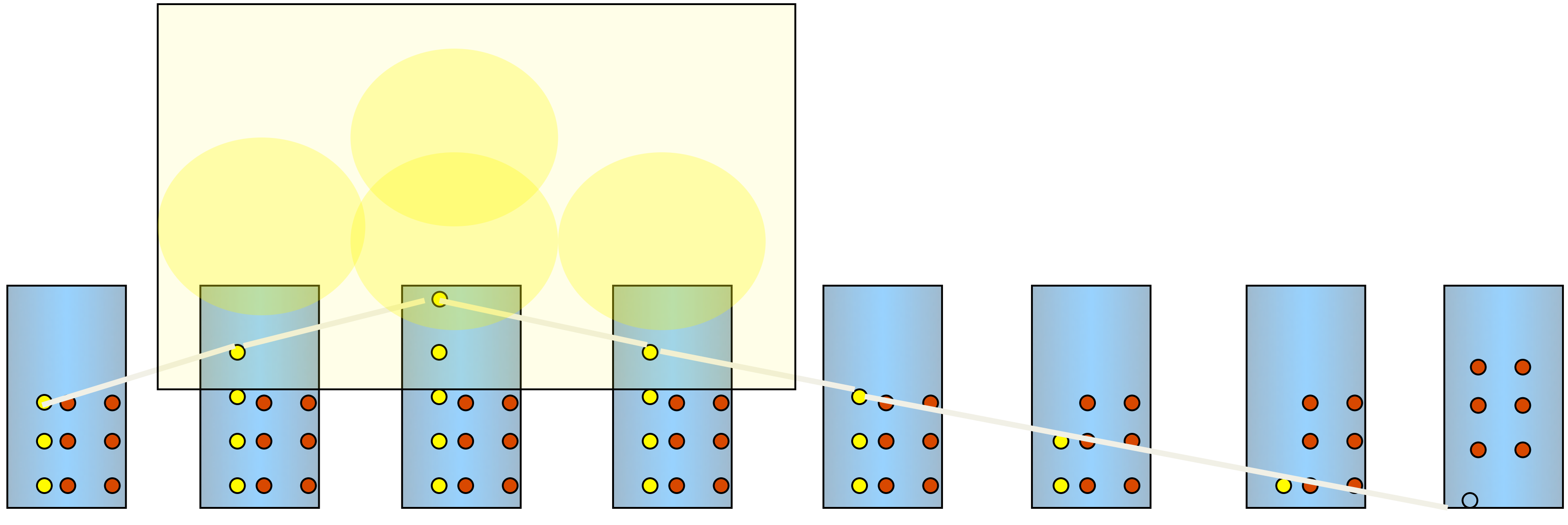

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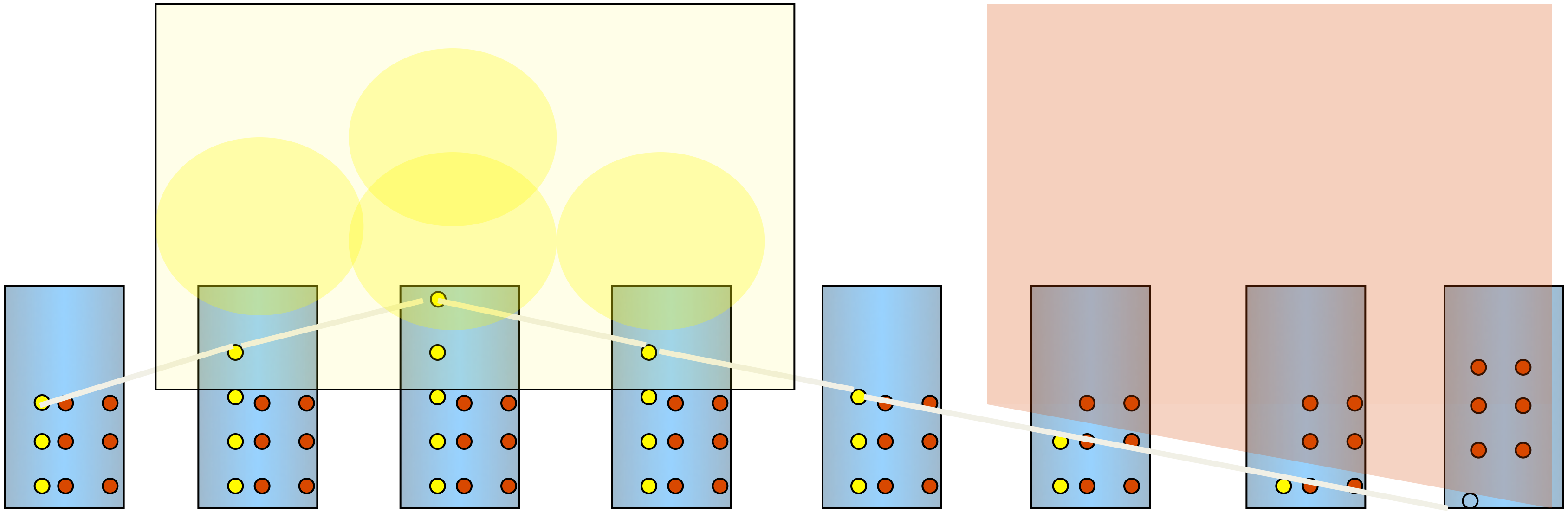

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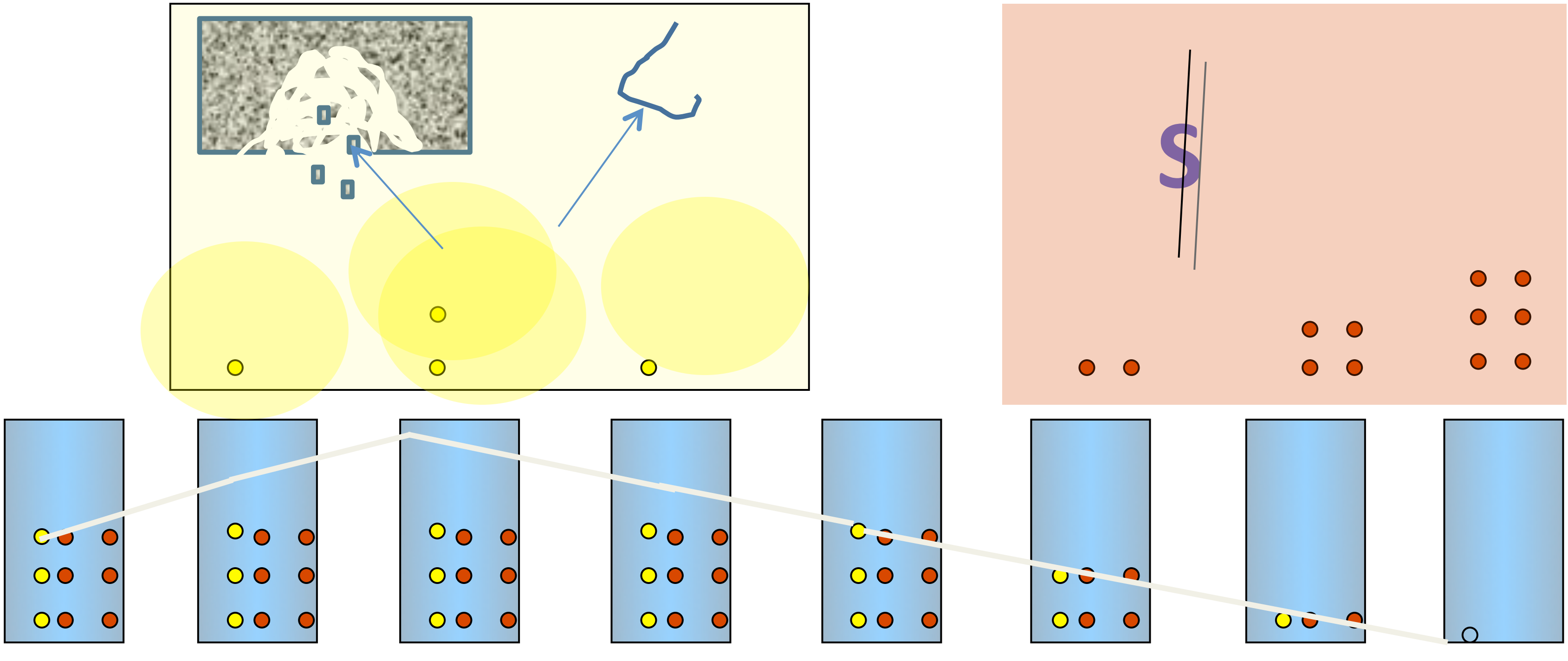

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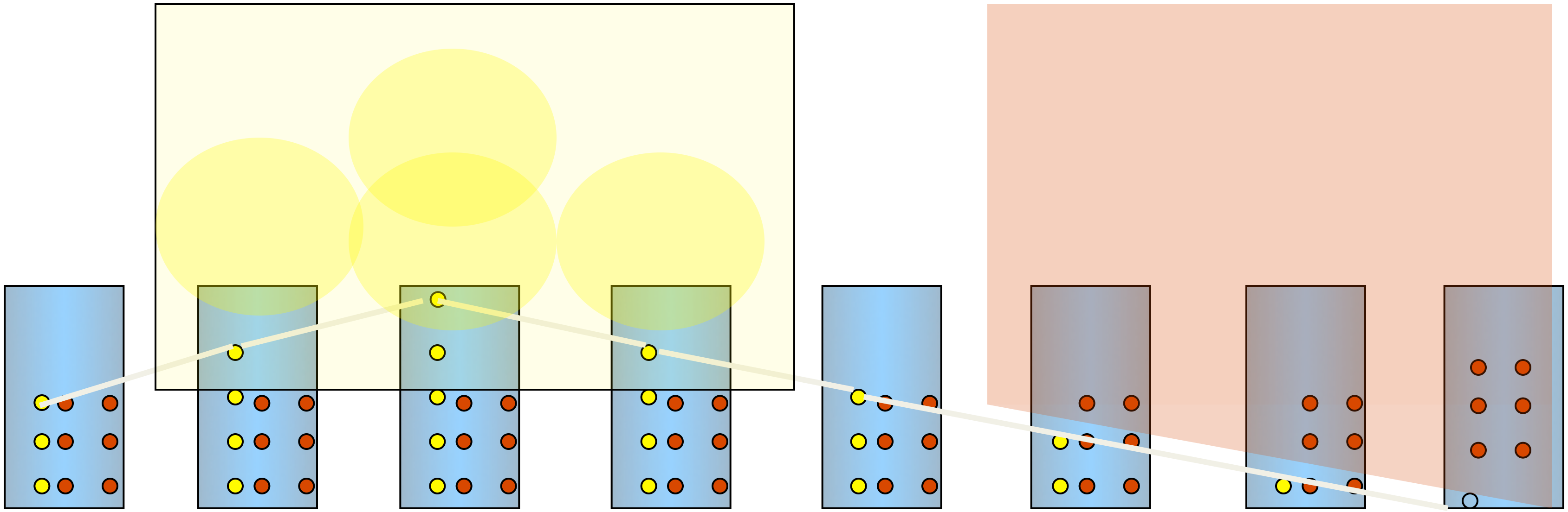

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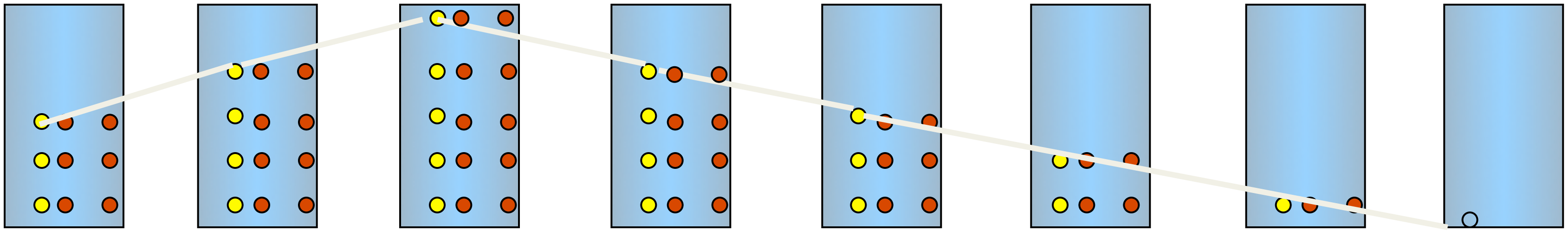

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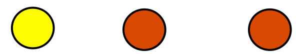
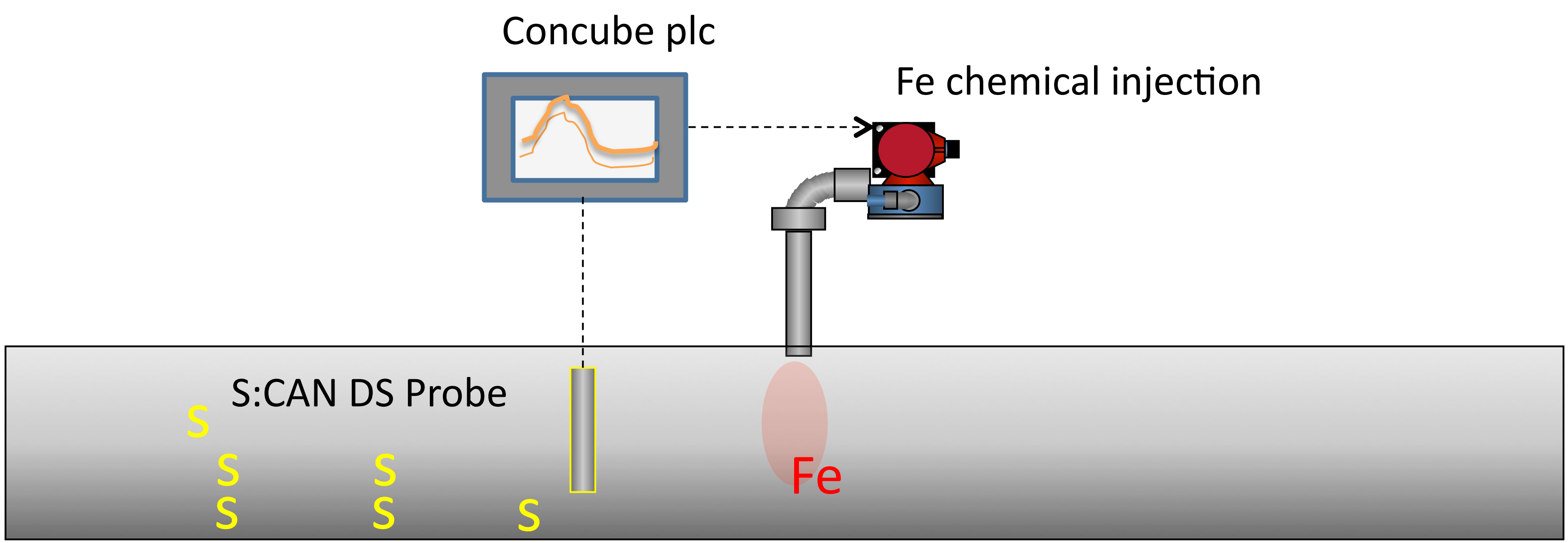
3) Future

3.1 Ideal treatment mass ratio DS-> Fe automated

 = Target Residual DS



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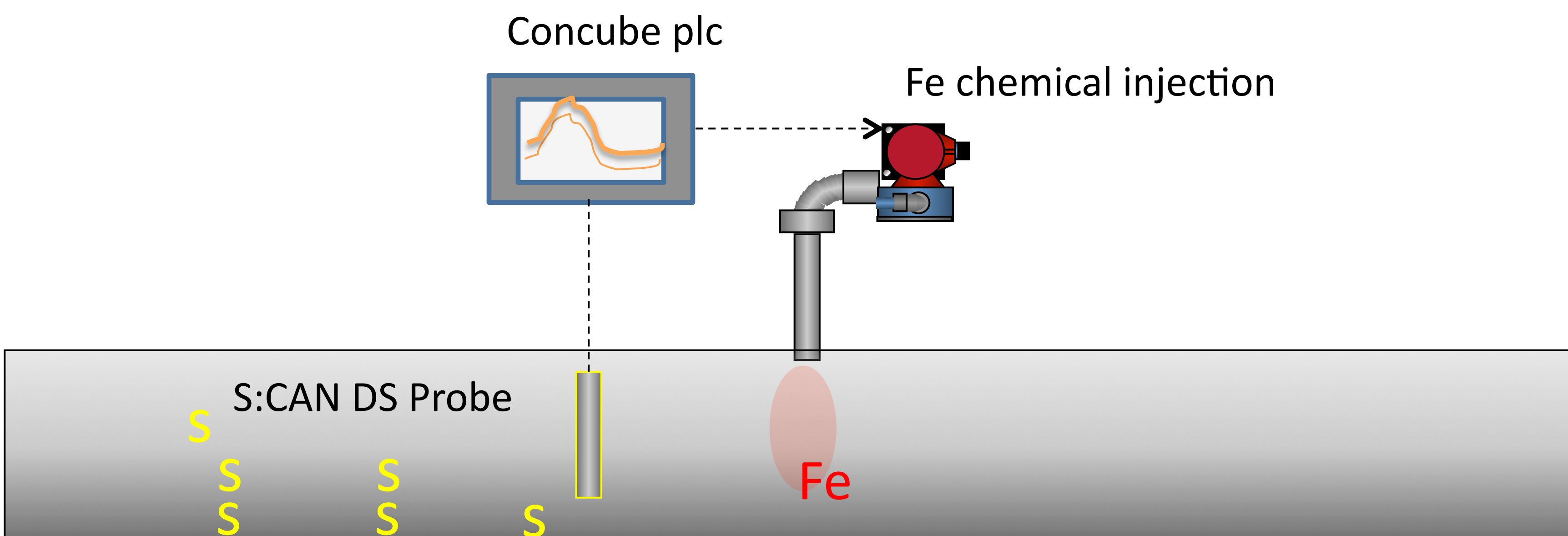
3) Future

3.1 Ideal treatment mass ratio DS-> Fe automated

= Target Residual DS



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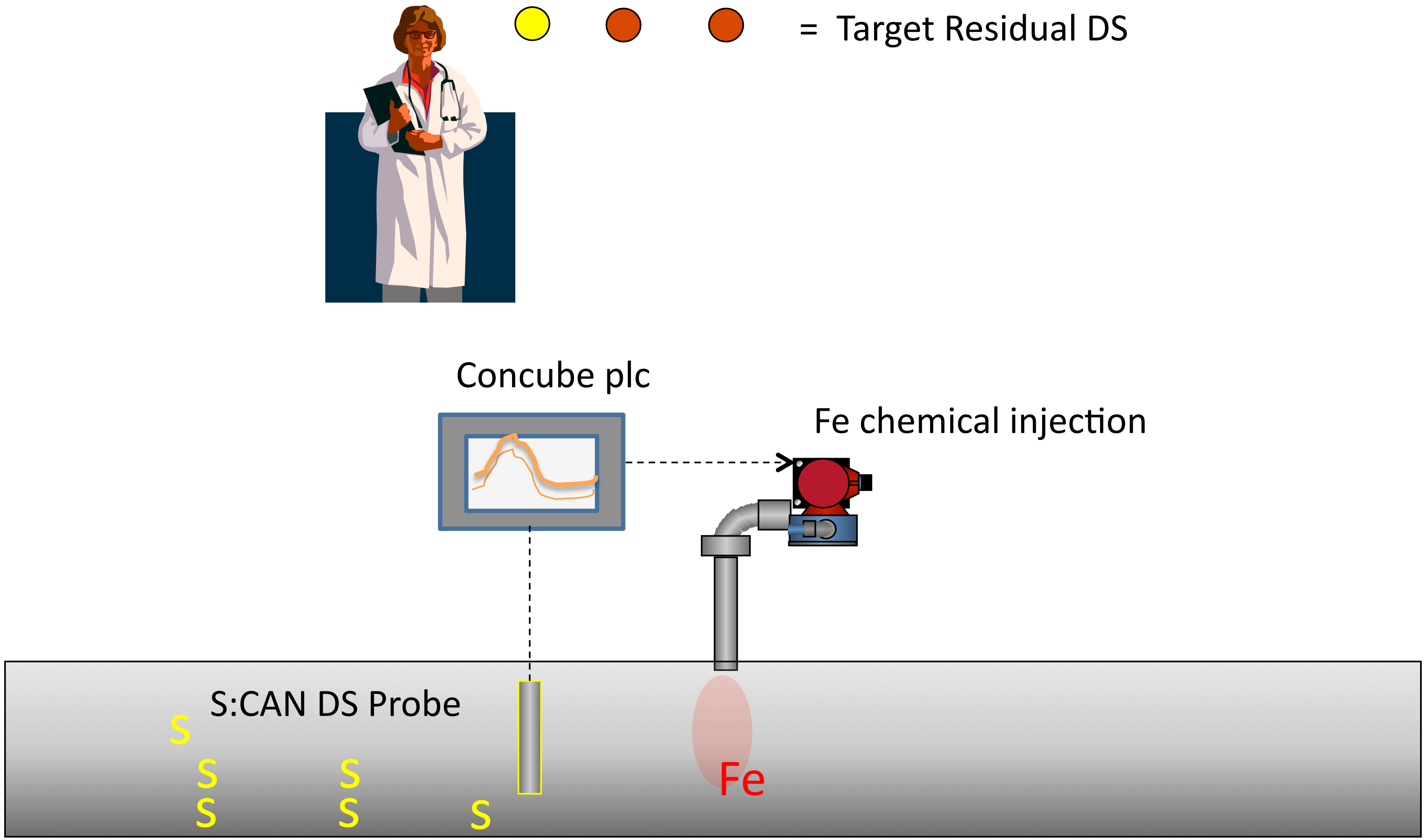
3) Future

3.1 Ideal treatment mass ratio DS-> Fe automated



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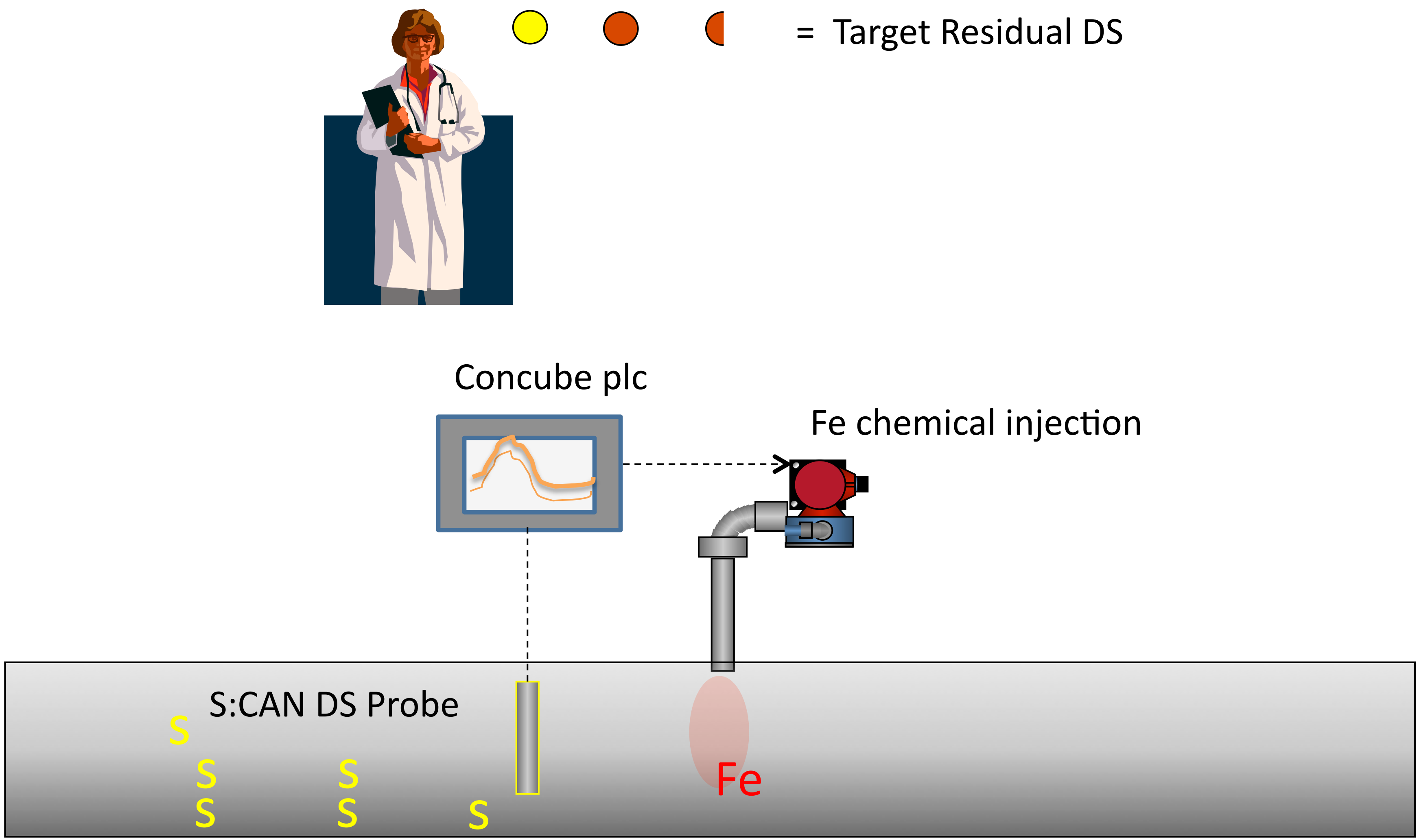
3) Future

3.1 Ideal treatment mass ratio DS-> Fe automated



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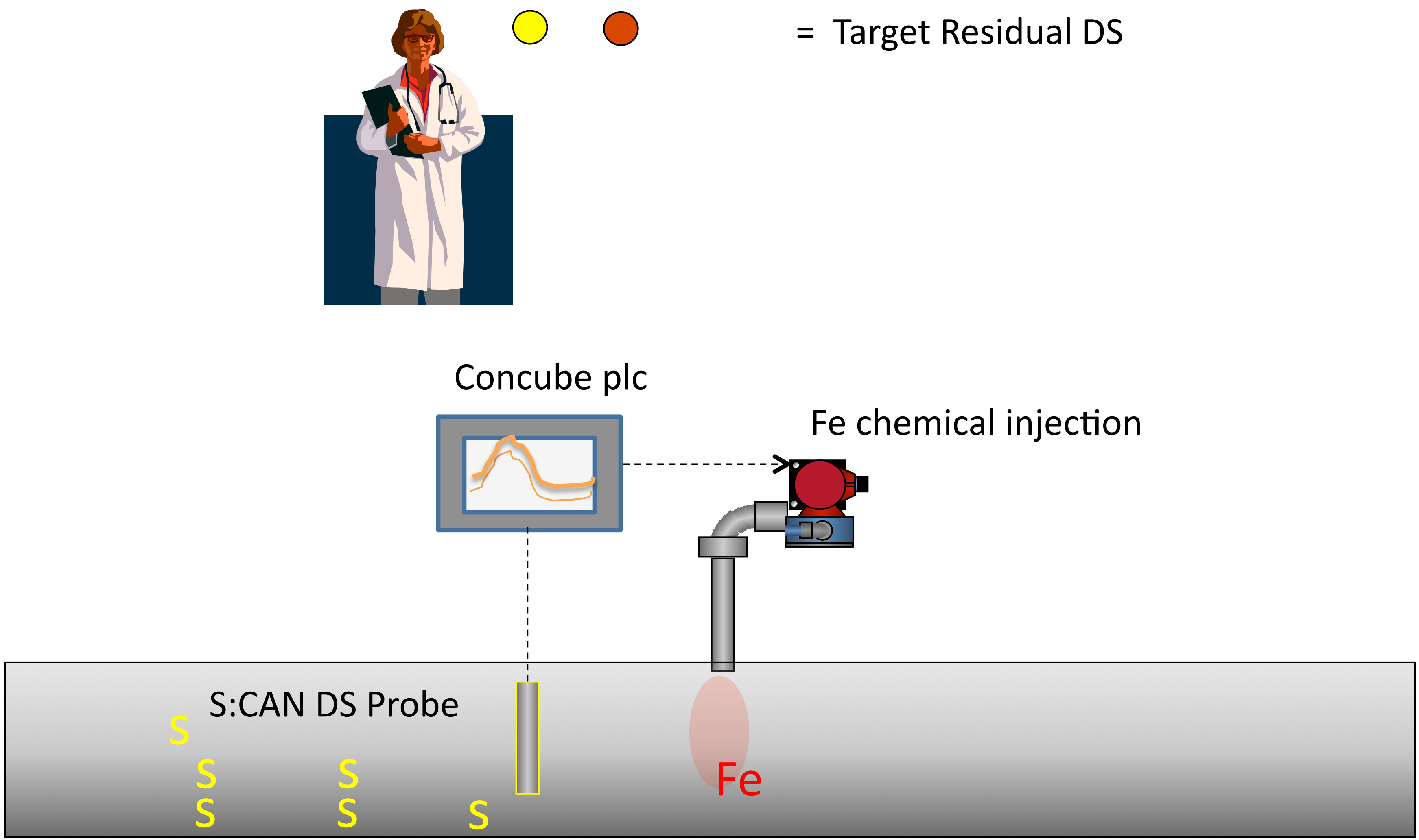
3) Future

3.1 Ideal treatment mass ratio DS-> Fe automated



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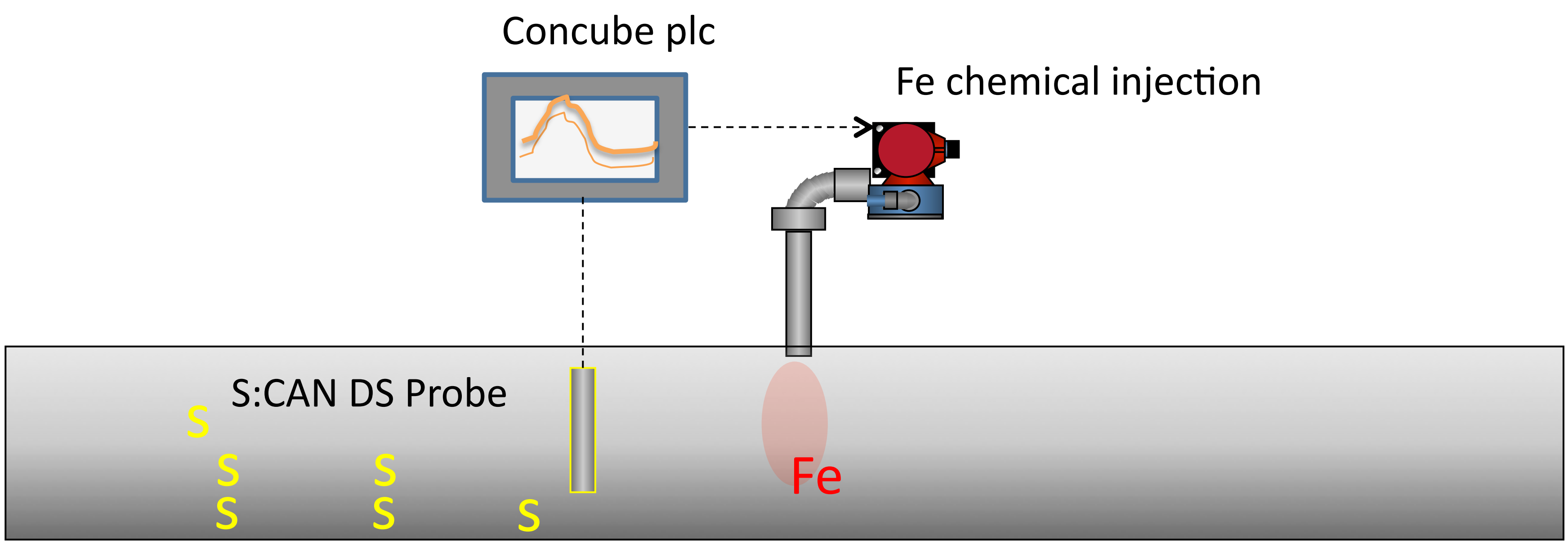
3) Future

3.2 Inclusion of BOD, COD, SS as control points



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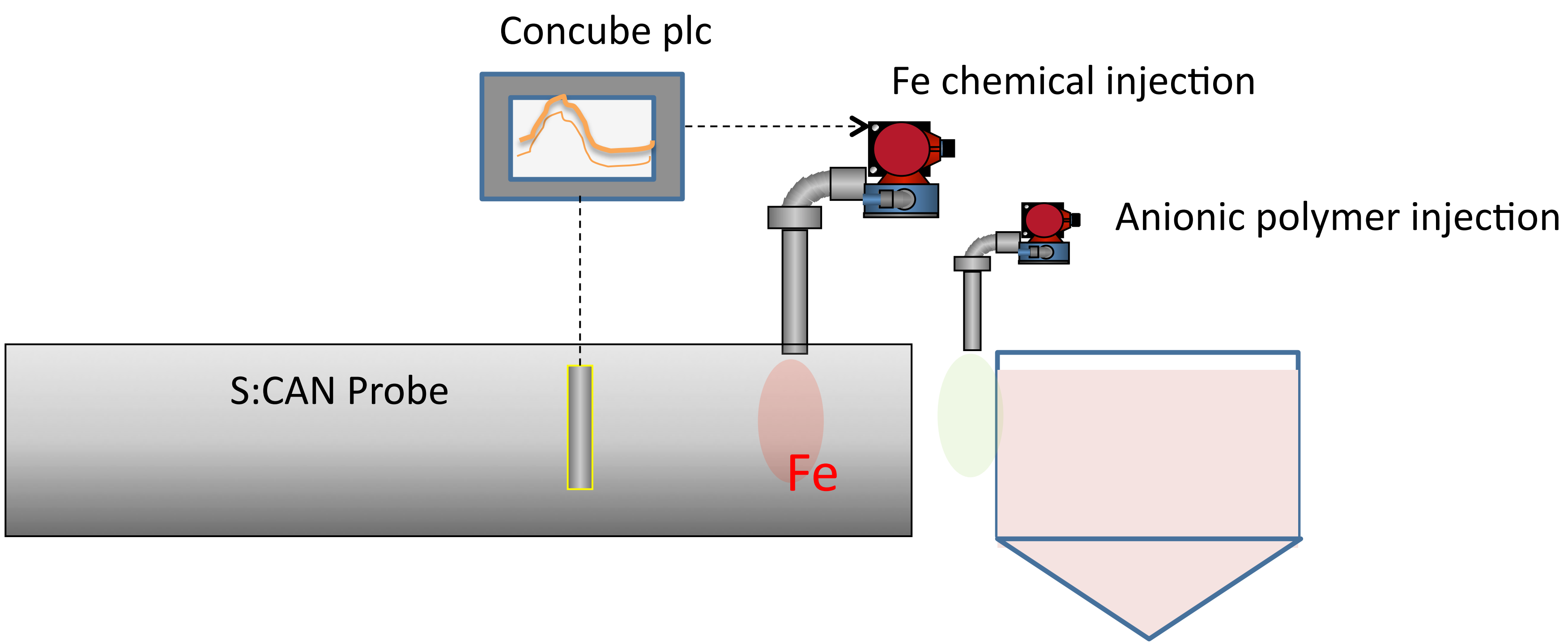
3) Future

3.2 Inclusion of BOD, COD, SS as control points



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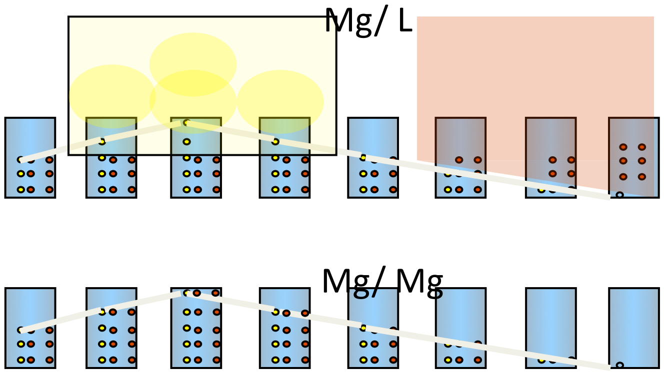
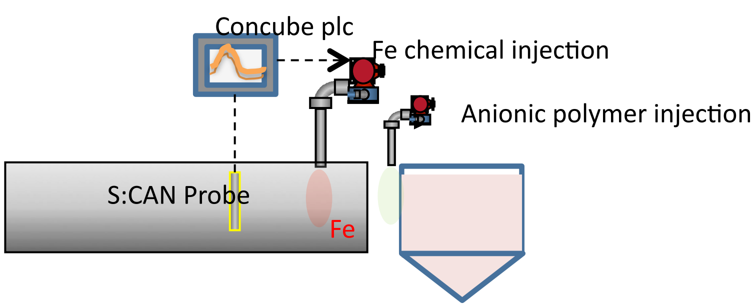
4) What This Means T0 You

4.1 Precision dose applications for odor control
4.2 Most effective chemical application
4.3 Expandable dose application for other process parameters





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Special Thanks!

- **PNCWA**
- **DCM Process Control**
- **Olivier Thomas** (his book UV-Visible Spectrophotometry of Water and Wastewater)
- **s::can Messtecknik GmbH**
- **Greg Land and Kemira**