

## THE STUDY OF LUMINESCENCE SPECTRA OF FOOD PRODUCTS

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### Abstract

*The visual analysis is express but not objective. The fluorometric methods are pretty lengthy and do not allow for the analysis of the product without splitting them. The luminescence spectral analysis method of food products has a bigger priority than the visual analysis method and the fluorometric methods (Budan Constanța, 1996). These methods of the luminescence spectral analysis are more precise and more convenient than the visual analysis methods or other methods.*

**Key words:** luminescence, substances, spectra

### INTRODUCTION

We present the results of the experimental results regarding the luminescence spectrum of food products, the methodical description of luminescence measurements of organic substances, the description of the installation and the analysis of experimental results.

### MATERIAL AND METHOD

#### **The method of measuring organic luminescent substances**

Most food glow in UV lights, the same as in visible spectral regions. The observation of luminescence spectra usually contain many irradiation bands conditioned by the existence of a number of luminescent components (aromatic amino acids, unsaturated fatty acids and their fermentation products, vitamins) (Budan Constanța, 1996).

Separating each luminescence bands in order to determine those to other luminescent components is only possible when using monochromatic excitation and selective recording (the use of light filters and monochromator) (Sfichi R., 1988).

The primary role of light filters is that they have high power of light. In large areas of light, the flux passing through the light filter is higher than the one going through the mono-chromator. As in the study of food products, the measurement of the illuminated region usually does not exceed few millimeters. This priority of light filters is done.

A big drawback of light filters is the big crossing strip, which consists of tens of nm. In the spectral research practice, 2 types of monochromators are used: in one of them is the prism, and the other network diffraction. In prism monochromator, the dispersion increases with the decrease of the long waves. In the diffraction network monochromator, the measurement of illumination power is proportional to the spectral intensity of the long wave tuning fork (Tutovan V., 1985).

The linear dispersion of the Monochromator with a diffraction network has a great value, that ensures priority in using these monochromators in luminescent research, as they ease the placing of recording facilities with automatic enrollment of spectral curves placed at the only signing and give the possibility to work with most broad partitions in the long-wave spectral regions. In studying food products photoluminescence as an excitation beam of luminescence, incandescent lamps, gas lamps and lasers can be used (Sears F. M., et al. 1983).

Incandescent lamps, are usually used in cases in which for the exiting of luminescence a part of the short waves visible spectrum is used.

For the excitation of food products photoluminescence gas lamps are used: low pressure mercury lamps, mercury - quartz lamps, high pressure xenon lamps, which can achieve the UV luminescence with high power long wavelengths, also lamps that have a continuous emission in the UV spectral region, filled with hydrogen, xenon, and deuterium (Schlett Z., 1998).

For the luminescence excitation in food products and their luminescent components gas lasers or liquid lasers can be used, with a slight adjustment of the frequency. Using the laser allows the increase of the intensity of the excitation and that increase, raises the sensitivity of the measuring apparatus. For this, it must always be considered the possibility of photochemical decomposition of the molecules of the analyzed substance. The excitation of cathode-luminescence is possible with electrons with a high speed in the electric field of up to 100 - 1000 eV energy (Walter Czech, 1998).

All food products and their basic components are dielectrics. When irradiating these substances with an electronic link, on their surface an electric charge is formed, so as the conductivity of the electric surface is very low to be removed. Meeting this target and increasing the delayed electric field is adjusted with a 2-a electric emission. At lower tension elevations, when the number of repeatedly flying electrons from the surface of the luminescent substance, the reduced number of excited electrons of the large field does not allow excited electrons to reach the surface of the luminescent substance (Edward M., 1982).

Stable cathode-luminescence can be obtained starting with a tension that increases the electric field, when the number of electrons is equal to the

number of excited electrons. The increased voltage region corresponds to a stable lighting, the output of cathode-luminescence practically does not depend on increasing of the voltage. The output of cathode-luminescence usually decreases with the increase of current density which may be a rich light medium, increasing the delayed electric field and the temperature of the luminescent surface of the body, which causes temperature quenching.

Through experiments it was found that typical cathode-luminescence spectra of cathode-luminophor do not depend on increasing the tension but on the excited current density. Luminescence excitation of different substances is usually done by three cases situated at the excitation source of the recording apparatus (Alfred Kasler, 1990).

In the first case we examine the luminescent light emerging from one side of the sample parallel to the link of the excitation of light.

In the second case – it arises from the opposite side that the excited light falls. In the 3rd case - appeared from the same part of the sample, on which the excited light falls. All marked options of the measuring machine took into account the processing and training devices for the studying of food products luminescence spectrum and their components whose scheme is shown in Fig. 1. As mono-chromator luminescence excitation 3 and luminescence 10 are used mono-chromatoare difracționale type MDP -2 -3 MDP or MDP- 23.

The 11 receiver serves as the photoelectromultiplier (fototelectromultiplicator) ФЭУ - ЫІФГ ФЭУ 100 - 106, the signal that is giving the current amplifier 12 and then to the transcript 13, when the electric potentiometer type КСП - 4 is used. The source of irradiation excitation 1 - gas lamps are used, pulse laser with nitrogen molecules ЛПИ - 21 type, or the piston with electric light beam, the high-voltage power source which is serving the 7kW current, at the excited current density of 10A \ m (Christoph Von Rhoneck, 1989).

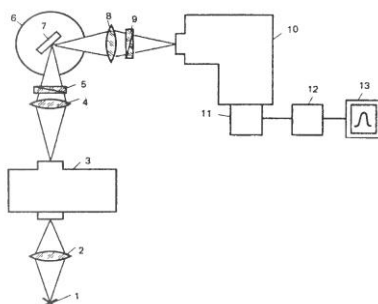


Figure 1. The elements of the recording apparatus for the luminescence and excitation spectrum: 1. Xenon lamp; 2. Optical system; 3. Mono-chromator 4. Quartz lens; 5. Polarizer; 6. sample holder; 7. Sample; 8. Lens; 9. Analyzer; 10. Mono-chromator; 11. Photoelectromultiplier; 12. selective amplifier; 13. transcriber.

At the laser and electronic excitation, the necessity to use the excitation mono-chromatorul and the quartz condenser 3 and 2, 4 and 8 is declining. For the polarizing measurements analyzer 5 and 9 a GLANA prism is used which allows the polarization throughout the whole polarization region (Maxwell J. C., 1989).

### **Calibration of the apparatus for measuring the luminescence spectra**

Before carrying out the measurements, the grading of the spectrophotometric apparatus is realized according to the wavelengths. In creating the grading system of the apparatus, we proceed as follows: the spectrograph entrance slit is illuminated with the help of a light source (mercury, helium), which has a discrete spectrum, whose wavelengths are well known. With the help of the received spectrum, the dependence between the wavelengths and gauge on the drum are constructed, which are connected to the motor that rotates the spectrograph prism, and then the dispersion curve of the apparatus is constructed (Manda D., 1974).

Knowing that the sensitivity of the photomultiplier and the dispersion of the apparatus depends on the wavelength, for the measuring of the distribution of the luminescence energy spectrum, the system should be graded with the help of a standard source for which is known to the energy distribution of the spectrum. For the purpose of this paper, we are using an ordinary incandescent lamp with the filament temperature of 2800K, which is determined with the help of the pyrometer. Energy distribution in the spectrum of tungsten irradiation within the visible spectrum limits, coincides quite well with the energy distribution in the spectrum of the absolute black body. The size of the deviation I registered for a specific wavelength can be written as:  $I_{\text{recorded}} = I_{\text{recorded}} \times K \times D$ , where  $I_{\text{recorded}}$  is the actual intensity recorded of the calibration source wavelength, as determined by tabular data, which correspond to the temperature value of the source gauge, expressed in units of the galvanometer scale values  $K = 1$  and  $H = 1$ , where  $K$  - photomultiplier sensitivity to the wavelength,  $D$  - spectrograph dispersion measured in (A / mm) (Moisil G., 1981).

The  $K \times D =: I_{\text{recorded}} / I_{\text{source}}$ . Performing similar measurements along the entire spectrum, we find the dependence of  $K \times D$  to the wavelength. This dependence represents the graph of the sensitivity of the system. For the first real spectrum of luminescence the ordinates of the experimental curve  $I_{\text{registered}}$  ( ) are divided by the corresponding ordinates of the sensitivity curve of the apparatus. In the following figure. is

shown the grading curve for the apparatus for the removal of luminescence spectra and that of excitation (Alexander Hellmans, Byron Bunch, 1998).

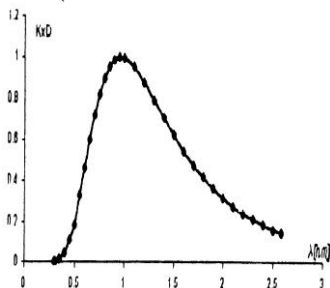


Figure 2. Equipment grading curve

### Quantitative analysis of luminescence

The quantitative analysis of luminescence allows us to determine the substance concentration in the sample. It should be noted that the difference between quantitative and qualitative analysis consists of those that the detected effects with the help of qualitative analysis to quantitative analysis are measured and processed with the introduction of all necessary remedies. All methods of this type of analysis are based on the existence of certain dependencies between luminescence intensity and concentration in the sample. Analysis should be performed under conditions allowing direct proportionality between studied sizes. In this case the concentrations of the examined elements is determined by comparing the intensities of the studied substance and the standard one. At certain concentrations greater than 10, 10 mol/l proportionality is usually broken after concentration quenching. Generally, the quantitative analysis of luminescence is reduced to preparing of standard series containing known concentrations of the analyzed substance, is reduced to the measurement of luminescence intensity. After obtaining data, we build an analytical curve of dependency between the intensity of the luminescence and that of concentration. By measuring the intensity of illumination of the studied model, with the help of the analytical curve it can be determined the concentration in the sample (Atanasiu V., 1970).

Quantitative analysis of the luminescence, it is often used the own luminescence of the analyzed substance. For objects that do not have luminescence, we resort to different luminescent reactions and after the irradiation intensity of the final product we determine the concentration. Using the well-arranged remunerate methods in the analytical chemistry we determine the final product concentration of this reaction.

In carrying out the successful analysis, we are often confused by the fact that the intensity of the researched product irradiation can be determined not only by its concentration but also by many other factors.

Example: On a high intensity lighting solution, a big reaction is caused by extinguishing processes, absorption by a substance that glows, by solutions, and repeated absorption of luminescence by those at whose analysis methods to achieve different classes of bonds is necessary to study the intensive nature of processes that can occur in solutions of these substances. In carrying out the analysis, we must first obey all the rules relating to the excitation and registration of luminescence, to obtain good results, the standard model and the one researched should be found during the complete analysis under the same conditions. This requires that the spectral composition of the standard to use standard concentration solution which is studied in the researched sample. In those cases where the preparation of such a solution is not possible, in the place of the standards from different standards that poses luminescence, similar to the spectral composition of the examined sample, first it shall be graded according to the analyzed solutions substances, the concentration of which is known in special cases, as benchmarks are used some samples of luminescent glass that is not subject to photo chemical changes and give a permanent continues luminescence.

#### **Luminescence spectra of fruit juice and apple**

The luminescence spectra of fruit juice and apple were measured at 293 K temperature of the excitation light with a wavelength of 253nm (Fig. 3).

From the figure it can be seen that the two spectra consist of a single band of irradiation, the maximum of which is located close to 420nm, the settlement of the strip coincides with the maximum of the luminescence spectrum of water solution of ascorbic acid which content in the apple corresponds on average to 10-16 mg/100g, and in fruit to 6 mg/100g. Other luminescent components of fruit juice and apples, have irradiation maxima near 420nm, more pronounced are highlighting fermented products of unsaturated fatty acids. That is, the fermented products of unsaturated fatty acids are also excited by light with a wavelength of 253nm, in which the luminescence spectra are taken out of fruit juice and apple (Figure 3). From the analyzed spectra we can draw the conclusion that a great contribution to the luminescence of fruit juices and apples have components that are responsible for their quality and depending on the condition of these components, which are outlined in the analyzed spectra the state of the product can be valued. The results of the investigations were established, that depending on the duration of the storage, the luminescence spectrum structure strips changes. With the increase shelf life the peak characteristic practically disappear and the luminescence intensity decreases.

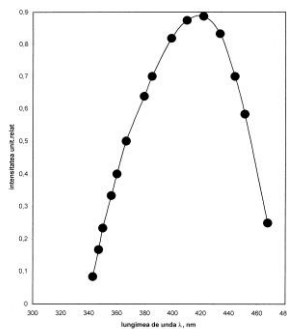


Figure 3.a. Luminescence spectrum

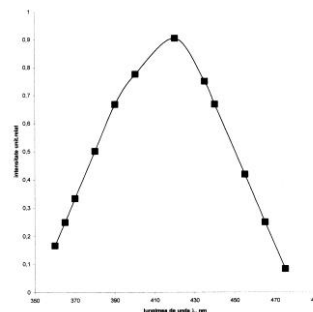


Figure 3.b. Luminescence spectrum

### Cooked and smoked salami

The study analysis of luminescence spectra of cooked and smoked salami quality was performed on freshly prepared products of two kinds, natural and artificial packaging, kept at low temperatures over 30, 60 days. Luminescent measurements were spent at 293 K temperature. Spectral-luminescent characteristics of such salami products are shown in Fig. 4. The luminescence spectra of the freshly prepared products measured with excitation radiation wavelength of 365nm consist of a single band of irradiation near 440nm (Fig. 4). Keeping the salami at a temperature of 267-269 K over a period of 30 days leads to the appearance on the luminescence spectrum of a band of irradiation located at 450 nm. The subsequent preservation of the salami at the same temperature leads to significant changes in their luminescence spectra. Following the chemical processes that occur in the luminescence spectra essential changes occur characteristic to the length of time. With the increase in the duration of time from 30 to 60 days in spectrum, it is revealed that a single band with a maximum of irradiation at 460nm. It was established that this rule was respected for the same type of salami in several experiments. This regularity can be successfully used as express analysis to determine shelf life. 0 essential influence on the structural shape of the luminescence curve is seen in the composition of salami, meaning the chemical and biological composition. It has been established that the degradation of the sausage is based on the type of package. Product quality is more stable in the first period of storage, for 15 days, for natural packed salami. At the second stage of storage, in the luminescence spectrum curve there are some features which are probably caused by the degradation of the package. For both the first artificial packaging both in the first and the second period, luminescence spectrum appear packaging characteristic. These features do not change depending on the duration of storage.

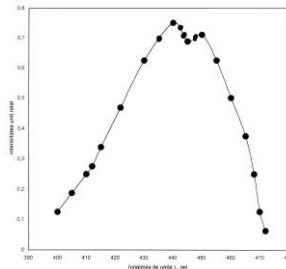


Figure 4.a. Luminescence spectral characteristics of salami after keeping for 30 days

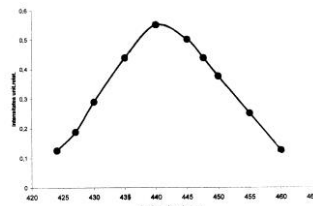


Figure 4.b. Luminescence spectral characteristics of salami after storing for 30 days

### Dairy products

From the dairy products, the main animal product is cow's milk which is used extensively in children nourishment and for people with different ailments which also require a trustworthy and prompt control. The chemical composition of cow milk is quite complicated in terms of the structure of organic components and the presence of harmful components and stages of fermentation processes is difficult to determine using traditional methods. Milk mostly contains water and fat soluble vitamins, pigments, enzymes etc. Under normal conditions the fat content in milk varies in the range of 2.8 to 6 %. The principal components are found in milk in the form of a suspension and emulsion, consisting of fat round or slightly oval bubbles, with the diameter of 0.5 - 20 $\mu$ m. Fat bubbles are covered with an albumin blanket which does not allow a union and really helps protect the fermentation of milk. The destruction of the protection layer albumin may appear in the result of lifting milk acidity, over a long period of heat treatment or short physical processes. Albumin milk contains amino acids that are part of the irreplaceable groups. The milk contains almost all known vitamins known in the present. Vitamin A is contained in milk in an amount of about 2-6%, also they contain carotenoids, which are pigments of milk fat and give butter the yellow color. The content of vitamin A in milk and dairy products depends on a number of factors. The fresh cow milk contains about 0.2 to 0.6 mg / kg of vitamin D in two forms of vitamin: D2 and D3. The content of this vitamin in milk increases during the animals grazing, and decreases in winter regardless of the feeding diet. The milk fats contains about 0.0025 mg / kg of vitamin D. Vitamin E is contained in the milk in an



amount of 0.9 mg / kg, and in butter about 22 mg / kg. Tocopheryl content in summer is higher than during winter which also is linked to the food content. Vitamin K is found in milk and powder milk. However, the concentration of this vitamin is very small, the urine of this vitamin occurs only in pasteurized milk. Vitamins present in the milk content are stable and are destroyed at high temperatures, but the damage is small. Vitamin B I in a free state occurs in milk, the average content of this vitamin is 0.02 - 0.6, cream - 0.3; Cheese - 0.4, condensed milk -0.6 mg/kg. After pasteurization of milk independently from the conditions of the preservation of the contents of the vitamin drops by 10-15 %. Vitamin B2 in an amount of 65-95 % is contained in the free form, there are small changes when pasteurizing. Vitamin B3 - stimulates the growth of lactic acid and other bacteria. In fig. 5 is analyzed the luminescence spectrum of cow milk amounted to excitation light with a wavelength of 365nm following the analysis results obtained, it can be noted that a large responsibility to the luminescence curve structure bear the remains of tryptophan in the milk albumin substances. The characteristic features are highlighted within 450 460nm wavelength, have a great contribution, respectively the vitamin groups A, D, and B1, but the strip irradiation at 495nm (Fig. 5) - is subject to free riboflovinului.

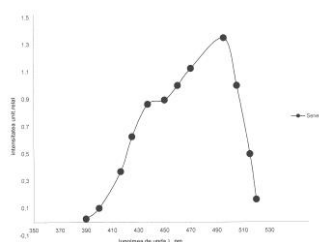


Figure 5. Spectral characteristics of cow milk

## RESULTS AND DISCUSSIONS

The results of the analysis of luminescence spectra collected from milk from different races, was established that their characteristic features depend on the concentrations of the components that largely depend on their food supply. To a certain race in similar food conditions the spectrum structure remains the same. With the increase of storage time regardless of the preservation of the luminescence spectrum, we see characteristic features whose intensity are in direct dependence to temperature and time. These characteristics strongly outlined in the spectra of highly elevated room temperatures can be used as parameters for determining the quality of dairy products. In the case of dairy products, the use of the Shpolski method gives the possibility of determining both the quality on the duration of

storage as well as information about the state of the elements in their composition.

## CONCLUSIONS

For cooked and smoked salami, it was found that the degradation of the salami is dependent on the type of packaging. Product quality is more stable in the first period of storage, for 15 days for naturally packaged salami. At the second storage stage in the luminescence spectrum curve there are some features which are caused probably by the degradation of the packaging. For the artificial packaging both in the first and second storage period, on the spectrum of luminescence appear characteristic peculiarities of the packaging. These features do not change depending on the duration of the storage.

In Fig.5 is analyzed the luminescence spectrum of cow milk amounted to excitation light with a wavelength of 313 nm, as a result of the analysis of results can be noted that a large task to the structure of the luminescence curve has the tryptophan remains of the milk albumin substances. The luminescent strip irradiation at 380 and 425 nm (Fig. 5), has a great contribution, respectively vitamins A, D, and B 1, but strip irradiation at 495 nm (Figure 5) - is subject to free riboflovinului.

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