



VOLATILE SECONDARY METABOLITES FROM ORGANIC APPLES BY HS-SPME IN COMBINATION WITH COMPREHENSIVE TWO-DIMENSIONAL GC-MS

Intro

Trentino Alto Adige produces about 1.5 M of tons of apples per year (~15% of total EU production) [1]. The high production density brings a burden for soil exploitation. In the last decade efforts have been done to make apple production more eco-sustainable by adopting organic farming practices. Organic farming is a production system which avoids or excludes the use of synthetic preparations (artificial fertilizers, pesticides, growth accelerators and fodder additives) [2]. Furthermore, recent works showed a positive willingness to purchase organic apples and consumer preference for apples organically rather than conventionally produced [3-5] providing important information about market opportunities. Despite this, many producers are afraid about lower sensory quality of organic fruits.

Instrumental and sensory analyses were applied to investigate the impact of organic farming on apple quality.

Here only preliminary data on volatile secondary metabolites obtained by HS-SPME in combination with comprehensive two-dimensional gas chromatography coupled to a quadrupole MS (HS-SPME GCxGC-MS) are presented.



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Material & Methods

Samples

Apple varieties:



Season: 2013

Farming: organic farming (bio); integrated production system (int)

Orchard: Maso delle Part (210 m asl); 2 separate parcels

Sample preparation: according to Aprea et al [6]

Experimental set up

SPME: 2cm DBV/CAR/PDMS; extraction time 30 min at 40 °C
GC7890B Agilent coupled to a 5977A extractor ion single quad

1st D: Zebron 5% 20m 0.18mm x 0.18μm

2nd D: WAX 5m x 0.32mm + 30cm x 0.1mm x 0.15μm

Modulation: differential flow modulator (Agilent's Capillary Flow Technology)

Carrier Helium

Data processing: GC Image (Zoex Corporation)

Compound identifications: NIST2011 and in-house database

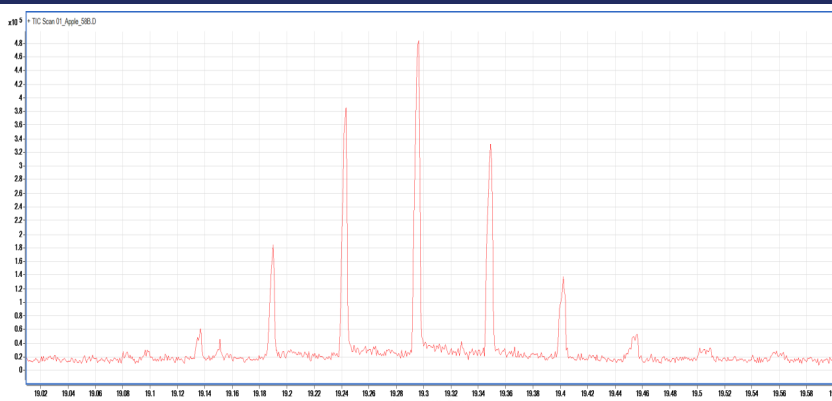
Statistical analysis: SimcaP+ v12 (Umetrics) and STATISTICA 9.1 (StatSoft)

Results

Set up optimization

Helium flow rates for 1st column: 0.3 mL/min
 Helium flow rates for 2nd column: 7.5 mL/min
 Modulation time: 3.2 s
 Sampling rate 22.857 Hz

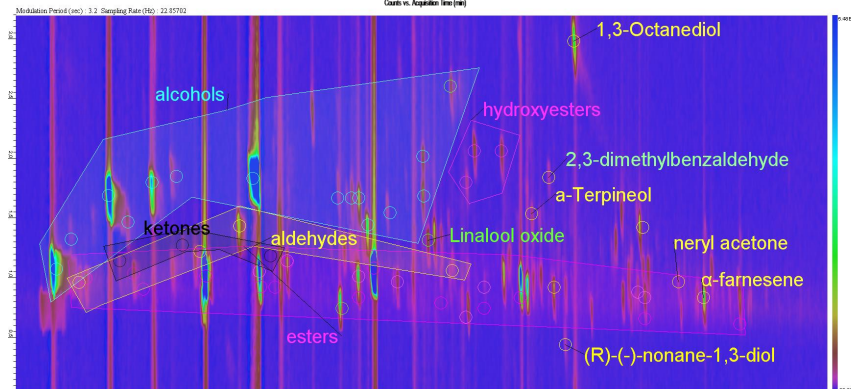
Fig.1. Modulated peak at 3.2 s with a sampling rate of 22.857 Hz.



Data extraction

More than a hundred compounds were detected and the identity of 63 compounds matching both LRI and spectra of our database and NIST2011 MS spectra were confirmed.

Fig.2. The total ion contour plot of apple headspace. Only full identified peaks are marked.



PLS-DA was used to group samples according to farming practices (bio: organic farming; int: integrated production system) and highlight the main compounds responsible of differences in the fruit headspace.

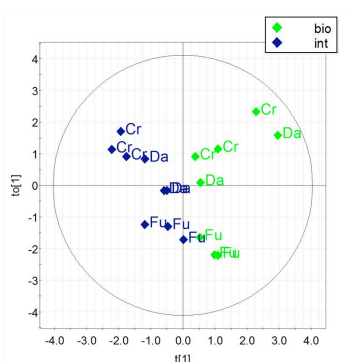


Fig.3. PLS-DA plot of apples using identified volatile compounds data (normalized peak areas).

The main contributors to the separation were the α -farnesene and the (Z)-geranyl acetone

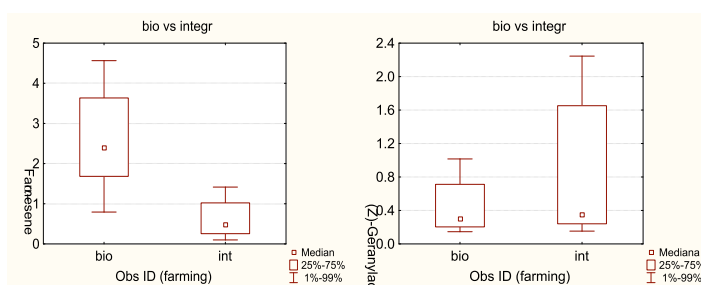


Fig.4. Box-plots of α -farnesene and (Z)-geranyl acetone

The cultivars are very different in terms of emitted volatile compounds. Nevertheless farming practices induce sistematic effects.

Conclusions & Perspectives

An SPME-GC-MS method, developed to study apple headspace [6], was adapted and checked for comprehensive two-dimensional gas chromatography;
 The use of helium and the optimized column setup avoid split before MSD and allow an excellent sensitivity;
 Preliminary results indicate an effect of farming practice on volatiles emitted by apples;
 Other combinations of columns will be tested in order to further improve peaks separation and compounds identification;
 The study will be extended with a wider sampling in order to confirm the preliminary results of farming practice influence on apples volatile emission.

References

- [1] <http://www.cooperazionetrentina.it/Ufficio-Stampa/Notizie/Le-previsioni-di-produzione-dimele-per-la-stagione-2013-2014>.
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- [6] Aprea E. et al., Food Research International 49 (2012) 677.

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