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PCA Test Methods

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A GUIDE TO TURPENTINE TEST METHODS

Introduction

A number of years ago the Pine Chemicals Association, then the Pulp Chemicals Association prepared a collection of the analytical methods used by the tall oil industry. This collection covered methods used for the analysis of tall oil and its precursors such as black liquor soap. It did not include the analysis of the other major product of pine chemicals industry, namely turpentine as that topic was covered in a chapter of the book Sulfate Turpentine Recovery published in 1971. This current guide is designed to update that chapter and bring together the methods now in use in the turpentine industry and in particular in the turpentine fractionation industry. It also includes the method for measuring the turpentine content of pine wood described in the 1971 book.

This guide was assembled by a small subcommittee of the PCA's Testing Committee and chaired by James Russell. Other members of the subcommittee were Henri Jobard of DRT, Donald Scott of Arizona Chemical Company and John Bailey of Rennessenz The aim of the subcommittee was to bring together the test methods of the industry so that these would be readily available to PCA members, their customers and their suppliers.

As the work of the committee proceeded it was realized that emphasis should be on purpose and scope of the test methods rather than the laboratory details. The details of the test methods were readily available in the publications of various standards organizations such as ASTM International, ISO, and the PCA and so it was considered unnecessary to reproduce them as they are all available for purchase. This present guide therefore summarizes the methods in use by the industry, their significance and scope and references where a detailed method is published.

Both physical and chemical analyses are used for the characterization of turpentine. When the chief use for turpentine was as a solvent, the physical characteristics were the most important but now that the main use for turpentine is as a raw material for the production of fine chemicals and terpene resins, chemical analysis, especially gas chromatography, has become of far greater importance.

PHYSICAL METHODS

Appearance and odor are important. Refined turpentine is a water white liquid with a mild characteristic odor. The color of crude turpentine can range from various shades of yellow to brown and, in the case of sulfate turpentine a very foul odor due to the presence of volatile sulfur contaminants overwhelms the characteristic smell. Refined turpentine is clear and any haze is most likely due to the presence of water. (The measurement of sulfur and moisture content are described in other parts of this guide.)

Obtaining a test sample is essential in every instance. Details are given in ASTM Test Method D233.

Specific gravity should be measured at 15.6 degrees Centigrade using any available method having a precision of 0.0005. Details on how to correct for specific gravities measured at other temperatures are given in ASTM Test Method D 233.

Refractive index should be measured at 20 degrees Centigrade. Again details for any temperature correction can be found in ASTM Test Method D 233

Optical rotation can be measured by any accurate polarimeter. Optical rotation is a characteristic of many terpenes and is a measure of the purity of these terpenes. With refractive index it is valuable for characterizing the turpentine source.   It should be measured at 589nm (sodium) at 20 degrees Centigrade.

CHEMICAL METHODS

Moisture content

Knowledge or water content is important in two phases of turpentine processing. On delivery, turpentine containers may be contain some water and during processing moisture can interfere with the chemical reactions. Usually, the moisture content is determined by the Karl Fischer titration method. This involves the reaction between water and Karl Fischer Reagent, a complex mixture of iodine, sulfur dioxide, pyridine and methanol. This method is very suitable for measuring small amounts of water in a wide variety of turpentine derived products as well as turpentine itself. It is not appropriate for measuring high levels of water such as might occasionally be found in a shipping container as the amount of titrant would be large. In such cases a sample should be drawn from the bottom of the container and then, if water is found it should be drawn from the container and measured gravimetrically

Details of the Karl Fischer method are given in ASTM Standard Test Method D890.

Sulfur Content

Foul smelling sulfur compounds such us dimethyl sulfide, are contaminants in crude sulfate turpentine, a by-product of the kraft wood pulping process. These need to be removed if the turpentine is to be used as a raw material for the production of end products such as flavors, fragrances and polymers.

Determining the sulfur content of turpentine uses the same techniques as the determination of sulfur in any other media such as petroleum, i.e. UV fluorescence or X-ray fluorescence.

In both methods the fluorescence emitted by the test samples is compared to the emission from standard samples containing known amounts of sulfur. Suitable standards can be obtained from the manufacturer of the testing equipment or can be prepared in the laboratory. It is preferable to use a standard similar in composition to the test substance.

Detailed procedures for these standard test methods are described in ASTM D5453 (UV fluorescence) and ASTM D4294 (X Ray fluorescence).

Composition by Capillary Gas Chromatography

Gas chromatography is an extremely important technique for the analysis and characterization of turpentine and related products as all its components are volatile. Knowledge of the composition and purity is critical as many of the fractions are used as intermediates in the production of flavors, fragrances and polymers. Gas chromatography is by far the most widely used technique for determining the individual components of turpentine and their concentrations.

The method involves injecting the test sample into a temperature programmed gas chromatograph fitted with either a polar or non polar column. The relative concentrations of the various components can be calculated from the resulting chromatogram using the area percent method and assuming the response factors are equal. If greater precision is required, especially if a large amount of heavy components is expected, first determine the response factors using known standards or an internal standard and then use those to calculate the concentrations.

Complete details of the methods can be found in ASTM Test Method D6387 (Turpentine), D801 (Dipentene) and D802 (Pine oil)

Peroxide value

The peroxide value of turpentine and related products is a measure of the degree of degradation of the material. When exposed to oxygen the double bonds of the terpene react to form peroxides. The peroxides catalyze other reactions leading to increased color and instability.

The peroxide value is determined by the reaction of the peroxide with potassium iodide solution. The iodine released in the reaction is measured by titrating with sodium thiosulphate solution using a starch indicator. A typical good quality turpentine can be expected to have an active oxygen content of 50 mg per liter.

Details of this determination are given in ASTM Test Method D1832-65 and AOCS Test method 8b-90.

Chirality is sometimes very important in characterizing turpentine. This property, which pertains to stereochemical structure of certain terpenes, differentiates between dextro and levo optical rotations in certain species i.e. alpha pinene + and alpha pinene -.   It can be measured by gas chromatographic analysis using a beta cyclodextrin column.

TURPENTINE CONTENT OF PINE WOOD

No standard method has been published describing a procedure for determining the turpentine content of wood although the PCA's book Sulfate Turpentine Recovery describes a method developed by John Drew.   That method was later adapted for the determination of crude tall oil in wood chips and published by the PCA as PCTM 25.

In this procedure wood chips are ground and digested in hot caustic soda. During the digestion the turpentine distils off. Details of the method are given in Sulfate Turpentine Recovery. The turpentine content of wood can also be obtained by following the first steps of   PCTM 25 but, in step 6, the turpentine should be collected and measured and not discarded. The of composition of the turpentine can be determined by gas chromatography and the other techniques described in this guide.

Information Sources

Sulfate Turpentine Recovery: J. Drew, J. Russell and H. W. Bajak published by the Pine Chemicals Association, 1971.

Copies of ASTM standard test methods can be obtained by contacting ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 or on their website: www.astm.org

Copies of PCA PCTM standard test methods can be obtained by contacting Pine Chemicals Association, Inc., PO Box 17136, Fernandina Beach, FL 32035 or on their website: www.pinechemicals.org.

STANDARD TEST METHODS
OF THE PINE CHEMICAL INDUSTRY

PRODUCT	TEST METHOD	ASTM	PCA	ISO	CHINA
ROSIN					
	Softening Point, Ring & Ball	E-28		ISO 4625-1	GB 8146-2003
	Softening Point Mettler	D-6090		ISO 4625-2	
	Acid Number	D--465			GB 8146-2003
	Rosin Acid Content	D1240			
	Fatty Acid Content	D1585			
	Unsaponifiables	D-1065			GB 8146-2003
	Insoluble Matter	D269			GB 8146-2003
	Gas Chromatographic Analysis	D5974		ISO 19334	
	Grading	D-509		ISO/CD 13632	GB 8145-2003
	Volatile Oil Content	D889			
	Water Content	D-890			
	Color USDA	D-509			
	Color Gardner	D6166		ISO 4630-1&2	
	Color Pt Co Scale			ISO 6271-1&2	

PRODUCT	TEST METHOD	ASTM	PCA	ISO	CHINA
TALL OIL FATTY ACID or DISTILLED TALL OIL					
	Saponification Number	D464			
	Acid Number	D465			
	Water Content	D890			
	Unsaponifiable Matter	D1065			
	Rosin Acid Content	D1240			
	Fatty Acid Content	D1585			
	Color Gardner	D1544			
	Color Instrumental	D6166			
	Titer	D1982			
	Iodine Value	D5768			
	Gas Chromatographic Analysis	D5974			
	Color After Heating	D1981			

CRUDE TALL OIL

Product	ASTM/PCA
Acid Number	PCTM 1&2
Water Content	PCTM 4A,4B&4C
Residual Soap	PCTM 13
Saponification Number	PCTM 16
Rosin Acid Content	PCTM 17
Unsaponifiable matter	PCTM 19
Fatty Acid Content	PCTM 20
Solvent Insolubles	PCTM 21
Viscosity	PCTM 26
Tall Oil in Wood Pulp	PCTM 23
Tall Oil in Wood Chips	PCTM 25
Tall Oil in Black Liquor	PCTM 24
Tall Oil in Tall Oil Soap	PCTM 7
Lignin in Tall Oil Soap	PCTM 8
Ash Content of Tall Oil Soap	PCTM 12
Tall Oil in Spent Acid	PCTM 10
Mineral Acid in Crude Tall Oil	PCTM 14

TURPENTINE AND ITS FRACTIONS

Product	ASTM	PCA
Sampling and Testing Turpentine	D 233	
Testing Dipentene	D 801	
Testing Pine Oil	D 802	
Gas Chromatographic Analysis	D 6387	
Turpentine in Wood		PCTM 25

Method of determining acid number of tall oil using a potentiometric end point

Scope

This method is used to determine the acid number of crude tall oil using the potentiometric technique for determining the equivalence point of the titration.

The test is used to determine the acid number of crude tall oil (CTO) and other related products. The potentiometric method yields a more accurate value with better precision compared to the colorimetric indicator method.

The sample is dissolved in an isopropyl alcohol/toluene solvent and titrated with a standardized alcoholic potassium hydroxide to a potentiometric equivalence point.

Apparatus

1.   Glass electrode pH meter. Use either standard or alkali-resistant electrodes for this test. An automatic potentiometric titrator may be used in place of a pH meter.
2.   Burette, 50-mL with 0.1 mL divisions.
3.   Stirrer, variable-speed with PTFE coated magnetic stir bar or other type mechanical stirrer.
4.   Beaker, 400-mL.

Reagents

1.   Standard alcoholic alkali (potassium hydroxide) solution, 0.5N - Purchase or prepare by dissolving 33 g of potassium hydroxide (pellets or sticks) in methyl alcohol or 39 mL of 45% KOH solution in a one liter bottle, and dilute to approximately one liter with the alcohol. Standardize to t 0.001N by dissolving approximately 2.5 g of potassium

acid phthalate (KHP) in 60 mL of water followed by the addition of 40 ml. of isopropyl alcohol once the KHP has dissolved; 2.553 g of KHP will be neutralized by 25.0 mL of 0.5N KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO_2) from the air. The solution should be standardized weekly potentiometrically. The standardization should use the same equipment and techniques as used in the actual acid number determination.
2.   Methanol, reagent grade.
3.   Isopropanol, reagent grade.
4.   Toluene, reagent grade.
5.   Potassium acid phthalate (KHP), primary standard grade.
6.   Buffer, pH 10, commercially available.

Procedure

1.   Accurately weigh 3-5 g of sample to the nearest 0.001 g, and transfer it to a 400-mL beaker. Add 25 mL of toluene and swirl to dissolve.
2.   Add 75 mL of isopropanol and swirl to mix.
3.   Adjust the beaker so the lower half of each electrode of the pH meter is immersed in the solution. Add the stir bar. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering.

NOTE 1:   If an autotitrator is employed, follow the manufacturer's operating instructions.

NOTE 2-   Glass *electrodes* read to dehydrate in nearly anhydrous solvent medium. Condition the *electrode* in water between tests and check with known pH buffers frequently.

4.   Titrate with the standard alkali solution, recording the burette and pH meter readings. Sufficient alkali may be added initially to bring the pH of the solution to approximately 8. Allow sufficient time for the electrode system to reach equilibrium. Add alkali in 1.0 mL portions until the change in pH per increment added amounts to about 0.3 pH unit. Reduce the additions of alkali to 0.1 mL or smaller until the end point has been passed, as indicated by a significant decrease in pH units per 0.1 mL added. Continue the titration with 1.0 mL ,portions until it becomes apparent that the inflection point has been well defined.

Determine the inflection point (point of maximum change in pH per milliliter of alkali solution) to the nearest 0.05 mL by plotting the pH readings against the milliliters of alkali used. For greater accuracy, a plot may be made of the change in pH per milliliter of alkali, against the pH. The peak of this curve will indicate the exact inflection point The inflection point is considered the end point of the titration. Alternatively, if an automatic titrator is used, the end point is either the inflection point from the plotted curve or the pH determined to coincide with the inflection point in the laboratory performing the analysis.

NOTE 3: The valued 10.8 is the average pH encountered at the inflection point by the above procedure using closely controlled conditions, solvent, etc. For less accurate work, a titration directly to the pH of 10.8 may be used.

Calculation

Calculate the acid number of the sample, expressed as milligrams of KOH per gram of sample as follows, and report the value to the nearest whole number.

Acid number = $\frac{(A \times N \times 56.1)}{B}$

where:
A   =   volume of alkali solution required for titration of the specimen, mL
N   =   normality of the alkali solution
B   =   sample weight, g
56.1 =   equivalent weight of KOH and is used in the equation to express the acidity based on an equivalent amount of milligrams of KOH.

Precision Statement

Based on an ASTM round-robin study, the within laboratory (repeatability) standard deviation for this test is 0.41 and the between laboratory (reproducibility) standard deviation for this test is 1.18.

Reference

ASTM D465 "Acid Number of Naval Stores Products Including Tall Oil and Other Related Products. "

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Method of determining acid number of tall oil using a colorimetric end point

Scope

This method is used to determine the acid number of crude tall oil (CTO) and other related products using the colorimetric indicator technique for determining the equivalence points of the titration.

Use of a colorimetric indicator yields a less accurate value with lower precision compared to the potentiometric technique. Dark samples (Gardner $\geq$12) are difficult to analyze using the colorimetric end point.

The sample is dissolved in a mixture of isopropyl alcohol/toluene and titrated with standardized alcoholic potassium hydroxide to a colorimetric end point.

Apparatus

1. Buret, 50-mL with 0.1 mL divisions.
2. Stirrer, variable-speed with polytetrafluoroethylene (PTFE) coated magnetic stir bar or other type of mechanical stirrer.
3. Erlenmeyer flask, 250-mL.

Reagents

1. Standard alcoholic alkali (potassium hydroxide) solution, 0.5N - Purchase or prepare by dissolving 33 g of potassium hydroxide (pellets or sticks) in methanol or 39 mL of 45% KOH solution in a one liter bottle, and dilute to approximately one liter with the alcohol. Standardize to t 0.OO1N by dissolving approximately 2.5 g of potassium acid phthalate (KHP) in 60 ml, of water followed by the addition of 40 ml, of isopropanol once the KHP has dissolved; 2.553 g of KHP will be neutralized by 25.0 ml, of 0.5N KOH. solution.

Protect the standardized solution against evaporation and absorption of carbon dioxide (CO_2) from the air. The solution should be standardized weekly. The standardization should use the same equipment and techniques as used in the actual acid number determination.

2. Methanol, reagent grade.
3. Isopropanol, reagent grade.
4. Toluene, reagent grade.
5. Potassium acid phthalate (KELP), primary standard grade.
6. Indicator solution, dissolve 0.1 g of phenolphthalein or thymol blue in 100 mL of isopropanol.

Procedure

1. Accurately weigh 3-5 g of sample to the nearest 0.001 g, and transfer it to a 250-mL flask. Add 25 mL of toluene and swirl to dissolve.
2. Add 75 mL of isopropyl alcohol and swirl to mix.
3. Add four drops of indicator solution. Add the stir bar. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering

NOTE 1:   For a dark solution, additional indicator may be needed to detect the endpoint

NOTE 2:   As the end point is approached, the addition rate of titrant should be reduced to more accurately determine the end point

4. Titrate with the standard alkali solution to the first permanent faint pink color when using phenolphthalein or a faint blue-green color using thymol blue.

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PC*TM 2*   *Method of determining acid number of tall oil using a colorimetric end point /2*

5.   Read the buret to 0.05 mL titrant. Calculation

Calculate the acid number of the sample, expressed as milligrams of KOH per gram of sample, as follows, and report the value to the nearest whole number:

$$Acid\ number = \frac{(A \times N \times 56.1)}{B}$$

where:

A   =   volume of alkali solution required for titration of the specimen, mL
N   =   normality of the alkali solution
B   =   sample weight, g
56.1   =   equivalent weight of KOH and is used in the equation to express the acidity based on an equivalent amount of milligrams of KOH.

Reference

ASTM D465 "Acid Number of Naval Stores Products Including Tall Oil and Other Related Products."

Specific gravity of tall oil

Scope

This method describes a method for determining the specific gravity of tall oil by use of a hydrometer. Knowledge of this property is important in process engineering studies, especially those related to pipelines and tanks. Although this method only describes the use of a hydrometer, other instruments such as density meters can be used.

Apparatus

1.   Hydrometer - The hydrometers to be used shall fall in the following nominal specific gravity ranges:
>   0.850 to 0.900
>   0.900 to 0.950
>   0.950 to 1.000

2.   Hydrometer Cylinder - The vessel in which the sample for the gravity test is confined shall be made of clear glass and shall be cylindrical in shape. The inside diameter shall be at least 1.0 inch greater than the outside diameter of the hydrometer to be used in it. The height of the cylinder shall be such that after equilibrium has been reached, the lowest point of the hydrometer will be at least 1.0 inch off the bottom of the cylinder.

3.   Thermometer, range 20 to 102°C graduated in 0.1°C.

4.   Waterbath or oven, capable of maintaining a temperature
of 15.6°C (60°F) ± 0.1 °C during the test.

Procedure

1.   Cool the sample in the original container to about 14°C.

2.   Rinse each piece of equipment with a portion of the sample and discard the rinse liquid. Pour the sample into the clean hydrometer cylinder so as to avoid the formation of air bubbles. Remove any air bubbles adhering to the surface.

3.   Place the cylinder vertically in the waterbath and let the temperature of the sample rise towards 15.6 ± 0.1°C. When the temperature of the sample reaches 15.3°C, slowly and carefully lower the hydrometer into the sample to a level two smallest scale divisions below that at which it will float and then release the hydrometer. Allow the equipment to equilibrate.

4.   When the temperature reaches 15.6 ± 0.1 °C, read the specific gravity, to the. nearest 0.001 unit, as the point at which the surface of the sample apparently cuts the hydrometer scale.

Moisture content of tall oil by azeotropic distillation

Scope

A sample is dissolved in toluene or xylene, then the azeotrope of the solvent and water is distilled and the water is collected. The volume of the separated water is used to calculate the percent moisture.

Apparatus

1. Flask, 0.5- or 1-liter short-neck, round-bottom or Erlenmeyer flask, depending upon the weight of the sample used. The larger size is preferred to avoid foaming.
2. Hot plate or heating mantle.
3. Reflux condenser, condenser connected to the flask and discharging into a trap.
4. Trap, 5-mL trap, subdivided into 0.1 mL, divisions, with each I mL line numbered.

Reagents

Toluene or xylene - reagent grade, moisture free.

Procedure

1. Weigh 100 grams of tall oil into the flask Add a few boiling stones. Fit the flask with a moisture trap and a reflux condenser. Add 150 mL of toluene or xylene to the flask and fill the moisture trap with solvent.
2. Heat gently until the solvent begins to reflex. Continue vigorous refluxing for 2 hours. Wash down the condenser with 5 mL portions of solvent from time to time during the reflux period and with four 5 mL, portions of solvent at the end. A drop of water remaining on the condenser may be dislodged with a fine wire or a stirring rod wet with methanol. Record the volume of water in the trap.

Calculation

$$Moisture, \% = \frac{V}{W} \times 100$$

where:

V = Volume of water, n1L
W = Weight of sample, g

Alternate methods

PCTM 4B, PCTM 4C

Reference

ASTM D803 "Methods for Testing Tall Oil."

Moisture content of tall oil by coulometry

Scope

This test method covers the determination of water in liquid organic materials containing <2% water. The moisture content of tall oil is determined by automatic titration with coulometrically generated Karl Fisher reagent In the Karl Fisher reaction, iodine reacts with water in the presence of sulfur dioxide, an organic nitrogen base like pyridine and an alcohol:

$$I_2 + H_2O + SO_2 + ROH + 3RN \rightarrow 2RN \cdot H1 + RN \cdot HSO_4R$$

With coulmettic titrators the required iodine is produced by anodic oxidation of an iodide contained in the cell reagents. The sample water content is then determined directly by electronically integrating the current required to generate sufficient iodine to precisely react with the water in the sample.

Safety precautions

Always operate the titrator in a fume hood. Most of the reagents, including some of the pyridine-free systems are noxious or toxic and inhalation or direct skin contact with them should be avoided.

Apparatus

1. Coulometric Karl Fisher titrator.
2. Sample vials, 8-nt or 4-dram.
3. Medicine droppers.
4. Disposable plastic syringes, 1-cc with 16, 18 or 20 gauge needles.
5. Syringe, 10-uL.

Reagents

Karl Fischer pyridine-free reagent. Reagents are available from the manufacturer of the apparatus.

Instrument preparation

Prior to sample analysis the analyst must become familiar with the operation of the titrator which differs slightly depending on the manufacturer of the apparatus.

1. Prepare and calibrate the apparatus as specified in the operating manual supplied by the manufacturer. This generally includes the following steps:
    a. Clean and assemble the titration chamber.
    b. Pour the titration solution into the chamber.
    c. Add the iodine generator solution to the generator assembly.
    d. Put the instrument in STANDBY position.
    e. Slowly add neutralizing solution normally by injection with a syringe)
    f. Continue the addition until the instrument indicates by a light or a message on an LCD that excess water is present.
    g. Stop the addition of neutralizing solution.
    h. Let the instrument stabilize for 1 hour in the STANDBY position.
2. Verify the instrument by injecting a known amount of water, usually 1 uL to 5 uL below the surface of the titration solution.
3. Put the instrument in the TITRATE or RUN position and record the reading when the END light comes on or a message appears that the titration is complete.

Moisture content of tall oil/2

4. Record the reading. This reading is usually in micrograms or milligrams of water and should be within ± 5% of the amount of water that was added.

   Example: for 5 uL of water the reading should be 5000 ug ± 250 ug.

Procedure

1. Some coulometric titrators require that the sample be injected through a septum. If this is the case proceed as follows:

   a. Draw approximately 0.5 ml, of the tall oil into a 1-cc disposable syringe. Wipe the needle clean with a dry paper towel.
   b. Weigh the syringe with the sample to the nearest 0.001 g. Record this weight.
   c. Inject about 0.1 to 0.2 mL of the sample into the titrator. Withdraw the syringe.
   d. Weigh the syringe to the nearest 0.001 g and record this weight.
   e. Proceed to step 6.

   For instruments which do not require through-septum injections go to step 2.

2. Put approximately 4 mL of tall oil into a small sample vial. Do not allow the sample to touch the outside of the vial.
3. Put a medicine dropper into the vial and weigh the vial, sample and medicine dropper together on an analytical balance to the nearest 0.0019. Record this weight.
4. Using the medicine dropper, introduce one to two drops of the sample into the coulometric titrator.
5. Put the medicine dropper back into the vial and weigh to the nearest 0.001 g.. Record this weight.
6. Begin the titration.

Calculation

Moisture, % = $\dfrac{\text{(micrograms of water found)}}{\text{weight of sample in g} \times 10{,}000}$

Report to the nearest 0.001%.

Alternate methods
PCTM 4A, PCTM 4C

References

ASTM D1364 "Water in Volatile Solvents."
ASTM D890 "Water in Liquid Naval Stores."

Appendix

In general, the coulometric reaction cell consists of a small vessel which houses an iodine generating electrode and a sensing electrode. To keep out moisture, the vessel is sealed except for a sample and reagent introduction port which may be opened as needed. The iodine generating electrodes consist of an (inner) cathode and an (outer) platinum screen anode, separated by a glass frit. Iodine generation takes place at the anode. An equivalent amount of reducing species is created at the cathode. The glass frit and spatial arrangement of the electrodes prevents unwanted migration of the reducing species.
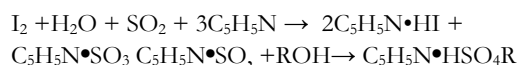
The sensing probe is a dual platinum electrode to which a voltage is continuously applied. A sharp decrease in cell resistance is recorded when the highly conductive excess iodine appears, after all the water in the sample has reacted. This is the equivalent of the end point in the volumetric titration with Karl Fisher reagent. (Reference ASTM D1364).

In the stand-by mode a coulometric titrator continues to generate iodine on demand as trace quantities of atmospheric moisture enter the apparatus. Between samples, the end-point is always held in this way and the instrument is always ready for use, provided reagent solutions are replenished when needed. All current models of coulometric Karl Fisher titrators have warning indicators to alert the analyst when reagents need replacement.

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Moisture content of tall oil by Karl Fischer titration

Scope

This test method covers the determination of water in liquid organic materials containing 0.5 to 10% water. It is based on the reduction of iodine by sulfur dioxide in the presence of water. The moisture content of tall oil is determined by automatic, volumetric titration with Karl Fischer reagent. In the Karl Fischer reaction, iodine reacts with water in the presence of sulfur dioxide, an organic nitrogen base like pyridine and an alcohol:

$I_2 + H_2O + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N \bullet HI + C_5H_5N \bullet SO_3 \ C_5H_5N \bullet SO, + ROH \rightarrow C_5H_5N \bullet HSO_4R$

The Karl Fischer reagent is the titrant. It normally consists of iodine, pyridine and sulfur dioxide, in a molar ratio of 1 : 10 : 3, dissolved in anhydrous 2-metboxyethanol.

Safety precautions

Always operate the titrator in a fume hood. Most of the reagents, including some of the pyridine-free systems are noxious or toxic and inhalation or direct skin contact with them should be avoided.

Apparatus

1. Automatic Karl Fischer titrator.
2. Sample vials, 8-mL or 4-dram.
3. Medicine droppers.
4. Disposable plastic syringes, 1-cc with 16, 18 or 20 gauge needles.
5. Syringe, 10- and 25-uL.
6. Weighing pipet (optional).

Reagents

Karl Fischer reagent or Karl Fischer pyridine-free reagent Reagents are available from the manufacturer of the apparatus.

Instrument preparation

Prior to sample analysis the analyst must become familiar with the operation of the titrator which differs slightly depending on the manufacturer of the apparatus.

1. Prepare and calibrate the apparatus as specified in the operating manual supplied by the manufacturer. This generally includes the following steps:
   a. Clean and assemble the titration chamber.
   b. Introduce a volume of anhydrous titration solvent into the titration vessel. This solvent is normally ethylene glycol- pyridine and is supplied by the manufacturer.
   c. Titrate the solvent to the instrument end point with Karl Fischer reagent. This insures that all water due to the solvent and due to moisture on the surfaces of the apparatus is consumed.
   d. Now standardize the Karl Fischer reagent.
2. Standardize the Karl Fischer reagent each day. Inject exactly 10 uL or exactly 25 uL of water below the surface of the titration solution. Larger volumes of water are undesirable because they require large volumes of titrant which fills the vessel so that the solvent has to be poured out and new solvent introduced. A weighing pipe may also be used to introduce the water.
3. Put the instrument in the TITRATE or RUN position and record the volume of titrant used when the END light comes on or a message appears that the titration is complete.

4.   Calculate the weight of water in milligrams per mL of titrant. This is the equivalency factor and will be used later in the calculation of the water content of the sample:

$$F : \frac{A}{B}$$

where:
 F   =   equivalency factor, mg of water per mL of titrant
 A   =   weight of water used, mg (10 or 25)
 B   =   volume of Karl Fischer titrant used, mL

Procedure

Add the sample to the titrator after the standardization has been completed.

1.   Put approximately 4 mL of tall oil into a small sample vial. Do not allow the sample to touch the outside of the vial.
2.   Put a medicine dropper into the vial and weigh the vial, sample and medicine dropper together on an analytical balance to the nearest 0.001 g. Record this weight.
3.   Using the medicine dropper, introduce 0.5 to 1.0 mL of the sample into the titrator.
4.   Put the medicine dropper back into the vial and weigh to the nearest 0.001 g. Record this weight.
5.   Begin the titration and record the end point in mL as before.
6.   Calculate the water content of the sample as shown below.

Calculation

Moisture, %ov $= \dfrac{(V \times F)}{10 \times W}$

where:
V =   volume of Karl Fischer reagent required to titrate the sample, mL
F =   equivalency factor, mg of water per mL of titrant
W=   weight of sample added to the titrator, g

Report to the nearest 0.01%.

Alternate methods

PCTM 4A, PCTM 4B

References

ASTM D890 "Water in Liquid Naval Stores."
ASTM D1364 "Water in Volatile Solvents."

Recovery of tall oil from black liquor soap skimmings

Scope

This method describes a laboratory procedure for conversion of black liquor soap skimmings to crude tall oil.

The procedure utilizes acidulation of the soap using sulfuric acid, to produce the crude tall oil and an aqueous sodium sulfate brine layer. The crude tall oil is washed with water to remove any residual brine or acid.

The resultant product crude tall oil is suitable for characterization by other chemical analyses as desired.

Safety

Procedure steps 4 - 8 should be conducted in an appropriate fume hood, since toxic and noxious hydrogen sulfide maybe released from the acidification of residual sulfide present in black liquor and soap skimmings.

Apparatus

1. Top-loading balance, 0.01 g precision.
2. Hot plate, with suitable magnetic or mechanical stirrer.
3. Large oven maintained at 74-85 °C.

Reagents

1. Sodium sulfate, anhydrous.
2. 79% Sulfuric acid (60° Baumé), commercial grade.
3. Methyl orange indicator, 1 % solution.

Procedure

1. Place 300 mL of hot water into a 4liter beaker.
2. While agitating and heating, add 60 g of Na_2SO_4, (to facilitate the subsequent phase separation).
3. Add 25 mL of H_2SO_4 (60° Baumé) and bring to a boil.
4. Decant any free black liquor present in the soap sample, and add 400 g of soap skimmings, in portions while maintaining agitation.
5. Again bring the solution to a gentle boil and hold for five minutes.
6. Remove the beaker from the heat and allow the brine to separate.
   Draw off a small portion of the brine and check the pH. The desired pH is between 3.0 and 3.5. If the pH is high, add Na_2SO_4 and if the pH is low, add soap skimmings.
8. Once the correct pH range is obtained, allow the solution to gently boil for 30 minutes with agitation.
   Pour the mixture into a 1000 mL separatory funnel, and place in the oven at 74-85°C for approximately one hour to obtain separation of oil, lignin, and brine. Drain and discard the brine and lignin layer.
10. Wash the oil by adding 250 mL of water to the funnel, invert and mix moderately several times. Avoid vigorous mixing that may result in an emulsion. Then return the funnel to the oven to allow the aqueous phase to separate, as in Step 9. Repeat this washing step until the aqueous phase is neutral (pH 5.5 to 7.0) to methyl orange.
11. Remove the funnel from the oven, and discard the aqueous layer.
12. Retain the top layer, which is the crude tall oil.

■

Content of tall oil in tall oil soap

Scope

This test method covers the determination of the quantity of crude tall oil (CTO) which may be obtained from a representative sample of tall oil soap.

This method is useful in predicting the yield of crude tall oil which may be obtained in commercial acidulation of tall oil soap as obtained from storage tanks, tank cars or process equipment.

Care must be taken to be sure that the sample being analyzed is representative of the material in the vessel, tank car or tank truck. Since some black liquor may separate from the soap in the sample container, the material should be homogenized just before removing an aliquot for this analysis.

Safety

Ethyl ether is extremely flammable and must be kept from sources of ignition. Perform all work in a fume hood.

Apparatus

1. Separatory funnels, 1000 mL and 500 mL.
2. Beaker, 250 mL for weighing soap sample.
3. Beaker, 400 mL.
4. Beaker, 600 mL.
5. Forced draft oven, maintained at 110 to 120°C.
6. pH indicator paper.

Reagents

1. Ethyl ether, reagent grade.
2. Sulfuric acid, 30% solution.
3. Sodium sulfate, 10 to 15% solution.

Procedure

1. Transfer approximately 50 g of tall oil soap into a 1000 mL separatory funnel. An efficient transfer can be made using portions of the 10-15% sodium sulfate solution.

2. Add 17 mL of 30% sulfuric acid solution, and shake the contents vigorously for 2-3 minutes, venting pressure at intervals as necessary.

3. Add 100 mL of ethyl ether and shake moderately until all of the soap has been reacted. Some lignin will be present but it will be indistinguishable from the soap. The pH of the aqueous layer should be between 2 and 3.

4. Allow the ether layer to separate, then draw off the aqueous layer into a 600 mL beaker. Leave the ether and lignin layers in the separatory funnel. Pour the ether extract from the top of the separatory funnel into a second 500 mL separatory funnel, taking care to exclude as much lignin as possible.

5. Add the aqueous layer from the 600 mL beaker back into the lignin layer remaining in the first separatory funnel. Extract with 3 more 100 mL portions of ether, adding each ether extract into the second separatory funnel. Wash the combined ether extracts with four (4) 50 mL portions of distilled water. The aqueous layers may be retained to determine the lignin and fiber content.

6. After washing the combined ether extract four times, incrementally add the extract into a tared 400 mL beaker containing a boiling stone, and evaporate to dryness on a steam bath. Rinse the separatory funnel with 30 mL of ether, add the ether rinse to the beaker, and evaporate to dryness.

7.   After evaporating the ether from the combined extracts to dryness, dry the remaining extracted crude tall oil residue in the beaker in a 110 - 120°C oven for one hour, or as required to obtain a constant weight.

Calculation

Calculate the percent crude tall oil as follows:

$$Crude\ Tall\ Oil, \% = \frac{A}{B} \times 100$$

where:

A   =   grams of extracted crude tall oil
B   =   sample weight of soap skimmings, g

Report

Report the crude tall oil content in the tall oil soap to the nearest 1.0%.

Reference

TAPPI Method T 635 om.

■

Method to determine lignin, fiber, and foreign matter in tall oil soap

Scope

This method is used to determine lignin as well as fiber and foreign matter in tall oil soap. The soap sample is acidulated to convert soap to tall oil. The mixture is filtered and the tall oil dissolved in hexane. The undissolved solids which contain lignin, fiber, and foreign matter are washed with methanol to remove lignin. The material remaining on the filter paper is dried and weighed to determine fiber and foreign material. Water is used to precipitate the lignin from the methanol filtrate. The lignin is filtered and weighed.

Apparatus

1. Beaker, 400-mL.
2. Filter paper, No. 40 Whatman, 2 pieces.
3. Buchner funnel with 1-liter side arm flask.
4. Balance sensitive to 0.001 g.
5. Graduated cylinder, 100-m1.

Reagents

1. Hexane, reagent grade.
2. Methanol, absolute.
3. Sulfuric acid, 30% solution.

Procedure

1. Weigh 200 g of a representative soap to the nearest 0.001 g. Record this weight as W.
2. Convert the soap to oil using PCI'M 6.
3. Tare a piece of filter paper (to 0.001 g) and record this weight as D. This value will be used to calculate % fiber and foreign matter.
4. With vacuum, filter the tall oil and brine using the Buchner funnel. Filter the oil first (thinning the oil with hexane will save time) then the brine.

5. Wash the filter paper with hexane to remove residual tall oil. The filter now contains lignin, fiber, and other foreign matter.
6. Discard the filtrate.
7. Wash the filter with methanol until all of the lignin has dissolved and the filtrate is clear. Collect the methanol wash. The methanol must be dry to dissolve the lignin.
8. Dry the filter paper to a constant weight in an oven at 105 °C. Record this weight to the nearest 0.001 g, as C. This value will be used to determine % fiber and foreign matter.
9. To the methanol, add twice as much water as methanol to precipitate the lignin.
10. Tare a second piece of filter paper to the nearest 0.001 g, and record this weight as B. This value will be used to calculate % lignin.
11. Filter the precipitated lignin through the tared filter paper.
12. Dry the filter paper to a constant weight at 105 °C measured to the nearest 0.001 g. Record this weight as A. This value will be used to determine % lignin.

Calculations

$$Lignin, \% = \frac{(A - B)}{W} \ x \ 100$$

Method to estimate crude tall oil in spent acid

Scope

This method describes a procedure for estimating the amount of residual tall oil in tall oil brine (spent acid). Such information is important in order to quantify losses during and after the acidulation process. The method is based on centrifuging the tall oil brine and measuring the tall oil that separates.

Apparatus

1.   Centrifuge.
2.   Centrifuge tubes, calibrated.

Procedure

Centrifuge a 15 mL sample of spent acid for five minutes. Read the volume of oil in milliliters that separates at the top of the tube.

Calculation

$$Tall\ Oil,\% \ = \ \frac{A}{B} \ X\ 100$$

where
A   =   milliliters of separated oil
B   =   milliliters sample of spent acid

Determination of solids content of black liquor soap skimmings

Scope

This method describes a laboratory procedure for determining the solids content of black liquor soap skimmings.

The method is used to determine the amount of total contained solids in a given sample on a dry-weight basis. Solids are assumed to be all species that are not volatile under the specified oven drying conditions.

The water content of a sample is measured by drying a known mass of sample in an oven at 105°C.

Apparatus

1.   Top-loading balance, 0.001 g precision
         Evaporating dish or 50-mL beaker with matching
3.   watch glass cover
         Heat lamp or steam bath
4.   Desiccator
5.   Oven, maintained at 105°C

Procedure

1.   Weigh the clean dry beaker or dish (B), add 1.5 - 2.5 g (to the nearest 0.001 g) of the material to be tested into the beaker or dish, and reweigh (C). Record the weights as B and C.
2.   Place the beaker or dish with watch glass on a steam bath or under a heat lamp and apply heat until dryness is obtained.
3.   Place the container from step 2 into the oven (105° C) for one hour.
4.   Cool the container in a desiccator, and then reweigh (A). Record the weight as A.

Calculation

$$Solids, \% = \frac{A - B}{C - B} \times 100$$

where:

A   =   weight of dish plus residue, grams
B   =   weight of dish, grams
C   =   weight of dish plus sample, grams

Alternate methods

1.   Report the percent solids to the nearest 0.1%. Use a moisture balance (IR - heated balance) according to manufacturer's guidelines to determine the solids content, or measure the moisture content and report the solids as solids = 100 - % moisture. Sample presentation and amount must be considered, since the results may be influenced bee these factors.

2.   Use an azeotropic solvent-reflux technique (as in PCTM 4A) to measure the moisture content of the sample. The solids content can be reported as solids =100 - % moisture.

                                                                        ▪

Method to determine ash content of tall oil soap

Scope

This procedure is used to determine the residue after ignition at red heat.

Apparatus

1. Crucible - porcelain, silica or platinum, 70-mL capacity.
2. Desiccator.
3   Bunsen burner.
4. Muffle furnace.
5. Oven, general purpose, laboratory.

Reagents

Anhydrous ethanol or 3A ethanol (optional).

Procedure

1. Heat a clean crucible at 750° ± 25 °C in a muffle furnace for 20 minutes.

NOTE 1:   A platinum crucible is preferred if the ash is to be analyzed later for metals.

2. Place the crucible in a desiccator and allow to cool to ambient temperature.
3. Weigh the crucible to the nearest 0.001 g. Record the Weight
    4. Place approximately 20 g of the sample in the crucible and weigh to the nearest 0.001 g. Record this weight.
5. Pre-dry the sample overnight at 110°C in a drying oven.

NOTE 2: If a more rapid determination is desired, do not pre-dry. Instead add 1-2 mL of anhydrous ethanol (3A ethanol may also be used). Then using a bunsen burner, gently heat the crucible until the sample is completely dry and carbonized if the sample ignites, allow to bum until the flame goes out.

6. Put the crucible and sample back into the muffle furnace for 30 minutes (at 750°C).
7. Return the crucible to the desiccator and allow to come to ambient temperature. Weigh the crucible and residue to the nearest 0.001 g. Record this weight.

Calculation

$$Ash, \% = \frac{(A - B)}{C - B} \ x \ 100$$

where:

A	=	Weight of crucible plus residue, g
B	=	Weight of crucible, g
C	=	Weight of crucible plus sample, g

Reference

ASTM D803 "Methods for Testing Tall Oil."

Method of determining residual soap in crude tall oil

Scope

This method is used to determine the residual soap content of crude tall oil using either a potentiometric or pH end point.

The test is used to determine the residual soap content of crude tall oil and other related process samples. The potentiometric method yields a more accurate value, with *better* precision, than the pH method. A weighed amount of crude tall oil is dissolved in toluene and isopropyl alcohol, and the residual soap titrated electrometrically with standardized hydrochloric acid.

Reagents

1. Standard hydrochloric acid solution, 0.1 N - Purchase or prepare by filling a 2-L volumetric flask approximately three quarters full with distilled water. Using a 250-mL graduated cylinder, transfer 17 mL of concentrated hydrochloric acid to the volumetric flask and dilute to the line with distilled water. Mix well by inverting the stoppered flask several times. Pipet 25 mL of the HCl solution into a 250-mL beaker containing 50-75 mL of distilled water. Titrate with standardized 0.1 N KOH using the same type of end point detection to be used with the actual analysis. Use pH 7 as the end point when using a pH meter.
2. Isopropanol, reagent grade.
3. Toluene, reagent grade.
4. Buffer, pH 4, commercially available.

Sample Preparation

I. Accurately weigh 25 g of CTO to the nearest 0.001 g into a 250-mL beaker.
2. Add 25 mL of toluene and swirl to' dissolve.
3. Add 75 mL of isopropanol to the beaker and swirl to mix.

Method A- Potentiometric Titration (referee)

Apparatus

1. Automatic potentiometric titrator.
2. Analytical balance, capable of reading ±0.001g.
3. Beaker, 250-mL.
4. Magnetic stirrer with stir bar.

Procedure

1. Add a magnetic stir bar to the beaker if necessary.
2. Set up the autotitrator with the proper operating parameters and hydrochloric acid titrant.
3. Place the sample on the titrator and start the titration.
4. After the titration is complete, record the % soap printed out by the instrument or calculate the soap or soap number as in Calculations.
5. After each titration, rinse the electrode first with alcohol followed by water and store in buffer solution.

Method B- pH Meter

Apparatus

used in the equation to express soap

1.   pH meter with glass electrodes.
2.   Buret, 10-ml, with 0.1 mL divisions.
3.   Analytical balance, capable of reading
4.   Beaker, 250-mL.
5.   Magnetic stirrer with stir bar.

milligrams of KOH.

±0.001g.

Procedure

1.   Standardize the pH meter using pH 4 buffer.
2.   Add a magnetic stir bar to the beaker and place on stirrer.
3.   Insert the buffered electrode into the sample.
4.   Titrate the sample to a pH of 4.0 with 0.1 N HCL and record the amount of titrant used.
5.   After each titration, rinse the electrode first with alcohol followed by water and store in buffer solution.

Calculations

1.   Calculate the percent residual soap content of the CTO to the nearest 0.1 %.

$$Residual\ soap,\ \% = \frac{A \times N \times 32.4}{B}$$

where:

A   =   volume of acid solution required for titration of the specimen, mL
N   =   normality of the acid solution
B   =   sample weight, g
32.4   =   value used to calculate the residual soap as sodium abietate.

2.   Calculate the residual soap number of the CTO to the nearest 0.1 unit.

$$Residual\ soap\ number = \frac{A \times N \times 56.1}{B}$$

where:
56.1   =   the equivalent weight of KOH and is used in the equation to express soap based on an equivalent amount of mg of KOH

Method to determine free water-soluble acid in crude tall oil

Scope

'Ibis method describes a procedure for determining the free water soluble acid in crude tall oil by titration with alkali. A knowledge of the free water soluble acid is important in ensuring correct acidulation of tall oil soap. The presence of excess free acid in tall oil can cause corrosion of distillation equipment.

Apparatus

1. Separatory funnel, 250-mL.
2. Erlenmeyer flask, 250-mL.

Reagents

1. Toluene.
2. Distilled water.
3. Phenolphthalein indicator, I%.
4. Potassium hydroxide, 0.1 N solution, standardized to + or - 0.001.

Procedure

1. Heat the sample at 80^0 to $90°C$ for at least 30 minutes. Stir vigorously to homogenize.
2. Weigh a 10 g sample into a 250-mL separatory funnel and cool to room temperature.
3. Add 50 mL of toluene to the funnel and shake to dissolve. Vent the funnel.
4. Add 20 niL of distilled water and shake vigorously. Vent, allow the layers to separate and draw off the lower, aqueous layer into a 250-ni flask.
5. Repeat the water wash four times.
6. Combine the extracts in the 250-mL flask and add 1-2mL of phenolphthalein indicator solution.
7. Titrate with 0.1 N KOH to the fast faint permanent pink color. Alternately, use an automatic titrator.

Calculation

Water soluble acid as H_2SO_4, % $= \dfrac{A \times N \times 4.9}{W}$

where:

A = KOH, mL
N = normality of KOH solution
W = weight of sample (dry basis), g
4.9 = equivalent weight of sulfuric acid/10
   This is used in the equation to express water soluble acid as sulfuric acid.

Method to determine free acid in tall oil spent acid

Scope

This method describes a titrimetric method for determining the free acid in tall oil brine (spent liquor). This method, like PCTM 14, is important in ensuring correct acidulation of soap as the presence of excess free acid in tall oil can cause corrosion of distillation equipment.

Apparatus

1. Beaker, 600-mL.
2. Magnetic stirrer and stir bar.
3. Buret, 50-mL capacity.

Reagents

1. Potassium hydroxide, 0.25 N solution, standardized to $\pm$ 0.001.
2. Phenolphthalein indicator, 1%.

Procedure

1. Weigh 10 g of the spent acid sample into a 600-mL beaker.
2. Add 200 mL of distilled water and 1 mL of phenolphthalein indicator.
3. Stir using a magnetic stirrer and titrate with standard potassium hydroxide to appearance of the first permanent faint pink color.

where:.

A	=	KOH solution, mL
N	=	normality of KOH solution
W	=	weight of sample, g
56.1	=	equivalent weight of KOH
4.9	=	equivalent weight of sulfuric acid/10 . This is used in the equation to express the water-soluble acid as sulfuric acid.

Calculations

$$Free\ acid,\ mg\ KOH\ per\ g\ of\ sample = \frac{A \times N \times 56.1}{W}$$

$$H_2SO_4,\ \% = \frac{A \times N \times 4.9}{W}$$

Method to determine the saponification value of tall oil

Scope

This method is used to determine the total acid content, both free and combined, of tall oil. (Acid number only measures the free acid). The combined acids are primarily esters formed by reaction with the neutral components present in the original tall oil. The saponification value is therefore a <u>measure</u> of tall oil quality. It is determined by measuring the alkali required to saponify the combined acids and neutralize the free acids.

Apparatus

1. Erlenmeyer flask, 300-mL with S/T 24/40 neck and reflux condenser.
2. Pipet, 25-mL.
3. Automatic titrator (optional).

Reagents

1. Potassium hydroxide, 0.5 N solution in 3A etjyl alcohol, standardized to $\pm$ 0.005
2. Hydrochloric acid, 0.5 N solution, standardized to $\pm$ 0.005.
3. Phenolphthalein indicator, 1% (visual titration only).

Procedure

1. Weigh 2 g of sample, to the nearest 0.01 g, into a 300-niL Erlenmeyer flask.
2. Using a pipet, add 25 n1L of 0.5 N ethanolic potassium hydroxide.
3. Reflux for 60 minutes.
4. Titrate between 60 and 70°C with 0.5 N hydrochloric acid using phenolphthalein indicator or an automatic titrator.
5. Run a blank in the same manner.

Calculation

$$Saponification\ Value = \frac{(A - B) \times N \times 56.1}{W}$$

where:

A =	H_2SO, for blank, mL
B =	H_ZSO, for sample, mL
W =	weight of sample (dry basis), g
N =	normality H_2SO_4 solution
56.1 =	equivalent weight of potassium hydroxide

Precision statement

Based on an ASTM round-robin study, the within laboratory (repeatability) standard deviation for this test is 0.8 and the between laboratory (reproducibility) standard deviation for this test is 1.4.

Reference

ASTM D464 "Saponification Number of Naval Stores Products Including Tall Oil and Other Related Products."

Method to determine rosin acids in tall oil

Scope

This method covers the determination of rosin acids in tall oils containing more than 15% rosin acids.

This method may not be applicable to adducts or derivatives of tall oils, or other naval stores products.

Fatty acids are esterified by methanol in the presence of sulfuric acid catalyst, and rosin acids are determined by titration after neutralization of the sulfuric acid.

Apparatus

1. Beaker, tall-form, 300-mL capacity.
2. Buret, 50-mL capacity with 0.1-mL divisions. Electronic burets are preferable for increased accuracy and precision.
3. Erlenmeyer flask, 250-mL flat-bottom fitted with a condenser.
4. pH meter, capable of reading ± 0.1 pH over a range of pH 1 to pH 13 in alcoholic "solutions.
5. Pipet, 5-mL. Volumetric dispensers are preferred over standard pipets for convenience purposes.
6. Stirrer - A mechanical stirrer is preferred since improper mixing could affect precision.

Reagents

1. Methanol, anhydrous 99.5%.
2. Methanolic potassium hydroxide solution, 0.5 N - Dissolve 33 g of KOH in methanol and dilute to 1 L Standardize to ± 0.001 N with potassium acid phthalate (KHP) in 100 mL of methanol with sufficient water for a clear solution; 2.553 g of KHP will be neutralized by 25.00 mL of 0.5 N KOH. The standardized solution should be protected against evaporation and absorption of CO, from the air, and should be standardized frequently.

3. Methyl sulfuric acid solution, 20% - Caution: Slowly pour 100 g of concentrated sulfuric acid (-96%), while stirring constantly, into 400 g of methanol.
4. Thymol blue indicator - Weigh 0.1 g thymol blue in 100 mL methanol.

Sample Preparation

1. Dissolve 5 ± 0.5 g of sample, weighed to the nearest 0.001 g, into a 250-m1. Erlenmeyer flask.
2. Add 100 mL of methanol and swirl to dissolve.
3. Add 5.0 mL of methyl sulfuric acid solution.
4. Connect the flask to the condenser and reflux for 30 minutes. Allow the flask to cool to approximately room temperature.

Method A - Potentiometric Titration

1. Titrate with the KOH solution to a fixed pH of 4.0, the first end point.
2. Record the reading.
3. Continue the titration to the fixed pH of 10.8, the second end point.
4. Record the amount of KOH required for the titration between the first and second end points.

PCTM 17   *Method to determine rosin acids in tall oil /2*

Method B - Colorimetric Titration
1.   For colorimetric endpoints, add 1 mL of thymol blue indicator solution. Titrate with the methanolic KOH solution.
2.   Record the first endpoint when the color changes from red to yellow.
3.   Record the second endpoint when the color changes from a yellow-green to a greenish blue.
4.   For dark solutions, use a spot plate to determine the end points. This is done by withdrawing a few drops of the solution and placing it on a spot plate and adding a drop of indicator.

Calculation

$$\text{Rosin Acids, \%} = \frac{(V2 - V1) \times N \times 302}{W}$$

where:

$V,1 =$ KOH solution required to first endpoint, mL
$V2 =$ KOH solution required to second endpoint, mL
$N =$ normality of KOH solution
$W =$ weight of sample, g
$30.2 =$ equivalent weight of abietic acid, a typical rosin acid/10

Report the rosin acids to the nearest 0.1 %

Precision statement

Based on an ASTM round-robin study, the within laboratory (repeatability) standard deviation for this test is 0.2% and the between laboratory (reproducibility) standard deviation for this test is 0.5%.

Reference

ASTM D1240 "Rosin Acids Content of Naval Stores, Including Rosin, Tall Oil and Related Products."

Method to determine unsaponifiables in tall oil

Scope

This method is used to determine the amount of <u>unsaponifiable</u> matter in tall oil. It is a gravimetric test for constituents which cannot be saponified by potassium hydroxide.

Apparatus

1. Erlenmeyer flask, 250-mL flat-bottom fitted with a condenser.
2. Erlenmeyer flask, wide-mouth, 300-mL capacity.
3. Separatory funnel, 500-mL capacity with glass stopper.

Reagents

1. Alcoholic potassium hydroxide solution, -2N - Dissolve 132 g of KOH in 150 m, of water and dilute to 1 L with ethanol.
2. Alcoholic potassium hydroxide solution, 0.1N - Dissolve 6.6 g of KOH in ethanol and dilute with ethanol to 1 L. Standardize against a known standard to $\pm$ 0.001N. The solution should be standardized frequently.
3. Ethyl ether - reagent grade.
4. Ethanol, 95%.
5. Isopropanol, reagent grade.
6. Phenolphthalein indicator solution, 1% in ethanol.

Procedure

1. Weigh a 5 g * 0.5 g sample to the nearest 0.001 g into a 300-mLErlenmeyer flask, add 15 mL of the alcoholic potassium hydroxide (2N).
2. Attach condenser and reflux for 90 minutes.
3. Allow the flask to cool to approximately room temperature, and add 50 mL of water.
4. Transfer the solution into a separatory funnel.

Rinse the flask with 40 mL of ether, and add to the funnel.

5. Shake the funnel well, and allow to stand until the ether layer separates.
6. Draw off the aqueous soap solution (lower layer) into a second separatory funnel allowing a few drops of the water to remain above the stopcock to prevent loss of the ether layer by creeping through the ground-glass joint.
7. To the soap solution in the second separatory funnel add 30 n1L of ether and extract as before, drawing off the soap layer into the original Erlenmeyer flask. Add the ether in the second funnel to the ether in the first funnel; extract the soapy water again with 30 mL of the ether.
8. Draw the soap layer off into the Erlenmeyer flask again and add the ether layer to the first separatory funnel as before. At this time draw off all but a few drops of the soap solution which has collected below the combined ether layers in the first funnel and add to the soap solution before the final ether extraction.
9. Extract the combined soap solutions for the fourth time with 30 mL of ether and again add the ether layer to the first separatory funnel. The soap layer may now be discarded.
10. To the first separatory funnel containing the four combined ether extracts, add 2 mL of water after first drawing off any soap solution that may again have collected above the stopcock. Swirl the funnel gently and draw off the water, which may be discarded. Wash the ether layer by shaking with 5 mL of water and then with two 30 mL water washes.
11. Draw off the washed ether extract into a dry, tared wide-mouth Erlenmeyer flask. Rinse the funnel with 15 mL of ether and add to the flask. Evaporate the solvent on a steam bath. If water droplets are observed, add a few milliliters of

12. methanol, and continue to evaporate until a clean, dry residue is obtained.
13. Place the flask in an oven at 100° to 105°C for 10-15 minutes, or longer, if necessary. Cool in a desiccator, and weigh to the nearest 0.001 g.

Calculation

$$\textit{Unsaponiftables, \%} = \frac{A \times 100}{W} - \frac{B \times N \times 30.2}{W}$$

where:

A   =   dried residue, g
B   =   KOH solution used, mL
N   =   normality KOH solution
W   =   sample used, g
30.2   =   equivalent weight of abietic acid, a typical rosin acid/10

Report the unsaponifiable results to nearest 0. 1 %.

References

ASTM D 1065-92 "Unsaponifiable Matter in Naval Stores, Including Rosin, Tall Oil and Related Products."

TAPPI Method T 621 cm-82

■

Method of calculating fatty acid content of tall oil

Scope

This method is used to calculate the fatty acid content of crude tall oil using results from other tests previously performed.

Two procedures are available for calculating the fatty acid content of crude tall oil and other related products. If the fatty acid content is z 5%, the first procedure is used. For products with fatty acid contents < 5% (e.g. rosin), the second procedure is used.

The fatty acid content is calculated by subtracting rosin, unsaponifiables, and water from 100% or using the acid number and rosin acid content in a calculation to obtain the fatty acid content.

Calculations

Procedure 1(FA z 5%):

1. From other PCA o ASTM test procedures, obtain the rosin acid, unsaponifiable, and water content.
2. Calculate the fatty acid content and report the value to the nearest 0.1%.

Fatty acid,% =100 - IRA + UNS + Water)

where:
RA   =   % rosin acids
UNS   =   % unsaponifiable matter

Procedure 2 (FA < 5%):

1. From other PCA or ASTM test procedures, obtain the percent rosin acid and acid number.

2. Calculate the fatty acid as oleic acid and report the value to the nearest 0.1 %.

$$Fatty\ acid,\ \% = \frac{AN - (PA \times 1.855)}{1.986}$$

where:
AN   =   acid number (as oleic acid)
RA   =   rosin acids, %
1.855   =   conversion factor for converting rosin acid percentage to acid number
1.986   =   conversion factor for converting acid number to oleic acid

Precision statement

Based on an ASTM round-robin study, the within laboratory (repeatabiliby) standard deviation for this test is 0.2% and the between laboratory (reproducibility) standard deviation for this test is 0.7%.

References

ASTM D1585 "Fatty Acid Content of Naval Stores, Including Rosin, Tall Oil and Related Products."

ASTM D465 "Acid Number of Naval Stores Products Including Tall Oil and Other Related Products."

ASTM D1065 "Unsaponifiable Matter in Naval Stores, Including Rosin, Tall Oil and Related Products."

ASTM D1240 "Rosin Acids Content of Naval Stores Including Rosin, Tall Oil, and Related Products "

ASTM D803 "Standard Test Methods for Testing Tall Oil:

Method to determine insolubles in crude tall oil

Scope

This method covers the determination of the amount of insoluble matter in crude tall oil (CTO). Crude tall oil is soluble in numerous organic solvents whereas most common contaminants are not.

Apparatus

1. Beaker, 800-mL.
2. Magnetic stirring hot plate with polytetrafluoroethylene-coated stir bar.
3. Filter paper, Whatman No. 40.
4. Two-piece filter apparatus appropriate to hold the filter without leaking.
5. Analytical balance, capable of weighing 0.0001 g.
6. Laboratory tweezers.
7. Forced draft oven, maintained at 105 to 110°C.
8. Desiccator.

Reagents

Toluene, Hexane, Mineral Spirits, or other good solvent for tall oil as defined by the customer and supplier.

Procedure

1. Wash a filter with solvent, dry and store in a desiccator until ready to use.
2. Place a pre-weighed filter in the filter apparatus and secure it to prevent leakage. Record the weight (A), to the nearest 0.0001 g.

NOTE 1: Always use tweezers when handling the filter.

Weigh 100 t 0.1 g of sample into an 800-mL beaker. Record the weight (B). Add 150 mL of solvent. Place a PTFE-coated magnetic stir bar

into the beaker, and place the beaker on a hot plate. Heat and stir the material until it is completely dissolved. Do not boil the solvent.

4. Immediately pour the solution through the filter. Rinse the beaker and filter apparatus three times with additional hot solvent.
5. Disassemble the filter apparatus, remove the filter, and place it, contaminated side up, in a forced draft oven. Dry the filter to constant weight at 105 to 110°C (1 hr. is usually sufficient), cool in a desiccator, and weigh. Record the weight of the dry contaminated filter to the nearest 0.0001 g (C).

Calculation

$$\text{Insolubles, \%} = \frac{C - A}{B} \ X \ 100$$

where:

A = weight of clean, dry filter paper, g
B = weight of sample, g
C = weight of filter paper and insolubles, g

Report

Report the percent insoluble matter to the nearest 0.01%.

References

TAPPI Method T 621 cm
ASTM D269 "Insoluble Matter in Rosin and Rosin Derivatives."

■

Method of estimating total crude tall oil in wood pulp

Scope

This test is used to estimate the total amount of crude tall oil in a given wood pulp sample. Washed pulp will contain (1) tall oil soaps which were not effectively washed from the pulp and (2) unsaponified resin and fatty acids which were not converted to sodium soaps in the digester. In this procedure, the pulp sample is boiled in strong caustic to convert the unsaponified tall oil components to their sodium soaps. The pulp is then washed well and the filtrate recovered from the digesting and washing steps is combined and analyzed to estimate the total crude tall oil in the pulp. If this number exceeds 5 kg CTO/ton of pulp, it can indicate problems with either the digesting or washing operations.

To differentiate between the unsaponified tall oil components and the unwashed soap, a second portion of the pulp sample should be washed well using dilute caustic. Analysis of the washing filtrate (using PCTM 24) will give the unrecovered soap content of the washed pulp. The difference between that number and the total crude tall oil in the pulp is an estimate of the unsaponified tall oil content If this number exceeds 1 kg CTO/ton of pulp, problems with the digester or with calcium soap formation are indicated.

Apparatus

I.   A four liter resin reaction kettle or flask, 2000-mL heating mantle, variable transformer, thermometer, Pyrex stoppers, oil trap and reflux condenser assembled as illustrated in Fig. 1.
2.   Three stainless steel screens - 30, 80 and 200 mesh.
3.   Separatory funnel, 500-mL.
4.   Graduated cylinders, 10-mL, 100-ml, 250-mL, and 1-liter.
5.   Beakers, 400-nilL and 600-mL.
6.   Evaporating dish.
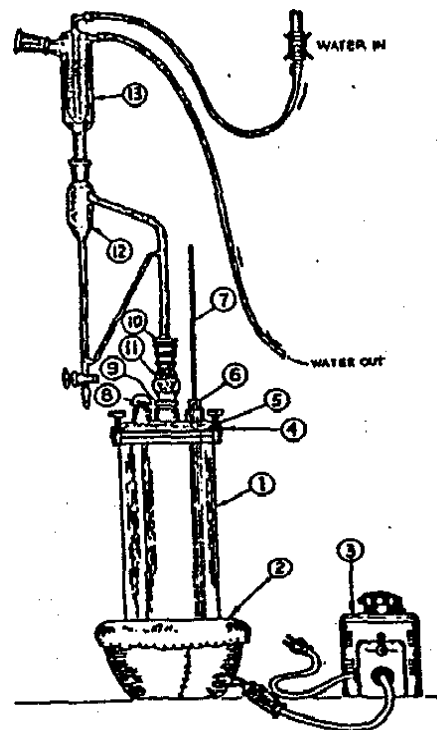7.   Steam bath.
8.   Coarse filter paper.

Fig. 1.   Apparatus for determining turpentine in pulp or wood chips.

1 =   4-liter resin reaction kettle;
2=   2,000-mL electric heating mantle;
3 =   variable transformer,
4=   resin reaction kettle cover;
5=   resin reaction kettle damp;
6 =   thermowell;
7=   centigrade thermometer, 0 to 200°C;
8=   Pyrex glass stoppers, 24/40;
9 =   glass adapter, joints 34/45 to 29/42;
10=   glass adapter, joints 29/42 to 24/40;
11 =   packing retainer and packing, joints 29/42 and 24/40; 12 = modified oil trap, ASTM D889 type, altered to have a 10-ml. graduated section;
13 =   reflux condenser.

Reagents

1. Caustic solution, 0.5N - Mix 20 g of NaOH per liter of water.
2. HCl (1:1) - Dilute conc. HCl with an equal volume of water.

NOTE 1: **For safety, add the acid to the water, not the water to the acid.**

3. Acetone-methanol - Add 1 volume of methanol to 4 volumes of acetone. Mix well.
4. Water-acetone-methanol - Mix 2 volumes of acetone with 1 volume of water and 1 volume of methanol.
5. Petroleum ether, boiling range 40-60°C.
6. Isopropanol, neutralized to a phenolphthalein end point.
7. Standardized alcoholic KOH solution, 0.05 N;

   maybe prepared by 1:10 dilution of standardized 0.5 N alcoholic KOH (see PCTM 1).
8. Phenolphthalein indicator solution, 1% in ethanol.

Procedure

1. Obtain a 100 g representative pulp sample for the tall oil availability determination and a 200 g sample for the TAPPI standard moisture determination. In sampling from a drum washer,

   sample at several locations and include the full pad profile in the composite pulp sample.
2. Add 100 g of pulp (wet' weight) to a four-liter resin reaction kettle along with 2,000 mL of 0.5 N caustic.
3. Set the kettle up for a turpentine determination, as illustrated in Fig. 1.
4. Reflux the turpentine for 5 hours. Control the reflux rate using the variable transformer to prevent foaming problems.
5. After five hours discard the turpentine and separate the pulp from the caustic solution using 30, 80 and 200 mesh screens in series. Save the caustic solution.
6. Transfer the pulp from all three screens back to the kettle and add 2,000 mL of fresh caustic solution. Mix and separate as before. This is a simple washing step - do not recook the sample.
7. Mix the 4000 mL of caustic solution and allow an hour for the solution to become homogeneous. Measure the total solution volume accurately using the graduated cylinders and record the volume as (E).
8. Filter about 1000 mL of the solution through coarse filter paper and discard the remaining solution. Ibis will give enough solution for ten runs.

9. Transfer 100 mL of the solution to a 500 mL separatory funnel.
10. In a fume hood, acidify the solution by adding 15 mL of HCl. Shake and vent continuously for one minute.
11. Add 250 ml, of the acetone-methanol solution, and mix thoroughly for 30 seconds to dissolve any lignin.
12. Add 150 mL of petroleum ether, shaking for about two minutes. Watch gas evolution. Vent frequently, particularly at the start of this step.
13. After shaking, allow about 5 minutes for the phases to separate. Transfer the lower phase to a 600 ml, beaker.
14. Wash the petroleum ether phase in the separatory funnel once with 25 mL of the water-acetone-methanol mixture and add the washings to the aqueous phase in the 600 ml, beaker.
15. Pour, from the top of the separatory funnel, the washed petroleum ether extract into a 400 mL beaker. Start evaporating the petroleum ether by placing the <u>beaker</u> on a steam bath at 80°C.
    Caution - A hot plate should not be used to evaporate petroleum ether as ether vapors are heavier than air and a spark could result in a fire or explosion.
16. Pour the aqueous phase from the 600 mL beaker back into the separatory funnel, making sure all solids in the water phase are transferred into the funnel. Extract with 100 mL of petroleum ether. Wash the ether as described above. Combine this extract with the original petroleum ether extract.
17. Evaporate the petroleum ether extract over a water bath at 80°C just until the off appears on the bottom of the beaker. Then add 25 mL of neutralized isopropanol to redissolve the oil.
18. Filter the dissolved oil through coarse filter paper into a 100 ml, beaker. Wash the 400 mL beaker thoroughly with neutralized isopropanol and pour over the filter paper. Then wash the filter paper with neutralized isopropanol until the final filtrate volume is approximately 50 or 60 mL.
19. Add about one mL of 1% phenolphthalein indicator solution and titrate with standardized alcoholic KOH solution, 0.05 N. For a 100 mL sample from pulp off a third washer or decker, the titration is typically only 1-2 mL.

Calculations

1. Assuming an acid number of 160, calculate the weight of tall oil present.

Weight tall oil, g = AxNx56.1 / 160
where:

A   =   mL KOH used

N   =   normality of KOH solution

2.   Calculate the pounds of available tall oil per
          ton of oven-dried pulp.

Pounds tall oil available/ton OD. pulp =

$$(C \ / \ 100 \ mL \ solution) \ \text{x} \ (E \ / \ 100 \ g \ pulp) \ \text{x} \ 20 \ D \ lbs./ton$$

where:
C   =   weight tall oil, g (from the calculation above)
D   =   pulp consistency, % or g dry pulp/100g pulp mat (measured separately) using Tappi standard method T240 om-93 or T 258 om-94.
E   =   total volume of caustic used for digesting and washing, mL

Method of estimating crude tall oil (CTO) in black liquor

Scope

This is an analytical method for the estimation of tall oil in Kraft black liquor. This method involves the extraction of the oil from an aqueous-alcohol-acetone solution in which the acidified liquor residues are soluble.

Apparatus

1. Buret, 50-mL capacity with 0.1 mL divisions.
2. Pipets, 10-niL and 100-mL.
3. Graduated cylinders, 10-mL, 100-mL and 250-mL.
4. Beakers, 400-mL and 100-mL capacity.
5. Separatory funnels, two 500-mL.
6. Sample container, 1 pint or larger, glass or polypropylene.

Reagents

1. H202 Solution - Mix 3 volumes of commercial 30% H202 with 2 volumes of water.
2. Na2S0, - Dissolve 20 g of anhydrous Na2SO, in 100 nil, of water.
3. HCl (1:1) - Dilute conc. HO with an equal volume of water.

NOTE 1:   For safety, add the acid to the water, not water to the acid.

4. Acetone - methanol - Add 1 volume methanol to 4 volumes acetone. Mix well.
5. Water-acetone-methanol - Mix 2 volumes of acetone, 1 volume of water and 1 volume of methanol.
6. Petroleum ether, boiling range 40-60°C.
7. lsopropanol, neutralized to a phenolphthalein end point.
8. Standardized alcoholic KOH solution, 0.05N - maybe prepared by 1:10 dilution of standardized 0.5 N alcoholic KOH.

9. Phenolphthalein indicator solution in ethanol (1%).

Procedure

Note 2: The sample must be representative of the process for this test to be of any value. Sampling lines (particrdarly those near skimmers) must be cleared of my accumulations of soap or other debris by opening the s°milling line for several seconds before collection. The sample should be collected directly into water to give an approximate solids concentration of 5%.

1. Estimate the solids concentration of the liquor stream to be sampled. Calculate the volume of black liquor required to give an approximate 5% solids concentration in a measured and marked container.
2. Calculate the amount of distilled water required for the 5% solids concentration and fill the container with that amount of distilled water. Mark the container where the total volume will be after the calculated volume of black liquor has been added.
3. Sample the black liquor directly into the water filling it to the mark made in step 2.
4. Determine the total solids content by drying 10 mL of the dilute sample prepared in step #1 in a tared crucible at 105° t 5°C for 24 hours. Alternatively, determine the solids with a moisture balance.

NOTE 3:   If the soap content of the liquor is low, the sample volume may be increased The volumes of the reagents used in steps 5- 7 and the value of D in the calculation should be similarly increased.

5. Pipet 100 mL of the dilute sample into a 500-mL separatoryfunnel. Add 5 mL of HZOZ solution and shake vigorously for 45 seconds, venting the funnel intermittently.

6. Within 1 minute after adding HO, add 5 mL Na_2SO_3 solution. Shake and vent for 1 minute.
7. Acidify by adding 10 mL of the 1:1 HCl. Shake and vent intermittently for 1 minute.
8. Add 250 mL of the acetone-methanol, and mix thoroughly for 30 seconds (to dissolve the lignin). Occasionally a precipitate is found that does not redissolve. Note this, but proceed with the test.
9. Add 150 mL of petroleum ether, then shake and vent for about 2 minutes.
10. After shaking, allow about 5 minutes for the phases to separate. Transfer the lower phase to a second 500-ml, separatory funnel.
11. Wash the petroleum ether phase in the first separatory funnel twice with 25 mL portions of the water-acetone-methanol mixture and add the washings to the aqueous phase in the second separatory funnel.
12. Pour the washed petroleum ether extract into a 400 mL beaker. Start evaporating the petroleum ether by placing the beaker on a steam bath at 80°C.

NOTE 4:   Do not use a hot plate for this evaporation. Petroleum ether vapors could result in a fire.

13. Extract the phase in the second separatory funnel with 100 ml, of petroleum ether. Draw off the lower phase, leaving the petroleum ether in the separatory funnel.
14. Wash the ether twice with 25 mL portions of the water-acetone-methanol. Allow the phases to separate after each wash and discard the water-acetone-methanol phase after each wash. Combine the washed petroleum ether phase with the original petroleum ether extract in the 400 ml, beaker on the steam bath.
15. Evaporate the petroleum ether extract over a waterbath at 80°C until just the oil appears on the bottom portions of isopropyl alcohol and pour them over the filter
    of the beaker. Add 25 mL of neutral isopropyl alcohol to redissolve the oil.
16. Filter the dissolved oil through coarse filter paper or coarse glass frit into a 100 mL beaker. Wash the 400 mL beaker thoroughly with additional paper or frit.

Then wash the filter paper with isopropyl alcohol until the final filtrate volume is approximately 50 mL.
17. Add 1 mL of 1% phenolphthalein indicator solution and titrate with 0.05 N alcoholic KOH solution. The endpoint is taken at the point where the first pink color persists for 30 seconds.

Calculations

1. Assuming an acid number of 160, calculate the weight of tall oil present.

Weight Tall Oil, g= $\dfrac{A \times N \times 56.1}{160}$

where:

A   =   mL KOH used
N   =   normality KOH solution
56.1 =   equivalent weight of potassium hydroxide

NOTE 5:   When the actual acid number for the CFO being produced is known, the actual acid amber should be used in place of the assumed acid number.

2. Calculate percent tall oil on liquor solids basis using weight of tall oil calculated above.

Percent Tall Oil on Liquor Solids Basis = $\dfrac{C \times 10}{D}$

Where:

C   =   weight of tall oil, grams
D   =   solids in 10 L dilute black liquor, grams.

                                        ∎

Method of estimating crude tall oil in wood chips

Scope

This test is used to determine the amount of available tall oil in a given wood supply. A wood chip sample is ground and then digested twice in 0.5 N caustic. During the digestion the tall oil components are saponified to form their soluble sodium soaps. The resulting pulp is washed to recover the sodium soaps. The digesting and washing filtrates are combined and analyzed to estimate the total crude tall oil in the wood chip sample.

Apparatus

1. Waring blender.
2. A four liter resin reaction kettle or flask, 2,000 mL heating mantle, . variable transformer, thermometer, Pyrex stoppers, oil trap and reflux condenser assembled as illustrated in Fig. 1.
3. Three stainless steel mesh screens - 30, 80 and 200 mesh.
4. Separatory funnel, 500-mL.
5. Graduated cylinders, 10-mL, 100-mL, 250-mL, and 1-liter.
6. Beakers, 400-mL and 600-mL.
7. Evaporating dish.
8. Steam bath.
9. Filter paper, coarse

Reagents

1. Caustic solution 0.5 N - Mix 20 g of NaOH per liter of water.
2. HCl (1:1) - Dilute cone. HG with an equal volume of water.

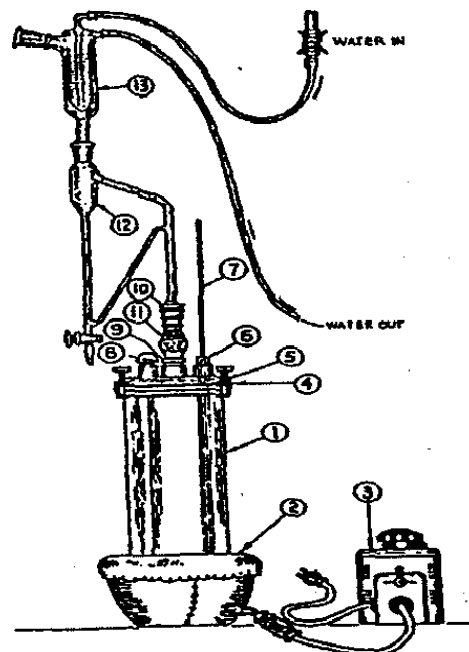NOTE 1: *For* safety, add the acid to the water, not water to the acid.

Fig. 1. Apparatus for determining tall oil and/or turpentine in pulp wood chips.

1 = 4-liter resin reaction kette;
2 = 2,000-mL electric heating mantle;
3 = variable transformer,
4 = resin reaction on kettle cover;
5 = resin reaction kettle clamp;
6 = thermowell;
7 = centigrade thermometer, 0 to 200°C;
8 = Pyrex glass stoppers, 24/40;
9 = glass adapter, joints 34/45 to 29/42;
10 = glass adapter, joints 29/42 to 24/40;
11 = packing retainer and packing, joints 29/42 and 24/40;
12 = modified oil trap, ASTM D889 type, altered to have a 10-mL graduated section;
13 = reflux condenser.

Method of estimating crude tall oil in wood chips

Scope

This test is used to determine the amount of available tall oil in a given wood supply. A wood chip sample is ground and then digested twice in 0.5 N caustic. During the digestion the tall oil components are saponified to form their soluble sodium soaps. The resulting pulp is washed to recover the sodium soaps. The digesting and washing filtrates are combined and analyzed to estimate the total crude tall oil in the wood chip sample.

Apparatus

1. Waring blender.
2. A four-liter resin reaction kettle or flask, 2,000 mL heating mantle, variable transformer, thermometer, Pyrex stoppers, oil trap and reflux condenser assembled as illustrated in Figure 1.
3. Three stainless steel mesh screens- 30, 80 and 200 mesh.
4. Separatory funnel, 500-mL.
5. Graduated cylinders, 10-mL, 100-mL, 250- mL, and 1-liter.
6. Beakers, 400-mL and 600-mL.
7. Evaporating dish.
8. Steam bath.
9. Filter paper, coarse

Reagents

1. Caustic solution 0.5 N – Mix 20 g of NaOH per liter of water.
2. HCl (1:1) - Dilute cone. HG with an equal volume of water.
   a. **NOTE 1:** **For safety, add the acid to the water, not water to the acid.**

3. Acetone-methanol - Add 1 volume of methanol to 4 volumes acetone. Mix well.

4.   Water-acetone-methanol - Mix 2 volumes of acetone with 1 volume of water and 1 volume of methanol.

5.   Petroleum ether,

6.   Isopropanol, neutralized to a phenolphthalein end point.

7.   Standardized alcoholic KOH solution 0.05 N; may be prepared by 1:10 dilution of standardized 0.5 N alcoholic KOH (see PCTM 1)

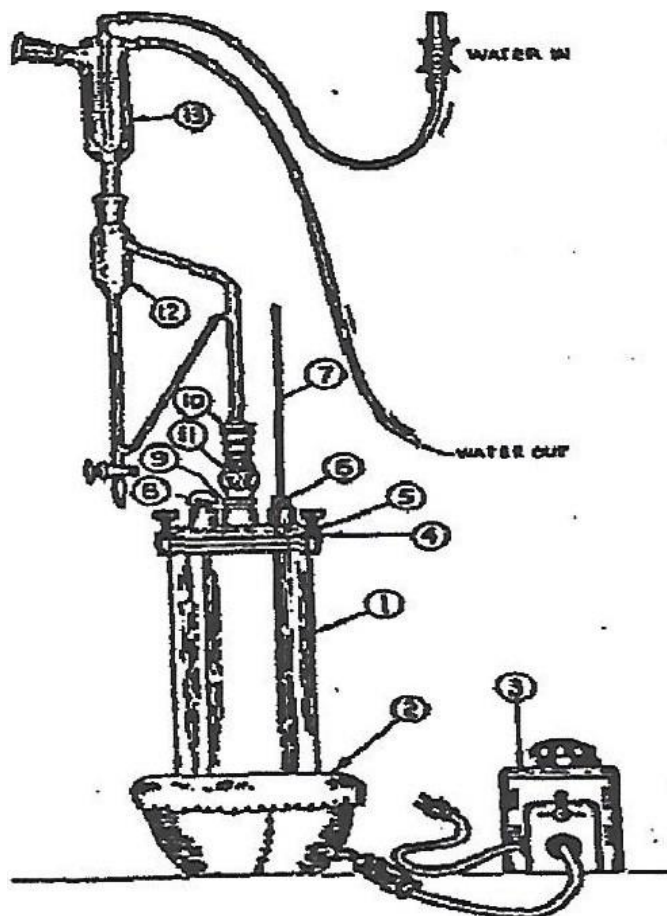8.   Phenolphthalien indicator solution 1% in ethanol.

Fig.1. Apparatus for determining crude tall oil in pulp wood chips.

1. 4-liter rosin reaction kettle;
2. 2,000-mL electric heating mantle;
3. Variable transformer;
4. Rosin reaction kettle cover;
5. Rosin reaction kettle clamp;
6. Thermowell;
7. Non mercury centigrade thermometer, 0° to 200° C   or other temperature measuring device;
8. Pyrex glass stoppers, 24/40;
9. Glass adapter, joints 34/45 to 29/42;
10. Glass adapter, joints 29/42 to 24/40;
11. Packing retainer and packing, joints 29/42 and 24/40;
12. Mmodified oil trap, ASTM D889 type, altered to have a 10-mL graduated section;
13. Reflux condenser.

Procedure

Wood Chip Digestion

1. Use the TAPPI standard for sampling a chip population to get a 100 g sample for tall oil availability and a 200 g sample for the TAPPI standard moisture determination.
2. Reduce the 100 g sample of chips (wet weight) to fines in a laboratory Waring blender. Add a small amount of the 0.5 N caustic to the fines to help the blender.
3. Transfer the fines and caustic to a four-liter resin reaction kettle using caustic solution to wash the blender. Add the wash to the fines and bring the total volume of 0.5 normal caustic to 2000 ml.
4. Set the kettle up as shown in Figure 1.
5. Reflux for five hours. Use the variable transformer to control refluxing. Watch that fines do not plug the necks of the condensers. Use a straightened coat hanger or heavy gauge wire to periodically clean the throat of the condenser if necessary.
6. After five hours, discard the volatile oil and separate the fines from the caustic solution using the 30, 80, and 200 mesh screens in series. Save the caustic solution.
7. After draining, transfer all of the fines to the Waring blender, add a small amount of fresh 0.5 N caustic solution and blend until the fines are reduced to pulp.
8. Transfer the pulp and caustic solution from the blender back to the kettle, once again washing with caustic and bringing the caustic volume to2000 ml.
9. Reflux, as before, for five (5) hours.
10. After five hours, separate the pulp from the caustic solution using the screens. Combine the caustic solution with the caustic solution used in the first digestion.
11. Transfer the pulp back to the kettle and add 2000 ml of fresh caustic solution. Mix and separate as before. Repeat with 2000 ml of fresh caustic solution and separate again. These are simple washing steps. Do not reflux.
12. Mix the 8000 mL of caustic solution and allow one hour for the solution to become homogenous. Measure the volume of the combined digestion and washing liquors accurately using the 1-liter graduated cylinder and record this volume as **(E).**
13. Filter about 1000 mL of the solution through coarse filter paper and discard the remaining solution. This will give you enough solution for ten (10) runs.

Tall Oil Extraction

14. Transfer 100 mL of the filtered solution to a 500 mL separatory funnel..
15. In a fume hood, acidify the solution by adding 15 mL of HCl. Shake and vent continuously for one minute.
16. Add 250 ml, of the acetone-methanol solution, and mix thoroughly for 30 seconds to dissolve any lignin.
17. Add 150 mL of petroleum ether, shaking for about two minutes. Watch gas evolution. Vent frequently, particularly at the start of this step.
18. After shaking, allow about 5 minutes for the phases to separate. Transfer the lower phase to a 600 ml, beaker.
19. Wash the petroleum ether phase in the separatory funnel once with 25 mL of the water-acetone-methanol mixture and add the washings to the aqueous phase in the 600 ml, beaker.
20. Pour, from the top of the separatory funnel, the washed petroleum ether extract into a 400 mL beaker. Start evaporating the petroleum ether by placing the beaker on a steam bath at 80°C.

21. Caution - A hot plate should not be used to evaporate petroleum ether as ether vapors are heavier than air and a spark could result in a fire or explosion.
22. Pour the aqueous phase from the 600 mL beaker back into the separatory funnel, making sure all solids in the water phase are transferred into the funnel. Extract with 100 mL of petroleum ether. Wash the ether as described above. Combine this extract with the original petroleum ether extract.
23. Evaporate the petroleum ether extract over a water bath at 80°C just until the off appears on the bottom of the beaker. Then add 25 mL of neutralized isopropanol to redissolve the oil.
24. Filter the dissolved oil through coarse filter paper into a 100 ml, beaker. Wash the 400 mL beaker thoroughly with neutralized isopropanol and pour over the filter paper. Then wash the filter paper with neutralized isopropanol until the final filtrate volume is approximately 50 or 60 mL.
25. Add about one mL of 1% phenolphthalein indicator solution and titrate with standardized alcoholic KOH solution, 0.05 N.

Calculations

1. Assuming an acid number of 160 calculate the weight of tall oil present:

$$\textit{Weight Tall Oil, g} \ = \ \frac{A \ x \ N \ x \ 56.1}{160} \ = C$$

where:

A = mL KOH used
N = normality of KOH solution (about 0.05N)

2. Calculate the pounds of available tall oil per ton of oven- dried wood:

Pounds of tall oil available/ton O.D. Chips =

$$\frac{C}{100 \ ml. \ Solution} \ x \ \frac{E}{100 \ g \ Chips} \ x \ \frac{100 \ g \ chips}{D} \ X \ \frac{2000 \ lb.}{ton}$$

where:

C - Weight tall oil, g

D - Chips solids content, % or g dry wood/100 g of wood chips. measured separately.

E - Total Volume of caustic digestion solution.

Method to determine viscosity of crude tall oil

Scope

This method covers the determination of viscosity of crude tall oil using a Brookfield viscometer. Viscosity values are useful for sizing pumps in commercial tall oil plants.

NOTE 1:   Special adapters for ultra low viscosities or small samples are also available from Brookfield.

Apparatus

1. Brookfield Viscometer - Digital or dial reading models, as listed below, are available from Brookfield Engineering Laboratories, 240 Cushing Street, Stoughton, MA 02072.
2. Beaker, 600-mL.
3. Constant temperature water bath.
4. Thermometer (range as desired).

Reagents

Standard oils, calibrated in absolute viscosity, centipoise - available from Brookfield Engineering Laboratories or Cannon Instrument Company, P. 0. Box 16, State College, PA 16801. The oils have a shelf life of about 1 year.

Procedure

This method assumes the user has the manufacturer's operating instructions and is familiar with the operation of the instrument.

1. Select the proper spindle for the viscosity range expected and attach it to the shaft.
2. Level the viscometer.
3. Fill a 600-mL beaker with the sample to be tested. The sample should be held at the desired temperature in a thermostatted water bath and the viscosity determination should be completed as rapidly as possible if that temperature is above room temperature. Immerse the spindle in the sample to the indentation in the neck of the spindle.
4. Turn on viscometer and select *speed* which will give a reading between 10 and 90.
5. After obtaining three consistent readings about 1 minute apart, take readings and measure the temperature of the material.
6. A viscosity/temperature curve can be made as a hot sample cools. Readings from the viscometer and temperature readings must be recorded at the same time.

Calculation

Viscosity, cP (centipoises) = reading x factor.

NOTE 2:   The factor is supplied with the viscometer and is dependent on the spindle used and its speed (rpm).

Report

Report the viscosity as centipoise to nearest 10 cP and the temperature, for example, 3470 cP at 50°C. Also include the spindle number and speed in the report.

Reference

ASTM D2196'Rheological Properties of non-Newtonian Materials, by Rotational (Brookfield), Viscometer"

Dial Reading Models	LVF	Low Viscosity		Medium Viscosity		High Viscosity	
		LVT	RVF	RVT	HAT	HBT	
Models		LVDV-44	LVDV-I	RVDV-11	RVDV-I HADV-44	HADV-4 HBDV-II	
No. of Speeds		4	8	4	8	8	8
No. of Spindles		4	4	7	7	7	7
Min. Viscosity (centipoise)		15	15	100	100	200	800
Max Viscosity (centpoise)		100M	2MM	2MM	8MM	16MM	64MM

(M=1000; MM=1,000,000)

Method for Characterization of Gum Rosin by Capillary Gas Chromatography

1. Scope

1.1 These test methods cover the determination of the amounts of certain rosin acids in gum rosin using capillary gas chromatographic separation of the volatile methyl esters of these acids.

1.2 Three methods for forming the methyl esters are described. The classic method for the formation of methyl esters is through the use of diazomethane, but diazomethane is a hazardous and toxic material, and so is no longer the preferred reagent. Methyl esters may be formed through the use of tetramethylammonium hydroxide (TMAH), trimethylphenylammonium hydroxide (TMPAH), or N,N-dimethylformamide dimethyl acetal (DMF-DMA).

1.3 This method is primarily for the identification of gum rosins from specific species of pine trees. It is not designed for the quantitative analysis of gum rosin mixtures. If such analyses are required the internal standard technique described in ASTM Method D5974 should be used.

1.4 *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:*
D 509 Test Methods of Sampling and Grading Rosin
D 804 Terminology Relating to Naval Stores, Including Tall Oil and Related Products
D 5974 Fatty and Rosin acids in Tall oil fractionation Products by Capillary Gas Chromatography

3. Significance and Use

3.1 Gum rosins are important commercial materials, primarily composed of rosin acids, but also containing some neutral material. For many applications, it is necessary to know the level of the individual rosin acids present in these products. Gas chromatography has proven to be a useful tool for such determinations (see ASTM Test Methods D 509), and capillary chromatography, described in these test methods, is considered to be the most effective gas chromatographic technique currently available.

3.2 Due to hydrogen bonding, unmodified rosin acids cannot be volatilized at atmospheric pressure without undergoing decomposition. So, it is necessary to convert the free acids to the more volatile and more stable methyl esters, prior to chromatographic separation.

3.3 These test methods describe three ways to prepare methyl esters. The classic method is through the use of diazomethane, but diazomethane is a hazardous and toxic material, and so is no longer the preferred agent.

3.3.1 TMPAH or TMAH are satisfactory methylating agents as both produce results that are very similar to those of diazomethane, but without the hazards that are associated with diazomethane.

3.3.2 DMF-DMA gives results comparable to TMPAH and TMAH and is easy and safe to use. However, the reagent is moisture sensitive, requiring samples to be free of any significant levels of water.

4. Conversion By Means of Tetramethylammonium Hydroxide (TMAH)

4.1 *Apparatus*
4.1.1 *Standard Laboratory Equipment*

.

4.2 *Reagents and Materials*
4.2.1 *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. 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.
4.2.2 *Tetramethylammonium Hydroxide Solution*, 24 % in methanol, CAS No. 75-59-2.
4.2.3 *Tetramethylammonium Hydroxide Solution*, 6 % (v/v) in methanol. Dilute 25 mL of the reagent described in 4.2.2 with 75 mL of methanol.
4.2.4 *Phenolphthalein Solution*, 1 % (w/v) in methanol.
4.2.5 *Diethyl Ether*, anhydrous.
4.2.6 *Methanol*, anhydrous.
4.2.7 *Acetic Acid*, 5 % volume/volume (v/v) in methanol.
4.2.8 *Toluene*, optional.
4.3 *Procedure*:
4.3.1 Dissolve the sample from 9.1 in 0.5 to 3.0 mL of a 50:50 ether/methanol mixture, add 2 to 3 drops of phenolphthalein indicator solution, and titrate to a pH of 7.8 to 8.1 or to the very first permanent pink color, with the 6 % solution of TMAH. If the solution is overtitrated, it can be back titrated with the acetic acid in methanol solution to the end point. When the solution is injected into the heated injection port of the chromatograph, the tetramethylammonium salts are pyrolyzed to methyl esters.

NOTE 1—For solid rosin 2 to 3 drops of toluene may be added to the vial prior to the addition of TMAH, to assist in dissolving the sample.

5. Conversion By Means of Trimethylphenylammonium Hydroxide (TMPAH)

5.1 *Apparatus*:
5.1.1 *Standard Laboratory Equipment*.
5.2 *Reagents and Materials*:
5.2.1 *Purity of Reagents*, see 4.2.1.
5.2.2 *Trimethylphenylammonium Hydroxide Solution*, 0.2 M or 0.1 M in methanol, CAS No. 1899-02-1.
5.2.3 *Diethyl Ether*, anhydrous.
5.2.4 *Methanol*, anhydrous.
5.2.5 *Toluene*, optional
5.3 *Procedure*:
5.3.1 Add 0.5 to 3.0 mL of a 50:50 ether/methanol, to the sample from 9.1. Add 2 to 3 drops of phenolphthalein indicator solution and titrate to the very first permanent pink color with the TMPAH in methanol solution. When the solution is injected into the heated injection port of the chromatograph, the trimethylphenylammonium salts are pyrolyzed to their respective methyl esters.

NOTE 2—For rosins that are difficult to dissolve, 2 to 3 drops of toluene may be added to the vial prior to the addition of TMPAH, to assist in dissolving the sample.

6. Conversion by Means of N,N-Dimethylformamide Dimethyl Acetal (DMF-DMA).

6.1 *Apparatus*:

6.1.1 *Standard Laboratory Equipment .*

6.2 *Reagents and Materials*:

6.2.1 *Purity of Reagents*, see 4.2.1.

6.2.2 *N,N-Dimethylformamide dimethyl acetal (DMF-DMA)*, CAS No. 4637-24-5.

6.2.3 *Methanol*, anhydrous.

6.2.4 *Toluene*.

6.3 *Procedure*:

6.3.1 Place the sample from 9.1 in an appropriate anhydrous vial, and dissolve with approximately 0.5 mL of either methanol or toluene. Add approximately 1 mL of DMF-DMA, mix well, and maintain the sample at 30–40°C for 15 minutes

7. Apparatus

7.1 *Gas Chromatograph*— An instrument equipped with a flame ionization detector (FID) that can be operated at conditions given in 10.1.

7.2 *Column*— The recommended (referee) column is a fused silica BDS column 25 m in length, 0.32 mm internal diameter, with a 0.20 μm film thickness, and provides separations equivalent or better than that displayed in Fig. 1 - 3. Other suitable columns are high resolution columns between 15 and 60 m in length, 0.25 to 0.53 mm internal diameter, with a 0.20-μm film thickness of biscyanopropylsiloxane type liquid phase.

7.3 *Analytical Balance*, accurate to 0.1 mg

8. Reagents and Materials

8.1 *Purity of Reagents*—See 4.2.1

8.2 *Rosin*— Rosin should be sampled following the procedures described in publications such as the Chinese National Standard,GB 8145-87, ASTM Test Method D 509 or the Naval Stores Act of 1923 (42 Stat 1435.7 USC-91-99) as amended in 1951.

NOTE 3—Rosin samples need to be freshly broken from a larger mass to ensure the results are not affected by air oxidation of the rosin.

9. Procedure

9.1 ***Preparation of Test Sample—***Weigh approximately 50 mg of sample into a suitable vial, and convert to methyl esters or substituted ammonium salts as described in Sections 4, 5, or 6.

10. *Set-up of Gas Chromatograph (GC)*

10.1 Set the GC conditions so that they are approximately (see Note 4) as follows:

Column temperature; Isothermal	195°C
Injection port temperature	300°C
Injection port liner	glass split
Detector temperature	280°C
Carrier gas	Hydrogen or Helium
Linear gas velocity	40 cm/s
Split ratio	40 to 1
Detector	FID
Hydrogen	50 kPa
Air	100 kPa

NOTE 4—These are the typical operating conditions for the instrument using the BDS column.. The individual instrument should be adjusted in accordance with manufacturer's instructions to optimize desired performance. Ongoing adjustments in operating temperature and flow rate may be necessary to maintain optimum performance of the column due to aging. If other columns are used (see 7.2) operating conditions should be used to give separations equivalent or better than that displayed in Fig. 1 - 3. In the US suitable BDS columns can be obtained from Restek Corporation (800 356 6801) and in Europe from HNU Nordion (358 9 565 7240).

11. Analysis

11.1 Inject 0.5 to 1.0 μL of the test sample prepared in 9.1.

NOTE 5—Dilution of the sample with additional solvent may be necessary to obtain injections that do not overload the column or detector.

12. Calculation

12.1 Sum all the areas of the individual peaks, exclusive of the solvent peak, to obtain the total peak area.

12.2 Calculate the relative percent of each rosin acid methyl ester present, uncorrected for the amount of polymeric materials present, as follows:

$$\text{Rosin acid \%} = (A \times 100) / TA$$

where:

A	=	peak area for rosin acid methyl ester being determined, and
TA	=	sum of areas of all rosin acid methyl ester peaks.

NOTE 6—See Fig. 1-3 for typical chromatograms of selected gum rosins and Table 1 for their compositions estimated from these chromatograms

13. Report

13.1 Report the area percent of the individual rosin acids to the nearest 0.1 %

13.2 By comparison with the data in Table 1 and Fig.1, 2 and 3, establish the identity of the gum rosin

Table 1   *Typical Composition of Characteristic Resin Acids in Gum Rosins from some Pine Species*

| Resin Acid	Pinus Massoniana	Pinus Merkusii	Pinus Elliottii	Relative Retention
	(%)	*(%)*	*(%)*	
Communic	0	0	5	0.588
Palustric	25	20	19	0.634
Isopimaric	2	15	17	0.664
Abietic	35	35	23	0.967
Dehydroabietic	4	5	5	1.000
Neoabietic	16	5	20	1.092
Mercusic	0	7	0	1.514

NOTE 7—Capillary Gas Liquid Chromatography (GLC). Conversion of Rosin resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2µm. T = 195°C isotherm, column flow = 50 kPa H_2
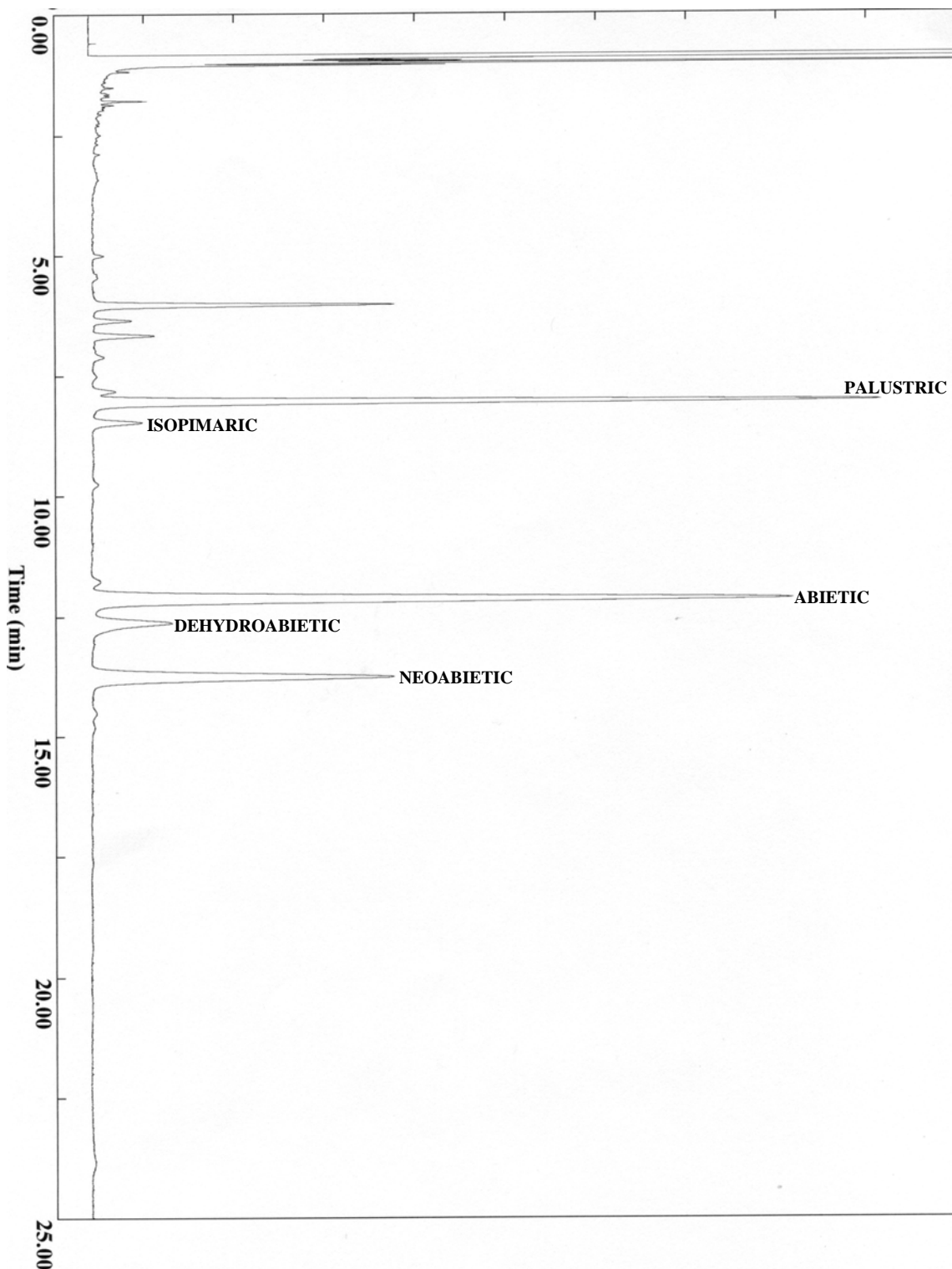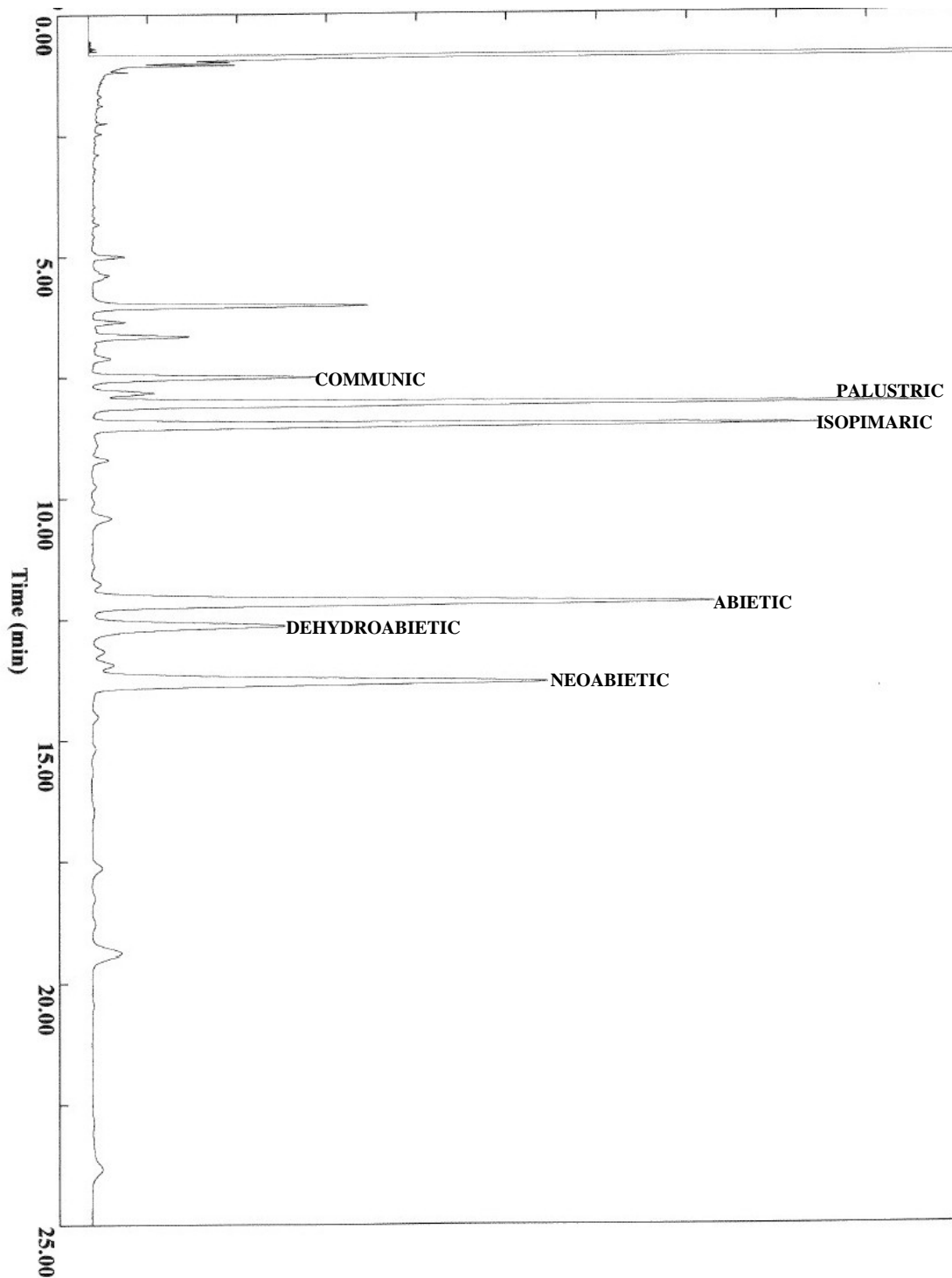
Figure 1   *Chromatogram of Resin Acid Methyl Esters from Pinus Massoniana Rosin*

NOTE 9—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2µm. T = 195°C isotherm, column flow = 50 kPa H_2.
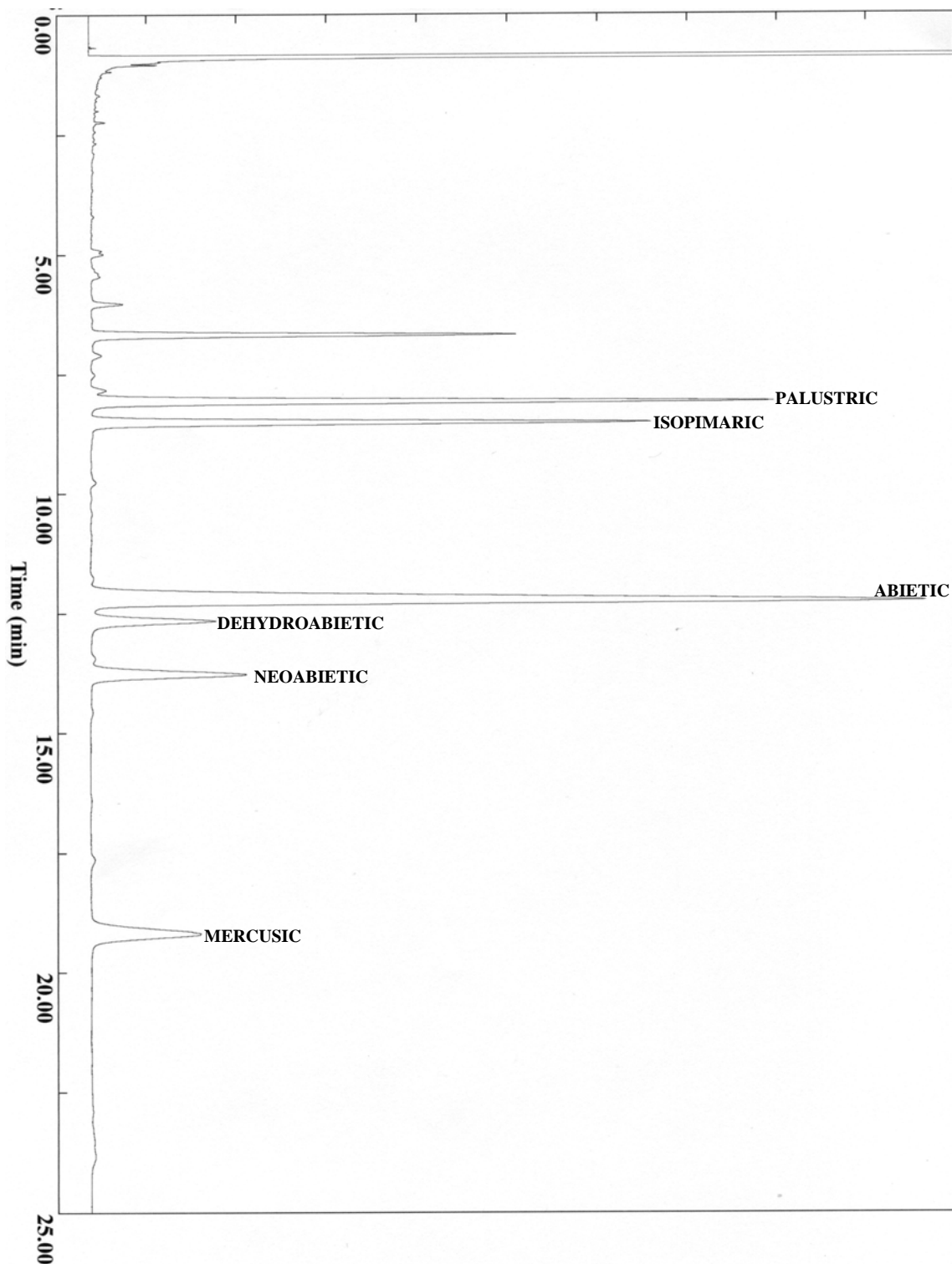
Figure 2   *Chromatogram of Resin Acid Methyl Esters from Pinus Merkusii Rosin*

NOTE 10—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2µm. T = 195°C isotherm, column flow = 50 kPa H_2.

Figure 3   *Chromatogram of Resin Acid Methyl Esters from Pinus Elliottii Rosin*

NOTE 11—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2µm. T = 195°C isotherm, column flow = 50 kPa H_2.

Determination of anthraquinone in crude tall oil by HPLC

1. Scope

1.1   The purpose of this method is to determine the amount of anthraquinone (AQ) in crude tall oil. It has been demonstrated at levels of approximately 100 - 2000 ppm AQ.

2. Applicable Documents

2.1   ASTM Standards
D804 standard definition of terms relating to Naval Stores and Related Products

3. Summary of Methods

3.1   The method is based on external standard calibration of high pressure liquid chromatography, utilizing a UV-VIS detector.

4. Purity of Reagents

4.1   Tetrahydrofuran, HPLC grade
4.2   Anthraquinone (AQ), 99+%
4.3   Water "Baker Analyzed" HPLC grade, filtered before use. Bacterial growth must be avoided.

5. Apparatus

5.1   Liquid chromatograph, Hewlett-Packard 1090 or equivalent, equipped with a gradient pumping system, flow rate controller and a diode array detector.
5.2   Guard column, Zorbax, Rx C-18, 4.0 mm x 12.5 mm - available from Mac Mod Analytical, Inc., 127 Commons Court, Chadds Ford, PA 19317, Part Number 820674-914, or equivalent.
5.3   Column Zorbax Rx C-18, 4.6 mm x 250 mm - Ibid., Part Number 880967-902, data system, or strip chart recorder with integrator suitable for determining peak areas, or equivalent.
5.4   Injection valve, equipped with a 5 μ L loop - Rheodyne Model 7125 or equivalent.
5.5   Volumetric flasks, 10 mL and 100 mL.
5.6   Balance, capable of weighing to 0.0001 gram
5.7   Vortex mixer - available from VWR Scientific, Bridgeport, NJ, Cat. No. 58815-178 or equivalent.
5.8   Filters, Nylon-66,0.2 Fm, disposable - available from Rainin Instruments Co., Woburn, Mack Rd., MA, Cat. No. 38-151.
5.9   Syringe, 3 mL disposable - available from VWR, Cat. No 9585 or equivale
5.10   Autosampler vials, 2 mL.

6. Procedure

Chromatographic Operating Conditions

Pump	Hewlett Packard 1090
Detector	HP 1090 Diode Array, Wavelength Setting, 254, 220, 275, 330 NM, Reference 550, 100, Bandwidth 4.
Injection Volume	5 .µL
Temperature	40°C
Column	Zorbax RX-C-18; 5 .µm particle size, 4.6 mm x 250 mm + 4 mm x 12.5 mm guard column.

Mobile Phase Gradient Composition			
Time (Min.)	%A (Methanol)	%B (Water)	%C (THF)
Initial	2	98	0
1.0	2	98	0
40.0	100	0	0
40.1	0	0	100
60.0	0	0	100

20 minute post run equilibration time

A. Preparation of Standard
6.1 Weigh , to the nearest 0.0001 g, 0.05 g of anthraquinone into a tared 100 mL volumetric flask. Record the weight of anthraquinone.
6.2 Fill to the mark with THF, and shake until dissolved.
6.3 Pipet 10 mL of the solution into a 100 mL volumetric flask, and fill to the mark with THF. Shake to mix.
6.4 Filter the solution through a 0.2 .µm -filter, known to be resistant to THF, into an autosampling vial.
6.5 With the chromatograph equilibrated at the operating conditions, inject 5 µ L of the filtered anthraquinone standard solution and obtain the chromatogram. Obtain the area of the anthraquinone peak.

B. Preparation of Sample
6.6 Weigh, to the nearest 0.0001 g, 0.5 to 0.6 g of sample into a 10 mL volumetric flask.
6.7 Fill to the mark with tetrahydrofuran and shake until dissolved.
6.8 Filter the solution through a 0.2 µm filter known to be resistant to THF, into an autosampler vial.
6.9 With the chromatograph equilibrated at the operating conditions, inject 5 µL of the filtered sample

solution and obtain the chromatogram. Obtain the area of the anthraquinone peak. A typical chromatogram of a CTO sample is shown in Figure 2.

> NOTE: There are two ways to confirm the identity of the anthraquinone peak:
> (1) Compare the spectrum of the anthraquinone standard to the spectrum for the peak eluting in the time frame for anthraquinone. A significant signal (minimum of 20 mAU) is needed to generate a UV spectrum. The spectrum for the standard should match that of the peak in the sample.
> (2) If the signal for the peak of interest is not high enough in the method above to obtain spectral information, then a wavelength ratio technique can be used. Select several wavelengths that represent peaks and valleys for the anthraquinone. The highest signal is 254 nm, the second highest is 275 nm and the third is 330 nm. This relationship (ratio) should be the same for the sample and the anthraquinone standard. If the ratio is different, then it indicates either that the peak is not due to anthraquinone or that an interfering peak is present. In these cases, the peak can be used to calculate the anthraquinone content, but it should be stated that this represents a maximum value.

6.10   Calculate the anthraquinone content (ppm) in the sample using Equation 1.

Calculation

$$\frac{As \times Cstd \times P \times 1{,}000{,}000}{Astd \times Cs} = \text{anthraquinone (ppm)} \qquad \text{Eq (1)}$$

Where:

    As = area of the anthraquinone peak in the sample
    Cstd = concentration of the AQ standard, mg/mL
    P = Purity of AQ standard , expressed as a fraction (i.e.if the AQ purity is 97%, then the P = 0.97)
    Astd = area of the AQ peak in the standard
    Cs = sample concentration, mg/mL

7. Report

7.1   Report the anthraquinone as parts per million (ppm) of the CTO sample.

8. Precision and Bias

8.1   The standard deviation of the method was found to be 0.89 ppm with 10 degrees of freedom at the 91 ppm level in a single laboratory. Duplicate determination from one laboratory should agree within 2.5 ppm (95% confidence). Such values are suitable for averaging. There is only limited data available from interlaboratory studies.

Determination of Anthraquinone in Crude Tall Oil by Gas Chromatography

1. Scope

1.1   The purpose of this method is to determine the amount of anthraquinone(AQ) in crude tall oil. It has been demonstrated at levels of approximately 100-2000 ppm AQ.

2. Applicable Documents

2.1   ASTM Standards

D804 standard definition of terms relating to naval stores and related products
D5974, Gas chromatography of fatty and rosin acids

3. Summary of Methods

3.1 The gas chromatographic method is based on internal standard quantitation utilizing a flame ionization detector and capillary column. Eicosane(C20) is used as the internal standard, with 9-anthracenecarboxylic acid as an alternate.

4. Purity of Reagents

4.1   Chloroform or tetrahydrofurane   ACS grades
4.2   Tetramethylammonium hydroxide, or diazomethane reagents (See D5974-96)
4.3   Eicosane (C20), 99+% or 9-anthracenecarboxylic acid (internal standard) 4.4 Anthraquinone (AQ), 99+%

5. Apparatus

5.1   Suitable GC equipped with an FID split or splitless flow injector and integration capabilities
5.2   Column: 30 meter Restek 2330, 0.25 mm I.D., 0.2 µ film, or functional equivalent
5.3   Analytical balance capable of measuring to ± 0.0001 g.
5.4   Derivatization equipment for GC analysis of fatty and rosin acids (D5974-96)
5.5   20 mL scintillation vial or equivalent
5.6   Syringe compatible with injector and capable of accurately delivering I µl.
5.7   100 mL volumetric flasks
5.8   Pipette capable of accurately delivering 1 mL.

6.   Chromatographic Conditions

6.1   He carrier gas, 10 psi head pressure
6.2   Split flow 25 mL/min.
6.3   Injector and Detector Temp. 275°C
6.4   Initial Column Temp. 150°C (5 min hold)
6.5   Rate 15°C/min
6.6   Final Column Temp. 250°C (30 min hold)

Procedure

I.   Preparation of Calibration Standards and Determination of Response Factor

6.7   Accurately weigh out approximately equal amounts of internal standard and anthraquinone (typically between 35 and 50mg each) into a 20 mL scintillation vial and record the weight of each to the nearest 0.0001 g.

6.8   Dissolve the mixture in approximately 10 mL of chloroform (mild heat may be used if necessary)

6.9   Determine the % of eicosane (C20) and anthraquinone (AQ) using equations 1 and 2 respectively.

6.10   Inject 1.0 μl of this solution into the GC using the conditions described above and determine the retention time of AQ and C20. Repeat as needed.

6.11   Determine the response factor from equation 3 and enter this value as the RF in the integration data file if needed.

II.   Preparation of Internal Standard Stock and Samples

6.12   Prepare a C20 internal standard stock solution by weighing out approximately 0.1g (record exact weight to the nearest 0.0001g) into a 100 mL volumetric flask and dilute to volume with chloroform. Shake well until complete dissolution is achieved.

6.13   Weigh out approximately 1.0g of CTO (record exact weight to the nearest 0.0001 g) into a 20mL scintillation vial. Accurately pipette 1.0 mL of the C20 internal stock solution into the vial. Determine the amount of C20 internal standard using equation 4.

6.14   Derivatize the sample using one of the techniques for conversion to methyl esters, as in D5974.

6.15   Dilute the sample to approximately 10mL with chloroform and mix well until the entire sample is dissolved. Mild heat (i.e. steam bath) may be used if necessary to completely dissolve the sample.

6.16   Inject 1 μl of the sample and determine the amount of AQ by internal standard quantitation using equation 5. This calculation (Eq 5) may be performed manually, or in the integration software.

Calculations

Equation 1: % C20 in Standard

$$\% \, C20 = \frac{(Wt.C20) \times 100}{(Wt.C20 + Wt.Aq)}$$

Equation 2: **%AQ in Standard**

$$\% AQ = 100\% - \% C20$$

Equation 3: Response factor for AQ

$$Rf\ (AQ) = \frac{\%\,AQ\ \text{weighed in (eq. 2)}}{\%\,AQ(GC)}$$

$$\text{where } \%\,AQ(GC) = \frac{(\text{area AQ}) * 100}{(\text{area AQ} + \text{area C20})}$$

Equation 4: Determination of IS amount in sample

(This calculation is based on adding exactly 1.0 mL of the C20 Internal Standard Stock Solution to the sample)

$$\mu g\ C20/\ g\ CTO = \frac{Wt.C20is \times 10{,}000}{Wt.CTO}$$

Equation 5: Concentration of AQ in CTO Samples

$$\mu\ g\ AQ/g\ CTO = \frac{(\mu g\ C20\,/\,g\ CTO) \times (\text{Area Count AQ}) \times Rf\ (AQ)}{\text{Area count C20}}$$

7. Report

7.1   Report the anthraquinone content as µg AQ/g CTO (parts per million, ppm) for each sample.

8. Precision and Bias

8.1   During a preliminary interlaboratory study a single sample of CTO was analyzed 5 times with an average of 755.8 ppm AQ and a standard deviation of 18.5 ppm. The same sample was spiked with 300 ppm of AQ and analyzed 5 times with an average value of 1035.8 with a standard deviation of 31.2 ppm.

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