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EXPLOITING THE POTENTIAL OF MULTIPLE ANALYTICAL DIMENSIONS**

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1676266> since 2018-09-10T10:09:28Z

Publisher:

Società Chimica Italiana Divisione di Spettrometria di Massa

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ABSTRACT SUBMISSION FORM

To be sent by July 31st, 2017 to

http://www.spettrometriadi massa.it/Congressi/5MS-FoodDay/5MSFoodDay_SubmissionForm.php

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Preference: Oral presentation Poster

EXTRA VIRGIN OLIVE OIL VOLATILES FINGERPRINTING BY GC×GC-TOF MS AND SOFT IONIZATION: EXPLOITING THE POTENTIAL OF MULTIPLE ANALYTICAL DIMENSIONS

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Extra Virgin Olive Oil Volatiles Fingerprinting by GC×GC-TOF MS and Soft Ionization: Exploiting the Potential of Multiple Analytical Dimensions

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Summary: *The study exploits the unique capabilities of comprehensive two-dimensional gas chromatography (GC×GC) coupled with Time of Flight Mass Spectrometry (TOF-MS) and tandem ionization of being an extremely powerful profiling platform with intrinsic potentials as fingerprinting tool. Within a fully automated work-flow, the comprehensive mapping of extra-virgin olive oil volatiles is directed to define ripening indicators and odor active compounds distribution.*

Keywords: *Extra Virgin Olive oil; odor active analytes and ripening indicators; comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry and tandem ionization*

1 Introduction

Comprehensive two-dimensional gas chromatography (GC×GC) is the most effective multidimensional separation technique for in-depth investigations of complex samples of volatiles (VOC) in food. It enables highly informative fingerprinting and, if combined with Mass Spectrometry, it has the intrinsic potential to provide a detailed profiling giving access to the higher level of information encrypted in the peculiar distribution of sample's components [1–3].

Time of Flight Mass Spectrometry (TOF MS) with soft electron ionization adds a further dimension to the analysis thereby enabling more confident identifications but also new challenges for the data processing. The possibility to operate by switching between hard (70 eV) and soft ionization (12, 14 and 16 eV) generates complementary MS signatures (about each component and for each

2D pattern), increasing the dimensionality of the analysis. In this study the focus is on the complex volatile fraction from Extra Virgin Olive oils from Spain, variety *Picual* and obtained from fruits at four different ripening stages. The analytical strategy combines extra-dimensions from volatiles sampling by High Concentration Capacity (HCC) sample preparation (Head Space Solid Phase Microextraction with different polymer(s) combinations) to analytes detection by hard (-70eV) and soft ionization at 12 eV.

The distribution of olives ripening indicators, key-odorants responsible of positive attributes [4] and off-odors for defects assessment is studied; fingerprints from different samples are compared to evaluate critically the beneficial role of adding an extra-dimension to the analysis.

2. Experimental

Samples: olive oil samples from *Picual* variety and harvested in 2014 were supplied by Altipiano de Granada (Spain). *Baza*: conventional production and drip irrigation; *Benamaurel*: conventional production and drip irrigation. Olives were harvested at four different ripening stages between November 2014 and January 2015.

Samples were analyzed by an accredited laboratory to define quality parameters; sensory evaluation was by a recognized panel.

Head Space Solid Phase Micro Extraction sampling: different amounts of samples were analyzed in headspace glass vials (20 mL) with single or multi-component SPME fibers from

Supelco, Bellefonte, PA, USA. Sampling time and temperature conditions were changed according to an experimental design aimed at maximize the number of detected analytes in each analytical session.

GC×GC-TOF-MS instrument set-up: Agilent 6890 GC coupled with Markes Bench-TOF Select™ (Markes International, Llantrisant, UK) operating in tandem ionization (70 eV and 12 eV). Transfer line 270°C; Ion source 250°C. Thermal modulation by KT 2004 loop-type modulator (Zoex Corporation, Houston, TX) cooled with liquid N₂ and controlled by Optimode™ V.2 (SRA Instruments, Italy). Hot jet pulse time 250 ms,

modulation time 4s. Column set: ¹D SolGelWax -100% PEG (30 m × 0.25 mm d_c, 0.25 μm d_f) and ²D OV1701 (86% PDMS, 7% phenyl, 7% cyanopropyl) (1 m × 0.1 mm d_c, 0.10 μm d_f), from J&W. Carrier gas: He, const flow 1.3 mL/min. Oven from 40°C (1 min) to

3. Results

The first step of the study aimed at defining optimal sampling conditions to obtain 2D patterns from samples volatile fraction with the highest information potential. Different SPME fibers were tested: polyacrylate (PA), polydimethylsiloxane (PDMS), PDMS/divinylbenzene (DVB) and Carboxen (CAR)/PDMS/DVB and a group of 155 targeted analytes chosen to evaluate sampling performances. Analytes were reliably identified at 70 eV by matching MS spectra with those from commercial and in-house databases (NIST Identity Search algorithm Match quality threshold ≥ 900 and I_s^T coherence) was mapped across 2D patterns from four different commercial fibers.

Results are visualized as heat-map (Figure 1) based on Quantifier responses (mean and centering normalization) from **Baza** plot sample at the second stage of harvest.

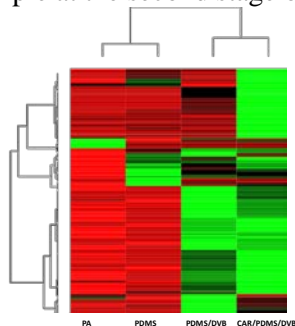


Figure 1

To make data comparable, the sample amount was kept constant and within headspace linearity (100 mg) and sampling was at 40°C - 60 minutes.

The combination of different polarities and extraction mechanisms (absorption/adsorption) has a clear impact on the fingerprint information potential. The best combination included CAR/PDMS/DVB (1 cm - Stableflex) with, on average, higher analyte concentration factors and wider polarity range.

Once defined optimal sampling conditions, oils obtained from olives at differing ripening stages, were analyzed and compounds with a meaningful variation across harvesting periods located over the 2D space and monitored on the basis of their relative

200°C at 3°C/min and to 260°C at 10°C/min (5 min).

Data acquisition and data elaboration: data were acquired by TOF-DS and processed by GC Image 2.7 (GC Image, LLC Lincoln NE, USA).

abundance in the sample. Figure 2 shows the heat-map based on Quantifier responses for 155 targeted analytes (mean and centering normalization) for *Baza* samples. Samples are ordered from left to right according to olive harvest stage.

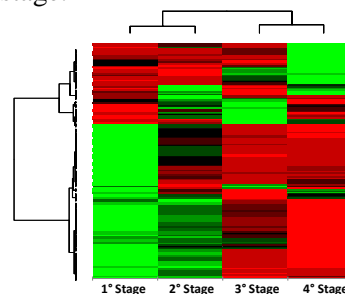


Figure 2

Coloring from red (low abundance) to green (high abundance) illustrates the evolution of volatiles from Stage 1 (predominance of C6 LOX derivatives and low-molecular weight hydrocarbons) to Stage 4 where reach their maximum abundance, e.g. 2-nonanone, (*E*)-2-nonanal, nonanal, octane, 6-methyl-5-hepten-2-one and octanol.

Stage-dependent evolution of ripening indicators based on Quantifier ions response ratios between key-analytes was used to define a “cut-off” value for quality classification from EVO to LO and Lampante (*) as illustrated in Figure 3.

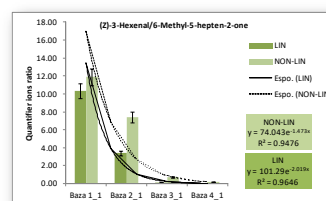


Figure 3

4. Conclusions

Accurate profiling and effective fingerprinting enables the comprehensive investigation of complex fractions of volatiles providing interesting insights on the distribution of analyst with high information potential. The adoption of multiple analytical dimensions, at the separation and detection level with the tandem ionization, result fundamental for reliable and consistent results.

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