



Monitoring in real time the changes in VOCs emission in sunflower and extra virgin olive oil upon heating by PTR-ToF-MS

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All relevant data are within the paper and its Supporting Information files.

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The authors declare no competing interests.

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Abstract: In this work the emission of volatile organic compounds (VOCs) upon the heating process of an extra virgin olive oil (EVOO) and a high oleic sunflower oil (SFO) was evaluated in real time by spectrometry. Two tests were carried out, in the first VOCs emitted from both kinds of oil were measured at room temperatures (not heated, NH) and at 180°C; in the second test, VOCs emission for selected masses were monitored under increasing temperatures over time: at room temperature not heated oils (NH), 60, 90, 120, 150, and 180°C, respectively. The spectra were acquired using a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-ToF-MS). The total VOCs emission increased at 180°C, determined both by the rise of the amount of compounds present in the NH samples and by the formation of new masses generated by oxidative chemical reaction from triglycerides and fatty acids. From the set of results it is evident that a good control of the temperatures can be useful in reducing the quantities of masses potentially harmful to health in human food.

1. Introduction

A common worldwide operation extensively used in food preparation is cooking by immersion in hot oil, as for fried and deep fried operations. Types of oils used for fried and deep frying operations vary with different cultures and are widely used both domestically and commercially. When frying and deep frying are used, fats and oils are carried at elevated tem-

peratures often over 180°C, which in presence of atmospheric oxygen (between 160 and 240°C) produce many flavor compounds (alkanes, fatty acids, aldehydes, ketones, polycyclic aromatic hydrocarbons), pleasant or unpleasant, and change their flavor stability. The flavor compounds released during the heating process are affected by some parameters such as cooking temperature, preparation time, chemical composition of the oils, physical and physicochemical constants and the presence of additives and contaminants (Fullana *et al.*, 2004). The volatile compounds and sensory characteristics from different edible oils (Brewer *et al.*, 1999; Katragadda *et al.*, 2010) were altered after intense heating and the main alterations were in the emission of volatile compounds linked to the oxidation process, compounds which are negatively related with the sensory attributes. In particular, the oxidation process in oils mainly lead to the formation of alkyl radicals, alkylperoxyl radicals and decomposition of hydroperoxide and cause the decay of both their nutritional and sensory quality (Velasco and Dobarganes, 2002; Silvagni *et al.*, 2012). Moreover, there are some human health risks both linked to oil oxidations process and to many of the originated compounds released by the heating process (Vaclavik *et al.*, 2013).

The PTR-ToF-MS tool represents a simple, and high-throughput strategy, applicable without any laborious sample preparations and treatments, particularly suited for analysis in real time of dynamic flavor release (both *in vitro* and *in vivo*) from diverse food matrices along the food-to-fork production chain (Costa *et al.*, 2016).

The aims of this study are (1) to test the PTR-ToF-MS as a sampling system for the detection of the released compounds from not heated olive and sunflower oils and to compare with heated oils at their smoking point (180°C); (2) to monitor and evaluate in real-time the VOCs emitted from different oils, upon the heating from 25°C to 180°C, to understand the dynamic of oxidation phenomena.

2. Materials and Methods

Vegetable oil material

Two different types of commercial oils were used for this experiment, extra virgin olive oil (EVOO) and a high oleic sunflower oil (SFO). They have different heating temperatures, this latter (SFO) considered more resistant to thermal increases (Smith *et al.*,

2007). Both oils were acquired at the local supermarket in Florence city (Italy). The analysis of volatile organic compounds (VOCs) emitted from both oils virgin has been obtained through a PTR-ToF-MS (Ionicon Analytik GmbH, Innsbruck, Austria), which is an instrument with high resolution mass and sensibility (5-10 ppt) and makes analysis possible without any pretreatment of samples. H_3O^+ was used as a reagent ion for the proton transfer reaction.

Sample preparation and analysis

First experiment. For this experiment, 100 ml of each type of oil was placed inside a 250 ml Pyrex glass jar, hermetically sealed; the jar's lid was equipped with two holes that permitted the insertion of Teflon tubes, which were respectively connected to a zero-air generator (Peak Scientific instruments, USA) and to the PTR-ToF-MS system. It was essential to avoid the entry of foreign substances inside the jar, and that was obtained by means of a sealing paste placed around the lid and the two entry holes. Oil samples were analyzed at two points: Room temperature (25°C) and at 180°C.

Second experiment. The same steps of the first experiment was followed, in addition each oil sample was heated by using a round electric heating plate and analyzed in real time to verify the VOCs emitted from both types of oil at different temperatures: room temperature (25°C), 60, 90, 120, 150, 180°C. Once reached each of the five thermal steps, the temperature was kept constant for 5 minutes and then passed to the subsequent thermal step. The evaluation of the aromatic profile of each oil examined was carried out in real time in order to monitor the behavior of the various volatile substances during the heating process. For each sample the analysis lasted for a period of about 50 minutes, recording a spectrum *per second* for a total of 60 spectra per minute. To determine the achievement of the selected temperatures, a trial was performed in parallel; in details, a thermometer was placed into the jar contained 100 ml of different kinds of oil and the times required to reach each temperature, for both samples, were measured as well. The whole analyses were carried out inside a conditioned room, with an internal temperature of 25°C in order not to condition the chemical reactions, as they are strongly sensitive to variations in temperature and humidity. The value of the white (control) represented by an empty sealant jar was recorded before starting with samples analysis, and the volatile profile of the white (control) has always been subtracted from the final value of

each sample.

The VOCs in the headspace were observed by direct injection into the PTR-ToF-MS and separation of single ions happened accordingly to their mass to charge (m/z) ratio. All the instrumental parameters were settled in the following way as in Taiti *et al.* (2017): drift tube ionization condition at 600 V and a continuous pressure of 2.20 ± 0.02 mbar; while instrument internal calibration was based on: $m/z = 29.997$ (NO^+); $m/z = 59.049$ ($\text{C}_3\text{H}_7\text{O}^+$) and $m/z = 21.022$ (H_3O^+) and was performed off-line. The experiment data was acquired through the TofDaq software (Tofwerk AG, Switzerland) and all spectra were analyzed and acquired using a dead time of 20 ns for the Poisson correction and peak extraction following the methodology described in Cappellin *et al.* (2011), using a modified Gaussian peak shape.

3. Results

The signal intensity (ncps) generally vary among different oils. In figure 1 the signal intensity (ncps) of protonated m/z detected at 25°C and 180°C in sunflower oil (SFO) and extra virgin olive oil (EVOO) are clearly indicated. As a general consideration, the intensity of the signals is always higher in EVOO than in the SFO at the same temperature. At room temperature (25°C) the SFO spectrum is smoother, characterized by only 16 signals, being a very refined oil compared to EVOO. The EVOO presents instead 33 signals at room temperature when not heated, which are characteristics of the extra virgin olive oil in general, even if among them there are some masses that could generate off-flavor ($m/z = 47.049$, $m/z = 61.028$, $m/z = 89.060$) (Marone *et al.*, 2017; Taiti and Marone, 2017). At temperatures of 180°C, 43 m/z were measured in EVOO and 39 m/z in SFO, with the formation of 23 new masses generated as a result of the high temperature in SFO and 11 new m/z in EVOO, of which only 7 common to both matrices.

To better verify the intensity of the signals at temperatures below 180°C, some masses of particular relevance have been selected in SFO and EVOO, found in the most recent literature (Klein *et al.*, 2016). In particular, in the SFO emerge the masses $m/z = 57$, $m/z = 101$, and $m/z = 113$ (Fig. 2); these masses are also reported in Klein *et al.* (2016) as particularly relevant emissions by SFO. For olive oil emerge the masses $m/z = 57$, $m/z = 101$, $m/z = 115$, $m/z = 143$, also reported in Klein *et al.* (2016). Moreover, as its peculiar trend, it should be noted

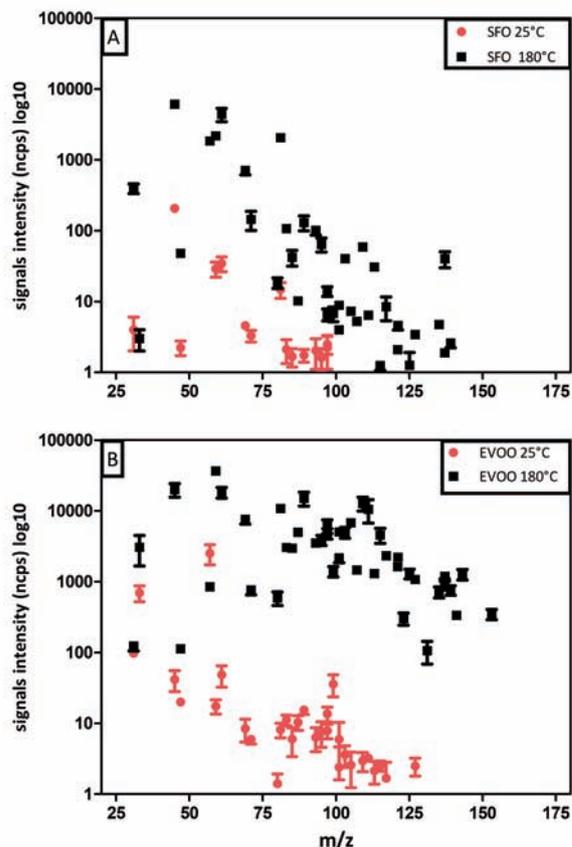


Fig. 1 - Signal intensity (ncps) of VOCs compounds in sunflower oil (SFO) and extra virgin olive oil (EVOO) at 25°C and 180°C. Bars represent standard deviations ($n = 3$).

the mass $m/z = 45$ (Fig. 2), that sharply increases in EVOO starting from 150°C.

The emission assessment of the selected masses by PTR-ToF-MS allows to directly examine in real time the trend of their quantities in SFO and EVOO in relation to the heating temperatures, avoiding alterations due to foods present together with the cooking oil, as generally found in the current scientific literature (Ontanón *et al.*, 2013; Klein *et al.*, 2016). The increasing temperature determines the increase of the emission of the total VOCs produced at each temperature point for both SFO and EVOO. The intensity of VOCs emission by the refined SFO, always appears lower than that of the EVOO. In both oils the increases are progressive, and related to the increasing temperature, in agreement with Katragadda *et al.* (2010). Both in SFO and EVOO the mass $m/z = 57$, still absent at 90°C, present at 120°C, showed a dramatic increase at 150°C according to Katragadda *et al.* (2010), and subsequently restart a trend proportional to the increase in temperatures. For each matrix all the other selected masses showed a common trend;

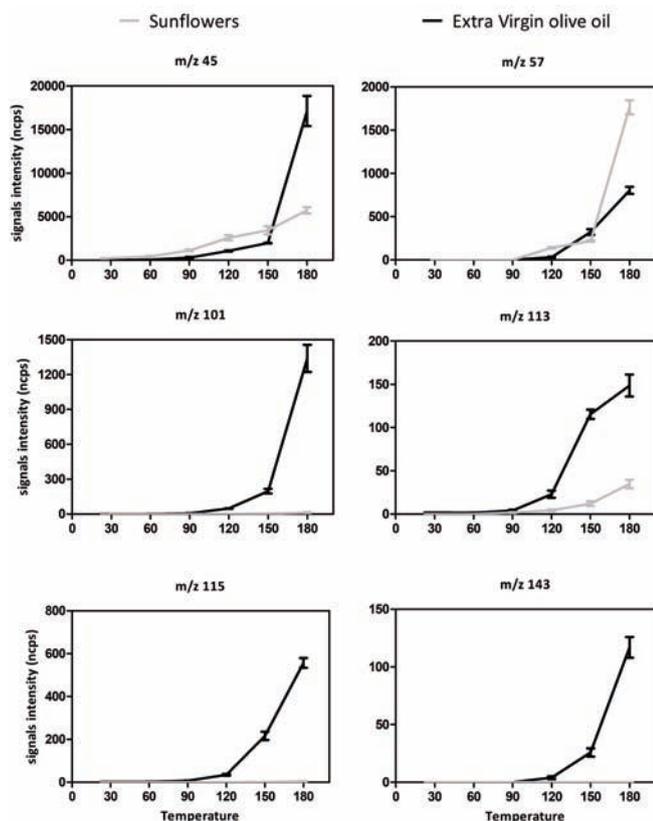


Fig. 2 - Trend of signal intensity (ncps) of different protonated m/z in sunflower oil (SFO) and extra virgin olive oil (EVOO) at different temperatures (25, 60, 90, 120, 150, and 180°C) upon heating

while they were absent, or present in small quantities, up to a temperature of 90°C, they have a relatively modest rise to 120°C, and showed a dramatic increase from 150°C, according to Nunes *et al.* (2013). The mass $m/z = 57$, always absent in the unheated oils, would derive from the dehydration of glycerol subjected to high temperatures (Klein *et al.*, 2016), and this would be a phenomenon common to all vegetable oils: the aldehydes that may be present in virgin olive oils as a result of a natural enzymatic oxidation of polyunsaturated fatty acids (Lipoxygenase cascade, LOX) increase due to the temperature through a chemical oxidative reaction of the same polyunsaturated fatty acids (Muik *et al.*, 2005).

4. Discussion and Conclusions

The PTR-ToF-MS tool represents a simple, and high-throughput strategy, applicable without any laborious sample preparations and treatments, for the real-time detection of oxidative changes occurred

during the heating process of both vegetable oils. There are numerous studies that examine the quality of the oil, as well as its composition and characteristics during the heating or frying process; nevertheless, a fewer number of studies examine the composition of the fumes generated during this process.

In this work, it is pointed out that EVOO emissions are always higher than those of the SFO; the effect of the heating causes an increase in the emission of the masses present at the origin and the generation of new compounds, deriving from transformations of triglycerides and above all of the polyunsaturated fatty acids (Moreno *et al.*, 1999). In particular, the trend of emissions in relation to the temperature has been highlighted for some selected masses, and it is clear that change due to chemical oxidation occur between 120 and 150°C, temperatures above which the production of volatiles increases enormously for all the examined masses. Since the increase in oil temperature proportionally increases the emission of VOCs, including some compounds that could be considered as pollutants, it is clear that an accurate control of the temperatures of oils used for frying food is important for the industry and for the home cooking. Many VOCs depend on the temperature, emissions at temperatures below the *smoke* point will be actually reduced. Some compounds, such as mass $m/z = 57$, start to form consistently already at relatively low temperatures (150°C). It should be noted that in the case of EVOO, masses of naturally occurring compounds are also very high, as they are derived from an oxidative process linked to enzymatic reactions of the polyunsaturated fatty acids (Lipoxygenase pathway, LOX) (Campestre *et al.*, 2017). The increase determined by high temperatures is no longer enzymatic but chemical oxidative. Further studies are needed to deepen the knowledge on the effect of heating temperature in the formation of compounds potentially harmful to human health, in order to reduce the effect of pollution not only at commercial but also at the domestic level, for the daily use of fried oils.

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