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SM2120B – Color – Visual Comparison Method

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1. Scope and Application

1.1. The Platinum-Cobalt method is useful for measuring color of potable water and water in which color is due to naturally occurring materials. It is not applicable to most highly colored industrial wastewaters. The platinum-cobalt method of measuring color is the standard method, the unit of color being that produced by 1 mg platinum/L in the form of the chloroplatinate ion.

1.2. This procedure is restricted to use by an analyst experienced in the operation of Hellige Aqua Tester. Additionally, the analyst must complete the requirements of the GA EPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GA EPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2. Definitions

2.1. Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

2.2. Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3. Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4. Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve. There is no ICV in this analysis.

2.5. Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6. Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK) or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7. LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision. In this method, the CCC results are used for LCS/LCSD for Labworks purposes.

3. Interferences

3.1. Even a slight turbidity causes the apparent color to be noticeably higher than the true color; therefore, remove turbidity before approximating true color by centrifugation or by filtration.

3.2. The color value of water is extremely pH-dependent and invariably increases as the pH of the water is raised. When reporting a color value, specify the pH at which the color is determined.

4. Safety

4.1. Refer to Laboratory Chemical Hygiene Plan & Fire Safety Plan, online revision.

5. Apparatus and Equipment

5.1. Sample Container: plastic half-gallon container
5.2. Hellige Aqua Tester
5.3. Hellige Color Disc # 611-11
5.4. #611-T Nessler Tubes
5.5. Suction Apparatus
5.6. #611-P1 Plungers
5.7. Gooch Crucible

5.8. 0.45µm pore size and 47 mm diameter Filter Paper Whatman PN#7184-004 or equivalent.
5.9. Lint free tissue
5.10. Glassware – Class A volumetric flasks, graduated cylinders and pipettes
5.11. Laboratory vacuum system
5.12. Approved pH meter, pH electrode and reference electrode with automatic temperature compensation.

6. Reagents

6.1. Reagent Water – Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18.2 [MΩ·cm] @ 25° C and a TOC of 50 µg/L or less).
6.2. Calibration Standard:
6.2.1. The No. 611-11 Color Disc reads directly in terms of APHA Platinum-Cobalt Units (CU).
6.3. Color Stock Solution (500 CU):
6.3.1. Hach Color Standard Solution 500 CU – Catalog no. 141453
6.3.2. Store standard at room temperature and in the dark when not in use.
6.3.3. This purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.
6.4. Laboratory Control Sample Solution (50 CU) also used for Continuing Calibration Check:
6.4.1. 100 ml of a Stock Solution (500 CU) is diluted to 1 L with reagent water for a final concentration of 50 CU.
6.4.1.1. Keep standard in the dark when not in use. Prepare fresh monthly.

6.5. 1:100 H_2SO_4 for adjusting pH:
6.5.1. In a 100 ml volumetric flask containing approximately 40 ml of reagent water, slowly and carefully pipette 1 ml of concentrated sulfuric acid(reagent grade), swirling while adding the acid to mix. Bring to final volume with reagent water.
6.6. 1:100 NaOH for adjusting pH:
6.6.1. In a 100 ml volumetric flask containing approximately 50 ml of reagent water, pipette 1 ml of 50% NaOH solution and bring to volume with reagent water.

7. Sample Collection

7.1. Samples are collected in opaque plastic half-gallon containers. No chemical preservation is required.

7.2. Samples must be stored at 0 – 6 °C (not frozen).

7.3. Holding time is 24 hours.

7.3.1. Samples analyzed outside of the holding time must be J qualified as estimated.

7.3.2. Comment as follows:

7.3.2.1. Color – SM2120B -<J>- Value Estimated – Sample was analyzed outside of the method required holding time of 24 hours.

7.3.2.2. If a source approval sample is J flagged for color and the result is above 10 CU, then the sample must be recollected.

8. Calibration

8.1. <u>Calibration Standards</u>:

8.1.1. The No. 611-11 Color Disc reads directly in terms of APHA Platinum-Cobalt Units at the following values: 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 100. One color unit is equivalent to the color of a solution containing 1 mg of Platinum/L.

8.2. <u>Calibration Curve</u>:

8.2.1. Not applicable.

8.3. <u>Calibration Verification</u>:

8.3.1. The Hellige Aqua Tester is checked against a Laboratory Control Sample (LCS) to verify the Hellige Color Disc# 611-11. For this method, there is no difference between a Continuing Calibration Check (CCC) standard and a Laboratory Control Sample (LCS). The LCS must be within 20% of its true value. A blank is also analyzed and must be less than the method RL.

9. Quality Control

9.1. Refer to Table 14.1for the Reporting Limits (RL), Table 14.2 for Quality Assurance Criteria and Table 14.3 for Quality Control (QC) procedures associated with this method.

9.2. Refer to reference 13.3 for training and certification procedures.

9.3. Refer to reference 13.4 for control charting procedures.

9.4. All Color acceptance criteria are static (i.e. not based on control charts).

9.5. Quality control limits are static, but control charts are created and reviewed twice per year for trend monitoring.

9.6. Color analyses are exempt from the requirement to perform MDL studies.

9.7. <u>Control Limits</u>

9.7.1. Because the LCS is essentially the same as a continuing calibration confirmation standard (CCC), the EPD Laboratory sets the default LCS control limits as static and a range of 80% - 120% recovery.

9.7.2. The EPD Laboratory sets the LCSD recovery to the same limits as the LCS recovery.

9.7.3. The EPD Laboratory sets the default precision limits for the LCS/LCSD to be 0 – 15% RPD (see calculation 11.2).

9.7.4. 10% of samples must be analyzed in duplicate. Precision of duplicates must agree within 15% RPD (see calculation 11.2).

9.7.5. The default control limits are presented in Table 9.4.5.1.

Table 9.4.5.1 Default QC Limits for SM 2120B

Analyte	**QC Type**	**Accuracy (%R) LCL**	**UCL**	**Precision (%RPD)**
Color	LCS/LCSD	80 -	120	15
	Duplicates	NA		15

9.8. Because the limits for this method are static, no Appendix A will be created for this SOP.

9.9. Duplicates must be analyzed at a frequency of 10% of all samples.

9.9.1. For batches of 1 – 9 samples, a minimum of one duplicate analysis is required.

9.9.2. For batches of 10 – 18 samples, a minimum of two duplicate analyses are required.

9.9.3. For sample duplicates, the entire procedure must be duplicated to assess method precision.

10. Procedure

10.1. Remove sample bottles, standards, and reagents from cold storage and allow equilibration to room temperature prior to sample preparation and/or analysis.

10.2. Perform backlog of pending samples. Batch samples in groups of 18 or less. At least 10% of samples must be analyzed in duplicate (see 9.6).

10.3. For each batch of samples, prepare an LCS (CCC), LCSD and Blank.

10.3.1. A Blank consists of an aliquot of reagent water of sufficient volume (approximately 100 ml) taken through the entire procedure, including filtration.

10.3.2. The LCS (CCC) and LCSD each consist of an aliquot of the LCS Stock Solution (500 CU) analyzed per steps 10.3.5.1 through 10.3.5.6.

10.3.3. Turn on the instrument lamp and warm up for 30 minutes.

10.3.4. All drinking water and source water samples will have previously had pH checks by SM4500-H+B (see reference 13.2). Record the pH found for each sample on the color worksheet.

10.3.4.1. If the pH was found to be outside of the range of 4 to 10, adjust the pH to 7 (between 6 and 8 is acceptable). If pH adjustment is necessary, comment the adjustment on the color test code in Labworks.

10.3.4.2 Adjust pH by adding 1:100 H_2SO_4 or 1:100 50% NaOH drop wise with stirring. Measure the pH with a pH meter calibrated as described in SM4500-H+B (batching and batch QC exempted for this adjustment).

10.3.5. <u>Procedure</u>:

10.3.5.1. Assemble filter assembly with a filter and wash the filter and assembly by passing at least 50 ml of reagent water through the filter.

10.3.5.2. Filter approximately 25 ml of sample. Discard the filtrate.

10.3.5.3. Filter about 50 ml through the same filter and retain for analysis.

10.3.5.4. Fill one of the Nessler tubes to the mark with filtered sample. Wipe down tube with lint free tissue paper and then insert plunger and place in right slot of Aqua Tester.

10.3.5.5. Fill the second Nessler tube to the mark with reagent water. Wipe down tube with lint free tissue paper, insert plunger and place in the left slot of Aqua Tester. Close back cover.

10.3.5.6. Make the color comparison by revolving the color disc. When a color match is obtained, the result is read directly from the figure seen in the circular opening within the light shield. The values can be between two readings: example 40-50 would read 45.

10.3.5.7. If the color exceeds 100 units, dilute sample with reagent water until the color is within the range of the color disk. Determine the Dilution Factor (DF) (see calculation 11.3.). Multiply color reading by this dilution factor.

10.3.5.8. For sample duplicates, the entire procedure (steps 10.3.5.1 through 10.3.5.6) must be duplicated to assess method precision.

10.3.5.9. Comment on all diluted samples: Reporting limit elevated due to high level of target analyte.

10.3.5.10. Rinse each Nessler tube thoroughly with deionized water between samples and wash with RBS and deionized water solution weekly.

11. Calculations

11.1. Percent Recovery:

$$\text{LCS (CCC), LCSD, ICV \%Recovery} = \frac{R_{spike}}{\text{Expected Result}} * 100$$

11.1.1. Where:

R_{spike} = Calculated spike concentration in CU

11.2. Duplicate or LCS/LCSD Precision:

11.2.1. *Relative Percent Difference (%RPD)*:

$$\%RPD = \frac{|R_{sample} - R_{duplicate}|}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} * 100$$

11.2.2. Where:

%RPD = Relative percent difference
R_{sample} = Result of the sample replicate
$R_{duplicate}$ = Result of the duplicate replicate

11.3. Dilution Factor:

$$\text{Dilution Factor} = \frac{\text{Volume}_{\text{final}}}{\text{Volume}_{\text{initial}}}$$

11.3.1. Where:
$\text{Volume}_{\text{final}}$ = Final volume after dilution
$\text{Volume}_{\text{initial}}$ = Initial volume of aliquot diluted

11.4. Sample Concentration Calculation:

11.4.1. Sample concentration is read directly from the dial and multiplied by a dilution factor, if necessary:

$$\text{Color (CU)} = \text{Color}_{\text{reading}} * \text{DF}$$

11.4.2. Where:
$\text{Color}_{\text{reading}}$ = Color (CU) read directly from the instrument
DF = Dilution Factor

12. Waste Management

12.1. See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures. See reference 13.5.

13. References

13.1. Standard Methods 2120B, Color by Visual Comparison Method, 2001, editorial revision 2011, 21st Edition.
13.2. GA EPD Laboratory SOP – SM4500-H+B – pH, SOP 3-003, online revision.
13.3. GA EPD Laboratory SOPs- Initial Demonstration of Capability SOP 6-001, online revision or later and/or Continuing Demonstration of Capability SOP 6-002, online revision.
13.4. GA EPD Laboratory SOP- EPD Laboratory Procedures for Control Charting and Control and Control Limits SOP, SOP 6-025, online revision.
13.5. GA EPD Laboratory SOP- EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.6. Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005 or later.
13.7. GA EPD Laboratory SOP- Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.
13.8. GA EPD Laboratory – Quality Assurance Manual, online revision.

14. Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14. 1 RLs for Method SM 2120B

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
SM 2120B	Color	5	CU

Table 14. 2 Acceptance Criteria for Method SM 2120B

QC Type	Analyte	Accuracy Water (%R)	Precision Water (%RPD)
CCC(LCS)[1]	Color	80-120	15
Sample Duplicate	Color (Sample Duplicate)	--	15

[1] *LCS/LCSD for this analysis are interchangeable with CCCs. Therefore control limits are static.*

Table 14. 3 Summary of Calibration and QC Procedures for Method SM 2120B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 2120B	Color	Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table 14. 2 and Initial Demonstration SOP	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	

Table 14. 3 Summary of Calibration and QC Procedures for Method SM 2120B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table, SOP 3-014 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.4)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Method Blank (MBLK)	Prior to sample analysis	Value must be < RL	Correct problem then analyze blank and all samples processed with the contaminated blank	If unable to re-analyze, flag with a "B"
		Continuing Calibration Check (CCC). CCCs are used for LCS/LCSD	Prior to analysis, after every 10 samples and at the end of the sample run	QC Acceptance Criteria Table 14. 2	Correct problem then reanalyze all samples associated with the out of control CCC	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run.	Value must be < RL	Correct problem then analyze blank and all samples processed with the contaminated blank	
		Sample duplicate	Minimum frequency of 10% of samples	QC Acceptance Criteria Table 14. 2	Evaluate out of control event and reanalyze sample	

Updates to Previous Version:
Section 2
Section 4
Section 13
Table 14.3