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Characterization of the aroma profile of novel Brazilian wines by solid-phase microextraction using polymeric ionic liquid sorbent coatings

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Abstract

In this study, a series of polymeric ionic liquid (PIL) sorbent coatings is evaluated for the extraction of polar volatile organic compounds (VOCs) from Brazilian wines using headspace solid-phase microextraction (HS-SPME), including samples from 'Isabella' and 'BRS Magna' cultivars—the latter was recently introduced by the Brazilian Agricultural Research Corporation – National Grape & Wine Research Center. The structurally tuned SPME coatings were compared to the commercial SPME phases, namely poly(acrylate) (PA) and divinylbenzene/carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS). The separation, detection and identification of the aroma profiles were obtained using comprehensive two-dimensional gas chromatography mass spectrometry (GC×GC-MS). The best performing PIL-based SPME fiber, namely 1-hexadecyl-3-vinylimidazolium bis[(trifluoromethyl)sulfonyl]imide with 1,12-di(3-vinylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide incorporated cross-linker supported on an elastic nitinol wire, exhibited superior performance to DVB/CAR/PDMS regarding the average number of extracted peaks and extracted more polar analytes providing additional insight into the aroma profile of 'BRS Magna' wines. Four batches of wine were evaluated, namely 'Isabella' and 'BRS Magna' vintages 2015 and 2016, using highly selective PIL-based SPME coatings and enabled the detection of 350+ peaks. Furthermore, this is the first report evaluating the aroma of 'BRS Magna' wines. A hybrid approach that combined pixel-based Fisher ratio and peak table-based data comparison was used for data handling. This proof-of-concept experiment provided reliable and statistically valid distinction of wines that may guide regulation agencies to create high sample throughput protocols to screen wines exported by Brazilian vintners.

Keywords Biomarkers · Flavor and aroma · Food chemistry · Foodomics · Sensomics

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Introduction

Wine is the second most consumed alcoholic beverage worldwide (~ 28.2 billion liters per year) and it has reported benefits to human health, which has imposed increasing demands on the art of wine making [1]. As a result, significant technological advances in viticulture and enology have been pursued to improve the quality and productivity of wine to supply market demand [1]. Viticulturists and vintner carefully address *terroir*, plasticity of the grape genome, and the chemistry of winemaking (ripening, fermentation, and maturation) to bestow a symphony of flavors to the final bottled product.

Wine is an aqueous solution, with concentrations of ethanol ranging from 10 to 20% of its total volume, and roughly 4% of such matrix is composed of organic compounds—responsible for quality attributes and consumer acceptance [2]. Despite such low weight fraction, volatile organic compounds (VOCs) are a

highly complex fraction of wine with more than 1000 volatile compounds reported so far [2]. Hence, exploratory analysis of such complex matrix requires efficient sampling and sample preparation techniques, as well as powerful instrumentation to extract meaningful information from the sample.

Sample preparation is a vital part of the analytical process. More than 75% of analysis time is spent on sample collection and preparation [3], which demands prospection of techniques with reduced solvent consumption (green chemistry) that are also compatible with miniaturization [4]. In this context, microextraction techniques are well-established alternatives to exhaustive solvent extractions, and may take on many forms and principles. Solid-phase microextraction (SPME) is a solvent less technique that combines non-exhaustive analyte extraction and pre-concentration into a one-step equilibrium process [5], exhibiting small sample requirements, and it has been extensively applied to the analysis of complex food matrices [6, 7].

Selection of sorbent phases demands careful considerations, as beverage sensory quality requires a consistent and meaningful characterization of VOC, including the sensory-active components [8]. This challenges analysts, as in exploratory analysis a large fraction of the matrix itself is often the subject of interest, unlike other applications in which only a group of analytes must be isolated from the sample. Hence, the sorbent phase must exhibit multiple solvation characteristics to effectively enhance the profile of extracted analytes from food matrices, such as wine. Until the past decade, most SPME methods employed poly(dimethylsiloxane) (PDMS), poly(acrylate) (PA), divinylbenzene (DVB), Carboxen®-based extractants for VOC isolation, which exhibited limited sorbent properties [9]. Thereby, new phases with unique selectivity are urgently needed.

Polymeric ionic liquids (PIL) are a promising class of sorbent coatings for SPME that exhibits unique selectivity by combining multiple solvation properties [9–14]. The PIL may be structurally tuned to impart desirable characteristics by carefully grafting substituents to the cationic/anionic moieties or by interchanging the combination of ion pairs [15]. Furthermore, the presence of weak ionic interactions imparts negligible sorbent bleed and high maximum allowable operating temperature (MAOT) to PIL-based materials [14, 16, 17].

An ideal match to SPME experiments is comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GC×GC-MS). Such technique is considered the most valuable tool for the separation and identification of volatile and semi-volatile organic compounds [18]. GC×GC harnesses the peak capacity of sequential GC separations by exploring complementary selectivity (i.e., solvation properties). Furthermore, GC×GC-MS has allowed the unprecedented detection of several hundred analytes from a single measurement [19]. Today, such techniques are embodied by thermal, valve-based, and flow interfaces. Excellent reviews describing the most important developments of GC×GC are available for the interested reader [19–23].

Zini and co-workers [24] have illustrated the advantages of GC×GC for wine aroma profiling enabling the successful identification of 220 compounds, which included esters, alcohols, terpenes, acids, aldehydes, ketones, lactones, phenols, furans, and sulfur compounds. Furthermore, 37 of 220 analytes that were identified in Merlot wines exhibited severe peak overlap in the first dimension but were resolved in the second dimension enabling proper identification. For instance, 5 out of 8 sensory active compounds could only be identified and quantified by GC×GC. Similarly, GC×GC-based methods have been employed to unveil the chemical composition of VOC in Cabernet Sauvignon [25], Merlot [26], Muscat [27], Marsala [28], and Moscatel [29] wines. Consequently, such investigations have improved the correlations between wine production variables and the volatile composition, such as regional feature of grapes [30], ripeness and maceration of grapes [31], fermentation [32], and aging [33]. Moreover, Welke et al. [34] profiled the VOC in Merlot, Chardonnay, Pinot Noir, Sauvignon Blanc, and Cabernet Sauvignon wines using GC × GC. Important compounds such as 1-hexanol, 1,4-butanediol, 3-methyl butanoic acid, 6-methyloctan-1-ol, ethyl hexanoate, ethyl nonanoate, ethyl decanoate, ethyl tetradecanoate, methyl octanoate, and dehydro-2-methyl-3(2H)-thiophenone were responsible for distinguishing Merlot and non-Merlot wines grown in Serra Gaúcha region (RS, Brazil).

The viticulture in tropical regions is improving its quality and has been achieving international acceptance over the last few decades. Traditional grape species used to produce wine and juices are usually restricted to temperate zones, which exhibits troublesome adaptations in hot climates. The Grape Breeding Program, maintained by Embrapa Grape and Wine, has released the 'BRS Magna', a new grape cultivar that resulted from the crossing of 'BRS Rúbea'×'Traviú', exhibiting intermediate cycle and wide climatic adaptation. The 'BRS Magna' has been successfully breed at the Experimental Station of Tropical Viticulture in Jales (SP). It was also evaluated at Nova Mutum (MT) and Serra Gaúcha (RS, Brazil) presenting good agronomic and industrial performance. The full ripe 'BRS Magna' grapes exhibits a pleasant raspberry flavor, similarly to *V. labrusca*, and chemical traits such as 17–19° Brix sugar content, 90 meq L^{-1} average total acidity, and pH value of 3.60 [35]. The color of the juice and wine of 'BRS Magna' is intense violet. Since its inception, 'BRS Magna' has been used for grape juice making, improving the color, sweetness, and flavor of grape juices in Brazil [35]. However, to the best of our knowledge, there are no reports evaluating the aroma of 'BRS Magna' wines and comparison to the traditional 'Isabel' (or 'Isabella') wines. Therefore, the application of SPME and GC×GC-MS may be an interesting solution to determine the VOC profile of such wine samples.

Although comparative analysis using peak tables is a widespread practice among GC practitioners, important information may be lost or overlooked during univariate data processing. The application of chemometric techniques and computational tools to extract meaningful and context-oriented information is critical to provide reliable and unbiased assessments [36–41]. Two aspects of data generated by GC×GC-MS that challenges univariate processing are the enormous size and complex structure of the raw measurements. In addition, GC×GC-MS generates native third-order data, which requires pixel-based chemometric techniques for proper pattern recognition and classification.

To address these restrictions, we propose an orthogonal workflow for exploratory analysis using SPME and GC×GC-MS. Several non-ionic and PIL-based sorbent coatings for SPME were evaluated for the extraction of polar VOC in wine samples. The best performing fibers were selected for GC×GC-MS profiling of Brazilian wines. A side-by-side protocol was established using two SPME fibers. First, a pixel-based approach, namely multilinear principal component analysis (MPCA), was applied to the four-way data for pattern recognition. This step was important to compare the chemical information probed by each of the SPME-based methods. Next, pixel-based Fisher ratios were calculated using the four-way GC × GC-MS data. This computational approach allowed for assignment of important volatile organic compounds that may be explored to differentiate Isabella and Magna wines. This proof-of-concept application may guide regulation agencies to create high sample throughput protocols to screen wines exported by Brazilian vintners.

Materials and methods

Samples

Wine samples were kindly provided by the Brazilian Agricultural Research Corporation – National Grape & Wine Research Center (Bento Gonçalves, RS, Brazil). Fermentation in winemaking was kept constant and used PDM yeast. Two wine samples 'i88' and 'm06' were produced in January/February of 2015, while the other two, 'i97' and 'm16', in January/February of 2016. 'i' and 'm' wines derived from 'Isabella' and the new 'BRS Magna' cultivars. Table S2 (see Electronic Supplementary Material, ESM) summarizes the samples analyzed.

Materials and reagents

A standard mixture of n-alkanes (C_8–C_{20}) from Merck (St. Louis, MO, USA) was used to determine the linear temperature programmed retention indices (LTPRI) of the analytes. Three different cross-linked PIL-based SPME fibers were used for analyte isolation. The PIL-based fibers were manufactured at Iowa State University (Ames, IA, USA) and evaluated at the University of Campinas (Campinas, SP, Brazil). PIL-based fibers were prepared as described in previously published methods [42, 43]. Table S1 (see ESM) summarizes the monomers and crosslinkers used in each fiber. The PIL-based SPME coatings were 1 cm length and exhibited an average coating thickness of 15 ± 2 μm ($n = 3$). For comparative analysis, a 2 cm 50/30 μm DVB/CAR/PDMS and 75 μm PA SPME fibers (Supelco – St. Louis, MO, USA) were also investigated. 20 mL glass vials, plastic screw caps, and PTFE-PDMS septa were used throughout the SPME extractions.

SPME method

All fibers were conditioned prior to the headspace (HS) SPME extractions. The commercial SPME fibers were conditioned as recommended by the manufacturer and the PIL-based fibers were conditioned for 30 min at 175 °C and 250 °C for $[Cl]^-/[Br]^-$ and $[NTf_2]^-$-based sorbent coatings, respectively.

A commercially available red wine was used as the model mixture to optimize the SPME procedure. The variables chosen for the optimization were the volume of wine (1.50, 2.25 and 4.50 mL) and concentration (10, 20 and 30% *w/v*) of a fixed volume (1.50 mL) saline solution, and the extraction temperature (30, 40 and 60 °C). Samples were pre-equilibrated for 5 min at the same temperature of the extractions. Extraction profiles were determined for the time interval of 15 to 60 min. Longer extractions were not evaluated to improve sample throughput. Continuous agitation at 300 rpm was used to ensure adequate mass transfer. Extractions were performed using 20 mL glass vials and aliquots of 4.50 mL of wine. All experiments of the optimization were obtained in triplicate. The final SPME extractions were attained by mixing 1.50 mL of 30% *w/v* aqueous solution of sodium chloride and 4.50 mL of wine, followed by 5 min pre-equilibration and 60 min sampling time at 40 °C. A continuous stirring rate of 300 rpm was used in the SPME experiments. Four replicates were obtained for each sample. The best performing SPME coatings were Fiber 2 and DVB/CAR/PDMS. Sample introduction to the GC × GC was attained by thermal desorption of the fibers at 250 °C for 5 min except for 175 °C for the $[Cl]^-$ / $[Br]^-$ PIL-based phases.

GC × GC-QMS

Analyses of volatile organic compounds from red wine samples were performed on a GC×GC, which comprised of a TRACE 1310 GC equipped with a flame ionization detector (FID) and a ISQ single quadrupole mass spectrometer (QMS) (Thermo Scientific, Waltham, MA, USA). Differential flow modulation using the reverse fill/flush configuration was

attained using INSIGHT modulator (SepSolve Analytical – Frankfurt, Germany). Data digitalization using FID was attained at 120 Hz. A 50–400 m/z scanning range was used producing 19 scans s^{-1}. Transfer line and the ion source were operated at 300 and 220 °C, respectively. Helium was used as carrier gas and auxiliary gas at constant flow rates of 1.0 mL min^{-1} and 12.5 mL min^{-1}.

The column set consisted of a primary 30 m × 0.25 mm-id × 0.25 μm (β of 250) HP-5MS and a secondary 5 m × 0.25 mm-id × 0.25 μm (β of 250) HP-50+ wall coated open tubular (WCOT) capillary columns (Agilent Technologies – Santa Clara, CA, USA). The effluent of the ^{2}D was split using a 3-port planar microfluidic device (Trajan – Victoria, Australia). Deactivated fused-silica capillaries, namely 5 m × 0.32 mm-id and 5 m × 0.18 mm-id, were used to transfer the effluent from the 3-port splitter to the FID and MS, respectively. This setup ensured a reproducible division of the ^{2}D effluent to FID (80%) and MS (20%). Sample introduction was performed using splitless injection and 1.00 min sampling time. The GC oven temperature was programmed from 45 to 250 °C at 4 °C min^{-1}. Modulation and flush periods were set to 3.0 s and 150 ms, respectively.

Identification

XCalibur (Thermo Scientific – Waltham, MA, USA) software was used for data acquisition. GC Image (Zoex – Houston, TX, USA) was used to perform peak table-based data analysis by template matching. Tentative identification of analytes was performed by combining mass spectrum similarity searches guided by LTPRI filtering. The minimum similarity match was 80%. A commercial NIST14 MS library (National Institute of Standards – Gaithersburg, MD, USA), was used for qualitative analysis. The NIST Web Book was consulted to determine the reported values of LTPRI, while the Pherobase and the Good Scents Company were used to obtain the odor descriptors.

Pixel-based chemometric analysis

The '.raw' Xcalibur (Thermo Scientific) native files were converted to '.cdf' ANDI/netCDF format using the File Converter plug-in. Multivariate data analysis was performed on MATLAB R2017b (MathWorks – Natick, MA, USA) environment. The netCDF files were imported to MATLAB to generate three-way data tensors. MPCA was performed using PLS Toolbox 7.5 (Eigenvector Research Inc. – Wenatchee, WA, USA) and it was used to compare the chemical information probed by each SPME sorbent coating. Fisher ratio calculations were performed using homemade MATLAB routines [44, 45]. MATLAB bi-plots highlighted the high-ranked F-ratio regions aiding in the selection of the grape-specific peaks in the GC × GC chromatograms.

Results and discussion

Method optimization

SPME relies on the diffusion of the analytes from the sample matrix to the extraction phase reaching thermodynamic equilibrium in the multiphasic system [44]. The distribution coefficient determines the affinity of a sorbent phase toward the analyte, which depends on the physical and chemical properties of the coating.

Solid coatings, such as DVB and Carboxen, which dispersed in PDMS, exhibit a large internal surface area promoting strong adsorption of analytes. Despite the high extraction efficiencies of solid coatings, they exhibit limited adsorption capacity resulting in short linear range for calibration [44], as well as displacement effects caused by high concentration of alcohol, for instance. Hence, polymeric liquid coatings were also evaluated, such as PA and PIL-based phases [17], as this limitation is avoided. In these coatings, analyte sorption is based on the partitioning process.

In this context, sampling a broad diversity of volatile organic compounds is required for profiling wine aroma, which comprises polar VOCs. PILs provide better selectivity toward polar analytes in comparison to commercially available phases, such as PA [12, 46]. Therefore, three custom-made PIL-based SPME coatings were carefully selected based on our group's past experience with food matrices [10, 12, 13, 45, 47–49], as described in Table S1 (see ESM). Also, two commercial coatings, namely PA and DVB/CAR/PDMS, were adopted as references for comparative analysis.

Preliminary experiments allowed the selection of extraction temperature (40 °C) and sample dilution factor (4.5 mL of wine mixed with 1.5 mL of 30% w/v aqueous solution of sodium chloride). Frequently, analyte uptake by SPME sorbent phase is an exothermic process, therefore increased temperature values results in undesired lowering of partitioning constant, although higher temperatures favors improved mass transfer. Hence, an intermediate extraction temperature, 40 °C, was selected for SPME experiments. In addition, mild temperatures also diminish the likelihood of producing extraction artifacts during analyte equilibration [50]. For instance, our group has ascertained that the concentrations of the extraction artifacts hydroxymethylfurfural, methyl-furone, and furfural increased with high equilibration temperatures and exposure periods, e.g. 240 min at 60 °C, which favored the occurrence of hydrolysis and thermal decomposition in honey samples. The addition of strong electrolytes, such as sodium chloride, to multiphasic equilibrium in high-ethanol beverages has no effect on the vapor pressure of ethanol but impacts the most on the water activity and salting out effect of most trace volatile and semi-volatile organic compounds [51]. Therefore, wine was diluted to reduce the vapor pressure of ethanol, while

the aqueous saline solution provided enhanced distribution constants of VOCs because of the salting out effect.

The extraction profiles were determined using all SPME fibers and are shown in Fig. S1 (see ESM), with relative standard deviations lower than 15%. Longer equilibration periods were not evaluated to maintain sample throughput, thus the extraction time selected was 60 min. Selection of the best performing SPME fibers within each group of sorbents, namely ionic and non-ionic, was performed considering the total number of extracted analytes (i.e., sum of peak areas) and the number of peaks in the respective GC × GC-FID chromatograms. The chromatograms obtained for the model red wine using all five fibers are shown in Fig. 1. It is readily noticed that at least 17 peak clusters that overlapped in the ^{1}D are resolved in the ^{2}D illustrating the benefits of GC × GC-MS profiling. For instance, ethyl sorbate and hexanoic acid overlaped in the ^{1}D but are baseline resolved in the ^{2}D, enabling proper identification of both analytes. Similarly, the pairs ethyl octanoate/octanoic acid and β-damascenone/decanoic acid also overlap in the ^{1}D but are separated in the ^{2}D.

The best performing fibers were the commercial DVB/CAR/PDMS assembly and the PIL-based Fiber 2, which were selected for further evaluation. It is worth noting that, although a large difference in the sum of peak areas was observed between the selected coatings, the total number of extracted analytes was significantly higher, 372 for Fiber 2 and 331 for DVB/CAR/PDMS.

Noteworthy, an important issue in fiber-based SPME is that the non-ionic liquid coatings may exhibit significantly lower distribution coefficients compared to the solid coatings [44]. Thus, a larger volume of the extraction phase must be used to improve sensitivity, especially for analytes that present low phase/sample distribution values. However, the PIL-based sorbent phases exhibited comparable extraction performance, although the average PIL coating thickness was only 15 μm (ESM Fig. S2) compared to 85 μm for PA and 50/30 μm for DVB/CAR/PDMS.

The evaluated PIL-based coatings are known to exhibit unique selectivity allowing the extraction of challenging and polar VOCs. For instance, the presence of a halide anion in the structure of Fiber 1 enhances the hydrogen bond basicity of the sorbent, which increases the selectivity toward analytes that can undergo hydrogen-bonding interactions, such as alcohols, carboxylic acids and amines [52, 53]. The PIL structure in Fiber 2 contains a long free alkyl side chain, increasing the ability to engage in non-specific dispersive interactions with aliphatic hydrocarbons [54]. The chemistry of Fiber 3 also contains a long alkyl side chain, but its cation is functionalized with a benzyl moiety, enabling the establishment of π-π interactions with aromatic VOCs [9]. Furthermore, all PIL-based SPME coatings exhibited excellent extraction of alcohols and fatty acids from the wine-diluted sample, as illustrated in Table 1.

Wine profiling using GC × GC

The GC × GC-QMS chromatograms of the wines produced from cultivars 'Isabella' and 'BRS Magna' vintages 2015 and 2016 using PIL-based Fiber 2 are shown in Fig. 2. Although 372 peaks were detected, only 103 (~28%) of the analytes could be successfully. This fact evidences the need for coupling high-resolution mass spectrometers to complement the extraordinary peak capacity of GC × GC to provide accurate mass measurements for qualitative analysis.

The main chemical classes found in wine aroma (see Table 1) were esters, alcohols, terpenes, phenylpropanoids, and organic acids—which are consistent with previous reports [2, 26, 55–57]. In addition, analytes with important sensory characteristics were successfully isolated. Esters are naturally found in grapes, although most of them are formed during fermentation and wine aging. Esters at low concentrations impart a sweet-fruity aroma to wines. Such group of analytes are derived from alkyl acetates or condensation reactions of fatty acids with ethanol, such as ethyl hexanoate (aniseed,

Fig. 1 GC × GC-QMS chromatograms of a model red wine aroma using HS-SPME sampling with different fiber coatings, namely PA (**a**), DVB/CAR/PDMS (**b**), PIL-based Fiber 1 (**c**), PIL-based Fiber 2 (**d**), and PIL-based Fiber 3 (**e**). Reverse fill/flush flow modulation was executed using INSIGHT™ modulator
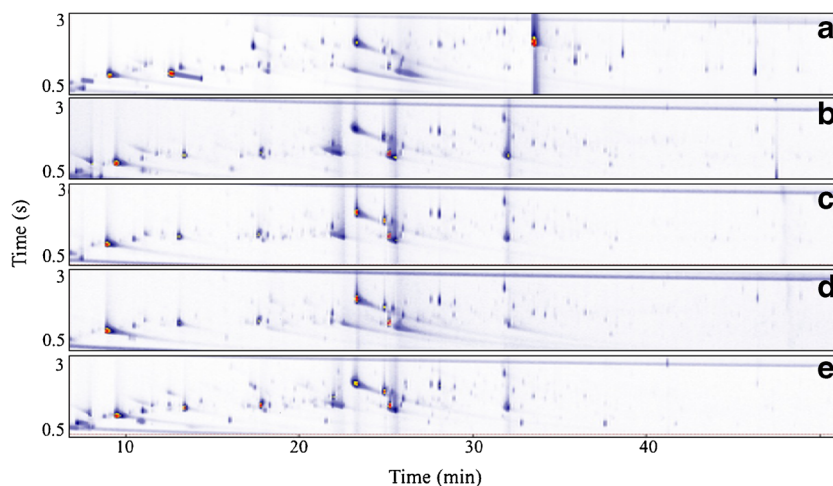
Table 1 Tentative identification of the analytes found in the volatile and semi-volatile fraction of Isabella and BRS Magna samples by HS-SPME and GC×GC-QMS. The selectivity of the investigated SPME coatings was demonstrated by highlighting the analytes extracted by the PIL-based sorbent materials and commercial fibers. The "x" entries indicate the extraction of such analyte by the SPME fiber. Retention indexes were obtained from NIST. Odor and flavor descriptors were attained from The Good Scents Company. Blob detection was attained using GC Image by adopting the following criteria: minimum area of 20, minimum volume of 50, and minimum peak value of 50. All analytes were identified by considering a minimum similarity match of 80% and a ±15 LTPRI deviation from NIST Web Book

Compound name	Match	Formula	CAS	LTPRI	LTPRI, NIST	PA	DVB/CAR/PDMS	Fiber 1	Fiber 2	Fiber 3	Odor	Flavor
Ethyl propanoate	88	$C_5H_{10}O_2$	105-37-3	708	739					x	sweet, fruity, grape, pineapple	fruity, sweet, winey, apple and grape nuances
3-methyl-1-heptene	86	C_8H_{16}	4810-09-7	742	732	x		x		x	–	intense fusel, fermented, bready and cereal with a fruity undernote
1-pentanol	91	$C_5H_{12}O$	71-41-0	759	763	x	x	x		x	fusel oil, sweet balsam	–
5-methyl-2-heptene	88	C_8H_{16}	22487-87-2	760	773			x	x		–	–
1-hexyn-3-ol	81	$C_6H_{10}O$	105-31-7	778	790			x			–	green, woody, apple, grassy, citrus and orange with a fresh, lingering aftertaste
hexanal	81	$C_6H_{12}O$	66-25-1	801	813			x			fresh green, grass leafy, fruity	–
ethyl butanoate	91	$C_6H_{12}O_2$	105-54-4	803	811		x	x	x	x	fruity, pineapple, cognac	fruity, sweet, tutti frutti, apple, fresh
propyl propanoate	83	$C_6H_{12}O_2$	106-36-5	807	800			x			sharp pungent, sweet, fruity, pineapple, winey	sweet, lift, tropical green fruity notes
isopentyl formate	85	$C_6H_{12}O_2$	110-45-2	818	830	x	x	x	x		plum, blackcurrant, vinous dry, earthy, green	sharp, green, apple and fruity with winey, fatty notes
E-2-octene	84	C_8H_{16}	13389-42-9	824	820				x		–	–
Z-2-octene	80	C_8H_{16}	7642-04-8	824	823	x					–	–
ethyl crotonate	87	$C_6H_{10}O_2$	623-70-1	839	853		x			x	pungent, sweet, caramel rum	musty, caramellic and brown notes
furfural	81	$C_5H_4O_2$	98-01-1	845	833		x				sweet woody, almond fragrant, baked bread	brown, sweet, woody, bready, nutty, caramellic with a burnt astringent nuance
1-hexanol	89	$C_6H_{14}O$	111-27-3	867	876	x	x	x			fusel oil, fruity, alcoholic, sweet green	green, fruity, apple-skin and oily
isoamyl acetate	89	$C_7H_{14}O_2$	123-92-2	871	887	x	x	x	x	x	sweet fruity, banana	sweet fruity, banana-like with a green ripe nuance
3,7-dimethyl-1-octene	88	$C_{10}H_{20}$	4984-01-4	877	866	x	x	x	x	x	woody, piney, herbaceous	–
ethyl pentanoate	83	$C_7H_{14}O_2$	539-82-2	884	873		x	x	x		sweet fruity, apple, pineapple, green tropical	fruity, strawberry, sweet, pineapple and tropical fruit
1,3,5,7-cyclooctatetraene	81	C_8H_8	629-20-9	888	898		x				–	–
3-methyl-1-hexanol	86	$C_7H_{16}O$	13231-81-7	896	880			x			–	–
5-methyl-1-hexanol	89	$C_7H_{16}O$	627-98-5	896	890	x	x	x	x		–	–
1-nonene	85	C_9H_{18}	124-11-8	906	900	x	x				–	–
bicyclo[4.2.0]octa-1,3,5-triene	83	C_8H_8	694-87-1	927	923	x		x			–	–
hexyl formate	83	$C_7H_{14}O_2$	629-33-4	929	937			x			–	–
1-heptanol	88	$C_7H_{16}O$	111-70-6	960	971		x	x	x		musty, leafy, violet, herbal, green, sweet, woody, peony	fermented with oily nutty and fatty notes, and a slight green aldehydic under note
benzaldehyde	88	C_7H_6O	100-52-7	982	1002	x	x	x			strong, sweet, bitter, almond, cherry	sweet, oily, almond, cherry, nutty and woody
2-ethyl-hexanol	89	$C_8H_{18}O$	104-76-7	984	1000		x				citrus, fresh, floral, oily, sweet	sweet, fatty, fruity
ethyl hexanoate	96	$C_8H_{16}O_2$	123-66-0	984	1009	x	x	x	x	x	sweet, fruity, pineapple, green, banana	sweet, pineapple, fruity, waxy and banana with a green, estry nuance
4-pyridinamine	83	$C_5H_6N_2$	504-24-5	986	999			x			–	–

Table 1 (continued)

Compound name	Match	Formula	CAS	LTPRI	LTPRI, NIST	PA	DVB/ CAR/ PDMS	Fiber 1	Fiber 2	Fiber 3	Odor	Flavor
ethyl E-4-hexenoate	91	$C_8H_{14}O_2$	629-33-5	992	1000			x			–	–
2-carene	82	$C_{10}H_{16}$	554-61-0	1000	1012			x	x	x	–	–
3-methyl-pentanoic acid	84	$C_6H_{12}O_2$	105-43-1	1002	999		x	x	x	x	sharp, acidic, cheesy, green, fruity, sweaty	sour, cheesy, fresh with fruity notes
1-decene	83	$C_{10}H_{20}$	872-05-9	1005	1015		x	x	x		–	–
hexyl acetate	94	$C_8H_{16}O_2$	142-92-7	1012	1025	x	x	x	x	x	fruity, green, apple, banana, sweet	fruity, green, fresh, sweet, banana peel, apple and pear
limonene	84	$C_{10}H_{16}$	138-86-3	1018	1046					x	citrus, herbal, terpene, camphor pungent, fruity, licorice	–
methyl sorbate	84	$C_7H_{10}O_2$	689-89-4	1019	1030			x			–	fruity, sweet, brown, vanilla and nutty
β-phellandrene	82	$C_{10}H_{16}$	555-10-2	1031	1022					x	mint, terpentine	–
3-methyl-1,2-cyclopentanediol	85	$C_6H_{12}O_2$	27583-37-5	1037	1044		x				–	–
ethyl E-2-hexenoate	91	$C_8H_{14}O_2$	27829-72-7	1041	1036		x	x		x	sweet, green, fruity, vegetable	fruity, green, sweet, with a juicy fruity undernote
eucalyptol	82	$C_{10}H_{18}O$	470-82-6	1059	1050		x	x			eucalyptus, herbal, camphor balsam	minty, camphoreous, eucalyptus
cis-sabinene hydrate	81	$C_{10}H_{18}O$	15537-55-0	1069	1078		x				balsam	–
1-octanol	81	$C_8H_{18}O$	111-87-5	1076	1063	x	x	x		x	green, orange, rose	green, citrus, orange and aldehydic with a fruity nuance
E-linalool oxide	83	$C_{10}H_{18}O_2$	34995-77-2	1086	1077		x	x			floral	–
o-tolualdehyde	89	C_8H_8O	529-20-4	1095	1099		x	x			cherry	–
p-tolualdehyde	89	C_8H_8O	104-87-0	1095	1101		x	x			fruity, cherry, deep phenolic	sweet, spicy, cinnamon, fruity, bitter almond
methyl benzoate	84	$C_8H_8O_2$	93-58-3	1096	1100	x		x			phenolic, wintergreen, almond, floral, cananga woody, balsam	phenolic and cherry pit with a camphoraceous nuance
E-sabinene hydrate	81	$C_{10}H_{18}O$	17699-16-0	1099	1087	x					–	–
linalool	88	$C_{10}H_{18}O$	78-70-6	1101	1119	x	x	x		x	citrus, floral, sweet, bois de rose, woody, green, blueberry	citrus, orange, lemon, floral, waxy, aldehydic and woody
ethyl sorbate	85	$C_8H_{12}O_2$	2396-84-1	1102	1121	x	x	x	x	x	warm fruity, anise, licorice	fruity, sweet, green, pineapple, juicy tropical nuances
nonanal	83	$C_9H_{18}O$	124-19-6	1107	1114	x	x	x		x	aldehydic, rose, fresh, orris, orange peel	effervescent, aldehydic citrus, melon rindy
E,E-2,4-hexadienoic acid	92	$C_6H_8O_2$	110-44-1	1109	1129	x	x	x	x	x	–	–
ethyl methyl succinate	95	$C_7H_{12}O_4$	627-73-6	1120	1134				x	x	–	–
2-phenylethanol	96	$C_8H_{10}O$	60-12-8	1136	1156	x		x	x	x	floral, rose, dried rose	floral, sweet, rosey and bready
6-methyl-2-pyrazinylmethanol	81	$C_6H_8N_2O$	77164-93-3	1137	1126		x				–	–
benzylmethoxymethyl ether	87	$C_9H_{12}O_2$	31600-55-2	1144	1150			x	x	x	–	–
1-phenyl-2-propanol	84	$C_9H_{12}O$	698-87-3	1155	1149	x		x	x	x	weak rose	sweet, pineapple
E-2-nonenal	81	$C_9H_{16}O$	18829-56-6	1163	1178	x		x	x	x	green, aldehydic, citrus	green, soapy, cucumber/melon-like with an aldehydic/fatty nuance
ethyl benzoate	80	$C_9H_{10}O_2$	93-89-0	1170	1155	x					fruity, dry, musty, sweet, wintergreen	sweet, green, minty, fruity, birch beer and wintergreen like
octanoic acid	84	$C_8H_{16}O_2$	124-07-2	1173	1177		x	x	x		vegetable, cheesy	rancid, soapy, cheesy, fatty, brandy
1-nonanol	86	$C_9H_{20}O$	143-08-8	1176	1164			x			fresh, floral, rose, orange	citrus, rue, aldehydic, orange, oily, fatty, spicy
3,5-dimethylphenol	84	$C_8H_{10}O$	108-68-9	1178	1185	x	x	x	x	x	–	balsamic, coffee
diethyl succinate	93	$C_8H_{14}O_4$	123-25-1	1183	1198	x	x	x	x	x	mild, fruity, apple, ylang	fruity, tart, tropical, floral, passion fruit

Table 1 (continued)

Compound name	Match	Formula	CAS	LTPRI	LTPRI, NIST	PA	DVB/CAR/PDMS	Fiber 1	Fiber 2	Fiber 3	Odor	Flavor
ethyl octanoate	93	$C_{10}H_{20}O_2$	106-32-1	1183	1207	x	x	x	x	x	fruity, wine, sweet, apricot, banana, brandy, pear	sweet, fruity and pineapple with creamy, fatty, mushroom and cognac notes
3,4-dimethylphenol	82	$C_8H_{10}O$	95-65-8	1191	1185	x	x	x			flat, dry	smoky, sweet and earthy notes
pentylbenzene	82	$C_{11}H_{16}$	538-68-1	1191	1208	x	x				–	–
α-terpineol	89	$C_{10}H_{18}O$	98-55-5	1195	1229	x	x	x	x	x	pine, terpene, lilac, citrus, woody, floral	citrus, woody, lemon, lime, soapy
butyl sorbate	80	$C_{10}H_{16}O_2$	7367-78-4	1199	1211		x	x			–	–
cyclodecane	86	$C_{10}H_{20}$	293-96-9	1199	1189					x	–	–
γ-terpineol	81	$C_{10}H_{18}O$	586-81-2	1200	1187		x		x	x	terpineol, lilac	–
decanal	93	$C_{10}H_{20}O$	112-31-2	1204	1224	x	x		x	x	sweet, aldehydic, orange peel, citrus, floral	citrus and orange peel with a slight green melon nuance
nonyl-cyclopropane	86	$C_{12}H_{24}$	74663-85-7	1216	1225	x	x	x	x	x	–	–
α-citronellol	80	$C_{10}H_{20}O$	141-25-3	1228	1220	x	x		x		floral, red rose, spicy, geranium	floral rosy, with waxy, powdery and heavy citrus and tropical nuances
β-citronellol	83	$C_{10}H_{20}O$	106-22-9	1232	1252	x	x		x	x	floral, rose bud, citrus	floral, rose, sweet, green with fruity citrus nuances
thiobenzoic acid	81	C_7H_6OS	98-91-9	1233	1247	x		x	x		–	–
ethyl phenylacetate	86	$C_{10}H_{12}O_2$	101-97-3	1246	1274	x	x	x	x	x	sweet, floral, honey, rose, balsam, cocoa	strong, rosy, honey and balsamic cocoa-like with molasses and yeasty nuances
2-phenylethyl acetate	84	$C_{10}H_{12}O_2$	103-45-7	1257	1287	x	x	x	x	x	floral, rose, sweet, honey, fruity, tropical	sweet, honey, floral, rosy
nonanoic acid	82	$C_9H_{18}O_2$	112-05-0	1272	7166	x		x	x		cheesy, cultured dairy	fatty, waxy and cheesy with a mild sweet creamy background
4-ethylguaiacol	88	$C_9H_{12}O_2$	2785-89-9	1303	1311	x	x	x	x	x	spicy, smoky, phenolic	woody, smokey and spicy with a sweet vanilla background
terpinyl formate	84	$C_{11}H_{18}O_2$	2153-26-6	1306	1314	x	x				floral, lavender, citrus, fruity	dry, fruity, raspberry
undecanal	86	$C_{11}H_{22}O$	112-44-7	1309	1299	x				x	floral, aldehydic, citrus, green	aldehydic, soapy with a citrus note and slight laundry detergent nuance
methyl E-4-decaenoate	86	$C_{12}H_{22}O_2$	76649-16-6	1380	1369	x					green, fruity, cognac	fatty, waxy, green, pineapple and pear nuances
hexyl hexanoate	82	$C_{12}H_{24}O_2$	6378-65-0	1381	1377			x			herbal, fresh, cut grass, vegetable, fruity	sweet, fruity and green with tropical notes
ethyl Z-4-decenoate	82	$C_{12}H_{22}O_2$	7367-84-2	1389	1398	x	x	x			–	soapy, waxy, fruity
decanoic acid	86	$C_{10}H_{20}O_2$	334-48-5	1398	1405	x	x		x	x	unpleasant, rancid, sour, fatty, citrus	–
ethyl decanoate	91	$C_{12}H_{24}O_2$	110-38-3	1399	1406	x	x	x		x	sweet, waxy, fruity, apple, grape, oily, brandy	waxy, fruity, sweet apple
1-tetradecene	82	$C_{14}H_{28}$	112-36-1	1403	1388		x				–	–
dodecanal	86	$C_{12}H_{24}O$	112-54-9	1410	1420		x			x	soapy, aldehydic, citrus, green, floral	soapy, waxy, citrus, orange mandarin
β-damascenone	86	$C_{13}H_{18}O$	23726-93-4	1440	1432	x		x	x	x	apple, rose, honey, tobacco, sweet	–
2,4-di-tert-butylphenol	88	$C_{14}H_{22}O$	96-76-4	1555	1545		x		x	x	phenolic	–
3,5-di-tert-butylphenol	83	$C_{14}H_{22}O$	1138-52-9	1555	1564	x	x		x	x	–	–

Table 1 (continued)

Compound name	Match	Formula	CAS	LTPRI	LTPRI, NIST	PA	DVB/ CAR/ PDMS	Fiber 1	Fiber 2	Fiber 3	Odor	Flavor
E-nerolidol	86	$C_{15}H_{26}O$	40716-66-3	1561	1584	×		×	×		floral, green, citrus, woody, waxy	green, floral, woody, fruity, citrus, melon
dodecanoic acid	83	$C_{12}H_{24}O_2$	143-07-7	1570	1563				×		coconut bay, oil	–
1-tridecanol	87	$C_{13}H_{28}O$	112-70-9	1580	1595	×		×		×	musty	–
hexyl octanoate	93	$C_{14}H_{28}O_2$	1117-55-1	1583	1594			×			fruity, green, berry, apple, ester	green, apple, fruity, berry with fresh waxy nuances
ethyl dodecanoate	85	$C_{14}H_{28}O_2$	106-33-2	1598	1605					×	sweet, floral	waxy, soapy and floral with a creamy, dairy and fruity nuance
1-hexadecene	92	$C_{16}H_{32}$	629-73-2	1602	1593				×		–	–
cyclohexyl benzoate	86	$C_{13}H_{16}O_2$	2412-73-9	1621	1633			×			mild, balsamic floral, herbal	–
benzophenone dimethyl ketal	81	$C_{15}H_{16}O_2$	2235-01-0	1733	1730			×			–	–
hexyl decanoate	90	$C_{16}H_{32}O_2$	10448-26-7	1779	1793			×			fresh green	–
1-pentadecanol	81	$C_{15}H_{32}O$	629-76-5	1784	1769				×		–	–
diisobutyl phthalate	84	$C_{16}H_{22}O_4$	84-69-5	1908	1905	×	×		×		–	–
methyl hexadecanoate	87	$C_{17}H_{34}O_2$	112-39-0	1925	1911				×		oily, waxy, fatty, orris	–
benzoyloxy-succinimide	83	$C_{11}H_9NO_4$	23405-15-4	1932	1947			×			–	–
2,2-dimethyl-1,3-diphenyl-1, 3-propanedione	88	$C_{17}H_{16}O_2$	41169-42-0	2052	2042			×			–	–

apple) and ethyl octanoate (pineapple). Isoamyl acetate is associated with the artificial banana smell, while the presence of ethyl acetate (fruity) is not always pleasant. 2-phenylethyl acetate is related to honey and tobacco notes. Also, terpenes such as linalool and α-terpineol are responsible for floral attributes, whereas phenylpropanoids contribute to tobacco and chocolate aroma. Lastly, free acids have been associated with aged wines [2, 26, 55–57].

Interestingly, GC×GC-QMS profiling of the wine aromas using all five SPME coatings indicated the absence of most common off-flavors: acetaldehyde (oxidation-related fault); short-chain organic acids like formic, lactic, propionic and butyric acids (i.e., volatile acidity); 2-acetyl-pyrroline (mousy taint); mercaptans and dissulfides (reduction-related fault); 2,3-butanedione (buttery scent); trichloroanisole and tribromoanisole (cork taint); 2-methoxy-3,5-dimethyl-pyrazine (fungal musk); and geosmin (earthy taint) for example. However, 4-ethyl-guaiacol was detected in the 'Isabella' and 'BRS Magna' red wines and it is frequently associated with spicy and smoke aroma, which negatively affect the overall perception. Noteworthy, this off-flavor is usually found in higher concentrations in Cabernet Sauvignon wines compared to contemporary red wines.

PIL-based Fiber 1 and Fiber 3 exhibited the highest number of exclusive compounds that were not extracted by the commercial SPME coatings (Table 1). Fiber 1 isolated some esters and phenylpropanoids, including benzaldehyde, phenylacetaldehyde, hexyl octanoate, hexyl benzoate, and hexyl decanoate that possesses important attributes [56, 57]. For example, many aldehydes are yeast fermentation by-products and convey nutty and bruised apple aroma. Accordingly, Fiber 2 also extracted decanoic acid [57] and nerolidol (woody aroma) [58]. Fiber 3 was the only coating that isolated limonene and α-terpinene, which are related to lemony-citrusy and sweet-citrusy smells [59, 60].

SPME fiber comparison using exploratory analysis

Careful considerations are required when developing new sorbent phases for sample preparation. In this study, we probed five SPME coatings, namely three PIL-based and two commercially available phases. The initial criteria for fiber selection was the number of extracted peaks, which enabled the selection of the two best performing extractants, DVB/CAR/PDMS and PIL-based Fiber 2. Although analysis of the qualitative table allows for the establishment of general relationships between the structural features of the PILs and the extracted analytes, we could not ascertain nor compare the chemical information probed by each of the best performing fibers.

To compare the chemical information probed by the best performing SPME coatings, DVB/CAR/PDMS and PIL-based Fiber 2, a pixel-based exploratory analysis was selected. A conventional approach using peak tables and template

Fig. 2 Total ion chromatogram of the investigated wines aroma using HS-SPME sampling with PIL-based Fiber 2. Investigated wine samples were produced from grape cultivars: "Isabella" vintages 2015 (**a**) and 2016 (**c**); "BRS Magna" vintages 2015 (**b**) and 2016 (**d**)
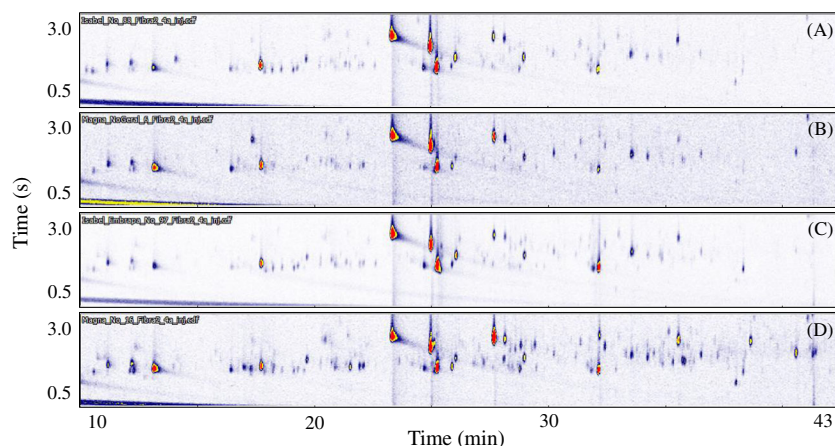
matching would require careful analyte integration and creation of a template, which we considered to be a time-consuming task at this point for comparative analysis, considering the hundreds of peaks and their wide intensity range. Furthermore, pixel-based data handling made more efficient use of the chemical information contained within the experimental measurements. It is also important to highlight that careful inspection of the unfolded chromatograms indicated insignificant retention time shifts between GC×GC-QMS runs, as shown in Fig. S3 (see ESM).

MPCA analysis enabled successful data projection and reduction, unveiling the chemical information contained within the native signals. A two-component MPCA model explained 62.78 and 76.79% of the aroma profiles obtained using DVB/CAR/PDMS and PIL-based Fiber 2, respectively (ESM Fig. S4). The presence of anomalous samples (i.e., outliers) was discarded by visual inspection of the plot of Q residuals versus Hotelling's t^2 ($\alpha = 0.05$) (ESM Fig. S5). The MPCA scores graph of the data obtained using DVB/CAR/PDMS and PIL-based Fiber 2 are shown in Fig. 3. Clustering of wine samples from 'Isabella' and 'BRS Magna' grapes was readily detected in the scores graph, except that DVB/CAR/PDMS data was more sensitive to the season of the grapes. Although both SPME coatings may be used to differentiate 'Isabella' and 'BRS Magna' wines, Fiber 2 was selected because it seemed less sensitive to the vintage/seasonality of samples.
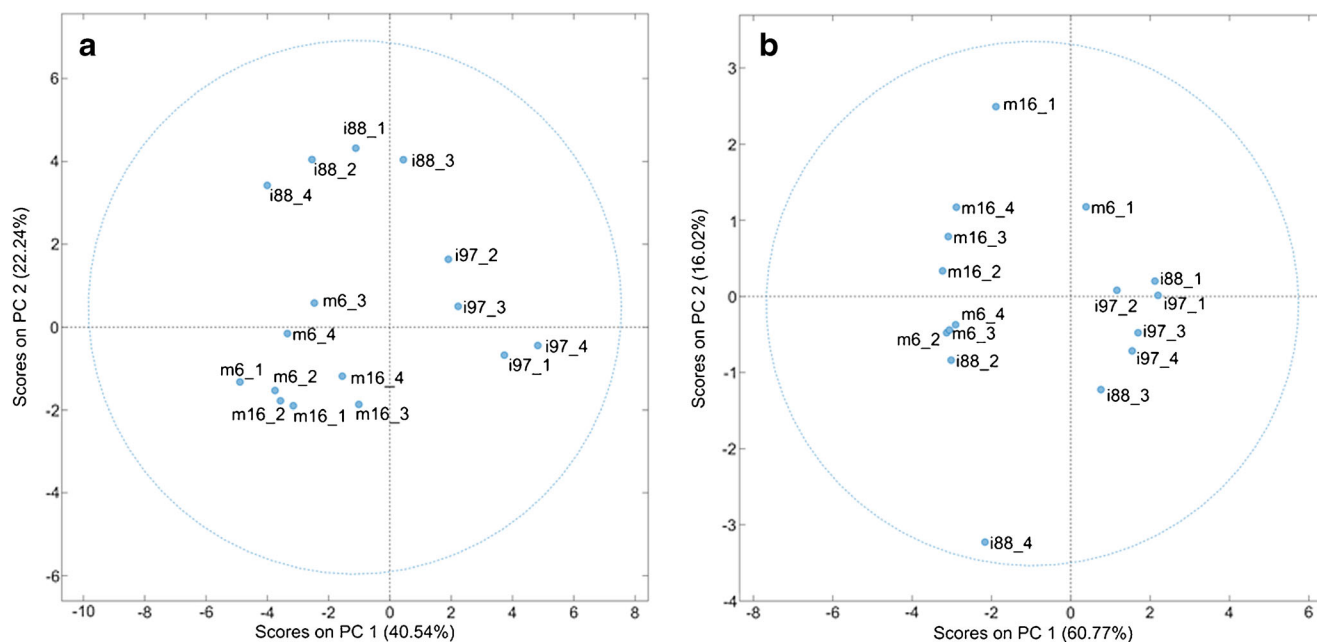

Fig. 3 Pixel-based two-component MPCA of Brazilian wines using four-way GC×GC-QMS data. Aroma profiles were obtained using the 50/30 DVB/CAR/PDMS (**a**) and PIL-based Fiber 2 (**b**). Caption: "Isabella," 2015—i88; "Isabella," 2016—i97; "BRS Magna," 2015—m6; "BRS Magna," 2016—m16

Fig. 4 Fisher bi-plot using GC Image to create a peak template from the high F-value regions (**a**). Example of template matching using GC Image to assign potential cultivar-specific peaks in the GC×GC-QMS total ion chromatogram of a "BRS Magna" vintage 2016 wine sample (**b**)
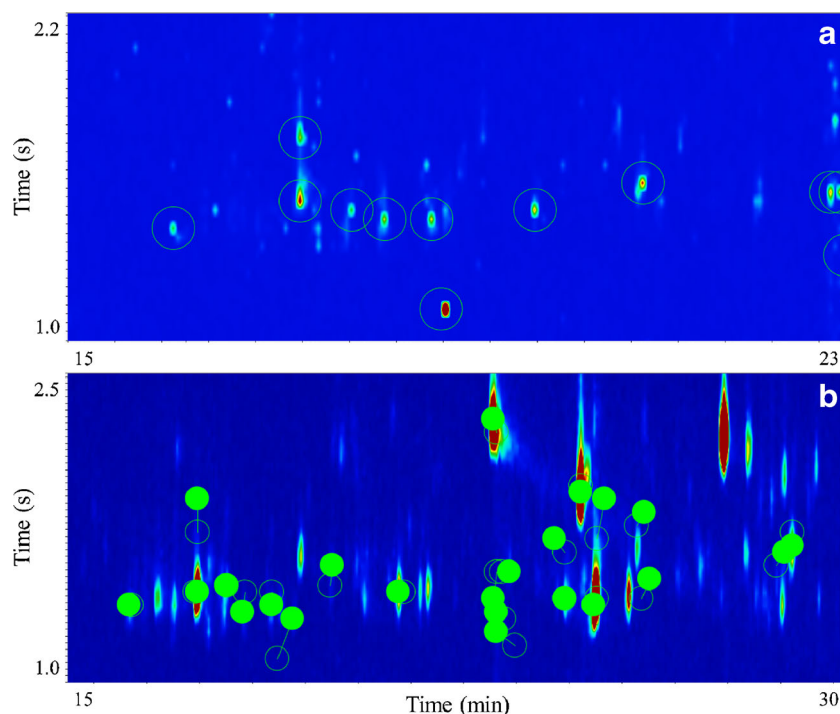
Discriminating analysis using pixel- and peak table-based data handling

To ascertain an important application of PIL-based SPME coatings to wine analyses, a protocol to differentiate Isabella and Magna-wines was elaborated. Chemometric methods are known to mathematically extract intrinsic information of GC×GC measurements in an analyst-independent and parsimonious way. Fisher ratio analysis is a conceptually simple but effective method to assign class-dependent VOCs in complex measurements. Investigation of the varietal diversity of wines is often dampened because a fraction of information contained within the data is unrelated with the grape, e.g. the wine vintage. Fisher ratio, however, highlighted the portions of the chromatograms that were statistically relevant by differentiating the pixels with large class-to-class variation (σ^2_{cl})

and the within-class variation (σ^2_{err}) [37, 39, 46, 61, 62]. Fisher ratio is calculated at every point in the separation space and may be calculated by the ratio of σ^2_{cl} of the detector signal and the sum of the σ^2_{err} of the detector signal. By highlighting these regions, Fisher ratio allows the extraction of statistically relevant information from the experimental measurements [63].

In this study, we have used an in-house MATLAB script to determine the F-value for each pixel available in the GC×GC-QMS chromatogram. Afterwards, tensor reduction was performed by calculating the sum of the F-values for each of the m/z channels. This procedure generated a two-dimensional tensor, equivalent to a GC×GC-MS total ion chromatogram, which was unfolded into a column-vector that contained all F-values and exported to a '.txt' or '.csv' file. The following file was imported by GC Image and plotted as a conventional GC×GC-MS chromatogram, as shown in
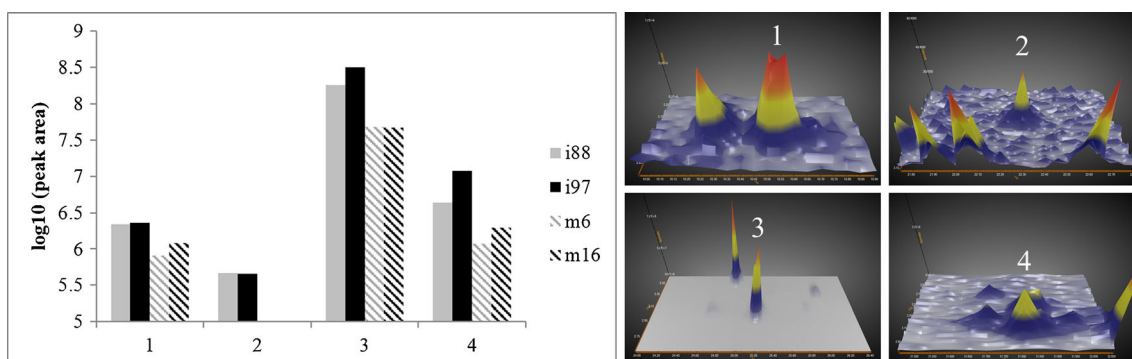

Fig. 5 Average peak areas (log$_{10}$ base) of analytes relevant to class differentiation, using pixel-based Fisher ratio analysis (left). 3D chromatographic profiles of 1—ethyl butanoate; 2—ethyl methyl succinate; 3—ethyl octanoate; 4—n-octanoic acid (right). Caption: "Isabella," 2015—i88; "Isabella," 2016—i97; "BRS Magna," 2015—m6; "BRS Magna," 2016—m16

Fig. 4. However, instead of chromatographic peaks in the two-dimensional contour plot, we obtained an image with a broad distribution of *F*-values. In this 'Fisher bi-plot', the regions with high-ranked *F*-values indicated the elution windows of peaks that were statistically different between the two groups of samples, 'Isabella' and 'BRS Magna'. Hence, such elution windows were used to guide the creation of a template in GC Image. The Fisher ratio-based template was then loaded, matched, and applied to the individual GC×GC-QMS chromatograms (see Fig. 4), after automated baseline correction and blob detection. The highlighted peaks and their peak values were used to assign of class-specific analytes.

Ethyl butanoate, ethyl methyl succinate, ethyl octanoate, octanoic acid, and α-terpinene were the analytes with the highest Fisher values (values above 10^5 in ESM Fig. S6). To illustrate the feasibility of such hybrid approach for class differentiation, the average peak values of four VOCs with high-ranked F-values were plotted in Fig. 5. Ethyl butanoate, ethyl octanoate, and octanoic acid were found in higher intensities in Isabella-wines compared to 'BRS Magna' samples. Remarkably, ethyl methyl succinate was detected exclusively in Isabella-samples. Also, a major hallmark of the proposed approach was that the statistical-assignment of the markers was independent of the signal-to-noise ratio of the analytes, Fig. 5 (right), as the analytes with highest *F*-values were found in trace concentrations. Noteworthy, two of the four potential markers, namely ethyl butanoate and ethyl methyl succinate, were only detected by the extractions using the PIL-based SPME fibers (see ESM Table S1), which shows the potential of these coatings to extract important chemical information from the wine samples.

Conclusions

Polymeric ionic liquids have drawn increased attention as SPME coatings because of their unique solvation properties. In this study, we carefully evaluated three PIL-based SPME coatings and compared their analytical performance with two commercial SPME sorbents, namely PA and PDMS/CAR/DVB. The best performing fibers, Fiber 2 and DVB/CAR/PDMS, exhibited improved selectivity toward a broad range of VOCs present in wine aroma. Our data has ascertained that PIL-based Fiber 2 exhibited higher selectivity toward the analytes found in wine aroma compared to DVB/CAR/PDMS. This study demonstrated that SPME using polymeric ionic liquids can provide greater analytical performance if oriented structural design of ILs monomer/crosslinker is performed.

Furthermore, a hybrid data handling protocol was proposed that comprised two simple steps. Firstly, a supervised pixel-based approach using Fisher ratio allowed the guided creation of a peak template. Secondly, after automated processing of the GC × GC-MS chromatograms, namely baseline correction and blob detection, template matching was performed to enable peak table-based data analysis. This simple procedure may be executed by non-expert users and it has allowed for efficient data mining by accurately assigning key markers from a total of 372 detected analytes. A major hallmark of the proposed method is that the occurrence of false positives in the F-ratio plot is eliminated by using template matching resulting in a powerful combination for GC × GC-MS big data analysis.

This outcome has enabled successful distinction of 'Isabella' wines from the new cultivar 'BRS Magna'. We expect to continue this research by significantly profiling more samples and applying such important aroma-related information to sensorial analysis of Brazilian wines.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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