



Designation: D 2085 – 89 (Reapproved 2002)

Standard Test Method for Determining Chloride Used in Calculating Pentachlorophenol in Solutions or Wood (Lime Ignition Method)¹

This standard is issued under the fixed designation D 2085; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These procedures cover the chemical analysis by the lime ignition method of treating solutions containing pentachlorophenol and of wood treated with pentachlorophenol. The method is suitable for the determination of up to 0.05 g of pentachlorophenol in treating solutions (Section 8), up to 0.05 g of pentachlorophenol in wood volumes up to 0.25 in.³ (Section 9), and up to 0.25 g of pentachlorophenol in wood volumes up to 2.0 in.³ (Section 11).

1.2 This test method is not applicable to samples containing halogens other than chlorine unless appropriate correction can be made. Total halogen (excluding fluorine) is calculated as its pentachlorophenol equivalent of chloride.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

- 2.1 *ASTM Standards:* <http://www.astm.org/catalog/standards/sist/413d3039-55>
D 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 An excess of silver nitrate is added to a nitric acid solution containing the chloride. The silver chloride is filtered off, and the excess of silver is titrated with thiocyanate in the presence of a ferric salt. A pinkish-brown color is formed when excess ferric thiocyanate is produced.

4. Significance and Use

4.1 This test method covers tests for pentachlorophenol content in the treating solutions and the wood specimen.

5. Apparatus

- 5.1 *Crucibles*, iron, nickel, or porcelain.
5.2 *Ignition Sources:*
5.2.1 *Gas Burner*, high-temperature of the Meker type, or
5.2.2 *Electric Muffle*.
5.3 *Analytical Balance*, sensitive to 0.001 g.
5.4 *Magnetic Stirrer*, with stirring bars (optional).
5.5 *Büchner Funnel*.
5.6 *Suction Flask*.
5.7 *Vacuum Source*.
5.8 *Food Blender*, equipped with a detachable lid and blade assembly that will fit a ½-pt fruit jar threaded top (Hamilton Beach Model 215 or equivalent).
5.9 *Fruit Jar*, ½-pt, 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.)
5.10 *Miscellaneous Glassware*, as required.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

6.3 *Ammonium Thiocyanate Solution (Approximately 0.1 N)*—Dissolve 7.6 g of ammonium thiocyanate (NH₄ CNS)

¹ This test method is under the jurisdiction of ASTM Committee D07 on Wood and is the direct responsibility of Subcommittee D07.06 on Treatments for Wood Products.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

crystals containing 0.005 % or less chloride in water. Quantitatively transfer to a 1-L volumetric flask and add water exactly to mark. Mix well. Certified, commercially prepared NH_4 CNS solutions are suitable.

6.4 *Calcium Hydroxide*—Powdered calcium hydroxide ($\text{Ca}(\text{OH})_2$) containing 0.025 % or less chloride.

6.5 *Ferric Ammonium Sulfate Solution (Volhard Indicator)*—Dissolve 10 g of ferric ammonium sulfate ($\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) crystals containing 0.001 % or less chloride in a dilute HNO_3 solution prepared by adding 10 mL of concentrated HNO_3 to 100 mL of water.

6.6 *Lime-Nitrate Mixture*—Thoroughly mix 10 parts of $\text{Ca}(\text{OH})_2$ with 1 part of the powdered KNO_3 .

6.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3), containing 0.00005 % or less chloride.

6.8 *Potassium Nitrate*—Potassium nitrate (KNO_3) crystals containing 0.002 % 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.

6.9 *Silver Nitrate, Standard Solution (0.100 N)*—Dissolve 16.99 g of silver nitrate (AgNO_3) crystals containing 0.005 % chloride or less in water. Quantitatively transfer to a 1-L volumetric flask and add water exactly to mark. Mix well and store in a dark place. Certified, commercially prepared AgNO_3 solutions are suitable.

7. Standardization of NH_4 CNS Solution

7.1 Transfer 10.00 mL of 0.100 N AgNO_3 solution to a 400-mL beaker. Dilute to approximately 150 mL with water. Add 5 mL of concentrated HNO_3 and 5 mL of Volhard indicator. Titrate to a permanent (5 min or longer) pinkish-brown end point with 0.1 N NH_4 CNS solution. The NH_4 CNS solution should be added from a buret whose smallest subdivisions are 0.05 mL. Estimate the amount of NH_4 CNS solution required to the nearest 0.01 mL. Record the volume used as quantity *E*.

7.2 Calculate the equivalence factor for NH_4 CNS, *F*, as follows:

$$F = 10.00/E \quad (1)$$

where:

E = NH_4 CNS solution required for the titration, mL.

8. Procedure for Treating Solutions

8.1 Place 10 g of lime-nitrate mixture in a 100-mL or No. 3 crucible, gently tapping the crucible on a hard surface to settle the contents. Add the sample of treating solution (filtered if necessary) dropwise 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 of pentachlorophenol. The sample size should approximately fit the following schedule:

Nominal Weight % Pentachlorophenol	Sample Size, g
2.5	1.6
5.0	0.8
7.5	0.6
10.0	0.4

Determine the size of the sample to the nearest 0.001 g 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 *A*.

8.2 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 min (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 to 1/4 in. (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 1 to 2 in. (25 to 50 mm). Heat in this position for 2 to 3 min. Readjust the distance between the burner grid and the bottom of the crucible to approximately 1/2 in. (12 to 13 mm). Heat in this position for an additional 20 to 30 min. The ignited sample should be free of carbon, but no appreciable error will be introduced unless large amounts of unburned carbon remain.

8.3 Cool the crucible and empty its contents into a 400-mL beaker by gently tapping the crucible. Rapidly add 70 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 scrubblings to the beaker. The total aqueous volume at this point should be approximately 100 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 buret or automatic filling pipet and a magnetic stirrer have been found useful in dissolving the sample. 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, add 5-mL increments of concentrated HNO_3 until these conditions are met.

8.4 Add 15.00 mL of 0.100 N AgNO_3 solution to 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 into a 500-mL Erlenmeyer suction flask by use of an appropriately sized Büchner funnel and a vacuum source (water aspirator source is adequate). Rinse the beaker with a small quantity of water and add the rinsings to the 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 0.1 N NH_4 CNS solution. An absence of turbidity in this test indicates that the washing is complete.

8.5 Add 5 mL of Volhard indicator to the contents of the suction flask. Titrate to a permanent (5 min or longer) pinkish-brown end point with 0.1 N NH_4 CNS. The NH_4 CNS solution should be added from a buret whose smallest subdivisions are

0.05 mL. Estimate the amount of NH₄ CNS solution used to the nearest 0.01 mL. Record the volume used as quantity *B*.

8.6 Determine a correction for the pentachlorophenol carrier unless it is known that the carrier is free of chloride. Follow the procedures of 8.1-8.5, inclusive, except that the weight of the sample should be approximately 2 g (determined to the nearest 0.001 g). record the sample weight as *A_c*. Record the volume of NH₄ CNS solution in 8.5 as quantity *B_c*.

8.7 Determine a reagent blank by following the procedures of 8.1-8.5, inclusive, but using no sample. Record the volume of NH₄ CNS solution in 8.5 as quantity *B_b*.

8.8 *Calculation:*

$$\begin{aligned}
 P_{\text{total}} &= \text{total (uncorrected) weight percent pentachlorophenol} \\
 &= 0.5327 [(B_b - B) \cdot F] / A_c \\
 P_{\text{carrier}} &= \text{weight percent pentachlorophenol blank of carrier} \\
 &= 0.5327 [(B_b - B_c) \cdot F] / A_c \\
 P_{\text{corrected}} &= \text{weight percent pentachlorophenol corrected for carrier blank} \\
 &= [(P_{\text{total}} - P_{\text{carrier}}) / (100 - P_{\text{carrier}})] \times 100
 \end{aligned}$$

where:

A = as defined in 8.1,
A_c = as defined in 8.7,
B = as defined in 8.5,
B_b = as defined in 8.8,
B_c = as defined in 8.7, and
F = as defined in 7.2.

9. Procedure for Treating Solutions Containing More Than 10.0 % Pentachlorophenol by Weight

9.1 Weigh approximately 4 g of original sample into a tared weighing bottle. Dilute with approximately four times its weight of heavy mineral oil⁴ and weigh again. Determine weights to the nearest 0.001 g.

9.2 Mix diluted solution thoroughly and transfer portions for analysis to crucible containing lime-nitrate mixture as set forth in 8.1. Follow analytical procedures as set forth in 8.2-8.7, substituting for *A* as follows:

$$A = (OS/DS_t) \times DS_a \quad (2)$$

where:

OS = weight of original sample,
DS_t = weight of original sample plus diluent, and
DS_a = weight of diluted sample used for analysis.

10. Precision and Bias

10.1 *Pentachlorophenol in Solution*—The following criteria should be used for judging the acceptability of the results:

10.1.1 *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.

10.1.2 *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.

10.2 *Pentachlorophenol in Wood*—The following criteria should be used for judging the acceptability of the results:

10.2.1 *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 .020 pcf.

10.2.2 *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.

10.3 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.

10.4 These precision statements are for the test 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.

11. Procedure for Wood Samples 0.25 in.³ (4 cm³) or Less in Volume

NOTE 1—Samples involving wood volumes greater than 0.25 in.³ should be subdivided into approximately equal parts and the results averaged. Samples involving wood volumes greater than 1.0 in.³ are more conveniently analyzed using the procedures of Section 10.

11.1 Place 10 g of lime-nitrate mixture in a 100-mL or No. 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 in such a manner that it does not contact the edge of the crucible. Record the volume of the sample in cubic inches as quantity *v*.

11.2 Cover the sample with an additional 20 g of lime-nitrate mixture and tap the crucible gently on a hard surface. Ignite the sample 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 min (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 for 1/8 to 1/4 in. (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 1 to 2 in. (25 to 50 mm). Heat in this position for 2 to 3 min. Readjust the distance between the burner grid and the bottom of the crucible to approximately 1/2 in. (12 to 13 mm). Heat in this position for an additional 20 to 30 min. The ignited sample should be free of carbon, but no appreciable error will be introduced unless large amounts of unburned carbon remain.

11.3 Cool the crucible and empty its contents into a 400-mL beaker by gently tapping the crucible. Rapidly add 70 mL of water to the beaker and immediately place a watch glass on the beaker. Scrub the crucible with water (or 2 % HNO₃ if desired)

⁴ Heavy mineral oil is described in National Formulary and is available locally.