



Simultaneous determination of free and bonded forms of odor-active carbonyls in wine using a headspace solid phase microextraction strategy



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ABSTRACT

This paper presents a new strategy for the direct evaluation of odor-active carbonyls in the wine headspace and for the simultaneous estimation of their amounts in odorless bonded forms. In the final developed strategy, 25 mL of wine are spiked with internal and surrogate standards and let to equilibrate for at least 12 h in an oxygen-free chamber. Ten milliliter of the sample are then transferred to a standard headspace vial. Carbonyls in the headspace are preconcentrated on a PDMS/DVD fiber keeping the sample unstirred at 45 °C for just 10 min and are further analyzed on a GC–MS equipped with a quadrupole in SIM mode. Normalized peak analyte areas interpolated in calibration plots built with synthetic wines give estimations of the concentrations of free forms, while the ratios of the areas of surrogates observed in wines to those observed in synthetic wine make it possible to get estimations of the proportion of each analyte present in bonded non-volatile form. The validity of this approach has been demonstrated both via standard recovery experiments and via the analysis of samples previously incubated with glyoxal in order to break aldehyde-bisulfite complexes. In general, method detection limits (below 1 µg L⁻¹), precision (RSD (%) < 10%) and accuracy are satisfactory for 12 studied carbonyls. Results demonstrate that wine contain relevant amounts of aldehydes (more than 95% in some cases) in the form of reversible odorless complexes, supporting a previous observation about the potential implication of these complexes on the development of oxidized aroma.

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1. Introduction

Carbonyls form a broad family of aroma compounds bearing a large diversity of descriptors. In wine, even if quantitatively they are not amongst the most important, they can contribute with odor nuances such as vanilla, caramel, butter, honey, potato, rancid oil, orange, lemon, violets, cider or plum. Some aldehydes in particular have been identified as the most important contributors to oxidative off-flavors [1–3], to the extent that the shelf life of many wines is closely related to its contents in methional and phenylacetaldehyde. Therefore, there is great interest in the development of analytical methods suitable to study these compounds.

Carbonyls are highly reactive molecules able to form interactions with many molecules. Remarkably, they can form reversible

adducts with sulphur dioxide (α -hydroxyalkylsulfonic acids) and with the amine groups of amino acids (Shift bases or imines) and proteins [4–8]. This fact has several potential implications. From the technical point of view it means that, at least potentially, wine can have a pool of odorless carbonyls which could be released back into odor-active forms during normal aging once SO₂ is depleted. From the analytical point of view this challenges the meaning and usefulness of the analytical data obtained with procedures which have not taken into account the possibility that the analyte exists in different interconvertible forms.

While there are yet several unclear aspects to this question [5], the existence of those bonded forms has been suggested by some authors to be an important clue related to the development of stale flavors in beer [5,8,9]. By contrast, and with the exception of acetaldehyde [10], the potential sensory relevance of those bonded forms is thought to be just of secondary importance in wine chemistry [4]. In fact, only in a recent work Grant-Preece et al. measured the apparent dissociation constants of the α -hydroxysulfonates formed by methional and phenylacetaldehyde with SO₂ (5.5×10^{-4} and 8.0×10^{-4} , [11] and suggested that these complexes could be

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the reason why red wines, with smaller levels of free SO₂, tend to show higher levels of methional and phenylacetaldehyde than white wines.

There are some other reports supporting a relevant role for bonded forms both in sensory and in aging potential terms. Free forms of long chain aliphatic aldehydes in normal wines (octanal, nonanal and decanal) were found to range from as low as 4% to up to 76% of the total content [12], and a significant part of the complexes (up to 89%) could not be recovered by incubation with acetaldehyde, but with heptanal, suggesting the existence of hydrophobic complexes, maybe with proteins [13]. Most recently, the apparent liquid–gas distribution coefficients of acetaldehyde and 2,3-pentanedione were found to differ by factors up to 17 or 11 between wines, respectively [14], far more than any other volatile studied, supporting a relevant role of carbonyl–matrix interactions on wine sensory properties. Moreover, carbonyl production rates upon wine oxidation have been found to be related to the wine content in combined SO₂, suggesting that a significant part of the aldehydes could be already present in wine under the form of SO₂ adducts [15].

The preferred techniques for the analysis of carbonyls involve the derivatization of the carbonyl group to introduce a pentafluorobenzyl [16], pentafluorophenyl [17] or dinitrophenyl [18] group in order to improve the extractability, chromatographic behavior and spectrometric signal of the carbonyls [19]. Such derivatizations can be carried out in different formats, in liquid phases [20,21], in solid phase extraction phases [22], in SPME fibers [23,24] or in liquid microextracts [25]. Some affordable procedures provide detection limits in the low ng L⁻¹ range [19,26]. However, in many of these approaches sample preparation is relatively forceful, so that part of the bonded forms and specific intermolecular interactions responsible for critical differences in volatility of a carbonyl in different samples may cleave. The exact extent of bonded forms and intermolecular interactions cleaved will depend on the specific strategy, but most often the analytical signal will refer to the free fraction plus an undetermined aliquot of the bonded fraction.

In this context, mild sample preparation strategies trying to minimize the disruption of the natural intermolecular equilibria of analytes in the samples should be preferred in order to get a reliable estimation of the amount of free forms. For instance, several authors have proposed the direct headspace extraction [27] or the SPME extraction of headspaces using short extraction times to assess the degree of interaction of aroma compounds with the matrix [28–30]. These approaches, however, require the previous knowledge of the total concentration of the analyte and need to be complemented by a second method and may have sensitivity problems. There are some more sophisticated alternatives that can provide a simultaneous estimation of the gas–liquid distribution coefficient and of the total amount, such as the phase ratio [31], multiple headspace extractions [32] or multiple headspace in tube extraction [14]. In all these cases, several determinations are also required and sensitivity and selectivity can be also of concern.

The main goal of the present paper is to develop an analytical method for the simultaneous determination of free and bonded forms of wine sensory relevant carbonyls. For addressing that goal, a mild headspace solid phase extraction strategy, combined with a careful selection of internal standards and surrogates for estimating total amounts has been developed.

2. Materials and methods

2.1. Reagents, standards, materials and samples

Ethanol was supplied by Merck (Darmstadt, Germany), tartaric acid 99%, glycerol 99.5%, 1,2-propanediol 99.5% and sodium

metabisulfite 97% were from Panreac (Barcelona, Spain), sodium hydroxide 99% was from Scharlau (Barcelona, Spain) and glyoxal 40% in water was from Aldrich (Madrid, Spain). Water was purified in a Milli-Q system from Millipore (Bedford, Germany).

The standards used for the analytical quantification, surrogates and internal standards were supplied by Aldrich, Fluka (Madrid, Spain), ChemService (West Chester, PA, USA) and Firmenich (Switzerland). Chemical standards: isobutyraldehyde 99%, 2-methylbutanal 95%, 3-methylbutanal (isovaleraldehyde) 97%, phenylacetaldehyde >90%, 3-(methylthio)propionaldehyde (methional) ≥97%, decanal 95%, 2,3-pentanedione 97%, acetovanillone 98%, β-ionone ≥97%, diacetyl 99%, benzaldehyde 99%, 5-methylfurfural 97%, furfural 99% and β-damascenone >93%. Chemical standards used as wine mayor compounds: 1-hexanol 99%, ethyl acetate 99.7%, ethyl octanoate 98%, ethyl hexanoate 99%, isoamyl acetate 98%, diethyl succinate 99%, heptanoic acid 99%, undecanoic acid 99% and 2-methylbenzyl alcohol. Surrogates: 2-methylpentanal 98%, hydrocinnamaldehyde ≥95%, β-damascone ≥90%, 3,5,5-trimethylhexanal ≥95%, 3-(methylthio)butanal ≥96%, 4,5-dimethylfurfural 97%, 3-octanone ≥98%. Internal standards: 4-methylpentan-2-ol 99%, methyl 2-methylbutyrate ≥98% and 2,6-dichloroanisole >97%.

Synthetic wine: 11% (v/v) in ethanol, 5 g L⁻¹ tartaric acid, 10 g L⁻¹ glycerol, 1.5% (v/v) in 1,2-propanediol and pH adjusted to 3.5 with sodium hydroxide 1 M. 1,2-propanediol is added in order to make the solubility and volatility of aroma compounds in the synthetic matrix more similar to that of real wine.

Polydimethylsiloxane/divinylbenzene (PDMS/DVB) 65 μm film thickness, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS 1 cm) 50/30 μm film thickness and polyacrylate (PA) 85 μm film thickness SPME fibers were purchased from Supelco–Spain (Madrid, Spain).

DB-WAXETR 30 m × 0.32 mm I.D. × 1 μm film thickness and DB5ms 30 m × 0.25 mm I.D. × 1 μm film thickness were purchased from J&W Scientific (Folsom, CA, USA) and SPB-1 Sulfur 30 m × 0.32 mm I.D., with 4 μm film thickness capillary columns was from Supelco.

Wines for the validation study and other applications were 8 whites, 6 rosés and 23 reds with alcoholic degrees comprised between 12.0% and 14.5% (v/v); all them were dry table wines with ages between 1 and 6 years old.

2.2. Method development

The three aforementioned GC-columns were tested in order to choose the one providing better peak shapes for the most active analytes (methional and phenylacetaldehyde). Three different SPME fibers (above mentioned) were also considered. The best fiber was chosen by comparing the peak areas of the different analytes obtained in the analysis of wines spiked with analytes. HS-SPME sampling was performed at various incubation times (10, 20 and 30 min), extraction times (1, 2.5, 5 and 10 min) and extraction temperatures (35, 40 and 45 °C) to determine the best conditions for the purpose of this work.

Candidates for internal standards and surrogates were first tested to ensure no coelution with critical analytes, a good peak shape and the absence in the standard of any impurity of analyte. Internal standards were compounds with polarity similar to analytes not bearing any carbonyl functional group. Surrogates were aldehydes or ketones. Candidates were further tested by repeated analysis of spiked wines and synthetic wines along different weeks. The best internal standards were those providing minimal intraday, interday and intersample (synthetic × real) variability in the normalized analyte and surrogate peak areas. Internal standards and surrogates finally chosen are given in Table 1.

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