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AMERICAN WOOD-PRESERVERS' ASSOCIATION STANDARD

(This Standard is under the jurisdiction of AWPA Committee P–5)

A5–91

STANDARD METHODS FOR ANALYSIS OF OIL-BORNE PRESERVATIVES

Note: Standard A5–90 consists of 15 pages dated 1990.

1. DETERMINATION OF TOTAL ACIDITY FOR CALCULATING PENTACHLOROPHENOL IN DRY CHEMICAL

Scope

This method covers the determination of the total acidity of a dry chemical sample expressed as the pentachlorophenol content of the sample. It does not distinguish between pentachlorophenol and other chlorinated phenols. All phenols, as well as other acidic compounds present, will be included as pentachlorophenol in the determination.

1. Reagents

a. Reagent grade water (non-referee grade) conforming to ASTM D1193 "Standard Specifications for Reagent Grade Water."

b. 0.1 normal sodium hydroxide—Dissolve 4.0 gm reagent grade NaOH in 1000 ml water (see Note 1).

c. 0.1 normal potassium acid phthlate—Weigh from 18 to 22 grams oven-dry primary standard grade potassium acid phthalate to the nearest mg. Quantitatively transfer to a 1 liter volumetric flask. Add water exactly to mark. Mix well (see Note 1).

d. Meta-cresol purple indicator solution—Transfer 0.1 gm m-cresol purple to a small mortar. Add 2.5 ml 0.1 normal NaOH and complete solution with the aid of a pestle. Transfer to a flask and add 100 ml water. (see Note 1).

e. 0.5% phenolphthalein indicator solution—Dissolve 0.5 gm phenolphthalein in 50 ml ethanol plus 50 ml water (see Note 1).

f. Methanol, reagent grade.

Note 1: Suitable solutions are commercially available from several chemical supply companies.

2. Standardization of Sodium Hydroxide

a. Transfer four 0.1 normal potassium acid phthalate replicates (from 1c) each of 25.00 ml volume into 125 ml Erlenmeyer flasks.

b. Add 3 to 5 drops phenolphthalein indicator to each replicate.

c. Titrate to a permanent faint pink end point with 0.1 normal sodium hydroxide (from 1b). Read the burette to the nearest estimated 0.01 ml. Record the volume of NaOH used for each replicate.

3. Sample Preparation

a. Weigh from 4 to 6 grams of oven-dry sample to be analyzed to the nearest mg.

b. Quantitatively transfer to a 500 ml volumetric flask.

c. Add methanol exactly to mark. Mix well.

4. Analytical Procedure

a. Transfer four replicates of the sample dissolved in methanol each of 100.00 ml volume into 250 ml flasks.

b. Add 3 to 5 drops m-cresol purple indicator.

c. Titrate each replicate from a yellow color to a faint purple color with 0.1 normal sodium hydroxide. Read the burette to the nearest estimated 0.01 ml. Record the ml sodium hydroxide used for each replicate.

d. Determine the reagent blank of four replicates of 100 ml methanol plus 25 ml water placed in 250 ml Erlenmeyer flasks. Follow Step c of this paragraph.

5. Calculations

a. Potassium acid phthalate normality

$A = (0.004897) \times (B)$

Where

A = normality of potassium acid phthalate (expressed to the nearest 0.0001 units)

B = gm potassium acid phthalate from Paragraph 1c

b. Sodium hydroxide normality

$$C = \frac{(A) \times (25.00)}{D}$$

Where

C = normality of sodium hydroxide (expressed to the nearest 0.0001 units)

A = normality of potassium acid phthalate from Paragraph 5a

D = ml sodium hydroxide used from Paragraph 2c

c. Percent pentachlorophenol

$$E = \frac{(F-G) \times (C) \times (133.2)}{W}$$

Where

E = total acidity calculated as percent pentachlorophenol by weight (expressed to the nearest 0.1 units)

F = ml 0.1 normal sodium hydroxide from Paragraph 4c

G = ml 0.1 normal sodium hydroxide reagent blank from Paragraph 4d (average of four determinations)

C = normality of sodium hydroxide from Paragraph 5b (average of four determinations)

W = gm sample from Paragraph 3a

6. Repeatability (95% Confidence Limits)

Individual values within a set of determinations should be no less than (0.9955) × (average for the set) and no greater than (1.0045) × (average for the set). The range of values (highest minus lowest) within a replicate set of four determinations should not exceed (0.0070) × (average for the set).

2. DETERMINATION OF ALKALI INSOLUBLE MATERIAL IN PENTACHLOROPHENOL

Scope

This procedure is used to determine the amount of alkali insoluble material present in a sample of dry pentachlorophenol.

1. Dissolve a 1-gram sample weighed to the nearest mg, in 100 ml. of 4 percent (± 0.1 percent) NaOH solution, warming to about 60° C. and crushing larger particles with a flattened glass rod.

2. Filter through a tared Gooch crucible with a fiberglass filter mat, weighed to the nearest mg, wash free from alkali with distilled water, and dry at 100° C. to constant weight. Weigh to the nearest mg. The increase in weight represents alkali-insoluble matter.

Calculation

$$\frac{\text{Gm. residue} \times 100}{\text{Gm. of sample}} = \text{Percent alkali insoluble}$$

3. DETERMINATION OF FREEZING POINT OF PENTACHLOROPHENOL

Scope

This method covers the determination of the freezing point of dry pentachlorophenol.

1. Fill an enameled cup or a nickel tube of at least 1 inch diameter with sample. Melt in the direct flame of a burner, in a hood, stirring constantly with a standardized 160° to 195° C. thermometer to avoid overheating.

2. When the molten material has a temperature about 10° above its expected freezing point, allow it to cool while maintaining constant stirring.

3. As the freezing point is reached, heat of crystallization usually causes the temperature to increase slightly. Read the freezing point as the highest point at which the temperature remains constant for at least 15 seconds.

4. DETERMINATION OF PENTACHLOROPHENOL SOLVENCY

Scope

This procedure is used to determine if a particular Hydrocarbon Solvent Type A has sufficient solvency for pentachlorophenol to be used as part of the oil-borne formulation.

1. Add ten grams (± 0.1 gram) of technical pentachlorophenol (AWPA P8) to 90 grams (± 1.0 gram) of Hydrocarbon Solvent Type A (AWPA P9) and maintain the mixture at 150° F. with constant stirring for 30 minutes. If there is visual evidence of undissolved pentachlorophenol remaining at the end of the heating period, the solvent shall be regarded as non-conforming. The solution shall be cooled to 75° F. for at least four hours. During the first two hours, the solution shall be stirred at intervals of 15 minutes. During the last two hours, it shall be permitted to stand undisturbed to allow any undissolved pentacholorphenol to settle to the bottom. If there is evidence of undissolved pentachlorophenol, the solvent shall be regarded as non-conforming. If there is no evidence of undissolved pentachlorophenol and in cases of doubt, a sample of the solution shall be removed from the supernatant liquid and analyzed by the method in Paragraph 5 below.

2. Add six grams (± 0.1 gram) of technical pentachlorophenol (AWPA P8) to the Hydrocarbon Solvent Type A (AWPA P9) fraction undistilled above 500° F. from a 100 ml ASTM Standard D-86 distillation and maintain the mixture at 150° F. with constant stirring for 30 minutes. After mixing, continue with the test procedure as in (1) above.

3. When it is desired to test the maximum solvency of a Hydrocarbon Solvent Type A prepare a gradient series of penta solutions in one percent concentration intervals spanning the range of anticipated solvency. When the approximate solvency is estimated using the method in (1) above, if desired, prepare another series to determine the solvency to the nearest 0.1 percent by preparing solutions in 0.1 percent concentration intervals and proceed as in (1) above.

5. DETERMINATION OF CHLORIDE FOR CALCULATING PENTACHOLOROPHENOL IN SOLUTION OR WOOD

1. Scope

1.1 The following Volhard Chloride procedure, commonly called the "lime ignition" method describes the chemical analysis of treating solutions which contain pentachlorophenol, of pentachlorophenol concentrates, and of wood treated with pentachlorophenol. The method as described is specifically suitable for the determination of the following:

- * Solutions which contain less than 10 percent by weight pentachlorophenol (refer to paragraph 5)
- * Solutions which contain more than 10 percent by weight pentachlorophenol (refer to paragraph 6)
- * Wood volumes of less than 0.25 cubic inches which contain less than 0.75 pounds per cubic foot pentachlorophenol (refer to paragraph 7)
- * Wood volumes of less than 2.0 cubic inches which contain less than 0.50 pounds per cubic foot pentachlorophenol (refer to paragraph 8)

1.2 This method is not applicable to samples containing halogens other than chlorine unless appropriate correction can be made because the pentachlorophenol concentration is calculated from the total (excluding fluorine) halogen content.

2. Apparatus

2.1 Crucibles, iron, nickel, or porcelain.

2.2 Ignition sources (either).

2.2.1 High temperature gas burner of the Meeker type.

2.2.2 Electric muffle.

2.3 Analytical balance, sensitive to 0.001 g.

2.4 Magnetic stirrer, with stirring bars (optional).

2.5 Buchner funnel.

2.6 Suction flask.

2.7 Vacuum source.

2.8 Food blender, equipped with a detachable lid and blade assembly that will fit a one-half pint fruit jar threaded top (Hamilton Beach Model 215 or equivalent).

2.9 Fruit jar, one-half pint with smooth inside walls and equipped with a protective cover over the assembly in case of breakage during blending. (Spraying the inside wall of the jar with silicone resin will prevent sticking of the lime-boring mixture.)

2.10 Miscellaneous glassware, as required.

3. Reagents

3.1 Purity of reagents—All chemicals used shall meet the requirements of the American Chemical Society Committee on Analytical Reagents (or equivalent promulgating agencies).

3.2 Purity of water—Reagent grade water (non-referee grade) conforming to ASTM D 1193 shall be used.

3.3 Calcium hydroxide—Powdered $Ca(OH)_2$ containing 0.025 percent chloride or less.

3.4 Potassium nitrate—KNO_3 crystals containing 0.002 percent or less chloride. Grind and powder the KNO_3 using an agate or porcelain mortar and pestle or food blender sufficiently to pass through a 40-mesh screen.

3.5 Lime-nitrate mixture—Thoroughly mix 10 parts of $Ca(OH)_2$ with one part of the powdered KNO_3.

3.6 Nitric acid—Concentrated HNO_3, specific gravity 1.42, containing 0.00005 percent or less chloride.

3.7 Silver nitrate solution—0.100 $AgNO_3$ solution (standard)—Dissolve 16.99 g $AgNO_3$ crystals containing 0.005% chloride or less in water. Quantitatively transfer to a one-liter volumetric flask and add water exactly to mark. Mix well and store in a dark place. (Hint: It is a good idea to transfer the above prepared 0.100N $AgNO_3$ into five (5) 200 ml amber bottles and store under refrigeration, rather than to continually use the 1 liter container). Certified, commercially-prepared $AgNO_3$ solutions are suitable. (Note: It is very important that the $AgNO_3$ be as close to 0.100N as practical. The analysis can be performed and standardized at Normalities greater or lesser than 0.100N, however the results will be in error).

3.8 Ferric ammonium sulfate solution (Volhard indicator)—Dissolve 10 grams $FeNH_4(SO_4)_2 \cdot 12H_2O$ crystals containing 0.001 percent or less chloride in a dilute nitric acid solution prepared by adding 10 ml concentrated HNO_3 to 100 ml water.

3.9 Ammonium thiocyanate solution (approximately 0.1N)—Dissolve 7.6 g NH_4SCN crystals containing 0.005 percent or less chloride in water. Quantitatively transfer to a one-liter volumetric flask and add water exactly to mark. Mix well. Certified, commercially-prepared NH_4SCN solutions are suitable.

4. Standardization of NH_4SCN Solution

4.1 Transfer 10.00 ml. of 0.100N $AgNO_3$ to a 400 ml. beaker. Dilute to approximately 150 ml. with water. Add 5 ml. concentrated HNO_3 and 5 ml. Volhard indicator. Titrate to a permanent (5 minutes or longer) pinkish-brown end-point with 0.1N NH_4SCN solution.

The NH_4SCN should be added from a burette whose smallest subdivisions are 0.05 ml. Estimate the amount of NH_4SCN required to the nearest 0.01 ml. Record the standardization volume used as quantity "S."

4.2 Calculate the Standardization Equivalence Factor (F) for NH_4SCN according to the following:

$$F = NH_4SCN\ \text{Factor} = \frac{10.00}{S}$$

Where: S = ml. NH_4SCN per paragraph 4.1.

5. Procedure for Treating Solutions or Other Solutions Containing Not More Than 10.0 Percent Pentachlorophenol by Weight

5.1 Place 10 g of lime-nitrate mixture in a 100 ml. or number 3 crucible, gently tapping the crucible on a hard surface to settle the contents. Add the sample of treating solution (filtered if necessary) drop-wise to little wells in the lime-nitrate mixture in such a manner as to give even distribution of the sample without having any sample touch the sides of the crucible. The sample should contain approximately 0.04 g pentachlorophenol. The sample size should approximately fit the following schedule:

Nominal % Pentachlorophenol by Weight	Sample Size in g
2.5	1.4
5.0	0.6
7.5	0.4
10.0	0.2

Determine the size of the sample to the nearest 0.001 grams by the weight difference in a weighing bottle containing the treating solution before and after sampling. Record the weight of sample in grams as quantity "Ws."

5.2 Cover the sample with an additional 20 g of lime-nitrate mixture and tap the crucible gently on a hard surface. Ignite the sample by either using an electric muffle or a gas burner. If an electric muffle is used, place the sample in the muffle and maintain at 800 C for 30 minutes (the muffle may be preheated if desired). If a gas burner is used, place the crucible on a supported nichrome triangle. Light the burner and adjust the gas and air so that a quiet flame is obtained and small cones of flame rise from 1/8 in. to 1/4 inch (3 to 6 mm) above the grid of the burner. Place the lighted burner under the supported crucible and adjust the height of the crucible so that the distance from the burner grid to the bottom of the crucible is one to two inches (25 to 50 mm). Heat in this position for two to three minutes. Readjust the distance between the burner grid and the bottom of the crucible to approximately 1/2 inch (12 to 13 mm). Heat in this position for an additional 20 to 30 minutes. The ignited sample should be free of carbon, but no appreciable error will be introduced unless large amounts of unburned carbon remain.

5.3 Allow the crucible to cool and empty its contents into a 600 ml. beaker by gently tapping the crucible. Rapidly add 150 ml. of water to the beaker and immediately place a watch glass on the beaker. Scrub the crucible with water (or 2 percent HNO_3 if desired) using a stirring rod equipped with a rubber policeman to loosen any remaining residue. Add the scrubbings to the beaker. The total aqueous volume at this point should be approximately 200 ml. Place the beaker in a cold water bath. Add 50 ml. of concentrated HNO_3 either down the side of the beaker covered with a watch glass or through the hole of a center hole watch glass covering the beaker. Addition of HNO_3 should be in small increments because of the vigor of the reaction. The use of an acid dispensing burette or automatic filling pipette and a magnetic stirrer have been found useful in dissolving the sample. A cold water bath is not absolutely required when using an acid dispensing burette or automatic filling pipet as long as a one hole cover glass is used and the condensate is recovered. After the addition of HNO_3, the beaker may be removed from the cold water bath and gently heated (contents not boiled) to promote the solution of the lime-nitrate mixture. The solution should be acid to Congo red paper and all lime should be in solution. If not, additions in 5 ml. increments of concentrated HNO_3 are to be added until these conditions are met.

5.4 Pipet 10.00 ml. of 0.100N $AgNO_3$ into the beaker. Cover with a watch glass and boil several minutes to coagulate the precipitate. Cool and filter the solution through a soft, rapid paper (Whatman 41 or equivalent) into a 500 ml. Erlenmeyer suction flask by use of an appropriately sized Buchner funnel and a vacuum source (water aspirator source is adequate). Rinse the beaker with a small quantity of water and add rinsings to precipitate on the filter paper. Rinse the precipitate thoroughly with water permitting the rinsings to be added to the contents of the suction flask. Test a few drops of the wash water with 0.1N NH_4SCN. An absence of turbidity in this test indicates that the washing is complete.

5.5 Add 5 ml. Volhard indicator to the contents of the suction flask. Titrate to a permanent (5 minutes or longer) pinkish-brown end-point with 0.1N NH_4SCN. The coloration is faint and occurs at the point where Ferric Thiocyanate is formed. Fading of the end-point color prior to the end of 5 minutes is a common occurrence. Care should be taken not to add excessive NH_4SCN. The NH_4SCN should be added from a burette whose smallest subdivisions are 0.05 ml. Estimate the amount of NH_4SCN used to the nearest 0.01 ml. Record the volume titrant used for the sample as quantity "Ts."

5.6 Calculate the Equivalent Sample (Es) volume of 0.100N NH_4SCN used according to the following:

Es = ml. 0.100N NH_4SCN (sample) = Ts × F
Where: Ts = ml. 0.100N NH_4SCN per paragraph 5.5
F = NH_4SCN factor per paragraph 4.2

5.7 Determine a correction for the pentachlorophenol carrier if it contains halogens other than those due solely to the presence of pentachlorophenol, unless it is known that the carrier being analyzed is free of additional halogens. Follow the procedures of paragraph 5.1 to 5.6 inclusive, using carrier without pentachlorophenol except that the weight of the sample should be approximately 2 grams (determined to the nearest 0.001 gram). Record the sample weight of the carrier as "Wc."

5.8 Calculate the equivalent carrier (Ec) volume of 0.100N NH_4SCN used according to the following:

$$Ec = \text{ml. } 0.100N\ NH_4SCN \text{ (carrier)} = Tc \times F$$

Where: Tc = ml 0.100N NH_4SCN per paragraph 5.7

F = NH_4SCN factor per paragraph 4.2

5.9 Determine a reagent blank by following the procedures of paragraphs 5.1 to 5.6, inclusive, but using no sample and 10.00 ml. of 0.100N $AgNO_3$. Record the volume of NH_4SCN titrant in paragraph 5.5 as quantity "Tb."

5.10 Calculate the equivalent blank volume (Eb) of 0.100N NH_4SCN used according to the following:

$$Eb = \text{ml. } 0.100N\ NH_4SCN \text{ (blank)} = Tb \times F$$

Where: Tb = ml. 0.100N NH_4SCN per paragraph 5.9

F = NH_4SCN factor per paragraph 4.2

5.11 Calculate the Reagent Blank (R) according to the following:

$$R = \text{ml. } 0.100N\ AgNO_3 \text{ Reagent Blank} = 10.00 - Eb$$

5.12 Calculations

Ptotal = Total (uncorrected) percent pentachlorophenol by weight

$$P_{Ptotal} = \frac{(10 - R - Es)\ 0.5327}{Ws}$$

Pcarrier = Percent pentachlorophenol by weight blank of carrier

$$Pcarrier = \frac{(10 - R - Ec)\ 0.5327}{Wc}$$

Pcorrected = percent pentachlorophenol by weight corrected for carrier blank

$$Pcorrected = \frac{(Ptotal - Pcarrier) \times 100}{(100 - Pcarrier)}$$

Where: 1.00 ml of 0.100N $AgNO_3$ = 0.005327 grams of pentachlorophenol.

R = as defined in paragraph 5.11
As = as defined in paragraph 5.6
Ac = as defined in paragraph 5.8
Ws = as defined in paragraph 5.1
Wc = as defined in paragraph 5.7

6. Procedure for Treating Solutions or Other Solutions Containing More than 10.0 Percent Pentachlorophenol by Weight.

6.1 Weigh approximately 4 g of the original sample into a tared weighing bottle. Dilute with approximately four times its weight of heavy mineral oil (1), and weigh again. Determine weights to the nearest 0.001 gram.

6.2 Mix diluted solution thoroughly and transfer portions for analysis to crucible containing lime nitrate mixture as set forth in paragraph 5.1. Follow the analytical procedures as set forth in paragraphs 5.2 through 5.8 substituting for "Ws" as follows:

$$Ws = \frac{Os \times Ds}{Dt}$$

Where: Os = Weight of original sample
Dt = Weight of the diluted total (sample + diluent)
Ds = Weight of the diluted sample used for analysis

(1) Heavy mineral oil is described in National Formulary and is available locally.

7. Procedure for Wood Samples 0.25 Cubic Inches (4cc) or Less in Volume

(Samples involving wood volumes greater than 0.25 cubic inches should be subdivided into approximately equal parts and the results averaged. Samples involving wood samples greater than 1.0 cubic inch should be determined using the procedures of paragraph 8.)

7.1 Place 10 g of lime-nitrate mixture in a 100 ml. or number 3 crucible, gently tapping the crucible on a hard surface to settle the contents. Add the wood sample to be assayed to the surface of the lime-nitrate mixture in such a manner that the sample does not contact the sides of the crucible. Record the volume of the sample in cubic inches as quantity "Vs." (Optional: If the results are desired in terms of weight percent, the weight of the sample should be determined to the nearest 0.001 grams and recorded as "Ws.")

7.2 Cover the sample with an additional 20 g of lime-nitrate mixture and tap the crucible gently on a hard surface. Ignite the sample by either using an electric muffle or a gas burner. If an electric muffle is used, place the sample in the muffle and maintain at 800 C for 30 minutes (the muffle may be preheated if desired). If a gas burner is used, place the crucible on a supported nichrome triangle. Light the burner and adjust the gas and air so that a quiet flame is obtained and small cones of flame rise from $\frac{1}{8}$ to $\frac{1}{4}$ inch (3 to 6 mm) above the grid of the burner. Place the lighted burner under the supported crucible and adjust the height of the crucible so that the distance from the burner grid to the bottom of the crucible in one to two inches (25 to 50 mm). Heat in this position for two to three minutes. Readjust the distance between the burner grid and the bottom of the crucible to approximately ½ inch (12 to 13 mm). Heat in this position for an additional 20 to 30 minutes. The ignited sample should be free of carbon, but no appreciable error will be introduced unless large amounts of unburned carbon remain.

7.3 Allow the crucible to cool and empty its contents into a 600 ml beaker by gently tapping the crucible. Rapidly add 150 ml of water to the beaker and immediately place a watch glass on the beaker. Scrub the crucible with water (or 2% HNO_3 if desired) using a stirring rod equipped with a rubber policeman to loosen any remaining residue. Add the scrubbings to the beaker. The total aqueous volume at this point should be approximately 200 ml. Place the beaker in a cold water bath. Add 50 ml of concentrated HNO_3 either down the side of the beaker covered with a watch glass or through the hold of a center hole watch glass covering the beaker. Addition of HNO_3 should be in small increments because of the vigor of the reaction. The use of an acid dispensing burette or automatic filling pipette and a magnetic stirrer have been found useful in dissolving the sample. A cold water bath is not absolutely required when using an acid dispensing burette or automatic filling pipette as long as a one hole cover glass is used and the condensate is recovered. After the addition of HNO_3, the beaker may be removed from the cold water bath and gently heated (contents not boiled) to promote the solution of the lime-nitrate mixture. The solution should be acid to Congo red paper and all lime should be in solution. If not, additions in 5 ml increments of concentrated HNO_3 are to be added until these conditions are met.

7.4 Pipette 10.00 ml of 0.100N $AgNO_3$ into the beaker. Cover with a watch glass and boil several minutes to coagulate the precipitate. Cool and filter the solution through a soft, rapid paper (Whatman 41 or equivalent) into a 500 ml Erlenmeyer suction flask by use of an appropriately sized Buchner funnel and a vacuum source (water aspirator source is adequate). Rinse the beaker with a small quantity of water and add rinsings to precipitate on the filter paper. Rinse the precipitate thoroughly with water permitting the rinsings to be added to the contents of the suction flask. Test a few drops of the water water with 0.1N NH_4SCN. An absence of turbidity in this test indicates that the washing is complete.

7.5 Add 5 ml Volhard indicator to the contents of the suction flask. Titrate to a permanent (5 minutes or longer) pinkish-brown end-point with 0.1N NH_4SCN. The coloration is faint and occurs at the point where Ferric Thiocyanate is formed. Fading of the end-point color prior to the end of 5 minutes is a common occurrence. Care should be taken not to add excessive NH_4SCN. The NH_4SCN should be added from a burette whose smallest subdivisions are 0.05 ml. Estimate the amount of NH_4SCN used to the nearest 0.01 ml. Record the volume titrant used for the sample as quantity "Ts".

7.6 Calculate the equivalent sample volume (Es) of 0.100N NH_4SCN used according to the following:

$$Es = \text{ml. } 0.100N\ NH_4SCN\ (\text{sample}) = Ts \times F$$

Where: Ts = ml. 0.100N NH_4SCN per paragraph 7.5

F = NH_4SCN factor per paragraph 4.2

7.7 Determine a correction for wood if it contains halogens other than those due solely to the presence of pentachlorophenol, unless it is known that the sample being analyzed is free of additional halogens. Follow the procedures of paragraph 7.1 to 7.6 inclusive using untreated wood. Record the volume of wood used as "Vc." (Optional: If the results are desired in terms of weight percent, the weight of the sample should be determined to the nearest 0.001 grams and recorded as "Wc.")

7.8 Calculate the equivalent correction volume (Ec) of 0.100N NH_4SCN according to the following:

$$Ec = \text{ml } 0.100N\ NH_4SCN\ (\text{carrier}) = Tc \times F$$

Where: Tc = ml 0.100N NH_4SCN per paragraph 7.5

F = NH_4SCN factor per paragraph 4.2

7.9 Determine a reagent blank by following the procedures of paragraphs 7.1 to 7.6, inclusive, but using no sample and 10.00 ml of 0.100N $AgNO_3$. Record the volume of NH_4SCN titrant in paragraph 7.5 as quantity "Tb".

7.10 Calculate the equivalent blank (Eb) volume of 0.100N NH_4SCN used according to the following:

$$Eb = \text{ml } 0.100N\ NH_4SCN\ (\text{blank}) = Tb \times F$$

Where: Tb = ml 0.100N NH_4SCN per paragraph 7.9

F = NH_4SCN factor per paragraph 4.2

7.11 Calculate the Reagent Blank (R) according to the following:

$$R = \text{ml } 0.100N\ AgNO_3\ \text{Reagent Blank} = 10.00 - Eb$$

7.12 Calculations

PCF/PPtotal = Total (uncorrected) pentachlorophenol

$$\text{by volume:}\quad PCFtotal = \frac{(10 - R - Es)\,0.02029}{Vs}$$

$$\text{by weight:}\quad PPtotal = \frac{(10 - R - Es)\,0.5327}{Ws}$$

PCF/PPwood = Correction for wood if it contains halogens other than those due solely to the presence of pentachlorophenol

by volume: $$\text{PCFwood} = \frac{(10 - R - Ec)\ 0.02029}{Vc}$$

by weight: $$\text{PPwood} = \frac{(10 - R - Ec)\ 0.5327}{Wc}$$

PCF/PPcorrected = Corrected pounds per cubic foot or percent by weight pentachlorophenol corrected for the wood blank.

by volume: PCFcorrected = PCFtotal − PCFwood

by weight: PPcorrected = PPtotal − PPwood

Where: R = as defined in paragraph 7.8
Es = as defined in paragraph 7.6
Ec = as defined in paragraph 7.8
Vs = as defined in paragraph 7.1
Ws = as defined in paragraph 7.1
Vc = as defined in paragraph 7.7
Wc = as defined in paragraph 7.7

8. Procedure for Wood Samples up to 2.0 Cubic Inches (33cc) in Volume

(Samples involving wood volumes greater than 2.0 cubic inches should be subdivided into approximately equal parts and the results averaged. Samples involving wood samples less than 1.0 cubic inch should be determined using the procedures of paragraph 7.

8.1 Record the volume of wood sample in cubic inches as quantity "Vs". (Optional: If the results are desired in terms of weight percent, the weight of the sample should be determined to the nearest 0.001 grams and recorded as "Ws"). Place the sample in a dry, half-pint fruit jar, attach a clean, dry lid assembly and, using the food blender, grind for one-half to one minute. Add 30 g of lime-nitrate mixture to the fruit jar, replace the lid assembly, and grind (blend) for an additional 2 to four minutes.

8.2 Transfer the contents of the fruit jar to a 200 ml, 250 ml, or number 5 crucible. Clean the remaining mixture from the fruit jar with a fine brush, adding these cleanings to the crucible. Add an additional 30 grams of lime-nitrate mixture to the crucible. Gently tap the crucible on a hard surface to settle the contents. Ignite the sample by either using an electric muffle or a gas burner. If an electric muffle is used, place the sample in the muffle and maintain at 800 C for 60 minutes (the muffle may be preheated if desired). If a gas burner is used, place the crucible on a supported nichrome triangle. Light the burner and adjust the gas and air so that a quiet flame is obtained and small cones of flame rise from ⅛ to ¼ inch (3 to 6 mm) above the grid of the burner. Place the lighted burner under the supported crucible and adjust the height of the crucible so that the distance from the burner grid to the bottom of the crucible is one to two inches (25 to 50 mm). Heat in this position for two to three minutes. Readjust the distance between the burner grid and the bottom of the crucible to approximately ½ inch (12 to 13 mm). Heat in this position for an additional 50 to 60 minutes. The ignited sample should be free of carbon, but no appreciable error will be introduced unless large amounts of unburned carbon remain.

8.3 Allow the crucible to cool and empty its contents into a 600 ml beaker by gently tapping the crucible. Rapidly add 250 ml of water to the beaker and immediately place a watch glass on the beaker. Scrub the crucible with water (or 2% HNO_3 if desired) using a stirring rod equipped with a rubber policeman to loosen any remaining residue. Add the scrubbings to the beaker. The total aqueous volume at this point should be approximately 300 ml. Place the beaker in a cold water bath. Add 100 ml of concentrated HNO_3 either down the side of the beaker covered with a watch glass or through the hold of a center hole watch glass covering the beaker. Addition of HNO_3 should be in small increments because of the vigor of the reaction. The use of an acid dispensing burette or automatic filling pipette and a magnetic stirrer have been found useful in dissolving the sample. A cold water bath is not absolutely required when using an acid dispensing burette or automatic filling pipette as long as a one hole cover glass is used and the condensate is recovered. After the addition of HNO_3, the beaker may be removed from the cold water bath and gently heated (contents not boiled) to promote the solution of the lime-nitrate mixture. The solution should be acid to Congo red paper and all lime should be in solution. If not, additions in 5 ml increments of concentrated HNO_3 are to be added until these conditions are met.

8.4 Cool the sample to room temperature and quantitatively transfer to a 500 ml volumetric flask. Rinse the beaker and cover glass with water, adding the rinsings to the volumetric flask. Add water exactly to the mark and mix well. Transfer 100 ml of the solution by pipette (do not use a graduated cylinder as they are too inaccurate) to a 600 ml beaker and add 150 ml of water. Pipette 10.00 ml of 0.100N $AgNO_3$ into the beaker. Cover with a watch glass and boil several minutes to coagulate the precipitate. Cool and filter the solution through a soft, rapid paper (Whatman 41 or equivalent) into a 500 ml Erlenmeyer suction flask by use of an appropriately sized Buchner funnel and a vacuum source (water aspirator source is adequate). Rinse the beaker with a small quantity of water and add rinsings to precipitate on the filter paper. Rinse the precipitate thoroughly with water permitting the rinsings to be added to the contents of the suction flask. Test a few drops of the wash water with 0.1N NH_4SCN. An absence of turbidity in this test indicates that the washing is complete.

8.5 Add 5 ml Volhard indicator to the contents of the suction flask. Titrate to a permanent (5 minutes or longer) pinkish-brown end-point with 0.1N NH_4SCN. The coloration is faint and occurs at the point where Ferric Thiocyanate is formed. Fading of the end-point color prior to the end of 5 minutes is a common occurrence. Care should be taken not to add excessive NH_4SCN. The NH_4SCN should be added from a burette whose smallest subdivisions are 0.05 ml. Estimate the amount of NH_4SCN used to the nearest 0.01 ml. Record the volume used for the sample as quantity "Ts".

8.6 Calculate the equivalent sample volume (Es) of 0.100N NH_4SCN used according to the following:

Es = ml 0.100N NH_4SCN (sample) = Ts × F
Where: Ts = ml 0.100N NH_4SCN per paragraph 8.5
F = NH_4SCN factor per paragraph 4.2

8.7 Determine a correction for wood if it contains halogens other than those due solely to the presence of pentachlorophenol, unless it is known that the sample being analyzed is free of additional halogens. Follow the procedures of paragraph 8.1 to 8.6 inclusive using untreated wood. Record the volume of wood used as "Vc". (Optional: If the results are desired in terms of weight percent, the weight of the sample should be determined to the nearest 0.001 grams and recorded as "Wc.)

8.8 Calculate the equivalent correction volume (Ec) of 0.100N NH_4SCN according to the following:

Es = ml. 0.100N NH_4SCN (carrier) = Tc × F
Where: Tc = ml 0.100N NH_4SCN per paragraph 8.5
F = NH_4SCN factor per paragraph 4.2

8.9 Determine a reagent blank by following the procedures of paragraphs 8.1 to 8.6, inclusive, but using no sample and 10.00 ml of 0.100N $AgNO_3$. Record the volume of titrant NH_4SCN in paragraph 8.5 as quantity "Tb".

8.10 Calculate the equivalent blank volume (Eb) of 0.100N NH_4SCN used according to the following:

Eb = ml 0.100N NH_4SCN (blank) = Tb × F
Where: Tb = ml 0.100N NH_4SCN per paragraph 8.9
F = NH_4SCN factor per paragraph 4.2

8.11 Calculate the Reagent Blank (R) according to the following:

R = ml. 0.100N $AgNO_3$ Reagent Blank = 10.00 − Eb

8.12 Calculations

PCF/PPtotal = Total (uncorrected) pentachlorophenol

$$\text{by volume:}\quad \text{PCFtotal} = \frac{(10 - R - Es)\,0.10145}{Vs}$$

$$\text{by weight:}\quad \text{PPtotal} = \frac{(10 - R - Es)\,2.6635}{Ws}$$

PCF/PPwood = Correction for wood if it contains halogens other than those due solely to the presence of pentachlorophenol

$$\text{by volume:}\quad \text{PCFwood} = \frac{(10 - R - Ec)\,0.10145}{Vc}$$

$$\text{by weight:}\quad \text{PPwood} = \frac{(10 - R - Ec)\,2.6635}{Wc}$$

8.12 Calculations continued

PCF/PPcorrected = Corrected pounds per cubic foot or percent by weight pentachlorophenol corrected for the wood blank.

by volume: PCFcorrected = PCFtotal − PCFwood

by weight: PPcorrected = PPtotal − PPwood

Where: R = as defined in paragraph 8.11
Es = as defined in paragraph 8.6
Ec = as defined in paragraph 8.8
Vs = as defined in paragraph 8.1
Ws = as defined in paragraph 8.1
Vc = as defined in paragraph 8.7
Wc = as defined in paragraph 8.7

9. Precision

The following criteria should be used for judging the acceptability of the results.

9.1 Pentachlorophenol in Solution Repeatability: Duplicate determinations on the same sample by the same operator using the same equipment should not be considered suspect at the 95% confidence level if they differ by 0.089% or less.

Reproducibility: Duplicate determinations on the same sample by different operators in different laboratories should not be considered suspect at the 95% confidence level if they differ by 0.152% or less.

9.2 Lime Ignition Method—Pentachlorophenol in Wood

Repeatability: Duplicate results from runs on the same sample by the same operator in the same laboratory should not be considered suspect at the 95% confidence level unless they differ by more than 0.02 pcf.

Reproducibility: Duplicate results from runs on the same sample by different operators in different laboratories should not be considered suspect at the 95% confidence level unless they differ by more than 0.031 pcf.

The foregoing precision statements are based on a round robin sample analysis on duplicate wood samples containing about 0.35 pcf of pentachlorophenol in Southern Yellow Pine sapwood as determined by six replicates of the sample run by each of ten laboratories.

These precision statements are for the method only and do not take into account the variability of treated wood in a given charge. They should not be used to measure the reliability of operators sampling and assaying material from a given charge or an individual piece of treated wood.

6. DETERMINATION OF PENTACHLOROPHENOL IN OIL OR WOOD BY THE COPPER-PYRIDINE METHOD

Scope

The copper-pyridine method is based on the formulation of a copper-pyridine-chlorophenol complex that is insoluble in water but readily soluble in chloroform to which it imparts a brownish-yellow color. Complexes are formed with pentachlorophenol; 2,3,4,6-tetrachlorophenol; 2,4,6-trichlorophenol; and 2,6-dichlorophenol. Chlorinated phenols that do not have both the 2 and 6 positions occupied by chlorine give no color.

This method is intended as an alternate for the lime-fusion method, when a method that is specific for chlorinated phenols is required. It can be used for the determination of technical pentachlorophenol in oil solutions or in wood. This procedure is not accurate for solutions containing less than 0.5 mg pentachlorophenol per 25 ml. Analysis of oils containing less than 1.0%, and wood containing less than 0.20 pcf pentachlorophenol require special handling.

Apparatus

1. Photoelectric colorimeter with a 450-millimicron light filter or a spectrophotometer.
2. Either exactly matched 1 cm cuvettes or exactly matched ½ inch test tubes shall be used as absorption cells. The use of ¾ inch or 1 inch test tubes is not recommended.
3. Separatory funnels, Squibb type, 125 ml or 250 ml capacity.
4. Boston round bottles, 8 ounce, with polyethylene-lined caps or 250 ml beakers.
5. Extraction apparatus (ASTM D 147) consisting of (see Figure 1):
   a. Block tin, spiral reflux condenser

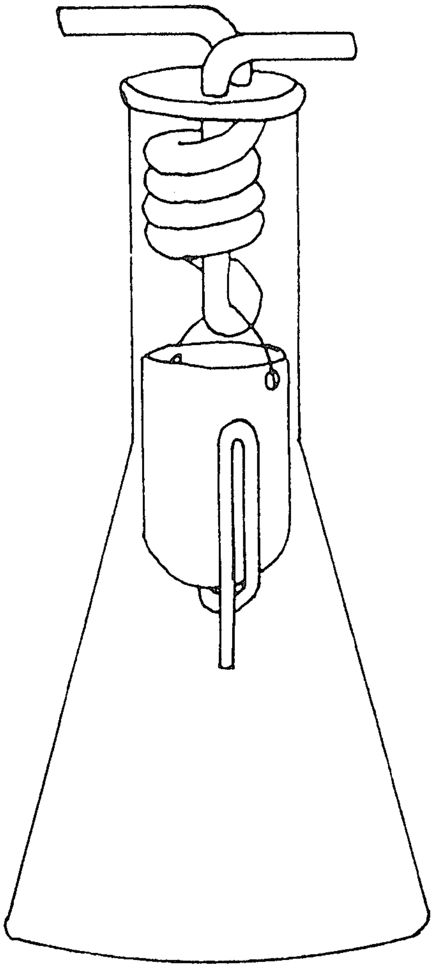

Figure 1.—Extraction Apparatus (ASTM D-147)

   b. Glass siphon tube
   c. Nickel wire to suspend siphon
   d. Long neck 400 ml Erlenmeyer flask
   e. Paper thimbles 22 mm diameter × 65 mm height.

Reagents

1. Standard pentachlorophenol solution, 0.2 mg pentachlorophenol per ml—Transfer 0.100 ± 0.002 grams of pure pentachlorophenol (Eastman No. 3462 or equivalent) to a clean, dry, 500 ml volumetric flask, dilute exactly to mark with chloroform, and mix well. Record the weight of pentachlorophenol transferred to the nearest 0.1 mg.

2. Copper-pyridine solution—Mix 50 ml of pyridine with 500 ml of water. Add 5 grams of copper sulfate, $CuSO_4 \cdot 5H_2O$, and mix until the salt has dissolved.

3. Ethanol toluol azeotrope solution—Mix 500 ml ethyl alcohol (Formula 30 denatured alcohol or J T Baker Chemical Company "Alcohol Reagent"

Number 9400 are acceptable substitutes) with 215 ml toluol and 2 ml acetic acid 1:9 (1 part glacial acetic acid + 9 parts water).

4. Sodium hydroxide solution, approximately 0.1N—Dissolve reagent grade sodium hydroxide in the ratio of 4.0 grams sodium hydroxide to 1 liter of water.

5. m-cresol purple indicator solution—Dissolve 0.1 gram of m-cresol purple in 10 ml of water containing one pellet of sodium hydroxide. Warm to effect solution, cool, and dilute to 100 ml with water.

6. Hydrochloric acid solution, approximately 0.1N—Mix 1 part concentrated hydrochloric acid with 90 parts of water.

7. Sodium sulfate, anhydrous granular.

8. Chloroform—reagent grade.

Procedure

Preparation of Calibration Curve.

1. Transfer by pipette *exactly* 5, 10, 15, 20, and 25 ml of the standard penta solution to clean, dry 25 ml volumetric flasks. Dilute contents of each flask to the mark with chloroform, stopper, and mix. Pipette 25 ml of chloroform into a 125 ml separatory funnel labeled reference. Pour the contents of each volumetric flask into a similar separatory funnel. (Do *not* wash out the traces of solution remaining in the flask.) Each sample will be treated with copper-pyridine solution, one at a time, because the optical density must be read within three minutes of treatment. Add 10 ml of the copper-pyridine solution to the reference sample. Stopper and shake vigorously for 30 seconds and release pressure. Allow to settle, drain all but approximately 2 ml of the lower layer into a dry, 50 ml beaker containing 2–3 grams of anhydrous, granular sodium sulfate. Swirl for about one minute, or until the water has been removed and the solution is clear. Set the colorimeter to 450 millimicrons and adjust to ∞ optical density with no sample in cell. Then decant a portion of the clear reference solution in the beaker into a dry absorption cell designated as the reference. Place the cell in the colorimeter and set the optical density to zero. Treat each of the samples containing penta in the same manner as the reference sample. Read and record the optical density for each sample within three minutes after adding the copper-pyridine and shaking the sample. Recheck the reference sample after each sample reading to check against voltage fluctuations.

Note: (a) It is advisable to read the percent transmittance and convert this to optical density from a standard conversion table. Transmittance is more easily read in the higher optical density range of 0.7 to ∞ especially. (b) When using a spectrophotometer such as a Beckman DB, the reference sample will be used in both cells to adjust the optical density to zero. The samples will then be added to the sample cell and compared to the reference solution in the reference cell.

Do not leave the solution in the cell for more than five minutes. Copper tends to plate out on glassware, separatory funnels, beakers, and absorption tubes. This equipment must be thoroughly cleaned upon completion of each test by rinsing successively with 1:1 hydrochloric acid, distilled water, acetone, and chloroform; then drying prior to reuse.

Prepare a calibration curve by plotting the milligrams of penta present in each sample vs the corresponding optical density on straight coordinate paper. Use the least squares method for determining the line, or determine calculation constant by least squares method. Calibration curve or calculation constant must be redetermined after parts replacement or mechanical adjustments made within the instruments. They must be checked for accuracy at least semi-annually (and advisably more often) for mechanical and electrical stability.

Analysis of Sample

2. For solutions.

2a. Solutions up to 10 percent penta by weight—Transfer approximately but no more than 1.000 gram sample to an eight ounce Boston round bottle or 250 ml beaker. The sample weight is to be known to at least the nearest milligram. (Proceed as in Paragraph 4.)

2b. (Solution stronger than 10 percent but less than 50 percent penta by weight)—Transfer approximately but no more than 0.4000 gram sample to an eight ounce Boston round bottle or 250 ml beaker. The sample weight should be known to at least the nearest 0.5 mg. (Proceed as in Paragraph 4.)

2c. (Solutions stronger than 50 percent penta by weight and dry chemical)—Transfer approximately but no more than 0.2000 gram sample to an eight ounce Boston round bottle or 250 ml beaker. The sample weight should be known to the nearest 0.1 mg. (Proceed as in Paragraph 4.)

2d. (Carrier only)—Transfer from 5 to 10 grams of carrier without penta to an eight ounce Boston round bottle. The sample should be known to at least the nearest 10 mg. (Proceed as in Paragraph 4.)

3. For wood borings.

Use 20 borings of approximately 0.20 inch diameter, cut to exact length specified for inspection and assay zone. Determine exact wood volume. Place the 20 borings without slicing or grinding in a paper thimble and place in the siphon tube (Figure 1). A two inch piece of straight wire fashioned from a paper clip and placed between the inside siphon wall and the thimble may serve to aid the siphoning and refill operation. Add 34 ml azeotrope into the 400 ml Erlenmeyer flask (azeotrope level should never come as high as the siphon tube). Heat to boiling. The siphon tube should fill and empty about every three to five minutes. Continue extraction for a minimum of 1.25 hours. After extraction, permit the siphon tube to fill almost to the point of emptying. Remove siphon tube and borings and discard the azeotrope in the tube. Place the flask on a steam bath and evaporate the solution to about 1 ml—a stream of low pressure air will aid in the evaporation. Caution: *Do not allow the sample to go dry.* Cool the flask immediately to room temperature in a water bath. Add 25 ml of chloroform from a graduated cylinder and swirl or stir to dissolve the penta. Any insoluble material on the walls and bottom of the flask may be ignored. Transfer the solution into a Boston round bottle or 250 ml beaker. Rinse the flask twice with 15 ml portions of chloroform and add each rinsing to the bottle. Proceed as in Paragraph 4 without adding additional chloroform.

4. Add 25 ml chloroform from a graduated cylinder and two drops of m-cresol purple indicator to the bottle. Swirl to accomplish solution. Add 100 ml 0.1 N NaOH. In the case of using Boston round bottles, cap the bottle and shake vigorously for one minute. In the case of using 250 ml beakers, stir vigorously either with a stirring rod or with the aid of a magnetic stirrer for one minute. Allow the chloroform and water to separate into two layers. (Proceed as in Paragraph 5.)

5. Conversion to sodium salt.

5a. For solutions up to 10 percent by weight and carrier only—Pipet exactly 10 ml of the aqueous (top-purple) layer from the bottle into a 125 ml separatory funnel. Proceed as in Paragraph 6. (Use an *aliquot factor* of 10 in the calculations.)

5b. For solutions stronger than 10 percent penta by weight and dry chemical—Pipet exactly 5 ml of the aqueous (top-purple) layer from the bottle into a 125 ml separatory funnel. Proceed as in Paragraph 6. (Use an *aliquot factor* of 20 in the calculations.)

5c. For wood samples containing from 50–400 mg penta—Pipet exactly 5 ml of the aqueous (top-purple) layer from the bottle into a 125 ml separatory funnel. Proceed as in Paragraph 6. (Use an *aliquot factor* of 20 in the calculations.)

5d. For wood samples containing less than 50 mg penta—Pipet exactly 25 ml of the aqueous (top-purple) layer from the bottle into a 125 ml separatory funnel. Proceed as in Paragraph 6. (Use an *aliquot factor* of 4 in the calculations.)

6. Add 25 ml 0.1N HCl and pipette exactly 50 ml chloroform into the separatory funnel. Shake funnel momentarily, release the pressure; then shake vigorously for 20 seconds. Allow layers to separate.

7. Drain 25 ml of the bottom chloroform (the aqueous, top layer must be a definite pink color) into a 25 ml volumetric flask and pour into a clean, 125 ml separatory funnel. Add 10 ml of the copper-pyridine solution, stopper and shake momentarily, release pressure, then shake vigorously for 30 seconds. Allow to settle, drain all but approximately 2 ml of the lower layer into a dry, 50 ml beaker containing 2–3 grams of anhydrous, granular sodium sulfate. Swirl for about one minute, or until the water has been removed and the solution is clear. Decant a portion of the clear solution in the beaker into a dry absorption cell designated "sample." Adjust the colorimeter at 450 millimicrons with a reference solution as described under "Preparation of Calibration Curve." Place the sample cell into the colorimeter and record the optical density at 450 millimicrons. Either read the milligrams of penta directly from the calibration curve, or calculate it by using the calculation constant determined during the calibration procedure.

8. Calculations.

A. Using calibration curve

Percent penta =

$$\frac{2 \times 100 \times \text{mg penta} \times \text{aliquot factor}}{\text{mg of sample}}$$

Pounds per cubic foot (PCF) penta =

$$\frac{2 \times \text{mg penta} \times .00381 \times \text{aliquot factor}}{\text{wood volume (cubic inches)}}$$

B. Using calculation constants

X	Y	XY
1.0		
2.0		
3.0		
4.0		
5.0	___	___
15		

1. X value; established from step (1) under Reagents and also Procedure. Equals mg penta per 25 ml.

2. Y value; observed optical density for each solution.

3. XY value; multiply value X times value Y for each solution.

4. Total columns (Σ) for Y and XY as shown for ΣX.

$$b = \frac{\Sigma XY - 3\Sigma Y}{10}$$

$$a = \frac{15b - \Sigma Y}{5}$$

5. $$\text{mg penta} = \frac{\text{optical density} + a}{b}$$

For determination of percent solution or pounds per cubic foot, substitute mg penta in formulae (A) and (B) above.

Using the values for "a" and "b" in step (4) above, the "least squares" calibration curve line may be determined by substitution in the following equation. By assuming values for X between 1 and 5, the corresponding value for Y can be calculated and the values for X and Y plotted on graph paper:

$$Y = bX - a$$

7. STANDARD METHOD FOR DETERMINATION OF COPPER IN COPPER NAPHTHENATE SOLUTION OR IN WOOD TREATED WITH COPPER NAPHTHENATE

Scope

This method is intended for the chemical analysis of wood treated with copper naphthenate. The procedure is fairly rapid, accurate and may be used where limited facilities are available. Copper naphthenate solutions or concentrates may also be analyzed by this method. The method is based on the oxidation of iodide ions to iodine by cupric ions, followed by titration of the iodine by thiosulfate. Many other oxidizing agents will interfere, such as nitric acid, dichromate, peroxides, permanganate, iron, arsenic, antimony, chlorate, hypochlorite, etc. Steps can be taken to overcome these interferences. This method will determine the total copper in the sample.

Reagents

Aqueous ammonium hydroxide, concentrate.

Sodium thiosulfate, 0.005 N.—Purchase 0.025 N and dilute 200 ml to make exactly 1.000 liter. If sulfur precipitates during preparation, or upon subsequent use, discard the solution and prepare a new one.

Stabilized starch indicator solution. Purchase. This solution is subject to slow decomposition and fresh solution should be purchased if a dark blue color is not produced with a drop of tincture of iodine in 100 ml of water upon addition of a drop of the starch indicator.

Nitric acid, concentrated. NOTE: All nitric acid must be boiled off before iodide is added.

Sulfuric acid, concentrated.

Potassium iodide, solution, 20 percent. Dissolve 20 grams of KI in 80 ml of water. NOTE: It should be water white or pale yellow. If it is a deep yellow, discard; or, titrate it and correct for the required thiosulate.

Potassium of sodium thiocyanate solution, 20 percent. Dissolve 20 grams. NaCNS or KCNS in 80 ml of water. NOTE: This reagent serves to prevent adsorption of triiodide ions onto cuprous iodide precipitate.

Phosphoric acid, concentrated. NOTE: This reagent serves to complex iron.

Procedure Treated Wood

1. Determine the density in pounds per cubic foot of the wood sample. Grind the sample to sawdust in a Wiley mill or cut into small pieces with a knife or cleaver, or use increment borings as is.

NOTE: Wet wood may be analyzed by weight but this should be so stated. Alternatively, the % moisture may be cited or the wet density. Or, simply the volume of the wood can be measured and the copper concentration in the wood may be expressed in weight per volume units such as g/cu. in. or pcf. These approaches avoid the need to dry the samples. If a drying step is used the evaporation loss of both water and organic solvent should be accounted for.

2. Weigh accurately into a tared porcelain crucible about 2.5 grams of the sample. (5 SYP borings). The sample in dilute solution should contain approximately 0.005 grams of copper. This is equivalent to 2.5 grams of wood treated to 0.08 pcf Cu. If 20 borings are used (about 10 grams of wood) then use the 0.025N Thiosulfate undiluted.
3. Char the wood sample slowly over a gas flame. When the sample is charred past danger of catching fire, heat strongly until all organic matter is destroyed, then continue as described below. (Note: An alternate method for destroying organic matter is as follows: Heat the sample in a furnace in an excess of air starting at 300°C and gradually increase to 600°C. Continue heating at 600°C until all organic matter is destroyed.)
4. Add 2 ml of sulfuric acid and 3 ml of nitric acid. Cover with a watch glass and heat gently until the sample is dissolved. If brown fumes appear, indicating the presence of organic matter, or if the sample is not completely dissolved, then add an additional 3 ml of nitric acid and heat gently.
5. Heat until dense white fumes of sulfur trioxide appear and a colorless or light green solution remains. All the nitric acid must be boiled off at this point, since nitric acid or any oxidizing agent will interfere with the copper titration. Generation of the sulfur trioxide fumes insures that all the nitric acid is gone.
6. Cool for about 5 minutes and cautiously wash down the sides of the crucible with about 5 ml of distilled water using a medicine dropper.
7. Carefully transfer the contents of the crucible into a 300 ml Erlenmeyer flask using distilled water. NOTE: If dichromate is present the addition of alcohol followed by warning at this point will reduce it to chromate. See AWPA Standard A2, p5. This should also reduce any permanganate present.
8. Wash down the sides of the flask with the water and neutralize cautiously with concentrated ammonium hydroxide until a deep blue color and a permanent precipitate just forms. Warming the solution at this point serves to flocculate any precipitate thus making it easier to see. NOTE: A brown precipitate is likely iron hydroxide if the sample has iron in it. The color will change from yellow to green to deep blue as the ammonium hydroxide is added

dropwise. If no iron is present, then no iron hydroxide precipitate will form and the color will change directly from a very light blue to a deep blue. Add concentrated phosphoric acid drop by drop until the precipitate just dissolves and add 2-3 drops of excess phosphoric acid. Dilute to about 125 ml with water. NOTE: If the pH is 3-4 at this point, then arsenic and antimony will not oxidize iodide ion to iodine.

9. Add 5 ml of 20 percent sodium thiocyanate solution and 10 ml of 20 percent potassium iodide solution. Mix thoroughly by rotating the flask. Titrate with 0.005N sodium thiosulfate solution, adding about 2 ml of starch solution just before the yellow color of the iodine disappears. Stop the titration when the blue color formed by the starch disappears and does not return for about 30-60 seconds.

Procedure Solutions

1. Weigh accurately into a tared crucible enough liquid sample to provide about 0.02 grams copper (2 grams of a 1% solution or 0.25 grams of an 8% concentrate).
2. Gently ignite the sample over a gas flame.
3. Continue as in step 3 and following in the procedure for wood, above, using the 0.025N thiosulfate.

Calculation

1. Percent copper $= \dfrac{\text{ml thiosulfate} \times 635 \times N}{\text{grams of sample}}$
2. Pounds of copper per cubic foot of wood $= \dfrac{\text{Percent copper} \times \text{wt. of cubic ft. of wood}}{100}$

8. METHOD FOR DETERMINING CONFORMANCE OF CO-SOLVENT USED WITH TYPE A HYDROCARBON SOLVENTS TO LEACHING RESISTANCE (PENTACHLOROPHENOL)

Scope

1.1 This method is suitable for determining whether a co-solvent used with a petroleum distillate or a blend of petroleum distillates contributes to pentachlorophenol leaching or loss from the preservative solution because of emulsion tendency or affinity for water. The method is intended only to be used as a qualitative tool.

1.2 This method utilizes the lime ignition method for chloride analysis (Par. 5 this Standard) as a measure of preservative loss from the test solution as compared to the control solution. A control blend consisting of five percent by weight pentachlorophenol in the petroleum oil portion of the solvent is extracted with distilled water by shaking in a separatory funnel. The test blend (with the co-solvent added) is also extracted. An analysis of the oil layers of the blends shall show no less penta in the test blend as in the control blend.

2. Make up a five percent by weight pentachlorophenol solution in the petroleum oil portion of the solvent blend. Allow to cool to 75°F.

Make up a five percent by weight pentachlorophenol solution in the co-solvent-petroleum oil solvent blend as it would be used. Allow to cool to 75°F.

3. Add 50 grams of the control blend to a 500 ml separatory funnel and add 200 grams of distilled water at 75°F to the funnel. Shake vigorously ten times. Allow to separate completely. Drain off the water layer and any permanent emulsion. Repeat, using the test blend of five percent penta with co-solvent and petroleum oil.

4. Analyze the two oil layers for pentachlorophenol. The amount of pentachlorophenol found in the oil layer of the penta-co-solvent-petroleum oil blend should be of no less than that found in the oil layer of the control blend.

9. METHOD FOR DETERMINING CONFORMANCE OF CO-SOLVENT USED WITH TYPE C HYDROCARBON SOLVENT TO WATER SOLUBILITY REQUIREMENT

Scope

This method is suitable for determining whether a co-solvent used with a petroleum distillate or a blend of petroleum distillates is miscible with water.

2. Add 50 ml of distilled water (75F ± 1°F) to a ground glass stoppered 100 ml graduated cylinder. Fill the cylinder to the 100 ml mark with the auxiliary solvent (75° ± 1°F). Stopper the cylinder and invert it ten times. Allow to stand 30 minutes.

3. At the end of the 30-minute period the point of interface between the auxiliary solvent layer and the water shall be read in ml.

10. DETERMINATION OF TRIBUTYLTIN OXIDE IN SOLUTION

Apparatus

The following apparatus is required:

1. pH meter, with glass and calomel electrode assembly. Essential performance requirements of the apparatus are given in BS 2586, 3145, and 3422.*
2. Magnetic stirrer.

Reagents

The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978* shall be used throughout.

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* British Std. 2586, Glass electrodes for measurement of pH.
British Std. 3145, Laboratory potentiometric pH meters.
British Std. 3422, Laboratory deflection pH meters.
British Std. 3978, Water for laboratory use.

The following reagents are required:

1. Propan-2-ol (isopropyl alcohol).
2. Hydrochloric acid, 0·5N volumetric solution.

Procedure

Weigh, to the nearest milligram, approximately 200 g of the sample and transfer to a 600 ml tall form beaker, add 200 ml of propan-2-ol and insert a magnetic stirring bar.

Insert the glass and calomel electrodes of the pH meter, commence stirring and titrate with 0·5N hydrochloric acid solution. Use 1·0 ml additions at the beginning of the titration and 0·5 ml additions when approaching the end point. Record the pH obtained for each addition of titrant. Determine the exact end point by plotting pH value against volume (in milliliters) of 0·5N hydrochloric acid solution. The end point occurs between pH 4·0 and 5·0.

Continuous flickering of the pH meter needle during titration may be corrected by earthing the pH meter to the magnetic stirrer case.

Calculation

Oxide content, expressed as tributyltin oxide,

$$((C_4H_9)_3Sn)_2O \text{ percent by mass} = \frac{14{\cdot}9V_1}{M_1}$$

where V_1 = volume, in milliliters, of 0·5N hydrochloric acid solution used, and M_1 = mass, in grams, of sample taken.

11. METHOD OF TEST FOR EMULSIFIABILITY OF TYPE A HYDROCARBON SOLVENTS AND/OR AUXILIARY SOLVENTS USED WITH TYPE A HYDROCARBON SOLVENTS

Scope

This method covers the measurement of the ability of petroleum oils or a mixture of petroleum oils and auxiliary solvent to separate from the water phase of treating plant cylinder and work tank drainings and/or effluent. This method is used as a guide to plant operators in selecting treating oils and is not intended to be a conformance test.

Summary of Method

A 50 ml sample and 50 ml of distilled water both at 160°F are shaken vigorously in a graduated cylinder. The separation of the cuff into distinct water phase and oil phase is measured in mls at 3, 15, and 30 minute intervals.

Apparatus

1. 100 ml graduated cylinder (ground-glass stopper type)
2. Fahrenheit thermometer (up to 200°F range)
3. Hot plate
4. Beaker (400 ml)
5. Stopwatch or suitable timer

Material

Penta-oil solution
Distilled water

Procedure

1. In separate beakers, heat the penta-oil solution and the distilled water to 160–170°F. The penta-oil solution is the solution in question, containing the concentration of penta in use and the concentration of auxiliary solvent, if any, in use.

2. Quickly pour penta-oil solution into graduated cylinder to 50 ml mark.

3. Quickly pour distilled water on top of the penta-oil solution up to the 100 ml mark.

4. Stopper cylinder and shake vigorously using up and down motions, ten times.

5. Quickly set cylinder down, vent, and start timer.

6. Record separation at intervals of 3 minutes, 15 minutes, and 30 minutes as follows:

	Water, ml	*Cuff, ml*	*Oil, ml*
3 minutes			
15 minutes			
30 minutes			

Notes:

Cuff is the intermediate layer which is found between the oil and water layers after shaking.

In recording the separation, note whether the water layer contains oil droplets and whether the oil layer contains water droplets. In both cases these usually adhere to the sides of the cylinder. Also note whether oil and water layers are clear or turbid. Note whether the emulsion of "cuff" layer is tight or loose or lacy at each time interval. This refers to the size of the bubbles in the "cuff."

The best results are those in which there is a minimum of "cuff" and a maximum of clean oil and water separation in the least time.

12. DETERMINATION OF THE COPPER CONTENT OF COPPER SOAPS

1. SCOPE

This method is applicable to the determination of copper in copper soaps.

OUTLINE OF THE METHOD

A buffered alcohol solution of the metal converted to chloride is titrated with an excess of standard EDTA solution and back-treated with standard copper sulfate solution.

3. SPECIFICATIONS AND DIRECTIONS

A. Apparatus
  1. Erlenmeyer Flasks, 300 ml
  2. Burets, 50 mL
  3. Hot Plates
  4. Analytical Balance

B. Reagents
  1. Isopropyl Alcohol, tech.
  2. Hydrochloric Acid Solution, 18% w.
  3. EDTA Solution, 0.01000 M, Standardized
  4. Copper Sulfate Solution, 0.01000 M Standardized
  5. Buffer Solution. Aqueous solution containing 67.5 grams per liter of ammonium chloride and 570 mL per liter conc. ammonium hydroxide solution.
  6. PAN Indicator Solution, 0.05% in Methanol. (PAN is 1 − (2 − pyridylazo) − 2 − naphthol or Kodak 7192)

C. Sample

0.4 − 0.5 grams for 1–2% copper.

D. Procedure
  1. Weigh sample to four decimal places and transfer to flask.
  2. Add 10 mL of isopropyl alcohol. Warm and swirl until dissolved.
  3. Add 12 drops of hydrochloric acid solution and swirl.
  4. Add 65 mL of isopropyl alcohol.
  5. Add an excess of EDTA solution from a buret. This can be estimated from the following formula:

$$\text{mL EDTA} = \frac{\text{Wt. Sample} \times \%\ \text{Copper} \times 1000}{63.54} + 10$$

  6. Add 10 mL buffer solution.
  7. Add 0.5 mL of indicator solution. Observe color.
  8. Titrate rapidly with copper sulfate solution to orange-red color.
  9. Titrate dropwise with EDTA solution back to original color (as in Step 7).
  10. Record total volumes of EDTA and Copper Sulfate used.

E. Calculations

Calculate % Copper present as follows:

$$\%\ \text{Copper} = \frac{(\text{mL EDTA} - \text{mL } CuSO_4) \times 63.54}{\text{Sample Wt.} \times 1000}$$

Procedure for Treated Wood
  1. Prepare ashed sample as in A5 Method, so as to provide about 4–10 mg. of copper.
  2. Titrate as in Section D above.

Precision Statement

The following statements and table should be used to judge the acceptability of an analysis under the conditions stated below:

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

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

Precision Table

Range of Copper Concentration (wt. %)	Range of Limiting Percentages	
	Repeatability	Reproducibility
0.5	0.026	0.042
1.0 to 2.0	0.015 to 0.038	0.033 to 0.114
8.0	0.100	0.218