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UV monitoring of sugars during wine making

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Abstract

A UV/UV system for the spectrophotometric determination of sugars during wine production is described. The methodology is based on the formation of a UV-absorbing byproduct produced by the photodegradation of sugars. Under the given experimental conditions, the influence of increasing the amount of acids and alcohol is negligible. The measurement by UV/UV is compared with FTIR as reference method and validated according to the French norm AFNOR XPT 90 210. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: UV monitoring; Sugar content; Wine making

1. Introduction

The determination of sugars is usually required by the wine industry during production of wine. It is important for routine quality control to follow the fermentation process and also to check the conformity to the requirements of certain types of wine.[1] The evolution of sugar concentration or sugar content is also studied during the aging of wines.[2] Numerous works have reported analytical methods for the measurement of sugars, as for example the redox titration reference method,[3] liquid chromatography,[4–6] electrophoretic methods[7] or flow injection analysis[8–10] as an alternative for automation.

On the other hand, UV spectrophotometry is used as a detection method coupled with separation techniques (HPLC), or directly for the quality control of water and wastewater, for the expression of global and specific parameters of water pollution such as total organic carbon (TOC) and dissolved organic carbon (DOC) or nitrate.[11–13] UV has also been described as an interesting tool for the monitoring of an organic photochemical reaction.[14]

In this paper, the monitoring of wine production by UV spectrophotometry is described. It is based on a UV/UV procedure (UV pretreatment + UV detection) which is a homemade system developed in previous work[15] and currently being industrialised. This system has demonstrated its effectiveness for the determination of specific parameters in wastewater: Kjeldahl nitrogen,[16] ammonium nitrogen,[17] total phosphorus.[18] The UV/UV procedure is applied in this work for the determination of sugars during wine making. Global sugars values obtained by the UV/UV method are compared with those obtained by FTIR analysis used as reference method.

2. Experimental

2.1. Apparatus

The UV/UV device was composed of a UV light source (for UV photodegradation) and a UV detector (for on line UV measurement). The UV source was a low-pressure mercury lamp (main emission at 254 nm), and the UV detector was an Anthelie (Secomam) UV/vis spectrophotometer controlled by a Dathelie version 4.1f software. The pathlength of the Suprasil quartz cell was 10 mm, and the scan speed was 1800 nm min^{-1}. Although FTIR spectroscopy is not yet accepted as an official method in wine analysis, it was used as a comparative method because it is a widespread analytical technique, and, moreover, has been used by the

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wine expert who supplied data for comparison. Spectra were acquired between 650 and 3000 cm^{-1} with a Spectrum One™ FTIR (Perkin–Elmer) equipped with an ATR cell and controlled by Spectrum One software. The technique was calibrated versus the sum of several sugars (glucose, fructose, sucrose).

2.2. Reagents and solutions

Buffer solution (pH 9): sodium tetraborate decahydrate (Aldrich), 38 g dissolved in 800 mL of ultrapure water, added to 30 mL of 2.5 M sodium hydroxide (Carlo Erba) solution and diluted to 1000 mL by ultrapure water. Glucose, galactose, fructose, lactose and sucrose (saccharose) (Riedel de Haen) were used without further purification. Solutions were prepared with a high-purity water from a MilliQ system (conductivity greater than 18 mΩ). A total of 20 samples coming from several wine production runs of red (Syrah) and white (Chardonnet) grape were analysed.

2.3. Principle of the UV measurement of sugar

Sugars are nonabsorbing compounds in the UV range. However, a UV/UV procedure based on the transformation of sugars into absorbent by products (carbonyl compounds) allows their indirect measurement. Fig. 1 represents the general scheme of the technique.

Firstly, after dilution and addition of a buffer solution (potassium tetraborate pH 9), the sample (25 mL) was irradiated in a closed-circuit with the UV lamp during 10 min. Under the influence of UV radiation, sugars were oxidised into UV absorbing compounds that were characterised by a peak around 268 nm (Fig. 2). These products have been identified as carbonyl compounds (aldehydes and/or ketones) by DNPH colorimetry.[19]

In a second step, the formation of these compounds was followed online by UV spectrophotometry, either at the maximum of absorbance (268 nm) using a calibration curve (obtained from irradiation of standard solutions), or from the whole spectrum using a multi-component exploitation method[20] (Fig. 2(b)). At first the increase of the absorbance at 268 nm can be observed, which corresponds to the oxidation of alcohol groups into carbonyl groups, followed (if UV irradiation is not stopped) by a decrease in absorbance value that corresponds to the oxidation into the carboxylic acid. Thus it was important to stop the UV photodegradation when the absorbance is at the maximum. Under the experimental conditions, this maximum was reached in 10 min, and remained stable for 15 min.

In case of a raw sample of wine, the deconvolution method is needed because of the presence of interferences (organic matter, suspended solids, etc.).

The total time of analysis was about 15 min, including the preparation of the sample (a simple dilution), the sugar transformation (by UV irradiation) and its measurement (by UV spectrophotometry).

3. Results and discussion

3.1. Standard solutions

The UV/UV procedure was first applied to standard solutions of glucose, fructose, galactose, lactose, saccharose, alone and in mixture. The concentrations obtained by the method were compared with those expected (Fig. 3), in a range of 20–400 mg L^{-1}.

The results show a good linear adjustment with a R^2 equal to 0.983. So, the determination of sugar content in non-complex aqueous solutions seems possible by using the UV/UV procedure. As the method is very

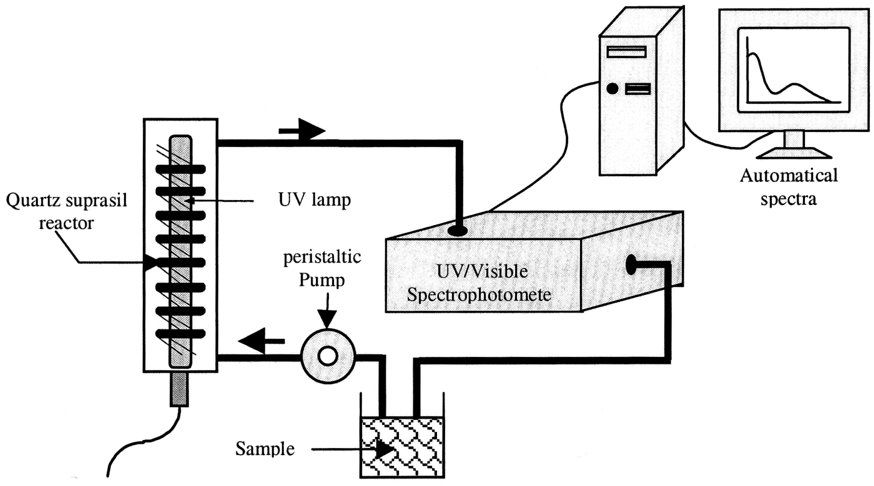

Fig. 1. Laboratory experimental device of the UV/UV concept.

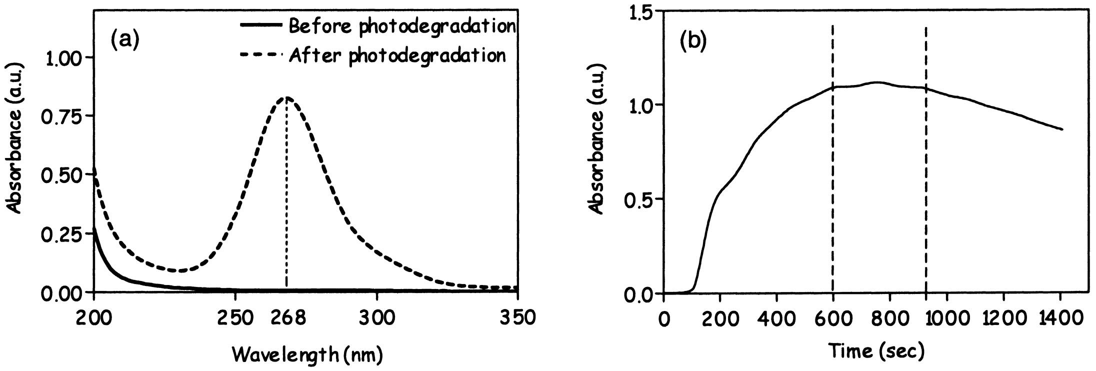

Fig. 2. Principle of sugar UV indirect detection: (a) effect of the irradiation on the UV signal; (b) evolution of the absorbance at 268 nm with time.

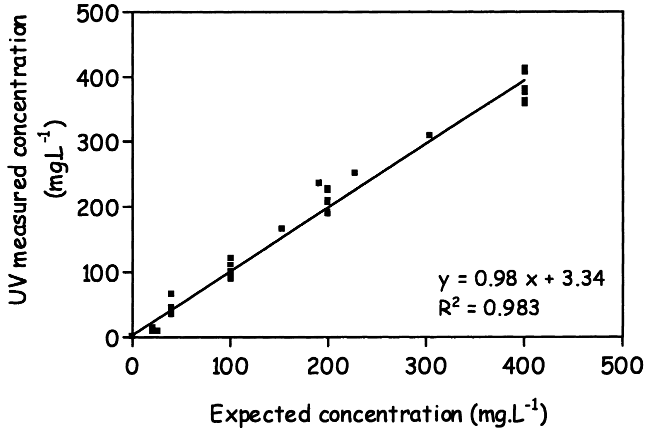

Fig. 3. Determination of sugar content by UV/UV method in standard solutions.

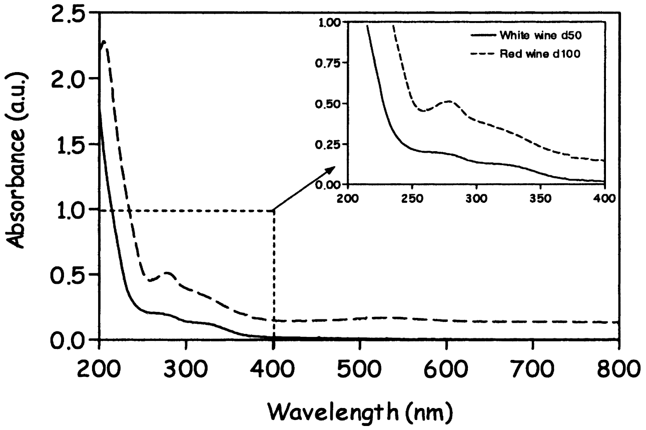

Fig. 4. UV spectra of wine samples.

sensitive (detection limit below than 20 mg L^{-1} with a 10-mm pathlength), a dilution will be necessary from sample containing high sugar concentrations.

3.2. Application on raw agricultural samples (wine production)

Raw samples containing sugar are studied all along the wine making process for both red and white varieties. Fig. 4 shows an example of UV spectra of both red and white wine samples. Characteristic absorbance of the main composant of wine could be observed: phenolic including tannins near 280 nm, antocyanidin around 520–530 mm and hydrocinnamic structure between 300 and 320 mm.

During the alcoholic fermentation of these wines, sugars were analysed by the UV/UV method and compared with the results obtained by the wine expert who was charged with the control of wine quality. Table 1 shows the wine expert's data. Notice that the sugar values obtained by the wine expert were acquired by FTIR spectroscopy.

As shown in Table 1, the alcoholic degree (which corresponds to the volume percentage of the quantity of alcohol contained in a liquid) and acid content increase during grape juice fermentation, whereas the concentration of the sugar decreases.

The evolution of acid concentration is not important because acidic compounds do not possess UV absorption and, moreover, do not interfere with sugar oxidation.

3.3. Effect of alcohol presence

An important parameter during the fermentation of grape juice is the production of ethanol (measured by the alcoholic degree defined previously). This product is well known for its scavenger properties and thus is able to interfere in the photochemical oxidation of sugars into carbonyl compounds. The effect of ethanol on UV/UV response was tested by standard addition into grape juice before its photodegradation. Fig. 5 confirms that the presence of an increased proportion of alcohol is detrimental to a precise sugar measurement. The

Table 1
Wine quality data

Sample	Alcohol degree	pH	Malic acid (g L^{-1})	Lactic acid (g L^{-1})	Total acids (g L^{-1})	Sugars (g L^{-1})
1	0	3.30	1.8	0	3.56	222
2	0	3.32	1.3	0	3.37	233
3	0	3.43	1.6	0	3.12	244
4	0	3.32	1.3	0	3.38	241
5	0	3.41	3.8	0	4.26	233
6	0	3.47	3.4	0	4.14	222
7	0	3.44	4.7	0	5.08	187
8	0	3.37	3.1	0	3.94	240
9	0	3.42	1.3	0	3.16	189
10	0	3.39	2.0	0	2.62	209
11	0	3.10	2.7	0	4.62	215
12	1.2	3.49	2.9	0	3.18	174
13	2.8	3.44	2.9	0	3.39	149
14	3.1	3.49	2.7	0	4.11	173
15	3.3	3.45	3.4	0	3.55	138
16	6.6	3.56	2.0	0.1	3.87	107
17	7.3	3.52	2.1	0.2	4.18	94
18	7.9	3.52	2.4	0.2	4.39	92
19	8.2	3.58	2.3	0.2	4.23	76
20	9.1	3.56	2.5	0.1	4.49	78

maximum alcohol degree should not be higher than 0.08° (%vol) in order to have results with an error of precision of < 10%.

For the raw samples analysed during the wine making, the alcohol degree varied between 0 and 9 (Table 1). But, as the method is very sensitive, a 250-fold dilution of the sample is needed. Thus, the alcohol maximum concentration measured into the analysed mixture (after dilution) is around 0.04°. In conclusion, the influence of ethanol can be, under experimental conditions, considered as negligible.

The samples analysed by the wine expert by FTIR spectroscopy were compared with the UV/UV values, and good linear regression was obtained (Fig. 6).

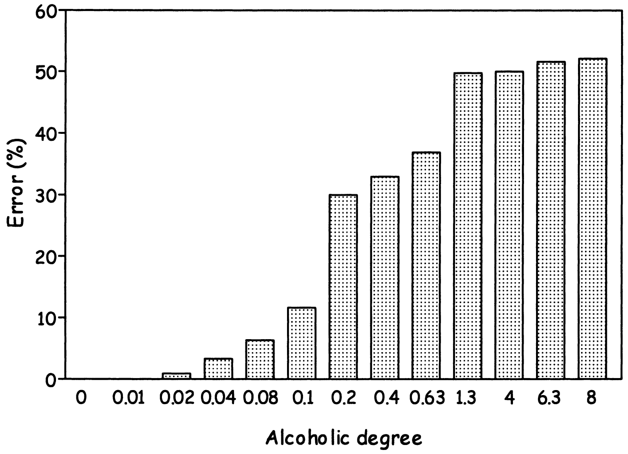

Fig. 5. Effect of the presence of ethanol.

The validation has been carried out according to the XPT 90-210 French standard[21] for the comparison of an alternative procedure with the reference method for water quality analysis. The acceptance of the UV/UV alternative method as a procedure equivalent to a reference procedure (for results) requires the test of the slope and intercept values of the regression line between experimental results. For that purpose, the previous data (Fig. 5) are considered. The conclusion of the t-Test of the slope and of the intercept, compared to the values 1 and 0, respectively, are presented in Table 2, and lead to the acceptance of the UV/UV method for sugar determination.

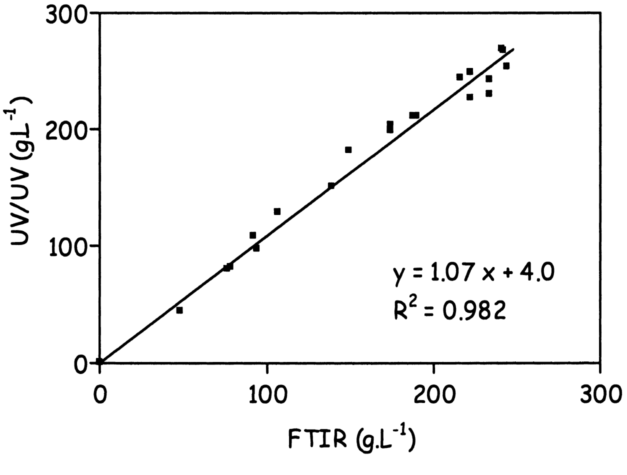

Fig. 6. Comparison between UV/UV measurement of sugars and the FTIR method.

Table 2
XPT 90-210 French standard results (from experimental results of Fig. 5)

Number of values (n)	20
Slope (δ)	1.07
Intercept (γ)	5.15
Standard deviation about regression $S_{y,z}$	11.49
Standard deviation S_δ of the slope δ	0.04
Standard deviation S_γ of the intercept γ	8.04
Value of *t*-Student's law ($t_{0.975}$)	2.1
$\delta-(t_{0.975})S_\delta<1$	0.98
$\delta+(t_{0.975})S_\delta>1$	1.16
$\gamma-(t_{0.975})S_\gamma<0$	−11.73
$\gamma+(t_{0.975})S_\gamma>0$	22.03

Under the experimental conditions the limit of determination and quantification in wine was calculated as 3.6 and 5.3 g L^{-1}, respectively.

4. Conclusions

The UV/UV method is a simple and rapid valuable method for the determination of sugar in wine samples. This technique was also used as a tool for following of the wine production process. Compared to a reference method, this procedure can be considered as an alternative method according the French AFNOR norm XPT 90 210. It can be used for online monitoring and control of the wine production process and for the measurement of sugar in agricultural effluents. Moreover, this technique is very sensitive, presents few interferences, and is carried out with devices usable for field measurement.

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