Application of comprehensive GCxGC-ToF-MS and sensory analysis to investigate the evolution in the aroma profile of a commercial grappa over storage

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INTRODUCTION

DEFINITION OF GRAPPA

Grappa is an Italian distillate obtained from fermented or semi-fermented grape pomace (Min. Decree no. 747/2016), which is a by-product of the winemaking process. Grappa is rich in volatile compounds (about 1% v/v) and each compound contributes to the aroma and flavor according to its concentration and sensory threshold. This aspect plays a fundamental role in the consumers' preference of the different styles of grappa present on the market. The constant application of new and improved analytical tools is fundamental to achieve a detailed description of a complex aroma profile in relation to its sensory descriptors.

CGxGC

Comprehensive bidimensional gas-chromatography (GCxGC-ToF-MS) can be used as an improved analytical tool to achieve a detailed description of a complex volatile profile in alcoholic beverage products (grappa). With respect to monodimensional gas-chromatography (GC-MS), the bidimensional separation allows for higher sensitivities as well as better peaks separation and identification.

THE AIM

The aim of this study is to compare GC-MS and GCxGC-ToF-MS (coupled with SPME) to investigate the evolution of the volatile profile of a commercial young grappa over storage in relation to its sensory profile.

MATERIALS AND METHODS

GRAPE POMACE → FERMENTATION → DISTILLATION → MATURATION → BLENDING → BOTTLING

Flow-chart for grappa processing

1- Materials

Samples of a dry, white (not aged in wood) Grappa-Treber (38% ABV) were provided by a local distillery in Termeno (Italy).

2 - SPME method

Volatile compounds were analysed through GC-MS after extraction with head-space (HS)-SPME. 4mL grappa samples were introduced into a 20mL vial, homogenized with 0.5g NaCl. Then, 4mL of prepared solution (1L milliQ water + 200µL of 4-methyl-2-pentanol) were added into the vial, and this was closed with a perforable screw cap. The vial was kept in a heating bath at 40°C for 5min in a continuous stirring at 500 rpm. Afterwards, a SPME fiber (DVB/CAR/PDMS, 50/30µm 2cm) was exposed into the headspace of the vial for 10 min under continuous heating and stirring.

3 - GC-MS method

The thermal desorption took place in a GC-MS Agilent 78908A at 240°C for 3.5min. Column: MEGA-Wax Spirit 0.30µm/0.18mm/40m. The injection was in split mode (1/10) and the temperature programme of the oven was: 40°C for 0.2 min, then raising up to 180°C at 3°C/min and to 230°C at 10°C/min. The mass range was 34-600m/z; ion source temperature 230°C; quadrupole temperature 150°C; EI: 70eV; acquisition rate 1 spectra/sec.

4 - GCxGC ToF-MS method

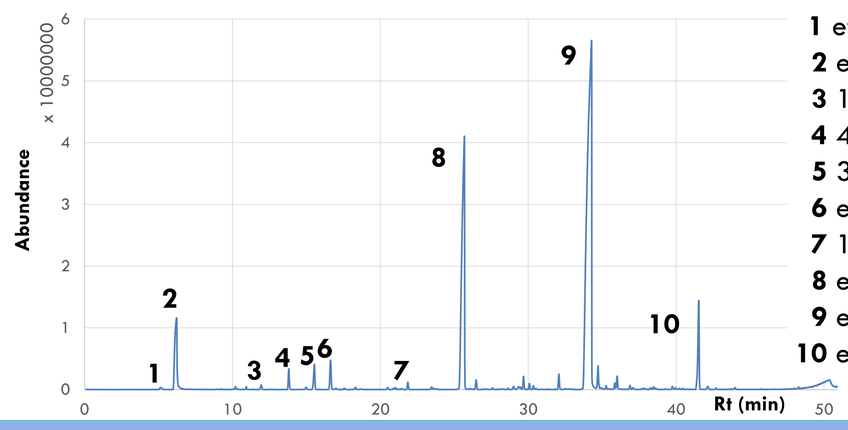
Samples were analyzed by GCxGC Agilent 7890 using the Novel Pegasus BT-4D system. Columns: 1D: Rxi-5 MS, 30m x 0.25mm i.d. x 0.25µm coating; 2D: Rxi-17Sil MS, 0.9m x 0.25mm i.d. x 0.25µm coating. Oven program: 40°C (hold 3 min), ramp 4°C/min to 220°C, ramp 15°C/min to 280°C hold 1 min; the secondary oven temperature was at +5°C. The MS transfer line was at 280°C, ion source temperature 250°C, mass range 34-600m/z, acquisition rate at 200 spectra/s, extraction frequency at 30Hz.

5 - Sensory evaluation

A group of 22 trained panelists (55% female and 45% male, 23±4 years old) was asked to describe the grappa samples for olfactory and gustatory evaluations.

RESULTS AND DISCUSSION

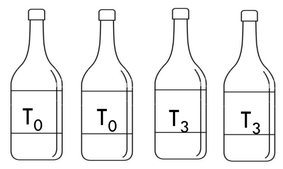
PROFILE OF GRAPPA BY GC-MS ANALYSIS



1 ethyl acetate (5.13)
2 ethanol (6.22)
3 1-butanol-3-methyl acetate (11.96)
4 4-methyl, 2-pentanol, **IS** (13.86)
5 3-methyl-1-butanol (15.52)
6 ethyl hexanoate (16.63)
7 1-hexanol (21.87)
8 ethyl octanoate (25.67)
9 ethyl decanoate (34.27)
10 ethyl dodecanoate (41.53)

EFFECT OF A 3-MONTH STORAGE ON VOLATILE COMPOUNDS

Storage time (months)	p-value
Control (T_0) *vs* 3-months (T_3)	> 0.05

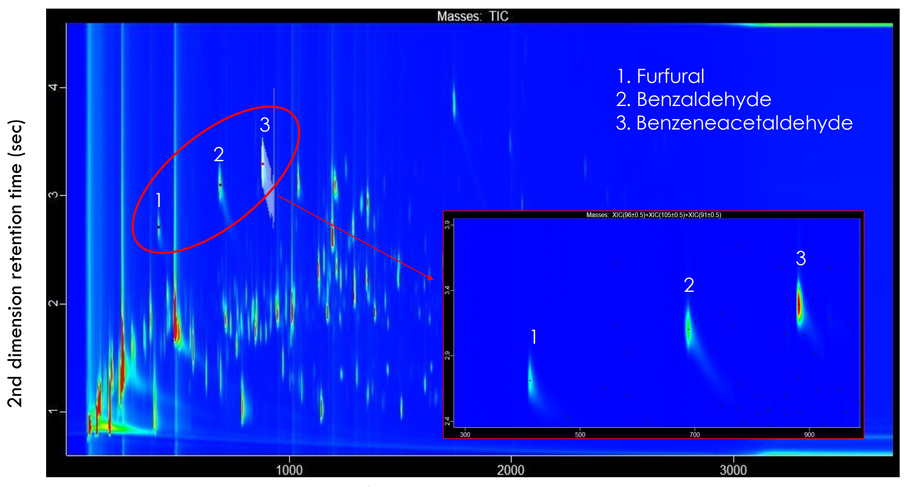


Grappa bottles (duplicate)

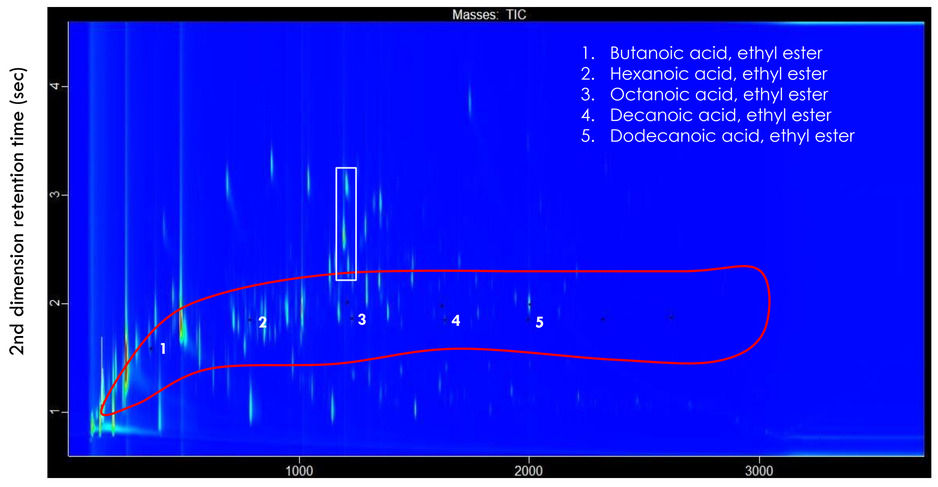
Statistical difference was evaluated by one-way ANOVA of all the peak areas normalized by the IS area. Differences were considered to be statistically significant when $p<0.05$ vs Control. Grappa samples did not differ for the volatile profile after 3 months of storage, suggesting that the sensory quality of grappa was kept over time.

PROFILE OF GRAPPA BY GCxGC ANALYSIS

1- Aldehydes



2- Fatty acids



With respect to GC-MS, in GCxGC many classes of volatile compounds was eluted in separate patterns according to their main chemical moiety (regions circled in red).

As an example, we have reported the identification of the regions of volatile aldehydes and ethyl esters in the GCxGC (2D) chromatograms.

This result is very helpful for the correct identification of congeners, compared to monodimensional GC, where the volatile classes of compounds are not resolved.

SENSORY EVALUATION

The sensory descriptors of grappa defined by the panel were reported in the sensory word cloud. The main aroma classes were floral, fruity (dried fruits and tree fruits), spicy, vegetative (dried and fresh) and caramelized (honey). The dimension of each word in the figure is directly correlated with the frequency of mentions by the panelists.

Ethyl esters of monocarboxylic acids (the series from butanoic to dodecanoic acid) are related to the pleasant fruity flavour. Benzaldehyde is usually associated with a dried fruit; furfural has a bitter and spicy flavour, whereas benzeneacetaldehyde is perceived as a floral and fresh aroma.

Sensory word cloud. a, aroma; f, flavour.

CONCLUSIONS

The use of GCxGC allowed a better understanding of the complexity of grappa volatile profile, since resolved peaks in the second dimension of bidimensional GC (such as the three spots included in the white box of the figure reporting the ethyl esters) are overlapped in a monodimensional system (GC-MS). Moreover, comprehensive bidimensional GC provides a peak list of about two hundred identified volatile compounds which can be useful to identify the molecules responsible for the main sensory descriptors reported by the trained panel.

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