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Quantitative determination of sotolon, maltol and free furaneol in wine by solid-phase extraction and gas chromatography–ion-trap mass spectrometry☆

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Abstract

A method for the analytical determination of sotolon [4,5-dimethyl-3-hydroxy-2(5*H*)-furanone], maltol [3-hydroxy-2-methyl-4*H*-pyran-4-one] and free furaneol [2,5-dimethyl-4-hydroxy-3(2*H*)-furanone] in wine has been developed. The analytes are extracted from 50 ml of wine in a solid-phase extraction cartridge filled with 800 mg of LiChrolut EN resins. Interferences are removed with 15 ml of a pentane–dichloromethane (20:1) solution, and analytes are recovered with 6 ml of dichloromethane. The extract is concentrated up to 0.1 ml and analyzed by GC–ion trap MS. Maltol and sotolon were determined by selected ion storage of ions in the m/z ranges 120–153 and 79–95, using the ions m/z 126 and 83 for quantitation, respectively. Furaneol was determined by non-resonant fragmentation of the m/z 128 mother ion and subsequent analysis of the m/z 81 ion. The detection limits of the method are in all cases between 0.5 and 1 μg l^{-1}, well below the olfactory thresholds of the compounds. The precision of the method is in the 4–5% range for levels in wine around 20 μg l^{-1}. Linearity holds at least up to 400 μg l^{-1}, and is satisfactory in all cases. The recoveries of maltol and sotolon are constant (70 and 64%, respectively) and do not depend on the type of wine. On the contrary, in the case of furaneol, red wines show constant and high recoveries (97%), while the recoveries on white wines range between 30 and 80%. Different experiments showed that this behavior is probably due to the existence of complexes formed between furaneol and sulphur dioxide or catechols. Sensory experiments confirmed that the complexed forms found in white wines are not perceived by orthonasal olfaction, and that the furaneol determined by the method can be considered as the free and odor-active fraction.

Keywords: Wine; Food analysis; Flavor–matrix interactions; Sotolon; Maltol; Furaneol; Aroma compounds

1. Introduction

Sotolon, maltol and furaneol are compounds of diverse chemical origin but with a certain similarity in their chemical structures. This similarity is evident in an analogy of physicochemical as well as olfactory properties which makes their determination as a

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whole advisable. The three have very sweet aromas of great power and are normally classified in the same group of aromas with notes of ''burnt sugar, caramel and maple'' by perfumers [1], therefore it is not surprising that they can act in an additive or synergic manner [2]. On the other hand, the threshold olfaction values for sotolon and furaneol in water–ethanol are very low, 5 $\mu g\ l^{-1}$, in both cases [2,3]. The olfactory threshold of maltol in water–ethanol has been estimated as 5000 $\mu g\ l^{-1}$ [4].

The role played by these components in the aroma of wines is not entirely known, although the data available in the literature indicate that their contribution could be substantial. At relatively high concentrations sotolon seems to be responsible for the characteristic flavors of wines elaborated with botrytic grapes [5], of wines elaborated by means of oxidative ageing [3,6] as well as of the nut-rancid note of some sweet fortified wines [7]. Other authors have indicated that sotolon could also exert a role in the aroma of oxidized dry wines [8]. Furaneol can be found in quantities above 1 $mg\ l^{-1}$ in wines elaborated with hybrid grapes, concentrations at which it produces a disagreeable strawberry scent [9]. It has been recently described that, by acting in a synergic manner with homofuraneol, relatively small quantities of this component exert a great impact in fruity and caramel notes of some rosé wines [2]. As far as maltol is concerned, this is a component present in the toasted wood used in the ageing of wines [11] and some authors have postulated that it can play an important role in the aroma of Chardonnay wines [12].

At present, there is no satisfactory analytical method for the quantitative determination of these components in wine. Some of the published methods can only be applied to wines which contain high amounts of the analytes. For instance, Guedes and Bertrand [10] used three simple successive extractions with ethyl acetate and further GC–MS for the quantitative analysis of furaneol at high concentrations. Similar techniques for the analysis of sotolon at high concentrations have been also proposed [14], and make use of HPLC. Another alternative makes use of three simple successive extractions with dichloromethane and further GC–MS [15]. More refined methods involve dual-column GC and further MS [13], a combination of several cleanup procedures including enrichment by HPLC on a diol column and further GC–MS [16]. The methods are, however expensive, tedious and time-consuming.

In the current work we present the results of a study aimed at the determination of these components by GC–MS. The proposed method takes advantage of the versatility of the new solid-phase sorbents to make an advantageous extraction and a powerful clean-up of the extract in the same extraction cartridge. The required additional selectivity for the determination of some of these components is obtained by means of the quantification in a GC-ion trap MS using different ion preparation techniques.

2. Materials and methods

2.1. Chemicals

LiChrolut EN resins, and diethyl ether, dichloromethane and methanol (all Lichrosolv quality), were supplied by Merck (Darmstadt, Germany). Pentane (''chemika quality''), and ammonium sulfate were from Panreak (Barcelona, Spain) The pure compounds furaneol, maltol and sotolon were supplied by Aldrich-España (Madrid, Spain). Catechol was from Merck and acetaldehyde from Aldrich. The internal standard solution contained 67 $mg\ \mu l^{-1}$ of 2-octanol in dichloromethane. Two different wines were used for the method development and validation. Wine A was a full bodied young red wine, 13.0% (v/v) in ethanol, pH 3.8, made with Tempranillo, grenache and mazuela in Cariñena (Spain). Wine B was a young dry white wine, 12.0% (v/v) in ethanol, pH 3.4 made with Macabeo also in Cariñena. Wines from other types and origins were used in method validation.

2.2. Proposed procedure

Eight hundred mg of LiChrolut EN resins were taken and packed between two frits in a 6-ml filtration tube from Supelco (Madrid, Spain). The tube was put in the extraction unit (Vac Elut 20 from Varian, CA, USA) and 8 ml of methanol and another 8 ml of an aqueous solution containing 13% (v/v) in ethanol were passed through the unit. Fifty ml of

wine were loaded (to which 7.5 g of ammonium sulfate have been previously added) in the filtration tube and passed through the solid-phase extraction (SPE) bed at a speed not higher than 2 ml/min. After this, the bed was washed with 5 ml of water, and dried by applying vacuum for 30 min, and interferences were removed with 15 ml of a mixture of pentane–dichloromethane (20:1). The analytes were eluted with 6 ml of dichloromethane, the volume in a centrifuge test tube was recovered and spiked with 50 μl of the internal standard solution. This volume was concentrated to 0.1 ml in a water bath at 47 °C, and transferred to an autosampler micro-vial, sealed and stored at −20 °C until its analysis.

2.3. Gas chromatography–mass spectrometry

The apparatus used was a Varian CP-3800 gas chromatograph with a Saturn 2000 ion trap mass spectrometric detector. The chromatographic column was a DB-WAXetr from J&W (Folsom, CA, USA), 60 m×0.25 mm I.D. and 0.25 μm phase thickness. The column was preceded by a 2-m fused-silica precolumn (intermediate polarity). The initial temperature of the column was 40 °C, which was held for 5 min, and was then raised first at 10 °C min^{-1} up to 150 °C, and later at 2 °C min^{-1} up to 220 °C. The column was kept at this temperature for 20 min. One μl of the extract was injected in splitless mode (splitless time, 1.50 min). The system had an electronic flow control. The carrier gas was set at a constant flow-rate of 1 ml min^{-1}, except during the splitless time, when it was set at about 2.5 ml min^{-1} by applying a pressure pulse of 40.0 p.s.i. (1 p.s.i. = 6894.76 Pa). The mass spectrometric acquisition mode and the mass fragments used for quantitation can be seen in Table 1. The area of the corresponding ionic peaks was normalized by that of the internal standard and was interpolated in a calibration graph built by the analysis of standard solutions in dichloromethane. The result was corrected by the corresponding recovery.

2.4. Method development and validation

The selection of the sorbent and the breakthrough volumes of the analytes were studied in previous work [17]. Different cleaning and elution solvents were tested (binary mixtures of diethyl ether or dichloromethane and pentane). The optimum mass spectrometric conditions were found by testing different ion acquisition systems (scan, selected ion storage, MS–MS) in the analysis of wine extracts obtained following the proposed procedure. The method was validated by the study of its reproducibility, linearity and existence of matrix effects following standard procedures. The determination of

Table 1
Mass spectrometric detection conditions

	Ion preparation methods	*m/z*	*S/N*	Observation	Interference
Maltol	Full-scan	126	78	–	No
	SIS	126	618	Range: *m/z* 120–135	No
Sotolon	Full-scan	83	36	–	Yes
	SIS	83	79	Range: *m/z* 120–135	No
	SIS	83	51	Range: *m/z* 79–95	No
Furaneol	Full-scan	128	21	–	Yes
	SIS	128	16	Range: *m/z* 120–135	Yes
	MS–MS	81	177	[(1)]Non-resonant	No
	Parent ion: 128			[(2)]60v	
	Product ion: 81			[(3)]20 mseg.	
				[(4)]0.85 seg.	
		81	345	[(1)]Non-resonant	No
				[(2)]60v	
				[(3)]20 mseg.	
				[(4)]1 seg.	

Dissociation parameters: [(1)]waveform type, [(2)]excitation amplitude CID, [(3)]excitation time, [(4)]scan time.

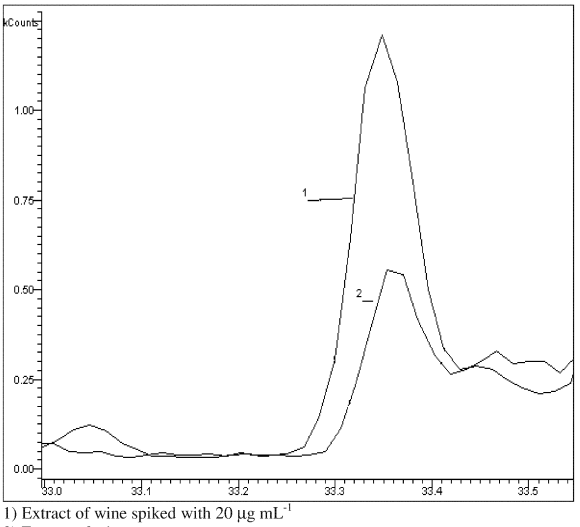
the recognition threshold of furaneol in different wines was carried out by triangle tests (10 panelists) [18].

3. Results and discussion

3.1. Extract preparation

The GC–MS analysis of extracts obtained by conventional means does not allow to obtain a sufficiently selective signal of some of the analytes under study. Fig. 1 shows the ionic chromatograms (m/z 128) at the furaneol time of retention of a wine extract obtained by direct extraction with dichloromethane and of the same extract spiked with 20 μg ml^{-1} of furaneol. It can be observed that the selectivity offered by the detection at m/z 128 is not sufficient. This causes the real limit of detection to be located around 20 μg l^{-1} of furaneol (concentration of compound for which $S/N \approx 3$). The same happens in the case of sotolon, which coelutes with 4-vinylguaiacol, as seen in Fig. 2a. Nevertheless, and although the fragment m/z 83 is selective for sotolon, as the figure suggests, the presence of high amounts of 4-vinylguaiacol makes the ionic peak of sotolon appear strongly deformed when present at low concentrations, as can be seen in the lower section of Fig. 2a. Although some of the above problems can be solved using strategies of ion treatment, the highly concentrated dichloromethane extracts contain relatively high amounts of non-volatile substances that in the long term, end up causing problems in the chromatographic systems. For all these reasons it is advisable to introduce a clean-up of the extract. From this point of view, SPE presents a clear advantage over the conventional liquid–liquid extraction, since the former allows to include a clean-up with solvents before the elution of the analyte.

In previous studies [17] we found that the LiChrolut-EN resins exhibit the best analyte extraction capacity, and therefore this resin was the one used in this study. Different clean-up solvents were tested, and the mixture pentane–dichloromethane (20:1) was found to be an optimal solution for the later GC–MS determination. The results are shown in Table 2 and Fig. 2b. In agreement with the data from the table, it is possible to percolate up to 15 ml of clean-up solution (through an 800 mg cartridge) without analyte losses greater than 5%, whereas the improvement in the GC–MS is noticeable, as shown in Fig. 2b for the case of sotolon.



1) Extract of wine spiked with 20 μg mL^{-1}
2) Extract of wine

Fig. 1. Ionic chromatograms (m/z 128) of furaneol. (1) Extract of wine spiked with 20 μg ml^{-1}, (2) extract of wine.

3.2. MS determination

Once the protocol for extract preparation was selected, we studied the effect that different modes of ion manipulation in the ion trap would have on the spectrometric signal. In the case of maltol, which elutes in a quite clean area of the chromatogram, its determination in full scan mode is feasible, although the sensitivity and the detection limits are improved if the selective ion storage (SIS) mode is used, as can be seen in Table 1. In this SIS mode, ions of a limited range of masses are accumulated within the trap. In the case of sotolon, and although the effect of the coeluent peak (4-vinylguaiacol) is further reduced in SPE extracts, the determination in scan mode is not advisable. A selection of ions in the range 79–95 provides an acceptable signal–noise relationship and eliminates the interferences. Furaneol, however, requires MS–MS to obtain a satisfactory signal–noise ratio.

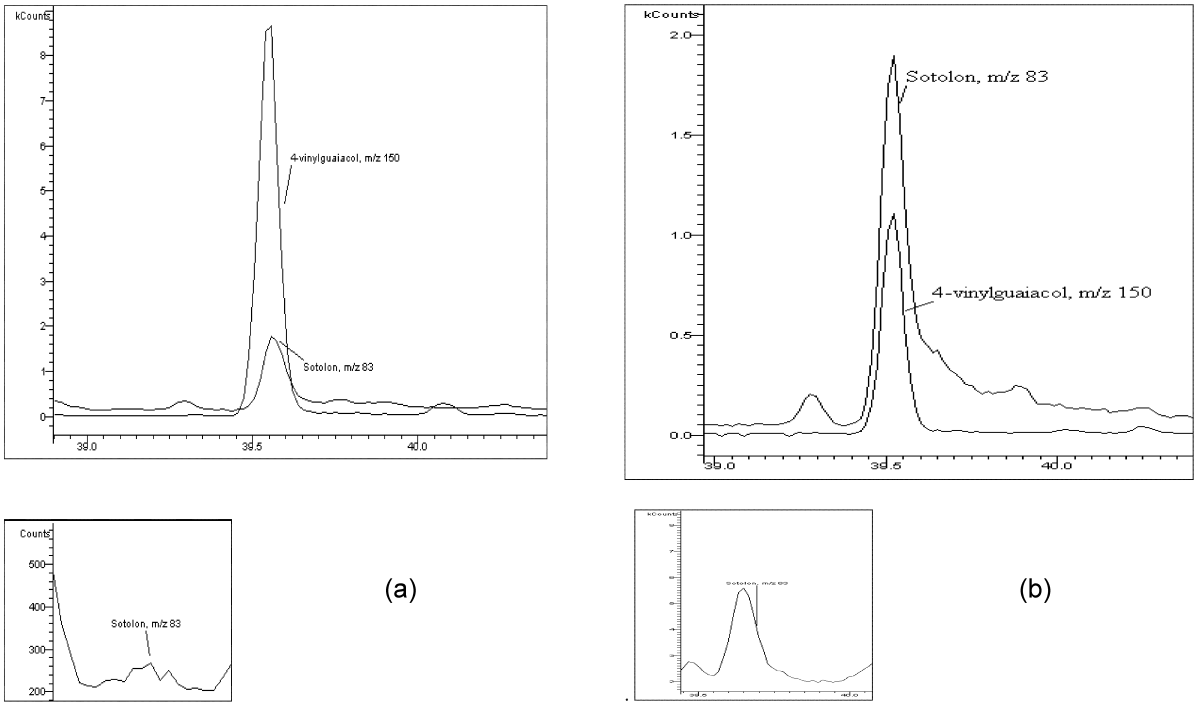


Fig. 2. (a) Ionic chromatograms of an extract of a dichloromethane wine extract spiked (the extract) with 10 μg ml^{-1} of sotolon. The small window shows the deformed peak of sotolon obtained in the GC–MS analysis of a dichloromethane extract from a wine which contained about 8 μg l^{-1} of sotolon. (b) Ionic chromatograms of an SPE extract of wine spiked (the extract) with 10 μg ml^{-1} of sotolon. The small window shows the peak of sotolon obtained in the GC–MS analysis of an SPE extract of a wine which contained 8 μg l^{-1} of sotolon.

3.3. Method validation

The accuracy of both the method and the chromatographic process was determined by means of replicated analysis of a given wine and repeated injection of the extracts. The results are shown in Table 3, indicating that the uncertainty of the global method stands at 5% for a concentration of 20 μg l^{-1}, which can be considered satisfactory. The decomposition of this uncertainty into the two individual operations (extraction + GC–MS determination) showed that both of them contribute to the global imprecision in similar proportion.

The calibration of the method cannot be accomplished by analysing synthetic wines containing only water, ethanol and the analytes, since most of these are lost during the process of concentration of the extract. The evaporation of dichloromethane solutions containing only the analytes brings about losses higher than than 60%. These losses are not observed,

Table 2
Elution of analytes with the potential clean-up solvents

	% Losses in clean-up step							
	Pentane–ethyl ether (20:1)				Pentane–dichloromethane (20:1)			
	5 ml	10 ml	15 ml	20 ml	5 ml	10 ml	15 ml	20 ml
Maltol	–	1	19	41	–	–	2	5
Furaneol	–	7	32	67	–	–	2	9
Sotolon	–	8	44	77	–	–	1	5

Table 3
Precision of the method

	GC–MS determination		SPE isolation		Global method	
	RSD (%)	SD[a]	RSD (%)	SD[a]	RSD (%)	SD[a]
Maltol	2.64	1.36	4.46	2.29	5.18	2.15
Furaneol	3.34	2.39	2.42	1.73	4.12	1.58
Sotolon	3.62	2.15	2.65	2.33	4.49	2.19

[a] SD, $\mu g\ l^{-1}$.

however, during the evaporation of extracts obtained from real wine (losses lower than 15%), due to the retentive effect exerted by the less volatile and matrix components present in the extract [19]. In order to evaluate both the linearity and the existence of matrix effects, three calibration lines were built, one using synthetic solutions and two others by means of standard additions on different wines. The most important results of this study are given in Table 4. The table shows that the slopes of the lines for the addition of maltol and sotolon are the same in both wines, and have, respectively, a magnitude 0.70 and 0.63 times the value of the slope obtained in the case of the synthetic solutions. This result suggests that both components are extracted and determined in an equivalent manner in any type of wine, and that the calibration can be done using the synthetic solution and a further correction by the corresponding recovery factor.

The case of furaneol is much more intriguing, inasmuch as in red wines the slope of the standard addition line is similar to that obtained in the analysis of synthetic solutions, but the slope obtained in the standard addition on white wines is far lower. In order to confirm this result, two new standard addition experiments were conducted on another pair of different wines. The results confirmed the previous observation and can be seen in Table 4. These results suggest that in white wines there is a strong matrix effect that causes the recovery to be far inferior to the levels expected. In these cases the calibration should be performed by means of standard addition; however if the analytical data try to reflect the possible sensory contribution of furaneol to aroma of wine, it will be necessary to study if this matrix effect is due to the presence in the wine of forms of furaneol aromatically nonactive. This question will be approached in the following section.

The detection limits obtained for maltol, furaneol and sotolon were 1.0, 0.45 and 0.84 $\mu g\ l^{-1}$, respectively. These values are adequate to evaluate the sensory contribution of these components to wines, since they are well below the corresponding threshold values.

3.4. Nature of the matrix effect of furaneol

In the first place, we investigated if the matrix effect originated in the extraction or in the spectrometric determination. Two extracts, one from a white wine (wine B) and a second from a red wine (wine A) when taken, were then spiked with a known quantity of furaneol and the area increments observed in both cases were determined. The increases were similar (9.31 and 9.34 units of relative area), therefore the matrix effect must be attributed to the isolation stage. The causes of this finding are not easy to explain a priori, since red wines are in general richer in almost all the components. Two initial hypotheses were formulated; firstly, the extraction could be extremely dependent on pH, since white wines usually have a lower pH than red ones. Secondly, furaneol in a white wine may be forming some type of nonextractive complex species, which could justify a diminution in the breakthrough volume and therefore in the recovery. The first hypothesis was discarded given the existing relationship between the signal and pH of the wine, shown in Fig. 3.

The possible existence of nonextractive complex forms was verified by the addition to the wine of substances which are in greater proportion in white than in red wines, or at least, are more easily available to form complexes. The first of these substances added was pyrocatechol (*ortho*-diphenol). The results are shown in Fig. 4, and demonstrate that

Table 4
Method linearity and standard addition experiments

Analyte	Synthetic solution		Red wine (A)			White wine (B)			Red wine 2			White wine 2		
	Slope	R^2	Slope	R^2	Recovery (%)	Slope	R^2	Recovery (%)	Slope	R^2	Recovery (%)	Slope	R^2	Recovery (%)
Maltol	13.026±0.512	0.999	8.161±0.613	0.992	62.6	8.228±0.496	0.989	63.2	–	–	–	–	–	–
Furaneol	0.055±0.007	0.999	0.054±0.008	0.974	97.4	0.019 ± 3.3^{-4}	0.998	34.5	0.053±0.012	0.997	98.1	0.0369±0.002	0.981	67.1
Sotolon	3.480±0.012	0.999	2.451±0.234	0.990	70.4	2.569±0.079	0.997	73.8	–	–	–	–	–	–

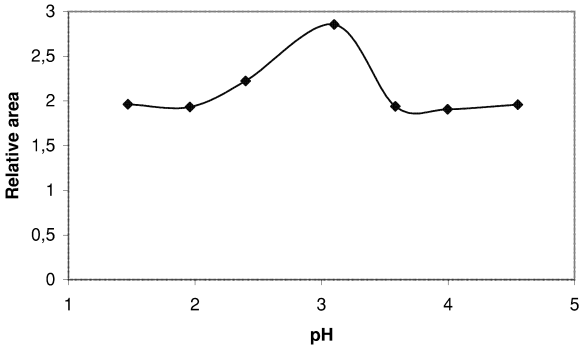


Fig. 3. Effect of the wine pH on the relative area of furaneol.

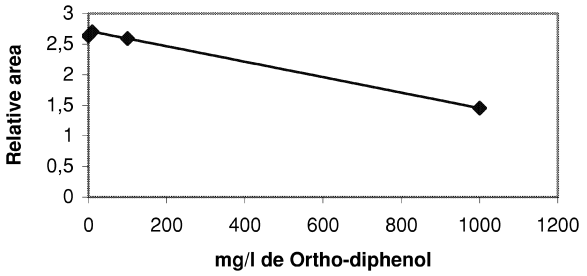


Fig. 4. Effect of the addition of cathecol to wine on the relative area of furaneol.

indeed, the presence of pyrocatechol causes a clear diminution of the furaneol signal. White wines do not contain more *ortho*-diphenols than red ones (normal contents range from 0.1 to 4 g l^{-1}), but these components are found in red wines mainly polymerised and forming complex associations with anthocyanins, proteins and other substances [20]. Another component that can be usually found in higher amounts in white wines is the sulphur dioxide (normal free SO_2 content ranges from 5 to 50 mg l^{-1}), which is added to wines to protect them from oxidation and from microbiological attacks. The addition of sulphur dioxide to the wine resulted as well in a diminution of the signal of furaneol in the case of red wine (see Fig. 5).

Next we studied if it was possible to displace furaneol from these complex forms by means of the addition of a competing substance. The substance we investigated was acetaldehyde, whose capacity to react both with the sulphur dioxide and with tannins and other polyphenols is well known. The addition

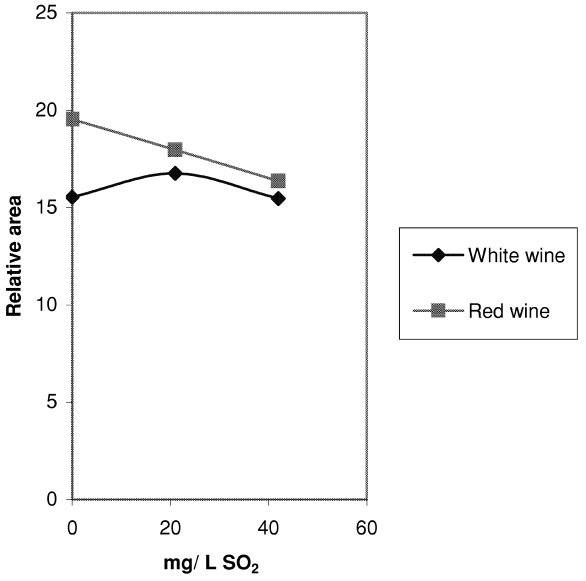


Fig. 5. Effect of the addition of sulphur dioxide on the relative area of furaneol.

of acetaldehyde improved indeed the signal, as can be appreciated in Fig. 6. The addition of 1000 mg l^{-1} of this component almost doubled the furaneol signal after 17 h of incubation. In spite of this improvement, the recovery of furaneol did not reach the levels obtained in red wines, which indicates that the displacement of the reaction is not complete. Experiments carried out at different temperatures could not improve this result.

3.5. Sensory implications of the existence of complex forms of furaneol

The existence of interactions between aromas and substances of diverse character has been documented by several authors [21,22], although most of the studies have been centered in the existence of interactions with proteins, fats and derivatives of cellulose. Nevertheless, two previous studies document that the addition of oak wood extracts, rich in tannic substances, to hydroalcoholic solutions hinders the extraction to organic phase of some ethyl esters [21,23], which seems to corroborate the results presented here. The effect of these interactions may not be limited to hampering the extraction of furaneol, but they could have consequences on the sensory effect exerted by the molecule in the wine. In order to evaluate this fact the amount of furaneol that must be added to a wine for its aroma to change significantly was determined by sensory analysis. The tasters were able to recognize the addition of 600 μg l^{-1} of furaneol to red wine (A), whereas in the white wine (B) the addition of 1600 μg l^{-1} was necessary to detect a significant sensory change (at $P \leq 0.05$), which seems to confirm that in this wine the proportion of free furaneol is three times lower than in the red and demonstrates that the complex form of furaneol cannot be perceived by the orthonasal route.

Once the existence of interactions capable of reducing the olfactory power of furaneol was confirmed, it is possible to wonder what information is of interest to the technologist or to the flavor chemist. The concentration of furaneol obtained by interpolation in the calibration graph is related to the fraction of free furaneol in the wine, whereas the determination of total furaneol demands the determination of the recovery of the component in such wine.

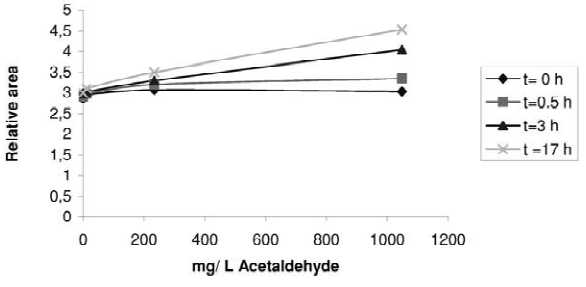


Fig. 6. Effect of the addition of acetaldehyde to wine on the relative area of furaneol at different reaction times.

4. Conclusions

The proposed method allows a satisfactory GC–MS determination of furaneol, maltol and sotolon in normal wines. The limits of detection attained are well below the olfactory threshold of the compounds. It has been also demonstrated that furaneol can exist in odor-less complexes in white wines, and that the amount of furaneol recovered in the proposed procedure is related to the free form.

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