APPLICATION NOTE

# Color of pulp mill wastewater at 465 nm

#### **Key words**

Color units, true color, turbidity, filtration, pH stability, spectrophotometer, platinum cobalt, pulp mill wastewater, colorimetry, 465 nm wavelength, NCASI, Bulletin 803, effluent

#### Goal

This application note utilizes a Thermo Scientific<sup>™</sup> Orion<sup>™</sup> AquaMate<sup>™</sup> UV-Vis or Visible-Only Spectrophotometer to measure the absorbance of color in pulp mill wastewater at 465 nm wavelength.

#### Introduction

This method utilizes a spectrophotometer to measure the absorbance of color in pulp mill wastewater at 465 nm wavelength. The method is adapted from the NCASI Technical Bulletin 803 for pulp and paper effluent<sup>[1]</sup>, which supersedes NCASI Technical Bulletin 253. The true color is determined in a sample with the pH adjusted to 7.6  $\pm 0.05$  and then passed through a 0.8  $\mu m$  filter.

#### **Equipment**

- Orion AquaMate UV-Vis Spectrophotometer or Orion AquaMate Visible-Only Spectrophotomer
- Water filters, pore size 0.80 µm
- Sample cell: 50 mm glass cell, 25 mm vial (Cat. No. AC3V25), or 24 mm vial (Cat. No. AC2V24)
- pH meter
- pH electrode



#### **Solutions**

- Platinum-Cobalt (Pt-Co) color standard solution,
  500 PCU (purchased separately or prepared by user<sup>[2]</sup>)
- Pt-Co color verification standard(s), per SOP, or near the expected sample color
- Reagents for pH adjustment: sodium hydroxide, 20%;
  hydrochloric acid, 10%; Hydrion™ pH 7.00 buffer capsules
- pH 7.00 and 10.01 buffers
- Reagent-grade water (RGW)



#### **Solutions preparation**

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

#### **Meter setup**

- Turn on the spectrophotometer. Allow the Orion AquaMate Visible Spectrophometer to warm up per the user guide. The Orion AquaMate UV-Vis Spectrophotometer does not require warm up.
- Choose a sample cell size (50, 25, or 24 mm). For example, 24 or 25 mm cells are convenient and inexpensive, while a 50 mm cell may achieve a lower detection limit.
- 3. Depending on the sample cell size, locate and select the desired preprogrammed method\* from the AquaMate Orion methods menu<sup>[3]</sup>.

#### **Calibration verification**

- Open the sample compartment and insert the sample cell containing RGW (the blank) into the sample holder with the orientation mark forward (for round vials).
   Close the lid and press Blank.
- 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 Measure. Results will be logged automatically.
- 3. The reading for the calibration verification standard should be within the desired criteria, per your QA plan.

#### Sample storage and preparation

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 analysis (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  $\pm$  0.05 (see details under "pH adjustment of sample"), if necessary.

After the pH adjustment, pass the sample through a  $0.8 \mu m$  filter. Prepare a method blank from RGW 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 cell(s) per instructions in the Orion AquaMate User Guide.

#### Sample meaurement

Clean the cell by rinsing three times with RGW. Fill the clean sample cell with about 10 mL of a sample or a method blank. Open the meter lid and insert the sample cell into the sample holder, close the lid, and press Measure. The results will be logged automatically and can be exported directly to a network location or can be saved to a 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.

#### pH adjustment of sample

- 1. Calibrate the pH probe in pH 7.00 and 10.01 buffers.
- 2. Warm color sample to room temperature.
- 3. Shake the sample to ensure homogeneity.
- 4. Add 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. Add one-half of a pH 7.00 Hydrion buffer capsule to the sample. Stir until the buffer has dissolved. Adjust the sample pH to 7.6  $\pm$  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 prepare again if the volume changes more than 1%.
- 8. Record the adjusted pH. Filter the sample through a 0.80  $\mu$ m filter.

## Results of color testing by platinum-cobolt method for pulp mill water on Orion AquaMate spectrophotometers

**Bias:** readings of color standards in various light path length cells on Orion AquaMate spectrophotometers demonstrate good accuracy.

- Lower-level standards (0 to 50 PCU) gave readings within ±2 PCU of expected values.
- Higher-level standards (250 PCU and 500 PCU) gave readings within ±2% of expected values.

**Precision:** water sample readings at various color values on Orion AquaMate Spectrophotometers 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 Figure 1.

Sample cell path length and precision: readings of true color in different surface water samples (see Figure 2) indicate good agreement between various cells (50 mm, 25 mm, and 24 mm) 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.

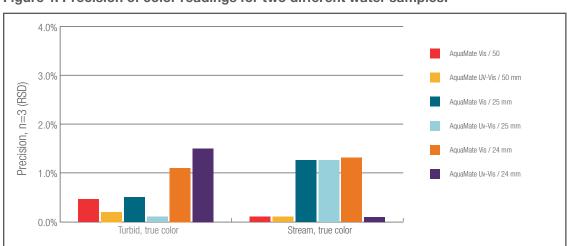
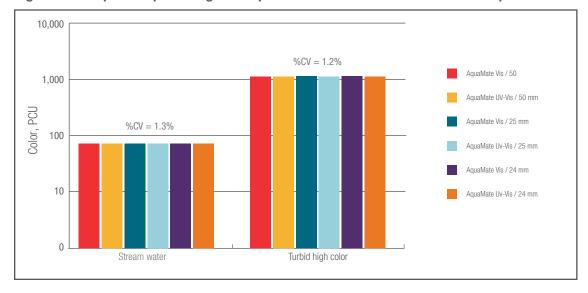


Figure 1. Precision of color readings for two different water samples.

Figure 2. Sample cell path length and precision for two different water samples.



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- \* For 50 mm cell, use CLRPT50; for 25 mm cell, use CLRPT25; for 24 mm cell, use CLRPT24. To make your own method, please refer to instructions in your Orion AquaMate User Guide.
- \*\* For best accuracy, use the same sample cell for measuring the standard, the blank, and the samples.

#### References

- NCASI, Technical Bulletin No. 803, June 2000. https://www.ncasi.org/resource/ technical-bulletin-no-0803-an-update-of-procedures-for-the-measurement-of-color-inpulp-mill-wastewaters/
- Standard Methods for the Examination of Water and Wastewater, Method 2120B. www.standardmethods.org.
- 3. Orion AquaMate Vis and Orion AquaMate UV-Vis User Guide.

To purchase Orion AquaMate meters, electrodes, and solutions, please contact your local equipment distributor and reference the Cat. Nos. listed below:

Product	Cat. No.
Instruments	
Orion AquaMate UV-Vis Spectrophotometer	AQ8000 / AQ8100
Orion AquaMate Visible Only Spectrophotometer	AQ7000 / AQ7100
Orion pH Meter	Multiple
Orion pH Electrode	Multiple
Accessories	
Orion AQUAfast 24 mm Round Vials (12 pack)	AC2V24
Orion AQUAfast 25 mm Round Vials (12 pack)	AC3V25
Nalgene 100 mL Polypropylene Copolymer (PPCO) Volumetric Flask	4000-0100
Nalgene Polypropylene Graduated Cylinder, 50 mL	3662-0050
Nalgene Polypropylene Beaker, 100 mL	1201-0100
Consumables	
Orion pH 7.0 Buffer	910107
Orion pH 10.01 Buffer	910110
Reagent-grade water	
Barnstead Smart2Pure 12 UV Water Purification System	50129890*

<sup>\*</sup>Please contact your local Thermo Fisher Scientific representative for support to order the best water purification system for your application, and visit our website at thermofisher.com/labwater.

