NCASI METHOD COLOR 71.01

COLOR MEASUREMENT IN PULP MILL WASTEWATERS BY SPECTROPHOTOMETRY

NCASI
West Coast Regional Center
Organic Analytical Program
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Acknowledgments

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This method is included in the NCASI Methods Manual as an update to NCASI Method 253. The purpose of including this updated method in the NCASI Methods Manual is to make it known that a method revision is under development and to solicit comments regarding the technical merit and applicability of the revised method. Those electing to apply the method are strongly encouraged to conduct rigorous QA/QC or validation so that the quality of the data generated can be evaluated.

NCASI METHOD COLOR 71.01

COLOR MEASUREMENT IN PULP MILL WASTEWATERS BY SPECTROPHOTOMETRY

1.0 Scope and Application

1.1 This procedure utilizes a spectrophotometer to measure the absorbance of light as it passes through a sample. The color is determined by comparison of the absorbance of the sample to the absorbance of colored solutions of known concentrations. The colored solutions used in this procedure are platinum cobalt stocks. The unit of color is the color produced by 1 mg platinum/liter in the form of the chloroplatinate ion, or PCU.

The term "color" represents the true color of an aqueous sample from which turbidity has been removed (1). Turbidity can cause the color value determined for a sample to be elevated due to an increase in light scattering. In this procedure, filtration is used to remove turbidity from the sample. The optimal method for removing turbidity without affecting the color value determined has not been found, but filtration using a 0.8-micron (µm) membrane filter has been demonstrated to be effective for most pulp mill effluent samples.

The color value determined for a specific sample is pH dependent and increases as the pH of an aqueous sample increases. Therefore, a buffer is used to stabilize pH during the filtration and measurement process.

1.2 This method has been validated at the single and inter-laboratory level in wastewater treatment plant influents, biologically treated effluents from kraft pulp and paper mills, and receiving waters. Demonstration of method performance for specific matrix types is recommended.

1.3 The estimated method detection limit (MDL) achievable is instrument and light path length dependent and was found to be 4 PCU for a river water sample using a 10-mm light path length (2). The MDL determined in a kraft mill treated effluent was found to be 7 PCU using a 10-mm light path length. These values are provided as guidance. Due to improvements in instrumentation and changes in matrix effects, each laboratory should establish its own MDL. The lower instrument calibration limit (LCL) for this method is approximately 10 PCU. Lower calibration levels can be obtained by using an increased light path length. The concentration range used during the single and inter-laboratory method validation was from 10 to 500 PCU. Sample values above 500 PCU may be determined by quantitative dilution.

2.0 Summary of Method

2.1 Biologically treated effluents and wastewater influents

Place a 50-mL aliquot of unpreserved influent (effluent) into a 100-mL beaker. Measure the initial pH of the sample and add approximately one-half of the solid from a pH 7 buffer capsule. Dissolve the buffer capsule completely using a mechanical stir plate and stir bar. Add an appropriate amount of sodium hydroxide solution (NaOH) or hydrochloric acid (HCl) to adjust the pH to 7.6 ±0.05. Filter the sample through a 0.8-µm membrane filter. If the analyst cannot filter the sample through the membrane because of significant clogging, a pre-filtration step may be added prior to pH measurement and adjustment. To verify pH stability, periodically measure the post-filtration pH.

2.2 Quantitative analysis

Assess the color load by measuring the absorbance of the solution in a spectrophotometer set at a wavelength of 465 nanometers (ηm). Calculate the color units using the linear regression equation developed in Section 12.1.

2.3 Quality assurance

Quality is assured through reproducible calibration and testing of the sample preparation and spectrophotometer system. A method blank is analyzed with each sample set (samples started through the process on a given day, to a maximum of 20, along with sample duplicates to ensure quality data). A complete description of quality control procedures, calculations, and method performance criteria are listed in Sections 9.0 and 10.

3.0 Definitions

3.1 These definitions are specific to this method, but conform to common usage as much as possible.

3.1.1 PCU—platinum cobalt color unit

3.1.2 May—this action, activity, or procedural step is neither required nor prohibited

3.1.3 May not—this action, activity, or procedural step is prohibited

3.1.4 Must—this action, activity, or procedural step is required

3.1.5 Should—this action, activity, or procedural step is suggested, but not required

4.0 Interferences

4.1 Reagents, glassware, and other sample processing hardware may contribute analytical interferences resulting in inaccurate absorbance readings. Run method blanks initially and with each subsequent sample set to demonstrate that the reagents, glassware, and other sample processing hardware are free from interferences under the conditions of the method.

4.2 Turbidity causes the measured color value to be greater than the true color value. Therefore, it is necessary to remove turbidity in the sample prior to measuring the sample's absorbance in a spectrophotometer. Interferences will vary considerably from source to source, depending on the diversity of the site being sampled. This procedure recommends the use of a 0.8-µm membrane filter to remove turbidity prior to measuring the absorbance in the spectrophotometer. As needed, the analyst can pre-filter the sample with a 1.0 µm glass fiber filter or use more than one 0.8-µm membrane filter if clogging prevents the sample from readily passing through the membrane filter.

4.3 The color value determined for a given sample is highly pH dependent. As pH increases the color value determined for the sample also increases. Therefore, stabilization of the pH at a given value for all measurements is required. This procedure is conducted with the sample at a pH of 7.6 ±0.05 to maintain consistency with standard methods currently in use.

4.4 All glassware must be clean and free of scratches. In addition, the cells used for spectrophotometric measurement of the samples must be free of all oil or residue that may cause interference in the absorbance measurement. It is recommended that the same cell be utilized for the measurement of the calibration curve, daily calibration checks, blanks, and samples.

5.0 Safety

5.1 Each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to a level protective of human health. This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses.

5.2 The platinum cobalt solution is corrosive and a suspected carcinogen. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) are also corrosive and should be handled with caution. Take appropriate measures to avoid contact with the chemicals by wearing chemical-resistant gloves, eye protection, and other protective clothing.

5.3 As with all samples, precautions should be taken to avoid exposure to potentially toxic, caustic, or nuisance odor compounds. Samples should be handled with gloves and opened in a fume hood.

6.0 Equipment and Supplies

Note: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 A spectrophotometer with a tungsten lamp source and a 10-ηm spectral slit width is required. The instrument must be capable of emitting light at a selectable wavelength of 465 ηm with an operating range of 400 to 700 ηm. Verify that the spectrophotometer is calibrated correctly by following the directions from the manufacturer for your specific instrument.

6.2 Do not use glassware with any star fractures, cracks, or severe scratches. All glassware should be washed with detergent, rinsed with tap water, then rinsed with reagent grade water prior to use.

6.3 Equipment for sample preparation

6.3.1 Filtration apparatus consisting of a flask, a vacuum source, and a filtration holder that will accommodate a 47-mm filter

6.3.2 Pasteur pipettes

6.3.3 50-mL graduated cylinder

6.3.4 Teflon™-coated stir bar

6.3.5 100-mL beaker

6.3.6 47-mm, 1.0-µm glass fiber filters for pre-filtration

6.3.7 47-mm, 0.8-µm membrane filters

6.4 Other apparatus

6.4.1 pH meter calibrated using a two-point calibration procedure at pH 7 and pH 8 using the appropriate buffer solutions

6.4.2 Magnetic stirrer

6.4.3 Sample cuvettes (absorption cell) for the measurement of absorbance, cell path length is determined by the required MDL, refer to Table 1 for the path length specific MDLs (3)

7.0 Reagents and Standards

7.1 Reagents

7.1.1 Metrepak pHydrion buffer capsules, or an equivalent supplier (dibasic sodium phosphate and monobasic potassium phosphate, pH 7.0), to stabilize sample pH

7.1.2 Organic-free reagent water in which color is not detected by this method

7.2 Standards

7.2.1 Fisher or an equivalent supplier, platinum cobalt color standard, 500 PCU stock

7.2.2 If a reliable source of platinum cobalt color standard is not available, prepare a solution of potassium chloroplatinate. Dissolve 1.246 g of potassium hexachloroplatinate, K_2PtCl_6 (Aldrich or an equivalent supplier), and 1.00 g of crystallized cobalt (II) chloride hexahydrate, $CoCl_2 \cdot 6\ H_2O$ (Aldrich or an equivalent supplier), in a portion of organic free reagent water containing 100 mL of concentrated HCl. Dilute this solution with distilled water to the desired color value. For example, dilution to 1000 mL will provide a standard with a color value of 500 PCU. Dilution to 500 mL will provide a standard with a color value of 1000 PCU.

7.2.3 Prepare a five-point calibration curve encompassing the sample concentration range. Prepare a calibration curve by diluting 5, 10, 20, and 50 mL of 500 color unit stock solution of platinum cobalt in 100 mL of deionized water. Include the absorbance measurement of the 500 color unit stock solution of platinum cobalt in the curve. The prepared calibration standards will have color units of 25, 50, 100, 250, and 500. It is necessary to prepare a calibration curve that brackets the expected values of color in the samples.

7.2.4 Stock solutions of the color standards do not need to be refrigerated, but care should be taken to protect the standards from evaporation, light, and contamination when not in use. Remember that the color standard solutions have pHs less than 2.0 and should be handled with care. Stock solutions of all standards should be checked for signs of concentration or formation of precipitates prior to the preparation of calibration or performance test standards. Replace the stock solutions if a change in concentration is indicated by the inability to meet the criteria specified in Sections 9.2 and 10.3.

7.3 Reagents for sample preservation and pH adjustment

7.3.1 Sodium hydroxide, ACS reagent grade, is used to adjust sample pH during processing. Prepare a 20% solution by adding 20 grams of sodium hydroxide pellets very slowly to 100 mL of reagent grade water using a stir bar and stir plate. Because this reaction is exothermic, take care that the heat generated by the addition of the NaOH to the water does not break the glassware.

7.3.2 Hydrochloric Acid, ACS reagent grade, is used to adjust sample pH during processing. Prepare a 10% solution by adding 10 mL of concentrated HCl to approximately 85 mL of reagent grade water using a stir bar and stir plate. Bring the volume to 100 mL once the heat has dissipated.

8.0 Sample Collection, Preservation, and Storage

8.1 Sample collection

Collect grab or composite samples using clean sampling containers that are free from contaminants which may interfere with the analyses. Composite samples should be refrigerated during the sampling period. The color determination should be made as soon as possible following sample collection. An assessment of sample stability should be done on a matrix specific basis since biological changes which can occur during storage may affect the color and alter the pH of the sample.

8.2 Sample preservation

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). Sample refrigeration should occur as soon as possible after sample collection.

9.0 Quality Control

9.1 Each laboratory that uses this method should operate a formal Quality Assurance Program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and ongoing analyses of standards and blanks as a test of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.2 Spectrophotometer performance and calibration verification

9.2.1 Fill the sample cuvette with reagent grade water and place it in the spectrophotometer. Adjust the absorbance reading to zero. Verify zero after every four to six samples using the same process.

9.2.2 Determine that the spectrophotometer system is operating within acceptable parameters by conducting a calibration check before each set of analyses

(samples started through the measurement process on a given day). The calibration check involves reanalyzing one of the standard calibration solutions used to prepare the calibration curve (Sections 7.2.3 and 10.3). The percent recovery determined for the calibration check should be within the calculated warning limits (Section 17, Table 2). The color determination may be sensitive to spectrophotometer and cell conditions such as dirty glassware. If the calibration check fails to meet the acceptance criterion, locate a new sample cuvette or perform appropriate maintenance and reanalyze the calibration check sample. If this fails to correct the calibration verification difficulties, the calibration curve should be re-prepared and analyzed.

9.2.3 Verify that the spectrophotometer is calibrated properly by periodically measuring an independent color standard check sample. If all calibration checks and adjustments fail to correct the problem, calibrate the instrument electronically. Electronically calibrate the instrument by first selecting the transmittance option and setting the wavelength to 450 ηm. With the 100% T/Zero control, set the display to read 100.0, insert an occluder in the sample well, and close the cover. Adjust the %T adjustment knob to read exactly 0.0 and remove the occluder.

9.3 Frequency

One sample per analytical batch of no more than twenty samples of similar matrix type should be allocated for quality control (i.e., duplicate analyses). A representative sample from each new or untested source or sample matrix should be treated as a quality control sample.

9.4 Blanks

9.4.1 Demonstrate that the analytical system is free of color by preparing and analyzing a blank with each sample set (20 samples or less). Prepare a method blank using the same procedure outlined in Section 11.0 utilizing reagent grade water for the sample.

9.4.2 If color is found in the blank at a value greater than 10% of the method detection limit or the lowest calibration limit, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

9.5 Sample and duplicate precision

Analyze a sample and duplicate for each matrix type with each set of samples to assess the precision of the analyses. Calculate the relative percent difference (RPD) in color for each sample and duplicate pair using Equation 1. The calculated RPD should be less than 14%.

Equation 1

$$Relative\ Percent\ Difference = \frac{(Highest\ Color\ Value - Lowest\ Color\ Value)\ x\ 100}{Average\ Color\ Value\ of\ the\ sample\ and\ duplicate}$$

A summary of the precision determined in the single laboratory validation is provided in Section 17, Table 3 for treatment system influent and biologically treated effluent samples. The average relative standard deviation for the single laboratory precision was 2.8% in biologically treated effluents and 7.1% in treatment plant influents. A summary of the accuracy and precision determined during an inter-laboratory validation is provided in Section 17, Tables 4 and 5 for treatment system influent, biologically treated effluent, and a receiving water sample.

9.6 Field replicates and field spikes

Depending on specific program requirements, field replicates may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1 Zero the spectrophotometer (Section 9.2.1) and establish the operating conditions outlined below. Use the same operating conditions to analyze all samples, blanks, calibration curves, and calibration verification samples.

10.2 Quantitation

10.2.1 Analyze the calibration standards (Section 7.2.3) at a wavelength of 465 ηm using the procedure described in Section 11.2.3. Construct a calibration curve by plotting the absorbances and the color units of the calibration curve points. An example of a calibration curve plot is located in Section 17, Figure 1.

10.2.2 If the r-squared value determined for the curve is 0.991 or greater, the calibration curve is assumed to be linear and acceptable. The linear equation determined from the curve can then be used to calculate sample color (Section 12.1). If the curve is not linear, evaluate the problem, undertake the appropriate remedial action, and reanalyze the calibration curve solutions. If remedial actions and reanalysis fail to produce an r-squared value of at least 0.991, prepare new calibration curve solutions and analyze them. The statistics for calibration curve linearity determined during a single laboratory validation of this method are included in Section 17, Table 6.

10.3 Verify calibration prior to the analysis of each set of samples (Sections 9.2). Analyze one of the calibration standards (Section 7.2.3) prior to the analysis of each set of samples. It is recommended that the selected calibration standard vary over time in order to verify the calibration of the instrument over the full calibration range of the

method. Recalibrate if the percent recovery for the color standard of the analyzed calibration solution is outside of the warning criteria (Table 2).

10.4 Process a blank with the curve to confirm that the glassware, sample cuvette, reagents, and other components are free from contamination. Prepare the blank with deionized water using the procedure for the preparation of the samples (Section 11).

10.5 Demonstrate that color is detectable at the minimum level using the lowest level calibration curve solution and the same path length of the sample cuvette that will be used to analyze all curve points, calibration verifications, and samples.

11.0 Procedure

This section includes the procedures used to adjust pH, and filter the treatment plant influent and biologically treated effluent samples. The pH adjustment and filtering procedures are used for all types of samples and method blanks.

11.1 pH adjustment of the sample

11.1.1 Remove the sample from the refrigerator and allow the sample to come to room temperature. Calibrate the pH meter using a two-point calibration with pH 7 and pH 8 buffer solutions. Shake the sample to ensure homogeneity and immediately measure 50 mL of the sample using a 50-mL graduated cylinder. For method blanks, measure 50 mL of reagent grade water.

11.1.2 Measure and record the sample pH (initial pH). Gently open a pH 7 Metripak pHydrion (or equivalent) buffer capsule and add approximately one-half of the contents (powder only) to the sample. Stir until all of the buffer has dissolved. Reserve the remaining half of the buffer for the next sample. Adjust the sample pH to 7.6 ±0.05 by adding a small volume of sodium hydroxide solution (preferably 20%) dropwise. If the pH is adjusted slightly too high, hydrochloric acid (preferably 10%) may be added dropwise to readjust the sample pH. The sample aliquot must be discarded and re-prepared if the sample volume changes by more than 1% before the pH is within the desired range. Differing strength acid and/or base solutions may be used to meet this criteria. Record the adjusted pH.

11.1.3 Assemble an aspiration-type filtering apparatus and pre-wet a 0.8-µm membrane filter with approximately 1 mL of deionized and/or distilled water on each side of the membrane. Gently shake off the excess water, place the filter onto the filter support, secure the filter holder/funnel in place, turn the aspirator on, and slowly add the sample. A rapid decline in the rate of flow through the membrane or foam coming off the membrane filter, can indicate filter plugging. If the filter plugs, immediately replace the filter with a new filter pre-wet with deionized and/or distilled water, and continue filtering the remaining sample.

11.1.4 If filtration through the 0.8-µm membrane filter is excessively difficult, the 50 mL of sample can be pre-filtered through a 1.0-µm glass fiber filter prior to sample manipulation. Transfer the sample filtrate to a 100 mL beaker equipped with a Teflon stir bar. Place the beaker on a mechanical stir plate and gently stir the sample. Buffer, adjust pH, and filter through a 0.8-µm membrane filter as described in Sections 11.1.2 and 11.1.3.

11.2 Spectrophotometer analysis

11.2.1 The spectrophotometer conditions should be set according to the criteria described in Section 9.2.3.

11.2.2 Perform the calibration verification as outlined in Section 9.2.2.

11.2.3 Verify that the spectrophotometer is zeroed (Section 9.2.1). Rinse the cell with a small amount of the filtered sample. Discard the rinse. Transfer enough of the filtered samples to the sample cuvette, filling to the reference line. Measure and record the absorbance at 465 ηm and discard the sample. Rinse the cell thoroughly with deionized and/or distilled water. Periodically verify that the spectrophotometer is zeroed.

12.0 Data Analysis and Calculations

12.1 Quantitation

12.1.1 The linear regression equation from the calibration curve (Section 10.2) is used to calculate the corresponding color value of the samples. Calculate the color value in the sample using Equation 2.

Equation 2

$$y=mx+b$$

where:
y is the absorbance
m is the slope
b is the y-intercept
x is the calculated color value

Calculate the color units for each sample by utilizing the measured absorbance value and the linear equation derived from the calibration curve (Section 10.2).

12.1.2 The calibration curve slope and y-intercept will vary depending on the light path length of the sample cuvette used in each different spectrophotometer. Therefore it is important to use the same light path length for all measurements. The following is an example calculation from a calibration curve prepared in one laboratory.

Example Calculation:

Absorbance measured for the sample (y)	0.039
Equation	$y = 0.0003x + 0.0016$ $x = \frac{y - 0.0016}{0.0003}$
Substitution	$x = \frac{0.039 - 0.0016}{0.0003}$
Calculated Color Units (x)	x = 125 PCU

12.2 Data review requirements

12.2.1 Review the data to assess the accuracy and precision of the determined color value, spectrophotometer problems, interferences, and bias using the guidance provided in Section 9.0 and 10.0. Correct any problems prior to reporting the analytical results.

12.2.2 Assess the need for sample dilutions. The procedure for conducting sample dilutions and reanalysis is described in Section 12.3.

12.2.3 Resolve inconsistencies between duplicates as necessary.

12.2.4 If review of the data shows any problems which could affect subsequent analyses, discontinue the analyses until the problems are resolved.

12.3 Results outside the calibration range

If the calculated color value exceeds the highest color calibration point, dilute an aliquot of the sample with reagent grade water prior to sample processing to bring the concentration within the calibration range of the method and continue the sample preparation process from Section 11.

13.0 Method Performance

Single laboratory performance for this method is detailed in Section 17, Tables 2, 3, and 6. Acceptance criteria were established from an inter-laboratory study using the draft method. The data from this study are given in Tables 4 and 5.

14.0 Pollution Prevention

Pollution prevention approaches have not been evaluated for this method.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 Instructions for sample and waste handling and disposal

15.2.1 Dispose of all samples as required by federal, state and local regulations.

15.2.2 Neutralize the sodium hydroxide solution and pour it down the drain with copious amounts of water.

15.2.3 Neutralize the calibration standard solutions to pH 7 and pour the aqueous portion of the extracted sample aliquot down the drain with copious amounts of water.

15.3 For further information on waste management, the Environmental Protection Agency suggests you consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*. Both are available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC, 20036.

16.0 References

1. *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, American Public Health Association, Washington, DC, 1998, 2-1 to 2-8.

2. *Federal Register*, "Appendix B to Part 136-Definition and procedure for the determination of the method detection limit-revision 1.11." Vol. 49, No. 209. October 26, 1984.

3. National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). *An investigation of improved procedures for measurement of mill effluent and receiving water color.* Technical Bulletin No. 253. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc. 1971.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Minimum Detectable Color for Various Light Path Length Sample Cuvettes

Sample Cuvette Light Path Length	Minimum Detectable Color Units
30	1
20	5
10	7[a]
5	10
1	25

[a] determined using a treated effluent from a kraft mill

Table 2. Daily Calibration Verification Criteria

Average Recovery[a] (%)	Standard Deviation[b]	Warning Limits[c] (%)	Action Limits[d] (%)	Color Unit Range (PCU)
94.9	6.7	81 - 108	75 - 115	10 - 500

[a] average recovery for 47 daily calibration checks
[b] standard deviation of the recoveries for 47 daily calibration checks
[c] average recovery plus or minus two times the standard deviation
[d] average recovery plus or minus three times the standard deviation

Table 3. Single Laboratory Precision: NCASI Color-71.01

Sample Type[a]	Range RPD[b]	Average RPD[c]
Effluent[d]	0.4 - 14.1%	2.8%
Influent[e]	0.1 - 13.2%	7.1%

[a] precision of the target analytes native to treatment system influents and biologically treated effluents
[b] range of relative percent differences observed between a sample and a duplicate
[c] pooled average relative percent difference for all sample and duplicate pairs analyzed
[d] range and average RDP for 12 duplicate pairs
[e] range and average RDP for 12 duplicate pairs

Table 4. Inter-Laboratory Accuracy[a]

Average Percent Recovery	Standard Deviation	Relative Standard Deviation (%)
94	10.6	11.3

[a] summary of the percent recoveries for a 125 PCU color standard analyzed by eight different laboratories using eight different spectrophotometers

Table 5. Results of an Inter-Laboratory Study Youden Pair Analyses to Assess Intra and Inter-Laboratory Precision

Parameter	Lignin Solution	Effluent Mill A	Effluent Mill B	Influent Mill A	Influent Mill B	Receiving Water Mill D
Number of Labs	7	7	6	6	7	6
Mean of Lab Averages	58.0	562	169	665	128	141
s(r) repeatability standard deviation	5.8	17.2	7.1	15.4	17.6	13.2
s(R) reproducibility standard deviation	13.9	95.2	22.1	87.7	44.8	25.6
RSD (r) repeatability relative standard deviation[a]	10.0	3.1	4.2	2.3	13.8	9.3
RSD (R) reproducibility relative standard deviation[b]	24.0	16.9	13.1	13.2	35.0	18.1

[a] intra-laboratory (repeatability) precision of the method

[b] inter-laboratory (reproducibility) precision of the method

Table 6. Calibration Curve Linearity

Linear Equation y = mx +b	R-squared	Light Path Length (mm)
y = 0.0153x - 0.0108	0.9981	10
y = 0.0003x + 0.0052	0.9968	10
y = 0.0003x + 0.0016	0.9999	10
y = 0.0003x + 0.0010	0.9997	10
y = 0.0005x + 0.0014	0.9999	20
y = 0.0003x + 0.0004	1.0000	10
y = 0.0005x + 0.0004	0.9999	20
y = 0.0003x + 0.0003	0.9999	10
y = 0.0003x - 0.0030	1.0000	10
y = 0.0005x + 0.0028	0.9988	20
y = 0.0006x - 0.0004	0.9999	25
y = 0.0014x - 0.0003	1.0000	50
y = 0.0027x + 0.0018	1.0000	100

Figure 1. Typical Calibration Curve

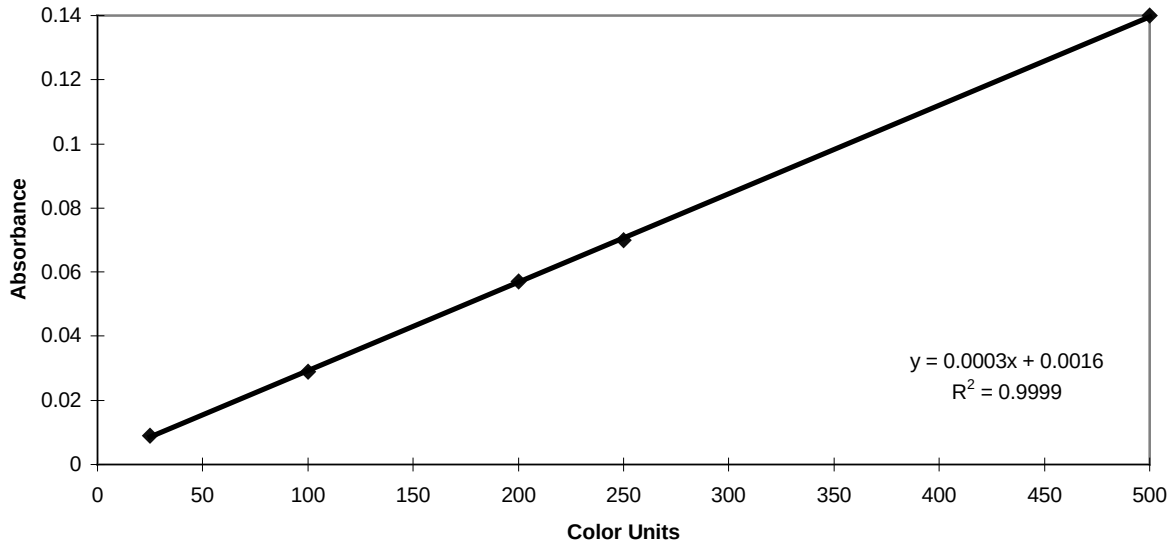

Figure 2. EPA Approval Letter

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

NOV 8 2001

Diana Cook
National Council for Air and Stream Improvement, Inc.
West Coast Regional Center
P.O. Box 458
Corvallis, OR 97339

OFFICE OF WATER

Dear Ms. Cook:

We are pleased to inform you that EPA's Statistics and Analytical Support Branch has determined that NCASI Method Color 71.01, "An Update of Procedures for the Measurement of Color in Pulp Mill Wastewaters," dated May 2000, (ATP Application # N01-0005) is an acceptable version of NCASI Method 253 which is currently approved at 40 CFR part 136. Consequently, NCASI Method Color 71.01 may be used in place of NCASI Method 253 for determining color under National Pollutant Discharge Elimination System compliance monitoring requirements.

Both methods use the same chemistry and analytical technique for determining color by spectrophotometer. NCASI Method Color 71.01 differs from NCASI Method 253 by incorporating a buffer to stabilize sample pH at the required 7.6 and allowing the use of a 1 micrometer glass fiber filter to reduce filter clogging (a 0.8 micrometer membrane filter is specified in NCASI Method 253).

We appreciate your interest in the development of environmental monitoring methods. If you have any questions regarding review of your method, please contact Khouane Ditthavong at (202) 260-6115 at your convenience.

Sincerely,

William A. Telliard, Director
Analytical Methods
Engineering and Analysis Division (4303)

cc: USEPA Regional Administrators (all Regions)
Quality Assurance Managers (all Regions)
Water Management Division Directors (all Regions)
ATP Coordinators (all Regions)
Maria Gomez-Taylor, U.S. EPA, SASB
Khouane Ditthavong, U.S. EPA, SASB
James Boiani, DynCorp I&ET, SCC