Thus, the use of mathematical analysis of the IR spectra in investigating the structure of cotton and wood cellulose allows a whole set of absorption bands to be detected; it may also be established that these types of cellulose are characterized by the same physical structure but differ in the relative content of hydroxyl-group rotamers.

LITERATURE CITED


QUANTITATIVE ANALYSIS OF MULTICOMPONENT SYSTEMS BASED ON THE
MATHEMATICAL ANALYSIS OF VIBRATIONAL SPECTRA

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The possibility of quantitative analysis of multicomponent mixtures based on the calculation of vibrational spectra was confirmed in [1-5]. However, these investigations paid insufficient attention to the errors of such methods and the choice of optimal standard information for specific multicomponent systems. Below, for the sake of simplicity, the mathematical analysis of vibrational spectra by means of a computer will be referred to as the spectral-calculation method.

It was shown in [1, 2] that the error of the method depends on the choice of the absorption region, the degree of overlap of the absorption bands there, the form of the bands, the number of standards, and the corresponding ratio of the components, and that the efficiency of the method increases on using excess information, i.e., when the number of points considered in the spectrum is greater than the number of components k. The present work outlines the results of investigating the influence of excess information on the error of the method in calculating the concentrations of the components from the spectra of artificial mixtures, as well as considering the choice of the schemes of standard artificial mixtures and the development of specific methods of quantitative analysis of commercial objects illustrating the efficiency of the method.

The experiment is undertaken on a UR-20 IR spectrophotometer and a unit for automatic collection and processing of experimental information for input to the computer [6].
TABLE 1. Schemes of Standards for Calculating the Mass Fraction of Three-Component Mixtures

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Fig. 1. Dependence of the arithmetic mean standard deviation $\bar{S}$ on the number $k$ of components in the mixture: $m \gg k$ (1, 2) and $m = k$ (3, 4).

The basis of the given method is that the spectra of the standards are described by functions

$$D_{i\lambda} = f_{i\lambda}(\nu) \quad (j = 1, \ldots, l; i = 1, \ldots, m),$$

where $D_{i\lambda}$ is the optical density of the $i$-th standard at the $\lambda$-th frequency $\nu$, and are introduced in the computer memory in the form of initial data. Values of $b_{ij}$ such that the synthesized $\sum_{i=1}^{m} \sum_{j=1}^{l} b_{ij}D_{ij}$ is practically the same as the spectrum of the given mixture are chosen.

The program used to calculate the concentrations is written for M-6000 and EC-1030 computers. The algorithm of the program is based on finding the vector of unknown coefficients ensuring a minimum of the sum of squares of the deviations of the optical densities of the standards with the given vector. To this end, a version of the gradient method is chosen.

The influence of excess information on the error in analyzing multicomponent mixtures is investigated for two-, three-, four-, and five-component mixtures. The standards are prepared as artificial mixtures containing all the components in the mixture being analyzed, and also from the individual components of the given mixtures.

The arithmetic mean of the standard deviation $\bar{S}$ is shown as a function of the number of mixture components $k$ in Fig. 1. Curves 1-4 depend not only on the number of analytical points but also on how the calculation is performed: from the spectra of individual components (curves 2 and 4) or from the spectra of artificial mixtures (curves 1 and 3). It is evident from Fig. 1 that the error of the analysis for calculation from the spectra of artificial mixtures is 2-4 times lower than for calculation from the spectra of the individual components and 3-9 times lower when excess information is used.

In comparing standards in the form of artificial mixtures, the number of mixtures and the ratio of their components is chosen experimentally on the basis of methods of experiment planning. The criterion for their choice is a minimum of the standard deviation $S$. The ini-