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A2–91

STANDARD METHODS FOR ANALYSIS OF WATERBORNE PRESERVATIVES AND FIRE-RETARDANT FORMULATIONS

Note: Standard A2-88 consists of thirteen pages dated as follows: Pgs. 1-13, 1988

Scope

Methods for analysis of materials used in standard water-borne preservatives and fire-retardant formulations are given for the determination of the following:

All chemical reagents should be of a quality complying with recommendations of the committee on analytical reagents of the American Chemical Society or of reagent grade. Distilled or deionized water should be used wherever water is called for in the analytical procedures.

Sampling

The accuracy of any analysis cannot be better than the accuracy of sampling, hence every precaution should be taken to insure a representative sample. The following directions should be helpful:

1. When the material under consideration is a liquid, it should be mixed to insure uniformity and the sample should be at least a pint and preferably a quart. This may be taken by a "thief" or any other device which will aid in obtaining a representative sample. When the material is a water solution, properly closed containers of glass or other suitable material shall be used.

2. When the shipment consists of mixtures of solid compounds, the sample should be at least 5 lb., taken at various points in the container or containers so that a true sample is obtained. It should be kept in an air-tight container to prevent changes in the composition by reason of changes in moisture content or chemical action with the air.

Preparation of Sample. In general, the methods of analysis given in the text specify samples from 0.2 to 0.5 gram of the ingredient to be determined in the solid, or an equivalent quantity of solution. Unless the solid is a finely divided material, it is preferable to weigh a larger sample than specified and dissolve this in a definite quantity of solvent from which aliquots containing the specified quantity are taken for analysis. Samples having a context of 10 to 14 g. of solid per liter of solution are generally satisfactory. Samples of solutions from working tanks or other treating plant equipment should be filtered at working temperature immediately on obtaining, and should not be filtered at the time the analysis is performed. Should any precipitate or solid adhering to the container be present when the sample is analyzed, the solution should be thoroughly mixed before analysis in order to obtain a proper sample.

When a sample consists of a solution made by the wet ashing of wood borings, this solution may be suitably aliquoted if more than one component is to be determined. Because of variations of sample size and standard retentions of salt treated wood, the normality of standard solutions may be raised or lowered as necessary, and buret capacity size increased, where high retentions are expected.

1. DETERMINATION OF AMMONIA IN AMMONIACAL COPPER ARSENATE AND OF AMMONIUM IN FIRE-RETARDANT FORMUATIONS

The sample should contain ammonia or ammonium in amounts approximating but not exceeding 0.15 g. NH_3 or NH_4.

Reagents

Bromocresol green indicator, 0.1% solution—dissolve 1.0g bromocresol green in 1.5 ml. 0.1 normal sodium hydroxide and dilute to 100 ml. with distilled water.

Magnesium oxide powder.

Potassium acid phthalate, Primary Standard Grade.

Boric acid solution, 4%—dissolve 40 g boric acid in 960 ml. distilled water.

Phenolphthalein indicator, 1.0% solution—dissolve 1.0 g. phenolphthalein in 10 ml. ethyl alcohol (such as J. T. Bakers #9400, alcohol, reagent).

Sulfuric acid solution, 0.2N—place about 10 ml. distilled water in a 1000 ml. volumetric flask, add 6.6 ml. concentrated sulfuric acid and cool to 20° C. Dilute to 1 liter with distilled water. (See standardization procedure below).

Sodium hydroxide solution, 0.2N—dissolve 8.1 g. sodium hydroxide in CO_2-free distilled water, cool to room temperature and dilute to 1 liter with CO_2-free distilled water.

Apparatus

The apparatus consists of a 500 ml. Kjeldahl flask to which is attached a spray trap by means of a rubber stopper. The spray trap can be found under "Kjeldahl distillation apparatus" in equipment catalogs where it is referred to as a "bulb". The trap returns liquid to the distillation flask and permits vapor to pass to a water-jacket condenser which directs the condensing vapor downwards, then through a condenser adaptor, into a 500 ml. Erlenmeyer flask.

Analysis Procedure

1. Assemble the apparatus as described above but do not connect the 500 ml. Kjeldahl flask. Place approximately 75 ml. of the boric acid solution in the 500 ml. Erlenmeyer flask, add 4-5 drops of bromocresol green indicator, and position the Erlenmeyer flask so that the tip of the condenser adaptor just dips into the boric acid solution.

2. Place the sample for analysis in the Kjeldahl flask. Dilute with distilled water to a volume of about 200 ml. Add a few glass beads to prevent bumping. Add 5.0 g. of magnesium oxide and immediately attach the flask to the rest of the apparatus by means of the rubber stopper on the spray trap.

3. After making sure that all connections are tight, and the tip of the condenser adaptor is just below the surface of the boric acid solution, commence heating the contents of the Kjeldahl flask.

4. Distill off about 150 ml. of liquid. Adjust the height of the Erlenmeyer flask throughout the distillation so that the tip of the condenser adaptor is always under, but near, the surface of the boric acid solution in the receiving vessel.

5. When the distillation is complete, lower the receiving vessel and remove the heat source. Wash down the condenser tube and adaptor into the receiving vessel, using distilled water.

6. Titrate the ammonium borate solution so formed with standard 0.2N sulfuric acid.

7. For standardization of sodium hydroxide solution, weigh two portions of potassium acid phthalate 1.6000 g. ± 0.1000 g. transferring each to 500 ml. Erlenmeyer flasks. Dissolve in 100 ml. freshly boiled and cooled water, adding 2 drops phenolphthalein. Titrate with the sodium hydroxide solution until a faint permanent pink color appears. Replicate titrations should yield normalities within 0.0005N.

8. For standardization of the sulfuric acid solution, pipet exactly 25 ml. of the sulfuric acid solution into a 250 ml. Erlenmeyer flask. Add two drops of phenolphthalein indicator and titrate with the standardized sodium hydroxide solution until a faint permanent pink color appears. Duplicate titrations should agree to within 0.10 ml. Record the average.

Calculations

Normality of sodium hydroxide =

$$\frac{\text{g. Potassium acid phthalate}}{\text{ml. NaOH} \times 0.2042}$$

Normality of sulfuric acid =

$$\frac{\text{Normality of NaOH} \times \text{ml. NaOH}}{25}$$

Percent active ingredient =

$$\frac{(\text{ml. } H_2SO_4)\ (\text{normality } H_2SO_4)\ (\text{Factor})}{\text{g. of sample}}$$

Active ingredient	Factor
NH_3	1.703
NH_4	1.804

2. DETERMINATION OF ARSENIC IN AMMONIACAL COPPER ARSENATE AND CHROMATED COPPER ARSENATE

The sample in solid form, solution or a solution aliquot from wet ashed wood borings should contain arsenic equivalent to about 0.03 g. of As_2O_5.

Reagents

Hydrochloric acid, concentrated.
Hypophosphorus acid, 50%.
Sulfuric acid, concentrated.
Potassium bromate, 0.1000 normal—dissolve 2.784 g. of pure dry potassium bromate in distilled water and make up to 1.000 liter in a volumetric flask.
Methyl orange—0.1 percent water solution.

Analytical Procedure

1. Place the sample in a 250-ml. wide-mouth Erlenmeyer flask and add sufficient water to make a total volume of about 50 ml.
2. Add 50 ml. of hydrochloric acid.
3. Add 20 ml. of hypophosphorous acid, mix thoroughly and warm the solution on a steam bath until a precipitate forms.
4. Boil the mixture gently for about 15 minutes.

IMPORTANT WARNING

If the sample being analyzed is a wood sample digested with a perchloric acid mixture as in Standard A7, it now contains perchloric acid and a strong reducing agent, hypophosphorus acid. If it is evaporated too much, *it may explode with dangerous violence.* Do not boil longer than the specified time and cover the mouth of the Erlenmeyer flask with a small watch-glass to minimize evaporation.

5. With the aid of suction, filter the hot solution through a 10 ml. Gooch crucible-containing a Whatman 934 AH glass microfiber filter or equivalent, washing the flask and precipitate thoroughly with water.
6. Place the crucible containing the precipitate in the same flask in which precipitation was carried out. Discard the filtrate.
7. Pour 10 ml. of sulfuric acid into the flask and heat over an open flame, while agitating, until copious fumes are evolved. (This should be carried out in a fume hood).
8. Allow the flask and contents to cool and then add 100 ml. of water very slowly and carefully, especially at first, as much heat is generated during this addition.
9. Next add 5 ml. of hydrochloric acid and 2 drops of methyl orange solution and immediately titrate with standard potassium bromate solution from a 10 ml. class A buret.
10. When the solution becomes colorless the end point has been reached.

Calculations

$$\frac{(\text{ml KBrO}_3)\,(0.5746)\,(\text{Aliquot Factor})}{\text{grams of sample}} = \%\ \text{As}_2\text{O}_5$$

$$\text{As}_2\text{O}_5\ \text{PCF} = \frac{(\%\ \text{As}_2\text{O}_5)\,(\text{wood density PCF})}{100}$$

3. DETERMINATION OF BORON IN FIRE-RETARDANT SOLUTIONS

The sample should contain boron equivalent to about 0.90 g. H_3BO_3.

Reagents

Phenolphthalein—dissolve 1 g. of phenolphthalein in 100 ml. alcohol.

Methyl red—dissolve 0.1 g. of methyl red in 50 ml. of 90% alcohol, dilute to 100 ml. with distilled water. Filter if necessary.

Barium chloride solution, 10%—dissolve 10 g. of $BaCl_2 \cdot 2H_2O$ in 90 ml. of distilled water.

Barium hydroxide solution—saturated water solution of $Ba(OH)_2 \cdot 8H_2O$.

Hydrochloric acid solution, about 0.5N; dilute 50 ml. of concentrated hydrochloric acid to 1 liter.

Sodium hydroxide solution, 1 N—dissolve 42 g. of sodium hydroxide in water and dilute to 1 liter. (See standardization procedure below.)

Hydrochloric acid, concentrated.

Mannitol, (mannite).

Hydrogen sulfide, compressed gas; or generated by other convenient means.

Sodium hydroxide solution, 10%—dissolve 10 g. of sodium hydroxide in 90 ml. water.

Potassium acid phthalate.

Litmus paper.

Analytical Procedure

Note: Steps 4, 5, 6 of this procedure are unnecessary when working with Type C.

1. Place the sample in a 250 ml. beaker and add sufficient water to make a total volume of about 100 ml.
2. Add 1 ml. of concentrated hydrochloric acid, heat just to boiling and add 25 ml. of 10% barium chloride solution from a pipette. Avoid continued boiling.
3. Digest for 30 minutes on a hot plate and allow the precipitate to settle. Filter through a Whatman No. 42 paper or equivalent and wash with hot water, collecting the filtrate in a 300 ml. Erlenmeyer flask.
4. Dilute the filtrate and washings to about 200 ml. and make slightly alkaline to litmus with 10% NaOH solution.
5. Pass a stream of hydrogen sulfide through the cold solution for 20 minutes, at the rate of 8 bubbles per second. (Insert a trap between the hydrogen sulfide evolution flask or cylinder and the flask containing the sample to prevent any iron from contaminating the latter.)
6. Allow the precipitate to settle for 15 minutes, filter and wash with cold water, collecting the filtrate and washings in a 600 ml. beaker.

7. Add sufficient saturated barium hydroxide solution to make the filtrate alkaline, avoiding a large excess.

8. Boil until all ammonia has been expelled. (Test vapor with moistened litmus paper.)

9. Filter, wash and boil down the filtrate to a volume of about 150 ml.

10. Make the solution slightly acid with 0.5N hydrochloric acid, cover beaker with a watch glass and boil for 5 minutes.

11. Wash down sides of beaker and watch glass and cool by placing beaker in cold water.

12. Add 3 drops of methyl red indicator and carefully neutralize by adding standard sodium hydroxide solution, until color of the solution just changes from pink to yellow. (If the neutrality point has been exceeded, add a small excess of 0.5N hydrochloric acid solution and repeat the neutralization carefully with 1 N sodium hydroxide solution).

13. Add 2 g. mannitol and 4 drops phenolphthalein indicator. Titrate with standard sodium hydroxide to the appearance of a pink color.

14. Add 2 g. of mannitol and if pink color disappears continue addition of standard alkali until it reappears. Repeat procedure until addition of mannitol has no further action on the end-point. Record the amount of standard sodium hydroxide used after mannitol is added as the titration.

15. For standardization of sodium hydroxide solution, weigh two portions of potassium acid phthalate 4.0000 g. ± 0.1000 g. transferring each to 500 ml. Erlenmeyer flasks. Dissolve in 100 ml. freshly boiled and cooled water, adding 2 drops phenolphthalein. Titrate with the sodium hydroxide solution until a faint permanent pink color appears.

Calculations

Standardization of sodium hydroxide: Normality of sodium hydroxide

$$= \frac{\text{g. potassium acid phthalate}}{\text{ml. NaOH} \times 0.2042}$$

Calculation of results:

For Type B or Type D:

Percent H_3BO_3 =

$$\frac{\text{ml. NaOH} \times \text{normality of NaOH} \times 6.18}{\text{g. of sample}}$$

For Type C:

$$\frac{\text{ml. NaOH} \times \text{normality NaOH} \times 1.915}{\text{g. of sample}} = \text{Percent } Na_2B_4O_7.$$

$$\frac{\text{ml NaOH} \times \text{normality NaOH} \times 3.83}{\text{g. of sample}} = \text{Percent } H_3BO_3.$$

4. DETERMINATION OF CHLORIDE IN CHROMATED ZINC CHLORIDE, AND FIRE-RETARDANT FORMULATIONS

The sample in solid form or solution should contain chloride equivalent to approximately 0.20 g. $ZnCl_2$.

Reagents

Sodium bicarbonate.

Silver nitrate solution, 0.1467N—dissolve 24.93 g. of pure dry silver nitrate in water and dilute to 1.000 liter.

Analytical Procedure

1. Place the sample in a 300-ml. Erlenmeyer flask and dilute with water to about 50 ml.

2. Add 2 g. of sodium bicarbonate. Then titrate with the silver nitrate solution to the first appearance of the permanent reddish brown color of silver chromate.

3. When the foregoing method is used to determine the strength of treating solutions, the chloride content of the water used to make up said solutions shall be determined in the same manner and appropriate deductions made.

Calculation

To express the chloride content of the solution in terms of preservative:

$$\frac{(\text{ml. } AgNO_3 - \text{ml. blank requirement}) \times \text{factor}}{\text{g. of sample}} = \text{Percent preservative}$$

To convert to the various preservatives, use the following factors:

Chromated zinc chloride or Fire-Retardant Formulation Type A	1.227
Fire-Retardant Formulation Type B	1.534
Copperized chromated zinc chloride	1.272
Fire-Retardant Formulation Type D	2.857

The above factors apply only to unused solutions, since these preservative solutions change during use. The above method is not a required control method, but affords a rapid method of estimating the strength of a freshly prepared treating solution.

5. DETERMINATION OF CHROMIUM (HEXAVALENT IN ACID COPPER CHROMATE, CHROMATED COPPER ARSENATE AND CHROMATED ZINC CHLORIDE)

The sample in solid form, solution or a solution aliquot from wet ashed wood borings should contain chromium equivalent to about 0.03 g. of CrO_3.

Reagents

Phosphoric acid, 85% (sp. gr.—1.71).

Barium diphenylamine sulfonate solution—0.20 g. barium diphenylamine sulfonate made up to 100 ml. with water.

Ferrous ammonium sulfate—sulfuric acid solution—50 g. 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 water.

Sulfuric acid, 1:1 solution—add one volume of concentrated sulfuric acid slowly and with constant stirring to one volume of water. Cool before use.

Potassium dichromate solution, 0.2000N—weigh 9.807 g. of oven-dry potassium dichromate into a 1-liter volumetric flask and adjust to a volume of exactly 1.000 liter with water at laboratory temperature.

Analytical Procedure

(The analysis should be performed as soon as possible after sampling).

1. Place the sample in a 500-ml. Erlenmeyer flask and add sufficient water to make a total volume of about 200 ml.
2. Add 3 ml. of phosphoric acid and 6 ml. of 1:1 sulfuric acid and stir the solution well.
3. Immediately pipet exactly 10 ml. of ferrous ammonium sulfate solution into the solution and add 10 drops of barium diphenylamine sulfonate solution.
4. Immediately titrate the solution with standard 0.2000 normal potassium dichromate solution from a 10 ml. class A buret.
5. The end-point has been reached when the color of the solution becomes deeply purple or deep greenish.
6. Titration of ferrous ammonium sulfate solution alone—Pipet exactly 10 ml. of the same ferrous ammonium sulfate solution used in the foregoing determination into another 500-ml. Erlenmeyer flask. Dilute to about 200 ml., add 3 ml. of phosphoric acid; 6 ml. of 1:1 sulphuric acid and 10 drops of barium diphenylamine sulfonate and titrate with standard potassium dichromate solution from a 10 ml. class A buret. Ferrous ammonium sulfate solutions change strength quite rapidly. This solution should, therefore, be restandardized at frequent intervals.

Calculations

The difference between the titration of the ferrous ammonium sulfate solution alone and that of the ferrous ammonium sulfate solution plus sample is the measure of the hexavalent chromium content of the sample.

$$\frac{(\text{Difference in Titrations in ml.})\,(0.6668)\,(\text{Aliquot Factor})}{\text{Grams of Sample}} = \%\ CrO_3$$

$$CrO_3,\ \text{pcf} = \frac{(\%\ CrO_3)\,(\text{wood density, pcf})}{100}$$

6. DETERMINATION OF COPPER IN ACID COPPER CHROMATE, AMMONIACAL COPPER ARSENATE AND CHROMATED COPPER ARSENATE.

The sample in solid form, solution or a solution aliquot from wet ashed wood borings should contain copper equivalent to about 0.02 g. of CuO.

Reagents

Ammonium hydroxide, concentrated.

Hydrochloric acid, concentrated.

Sulfuric acid, concentrated.

Alcohol, methyl or ethyl.

Potassium iodide solution, 20 percent. Dissolve 20 g. KI in 80 ml. of water.

Sodium thiocyanate solution, 20 percent. Dissolve 20 g. NaCNS in 80 ml. of water.

Starch indicator solution. Make a paste of 1 gram soluble starch in about 5 ml. of water, add 100 ml. water and boil for 1 minute with stirring. Cool and add 1 drop of chloroform. This solution is subject to decomposition and fresh solution should be prepared if a dark-blue color is not produced with a drop of tincture of iodine in 100 ml. water on addition of a drop of indicator.

Acetic acid, glacial.

Copper foil or shot.

Nitric acid, concentrated.

Urea solution, 5 percent. Dissolve 5 g. urea in 95 ml. water.

Sodium thiosulfate solution, 0.1N. Dissolve 24.85 g. $NA_2S_2O_3 \cdot 5H_2O$ in water, add 1.0 g. of Na_2CO_3 as a preservative and dilute to 1 liter.

Sodium thiosulfate solution, 0.05N. Dilute exactly 25 ml. of the standardized 0.1N sodium sulfate solution to exactly 50 ml. with freshly boiled distilled water, which has been cooled to room temperature. The normality of this solution, which should be made up immediately before use, is exactly 0.5 times that of the 0.1N solution as determined by standardization procedure in paragraph 4.

Potassium chlorate-nitric acid mixture—dissolve 5 grams potassium chlorate in 100 ml. concentrated nitric acid. Make up this solution just before use and do not save any surplus solution for reuse.

Analytical Procedure

1. Place the sample in a 300-ml. Erlenmeyer flask and add 10 ml. water. Add 10 ml. concentrated hydrochloric acid and a few glass beads. Add 15 ml.

alcohol carefully, warm to boiling and heat until all chromium is reduced, as evidenced by the absence of any yellowish-green color. The solution should be clear bluish-green. (With ammoniacal copper arsenate a hood should be used for the boiling.)

IMPORTANT WARNING

If the sample being analyzed is a wood sample digested with a perchloric acid mixture as in Standard A7, it now contains perchloric acid and a strong reducing agent, alcohol. If it is evaporated too much, *it may explode with dangerous violence.* Keep the Erlenmeyer flask covered and boil gently in the above step to minimize evaporation.

2. Wash down side of flask with water. Boil for 1 minute, cool and neutralize cautiously with concentrated ammonium hydroxide until a permanent precipitate just forms. With samples containing small amounts of copper, a precipitate may not form. In this case, adjust the pH to slightly basic with concentrated ammonium hydroxide as measured with pH indicating paper. Add concentrated sulfuric acid drop by drop until the precipitate just dissolves or until the solution becomes acidic. Boil down to a volume of 30 ml. Cool to below 20°C. Dilute to 125 ml.

3. Add 10 ml. 20 percent potassium iodide solution and 5 ml. 20 percent sodium thiocyanate solution and mix thoroughly by rotating the flask. Titrate from a 10 ml. Class A buret with 0.05N sodium thiosulfate solution, adding 2 ml. starch solution just before the brownish color of the iodine disappears. Stop the titration when the color changes from dark blue to light green. With ammoniacal copper arsenate, the end-point change is from dark blue to cream color. (If poor end-points or checks are obtained, see Note below.)

4. For standardization of the 0.1N sodium thiosulfate solution, dissolve in a 250 ml. Erlenmeyer flask an accurately weighed portion of pure copper foil or shot (about 0.25 g.) in 10 ml. of concentrated nitric acid. Evaporate the solution until about 3–4 ml. remains. Cool. Wash down sides of flask with distilled water. Add 10 ml. 5 percent urea solution and boil 3 minutes. Cool the solution to room temperature and add concentrated ammonium hydroxide cautiously until the solution just turns to a deep blue color. The use of a dropping bottle facilitates this step. Add 5 ml. glacial acetic acid, swirl, and wash down the sides of the flask with distilled water. Dilute to 50 ml. with distilled water and cool to room temperature. Add 10 ml. 20 percent potassium iodide solution, do not swirl, and 5 ml. of 20 percent sodium thiocyanate solution. Titrate with sodium thiosulfate solution. When about 20 ml. of sodium thiosulfate have been added, swirl the flask and continue the titration until the solution color changes from dark brown to light tan. Add 5 ml. of fresh starch indicator solution and continue the titration until the solution color just changes from blue to cream-white.

Calculations

Standardization of sodium thiosulfate:
Normality of sodium thiosulfate solution =

$$\frac{\text{grams copper} \times 15.74}{\text{ml. titration}}$$

Calculations of results:

$$\frac{(\text{mL. } Na_2S_2O_3)\ (\text{Normality } Na_2S_2O_3)\ (\text{Aliquot Factor})\ (7.96)}{\text{Grams of Sample}} = \%\ \text{CuO}$$

$$\text{CuO, pcf} = \frac{(\%\ \text{CuO})\ (\text{wood density, pcf})}{100}$$

Note: Inconsistent copper titrations. In used solutions, the accumulation of organic materials may interfere with the copper analysis. These may be destroyed as follows; before proceeding with the analysis:

1. Place the sample in a 300-ml. Erlenmeyer flask, add 10 ml. of the potassium chlorate-nitric acid mixture, and boil to dryness, with constant agitation. When dry, bake the residue over an open flame for about 1 minute.

2. Cool, then add 20 ml. water and 10 ml. concentrated hydrochloric acid. Boil to destroy excess chlorate and dissolve salts.

3. Cool, and proceed as in "Analytical Procedure" starting with the addition of 15 ml. alcohol in paragraph 1.

7. DETERMINATION OF THE FLUORIDE IN WOOD AND SOLUTIONS

1. Scope

The steam distillation of samples containing fluorides and the subsequent analysis using a specific ion electrode for fluoride is a suitable method of fluoride analysis.

The procedure for a single analysis takes approximately 2½ hours for a solution and 4½ hours for a wood sample. When sufficient numbers of samples are run, a train of distillation flasks fed by a single steam generator can be set up. A train of four flasks will enable one operator to analyze eight samples in an eight hour day.

In this procedure, wood samples are prepared for analysis by burning in the presence of sodium carbonate. The organic material is eliminated and the fluoride trapped as the sodium salt. The sample is then treated with sulfuric acid in the distillation flask, and carbon dioxide is evolved. Solution samples are added directly to the distillation flask along with sulfuric acid. The sodium fluoride is converted to hydrofluoric acid. The latter forms an azeotrope with water, which has a boiling point of 120°C. The azeotrope distills over during the steam distillation process. The distillate is collected in a plastic beaker containing a small volume of sodium hydroxide solution. This converts the hydrofluoric acid back to sodium fluoride, which cannot be lost through evaporation.

The distillate is analyzed for fluoride using the specific ion electrode for fluoride. This method is used in lieu of the thorium-nitrate method which has an end-point that can be difficult to observe.

2. Apparatus

2.1 Distillation Train—See Figure 1.
2.2 Crucibles, Nickel—50 ml.
2.3 Plastic Beakers—500 ml., wide-mouth
A. Florence flask, 2000 ml.
B. Claissen flask, 250 ml.
C. Liebig condenser
D. Thermometer
E. Pinch cock
F. Pinch cock
G. Bunsen burner
H. Separatory funnel
I. Orion pH millivolt meter 611 or equivalent
J. Orion F^- electrode 94-09A or equivalent
K. pH Electrode

Note: A number of stills can be operated from a single 2000 ml. Florence flask.

3. Reagents

3.1 Sodium carbonate—Reagent grade, anhydrous powder.
3.2 Potassium permanganate solution—Saturated water solution.
3.3 Sodium hydroxide solution, approximately 2%—Dissolve 2 grams of NaOH in 100 ml. of distilled water.
3.4 Hydrochloric acid solution, 1:200—Add 1 ml. of concentrated HCl to 200 ml. of distilled water.

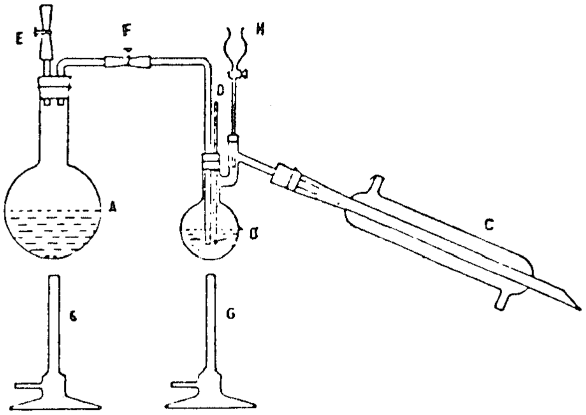

Figure 1. Distillation Train

3.5 Sulfuric acid, concentrated reagent grade.
3.6 Standard sodium fluoride solution—Orion Application Solution Fluoride Standard.
3.7 Certified Buffer Solution pH 7.00.

4. Analytical Procedure

4.1 For solutions.

Weight accurately a sample containing the equivalent of from 0.001 to 0.065 g. of sodium fluoride. Quantitatively transfer the sample to the distillation flask (B) shown in Figure 1. Dilute with 30 ml. of distilled water and slowly add 35 ml. of concentrated H_2SO_4, using the precautions outlined in paragraph 4.2.6. Proceed as in paragraph 5.

4.2 For Wood Samples.

4.2.1 Measure and record the sample volume, in cubic inches, or weight accurately, a sample containing the equivalent of from 0.001 to 0.065 g. of sodium fluoride. Slice the wood into 1 / 16 inch discs, or grind the sample.

4.2.2 Place about 15 g. of Na_2CO_3 anhydrous powder in 50 ml. nickel. Make a well with a spatula and quantitatively transfer the entire volume of wood into it. Intimately mix some Na_2CO_3 with the sample. Add about 15 g. of Na_2CO_3 to the crucible and tap lightly.

4.2.3 Place the crucibles in a muffle furnace at 700°C for 2½ hours. Remove crucibles and allow to cool slowly at first (on top of muffle furnace) to prevent crucible cracking.

4.2.4 Break up the Na_2CO_3 cake with a spatula. Quantitatively transfer the sample into the distillation flask (B) shown in Figure 1.

4.2.5 Add a small amount of distilled water to the crucible. Swirl to clean out the crucible, and carefully pour into the distillation flask. Wash crucible again with 20 ml. of distilled water. Volume in the distillation flask may be adjusted from 20 to 100 ml. for convenience in adding concentrated sulfuric acid and efficient steam distillation.

4.2.6 Pour 50 ml. of concentrated H_2SO_4 into a separatory funnel (H) shown in Figure 1 fitted into the distillation flask. Add the H_2SO_4 dropwise to sample in the distillation flask. Close the separatory funnel stopcock, and keep closed during the steam distillation.

5. Steam Distillation

5.1 Add 10-15 drops of saturated $KMnO_4$ solution to the distillation flask. Rinse down the neck and sides of the flask with distilled water. Add 2-3 boiling chips.

5.2 With pinchcock (E) open, bring the distilled water in the steam generator flask (A) to a boil. Concurrently, and with pinchcock (F) closed, heat the sample in the distillation flask (B) until a temperature of 135°C is attained. Open pinchcock (F) and close pinchcock (E). Maintain 135–140°C in the distillation flask (B) during the steam distillation.

5.3 Collect about 250 ml. of distillate in a wide-mouth flask containing 1-2 ml. of 2% NaOH solution. Remove heat source but maintain steam distillation until 300 ml. is collected. Open pinchcock (E) and close pinchcock (F), and immediately disconnect distillation flask (B) at (F).

5.4 Disconnect the distillation flask (B) from the condenser (C). Rinse the inside of the condenser with a small amount of distilled water, and allow the rinse water to flow into the flasks containing the distillate.

6. Specific Ion Electrode Method

6.1 Standardize pH meter with pH 7.00 standard solution. Buffer distillate sample with NaOH and HCl to the range of 5.9–6.1. Final sample volume should be 300 ml.

6.2 Make up fluoride standards: 1, 2, 5, 10, 20, 50 and 100 ppm fluoride. Buffer standards to the same pH range as the samples.

6.3 Zero the fluoride electrode using the millivolt scale with the 1 ppm fluoride standard. Record the millivolt measurement for each of the remaining standards. Draw a standard curve (ppm F^- vs. mV).

6.4 Record millivolts for each of the sample distillates. Use standard curve to get the ppm fluoride that corresponds to the millivolt measurement. Calculate the pounds per cubic foot for each sample.

7. Calculations

7.1 For Solutions (PPM F^- from standard curve).

$$\frac{\text{PPM } F^- \times (6.67 \times 10^{-2})}{\text{Sample Wt. in Grams}} = \%\ \text{NaF}$$

7.2 For Wood (PPM F^- from standard curve).

$$\frac{\text{PPM } F^- \times (2.54 \times 10^{-3})}{\text{Sample Vol. in Cu. In.}} = \text{NaF, pcf}$$

8. DETERMINATION OF pH OF TREATING SOLUTIONS C

The pH should be determined by glass electrode or any conventional method which gives results that agree within 0.1 pH of that obtained with the glass electrode.

9. DETERMINATION OF PHOSPHATE IN FIRE-RETARDANT FORMULATION TYPE C

Reagents

Phenolphthalein—dissolve 1 g. of phenolphthalein in 100 ml. of alcohol.

Hydrochloric acid solution, 1N—dilute 100 ml. of concentrated hydrochloric acid (specific gravity approximately 1.19) to 1 liter. (See standardization procedure below.)

Sodium hydroxide solution, 1N—dissolve 42 g. of sodium hydroxide in water and dilute to 1 liter. (See standardization procedure below.)

Ammonium molybdate solution—dissolve 150 g. of ammonium molybdate in 1 liter of distilled water. Pour 390 ml. of concentrated nitric acid into 610 ml. of distilled water. Then add the diluted nitric acid solution to the molybdate solution. Let stand several days and decant clear liquid. Score in a glass bottle.

Nitric acid solution, 1%—dilute 1 ml. of concentrated nitric acid with 99 ml. of water.

Nitric acid, concentrated.

Hydrochloric acid, concentrated.

Ammonium hydroxide, concentrated.

Ammonium nitrate solution, 1%—dissolve 1 g. ammonium nitrate in 99 ml. of water.

Potassium acid phthalate.

Litmus paper.

Analytical Procedure for Volumetric Method

1. Pipette exactly 10 ml. of solution into a 500-ml. Erlenmeyer flask.
2. Add 30 ml. of concentrated nitric acid and 5 ml. of concentrated hydrochloric acid. Boil until there is a change from brown fumes to clear vapors. Continue boiling until approximately 5 ml. of liquid remain.
3. Cool to about 100° F.
4. Add 5 ml. of concentrated ammonium hydroxide and drop a piece of litmus in the solution. The litmus paper should turn blue. If not, add ammonium hydroxide a few drops at a time until the litmus paper turns blue.
5. Adjust the acidity of the solution by adding concentrated nitric acid until fresh litmus paper just turns red. Add 3 drops of concentrated nitric acid in excess.
6. Hold to approximately 75 to 80° F., by means of constant temperature bath.

7. For solutions of 15 percent concentration or less, add 50 ml. of filtered ammonium molybdate solution; for solutions between 16 and 25 percent concentration add 75 ml. of the molybdate solution; and for solutions greater than 25 percent, add 100 ml. of the molybdate solution.

8. Shake vigorously upon addition of the molybdate solution, and shake intermittently for 30 minutes.

9. Filter at the end of one-half hour through a Gooch crucible with medium-fibre asbestos mat on a vacuum filtration apparatus.

10. Wash the flask clean with 1 percent nitric acid solution. Wash the precipitate in the Gooch crucible twice with 1 percent nitric acid solution.

11. Wash the precipitate several times with 1 percent ammonium nitrate solution.

12. Wash the precipitate with water once, discarding all filtrates.

13. Transfer the Gooch crucible containing the yellow precipitate to a 400 ml. beaker. Pipette 25 ml of 1N sodium hydroxide solution into the crucible and loosen the mat with a stirring rod.

14. Wash the crucible well with water and remove crucible. At this point all the yellow precipitate should be dissolved; if not, add further 25 ml. portions of standard alkali until solution is complete.

15. Add 3 drops of phenolphthalein and titrate with 1N hydrochloric acid solution until the solution changes from red to colorless.

16. Titrate a blank, using the same quantity of 1N sodium hydroxide required to dissolve the yellow precipitates, the phenolphthalein, and the same 1N hydrochloric acid.

17. For standardization of 1 N sodium hydroxide, see standardization procedure under "Determination of Boron". Standardize 1 N hydrochloric acid by pipetting exactly 25 ml. of acid into a 100 ml. Erlenmeyer flask. Add 2 drops phenolphthalein and titrate to a pink color with the standard sodium hydroxide. Then:

$$\text{Normality of HCl} = \frac{\text{titration} \times \text{normality of NaOH}}{25}$$

Calculation

To express the results in terms of diammonium phosphate:

$$\frac{\text{(ml. blank titration—ml. sample titration)} \times 0.05744 \times \text{normality of HCl}}{\text{Sp. gr of solution}} = \text{Percent } (NH_4)_2HPO_4$$

Analytical Procedure for Gravimetric Method

1. Digest a 10 ml. pipetted sample of the solution in the same manner as outlined in the foregoing volumetric procedure.

2. Wash the solution into a 400-ml. beaker.

3. Continue with method through the addition of molybdate solution up to and including the intermittent shaking for 30 minutes.

4. Filter at the end of one-half hour through a pre-weighed Gooch crucible with medium fibre asbestos mat.

5. Wash the beaker with 1 percent nitric acid solution until all the yellow precipitate is transferred to the Gooch crucible assembled on a vacuum filtering apparatus.

6. Wash the yellow precipitate by filling the Gooch crucible five times with 1 percent nitric acid, sucking dry between fillings.

7. Finally, fill the Gooch crucible with distilled water and suck the precipitate as dry as possible.

8. Heat the crucible and precipitate in an oven of 220° F. for two hours. Weigh.

Calculation

To express the results in terms of diammonium phosphate:

$$\frac{\text{Weight of yellow precipitate} \times 0.704}{\text{Sp. gr. of solution}} = \text{Percent of } (NH_4)_2HPO_4$$

10. DETERMINATION OF SULFATE IN FIRE-RETARDANT FORMULATIONS TYPES B, C, AND D

The sample solution should contain sulfate equivalent to approximately 0.15 g. $(NH_4)_2SO_4$.

Reagents

Barium chloride solution, 10%—dissolve 10 g. of $BuCl_2 \cdot 2H_2O$ in 90 ml. of distilled water.

Alcohol, ethyl or methyl.

Hydrochloric acid, or methyl.

Hydrochloric acid, concentrated.

Silver nitrate solution, 1%—dissolve 1 g. silver nitrate in 99 ml. of distilled water.

Analytical Procedure

Note: Since Type C contains no hexavalent chromium requiring reduction, the addition of alcohol and boiling in step 2 may be omitted.

1. Place the sample in a 400-ml. beaker and dilute to about 100 ml.

2. Add 5 ml. of hydrochloric acid and 20 ml. of alcohol. Boil gently until solution has a green color and excess alcohol has been evaporated.

3. Dilute the solution to 200 ml. and heat to boiling. Add 20 ml. of barium chloride solution from a pipette, dropwise, with vigorous stirring.

4. Cover the beaker with a watch glass and allow to settle on a hot plate (low heat) for an hour.

5. Cool, and filter through a Whatman No. 42 paper or equivalent, scrubbing the beaker.

6. Wash the precipitate on filter with hot water until filtrate is free from chlorides. (Test with 1 percent silver nitrate solution until washings give no precipitate.)

7. Transfer paper and precipitate to a weighed porcelain crucible, dry and ignite in an electric furnace. Cool in desiccator and weigh as barium sulfate. (A Bunsen or Meker burner may be used for the ignition.)

Calculation

To express the results in terms of ammonium sulfate:

$$\frac{\text{Weight of } BaSO_4 \times 56.62}{\text{g. of sample}} = \text{Percent of } (NH_4)_2SO_4$$

11. DETERMINATION OF ZINC IN CHROMATED ZINC CHLORIDE, AMMONIACAL COPPER ZINC ARSENATE AND FIRE-RETARDANT FORMULATIONS

Reagents

Hydrochloric acid, concentrated.

Hydrochloric acid 1.20—add one volume concentrated acid to 20 volumes water.

Alcohol, ethyl or isopropyl.

Hydrogen sulfide gas.

Ammonium hydroxide, concentrated.

Uranyl acetate, 1/10N, 4.3 g. dissolved in 100 ml. water.

Potassium ferrocyanide solution, 0.15N—weigh accurately 21.12 g. of pure $K_4Fe(CN)_6 \cdot 3H_2O$, and dissolve it in distilled water. Add 0.2 gram sodium carbonate to stabilize the solution and make the volume up to 1.000 liter. The solution should be kept in a dark bottle. (See standardization procedure below.)

Zinc chloride standard solution, 0.15N—weigh out 2.4518 g. of pure zinc. Place the zinc in a 500 ml. volumetric flask. Add 10 ml. concentrated hydrochloric acid. After the initial reaction, dissolving may be hastened by heating. Cool to room temperature and dilute to mark. Use this solution for standardizing potassium ferrocyanide and back titrating procedure.

Analytical Procedure

1. Accurately weigh approximately 10 g. of treating solution into a 500 ml. Erlenmeyer flask. Add 5 ml. concentrated HCl and 5 ml. ethyl or isopropyl alcohol. Warm on hot plate and when alcohol fumes begin to come off, ignite them, leaving flask on the hot plate until the flame extinguishes. Dilute with 100 ml. water and heat to boiling. Remove from hot plate and bubble H_2S gas through until canary yellow precipitate comes after the initial black precipitate.

2. Filter using Whatman No. 40 paper receiving filtrate in 400 ml. beaker. Wash precipitate with three 20 ml. portions of 1:20 HCl. Boil solution down to about 50 ml. to expel H_2S. Cool. Add 75 ml. water, 15 ml. concentrated HCl, 12 ml. concentrated NH_4OH.

3. Titrate with $K_4Fe(CN)_6$ solution 0.15N using uranyl acetate as an external indicator. Place 2 drops of indicator in each of a series of depressions of a glazed white ceramic spot plate or ¼-inch depressions in a block of paraffin. (The latter can best be made by cutting them out with the tip of a ⅜-inch metal drill.)

4. If the approximate number of milliliters of $K_4Fe(CN)_6$ required is unknown, add 1 ml. of it to the sample, stir thoroughly, then transfer a drop of the sample to one of the uranyl acetate spots. Wait one minute. When the spot turns brown the end-point has been passed. Back titrate with $ZnCl_2$ solution 0.15N from a burette, adding a drop at a time, stirring thoroughly, then transferring a drop of the sample to the spot plate and recording the reading of the burette after each drop is added. When the uranyl acetate spot remains colorless after a drop of sample is added, the end-point has been passed in the opposite direction. Match up the burette reading with the last drop in which the brown color is plainly visible.

5. Subtract the ml. of $ZnCl_2$ solution used to back titrate, from the ml. of $K_4Fe(CN)_6$ and this will give the net ml. of $K_4Fe(CN)_6$ required by the zinc in the sample.

Calculations

To calculate the percentage of active ingredient:

$$\text{Percentage} = \frac{\text{ml. titration} \times \text{normality of } K_4Fe(CN)_6 \times \text{factor}}{\text{g. of sample}}$$

The factors are as follows:

Active Ingredients	Factor
ZnO	4.068
$ZnCl_3$	6.814
$ZnSO_6 \cdot 7H_2O$	14.373

Note: The above procedure is based on the assumption that both the potassium ferrocyanide and zinc chloride solutions are made up to exactly 0.15N.

If some different weight (g.) of zinc metal is used, calculate the normality of the zinc chloride for the above procedure as follows:

$$\text{Normality } (ZnCl_2) = \frac{\text{g. Zinc} \times 2}{32.69}$$

The normality of potassium ferrocyanide is determined by pipetting a 25.00 ml. aliquot of the standard zinc chloride solution into a 250 ml. Erlenmeyer flask. Add 20 ml. concentrated hydrochloric acid and 12.5 ml. concentrated ammonium hydroxide, and then proceed according to steps 4, 5, 6, 7, and 8 of standard A2–59 (Section 12). Normality of potassium ferrocyanide is calculated as follows:

$$\text{Normality } (K_4Fe(CN)_6) = \frac{\text{g. zinc}}{.6538 \times \text{ml. titration } K_4Fe(CN)_6}$$

In the event that the normalities of the two solutions are not equal, a multiplier will have to be applied to the quantity of zinc chloride solution subtracted in step 5. Using the 25.00 ml. zinc chloride and the potassium ferrocyanide titration volume obtained in the standardization, this multiplier (M) can be calculated:

$$M = \frac{\text{ml. } K_4Fe(CN)_6}{\text{ml. } ZnCl_2}$$

Calculation in step 5:
net ml. $K_4Fe(CN)_6$ = ml. $K_4Fe(CN)_6$ − ml. $ZnCl_2 \times M$

12. DETERMINATION OF THE VALENCY STATE OF THE ARSENIC COMPONENT OF AMMONIACAL COPPER ARSENATE SOLUTIONS

Scope

This method is intended for testing batches of concentrate solution, prepared via air-oxidation of trivalent arsenic. The method provides a means of confirming that oxidation has been completed and that at least 99.5% of the arsenic has been oxidized. The sample for testing should contain 100 ± 20 mg. of potential As_2O_5. A 200 ml aliquot of a concentrate containing 8–12% of preservative oxides is suitable.

Reagents

Tartaric acid solution: Dissolve 27 g. of tartaric acid in 400 ml of water:

Saturated sodium bicarbonate solution: Add 45 g. of sodium bicarbonate to 400 ml. of water, and swirl occasionally until most of the sodium bicarbonate goes into solution. Do not use heat to dissolve the salt. This solution can be kept in a stoppered flask.

Starch indicator solution: Make a paste of about 1.0 g of *soluble* starch in 5 ml of water. Pour the paste into 200 ml. of water, near the boiling point, and then boil for one minute. When the solution has cooled, add a few drops of chloroform as a preservative and keep in a stoppered bottle. Some batches of starch will not dissolve properly. If the solution separates into two layers, use the clear, top layer. If the whole solution is cloudy, prepare a fresh solution, or obtain a different supply of starch.

Iodine solution: Add 6.3–6.4 g. of resublimed iodine to a 500 ml. standard flask. Add 10–12 g. of potassium iodide and not more than about 20 ml. of water. Swirl the contents of the flask at room temperature until all the iodine has dissolved, and dilute to the graduation mark. This solution can be kept for a few weeks if stored in a tightly-sealed, glass-stoppered, dark bottle in a cool place.

Procedure:

1. Take a sample of the ACA concentrate and place in a stoppered container (contact of the sample with air should be kept to a reasonable minimum or else misleading results could be obtained.) Allow the sample to settle for at least 5 min. before analysis.
2. Add 20 ml of the tartaric acid solution to a 250 ml Erlenmeyer flask.
3. Using a rubber pipetting bulb, pipet exactly 2.00 ml of the ACA concentrate into the tartaric acid solution. The color of the solution should now be light blue-green. If a reddish, grey, cloudy suspension is obtained, it means that aeration of the concentrate is required.
4. To the light blue-green solution, add 20 ml of saturated sodium bicarbonate solution. The solution will now be light blue. Add 2 ml of the starch indicator solution.
5. Add *one drop* of the iodine solution. This should be done from a buret so that the drop will be about 0.05 ml. Swirl the solution in the flask. If it immediately becomes dark blue (similar to the color of an ACA treating solution), and remains dark for at least one minute, it means that aeration of the concentrate was complete, and that at least 99.5% of the arsenic is in the pentavalent form. If this result is not obtained, aeration should be continued, and another sample tested later.

13. DETERMINATION OF CARBONATE IN AMMONIACAL COPPER ZINC ARSENATE

This analysis provides for the determination of carbonate in an ammoniacal copper zinc arsenate solution.

Reagents

CO_2 free water—distilled or demineralized water freshly boiled or boiled and stored in a closed container. Use whenever CO_2 free water is called for.

Phenolphthalein, 1.0% solution in 50% alcohol.

Potassium Acid Phthalate. Primary Standard Grade.

Sodium hydroxide solution. 0.1 N—purchase standardized solution or—dissolve 4.0 gms. sodium hydroxide in CO_2 free water, cool to room temperature and dilute to 1 liter with CO_2 free water. (See standardization procedure below.)

Hydrochloric acid solution. 0.1 N—purchase standardized solution or dilute 8.3 ml concentrated hydrochloric acid to 1 liter with CO_2 free water. (See standardization procedure below.)

CO_2 absorbant, for drying tube.

Ammonium hydroxide, reagent grade, 28 to 30%.

Calcium chloride solution, 10%, 100 gms. in 900 gms. Co_2 free distilled water.

Sulfuric acid solution, 1:9, 10 gms. in 90 gms. water.

Apparatus

Plastic tubing connector—two piece.
Dropping bottle.
Gas washing bottle.
Filter flask—250 ml.
Magnetic Stirrer-hot plate.
Magnetic stirring bar, 1".
Aspirator (or vacuum pump).
Gas drying tube.
Glass wool, for drying tube.
One hole rubber stopper, #6 (to fit filter flask).
Plastic thistle tube with removable funnel.
Vinyl or latex tubing, 1 / 4" i.d.

Procedure

Assemble and test apparatus as follows:

1. Vacuum flask containing stirrer, one hole stopper and thistle tube are set on stirrer-hot plate. Thistle tube should extend as near bottom of flask as possible without interfering with stirring bar.
2. Add 200 ml. water to gas bottle.
3. Connect vacuum flask tubule to the gas bottle tubule leading to the frittered glass gas disperser near the bottom of the bottle. Plastic two-piece tubing connectors on each side of the gas bottle make later manipulations quite convenient.
4. Connect the outlet of the gas bottle to the vacuum system, using a short section of light tubing with a pinch clamp on it next to the gas bottle.
5. Start vacuum system and adjust air to a moderate flow with pinch clamp.
6. Add about 50 to 60 ml. water to thistle tube as it sucks into flask.
7. Using the pinch clamp, adjust airflow to about 2 to 4 bubbles per second through the bottom of the thistle tube.
8. Without disturbing the pinch clamp setting, disassemble and dump water.
9. Add 150 ml. CO_2 free water and 50 ml. reagent ammonium hydroxide to the gas bottle. Reassemble, check air flow for 2 to 4 bubbles per second and adjust if needed.
10. Weigh sample of solution containing 0.24 to 0.38 gms of ammonium bicarbonate (or 0.13 to 0.21 gms. CO_2), into thistle tube. This is a done conveniently with a weighed dropping bottle. Follow immediately with 50 ml. CO_2 free water. Note that 10 ml. of a 6% ACZA solution contains about 0.3 gms. of ammonium bicarbonate.
11. Turn on stirrer to medium stirring action, and heat high enough to boil in about five minutes.
12. As soon as heat switch is on, start adding 1:9 sulfuric acid about 1 ml. at a time until first sign of solids appear in flask. Then slow acid addition to a drop at a time, a drop to each 2 or 3 air bubbles. Rapid acid addition at this point will blow CO_2 out the thistle tube. When solids have redissolved, add 2 ml. excess 1:9 acid.
13. As soon as acid addition is complete (about 2 minutes), remove funnel top from thistle tube and attach drying tube filled with CO_2 absorbent in place.
14. At first sign of boiling, or when heat reaches top of filter flask, shut heat off. Continue air flow 15 minutes more, to a total of about 20 minutes.
15. Disassemble, wash gas bottle contents into 500 ml wide mouth Erlenmeyer flask, using CO_2 free water.
16. Add 10 ml. 10% calcium chloride solution, dilute to about 400 ml. with CO_2 free water, and digest on steam bath 2 hours.
17. Filter through asbestos matt in Gooch crucible, wash flask and crucible with CO_2 free water. Return crucible to Erlenmeyer flask and dry in an oven at 225 F for 1 hour.
18. Add 100 ml standardized hydrochloric acid (pipete). Tilt and rotate flask to wash sides and dissolve any adhering calcium carbonate. Dilute to about 150 ml with CO_2 free water, washing sides of flask.
19. Boil gently 1 minute to expel CO_2.
20. Titrate to phenolphthalein end-point with 0.1 N standardized sodium hydroxide.
21. Standardization of sodium hydroxide solution. Weigh out replicate portions of potassium acid phthalate, 1.6000 g. + − 0.1000 g., transfer to Erlenmeyer flasks. Dissolve each in 100 ml. CO_2 free water, adding 2 drops phenolphthalein. Titrate with the sodium hydroxide solution to a faint permanent pink color. Replicate titrations should yield normalities within 0.0005.
22. Standardization of hydrochloric acid solu-

tion. Pipet 50 ml. of hydrochloric acid solution into 250 ml. Erlenmeyer flask. Add 2 drops phenolphthalein indicator and titrate with standardized sodium hydroxide solution until a faint permanent pink color appears. Duplicate titrations should agree within 0.1 ml. Record average.

23. Run blanks, i.e. run the complete analysis without a sample added. At step 12, only the 2 ml. excess of 1:9 sulfuric acid is needed. At step 18, use 50 ml. of the standardized HCl as in step 22. The ml. used to titrate this solution will be less than that used in the standardization, step 22. The difference is the blank used in the calculations.

Calculations

Legend:

Normality HCl = N_{HCl}
Normality NaOH = N_{NaOH}
Active Ingredient = AI
Factor = F
Blank = ml. NaOH in step 22 − ml. NaOH in step 23

$$N_{NaOH} = \frac{\text{grams potassium acid phthalate}}{\text{ml. NaOH} \times 0.2042}$$

$$N_{HCl} = \frac{N_{NaOH} \times \text{ml. NaOH}}{50}$$

$$\% \text{ AI} = \frac{\{\text{ml. HCl} \times N_{NaOH}\ (\text{ml. NaOH} + \text{Blank})\} \times F}{\text{sample weight}}$$

Active Ingredient	Factor
Ammonium bicarbonate	3.953
CO_2	2.201

14. PRECISION STATEMENTS

CCA IN SOLUTION BY A2 METHODS 2, 5 AND 6

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

Repeatability:	Duplicate single determination 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 that 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 limited percentages shown in the following table.

PRECISION TABLE

Element	Expressed As Oxide	Solution Oxide Concentration Level (%)	Limiting Percentages Repeatability	Limiting Percentages Reproducibility
Chromium		0 to 9.95	.021	.045
Chromium	CrO_1	0.96 to 2.50	.027	.040
Chromium		2.51 to 4.00	.041	.121
Copper		0 to 0.45	.008	0.38
Copper	CuO	0.46 to 1.05	.021	.085
Copper		1.06 to 1.60	.014	.236
Arsenic		0 to 1.00	.029	.036
Arsenic	As_2O_5	1.01 to 2.20	.020	.050
Arsenic		2.21 to 3.00	0.71	.330

The above precision statements are based on round robin data by six laboratories, each running three replicate determinations on each of three sample covering the concentration range 1.40% to 8.12% CCA in solution. The samples included both CCA-B and CCA-C.

15. DETERMINATION OF BORON IN TREATED WOOD—USING AZOMETHINE-H

1.0 EQUIPMENT

1.1 Crucibles—for example VWR #23967-067, 50 ml fused silica—boron free, glazed inside and out

1.2 Covers for above VWR #23968-060

1.3 Furnace—Programmable preferred (for example Thermolyne, Programmable Ashing Furnace Type 6000—Model #F6050-60, 240 volts)

1.4 Whatman #4 filter paper

1.5 Standard laboratory glassware

1.6 Wood Grinder

2.0 PROCEDURE

2.1 Dry wood, at 50°C, overnight.

2.2 Grind wood sample to a fine powder, −30 mesh (U.S. Standard).

2.3 Place 1 to 3 g of sample, to nearest 0.01 g, into crucible.

2.4 Cover, leaving slightly ajar.

2.5 Place crucible in oven and increase temperature to 500°C at a rate of 20°C/minute to prevent flashing. When the temperature has reached 500°C, hold at that temperature for 16 hours.

2.6 After 16 hours, cool the oven at approximately 50°C/minute to prevent crucible from cracking.

2.7 Remove from furnace when under 150°C.

2.8 Add 3 drops of 6N HCl to the crucible.

2.9 Wash acidified residue with hot water (approx. 20 ml) into a beaker. Stir for 5 minutes, then filter through Whatman #4 filter paper. Wash filter paper 3 times with 10 ml of hot water. Dilute to 250 ml in a volumetric flask.

3.0 EQUIPMENT

3.1 Spectronic 20, or Beckman DU-6 spectrophotometer or equivalent.

3.2 1 cm pathlength cuvettes with about 3.5 ml capacity

3.3 Burettes and Pipettes (automatic pipettes are convenient)

3.4 Volumetric flasks

3.5 Magnetic stirrer and stirring bars

3.6 Balance

3.7 30 ml bottles with ground glass stoppers (for example VWR Scientific Catalog Number 16711-100)

4.0 REAGENTS

4.1 Concentrated sulfuric acid, analytical reagent grade, 96% or greater concentration.

4.2 Standard boron solutions.

4.3 The standard boron solutions are prepared as described above for the azomethine-H procedure.

4.4 **Carminic Acid Solution:**
Add 0.250 g of carminic acid, about 950 ml of concentrated sulfuric acid (caution: corrosive) and a magnetic stirring bar to a one liter volumetric flask. Stopper flasks and stir magnetically for 3 to 4 hours. Remove the magnet with a magnet thief, add concentrated sulfuric acid to the mark and mix well. The solution should be stored preferably in a boron free glass stoppered bottle. However, if none is available, a clean commercial 9 lb. concentrated sulfuric acid bottle is adequate. Fresh carminic acid solutions should be stored in the same bottle. The bottle should be tightly closed when not in use.

5.0 PROCEDURE

5.1 1.0 ml of each standard and unknown solution, as well as 1.0 ml of a water blank (0 ppm boron), is pipetted into separate 30 ml glass bottles equipped with ground glass stoppers. (A set of standards should be run each time the unknown solutions are analyzed.)

5.2 From a burette or pipette, add 5.00 ml concentrated sulfuric acid to each bottle at a fast drop rate. Because of the viscosity of the sulfuric acid, it may be necessary to cut tips to allow a fast drop delivery.

5.3 Stopper the bottles, cool and swirl gently to mix.

5.4 From a separate burette, add 5.00 ml of carminic acid solution to each bottle at a fast drop rate.

5.5 Again, stopper the bottles, cool and swirl gently to mix.

5.6 Allow solutions to stand for 1-1/2 hours to insure full color development.

5.7 Transfer to cuvette and measure the absorbance at 585 nm.

5.8 Prepare a standard curve by plotting the absorbance on the y-axis and the ppm boron of the standard solutions on the x-axis.

5.9 The ppm boron of the unknown(s) can be determined from the graph by reading the concentration on the x-axis.

6.0 CALCULATIONS

$$\% \ B_2O_3 = \frac{(\text{ppm boron } (0.0805)}{\text{grams of sample}}$$

If the absorbance of the unknown is greater than the absorbance for the 10 ppm standard, take 1 ml of the unknown solution and dilute to 5 ml using a volumetric flask and repeat the procedure. The % B_2O_3 obtained must then be multiplied by 5 to obtain the correct answer.

To convert % B_2O_3 to pounds B_2O_3/cubic foot:

$$\text{pounds } B_2O_3/\text{cubic foot} = \frac{(\%B_2O_3)\ (\text{wood density in PCF})}{100}$$

7.0 PRECISION STATEMENT

A ground, well homogenized wood sample was prepared. Ten individual samples were analyzed. The results at the 95% confidence level were 0.74 ± 0.03 expressed as % B_2O_3.

NOTES

Note 1. A blank wood sample should be analyzed with each batch of boron treated wood. The % B_2O_3 value determined should be subtracted from the value of the unknown.

Note 2. All blank glassware should be dry before using.