Optical luminescent properties of stalked and concentrated feeds

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Abstract. There is a growing consumer demand among livestock professionals for compact devices that allow to determine the nutritional value of field-grown forage, bypassing a long chain of laboratory tests. This allows for the most efficient operation of the feeding management process. Among commercial instruments, the most common diagnostic method is the use of near infrared spectroscopy, however, our study shows that spectroscopy in the visible range, in some cases, may be considered as a more representative method. The use of excitation for photoluminescence by radiation with the wavelength of 424 nm (luminescence measurement range 450-600nm) is the most promising method within the analysis of the feeding mixtures composition. It is expedient to take the excitation wavelength of 485 nm (luminescence measurement range 510-670nm) as the reference one. The difference between the most luminescent fraction of silage and mixed fodder is λ_e=424 nm being 1.96 times.

1 Introduction

Today, modern livestock complexes for keeping large cattle that get milk and beef are enterprises with a high level of technological processes automation, however, some farming processes cannot be performed 100% efficiently without human intervention. In particular, the example of such a process is feeding, formed by a long chain of successive technological operations performed by mechanized means, robots, or directly by specialists.

Forming the diet for feeding animals that are kept in livestock complexes, the farmer pursues an exclusively rational approach in terms of livestock productivity, health and productive life. First of all, the provision of these indicators forms the quality of livestock feeding and the nutritional value of the diet provided, being the subject to constant change through the appearing external factors.

The first important indicator of the forage consumed by animals is the dry matter content. The point is that it shows the amount of nutrients the animal's body receives applying the gravimetric, dielcometric and spectroscopy methods in various measurement ranges.

Due to the fact that milk flow or livestock weight gaining is the key indicator of livestock efficiency for a farmer, the protein content in livestock forage, being its building

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material, is crucial since its specificity in the forage of natural origin. The said indicator may vary depending on weather and climatic conditions, as well as the time of harvesting of the farming material used and other factors, too.

The content of dry matter in the forage is estimated via the weight method. This implies the determination of the primary mass of a particular component, applying drying units that complete moisture extraction and comparing the primary mass and secondary indicators. The dielcometric method implies measuring voltage potentials, being less labor-intensive and allowing for the quicker obtaining of measurement results. However, the result of measuring the dry matter content often implies inefficiency of up to 2-3%. Spectroscopy in various measurement ranges allows not only to determine the dry matter content, but also to identify the content of starch, protein and other nutrients. This method is more expensive in terms of practical implementation, but it is much more functional by application.

The last 10 years trend is the technological transition from the methods of "wet" chemistry to the methods of forage spectral analysis. Spectral technologies cannot be considered a panacea that supplants other methods, but there exist numerous key features that indicate the certain advantages in the analysis of forage in non-laboratory conditions.

The research by the Portable IoT NIR spectroscopic system to analyze the quality of dairy farm forage research presents the portable instrument system for analyzing the nutritional value of dairy farm forages using near infrared spectrometry techniques. Applying IoT tools, the data is sent to the cloud for further processing; then they become available for any device. To analyze the nutritional value of dairy farm forage, the chemometric model and an implemented tool were developed allowing to understand the correlations between the measured spectrum and the concentration of matters of interest.

The spectroscopy of various ranges is also used in other areas, for example, by a group of researchers under Guangxin Ren. In Cognitive spectroscopy for evaluating Chinese black tea grades (Camellia sinensis): near-infrared spectroscopy and evolutionary algorithms the way for assessing the quality of black tea using the NIRS measurement system is described. The spectra of the samples were pre-processed by the transformation of variables, multiplicative scattering correction and minimum/maximum normalization. The experimental results showed that the predictive model for determining the qualitative indicators of the tea by its spectral characteristics operates without any human intervention with the efficiency confirmed by the correlation coefficients within the predictions of 0.9838.

The paper, describes the method for determining the dry matter content of cultivated peppers of 2 various types, and the reliability of spectroscopy was from 88.28 up to 91.37%.

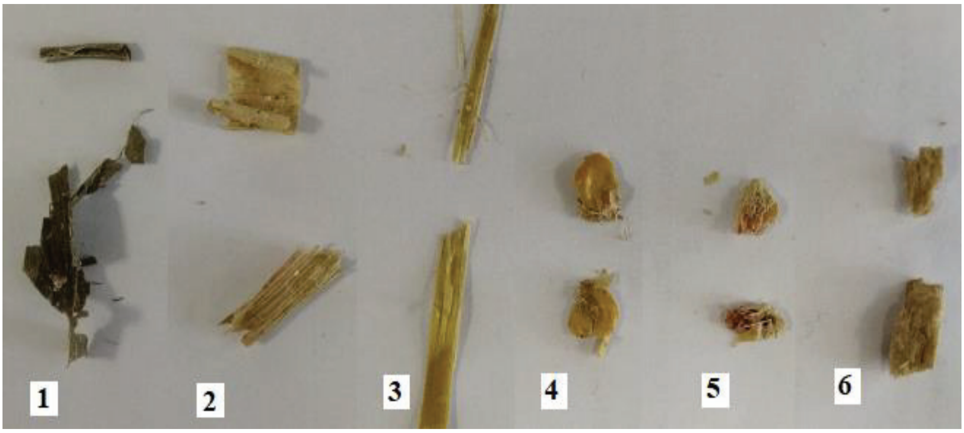
The paper describes the development of mathematical models allowing to determine by the intensity of the spectra for nine features of peas, such as the percentage of moisture, dry matter, total nitrogen, crude protein, ADF, NDF, AD-lignin, cellulose and carbohydrates, and the results reliability is estimated by R^2 from 0.88 to 0.98.

The purpose of the work is to study the optical photoluminescent characteristics of silage and compound feed and their components to determine the most informative spectral ranges.

2 Materials and methods

The research implied the determination of the optical properties and the achievement of the correlating spectral dependences for the components within a complete forage mixture for large cattle. The mixture also includes corn silage and concentrated combined forage, consisting of grinding of grain corn, beet pulp, corn stillage (wastes from ethyl alcohol production), rapeseed meal (wastes from oilseed production).

To obtain reliable optical properties, dissimilar materials were decomposed by their structure into separate elements, for example, corn silage. The data is provided in Figure 1.



1 - leaves, 2 - cob shell, 3 - stem part, 4 - grain surface, 5 - inner part of the grain, 6 - cob core

Fig. 1. Photos of silage fractions.

Since grown corn has heterogeneous structural elements, both in terms of color and nutritional value, the spectral characteristics of the leaf part (1), the cob shell (2), the stalk part (3), the grain part shell (4), the inner part of the grain (5), the inner part of the cob (6), were determined separately, and then the total spectrum of all materials in the aggregate was analyzed as well.

The nutritional characteristics of corn silage and concentrated forage were measured with the device "Kapel' 205" - Lumex, functioning on the basis of the capillary electrophoresis method, arbitration method and certified result as well, and it also requires the significant labor costs for sample preparation of the analyzed material.

The resulting nutritional characteristics are presented in the Table 1.

Device specification:

- Operating wavelength range from 190 to 380 nm.
- Registration of absorption spectra for the analyzed sample.
- Autosampler for 59 positions using disposable Eppendorf tubes (1.5 ml).
- Liquid capillary cooling.
- Distilled water is used as heat carrier.
- Setting and control of the coolant temperature is possible in the range from 10 degrees below the ambient temperature up to +50°C.
- Sample injection methods: hydrodynamic method (pressure of -100 to 100 mbar), electrokinetic method (voltage of -30 to +30 kV).
- Capillary flushing is automatic (constant pressure from 500 mbar to 2000 mbar), that allows to work with high-viscosity background electrolytes in the capillary gel electrophoresis mode.
- High voltage power supply with automatic polarity switching (DC voltage from -30 to +30 kV, with the lead of 1 kV, and the current of 0–300 μA).
- Full control of the device, data collection and processing with the specialized software "Elforan".

Table 1. Silo parameters.

Parameters	Total, %	Dry matter, %

Moisture degree	66.8	35.7
Starch	12.0	33.1
Protein	2.6	7.3
ADF	8.5	23.8
NDF	15.3	43.0
Ash	1.8	4.9
Crude fat	1.2	3.4

Similarly, the characteristics of the concentrated forage and its components were determined by the following parameters:

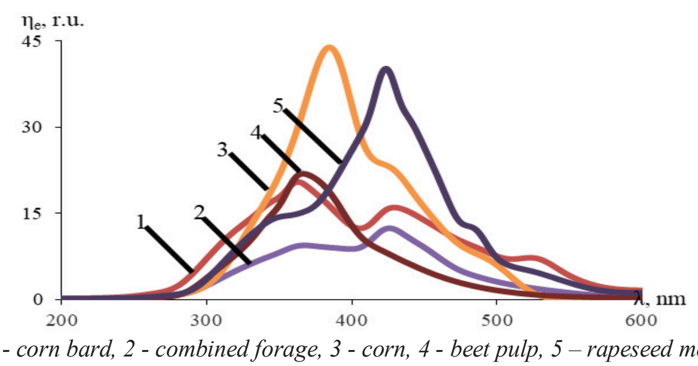
- Moisture degree.
- Crude protein.
- Crude fiber.
- Lysin.
- Methionine.
- Calcium, phosphorus and natrium.

The study of the spectral luminescent properties was carried out with a hardware-software complex consisting of the spectrofluorometer “Fluorat-02-Panorama” (Lumex), being the computer with the Panorama Pro software, and the external camera for the analyzed samples. The measurement and photoluminescence spectra were applied similarly to the previous ones.

The excitation (absorption) spectra $\eta_e(\lambda)$ were measured under the synchronous scanning by the monochromators of the spectrofluorometer based on the luminescence spectra $\varphi_l(\lambda)$. The statistical processing was carried out as well, averaging the obtained results by 20 measurement parameters.

3 Results and Discussion

The spectral characteristics of the excitation of combined forage and its components, averaged by 20 measurements, are provided in Figure 2.



1 - corn bard, 2 - combined forage, 3 - corn, 4 - beet pulp, 5 – rapeseed meal

Fig. 2. Spectral characteristics of excitation of combined forage and its components.

For combined forage and its components, excitation starts at 260-280nm and ends at about 530nm (for corn grains) - 580nm (for stillage and meal).

The spectral characteristics of the silo fractions excitation are shown in the Figure 3.

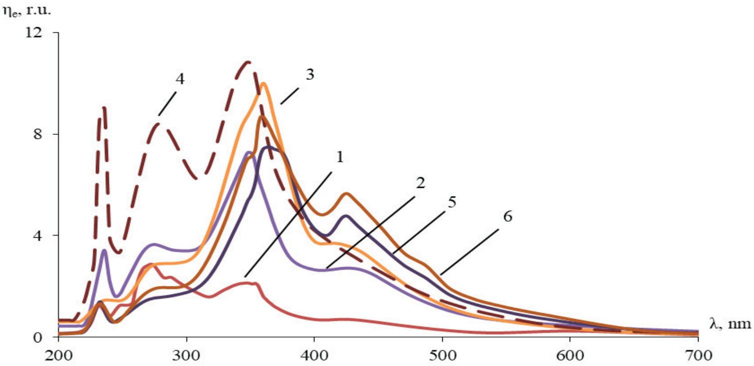
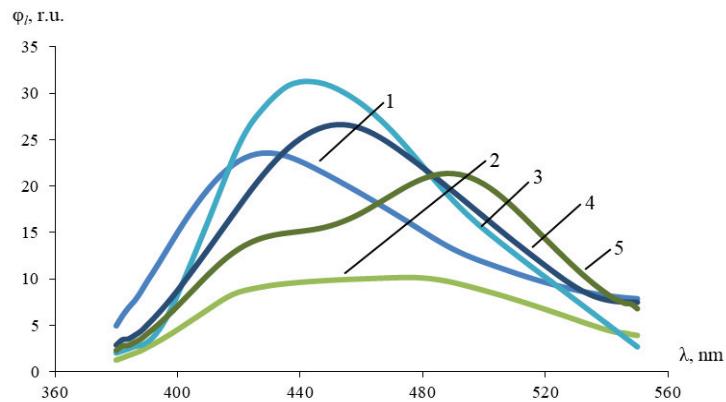


Fig. 3. Spectral excitation characteristics of the silage fractions.

The silo fractions are excited much weaker than those of the combined forage, which can be caused by their high moisture degree and the associated quenching of luminescence.

The excitation of the silo occurs at the range from 220nm to 550-600nm. Attention shpuld be given to the excitation are the regions of 232 nm (absorb fractions 4, 2 and the other to a lesser extent), 260-280 nm (fractions 4, 2, 1), 350-365 nm (the strongest absorption of fractions 4, 3, 6, 5, 2 and, to a lesser extent, fraction 1), 424 nm (fractions 6, 5, 3). At the same time, in the region of 350-365 nm, the greatest absorption of radiation is observed: for fractions 1, 2, 4 this occurs at 350 nm, while for fractions 3, 5, 6 this occurs at 362-364 nm.

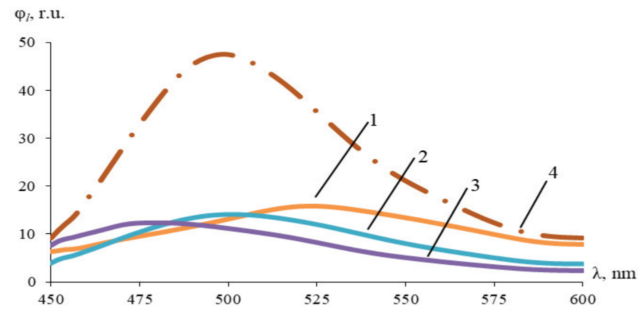
The spectral characteristics of the photoluminescence of the combined forage and its components excited by radiation at wavelengths of 362, 424 and 485 nm are provided in Figures 4, 5 and 6, respectively.



1 - corn bard, 2 - dark combined forage, 3 - corn, 4 - beet pulp, 5 - rapeseed meal

Fig. 4. Luminescence spectral characteristics at λ_e = 362 nm.

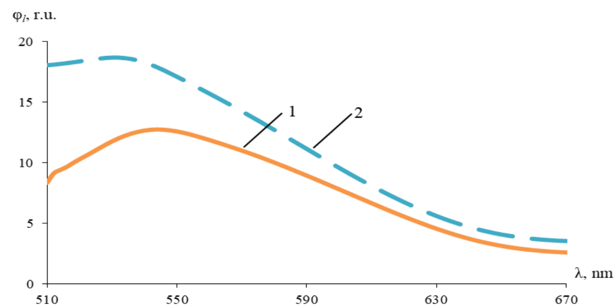
As for the combined forage and all its constituents, the photoluminescence spectra at λ_e=362 nm are in the range of 380-550 nm. The maximum indicator for corn is at about 445nm, while for beet pulp it is at 455nm, for stillage it is at 430nm, and for meal it is at 495nm. Therefore, the photoluminescence spectrum of the combined forage is flat-topped, with negative kurtosis.



1 - corn bard, 2 - dark combined forage, 3 - beet pulp, 4 - rapeseed meal

Fig. 5. Luminescence spectral characteristics at λ_e = 424 nm.

When excited by radiation λ_e=424 nm, the spectral range of photoluminescence is 450-600nm.

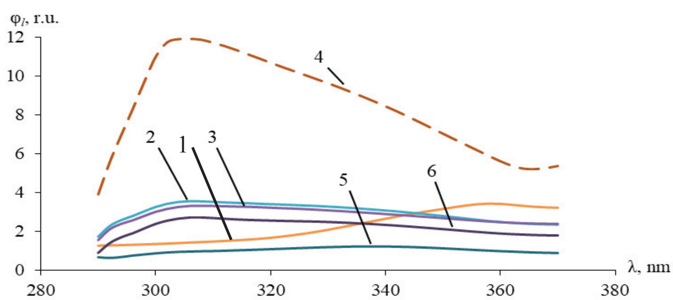


1 - corn bard, 2 – rapeseed meal

Fig. 6. Luminescence spectral characteristics at λ_w = 485 nm.

When excited λ_e=485nm, only stillage and meal demonstrate luminesce, but the indicator is less than the one for shorter-wavelength excitation. This wavelength can be used as the control one to determine the relative amount of stillage and meal in combind forages and feeding mixtures.

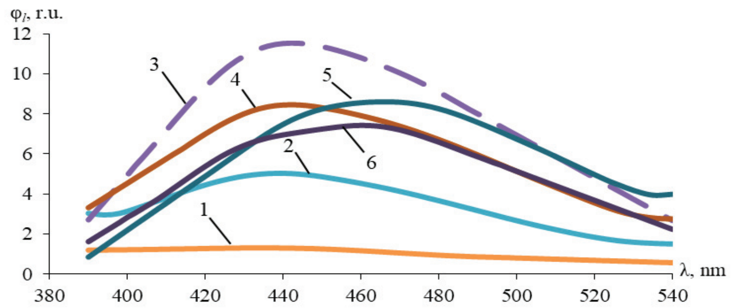
The photoluminescence spectral characteristics of corn silage fractions when excited by radiation at wavelengths of 323, 362, and 424 nm are shown in Figures 7, 8, and 9, respectively.



1 - first fraction, 2 - second fraction, 3 - third fraction, 4 - fourth fraction, 5 - fifth fraction, 6 - sixth fraction

Fig. 7. Spectral characteristics of silage luminescence at λ_e = 232 nm.

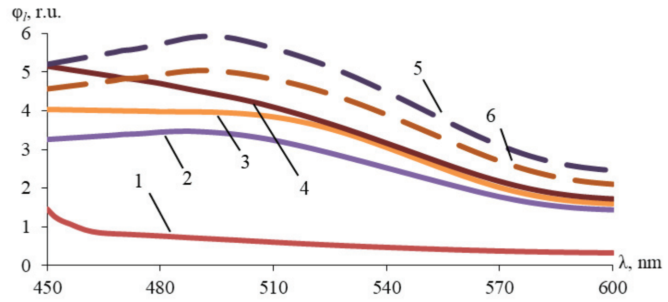
When the silo is excited by radiation λ_e = 232 nm, only the fourth fraction noticeably luminesces.



1 - first fraction, 2 - second fraction, 3 - third fraction, 4 - fourth fraction, 5 - fifth fraction, 6 - sixth fraction

Fig. 8. Spectral characteristics of silage luminescence at λ_e = 362 nm.

The better luminescence is presented when excited by radiation with a wavelength of 362 nm. In the range of 390-540nm, the third, the fourth, the fifth.



1 - first fraction, 2 - second fraction, 3 - third fraction, 4 - fourth fraction, 5 - fifth fraction, 6 - sixth fraction

Fig. 9. Spectral characteristics of silage luminescence at λ_e = 424 nm.

Upon excitation of λ_e = 424 nm, the luminescence is weak.

The research made it possible to evaluate the higher sensitivity of the visible range spectroscopy method for the express analysis of forage mixtures.

Theoretically, the luminescence intensity I_l is proportional to the luminescence quantum yield η_e, as well as the intensity of the exciting light I_0, the absorption coefficient at the excitation wavelength ε, the layer length l and the concentration of the phosphor c_l:

$$I_l = 2.3 I_0 \varepsilon l c_l \eta_e \tag{1}$$

This equation underlies the quantitative luminescent analysis. The dependence of the luminescence intensity on the phosphor concentration often remains linear within three to four orders of magnitude of the concentration. It is possible to assume that in excitation at 424 nm, the luminescence intensity is determined by the concentration of tryptophan, which is highly presented in meal (5.5 g per 1000 g of meal), while for the excitation at 485 nm it is protein (328 g/kg for meal and 216 g/kg for bard).

The results for silage and compound feed are consistent with previously performed integral measurements.

4 Conclusion

The use of excitation for photoluminescence by radiation with the wavelength of 424 nm (luminescence measurement range 450-600nm) is the most promising method within the analysis of the feeding mixtures composition. It is expedient to take the excitation wavelength of 485 nm (luminescence measurement range 510-670nm) as the reference one. The difference between the most luminescent fraction of silage and mixed fodder is λ_e=424 nm being 1.96 times.

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