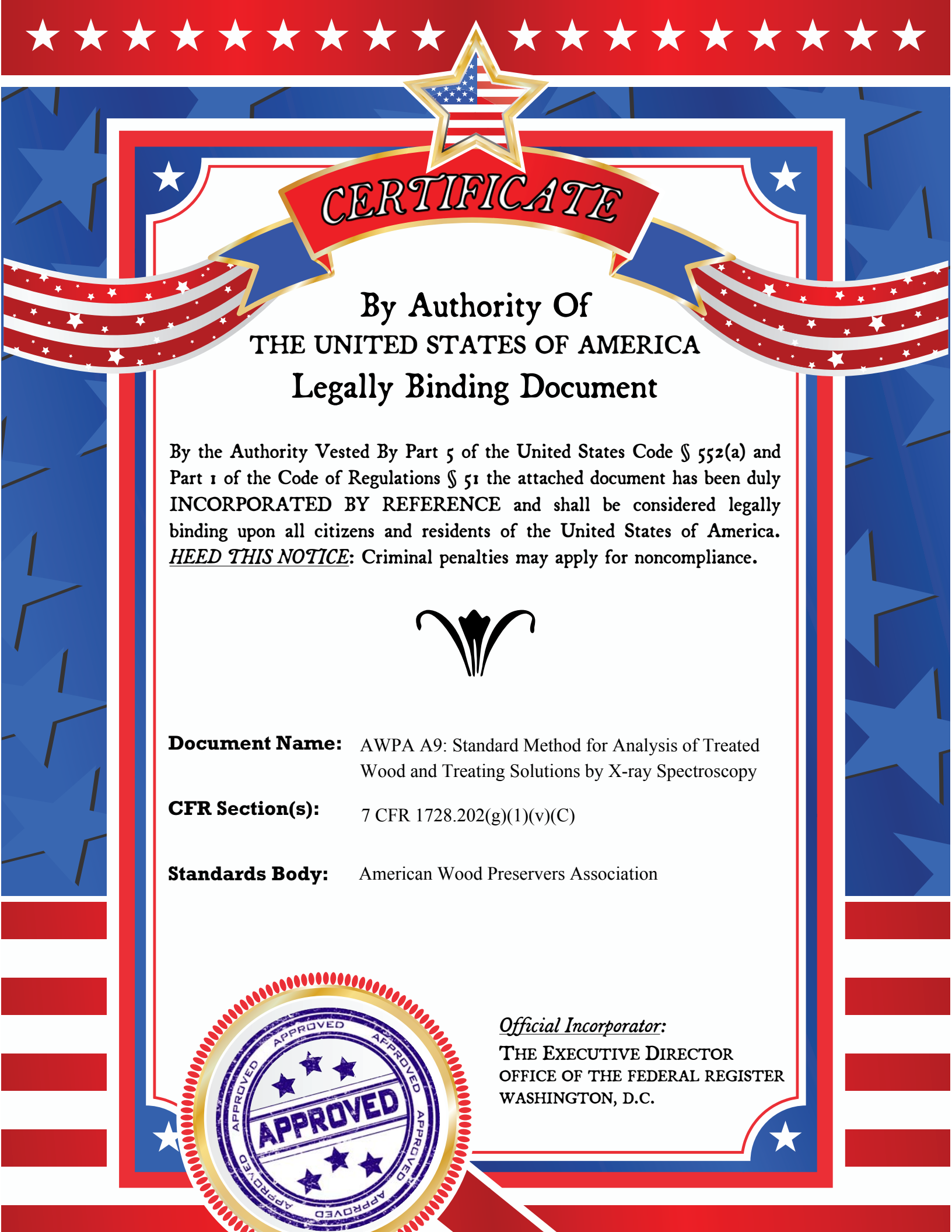




CERTIFICATE

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Document Name: AWP A9: Standard Method for Analysis of Treated Wood and Treating Solutions by X-ray Spectroscopy

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

Standards Body: American Wood Preservers Association



Official Incorporator:

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**AMERICAN WOOD-PRESERVERS' ASSOCIATION
STANDARD**

**(This Standard is under the jurisdiction of AWPA Committee P-5)
A9-90**

**STANDARD METHOD FOR ANALYSIS OF TREATED WOOD AND
TREATING SOLUTIONS BY X-RAY SPECTROSCOPY**

Note: Standard A9-90 consists of four pages dated as follows: Pgs. 1-4, 1990.

1. Scope

1.1 This method provides for X-ray spectroscopic analysis of treated wood and treating solutions.

1.2 The method is applicable to the determination of elements of atomic number 11 or higher than are present in significant quantity in the wood (usually above 0.01 percent).

1.3 The specific elements covered in this method, and now specified for use in preservative and fire-retardant treatment of wood, are, with their atomic numbers, P(15), S(16), Cl(17), Cr(24), Cu(29), Zn(30), and As(33).

1.4 Energy dispersive and wavelength dispersive spectrometers can both be used. The instructions for operating each type of spectrometer are provided by the manufacturer and are not described here. General information concerning sample preparation and calculation of preservative retention are described.

2. Summary of Method

2.1 If the sample is of treated wood, it is ground and the powder is compacted and mounted in a sample holder. (In the event the sample is of wood treated with an oil-borne preservative such as pentachlorophenol, extraction may be required with the preservative being measured in the solution. The sample is then irradiated. The characteristic X-rays of the atom that are emitted are measured by sensitive detectors. Detector output is related to concentration of calibration curves.

2.2 If the sample is a solution, either aqueous or organic, it is transferred to a Mylar cell after preparation and then irradiated and measured as in 2.1.

2.3 The K spectral lines are used.

3. Interferences

3.1 In general, the total X-ray fluorescence of an element in the sample is determined not only by quantity of the element being measured, but is also influenced by the quantities of the other elements in the sample. For this reason, any standards should match closely the unknowns in kinds and amount of

elements present and species and density of wood or solvent employed. The interelement interference and matrix correction equation should be generated over the range of retentions of interest.

4. Safety Precautions

4.1 When the X-ray equipment is installed, it should be checked for radiation leakage by factory installers or other competent personnel.

4.2. Normal safety precautions for X-ray spectrographic installations are to be observed. It is recommended that suitable monitoring devices, such as film badges, be worn by participating personnel, and that effective control and regulation of the monitoring procedure be maintained.

5. Apparatus

5.1 Sample Preparation Equipment

5.1.1 Wiley mill or equivalent comminuting equipment, capable of producing a product passing a U.S. Standard 30 mesh sieve.

5.1.2 Sieves.—U.S. Standard 30 mesh, (589 μm) minimum as specified in ASTM Specification E11.

5.1.3 Compacter.—A suitable press, equipped with a gauge giving reproducible readings and capable of exerting a pressure of at least 50,000 psi, (3515 kg/cm^2) is required.

5.1.4 Special Equipment—For samples in which the preservative is applied in a large amount of nonvolatile solvent, so that the solution is likely to be expressed during milling and compacting, extraction is required prior to analysis. The borings may be extracted with ethanol-toluene azeotrope, using a Soxhlet or similar apparatus. Alternatively, borings may be sliced and boiled on a steam bath with ETA solution.

5.2 X-ray Generation and Measuring Equipment

5.2.1 A large number of X-ray spectrometers are now available, many of which allow computerized fitting of spectra and integration of peak areas. Equipment manufacturers can also provide advice on operation and suitability of electronic components. For elements with X-ray energy less than 3keV, then special sample chambers which are

either evacuated or flushed with helium, are used. A few of the essential requirements in the X-ray equipment are summarized below.

5.2.1.1 **Stable Electrical Power Supply** (± 1 percent).

5.2.1.2 **Excitation Source.**—Source of high-intensity X-rays of the proper energy distribution. The target should be selected with consideration for the element being determined.

5.2.1.3 **Atmosphere Control.**—(Air is normally used). Special procedures are required for the lighter elements when helium and vacuum atmospheres are recommended.

5.2.1.4 **Detector.**—A flow-proportional counter using argon-methane is suitable for light elements; a scintillation counter for heavy elements. A Li(Si) solid state detector is suitable for all elements, but is less sensitive to the light elements.

5.2.1.5 Amplifiers, rate meters, recorders, scalars, and printout, as required.

6. Reagents

6.1 **Purity of Reagents.**—Reagent grade chemicals shall normally be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 **Purity of Water.**—Unless otherwise indicated, references to water shall be understood to mean deionized water.

7. Sampling

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

7.2 Alternatively, the method may be used for bulk wood samples or larger ground wood samples.

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 The wood shall be dried to achieve 0% moisture content, ground, and pelletized as specified in Paragraph 8.1.4 below, and read as rapidly as possible to avoid significant increase in moisture content. Significant errors are introduced when samples are run at moisture contents above 3-5%.

For greatest accuracy, the use of the actual specific gravity of the wood is preferred to using the assumed average species density. For a referee analysis, actual wood specific gravities must be determined and used.

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 minimum fineness is achieved, returning oversize to the mill.

8.1.3 If the sample is of less than 100 g weight, the entire sample shall be so milled. If the sample

is of greater weight, it shall be reduced by quartering in accordance with accepted practice.

8.1.4 Compress a portion of the ground sample to a briquet suitable for use in the sample holder of the X-ray instrument. Care must be taken to maintain uniformity of pellet thickness in both standard and unknown pellets. A pressure of about 30,000 psi is usually required; however, reproducibility usually improves as the density of the briquetted sample increases. Sufficiently high pressure should be used to eliminate sample preparation as a significant source of error.

8.1.4.1 As an alternate to 8.1.4, the ground sample, preferably reduced to flour, may be packed firmly into a plastic holder with a spatula and the sample sealed with Mylar film, provided it can be shown that satisfactory precision is thus attained.

8.1.5 In the event the wood sample is treated with an oil-soluble preservative in a non-volatile solvent, the procedures of 8.1.2-8.1.4 may cause oil to be squeezed out and deposited on the mill and press, or unevenly distributed in the briquet. In this case, better accuracy and precision will be obtained by the following procedure which is recommended.

8.1.5.1 The sample borings are extracted with ethanol-toluene azeotrope in a Soxhlet extractor, the extract diluted to volume in a volumetric flask, and a portion transferred to a Mylar cell adapted to the instrument using the same technique as directed in 8.2 for solutions. Alternatively, borings may be sliced and boiled on a steam bath with ETA solution. After filtering, the solution is evaporated on a steam bath using forced air to a volume of 10 ml and quantitatively transferred to a 25 ml volumetric flask and then made up to 25 ml with ETA solution. Standard curves are made up using analytical grade PCP in ETA solution.

8.2 Solution Samples

8.2.1 Working solution samples may be measured without further preparation if substantially free of insoluble matter. Concentrated solutions should be diluted by weight to be compatible with the range of the standard curve.

8.2.2 Samples containing appreciable quantities of sludge or insoluble matter should be filtered free of it before use. Do not wash the filter.

8.2.3 Used solutions of waterborne preservatives containing chromium are photosensitive. Store in a dark container or storage area before testing.

8.2.4 For measurement, transfer a portion of the solution sample to a Mylar cell and measure as described in Section 10.

8.2.5 Treat solutions of pentachlorophenol or the like, prepared by extraction of borings as in 8.1.5.1, by the above procedure.

9. Preparation of Apparatus

9.1 Follow the manufacturer's instructions for

the initial assembly, conditioning, and preparation of the fluorescent X-ray apparatus.

9.2 Follow the manufacturer's instructions with respect to control settings.

10. Excitation and Exposure

10.1 Position the sample in the special chamber provided for this purpose. Produce and record the spectrum.

11. Calibration and Standardization

11.1 The most accurate evaluations can be made by preparing special standards containing the same components as the sample. The ratios of the components should be that indicated by the nominal composition of the preservative being analyzed for, as well as other ratios beyond those specified in the AWWA P and C1 Standards. This will allow the correction to be made for each element for interference and matrix effects due to the other components in the sample. Standard samples should be analyzed at the same time as unknown samples, to determine correction for electronic drift in the instrument, and to confirm the correct operation of the spectrometer.

11.2 Wood Samples

11.2.1 For best results, standards should be prepared by impregnating sawdust of the same species and approximate density with known amounts of solutions or preservative in the same solvent. The sawdust, of a mesh size meeting the requirements of Paragraph 8, shall be dried to 0 percent moisture content before processing and then processed as specified in Paragraph 8.

11.2.2 For inorganic constituents, the materials used in impregnating standards can be directly weighed if it can be shown that the chemical has a purity based on active ingredients present at the time of use, of 99-100 percent. The same chemicals shall be used in making up standards as those present in the preservative being used in order to compensate for interferences from inert elements. For hygroscopic materials, the standards should be analyzed by wet procedures.

11.2.3 For organic constituents; Pentachlorophenol standard solutions shall use oils of the same character as those in plant use, and shall be standardized by analysis by the lime-ignition method, (AWWA Standard A5, Section 5). If the extraction option (Section 8.4.1) is used, the standards shall be made up in ethanol-toluene azeotrope, and the chlorine emission measured in a liquid cell. Copper naphthenate shall be standardized by analysis for copper (AWWA Standard A5, Section 7) and the same general procedures shall apply as for pentachlorophenol.

11.3 Solution samples

11.3.1 If the chemicals involved can be shown to have a purity of 99-100 percent, prepare standards of inorganic materials by direct weighing. Other-

wise, analyze the standard solutions by the methods of AWWA Standard A2. Where possible use the same chemical species as those present in the preservative to compensate for possible interference from inert elements.

11.3.2 Solutions of organic preservatives shall be standardized as described in 11.2.3

11.4 At least ten standards spanning the entire expected range of retentions for the preservative in question shall be used in determining calibration curves for the elements to be determined. See AWWA C-Standards for lists of elements and reference to chemical analysis methods.

11.5 Because drift is sometimes encountered in the X-ray readings, standardization curves shall be checked regularly when the equipment is in operation. At least one standard sample should be run with every batch of analyses run sequentially on the same day.

11.6 Internal standards should be used to provide direct comparison.

12. Calculations

12.1 Average the results for each component from three exposures of each sample. The number of replicates used shall be sufficient to afford repeatability in this operation substantially better than that of the entire method. For routine control, replicates may be unnecessary. Use the averaged values to compute retentions from prepared calibration curves, or curve formulas.

12.2 The method of calculating results is determined by the provisions of the applicable AWWA C-Standards and is best illustrated by examples.

12.2.1 Example 1. Pentachlorophenol, compressed wood method. Standards are prepared using analyzed penta-in-oil, and sawdust of the species used in treatment. Standards are prepared using sawdust analyzed for its penta content by the methods of AWWA Standard A5. The retention of penta in each standard is given by:

$$\frac{\% \text{ Penta in wood} \times \text{density of wood, pcf}^*}{100} = \text{lb. penta/cu. ft.}$$

12.2.2 Example 2. Pentachlorophenol, extraction method. Known amounts of analyzed penta-in-oil are transferred to a volumetric flask of the same size as that used for the Soxhlet extraction of the sample, and made to the mark with toluene-methanol azeotrope. After shaking thoroughly, transfer a portion of the solution to the Mylar cell and measure on the X-ray spectrometer. Prepare a calibration curve, plotting grams of penta in standards against counts. Values on unknowns, taken from this curve,

* Obtained from appropriate C-Standard

may now be combined with the volume of the borings to calculate retention.

12.2.3 Example 3. CCA. Type C, compressed wood method. Sawdust is impregnated with known amounts of all three active constituents, in the approximate ratio used in the preservative or encountered in wood. The retention in each standard is calculated for each ingredient.

$$\begin{aligned} & \frac{\text{g. As (as As}_2\text{O}_5\text{)}}{\text{g. dry sawdust}} \\ & \times \text{density of wood, pcf} \quad (A) \\ & = \text{lb. As}_2\text{O}_5 / \text{cu.ft.} \\ & \frac{\text{g. Cu (as CuO)}}{\text{g. dry sawdust}} \\ & \times \text{density of wood, pcf} \quad (B) \\ & = \text{lb. CuO} / \text{cu.ft.} \\ & \frac{\text{g. Cr (as CrO}_3\text{)}}{\text{g. dry sawdust}} \\ & \times \text{density of wood, pcf} \quad (C) \\ & = \text{lb. CrO}_3 / \text{cu.ft.} \end{aligned}$$

The sum (A) + (B) + (C) is taken as the retention of CCA (on an oxide basis) standard.

A separate calibration curve is prepared for each element and the retention in the unknown calculated by adding the total values for As_2O_5 , CuO, and CrO_3 determined from the curve. Sufficient standards shall be used to prepare reliable calibration curves.

13. Precision Statement

The following statements and tables should be used to judge the acceptability of analysis on duplicate samples under the conditions stated below.

Repeatability: Duplicate single determinations on the same sample by the same operator using the same equipment should not be suspect at the 95% confidence level if they do not differ from one another by equal to or less than the limiting percentages shown in the following table.

Reproducibility: Duplicate single determinations on the same sample made by different operators in different laboratories should not be considered suspect at the 95% confidence level if they do not differ from one another by equal to or less than the limiting percentages shown in the following table.

PRECISION TABLE

Element	Expressed as Oxide	Concentration Level (wt %)	Limiting Percentages	
			Repeatability	Reproducibility
chromium	CrO_3	0.16	.025	.059
chromium		0.31 to 0.46	.056	.066
chromium		0.47 to 0.85	.090	.108
chromium		0.86 to 1.52	.152	.179
chromium		1.53 to 3.03	.236	.651
copper	CuO	0.07 to 0.13	.016	.028
copper		0.14 to 0.31	.036	.067
copper		0.32 to 0.55	.046	.110
copper		0.56 to 1.10	.088	.308
copper		1.11 to 1.59	.129	.415
arsenic	As_2O_5	0.12	.016	.055
arsenic		0.22 to 0.43	.033	.102
arsenic		0.44 to 0.78	.053	.139
arsenic		0.79 to 1.05	.105	.180
arsenic		1.06 to 2.16	.261	.655

The above precision statements are based on round robin data by ten laboratories, each running four replicate determinations on each of ten samples covering the retention range 0.1 to 2.5 lb/ft³