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Quantification of varietal aroma compounds, oak markers, and Strecker aldehydes in wines by SPE and gas chromatography–tandem mass spectrometry

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Abstract

This protocol outlines the conditions for the assaying volatile impact compounds in white and red wines by gas chromatography–tandem mass spectrometry (GC–MS/MS). This method enables the quantification of volatile thiols (3SH: 3-sulfanylhhexanol; 3SHA: 3-sulfanylhhexyl acetate; 4MSP: 4-methyl-4-sulfanylpentan-2-one; BM: benzenemethanethiol; E2SA: ethyl 2-sulfanylacetate; and FFT: furfurylthiol), odoriferous oxidation markers (methional, ortho-acetaminophenone, and phenylacetaldehyde) in dry white wines, the main furanones and lactones associated with jammy fruit notes in red wines, terpenes (linalool, α -terpineol, nerol, geraniol), C13-norisoprenoids (β -damascenone and β -ionone), and oak wood markers (vanillin, eugenol, whisky lactone, guaiacol, nerol). This method represents an optimization and automation of the one described by Thibon et al (2015).

Materials

Gilson GX-274 ASPEC solid-phase extraction system (Villiers-Le-Bel, France)

HR-X CHROMABOND (500 mg, 6mL, Nacherrey-Nagel, France)

Trace GC Ultra gas chromatograph coupled to a TSQ Quantum XLS triple quadrupole mass spectrometer (Thermo Electron SAS, Courtaboeuf, France)

OPTIMA WAX, 100% Polyethylene glycol, 60 m; 0.25 mm; 0.25 μ m (Macherey-Nagel, Germany)

Extraction of volatile compounds

- 1 The SPE procedure was automated with a Gilson GX-274 ASPEC solid-phase extraction system (Villiers-Le-Bel, France). HR-X CHROMABOND (500 mg, 6mL, Nacherey-Nagel, France) was first activated with methanol (7 mL, 6 mL/min), washed twice with ultrapure water/ethanol (90/10, v/v; 2 mL, 5 mL/min). 20 mL of wine spiked with 50 µL an internal standard mix (6-sulfanyhexanol (1.5 mg/L), 4-methoxy-2-methyl-2-sulfanylbutan (1.5 mg/L), 3-octanol (1 mg/L), and EDTA (12 mg/L)) were then loaded onto the SPE cartridge at 3 mL/min. The cartridge was rinsed with water (2 mL, 5 mL/min), dried by air push (8 mL, 6 mL/min), and then the analytes were recovered by passing 3 mL of a solvent mixture of pentane/dichloromethane (50/50, v/v, 2 mL/min) and 3 mL of dichloromethane/methanol (95/5, v/v, 2 mL/min). The final organic phase was dried with anhydrous sodium sulfate and concentrated to 150 µL under a nitrogen stream.

GC-MS/MS analysis

- 2 Samples were analyzed using a chromatographic system comprising a Trace GC Ultra gas chromatograph (Thermo Electron SAS, Courtaboeuf, France) coupled to a TSQ Quantum XLS triple quadrupole mass spectrometer. GC separation was carried out on a polar wax capillary column (OPTIMA WAX, 100% Polyethylene glycol, 60 m; 0.25 mm; 0.25 µm) from Macherey Nagel (Germany). The carrier gas was helium (Messer, France), 6.0 grade, with a flow rate of 1 mL/min. A 1µL sample was injected via the autosampler (Triplus RSH autosampler, Thermo Electron SAS) into a split/splitless programmable-temperature injector (splitless time: 1 min, split flow 20 mL/min) set as follows: 0.05 min at 180°C, then raised to 230°C at 14°C/min, maintained for 1 min, and then raised to 250°C at 14°C/min and kept at that temperature for 10 min. Oven temperature was initially set at 45°C, held for 1 min, then raised to 230°C at 4°C/min, raised to 250°C at 20°C/min, and finally held at this temperature for 10 min. The MS transfer line temperature was set at 260°C. The source parameters including source temperature, electron energy, and emission current were set at 230°C, 70 eV, 50 µA and 100 V respectively. The collision gas was argon and the mass spectrometer was operated in electron impact (EI) mode. The SRM conditions were optimised for each compound in terms of collision energy and gas pressure values applied to each precursor ion depending on the transition. Precursor ion (m/z), product ion (m/z) and collision energy (V) selected as follows for compounds were indicated in table. Instrument set-up, data acquisition, and processing were performed using Xcalibur software (version 2.1.0). PFTBA (perfluorotributylamine) was used for mass calibration.

Compound	RT (min)	Precursor (Da)	Product (Da)	CE (volts)
3MMMB (IS-1)	17.80	134.00	100	5
3-octanol (IS-2)	18.90	101.00	83	5
4MSP	19.10	132.00	89	5
E2SA	19.35	119.95	74	5
FFT	20.60	114.00	81	5
methional	21.40	104.00	48	10
Furfural	21.50	96.00	95	10
Linalol	23.70	136.00	121.3	10
BM	26.40	123.95	91	10
phenyl acetaldehyde	27.10	120.00	91	10
A-terpineol	28.30	93.00	77	13
A3SH	29.30	115.95	88	10
Geraniol	31.00	69.05	53	17
β -damascenone	31.85	190.00	121	10
3SH	32.20	134.00	67	5
Nerol	32.30	111.00	77.1	17
Galacol	32.80	124.00	109	10
Wiskylactone	33.5/39.5	99.00	71	5
γ -octalactone	34.75	84.95	57	10
β -ionone	35.10	177.15	162	10
6SH (IS-3)	35.70	115.95	87	10
Furaneol	37.13	128.00	85	5
γ -nonalactone	37.60	84.95	57	10
Homofuraneol	38.45	142.00	127	10
Nor furaneol	39.25	114.00	85	10
γ -decalactone	40.30	127.95	94.95	5
Eugenol	40.40	164.00	149	10
δ -decalactone	41.60	99.00	73	10
<i>o</i> -acetoaminophenone	41.80	135.00	92	18
Massoialactone	42.45	97.00	41	15
Vanilline	47.1	152.00	151	10

Retention time (RT), precursor ion (m/z), product ion (m/z) and collision energy (V) selected for each compound.



Protocol references

Bruez É., Cholet C., Thibon C., Redon P., Lacampagne S., Martignon T., Guidicci M., Darriet P., Gény L., 2021. Influence of curettage on Esca-diseased *Vitis vinifera* L. cv. Sauvignon blanc plants on the quality of musts and wines. *OENO One*, 55 (1), 171-182.

Pons A., Lavigne V., Suhas E., Thibon C., Redon P., Loisel C., Darriet P., 2022. Impact of the Closure Oxygen Transfer Rate on Volatile Compound Composition and Oxidation Aroma Intensity of Merlot and Cabernet Sauvignon Blend: A 10 Year Study. *Journal of Agricultural and Food Chemistry*, 70 (51), 16358-16368.

Thibon C., Pons A., Mouakka N., Redon P., Méreau R., Darriet P., 2015. Comparison of electron and chemical ionization modes for the quantification of thiols and oxidative compounds in white wines by gas chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1415, 123-133.