

Optimization of HS-SPME-GC-MS Quantitation of Volatile Compounds and Application to more than 1000 Samples for Supporting the Panel Test in Virgin Olive Oil Classification and For Authentication of the Geographic Origin

Cecchi L.

Department of NEUROFARBA, University of Florence, Via Ugo Schiff 6, 50019 Sesto F.no (Florence), Italy

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Objectives

Extra Virgin Olive Oil (EVOO) is considered as the highest quality product among edible oils, and economic frauds regarding false claim of geographical origin and commercial category cannot be fully avoid to date [1,2]. The use of HS-SPME-GC-MS analysis for quantification of volatile organic compounds (VOCs) has gained great attention in the last years and the possibility of using reliable chemical data from this analysis, has been recognized as more and more crucial for support both the virgin olive oil classification and the authentication of its geographical origin [3].

In this study, we collected and analyzed more than 1000 virgin olive oil samples over three olive oil campaign, with the aim of developing chemometric approaches for the quality control of virgin olive oil. To reach this goal, we optimized and validated the HS-SPME-GC-MS quantification of 73 Volatile Organic Compounds (VOCs) of virgin olive oil by using several internal standards. The validated method was the used for the analysis of approx. 1200 oil samples; the obtained set of data has been analyzed using several statistical tools in order to propose reliable and robust approaches suitable to support the panel test in virgin olive oil classification and to authenticate the geographical origin of virgin olive oils from the main worldwide producing countries.

Methods

More than 1000 virgin olive oils from different geographical origin (Italy, Spain, Greece, Tunisia, Portugal) and category (EVOO, VOO, LVOO) were collected in the olive oil campaign 2016/17, 2017/18, 2018/19, and analyzed by both HS-SPME-GC-MS and Panel Test. The quantitative analysis was optimized using up to 11 internal standards and the validated method was applied to the samples using a 6890N GC system equipped with a MS detector, model 5975 by Agilent. A HP-Innowax capillary column 50 m × 0.2 mm ID, 0.4 µm DF was employed. A SPME fiber 50/30 µm DVB/CAR/PDMS was exposed under orbital shaking at 400 rpm for 20 min in the headspace of a 20 ml screw cap vial fitted with a PTFE/silicone septa containing 4.3 g of sample and 0.1 g of internal standard solution vial, then the adsorbed VOCs were desorbed in the injection port of the GC system. Mass detector worked in scan mode within the range of 30-350 Th, 1500 Th/s at ionization energy of 70 eV. Each VOC was quantified using a calibration curve in which the area ratio (ratio between areas of that VOC and the selected ISTD) was plotted versus the amount ratio.

Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA), Analysis of Variance (ANOVA) and *t*-test were employed for data analysis, aiming at building the chemometric approaches above mentioned.

Results

The method for quantification of 73 VOCs was optimized and validated using 11 internal standard and selecting the more suitable one for each of the quantified VOCs, allowing obtaining reliable data in wide ranges of calibration in spite of the several critical issues pointed out for quantitative analysis by HS-SPME-GC-MS. The method was then used for analyzing the selected samples for building chemometric approaches aimed to:

- Supporting the panel test in virgin olive oil classification (n=1223)
- Authenticate the geographical origin of virgin olive oils from the main worldwide producing countries (n=1217).

The proposed approaches were built and internally validated using a training-set, and then externally validated using a set of independent samples. The PCA-LDA model gave the best results for supporting the panel test in virgin olive oil classification, while a simplified model allowed obtaining a very good predictive capability only using data from 10 VOCs, thus strongly simplifying the analytical work.

Our data also allowed pointing out octane, heptanal, pent-1-en-3-ol, Z-3-hexenal, nonanal and 4-ethylphenol as the more suitable VOCs for discriminating the different classes of virgin olive oils (i.e., extra virgin olive oil and virgin olive oil defective for different kinds of defects).

The ANOVA-LDA model, only using 25 selected VOCs was the best approach for authentication of the geographical origin of virgin olive oils from the main worldwide producing countries, with a prediction capability higher than 97% for some specific origins. In conclusion, reliable and robust chemometric approaches suitable for virgin olive oil quality control have been proposed based on quantitative data obtained by an optimized HS-SPME-GC-MS quantitation method, developed using several internal standard. The proposed approaches allow protecting consumers and producers from incorrect claiming of commercial classification and geographic origin.

1. T. Cajka, K. Ridellova, E. Klimankova, M. Cerna, F. Pudil, J. Hajslova, *Food Chem*, 121 (2010), pp 282-289.
2. L. Cecchi, M. Innocenti, F. Melani, M. Migliorini, L. Conte, N. Mulinacci. *Food Chem*, 219 (2017), pp 148-157