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QUANTITATIVE DETERMINATION OF THE SUM OF THE ACIDS OF THE ABIETIC TYPE IN ROSIN

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A method has been developed for the quantitative determination of the sum of acids of the abietic type from the intrinsic absorption of abietic acid, which simplifies the performance and decreases the random error.

One of the important directions of the use of rosin is the synthesis from it of rosin-maleic resins. The latter are obtained as the result of the Diels–Alder reaction between maleic anhydride and levopimaric acid. In an acid medium, a dynamic equilibrium arises between the levopimaric, abietic, palustric, and neoabietic acids (acids of the abietic type) [1]. At the same time, the equilibrium mixture contains abietic acid in overwhelming amount. The content of levopimaric acid amounts to a fraction of a percentage part, but this amount is sufficient for the whole of the acids to be converted into the maleic anhydride adduct of levopimaric acid. The quality of the rosin as a starting material before the synthesis of rosin-maleic resins is therefore determined by its content of the sum of the above-mentioned acids [1, 2].

The basic scheme of the simplest method for the quantitative determination of the sum of the acids of the abietic type in rosin includes their isomerization to abietic acid and the quantitative determination of the latter in the equilibrium mixture. A method has been described in the literature [3, 4] which is based on the isomerization of these acids to abietic acid and its quantitative photometric determination with the preliminary performance of a color reaction with diazonium salt of 1-amino-2-naphthol-4-sulfonic acid or with Diazole Rose O.

We have developed a method for the quantitative determination of the sum of the acids of the abietic type from the intrinsic absorption of abietic acid which simplifies the performance of the analysis and decreases the random error of the determination. The method developed is based on the isomerization of the sum of the acids mentioned to abietic acid and the direct photometric determination of it by measuring the optical density of the solution at three wavelengths (the Beins–Ébi method) [5]. The only condition for the applicability of this approach to a particular "substance to be determined–impurity" system is the linear nature of the absorption of the impurity in the wavelength interval used.

The UV spectrum of abietic acid in ethanol has absorption maxima at 234 and 241.5 nm and a shoulder at 249-250 nm. The symmetrical arrangement of a short-wave maximum and the long-wave shoulder relative to the maximum at 241.5 nm is extremely convenient for quantitative measurements at three wavelengths, since it permits the determination of the density of a solution in horizontal sections of the spectrum. To check the applicability of the three-point method to the mixture to be analyzed (i.e., to check the hypothesis of the linearity of the absorption of the impurity in the working section of the spectrum) we studied the absorption of solutions of isomerized rosin at four different concentrations. As the analytical wavelength we selected two sets of three equidistant wavelengths – 234, 241.5, and 249 nm, and 237, 241.5, and 246 nm. The results are summarized in Table 1.

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TABLE 1. Results of an Analysis Confirming the Applicability of the "Beins–Ébi" Method for the Determination of Abietic Acid in Rosin

Line No.	λ, nm	$E^{1\%}_{1\,cm}$ of abietic acid	Optical densities of the solutions analyzed			
				II	III	IV
1	234	656	0,528	0,362	0,259	0,184
2	237	642	0,528	0,360	0,259	0,184
3	241,5(max)	696	0,561	0,390	0,284	0,200
4	246	506	0,416	0,284	0,205	0,145
5	249	453	0,385	0,260	0,188	0,133

TABLE 2. Results of Experiments with Additions of Abietic Acid to a Rosin Solution

Abietic acid, g				Relative error, %
determined in 1 ml of rosin solution	added	total should be	found	
$7,98\cdot10^{-4}$	$4,02\cdot10^{-4}$	$12,00\cdot10^{-4}$	$11,7\cdot10^{-4}$	−2,5
$7,98\cdot10^{-4}$	$8,04\cdot10^{-4}$	$16,02\cdot10^{-4}$	$16,35\cdot10^{-4}$	+1,9
$7,98\cdot10^{-4}$	$12,06\cdot10^{-4}$	$20,04\cdot10^{-4}$	$20,21\cdot10^{-4}$	+0,

A criterion of the applicability of the "Beins–Ébi" method to the substance to be determined–impurity system is the constancy of the ratio R_1/R_2 for the solutions and its equality to the magnitude R_1^{AA}/R_2^{AA}, where $R_1 = 2D^{241.5} - D^{37} - D^{246}$, $R_2 = 2D^{241.5} - D^{234} - D^{249}$ [5]. For abietic acid, $R_1^{AA} = 244$, $R_2^{AA} = 284$, $R_1^{AA}/R_2^{AA} = 0.862$.

The corresponding values of R_1/R_2 for the four rosin solutions analyzed were: I) 0.876; II) 0.861; III) 0.876; IV) 0.855.

The concentrations of abietic acid in the solutions analyzed calculated for the two sets of wavelength as $C_{AA} = R_1/R_1^{AA}$ and $C_{AA} = R_2/R_2^{AA}$, respectively, proved to be $0.750\cdot10^{-3}$ and $0.739\cdot10^{-3}$; $0.557\cdot10^{-3}$ and $0.558\cdot10^{-3}$; $0.434\cdot10^{-3}$ and $0.427\cdot10^{-3}$; $0.291\cdot10^{-3}$ and $0.293\cdot10^{-3}$.

The results obtained permit the use of both sets of wavelengths for the quantitative determination of abietic acid, the ratio R_1/R_2 for the four concentrations being constant and practically equal to the ratio R_1^{AA}/R_2^{AA}, which shows that the absorption of solutions of abietic acid obeys Beer's law and that the assumption of a relatively linear change in the absorption of the impurity with wavelength is valid. (In the recommended procedure, the measurements are performed at 234, 241.5, and 249 nm, since at these wavelengths the change in the optical density with a change in the wavelength is minimal.)

To develop the method we obtained a standard sample of abietic acid, which was characterized by its melting point (168-171°C), by TLC, and by PMR spectroscopy.

The study of the process of isomerizing acids of the abietic type to abietic acid showed that at a concentration of hydrochloric acid of ~1.5% at the boiling point of alcohol isomerization took place practically completely in 10 min.

The solution of isomerized rosin did not change its optical density for at least seven days on storage in the refrigerator.

The metrological characteristics of the method are given below:

f	$\bar{X}$	S	P, %	$t(P,f)$	$\Delta\bar{X}$	E, %	B_3
6	75,8	±1,35	95	2,45	∓3,31	∓4,4	±2,5

It follows from this that the relative error of a single determination with 95% probability does not exceed 4.4%. To demonstrate the absence of a systematic error, we carried out experiments with additives (Table 2). The relative errors of the determination had different signs and fell within the limits of the random error of the method, which shows the absence of a systematic error.

EXPERIMENTAL

About 0.05 g of rosin (accurately weighed) was placed in a 50-ml measuring flask, the rosin was dissolved in approximately 30 ml of alcohol, the volume of the solution was made up to the mark with alcohol, it was carefully mixed (solution I); 0.5 ml of this solution was transferred to a 10- to 25-ml round-bottomed flask, one drop of concentrated hydrochloric acid was added, and the mixture was heated under reflux (an air condenser is possible) in the water bath at 80°C for 10 min.

The resulting solution was transferred quantitatively (the flask being washed with 5-ml portions of alcohol) into a 50-ml measuring flask, and the volume of the solution was made up to the mark with alcohol and it was mixed (solution II).

The optical density of solution (II) was measured on a spectrophotometer at 234, 241.5, and 249 nm against a background of alcohol in the cell with a layer thickness of 1 cm. The percentage content of the sum of the acids of the abietic type in the rosin (X) was calculated from the formula

$$X\% = \frac{V_1 \cdot V_3\,(2D^{241,5} - D^{234} - D^{249})}{V_2 \cdot P\,(2E^{241,5} - E^{234} - E^{249})},$$

where V_1 is the volume of solution (I) (50 ml); V_3 is the volume of solution (II) (50 ml); V_2 is the volume of solution (I) taken for isomerization (0.5 ml); P is the weight of rosin, g; D^{λ} is the optical density of solution II at wavelength λ; and E^{λ} is the specific absorption coefficient of abietic acid at wavelength λ ($E^{241.5} = 696$; $E^{234} = 656$; $E^{249} = 453$).

On inserting the values of the magnitudes determined by the conditions of the experiment, we obtain

$$X\% = \frac{50 \cdot 50 \cdot (2D^{241,5} - D^{234} - D^{249})}{0,5 \cdot P \cdot (2 \cdot 696 - 656 - 453)} = \frac{5000 \cdot (2 \cdot D^{241,5} - D^{234} - D^{249})}{284 \cdot P}.$$

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