Development of a Method of Luminescent Analysis of Grain Products Grinding Degree

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Abstract. The aim of this work is to develop a luminescent method for assessing the quality of grinding of grain processing products. In the course of the study, we studied luminescent characteristics of peas and lentils, as well as their grinding on a spectrofluorimeter. The spectra were measured by means of a synchronous scanning, then were measured excitation and luminescence spectra, which was followed by calculation of integral parameters, namely the excitation energy and the luminescence flux. The excitation spectra of pea grindings have maximums at wavelengths of 288, 362 and 424 nm, and of lentils grindings reach 288, 424 and 530 nm. In the range of 410-470 nm, the dependence of the excitation energy on the grinding diameter is systemic. The dependences of the photoluminescence flux on the average particle diameter can be approximated with sufficient accuracy by means of linear regression models. The express-analysis technique developed on the basis of these models of analysis of the average particle size of the fractions in the grinding includes sample preparation, excitation and registration of photoluminescence, amplification of the received signal, and size determination based on previously obtained calibration curves. The technique can be applied in grain processing and food industries.

1. Introduction

In the modern economy, the development of various branches of the food industry is rapidly progressing and requires special methods for assessing the quality of raw materials and of finished products. In order to solve the described problems, it is necessary to introduce modern express methods of quality assessment. Such technical solutions allow to produce fairly accurate analyzes in a production laboratory and to solve certain problems in the shortest possible time. These technologies include near-infrared spectroscopy, which was used to authenticate agricultural materials and finished products [1]. Also, computer vision methods and spatial radiation scattering measurements are used for the diagnosis of fruits [2-5]. In addition, the spectral luminescent analysis is widely used in agriculture and the food industry. It is based on the difference between the luminescence of fresh and low-quality raw materials or on the intrinsic luminescence of the product components [6-8].

The aim of this work is to develop a luminescent method for assessment of the quality of grinding of grain processing products.

The main areas of research are the following:
1. Study and identification of dependences between the spectral luminescent properties of grain products and their grinding on the average size of the fraction, as well as identification of the most informative parameters of express diagnostics;
2. Development of a methodology for luminescent analysis of the quality control of grain products, based on the results obtained.

2. Materials and methods
The study of luminescence of grains and of grindings was performed on a Fluorat-02-Panorama spectrofluorimeter, which is controlled using a computer with Panorama Pro software installed using an external camera for the samples to be studied. The obtained results were processed in the Panorama Pro software and MS Excel.

The Fluorat-02-Panorama spectrofluorimeter is used to measure the mass concentration of various impurities in various media, technical materials, food products, biological objects in accordance with the measurement procedure. The device can be used to register and study the excitation and luminescence spectra, to study the photometric parameters and phosphorescence characteristics of various objects.

For the experiments, we performed sample preparation. The grinding was carried out in an electric mill equipped with metal knives. In order to obtain optimal fractional distribution, the grinding time and the loading portion of the product were different. After this, the resulting mixture was sorted using sieves. For sieve separation we used sieve numbers 60, 50, 40, 30, 15, 050 and 0315. In this paper we studied only similar fractions from these sieves, the passage through the sieve 0315 was not considered. As a result, we obtained samples with varying degrees of grinding.

The average particle size of each fraction is determined by the formula:

\[ d = \frac{d_2 + d_1}{2} \]

where \( d_1 \) is the size of the sieve cells retaining the fraction, mm; \( d_2 \) is the size of the sieve cells located above the sieve retaining the fraction, mm.

For all the studied samples, excitation spectra were measured by synchronous scanning. Such a measurement makes it possible to determine the effect of radiation of a certain wavelength on luminescence of the object to be studied. The synchronous spectrum is measured in the widest spectral range for this device, which is of 180-700 nm, with an average sensitivity of the photomultiplier. The number of flashes of the radiation source is of 25 pcs, and the monochromator tuning step is of 2 nm, with a shift of 70 nm [9].

After analyzing the obtained curves, we obtained the spectral characteristics of excitation \( \eta_e (\lambda) \) and of luminescence \( \phi_l (\lambda) \) of integral grains and of grindings. In order to obtain each curve, we averaged 15 curves of individual measurements. After analyzing the spectra, we determined the maximum values of excitation and luminescence characteristics such as the maximum value (\( \eta_{e, \text{max}} \), \( \phi_{l, \text{max}} \)) and the corresponding wavelength value. In addition, the integrated values of excitation (H) and luminescence (Φ) were calculated in the given ranges. The latter has the physical meaning of a relative photoluminescence flux. All necessary mathematical processing was carried out similarly [10].

3. Results and discussion
Excitation spectra of grindings during synchronous scanning \( \eta_e (\lambda) \) of peas have maxima at wavelengths of 288, 362 and 424 nm, and for lentils they reach 288, 424 and 530 nm [11]. The analysis of the whole spectra did not give us a clear idea of dependences between the average particle size of the fraction and the relative excitation energy \( H \), because sometimes the spectra crossed each other and the dependences were broken. This is especially noticeable in peas, therefore, all spectra were divided into 3 sections, each of which included a maximum point on the graph, as well as a part of the spectrum for which it is characteristic. The results are presented in Tables 1 and 2.

An analysis of the results (Tables 1 and 2) in the section of 250-310 nm shows that maximum increases in the relative excitation energy relatively to the integral grain are exactly characteristic of it. All spectra are characterized by trimodality and the maximum peak is located at 286–290 nm. With a decrease in the size of the fraction, the spectra and the integral value of energy increase, but unevenly.
Table 1. Integral values of $H$, rel. un. of the pea excitation spectra in different parts of the spectrum.

| Particle size of the fraction, mm | 250 – 310 nm | 320 – 400 nm | 410 – 470 nm | Integral spectrum |
|----------------------------------|--------------|--------------|--------------|------------------|
| 0.41                             | 604          | 802          | 615          | 2312             |
| 1.0                              | 488          | 652          | 605          | 2006             |
| 2.25                             | 713          | 616          | 405          | 1989             |
| 3.5                              | 723          | 573          | 380          | 1922             |
| 4.5                              | 674          | 560          | 345          | 1815             |
| 5.5 (Integral grain)             | 656          | 556          | 322          | 1764             |

Table 2. Integral values of $H$, rel. un. of the lentil excitation spectra in different parts of the spectrum.

| Particle size of the fraction, mm | 250 – 310 nm | 410 – 470 nm | 480-580 nm | Integral spectrum |
|----------------------------------|--------------|--------------|------------|------------------|
| 0.41                             | 667          | 276          | 760        | 2208             |
| 1.0                              | 705          | 244          | 612        | 2012             |
| 2.25                             | 535          | 241          | 546        | 1710             |
| 3.5                              | 424          | 204          | 490        | 1446             |
| 4.5 (Integral grain)             | 378          | 194          | 530        | 1390             |

In the range of 410-470 nm, the dependence of $H$ on the grinding diameter $d$ has a systemic character. The wavelength of the maximum excitation for this range is of 424 nm. In the future, this wavelength will be used in order to obtain the luminescence and excitation spectra.

Spectral characteristics of excitation $\eta_e(\lambda)$ and of luminescence $\phi_l(\lambda)$ of peas and lentils of varying degrees of grinding are shown in Figures 1 and 3. Each curve in the graphs is an average value obtained from 15 curves of separately weighed samples of a certain fraction. Processing results of these spectra are summarized in Tables 3 and 4. In addition, the integral of the curve and the excitation energy were found for luminescence and excitation spectra, respectively. The results were also approximated in Excel using a linear function.
Figure 1. Spectral characteristics of excitation and luminescence of peas of various sizes: 1, 2 - 0.41 mm; 3, 4 - 1.0 mm; 5, 6 - 2.25 mm; 7, 8 - 3.5 mm; 9, 10 - 4.5 mm; 11, 12 - 5.5 mm.

Table 3. Results of processing luminescence and excitation spectra of peas.

| Average particle size d, mm | Excitation spectrum | Luminescence spectrum |
|-----------------------------|---------------------|-----------------------|
|                             | H, r. u.            | $\lambda_{w, \text{max}}$, nm | $\eta_{\lambda_e, \text{max}}$, r.u. | $\Delta\lambda_e$, nm | $\Phi_e$, r. u. | $\lambda_{\text{max}, \Phi_e}$, nm | $\Phi_{\text{max}, \Phi_e}$, r.u. |
| 5.5 (Integral)              | 197                 | 424                   | 5.27                                    | 54                    | 467            | 478                               | 4.99                                 |
| 4.5                         | 258                 | 424                   | 6.76                                    | 56                    | 585            | 480                               | 6.51                                 |
| 3.5                         | 302                 | 424                   | 8.05                                    | 54                    | 649            | 478                               | 7.17                                 |
| 2.25                        | 252                 | 426                   | 6.74                                    | 54                    | 752            | 478                               | 8.03                                 |
| 1.0                         | 283                 | 424                   | 7.63                                    | 56                    | 783            | 480                               | 8.62                                 |
| 0.408                       | 357                 | 424                   | 9.54                                    | 56                    | 948            | 480                               | 11.24                                |

Table 4. Results of processing the spectra of luminescence and excitation of lentils.

| The average particle size d, mm | Excitation spectrum | Luminescence spectrum |
|---------------------------------|---------------------|-----------------------|
|                                 | H, r. u.            | $\lambda_{w, \text{max}}$, nm | $\eta_{\lambda_e, \text{max}}$, O.e. | $\Delta\lambda_e$, nm | $\Phi_e$, r. u. | $\lambda_{\text{max}, \Phi_e}$, nm | $\Phi_{\text{max}, \Phi_e}$, r.u. |
| 4.5 (Whole)                    | 96                  | 424                   | 2.55                                    | 52                    | 174            | 476                               | 2.32                                 |
| 3.5                             | 130                 | 424                   | 3.48                                    | 54                    | 241            | 478                               | 3.28                                 |
| 2.25                            | 140                 | 424                   | 3.79                                    | 54                    | 277            | 478                               | 3.81                                 |
| 1.0                             | 152                 | 424                   | 4.12                                    | 54                    | 314            | 478                               | 4.13                                 |
| 0.408                           | 182                 | 424                   | 4.91                                    | 54                    | 407            | 478                               | 5.36                                 |

A graph showing the dependence of the luminescence flux on the average particle size of the fraction for peas is presented in Figure 2.
Figure 2. Dependence of the luminescence flux on the particle size for peas.

The obtained dependence is with sufficient reliability (determination coefficient $R^2 = 0.945$) approximated by the following linear regression model:

$$\Phi = -81.86d + 931.5$$

(2)

A graph showing the dependence of the luminescence flux on the average particle size of the fraction for lentils is presented in Figure 4. The obtained dependence is with sufficient reliability (determination coefficient $R^2 = 0.920$) approximated by the following linear regression model:

$$\Phi = -48.88d + 396.7$$

(3)

The studied samples are characterized by the following dependence: with a decrease in the average particle size in the fraction, the luminescence flux increases. Critical points of the luminescence spectra are at 475 - 485 nm for peas and lentils. The working range tightens when the size is reduced: the peak becomes less noticeable in contrast to smaller fractions.

Figure 3. Spectral characteristics of excitation and luminescence of lentils of various sizes: 1, 2 - 0.41 mm; 3, 4 - 1.0 mm; 5, 6 - 2.25 mm; 7, 8 - 3.5 mm; 9, 10 - 4.5 mm
Figure 4. Dependence of the luminescence flux on particle size for lentils

An analysis of the Stokes shift ($\Delta \lambda$) shows that mechanical grinding does not affect the difference between the critical points of excitation and luminescence spectra of integral grains and of grindings of various degrees. The studied parameter is almost always constant and possible deviations of 2 nm can be explained by a measurement error. The dependence of the size $d$ of the pea fraction on the luminescence flux $\Phi$ (Figure 5) can be used as a calibration curve of an optical device for measuring the sizes of fractions of bulk materials.

The equation of approximating dependence for peas is the following:

$$d = -0.0116\Phi + 10.915.$$  \hspace{1cm} (4)

For lentils, the dependence $d$ ($\Phi$) is also decreasing:

$$d = -0.0188\Phi + 7.653.$$  \hspace{1cm} (5)

Formulas (4) and (5) are applicable for measuring fractions with average particle sizes from 0.4 to 6 mm. Figure 6 presents a structural diagram of the developed methodology for express analysis of the average particle size of a fraction in grinding.

Figure 5. Dependence of the average particle size of peas on the degree of grinding due to the luminescence flux magnitude.
For analysis, the grinded grain should be placed in a dark and isolated from external light chamber. In the chamber, the studied material is placed in a bulk layer of small thickness. Initially, the sample is irradiated with radiation from a source in order to excite photoluminescence. The luminescent radiation of the material is detected by a photodetector, amplified by an amplifier, and using a microcontroller, the signal is processed in accordance with the equation of dependence of \( d \) on \( \Phi \) obtained earlier, i.e., the average particle size in a fraction is calculated. On this basis, a further decision is made whether this size is satisfactory for further operations. If the grinding size meets the requirements, the product is sent to the next stage of production processing, otherwise the product can be sent to an additional grinding cycle.

4. Conclusion

In the course of the work, we obtained results proving that there is a close to linear dependence of the luminescence flux on the average particle size of the fraction. It should be noted that such a dependence exists only for photoluminescence, since it was absent or very illegible when studying excitation spectra. Based on the obtained measurement results, calibration curves for the optical grinding degree control device were constructed, and a quality control technique was developed. The developed technique allows us to determine the average particle size in the grain fraction quickly, does not require special training and skills from the equipment operator. During the studies, we established good repeatability of the experimental results, which indicates the possibility of certification of the developed methodology. The technique can be applied in various sectors of the grain processing, in food and agricultural industries. Its use does not require special skills, which allows reducing of the costs of staff training, the technique is also remarkable by its expressiveness and does not demand special sample preparation. All this allows us to increase the capacity of the production laboratory, to reduce financial and time costs, to increase the overall productivity of grain processing.

5. References

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