

INTRODUCTION

Food Contact Materials (FCMs) are all materials and articles intended to come into contact with food. Plastic represents in Europe one of the most common FCMs; recycled plastics may also be used in FCMs under certain conditions. Even if perfectly aligned with the Circular Economy and the EU Green Deal program, the safety of recycled plastics requires evaluation, as chemicals can migrate from the materials into food. All the plastic materials should be manufactured in compliance with EU regulations, including good manufacturing practices, so that any potential transfer to foods does not raise safety concerns; otherwise, they could change the composition of the food in an unacceptable way, or they could have adverse effects on the quality of foods (for instance, taste and/or odor). Some recycled plastic materials significantly impact the overall "volatilome" of foods, potentially releasing off-notes, changing their typical profile during processing or their shelf life. Mono- and multidimensional GC-MS were largely used in the past to evaluate the specific migration of volatiles compounds in foods; Head Space-Gas Chromatography coupled with Ion Mobility (HS-GC-IMS), an underexploited technique in this area of interest, should be considered a powerful tool useful to rapidly evaluate the release of off-notes as well as the change of the volatile profile in foods.

Aim of this work was focused on the application of HS-GC-IMS to study volatile profiles of recycled plastics produced by different technologies, investigating the release of off-notes, particularly in edible oil (grape seeds)

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 components released from plastic materials and grape seed oil samples. GC-IMS system was coupled with an automatic sampler capable of heating and stirring the samples before analysis. By GC with Ion Mobility Spectrometry, the instrument is configured to lead a 2D profile of the low boiling flavoring compounds obtained from the head-space analysis of the various samples.

Sample preparation: the grape seed oil samples were brought into contact with two types of recycled plastic pellets (deodorized and not) in a ratio of 1:10 (plastic : oil). The hermetically sealed samples were subjected to modified migration tests under critical conditions, preliminarily selected according the Reg. (EU) No 10/2011 "on plastic materials and articles intended to come into contact with food". 1 mL of oil sample was transferred without pretreatment into a 20 mL glass vial, immediately sealed through a special screw cap to avoid partial loss of the Volatile Organic Compounds (VOCs) fraction. The equilibrium between the liquid and the gas phases was obtained setting the automatic sampler at 50 ° C for 10 minutes, following the positioning of the vials.

Analytical method: 300 µL of the headspace of the vials containing different samples were injected (syringe temperature: 70 ° C). The duration of the analysis was set at 20 minutes; the carries gas (N₂) 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 (N₂) 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, exploiting the Kovats indexes. 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) using the libraries supplied in the instrument software.



RESULTS

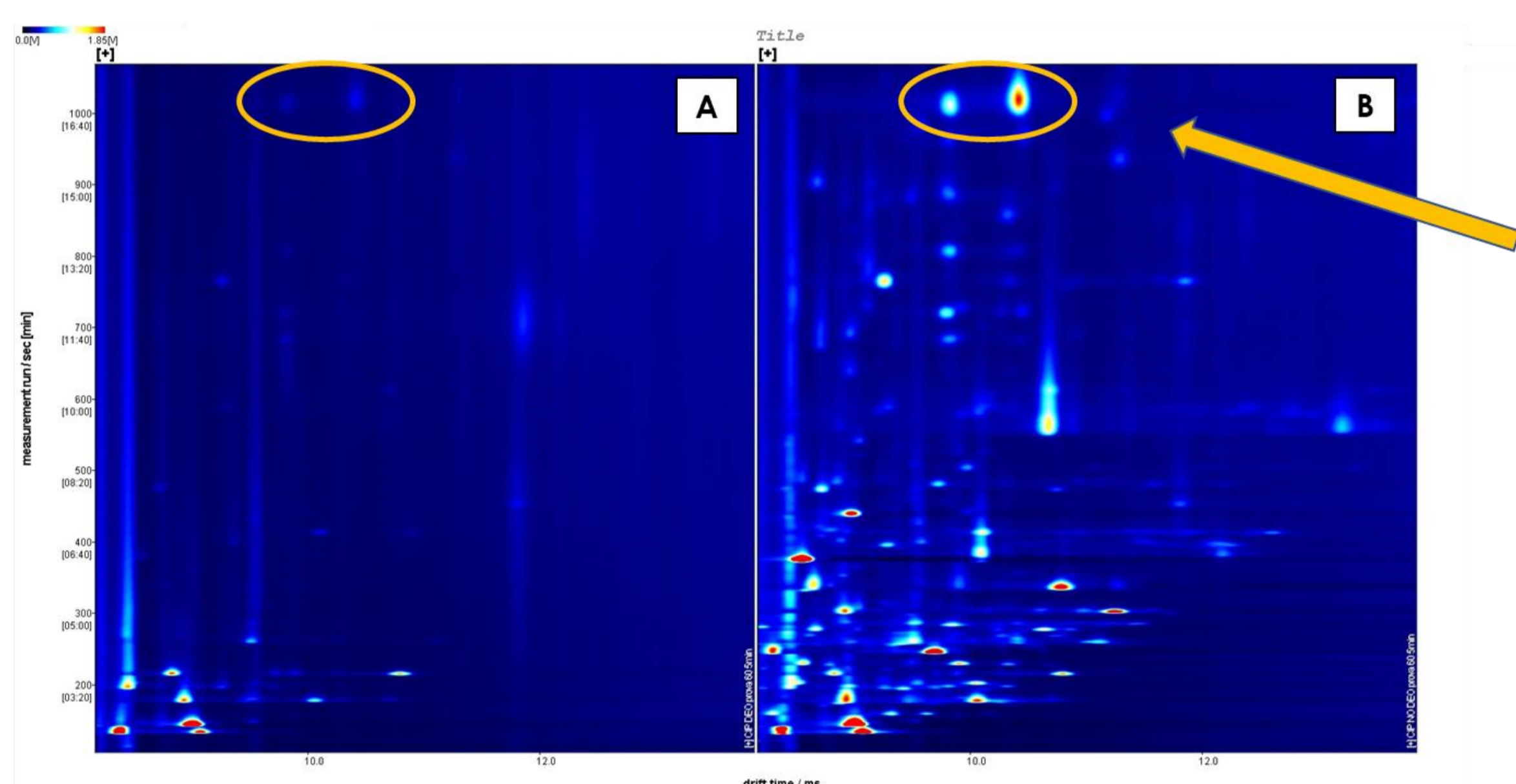


Fig. 1. VOC's profiles from deodorized plastic pellets (A) and not deodorized plastic pellets (B)

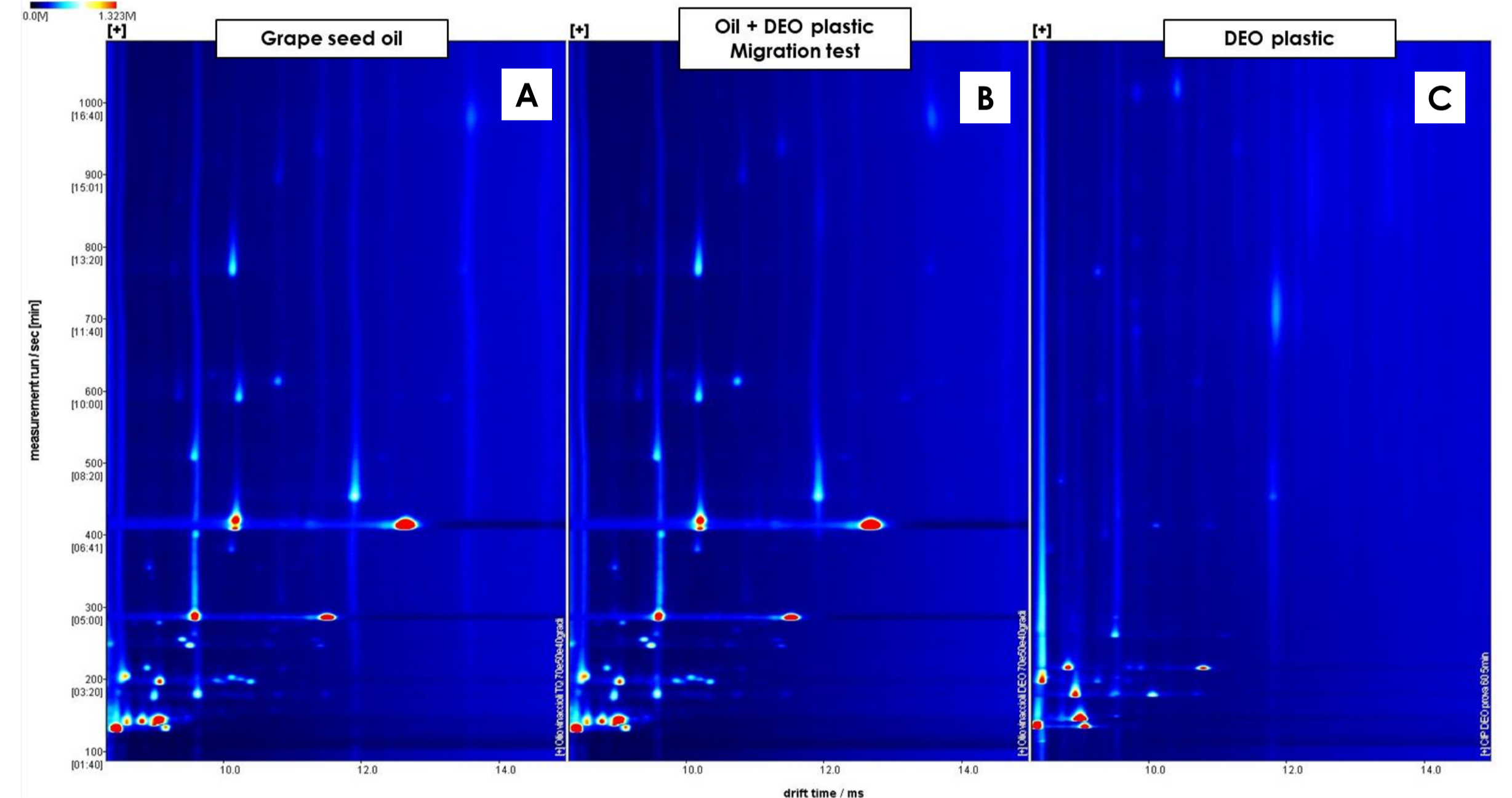
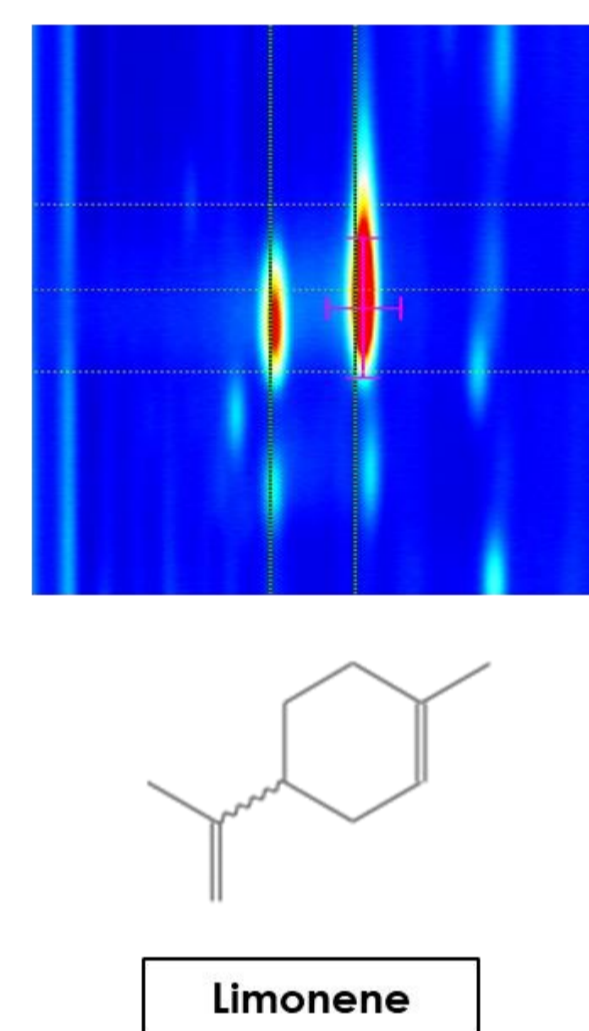


Fig. 2. Comparison among the VOC's profiles of the grape seed oil (after accelerated thermal treatment, A), deodorized plastic (C) and oil exposed to deodorized plastic material (B)

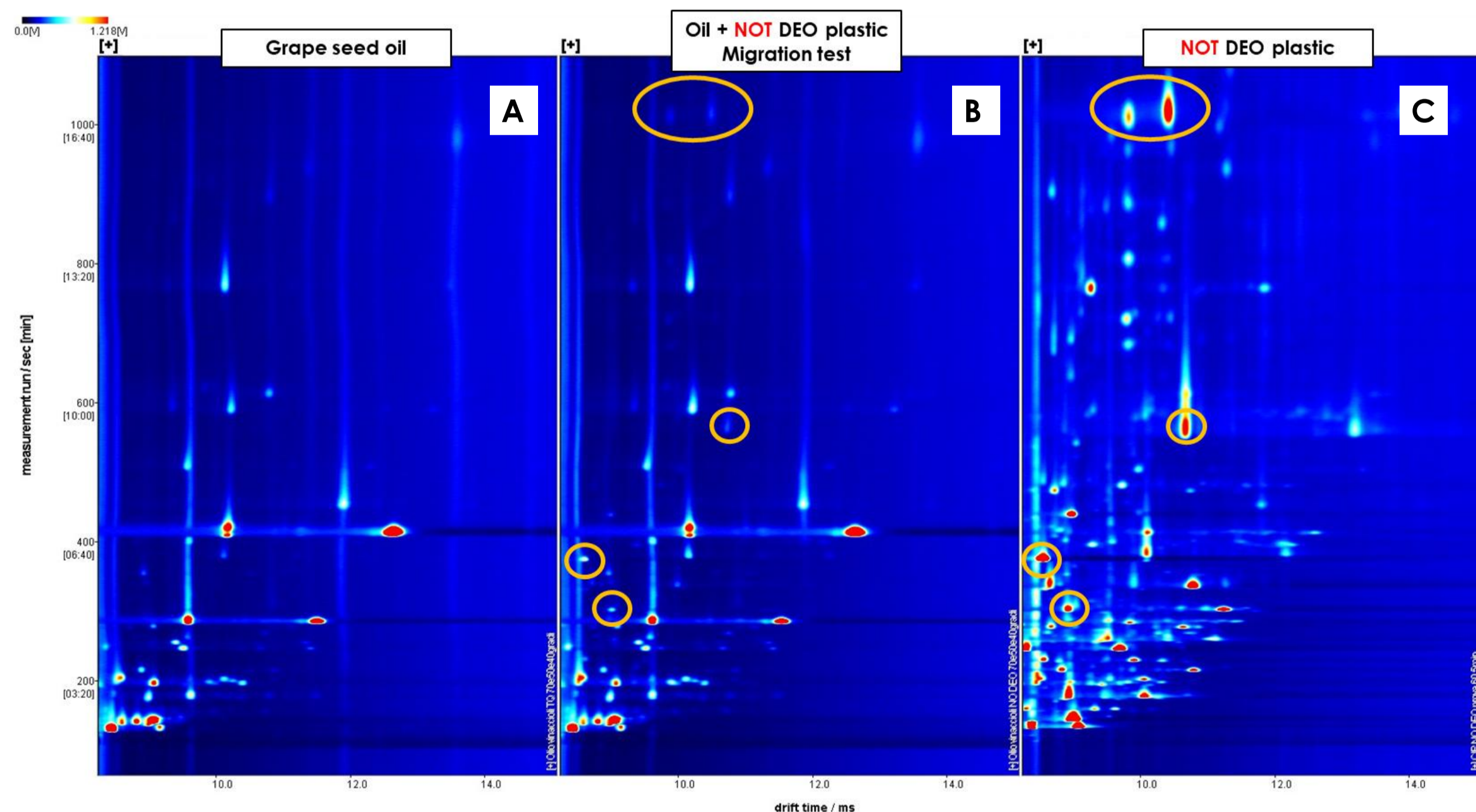


Fig. 3. Comparison among the VOC's profiles of the grape seed oil (after accelerated thermal treatment, A), not deodorized plastic (C) and oil exposed to not-deodorized plastic material (B)

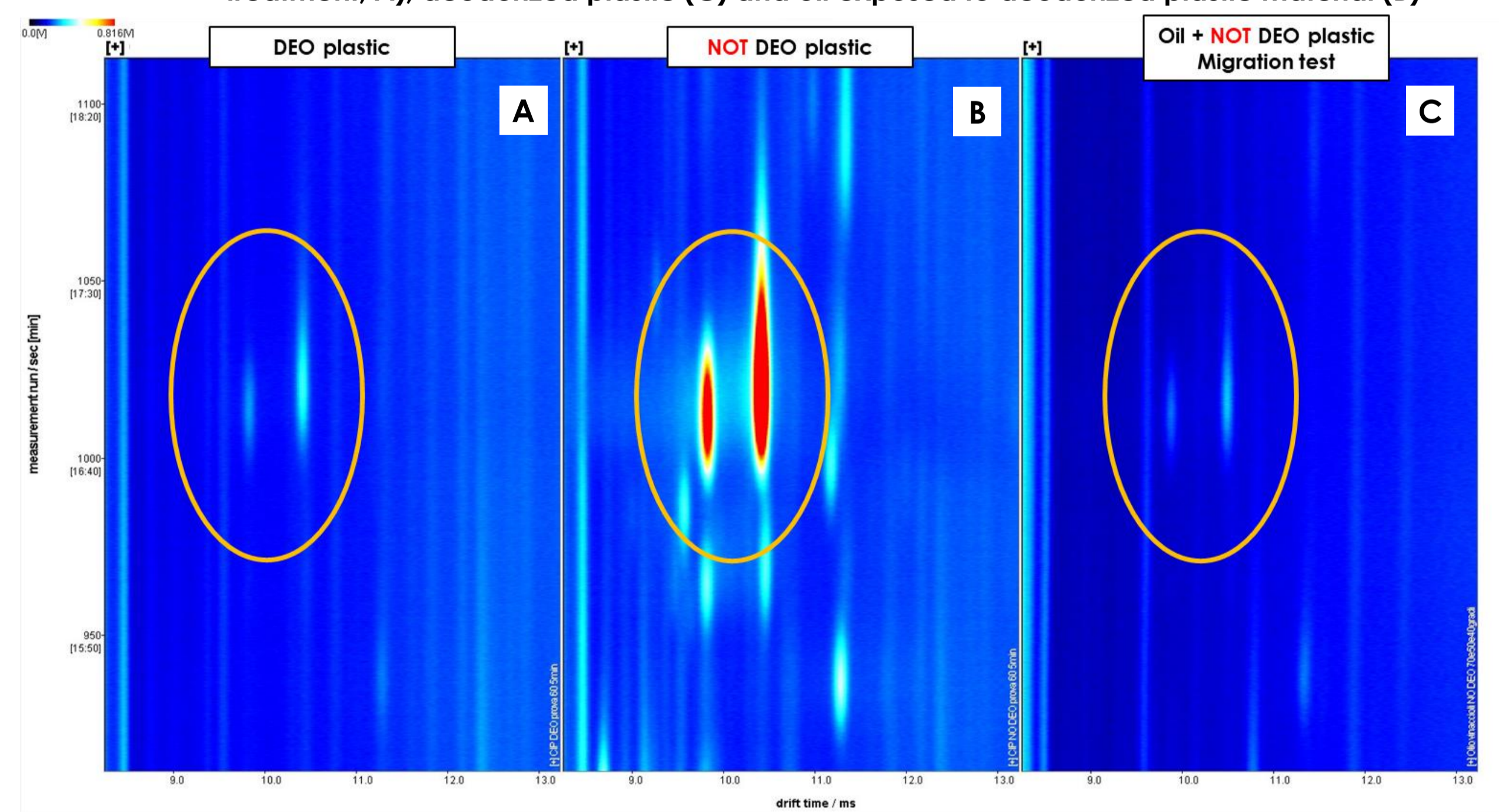


Fig. 4. Magnification of the 2D chromatographic profiles of the deodorized plastic pellet (A), not deodorized plastic pellet (B), and grape seed oil exposed to not-deodorized pellet (C). Limonene (monomers and dimers) presence is highlighted in yellow circles.

2D fingerprints of recycled plastic material (deodorized and not, pre-formed extruded pellets) are reported in Fig. 1 A and B, respectively. As showed in Fig. 1B, the VOC's profile obtained from the not deodorized recycled plastic sample is complex when compared with that obtained from the deodorized one, as expected. Arrow in Fig. 1B shows the presence of limonene, a cyclic monoterpene impact-flavoring compound often recovered in recycled plastic materials. The chromatogram of grape seeds oil obtained by HS-GC-IMS is reported in Fig. 2 A. The thermal treatment didn't affect significantly the overall 2D profile of the oil Volatilome (data not shown). The analysis of the thermally-treated oil in presence of recycled plastic pellets (accelerated test in oven) is reported in Fig. 2 and 3 (Fig. 2: deodorized plastic; Fig. 3: not deodorized plastic pellets). The magnification reported in Fig. 4C clearly shows the presence of limonene in oil samples, confirming the capacity to migrate of this compound in the adopted conditions and parameters.

CONCLUSIONS

Rapid analysis through HS-GC-IMS confirmed its usefulness, particularly reducing time in sample handling and preparation. Peculiar volatiles fingerprints obtained from the stripped deodorized recycled plastics were confirmed. 2D profiles allowed us to obtain molecular fingerprints, highlighting the release and migration of odorant compounds, and confirming the need to explore in deep this class of materials. Finally, this analytical approach will open new perspectives, particularly regarding the quality control of FCMs, including at-line monitoring.