

Sam-02: Influence Of Headspace Sampling Strategy On Volatile Fingerprint GC×GC–MS And Multivariate Discrimination Of Monovarietal EVOOS

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Abstract

The characterization of volatile organic compounds (VOCs) plays a central role in the chemical profiling of extra virgin olive oil (EVOO), as the volatile fraction is closely associated with product identity and sensory characteristics. Headspace solid-phase microextraction (HS-SPME) is widely used for VOC analysis; however, recent methodological developments have introduced alternative approaches, such as vacuum-assisted HS-SPME (Vac-HS-SPME) and high-throughput adsorptive extraction (HiSorb), which remain relatively underexplored in the EVOO field. In this study, the three aforementioned sampling strategies were evaluated in combination with comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GC×GC–MS) for the analysis of monovarietal EVOOs from three renowned Italian regions and different harvest seasons. The analytical protocol was based on previously published methodologies (Mascrez et al., 2024; Cecchi et al., 2019), and a set of 32 analytes was selected based on their sensory relevance. The techniques were systematically compared in terms of extraction performance and chemometric behaviour. Technique-dependent differences were observed, affecting not only signal intensity and analyte coverage but also the resulting chemical fingerprints. In particular, the pressure-reducing characteristic of Vac-HS-SPME improved the extraction of several VOCs associated with sensory defects, highlighting selectivity differences compared to HSSPME and HiSorb. Multivariate data analysis was applied to explore sample distribution in multivariate space and to evaluate the influence of sampling strategy on discriminative performance. Rather than focusing solely on extraction yield, particular attention was paid to evaluating how each analytical configuration shapes the structure of the dataset and influences sample differentiation within the studied set. These results highlight the importance of carefully selecting headspace sampling conditions when volatile fingerprints are intended for discrimination-oriented applications. Overall, this work emphasizes that the volatile fingerprint of EVOOs cannot be interpreted independently of the extraction regime adopted, as the sampling strategy intrinsically contributes to defining the chemical identity represented in the multivariate space.