Extraction of MDMP *via* supercritical CO_2

Application to cork

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TECHNIQUE

Introduction

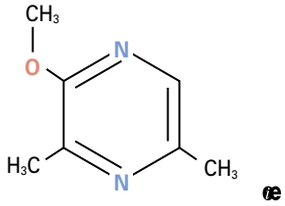
In 2004, Simpson et *al.* ***(1)*** revealed the presence of 2-methoxy-3,5-dimethylpyrazine (MDMP) in cork. These authors describe its aroma impact as having notes of wet cork, earth, dust, potato and unripe hazelnut, and they found its threshold of perception in wine to be around 2.0 ng/L.

In 2010, Chatonnet et *al.* ***(2)*** identified a bacterium, Rhizobium excellensis, which is at the origin of the biosynthesis of this compound from L-alanine and L-leucine. This bacterium, which may be present in the soil, can contaminate cork planks and bundles by direct contact when they are stored under poor conditions. Consequently, cork and lightly toasted oak chips can be the source of contamination in some wines.

The determination of MDMP content ***(figure 1)*** in 43 batches of natural cork closures from 5 different suppliers for 36 months reveals the presence of this contaminant in more than 86% of the samples (> 2 ng/closure) ***(2)***.

The main objective of this study is to verify whether the Diamant® supercritical carbon dioxide extraction process, developed by the Diam Bouchage company, to eradicate 2,4,6-trichloroanisole from their high-tech closures, is also effective in extracting MDMP from cork, and, if so, in what proportions.

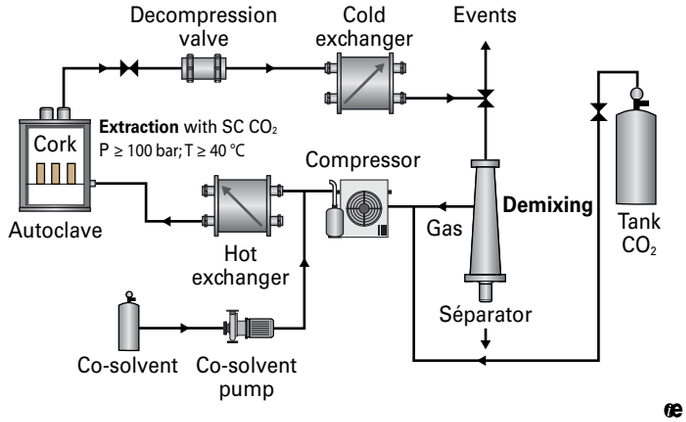
■ Figure 1: Formula for 2-methoxy-3,5-dimethylpyrazine (MDMP)



Review of the Diamant® process

The Diamant® process consists in an extraction of volatile compounds from cork by carbon dioxide in the supercritical phase (SC CO_2). Above 31°C and 73.8 bar, the CO_2 goes into an intermediate state between the liquid and gaseous phases, which gives it multiple properties. SC CO_2 thus has the diffusivity of a gas and the solvency of a liquid ***(3)***. ***Figure 2*** summarizes the extraction principle of this process, which was patented in 2000 (EP 1216123).

■ Figure 2: Operating principle of the Diamant process (extraction with supercritical CO_2).



The first step consists in compressing and heating the CO_2 above its critical point, with the addition of an aqueous co-solvent.

The SC CO_2/co-solvent mix is put in an autoclave filled with cork powder for selective extraction of the target compounds in accordance with a dynamic process (the fluid is always in circulation). At the end of the extraction, the supercritical fluid is progressively evacuated from the autoclave and is subjected to decompression (below the critical pressure), and to cooling (below the critical temperature).

The CO_2 is then in the gas phase. The extracted compounds which are soluble in SC CO_2 are no longer soluble in CO_2 gas, and thus demixing occurs in the separator. The purified CO_2 gas then returns to the circuit (recycling), and the continuous extraction process continues until all of the cork has been processed.

The work performed by Bobé et *al.* ***(4)*** shows that this Diamant® process, originally developed for the eradication of 2,4,6-trichloroanisole from cork powder, can also extract a very large number of other aroma compounds from various chemical families (alcohols, ketones, aldehydes, terpenes, sesquiterpenes, hydrocarbons, phenolics, furans, etc.). This extraction induces a very significant change of the sensory profile of the cork powder after treatment. The purified cork powder is characterized by greater organoleptic neutrality. However, we do not currently have any studies dealing specifically with the elimination of MDMP *via* a supercritical fluid extraction process.

■ Table 1: Evaluation of the effectiveness of the supercritical CO_2 process.

Contamination level	Theoretical MDMP content (ng/g)	Measured MDMP content (ng/g)	
		Before CO_2 SC treatment	After CO_2 SC treatment
Medium	5.0	4.0	nd
		4.1	nd
		3.8	nd
High	15.0	9.8	nd
		10.3	nd
		10.2	nd
Very high	50.0	42.2	nd
		41.5	nd
		41.8	nd

Extraction of pyrazines with supercritical carbon dioxide

While there are no bibliographic references dealing specifically with MDMP, there is a lot of bibliographic data dealing with the solubility and extraction of pyrazines using SC CO_2.
Studies were conducted by Shen et *al.* ***(5),*** measuring the solubilities of pyrazine, 2-methoxypyrazine, 2-methylpyrazine and 2,3-dimethylpyrazine in carbon dioxide at temperatures ranging from 25 to 100°C and at pressures up to 200 bar. These compounds are very soluble in CO_2 at low temperatures and pressures.
The data obtained justify the use of CO_2 as a supercritical fluid in order to extract pyrazine-type compounds from natural materials.
The extraction rates of 2-methylpyrazine, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine, trimethylpyrazine and tetramethylpyrazine from samples of cocoa beans by means of SC CO_2 are greater than 95% at a temperature of 60°C and a pressure of 150 bar, with a dynamic mode for 30 minutes followed by 1 minute in static mode ***(6).***
Other applications should be mentioned. Pyrazine and its derivatives are the main compounds involved in the aroma of roasted peanuts. Deodorization trials on raw oil obtained from the pressing of roasted peanuts have been conducted using extraction with SC CO_2 ***(7).***

Determination of MDMP in granulated cork

To select batches of granulated cork containing variable contents of MDMP, a systematic check was put in place for 3 months on 40 cork batches used in production and sampled before SC CO_2 treatment.
The analytical method used is an extraction with organic solvent and quantification by means of gas chromatography coupled with mass spectrometry, with internal calibration (method available upon request). ***Figure 3*** shows the distribution of the batches analyzed each month and the number of contaminated batches during this 3-month period.
No contamination of the cork was found in the 40 production batches subject to analysis (limit of detection < 0.9 ng/g).

Evaluation of the effectiveness of the SC CO_2 extraction process

During the study period, we did not identify any granulated cork naturally contaminated with MDMP. Consequently, to assess the effectiveness of the elimination of MDMP via the SC CO_2 extraction process, we enriched the granulated cork with this compound.
A sample of granulated cork was impregnated with a solution of MDMP in methanol, then dried and evaporated (operating protocol upon request). The enrichments were done in triplicate and at 3 different concentration levels: 5 ng/g (medium contamination), 15 ng/g (high contamination) and 50 ng/g (very high contamination). A portion was treated with the SC CO_2 extraction process, and another was kept as a control to evaluate the recovery rates.

Figure 4 shows the correlation obtained between the theoretical target values and the measured values. The measured contamination levels for theoretical concentrations of 5, 15 and 50 ng/g are, respectively, 4 (+/- 0.2); 10.1 (+/- 0.3) and 41.8 (+/- 0.4) ng/g. The recovery rates obtained are satisfactory, on the order of 79 (+/- 3)%; 67 (+/- 3)% and 84 (+/- 1)%, respectively, for 5, 10 and 50 ng/g. The results in ***table 1*** show the very great effectiveness of the Diamant® process to eradicate MDMP from cork powder. Even at very high concentrations (50 ng/g) that go well above those cited in the literature, cork powder treated with SC CO_2 no longer shows any detectable MDMP.

Conclusion

This study confirms that the use of SC CO_2 is of interest for eliminating pyrazines in various agricultural and food applications. During this work, we have demonstrated that MDMP, a potential contaminant of cork causing earthy-type organoleptic deviations in wines, may be completely extracted, even at initial contents that are much higher than those cited in the literature.
These new results are thus an addition to those already published in 2006 concerning the extraction of more than 150 other compounds from cork using this same SC CO_2 process ***(4).*** ■

Note: *The bibliographical references concerning this article are available on request from the Revue des Œnologues.*
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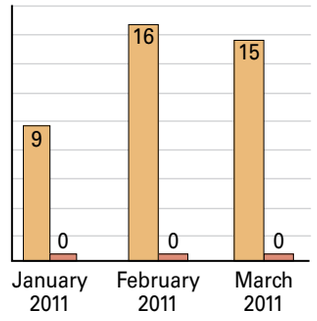
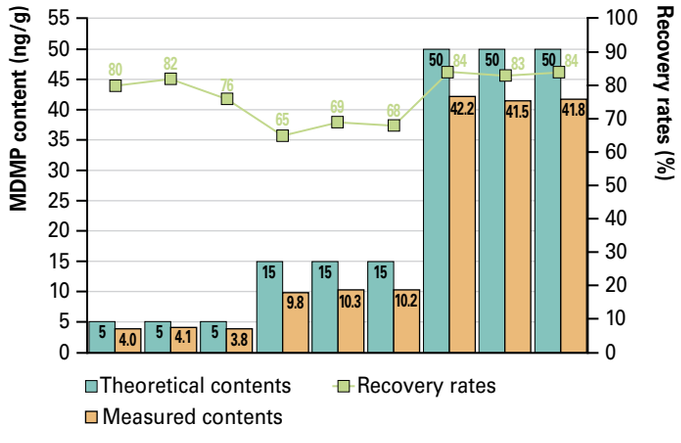
- On the Internet : ***www.oeno.tm.fr***

■ **Figure 3: Monitoring of MDMP contamination under real production conditions.**



■ **Figure 4: Evaluation of MDMP enrichment in granulated cork.**



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