Honey discrimination by Volatile Organic Compounds analysis: comparison between GC-IMS and GC-E-Nose

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Introduction

Food safety and quality are becoming more and more considered by food companies and consumers that are daily exposed to food fraud risk. To face food fraud, the development of new analytical techniques that can identify and recognize the authenticity of food products has become essential. One of the most innovative analytical approaches is the assessment of the volatile fraction combined with chemometric techniques. The composition of volatile organic compounds (VOCs) from Acacia and Millefiori honey samples were analyzed, to identify molecules relevant for their classification according to the botanical origin. Honey is one of the most exposed food to fraud, due to its economic value, its worldwide production and the current problems associated with the control and maintenance of bees' farms. The honeys' volatile fraction was analyzed by using two diverse gas chromatography (GC) instruments (GC-E-Nose and GC-IMS), and the data obtained were compared after chemometric processing.

Experimental

Fifty four honey samples (26 Acacia and 28 Millefiori) were selected, prepared and treated under standardized operating conditions. About 1 g of sample was placed in a 20-mL vial, without any further treatment before chromatographic analysis. The two GC instruments used for the study were: - GC-E-Nose (Fig.1): Ultrafast Heracles GC instrument with 2 GC capillary columns of different polarity and 2 flame ionization detectors (FID), used in untargeted mode. - GC-IMS (Fig.3): GC instrument with a GC column coupled to an ion mobility spectrometer (IMS), used in both untargeted and target mode. Finally, the raw data of the samples' volatile composition were subjected to Principal Component Analysis (PCA) statistical analysis.

Fig.1 GC-E-Nose Heracles

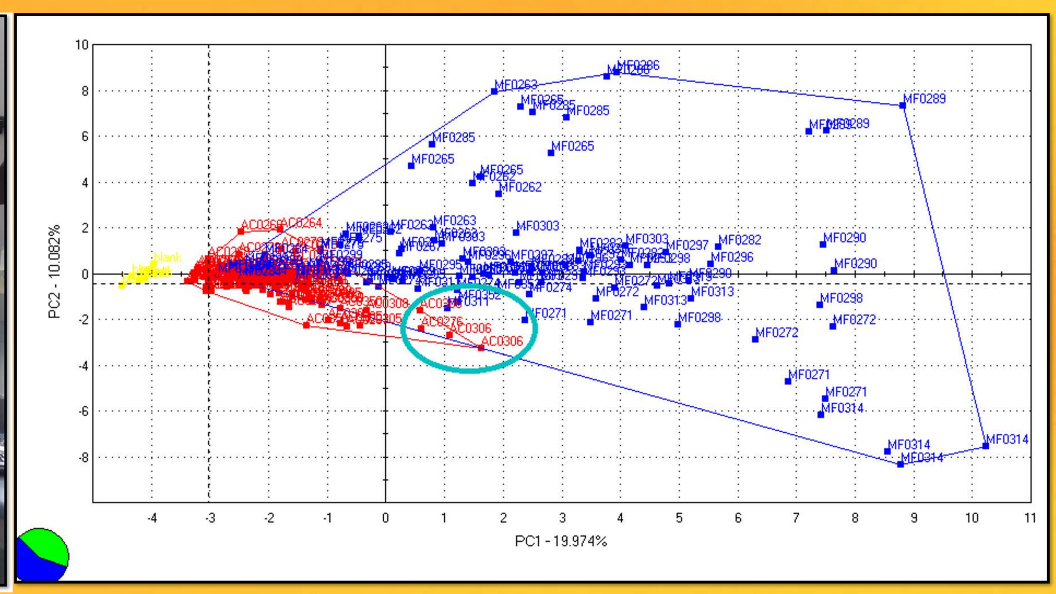

Fig.2 PCA data obtained from GC-E-Nose: Millefiori (blue), Acacia (red), Blank (yellow)

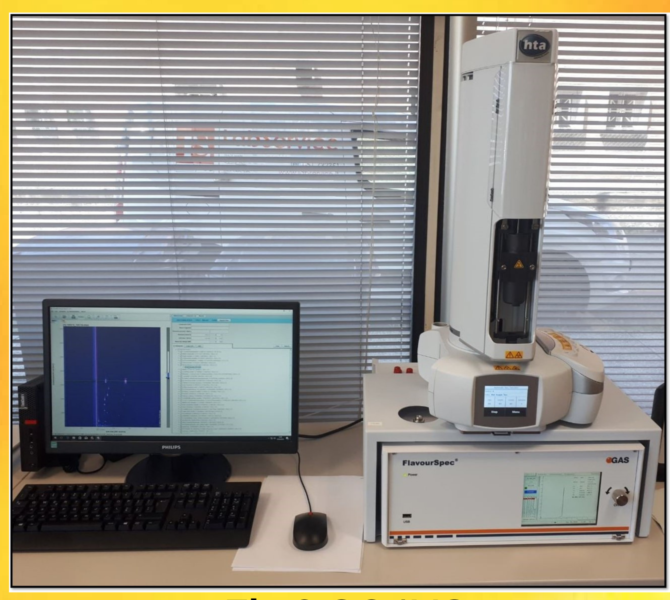

Fig.3 GC-IMS

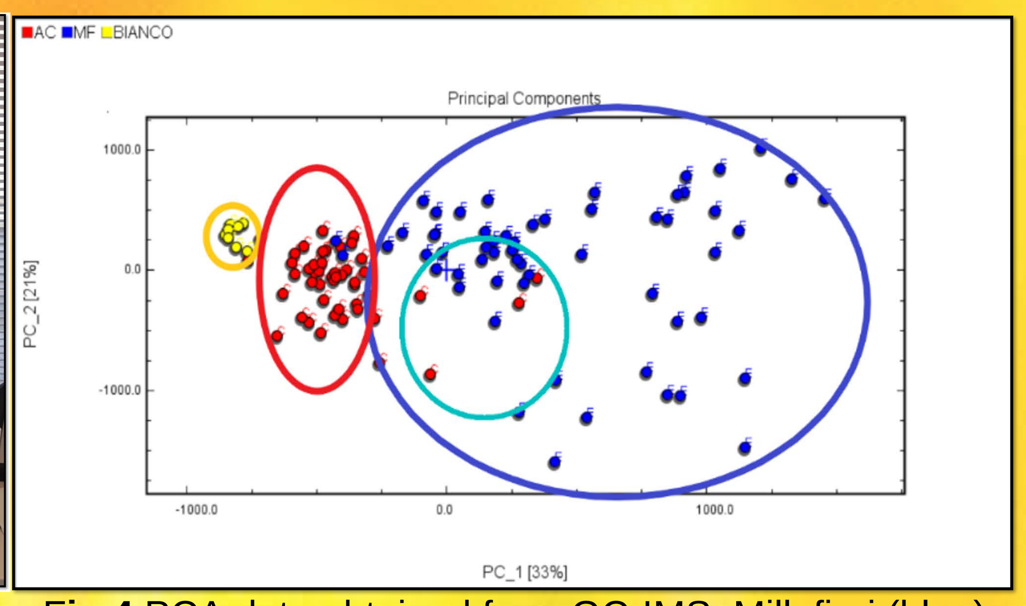

Fig.4 PCA data obtained from GC-IMS: Millefiori (blue), Acacia (red), Blank (yellow)

Results

The VOCs raw data obtained with the two different GC instruments, were separately processed by using PCA statistical analysis. PCA analysis was able to similarly discriminate samples into the two main honey classes (Millefiori and Acacia) regardless of the type of GC instrument used, as shown in Fig. 2 and Fig. 4. Furthermore, both PCA evidence that a sample of Acacia honey (grouped with a light blue circle) was not correctly positioned with respect to the honey classification. The latter sample is an organic honey, which might contain characteristic volatile molecules that are related to unconventional breeding techniques or a different production process. When the PCA was applied to the data obtained by the untargeted approach, the acacia honey samples were divided into conventional and organic ones (Fig. 5). The non-compliant sample was studied more in depth by GC-IMS, with a target approach, where acetic acid was identified as a "marker" molecule of this type of sample. In fact, according to the EU Reg. 2018/8481, acetic acid can be used against Varroasis in the prodution of organic honey.

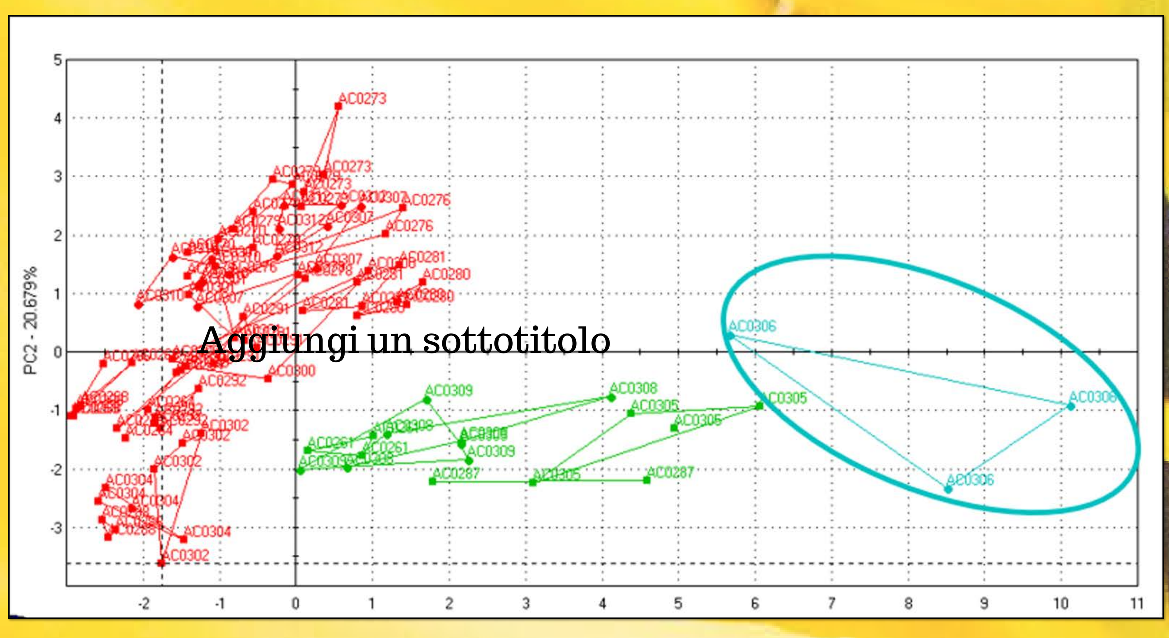

Fig.5 PCA Acacia Samples: Conventional acacia (red), Organic acacia (green), Non-compliant Acacia with this classification (blue)

Conclusions

The results obtained show that the two GC instruments are able to generate very similar outputs, when used under the same operating, analytical, and statistical conditions. The untargeted analytical approach associated with chemometric data processing allows the formation of different sample classes according to qualitative differences detected in the honey volatile fraction. Clustering of untargeted data proved to be a useful tool for preliminary identification of differences among samples, but it does not allow the identification of discriminating molecules. To recognize the chemical nature of discriminating molecules, it should be used a target approach, such as the one carried out with GC-IMS in the present work. The identification of discriminating molecules allowed to justify the obtained sample classification, being thus useful to distinguish with greater certainty a conventional honey from an organic one.

References: Reg EU of 30 May 2018, No 848 relating to organic production and labelling of organic products.