CURRENT STUDY OF RESEARCH REGARDING THE LUMINESCENT ANALYSIS OF ORGANIC SUBSTANCES

Bogluţ Angela*, Tudoran Dan **

*****Banat´s University of Agricultural Sciences and Veterinary Medicine "King Michael I of Romania" from Timisoara, 300645 - Timisoara, Calea Aradului, 119, Romania
******University of Oradea, 410087 – Oradea, Universitatii street, 1, Romania

Abstract

The luminescence analysis has found its application in diverse domains of science and technology. In agriculture and the food industry, the usage of luminescence is based on different illumination colors of food products, of low and high quality, of the personal luminescence of some vitamins.

Key words: excitation, luminescence, spectrum luminescence

INTRODUCTION

In one case, the analysis takes place specifically with the help of the visual effect of the analysed products with the help of luminesence. In other case, the analysis takes place with the help of the calculation of the quantity of the vitamin intake in food products with the usage of the florometric method, which includes different splitting operations, cleaning of the contents of the product process with a flurophore.

MATERIAL AND METHOD

Excitation and luminescence spectrum analysis

Absorption and luminescence spectra of molecules

Absorption and emission spectra in the visible and near ultra-violet energy domain are conditioned by the energetic transitions between different electronic states of the molecule, which is why they are called electronic. The transition from one electronic state to another can happen at different rotating or vibrating levels, the energy difference between electronic states of the molecule is usually higher than that of the rotating and vibrating on which the latter are received for testing as electronic sublevels of energy levels (Schlett Zeno, 1998). The electronic state with the lowest energy (E) is called the fundamental state of the molecule, and the other states are called excited states. In fig. 1 is the diagram of the energy levels of a molecule and electronic transitions (Purcell E. M., 1982).

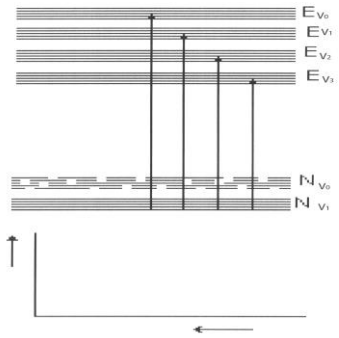

Figure 1. Scheme of the energy levels of a multi-atomic molecule and electronic transitions: N - fundamental electronic state, E - excited electronic state, v0 , v1, v3 - various vibrational states; (v - vibrational state of the molecule which is the fundamental electronic state; through the close thin lines are represented the rotary sublevels; vertical arrows represent the transition from the null vibrational sublevel of the fundamental electronic state on different vibrational sublevels of the excited electronic state).

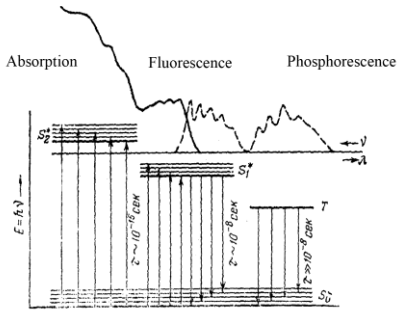

Figure 2. Electronic – vibrational scheme of levels and the overall shape of the absorption and luminescence spectra of molecules.

Representation of electronic line spectrum depends mostly on rotary-electronic transitions – such as multi-atomic molecules the difference of the energy between the neighboring rotary levels is small (≤ ΔErot 1cm -1). In reality, the analyzed spectra typically have the form of broad lines (Fig. 1). Lines of an electronic transition hold a spectral tuning fork of 5000-10000 cm -1 (Von Rhoneck Christoph, 1989). A more general electronic state (and transitions respectively) of atoms and molecules depends on the value of multiplicity characterized by the spin quantum number: J= $\left| 2S \right|$ + 1 where S - entire spin of the molecule. The full spin state with S=0 and T=1 is called a singlet and is denoted by (S); State with S=1 and J=3 is called a triplet and is denoted by (T). The nature of electronic spectra of multi-atomic molecules is determined exactly by these two types of states. Transitions between states with different multiplicities (singlet ↔ triplet) are called inter-combination (Maxwell J.C., 1989).According to the interdiction law of inter-combination, allowed transitions are transitions between states of

multiplicity. The multiplicity of electronic states and the interdiction law of inter-combination give us a general characteristic of the absorption and luminescence spectra of multi-atomic molecules (Sfichi R., 1988). At room temperature, almost all the molecules are in fundamental state. In most known molecules, this state is singlet and is denoted by S0 (index below shows the electronic level). In single light source molecule excitation of mild intensity, the investigated absorption spectrum (Fig. 2) is subject to transitions from the ground state to the excited single state (S0 transitions - S*i). Given the short life span of the excited state (S*i - state molecule lives only 10-7 - 10-9 seconds and S * 2, S * 3 even less) singlet and that the light excites only a small part of the molecule, the excited molecules concentration is very small and the lines S * i> 0 → S * k transitions in these conditions are not being investigated. They can be seen when using the laser light as a source (Manda D., 1974). How the process of luminescence arising from molecules results At the absorption of light quantum, the molecule passes from the fundamental state S0 to the excited S'', which in the visible and ultraviolet spectrum is connected with the passage of the electron (e) on a superior energy level. (Moisil G., 1981). The energy (E) of electronic excitation reserved in the molecule at a singlet level can be used in a range of molecular processes, such as: a) Energy use in thermal oscillations – non-luminescent transition; b) Passing of the electron at a fundamental level accompanied by the irradiation of the fluorescent quantum; c) Transition of the molecule in a triplet state at the rotation of the excited electron - non-luminescent transition. Then, at the passing of the electron from the triplet level to the fundamental one, the irradiated energy is used for the heater, which is a non-luminescent process, or at illumination, which represents the luminescence process called phosphorescence; d) Delivering electronic excitation energy to the neighboring molecule - energy migration; e)Energy use in the photochemical process.

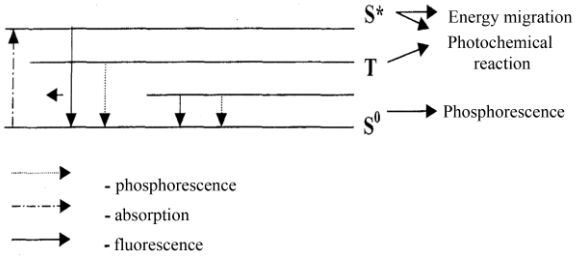

Figure 3.

After the phosphorescence spectrum, we determine the accumulated energy of a molecule at a triplet level. Usually, in the singlet excited state,

the molecule is 10 " 9 - 108s then there takes place the usage of energy at thermal oscillations or lights at a fluorescent quantum. In the triplet state, the molecule remains for a longer period (Hellmans A., B. Bunch, 1998).

Experimental measurements of luminescence

After executing the electron at room temperature, a part of the energy is lost in the heating and the molecule passes to the lowest sublevel of oscillations, from which the luminescent quantum starts irradiating. No matter how many electrons and the wavelength (λ) they get excited by, the luminescence starts at the above mentioned sublevel. Here, it's the fair Vavilov's law: "the luminescence does not depend on the characteristics of the quantum absorbed by the molecule." The radiation transition in the molecule, also occurs at different sublevels of the fundamental level. Because of the loss of a unit from the energy absorbed in heating, the energy value of the luminescent quantum is smaller than the absorbed one, corresponding to the luminescence spectrum and will permanently be situated in the large wavelength in regards to the highest maximum absorption wavelength. Since the oscillating configuration of the molecules coincides, even in the excited electronic state, it is clear that the absorption and luminescence spectra are symmetrical in dependence on the wavelength corresponding to the electronic transition (Atanasiu V., 1970). The luminescence spectra represent the intensity dependence curb of luminescence intensity in the wavelength or frequency.

$$d\tau / d\lambda = f (\lambda) [\tau] = [j] = [n \times hv]$$

The influence of temperature on luminescence

When measuring luminescence at low temperatures, close to liquid nitrogen temperature, a deceleration of biochemical processes occurs and thus the compound is guarded by the photochemical action of light intensity excitation. Low temperature spectra analysis allows to obtain new information about the properties of the substance and its status in the composition of the medicinal preparation. Increasing the drug temperature leads to the decrease of luminescence intensity. The decrease of temperature leads to the increase in fluorescence of the compounds with a weak luminescence at room temperature. Low temperatures better highlight the fine structure of luminescence spectra and besides fluorescence, phosphorescence appears. The upper limit for shorter wavelengths belongs to the fluorescence, and the long-wave maximum sites belong to the phosphorescence.

Luminescence excitation spectra

If the fluorescent object glows with monochromatic light, then, the intensity of the fluorescence will be different from different wavelengths. This is linked to the fact that the fluorescence intensity depends on the intensity of the exciting light which falls on every wavelength and the degree of absorption of this excitation light.

nfe = n0 (1- T) φ; nfe/n0 (1- T) φ

n0 - the intensity of the exciting light at a given wavelength; (1-T) - the light absorbed by the substance; φ - quantum of light output

nfe the total intensity of the fluorescence of the excited substance at a given wavelength. Luminescence excitation spectrum is called the curve dependence nfe/n0 of λ light excitation nfe/n0 = f (λ). From the relation (1) for φ = constant results that the excitation spectrum coincides with the absorption spectrum of the substance. At low absorptions (1- T) ~ D, where D - optical constant. Therefore, in the case of diluted solutions, diluted and individual substances at a suitable choice of calibration of the excitation spectrum coincides with the absorption spectrum. At a total absorption of light by excitation - (1-T) = 1 in this case means that the excitation spectrum φ (λ) represents dependence (Atanasiu V., 1970).

Luminescence analysis of food products

The luminescence analysis is used for sorting food products, seeds, roots. According to the luminescence color of food products, food spoilage can be seen beginning long before it is seen in an ordinary light, so it gives the possibility of long-term storage of products and is useful for the canning process. This way, the analysis methods are simple and accessible to everyone. They are reduced to the illumination of the analyzed product by UV or with shortwaves. To analyze the products, sunlight is also used, in these cases the products are arranged in solar light scope. Thus decay is detected in cucumbers, potatoes and other vegetables and fruits. This way, quality vegetables differ from those vegetables that are attacked by mold and frost (Krumbach W. C., et al., 1998). Example: therefore, fresh mandarin oranges possess a dark orange luminescence, and tangerines attacked by unnoticed to the naked eye mold illuminate the places attacked with a blue light. With the help of luminescent methods other food products can be analyzed. Thus, according to the luminescence color, the quality of the flour can be determined. The more grain it contains the more intense the luminescence becomes, which changes from bluish to dark bluish. Illuminating the products with UV rays, a control is be conducted of products such as: eggs, milk, egg powder and other products.

RESULTS AND DISSCUSIONS

Wheat flour

The luminescence spectra and luminescence excitation of rye whole flour were calculated at liquid nitrogen temperature for freshly milled flour, stored at room temperature for a year. It was found that the luminescence spectra of freshly ground rye flour out at 313nm, consisted of two strips of irradiation at 405 and 420nm (Fig. 1, curve 1). Such strips of irradiation, which peak at 77K so are within 405-420nm wavelength, lie in on the luminescence spectra of unsaturated fatty acids in their first stage of fermentation, and according to their formation and others, luminescence excitation spectrum of freshly ground product such as: whole flour rye, brought out at 405 nm, that peaks near 210, 325 and 55nm, and so on, corresponds to that of the original spectra of the fermented products of unsaturated fatty acids. Accordingly, it can be considered that a great contribution in both luminescence bands of radiation, appeared on the luminescence spectra on studied examples, of freshly ground products, the rye flour, shown above, excitement of wheat acids investigated in the process of conservation and practically totally switches in the milled rye flour (Sears F.M., M.W. Zemansky, H.D. Young, 1983). Measured after storage, during the year, in the same conditions of excitation of luminescence, the luminescence spectrum of the samples studied of rye flour consists of a single unstructured strip located at 435nm (Fig. 4, curve 2). On the luminescence excitation spectrum of the studied examples, took out at 435nm, there is a single strip of excitement, located near 365nm. The analysis of experimental data obtained, shows with the help of spectral luminescent characteristics calculations of grain products in the process of their conservation, we can appreciate the degradation of lipid fractions and thus can appreciate the quality and duration of storage of these products under the given circumstances (Budan Constanţa, 1996).

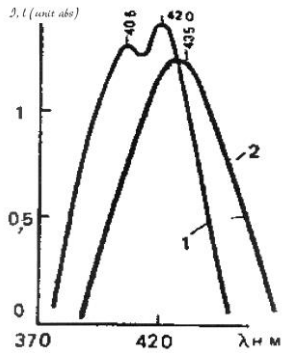

Figure 4. Luminescence spectra of wheat flour;

1 - fresh flour; 2 - after storage

Maize flour

Spectral - luminescent characteristics of moldy maize flour were determined in the temperature range of 77 - 300K after the immediate excitement of luminescence. The luminescence spectrum of moldy maize flour, measured at room temperature, consists of a single strip of irradiation at 470nm (Figure 5, curve 5) in decreasing the temperature to 77K, the maximum of this spectrum is moving with 30nm in the short wave spectrum (Figure 5, curve 6). [15] On the luminescence excitation spectrum of moldy maize flour raised to 470nm, it highlights a peak at 380nm (Figure 5, curve 2). A similar maximum appears in the luminescence spectrum. The position of the occurred irradiation strips, corresponding to 300 and 700K in luminescence spectra of moldy maize flour, are characteristic for this product. Meanwhile, the luminescence spectra and excitation of normal and healthy maize flour luminescence spectra differ from moldy maize flour, so as the analog spectrum. Therefore, the normal and unaffected by different fungi maize flour luminescence spectrum is moved to the short wavelength compared to the moldy wheat flour spectrum at a 300K temperature, so as to 77K. In the first case, the amount of movement is 25nm, 10nm in the second (Fig. 5, curve 3 and 4 as appropriate). Moved by 20nm in the short wavelength the maximum luminescence excitation spectrum of normal and healthy maize flour, unlike the corresponding maximum moldy wheat (Fig. 5, curve 1 and 2 as appropriate).

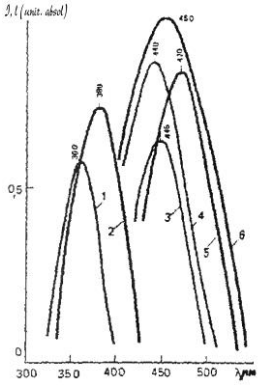

Figure 5. Luminescent Spectral characteristics of maize flour : I - II - luminescence excitation spectra; 1 - normal and healthy grain; 2 - moldy grain; 3-6 - luminescence spectra; 3 - normal and healthy grain (300K); 4 - normal and healthy grain (77K); 5 - moldy grain (300K); 6 - moldy grain (77K)

Vegetable oils

Vegetable oils can be used as ready food products and for the purpose of unfinished goods for the production of for example: margarine and other food products. Vegetable oils are added to food products (margarine, dairy products for nourishing children) in order to enrich primarily unsaturated fatty acids. That is, lots of oil containing vitamins (especially vitamins of the germ-rich grain). This is necessary to be taken into account in the production of food vitamins, this feature is considered in the adjustment of vitamins in the composition of dairy products for children, pointing to near their maximum biological effects. The luminescence spectral analysis of vegetable oils can be used to control the detection of the contents of active biological substances and for the determination of their state. As an example, at liquid nitrogen temperature luminescence spectra of vegetable oils (sunflower, cotton and palm) out at 313nm (Figure 6a) and 365nm (fig.6,b). From the figure it can be seen that the structure of the vegetable oils luminescence spectra (Fig.6, curve 1) and of cottonseed oil (curve 2), with the more complicated curve 3 of palm oil. That is, the luminescence of palm oil is calculated, in essence, only with the luminescence β - carotene (the palm oil contents is 0.05 0.2%). Indeed, at a temperature of 77K in the luminescence spectrum of palm oil, photographed at 365nm (Figure 6, curve 3) appear three radiation bands 420, 445 and 515nm, which coincide with the corresponding lines, as monitored at 77K temperature, on the luminescence spectrum of trans - β - carotene standard solutions. The wavelength of the excited light from which we calculate the luminescence spectrum of the palm oil investigated that is within the area of the total excited luminescence spectrum trans - β-carotene. Maximum luminescence excitation spectrum of this pigment is at 345nm. The structure of the luminescence spectrum of palm oil is measured at 313nm (Fig. 6, curve 3), is less than the characteristic structure discussed above. That is, this luminescence spectrum reflects a narrow structure near 515nm and a broad luminescence band structure within the wavelength 420nm to 44nm so the total luminescence coincides with Trans - β- carotene. Narrow structure near 405nm, is seen as such even on the luminescence spectra of palm oil brought to 313nm, can be registered, and the luminescence of acids contained in this oil is in the amount of 8-10%. Indeed the narrow line of excitation of acids (located at 310Nm) are distinguished by 3nm from the used wavelength of excited light, the high band of luminescence of such fatty acids located at 400nm. The luminescence of acids can be structured from shortwave luminescence spectrum of cotton and palm oil from which the content of these fatty acids makes up 31.8%. On this spectrum (Fig. 6, curves 1 and 2) besides the irradiation line at 405nm bands appear at 385nm coinciding with a more intensive irradiated stretch discovered on the luminescence spectra acid of these fatty acids at a temperature of 77K. The

last irradiation strip appears on the spectrum of the sunflower and cotton oil luminescence removed at 365nm (Figure 6 a, b, curves 1 and 2), and also, on the luminescence spectrum of the sunflower oil measured at 313nm (Figure 6 is a curve 1). Mixing them in the region of 5 nm with the comparing of the total corresponding solutions lines trans - β - carotene standards, may be called by the presence of sunflower oil and cotton fermented β -carotene products. Indeed, the fermentation of β - carotene aims at mixing the irradiated bands in this long waves region pigment. Therefore, based on the spectral luminescent analysis of vegetable oils measured at liquid nitrogen temperature for different light excitation wavelengths the identification of β - carotene and unsaturated fatty acids can be made.

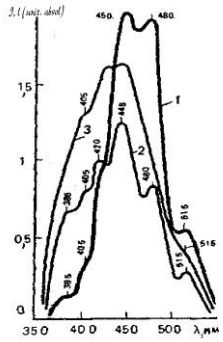

Figure 6.a. Luminescence spectra of vegetable oils: 1 - sunflower oil; 2 - cottonseed oil; 3 - palm oil

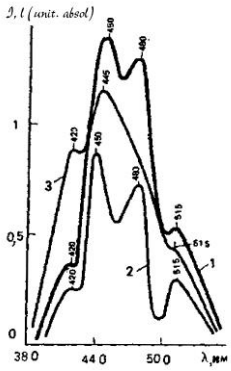

Figure 6.b. Luminescence spectra of vegetable oils: 1 - sunflower oil; 2 - cottonseed oil; 3 - palm oil

Food fat

The following examples of prepared food fat were carried out based on soy bean oil and soy fat, which were kept at a temperature of about 277K during 30 to 90 days. The luminescence spectra of these examples,

measured at a temperature of 77K to 313 and 365nm which are shown in Figures 7a and b accordingly. From the figure it can be seen that in the higher wavelength regions, 440Nm, the structure of the luminescence spectra of the studied sample, of culinary fats, similar practices, correspond to the occurred settlement in this spectral irradiance strip region, so does their intensity correlation. All moved irradiation strips in the long-wave region with the corresponding comparing radiation of soybean oil belts (strips 450, 485nm - to 5 nm, 530nm strip - at 15nm) (Fig. 7 a and b, Fig. 7 a and b - curve 1). Based on those mentioned above, it can be assumed that the main deposit in the luminescence irradiation culinary fats belts, located near 485nm, introduces fermented tocoferie, the highs of the irradiation strips which are located within the 77K temperature within the limits of 480-490nm wavelengths. The presence of culinary fat strips irradiation at 450 and 530nm on the luminescence spectra, mixed in the direction of long-wave corresponds to the total radiation belts of trans - β-carotene, may be incurred due to the existence in the study of the samples of culinary fats and fermented β-carotene products. Fermented foods β-carotene have a great contribution to the luminescence stripe at 425nm, appeared on the luminescence spectra of several samples of culinary fat (Fig.7 curve 1 and curve 2).

Thus it can be assumed that the fermentation tacoferolov and β - carotene products, emerged as well as in the food preparation, similar to preservation, in the first 30 days, do not support significant changes in the long storage that occurs without changes in the structure of these fats luminescence spectra in legions of wavelengths that exceeded 440Nm. On the other hand, the structure of the short wave spectrum of the luminescence spectra from fat for the stored samples between 30 to 90 days is different. At excitation light with 313nm this difference appears in the exchange process of storing the irradiation strips at 405 and 425nm, a great contribution is given by the unsaturated fatty acids and their products of fermentation (Figure 7 a, curves 1 and 2), while for the specimens that are kept 30 days, the intensity of these bands for irradiated specimens kept for 90 days is the same.

This can serve as a witness to increasing the degree of fermentation to preserve the control of fatty food samples for 60 days. As confirmation may serve the observed changes in the storage process the samples of culinary fats in the structure of short wavelength side of the luminescence spectra, taken to 365nm.

Thus, on the luminescence spectra samples kept for a period of 30 days appear intensity irradiation bands approximately equally placed at 425 and 435nm, a large contribution to the luminescence made by the fermented products of unsaturated fatty acids, corresponding to different depths of

fermentation reactions (Figure 7b, curve 1). In the short -wave luminescence spectrum of samples of fatty food kept over 90 days, there is only one strip of irradiation at 435 nm (Fig. 7 b, curve 2). [16]

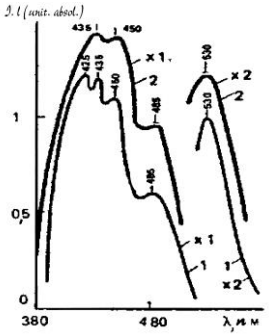

Figure 7.a. culinary fats luminescence spectra at π = 313nm; 1-30 days; 2-90 days

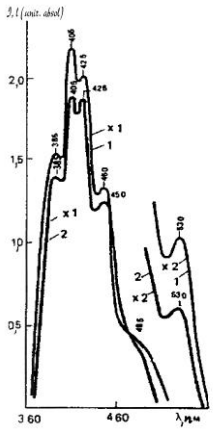

Figure 7.b. culinary fats luminescence spectra at π = 365nm; 1-30 days; 2-90 days

CONCLUSIONS

After analyzing the spectral - luminescent characteristics experimentally obtained at the facility for measuring luminescence and excitation spectra results the following: for fruit and apple juice we have the following results.

he results of the investigations it was established that depending on the duration of storage, the structure of luminescence spectrum strips changes. With the increase of shelf life, peak characteristics practically disappear, and luminescence intensity decreases.

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