



Parameter and Sample Type

Color of Pulp Mill Wastewater at 465 nm.

Introduction

This method utilizes a spectrophotometer to measure the absorbance at 465nm wavelength. The method is adapted from the NCASI Technical Bulletin 803 for pulp and paper effluent¹ (which supersedes NCASI Technical Bulletin 253). The true color is determined in a sample with the pH adjusted to 7.6 ±0.05 pH and then passed through a 0.8 µm filter.

References

1. NCASI, Technical Bulletin No. 803, June 2000. <http://www.ncasi.org/Downloads/Download.ashx?id=3089>
2. Standard Methods for the Examination of Water and Wastewater, Method 2120B. www.standardmethods.org.
3. Orion AquaMate 7000 Vis and Orion AquaMate 8000 UV-Vis User Guide

Recommended Equipment

Thermo Scientific Orion AquaMate AQ8000 or AQ7000 spectrophotometer; Water filters, pore size 0.80-microns; Sample cell - 50 mm glass cell (Cole-Parmer Cat. No. R-83301-07), or 25 mm vial (Orion AC3V25), or 24 mm vial (AC2V24); pH meter; pH electrode.

Required Solutions

1. Platinum-Cobalt (Pt-Co) color standard solution, 500 PCU (Fisher SP120-500 or prepared by user²).
2. Pt-Co color verification standard(s), per SOP, or near the expected sample color.
3. Reagents for pH adjustment. Sodium hydroxide, 20%; Hydrochloric acid, 10%; pHydron buffer capsules (Fisher Cat. No. 15-420-2X), pH 7; pH 7.00 and 10.01 Buffers.
4. Deionized water (DI).

Solutions Preparation

Prepare standards by diluting an appropriate volume of the 500 PCU Pt-Co standard with DI water in 100 mL volumetric flask. For example, to prepare 50 PCU color standard, dilute 10 mL of 500 PCU Pt-Co color standard with DI water in 100 mL volumetric flask.

Meter Setup

Turn on the spectrophotometer. Allow warm up per the User Guide. Choose a convenient cell size (50, 25, or 24mm). For example, 24 or 25 mm cells are convenient and inexpensive, while a 50 mm cell may achieve a lower detection limit. Select the desired cell holder position by pressing the cell position key³. Access the USB memory stick using a computer. Depending on the sample cell size, copy the desired preprogrammed method* from the Orion folder to the Thermo folder. Remove the USB memory stick from the

computer and insert it into the USB port on the front of the AquaMate. Select the method and load it. Press Run Test to start the analysis.

Calibration Verification

1. Open the sample compartment and insert the sample cell containing DI water (the blank) into the sample holder with the orientation mark forward (for round vials). Close the lid and press the Measure Blank key.
2. Empty and fill the same cell** with the prepared color standard (e.g. 50 PCU), and insert it into the sample holder, with the orientation mark facing forward. Close the lid, and press the Measure Sample key. Record the displayed result.
3. The reading for the calibration verification standard should be within the desired criteria, per your QA plan.

Sample Storage

Samples are not preserved prior to analysis, as a change in pH can greatly affect the resulting color determination. Samples should be refrigerated prior to analyses (4°C) as soon as possible after sample collection. Refer to 40 CFR Part 136.3 for EPA compliance requirements.

Sample preparation

Before the color measurement, measure and record sample initial pH, then adjust it to the pH 7.6 ±0.05 (see details on page 2), if necessary. After the pH adjustment, pass the sample through a 0.8 µm filter. Prepare a method blank from the deionized water using the same pH adjustment and filtration procedure as for a sample.

Sample Cell Storage and Cleaning

In order to obtain reproducible results, clean and store sample cells per instructions in the Orion AquaMate User Guide.

Sample measurement

Clean the cell by rinsing three times with DI water. Fill the clean sample cell with about 10 mL of a sample or a method blank. Open the lid, insert the sample cell into the holder, close the lid, and press the Measure Sample key. Record the displayed result. The results can be saved to the USB stick, if desired. If reading is >500 PCU, dilute and retest. Multiply the reading by the dilution factor.

Quality Control (QC)

Run a calibration verification, duplicate samples, and method blank (if filter samples) with each batch or per your QA plan.

*For 50mm cell - CLRPTP50, for 25mm - CLRPTP25, for 24mm - CLPTP24. To make your own method, use the Standard Curve application described in the section 20 of the AquaMate User Guide.

**For best accuracy, use the same sample cell for measuring the standard, the blank, and the samples.

pH Adjustment of Sample

1. Calibrate the pH probe in pH 7.00 and 10.01 buffers.
2. Warm color sample up to room temperature.
3. Shake the sample to insure homogeneity.
4. Measure 50 mL of the sample to a 100-mL beaker using a graduated cylinder.
5. Immerse the pH probe in the sample and record the initial pH.
6. Empty one-half of a pH 7 pHydrion buffer capsule to the sample. Stir until the buffer has dissolved. Adjust the sample pH to 7.6 ± 0.05 by adding 20% NaOH or 10% HCl solutions dropwise. Different strength acid and base can be used if needed.
7. Note that the overall volume change should not be greater than 1% (0.5 mL). Discard and re-prepare if the volume changes more than 1%.
8. Record the adjusted pH. Filter the sample through a 0.80-micron filter.

Results of Color Testing by Platinum-Cobalt Method for Pulp Mill Water on the Orion AQ7000 and AQ8000 Spectrophotometers

Bias: readings of color standards in various light path length cells on AQ8000 and AQ7000 demonstrate good accuracy:

- Low level standards (0 to 50 PCU) gave readings within ± 2 PCU of expected values.
- High level standards (250 PCU and 500 PCU) gave readings within $\pm 2\%$ of expected values.

Precision: water sample readings at various color values on the AQ8000 and AQ7000 demonstrate good precision.

- Filtered (true color) readings for a turbid sample and a stream sample showed precision near or less than 1.5% relative standard deviation (RSD). See precision chart below.

Sample cell path length and precision: readings of true color in different surface water samples (see chart below) indicate good agreement between various cells (50mm, 25mm, and 24mm) and both meters. Good readings are achieved in all cases.

- True color readings on two different meters and three different cell sizes all agree to within 1.2% RSD for turbid sample and 1.3% RSD for stream water. Therefore, both meters and all three cell sizes give similar readings. See sample cell pathlength chart below.

