The Importance of Corrosion Product Monitoring

2021 Virtual ACCUG Meeting

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Agenda

1. Guidelines
2. Sample Conditioning
3. Methods of analysis
4. Online technology
5. Validation

Fossil, CC and HRSGs with Air-Cooled Condensers (ACC)

Corrosion Product Guidelines

- Monitoring corrosion products in the condensate before and after a condensate filter provides an indicator of whether corrosion and FAC are minimized in the ACC at the tube entries in the upper transport ducts (streets).
- The level of total iron (dissolved and particulate) is directly dependent on the feedwater/condensate pH.
- Levels of total iron < 10 ppb are consistently achievable with pH levels around 9.8.
- Downstream of a typical filter (5 µm absolute) the levels can be consistently controlled to around 5 ppb.

Sample Conditioning

Key Parameters

A – Pressure Reduction B – Cooling

C – Isolation valves D – Sample Lines

1) Length
2) Routing
3) Size
4) Flow rate / velocities

Sample Conditioning

Key “Keep in Minds”

- Continuous stream of sample flow under steady state conditions (full load if possible)
- Particle filters removed
- Cleaned bottles (for grab samples)
  - using high purity concentrated acid

Methods of Analysis

- Atomic Absorption (AA): 7 ppb LOD
- Graphite Furnace Atomic Absorption (GFAA): 0.3 ppb LOD
- Inductively Coupled Plasma (ICP)
  - Atomic Emission Spectroscopy (AES): 7 ppb LOD
  - Mass Spectroscopy (MS): 1 ppb LOD
- Babcock & Wilcox Membrane Filter Comparison Charts
- Corrosion Product Sampler
- Visible Spectroscopy

Method of Analysis

Babcock & Wilcox Membrane Filter Comparison Charts

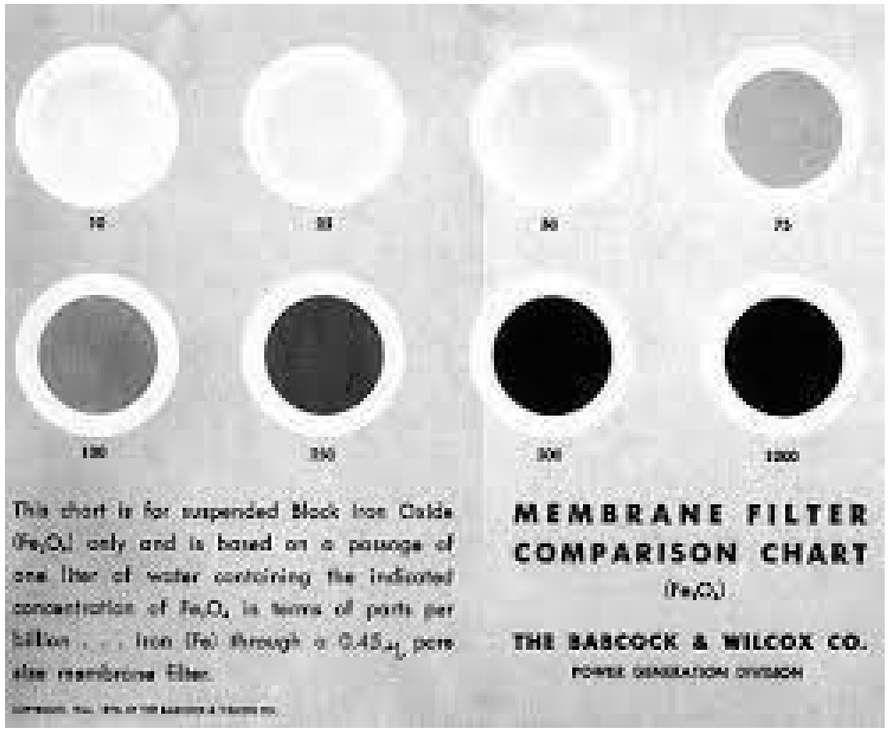


Photo courtesy of Babcock & Wilcox

Method of Analysis

Corrosion Product Sampler

Samples water for quantifying of particulate an ionic matter (corrosion products) circulating in the piping of condensate/feedwater systems

- Locates and identifies cause / source of corrosion products
- Quantifies rate of corrosion
- Track the path of corrosion products
- Measure effectiveness of chemical treatment
- Contains a particulate filter and a digital totalizing meter

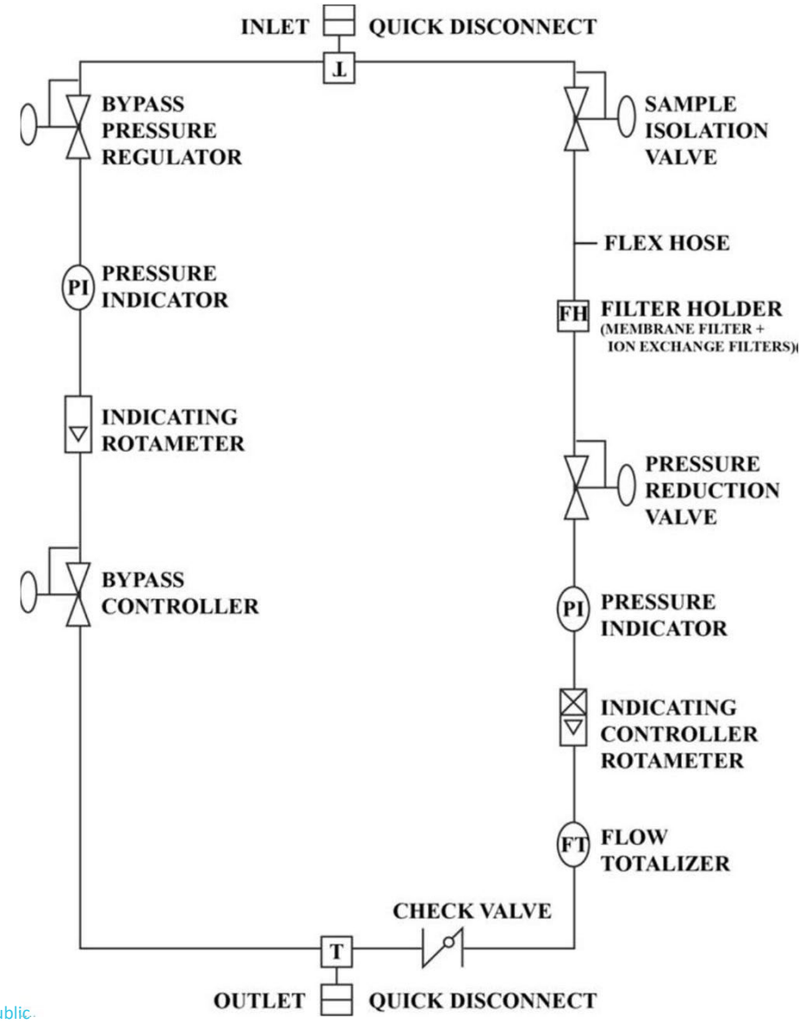
Photo and description courtesy of Sentry Equipment

Method of Analysis

Corrosion Product Sampler

Key steps:

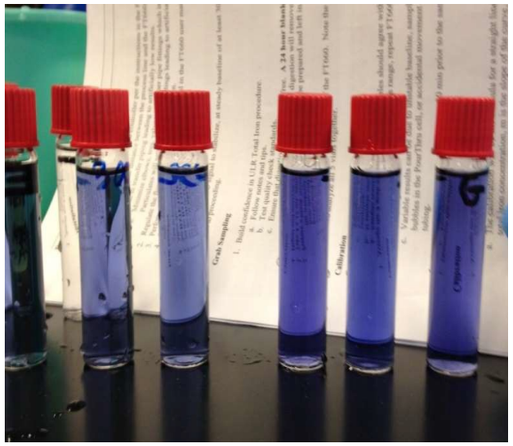
1) Particles collected on an acid digestible filter of pore size 0.1 to 0.45 µm and the dissolved fraction on an ion-exchange membrane filter placed after the particle filter
2) Volume of filtered sample fluid over 1 – 24 hours is recorded
3) Remove filters, dry and digest in acid
4) Determine mass of corrosion product using appropriate analytical method



Method of Analysis

Visible Spectroscopy

Measured at 562 nm



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

Iron, Total

DOC316.53.01520

FerroZine® Method[1] **Method 10287**

1.00 to 100 µg/L Fe (1-inch cell) **Reagent Solution**

Scope and application: For ultrapure water.

[1] Adapted from Stookey, L.L., *Anal. Chem.*, 42 (7) 779 1970.

STEP 1 – PREPARATION OF SAMPLE CELL

- 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

STEP 2 – PREPARATION OF DIGESTION VIALS

- Add 8 drops of FerroZine to each digestion bottle and dilute to 12mL with DI water
- Heat for 24 hrs. @ 135°C in DRB200 digestion block

STEP 3 – COLLECTING THE SAMPLE

Sample should be taken from continuous stream

- From outlet on sample panel
- From outlet of laser nephelometer

Critical that outlet and flow is not disturbed when taking sample

Digestion vial should first be rinsed out *at least 3 x* with the sample before collecting

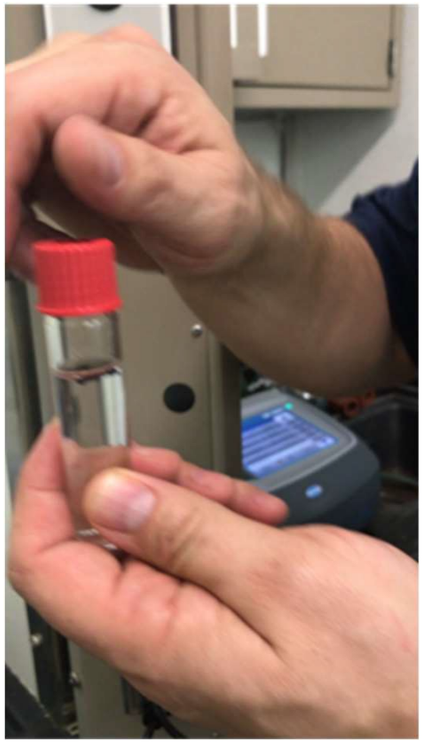
STEP 4 – PREPARATION & DIGESTION OF SAMPLE

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 ℃ for 30 minutes

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



STEP 5 - DETERMINE THE REAGENT BLANK

1. Fill clean sample cell with DI water and wipe the outside surface with KimWipe
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

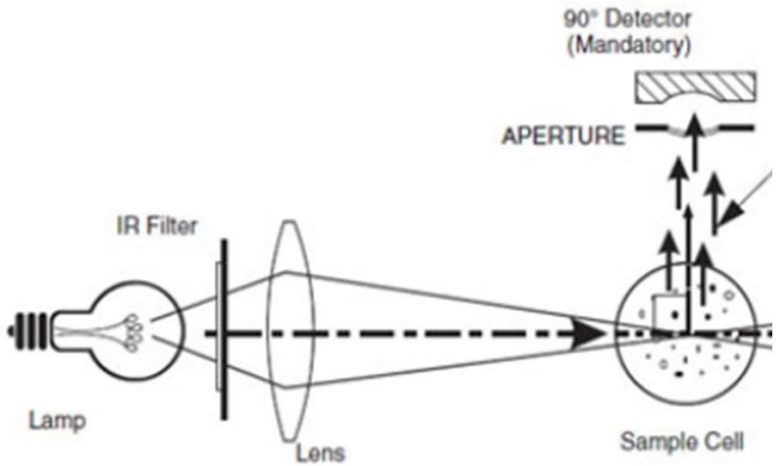
STEP 6 – DETERMINATION OF TOTAL Fe

1. Place DI water in the cell and **ZERO** the DR3900/6000
2. Remove cell from spec, dump the DI water and rinse with a few ml of the digested sample.
3. Add the digested sample to the sample cell
4. Place sample cell in spec and press **READ** to obtain value.
5. **(Reading – Reagent Blank) = Total Iron (ppb)**

Online Technology

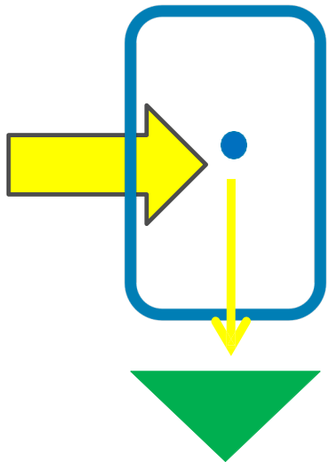
Laser Nephelometer

Detection of light energy scattered or reflected toward a detector that is not in the direct path of the transmitted light, typically measured at 90° to the incident light.

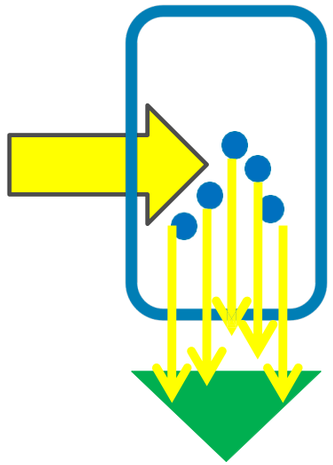


Online Technology

Laser Nephelometer



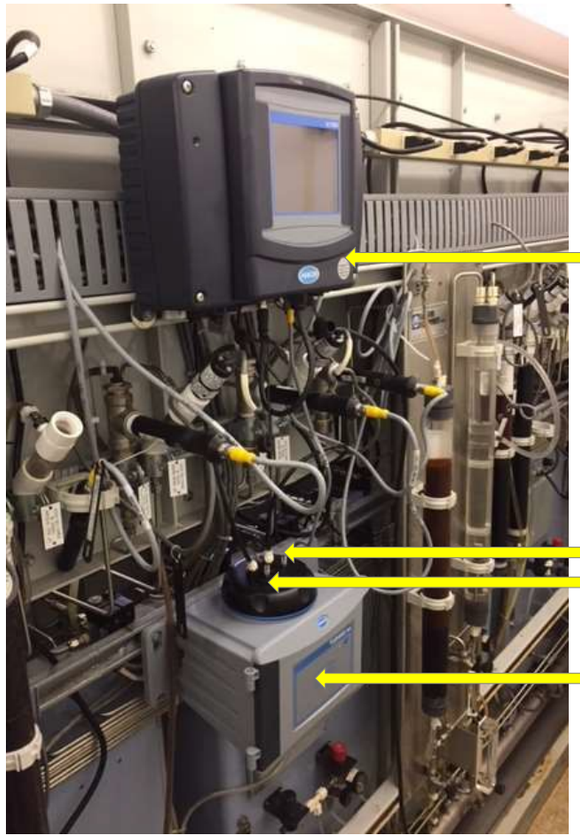
Non-detectable



Detectable

ON-LINE SURROGATE METHOD FOR IRON ANALYSIS

Laser Nephelometer



Example of an online laser nephelometer installation

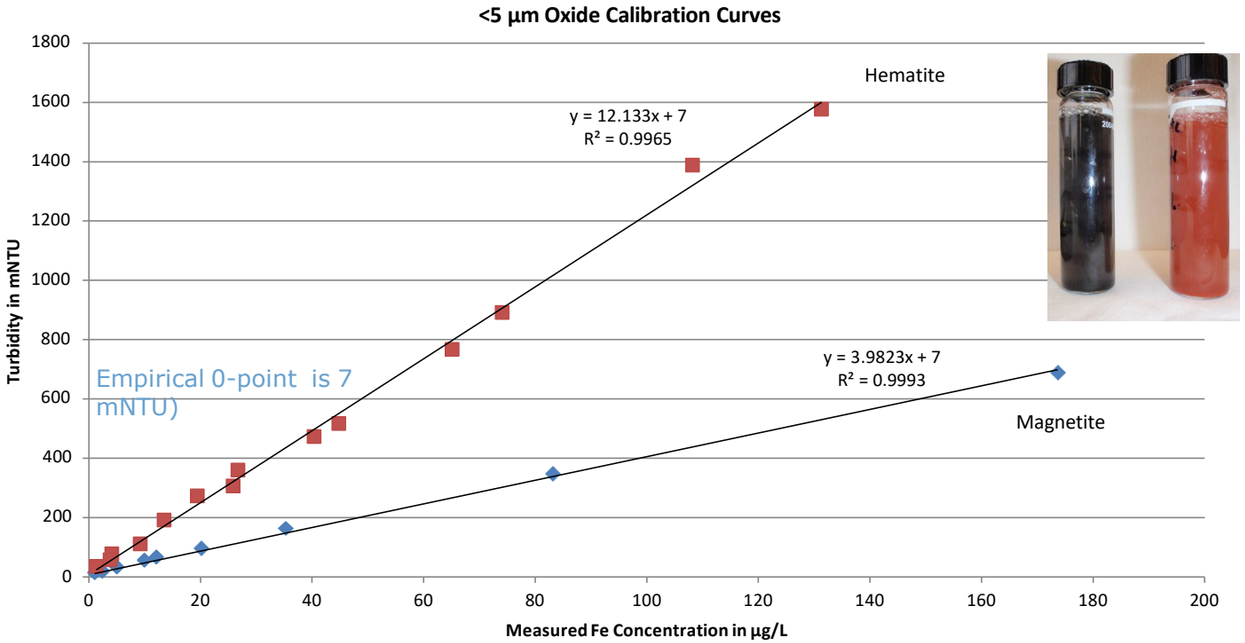
Controller with readout of iron concentration in ppb and/or nephelometric units (NTU)

Process sample outlet – ¼” tubing
Process sample inlet – ¼” tubing

Laser nephelometer with detector

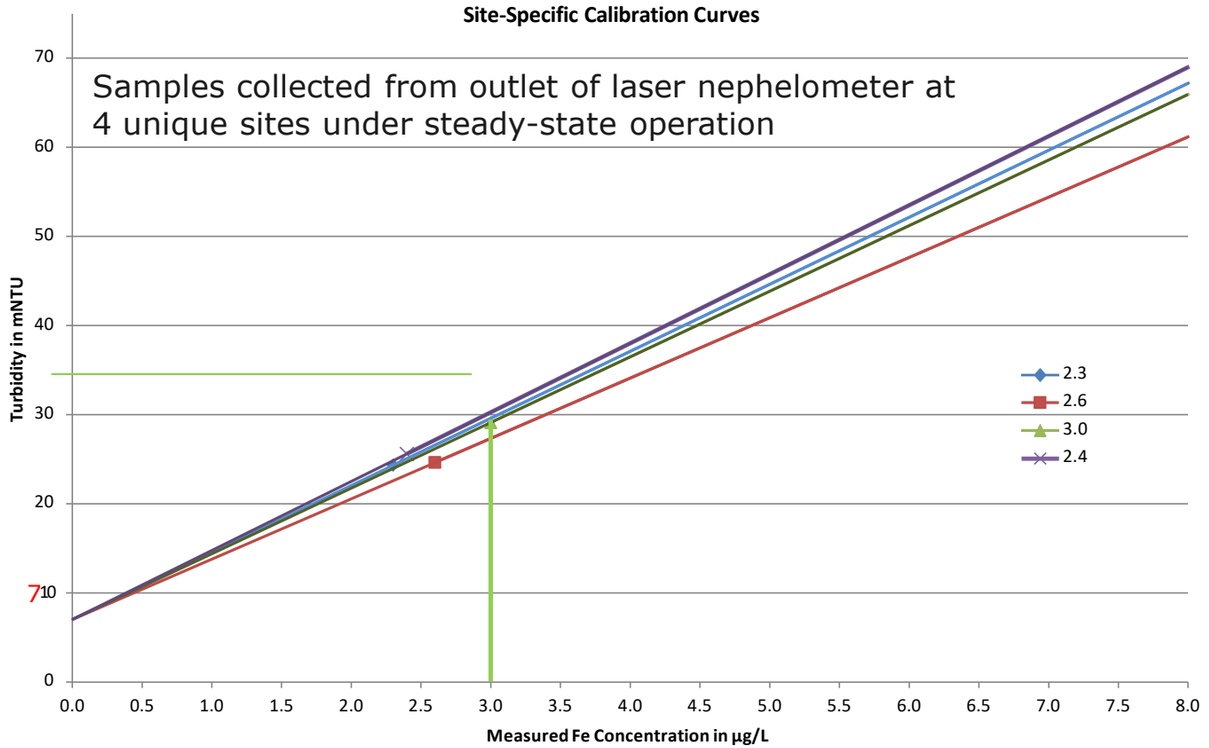
Nephelometer Correlation

Linear relationship for both hematite and magnetite



Site-Specific Correlation

Laser Nephelometer



Calculations

Laser Nephelometer

Measured Values		**(in Excel Spreadsheet)**	
Data Input in Blue area			
Lab - Fe2		**3.4**	(grab sample reading from spectrophotometer: **ppb Fe**)
In-Line Analyzer - mNTU2		**16**	(reading from nephelometer at time of grab sample: **mNTU**)
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

$$y = mx + b$$

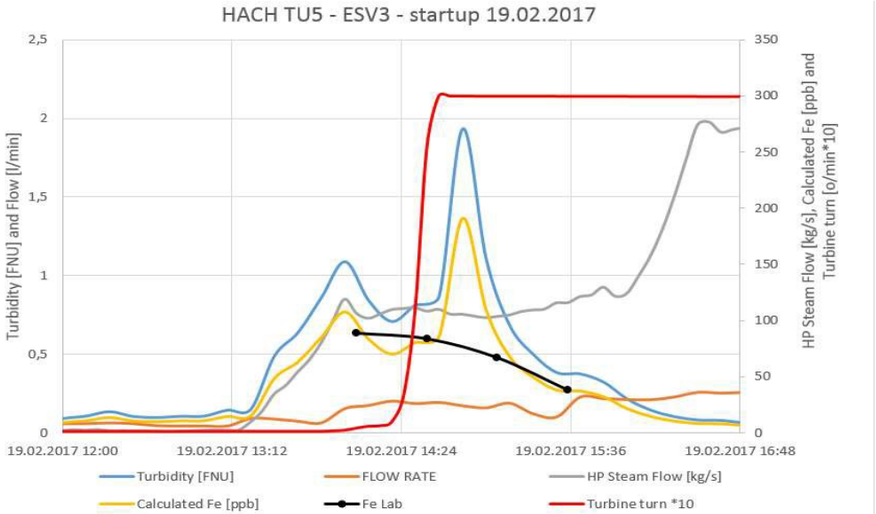
Actual Data

Laser Nephelometer

Date	Lab Fe_{total}		Turbidity	Flow	$Fe_{calculated}$
	ppb		FNU	L/min	ppb
04.03.17 13:40	<2	8	0,011	0,36	2
05.01.17 08:45	5	-	0,045	0,20	5
17.01.17 08:25	5	-	0,050	0,23	6
27.01.17 13:15	16	31	0,056	0,19	6
02.02.17 11:15	17	2	0,027	0,20	4
14.02.17 08:45	6	14	0,028	0,16	4
19.02.17 14:05	88	89	1,020	0,16	101
19.02.17 14:35	83	84	0,920	0,19	91
19.02.17 15:05	71	67	0,800	0,17	80
19.02.17 15:35	39	38	0,370	0,16	37
28.02.17 10:00	<2	-	0,020	0,14	3
14.03.17 09:00	4	31	0,034	0,27	4

Calibration points for the Fe calculation

[Fe2]	83,5	ppb
[Fe1]	2	ppb
mNTU2	840	mNTU
mNTU1	11	mNTU
m	0,098311	
b	0,918577	



i. Calculate the slope, m.

$$m = \frac{[Fe2] - [Fe1]}{mNTU2 - mNTU1}$$

$$m = \frac{5-0}{50-7} = \frac{5}{43} = 0.116$$

ii. Calculate the intercept, b.

$$b = y - mx$$

$$b = 5 - 0.116 \times 50 = -0.8$$

Validation

Corrosion Monitoring Program

Main quality parameters that should be considered:

- Linearity over the relevant measuring range
- Accuracy – this is a measure of the systematic error
- Repeatability over the measuring range – random variation when measurements are performed within short time intervals under otherwise constant conditions
- Reproducibility at selected levels – random variation taking into account the small contributions to errors that vary from batch to batch of samples
- Detection limit – describes the lowest measurable concentration that is statistically different from zero.

Thank You

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