Hach's Iron Monitoring Technologies

Best Practices

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EPRI Filming Amine Workshop

Charlotte, NC

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In ultrapure water your goal is to measure at parts per billion concentration.

Have you ever really thought what a part per billion means in water analysis?

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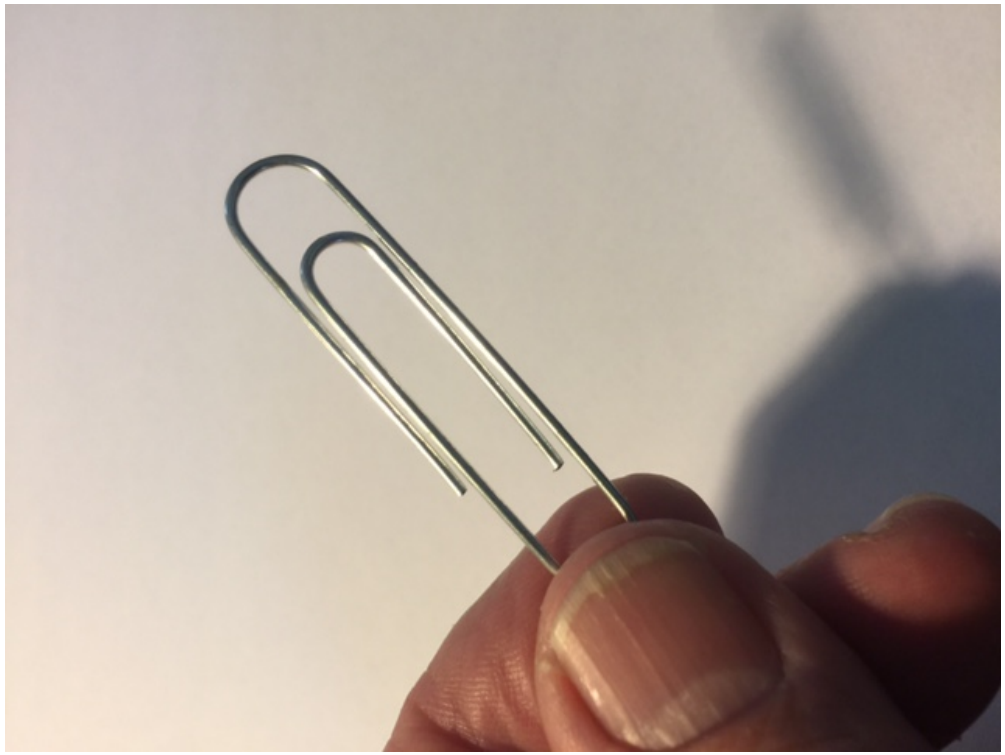
This paper clip weighs about 1 gram



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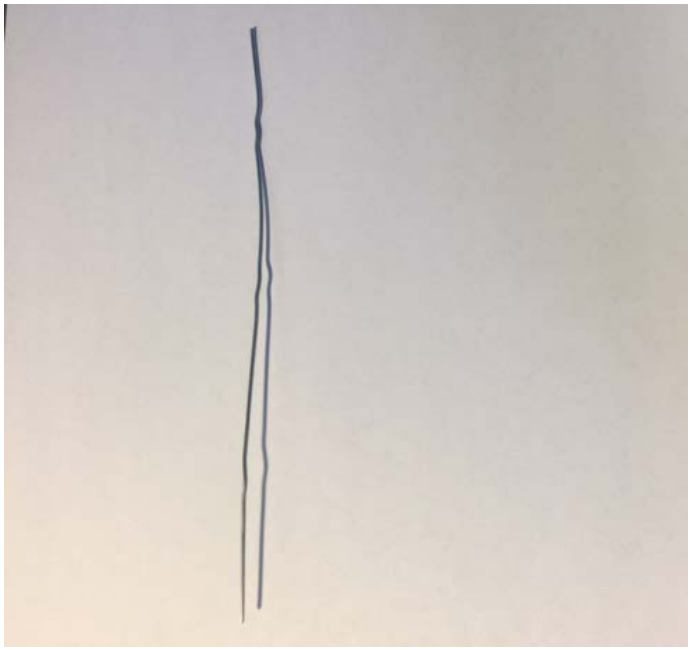
- Unfolded it's length is 6.5 inches or 165 mm
- Now let's cut the clip into 1000 separate pieces ….. Each piece is 0.165 mm in length and would weigh approximately 1 mg. (Human hair is about 0.05 mm in thickness.



- Dissolve one of those pieces in 1 liter of water and you would have 1 mg/L or 1 ppm.
- To get to 1 µg/L (ppb) one would then have to dilute the above 1 mg/L solution by 1000.
- ***In other words 1 ppb would be 1 millionth of the paper clip in 1 liter of water.***

Sample Collection

The sample is usually the greatest limiting factor in obtaining a true or representative result.

WHETHER GRAB OR CONTINUOUS, THE ANALYSIS IS ONLY AS GOOD AS THE SAMPLE

EPRI Target for Total Iron

The lower level target is 2.0 µg/L (ppb) of total iron

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Hach has developed technologies to improve both lab and continuous monitoring of ultra-low iron levels in the steam cycle.

Grab sample lab method for total iron

- *Quantitative to < 1.0 ppb*
- *Results in < 1 hour*
- *Utilizes laboratory spectrophotometer*

On-line method with laser nephelometer for suspended iron

- *Surrogate*

Correlate lab method to on-line

- *Quantitative but correlation is site specific*

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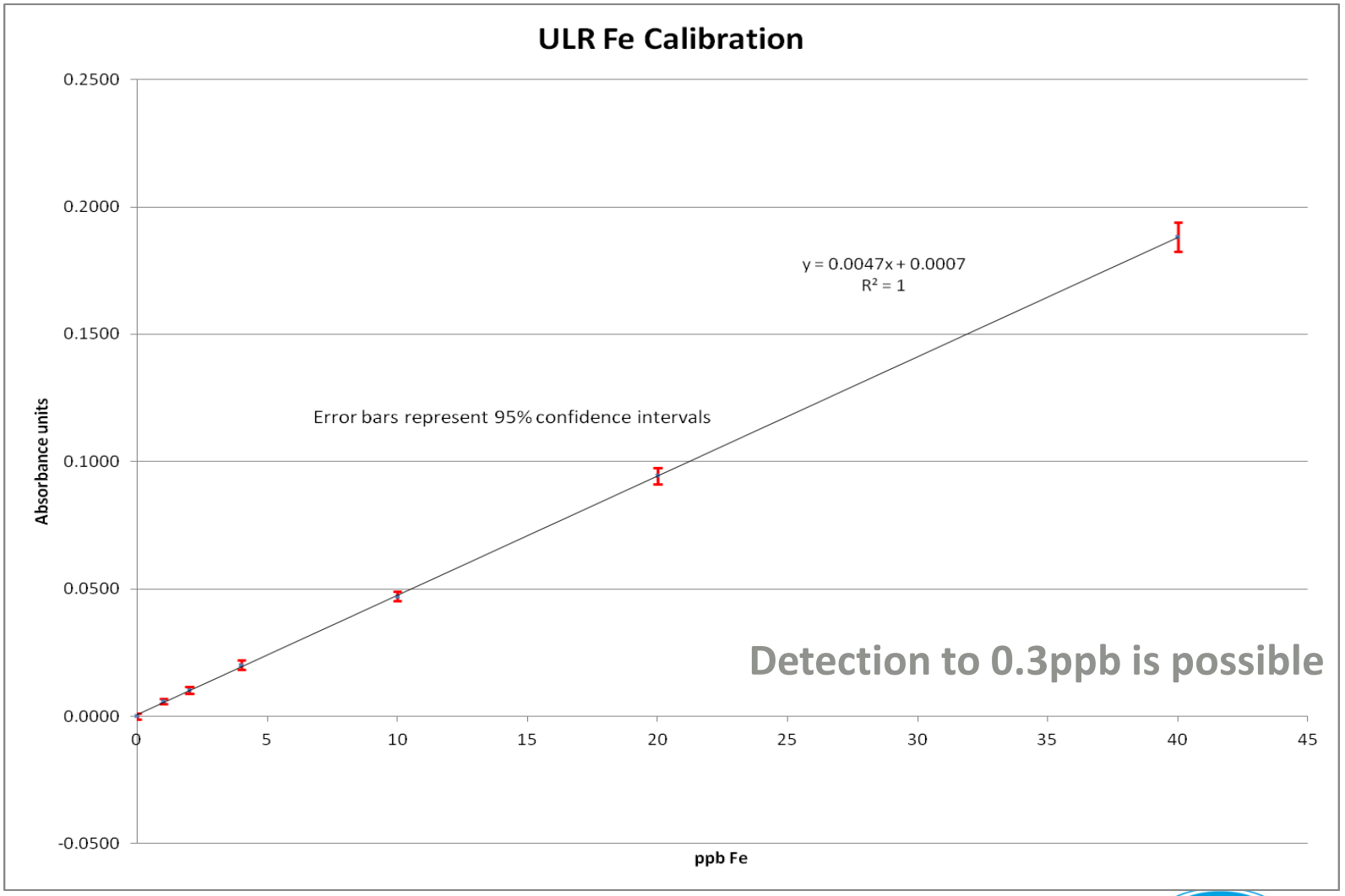
Grab Sample -ULR FerroZine Method

- *Combination* reagent - FerroZine + TGA
  - TGA is responsible for digestion / dissolution
  - FerroZine color reagent complexes with ferrous ions to form purple complex
  - Intensity of color complex is proportional to iron concentration
- Digestion at 135°C for 30 mins reduces *all Fe* including magnetite & hematite

Ultra Low Range Iron Analysis



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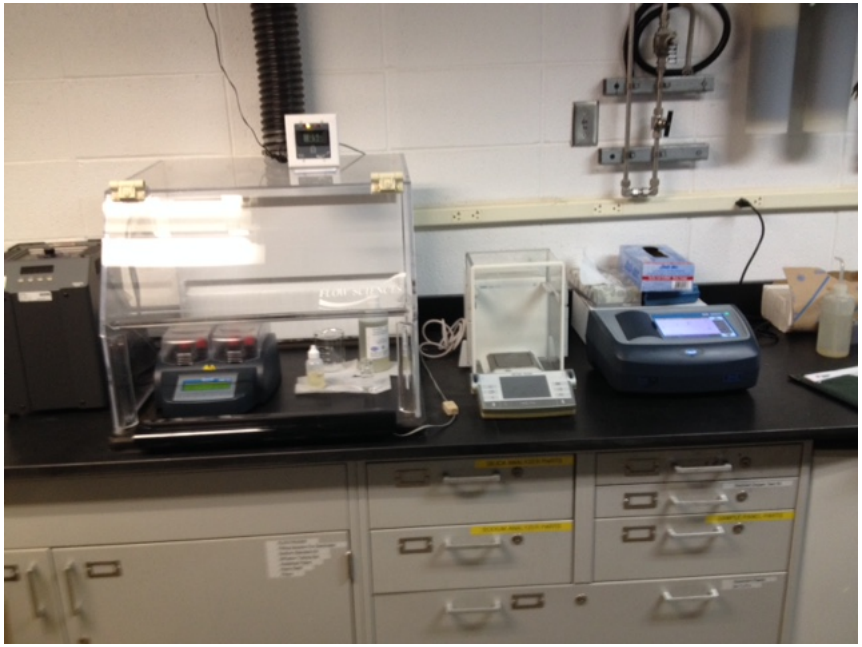
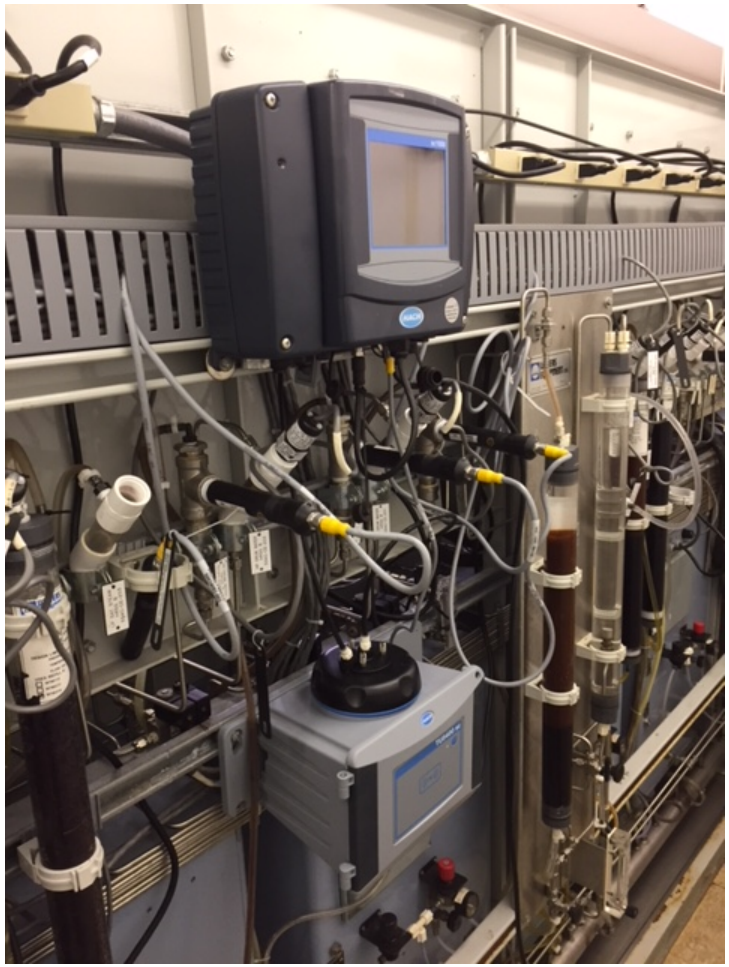
Determination of Total Iron (Bench Method)

2 Objectives

- In-plant analysis of iron – 1 hour
- Correlation of iron to laser turbidity





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The Method is Accurate If .....

Contamination is eliminated

Never digest more than 12 mL of sample ….. *but store the vial full*

Cook new vials with 12 mL of ultrapure water + 8 drops of Ferrozine for 12 hours at 135˚C

Store sample cell with ultrapure water containing Ferrozine. Cover with Parafilm

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Remove Contamination

- Add 8 drops of FerroZine to each digestion bottle and dilute to 12mL with DI water
- Heat for 24 hrs. @ 135°C in digestion block

Mark level in advance with marker

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Remove Contamination

- Add 8 drops of FerroZine to 1” sample cell, fill with DI water
- Cover with Parafilm and let stand for at least 30 mins at room temperature

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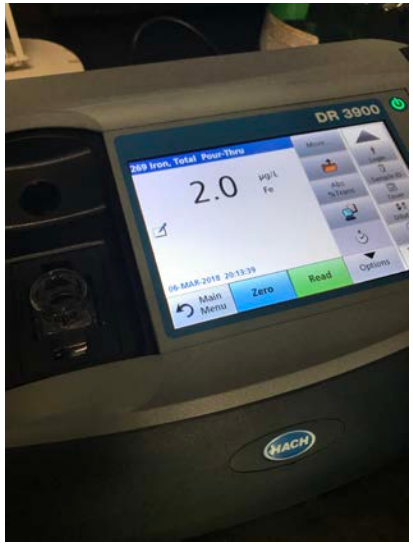
Determine the Correct Reagent Blank

1. Fill clean sample cell with your best water and wipe the outside surface
2. Place sample cell in spectrophotometer and **ZERO**
3. Remove sample cell and add 8 drops of Ferrozine and Swirl to mix.
4. Wipe surface and place back into the spectrophotometer
5. Press READ and note concentration.
   EXAMPLE 1.3 ppb
6. Remove sample cell and add an additional 8 drops of Ferrozine and swirl to mix.
7. Wipe surface and place back into the spectrophotometer
8. Press **READ** and note concentration.
   EXAMPLE 2.0 ppb

The difference between the two values = REAGENT BLANK



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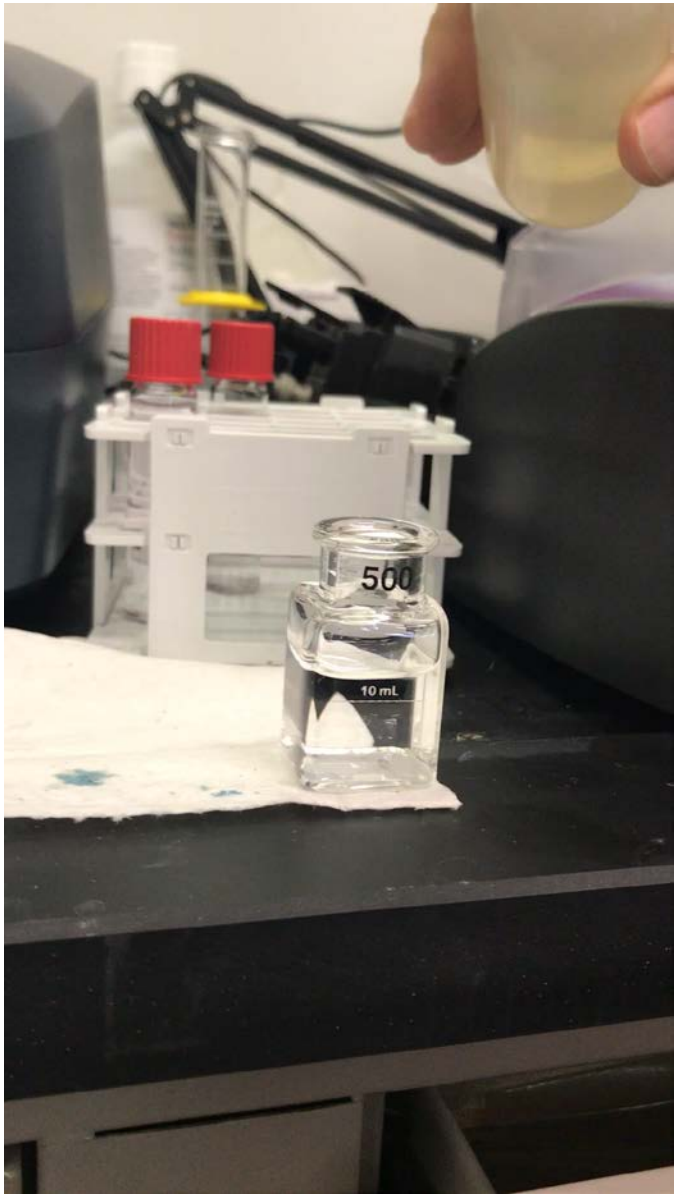

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TAKING THE GRAB SAMPLE IS ONE OF THE MOST CRITICAL TASKS

Sample should be taken from continuous stream

- From outlet on sample panel
- From outlet of Laser Turbidemeter

It is critical that the outlet and the flow is not disturbed when taking sample.

When obtaining the sample the digestion vial should first be rinsed out at least 3 times with the sample.

Procedure – Sample Digestion

1. Once 12 mL of the sample is added to the digestion vial, add 8 drops of Ferrozine.

2. Tightly replace cap and invert to mix

3. Place vial in digestion block and heat at 135˚C for 30 minutes

4. After 30 minutes remove vial from block and allow to cool.

Procedure – Determination of Total Iron

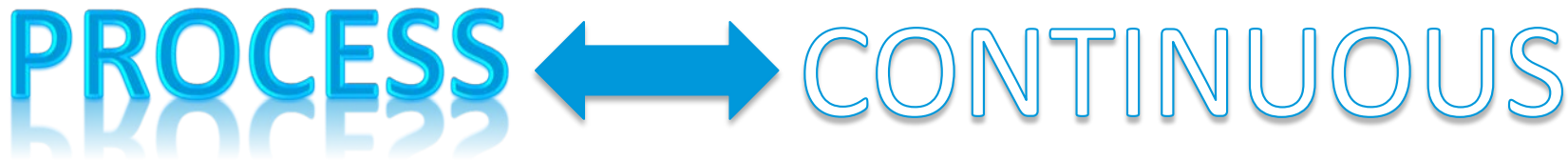
1. Remove storage water from the sample cell and add unreacted DI water to the cell and **ZERO** the spectrophometer.
2. Remove cell from spectrophotometer dump the DI water and add a small amount of the digested sample and rotate to pre-rinse the inside surface of the sample cell.
3. Add the remaining digested sample to the sample cell
4. Place sample cell in spectrophotometer and press **READ** to obtain value.
5. **(Reading – Reagent Blank) = Total Iron (ppb)**

**** HINT: For more consistent results press ZERO / READ to obtain several readings. This allows for most consistent results.***

Procedure – Determination of Dissolved Iron

Run the same procedure on the sample without prior digestion.

Monitoring of Iron Transport using a laser nephelometer



Turbidity can be more than just a trend monitoring tool

- The FerroZine total iron lab analysis accurately measures ppb levels of iron oxides
- The laser nephelometer can be calibrated on site using the lab ULR Fe procedure
- Site-specific calibration means that the laser nephelometer will respond accurately to the specific corrosion products present at each installation in the steady-state corrosion regime
- **Steady-state iron concentrations can be measured accurately for correlation.**

Monitoring Iron Transport with a laser nephelometer

Equipment:

- TU5400
- sc200/sc1000

Procedural Steps:

- Plumb the TU5400 to the sample line
  - Condensate pump discharge
  - Economizer inlet
- Adjust the flow to **<u>>500 mL/min</u>**
- Connect the controller to plant data system

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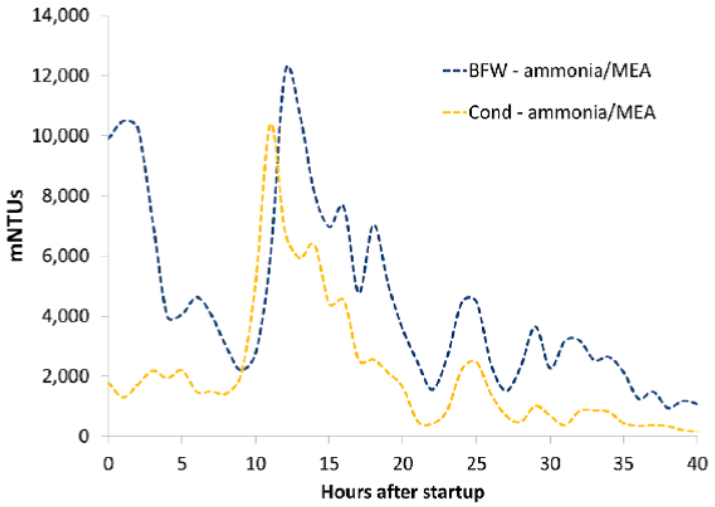
Cold start w/ ammonia:MEA AVT

Turbidity peaked ~12K mNTU

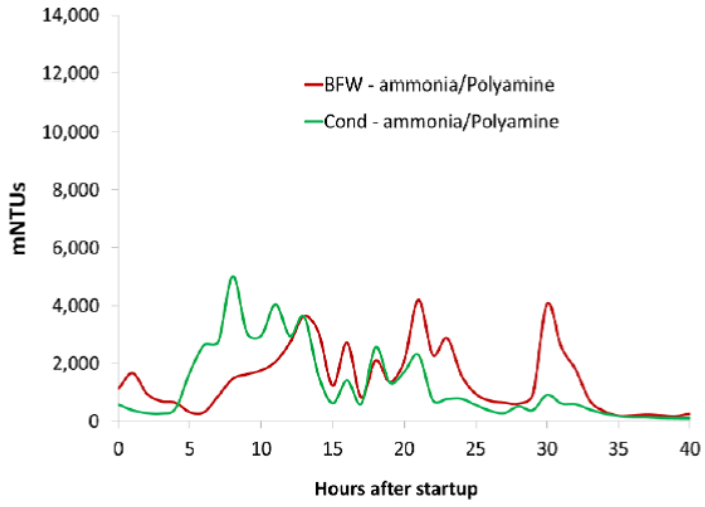
Condensate turbidity in 2-10K mNTU range

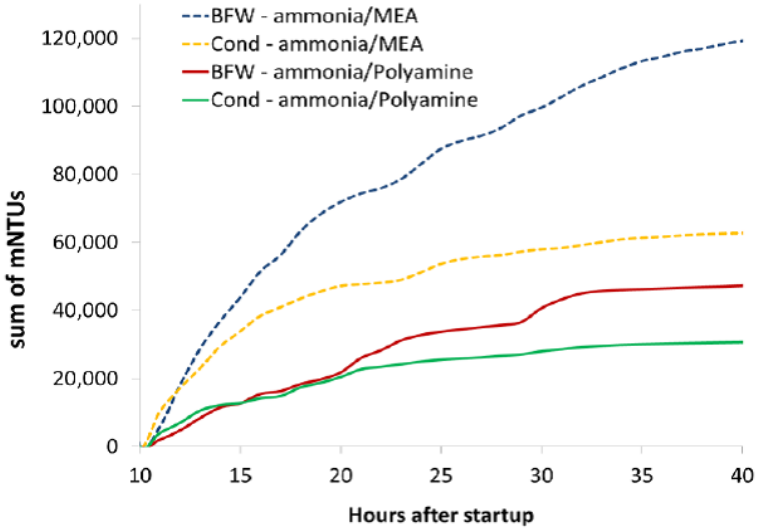


Cold start after Polyamine addition

Turbidity peaked ~5K mNTU

Condensate turbidity in 1-5K mNTU range

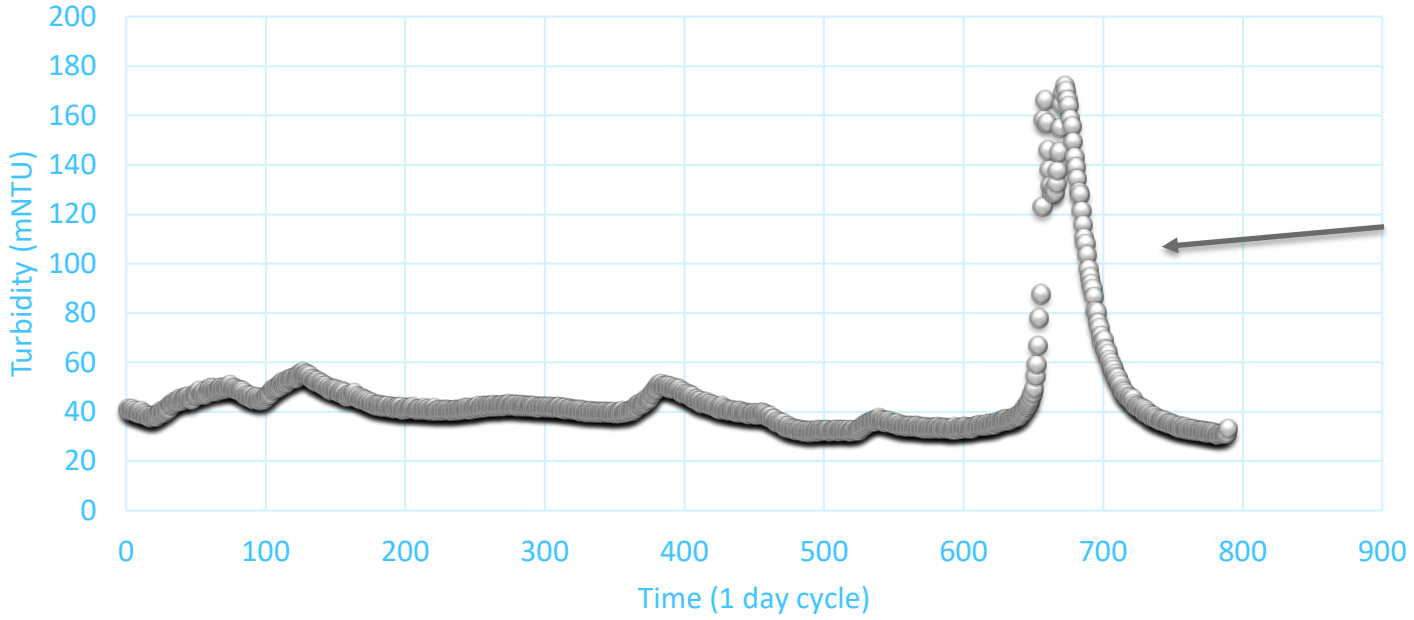




Courtesy GE Power & Water

Corrosion monitoring options

- Grab Samples
  - Quantitative
  - Time intensive
  - Easy to miss large transport events
- Process Analyzer
  - Surrogate particle analyzer allows for real-time measurement
  - Quantitative based on site specific calibration.



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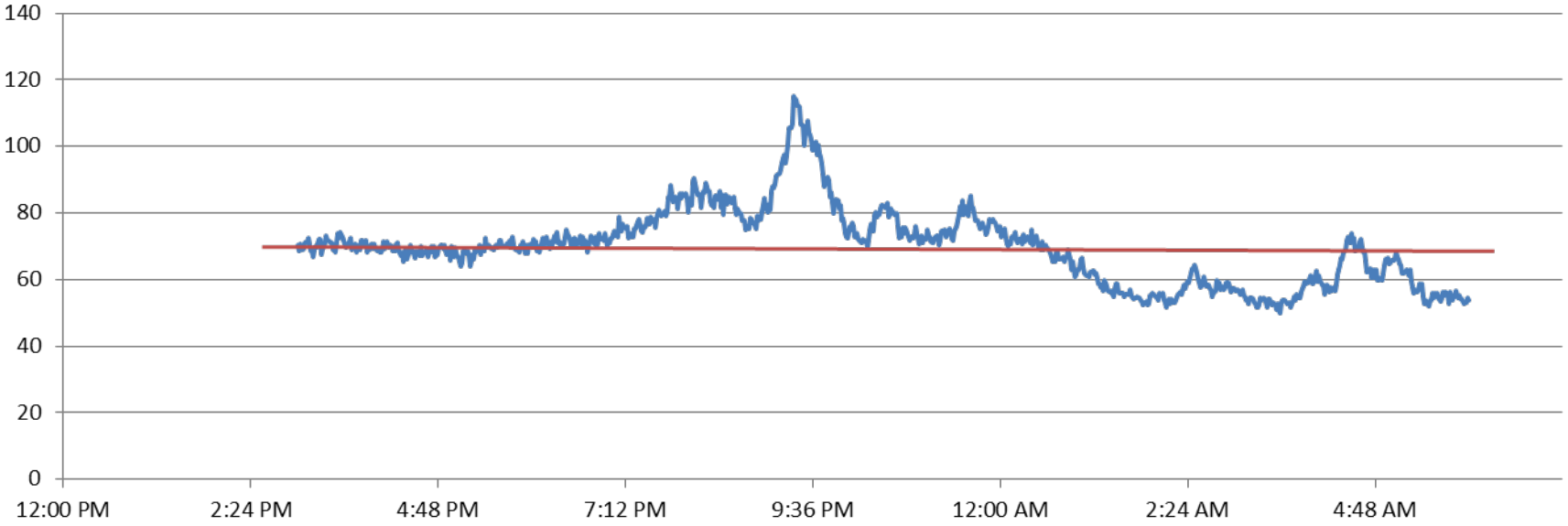
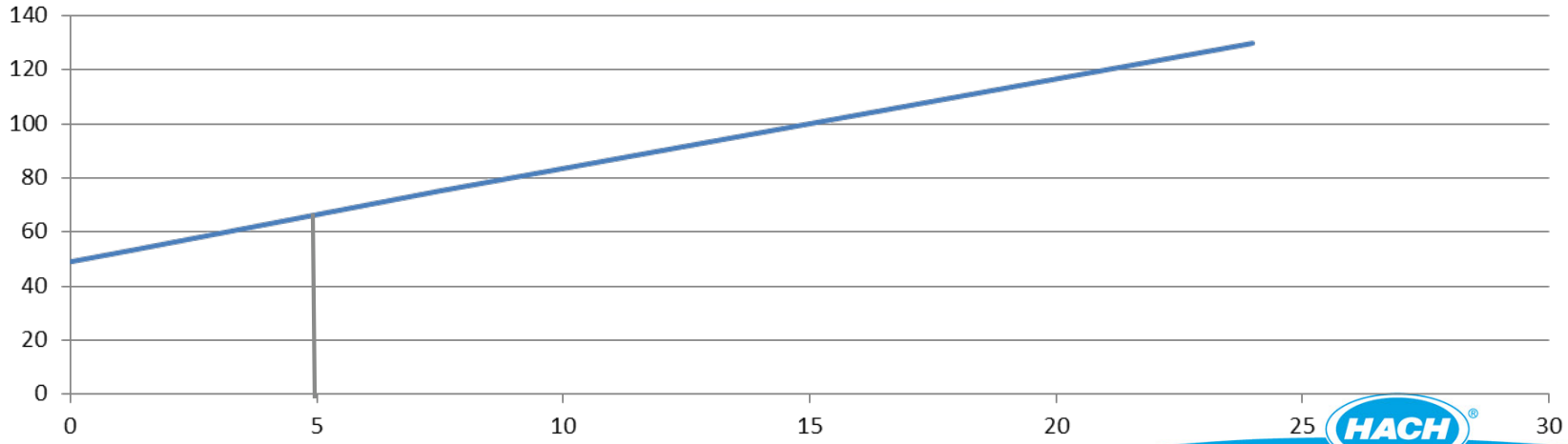
EXAMPLE from an installed Laser Nephelometer



Correlation Curve



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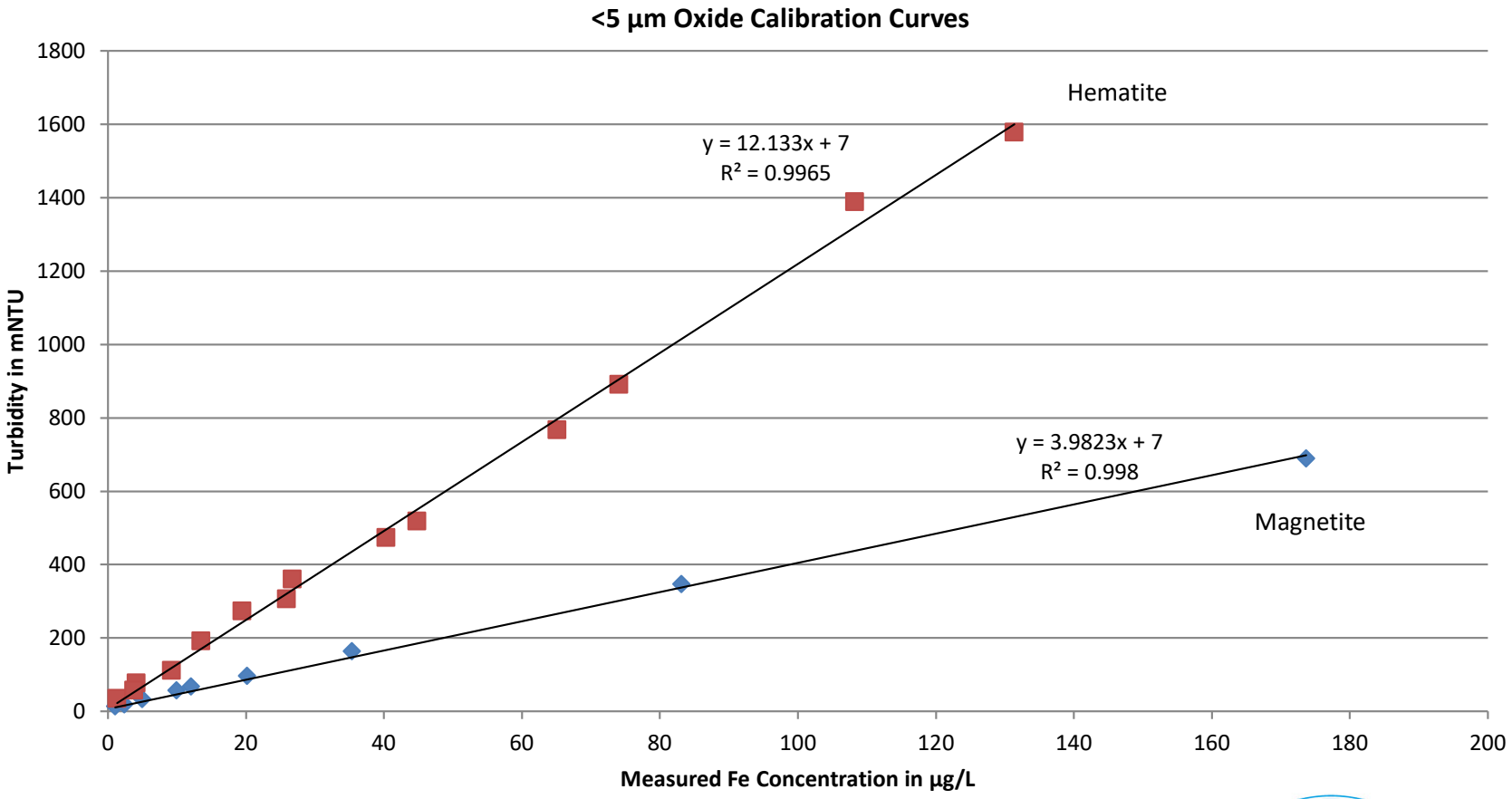
Nephelometer calibration for active corrosion

Nephelometer calibration curves are linear but oxide dependent



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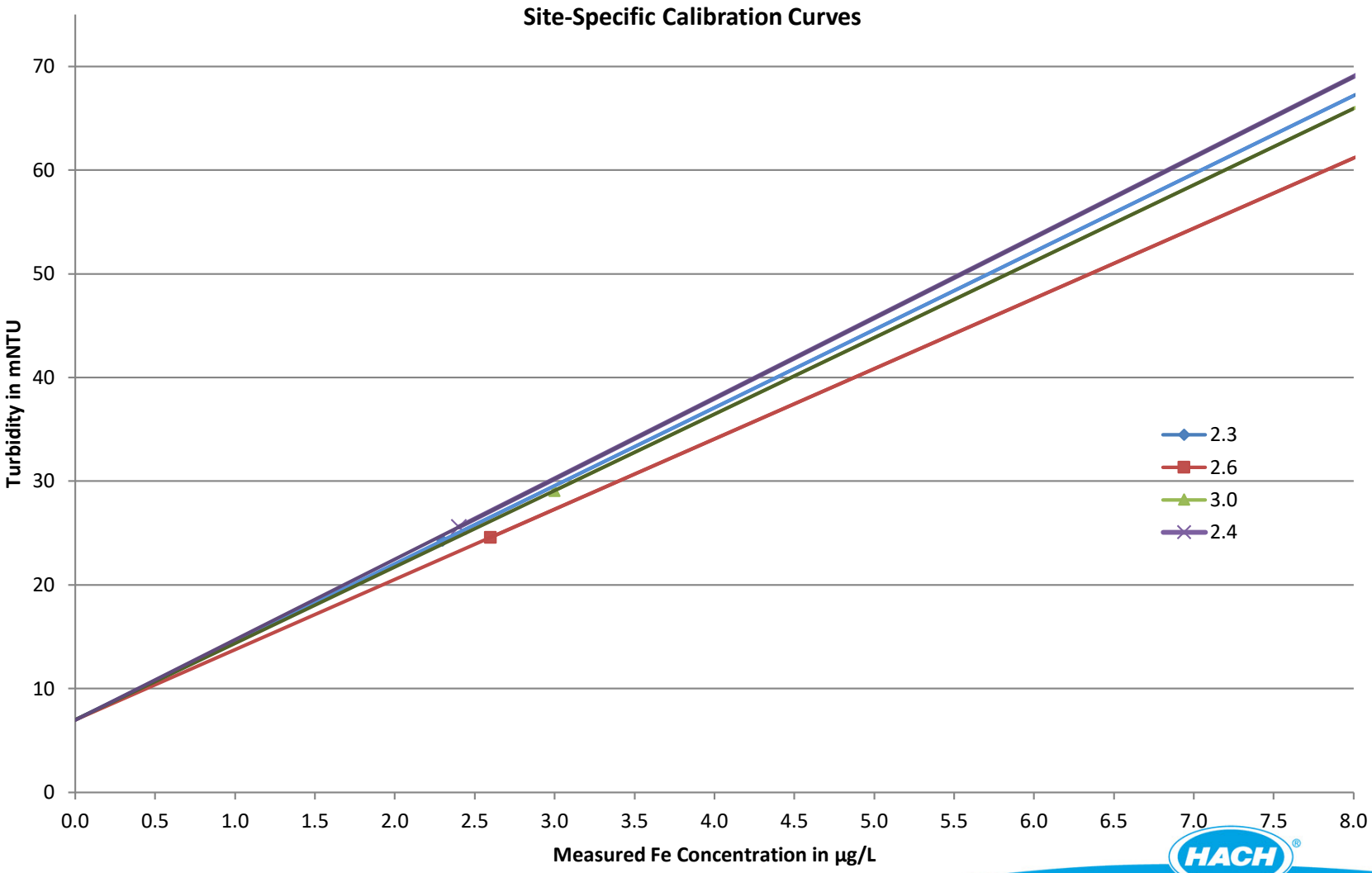
Site-specific calibration



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SUMMARY OF PROCESS Fe MONITORING

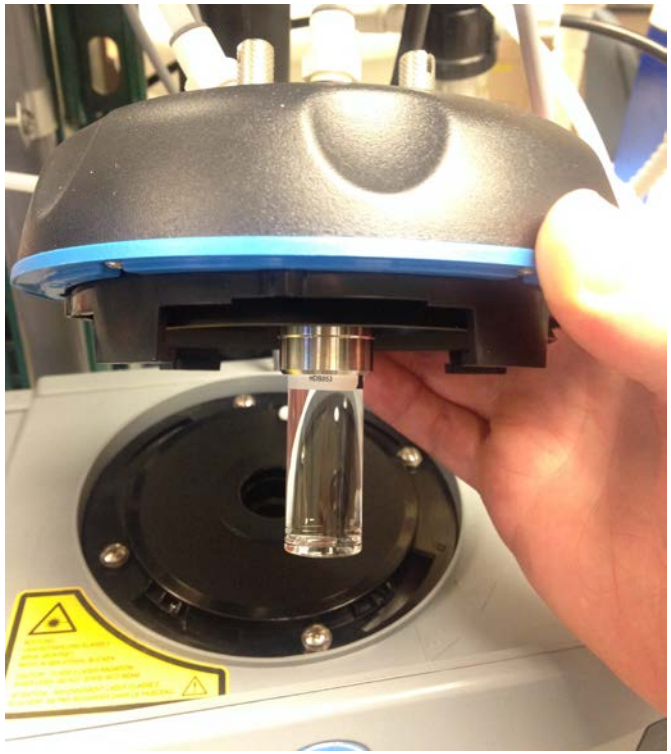
Nephelometer can be more than just a trend monitoring tool

- Can be calibrated on site using the lab ULR Fe procedure
- Site-specific calibration means that the nephelometer will respond accurately to the specific corrosion products present at each installation in the steady-state corrosion regime
- **Steady-state iron concentrations can be measured accurately**
- **Large transport events can be monitored qualitatively and quantitatively**

Site-specific calibration

Single-point site-specific calibration of sample:

- Grab samples collected from outlet of laser nephelometer during steady-state operation
- Curve forced through the empirical 0-point (7 mNTU)
- Calibration curve created with a single data point



CALCULATIONS

Measured Values			
Data Input in Blue area			
Lab - Fe2	**3.4**		**EXCEL**
In-Line Analyzer - mNTU2	**16**		**Spreadsheet**
Theoretical Values			
Zero - Fe1	0		
Zero - mNTU1	7		
Slope (m= Fe2-Fe1/mNTU2-mNTU1)			
Slope - (m)	0.378		
Intercept (b= Fe2-Slope(m)*mNTU2)			
Intercept - (b)	-2.644		
Analyzer Formula (Fe = Slope (m)*Reading (A) + Intercept (b))			
Fe =	0.378	*A	-2.644

$y = mx + b$

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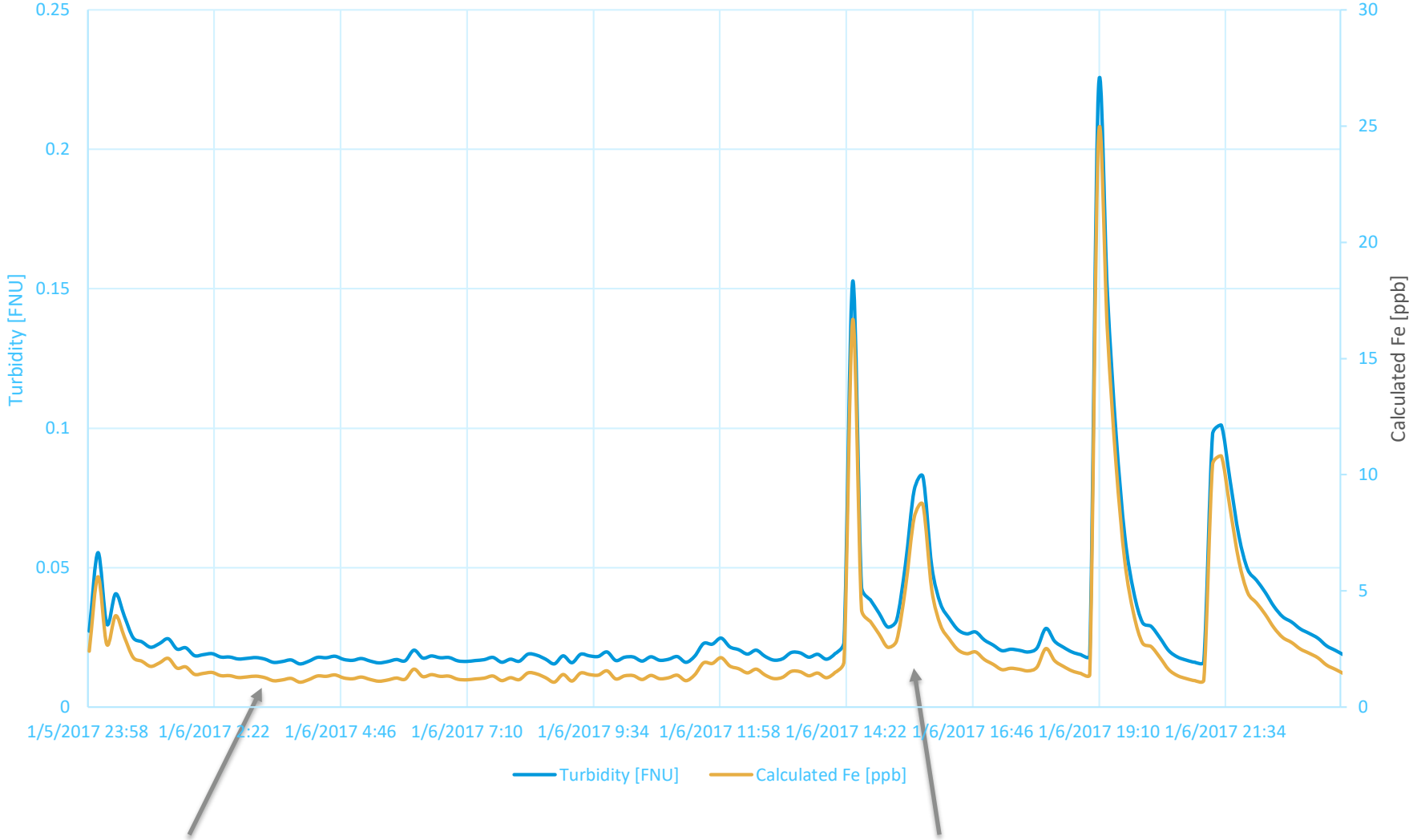
Monitoring Iron Transport with a nephelometer

Challenges for Monitoring Corrosion Transport with Nephelometers

- Nephelometers are sensitive to particle **color**. Oxides are different colors.
- Nephelometers don't detect **dissolved** species.
- Nephelometers are sensitive to **particle sizes**.
- Accurate universal turbidity/iron calibration is **impossible**

Monitoring Iron Transport with Nephelometry



Baseline active corrosion

Transient corrosion product transport

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SETTING UP THE TU5400 LASER TURB

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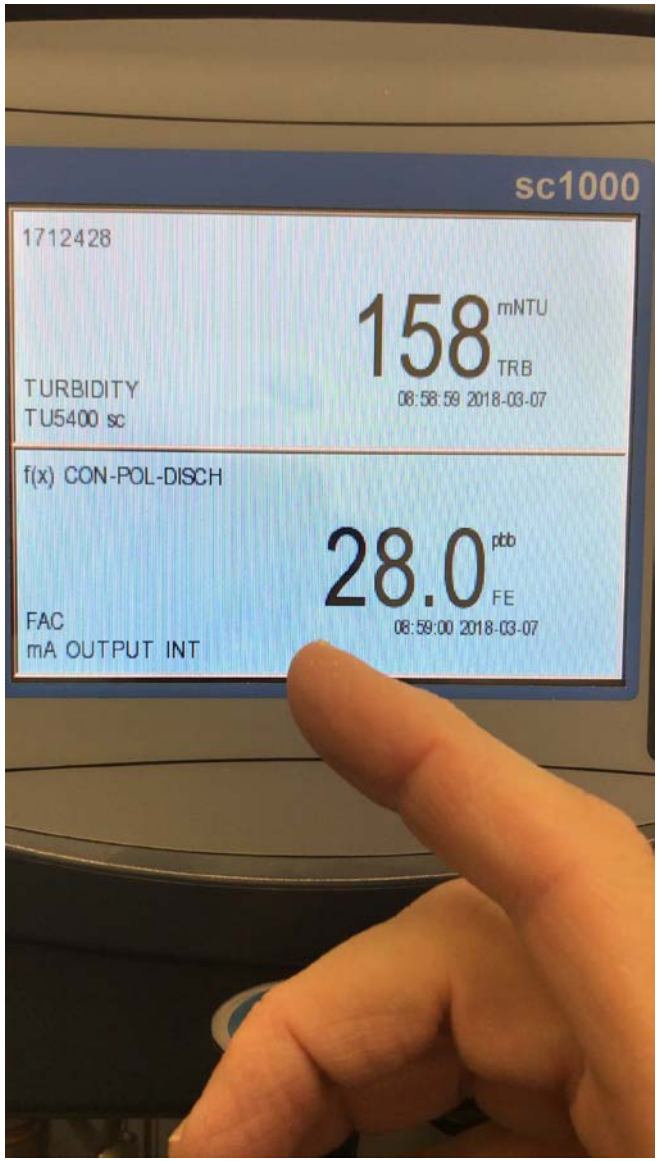
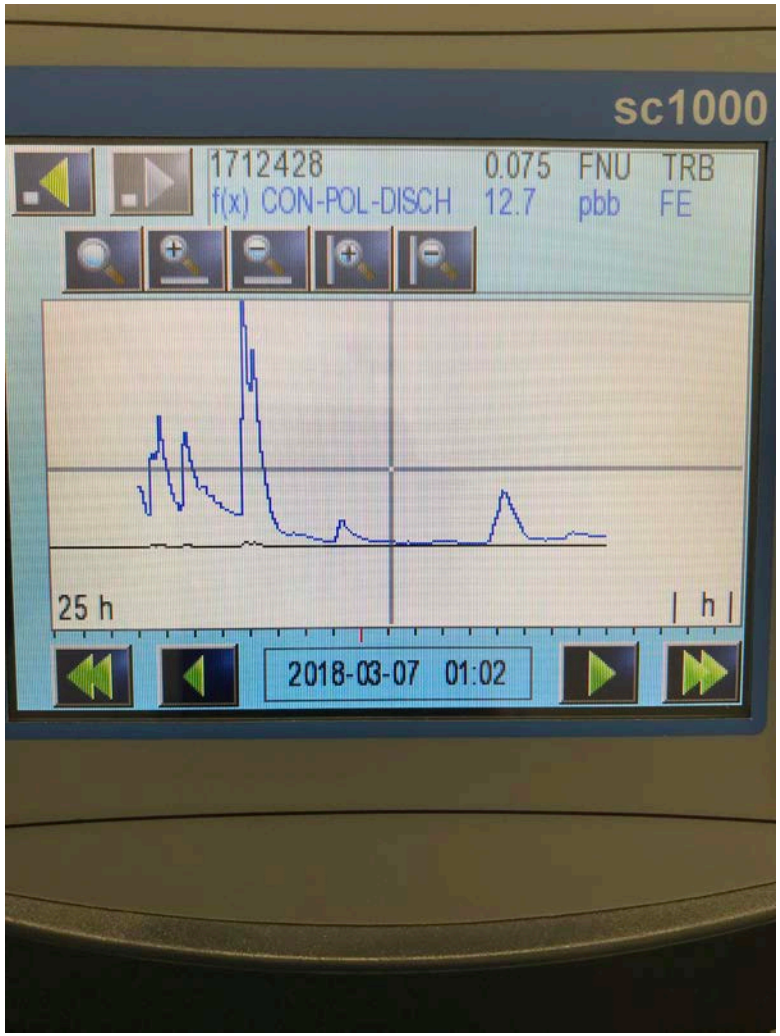
SETTING UP A GRAPHICAL DISPLAY ON THE SC1000





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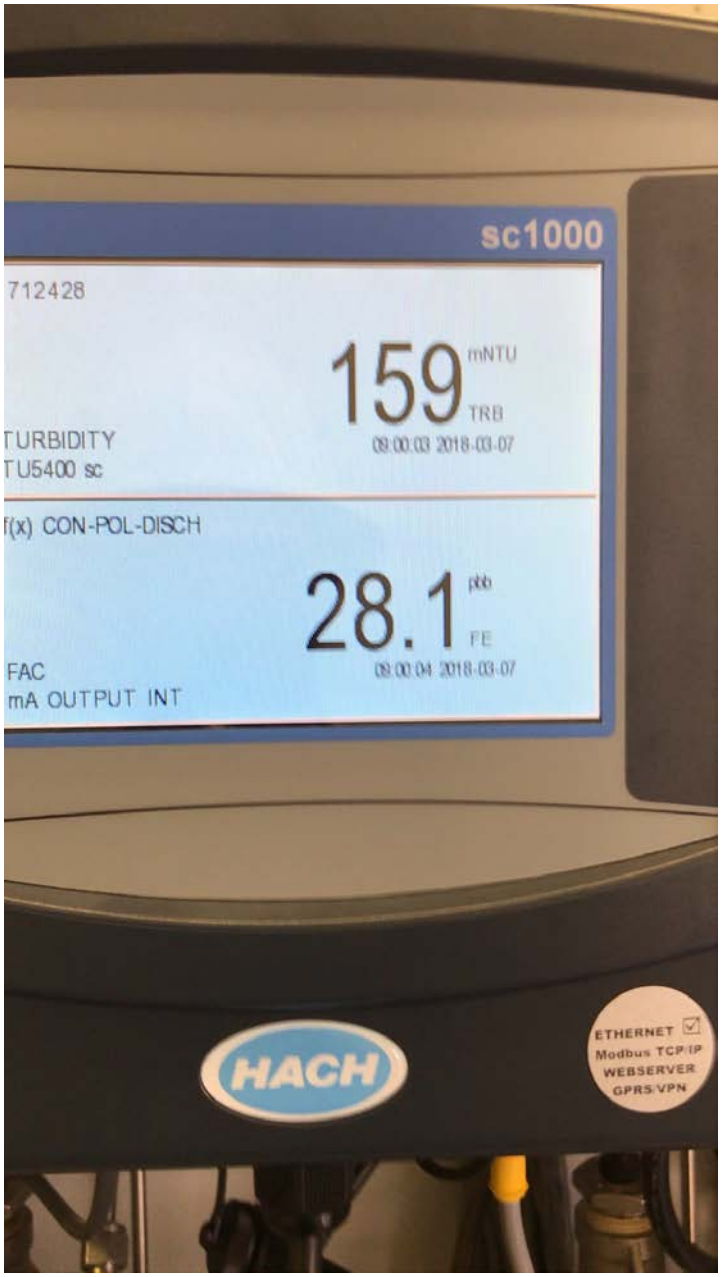
Speed of response to upset in sample line.



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RESEARCH REGARDING EFFECT OF FILMING COMPOUNDS ON IRON MEASUREMENT

Hach ULR Iron FFA/FFP interference

- Concern that film forming amines (FFA) or film forming products (FFP) may interfere with Hach ULR Fe method
  - Either direct interference with the color chemistry (FerroZine) or the digestion (reduction via thioglycolic acid at 150C in a closed vessel)
  - Potential for common FFA functional group, diamine, to function as chelator with iron, thereby inhibiting digestion

- Analyzed 6 FFA/FFP products for interference
  - Solenis DPL-674
  - Helamin 90H Turb
  - GE Steamate PAS6079
  - Chemtreat Titan360
  - Anodamine HPFG
  - Nalco Powerfilm 10000

Hach ULR Iron FFA/FFP interference

- Each product was spiked to an iron standard at the manufacturer's recommended concentration as well as at 20x the recommended concentration (highest recommended concentration at feed point or as residual depending on product).

- Each product spike was tested with dissolved iron (Fe^{2+}), magnetite particulates(~1µm), and hematite particulates(~1µm).

- Unspiked standards were measured concurrently for reference.

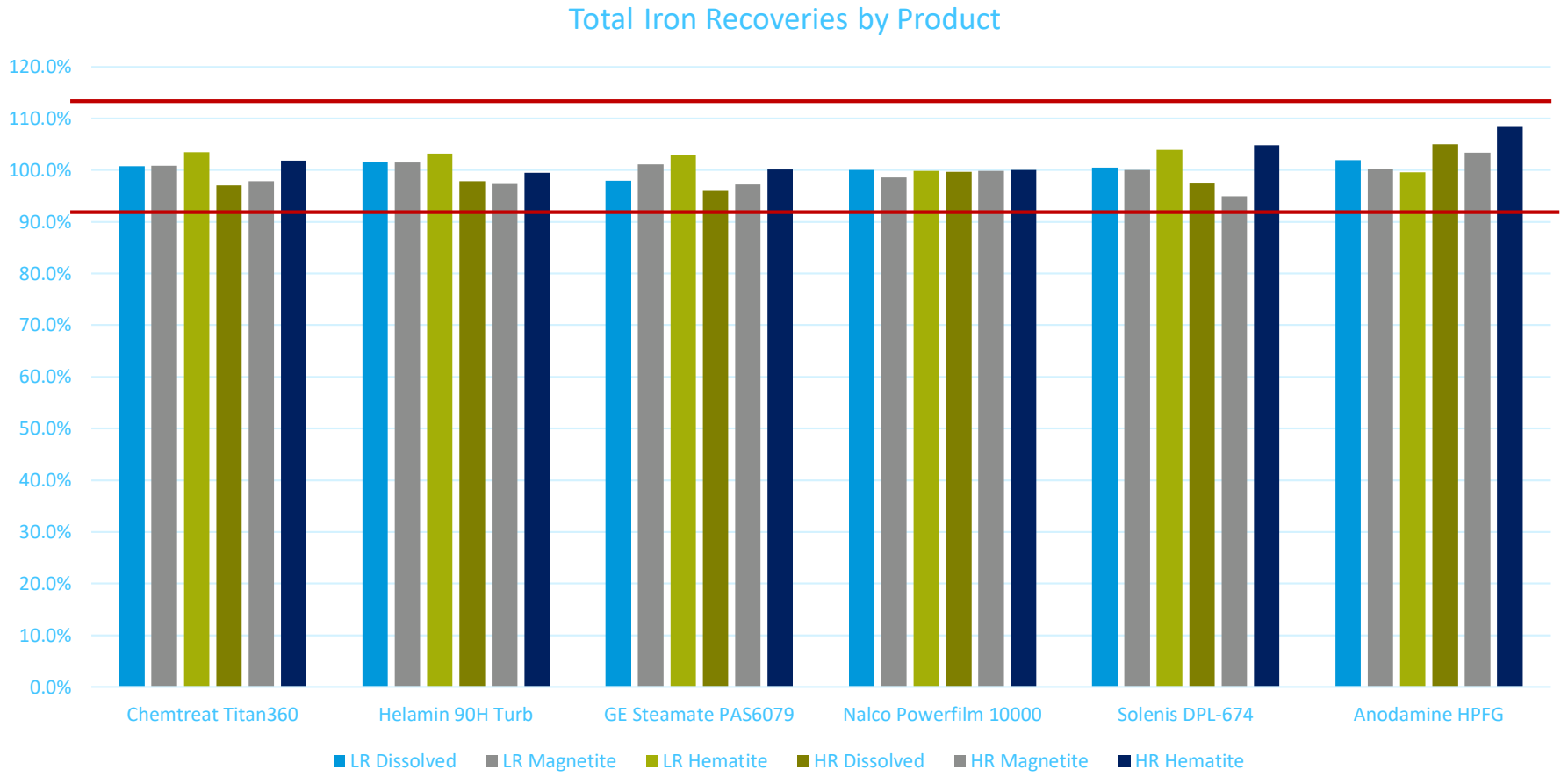
- Average spike results were compared with average standard results to determine percent recovery.

- Low percent recovery (<90%) would indicate some kind of interference.

Hach ULR Iron FFA/FFP interference

No interference was observed for any product at any concentration with any iron species.

Hach ULR Iron FFA/FFP interference



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THANK YOU FOR YOUR TIME