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# Development and validation of method for heterocyclic compounds in wine: Optimization of HS-SPME conditions applying a response surface methodology

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## ARTICLE INFO

### Article history:

Received 31 May 2013

Received in revised form

7 August 2013

Accepted 23 August 2013

Available online 30 August 2013

### Keywords:

Wine

Heterocyclic compounds

Method validation

Response surface methodology

HS-SPME optimization

## ABSTRACT

Considering the importance of the heterocyclic compounds in terms of wine flavor, this study aims to propose a new rapid and solvent free method to quantify different classes of heterocyclic compounds, such as furans, thiophenes, thiazols and pyrazines, which are products of the Maillard reaction, in wines. The use of a central composite design and the response surface methodology to determine the best conditions allows the optimum combination of analytical variables (pH, NaCl and extraction time) to be identified. The validation was carried out using several types of wine as matrices. The method shows satisfactory repeatability ( $2.7\% < \text{RSD} < 12\%$ ), reproducibility ( $2.8\% < \text{RSD} < 12\%$ ), accuracy and specificity. The optimized method was applied to 29 French wines and significant concentrations of the different heterocyclic compounds were determined, mainly for red wines.

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## 1. Introduction

Wine aroma originates from a large number of volatile compounds belonging to heterogenic chemical groups, which may be classified as primary (derived from grape), secondary (formed during the fermentation) and/or tertiary aromas (from chemical reactions or physical interactions with containers, such as barrels) [1]. However, the origins of many odorous molecules present in wines are still not well defined. Some wines have aromatic notes close to those of “coffee”, “toasted”, “roasted”, which are associated with the Maillard reaction. The Maillard reaction is responsible for the characteristic flavor and color of many processed food products (baked, fried or roasted) [2]. Typically, a carbonyl compound derived from carbohydrate degradation reacts with a single amino acid. This well-known reaction occurs between a reducing sugar and an amino acid, and the mechanism can be divided into the Amadori and Heyns rearrangement or into the Strecker degradation and melanoidin formation. The most odorous products of the Maillard reaction are heterocyclic compounds with

5 or 6 members, which contain nitrogen-, sulfur- and oxygen-, notably including the compounds belonging to 4 different classes: furans, thiazoles, thiophenes and pyrazines [3].

In wines, some of these compounds have been identified and quantified and in some cases their chemical generation pathways and origins have been studied. Pripis-Nicolau et al. [4] showed that some carbonyl compounds mixed with amino acids in wine-like solutions reacted, even if kept in a reducing medium and under mild conditions similar to those of in bottle wine aging (pH close to 3.5, temperature close to 20 °C, and aqueous medium). The authors observed that the most interesting molecules were produced in the presence of the sulfur amino acids, in particular cysteine, with the production of heterocycles such as pyrazines, alkylpyrazines, methylthiazoles, acetylthiazole, acetylthiazoline, acetylthiazolidine, trimethyloxazole, and dimethylethyloxazoles. These mixes generate notes described as ‘popcorn’, ‘hazelnut’, ‘toasted’ and ‘roasted’ which are known to contribute to the aged wine bouquet [5]. Later, Marchand, de Revel and Bertrand [6] also studied the products of the reaction between cysteine and dicarbonyl compounds, under similar conditions. The compounds formed in solution included five of the most abundant and odorous compounds, that is, thiazol, 2-acetylthiazole, trimethyloxazole, 2-furanmethanethiol and thiophene-2-thiol, which were identified and quantified in French wines from different origins.

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These are known products of the Maillard reaction that occurs in several agribusiness processes and leads to roasted food flavors. These molecules were described for the first time in the wines by these authors, and may play an important role in their flavor. Researchers studied the reaction between diacetyl and cysteine, and proposed new pathways for the generation of odorous heterocyclic compounds under wine-like physicochemical conditions [7,8].

Considering the importance of these compounds in terms of the flavor of wines, and that no analytical method to identify and quantify of 4 different families of heterocyclic compounds in single chromatographic run could be found in the literature, this study aimed to propose a new rapid and solvent-free quantification method to quantify different classes of heterocyclic compounds, such as furans, thiophenes, thiazoles and pyrazines, which are products of the Maillard reaction. However, there are several methods for their quantification described in the literature using gas chromatography (GC) and various detectors: GC/FPD, GC/NPD, GC/FID, and GC/MS [9,4], thus a method using GC coupled to mass spectrometry was developed and validated. In relation to the extraction method for the compounds, researchers have been using liquid–liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME) [10–12]. In this study SPME was used because it offers many advantages over conventional sample preparation techniques. Simplicity, speed, solvent-free extraction and minimal sample manipulation are amongst the advantages offered by this technique [13]. As many factors can influence SPME extraction, a central composite design (CCD) using the response surface methodology (RSM) was applied to determine the best conditions. This methodology represents a combination of mathematical and statistical techniques aimed at optimizing the final response. The main advantage of this method is the reduced number of experiments required to provide sufficient information to obtain statistically acceptable results.

The RSM and CCD provide a complete factorial investigation of the simultaneous, systematic and efficient variation of important components, identifying the possible interactions, main effects and optimal conditions of operation [14].

## 2. Material and methods

### 2.1. Chemicals and Standards

Standard compounds (numbers given in Table 1) were obtained from commercial sources as follows: numbers 1 to 13, 16 and 18 to 24 (Sigma-Aldrich, Saint-Quentin-Fallavier, France); 15 (Alfa Aesar A Johnson Matthey Company, Bischheim, France); and 14, 17 and 22 (Acros organics, Geel, Belgium). The internal standard (25) was supplied by CDN Isotopes (Quebec, Canada). All solvents were HPLC grade. Absolute ethanol and methanol (purity > 99%) were obtained from Merck (Darmstadt, Germany). Milli-Q water was obtained from a Milli-Q Plus water system (Millipore, Saint-Quentin-en-Yvelines, France). Sodium chloride (99%) was supplied by VWR-Prolabo (Fontenay-sous-bois, France).

### 2.2. Sample preparation and spiking

The optimization of the type of fiber, sample dilution and the optimization of extraction of heterocyclic compounds were carried out on red wines spiked with 100  $\mu\text{g L}^{-1}$  of the standard solutions, prepared at 1000  $\text{mg L}^{-1}$  in water/ethanol solution (50% v/v).

Liquid–liquid extractions (LLE) was carried out with dichloromethane, 50 mL samples of wine were extracted 3 times with 5 mL of solvent. The combined extracts were dried over anhydrous

**Table 1**  
Flavor description, boiling point and ions monitored in SIM detection for each compound.

No	Compounds	Flavor description	BP ( $^{\circ}\text{C}$ ) <sup>a</sup>	Selected Ions <sup>b</sup>
<b>N,S-heterocycle</b>				
1	Thiazole	Popcorn, peanut	117–118 $^{\circ}\text{C}$	<b>85/58</b>
2	4-Methylthiazole	Green, nutty	133–134 $^{\circ}\text{C}$	<b>99/71/72</b>
3	2-Ethylthiazole	Green, nutty	148 $^{\circ}\text{C}$	<b>113/112/98</b>
4	Benzo[thiazole]	Rubber	231 $^{\circ}\text{C}$	<b>135/108</b>
5	2-Acetylthiazole	Nutty, popcorn	89–91 $^{\circ}\text{C}/12$ mmHg	<b>127/99/112</b>
6	2-Methylthiazole	Green vegetable	129 $^{\circ}\text{C}$	<b>58/99</b>
<b>N,O-heterocycle</b>				
7	2,4,5-trimethyloxazole	Very ripe fruit, nutty	133–134 $^{\circ}\text{C}$	<b>111/96/82</b>
<b>O-heterocycle</b>				
8	3-Acetyl-2,5-dimethylfuran	–	62 $^{\circ}\text{C}/0.25$ mmHg	<b>123/138/91</b>
9	2,3-Dihydrobenzofuran	–	188–189 $^{\circ}\text{C}$	<b>91/121</b>
10	2-Acetylfuran	Powerful, balsamic, burning, sweet	67 $^{\circ}\text{C}/10$ mmHg	<b>110/95</b>
11	5-Methylfurfural	Sweet, caramel, nutty, spicy	187 $^{\circ}\text{C}$	<b>110/53/81</b>
<b>S-heterocycle</b>				
12	3-Acetylthiophene	–	208–210 $^{\circ}\text{C}/748$ mmHg	<b>111/126</b>
13	2-Acetylthiophene	Mustard-like, onion, malty, roasted	214 $^{\circ}\text{C}$	<b>111/126/83</b>
14	2,3-Dimethylthiophene	–	142 $^{\circ}\text{C}$	<b>97/111/112</b>
15	2,5-Dimethylthiophene	Green-like	134 $^{\circ}\text{C}/740$ mmHg	<b>111/95</b>
<b>N-heterocycle</b>				
16	2-methylpyrazine	Nutty	135 $^{\circ}\text{C}/761$ mmHg	<b>94/67</b>
17	Acetylpyrazine	Roasted, sweet	78–79 $^{\circ}\text{C}/8$ mmHg	<b>80/122/43</b>
18	2-Ethylpyrazine	Nutty, roasted	152–153 $^{\circ}\text{C}$	<b>107/108/80</b>
19	2,6-Dimethylpyrazine	Nutty, sweet, roasted, chocolate	154 $^{\circ}\text{C}$	<b>42/108/67</b>
20	2,3-Diethylpyrazine	Roasted, earthy	180–182 $^{\circ}\text{C}$	<b>121/136/80</b>
21	2-Ethyl-3-methylpyrazine	Potato, burnt nutty, roasted, cereal	57 $^{\circ}\text{C}/10$ mmHg	<b>121/122/94</b>
22	2-Acetyl-3-methylpyrazine	–	90 $^{\circ}\text{C}/20$ mmHg	<b>93/136/94</b>
23	2,3,5-Trimethylpyrazine	Nutty, roasted peanut, cocoa, burnt	171 $^{\circ}\text{C}$	<b>81/122/42</b>
24	2,3,5,6-Tetramethylpyrazine	Green, nutty, cocoa, musty, potato	190 $^{\circ}\text{C}$	<b>54/136</b>
25	2-Methylpyrazine-d <sub>6</sub>	–	–	<b>100</b>

<sup>a</sup> BP: Boiling point (not specified) was 760 mm Hg.

<sup>b</sup> Quantitative ions are marked in bold text and control ions are marked in regular character.

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