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Non-thermal plasma as preparative technique to evaluate olive oil adulteration

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ABSTRACT

In recent years adulteration of pure extra virgin olive oil (EVOO) with other types of vegetable oils has become an important issue. In this study, non-thermal plasma (NTP) is investigated as an innovative preparative analytical technique enabling classification of adulterated olive oil from an ascertained authentic batch of olive oil in a more sensitive manner. Non-thermal plasma discharges are a source of highly oxidative species such as singlet oxygen, and atomic oxygen. It was assumed that NTP-induced oxidation triggers unique lipid oxidation mechanisms depending on the specific composition of the oil matrix and minor constituents. In this work EVOO samples were adulterated with sunflower oil (1–3%) and submitted to NTP treatment. Results showed that while untreated samples could not be classified from the authentic olive oil reference, NTP treatments of 60 min (Ar/O_2 0.1%) on the oil batches resulted in the formation of a unique set of secondary volatile lipid oxidation products enabling classification of adulterated oil samples.

1. Introduction

Olive oil is a highly desirable food product on the international market due to its unique organoleptic properties, its high monounsaturated fatty-acid content and antioxidant properties (Bendini et al., 2007; Frankel, 2011). Safeguarding the quality of these olive oils is of utmost importance.

Much research is focusing on the aroma and flavor properties of olive oils. The organoleptic quality of olive oils is mostly assessed using trained taste panels or by means of headspace-solid phase microextraction (Romero, García-González, Aparicio-Ruiz, & Morales, 2015; Šarolić, Gugić, Friganović, Tuberoso, & Jerković, 2015). Recently, Uncu and Ozen (2015) described a Fourier transform infrared spectroscopy method to determine quality parameters such as oxidative stability, color pigments, fatty acid profile and phenolic composition of olive oils. Next to the abovementioned focus on overall quality of fresh olive oil, increasing research attention is given to oxidative deterioration of olive oils. Krichene et al. (2010) studied the stability of virgin olive oil and behavior of its natural antioxidants under medium temperature conditions. Equally important is the development of analytical techniques to verify the traceability of high-quality monovarietal olive oils (Garcia, Martins, & Cabrita, 2013). In order to verify the claimed botanical origin, multiple techniques have been developed such as Near Infrared (NIR) Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy, and Synchronous Fluorescence Spectroscopy (Garcia et al., 2013). Giacalone, Giuliano, Gulotta, Monfreda, and Presti (2015) reported how extra virgin olive oils of Italian and non-Italian origin were differentiated by GC-FID analysis of sterols and esterified sterols followed by chemometric tools. Garrido-Delgado, del Mar Dobao-Prieto, Arce, and Valcárcel (2015) described how combining a capillary column with Ion Mobility Spectrometry (IMS) enabled the quantification of 26 volatile metabolites (aldehydes, ketones, alcohols and esters) which might be used to verify the category of an olive oil sample. Garcia et al. (2013) applied headspace solid-phase micro-extraction (HS-SPME) to quantify a selection of C6 compounds and terpene hydrocarbons as suitable markers of the geographical origin and genotype of the EVOO.

Today, significant research attention is also given to the development of analytical techniques which can be used to detect olive oil adulteration. Due to its economic importance olive oils are prone to such adulteration. Garcia et al. (2013) reviewed that blending of extra virgin olive oil (EVOO) with refined olive oil (ROO) is a common type of adulteration. Extra-virgin olive oil (EVOO) is also often adulterated with less expensive oils (e.g. sunflower, soy, corn, and rapeseed oils, hazelnut and peanut oils). Several analytical chemical techniques have been developed for

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the detection of olive oil adulteration such as liquid chromatography (analyzing triacylglycerol content), gas chromatography–mass spectrometry (Mildner-Szkudlarz & Jelén, 2010), mid-infrared spectroscopy (Borràs et al., 2015), microwave reflectometry analysis (Cataldo, Piuzzi, Cannazza, & De Benedetto, 2012), electronic nose, DNA identification of adulterant markers (Zhang et al., 2016), detection of metabolite-based markers (Zhang et al., 2016). Borràs et al. (2015) studied mid-infrared (MIR) spectra (4000–600 cm^{-1}) of olive oils using chemometric methods to distinguish extra-virgin olive oils with lower quality olive oils. (Dais & Hatzakis, 2013) extensively reviewed current application of Nuclear Magnetic Resonance (NMR) Spectroscopy for olive oil quality and authenticity assessment. In particular two methodological approaches of metabonomics, metabolic profiling and metabolic fingerprinting were discussed in great detail.

Since the abovementioned techniques are rather time-consuming, often generate chemical aste, and require highly trained professionals, ongoing research attention is given in order to develop improved methods for vegetable oil adulteration. Zhang et al. (2014) detected adulteration based on fatty acid profiles by gas chromatography coupled with mass spectrometry (GC/MS) in selected ion monitoring mode. Using mass spectral characteristics of selected ions and equivalent chain length a model could detect adulteration of edible oil with other vegetable oils from a content of 10%. Zhang et al. (2016) proposed ion mobility spectrometry (IMS) fingerprinting as a simple and rapid detection technology for adulteration. Such IMS technology is based on the detection of ionized molecules that are separated under a weak electric field at ambient conditions. This innovative method proved to be able to classify sesame oil samples that were 10% adulterated. Agrimonti, Vietina, Pafundo, and Marmiroli (2011) reviewed methods based on assaying DNA present in the oil. Pérez-Jiménez, Besnard, Dorado, and Hernandez (2013) assessed the performance of cpDNA markers on olive oil matrices to determine the origin and authenticity. By using a combination of nine plastid loci, 6 haplotypes were fingerprinted which could be used to discriminate high-value commercialized cultivars. Very recently, Liang, Huang, and Chuang (2015) described the application of fiber grating sensors based on changes in refractive index to detect a minimum of 5% adulteration of pure olive oil with cottonseed oil. Mabood et al. (2015) investigated the effect of thermal treatment (8 h at 75 °C) on the discrimination of pure extra virgin olive oil (EVOO) samples from EVOO samples adulterated with sunflower oil. Using fluorescence spectra adulterated oil samples could be identified from 2%. van Wetten, van Herwaarden, Splinter, Boerrigter-Eenling, and van Ruth (2015) investigated the applicability of fast DSC for the detection of sunflower oil (SFO) in EVOO. Heating curves of adulterated EVOOs showed an decrease in the one of two endothermic peaks which therefore could be used in the detection of adulteration of EVOO by SFO. Depending on the type of olive oil, the presence of 2–10% SFO could be detected.

Based on the above literature overview it can be noticed that despite the recent advances in analytical methods for olive oil adulteration, minimal detection levels for adulteration are still too high. Additionally, techniques described above are typically time-consuming, require the use of harmful solvents and require highly expensive and complex technology and expertise. From literature it can be concluded that the currently available techniques are able to detect adulteration only from 2% oil addition. Garcia et al. (2013) concluded that further research is required to find new approaches or identify new compounds that could be assigned as reliable adulteration markers able to detect this fraudulent practice with high selectivity, sensitivity and accuracy.

In this work, the application of non-thermal plasma has been tested for the first time as an innovative preparation technique enabling the detection of low amounts of adulteration. In the recent study of Vandamme et al. (2015) and Van Durme, Nikiforov, Vandamme, Leys, and De Winne (2014) non-thermal plasma (NTP) proved to be an accelerated oxidation technique with great potential to study and predict lipid oxidation phenomena and/or oxidative stability. It was proven that such non-thermal plasma treatments enabled a controlled and standardized accelerated induction of lipid oxidation in complex food matrices due to the generation of high concentrations of reactive species such as singlet oxygen, hydroxyl radicals, atomic oxygen, etc. The application of non-thermal plasma technology to detect adulteration is unexplored, but highly promising since it can be assumed that each oil matrix oxidizes differently depending on its unique fatty acid profile, presence of polyphenols and specific composition of antioxidative compounds, etc. It is assumed that adulteration with different types of oil will result in small changes of oil composition and/or contents of minor compounds determining unique oxidation mechanisms and pathways. The result of such oxidative deterioration is the formation of volatile organic compounds (Bendini, Cerretani, & Salvador, 2009). A forced non-thermal oxidation could thus result in the formation of a unique headspace composition that can be used to classify authentic from adulterated oil matrices. The goal of this work is therefore to investigate whether the application of non-thermal plasma might indeed induce such different lipid oxidation kinetics in adulterated olive oil samples, leading to the formation of a unique headspace composition.

2. Materials and methods

2.1. Oil samples

Adulterated olive oil samples were prepared adding 1.00 g, 2.00 g and 3.00 g from the same batch of sunflower oil (commercial available 100% refined sunflower oil) to respectively 99.0 g, 98.0 g and 97.0 g from a batch of extra virgin olive oil (commercially available Carapelli Extra Virgin Olive Oil 'Classico', Firenze (Italy), immediately followed by a 10 min intensive mixing. All samples were stored in the dark at −80 °C to prevent oxidation. The commercial sunflower oil had following composition; total saturated fat (11%), total mono-saturated fat (27.3%), total poly-unsaturated fat (61.7%). The commercial extra virgin olive oil (EVOO) was composed as; total saturated fat (14.5%) (palmitic acid: 13.0%, stearic acid: 1.5%), total mono-unsaturated fat (70.3–73.5%) (oleic acid: 70.0%, palmitoleic acid: 0.3–3.5%), total poly-unsaturated fat (15.5%) (linoleic acid: 15.0%, α-linolenic acid: 0.5%).

Prior to analysis 0.5 g of oil sample was carefully weighed in a 20 mL glass vial and sealed air-tight with a silicon cap. Concentration of identified oxidation products were expressed semi-quantitatively, using an internal standard, 3 μL methylpyrazine (14.33 mg/mL). All samples were measured in quadruplicate (n = 4).

2.2. Plasma reactor for treatment of oil samples

A dielectric barrier discharge (DBD) plasma source was used for non-thermal plasma (NTP) treatments of the oil samples. The plasma jet was operated with oxygen (Ar/O_2) gas mixture. The species generated in the active zone of the discharge located in between electrodes can be divided in (listed according to increasing reactivity): charged particles (electrons, positive and negative ions); neutral excited states of Ar (metastables, resonance states and electron excited states); UV and VUV photons (appearing due to excimer radiation, OH and NO bands emission); oxygenated species including O_3, O_2 singlet, and O. The production mechanisms of these different excited species have been intensively studied in the last decade worldwide (Knake, Reuter, Niemi, der