Laser Nephelometer Calibration Guide for Monitoring Flow Accelerated Corrosion and Treatment Efficiency in the Steam Cycle

Introduction

The TU5400 and FT660 nephelometers may be used to monitor steel corrosion in steam cycle components. When properly calibrated, the nephelometric units provided by the nephelometer can be calibrated to total iron concentration values. The iron concentration of the process water is a direct indicator of steel corrosion.

Background

As the process waters used in power generation are particularly pure, the majority of insoluble matter present in a ferrous metallurgy process stream is due to steel corrosion in the form of particulate or colloidal iron oxides. Corrosion of steel components in power generation is generally found as iron(II, III) oxide (magnetite), α-iron(III) oxide (hematite), or dissolved iron. Each of these three species produces a different nephelometric response. Black magnetite absorbs more and reflects less light than red hematite. Dissolved iron does not produce any nephelometric response. Furthermore, these oxide particles may be present over a range of diameters. Nephelometers respond differently to different particle sizes.

The variables associated with iron corrosion (species, color, particle size) make it impossible to create a universal nephelometric calibration for quantification of this corrosion. A nephelometric calibration which is appropriate for a particular sample location with particular corrosion characteristics will not be accurate for a different location with different corrosion characteristics. For instance, 5 µg/L of iron present as 1 µm hematite particles might produce a nephelometric response of 70 mNTU. A concentration of 10 µg/L iron present as 3 µm magnetite might produce the same 70 mNTU nephelometric response. A nephelometer calibrated with 1 µm hematite, but installed at a location where corrosion was present as 3 µm magnetite, would under report the iron concentration by 50% at 70 mNTU. This simple example could be complicated significantly if the iron present at each location were assumed to be a mixture of species at variable particle sizes, as is expected in real-life applications.

Quantification of total iron by nephelometry must be accomplished through site-specific calibration. Site-specific calibration ensures that nephelometric response is calibrated to the specific corrosion characteristics present at each installation. A specific calibration curve must be generated for each nephelometer installation, even at different locations within the same plant. Variability in water chemistry, phase, and local piping configurations contribute to variable corrosion characteristics.

Site-specific calibration requires on-site total iron determination. This means that each nephelometer installation for iron corrosion monitoring must be performed in tandem with the colorimetric total iron lab procedure, 10263. This procedure can be used to quantify total iron down to 0.7 µg/L. Grab samples taken from the nephelometer must be analyzed with the total iron lab procedure, and the nephelometric values for each sample calibrated with the determined total iron concentration.

Methods and Materials

The calibration and calibration procedure is conceptually simple, but requires careful and deliberate analytical technique. Accurate calibration is dependent upon proper performance of the ULR Total Iron procedure. Consequently, it is highly recommended that the user become familiarized and comfortable with this procedure prior to attempting the calibration.

Iron is one of the most common elements on Earth. It is present in and on many of the items commonly used in the laboratory. This pervasiveness makes iron contamination an ever present concern for ultra-low-range (ULR) determination. The ULR Total Iron procedure contains multiple notes and tips for minimizing iron contamination during the analysis. Additional tips for this procedure can be found in the Ultra Low Range Total Iron Method video available at Hach.com/power. Confidence with the procedure can be built through preparation and analysis of check standards as described in the analytical method.

Once the lab procedure is mastered, the calibration can be generated from a single data point obtained during steady-state process operation. During steady-state process operation the nephelometric response is generally very consistent, indicating consistent corrosion characteristics. Grab samples are taken at this point, analyzed for total iron with the lab procedure, and calibrated to the steady-state nephelometric value. The calibration of total iron to nephelometric value can be entered into the SC1000 controller or site DCS which can then be used to monitor iron corrosion directly.

Single point calibration is common in nephelometry as nephelometric response is very linear. In conjunction with the empirically determined absolute minimum nephelometric value for a given nephelometer (7 mNTU for the TU5400 and FT660), this linearity makes a single point total iron calibration possible. This is especially valuable for iron corrosion monitoring as there is only one steady-state nephelometric value associated with each nephelometer installation.

While steady-state processing generates a stable nephelometric baseline suitable for calibration, nephelometric data produced during dynamic processing are not suitable for calibration. Very large spikes in nephelometric response are always produced during process start-up or shutdown, whenever a valve in the sampling line is turned, or whenever the sampling line or nephelometer are disturbed. These activities will flush high concentrations of settled iron oxides through the process piping, creating a transient particulate slug. This slug of particulates is not stable enough for use in calibration, nor is it representative of the corrosion characteristics present during normal operation. As a result, even if it were possible to accurately sample this transient slug, the calibration generated from these samples would be inaccurate after the slug had passed. The converse is also true; the calibration generated using steady-state samples will be inaccurate during slug transport. This guide uses a steady-state based calibration because this basis provides the most useful data for monitoring real-time corrosion and the best means of measuring various corrosion treatment efficiencies. While slug peak concentration values will be inaccurate when using this calibration, the relative concentrations can still be used effectively for monitoring iron corrosion during slug transport. These relative concentration values can be used to monitor the effectiveness of corrosion treatment simply by comparing the relative peak heights.

The following instrumentation, apparatus, reagents, and documents are required for this procedure:

TU5400SC or FT660SC Laser Nephelometer with SC200 or SC1000 Controller	See Hach.com for available options
Stablcal® Turbidity Standard, 800 mNTU	2788453
Ferrozine® Iron Reagent Solution	230149
DR6000 or DR3900 Spectrophotometer	LPV441 or LPV440
DRB200 digestion block	DRB200-04
59 mL dropping bottle	2937606
20-mm digestion vials	LZP065
Pourthru Cell Kit	LZV899
Deionized water	27256
6.0 N hydrochloric acid	88449
1 mg/L iron standard	13949
Pipet, 0.2-1.0 mL	BBP078
Pipet, 1.0-5.0 mL	BBP065
Pipet tips, 0.2-1.0 mL	BBP079
Pipet tips, 1.0-5.0 mL	BBP068
FT660 Calibration Instruction Sheet	5236489, may be downloaded from Hach.com
ULR Total Iron Method 10263	DOC316.53.01492, may be downloaded from Hach.com

The total iron analysis must be performed in a fume hood. The Ferrozine® reagent is toxic and noxious. Sample waste contains Ferrozine® and must be handled appropriately according to site waste protocols

Procedure

Nephelometer Installation

1. Install the nephelometer and associated controller per the instructions in the FT660 user manual
   a. Minimize the distance between the process line and the nephelometer. Particulates will settle in transfer piping leading to artificially low results.
   b. Minimize elbows, tees, valves, and other pipe fittings which impede or alter flow. Particulates will settle around these fittings leading to artificially low results.
2. Regulate the flow to the nephelometer to 200-700 mL/min. Higher flow rates will minimize particulate settling in the sample line.
3. Perform the Stablcal® calibration as described in the nephelometer user manual.
4. Set the BUBBLE REJECT to YES.
5. Set the SIGNAL AVG to 6 SEC.
6. Set the DATALOG INTRVL to 30 SEC.
7. Set DATE/TIME.
8. Allow the mNTU signal to stabilize, at steady baseline of at least 30 minutes is recommended.

Grab Sampling

1. Build confidence in ULR Total Iron procedure.
   a. Follow notes and tips.
   b. Test quality check standards.
   c. Ensure that digestion vials are iron free. A 24-hour blank digestion must be performed prior to first use. This digestion will remove iron contamination from the vial itself. The blank can be prepared and left in the heated block over the weekend.
2. Prepare a blank using iron-free water.
3. Take 4 x 15 mL samples from the outlet of the nephelometer. Record the sampling time.
4. Digest and analyze all 5 vials together.

Calibration

1. Average the 4 grab sample results.
   a. Sample results for the 4 grab samples should agree within ±10% of the average.
   b. If sample results are outside of this range, repeat nephelometer stabilization and grab sampling.
   c. Variable results can be due to unstable baseline, sample or vial contamination, bubbles in the Pourthru cell, or accidental movement of the Pourthru cell or tubing.
2. Average the mNTU values for at least 30 min prior to the sampling time.

Correlation

1. Determine the calibration curve.
   a. The calibration will be the formula for a straight line, y=mx+b, where y is the total iron concentration, m is the slope of the curve, x is the nephelometric value, and b is the intercept.
   b. These variables are determined by the two known data points, the known absolute zero value for the nephelometer, and the point measured with the lab procedure. The following example uses the known FT660 zero point, (7mNTU,0ppb Fe), and an example measured steady-state point, (50mNTU,5ppb Fe).

      i. Calculate the slope, m.

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

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

      ii. Calculate the intercept, b.

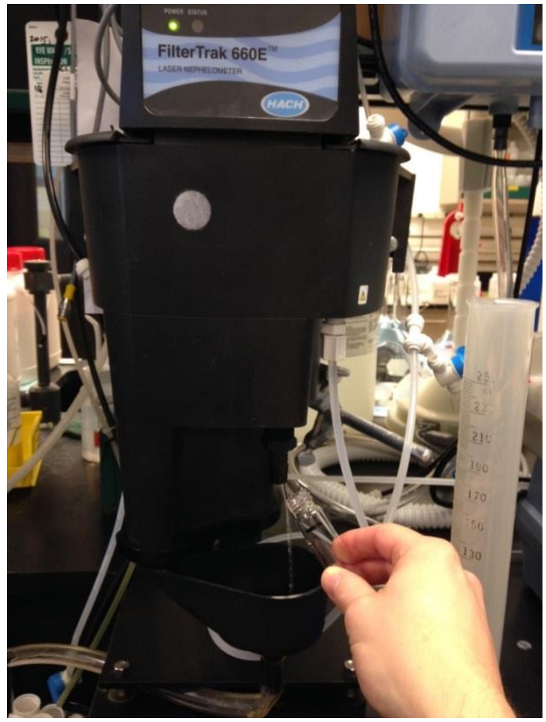
$$\mathrm{b} = \mathrm{y} - \mathrm{mx}$$
$$\mathrm{b} = 5 - 0.116 \times 50 = -0.8$$

      iii. Input the slope and intercept into to calibration curve.

$$\mathrm{y} = \mathrm{mx} + \mathrm{b}$$
$$[\mathrm{Fe}] = 0.116 \times \mathrm{mNTU} - 0.8$$

2. Input the curve into the controller or DCS. Refer to the SC1000 manual and the step-by-step instructions below for formula input instructions.

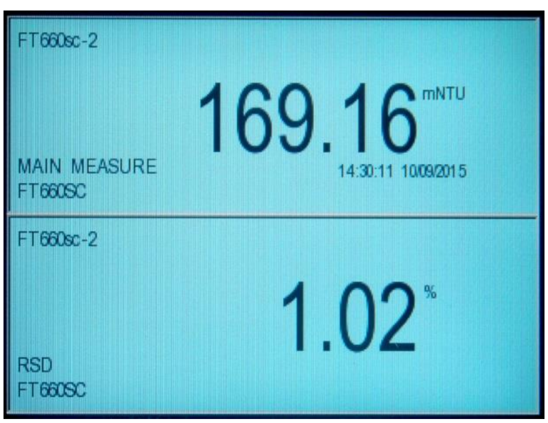
Illustrated Sampling Procedure



Sample from the nephelometer outlet

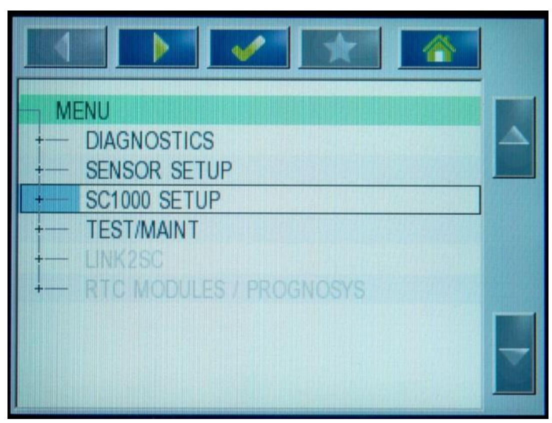
Programming a Formula in the sc1000

1



The formula will display the calculated iron concentration on the measurement value display.

2

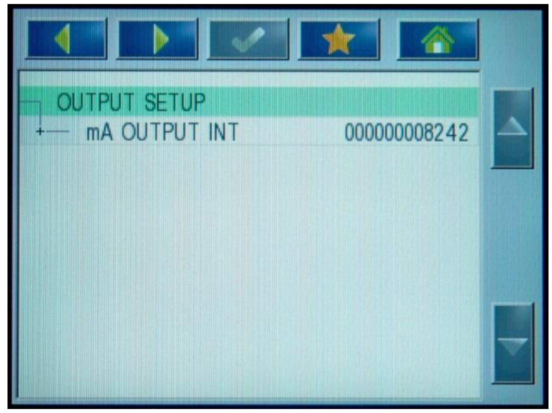


Select the SC1000 SETUP screen.

3

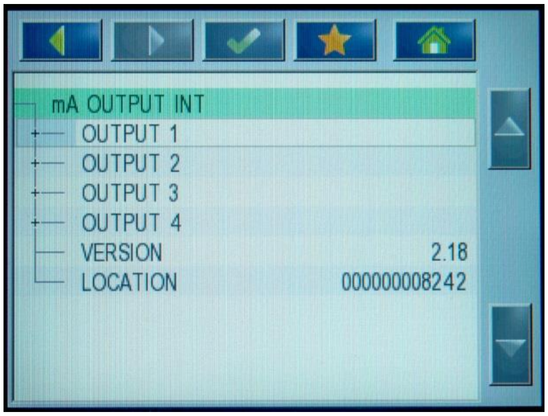
Choose either OUTPUT SETUP or RELAY. An output or relay card must be installed.

4



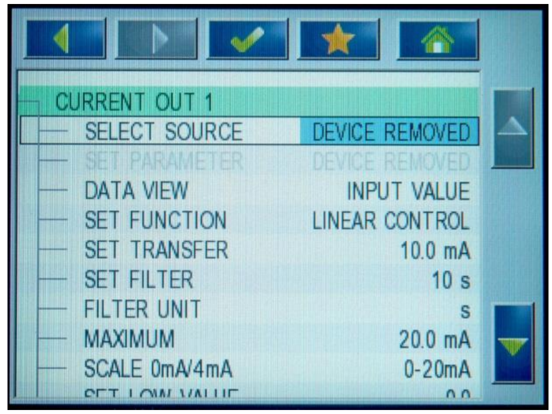
Select the location.

5



Choose the desired OUTPUT or RELAY.

6

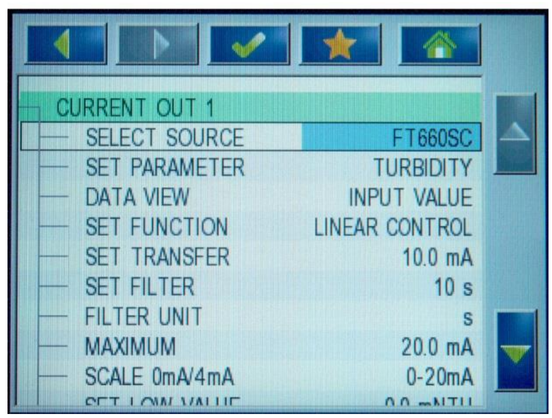


Choose SELECT SOURCE.

7

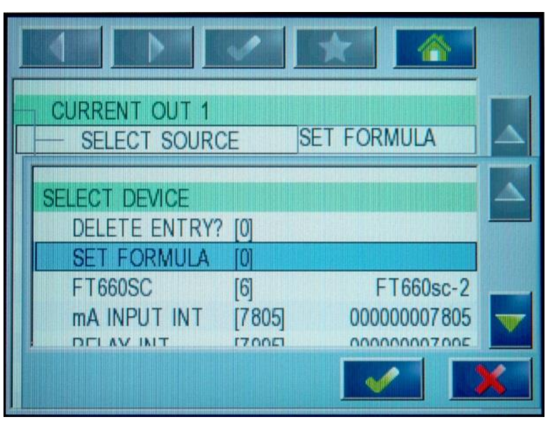
Locate and select the nephelometer.

8



Choose SELECT SOURCE again.

9



Locate and select SET FORMULA.

10

Choose ADD.

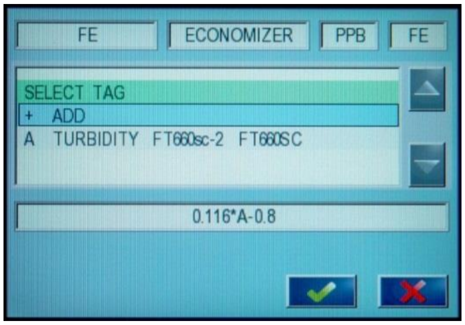
11

Enter the equation in the bottom line.

12

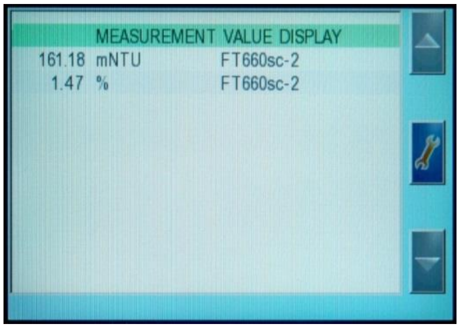
Modify the sample identification information.

13



The formula entry is complete.

14

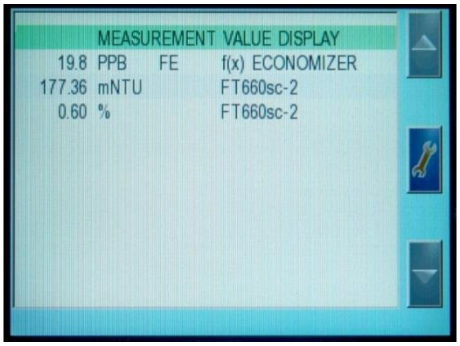


Press the List button to add the formula to the measurement value display. Press the WRENCH button to view display options.

15

Locate and select the formula. Add the formula to the measurement value display list.

16



The formula is added to the display list.

17

The measurement value display now shows the calculated iron value.

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