



Multiclass semi-volatile compounds determination in wine by gas chromatography accurate time-of-flight mass spectrometry



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ABSTRACT

The performance of gas chromatography (GC) with accurate, high resolution mass spectrometry (HRMS) for the determination of a group of 39 semi-volatile compounds related to wine quality (pesticide residues, phenolic *off*-flavours, phenolic pollutants and bioactive stilbenes) is investigated. Solid-phase extraction (SPE) was used as extraction technique, previously to acetylation (phenolic compounds) and dispersive liquid-liquid microextraction (DLLME) concentration. Compounds were determined by GC coupled to a quadrupole time-of-flight (QTOF) MS system through an electron ionization (EI) source. The final method attained limits of quantification (LOQs) at the very low ng mL^{-1} level, covering the range of expected concentrations for target compounds in red and white wines. For 38 out of 39 compounds, performance of sample preparation and determination steps were hardly affected by the wine matrix; thus, accurate recoveries were achieved by using pseudo-external calibration. Levels of target compounds in a set of 25 wine samples are reported. The capabilities of the described approach for the post-run identification of species not considered during method development, without retention time information, are illustrated and discussed with selected examples of compounds from different classes.

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1. Introduction

Wine quality is a concerning issue in a globalized market with new consumers and producers. Traditionally, quality has been associated with the sensorial properties of this foodstuff, which are correlated with volatile species displaying different odour threshold and activity values [1,2]. In addition, several groups of semi-volatile compounds must be also taken into account in order to define the quality of wines. Some examples are (1) ethyl and vinylphenols which, depending on their concentrations, exert positive or negative effects in the aroma of wine, (2) natural bioactive compounds, e.g. resveratrol, which have been correlated with healthy effects associated to a moderate wine consumption [3], (3) undesired anthropogenic species, resulting from wine contamination during elaboration and/or packaging (e.g. bisphenol A and alkylphenols from detergents degradation) [4], and (4) pesticides. The determination of pesticide residues in wine is of particular relevance since (1) several producer countries, particularly Australia and those from South and North America, have more restrictive legislations than the European ones [5]; and furthermore, (2) cer-

tain pesticides affect the formation of aromatic compounds during must fermentation [6].

Analytical chemists have developed a myriad of approaches dealing with separate groups of the above compounds, such as ethylphenols [7], stilbene derivatives [8], pesticides [9] and other anthropogenic pollutants [4] residues in wine. However, there is still a need for multiclass methodologies, covering the determination of species with different origins, concentration ranges and belonging to different chemical families. The main challenges to develop multiclass reliable methods are: (1) the optimization of compatible sample preparation (extraction and concentration) conditions for compounds with different chemical functionalities; (2) their simultaneous determination achieving suitable limits of quantification (LOQs) (taking into account the maximum residue limits, MRLs, of pesticides and the odour thresholds of *off*-flavours); (3) attaining linear response intervals covering the expected range of concentrations in wines with different origins; and (4) achieving enough selectivity to guarantee the unequivocal detection of target compounds in the complex chemical environment of wine extracts.

High resolution mass spectrometry techniques (HRMS) dramatically reduce the risks of mass spectral interferences when quantification ions are extracted using a mass window of a few milidaltons (mDa); furthermore, Orbitrap and time-of-flight (TOF) MS analysers provide an excellent sensitivity in the scan mode,

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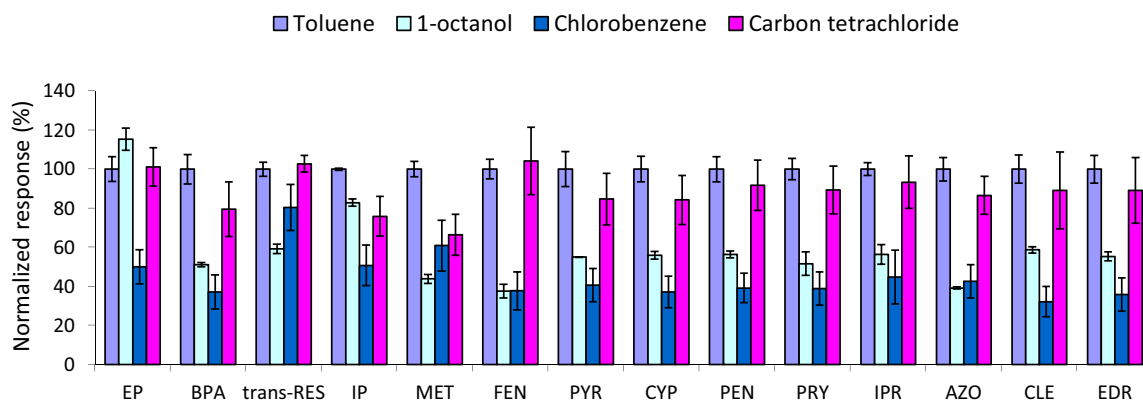


Fig. 1. Comparison of responses attained, for a selection of compounds, as function of the extractant during DLLME of SPE extracts from the same wine (red wine, *Mencía* variety). Normalized responses to those corresponding to toluene, $n = 3$ replicates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

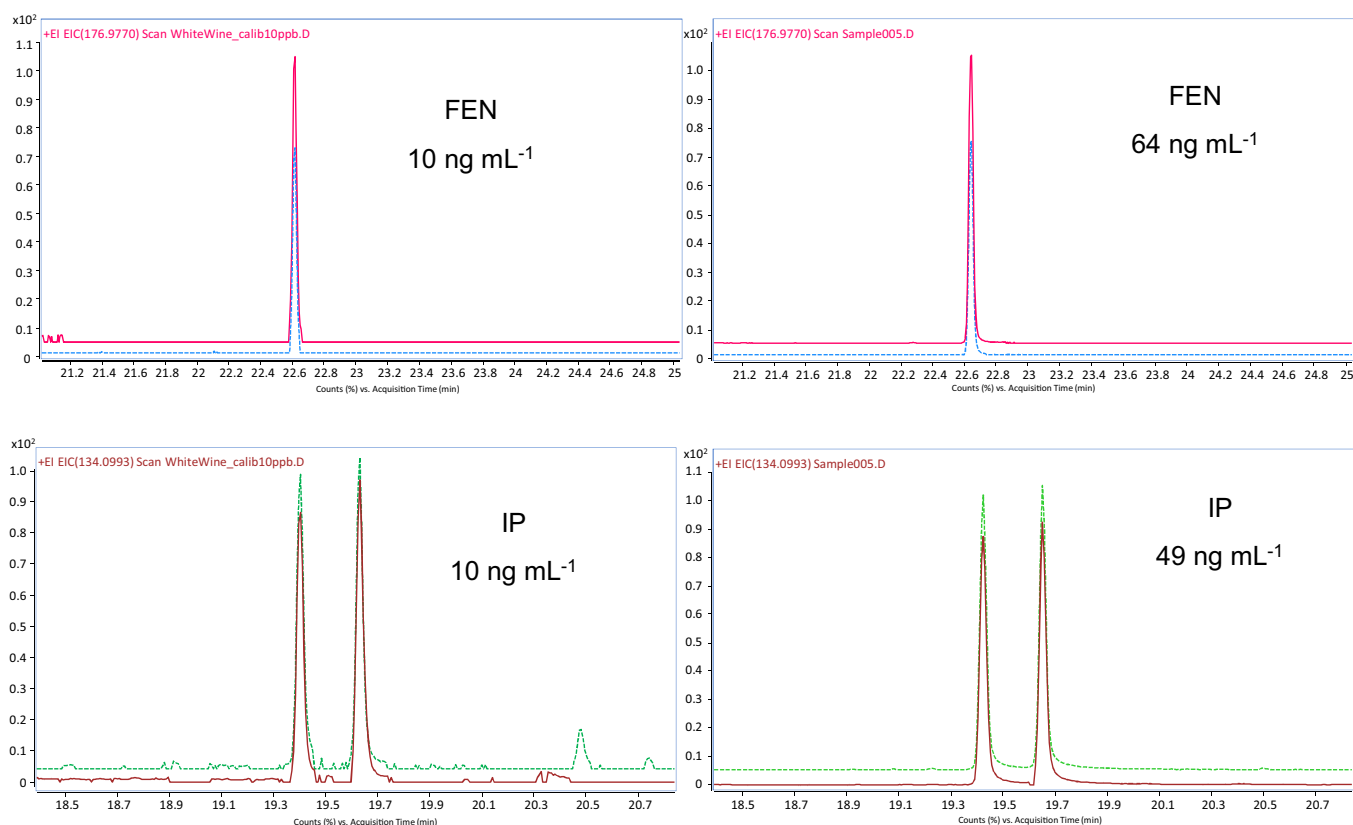


Fig. 2. EIC chromatograms for quantification (solid line) and qualification (dotted line) ions of fenhexamide (FEN) and iprovalicarb (IP) in a non-polluted wine spiked at 10 ng mL^{-1} (left) and in a non-spiked wine sample (right) containing 64 and 49 ng mL^{-1} of FEN and IP, respectively.

allowing to record data for an unlimited number of compounds. In this vein, the combination of liquid chromatography (LC) with quadrupole (Q) TOF-MS has already demonstrated an excellent performance for the analysis of phytochemical residues [9] and the investigation of resveratrol analogues [10] in wine. Replacement of electrospray (ESI) for a harder ionization source, e.g. electron ionization (EI), is expected to increase the spectral information associated to any chromatography peak. Also, the combination of HRMS with gas chromatography (GC) allows the determination of semi-volatile, small-size molecules poorly ionized in LC-MS interfaces. The qualitative applications of GC-EI-QTOF-MS have been already evaluated during the characterization of some food commodities [11], and for the identification of pesticide residues in

vegetable food samples [12] and organic pollutants in water matrices [13]. On the other hand, quantitative features of GC-QTOF-MS remain mostly unexplored.

Solid-phase extraction (SPE) is regarded as the most popular technique for extraction of natural and anthropogenic compounds from wine [14,15]. The relatively low breakthrough volumes of SPE sorbents for wine matrices (when compared with less complex environmental samples) can be compensated by further combination with dispersive liquid-liquid microextraction (DLLME), aiming not only to increase the obtained enrichment factors, but also to remove some undesired species from the primary SPE extract [16,17].

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