Detection of synthetic dyes in red wines

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Abstract. The falsification of drinks, syrups, extracts and concentrates, as a rule, is of a technological nature and is carried out by diluting, as well as completely or partially replacing natural ingredients with essences, sweeteners, colorants and other additives, including synthetic ones. Painted fruits are distinguished by the presence of anthocyanins - compounds that determine their color and have high antioxidant activity. The paper describes developments of libraries of spectra of artificial dyes used as additives in drinks and food products and of spectra of natural juices (containing anthocyanins) in the wavelength range of the visible part of the spectrum from 400 to 760 nm.

Currently, an urgent problem is the identification of falsifications of wine and fruit juices entering the consumer market. Many studies have found that the main source of free radicals and antioxidants in the human body, due to the high content of phenolic compounds, are alcoholic beverages (wines), tea, coffee, juices, vegetables and fruits. The insufficiency of food control methods does not allow for timely detection of deviations from the norm and the detection of counterfeit products. The strategy to improve the quality of food products in the Russian Federation until 2030 and current market trends require the establishment of additional criteria for the quality of products, including their identification features, which should be preceded by serious scientific work. Only after this is it possible to develop measurement methods and techniques with the participation of specialists from different fields [1].

Painted fruits are distinguished by the presence of anthocyanins - compounds that determine their color and have high antioxidant activity.

Anthocyanins are colored plant glycosides containing, as an aglycon, anthocyanides-substituted 2-phenylchromenes related to flavonoids. Anthocyanins have several forms of isomers. An experimental study was conducted at a pH of 3 to 4, which corresponds to the pH of natural red wine [3].

Figure 1. Total structure of Anthocyanidins.
The color of anthocyanins and anthocyanidins is determined by their sensitivity to pH: in an acidic environment (pH < 3), anthocyanins (and anthocyanidins) exist in the form of red pyrilide salts; when the pH is increased to 4-5, the hydroxide ion joins to form a colorless pseudo base; with a further increase in pH to ~ 6-7, water is split off to form a blue quinoid form, which, in turn, splits off a proton at pH ~ 7-8 to form a purple phenolate, and finally, at pH above 8, the quinoid phenolate hydrolyzes with a rupture of the chrome cycle and the formation of the corresponding yellow chalcone.

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Table 1. General structure of anthocyanidins

| Anthocyanin         | R1 | R2 | R3 | R4 | R5 | R6 | R7 |
|---------------------|----|----|----|----|----|----|----|
| Aurantinidin        | -H | -OH| -H | -OH| -OH| -OH|    |
| Cyanidin            | -OH| -OH| -H | -OH| -OH| -H | -OH|
| Dolphinidin         | -OH| -OH| -H | -OH| -OH| -H | -OH|
| Europinidine        | -OCH3 | -OH| -OH| -OH| -OCH3| -H | -OH|
| Luteolinidine       | -OH| -OH| -H | -OH| -H | -OH|    |
| Pelargonidine       | -H | -OH| -H | -OH| -OH| -H | -OH|
| Malvidin            | -OCH3 | -OH| -OCH3| -OH| -OH| -H | -OH|
| Peonidine           | -OCH3 | -OH| -H | -OH| -OH| -H | -OH|
| Petunidine          | -OH| -OH| -OCH3| -OH| -OH| -H | -OH|
| Rosinidine          | -OCH3 | -OH| -H | -OH| -OH| -H | -OCH3|
An analytical result is achieved by spectrophotometry of the test sample and comparative analysis of the characteristic curves obtained during spectrophotometry, a natural sample of cyanidin-3-O-glucoside, as well as a number of synthetic dyes, which increases the accuracy of the analysis taking into account the specific conditions of the test.

A group of specialists of VNIIFTRI conducted a study of changes in the extrema of the optical density of natural wine at pH values from 1 to 10. The resulting wave graphs of the function of the optical density of natural wine samples at various pH values propagating along the Ox axis, plotted at a fixed point in time (t = const) have all types of shift of the absorption band (Figure 1).

Hyperchromic and hypochromic shifts - increase and decrease in intensity, respectively. An increase in band intensity is called the hyperchromic effect, and a decrease is called the hypochromic effect.

With increasing solvent polarity due to an increase in the pH of a natural wine solution, the long-wavelength absorption band undergoes a bathochromic shift. The magnitude of the bathochromic and hypsochromic shift was determined by measuring as the distance between a pair of neighboring maxima \( x \). All data for natural wine are shown in Table 1, for synthetic dyes, all values of the absorption band offsets are shown in Table 2.

### Table 2: Table of Optical density depending on the pH value of the investigated sample of natural wine.

| Sample number | pH | Extremum, nm | Bathochromic shift, nm | Hypsochromic shift, nm | Hyperchromic shift, nm | Hypochromic shift, nm |
|---------------|----|--------------|------------------------|------------------------|------------------------|------------------------|
| 1             | 1  | 410          |                        |                        | 13,0                   |                        |
| 2             | 2  | 414          | -                      | 9,0                    |                        |                       |
| 3             | 3  | 420          | -                      | 3,0                    |                        |                       |
| 4             | 3,5| 423          | -                      | -                      |                        |                       |
| 5             | 4  | 704          | 281,0                  | -                      | Extraction coefficient | investigated wine varies from 45 to 52 |
| 6             | 5  | 785          | 362,0                  | -                      |                        |                       |
| 7             | 6  | 720          | 307,0                  | -                      |                        |                       |

According to normative documents concerning the quality of natural red wines (GOSTs and TU), the value of the hydrogen index of natural wine ranges from 3.0 to 4.0. Graphs of the dependence of
optical density on the wavelength, as well as the magnitude of the shift of the absorption band for all types of shifts are considered as criteria for determining the naturalness of wine.

Table 3. Table of Optical density depending on the pH value of the studied samples of synthetic dyes.

| Sample number | pH | The value of the extremum, nm | Bathochromic shift, nm | Hypsochrome shift, nm | Hyperchromic shift, nm | Hypochromic shift, nm |
|---------------|----|-------------------------------|------------------------|----------------------|-----------------------|----------------------|
| 11            | 3.5| 423                           | -                      | -                    | -                     | -                    |
| 12            | 3.5| 431                           | -                      | 9                    | 12                    | -                    |
| 13            | 3.5| 410                           | 12                     | -                    | -                     | 8                    |
| 14            | 3.5| 380                           | -                      | 43                   | 75                    | -                    |
| 15            | 3.5| 411                           | -                      | 12                   | -                     | 22                   |
| 16            | 3.5| 515                           | 88                     | -                    | -                     | 37                   |
| 17            | 3.5| 413                           | -                      | 11                   | -                     | 25                   |
| 18            | 3.5| 472                           | 49                     | -                    | -                     | 25                   |
| 19            | 3.5| 405                           | 18                     | -                    | -                     | 38                   |

Figure 4. Graphs of the dependence of Optical density on the wavelength of a sample of red wine at various pH values.

On Figure 4 plots of the dependence of optical density on the wavelength of natural wines of Cabernet and Isabella and dyes E 122, E 180 and E 124. Dye plots are outside the specified range.

As show the Figure 5 the spectrogram of the synthetic dye does not change at different pH values.

Red wines from Isabella grapes contain diglucoside malvidol, which causes a hypsochromic shift and the extremum of the optical density is at 411 nm, while the extremum of Cabernet wine is at 423 nm ± 2, that is, it falls into the specified wavelength range. The peculiarity of the chemical composition of wine from Isabella grapes must be known and taken into account when analyzing wine samples for naturalness.

In the course of the work, natural red wine was falsified in the laboratory by adding natural dyes (chokeberry and natural dye E 163, obtained from Isabella grape skins). In the study of falsifications, spectra similar in appearance were obtained, but the extrema are different. Dye E163 does not have an
extremum in the characteristic wavelength region of 410-425 nm, while natural wine has an extremum at 423 nm. (Figure 5).

**Figure 5.** Synthetic dye E122 and natural wine at control pH values.

Extreme graphs of the optical density of red wines with synthetic dyes at pH 3.0; 3.5 and 4.0 are outside the range of 410-425 nm.

**Figure 6.** Natural wine and wine falsifications.
Thus, it has been established that natural red wines, corresponding in terms of quality to the normative documents for wine, and in particular in terms of pH, have characteristic spectra and an extremum in the wavelength range from 410-425 nm. All extremum values of the optical density of the test sample that are not in this wavelength range (for the bathyromic and hypsochrome shifts) show the presence of a synthetic dye in the test wine sample. For pink and white wines, similar studies are being conducted, the results of which will be reported later. The spectrograms for natural juices containing anthocyanins, which provide the juice with a red color and juices containing dyes, were similarly studied. The results are shown in Figure 6. For natural juices, the extremum of the optical density is also in the wavelength range of 410-425 nm.

Conclusions.

- A library of spectra of artificial dyes used as additives in drinks and food products have been created; and a library of spectra of natural juices (containing anthocyanins) in the wavelength range of the visible part of the spectrum from 400 to 760 nm have been created as well
- A fast, low-labor and cost-effective method for assessing the naturalness of drinks based on spectrophotometry in comparison with HPLC, mass spectrometry and other expensive analysis methods has been developed.
- A patent application has been filed.
- A measurement technique (MVI) is being developed

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