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Document Name: AWP A6: Method for the Determination of Oil-Type Preservatives and Water in Wood

CFR Section(s): 7 CFR 1728.202(g)(1)(v)(A)

Standards Body: American Wood Preservers Association



Official Incorporator:

THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

AMERICAN WOOD-PRESERVERS' ASSOCIATION
STANDARD

A6-89

METHOD FOR THE DETERMINATION OF OIL-TYPE PRESERVATIVES
AND WATER IN WOOD

Note: Standard A6-89 consists of six pages dated as follows: Pgs. 1-2, 1989; Pages 3-4, 1976, Pages 5-6, 1989

1. STANDARD METHOD FOR DETERMINATION OF RETENTION OF OIL-TYPE PRESERVATIVES FROM SMALL SAMPLES

Scope

This assay method is suitable for the determination of creosote, coal tar, petroleum, and their solutions in treated wood when the sample contains at least 5.0 grams of wood and one gram of oil. Additives, such as copper naphthenate or pentachlorophenol, may not be quantitatively extracted by this method. The method can also be used for the determination of water in treated or untreated wood, but when it is so used, the directions on handling the sample in Standard M2 must be followed carefully.

Apparatus

1. **Extraction apparatus.***—A 500-ml. flask and thimble holder as shown in Fig. 1. Flask and holder may be combined in a single unit.

2. **Condenser.***—A water-cooled condenser of the cold-finger type as illustrated in Fig. 1.

3. **Water trap.***—A glass tube having an outside diameter of 12.0 to 13.0 mm. and sealed at one end as shown in Fig. 1. The graduated portion of the tube shall have a capacity of 10.00 ml., with smallest graduation of 0.1 ml., and with major divisions marked 1 to 10. In case the water content of the sample exceeds 10 ml., a similar tube of 20.00 ml. capacity with outside diameter of 15.0 to 17.0 mm. shall be used. The smallest graduation on this larger tube shall not be greater than 0.2 ml. with major divisions marked 1 to 20. Do *not* use this larger tube with samples containing less than 10 ml. of water. The trap shall be chemically clean (see Preparation of Water Trap Assembly and Condenser) so that the water meniscus is horizontal and well-defined and its shape the same at the end of the test as at the beginning. If these criteria are met, the volume of water in the trap can easily be estimated to the nearest 0.02 ml.

* A suitable apparatus is listed by Scientific Glass Apparatus Company as Catalog Number JM 8530.

4. **Extraction basket.***—A basket of about 45-mesh stainless steel gauze, 38 to 42 mm. in diameter and 55 to 125 mm. in height.

5. **Weighing bottle.***—A weighing bottle with stopper of a size to hold the extraction basket. Weight of bottle, basket, and sample shall not exceed the capacity of the balance.

6. **Electric hot plate.**

7. **Rod.**—A rod of about 3-mm. diameter made of water-repellent material such as polytetrafluoroethylene (Teflon)®. A coiled wire has also proven satisfactory.

8. **Oven.**—A vented drying oven maintained at $125^{\circ} \pm 5^{\circ}$ C. A forced draft, air-recirculation oven is not satisfactory.

9. **Desiccator.**—A desiccator with drying agent of the indicating type.

10. **Balance.**—An analytical balance sensitive to 0.001 g. with suitable weights.

Reagents

1. Toluene, meeting ASTM Specification D 846 for nitration grade toluene.

2. Xylene, meeting ASTM Specification D 846 for 10 degree xylene.

3. Toluene-Xylene Mixed Solvent.—A mixture of the specified toluene and xylene in any desired proportion.

Preparation of Water Trap Assembly and Condenser

1. Thoroughly clean the inner surface of the water trap section of the apparatus and the outer surface of the cold-finger condenser with a warm solution of household or industrial detergent in water. Rinse with clean water, drain a few minutes, then dry the outer surface of the water trap section with an absorbent, lintless towel. Carefully inspect its inner surface and the outer surface of the tip of the condenser. If drops or droplets of water remain on these surfaces, repeat the cleaning operation until these critical surfaces are chemically clean. Then proceed as directed under Procedure 1. Do not dry the equipment before use.

2. If repeated cleaning of the apparatus with detergent solution fails to leave a chemically clean sur-

face, rinse the equipment repeatedly with a warm, saturated solution of chromic acid in concentrated sulfuric acid. (Since this solution is very corrosive, care must be taken to prevent contact with skin or clothing. If contact does occur, wash at once and liberally with water.) After the treatment with the acid cleaning solution, rinse the apparatus thoroughly with clean water, drain, and inspect as before. Repeat the cleaning operation, if necessary.

Procedure

1. Place about 200 ml. of toluene, xylene, or mixed toluene-xylene solvent in the extraction flask and add 1 to 2 ml. of water. Assemble the apparatus on the hot plate, apply heat, and reflux for about 30 minutes.

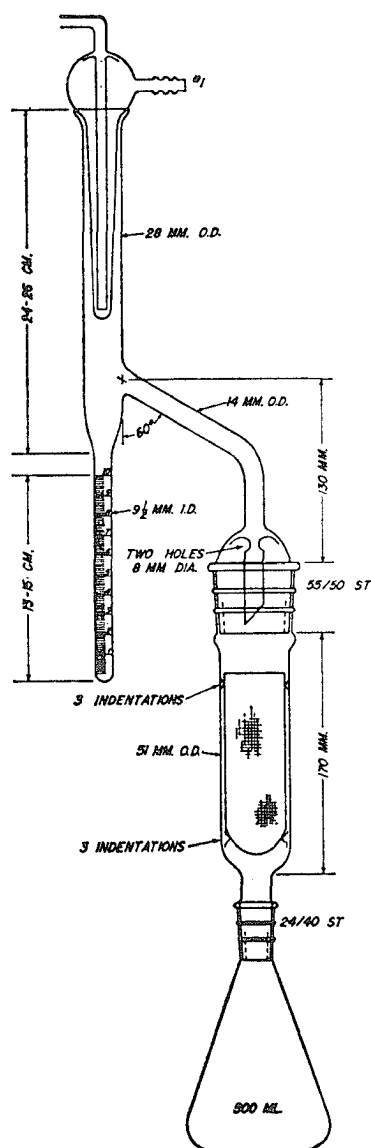


Figure 1.

Allow the contents of the water trap to cool to room temperature, then use the rod or coiled wire to transfer any water adhering to the walls of the condenser or water trap to the water layer in the trap. Spinning the coiled wire aids in freeing water droplets in the solvent layer. Read and record the volume of water in the trap to the nearest 0.02 ml.

2. Place the wood borings or shavings in the weighing bottle—either directly or contained in the wire basket, previously tared to the nearest 0.002 g.—and weigh to the nearest 0.002 g. Transfer the sample to the wire basket, if not already in the basket, and place the basket with sample immediately in the holder of the extraction apparatus. Then reassemble the apparatus. Weigh the empty weighing bottle to the nearest 0.002 g. and record the weight of sample, calculated by difference.

3. Apply heat and reflux the solvent at a rate that at least one drop per second falls from the tip of the condenser. Use the following reflux periods:

Wood freshly treated with creosote or petroleum	2 hours
Wood freshly treated with creosote-coal tar solution	5 hours
Wood exposed in service	5 hours

After the appropriate reflux period, allow the contents of the trap to cool to room temperature. Transfer any water adhering to the walls of the condenser or water trap to the water layer in the trap, using the rod or coiled wire as before. Then read and record the volume of water to the nearest 0.02 ml. The difference between this and the first reading is the water content of the sample.

4. Remove the wire basket and contents from the extraction flask and allow to stand under an effective hood for 10 to 15 minutes. Then place the basket and contents in the 125° C. oven in an open support. *Do not set the basket in a beaker.* After 90 minutes, place the wire basket and contents in the weighing bottle, previously tared with stopper. Cool the uncovered weighing bottle and contents in the desiccator to room temperature. Then stopper the bottle and weigh to the nearest 0.002 g. To ensure that all solvent has been removed in the drying operation, return the wire basket with extracted sample to the oven for 30 minutes, then remove and weigh as before. Repeat these operations if the additional weight loss is greater than 10 mg. Calculate and record the weight of dry, extracted wood.

Calculations

$$\text{Oil in sample, g.} = W_1 - W_2 - W_3$$

$$\text{Oil in sample, lb.} = 0.00220(W_1 - W_2 - W_3)$$

$$\text{Oil, \% of dry, extracted wood} =$$

$$\frac{W_1 - W_2 - W_3}{W_2} \times 100$$

Water in sample, lb. = $0.00220 W_3$

Water, % of dry, extracted wood = $\frac{W_3}{W_2} 100$

Water, % of dry, untreated wood =

$$\frac{W_3}{W_1 - W_3} 100$$

Where:

W_1 = weight of sample before extraction, g.

W_2 = weight of oven-dry, extracted sample, g.

W_3 = weight of water in sample, g. (1.00 ml. \approx 1.00 g.)

Conversion of Boring Assay to pcf

Weight of oil in borings, lb. = $0.00220 (W_1 - W_2 - W_3)$

Volume of borings, cu. ft. = $0.0004545 D^2 L$

Oil content of borings, pcf =

$$\frac{4.84 (W_1 - W_2 - W_3)}{D^2 L}$$

Where:

L = total length of borings, in.

D = inside diameter of borer used, in., or average diameter of borings before extraction, in.

Precision

The following criteria should be used to judge the acceptability of results at the 95 percent probability level:

Preservative Content

Repeatability

Duplicate values by the same operator should not be considered suspect unless they differ by more than 1.3 pcf.

Reproducibility

The values reported by each of two laboratories should not be considered suspect unless they differ by more than 1.5 pcf.

Note:

The estimated standard deviation of repeatability is 0.38, based on 15 degrees of freedom and of reproducibility is 0.51, based on seven degrees of freedom. The retention level of the sample on which the above is based, as analyzed by eight laboratories, was 7.2 pcf.

Moisture Content

Repeatability

Duplicate values by the same operator, as well as values reported by each of two laboratories, should not be considered suspect unless they differ by more than 2.29 percent.

Note:

The estimated standard deviation of repeatability and of reproducibility is 0.78, based on six degrees of freedom. The moisture content level of the sample on which the above is based, as analyzed by eight laboratories, was 9.4 percent.

2. STANDARD METHOD FOR THE QUANTITATIVE RECOVERY OF OIL-TYPE PRESERVATIVES FROM LARGE SAMPLES

Scope

This method is suitable for the quantitative extraction of oil-type preservatives from freshly treated and aged wood and the removal of residual solvent from the extracts.

Outline of Method

The sample is reduced to shavings, chips, or slivers and extracted with toluene in equipment similar to that used in Section 1, A6. Water is removed and measured by means of a side-arm trap. The bulk of the toluene is recovered by straight distillation from the extraction flask. Residual toluene is removed through a 5-ball distillation column.

Apparatus

1. **Extraction Flask.**—5-liter round-bottom flask fitted with suitable outer standard joint.

2. **Sample Holder.**—Similar in design to the thimble holder of Section 1 with inner standard joint at bottom to fit extraction flask and outer standard joint at top to fit adaptor for connection to water trap. The measurements of a sample holder capable of extracting up to 1000 g. of wood are: height (without joints) 38 cm., width 15 cm.

3. **Water Trap.**—Ungraduated with stopcock at bottom, capacity about 50 ml. Inner standard joint at bottom of side arm to connect with adaptor, and outer standard joint at top to connect with condenser. (See Fig. 1, Section 1.)

4. **Adaptor.**—With standard joints to connect sample holder with water trap.

5. **Condenser.**—Water condenser of suitable capacity, preferably of Friedrichs type, with inner standard joint to connect with top of water trap.

6. **Heating Mantle.**—Spherical mantle to fit 5-liter round-bottom extraction flask.

7. **Variable Transformer.**—For use with heating mantle.

8. **Wood Chipper.**—Wiley type. A Cumberland mill, size $\frac{1}{2}$, with $\frac{1}{2}$ -in. holes in the bottom screen has been found satisfactory.

9. **Distillation Equipment.**—5-ball column or equivalent with 1-liter round-bottom flask and spherical heating mantle, and water condenser.

Reagent

1. **Toluene, 2°C. boiling range.**—Meeting the Specifications for Industrial Grade Toluene (ASTM Designation: D 842).

Storage of Sample

Keep samples to be analyzed in tightly sealed cans or wrap in waxed paper followed by aluminum foil. Aluminum foil must not be used in contact with marine specimens. Storage under refrigeration is advisable.

Preparation of Sample

Determine the volume of the sample to be analyzed by suitable means. Water displacement, done very rapidly, has proven satisfactory. Weigh the sample and convert it quantitatively to shavings, chips, or slivers having at least one dimension that does not exceed 2.0 mm. A Wiley-type mill is recommended. Collect the converted sample under a measured volume of toluene to prevent vapor loss of preservative. Clean the mill with small, measured amounts of toluene and add the washings to the bulk of the converted sample.

Extraction

Set the extraction flask in the heating mantle and position the sample holder. Place a cotton bag of suitable size in the holder and quantitatively transfer the sample and toluene to the bag. Then tie the top of the bag. Add toluene to bring its total volume to about 2000 ml. Connect the sample holder to the water trap by means of the adaptor and connect the condenser to the water trap. Start refluxing and continue for 18 to 24 hours in the case of freshly treated wood, for 48 hours in the case of weathered wood. Draw off the water collecting in the trap periodically into a 500-ml graduated cylinder. Record the final volume of water. If a Soxhlet-type extractor is used, the reflux periods must be doubled; even then extraction may not be complete.

At the end of the reflux period withdraw all water from the trap and connect a suitable flexible hose to the bottom of the stopcock. Open the stopcock and continue refluxing until all but about 150 ml of the toluene in the system has been collected in a 2-liter graduated cylinder. When cool, remove the bag with extracted wood and hang outdoors in a protected place until free of toluene odor. Dry the wood to constant weight in an oven at 125°C. and record the weight of oven-dry, extracted wood.

Recovery of Oil-Type Preservative

Transfer the toluene extract to a tared 1-liter round-bottom flask, using small portions of recovered toluene for rinsing the 5-liter flask. Place the 1-liter flask in its heating mantle and connect to a 5-ball column with water condenser. Wrap the column with bright aluminum foil if a distillation shield is not available. Distill at a rate of about 1 drop per second until the vapor temperature at the top of the column reaches 200°C. Cool the flask and weigh. Record the weight of toluene-free extract.

Calculation

Calculate the retention of oil-type preservative as follows:

$$\text{Retention, pcf} = \frac{62.4 W}{a}$$

where: W = weight of toluene-free extract, g.
 a = volume of sample extracted, cc

If the volume of wood extracted is not known, report the percentage of oil-type preservative on the basis of dry, extracted wood.

The sum of the weights of recovered oil, recovered water, and oven-dry, extracted wood should about equal the weight of original sample.

3. RESEARCH STANDARD METHOD FOR THE DETERMINATION OF OIL-TYPE PRESERVATIVES IN SMALL QUANTITIES OF WOOD

Scope

This method is suitable for determination of creosote or creosote-coal tar solution and water in small samples of wood. The sample should not contain more than 3.0 grams of water and can be used for samples that contain as little as 0.1 grams of water. If electronic end point detectors are used, the sensitivity of the method can be increased by a factor of 30. See ASTM Standard E 203. This method should not be used for samples of wood larger than about 5 grams dry weight. For larger samples and for assay samples taken from treated charges, see Paragraph 1 of this Standard.

General

The sample is extracted in a 125 ml. Soxhlet apparatus, using 75 ml. of a 40/60 anhydrous benzene-methanol azeotropic mixture which boils at 58° C. After the extraction is completed, the solvent is diluted volumetrically to 100 ml. with azeotrope. An aliquot of this dilution is analyzed for water, using Karl Fisher reagent. The weight loss of the extracted sample can then be corrected for the water content, and an accurate retention value of the oil-type preservative can be obtained. Since the water content of the sample may not be the same as the water content of the wood from which the sample was taken, unless extreme care is used in sampling, the method should not be used to determine the moisture content of the wood.

Apparatus

1. Extraction apparatus—Soxhlet, with Allihn Condenser (Corning No. 3840), 125 ml. flask.
2. Extraction cup—A basket about 25 mm. x 80 mm. made of approx. 45-mesh stainless steel gauze, or a disposable paper extraction thimble 25 mm. x 80 mm. can be used.

3. Hot Plate.
4. Oven maintained at $105^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$
5. Desiccator.
6. Balance sensitive to .001 gram.
7. Automatic burete—One similar to the Shellbach which can be sealed off with desiccant to protect the Karl Fisher reagent from moisture contamination.
8. Two (2) 250 ml. Erlenmeyer flasks with either rubber or glass stoppers.

Reagents

1. Benzene Methanol Azeotropic Mixture—Make up a stock solution containing 40%, by weight, methanol and 60%, by weight, Benzene, both anhydrous grade.
2. Karl Fisher Reagent—This can be purchased from a chemical sales house.

Procedure

1. Measure and record the volume of the wood sample in the appropriate space on the sample work sheet.
2. Weigh the empty dry basket to .001 gram, then add sample and weigh again. Record both weights.
3. Using a graduate, add 75 ml. benzene-methanol azeotrope to Soxhlet flask. Place basket containing sample in extraction chamber and assemble apparatus, including water-cooled condenser.
4. Apply heat and reflux the azeotrope at the rate of at least one drop per second from the tip of the condenser. Continue refluxing for at least two hours, or until the extracting solvent in the syphon cup becomes clear.
5. Remove basket, dry in oven at least two hours, cool in desiccator, and then reweigh basket and sample. Record total weight loss of sample.
6. Cool, then carefully transfer the extraction solvent to a 100 ml. volumetric flask. Rinse the Soxhlet flask with azeotrope, and add to flask. Dilute up to volume with azeotrope.
7. Standardize Karl Fisher solution each day as follows:

Add 50 ml. of dry methanol to each of two Erlenmeyer flasks. Titrate the methanol with Karl Fisher reagent until the solution goes through yellow and deepens to an orange-red end point. The end point will vary with the operator.

Weigh one drop of water (0.3–0.4 grams) into the above flasks. The color will return to a yellow. Titrate with Karl Fisher solution to the same end point as above. It is advisable to hold one flask at the end point while titrating the water in the other. Then the duplicate determination can be run. Record the weight of water and the volume of Karl Fisher reagent used to titrate the sample. The *water factor*

is determined as the grams of water per milliliter of reagent.

8. Run a blank on the azeotrope by titrating a pipetted 10 ml. sample to the same end point used above. Record the blank titration in the appropriate space on the sample work sheet.

9. Pipete 10 ml. of the extraction solvent from the 100 ml. volumetric flask into the same solutions above. Titrate the sample with the reagent to the same end point as above. Record the volume of reagent used. Calculate the water in the sample by multiplying the net (blank subtracted) ml. reagent \times the water factor (grams $\text{H}_2\text{O}/\text{ml. reagent}$) \times *aliquot factor* of 10.

10. Calculate and record the weight of oil-type preservative in the sample by subtracting the weight of water from the total sample weight loss during the extraction.

11. Convert the results into pounds per cubic feet of oil-type preservative by using the factors shown under "CALCULATIONS."

Calculations

1. Water factor, Karl Fisher reagent, grams $\text{H}_2\text{O}/\text{ml. reagent}$

$$\text{FACTOR} = \frac{\text{Wt. of H}_2\text{O}}{\text{ml. reagent}}$$

2. Wt. of water in sample, grams = Net titration (ml.) \times Aliquot Factor (10) \times K. F. Factor.

3. W_1 = Weight of sample before extraction, grams.

W_2 = Weight of oven-dry, extracted sample, grams.

W_3 = Weight of water in sample, grams.

Wt. of oil extracted = $W_1 - W_2 - W_3$

4. Retention of oil preservative in sample:

$$\text{pcf} = \frac{\text{Wt. of oil preservative (gms.)} \times 3.809}{\text{Volume of sample, (cubic inches)}}$$

4. DETERMINATION OF TRIBUTYL TIN OXIDE IN WOOD

Scope

This method is suitable for the analysis of the total tin content of treated wood. It is important to note that the method is not specific to tributyltin oxide (TBTO), and can therefore only provide the total tin content of the treated wood, including in the analysis any other organotins (such as dibutyltin oxide) which may be present as impurities or degradation products. The method is suitable for the determination of up to 0.3% w/w of tin (or 0.5% TBTO).

1. Reagents

1.1 Standard tin solution 1

Dissolve 1.00g A.R. tin in 100 ml 80 percent v/v hydrochloric acid. Add 420 ml conc hydrochloric acid and dilute to 1 liter with distilled water. (1.00 ml = 1.00 μ g Sn).

1.2 Standard tin solution 2

Dilute 10 ml of tin solution 1 to 100 ml with 50 percent v/v hydrochloric acid (1.00 ml = 100 μ g Sn).

1.3 Standard tin solution 3

Dilute 10 ml of tin solution 2 to 10 ml with 50 percent v/v hydrochloric acid (1.00 ml = 10.0 μ g Sn).

1.4 Tartaric acid solution

Dissolve 300g A.R. tartaric acid in 1 liter distilled water.

1.5 Phenylarsonic solution

Dissolve 2g of 4 hydroxy 3 nitrophenylarsonic acid in about 50 ml water containing 0.5g NaOH (2.5 ml of 5N NaOH) and dilute to 100 ml. The solution is stable for only a few days.

1.6 Sulphuric acid

Concentrated (1.84 sp.gr.), A.R.

1.7 Nitric acid

Concentrated (1.42 sp.gr.), A.R.

2. Preparation of Standard Calibration Graphs

2.1 Upper Range: 100–500 μ g Sn per test

Pipete 1.0, 2.0, 3.0, 4.0, and 5.0 ml of standard tin solution 2 into 100 ml conical flasks. To each flask add 5.0 ml of concentrated sulphuric acid and 1 glass bead. Place a small filter funnel in the neck of each flask and heat on a hot-plate until fumes of sulphuric acid are seen. Take care not to evaporate the sulphuric acid. Cool and add 25 ml of tartaric acid solution and 10 ml of phenylarsonic reagent. Transfer to a 50 ml graduated flask, dilute to the mark and shake well. To an empty flask add 5.0 ml of concentrated sulphuric acid, 25 ml of tartaric acid solution and 10 ml of phenylarsonic reagent, dilute to 50 ml with water and shake well. The five standards and the blank must be allowed to stand for 18–20 hours before measurement. The solution should be thoroughly mixed before measurement. The reagent blank solution is placed in the comparison cell and the standard solutions are compared with this. If the E.E.L. absorptiometer is used then 1 cm cells and the 602 filter are required. If a spectrophotometer is used then a wave-length setting of 450 m μ is required. Plot the galvanometer readings against μ g of Sn.

2.2 Lower Range: 20–100 μ g Sn per test

Pipete 2.0, 4.0, 6.0, 8.0 and 10.0 ml of standard tin solution 3 into 100 ml conical flasks. Follow the above procedure, but use 4 cm cells when measuring the turbidity.

3. Determination of TBTO* In Wood

The sample to be analyzed should first be ground into wood-flour and thoroughly mixed. Weigh out a suitable quantity (containing between 0.05 and 1.25 mg of TBTO) of wood-flour into a 500 ml Kjeldahl flask and add about 10 ml of water. Add 5.0 ml of concentrated sulphuric acid and about 30 ml of concentrated nitric acid. Add one glass bead and heat until fumes of sulphuric acid are seen or until charring begins. Cool and add about 10 cc of nitric acid and heat again to fuming. Repeat the boiling with nitric acid until all the organic matter has been destroyed. Excessive fuming and therefore evaporation of the sulphuric acid must be avoided. Cool and wash down the walls of the flask with about 50 ml of water. Heat until fumes of sulphuric acid are seen. Cool and add a further 50 ml of water and reduce to fuming once more. Cool and add 25 ml of tartaric acid solution and 10 ml of phenylarsonic reagent. Transfer to a 50 ml graduated flask, dilute to the mark and shake thoroughly. Prepare a blank by diluting a mixture of 5.0 ml of concentrated sulphuric acid, 25 ml of tartaric acid solution and 10 ml reagent to 50 ml. After 18–20 hours shake the flasks thoroughly and measure the turbidity using the reagent blank in the comparison cell. Use the cells appropriate to the amount of tin present and determine the amount of tin from the appropriate calibration graph.

4. Calculation

1. The percent tributyltin oxide based on weight of wood =
$$\frac{(2.51 \times 10^{-4}) y}{w}$$

2. Para. 1.1: (1.00 ml = 1.00 mg Sn)

3. Para. 1.3: Dilute 10 ml of tin solution 2 to 100 ml.

where: y = μ g of tin determined from the calibration graph

w = original weight in grams of wood sample.

* Trademark M&T Chemical Co.