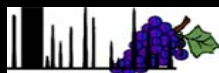


Analysis of Alkylmethoxypyrazines in Wine and Grapes by Mixed-Mode SPE and GC-MS

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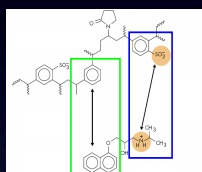
1. Introduction and Objectives

Alkylmethoxypyrazines (MPs) are responsible for the vegetative aromas found in some wines. Their extremely low sensory thresholds constitute an analytical def. with values ranging from 16 ng/l for 3-isobutyl-2-methoxypyrazine (IBMP), 2 ng/l for 3-isopropyl-2-methoxypyrazine (IPMP), and 1 ng/l for 3-secbutyl-2-methoxypyrazine (sBMP) [1-3].

Usually, concentration steps and selective detection are not enough to detect MPs without interferences [4-6]. In this work we present an approach based on the use of mixed-mode SPE to obtain a superior level of selectivity for the analysis of MPs in wine.

Slightly basic properties

SPE with mixed-mode sorbents

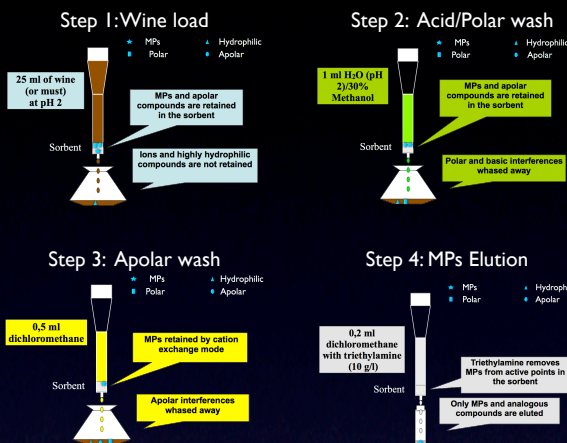


Mixed-mode SPE retention mechanism

Strong cation exchange

Hydrophobic interaction

2. Proposed Method



SORBENT
Best results obtained with Bond Elut Plexa PCX (Varian)

GC-MS CONDITIONS
Injection: 8 µl cold splitless
VF-5 MS (20m x 0.15mm x 0.15 µm)
QP2010 Shimadzu
SIM mode

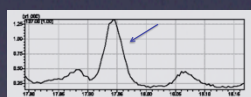
Analytes	Quantifier ions (m/z)	Qualifier ions (m/z)
IPMP	137	152, 124
sBMP	138	124, 151
IBMP	124	151, 94
IPMP*	123	151, 166

*IPMP: 3-isopropyl-2-ethoxypyrazine (internal standard)

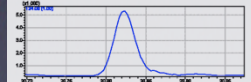
3. Figures of Merit

	LOD (ng/l)	Linear range (ng/l)
IPMP	0.4	1.7-25
sBMP	0.1	0.4-10
IBMP	0.3	1.0-25

	Recovery of 20 ng/l (%)	Repeatability (%RSD)
IPMP	20.1 ± 3.9	3.4
sBMP	19.3 ± 3.0	4.0
IBMP	24.0 ± 3.0	4.8



IPMP (4.9 ng/l) wine sample



IBMP (14.9 ng/l) wine sample

6. References and Acknowledgments

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4. Wine and Grape Analysis

Alkylmethoxypyrazines (ng/l) in Chilean Sauvignon blanc white wines

Wine	IPMP	sBMP	IBMP
"EQ Coastal", 2007	n.d.	n.d.	5.7
"Nimbus Estate", 2008	2.2	n.d.	10.5
"Casas del Bosque", 2008	1.4 ^a	0.2 ^a	8.8
"Floresta Leyda", 2007	n.d.	0.4 ^a	6.5
"Montes", 2007	1.9	n.d.	8.5
"Quintay", 2008	4.2	1.1	20.9
"Th Undurraga", 2007	1.1 ^a	n.d.	9.3
"Veramonte", 2008	n.d.	n.d.	2.9
"Castillo de Molina", 2008	7.8	0.3 ^a	19.8
"I20 Rua Especial", 2008	n.d.	n.d.	1.0
"De Martino", 2007	4.9	0.3 ^a	14.9
"J. Bouchon", 2008	n.d.	n.d.	2.2

LEGEND:
n.d.: not detected
^a Under Limit of Quantitation
¹ One week before ripeness
² Same parcel at ripeness

Alkylmethoxypyrazines (ng/l) in barrel aged Spanish red wines from D.O. Rioja and Ribera

Wine	IPMP	sBMP	IBMP
Ilurce Vendimia Seleccionada, Rioja	< 0.4	n.d.	1.7
Sierra Cantabria, Rioja	1.2 ^a	n.d.	2.7
Remelluri, Rioja	< 0.4	< 0.1	1.0
Luberri Monje, Rioja	< 0.4	n.d.	1.1
La Montesa, Rioja	< 0.4	n.d.	0.8 ^a
Viña Sastre, Ribera del Duero	n.d.	n.d.	5.9
Pago de los Capellanes, Ribera del Duero	2.6	n.d.	3.4
Arzuaga, Ribera del Duero	1.1 ^a	n.d.	6.6

Alkylmethoxypyrazines (ng/kg) in grapes

Grape cv.	IPMP	sBMP	IBMP
Grenache ¹	n.d.	n.d.	5.0
Grenache ²	n.d.	n.d.	n.d.
Mazuela ¹	n.d.	n.d.	3.3.
Mazuela ²	n.d.	n.d.	2.0
Gros Manseng ¹	n.d.	n.d.	n.d.
Gros Manseng ²	n.d.	n.d.	n.d.
Fer Servadou ¹	n.d.	n.d.	11.3
Fer Servadou ²	n.d.	n.d.	5.0

5. Conclusions

The proposed method allows the determination of IPMP sBMP and IBMP in their range of occurrence in grapes and wines. The high selectivity achieved through the use of mixed mode sorbents has provided a good tool for the study of MPs in grapes and wines.

According to the results obtained from the analysis of MPs in wines, Rioja and Ribera red wines have MPs quantities below their detection thresholds. However, this is not the case for Chilean white wines which in many cases have MPs contents above the detection thresholds as could be expected from wines elaborated with Sauvignon grapes.