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POSSIBILITIES OF USING FLUORESCENCE IN WINE RESEARCH

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Specific structure of fluorescence dye molecules may have an impact on their behavior in water solutions. It is possible that different water affinity of pigment molecules opposite ends (amphophility) may cause the densely packed and ordered, fluorescence layer on the solution free surface. The authors considered the possibility of the occurrence of such a phenomenon in the paper. The paper presents results that can confirm the thesis that flavonoids and anthocyanins contained in wine have a tendency to concentrate on the wine's surface, thus creating a layer. Clear, stable and repeatable spectra of wine surfaces have been obtained.

INTRODUCTION

Measurements of solution fluorescence are difficult [Kawski, 1992]. Single molecules with fluorescence properties are distributed among a large number of molecules which do not react with light, which causes relatively low fluorescence efficiency of solutions. Additionally, chaotic, thermal movements of pigment molecules cause fluctuations of emitted light intensity and the Doppler Disarray of the spectra obtained. Moreover the interpretation of solution fluorescence measurements is difficult due to such phenomena as: re-emission and re-absorption. Traditional approach to measure fluorescence of solutions which are so absorbent (red wine) could not give satisfactory results. However, fluorescence of wine surface is quite interesting. But it is more important that surface-fluorescence light is emitted directly from components of wine (flavonoids) which have a positive impact on human health [Campos & Lissi, 1996]. The objective of this work was to determine the usefulness of a new method of fluorescence measurement in wine research.

PHYSICAL BASE OF CONCENTRATION AND LONG--RANGE ORDERING OF PIGMENT MOLECULES ON SURFACES OF LIQUID SAMPLES

There are fluorescence dyes whose molecules have amphophilic structure, *i.e.* their ends have different water affinity. Flavonoids are such ones. These are specific substances of plant origin which are common in natural wines [Ghiselli *et al*., 1998]. The presented molecule of flavon pigment has the opposite ends with different chemical affinity towards water (Figure1). There is a hydrophobic phenyl group at the upper end of this molecule, while at the bottom there are hydrophilic hydroxyl groups. Molecules of such a structure are called amophilic. They can be found in wine - water solution with strong polar properties. Thus the above described flavonoid molecule structure may explain their concentrations on the free surface of samples (Figure 2). Densely packed molecules on the wine's surface may result in the creation of a long-range ordered structure, similar to a mono-

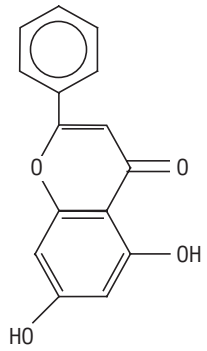

FIGURE 1. Flavon molecule.

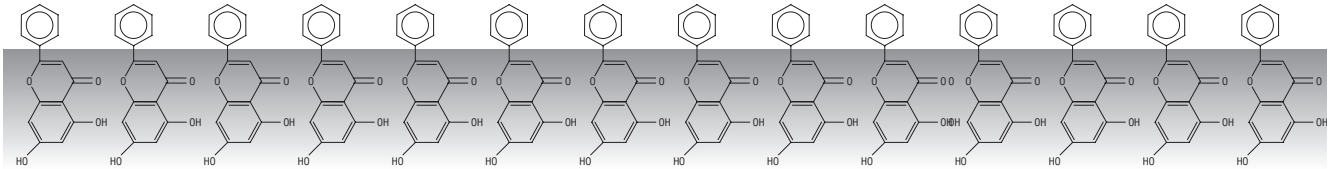

FIGURE 2. Flavon molecules on the surface of wine.

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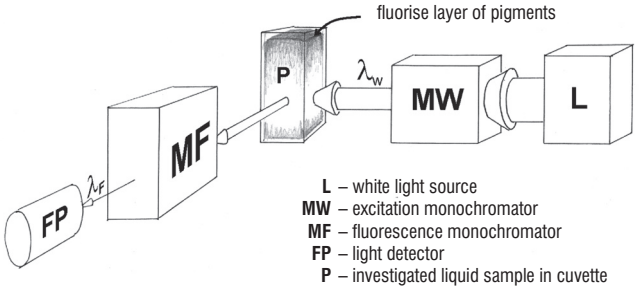

FIGURE 3. Fluorescence measurement with traditional method.

layer of smectic liquid crystal [Adamczyk, 1983]. Such natural transfer of amphophilic molecules of fluorescence dyes towards the surface may result in a failure to apply the traditional techniques to measure in wines (Figure 3). The measurement space of the available spectrofluorimeters and laboratory setups known to the authors do not cover the free surface of liquid samples. The presented modification of fluorescence measurement involves the change in geometry of its excitation and registration [Przybyłowski & Gębala, 2004]. The horizontal layer of fluorescence dyes on the free sample surface is excited vertically downwards, and the excited fluorescence radiation is registered from the top (Figure 4).

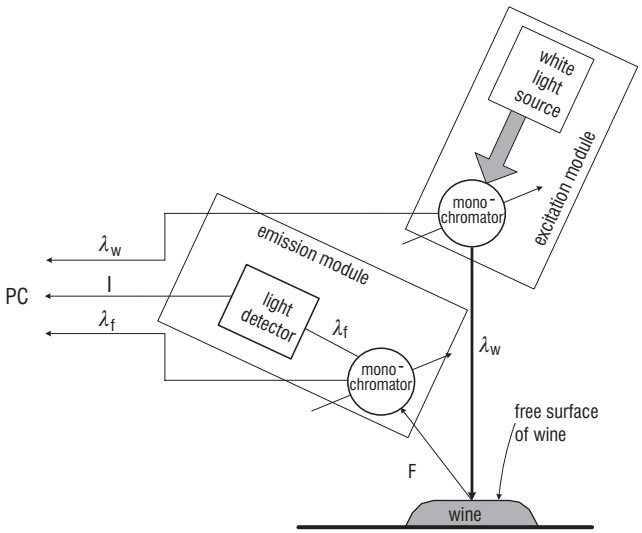

FIGURE 4. The new conception of fluorescence measuring.

MATERIALS AND METHODS

During the studies a "Fluorat-02-Panorama"-spectrofluorimeter made by "Lumex" was applied for measurements. In accordance with the new measurement idea a special adapter was made [Gębala, 2005], which facilitated the change in directions of fluorescence excitation and registration (Figure 4). The samples of unprocessed wine were placed in the adapter. If its objective was placed over the wine surface, a light of fluorescence from above sample F_{p+g} was analyzed. On the other hand, the apparatus analysed the fluorescence light from depth of the wine sample F_g, when the objective was placed under that surface. Then the samples of wine were excited with radiation of wavelengths changing from 210 to 550 nm, every 1 nm. The fluorescence intensity was measured for wavelengths higher by 80 nm, *i.e.* from the range between 290 and 630 nm. During each measurement the position of the excitation monochromator and registration monochromator were synchronized and always varied by 80 nm. The measurement results were stored in a computer and presented as two-dimensional synchronous spectra plots with 80 nm offset.

Fluorescence of 13 wine samples from different regions of the world and from years 1985–2004 was measured. There were samples of red (7), white (5) and rose (1) wine (Table 1).

RESULTS AND DISCUSSION

The measurement setup was built in accordance with the presented idea (Figure 4). It is designed to measure the sum of intensities of two fluorescence radiation fluxes: one – from the wine sample surface and the second – from the depth *(F_g)*.

$$F_{p+g} = F_p + F_g$$

TABLE 1. Wine sample origin.

Wine	Region	Kind	Importer
Rosso	Italia, Pirovano	red	Win – Cin Sp. z o.o., Olsztyn
Stony Cape	South Africa, Cisnault	red	Win – Cin Sp. z o.o., Olsztyn
Castillo del Llano	Spain, Valencia	red	Win – Cin Sp. z o.o., Olsztyn
Gato Negro	Chile, Central Valley	red	Żywiec Trade Sp. z o.o.
Kolkhida	Georgia, Eastern Georgia	red	WGM Sp. z o.o., Milanówek
Chabret	France, Illzach	red	Win – Cin Sp. z o.o., Olsztyn
Castillo Augustino	Spain, Valencia	red	Win – Cin Sp. z o.o., Olsztyn
Chabret	France, Illzach	rose	Win – Cin Sp. z o.o., Olsztyn
Tokaji	Hungary	white	
Ananas de oro	Spain, Valencia	white	AN.KA. Dystrybucja Sp. z o.o.
Furia	Argentina, Finca la Celia	white	Żywiec Trade Sp. z o.o.
Rudorfer	Italia, Selezione Ruvina	white	Win – Cin Sp. z o.o., Olsztyn
Vilarica	Chile, Central Valley	white	TIM S.A., Bielsko-Biała

The measurement of fluorescence radiation intensity at different wavelengths provides information on fluorescence spectra *(F(λ))*. The spectra are illustrated with diagrams.

$$F_{p+g}(\lambda) = F_p(\lambda) + F_g(\lambda)$$

The graph of fluorescence spectrum of the surface $F_p(\lambda)$ is thus the difference between the fluorescence spectrum graph $F_{p+g}(\lambda)$ and the spectrum graph $F_g(\lambda)$ of the same sample, obtained in a traditional way.

$$F_p(\lambda) = F_{p+g}(\lambda) - F_g(\lambda)$$

The surface fluorescence spectrum was obtained in the form of differential spectrum using the standard computer software.

Figure 5 presents the above discussed diagrams of the following spectra: fluorescence measured with the apparatus objective placed over the wine surface $(F_{p+g}(\lambda))$, fluorescence measured with the objective placed under the surface $(F_g(\lambda))$ and fluorescence from the surface of white wine $(F_p(\lambda))$. Figure 6 presents the same spectra obtained for rose wine. Similarly for red wine (Figure 7) fluorescence was measured over the sample surface, below it and the fluorescence of the surface itself was determined. Different shapes of fluorescence measured from above and from underneath the surface for three samples of different kinds of wine and similar shapes of the calculated surface fluorescence spectra can be seen. The presented diagrams indicate that fluorescent layers on wines free surface are existing and

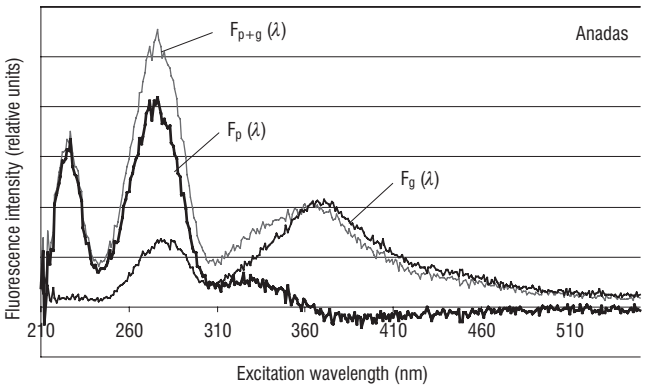

FIGURE 5. Fluorescence spectra of white wine registered above the sample surface ($F_{p+g}(\lambda)$), under the surface ($F_g(\lambda)$) and the calculated surface fluorescence spectrum ($F_p(\lambda)$).

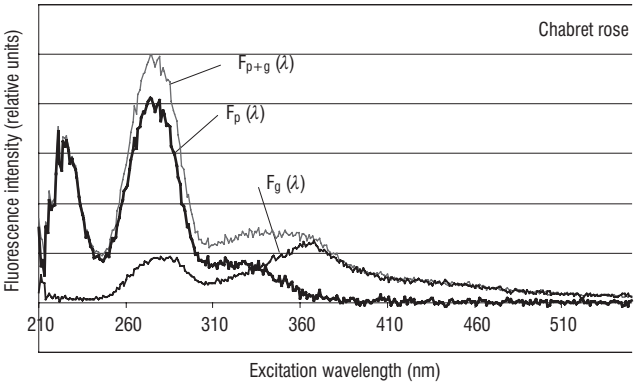

FIGURE 6. Fluorescence spectra of rose wine.

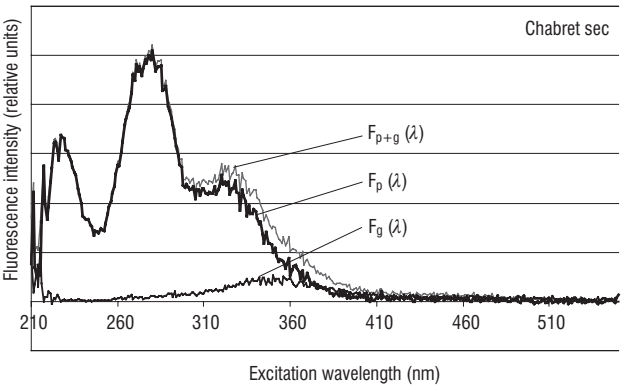

FIGURE 7. Fluorescence spectra of red wine.

that the layers of pigments are more effective on the surface of darker wines. Also the repeatability of spectra of the same sample and smooth plots which indicate small fluctuations during the measurement are presented. These features may be important for the applications of the new fluorescence measurement techniques. These surface fluorescence features may be important for their further application.

CONCLUSIONS

1. The presented spectra diagrams received the physical model created for the interpretation of the fluorescence of wine surface and justify the created innovated measurement setup solutions.

2. Dynamic and diversified shapes of synchronous plots of fluorescence spectra of wine surface can indicate that these spectra carry important information regarding the characteristic, qualitative wine features.

3. It is likely that the presented method of surface fluorescence measurement may become a basis for fast analytical methods which do not require time consuming and often costly preparation of samples.

4. The described method of surface fluorescence measurement may be used in wine traceability.

5. This method may also become a basis for fast analytical methods to determine the contents of fluorescent amphophilic molecules in liquids.

REFERENCES

1. Adamczyk A., Ciekłe kryształy. 1983, *in*: Encyklopedia Fizyki Współczesnej, PWN, Warszawa, pp. 489–499, (in Polish).
2. Campos A.M., Lissi E.A., Total antioxidant potential of Chilean wines. Nutr. Res., 1996, 16, 385–389.
3. Gębala S., Fluorescence of free surface of rheological water solutions. Zeszyty Naukowe Akademii Morskiej w Gdyni, 2005, 54, 53–61 (in Polish; English abstract).
4. Ghiselli A., Nardini M., Baldi A., Scaccini C., Antioxidant activity of different phenolic fractions separated from an Italian red wine. J. Agric. Food Chem., 1998, 46, 361–367.
5. Kawski A., Fotoluminescencja roztworów. 1992, PWN Warszawa, (in Polish).
6. Przybyłowski P., Gębala S., A device for fluorescence measurement from the free surface of samples. 2004, Polish patent No. P 366567 (in Polish).

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MOŻLIWOŚCI WYKORZYSTANIA FLUORESCENCJI W BADANIACH WIN

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Amfofilna budowa cząsteczek niektórych barwników może być powodem ich samoistnej koncentracji i gęstego upakowania na powierzchni swobodnej roztworów. Autorzy potwierdzili występowanie tego zjawiska w winach. Przedstawiono rezultaty potwierdzające tezę, że w winach występują barwniki fluorescencyjne, mogące tworzyć powierzchniowe warstwy uporządkowane. Przedstawiono stabilne i powtarzalne widma fluorescencji powierzchni win.