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Rapid headspace solid-phase microextraction/gas chromatographic/mass spectrometric assay for the quantitative determination of some of the main odorants causing off-flavours in wine

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Abstract

In this study we present a rapid and simultaneous assay method using headspace (HS) solid-phase microextraction (SPME)/gas chromatography (GC)/electron impact (EI) mass spectrometry (MS) (selected ion monitoring) for contaminants causing the principal organoleptic defects of wine (2,4,6-trichloroanisole, 2,3,4,6-tetrachloroanisole, pentachloroanisole, 2,4,6-tribromoanisole, 1-octen-3-ol, geosmin, 2-methylisoborneol, 3-isopropyl-2-methoxypyrazine, fenchol, fenchone, 2-methoxy-3,5-dimethylpyrazine, 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol, 4-vinylguaiacol, 3-isobutyl-2-methoxypyrazine, guaiacol and ethyl acetate). The method was validated according to protocols NF ISO 5725-1, 2 and NF V03-110. Its characteristics (limit of detection (LOD), limit of quantification (LOQ), uncertainties) were determined after having optimised the SPME parameters. The target contaminants were quantified in the wines below their threshold of perception with a satisfactory relative standard deviation for all the analytes except ethyl acetate (RSD = 36%); for that, the assay method permits clear differentiation of the wines that are at risk of presenting an acescent character, i.e. containing more than $120\,\mathrm{mg\,L^{-1}}$ ethyl acetate. The target volatile and odorous substances were determined at concentrations significantly below their threshold of perception in a hydroalcoholic context and their threshold of recovery in wines.
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1. Introduction

The control of the organoleptic quality of wines is indispensable if the consumer is to be presented with a high-quality product. To date, sensory analysis is a subjective technique subject to a number of problems. In addition, qualification of an organoleptic defect is very difficult in the absence of objective data regarding the identification and precise quantification of the contaminants responsible for the disorder that has been detected. Finally, when using these data, it is always necessary to link them to the thresholds of perception of the substances in question in order to be able to draw conclusions actually on the probable responsibility and origin of the adulteration. From this perspective it is interesting to employ a rapid analytical method that enables the simultaneous quantification of the principal molecules identified as responsible for the main olfactory disorders of wines.

The main organoleptic defects of wines involve molecules that have thresholds of perception that range from some $100\,\mathrm{mg\,L^{-1}}$ for ethyl acetate to nanograms per litre for 2,4,6-trichloroanisole. In order to determine the origin of these contaminants, it is necessary to quantify the molecules responsible on this side of their thresholds of perception in the wines by means of a method that is sufficiently simple and sensitive.

Solid-phase microextraction (SPME), developed by Arthur and Pawliszyn in 1990 [1], used in headspace mode (HS-SPME) and coupled with high-performance gas chromatography (GC), allows the quantification of a large number of molecules with sufficiently low limits of detection and good linearity over a considerable dynamic range. Mass spectrometry used in specific fragmentometry after ionization by constant-energy electron impact and in the selected ion monitoring mode (EI-MS–SIM) allows detection that is simultaneously versatile, sensitive and very specific. In addition, this method, easily automated and reliably repeatable, uses no solvent and little or no preparation of

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