

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 CO₂ 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-mL 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. Record the reading.
2. Continue the titration to the fixed pH of 10.8, the second end point.
3. Record the amount of KOH required for the titration between the first and second end points.

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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

$$\text{Rosin Acids, \%} = \frac{(V2 - V1) \times N \times 30.2}{W}$$

where:

V₁ = 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."