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Some limitations using optical sensors for determination of dissolved oxygen in wine

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Ru(II)-tris (4,7-diphenyl-1,10-phenanthroline) dichloride immobilized in matrices from sol-gel produced SiO_2, SiO_2-citric acid/ethylene glycol polyester hybrid or poly (methylmetacrylate) is explored as a sensor for determination of dissolved oxygen in white and red wines. The significant overlapping of the 612 nm spectral bands of the oxygen-sensitive chromophore with the analyzed products band imposes the necessity of accounting for the impact of the latter in the analysis. The SiO_2-based composite is rather sensitive to the prolonged action of wine causing a disturbance of the linearity of the Stren-Volmer dependence and significant decrease of the respective constant.

Key words: optical oxygen sensors, wine, Ru(II) complexes, immobilization matrices, Stern-Volmer constant, fluorescence microscopy.

INTRODUCTION

The control of the dissolved oxygen content is of primary importance for optimal processing of a number of fermentation processes in food industry. Few parameters responsible for beer quality (alcohol concentration, colloid stability, taste) as well as technological losses are determined by the oxygen content during and after fermentation. What is more, both low and high concentrations of oxygen are damaging. Optical oxygen sensors based on the quenching of the luminescence of Ru(II)-tris (4,7-diphenyl-1,10-phenanthroline) dichloride (Rudpp) immobilized in sol-gel prepared SiO_2 can be successfully used for monitoring oxygen concentration in the product [1].

Oxygen content is of crucial importance for the quality of wine. It has to be minimal and constant. In the excess of oxygen, color darkening, microflora propagation, flavor loss, and accelerated aging are observed. In the same time, especially red wine needs some amount of oxygen in the course of the fermentation. The increased oxygen content is necessary when H_2S is formed in the new wine and at appearance of an unsavoury tannin taste immediately after fermentation. In such a case, however, the oxygen concentration must not increase after bottling. The oxygen content has to be known for the precise dosage of the necessary H_2SO_3.

It is accepted that the optimal oxygen content in the wine at the moment of bottling has to be 0.2–0.6 or, at least, <1 mg/l, ensuring complete and optimal fermentation, good stability and optimal "fragrance profile" of the white and rose wines, stable color of the red ones, low content of the antioxidant H_2SO_3 [2]. A review of the role of the dissolved oxygen in wine production is presented in [3].

Along with the electrochemical sensors, optical sensors for determination of the oxygen content in wine are already commercially available [4, 5] due to their advantages: no calibration and spare parts are need, no polarization (specific for the electrochemical devices) takes place [2]. The interval of determination is 0.00–20.0 mg/l at a resolution of 0.01 or 0.1 mg/l; precision is ±1 % of the full scale.

Optical oxygen sensing is usually based on collision quenching by molecular oxygen of a fluorophore embedded in a support matrix. The quenching process is described by the Stern - Volmer equation $I_0/I = 1 + K[O_2]$, where I_0 and I are the emission intensities in the absence and presence of oxygen, respectively, $[O_2]$ is the concentration of O_2 and K – the Stern-Volmer quenching constant. Rudpp is, so far, the most often used chromophore due to the sensitivity of its red emission intensity (when irradiated with blue light) to the O_2 – content. The immobilization matrix has to satisfy two contradictory requirements – to ensure strong enough entrapping of the dye and, in the same time, to allow the smaller analyte species to diffuse into the matrix and to interact with the fluorophore. So, the matrix properties are of crucial importance for sensor sensibility, detection limit, calibration stability, areas of application and exploitation life.

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Apart from some technical data given in the production lists of the respective firms-manufacturers, literature data on the peculiarities of optical oxygen sensing in wines are rather limited. It is reported that Ru- [4] and Pt- [6] compounds are used as oxygen sensitive dyes. HIOXY type of sensor [5] with not-disclosed type of coating is recommended for monitoring oxygen in non-aqueous vapors and solutions. The sensor coating chemistry is described as ideal for use with oils, alcohols and hydrocarbon-based vapors and liquids. Polymerized sol gel coating is used in [6].

The applicability of the optical sensors to such an analytical object as wine is determined, besides the principal requirements to this type of sensors (sensitivity of the signal to the oxygen content, linearity of the Stern-Volmer dependence), by few peculiarities of the system: possible overlapping of the emission of the wine with the fluorescence signal of the optically active dye, rather low optical transparency of the red wines, stability of the complex doped matrix to the action of the analyzed medium. The present paper is a step in elucidating the influence of these factors on the optical measurement of dissolved oxygen in wines.

EXPERIMENTAL

Bottled dry red and white wines were analyzed immediately after the bottle opening.

The analysis were performed with films (deposited by dip-coating) containing Rudpp, immobilized in three types of matrices, consisting of sol-gel produced SiO_2, inorganic-organic hybrid (prepared by the simultaneous hydrolysis of tetraethoxysilane, esterification of the hydrolysed product with citric acid and esterification between the latter and ethylene glycol) and of poly(methylmetacrilate). Methods for production of the films are described in [7-9].

The photoluminescent response of the fabricated films to oxygen in liquids was measured by a Cary Eclipse (Varian) device. Due to the significant optical density of the red wines the spectral measurements were done in 1 mm-cuvette.

The relative mean square deviation of the photoluminescent signal intensity (determined by measuring of 5 parallel water samples containing $7.3.10^{-4}$ % O_2) is 0.5 %. The oxygen-free liquids were prepared by bubbling high-purity N_2 for 90 min through the pre-boiled water put in a closed vessel with a hydraulic gate, and fully oxygenated ones – by bubbling O_2 for 50 min through ice-cold liquid put in the same vessel.

The effect of the soaking of the SiO_2-based films in wine or other aggressive medium was evaluated by their performance in oxygen content measurement in gaseous phase. The photoluminescence response to oxygen was measured by the equipment described in [7] under illumination by blue LEDs with maximum of the spectral output band at 450 nm.

RESULTS AND DISCUSSION

1. Influence of the analyzed sample emission on the spectrum of the sensor film

The spectra of the films made from the above mentioned types of matrices and immersed in the analyzed wines are compared with the spectra of the analyzed samples (Fig. 1) in the spectral region of interest around the maximum in the Rudpp emission spectrum (612 nm).

Table 1. Ratios of the areas of the spectral bands at 612 nm of the wine and of the chromophore immersed in the same wine

Matrix	Wine	Ratio, %
SiO_2	red	13.4
	white	2.2
Hybrid	red	15.8
	white	8.0
PMMA	red	14.1
	white	12.2

Table 1 presents the ratios of the areas of the spectral bands at 612 nm of the wine and of the chromophore immersed in the same wine. The integration is performed in the wavelength interval 550-800 nm. It is seen that the overlapping is lowest for the SiO_2-based matrix due to the higher photoluminescence intensity obtained applying this matrix. The difference with other matrices for the analyzed red wines is <18 %. As can be expected the overlap for white wine is smaller but the differences between the different matrices are much stronger expressed.

2. Some peculiarities of O_2-sensitive films performance in wines

Influence of the film thickness on the fluorescence intensity. Table 2 presents data for the intensity of the main emission band (around 612 nm) of Rudpp immobilized in SiO_2 in few wine samples (with different oxygen content) in dependence of the film withdrawal rate in the course of its preparation. It is seen that with the increase of the film thickness a slight (approx. 5-6 % for samples 1-3) decrease of the fluorescence

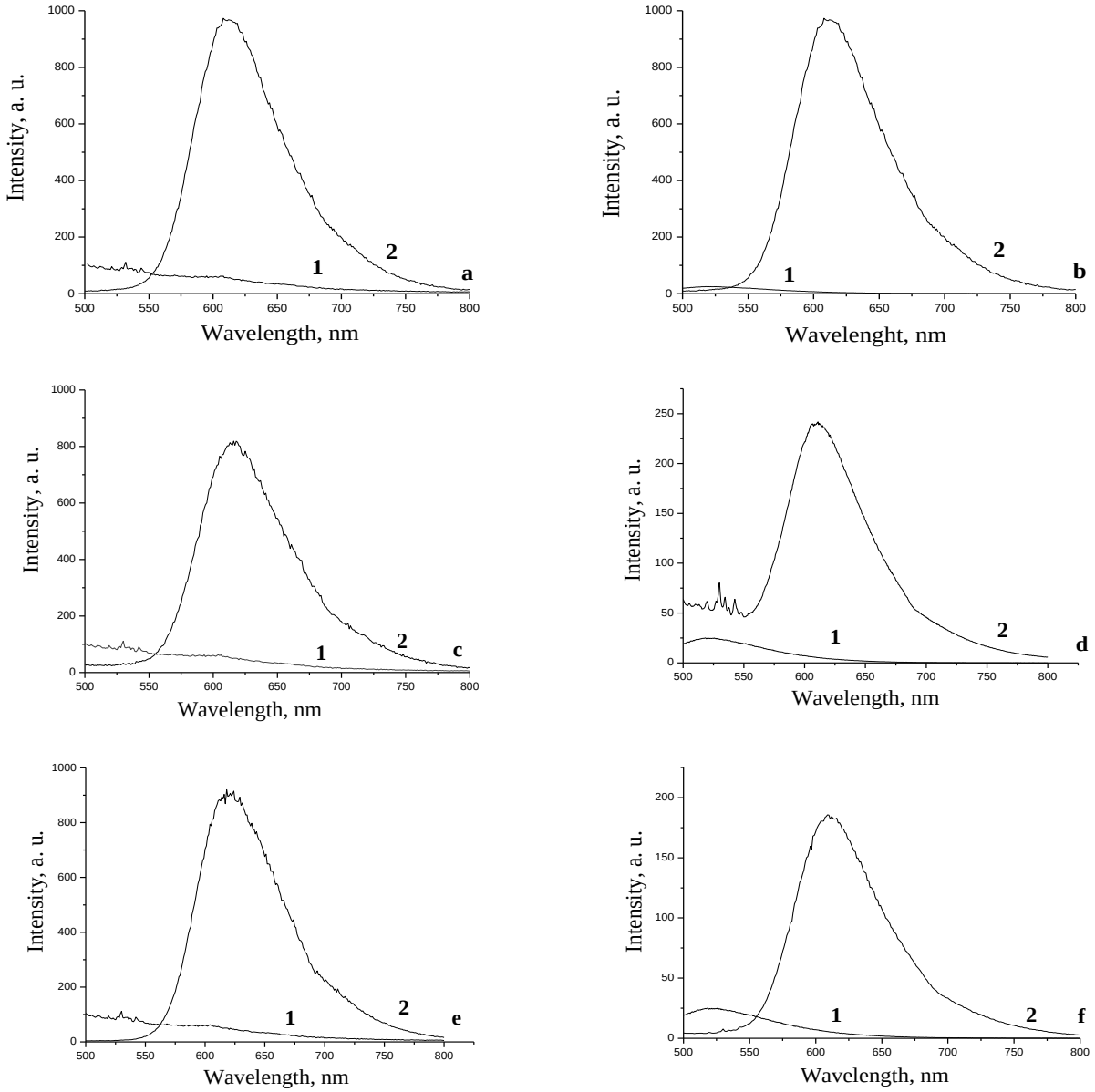


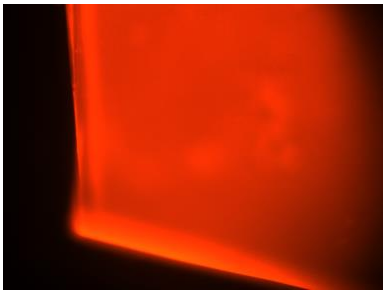
Fig. 1. Emission spectra of analyzed wines (1) and of Rudpp (2) in matrices from SiO_2 (a, b), hybrid (c, d) and from PMMA (e, f) immersed in red (a, c, e) and white (b, d, f) wine.

Table 2. Dependence of intensity (I) of the fluorescence at 612 nm of red wine samples with different oxygen content on the film thickness.

Film withdrawn rate, mm/s	I (arb. units), sample			
	1	2	3	4
0,015	79.5	84.4	95.5	111.5
0,75	76.0	78.8	91.8	99.1
[I(0,015)-I(0,75)]/I(0,015), %	4.4	6.6	5.3	11.1

intensity is registered. In some cases (sample 4) the effect is significant. It has to be mentioned that the data are related to films with rather great difference in the thickness, not commonly occurring in the practice. The typical withdrawal rate used for such films preparation (as well as in the present work) is 0.4 mm/s leading to a thickness of about 300 nm.

In a thicker layer, more chromophore molecules are available. Accounting for the high surface porosity of the dip-coated films (observed in the morphological study [11]) it can be expected that they can be reached by the analyte molecules and the quenching effect will be more pronounced.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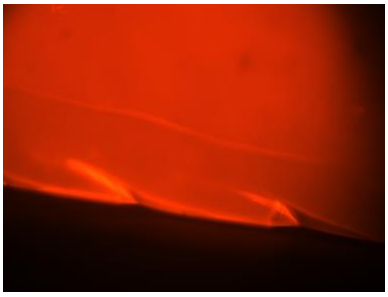
(2)

Fig. 2. Fluorescence microscopic images (x160) of Rudpp-SiO_2 after 330 h storage at 0 ^oC in white (1) and red (2) wine.

Table 3. Stern-Volmer constant (for hybrid matrix) and dissolved oxygen content in wine and distilled water

Sample	Dissolved oxygen content, ppm			Stern-Volmer constant	
	Without treatment	After bubbling with O_2	After bubbling with N_2	Value, $n.10^{-3}$ ppm^{-1}	Correlation coefficient*
Water	2.24	10.88	1.60	20 [8]	0.982
White wine	2.01	5.87	1.65	15	0.982
Red wine	2.04	5.56	1.46	22	0.979

* Linear fit.

Stern-Volmer relation. The data in Table 3 show that no significant difference exists in the linearity of Stern-Volmer dependence for distilled water and wines and in the values of the Stern-Volmer constant as determined by the O_2-sensitive film based on hybrid matrix [8]. So, it can be expected that the sensitivity of the determination of O_2 dissolved in wines will be of the same order as in distilled water.

Content of dissolved oxygen in wine. The data from the analysis of the oxygen content in red and white wine (as supplied or after bubbling for 1 h with O_2 or N_2) are compared with parallel analysis of distilled water treated in the same way (Table 3). The measurements are performed by the hybrid-based matrix [8]. The results show oxygen concentration in the analyzed samples (~2 mg/kg), approx. 2 times higher than the admissible one. As far as no special precautions are taken, the increased content may be due to the oxygen enrichment of the sample during the measurement. It is found that bubbling with N_2 leads to an oxygen concentration decrease with ~25 %. It seems that oxygen saturation of the studied wine samples at ambient temperature is reached at 5.5-6 mg/kg, i.e. the oxygen solubility in these types of wine is approximately twice lower than in water at the same temperature. It could be supposed that salting out action of species dissolved in wine is (at least, partially) responsible for this effect.

3. Stability of the Rudpp-SiO_2 composite on the wine action

The test was carried out by soaking of the studied films in red and white wine, stored at ~5 ºC (to avoid fermentation) for 384 h and compared with the effect of dilute HCl. The effect is evaluated through the influence on the value of the Stern-Volmer quenching constant Ksv. The value of Ksv determines the sensitivity and the detection limit of the analytical method. The data in Table 4 (see also [10]) show that the effect of the wine is much stronger than that of a hydrochloric solution with similar pH at higher temperature (the difference between the later and the value for fresh film is within the errors limit). The reasons for this strong effect are to be elucidated.

Table 4. Influence of the storage (384 h) in acidic media on the Stern-Volmer constant (Ksv, gaseous phase) of Rudpp-SiO_2 films

Aggressive medium	Correlation coefficient	$Ksv.10^{-3}$ $\%^{-1}$
Fresh film	0.994	28.3
HCl, pH 4.0,21 ^oC	0.914	30.9
Red wine, pH 3.6, ~5 ^oC	0.982	2.5
White wine, pH 3.6, ~5 ^oC	0.994	2.4

The fluorescence microscopy reveals some disruption of the sensor membranes surface after soaking in wine. The spots with paler color (Fig. 2) suggest some leakage of the chromophore. Such defects can explain the disturbance of the linearity of the Stern-Volmer dependence seen on Fig. 3 and the decrease of the correlation coefficients for linear fit of the experimental data (Table 4). It is known that surface non-homogeneity of the optically active film is one of the main reasons for the non-linearity of the dependence and the low value of the Stern-Volmer constant [7].

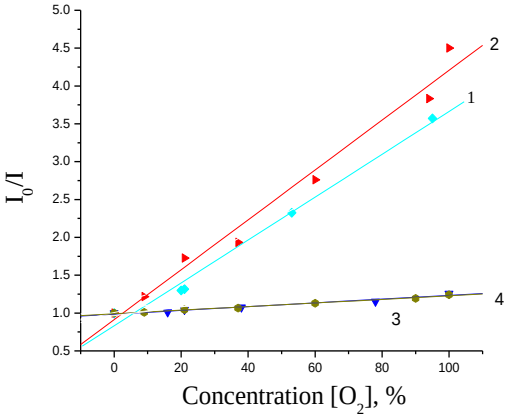

Fig.3. Stern-Volmer dependence (gaseous phase) of Rudpp-SiO_2 films: initial film (1), the same after storage for 384 h in HCl, pH=4, 21 ^{0}C (2), red (3) and white (4) wine (~5 ^{o}C).

CONCLUSION

The reported results lead to the following conclusions:

Microcomposites based on Ru(II)-tris(4,7-diphenyl-1,10-phenantroline) immobilized in matrices of sol-gel produced SiO_2, SiO_2-citric acid/ethylene glycol polyester and poly(methylmetacrylate) can be used for determination of oxygen dissolved in white and red wines. The significant overlapping of the spectral bands of the analyzed product and of the oxygen-sensitive chromophore imposes the necessity of accounting for the impact of the sample own emission in the analysis, i.e., the calibration of the sensor should be made in the same wine with controllable oxygen content. The use of SiO_2-based matrix is advantageous from this point of view because of smaller overlapping.

The value of the Stern-Volmer constant for the hybrid film immersed in wine is of the same order as for distilled water.

The SiO_2-based microcomposite described in this work is not suitable for continued measurement of oxygen in wine due to the relatively fast worsening of its functional properties under the action of the analyzed medium. Further evaluation of the applicability of the hybrid matrix from this point of view has to be done.

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НЯКОИ ОГРАНИЧЕНИЯ ПРИ ИЗПОЛЗВАНЕ НА ОПТИЧНИ СЕНЗОРИ ЗА ОПРЕДЕЛЯНЕ НА РАЗТВОРЕН ВЪВ ВИНО КИСЛОРОД

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(Резюме)

Ru(II)-трис(4,7-дифенил-1,10-фенантролин) дихрорид, имобилизиран в матрици от SiO_2, хибрид, състоящ се от SiO_2 и полиестер на лимонена киселина с етилен гликол или от поли(метилметакрилат) е изследван като сензор за определяне на кислород, разтворен в бели и червени вина. Значителното припокриване на спектралната ивица при 612 nm на кислородно-чувствителния хромофор със собствената ивица на анализирания продукт налага необходимост от отчитане на влиянието на последната при анализа. Композитът, базиран на SiO_2 е твърде чувствителен към продължително действие на виното, което води до нарушаване на линейността на зависимостта на Stren-Volmer и значително намаляване на стойността на константата на Stren-Volmer.