INFLUENCE OF pH ENVIRONMENT ON THE SPECTRAL AND OPTICAL PROPERTIES OF BETALAIN DERIVATIVES

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ABSTRACT
This article is devoted to the study of the influence of intermolecular interaction on the spectral and optical properties of food dyes. These studies make it possible not only to monitor the change in the color of dyes depending on the pH of the environment, temperature and other environmental factors, but also the use of food dyes in various branches of science and technology.

Keywords: Food dyes, spectral and optical properties, betalain, vulgaxanthin, betanin, beetroot dye, absorption maximum, polarization plane, pH environment, optical density.

INTRODUCTION
One of the tasks of the material well-being of the people is the production of nutritious food products that provide rational nutrition for the country's population; it requires a significant increase in the quality of biological values, taste and improvement of its range.

The study of photophysical and photochemical properties of food dyes and intermolecular interactions is one of the current areas of modern molecular spectroscopy. These studies make it possible to study the basic principles of the chemical structure, the nature of substituents and the effect of the solvent on the spectral and optical properties, to develop more effective methods for measuring metrological characteristics, to expand the areas of application of food dyes and vitamins. The study of the resistance of food dyes to heat and light is important when assessing their organoleptic characteristics, determining metrological characteristics, determining conditions of use in the food and pharmaceutical industries, and also has practical importance when conducting scientific research in laboratories of food enterprises.

It has long been known to color, improve or impart a certain appearance and color to food products such as confectionery, soft drinks, ice cream, jams, marshmallows, fruit and berry waters, etc. used natural vegetable dyes.

Betalain derivatives are the coloring pigments of beetroot dye. The optical properties of betalain derivatives are determined by the spectral parameters of betalain and vulgaxanthin. In the absorption and luminescence spectra, beet dye has two maxima λ_{max}^{abs}= 483 nm and 523

nm, as well as λ_{max}^{lum}= 580 nm and 640 nm. In these cases, mirror symmetry of the electronic absorption and emission spectra is observed. The chromatographic separation of the spectra of the beet dye showed that the absorption maximum λ_{max}^{abs}= 483 nm and 580 nm refers to vulgaxanthin, and λ_{max}^{abs}= 523 nm and 640 nm refers to betanin. From the analysis of the structural formulas it follows that betanin has three carboxyl groups, while vulgaxanthin has two carboxyl groups and one carboxylate ion group. Consequently, betanin molecules in relation to vulgaxanthin have more elongated chains of π-electron bonds, which lead to longer wavelength absorption and emissivity in relation to the vulgaxanthin molecule.

Low-temperature studies have shown that the fluorescence quantum yield at liquid nitrogen temperature increases ~180 times relative to the fluorescence yield obtained at room temperature. In these cases, a vibrational structure of the spectrum is observed in the emission and luminescence excitation spectra. Based on these results, a conclusion was made about the nature of the low quantum luminescence of betalain derivatives. It was found that the low fluorescence quantum yield is not due to the rigidity of either betanin or vulgaxanthin. The nuclear magnetic resonance spectrum and optical rotation dispersion of the beetroot dye were also measured. It was established that the appearance of the optical rotation dispersion curve is due to the smooth positive dispersion curve of the optical activity of sugary substances, as well as against the background of its *S*-shaped curve characteristic of a separate electronic transition in an asymmetric molecule. The maximum of the *S*-shaped curve was at wavelengths of 340 and 410 nm, the amplitude of these maxima was φ = 0,08°. To confirm the influence of sugary substances on the electronic spectra of beet dye, an NMR spectrum of deuterated water is given. Observed resonances in the region of 3,4-4,2 ppm. indicates the presence of sugars in dyes. Using the dispersion and optical rotation spectra in the plane of polarization, the concentrations of sugars in the beet dye were determined. It has been established that the concentration of sugars in dyes is more than 10-12%, depending on the physicochemical properties of the raw materials used.

The pH of the medium was studied for the absorption spectra of beet dye. The addition of alkali leads to a decrease in the intensity of the absorption bands both with λ_{max}^{abs}= 523 nm and with λ_{max}^{abs}= 483 nm. In this case, the spectrum broadens on the short-wavelength side. Further addition of alkali and, accordingly, an increase in the pH value of the medium leads to the appearance and strengthening of a new short-wave absorption band with λ_{max}^{abs}= 405 nm with the practical disappearance of the absorption bands of vulgaxanthin and betanin molecules. This leads to discoloration of dyes.

Of particular interest is the study of the dependence of the absorption spectrum of beet dyes on the content of additives of various acids, respectively (on the pH value of the medium). The results of the studies showed that the absorption capacity of an aqueous solution of beet dye decreases slightly as hydrochloric and citric acids are added, while maintaining the shape of the spectra. Increasing the temperature of the aqueous solution of beet dye from 293 to 323 K with further maintenance at 323 K leads to partial changes in the absorption spectra. In this case, the optical density of the acidified beet solution at λ_{max}^{abs}= 483 nm decreases, and at λ_{max}^{abs}= 523 nm it increases. Increasing the exposure time at 323 K leads to the development of this process, the final ratio of optical densities $D_{523}^{abs}/D_{483}^{abs}$ reaches 1,5. The color characteristics of the dye change towards a darker red color, which is what is required for the food industry.

It is important to note that the observed changes in the spectra of acidic solutions of beet dye with temperature influence are irreversible: the spectra are not restored when alkali is added. Heating and holding the solution at 323 K leads to the formation of a chemical bond of a proton with the carboxylate group and the transition of vulgaxanthin molecules to betanins. This assumption is confirmed by the fact that as the temperature exposure time increases, the betanin band increases, and the vulgaxanthin band decreases. The above assumption is confirmed by the IR spectra of beet dyes obtained without acid and stabilized with citric acid. Beetroot dye stabilized with citric acid has a higher intensity of bands in the region of 3650-2500 cm^{-1}, related to carboxyl groups. The change in the absorption spectra of beetroot dye in environments with high pH values OH$^-$ is also explained by the transition of the molecules of betalain derivatives to the base form. Apparently, the addition of alkali to aqueous solutions of beet dye leads to the localization of the OH group of the alkali in the molecules of coloring pigments.

Considering that when alkali is added, a decrease in the absorption capacity of both the $\lambda_{max}^{abs}=$ 523 nm and $\lambda_{max}^{abs}=$ 483 nm bands is observed, we can conclude that the resulting form of the bases betanin and vulgaxanthin has lower values OH$^-$ of the extinction coefficient in relation to their neutral forms , formation of the base shape. Apparently occurs as a result of the localization of the OH group of the alkali, which has a negative charge, near the positive infected nitrogen (N$^+$) of betalain derivatives. In this case, the most probable type of intermolecular interaction is ionic bonding. The absence of a chemical bond during the formation of the base form is indicated by the fact that the addition of an acid to an alkaline solution of beetroot dye leads to a complete restoration of the absorption spectra of neutral forms of betalain derivatives. The formation of binary molecules of the neutral form of the base in solution is also indicated by the appearance of an isosbestic point in the absorption spectra of the compounds under study..

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