



## Coupling laser desorption with gas chromatography and ion mobility spectrometry for improved olive oil characterisation



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### ABSTRACT

The investigation of volatile compounds in the headspace of liquid samples can often be used for detailed and non-destructive characterisation of the sample. This has great potential for process control or the characterisation of food samples, such as olive oil. We investigated, for the first time, the plume of substances released from olive oil droplets by laser desorption in a feasibility study and applied ion mobility spectrometry coupled to rapid GC pre-separation to enhance selectivity. Our investigation demonstrated that significantly more substances can be detected and quantified via laser desorption than in the usual headspace, enabling a rapid (5–10 min), sensitive (low ng/g range) and comprehensive analysis of the sample, with the potential for quality control and fraud identification. Therefore, laser desorption provides a useful sampling tool for characterising liquids in many applications, requiring only a few  $\mu\text{L}$  of sample.

### 1. Introduction

Many samples can be comprehensively characterised by their odour, as the use of trained dogs for the identification of drugs and explosives or even individuals impressively exemplifies. Furthermore, in the food and fragrance industries, sensory panels for olfactometric investigations are commonly applied. The odour of a sample is determined by the composition of volatile compounds released from its surface, which is obviously dependent on the temperature. From an analytical point of view, the characterisation of a sample by its odour is implemented by headspace analysis. This procedure requires a thorough consideration of experimental conditions, particularly with regard to the amount or surface area of the sample, temperature, headspace volume, sample heating time and saturation stability in the headspace (Kaiser, 2005; Jenner, 2005). Thus, sample preparation is time-consuming and cannot meet the requirements of many process control applications with regard to analysis time. In addition, only volatile compounds can be released by this technique, depending on the sample temperature, but excessive heating for a particular time period can significantly alter the sample. Nevertheless, headspace analysis is a very common technique for subsequent analysis in mass spectrometry, which is often coupled with gas chromatographic pre-separation in many fields of application (Boots et al., 2014; Zhang et al., 2015; Chappuis, Niclass, Vuilleumier, &

Starkenmann, 2015).

Facing the above-mentioned restrictions of headspace analysis and focusing on liquid samples, experiments for the investigation of the potential of laser desorption (LD) compared to common headspace analysis were designed. In particular, this study is focused on the release of not only highly volatile compounds but also semi- and non-volatiles, from a liquid sample in a few  $\mu\text{s}$  for subsequent analysis. To keep the analysis time as short as possible, we decided not to use pre-concentrators such as SPME (Solid Phase Micro Extraction) for laser thermal desorption GC mass spectrometry to analyse the released substances, but rather used ion mobility spectrometry (IMS) as a fast and sensitive detector (50–100 ms). Furthermore, considering the complex sample expected, we coupled IMS with a rapid GC pre-separation step (few minutes).

After initial studies of ion mobility dating back to 1880, ion mobility spectrometry as an analytical device was first developed for military use (chemical warfare agents) and security purposes (drugs, explosives) (Eiceman & Karpas, 1994). In recent years, the coupling of IMS with rapid gas-chromatographic pre-separation enabled the sensitive (down to the ppt<sub>v</sub> range) and selective analysis of extremely complex and humid samples by yielding fast on-site results. GC/IMS have already been used successfully for the characterisation of gas-phase samples in process control (Vautz, Mauntz, et al., 2009; Vautz and Baumbach,

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2008, Vautz, Baumbach, & Jung, 2006), breath analysis for medical applications (Vautz, Nolte, et al., 2009; Perl et al., 2009; Jünger et al., 2012; Pagonas et al., 2012) and food quality and safety. Previous studies with olive oil analysis were restricted to the volatile compounds in the headspace, as mentioned above (Boskou, 2015, Garrido-Delgado, Arce et al., 2011; Garrido-Delgado, Mercader-Trejo et al., 2011; Garrido-Delgado, Arce, & Valcárcel, 2012).

Laser desorption is a common method in modern analytical chemistry that is usually coupled to mass spectrometry, not only in food chemistry applications (see e.g., Shrivastava & Tapadia, 2015; Cheng, Chen, & Chang, , Chen, & Chang, 2015; Haslam et al., 2015; Gilbert-López et al., 2013). In some cases, ion mobility spectrometry is coupled to pre-separation of ions before their mass spectrometric detection (Jackson et al., 2005; Huang, Kolaitis, & Lubman, 1987; Cevallos-Cevallos, Reyes-De-Corcuera, Etxeberria, Danylyuk, & Rodrick, 2009). However, at present, only a few studies on the coupling laser desorption with ion mobility spectrometry have been reported, none using an additional GC pre-separation step (Weickhardt, Kaiser, & Borsdorf, 2012; Ehlert, Walte, & Zimmermann, 2013; Ilbeigi, Sabo, Valadbeigi, Matejcek, & Tabrizchi, 2016).

To validate the proposed LD-GC/IMS method for liquids, olive oil was chosen as a representative sample. The quality and origin of olive oils have a significant influence on price; quality, in particular, causes higher production costs. Therefore, fast on-site analytical methods for the characterisation of the real quality of olive oil and identification of fraud are required (Ruiz-Samblás et al., 2011; Aparicio & Harwood 2013; Flath, Forrey, & Guadagni, 1973). Such a tool would have high potential for applications in the olive oil industry and quality control, and would also be beneficial for the consumer.

### 1.1. Olive oil

The oil produced from olive fruits is a natural product and is available at different quality levels (EG regulation 1234/2007, 22.10.2007). The quality of olive oil is influenced by the production process, and additional effects on its taste can be expected from the climate and origin of the trees. Based on regulations, only olive oils with the following general sales descriptions are allowed for sale:

- Extra Virgin Olive Oil (EVOO)
- Virgin Olive Oil (VOO)
- Olive Oil (mixture of refined and native olive oils)
- Olive-Pomace Oil

First-class olive oils are directly extracted from olives by mechanical treatment, which can be mentioned as additional details, such as “cold press” or “first cold press”. In addition to the abovementioned general sales descriptions, there are many different types of olive oils, depending on the above-mentioned production process details.

According to EG regulation 640/2008, only a few attributes describing the taste, which is in general determined by sensory panels (Iraqi, Vermeulen, Benzekri, Bouseta, & Collin, 2005), are allowed to characterise the olive oil, with the additional specification of intensity (intensive, medium, light and mild):

- fruity
- fruity – green
- fruity – ripe
- bitter
- sharp

The official analytical methods approved by the International Olive Council (mainly gas chromatographic and spectrophotometric methods) are used to characterise the quality of an olive oil to identify fraud. These require extensive sample preparation, long analysis times, qualified personnel, and large amounts of sample, reagents and

solvents.

In summary, the quality of olive oil is determined by the production process alone and not by analytical quality control or sensory panels during the process. Numerous studies on the correlation of the particular constituents of oil with the tested characteristics are presently available and are in general performed using time-consuming GC-MS analysis, mostly using direct headspace analysis (López-Feria, Cárdenas, García-Mesa, & Valcárcel, 2007) or LC-ESI-MS of the olive oil itself (de la Torre-Carbot et al., 2007). Furthermore, infrared spectroscopy can be applied for the analysis of those oils (Casale et al., 2012).

However, complex regulations clearly demonstrate that a detailed, sensitive and selective (as well as rapid and reproducible) characterisation with regard to quality, odour and taste is required. It can be mapped via the relevant volatile and semi- to non-volatile compounds in the oil. In addition, with the attributed intensity of particular tastes, a quantitative description is required. Therefore, we investigated the potential of laser desorption for the provision of a gas-phase sample from a liquid—including volatiles as well as semi- and non-volatiles—for its detailed characterisation using a fast, sensitive detector with additional selectivity. In this case, ion mobility spectrometry coupled to gas-chromatography (GC/IMS) was used. Such an instrument could be a helpful tool for olive oil characterisation after analysis and comparison of a suitable number of samples.

## 2. Materials and methods

The general setup selected (Fig. 1) was the implementation of a laser desorption chamber in the carrier gas flow. The gas phase sample released from a liquid droplet by the laser beam is flushed through the sample loop of the analytical system, an ion mobility spectrometer coupled to a rapid gas-chromatographic pre-separation. The particular components of the complete system are described in the following paragraphs.

Furthermore, reference measurements for identification of unknowns in the sample were performed via adsorption of the samples on Tenax GR® adsorption tubes and later analysis using thermal desorption GC-MS.

For the present study, we used laser energy for desorption only and not for ionisation, due to the low ionisation yield usually obtained from laser ionisation. Instead, we used proton-transfer reactions induced by  $\beta$ -radiation ionisation of the present drift gas, as described in Section 2.3.

### 2.1. Laser desorption

For Laser Desorption (LD), a commercial, medical 2940-nm Er:YAG-laser (Limmer Laser, UNILAS 2940) with an energy of 0.1–1.2 J was used. The laser beam, guided by the attendant beam line, was focused by a CaF<sub>2</sub>-lens with a focal length of 75 mm into a desorption chamber. A controlled beam shutter (Thor Labs, SH05) was used to ensure a reproducible number of laser pulses for desorption.

The desorption chamber was made of stainless steel, with an inner diameter of 40 mm and a height of 20 mm. It is closed on the top with a disk of quartz-glass with a thickness of 3 mm. To ensure a reproducible laser position, the chamber and the laser were fixed on an optical bank (see Fig. 1). The sample was added to a 150- $\mu$ L stainless steel cup with a diameter of 8 mm, which was centred at the bottom of the desorption chamber. The chamber has two gas connections opposite each other, 3.7 mm above the bottom, which are connected to Swagelock®-fittings on the outside. A nitrogen flow (evaporated liquid nitrogen, Messer AG) of 100 mL/min, controlled by a mass flow controller (Bronkhorst, IQF-200-AAD-11-V), was applied as a carrier gas.

The emitted laser light has a wavelength of 2940 nm ( $3401\text{ cm}^{-1}$ ). It is absorbed by water, which has a strong absorption band at  $3404\text{ cm}^{-1}$ , a combination of the asymmetrical O–H stretching vibration ( $\nu_3$ ) at approx.  $3600\text{ cm}^{-1}$  (mostly due to hydrogen bridge

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