A COLORIMETRIC PROCEDURE FOR THE DETERMINATION OF ARSENIC, CHROMIUM, AND COPPER IN WOOD TREATED WITH WATER-BORNE PRESERVATIVES

Thesis for the Degree of Ph. D.

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Vishwa Nath Prasad Mathur

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THESIS

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ABSTRACT

A COLORIMETRIC PROCEDURE FOR THE DETERMINATION OF ARSENIC, CHROMIUM, AND COPPER IN WOOD TREATED WITH WATER-BORNE PRESERVATIVES

by Vishwa Nath Prasad Mathur

A colorimetric method is described for the rapid and accurate quantitative determination of arsenic, chromium, and copper in wood treated with water-borne preservatives. A wet digestion method, utilizing sulfuric acid and hydrogen peroxide, has been satisfactorily used for destruction of the wood substance and subsequently bringing the elements to be analyzed into water solution.

By reacting with sodium molybdate-hydrochloric acid solution, the arsenic present in the preservative solution or the digested wood solution is completely converted to 1,2 molybdoarsenic acid. The 1,2 molybdoarsenic acid is extracted from the water solution into Butan-1-ol. Following separation it is possible to make a colorimetric measurement of the alcohol layer at 370 mμ. Removal of suspected interfering ions is also described in the procedure. From the study of the determination of arsenic from different species of treated wood and various preservative formulations it is found that a precision of more than 95 per cent is achieved.

Chromium is extracted with ethyl acetate and determined colorimetrically at 565 mμ. in the form of blue perchromic acid. Only hexavalent chromium is converted to blue perchromic acid by the action of hydrogen peroxide. A procedure for oxidation of the chromium content into hexavalent state is also described. It is found that chromium can be determined by the blue perchromic acid method with an accuracy of more than 95 per cent, irrespective of the species of the treated wood and the preservative formulation tested.

Copper is determined by the "cuproine" method which is specific for copper (I). This method is satisfactorily used to determine copper with an accuracy of more than 98 per cent. All the copper content of the solution is brought to copper (I) state by reducing it with hydroxyl ammonium chloride (NH_2OH HCl). A copper (I)-cuproine complex is formed which can be extracted with isoamyl alcohol. The colorimetric measurements are then made on this alcohol layer at 546 mμ. Copper has been determined with an accuracy of more than 98 per cent from all the species of treated wood and preservative formulations tested.

A comparative test on the determination of arsenic, chromium, and copper by the volumetric method and the colorimetric method show excellent agreement between the two methods. However, the colorimetric method has additional advantages in that smaller sample sizes can be used and less time is taken for analysis.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

Wood preservatives are chemical substances which, when applied to or impregnated into wood, make it resistant to attack by fungi, insects, or marine borers. Preservatives may be classified into two main groups: the water-borne preservatives and the oily, or oil-borne, preservatives. This thesis is devoted to water-borne preservatives.

Water-borne Preservatives

The chief constituents of water-borne preservatives are the compounds of arsenic, chromium, copper, fluoride, and zinc. Almost all of the proprietary preservatives available on the market today consist of one or more than one compounds of these elements, as shown in Table 1. Toxicity of these preservatives towards various agencies of wood deterioration are different and have been under study since the evolution of the wood preserving industry. For effective preservation of wood and wood products, it is essential that the treated product contain more than the lethal dosages of these chemical constituents. Both the treating solution and the treated wood may be analyzed for determining the retention of the constituents involved. In practice, only the strength of the treating solution,

Table 1.--Active ingredients in various proprietary preservatives.

Preservative	Active Ingredients				
	Arsenic	Chromium	Copper	Fluorine	Zinc
1. Acid Copper Chromate (ACC) CELCURE*	-	+	+	-	-
2. Ammoniacal Copper Arsenate (ACA) CHEMONITE*	+	-	+	-	-
3. Chromated Copper Arsenate (CCA) ERDALITH* GREENSALT	+	+	+	-	-
4. Chromated Zinc Arsenate (CZA) BOLIDEN*	+	+	-	-	+
5. Chromated Zinc Chloride (CZC)	-	+	+	-	+
6. Copperized Chromated Zinc Arsenate (CuCZA) COPPERIZED BOLIDEN SALTS*	+	+	+	-	+
7. Copperized Chromated Zinc Chloride (CuCZC)	-	+	+	-	+
8. Fluor Chrome Arsenate Phenol, Type A (FCAP-Type) TANALITH* WOLMAN SALTS*	+	+	-	+	-
9. Fluor Chrome Arsenate Phenol, Type B, (FCAP-Type B) OSMOSALTS* OSMOSAR*	+	+	-	+	-

*Reg. U. S. Patent Office.

- Ingredients not present in this preservative formulation.

+ Ingredients present in the preservative formulation.

the volume of the wood to be treated, and the weight of the treating solution before and after treatment are recorded to give retention values. However, such information gives only an average retention value of the treating charge, because of many variables such as species, grain direction, heartwood and sapwood content, and moisture content. The average retention value does not give a true picture of the retention in the individual pieces nor the concentration of preservatives or ions at different depths from the surface of the treated wood.

Standard methods for analysis of water-borne preservatives are described in the American Wood Preservers' Association manual (2), American Society for Testing and Materials Standards (1), British Standard Institution Standards (10), and other standard agencies. All these methods can be classified into the general category of volumetric and gravimetric analysis. For example, arsenic is determined by taking an aliquot sample (.25 gm. of As_2O_5 content) in hydrochloric acid and precipitating it with hypophosphoric acid on heating. The precipitate is separated by filtering and later dissolving in sulfuric acid. This solution is then suitably titrated with standard sodium bromate solution. Many of the volumetric and gravimetric methods are time consuming and require a relatively large sample for analysis. In the case of a 2 per cent treating solution of Erdalith^R or wood containing 0.35 pounds of Erdalith per cubic foot, a sample of at least

43 ml. solution or 86 grams of treated wood is required for single analysis for the determination of the arsenic, chromium, and copper content. Such large sized samples are objectionable from the viewpoint of wet washing the sample. Also, when thin lumber or veneer is to be analyzed, or the retention is sought for the outer quarter or half inch zone of a boring from a utility pole at ground line, the large sample may spoil the specimen for its intended use.

These practical difficulties in the determination of the constituents of the preservatives in treated wood clearly call for the development of new techniques of analysis. Colorimetric methods and X-ray methods seem to be the answer for these needs. Since cost of installation and maintenance of X-ray equipment are beyond the reach of most wood preserving plants and many research laboratories around the world, this technique of analysis is not adopted. However, it should be pointed out that the X-ray methods save the time consuming task of wet or dry ashing of the sample.

The Principle of Colorimetry

The most fundamental law in colorimetry is the Beers-Lambert Law which states, "Successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of radiant energy traversing them." In mathematical terms it can be stated as

$$\frac{dI}{dn} = -kI$$

where dI is the intensity absorbed at the intensity level of the radiation I by an increment dn in the number of absorbing molecules; k is a constant of proportionality. By rearranging and integrating within limits we get

$$\int_{I_0}^{I} \frac{dI}{I} = -k \int_0^N dn$$

$$\text{or} \qquad \ln \frac{I}{I_0} = -kN$$

where I_0 represents the intensity of radiation entering the cell, and N is the number of absorbing molecules traversed at a point where the intensity of the radiation is reduced to I, for a beam of 1 cm^2 cross-section. For a beam of cross-section area, s cm^2, the equation becomes

$$\ln \frac{I}{I_0} = -kNs.$$

The quantity Ns is a measure of the number of particles which are effective in absorbing radiation. A more useful measure, however, is the product of concentration c and the length of the path b, so that we shall write

$$\ln \frac{I_0}{I} = kbc.$$

For convenience, we shall replace k by another constant a, which includes the factor of conversion from natural to common logarithms:

$$\log \frac{I_0}{I} = A = abc.$$

The quantity $\log \frac{I_0}{I}$ is so important that it is given a special symbol A and called the absorbance (some authors have called A the optical density). The symbol a is called absorptivity, and it is a characteristic of a particular combination of solute and solvent, for a given wave length.

To summarize, the colorimetric method is based upon measuring the light absorptive capacity of the system containing, or chemically equivalent to, the desired constituent. The application of a colorimetric method in a specific case usually involves two principal steps: (1) the separation of the desired constituent from the interfering constituent(s), and/or the development of a suitably colored system; and (2) the measurement of the colored system. The first is largely chemical and the second entirely physical.

Thus, to develop a colorimetric method for determining arsenic, chromium, and copper ions the problem has to be divided into two main parts: (1) the separation of the ion to be determined from any interfering ion and the formation of a stable colored system; and (2) measurement of absorbance of the colored system at such a suitable wave length, usually where the absorptivity value is at a maximum.

Statement of the Problem

Length of time and the quantity of treated wood required to analyze water-borne treated wood are too great when volumetric or gravimetric methods of analysis are used. These factors are the chief drawbacks to progress in method of analyzing treated wood and adhering to specifications based on actual retention of preservative ingredients in wood (such specifications are called result type specifications). The result type specifications have been proposed for pentachlorophenol or creosote treated wood for which colorimetric methods of analysis exist (4). Also, for quality control of treated wood it is essential that a method of analysis for its preservative content be both easy to follow and employ small samples.

It is apparent that new procedures of analysis should be developed, utilizing small samples and easy to handle equipment and reagents. The purpose of this investigation is to develop a procedure for quantitatively determining arsenic, chromium, and copper content in waterborne preservatives and treated wood by colorimetric methods. This problem is divided into four main parts:

1) Digestion of the organic matter of treated wood.
2) Determination of arsenic in treating solutions as well as in treated wood, in the presence or absence of copper and/or chromium.
3) Determination of chromium in treating solutions as well as in treated wood, in the presence or absence of arsenic and/or copper.
4) Determination of copper in treating solutions as well as in treated wood, in the presence or absence of arsenic and/or chromium.

The effect of interfering ions and species of treated wood is also studied.

REVIEW OF LITERATURE

Methods of Analysis

The manual of the American Wood Preservers' Association (2) deals with standard volumetric analysis procedures for determining arsenic, chromium, and copper in the preservative chemicals and solutions. It is also suggested that treated wood can be analyzed after wet digesting (2) the samples. Phillips and Baechler (31) reviewed articles on methods for determining arsenic, boron, etc. that might be useful in wood preservation. They realized the importance of looking for faster and better methods of determining these ions and felt that instrumental methods of analysis offer the best prospect. Belford (5) examined some of the physical methods which could be used for quantitative analysis. X-ray spectrographic and X-ray diffraction, spectrographic, colorimetric, and γ-ray techniques are discussed by Belford for use in the analysis of treated wood. X-ray spectrographic analyses can be satisfactorily used for the determination of metallic ions using small samples of wood.

Recent Developments in Colorimetric Reagents

Colorimetric principles are well known and such great treatises as Sandell (33) and Snell and Snell (36) have dealt with the subject exhaustively. Some recent developments and the theoretical background of the colorimetric reagents are discussed by Johnson (24). He describes the evolution of the pyridyl and phenanthroline reagents in recent years. The group common to these reagents is the $=N-\overset{\|}{C}-\overset{\|}{C}-N=$ chain called the ferroin group, and it is by the virtue of this arrangement that they and many other similarly constituted substances yield ferroin type complexes. G. F. Smith at the University of Illinois and F. H. Case at Temple University, with other co-workers, have prepared some 200 substituted derivatives of phenanthroline and other compounds containing the $=N-\overset{\|}{C}-\overset{\|}{C}-N=$ chain and have determined their characteristics as reagents for several anlytical purposes. Perhaps the most interesting outcome of research on dipyridyl and phenanthroline derivatives is the influence of their ability to react selectively with cuprous complex ions. A list of various derivatives of this group with their molar extinction coefficients or absorptivity for Fe (II) complex and Cu (I) complex is given in Table 2.

Colorimetric Method for Copper

Hoste (19) assigned to 2,2' Biquinoline the common name cuproine because of the analogy of the reagent and its reaction with cuprous ion to the ferroin reaction of ferrous ion with 1,10 phenanthroline. Subsequently, the reagent received considerable attention and was applied to the determination of copper in a variety of materials.

Table 2.--List given by Johnson (24) on the various derivates of ferroin group with their absorptivity values for Fe (II) complex and Cu (I) complex.

Chemical formula	Absorptivity for Fe (II) complex	Absorptivity for Cu (I) complex
2,2'-Dipyridyl	8,650	4,550
1,10-Phenanthroline	11,100	7,150
6,6'-Dimethyl-2,2'-dipyridyl	. .	6,570
2,2'-Biquinolyl (cuproine)	. .	5,490
2,9-Dimethyl-1,10-phenanthroline (neocuproine)	. .	7,950
4,7-Diphenyl-1,10-phenanthroline	22,400	. .
2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine)	. .	14,160

Other copper specific reagents in this series are neocuproine and bathocuproine. An excellent bibliography on cuproine, neocuproine, and bathocuproine is available in the pamphlet by Diehl and Smith (11). Sodium diethyldithiocarbamate, dithiozone, and potassium ethyl xanthate reagents have also been used for the colorimetric determination of copper. The limitations of these methods with their advantages and disadvantages are discussed by Snell and Snell (36). However, these reagents were not selected for the present work as they have been shown to lack sensitivity, selectivity, and stability.

Edge (13) has found that carboxylic acid cation exchange resins can be used with success in determining copper in chromated wood preservative solutions. He has used the resin column to separate copper from other metallic ions of the solution and later recovered the copper with hydrochloric acid. For the purpose of determination of copper he used the volumetric method. Ion exchange resins have also been used in industry for separation of copper from other ions.

From the various methods described the cuproine method was selected for this work. The major considerations for selecting this method were:

1) Specificity.--2,2' Biquinoline is specific for copper. Breckenridge, Lewis, and Quick (8), Hoste (15) (19-22), and later Guest (17) found that none of the following cations gave color

reaction with the reagent: NH_4^+, Li, Na, K, Rb, Cs, Be, Mg, Ca, Ba, Al, La, Ce (III), Ce (IV), Nd, Sm, Ti (IV), Zr, Th, V (V), Nb, Ta, Cr (II), Cr (III), Mo (VI), W (VI), UO_2^{++}, Mn, Fe (II), Fe (III), Ru, Co (II), Rh, Ir, Ni, Pd, Pt, Ag, An, Au, Zn, Cd, Hg (I), Hg (II), Ga, In, Tl, Ge, Sn (IV), Pb, As (III), As (V), Sb (III), Sb (V), Pn, Se (IV), Se (VI), Te (IV), Te (VI). The titanous ion gives a pale green color which cannot be confused with the purple color of cuprous-biquinolene compound. Some ions, of course, interfere because of their own color, nickel for example; none of these is extracted into isoamyl alcohol. Among the anions, the following anions do not affect the cuprous biquinoline cation: acetate, borate, bromide, chloride, chlorate, perchlorate, tartrate, nitrate, sulfate, and phosphate. Cyanide, thiocyanate, iodide, and oxalate anions do interfere.

2) According to Smith (11) 0.008 µg. of copper in 1 ml. of water gives a detectable color.

3) The sensitivity of the detection of copper with biquinoline may be improved by extracting the colored copper with an immiscible solvent. The purple cuprous-biquinoline compound is soluble in isoamyl alcohol, benzyl alcohol, hexyl alcohol, benzene, carbon tetrachloride, chloroform, ethyl

acetate and amyl acetate. The partition coefficient is greatest in isoamyl alcohol and this solvent is used in this work.

4) The extraction with isoamyl alcohol of cuprous biquinoline gives an excellent method of separation of copper from the digestion mixture obtained either from the usual perchloric acid method or the new peroxide method. The color is very stable for many days. However, fading has been reported and has been ascribed to oxidation of the cuprous compound either by air or by an oxidizing impurity in isoamyl alcohol used for extraction. No trouble is experienced if an excess of reducing agent is present.

Colorimetric Methods for Arsenic

Arsenic compounds have been used as wood preservatives for a long time. At the present time arsenic is determined volumetrically in research laboratories as well as in treating plant laboratories. Until recent years, small quantities of arsenic were determined nearly exclusively by the Gutzeit method (33), but now its position is seriously threatened by the rival molybdenum blue method and the 1,2 molybdoarsenic method.

An excellent review of the determination of arsenic has been reported by the Analytical Methods Committee of the Society for Analytical Chemistry, England, and reported in the Analyst (41). Arsenic used to be separated as arsenious chloride from hydrochloric acid solution or by volatization of arsenic as arsine, which in turn is decomposed into elemental arsenic by passage through a silica tube heated to 800°C. The chief source of error in the procedure is likely to be the incomplete absorption of arsine. Trivalent arsenic can be extracted, from acid solutions, as xanthate, by carbon tetrachloride. Other metal xanthates, which are also extracted, can be removed from carbon tetrachloride by washing with concentrated hydrochloric acid containing stannous chloride.

W. J. Wilson (44) determined arsenic in treated wood by modifying a volumetric method proposed by Schulek and Villecz (34). In this method a one gram sample of treated wood is decomposed with concentrated nitric acid and sulfuric acid, reduced with hydrazine sulfate solution, and the excess of the reagent decomposed by fuming. The solution is titrated with 0.01N ceric sulfate solution in the presence of osmium tetraoxide using ferrous O-phenanthroline perchlorate as a catalyst.

Sandell (33), Snell and Snell (36), and other standard treatises on colorimetric analysis give the details and variations of the molybdenum blue method. Of the several variants of the molybdenum blue method (23) (30) (37) (38) and (45), the procedure recommended by the Analytical Methods Committee of the Society of Analytical Chemistry, England, for the determination of small amounts of arsenic in organic matter follows most closely the method proposed by Wyatt (45). In this method the organic matter is destroyed by wet digestion and the arsenic, after extraction with diethylammonium diethyldithiocarbamate solution, is converted to the arsenmolybdate complex, which is then reduced by means of hydrazine sulfate to a molybdenum blue compound and determined absorptiometrically at a wave length of 840 mμ. Since working at 840 mμ. requires adjustment of the instrument (replacing the phototube with a red sensitive tube and putting a red filter in the path of incident radiation), this method was not considered further.

However, the arsenomolybdate complex mentioned earlier has been thoroughly investigated by Waldelin and Mellon (43). They investigated the character of the absorption spectrum of the colorless 1,2 molybdoarsenic acid solution in the near ultra violet region. They applied the familiar process of liquid-liquid extraction of the heteropoly acids from water into certain organic solvents. It was found that 1,2 molybdoarsenic acid can be extracted from the aqueous phase into butan-1-ol. Following extraction it is possible to make absorption measurements at 370 mμ. where the molar absorptivity for arsenic is 5100. Waldelin and Mellon have reported the effect of 48 diverse ions along with methods for preventing interference from soluble silica, iron, and small amounts of orthophosphates.

Tanaka and Hiiro have proposed several methods for determination of arsenic with quincetin (39), rutin (40), and morin (18) reagents. However, these methods require separation of arsenic from the organic matter by the usual arsine method followed by extraction with complex forming agents (rutin, morin, etc.) and later evaporation of the solvent. The arsenic complex is then brought into alcohol solution and the absorption read at known wave length (440 mμ.). As these methods require heating, evaporation, and waiting periods for the color to develop, they were not found useful for this work.

Colorimetric Methods for Chromium

Chromium salts in water-borne preservatives basically are used because of their property of fixing the other components (e.g., copper and arsenic) in the treated wood (25) (29). The fixation of chromates and dichromates consists of their reduction by the constituents of the wood to chromium ion, which forms a stable bond with the constituents of the wood. Somewhat similar but probably rather more complex changes take place when a copper-chrome-arsenic solution is used (42). Potassium or sodium dichromates, chromic acid, and sodium chromate have been in use in many of the patented water-borne preservatives. In the usual volumetric analysis chromium is determined as hexavalent chromium iodometrically or by a back titration method with ferrous ammonium sulfate and standard potassium dichromate solution (2).

Various colorimetric methods have been proposed for quantitative determination of chromium in the iron and steel, chromium plating, and leather tanning industries. According to Sandell (33) the most useful method for the separation of chromium involves oxidation in the basic media, whereby chromate is formed and remains in solution, while a great many metals such as iron, titanium, manganese, nickel and cobalt, etc. are precipitated. The oxidation can be effected in hot solution with sodium peroxide/hydrogen peroxide and sodium hydroxide. In acid media oxidation can be achieved with persulfate in the presence of silver as a catalyst. Other common agents for oxidation of chromium to the hexavalent state are bismuthate, permanganate, bromine, and silver oxide. It is always necessary to destroy the excess of the alkaline oxidant. Peroxide will reduce chromium (VI) in acid solution. Boiling in alkaline solution is the procedure employed for the destruction of peroxide, which is the usual alkaline oxidant employed. This reaction is very slow and the last traces of peroxide are very difficult to remove. If ferric ammonium sulfate is added as catalyst, or ferric or nickel oxides are present in the solution, ten minutes boiling is sufficient. For the highest accuracy, or in the case of traces of chromium, a secondary oxidation is employed with permanganate solution.

The outstanding colorimetric method for the determination of chromium is that which depends on the intense red-violet color developed on the addition of a solution of s-diphenyl carbazide to an acidified solution of a chromate or dichromate. Numerous research papers have been published on the nature of the reaction, preparation of the reagent, stability and sensitivity of the color reaction. A very good summary of the exhaustive work on s-diphenyl carbazide chromium complex is provided by Kolthoff, Elving, and Sandell (26). Mann and White (28) extracted the chromium (IV) with trioctyl phosphine oxide in benzene, then measured the color by addition of alcoholic diphenyl carbazide directly to the benzene extract.

There are too many interferences with the diphenyl carbazide method. It is reported (33) that the chromium reading will be about ten per cent low if copper is present in amounts 500 times the chromium concentration. Iron, mercury, and vanadium have also been found to affect the determination of chromium by this method.

A colorimetric determination of chromium has also been proposed (33) in which the absorption of its alkaline solution is read at a wave length of 374 mμ. The general procedure is to convert chromium to the hexavalent state, adjust the pH to 8.5 to 9.5, and take an aliquot of 5 to 100 parts per million of chromium. The absorbance is measured at 365 to 370 mμ, and is compared with the standard, which should be adjusted to the same pH and inert salt concentration as the unknown. Since preparation of a standard solution of the same inert salt content (copper,

arsenic, etc.) is laborious, this method is not very effective.

An extremely stable complex of chromium (III) is formed with ethylenediaminetetraacetic acid (6), but its formation is very slow at room temperature although it proceeds rapidly on heating. Several investigators have reported on the possible use of EDTA complex with chromium (III) and the effect of interfering ions, pH of the solution, etc. Boef, DeJong, Krijin, and Poppe (6) (7) critically investigated the spectrophotometric determination of chromium (III)-EDTA complex. They suggested that separation by EDTA or TTA produces better results than oxidation to chromate. However, their procedure is laborious and time consuming.

Majumdar and De (27) report on the use of TTA (2-thenoyltrifluoroacetone) for the direct determination of chromium (III) in the organic phase. Their method gives a simultaneous extraction and colorimetric method for milligram amounts of chromium (III) on the basis of the formation of an orange chelate with TTA, which is extractable with an organic solvent such as benzene. The colored system is reported to be stable for a week. The colored solutions produced by this method conform to Beers Law at 430 mμ. over the concentration range of 8 to 200 μg. of chromium (III) per ml. The wave length 430 mμ, is very critical; plus or minus 5 mμ. gives a very large difference in the absorbance reading. Due to the limitation of the colorimetric instruments used in this study, this method did not give satisfactory results.

Brookshier and Freund (9) report determination of chromium as perchromic acid, which can be extracted with ethyl acetate and determined photometrically as the blue perchromic acid at a pH of 1.7 ± .2 at 20°C. The perchromic acid could be formed by reducing dichromate ions with hydrogen peroxide in acid media. The presence of organic liquids and lower temperature stabilizes the perchromic acid formed. Large amounts of iron, manganese, vanadium, molybdenum, and tungsten do not interfere. Beers Law is observed. Glasner and Steinberg (16) proposed the separation of chromium from vanadium by extraction of perchromic acid with ethyl acetate, to be determined subsequently, by the possibility of using ethyl acetate extractions for determination of chromium without going through the diphenyl carbazide method. They confirmed the finding of Brookshier and Freund, i.e., that the aqueous solution at equilibrium should have a pH of 1.7 ± .2 and that the ethyl acetate extracts are fairly stable up to 20°C. They also compared their perchromic acid results with those of the diphenyl carbazide method and found that the perchromic acid method gave better results (see Table 3). Glasner and Steinberg also reported that the absorbances are a linear function of the concentration of the dichromate, up to and somewhat above the absorbance of one, and independent of the mineral acid used. Foster (14) of the U. S.

Table 3.--Comparative results from perchromic acid method and diphenyl carbazide method for determining chromium from ethyl acetate extraction, as reported by A. Glasner and M. Steinberg (16).

Initial amount of chromium	Chromium by perchromic acid method		Chromium by diphenyl carbazide method	
Mg.	Mg.	%	Mg.	%
0.05326	0.05334	100.2	0.05154	96.8
0.1065	0.1057	99.2	0.1025	96.3
0.1598	0.1611	100.8	0.1552	97.1
0.2130	0.2128	99.9	0.2058	96.6
0.2663	0.2647	99.4	0.2554	95.9

Geological survey reported that the perchromic acid method can be applied in mineral analysis, provided chromium is present in the amounts of 0.5 to 5 mg.

A modified blue perchromic acid method is used in this work because of the simplicity of the procedure and accuracy of the results.

Digestion Methods

All the colorimetric methods discussed so far can only be applied to the respective ions in solution. In the case of treated wood, the first problem is to bring the ions to be determined (e.g., arsenic, chromium, and copper) into solution by destroying the organic matter. This process is known as digestion or ashing. Dry ashing used to be the standard method for digestion in the wood preserving industry but in recent years the wet digestion (3) procedure has been utilized. The main disadvantages of the dry ashing method, according to Sandell (33), are that copper may be lost, owing to the reaction with other constituents of the ash. It is also probable that copper may react with the vessel used for ignition to form sparingly soluble copper compounds. Chromium could be volatized as chromylchloride if chloride ions are present in the wood.

The wet digestion of organic matter employing hot concentrated perchloric acid is discussed by Smith (35). The American Wood Preservers' Association has also incorporated the wet digestion method in their manual (2).

However, the most exhaustive study on the destruction of the organic matter (both dry and wet ashing) has been done by the Analytical Method Committee of the Society of Analytical Chemistry, England (42). They have considered various combinations of the acid (nitric, sulfuric, etc.) and oxidants (perchloric acid, hydrogen peroxide, etc.) according to the elements that are required to be analyzed after the destruction of the organic matter.

Because of the study reported above, it was not thought wise to repeat the work to find a suitable method of ashing the treated wood. A critical review of the method proposed indicated that the wet digestion using sulfuric acid and/or nitric acid with perchloric acid or hydrogen peroxide would give complete destruction of the organic matter as well as retain all the ions which are to be determined by colorimetric methods. Since the handling of perchloric acid is hazardous and serious accidents are possible, the hydrogen peroxide method has been adopted. The details of this method will be given later on pages 31, 33 and 34.

EQUIPMENT AND REAGENTS

1. Colorimeter.--The selection of the colorimeter for commercial testing plant use depends on its available wave length range, sensitivity, and the initial and maintenance cost. Though recording type instruments are available in the market, they were not used for these experiments for economic reasons. Table 4 gives a comparison of the features available in different reading types of colorimeters. Since a B and L Spectronic 20 colorimeter was available and its features qualify it for the present investigation, all the experiments were carried out on it. Many other instruments which give the same or better performance can also be used.

Bausch and Lomb's "Spectronic 20," shown in Figure 1, is a versatile instrument and is available at low cost. It is useful for both spectrophotometric and colorimetric measurements. The specifications and other details of this instrument are described in Table 4. B and L colorimetric specimen tubes of 3/4 inch diameter were employed in these experiments.

2. pH Meter.--Where not otherwise mentioned, a Beckman Model N pH meter was used throughout these experiments to determine the pH of the solution. At some

Table 4.--Comparison of visible ultraviolet non-recording spectrophotometers.*

	Beckman DU	Beckman B	B and L Spectronic 20
Range	210-1000 mµ.	325-1000 mµ.	350-950 mµ.
Source	Interchangeable tungsten and hydrogen discharge tube	Tungsten lamp	Tungsten lamp
Monochromator	Littrow quartz prism	Ferry prism	Grating
Design principle	Single beam, null balance	Single beam, direct reading	Single beam, direct reading
Resolution	Ultra violet 0.3 mµ. Visible 1.0 mµ.	0.5 mµ. 1.0 mµ.	0.20 mµ.
Detectors	Red and blue sensitive phototube	Red and blue sensitive phototube	Red and blue sensitive phototube
Slits	Continuously adjustable from 0.01 to 2.0 mm.	Adjustable from 0.01 to 1.5 mm.	Nonadjustable
Stray light	Maximum 0.1% in visible range	1% at 320 mµ. 1.7% at 580 mµ.	Not specified
Reproducibility	Ultraviolet 0.05 mµ.	0.05 mµ.	Not specified
Wave length transmittance	Visible 0.2 0.1%	0.2% full scale	Not specified

*Table 581V of Treatise on Analytical Chemistry Part I, Volume 5, Edited by Kolthoff, Elving, and Sandell. Interscience Publication, New York. 1964.

Figure 1.--Shows the Bausch and Lomb Spectronic "20" Colorimeter (WU1043X) with its Voltage Regulator (WU1159X). On the right hand side of the colorimeter are shown the B and L colorimetric tubes in their rack. In the foreground (from right to left) the first three watch glasses show the form of one gram samples of treated wood which can be used for colorimetric analysis. The fourth watch glass shows the treated and untreated wafer and the microsyringe used for treatment. The treating solution is shown in the volumetric flask. The two white capped bottles contain 84 grams of ground sample required for volumetric analysis.

places, pHydration paper AB-pH 1-11 and pH 1.2-2.4 manufactured by the Micro Essential Laboratories, Inc., Brooklyn 10, New York, was also used in the procedures for the determination of arsenic, copper, and chromium respectively, in order to obtain a general idea of the pH of the solution. For precise measurement (in the chromium analysis) the pH meter was used.

3. Reagents.--All the reagents used in these experiments pass A.C.S. specifications. The colorimetric reagents for the determination of copper were purchased from G. F. Frederick Smith Company of Columbus, Ohio. A complete list of reagents used for the volumetric method of analysis is given in Appendix I. The reagents for colorimetric analysis are described with the procedure for analysis.

4. Cleaning solution.--A "Wash acid" consisting of 50 ml. of nitric acid (sp. gr. 1.42) and 150 ml. of hydrochloric acid (sp. gr. 1.19) in 200 ml. of water is recommended by Saltzman (32) for cleaning glassware in which chromium in acidic media has been kept for a long duration. Saltzman's "Wash acid" was used for cleaning glassware. For general cleaning purposes, a detergent solution (Tide^R) was used in these experiments.

After cleaning with the detergent solution or wash acid, the glassware was thoroughly washed with tap water, followed by twice washing the glassware with double distilled water.

5. Redistilled water.--The copper content of distilled water obtained from the Chemistry Department was determined to be 0.2 μg/ml. This warranted another distillation in all glass vessels. The copper content of this redistilled water was found to be less than one hundredth microgram per milliliter.

EXPERIMENTAL PROCEDURE AND RESULTS

Preparation of Treated Wood Samples

The usual preservative impregnation techniques could not be applied successfully to impregnate microgram to milligram quantities of preservative ingredients to achieve an accuracy of 95 per cent or more. The procedure given below was followed for preparing treated wood samples:

> The wood to be treated was cut into a wafer (1/8" thick and 3/4" wide). A piece weighing one gram (±.05 gram) was cut from it. This weighed piece was laid flat on two glass rods which supported the edges of the sample. A known volume of the solution was introduced on the flat surface drop by drop through a microsyringe. Care was taken that all the solution introduced was absorbed by the wood sample only. Only 0.6 ml. of the solution could safely be placed on the surface at a time. If more solution had to be introduced, this was done after a time interval long enough for all previous treatments to be absorbed, so that the sample had dried sufficiently to be able to absorb more. Generally, with a drying time of 12 hours or overnight, the solution could be added in steps of 0.6 ml. or less. The sample was

dried for at least 48 hours at room temperature after the desired volume of the solution was introduced in it.

The dried sample of known ingredient content could either be placed on a glass plate and cut into thin slices (see Figure 2) or made into a powder by placing it in a micro Wiley mill (see Figure 2).* The treated wood sample could now be digested by the procedure given below.

Digestion Procedure

Reagents.--

1) Sulfuric acid, concentrated 96 per cent (arsenic content less than 6×10^{-7} per cent).
2) Hydrogen peroxide 30 per cent.

Acid/oxidant: Two volumes of 30 per cent hydrogen peroxide plus one volume of sulfuric acid.

Procedure.--The following procedure was used for one gram treated wood samples in sliced form:

The accurately weighed sample was placed in a 150 ml. beaker. Two or three boiling chips were added to prevent bumping. Fifteen milliliters of the acid/oxidant solution were gradually added. The beaker was then kept on a hot plate at medium heat and allowed to boil for ten minutes. If any charring was noticed or the color of the resulting solution

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*Figure 2 also shows the comparative sizes of samples required for colorimetric and volumetric analysis.

Figure 2.--Shows the comparative size of sample required for colorimetric and volumetric analysis. Each watch glass contains one gram of treated wood sample. The left hand bottom watch glass shows sliced wood, the top one shows ground wood sample, and the remaining watch glass shows sliced increment boring. The two bottles, shown on the right, contain 84 grams of ground wood sample required for volumetric method of analysis.

turned black, the beaker was removed from the hot plate and cooled. A few drops of hydrogen peroxide were added and the contents again boiled. This step was repeated until the final color of the solution was light orange to light yellow. The contents were cooled to room temperature.

In the case of treated wood of high chloride content (CZc, CuCZc treated wood), the above procedure was modified. Before addition of acid-oxidant solution, 10 ml. of nitric acid (1:10) were added and allowed to soak into the wood. The contents of the beaker were heated at low heat so as to start a vigorous reaction in which the sample seemed to be charred. The contents were cooled and acid/oxidant solution added. The procedure given in the previous paragraph was followed thereafter.

For the ground sample, the beaker was replaced with an appropriate Kjeldahl flask (for one gram sample 100 ml. flask was used and for ten gram sample 500 ml. flask was used). The Kjeldahl flasks were heated at low heat from gas burners instead of a hot plate. The procedure of digestion was the same as that followed for sliced wood with the only modification that for a five gram sample, 50 ml. of the acid/oxidant solution was used.

The digested solution was transferred into a 50 ml. volumetric flask. The beaker/Kjeldahl flask, in

which digestion was carried on, was washed twice with 5 ml. 1:1 ammonium hydroxide or 10 per cent sodium hydroxide solution and the alkaline solution added to the volumetric flask. This flask was then cooled to room temperature and redistilled water was added to bring the level of the contents up to the mark.

Determination of Copper

Copper has been used in water-borne preservatives as copper sulfate ($CuSO_4 \cdot 5H_2O$), copper hydroxide ($Cu(OH)_2$), and cupric chloride ($CuCl_2 \cdot 2H_2O$). The intention has been to analyze both preservative solutions and treated wood by a rapid method and to determine a content range of 20 to 200 µg. of copper per gram of treated wood or per milliliter of the treating solution with a precision of more than 95 per cent.

Separation Techniques

It has been mentioned that 2,2' Biquinoline (cuproine) forms a purple cuprous-cuproine compound which can be extracted by various organic liquids, e.g., isoamyl alcohol, benzene, carbon tetrachloride, chloroform, or ethyl acetate. Hoste, Eeckhout, and Gillis (22) have recommended isoamyl alcohol, since it has the highest partition coefficient. Guest (17) showed that a shaking time of one minute using isoamyl alcohol is sufficient to establish equilibrium if the pH of the aqueous solution is between 4.4 and 7.5. The extraction method fits in with

the procedure for quantitative determination of copper described in the next section.

Determination in Solution

Ion exchange resins have been used for the separation of copper from aqueous solutions containing chromium and arsenic. A screening experiment was performed to ascertain the suitability of this method. Amberlite 120 cation exchange resin was used. The copper cation is held by the resin while the anions containing chromium ($Cr_2O_7^{--}$) and arsenic (AsO_4^{---}) pass through the resin column. The effluent solution can then be analyzed for chromium and/or arsenic.

Preparation of ion exchange column.--A 25 ml. buret was used for the column. A paste of Amberlite 120 resin in water was prepared and poured into the buret so as to make a column. The resin column was supported on a glass wool plug. Ten millimeters of 6N sulfuric acid were then poured into the buret and allowed to soak through the resin at a flow rate of 0.25 ml. per minute. When the liquid level reached the top of the resin bed, another 10 ml. of 6N sulfuric acid were poured in and repeated the process of soaking. The resin bed was thus made ready for the separation of copper from the preservative solution containing 6N sulfuric acid. This normality of the acid was chosen because it was the same as that present in the digestion solution.

Procedure.--Five ml. of the preservative solution (2 per cent Erdalith), adjusted to 6N sulfuric acid concentration, were then poured gradually into the column and the flow rate adjusted to 0.25 ml. per minute. When the level of the preservative solution reached the top of the resin bed, 5 ml. of 6N sulfuric acid were added, followed by two 5 ml. portions of redistilled water. The effluent solution was collected in a 150 ml. beaker. The copper content of this effluent solution was determined by the cuproine method (described on pages 38-40). The copper from the resin bed was removed by passing 20 ml. of 3N hydrochloric acid through the resin bed at a flow rate of 0.25 ml. per minute.

Results.--Table 5 gives the amount of the copper ion detected in the effluent preservative solution. It is found that 98 to 99 per cent of the copper was extracted by the resin. The ion exchange resin method is effective in separating the copper of the preservative solution from chromium and arsenic ions of the solution. However, it has been found to be a very time consuming method, because one analysis takes at least 1-1/2 hours for 5 ml. of the sample. Further, in the determination of copper, the extracted copper from the resin has to be brought back into solution and then determined by the cuproine method. It was due to the time factor that this method was not adopted.

Table 5.--Determination of copper in the effluent solution after extraction of copper by ion exchange resin (Amberlite 120).

Copper present in Erdalith solution µg.	Copper found in effluent solution µg.	Recovery %
1680	34	98
3360	30	99.1
5040	36	99.3
6720	42	99.3
8400	50	99.4

Notes:

The 2 per cent Erdalith solution was prepared by dissolving 2.2431 grams of potassium dichromate in 50 ml. distilled water and 10 ml. of concentrated sulfuric acid. To this were added 1.32 grams of copper sulfate ($CuSO_4 \cdot 5H_2O$) and 0.44 grams of sodium arsenate. The volume of the solution was then adjusted to 100 ml.

Copper was determined by the cuproine method described on pages 38-40.

Determination of Copper by Cuproine Method

Reagents.--

Cuproine solution: A 0.1 per cent solution of cuproine was prepared in isoamyl alcohol.

Isoamyl alcohol: Redistilled isoamyl alcohol as supplied.

Hydroxylammonium chloride: A 10 per cent solution was prepared in water by dissolving ten grams of hydroxylammonium chloride in 100 ml. of redistilled water. Copper content of this solution was checked by adding a few ml. of cuproine solution and then 10 ml. of isoamyl alcohol. The solution was shaken and separated into layers. It was found that the copper content of isoamyl alcohol showed no purple color and the absorbance at 546 mμ. was zero as compared to pure isoamyl alcohol.

Standard copper solution: A standard solution containing 20 μg. copper per ml. was supplied by the G. Frederick Smith Company of Ohio. Another standard solution containing 100 μg. copper per milliliter was prepared by dissolving 0.3926 gram of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 1 liter of redistilled water.

Procedure.--The following procedure is used for extracting and determining copper content of 20 to 200 μg. from an aqueous solution of pH 5-6:

An aliquot sample of the preservative solution was pipetted into a 125 ml. separatory funnel. Five ml. of 10 per cent hydroxylammonium chloride were added. The pH of this solution in the separatory funnel was adjusted to 5 to 6 with dilute ammonium hydroxide solution or 1:10 sulfuric acid, using a pH paper.

Two ml. of the cuproine solution were added followed by the addition of 10 ml. of isoamyl alcohol. The separatory funnel was shaken for one minute and the contents allowed to separate into layers. The lower aqueous layer was poured into another separatory funnel and the alcohol layer poured into a 25 ml. volumetric flask. The aqueous layer was extracted again with 10 ml. of isoamyl alcohol and, after one minute of shaking, the layers were separated. The isoamyl alcohol layer was added to the volumetric flask and the volume was brought to 25 ml. with isoamyl alcohol. If desired, the aqueous layer could be saved for the determination of chromium or arsenic or both. The extraction of copper was thus complete.

The isoamyl alcohol collected was then poured into a 50 ml. beaker, and one gram of sodium sulfate was added to absorb any traces of water. The absorbance of this solution was then determined against isoamyl alcohol at 546 mμ. It was observed that it was better to find the transmittance first, as its scale is divided equally throughout the full range from zero to 100 per cent. From a standard conversion chart the transmittance could be converted to the absorbance reading.

Preparation of standard calibration curve.--Following the procedure laid down in the previous section, the absorbance was measured for known amounts of copper by taking samples from the standard solutions. The absorbance data have been presented in Table 6 and Figure 3.

Determination in Treated Wood

Samples of wood containing known amounts of copper were prepared with the standard copper solution (100 µg/ml.) according to the procedure described on pages 30 and 31. For bringing the pH of the digested solution to 5-6 both sodium hydroxide and ammonium hydroxide could be used. However, when sodium hydroxide was used, the pH was never allowed to go above 7, due to the possibility of precipitating the copper hydroxide. Copper hydroxide forms a soluble complexion in ammonium hydroxide; hence a 1:1 solution of ammonium hydroxide was used.

A standard calibration curve was prepared for treated wood, similar to the one described above for solutions. Treated wood samples containing 20 to 200 µg. copper were prepared and the absorbance data were collected, as reported in Table 7 and Figure 4. Sugar pine wood was used in this experiment. A control sample (one gram of untreated wood) was also used, and it

Table 6.--Calibration data for determining copper in standard solution by cuproine method.

Standard solution	Volume tested ml.	Copper present µg.	Absorbance
G. Frederick Smith Company standard solution containing 2 µg. copper/ml.	10	20	.114
	20	40	.232
	40	80	.460
	60	120	.690
	80	160	.920
	100	200	1.150
Standard solution prepared in lab. containing 100 µg. copper/ml.	0.2	20	.112
	0.4	40	.232
	0.6	60	.348
	0.8	80	.455
	1.0	100	.580
	1.2	120	.680
	1.4	140	.810
	1.6	160	.900
	1.8	180	1.020
	2.0	200	1.155

Figure 3.--Absorbance vs. copper content in solution, calibration graph.

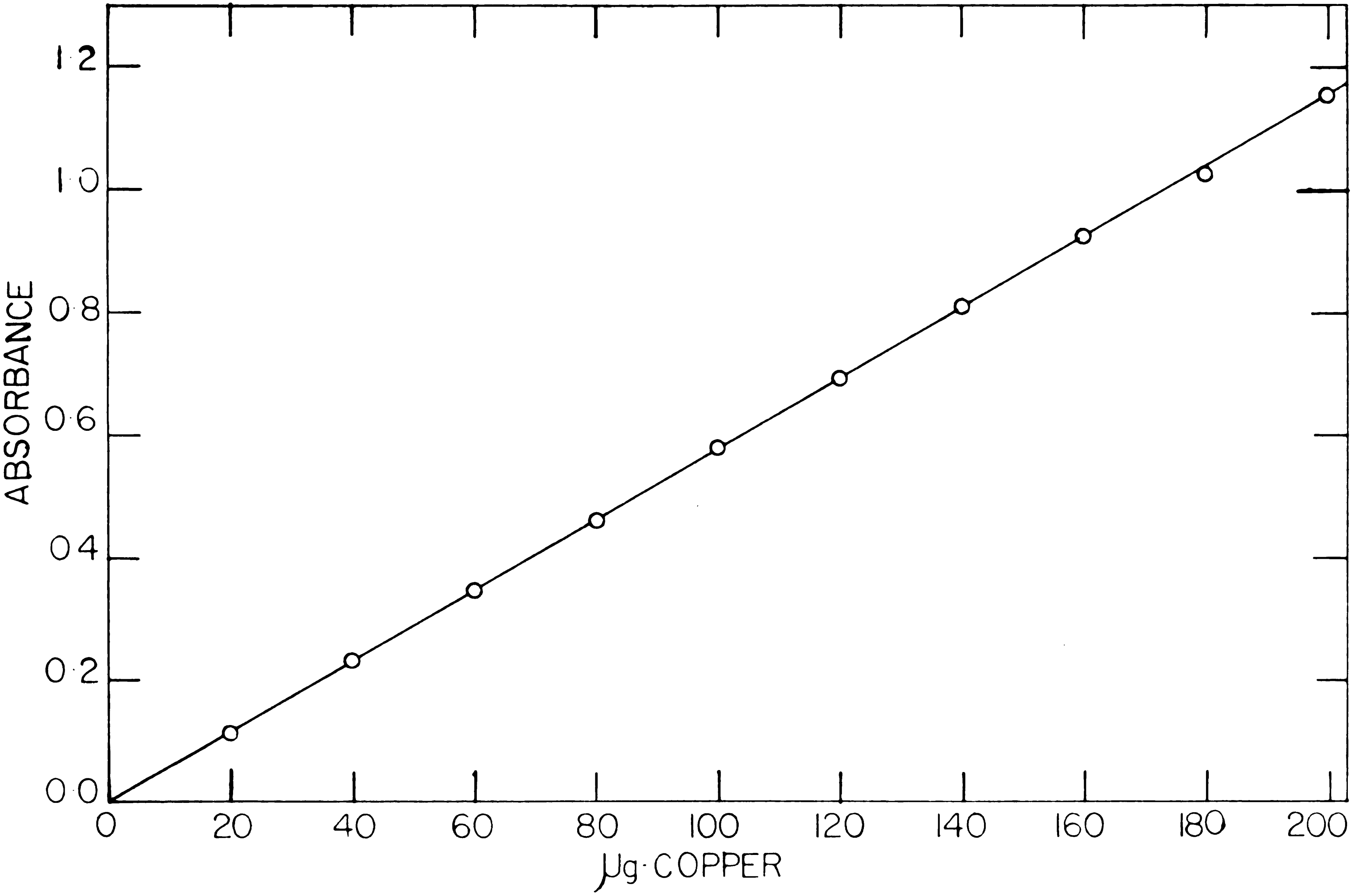
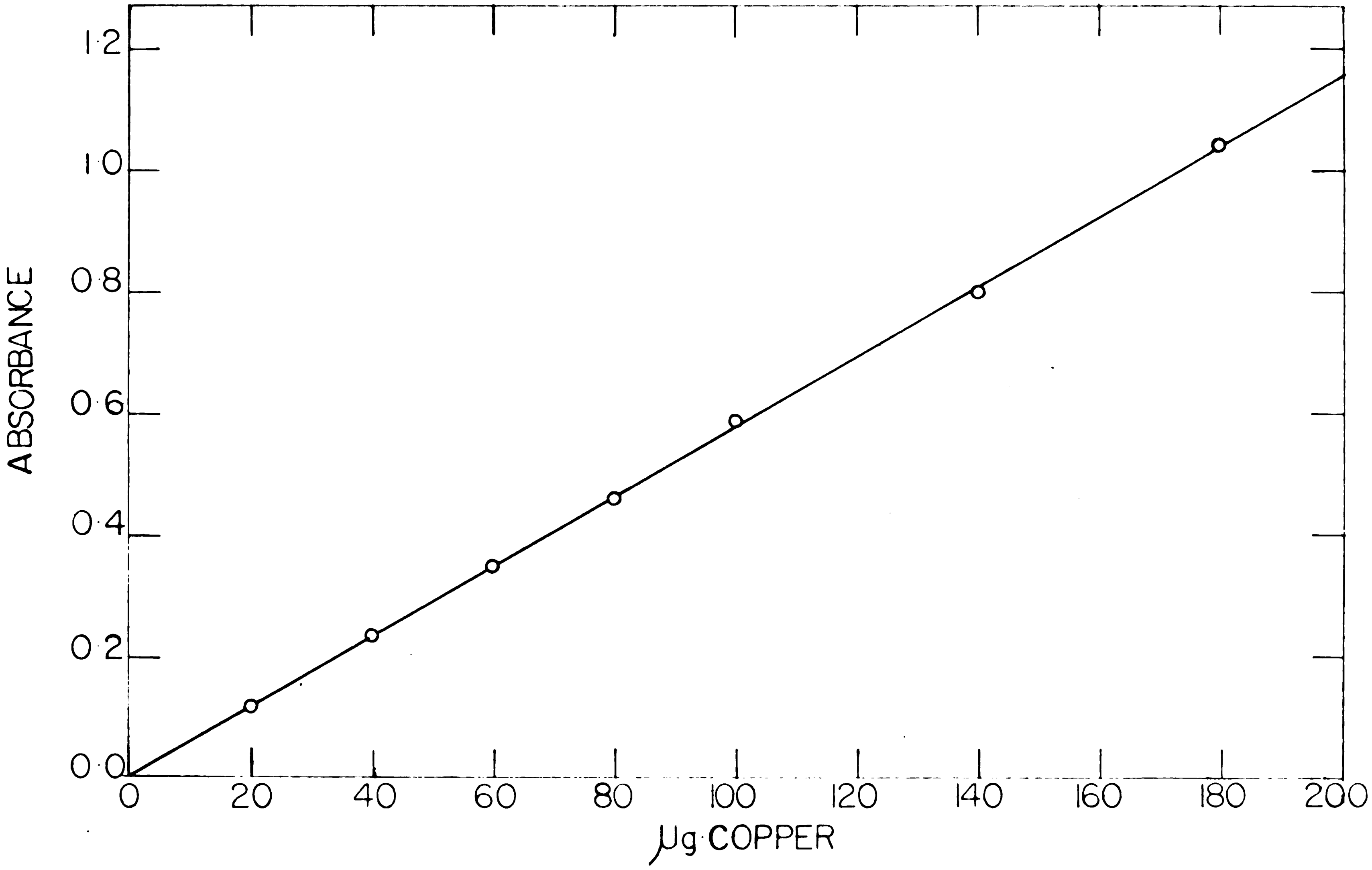


Table 7.--Calibration data for determining copper in treated wood by cuproine method.

Copper present in treated wood µg.	Absorbance
20	.120
40	.238
60	.350
80	.460
100	.590
140	.820
180	1.040
200	1.160

Figure 4.--Absorbance vs. copper content in treated wood, calibration graph.



furnished the zero reading of absorbance for the data of all treated wood samples.

The standard calibration curve was prepared as shown in Figure 4. The slopes of both graphs are the same, and the calibration curve is a straight line.

Effect of Arsenic and Chromium

Standard solutions for chromium (100 µg/ml.) and arsenic (100 µg/ml.) were prepared and known amounts of these were added to 1 ml. of the standard copper solution (100 µg/ml.). The procedure laid down in this section was followed and copper content was determined. From the absorbance data collected, the amount of copper was determined from Figure 3. Table 8 presents the collected data and the per cent of error in the determination of copper.

For studying the effect of chromium and arsenic ions on the determination of copper in treated wood, the samples of treated wood containing known amounts of copper, chromium, or arsenic, or both, were prepared by the procedure given on pages 30 and 31. These samples were digested and the cuproine method followed to determine copper with the aid of Figure 3. Table 8 presents the collected data and the per cent of error in the determination of copper.

Table 8.--Effect of arsenic and chromium on determination of copper by cuproine method.

Copper present µg.	Arsenic present µg.	Chromium present µg.	Copper found in solution µg.	Copper found in wood µg.	Error found in solution %	Error found in wood %
100	0	0	100	101.3	. .	1.3
100	10	0	100.6	101.4	0.6	1.4
100	30	0	100.2	101.8	0.2	1.8
100	60	0	101.0	98.6	1.0	-1.4
100	100	0	101.8	102.2	0.8	2.2
100	0	50	99.9	101.3	-0.1	1.3
100	0	100	100.8	101.6	0.8	1.6
100	0	200	100.6	99.8	0.6	-0.2
100	0	400	100.2	101.6	0.2	1.6
100	0	600	100.2	102.1	0.2	2.1
100	30	170	100.8	101.4	0.8	1.4

Effect of Suspected Interfering Ions

Contact with wood treating equipment sometimes results in pickup of ions such as iron and zinc by the preservative solution. Phosphates and silicate ions could be contributed by the wood or might enter treating solutions from other sources. These may affect the analysis of copper by the cuproine method. It has already been reported that the cuproine method is specific for copper (I) and iron, zinc, phosphate, or silicates do not interfere. However, to make sure that the method proposed on pages 38-40 can be successfully applied to the analysis of commercial treating solutions and treated wood, the effect of these ions was also tested. Table 9 gives the effect of these interfering ions.

Effect of Species of Treated Wood

All the work on the treated wood was done on one species only, namely, sugar pine. A study was undertaken at this stage to determine if there is any effect of the species of treated wood on the determination of copper by the colorimetric method described on pages 38-40. Southern yellow pine, Douglas fir, and red oak were the other three species of wood that were tested.

Only the colorimetric method of analysis for copper was used, and the samples were prepared according to the procedure given on pages 30 and 31 by adding 1 ml. of 2 per cent Erdalith solution to a one gram wood wafer of each species. Table 10 presents the data collected.

Table 9.--Effect of suspected interfering ions on the determination of copper (100 μg.) by the colorimetric method.

Suspected interfering ion	Added as	Amount added μg.	Error %
Fe	$FeCl_3$	400	1.80
SiO_3	Na_2SiO_3	400	0.30
PO_4	$NH_4H_2PO_4$	400	0.40
Zn	$ZnCl_2$	400	0.50

Table 10.--Effect of species of treated wood on the determination of copper by the colorimetric method.

Specie of wood	Copper present μg.	Copper found μg.	Error %
Sugar pine (*Pinus lambertiana*)	1680	1684	0.23
Southern yellow pine (*Pinus* sp.)	1680	1692	0.71
Douglas fir (*Pseudotsuga menziesii*)	1680	1686	0.36
Oak (*Quercus rubra*)	1680	1698	1.07

Determination of Chromium

Sodium chromate, sodium dichromate, and potassium dichromate are the most common ingredients of proprietary preservatives used in the wood preserving industry. The colorimetric method selected is based on the principle of formation of blue perchromic acid, which can be extracted in ethyl acetate followed by measurement of the absorbance of the extract at 565 mμ.

Only hexavalent chromium forms the blue perchromic acid. Therefore, the first step in the analysis is to convert all chromium present in the solution to the hexavalent state. In dichromate and chromate ions, chromium is present in the hexavalent state. If chromium is present in the trivalent state, it first has to be oxidized to the hexavalent state.

Reagents.--

1) Ethyl acetate--anhydrous--Baker's analyzed.
2) Hydrogen peroxide 30 per cent.
3) Dilute hydrogen peroxide solution: 11.4 ml. of 30 per cent H_2O_2 reagent was diluted to 100 ml. with redistilled water. 0.5 ml. of dilute H_2O_2 solution in 25 ml. aqueous solution would give 0.02M H_2O_2.
4) Sulfuric acid--1:1: Gradually added 10 ml. of redistilled water to 10 ml. of sulfuric acid.
5) pH 1.7 buffer solution: 107 ml. of 0.2N hydrochloric acid was added to 250 ml. 0.2N

potassium chloride solution and then diluted to 1000 ml. with redistilled water.

Standard chromium (VI) solution: Weighed 0.2844 gram of potassium dichromate. Redistilled water (850 ml.) was adjusted to pH 1.5 with 1:1 H_2SO_4 and poured into a liter volumetric flask. Weighed potassium dichromate was then added and volume adjusted to 1 liter. The chromium (VI) content of this solution was 100 µg/ml.

In Solution

An aliquot sample of the standard solution was pipetted into a 150 ml. beaker. The pH of the solution was adjusted to 1.7 ± .2 with either 1:1 sulfuric acid or 1:1 ammonium hydroxide. The volume of the solution was brought to 25 ml. with the buffer solution.

The sample was then transferred to a 125 ml. separatory funnel provided with a glass stopper. Thirty ml. of ethyl acetate (anhydrous) were pipetted into the beaker in which the pH was adjusted. Ethyl acetate was then transferred to the separatory funnel containing the sample solution. The separatory funnel was cooled to 0-10°C by keeping it in a refrigerator for fifteen minutes. Then 0.5 ml. of dilute hydrogen peroxide solution was added to the cooled sample-solvent mixture. The separatory funnel was gently shaken for thirty seconds and then the layers were separated. The lower layer (aqueous) was transferred to another 125 ml. separatory funnel and the ethyl acetate layer collected in a 50 ml. graduate. To the aqueous layer another 10 ml. of ethyl acetate were added and the separatory funnel shaken for thirty seconds. The layers were separated—the aqueous layer transferred to the first separatory funnel and the ethyl acetate layer to a 50 ml. graduate. One more extraction with 5 ml. of ethyl acetate was performed. The aqueous layer could be saved for determination of some other ions if required (e.g., arsenic). The ethyl acetate-perchromic acid solution in the graduate was brought up to the 50 ml. mark with ethyl acetate. The extraction of chromium (VI) was thus completed.

An aliquot of the blue perchromic acid-ethyl acetate solution was transferred to a 3/4" colorimeter test tube and the absorbance measured at 565 mμ. against a blank.

Aliquot samples of standard chromium (VI) solution were analyzed by the procedure just described. Table 11 presents the collected data on the absorbance reading for known chromium (VI) and the same data have been plotted in Figure 5.

In Treated Wood

Treated wood samples containing 100 μg. to 2 mg. were prepared by the procedure described on pages 30 and 31. The procedure laid down for digesting treated wood (pages 31, 33, and 34) was followed. The pH of the digested

Table 11.--Calibration data for determining chromium in solution.

Chromium present in solution µg.	Chromium present per ml. of ethyl acetate µg/ml.	Absorbance reading
50	1	.02
100	2	.042
150	3	.064
200	4	.083
250	5	.102
500	10	.205
750	15	.305
1000	20	.408
1250	25	.512
1500	30	.615
1750	35	.718
2000	40	.820
2500	50	1.030

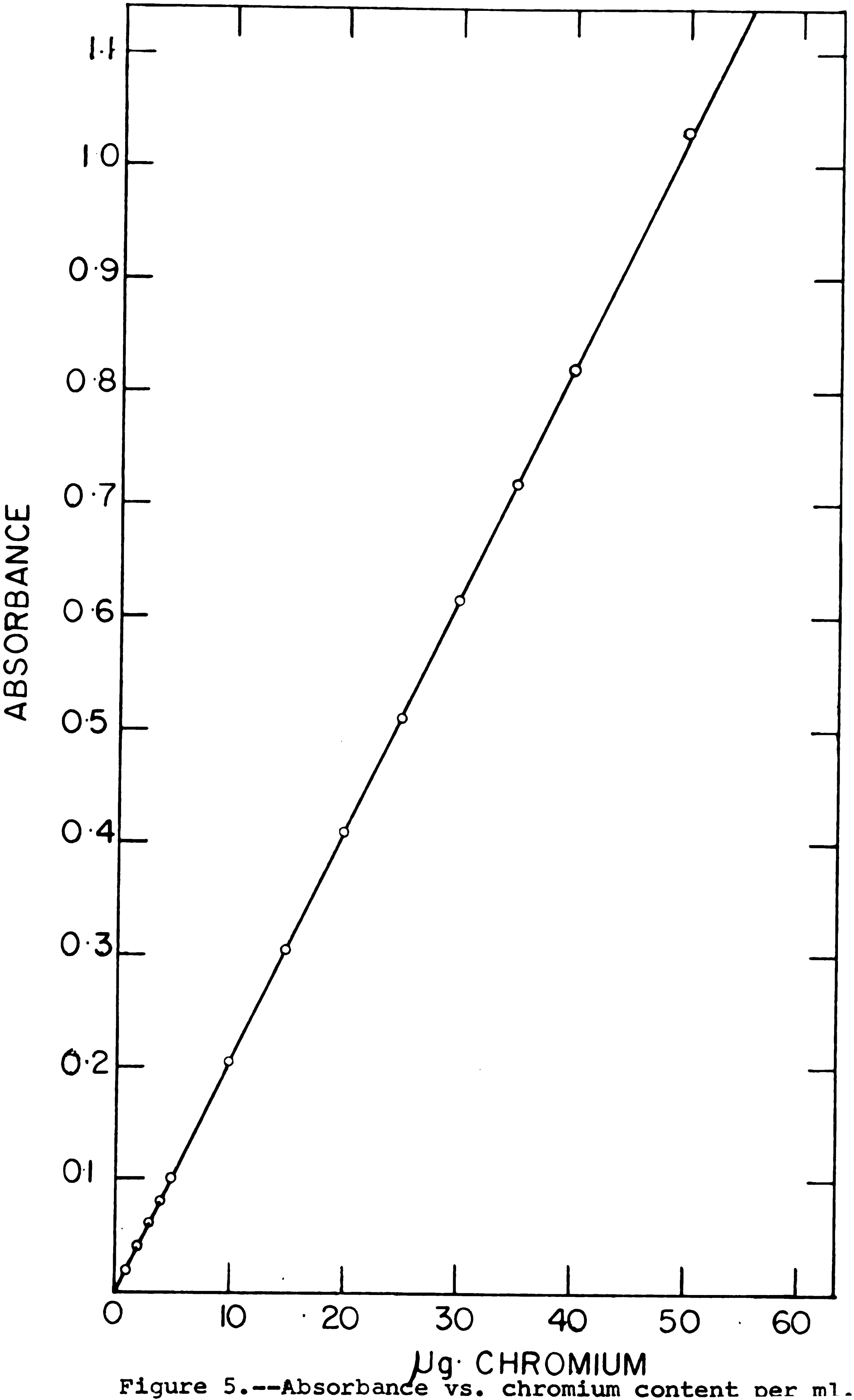


Figure 5.-- Absorbance vs. chromium content per ml. of ethyl acetate in the determination of chromium in solution.

Figure 5.--Absorbance vs. chromium content per ml.

solution was brought to 9 with 1:1 ammonium hydroxide. Then 1 ml. of 30 per cent hydrogen peroxide was added. It was shaken and boiled for ten minutes with 1 ml. of a 1 per cent solution of ferrous ammonium sulfate or nickel oxide as a catalyst. Nickel oxide was used if arsenic had to be determined later. After ten minutes of boiling, the solution was cooled and to it was gradually added 1:1 sulfuric acid until the precipitate redissolved. The solution was then transferred to a 50 ml. volumetric flask, and the solution adjusted to a volume of 50 ml. with redistilled water.

An aliquot sample was taken and the procedure for determination of chromium in solution was followed. The absorbance data collected were plotted against the concentration of chromium (VI)/ml. ethyl acetate. See Table 12 and Figure 6.

Effect of Copper and Arsenic

A known quantity of copper and/or arsenic was added to the standard chromium solution and the chromium was analyzed by the procedure described on pages 50 and 51. From the absorbance reading, chromium was determined from Figure 5. Table 13 presents the data collected and the per cent of error caused by the presence of copper and arsenic ions in determination of chromium.

Treated wood samples were prepared by following the method described on pages 30 and 31 with the modification that before chromium solution was put on the wood

Table 12.--Calibration data for determining chromium in treated wood.

Chromium present in wood µg.	Chromium present per ml. of ethyl acetate µg.	Absorbance reading
200	4	.100
500	10	.210
750	15	.302
1000	20	.405
1250	25	.518
1500	30	.612
1750	35	.720
2000	40	.822
2500	50	1.026

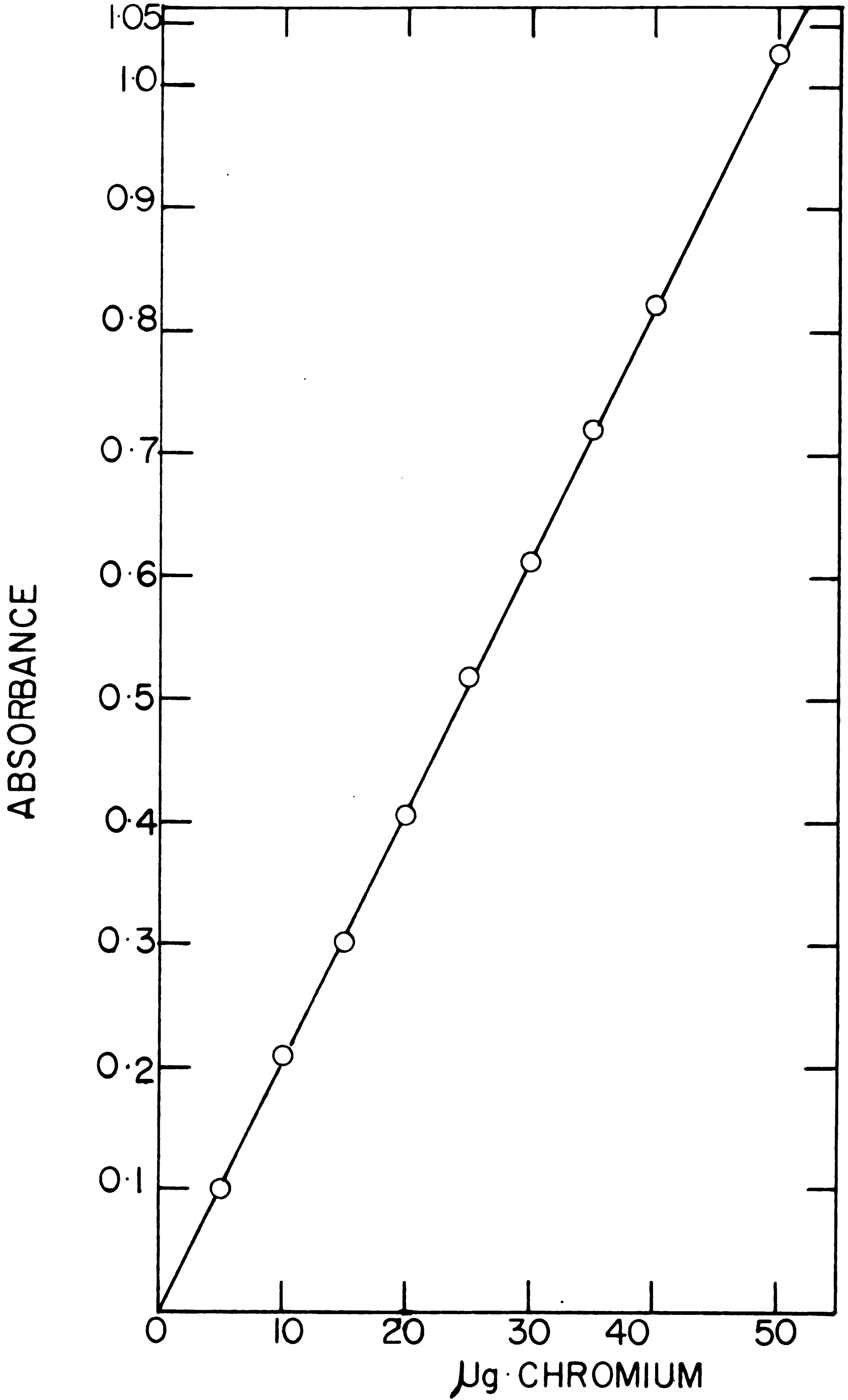


Figure 6.--Absorbance vs. chromium content per ml. of ethyl acetate in the determination of chromium from treated wood.

Table 13.--Effect of arsenic and copper concentrations on determination of chromium.

Chromium present µg.	Arsenic present µg.	Copper present µg.	Chromium found in solution µg.	Chromium found in wood µg.	Error found in solution %	Error found in wood %
500	0	0	500.0	500	. .	. .
500	10	0	506.0	515	1.2	3.0
500	30	0	521.5	490	4.3	-2.0
500	60	0	505.5	496.5	1.1	-0.7
500	100	0	495	508.0	-1.0	1.6
500	500	0	490	511.5	-2.0	2.3
500	0	100	526	522.5	5.2	4.5
500	0	200	518	524.5	3.6	4.9
500	0	300	496	502.0	0.8	0.4
500	0	400	505	486	1.0	-2.8
500	0	500	492	485	1.6	-3.0
500	100	300	495	510	-1.0	2.0

wafer for soaking, known quantities of copper and/or arsenic solutions were soaked into the wafer. The method of digestion and analysis for chromium (IV) was the same as described on pages 31, 33, 34, and 51, 54. Table 13 presents the data on the effect of copper and arsenic ions on determination of chromium in treated wood.

Effect of Suspected Interfering Ions

The suspected interfering ions studied were those of iron, zinc, phosphate, and silicate. The reason for selecting these ions has already been described on page 47. Known quantities of the suspected ions were added to known volumes of the standard chromium solution (100 µg/ml.) and, by following the procedure described on pages 51 and 54, absorbance was measured. From the standard calibration graph (Figure 5), the chromium content was calculated. Table 14 reproduces the collected data on the effect of various suspected interfering ions on the determination of chromium (VI).

Effect of Species of Treated Wood

The species of wood studied in this case are the same as reported on page 47. Only the colorimetric method of analysis for determination of chromium described on pages 51 and 54 was followed. The treated wood samples were prepared according to the procedure described on pages 30 and 31 by adding 1 ml. of standard chromium solution (500 µg/ml.) to a one gram sample of each wood species studied. Table 15 presents the collected data.

Table 14.--Effect of suspected interfering ions on the determination of chromium (500 μg) by the colorimetric method.

Suspected interfering ion	Added as	Amount added μg.	Error %
Fe	$FeCl_3$	400	-1.5
SiO_3	Na_2SiO_3	400	4.6
PO_4	$NH_4H_2PO_4$	400	3.5
Zn	$ZnCl_2$	400	2.8

Table 15.--Effect of species of treated wood on the determination of chromium by the colorimetric method.

Specie of wood	Chromium present μg.	Chromium found μg.	Error %
Sugar pine (*Pinus lambertiana*)	500	500	. .
Southern yellow pine (*Pinus* sp.)	500	490	-2
Douglas fir (*Pseudotsuga menziesii*)	500	485	-3
Oak (*Quercus rubra*)	500	520	+4

Determination of Arsenic

Arsenic compounds have found their place in water-borne preservatives, in association with compounds of chromium, copper, and/or zinc. Arsenic trioxide, arsenic pentoxide, arsenic acid, and sodium arsenate have been used in proprietary preservatives (described in Table 1).

The colorimetric method selected for the determination of arsenic (V) is based on the principle of forming 1,2 molybdoarsenic acid and extracting it with butan-1-ol (n-butyl alcohol), followed by measuring the absorbance of the alcohol extract at 370 mµ. Waldelin and Mellon (43) have reported interference due to $Cr_2O_7^{--}$, PO_4^{--}, SiO_4^{--} ions. Hence, to achieve a precision of 95 per cent or more in the determination of arsenic in the range 0-1 mg., it is essential to:

1) Bring arsenic to the pentavalent state.
2) If chromium is present, remove it completely or convert it to Cr^{+++} ions (Cr^{+++} does not interfere if present up to a maximum of 12 mg. with arsenic (V) in the range of 0-1 mg) before proceeding with the determination of arsenic.
3) Remove interference due to PO_4^{--} and SiO_4^{--} ions.

Trivalent arsenic could be converted to pentavalent arsenic by the action of a suitable oxidizing agent. For a solution of pH greater than 7, hydrogen peroxide has been used as an oxidizing agent. For solutions of pH less than 7 (pH 2-5), potassium bromate solution can be used according to the following equation: ($BrO_3^- + 3As^{3+} + 6H^+ \rightarrow Br^- + 3As^{5+} + 3H_2O$). In both cases the excess of oxidizing agent can be destroyed by boiling. However, it should be remembered that other ions which are present in their reduced form would also be oxidized. For example, cuprous ion, which would react as follows: ($6Cu^+ + BrO_3^- + 6H^+ \rightarrow 6Cu^{++} + Br^- + 3H_2O$). The presence of copper (Cu^{++}) does not affect the determination of arsenic. Chromium ions can be extracted from solution by the ethyl acetate extraction technique described on pages 35 and 36.

Phosphates and silicates present in the solution also form heteropoly acids similar to 1,2 molybdoarsenic acid. The 1,2 molybdophosphoric acid could be selectively extracted with chloroform, in which the partition coefficient for 1,2 molybdoarsenic acid is negligible. The 1,2 molybdosilicic acid forms slowly; hence the effect of silicate ions could be avoided if the absorbance measurements could be taken within six minutes from the time sodium molybdate solution has been added.

In Solution

Reagents.--

1) Sodium molybdate-hydrochloric acid solution: Fifteen grams of sodium molybdate dehydrate were dissolved in 200 ml. redistilled water. Eighty-four

ml. of concentrated hydrochloric acid were added and diluted to 500 ml. The resulting molybdate-hydrochloric acid solution was stored in a plastic bottle.

2) Butan-1-ol B.P 117.0 to 118.5°C.
3) Standard arsenic solution: 0.384 grams of As_2O_5, of purity 99.5 per cent, was placed in 150 ml. redistilled water and heated to 60°C. When dissolution was complete, the solution was cooled to 25°C and diluted to 250 ml. This solution contained 1.0 mg. arsenic/ml. and was stored in a plastic bottle.
4) Chloroform-butan-1-ol solution: 300 ml. of chloroform and 100 ml. of butan-1-ol.
5) Hydrochloric acid 1:1.
6) Sodium hydroxide 10 per cent, stored in a plastic bottle.

An aliquot sample from the standard arsenic solution (containing 0-1 mg. arsenic) was pipetted into a 125 ml. beaker and the volume of the sample brought to 20 ml. with redistilled water. The pH of this solution was then adjusted between 5 to 9. The contents were transferred to a separatory funnel.

Ten ml. of sodium molybdate solution were then poured into the beaker used for adjusting pH, and next transferred to a separatory funnel. Twenty ml. of chloroform-n butyl alcohol solution were added and the funnel shaken for thirty seconds. The layers were then allowed to separate and the bottom chloroform layer was discarded. The process of extraction with 20 ml. of chloroform-n butyl alcohol solution was repeated twice. The phosphate ions, if present, would be extracted with the chloroform layer.

To the chloroform washed aqueous solution, 20 ml. of n butyl alcohol were added. The separatory funnel was shaken for thirty seconds and then allowed to separate into layers. The aqueous layer was transferred to another separatory funnel and the butanol layer was collected in a 50 ml. graduate. The extraction procedure was repeated with 20 ml. n butyl alcohol and the butyl alcohol layer added to the 50 ml. graduate. The alcohol layer was then brought up to the 50 ml. mark with the addition of n butyl alcohol.

The absorbance was read immediately, if the presence of silicate ions were suspected, at 370 mμ. against a blank in 3/4" colorimetric test tubes.

The absorbance A was measured by following the procedure described for the determination of arsenic in solution, using known amounts of arsenic and taking aliquot samples from the standard solution. The absorbance data have been presented in Table 16 and plotted in Figure 7.

Table 16.--Calibration data for determining arsenic in solution.

Arsenic present µg.	Absorbance
5	.011
15	.028
25	.048
35	.066
50	.090
65	.118
75	.140
90	.164
100	.180
150	.280
200	.400
400	.690
800	1.300
1000	1.600

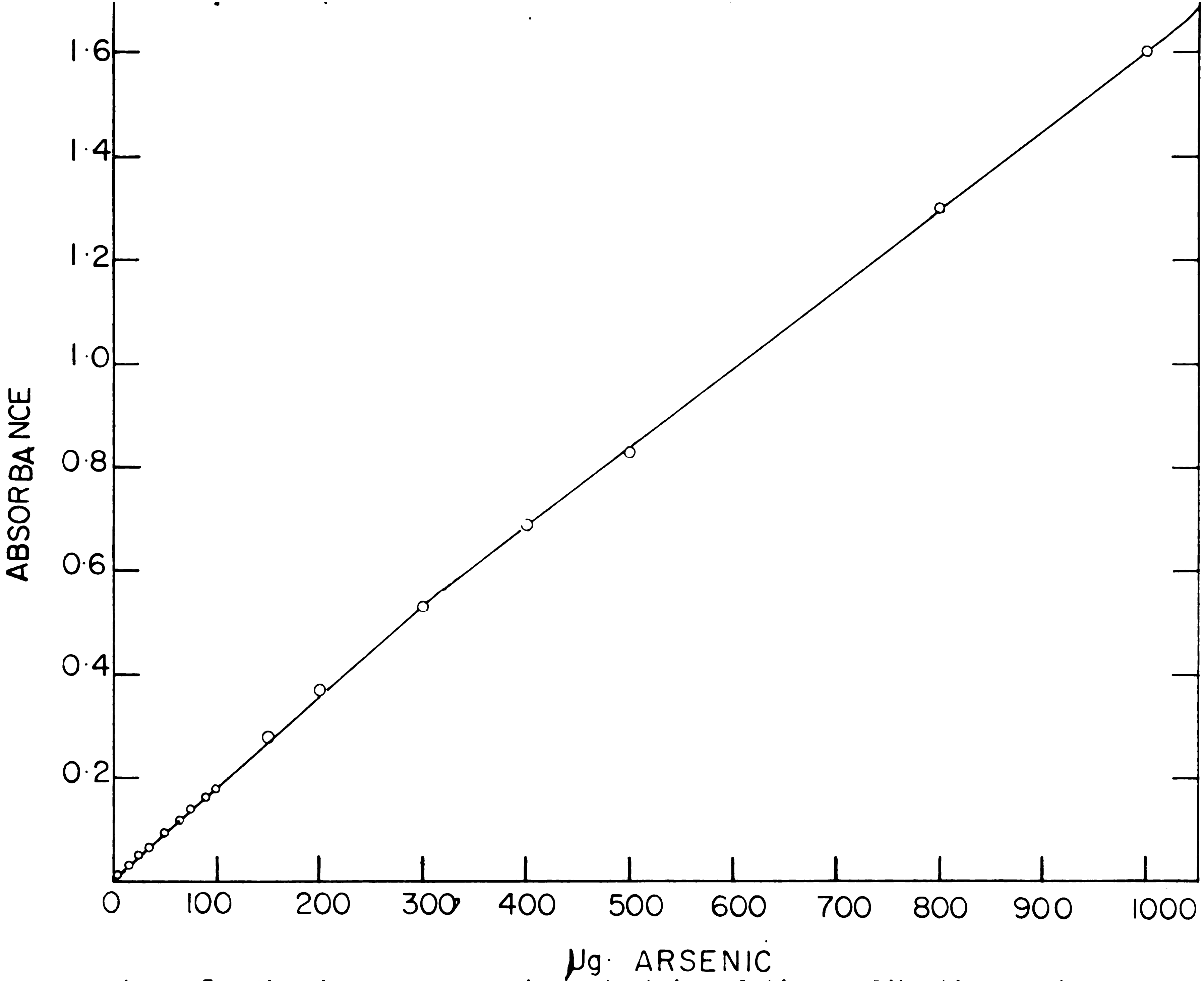


Figure 7.--Absorbance vs. arsenic content in solution, calibration graph.

In Treated Wood

Treated wood samples were prepared by following the procedure given on pages 30 and 31. Treated wood samples were digested according to the procedure described on pages 31, 33 and 34. To assure that the arsenic present in the digested wood solution was in pentavalent form, the pH of the solution was raised to 9 with 1:1 ammonium hydroxide or 1N sodium hydroxide. Then 1 ml. of 30 per cent hydrogen peroxide was added and the excess of hydrogen peroxide destroyed by boiling for ten minutes. (Nickel oxide can be used as a catalyst.) The solution was cooled and the volume made up to 50 ml. When chromium was not present the oxidation could be carried out in acid media by adding 5 ml. of 1N potassium bromate solution, removing the excess of bromate/bromine ion by boiling for ten minutes.

A 20 ml. aliquot of the solution was taken for the determination of arsenic, as described on pages 61-63. The absorbance measurements were recorded against that of a blank, which was made by following the same procedure on one gram of untreated wood.

A standard calibration curve relating the absorbance and arsenic content in wood was prepared by following the above procedure on wood containing known amounts of arsenic from 0-1 mg. The absorbance data collected has been recorded in Table 17 and the same has also been plotted in Figure 8.

Table 17.--Standard calibration for arsenic in treated wood.

Arsenic present µg.	Arsenic in aliquot µg.	Absorbance
50	10	.019
100	20	.038
150	30	.054
200	40	.072
400	80	.150
600	120	.226
800	160	.290
1000	100	.182

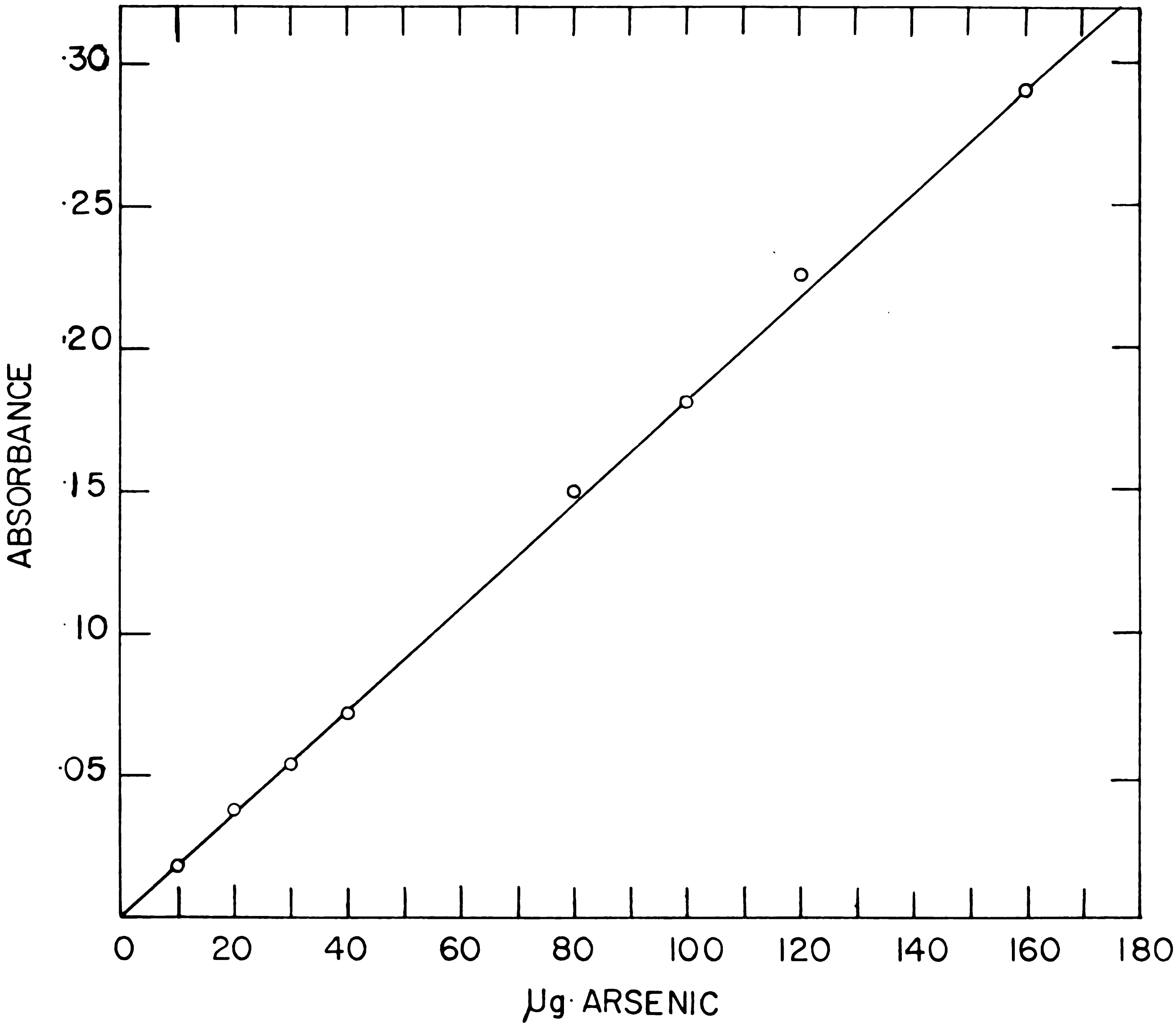


Figure 8.--Absorbance vs. arsenic content in treated wood, calibration graph.

Effect of Copper and Chromium

Standard solutions of copper (100 µg./ml.) and chromium (VI) (100 µg./ml.) were prepared and known volume of these were added to 1 ml. of standard arsenic solution (100 µg./ml.). The procedure laid down on pages 61-63 was followed and arsenic determined using Figure 7. Table 18 reports the collected data and the per cent of error in the determination of arsenic in the presence of copper and chromium.

The effect of the presence in wood of chromium and copper in addition to arsenic was also studied. The procedure followed in preparation of the sample was the same as described on pages 30 and 31, and the solutions used for impregnation were the same as described in the previous paragraph. Table 18 reports the collected data.

Effect of Suspected Interfering Ions

This study was already reported exhaustively by Waldelin and Mellon (43) who reported the effect of 48 ions, including metallic ions such as iron, zinc, copper, chromium (the ions which could be picked up by the solution in contact with wood treating equipment) and silicate and phosphate ions (which could be contributed to the treating solution by the wood itself or some other source). Table 19 presents the effect of these interfering ions on the analysis of arsenic.

Table 18.--Effect of copper and chromium ions on the determination of arsenic.

Arsenic present µg.	Copper present µg.	Chromium present µg.	Arsenic found in		Error found in	
			solution µg.	wood µg.	solution %	wood %
100	0	0	100	100	. .	. .
100	100	0	100.5	102	0.5	2
100	200	0	97.0	104	-3.0	4
100	300	0	102.0	100	2.0	0
100	400	0	102.0	104	2.0	4
100	0	100	850	1000	750	900
100	0	200	∞	∞	∞	∞
100	300	500	∞	∞	∞	∞

Table 19.--Effect of suspected interfering ions on the determination of arsenic.

Suspected interfering ion	Added as	Amount added µg.	Error %
Fe	$FeCl_3$	400	10.5
SiO_3	Na_2SiO_3	400	2.8
PO_4	$NH_4H_2PO_4$	400	4.9
Zn	$ZnCl_2$	400	-0.6

Effect of Species of Treated Wood

The species described on page 47 were studied for their effect on the determination of arsenic. The treated wood samples were prepared according to the procedure described on pages 30 and 31, by adding 1 ml. of standard arsenic solution (100 µg./ml. to one gram sample of each wood specie studied. Table 20 presents the collected data.

Table 20.--Effect of species of treated wood on the determination of arsenic by colorimetric method.

Specie of wood	Arsenic present µg.	Arsenic found µg.	Error %
Sugar pine (*Pinus lambertiana*)	100	100	. .
Southern yellow pine (*Pinus* sp.)	100	101.5	1.5
Douglas fir (*Pseudotsuga menziesii*)	100	98.0	-2.5
Oak (*Quercus rubra*)	100	103.5	3.5

Comparative Study of Volumetric and Colorimetric Methods

All the proprietary preservatives given in Table 1 were prepared according to the A.W.P.A specifications for per cent ingredients in each preservative (2). The treated wood samples were prepared by the following procedure:

> Five grams of sugar pine (*Pinus lambertiana*) were weighed to the nearest 0.01 gram. The weighed wafers were placed in a beaker and this beaker was kept in a dessicator, which was attached to a water vacuum pump. Full vacuum was pulled for ten minutes. The preservative solution was then introduced into the beaker, through the separatory funnel, and the vacuum pump was turned off. Sufficient solution was used so as to cover the wafers completely. The wafers were left submerged in the treating solution overnight to obtain maximum absorption. The waters were then removed from the solution, wiped lightly to remove surface preservative, and immediately weighed to the nearest 0.01 gram. The gain in the wafer's weight was recorded as the grams of treating solution absorbed and the retention was calibrated as:
>
> $$\text{Retention(gm./gm. wood)} = \frac{\text{(gm. of treating solution)(strength of treating solution)}}{\text{100 x grams of sample}}.$$

The treated wafers were dried at room temperature for two days followed by oven drying at 50°C for 24 hours. The dried wafers were converted into powder small enough (to pass 10 mesh) in a micro Wiley mill.

The powder was weighed to the nearest .01 gram and digested in a 500 ml. Kjeldahl flask. The wet digestion with sulfuric acid and hydrogen peroxide was carried out according to the procedure described on pages 31, 33 and 34. The digested solution was made up to 100 ml. in a volumetric flask.

Aliquot samples of the digested solution were analyzed for arsenic, chromium, and copper according to the procedure described in the A.W.P.A. Manual (2). Table 22 presents the collected volumetric data for each item.

A scheme followed for the colorimetric analysis of various water-borne preservative treated wood is shown in Table 21. The digested solution formed the starting point for the analysis.

An aliquot sample of the digested solution (1 ml. to 10 ml. containing 20 µg. to 200 µg. of copper) was taken for the determination of copper. The procedure followed has already been described on pages 38-40, which can be summarized as: added 10 ml. of 10 per cent $NH_2OH \cdot HCl$ and adjusted pH of the resulting sample solution to 5-6 in a 125 ml. separatory funnel. Two ml. of 0.1 per cent cuproine reagent solution were added and followed by 10 ml.

Table 21.--Scheme for analysis of water-borne preservative treated wood.

Digest sample with sulfuric acid and hydrogen peroxide mixture. Take aliquot sample to determine copper[1] and another aliquot to determine chromium.[2] For determination of arsenic[3] the aqueous solution remaining after chromium extraction was used. The following scheme was used to determine arsenic, chromium, and copper:

Preservative	First aliquot	Second aliquot
Ammoniacal Copper Arsenate (ACA)	Copper	Arsenic
Acid Copper Chromate (ACC)	Copper	Chromium
Copperized Chromated Zinc Arsenate (CuCZA)	Copper	Chromium $\xrightarrow{-Cr}$ Arsenic
Chromated Copper Arsenate (CCA)	Copper	Chromium $\xrightarrow{-Cr}$ Arsenic
Chromated Zinc Chloride (CAC)	Chromium	
Copperized Chromated Zinc Chloride (CuCZC)	Copper	Chromium
Chromated Zinc Arsenate (CZA)	Chromium $\xrightarrow{-Cr}$	Arsenic
Fluor Chrome Arsenate Phenol Type A (FCAP)	Chromium $\xrightarrow{-Cr}$	Arsenic
Fluor Chrome Arsenate Phenol Type B (FCAP)	Chromium $\xrightarrow{-Cr}$	Arsenic

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[1] Copper by cuproine method described on pages 40 and 45.

[2] Chromium by blue perchromic acid method described on pages 51 and 54.

[3] Arsenic acid-1,2 molybdoarsenic acid method described on page 66.

of isoamyl alcohol into the funnel. A shaking time of one minute brought the copper (I)-cuproine complex thus formed into the alcohol layer. The layers were separated and the alcohol layer was then transferred into a 25 ml. volumetric flask while the aqueous layer was transferred into another separatory funnel. Another extraction was made with 10 ml. isoamyl alcohol and the alcohol layer added to the volumetric flask. The contents of the flask were made up to the mark with fresh isoamyl alcohol. Any traces of water were removed from the alcohol collected by transferring it into a 50 ml. beaker containing one gram of sodium sulfate. An aliquot sample was transferred into a colorimetric tube and absorbance measured at 546 mμ. against the blank.

The absorbance reading was converted into the copper content of the sample (with the help of calibration graph, Figure 4). From the collected data (μg. copper/gram of sample), it was easy to determine the active ingredient present as gram per gram of the wood or as pounds per cubic foot by using the following conversion factors and equation:

Active Ingredient (gm./gm. wood)	Multiplying Factor
$CuSO_4$	2.511×10^{-6}
$CuSO_4 \cdot 5H_2O$	3.928×10^{-6}
$CuCl_2 \cdot 2H_2O$	2.682×10^{-6}

Ingredient in lb./cu. ft. = 62.43 x ingredient(gm./gm. wood) x specific gravity.

Chromium was determined by taking another aliquot sample from the digested solution. This procedure, given in detail on pages 50 and 51, calls for oxidation of the sample in alkaline media with peroxide. The excess of peroxide was destroyed by boiling for ten minutes in the presence of nickel oxide or ferric ammonium sulfate. The pH was then adjusted to 1.7 ± .2 with sulfuric acid. Addition of buffer solution brought the volume to 25 ml. which was transferred to a 125 ml. separatory funnel. Anhydrous ethyl acetate (30 ml.) was then added and the contents brought to a temperature of 0-10°C. To the cold contents of the funnel, 0.5 ml. of the dilute hydrogen peroxide was added to make 0.02M H_2O_2 content of the aqueous phase. A shaking time of thirty seconds was enough to form blue perchromic acid and extract it into the acetate layer. The acetate layer was collected in a 50 ml. volumetric flask and the aqueous layer transferred to another separatory funnel. The extraction procedure was repeated with 10 ml. and 5 ml. ethyl acetate, and the acetate layer added to the first acetate collection. The aqueous solution could be saved for the arsenic analysis. An aliquot sample was transferred into a colorimetric tube and absorbance measured at 565 mμ. against a blank. The absorbance reading for chromium was converted into the chromium content of the sample with the help of calibration graph, Figure 6. From the collected data on chromium content (in μg. chromium per gram of sample), it was easy to determine the active ingredient present as gram per gram of wood or as pounds per cubic foot of treated wood by using the following conversion factors and equation:

Active Ingredient (gm./gm. wood)	Multiplying Factor
Na_2CrO_4	3.115×10^{-6}
$Na_2Cr_2O_4 \cdot 2H_2O$	5.731×10^{-6}
$K_2Cr_2O_7$	5.657×10^{-6}

Ingredient in lb./cu. ft. = 62.43 x ingredient(gm./gm. wood) x specific gravity of wood.

Arsenic was determined by the procedure on pages 62 and 63. In the case of ammoniacal copper arsenite an aliquot sample from the digested solution could be taken for arsenic analysis, and in other preservative formulation the aqueous layer collected after chromium extraction formed the starting point for arsenic analysis.

An aliquot sample (20 ml.) was adjusted to a pH of 5-9 and 10 ml. of a sodium molybdate solution were added to it in a separatory funnel. Interference from phosphate ions was eliminated by thrice extracting with 20 ml. of a chloroform-normal butyl alcohol (3:1) mixture. The 1:2 molybdoarsenic acid was then extracted with 20 ml. of n butyl alcohol. A shaking time of thirty seconds was used and extraction with butan-1-ol was repeated with another 20 ml. of n butyl alcohol. The alcohol layers were

collected in a 50 ml. volumetric flask and made up to the mark with the addition of n butyl alcohol. An aliquot sample was transferred into the colorimetric tube and absorbance measured at 370 mμ. against a blank.

The absorbance reading for arsenic was converted into the arsenic content of the sample with the help of Figure 8. From the collected data of arsenic content (in μg. As/gm. of sample) it was easy to calculate the active ingredient present as grams/gram of wood or as pounds/cubic foot of wood by using the following conversion factors and equation:

Active Ingredient (gm./gm. wood)	Multiplying Factor
As_2O_3	1.30×10^{-6}
As_2O_5	1.534×10^{-6}
Na_2HAsO_4	2.482×10^{-6}
$Na_2HAsO_4 \cdot 7H_2O$	4.165×10^{-6}

Ingredient in lb./cu. ft. = 62.43 x ingredient(gm./gm. wood) x specific gravity.

The comparative analysis data collected has been presented in Table 22. From other sources* a few samples were received with their own analytical data. These samples were analyzed by the procedure laid above for the colorimetric determination of copper, chromium, and arsenic in preservative treated wood. The results are presented in Table 22.

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*A government agency and a private firm.

Table 22. Comparative analysis to determine water-borne preservatives by volumetric and colorimetric methods

Preservative Treatment	Ingredient Determined	Ingredient present in treated wood	Volumetric analysis data					Colorimetric analysis data					
			Ingr. in aliquot sample	Vol. of titrant	Calculated Ingredient		Error $\frac{b-f}{b}\times100$	Ingr. in aliquot sample	Absorbance	Calculated Ingr.		Error $\frac{k-b}{b}\times100$	Error $\frac{k-f}{f}\times100$
		gm. /gm.wood	gm.	ml.	gm.	gm ./gm.wood		µg.		µg.	gm./gm.wood		
	a	b	c	d	e	f	g	h	i	j	k	l	m
Acid copper chrome	Total Salt	.1680											
	$CuSO_4 \cdot 5H_2O$	.0840	.063	24.94	.0622	.0828	1.43	420	.611	416.4	.0833	.83	-0.6
	$Na_2Cr_2O_7 \cdot 2H_2O$	.0840	.210	20.85	.2042	.0817	2.74	420	.285	401.2	.0802	4.48	1.84
Ammoniacal Copper Arsenate	Total Salt	.2860											
	$CuSO_4 \cdot 5H_2O$	.2242	.1121	43.25	.1078	.2156	3.84	1121	1.600	1092	.2184	2.59	-1.3
	As_2O_3	.0618	.1545	29.45	.1457	.0583	5.66	309	.424	290.7	.0581	5.92	0.34
Chromated Copper Arsenate	Total Salt	.3220											
	$Cu\ SO_4 \cdot 5H_2O$	.1063	.0797	31.02	.0773	.1031	3.01	531	.760	518	.1036	2.50	-0.48
	$K_2Cr_2O_4$	.1803	.2705	28.10	.2756	.1837	-1.90	9020	.625	8768	.1754	2.75	4.51
	As_2O_5	.0354	.0531	9.15	.5026	.0351	1.04	1770	.211	1783	.0357	-0.68	1.70
Chromated Zinc Arsenate	Total Salt	.3040											
	$Na_2Cr_2O \cdot 2H_2O$	.0486	.1216	12.05	.1197	.0479	1.48	2432	.175	2436	.0487	-0.25	-1.67
	$Na_2H\ AsO_4$	.1246	.1869	19.95	.1855	.1237	.75	1246	.083	1253	.1253	-0.50	-1.29
Chromated Zinc Chloride	Total Salt	.3100											
	$Na_2Cr_2O_7 \cdot 2H_2O$	.0574	.1434	13.95	.1386	.0554	3.33	2867	.200	2810	.0562	2.00	-1.44
Flour Chrome Arsenate Phenol Type B	Total Salt	.3280											
	$Na_2Cr_2O_7 \cdot 2H_2O$	.1115	.2788	28.05	.2787	.1115	.00	5576	.39	5444	.1089	2.36	2.33
	$Na_2H\ AsO_4$	.0820	.1230	12.95	.1204	.0803	2.07	4100	.06	4095	.0819	0.12	1.99
Treatment Source #1 Sample #1	$CuSO_4$					.0066		1320	.300	1300	.0065		1.46
	Na_2CrO_4					.0039		1560	.210	1604	.0040		-2.82
	$Na_2H\ AsO_4$					.0049		1960	.270	1825	.0046		5.67
Sample #2	$CuSO_4$					.0147		2940	.680	2962	.0148		-0.75
	Na_2CrO_4					.0057		2280	.305	2336	.0058		-2.45
	$Na_2H\ AsO_4$					.0072		1440	.206	2805	.0070		2.64
Sample #3	$CuSO_4$					.0087		1740	.420	1823	.0091		-4.77
	Na_2CrO_4					.0057		2280	.315	2414	.0060		-5.79
	Na_2HAsO_4					.0058		1160	.164	1118	.0056		3.60
Sample #4	$CuSO_4$					.0002		40	.088	37.7	.000189		5.50
	NA_2CrO_4					.0015		600	.081	623	.00155		-3.8
	Na_2HAsO_4					.0011		440	.128	435	.00109		1.1
Treatment Source #2 Sample #1	Total Salt	.0144											
	$CuSO_4 \cdot 5H_2O$	.0048						476	.690	4714	.0047	1.01	
	$K_2Cr_2O_7$	.0081						3232	.215	3111	.0078	3.74	
	$As_2O_5 \cdot 2H_2O$	.0016						635	.075	672	.00168	-5.86	
Sample #2	Total Salt	.0106											
	$CuSO_4 \cdot 5H_2O$	.00349						349	.52	354	.00354	1.43	
	$K_2Cr_2O_7$	.00593						2372	.165	2263	.00576	4.57	
	$As_2O_5 \cdot 2H_2O$	.00117						466	.110	498	.00125	-6.95	

DISCUSSION OF THE RESULTS

Copper Analysis

The cation exchange resin method for extraction of copper ions from the treating solution was found to give sufficient accuracy (100 ± 5 per cent). However, this method suffers from the great drawback that it has been found to be very time consuming. The cuproine method has been found to be very sensitive and satisfactory as well as less time consuming. One hundred per cent recovery of copper was achieved and the precision of determination was plus or minus 2 per cent.

The calibration graphs (Figures 3 and 4), relating absorbance and copper content in solution, as well as in treated wood, turned out to be straight lines for the copper concentrations studied. Further, the slopes of these straight lines were also found to be equal which proves that the digestion and extraction procedure gave one hundred per cent recovery of copper content. The procedure described for the extraction of copper levels ranging from 20 to 200 μg. can also be extended to higher limits. Where more than 20 μg. of copper were present, extractions were continued until there was no visible purple color in the isoamyl alcohol layer. The total

alcohol layer was brought to the nearest multiple of 25 ml. and a sample of this was then taken for absorbance measurement at 546 mμ.

The results obtained in studying the effect of chromium, arsenic, zinc, iron, phosphate, and silicate (see Tables 8 and 9) show that these ions do not interfere in the determination of copper. This confirms the previous finding as reported in the literature survey on pages 12 and 13.

In studying the effect of the species of treated wood in the determination of copper, the results show (see Table 10) that copper can be determined accurately regardless of the species of treated wood. This is simply because the digestion procedure brings the entire copper content of the sample into solution form and because an untreated control specimen of the sample species was used for adjusting the zero scale of absorbance.

Chromium Analysis

The data collected on the standard calibration curves for chromium content in solution and in treated wood showed that the Beer's Law is obeyed from 0 to 2.5 mg. of chromium (VI) content. Figures 5 and 6 showed the chromium content of the ethyl acetate extract and not the chromium content of the solution or of the treated wood. In these tests 50 ml. of ethyl acetate were used for extraction in samples having 50 μg. to 2.5 mg. of chromium

content. However, if the sample was smaller than 10 ml. and pH paper was used for adjusting the pH to 1.7 ± .2, then a total of 25 ml. of ethyl acetate could be used for extraction of blue perchromic acid. Inasmuch as Figures 5 and 6 present the concentration of chromium per ml. of ethyl acetate, it was found easier to calculate the total chromium content of the sample by multiplying the chromium content in ethyl acetate by the ml. of ethyl acetate used for the extraction of chromium. Furthermore, it was found that the slopes of straight lines of the calibration graphs in Figures 5 and 6 were practically the same. Thus, it could be concluded that all the chromium present in the sample was brought into aqueous solution by the digestion procedure and that all dissolved chromium was extracted from this solution into the ethyl acetate.

Table 12 shows that arsenic has no effect on the determination of chromium while copper affects the determination of chromium to a level of 100 plus or minus 5 per cent or less. Thus, in a sample containing copper, chromium, and arsenic, one could take an aliquot sample and proceed directly to the determination of chromium without removing the copper, while still achieving an accuracy of ± 5 per cent. It was also found that if copper is extracted by the cuproine method and the remaining solution used for chromium analysis, the chromium present is not in the hexavalent state. This can be explained by the fact that the reducing agent used in the cuproine method also reduces chromium into the trivalent state. Hence, to proceed for the determination of chromium, an oxidation to Chromium (VI) was found essential. This was done by the action of peroxide in alkaline media and the procedure is described on pages 51 and 54.

The suspected interfering ions had no effect on the determination of chromium by the blue perchromic acid method (see Table 14). Table 15 presents the data on effect of species of treated wood, which is also found to be negligible. The explanation of this behavior is the same as that advanced for the effect of species in copper analysis (page 79).

Arsenic Analysis

The calibration curve (Figure 7) for arsenic content in solution shows that a linear relationship exists between the measured absorbance and the arsenic content, from zero to 350 µg. The slopes of the straight line between 0-350 µg. and 350-1000 µg. are different, which shows a negative deviation from the Beers-Lambert Law. For treated wood an aliquot sample was taken to give arsenic content between zero and 200 µg. The slopes of the calibration curves for the determination of arsenic in solution (Figure 7) and treated wood (Figure 8) are found to be equal for all practical purposes. Thus, it can be concluded that both digestion and extraction procedures gave excellent recovery of arsenic.

The presence of chromium was found to be detrimental to the determination of arsenic by the 1,2 molybdoarsenic acid method. Hence, if chromium ions are suspected, then it was found to be essential that they be extracted before proceeding with the determination of arsenic. The presence of copper did not interfere with the determination of arsenic.

It was found that iron, phosphate, and silicate would interfere with the determination of arsenic if their interference was not nullified. Traces of iron present (as tested up to 400 µg.) do not interfere, however, so that if excess of iron was present, it would be desirable to remove it by precipitation as iron hydroxide in alkaline media. To be more precise, any of the specific colorimetric reagents such as cupferron can be used. Since it was reported that up to 1 mg. of iron can be permitted without interfering with the absorbance measurements, cupferron was not used.

Phosphate and silicate interference was removed by slightly modifying the procedure. When the modified procedure was used, the error introduced is less than 5 per cent (see Table 19).

The species of treated wood did not affect the determination of arsenic as may be seen from Table 20. The reasoning given for copper holds also for arsenic.

Comparative Study of Volumetric and Colorimetric Analyses

Volumetric analysis requires a large sample if the treatment is made for 0-35 lb./cu. ft. retention from a 2 per cent treating solution. Hence, higher concentration solutions were used with greater retention values (see Table 22).

Aliquot samples for volumetric and colorimetric analyses were taken from the same digested wood solution for each ingredient to be analyzed (e.g., copper).

The comparative data presented in Table 22 for volumetric and colorimetric analyses of the water-borne preservative formulations tested show that equally reliable results are obtained by each method.

CONCLUSIONS

The colorimetric procedure described for the determination of arsenic, chromium, and copper in solution and treated wood follows the Beers-Lambert Law. The slopes of the standard calibration for the absorbance and concentration of the ion are found to be practically the same for preservative solution as for treated wood. This clearly proves that the digestion method utilizing hydrogen peroxide and sulfuric acid gives complete recovery of the ions to be analyzed.

Arsenic, chromium, and copper can be determined to an accuracy of plus or minus 5 per cent by the procedure described for the determination of each ion. The rangesof each ion which can be analyzed by the given procedure for the desired accuracy are given below:

As (V)	50 µg. to 1.0 mg.
Cr (VI)	50 µg. to 3.0 mg.
Cu	20 to 250 µg.

The upper limit for the determination of these ions is flexible because the preservative solution or the digested solution of treated wood can be diluted to give the desired size of samples.

The species of treated wood tested in these experiments have been found to have no significant effect on the determination of copper, chromium, and arsenic ions.

The expected interfering ions such as iron, zinc, phosphate, and silicate do not interfere in the colorimetric method of analysis. A comparative analysis of copper, chromium, and arsenic by the volumetric and colorimetric methods revealed that the colorimetric method described gave results as accurately as the volumetric method. All the water-borne preservatives containing arsenic, chromium, and/or copper in any combination can be analyzed both in solution and treated wood to an accuracy of 95 per cent or more by the colorimetric method described in this work.

FUTURE STUDIES

Copper, chromium, and arsenic form the major ingredients of the water-borne preservatives which are presently being used throughout the world. It would be useful to follow up this study with the development of a colorimetric method for analysis of zinc and fluoride ions also.

Further, it would be interesting to determine (1) how large (2) how many and (3) from which section of the treated wood the samples be taken for analysis purposes. The present information on this subject is not sufficient specially because the size of the sample can be very small (less than one gram) for X-ray and colorimetric methods of analysis.

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APPENDIX I

List of Reagents Used in Volumetric Analysis

Reagents Used in Volumetric Analysis of Arsenic

1) Hydrochloric acid, concentrated.
2) Hypophosphorous acid, 50 per cent.
3) Sulfuric acid, concentrated.
4) Potassium bromate, 0.1000 normal--dissolved 2.784 grams of pure dry potassium bromate in redistilled water and made up to 1.000 liter in a volumetric flask.
5) Methyl orange--0.1 per cent water solution.

Reagents Used in Volumetric Analysis of Chromium (Hexavalent)

1) Phosphoric acid, 85 per cent.
2) Barium diphenylamine sulfonate solution--0.20 gram barium diphenyl sulfonate made up to 100 ml. with water.
3) Ferrous ammonium sulfate--sulfuric acid solution--140 grams of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 25 ml. of concentrated sulfuric acid made up to one liter with redistilled water.
4) Sulfuric acid 1:1 solution--one volume of concentrated sulfuric acid was slowly added with constant stirring to one volume of water. Cool before use.
5) Potassium dichromate solution, 0.2000N--weighed 9.807 grams of potassium dichromate into a one liter volumetric flask and adjusted the volume to exactly 1.000 liter with redistilled water.

Reagents Used in Volumetric Analysis of Copper

1) Ammonium hydroxide, concentrated.
2) Hydrochloric acid, concentrated.
3) Alcohol, ethyl.
4) Potassium iodide solution, 20 per cent--dissolved 20 grams of potassium iodide KI in 80 ml. of water.

5) Sodium thiocyanate solution, 20 per cent--dissolved 20 grams NaCNS in 80 ml. of water.
6) Starch indicator--Made a paste of one gram soluble starch in about 5 ml. of water, add 100 ml. water to it and boiled for one minute with stirring. One drop chloroform was added after the starch solution was cooled.
7) Acetic acid, glacial.
8) Copper shot.
9) Nitric acid, concentrated.
10) Urea solution, 5 per cent--dissolved 5 grams urea in 95 ml. redistilled water.
11) Sodium thiosulfate solution, 0.1N.--dissolved 24,85 grams of $Na_2S_2O_3 \cdot 5H_2O$ in redistilled water and added 1.0 gram of Na_2CO_3 as a preservative and diluted to one liter.
12) Sodium thiosulfate solution, 0.01N. diluted exactly 50 ml. of the standardized 0.1N sodium thiosulfate solution to exactly 500 ml. with freshly prepared redistilled water.