Chromatographic Determination of Neutrals in Tall Oil Fatty Acids, Gum and Wood Rosin

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Abstract

A simple analytical method for the determination of the neutrals (nonacidics) in tall oil fatty acids, gum and wood rosin has been developed. The method is based on the use of chromatographic techniques for the separation of the acidic from the nonacidic fraction by using alumina as the adsorbent and acetone as the solvent. Data are presented which show good agreement between a calculated theoretical nonacidic content and the amount actually found by the chromatographic procedure as well as the standard AOCS procedure for unsaponifiables.

Introduction

With the great interest in tall oil products, gum and wood rosin, it has become necessary to improve their methods of analysis. Tall oil fatty acids, gum and wood rosins are similar in composition to the extent that each contains acidic and nonacidic or neutral components.

Several procedures have been developed for the separation of these neutral and acid fractions. One of the most widely accepted methods involves the conversion of the acidic component to its soluble salts and extracting the neutrals from an aqueous solution with either hydrocarbons (petroleum ether) or diethyl ether (1–4).

Work recently done by Joyce et al. (5,6) isolated the neutral fraction of wood rosin by converting and extracting the rosin acids as cyclohexylamine salts. This procedure involved a series of six washings with approximately 0.1 N HCl, followed by water washings until the water wash was neutral.

This paper presents a rapid, reliable method for separating and quantitatively determining the neutral components in tall oil fatty acids, gum and wood rosin. The method utilizes chromatographic techniques with commercial catalytic grade alumina as the adsorbent and acetone as the solvent. An acetone solution of the sample is added to the alumina column. The alumina retains the acidic constitutents, and the neutrals are eluted with additional acetone. The acetone is evaporated, and the residue that remains is weighed and calculated as percentage neutrals in the original sample.

The method should be applicable to samples of mixed acids of dark oils where a theoretical acid number cannot be obtained.

Experimental Procedures

Apparatus

1. Chromatographic column, size III, 38 × 230 mm—Scientific Glass Company, Bloomfield, N. J., Cat. No. J-1661.
2. Round wooden rod, ½ in. (a suitable length of wooden dowel may be used).
3. Fisher Filtrator—Fisher Scientific Company, Cat. No. 9–788.

Materials and Reagents

1. Acetone—ACS reagent grade.
2. Alumina, Matheson—Coleman and Bell alumina, activated chromatographic Grade A × 612, 80–200 Mesh.
3. Alcoholic KOH—approximately 0.1N prepared in methanol and accurately standardized.

Procedure

Assemble the chromatographic column on the Fisher Filtrator and insert a small plug of cotton in the bottom of the column. With suction off, add a sufficient amount of the alumina to the column to give a packed height of about 5 cm. Turn on suction and settle adsorbent by lightly tapping the side of the column with the wooden rod. Then insert the wooden rod and lightly tamp the adsorbent column, finally level the top of the surface by a circular motion of the rod.

Weigh 0.75 to 1.0 g of rosin or fatty acids into a small beaker, and dissolve in 20 ml of acetone. Place a tared 100-ml beaker in the Fisher Filtrator under the chromatographic column. With suction off, add the acetone solution to the top of the column. After the acetone solution has penetrated into the column packing, rinse the beaker with 10 ml of acetone, add the acetone wash to the top of the column, and allow it to penetrate into the packing. Finally, add 50 ml of acetone to the column; then turn on suction until the column is dry.

Disconnect the suction, remove the beaker with the acetone solution, and evaporate the acetone on a steam bath, directing a gentle stream of clean air into the top of the beaker to speed evaporation. Finally, heat the beaker and contents to a 105–110C oven for 15 min, cool, and weigh. Discard the used column packing after each determination.

Calculations

Percentage neutrals in sample = g of residue × 100/g of original sample. Percentage neutrals in sample (corrected)[2] = percentage neutrals in sample − [ml KOH × N × 56.1 × 186 × 100/wt of sample.] (Substitute 199 for 186 when analyzing tall oil fatty acids.)

Discussion

The published methods for the determination of unsaponifiables in an acid mixture are long and laborious; errors in the results can be caused by incomplete saponification, emulsions, and loss of sample during extractions.

It is advantageous for an analytical method to be reliable and relatively simple, and to require a

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[2] To correct for any acidity in the sample that might have been eluted from the column, dissolve the residue in 50 ml of neutral 2:1 benzene-methyl alcohol and titrate to a thymol blue end-point with approximately 0.1 normal alcoholic KOH. This value is usually zero unless the column is overloaded.

TABLE I

Chromatographic Determination of Neutrals in Tall Oil Fatty Acids, Gum and Wood Rosin

Sample	Theoretical neutrals (%)	Neutral by chromatography (%)
B118–6–1[a]	7.7	7.6
		7.7
		7.8
B131–6–1	8.6	8.6
		8.6
		8.5
B173–6–1	7.2	7.3
		7.3
		7.1
U582–6–1	11.0	10.4
		11.0
		10.4
H2–80	5.5	5.5
		5.1
		5.4
65–3682[b]	7.5	6.9
		7.2
		6.9
Acintol DyLR[c]	3.7	3.2
		3.6
		3.6
Pamak-I	3.5	3.1
		3.3
		3.2

[a] Gum rosin.
[b] Wood rosin.
[c] Tall oil fatty acids.

minimum amount of time. Such a method has been developed for the determination of the nonacidic (neutrals) in tall oil fatty acids, gum and wood rosin. The total time required to complete an analysis is about one-third of the time required in the published extraction procedures.

The neutral content of a rosin sample was calculated on an acid number of 186 for abietic acid. The percentage of rosin acids subtracted from 100 gives the "theoretical" percentage neutrals in a sample. The neutral content of the tall oil fatty acid was calculated in the same manner on the basis of 199 for oleic acid. An acid number is a measure of the available acid and is defined as the number of milligrams of potassium hydroxide required to neutralize the acids in one gram of sample (7,8).

An observation of the data presented in Table I show that the percentage of neutrals found by the chromatographic procedure agree well with the "theoretical" neutral content. All of the values are presented in triplicate determinations. The precision was within $\pm 0.1\%$ of the average value.

TABLE II

Determination of Neutrals by Chromatographic Separation and AOCS Method Tk-1z-64T

Sample	Theoretical neutrals (%)	Neutrals by chromatography (%)	Neutrals by AOCS Method Tk-1a-64T (%)
Acintol D6LR[a]	3.7	3.2	3.1
		3.6	3.2
		3.6	
Pamak I	3.5	3.1	3.5
		3.3	3.7
		3.2	
H2-80[b]	5.5	5.5	5.1
		5.1	5.3
		5.4	
65–3682[c]	7.5	6.9	6.3
		7.2	6.7
		6.9	

[a] Tall oil fatty acids.
[b] Gum rosin.
[c] Wood rosin.

The data presented in Table II show that the values obtained by the chromatographic procedure agree better with the theoretical neutral content than the standard AOCS extraction procedure.

The method presented herein is simple, precise, and short enough to be used in any industrial control analysis laboratory.

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REFERENCES

1. American Oil Chemists' Society Method Tk-1a-64T.
2. Harris, G. C., and T. F. Sanderson, J. Am. Chem. Soc. *70*, 3870–3872 (1956).
3. O'Connor, R. T., private communication, July 24, 1967.
4. Roberts, Edward, and R. V. Lawrence, J. Am. Chem. Soc. *78*, 4087–4089 (1956).
5. Joyce, N. M. Jr., et al., J. Org. Chem. *30*, 429–431 (1965).
6. Roberts, Edward, et al., Paper No. 16, published in the Naval Stores Research Section, Naval Stores Station, Olustee, Fla.
7. Lange, N. A., "Handbook of Chemistry," 7th ed., Handbook Publisher Inc., Sandusky, O., 1949, p. 1683.
8. Link, W. E., JAOCS *36*, 477–483 (1959).

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