

CERTIFICATE

By Authority Of THE UNITED STATES OF AMERICA Legally Binding Document

By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. HEED THIS NOTICE: Criminal penalties may apply for noncompliance.



Document Name: AWPA A11: Standard Method for Analysis of Treated Wood and Treating Solutions by Atomic Absorption

CFR Section(s): Spectroscopy
7 CFR 1728.201(i)(1)(iii)(B)

Standards Body: American Wood Preservers Association



Official Incorporator:

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

**AMERICAN WOOD-PRESERVERS' ASSOCIATION
STANDARD**

A11-83

**STANDARD METHOD FOR ANALYSIS OF TREATED WOOD AND TREATING
SOLUTIONS BY ATOMIC ABSORPTION SPECTROSCOPY**

Note: Standard A11-83 consists of five pages dated as follows:
Pgs. 1-5, 1983.

1. Scope

1.1 This method provides for atomic absorption spectrometric analysis of treated wood and treating solutions.

1.2 The method is principally applicable to the determination of metallic elements. It is highly applicable to analyses for Cu, Zn, Cr, and As, and is of no value for the analysis of Cl, F, or organic constituents.

2. Summary of Method

2.1 Atomic absorption is the process that occurs when a ground state atom absorbs energy in the form of light at a specific wavelength and is elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light absorbed and the concentration of analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light they absorb. Instrument readouts can be calibrated to display concentrations directly.

The basic instrumentation for atomic absorption requires a primary light source, an atom source, a monochromator to isolate the specific wavelength of light to be used, a detector to measure the light accurately, electronics to treat the signal, and a data logging device to show the results.

The atom source used must produce free atoms of analyte material from the sample. The source of energy for free atom production is heat, most commonly in the form of flame or a Heated Graphite Atomizer (HGA). The sample is introduced as an aerosol into the flame and as a liquid or solid into the graphite furnace. The flame burner head or surface is aligned so that the flame or graphite tube intersects the spectrophotometer light path, where the atomic absorption is measured.

3. Interferences

3.1 Interferences in atomic absorption are typically of five types: chemical interferences, ionization interferences, spectral interferences, matrix interferences, and background absorption. A general description of the interferences found in atomic absorption follows.

3.2 Chemical interference, also referred to as condensed-phase interference, occurs when the element of interest combines with some other cation or anion in solution to form a compound which influences the degree of reduction to neutral atoms in the flame used.

Chemical interferences can normally be overcome or controlled in two ways: use of a higher temperature flame or addition of a releasing agent (e.g., Lanthanum Oxide) to the sample (and standard) solution.

3.3 Matrix interferences, also known as viscosity or bulk interferences, occur when the physical characteristics (viscosity, surface tension, etc.) of the sample and standard solutions differ considerably. Matrix effects can often be controlled by matching the concentration of major constituents in sample and standard solutions.

3.4 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion.

Ionization interferences can generally be controlled by the addition to both standard and sample solutions of a large excess of an easily ionized element.

3.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. Methods of overcoming the potential interference include use of a smaller spectral slit width or suggested alternate wavelengths.

3.6 Background absorptions; certain samples, when atomized, may absorb or scatter light from the source lamp because of the existence of gaseous molecular species, salt particles, smoke, or other causes. Background absorption is a collective term used to describe the combined effects of such phenomena (flame absorption, molecular absorption, light scattering etc.) in atomic absorption determinations. Methods of correcting for background absorption effects include: 1. compensation using a nearby non-absorbing wavelength and 2. compensation using the Deuterium Background Corrector.

4. Safety Precautions

4.1 A proper venting system is required to remove the fumes and vapors from the flame to protect

laboratory personnel from toxic gases which may be produced.

4.2 Fasten all gas cylinders securely to an immovable bulk-head or a permanent wall. Locate gas cylinders away from heat or ignition sources. Use only approved regulators and hose connectors. When the equipment is turned off, close all gas cylinder valves tightly at the tank.

4.3 Never view the flame or hollow cathode lamps or electrodeless discharge lamps directly without protective eyewear due to potentially hazardous ultraviolet radiation which may be emitted.

5. Apparatus

5.1 No special apparatus is required for preparation of the sample, other than that used for regular chemical analyses.

5.2 Atomic Absorption Equipment.

5.2.1 Sources. The sources used in atomic absorption spectrometry must provide narrow line spectra of the elements of interest. These sources should be bright, stable, and long lived. Traditionally, hollow cathode lamps have been used to provide narrow line spectra. For some elements, hollow cathode lamps are not optimum; electrodeless discharge lamps are now available for some of these elements. A single-element lamp is generally preferred for each element to be determined although there are some multi-element lamps available. Single-element lamps generally provide greater light output than multi-element lamps. Therefore, single-element lamps are required when operating at or near detection limit levels.

5.2.2 Burner System. The atomizer of an atomic absorption spectrophotometer must generate ground state atoms in the optical path of the photometer. Several devices have been utilized for this purpose, each with its own special advantage. The widely applied technique around which the routine use of atomic absorption was developed is the direct aspiration of sample solution into a flame. Where applicable, this is still the easiest and fastest approach.

5.2.3 Flame. Air-acetylene is the flame most widely used for the determination of about 35 elements including Cu, Cr, Zn and As by atomic absorption. However, the selection of a flame type for a particular analysis is often dependent upon the type of instrument being used and the concentration range being analyzed. Therefore, please refer to the instrument operating manual to determine the proper flame conditions. Some of the flame temperatures obtainable are:

Mixture	Approx. Temp., °C
Air-propane -----	1900
Air-Hydrogen -----	2000

Air-acetylene -----	2300
N ₂ O-acetylene -----	2900
50% O ₂ — 50% H ₂ -acetylene -----	2815
O ₂ -acetylene -----	3100
N ₂ O-acetylene -----	3080
(CN) ₂ — O ₂ -----	4800
(CN) ₂ — NO ₂ -----	5000

5.2.4 Optical System. There are basically two types of atomic absorption instruments commercially available—single-beam and double beam. The single-beam system has a simple optical system. Energy from the primary source is focused into the sample compartment and then to the monochromator where dispersion occurs. In the double-beam system, light from the lamp is divided into two beams, the sample beam and the reference beam. The sample beam travels through the sample compartment, while the reference beam travels around it. The beams are recombined before entering the monochromator and the ratio of the two intensities is measured. The double-beam system compensates for any drift in lamp intensity, detector sensitivity, and electronic gain and ultimately results in improved detection limits and precision.

5.2.5 Power Supply. A reasonably constant voltage, in accordance with manufacturer's instructions, must be supplied.

6. Reagents

6.1 Purity of Reagents. Reagent grade chemicals shall be used throughout. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity so as not to affect the accuracy or precision of the determination.

6.2 Purity of Water. Unless otherwise indicated, references to water shall be understood to mean reagent water conforming the ASTM Standard D 1193 for Reagent Water.

6.3 Gases. Gases for use in the burner shall be of high purity and graded for use in atomic absorption wherever possible.

7. Sampling

7.1 A wood sample for analysis will normally consist of one or more borings, to be taken in accordance with the provisions of AWP Standard M2 and the appropriate commodity standards.

7.2 Alternatively, bulk wood or large samples of ground wood may be analyzed. Due precaution should be taken that such samples are indeed representative.

7.3 Solution samples should be taken in accordance with the provisions of AWP Standard A2.

8. Preparation of Sample

8.1 Wood samples

8.1.1 If analysis are performed on samples at different moisture contents, significant differences in analytical results will occur; therefore, it is critical that the wood samples shall be dried to a bone dry weight before processing.

8.1.2 If the sample is not of sufficient fineness to pass a 30-mesh screen, it shall be ground in a Wiley mill until this fineness is achieved.

8.1.3 If the sample weighs less than 100g, the entire sample shall be milled if necessary. If the sample is larger, it shall be reduced by quartering in accordance with accepted practice until a convenient weight, not less than 100g, is obtained for milling in accordance with 8.1.2.

8.1.4 If the samples are borings (about 20 borings, .2" diameter and .6" length) they can be digested without grinding.

8.1.5 After milling, a sample of the wood shall be treated chemically to prepare a solution containing the appropriate quantity of the element to be determined, using the equipment manufacturer's recommendations.

As an example, the final solution to be fed into the burner may have the following concentration ranges of the elements in ppm:

Cu	Cr	As	Zn
2-20	2-20	10-100	0.5-5

A suitable solution can usually be prepared by dissolving or extracting 5g of wood into 200 ml. This solution is used full-strength for As, and is diluted 1:10 for Cu, Cr, and Zn.

8.1.6 Dissolving techniques. One of the following procedures may be used.

8.1.6.1 Lambert (J. Inst. Wood Sc. 4 (24) 27-36 (1969)) has described the procedure which has probably had the widest acceptance. This is as follows:

Weigh 5.000g of sample prepared according to Sections 8.1.1-8.1.3 into a Soxhlet thimble and cover with a small plug of glass wool. Add 150 ml. 2N HCl to a 250 ml. Soxhlet flask fitted with extractor and thimble, and extract for about 12 cycles—requiring usually 4-8 hours. Make up the solution to 200 ml. with distilled water.

8.1.6.2 Dissolve 5.000g of sample according to Method One of A7-75. After solution is complete, add 20 ml. concentrated HCl and evaporate to a final volume of 20 ml. Dilute to 200 ml. with 2N HCl.

8.1.6.3 Dissolve 5.000g of sample according to Method Two of A7-75. Dilute final solution to 200 ml. with 2N HCl.

8.1.6.4 Weigh 5.000g of wood into a flask containing 40 ml. concentrated HNO₃. Allow to stand

until the wood is saturated and the evolution of brown fumes has ceased. Heat, adding HNO₃ 5 ml. at a time if necessary until brown fumes cease and the wood is all dissolved, except for a tarry residue. Add 20 ml. concentrated HCl and evaporate to about 20 ml. volume. Dilute to 100 ml., filter into a 200 ml. volumetric flask. Wash down the filter with 2N HCl and dilute to the mark with 2N HCl.

8.2. Treating Solutions

8.2.1 Prepare a dilution of the treating solutions with 2N HCl within the range of standard solutions. Use full-strength for As; dilute 1:10 for Cu, Cr, and Zn.

9. Standard Solutions

9.1 Certified standards containing known quantities (generally 1000 PPM) of each element are available and recommended to be used after appropriate dilution. However, standards may also be prepared using the following procedures.

9.2 Standard copper solution. Dissolve 0.5000g of pure copper foil or wire in 5 ml. of concentrated HNO₃. Evaporate to dryness and dissolve in 10 ml. of concentrated HCl. Add 300 ml. 2N HCl and dilute to 500 ml. with water. This solution contains 1000ppm Cu.

9.3 Standard chromium solution. Dissolve 1.414g of K₂Cr₂O₇ in 10 ml. heated distilled water, and dilute to 500 ml. with 2N HCl. This solution contains 1000ppm Cr.

9.4 Standard arsenic solution. Dissolve 1.320g of As₂O₃ (dried at 105-110°C for 2 hours) in 10 ml. of 20 percent sodium hydroxide solution. Dilute to 500 ml. with 2N HCl. This solution contains 2000 ppm As.

9.5 Standard zinc solution. Dissolve 0.5000g of pure zinc in 20 ml. of 2N HCl, warming if necessary. Dilute to 500 ml. with 2N HCl. This solution contains 1000ppm Zn.

9.6 Working standards. By appropriate dilution, prepare at least four standards covering the range of concentration to be expected from the unknowns.

	1	2	3	4
Cu & Cr (ppm)	5.0	10.0	15.0	20.0
As (ppm)	25.0	50.0	75.0	100.0
Zn (ppm)	.5	2.0	3.5	5.0

However, depending upon the type of instrument and the type of lamp used, the working range for each element can vary. Therefore, please refer to the operating manual for specific working ranges for each element.

In addition, it is recommended that each standard should contain the other elements present in the preservative in about the ratio present in the nominal composition.

10. Operation of Equipment

10.1 The equipment should be operated in accordance with manufacturer's recommendations. Usually the type of flame and wavelength will be about the same for all makes, but slit widths, pressure and rate of burning will vary from make to make. Examples of standard conditions for Cu, Cr, As, and Zn are:

	Approx. Wave length (nm)	Light Source	Flame	Approx. Linear Work Range
Cu	324.8	HCL	A-Ac	5µg/ml
Cr	357.9	HCL	A-Ac(N-Ac)	5µg/ml (10µg/ml)
As	193.7	EDL	A-Ac	50µg/ml
Zn	213.9	HCL	A-Ac	1µg/ml

HCL: Hollow Cathode Lamp

EDL: Electrodeless Discharge Lamp

A-Ac: Air-Acetylene

N-Ac: Nitrous Oxide-Acetylene

However, it should be understood that in actual practice, linear working ranges can vary, depending upon the operating conditions and instrumentations.

10.2 The determination of arsenic has presented some difficulty because of the low wavelength required. However, greater sensitivity and a lower detection limit can be obtained through the use of Electrodeless Discharge Lamps (EDL's). EDL's provide greater light output and longer life than corresponding hollow cathode lamps.

11. Standardization

11.1 Directly proportional behavior between absorbance and concentration is observed in atomic absorption. When the absorbances of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration, a calibration relationship is established. Over the region where the Beer's Law relationship is observed, the calibration yields a straight line. As the concentration and absorbance increase, nonidealities in the absorption process cause a deviation from straight line behavior. If the calibration curve extends beyond the linear working range, additional standards must be used. The working curve may change somewhat from day to day and should therefore be checked with every batch of samples.

After a calibration is established, the absorbance of solutions of unknown concentrations may be measured and the concentration determined from the calibration curve. In modern instrumentation, the cali-

bration can be made within the instrument to provide a direct readout of unknown concentrations. Since the advent of built-in microcomputers, accurate calibration even in the nonlinear region is feasible. However, if possible, it is recommended to operate in the region where the Beer's law relationship is observed.

11.2 Concentration on the conversion chart may be plotted as ppm of the element in the standard solutions. However, the elements are reported as oxides in AWWPA calculations, and the following factors may be used to obtain results in oxide form:

Multiply ppm Cu by 1.2518 to obtain ppm CuO
ppm As by 1.5339 to obtain ppm As₂O₅
ppm Cr by 1.9231 to obtain ppm CrO₃
ppm Zn by 1.2447 to obtain ppm ZnO

11.3 Standards should be made as frequently as possible. If very dilute standards are needed for a period longer than one day, stock solutions in concentrations greater than 500 µg/ml should be made up. The stock solutions can then be stored and diluted as required when standards are needed. This will avoid changes in concentration (as much as 2 to 3% in 3 days) that occur when very dilute solutions are left standing.

12. Calculations

12.1 Treating solutions

12.1.1 Calculate the percent oxide in the sample from the following formula:

$$\% \text{ oxide} = \frac{\text{ppm oxide} \times \text{degree of dilution}}{10000} \times \text{sp. gr. of orig. solution}$$

"Degree of dilution" is the product of all dilutions used in preparing samples.

Example: Pipet 10 ml. of treating solution into a 200 ml. volumetric flask and dilute to the mark. Analyze this solution for arsenic. Pipet 10 ml of the diluted solution into a 100 ml volumetric flask and dilute to the mark. Analyze this second solution for Cu and Cr.

Degree of dilution for As will be: 20

Degree of dilution for Cu & Cr will be: $20 \times 20 = 200$

12.2 Wood samples

12.2.1 Calculate the pcf oxide in the sample as follows: (sample was diluted into 200 ml V.F.)

$$\text{lb. oxide/cu. ft.} = \frac{\text{ppm oxide} \times \text{"degree of dilution"}}{5000 \times \text{wt. sample, g}} \times \text{density of wood, pcf}$$

12.2.2 If a single boring is dissolved for analysis, then the retention is:

$$\text{lb. oxide/cu. ft.} = \frac{\text{ppm oxide} \times \text{degree of dilution}}{5000 \times 453.6} \times \frac{1728}{\text{vol boring, cu. in.}}$$

13. Precision and Accuracy

13.1 Insufficient field data are available at this time to support precision and accuracy calculations for this method. Further study is required.