Kentucky Method 64-227-08
Revised 04/15/08
Supersedes 64-227-03
Dated 02/19/03

WATER-BORNE PRESERVATIVES

1. SCOPE: This test method covers water-borne timber preservatives used to treat wood that will be used in highway construction and maintenance. The chemical testing of water-borne timber preservatives is a modification of AWPA Method A2-71. Two methods are detailed in this method, "Wet Chemical Analysis" and "X-Ray Fluorescence" (preferred method).

2. SAMPLING: Preservatives shall be sampled and tested by the inspection company at the sources. When sampled by the Cabinet, a one-liter (quart) sample per lot will be taken and submitted to the Division of Materials. The test report for shipment of treated timber will show the laboratory approval number for the preservatives.

3. ALTERNATIVE WET CHEMICAL ANALYSIS AS STATED IN AWPA METHOD A2-71:

3.1. Apparatus/Materials:

3.1. Hydrogen Peroxide (30%)

3.2. Sulfuric Acid, Conc.

3.3. Perchloric Acid, 70%.

3.4. Nitric Acid, Conc.

3.5. Hydrochloric Acid, Conc.

3.6. Hypophosphorous Acid, 50%.

3.7. Potassium Bromate, 0.050N: dissolve 1.392 grams of pure dry potassium bromate in distilled water, and make up to 1.0 liter in a volumetric flask. For 0.100N, use 2.784 grams.

3.8. Methyl Orange: 0.1 percent water solution.

3.9. Ammonium Hydroxide, conc.

3.10. Alcohol, Methyl.

3.11. Potassium Iodine Solution, 20 percent: dissolve 20 grams KI in 80 ml of water.

3.12. Sodium Thiocyanate Solution, 20 percent: dissolve 20 grams NACNS in 80 ml of water.

3.13. Starch Indicator Solution: Make a paste of 1 gram soluble starch in about 5 ml water. Add 100 ml water, and boil, with stirring, until solution is clear. Cool, and add 1 drop of chloroform. This solution is subject to decomposition, and fresh solution should be made if a dark blue color is not produced when a drop is added to an iodide solution.

3.14. Acetic Acid, Glacial.

3.15. Copper foil, or shot: to be used for standardization of sodium thiosulfate solution.

3.16. Urea Solution - 5 percent: to be used in standardization of sodium thiosulfate solution. Dissolve 5 grams of urea in 95 ml water.

3.17. Sodium Thiosulfate Solution, 0.1N: purchase standard solution. For method of checking, see AWPA Methods.

3.18. Sodium Thiosulfate Solution, 0.01N: dilute 50 ml of standard 0.1N sodium thiosulfate solution to 500 ml in volumetric flask using freshly boiled distilled water which has been cooled to room temperature. This solution should be made up immediately before use.

3.19. Phosphoric Acid, 85% (Sp. Gr.- 1.71).

3.20. Barium Diphenylamine Sulfonate Solution: 0.20 g made up to 100 ml with water.

3.21. Ferrous Ammonium Sulfate - Sulfuric Acid Solution: 140 grams of ferrous ammomium sulfate, Fe $(NH_4)_2$.$6H_2O$ and 25 ml of concentrated sulfuric acid made up to one liter with water.***

3.22. Sulfuric Acid, 1:1 solution: add one volume of concentrated sulfuric acid slowly and with constant stirring to one volume of water. Cool before use.

3.23. Potassium Dichromate Solution, 0.2000N: weigh 9.807 grams of <u>dry</u> potassium dichromate into a 1 liter volumetric. Dissolve thoroughly, and dilute to 1 liter with water at room temperature. For 0.1000N, use 4.9035 grams of <u>dry</u> potassium dichromate.

3.2. Preparation:

3.2.1. Wet ashing of borings.

3.2.1.1. Add slowly two volumes of hydrogen peroxide (30%) to one volume of concentrated sulfuric acid. Mix well and cool.

3.2.1.2. Measuring from outside surface cut borings into 15 mm (0.6 inch) specimens. Count and divide into 2 or 3, 500 ml Phillips Beakers, depending on apparent concentration. To each beaker add 30 ml cooled mixture and let soak for 5 minutes. Warm slowly on hot plate. Increase heat, and digest until solution chars. Remove from hot plate. Add 10 ml perchloric acid. Wash down sides of flask with nitric acid, and return to hot plate. Solution will boil and become still. It boils again and changes color. Red or dark orange for CCA; light green for ACA. Remove from heat and cool. Combine into a 100 ml flask, rinsing each beaker well. Dilute to 100 ml, and mix well. Use 25 ml aliquot for each determination.

3.2.2. Liquid Preservatives: These samples should be mixed thoroughly. Samples may be obtained by filling a disposable syringe with the well mixed solution. The samples are then squirted into the appropriate receptacles, and weight by difference is recorded. 1 gram samples are usually taken, but 0.5 grams is better for CuO. 1 gram is equal to approximately 1 ml of solution.

3.3. Procedure:

3.3.1. By referring to AWPA Std. P5-72, it can be determined which tests should be run.

3.3.2. Arsenic (As_2O_5):

3.3.2.1. Place sample in 500 ml Phillips Beaker and add water to make a volume of about 50 ml. Add 50 ml of HC1 and 20 ml of hypophosphorous acid. Mix thoroughly, and warm on steam bath until precipitate is formed. Boil about 15 minutes until the precipitate separates out. Filter the hot solution through a 10 ml Gooch crucible containing a glass fiber pad, washing flask and precipitate thoroughly with water. Place the Gooch back into the Phillips beaker and discard the filtrate. To this beaker, add 15 ml of sulfuric acid and heat over an open flame, while agitating, until copious fumes are evolved and all the arsenic has been converted. Cool and gradually add 100 ml of water. Add 7 ml HC1 and 5 drops of methyl orange, and immediately titrate with standard potassium bromate solution to a colorless end-point.

3.3.2.2. Calculations:

Borings:

$$\frac{mL \times N \times \text{Dilution Factor} \times 0.218894 \times 16.01846}{\text{Volume}}$$

$= kg/m^3(16.01846 \times lbs/ft^3)\ As_2O_5$

Liquid:

$$\frac{mL \times N \times 5.746}{\text{Weight}} = \%\ As_2O_5$$

3.3.3. Copper (CuO):

3.3.3.1. Place samples in 300 ml Erlenmeyer flask, and add 50 ml H_2O. Add 10 ml HCl and a few glass beads. Add 20 ml methyl alcohol carefully, warm to boiling and heat until all chromium is gone. The solution should be clear bluish green and show no signs of presence of methyl alcohol. Wash down the sides of the flask with water, boil for 1 minute and cool. Add NH_4OH cautiously until a permanent precipitate just forms. Add H_2SO_4 drop by drop until the precipitate just dissolves. Dilute to 125 ml and cool. Add 10 ml 20 percent potassium iodide solution and 5 ml 20 percent sodium thiocyanate solution and mix thoroughly by rotating the flask. Add 2 ml starch solution and titrate with 0.01N sodium thiosulfate solution. With ACA, the end-point change is from dark blue to cream color. In CCA, it is from dark blue to light green.

3.3.3.2. Calculations:

Borings - (Using 0.01N sodium thiosulfate)

$$\frac{mL \times N \times \text{Dilution Factor} \times 0.218894 \times 16.01846}{\text{Volume}}$$

$= kg/m^3(16.01846 \times lbs/ft^3)\ CuO$

Liquid

$$\frac{mL \times N \times 7.96}{\text{weight}} = \%\ CuO$$

3.3.4. Chromium (CrO_3):

3.3.4.1. Place the sample in a 500 ml Erlenmeyer flask with sufficient water to make a total volume of about 100 ml. A blank must also be run. Add 5 ml of phosphoric acid and 7 ml of 1:1 sulfuric acid and stir the solution well. Immediately pipet exactly 10 ml of ferrous ammonium sulfate solution into the solution and add 8 drops of barium diphenylamine sulfonate solution. Immediately titrate the solution with standard 0.1N potassium dichromate solution. **The endpoint has been reached when the color of the solution becomes deep purple or deep greenish.

3.3.4.2. Calculations:

Borings (Using 0.1N Potassium Dichromate)

$$\frac{\text{Differences in ml x Dilution Factor x 0.0127 x 16.01846}}{\text{Volume}}$$

$$= \text{kg/meter}^3\ CrO_3\ (16.01846 \times \text{lbs/ft}^3)$$

Liquids

$$\frac{\text{Difference in ml x Factor}}{\text{Sample Weight}} = CrO_3$$

Factors

Using 0.2N - 0.6668
Using 0.1N - 0.3334

3.4. Calculations:

3.4.1. For each active ingredient, see calculations under Procedure.

3.4.2. Volume of borings = 0.01884 x no. of borings.

3.5. Precautions:

3.5.1. Special care must be taken with any solution containing perchloric acid, especially when combined with a strong reducing agent, such as hypophosphorous acid. It must not be evaporated too much and should be covered with a small water-glass during this procedure.

3.5.2. In the determination of arsenic the solution must be kept hot until after it is treated

with sulfuric acid.

3.6. Report:

3.6.1. Borings:

3.6.1.1. Kg/m^3 (lbs/ft^3 multiplied by 16.01846) of each active ingredient.

3.6.1.2. Kg/m^3 (lbs/ft^3 multiplied by 16.01846) total active ingredient.

3.6.2. Liquid:

3.6.2.1. Percent concentration of each active ingredient.

3.6.2.2. Total percent concentration active ingredients (salts).

3.6.2.3. Percent of total salts - each salts.

*NOTE 1: In used solutions, the accumulation of organic materials may cause inconsistent copper titrations. If this occurs, see NOTE on page 6 of AWPA Method A2 - 71.

**NOTE 2: 0.2N potassium dichromate may be used, but the end point is much more difficult to discern.

***NOTE 3: Since ferrous ammonium sulfate solutions change strength rapidly, solution should be standardized or blanks run for each determination.

4. X-RAY FLUORESCENCE (Preferred Method):

4.1. Apparatus/Materials:

4.1.1. Philips MagiX PRO Wavelength Dispersive x-ray fluorescence spectrometer.

4.1.2. SuperQ software

4.1.3. Carver hydraulic press

4.1.4. Tungsten Carbide 31mm die set

4.1.5. Spex 8000 mixer/mill

4.2. Procedure – X-Ray Fluorescence:

4.2.1. Dry wood sample in oven at 110°C for at least 2 hours.

4.2.2. Weigh approximately 6 grams of sample and place into the Spex 8000 mixer/mill

and grind until a powder is obtained and/or sample is completely uniform. This may take several minutes.

4.2.3. Place homogenous sample in the die. Press to 33,000lbs and allow pressure to release very slowly.

4.2.4. Enter names of samples in the measure sample screen on the measure and analyze program.

4.2.5. Place sample in 27mm steel cup. Then place in x-ray instrument and prepare to run wood application on the measure sample screen. Click on measure at the bottom of the screen. This may take a few minutes. The application chosen is dependent upon the sample type.

4.3. Quantification: Program quantifies data by using a least squares program. Similar samples with known chemical compositions are used as standards in the quantification technique. As many standards as possible are used for best quantification. The results are reported as oxides in weight percents.

4.4. Report:

4.4.1. % As_2O_5

4.4.2. % CuO

4.4.3. % CrO_3

APPROVED _____

DIRECTOR
DIVISION OF MATERIALS

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