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APPLICATION OF SPECTROSCOPY IN THE PROCESS OF OBTAINING DYES FROM ONION PELL

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A dye-receiving technology from waste products in the form of onion peel. Spectroscopic methods defined temperature extraction mode pigments. It is shown that bioflavony and extracts from onion peels tend to form complexes with metal ions. It was found that the reaction of complexation with the metal ion of quercetin are characterized by the formation of connection with metal by electron transfer from the metal d orbitals in the π^ orbital of quercetin. The Study of the natural scales dye staffs pommel and cortex of the plants ruyan applicable in textile industry. The Determination main dyeing pigment of the dye staffs and offers of the methods to stabilizations of the dye staff.*

Keywords: technology, spectroscopy, food coloring, quercetin, rutin, biflavones metal Ionia, electronic orbitals.

Introduction

Natural food colorings (carotenoids, anthocyanins, flavonoids, etc.) are environmentally friendly compounds that do not affect the human body carcinogenically, and are widely used in the food, pharmaceutical and other sectors of the economy [1]. Typically, natural food colors are used in the form of solutions, pastes or powders, where they can be in different molecular forms [1-4]. For effective use of dyes, it is necessary to have information about their spectral-luminescent, optical and other physicochemical characteristics and their changes under the influence of a number of external factors (the nature of the solvent, temperature, concentration, light radiation, etc.) [5,6]. In addition to the use of spectroscopy in the procession, the preparation of natural dyes makes it possible to develop effective methods for obtaining pharmacological preparations and biological active substances [7,8].

1. Objects and technique of research

To the questions of obtaining natural dyes from the onion husks in sufficient quantity there are scientific works. In work [9] the dye from the husk of onions was obtained according to which the plant raw material is extracted, sorbents are sorbed with an inorganic sorbent at a temperature of 70-80°C. Then, desorption is carried out in a continuous stream, an alcoholic solution with citric acid added to it with a mass fraction of 5-10% at a temperature of 80-85° C. In another method for producing a natural dye from an onion husk [10], an aqueous extract of the onion husk is carried out. Before the extraction of the raw material for the preparation of the dye, it is crushed and poured into water in a ratio of 1: 9 or 1:10. Extraction is carried out at 65-90°C and filtration is carried out. After filtration, the extract is evaporated under vacuum at a pressure of 0.3-0.5 MPa or dried to a powdery state. As food acids use citric or acetic acid. In the third, the method for obtaining a natural colorant of the raw material is extracted with water in the presence of a carbonic acid salt, the extraction mixture is heated to 69-79°C and carried out at a pressure of 7.2-10.0 MPa [11].

In the fourth method of obtaining natural dye from the onion husk, the extraction process of the coloring pigments is carried out by extraction, raw materials and before the extraction is added the crushed bark of coniferous trees by a ratio from 3 to 7 to 7 ÷ 3, the mixture is treated with a flow of

carbon dioxide [12]. We used onions for the production of the dye as a raw material. The choice of the object of the study was due to the fact that they contain about 0.4% of the antioxidant in the form of a biflavanoid - quercetin and a rutin with P - vitamin activity. Raw materials are pulverized in a pulverized manner. The resulting semi-finished product was wetted in cold water. Extraction is excreted in the course of ~ 30min. The temperature is 45°C. As an extractant, along with distilled water, ethyl alcohol was used. The chromaticity and concentration of coloring substances was determined by the spectroscopic method. The absorption spectra of the compounds studied were recorded on Specord 50 SA and SF-46 spectrophotometers. To produce them, depending on the concentration of the solution, we used quartz cuvettes with liners, which made it possible to vary the thickness of the measured layer from 0.1 to 50 mm. All measurements were taken at room temperature (297 K). It has been experimentally found that extracts from the onion husks do not have a fluorescent capacity at room temperature.

Therefore, we confined ourselves to considering only the absorption spectra. In order to determine the main coloring pigment of the dye from the onion husks, standard compounds of quercetin and rutin (brands of PTA), often found in the husks of onions, were selected.

2. Results and discussion

Solutions of standard compounds were made in 95% ethyl alcohol with a concentration of 1 mg/ml, which they prepared by accurately attaching the selected flavonoids. In order to select the analytical wavelength of the standard connected, the UV spectrum of the alcoholic solutions of rutin and quercetin and also the extracts of the onion husks were previously obtained. As an example, Figures 1 and 2 show the electronic absorption spectra of the reference extract from the onion husk and quercetin, respectively. The concentration dependence of the absorption spectra of solutions of quercetin, rutin and pigments from onion husks in ethanol in the concentration range 10^{-5} – 10^{-3} M was studied. It was found that the shape of the spectra of the investigated compounds and the intensity of the absorption bands remain practically constant (see Figures 1 and 2 of curve 1-3).

These indicate that the molecules of the derivatives of flavones at given concentration intervals are in monomer states. The absorption spectrum of quercetin in ethanol has three maxima, with $\lambda_{\max} = 258$ nm, $\lambda_{\max} = 301$ nm, $\lambda_{\max} = 377$ nm (Fig. 2).

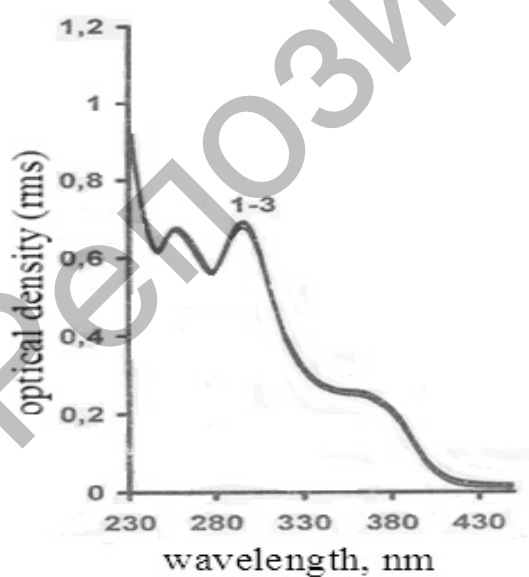


Fig.1. Concentration dependence absorption spectra of the extract from the onion husk:
 $1 \cdot 10^{-5}$, $2 \cdot 10^{-4}$, $3 \cdot 10^{-3}$ M

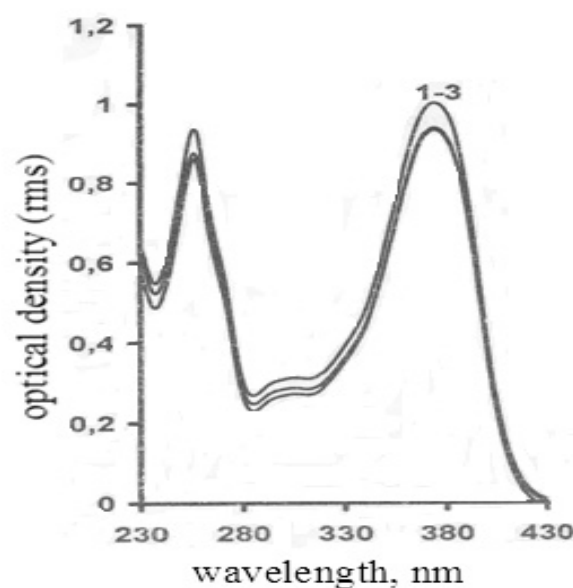


Fig.2. Concentration dependence absorption spectra in ethanol quercetin:
 $1 \cdot 10^{-5}$, $2 \cdot 10^{-4}$, $3 \cdot 10^{-3}$ M

In these cases, the main absorption bands of rutin are with $\lambda_{\max} = 257$ nm, $\lambda_{\max} = 298$ nm and $\lambda_{\max} = 360$ nm. The results of the experiment showed that the optical density of the alcohol extract of the onion husks outweighs the similar value of the results obtained in the aqueous extract. Taking into account the foregoing, for the preparation of coloring pigments.

The carried out researches have shown that in the case of replacing the extract and carrying out this process in ethanol, the optical density of the extract increases ~ 3 times. In this case, the optical density varies from 0.08 to 0.3 units of absorbance. It should be noted that the extraction time and temperature in both extractants remained the same. Further, a study is conducted to obtain an extract of an alcoholic solvent, depending on the temperature and extraction time. It was found that increasing the extraction temperature from 20°C to 48°C results in a significant increase in the optical density, which varied from 0.3 to 0.9 units of optical density, i.e. in these cases, the color of the extract increased ~ 3 -fold. It was found that the extraction is carried out in alcohol at a temperature of 45 - 48°C and in time of about 2 hours.

In order to determine the proportion of quercetin and rutin in the extracts of onion husks, the method of adding aluminum sulphate, which enters the complication reaction with the selected standard compounds, was used. First of all, we extracted the onion husks in water. Then, a spectroscopic study of the aqueous solution of quercetin and rutin with the addition of aluminum sulfate as an example in Fig. 3 shows the absorption spectrum of the aqueous solution of quercetin as aluminum sulfate $\{\text{Al}_2(\text{SO}_4)_3\}$ is added.

It follows from Fig. 3 that addition of aluminum salts to the aqueous solution of quercetin leads to a simultaneous decrease in the intensity of the band with $\lambda_{\max} = 420$ nm. It should be noted that the introduction of $\text{Al}_2(\text{SO}_4)_3$ ions in an amount from $2 \cdot 10^{-5}$ M to $5 \cdot 10^{-5}$ M deformation of the absorption spectra of the aqueous solution of quercetin is accompanied by the appearance of an isobestic point at $\lambda_{\max} = 405$ nm. Further introduction of aluminum ions from $4 \cdot 10^{-4}$ to $6 \cdot 10^{-2}$ M causes the isobestic point in the absorption spectra to disappear (see curve 4-6 of Fig.3). The appearance of an isobestic point in the absorption spectra indicates that at certain concentrations of the addition of metal ions leads to the formation of complexes.

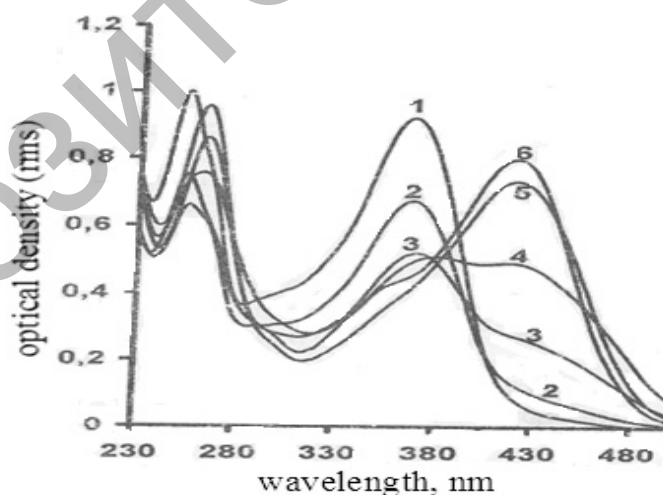


Fig.3. The absorption spectrum of quercetin in water ($c = 10^{-5}$ M) as different amounts of $\text{Al}_2(\text{SO}_4)_3$:
1 – 0; 2 - 10^{-5} ; 3 - $5 \cdot 10^{-5}$; 4 - 10^{-4} ; 5 - $5 \cdot 10^{-4}$; 6 - 10^{-2} M $\text{Al}_2(\text{SO}_4)_3$

In these cases, the solution turns out to be binary molecules of quercetin and complex them with metal ions. The absence of an isobestic point indicates that starting from the added aluminum ions with a concentration of more than $4 \cdot 10^{-4}$ M, complex complexes of biflavone molecules with metal ions are formed in their aqueous solutions. Similar phenomena of spectral changes are observed in the complication of the molecules of rutin with metal ions in aqueous solutions of rutin.

In contrast to quercetin for rutin, a new absorption band is observed and developed at $\lambda_{\max}=427$ nm and the isobestic point occurs at $\lambda_{\max}=410$ nm. Complexation of derivatives of flavonoid with metal ions are discussed in [13].

According to the authors of the complexation of metal ions with derivatives of flavonoids is due to the pronounced electron-donor properties of the latter and their low reduction potential, which for most flavonoids lies in the range of 0.25-0.75. The complication reaction of quercetin with metal ions is characterized by the formation of a ligand-metal bond by transfer of an electron from d-dwelling metal to π^* -orbital quercetin. The structure of the resulting complex compound depends on the nature of the electron density distribution in the ligand. In particular, on the charge on oxygen atoms, where the electron density is maximal. It was found that higher values of the negative charge are located on the oxygen atom of the carbonyl group (-0.312). Charges on other oxygen atoms range from -0.111 to -0.248. Proceeding from the above, it can be assumed that for the quercetin molecule, a complex with metal ions is formed through the oxygen atom of the carbonyl group [13].

On the basis of experimental studies and generalization of the literature data [14], it is established that the derivatives of flavone rutin and quercetin tend to form complexes with metal ions. Based on the results obtained, it is possible to develop spectroscopic techniques for determining the derivatives of flavonoids in aqueous dye extracts from onion husks. For this purpose, the gradient curves for quercetin and rutin were added as aluminum sulfate was added in their aqueous solutions.

In Fig. 4 shows the gradient curve of the aqueous solution of quercetin as the metal ions are added. The obtained dependences of the gradient curve are linear. Using the gradient curve, the proportion of biflavonides in the aqueous extract of the onion husk was determined. Quantitative determination of the content of the sum of flavonoids in onion husks was carried out on the basis of the gradient curves (Fig. 4).

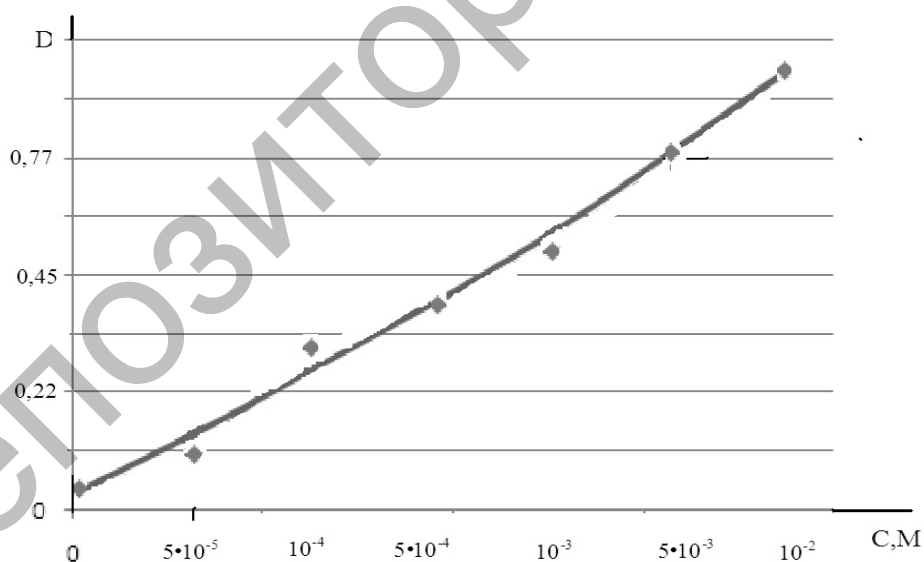


Fig.4. Grading chart for quercetin $\lambda = 440$ nm. Comparative solution: aqueous solution of aluminum sulphate.

Based on the results obtained, a method for the spectrophotometric determination of the total content of flavonoids in terms of their content for rutin or quercetin has been developed. It was found that the content of the sum of flavonoids (in terms of rutin) in the husks of onion -90.3 ± 4.8 $\mu\text{g} / \text{ml}$, (in terms of quartzite) -47.5 ± 2.6 $\mu\text{g}/\text{ml}$.

Conclusion

Thus it is shown that in extracts of onion husks the main coloring pigments are quercetin and rutin. The proportion of biflavonoids is determined in the band of complexes of coloring pigments with metal ions, based on spectroscopic methods of investigation.

Acknowledgment

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