Aceto Balsamico Tradizionale di Modena" PDO authenticity: detection of caramel-containing vinegar by HS-GC-IMS

Matteo BORDIGA[a], Vincenzo DISCA[a], Cesare ROSSINI[b], Thomas WORTELMANN[c] and Marco ARLORIO[a]

[a]Dipartimento di Scienze del Farmaco, Università degli Studi del Piemonte Orientale, Novara, Italy.
[b]LabService Analytica s.r.l, Via Emilia 51/c, 40011 Anzola Emilia (Bologna), Italy
[c]G.A.S. Gesellschaft für analytische Sensorsysteme mbH, Otto-Hahn-Str. 15, 44227 Dortmund, Germany

matteo.bordiga@uniupo.it

INTRODUCTION

The economic value of **Aceto Balsamico Tradizionale di Modena PDO (ABT PDO)** ("*affinato*" and "*extra-vecchio*" types, depending on the aging), prepared following a traditional way and aged for many years in a set of barrels (transferring a certain amount of vinegar from one cask to another in a decreasing "topping up" procedure) is great, when compared to **Aceto Balsamico di Modena PGI (AB PGI),** prepared with concentrated grape musts, with the potential addiction of caramel. AB PGI is certainly the most widespread industrial-type vinegar in the world, deriving from low-temperature condensed grape must (or cooked must) mixed with wine vinegar, obtaining balsamic vinegars with a caramel-like taste. Depending on its economic value, ABT PDO is often object of fraud, requiring to fight counterfeit products and imitations. Aim of the present study was to develop a quick authentication model for the recognition of the counterfeit ABT PDO products; different samples, prepared adding AB PGI in ABT PDO (5, 10, 20%, respectively) were analyzed using HS-GC-IMS, confirming the capacity to identify the presence of concentrated/cooked must-like products in ABT PDO from as little as 5%.

MATERIALS AND METHODS

Qualitative determination of aromatic compounds: A gas chromatograph coupled to an ion mobility spectrometer (**FlavourSpec®**, G.A.S., Dortmund, Germany) was used to analyze the volatile component in the vinegar samples. GC-IMS system was coupled with an automatic sampler capable of heating and stirring the samples before analysis. By combining gas chromatography with ion mobility spectrometry, the instrument is configured to obtain a 2D profile of the low boiling aromatic compounds obtained from the head space of the various samples.

Sample preparation: Different mixtures (5, 10, 20%) were prepared adding Aceto Balsamico di Modena PGI (two commercial types: AB1 and AB2) to Aceto Balsamico Tradizionale di Modena PDO (ABT PDO). The sample was transferred without pretreatment into a 20 mL glass vial by pipette (500 µL of diluted sample – 50 µL vinegar and 450 µL water). Once the transfer of each sample was completed, the respective vial was immediately sealed through a special screw cap to avoid partial loss of the Volatile Organic Compounds (VOCs) component. The equilibrium between the liquid and the gas phases (in order to obtain homogeneous data from all the samples) was obtained setting the automatic sampler at 40 ° C for 5 minutes, following the insertion of the vials.

Method: 100 µL of the headspace of the vial containing 500 µL of liquid sample was injected for all types under examination (syringe temperature equal to 70 ° C). The duration of the analysis was set at 20 minutes; the carries gas (N_2) ramp with an initial value of 2 mL/min gradually and steadily increased up to 25 mL/min at the end of the analysis. The column used for this study was a MXT-5 column (low polarity phase, Crossbond® diphenyl dimethyl polysiloxane; 15 m, 0.53 mm ID, 1 µm). The drift gas (N_2) was set to 150 mL/min and the chromatogram recording was carried out with positive polarization. The source of ionization was tritium. The retention index of each volatile compound was calculated using a mix composed of C4-C9 n-ketones (G.A.S., Dortmund, Germany) as the reference standard. The volatile compounds were identified by comparing the retention index and the drift time (the time in milliseconds taken by the ions to reach the collector moving through the drift tube) with the libraries supplied in the instrument software.

RESULTS

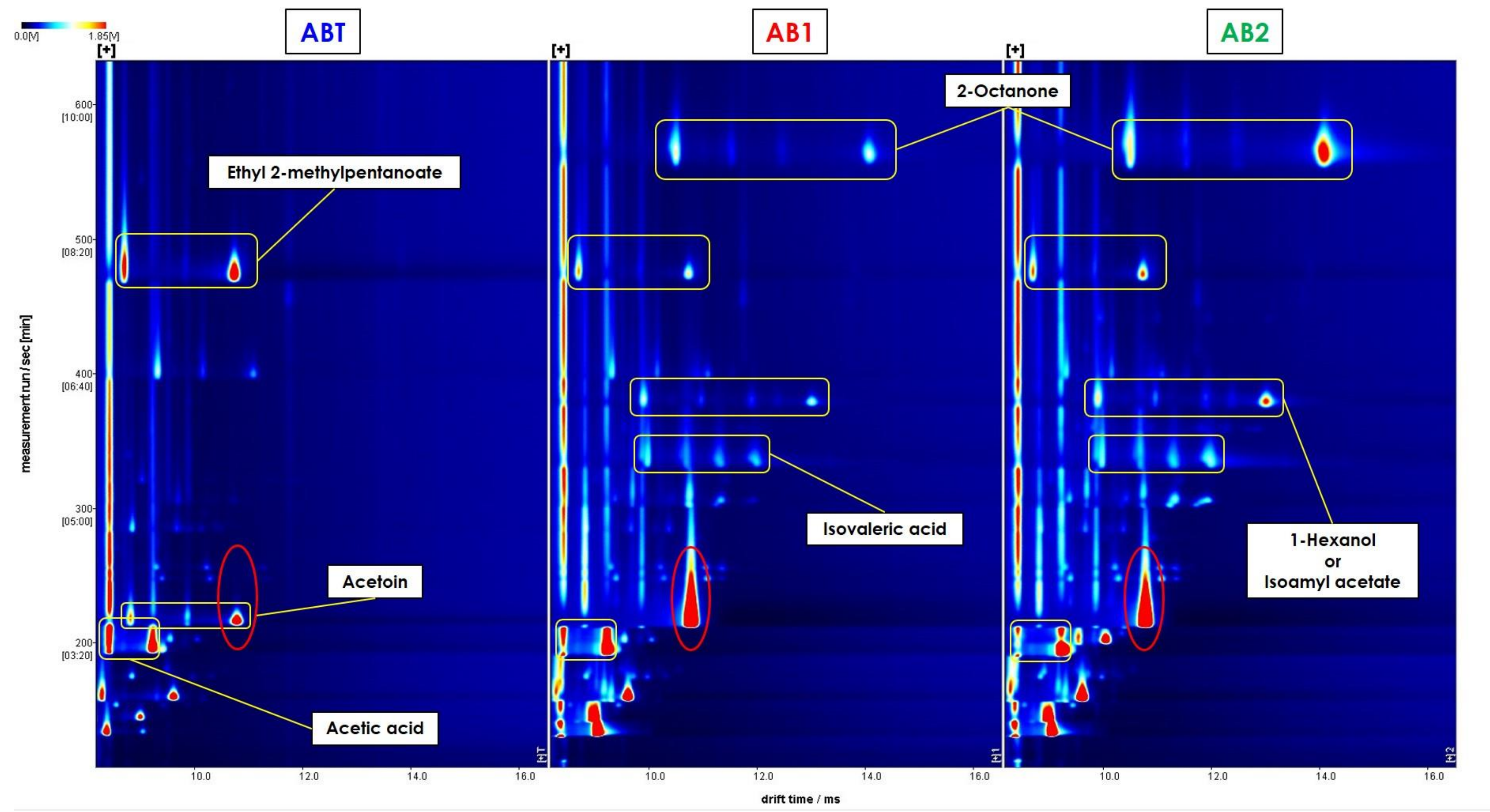


Figure 1. Chromatographic profiles of the three types of vinegar (ABT, AB1 and AB2)

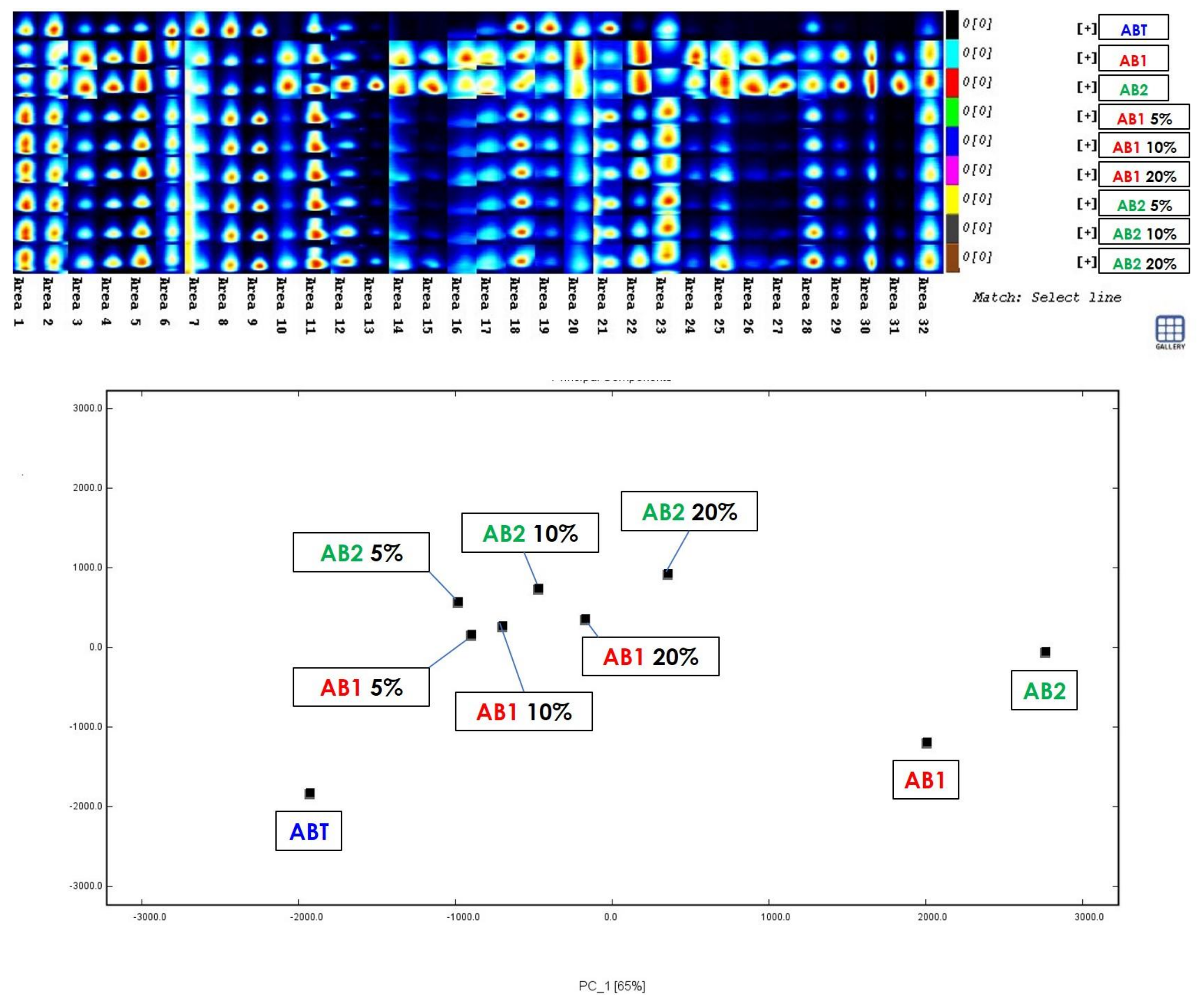


Figure 2. (upper part) characteristic compounds of the analyzed samples. (lower part) PCA obtained considering all the volatile compounds reported above.

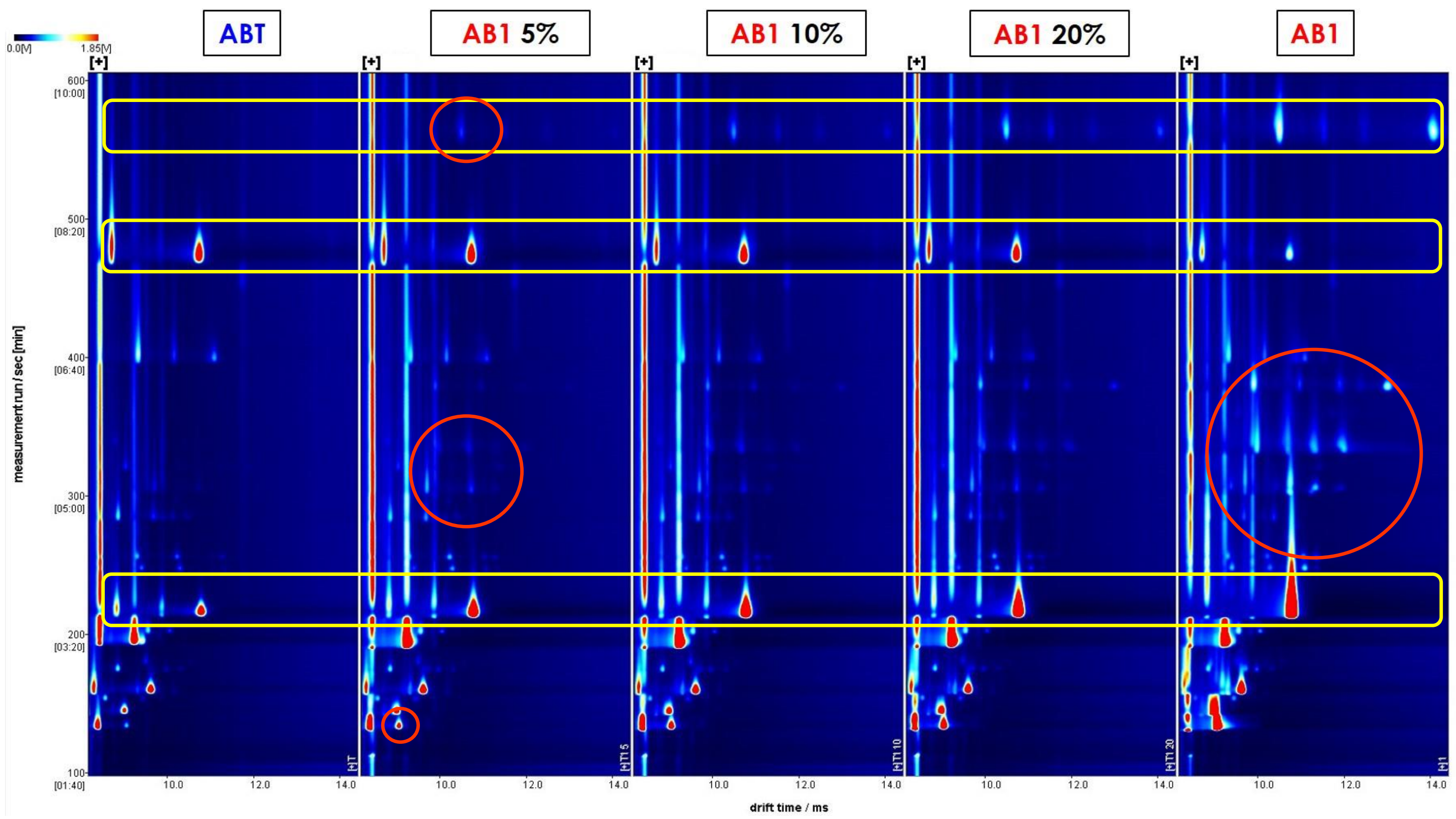
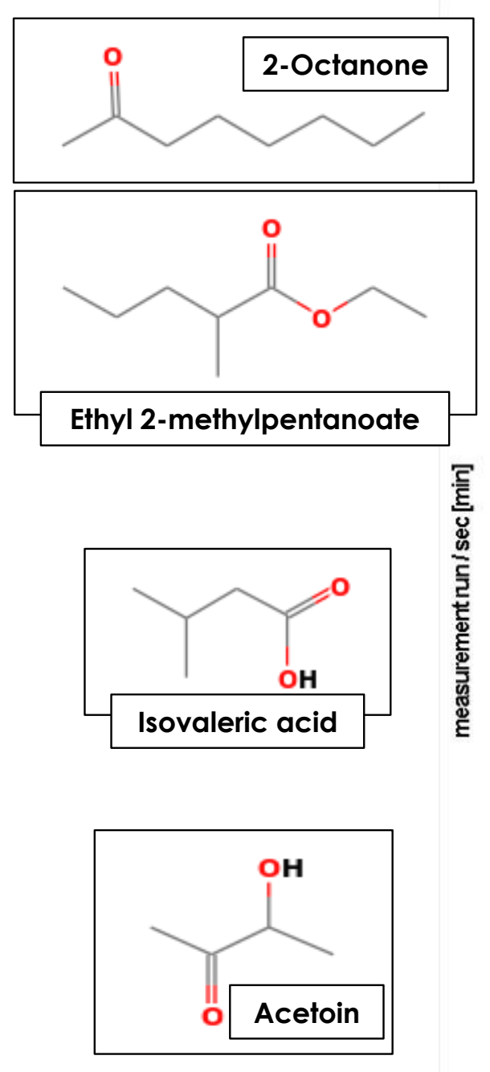


Figure 3. comparison between the volatile profiles of the ABT sample and the samples with the different percentages of AB1



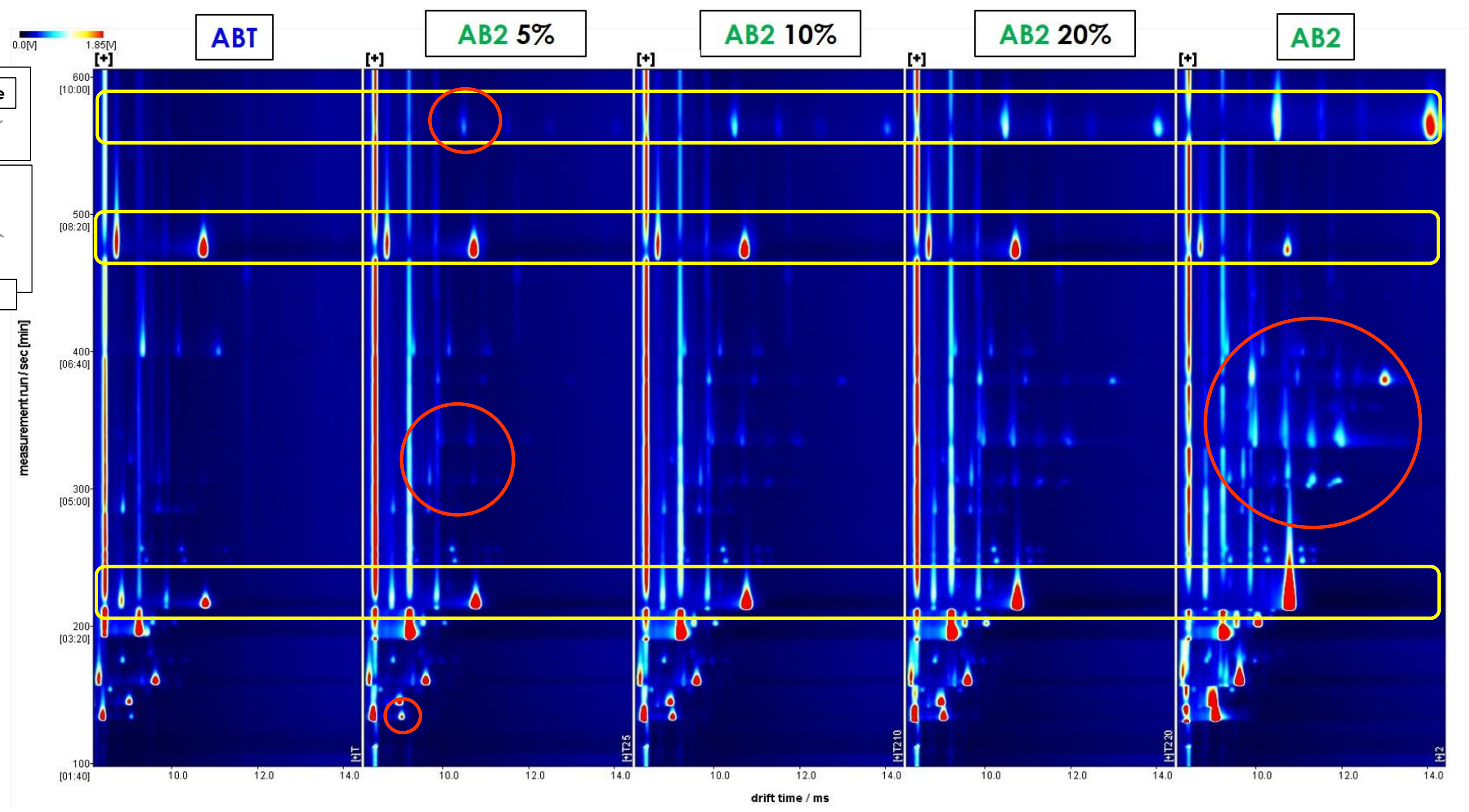


Figure 4. comparison between the volatile profiles of the ABT sample and the samples with the different percentages of AB2

The effectiveness of this technology in characterizing the fingerprints relating to the aromatic profile of different vinegar samples was evaluated. For the experimentation TQ samples of pure vinegar (**ABT**, **AB1** and **AB2** samples) were compared with mixed samples in different percentages of **AB** (**5**, **10** and **20%**). The final aim was to develop a quick method able to discover the integrity of the PDO product, permitting to fight frauds in this area by using HS-GC-IMS. The fingerprints of the two commercial samples of **AB** vinegar showed profiles characterized by more volatile molecules (among these ***2-octanone***, ***isovaleric acid***, ***1-hexanol***, ***isoamyl acetate*** and ***acetoin*** were clearly identified) when compared with **ABT** samples (**Figure 1**). The more complex fingerprint, together with the sensitivity of the instrument, made it possible to identify and differentiate the samples added with AB from that of ABT already at the percentage of 5%, identifying specific molecular markers. Subsequently, the data were statistically analyzed by applying principal component analysis (PCA) (**Figure 2**). **Figures 3** and **4** show how already at the 5% percentage it was possible to discriminate some volatile compounds (characteristic of the **AB** samples) such as ***2-octanone***. The confirmation of the nature of the molecules identified through the ***FlavourSpec®*** (processed by the software through direct recognition, using the Kovats indices) can possibly be carried out by comparison with standards (GC-FID) or by MS analysis (ongoing work).

CONCLUSIONS

Head Space-GC-Ion Mobility Spectrometry (HS-GC-IMS) is a rapid chromatographic technique useful to obtain 2D separation of VOCs from foods, allowing to obtain a specific fingerprint of the aroma with no pre-treatment of the samples. This analysis clearly demonstrates the ability of this rapid approach to distinguish samples with different percentages of AB PGI. This model study – focused on the determination of the authenticity of ABT PDO product – clearly showed that the application of HS-GC-IMS approach is useful to trace the adding of AB PGI industrial product up to 5% spiking in high value traditional vinegar. The implementation of the analysis enlarging the sampling as well as the further application of the Computer Vision Image Analysis on 2D fingerprints will made robust this approach, simplifying its application.

In Vino Analytica Scientia Neustadt2022
Analytical Chemistry for Wine, Brandy and Spirits