Alternate Method for the Determination of Unsaponifiable Matter

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Abstract

A method is described for the determination of unsaponifiable matter in fatty acids and mixtures of fatty and rosin acids by the use of a mixed bed ion-exchange resin.

Introduction

THE DETERMINATION OF UNSAPONIFIABLE matter in fatty oleoresinous materials has always been a tedious and time-consuming procedure. Aside from the necessity of doing a number of consecutive extractions, emulsions are a common problem which add greatly to the time required to complete an analysis.

Recently Linning[1] described a method for determining the lanolin content of soap by removing both anionic and cationic materials with a mixed ion-exchange resin. We have adapted this method in an attempt to develop a speedy and readily reproducible technique for determining unsaponifiable matter in tall oil products. Excellent results have been obtained with fatty acid-rosin acid mixtures containing up to 34% rosin acids. But the method does not appear to be satisfactory for the determination of unsaponifiable matter in rosin.

Experimental Procedures

Saponification of the tall oil products and of the coconut oil was carried out by using ASTM methods D803–61 and D1965–61 respectively. After saponification, 300 ml of mixed solvent (prepared from 70 parts ethanol [95%] and 25 parts toluene) was added, and the solution was passed through a 2.8 × 30.5-cm column, packed with 100 g of Amberlite MB-1 ion-exchange resin (Rohm and Haas Company) at a rate of 12 ml/min. The column was then washed at the same rate with 150 ml of the mixed solvent. The combined effluents were concentrated to about 25 ml, transferred to a tared dish, evaporated to dryness on the steam bath, and then dried 15 min in an oven at 105C. After weighing, the residues were redissolved and titrated for remaining acids, and their weights were corrected according to the ASTM method.

TABLE I

Determination of Unsaponifiable Matter

Method	Unsaponifiable content	
	ASTM	Ion exchange
	%[a]	%[a]
Material		
1 Tall oil fatty acid (4% R.A.)	1.27, 1.14	1.28, 1.24
2 Tall oil fatty acid (5.7% R.A.)	3.4	3.65
3 Tall oil fatty acid (34% R.A.)	1.3	1.2
4 Distilled tall oil (29% R.A.)	1.5, 1.3	1.29, 1.33
5 Tall oil fatty acid (0.3% R.A.)	0.25, 0.26	0.23, 0.23, 0.24[b]
6 Tall oil heads	15.1, 14.9	14.9
7 Tall oil fatty acid (28.5% R.A.)	1.19, 1.24	1.32, 1.28
8 Coconut oil	0.18, 0.21	0.196, 0.194

[a] Titration of residue required 0.1 to 0.3 ml of 0.1N base.

[b] Used 10 g of acid in the saponification and 150 g of ion-exchange resin.

In the case of the coconut oil, the glycerol formed during saponification was removed before the evaporation step by washing the effluent with three 50-ml portions of distilled water. The combined water washes were extracted with three 30-ml portions of petroleum ether, and the combined petroleum ether extracts were added to the washed toluene-ethanol effluent prior to the evaporation step.

The column was prepared in the following manner. Amberlite MB-1 mixed bed ion-exchange resin (100 g) was slurried with 100 ml of 95% ethanol and rapidly poured into the empty column with the stopcock closed, preventing separation of the anion and cation exchange resins. The ethanol was then drained from the column, and the column was washed with 120 ml of mixed solvent.

Discussion

The results obtained are shown in Table I. Comparison with the values obtained by ASTM methods for the same samples, also shown in Table I, shows that this method is useful for fatty materials with rosin contents from 0 to 34%. However, when the ion-exchange method was applied to the determination of unsaponifiable matter in rosin, values higher than the ASTM method were obtained. In the one case in which an oil was used (Example 8), agreement between the methods is excellent.

In Example 5 the amount of acid and base used were double the standard quantities, but only 150 g of ion-exchange resin were used. This indicates that 75 g of resin would be sufficient for the normal determination; however this was not investigated further.

This procedure eliminates the laborious washings which are necessary to obtain complete extractions of the unsaponifiable matter as required in the ASTM method.

REFERENCE

1. Linning, F. J., Soap Chem. Specialties 42 (No. 7), 55 (1966).

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