Rapid fingerprinting and classification of extra virgin olive oil by microjet sampling and extractive electrospray ionization mass spectrometry†

Wai Siang Law,[a] Huan Wen Chen,[b] Roman Balabin,[a] Christian Berchtold,[a] Lukas Meier[a] and Renato Zenobi*[a]

Received 16th November 2009, Accepted 5th February 2010
First published as an Advance Article on the web 12th February 2010
DOI: 10.1039/b924156f

Microjet sampling in combination with extractive electrospray ionization (EESI) mass spectrometry (MS) was applied to the rapid characterization and classification of extra virgin olive oil (EVOO) without any sample pretreatment. When modifying the composition of the primary ESI spray solvent, mass spectra of an identical EVOO sample showed differences. This demonstrates the capability of this technique to extract molecules with varying polarities, hence generating rich molecular information of the EVOO. Moreover, with the aid of microjet sampling, compounds of different volatilities (*e.g.* *E*-2-hexenal, *trans-trans*-2,4-heptadienal, tyrosol and caffeic acid) could be sampled simultaneously. EVOO data was also compared with that of other edible oils. Principal Component Analysis (PCA) was performed to discriminate EVOO and EVOO adulterated with edible oils. Microjet sampling EESI-MS was found to be a simple, rapid (less than 2 min analysis time per sample) and powerful method to obtain MS fingerprints of EVOO without requiring any complicated sample pretreatment steps.

Introduction

Mass spectrometry (MS) has emerged as one of the main techniques for analyzing and identifying chemical compounds in complex matrices, *e.g.* proteins in native biological systems,[1–3] metabolites in tissue samples[4,5] and non-covalent biomolecular complexes.[6,7] This is mainly because of the unparalleled ability of MS to provide qualitative and semi-quantitative data about samples of enormous complexity.

Several promising ambient ionization mass spectrometry techniques have been developed for direct and real-time analysis of samples.[8–10] The introduction of desorption electrospray ionization (DESI)[4,5,11] and direct analysis in real time (DART)[12,13] allowed, for the first time, the direct analysis of mainly solid samples in their native state. Since then, a number of other ambient ionization methods, such as laser ablation with electrospray ionization (LAESI),[14–16] low temperature plasma (LTP) probe,[17–19] electrospray-assisted laser desorption/ionization (ELDI)[20,21] and others[8–10] have been developed for rapid detection of analytes on solid surfaces. Extractive electrospray ionization (EESI) mass spectrometry (MS)[22–29] was introduced to analyze liquids and suspensions with dirty and complex matrices. Samples such as undiluted urine or milk can be directly injected into an electrospray plume. Analyte ions are created when neutral analyte droplets are collided with the droplets from the primary ESI spray solvent. This method is non-invasive and has hardly any memory or matrix effects.

Extra virgin olive oil (EVOO) is a product with high nutritional value and significant health benefits. Medical and epidemiological research conducted by the International Olive Oil Council has shown that, compared to other edible oils, the consumption of EVOO lowers the risk of cardiovascular diseases and diabetes. The EVOO also displays anti-inflammatory, antibacterial and antioxidant activity.[30–36] Due to these potential health benefits, it is not surprising that EVOO is one of the most widely consumed edible vegetable oils. However, adulteration of EVOO with lower quality vegetable oils is a relatively common fraudulent practice. Chemical fingerprinting of EVOO is a useful tool to detect such adulteration.[34] Due to the intricate matrix of EVOO, most current methods for detecting EVOO provenance and adulteration require extraction protocols such as liquid–liquid extraction and/or solid-phase extraction prior to analysis by MS.[37–40] An exception is headspace analysis, which can be directly performed by GC to analyse volatile compounds.[41,42] Although direct infusion mass spectrometry could be performed to analyze adulterated EVOO, adduct formation and sample carry-over effects are frequently observed.[43–46] Ambient ionization methods such as DART[47] and LTP[48] probe were employed for the mass spectrometric analysis of olive oil, showing the promise of this general approach for rapid and accurate detection of olive oil adulteration without sample preparation.

Here, we explore the use of another simple and rapid ambient MS method, microjet sampling combined with extractive electrospray ionization (EESI)-Mass Spectrometry (MS) to profile EVOO without any sample pretreatment. We also applied EESI-MS to distinguish admixtures of other edible oils with extra virgin olive oil. As shown in Fig. 1, a stream of nitrogen gas is directed into the liquid, causing bubble formation. Driven by the gas pressure, the bubbles move upwards to the liquid surface. Eventually, the bubbles burst and create microdroplets at the gas liquid surface *via* a mechanism known as microjetting.[49,50] Via microjetting, volatile, semi-volatile and even non-volatile molecules are liberated and transported to the EESI source *via* a heated Teflon tube (Fig. 1). Nitrogen gas is preferable to avoid oxidation or chemical contamination of the sample.

[a]*Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland. E-mail: zenobi@org.chem.ethz.ch; Fax: (+)41-44-632-1292*
[b]*Department of Applied Chemistry, East China Institute of Technology, Fuzhou, 344000, China*
† This paper is part of an *Analyst* themed issue on Ambient Mass Spectrometry, with guest editors Xinrong Zhang and Zheng Ouyang.

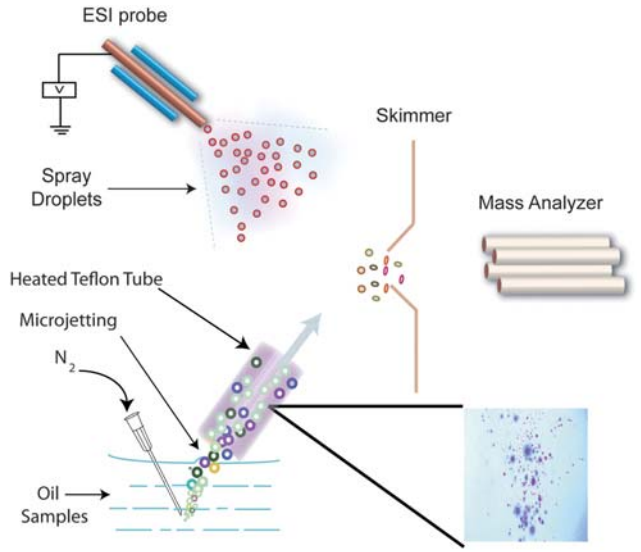

Fig. 1 Schematic illustration of the concept and set-up of EESI-MS. Inset: The aerosol is directed to the ion source of the mass spectrometer *via* microjet sampling. The fine droplets were collected at the outlet of the second neck of the flask. Other conditions were similar to those used for the EVOO adulteration detection. Deposition of rhodamine 6G on a paper surface caused a pink coloration.

The high nutritional value of EVOO arises from high levels of oleic acid, and from minor compounds such as phenolic acids.[30] Although a higher sensitivity for detection of fatty acids and phenolic acids could be achieved in negative ion mode, it is preferable to characterize phenolic acids in positive ion mode as it provides more characteristic fragments for identification purposes.[30,33–36] Moreover, oleic acid is present in high abundance in EVOO, and detection of this compound could be achieved simultaneously in positive ion mode. EESI-MS in positive ion mode was hence employed for mass spectrometric fingerprinting of EVOO samples.

Experimental

Materials and methods

EESI-MS fingerprints of EVOO, adulterated EVOO, and other edible oils were obtained in positive ion mode on a commercial quadrupole time of flight (Q-ToF) mass spectrometer (Q-ToF UltimaTM, Micromass/Waters, Manchester/UK) with minimal source modification. Typical EESI-MS conditions were as follows: source temperature 25 °C, desolvation temperature 50 °C, ESI and cone voltages were set to +3.8 kV and +40 V, respectively. An electrospray solvent mixture (MeOH–H_2O/acetic acid in a 2 : 2 : 1 ratio) was infused at 2 μL min^{-1}. Caffeine (10 μg L^{-1}) was added into the ESI spray as an internal standard to monitor the stability of the ESI spray. Mass spectra were acquired over the 50–500 Da range. CID of selected ions was performed with 10–35 units of collision energy. The Mass Lynx 4.0 software (Waters, Manchester, U.K.) was used for the Q-ToF-MS experiments. Mass spectra were typically collected for about 90 s with a single scan time frame of 1 s. Background subtraction of the spectra was performed using the background subtraction algorithm from the Mass Lynx Software.

A two-neck flask containing 2 mL of liquid sample was used in this study. Nitrogen gas (gas flow rate 100 L h^{-1}) was directed into the liquid sample *via* the first neck and the second neck was connected to a heated Teflon tube (i.d. 5 mm, 1.2 m in length and 80 °C) to deliver the aerosol produced by the microjetting process to the ion source of the mass spectrometer (Fig. 1). The outlet of the heated Teflon tube is 2 cm away from the sample cone of ESI. The velocity of the gas flow through the tube is approximately 141 cm s^{-1}. During the EESI experiments, it is not likely that EVOO droplets are transported to the sampling cone of the ESI source. Moreover, we have applied a counter-flow (≈ 5 L h^{-1}) at the outlet of the sampling cone to blow away the larger olive oil droplets. Caffeine was added as an internal standard to monitor the overall ion intensity during the EESI-MS experiments. No significant decrease in signal of protonated caffeine was observed after 12 h. This further demonstrates that oil droplets are not likely transported to and accumulated in and around the sample cone.

EVOO, sun flower oil (SFO), rapeseed oil (RSO) and sesame oil (SSO) were purchased from reliable sources. They were kept in a cool and dry place until analysis. Rancid EVOO extraction was performed using a procedure described previously.[39] In brief, 0.5 mL of rancid EVOO samples were mixed with 1.5 mL of a methanol–water mixture (50 : 50). The mixtures were centrifuged at 5000 *g* for 5 min. The hydroalcoholic layer was transferred to a sample vial, 20 μL of formic acid was added into the hydroalcoholic layer, and the EVOO hydroalcoholic extract (mainly polar compounds) was ready for analysis.

For adulteration of pure EVOO with edible oils, the EVOO samples were spiked with 5% of edible oils (sun flower oil, rapeseed oil and sesame oil). These admixtures were analyzed immediately after preparation.

For Principal Component Analysis (PCA),[51,52] the raw mass spectral data obtained were tabulated and normalized. Multivariate analysis was performed using the Matlab software. (MathWorks, Inc., Natick, MA, United States).

Results and discussion

We first investigated the microjet sampling mechanism. For this purpose, EVOO was mixed with a small amount of non-volatile rhodamine 6G (1 mM in ethanol). A sharp stream of nitrogen gas was directed into the sample, and the aerosol formed was collected at the outlet of the two-neck flask. The inset of Fig. 1 shows aerosol droplets consisting of both the EVOO and rhodamine 6G. This result demonstrates the capability of this microjetting mechanism to sample non-volatile compounds from this complicated viscous liquid *via* aerosolization.

Effect of primary ESI spray composition

Based on previous reports,[22] analytes are thought to be "extracted" in EESI from the sample spray into the charged droplets during droplet collision events. The composition of the primary ESI solvent spray is hence expected to strongly influence which analytes are efficiently extracted and detected in EESI. In order to investigate this "extraction "hypothesis, studies with different solvent compositions of the primary ESI spray were conducted.

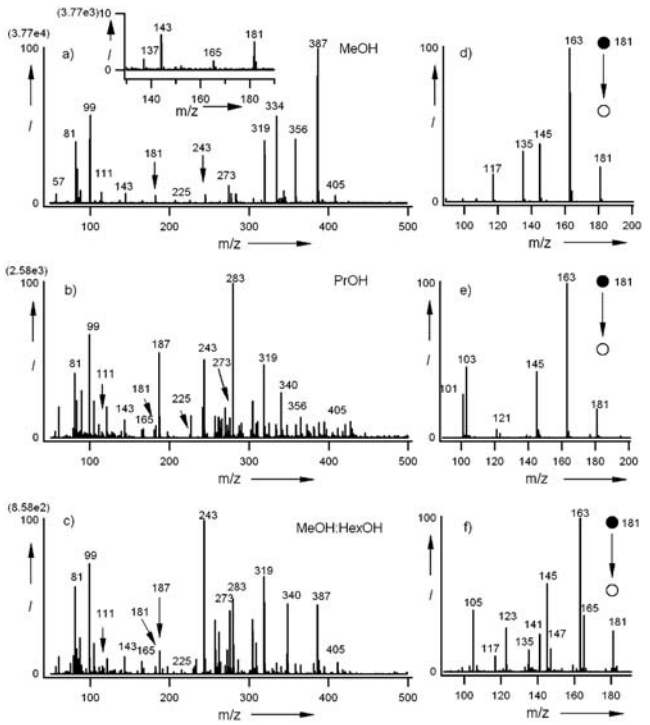

Fig. 2 Mass spectra fingerprints of EVOO obtained from different primary ESI spray solvent. a) methanol, b) propanol and c) methanol : hexanol in a 1 : 1 ratio. CID spectra of compounds at *m/z* 181 obtained from different ESI spray solvents. d) methanol, e) propanol and f) methanol : hexanol in a 1 : 1 ratio. Values in the parentheses are the absolute total ion counts. Inset: Zoomed segment of the positive microjet sampling EESI-MS mass spectrum of EVOO, showing relative abundances of phenolic acid compounds at *m/z* = 181 and 165.

As shown in Fig. 2 (a–c), spectral patterns with new peaks or with common peaks exhibiting different signal intensities result from changing the primary ESI spray solvent composition. Since hexanol is unable to generate a stable ESI spray independently, a primary ESI spray solvent mixture consisting of acidified methanol : hexanol in a 1 : 1 ratio, was used instead. The relative peak intensities of phenolic compounds (at *m/z* 137, 165, 181 and 225; identification see below and Table 1) were the highest when only acidified methanol was used as primary ESI spray solvent. The peak intensities of these compounds decreased progressively when the methanol : hexanol solvent mixture and propanol was separately employed as the primary ESI spray solvent. This suggests that the composition (*e.g.* polarity) of the primary ESI spray solvent strongly influences the type of molecules that are extracted into the charged droplets, thereby giving rise to different mass spectra.

To further investigate the effects of primary ESI spray solvent composition on the MS fingerprint obtained, MS/MS experiments were conducted on several selected peaks. For example, MS/MS of *m/z* = 181 generates fragments at *m/z* 163, 145, 135 and 117 when MeOH was used as the primary ESI spray solvent (Fig. 2d). The fragmentation pattern was established to be that of protonated caffeic acid. However, when propanol (Fig. 2e) was used as the primary ESI spray solvent, MS/MS of *m/z* 181 generates a different fragmentation pattern (*m/z* 163, 145, 121, 103 and 101) whereas the characteristic fragments observed in methanol/hexanol (Fig. 2f) were at *m/z* 181, 165, 163, 147, 145, 141, 123. Although the identities of the latter two components could not be established, this finding indicates that the compounds extracted from EVOO varied with the composition of the primary ESI solvent spray. Interestingly, when the compound at *m/z* 99 was subjected to MS/MS experiments, the

Table 1 Diagnostic ions found in EVOO by microjet sampling EESI MS

Compound	Boiling Point/°C [b]	*m/z*	MS/MS Product ions (*m/z*)	Neutral losses in MS/MS
Trans-2-Pentenal	118 °C	85	67	H_2O
1-Penten-3-ol	114 °C	87	69	H_2O
Pentanal	103 °C	87	69	H_2O
E-2-Hexenal	147 °C	99,81	81, 57	H_2O, C_2OH_2
Hexanal	122 °C	101	83, 55	H_2O, C_2H_5OH
Trans-trans-2,4-heptadienal	84.5 °C	111	93, 67	H_2O, CH_3CHO
Tyrosol[a]	158 °C	121	103, 93, 77	H_2O, CO, CH_3CHO
Octanal	172 °C	129	111, 83, 69	H_2O, C_2H_5OH, (C_2H_5OH, CH_2)
Hydroxytyrosol	355 °C	137	119, 91	H_2O, C_2H_5OH
Nonanal	192 °C	143	125, 97, 83	H_2O, C_2H_5OH, (C_2H_5OH,CH_2)
Coumaric acid	346 °C	165	147, 119, 91	H_2O, C_2H_5OH, (C_2H_5OH,C_2H_4)
Caffeic acid	419 °C	181	163, 145, 135, 117	H_2O, $2H_2O$, C_2H_5OH, (C_2H_5OH H_2O)
Sinapic acid	402 °C	225	207, 175, 147, 192, 164, 119	H_2O, (H_2O,CH_4O), (H_2O, CH_4O, CO), (H_2O, CH_3), (H_2O, CH_3, CO), (H_2O, CH_3, CO, CH_2OCH_3)
Elenolic Acid	225 °C	243	225, 211, 193, 183, 169, 139	H_2O, CH_4O, (H_2O, CH_4O), CH_3COOH, C_2H_5COOH, (CH_3COOH, CH_3CHO)
Oleic Acid	360 °C	283	265, 247, 223, 191, 177, 163, 149, 135, 121	H_2O, 2 H_2O, CH_3COOH, (H_2O, CH_3COOH, $[CH_2]_n$), $n = 1 \ldots 6$
Cholesterol/$C_{22}H_{27}O_6$	360 °C	387	369, 287, 243, 203, 189, 175,161, 147	H_2O, $C_6H_{12}O$, $C_9H_{20}O$, ($C_6H_{12}O$, $[CH_2]_n$), $n = 6 \ldots 10$

[a] Tyrosol is observed as M + H − H_2O. [b] Obtained from SciFinder Scholar 2007.

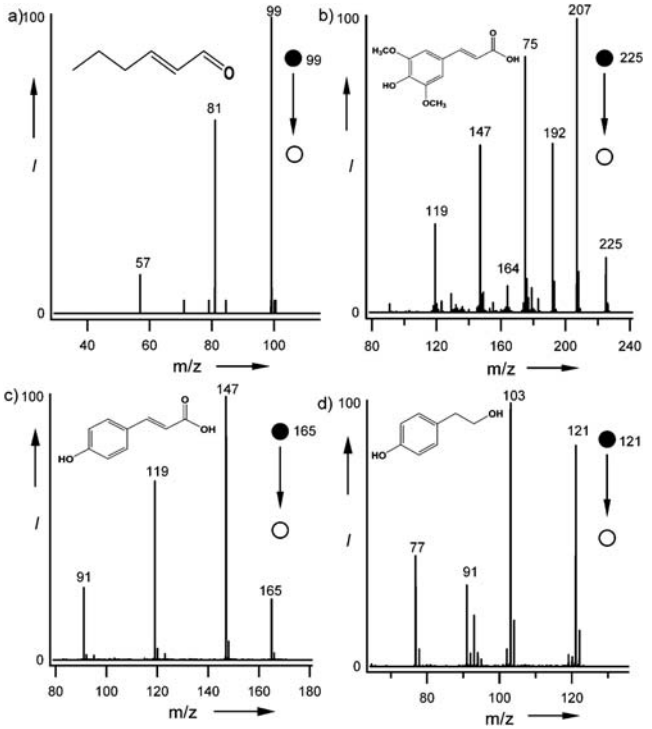

Fig. 3 CID spectrum and molecular structure of diagnostic ions of EVOO. a) *E*-2-hexenal b) sinapic acid c) coumaric acid and d) tyrosol.

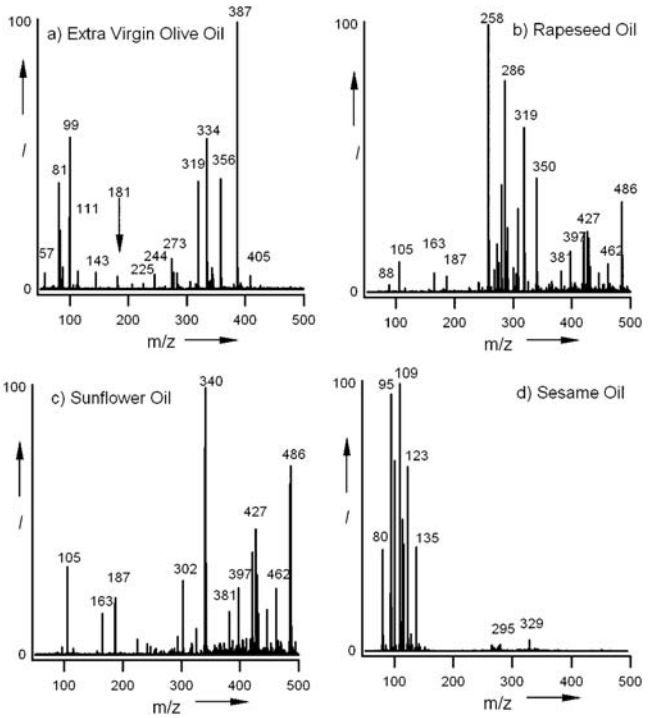

Fig. 4 Chemical fingerprints of a) Extra virgin olive oil b) Rapeseed oil c) Sunflower oil and d) Sesame oil.

fragments obtained with the three different primary ESI solvents are identical (Fig. 3a) in which the parent ion (*m*/*z* 99) generates fragments at *m*/*z* 81 and 57 by loss of H_2O and C_2OH_2, respectively. The fragmentation pattern was established to be that of protonated *E*-2-hexenal.[48] It is thus quite probable that only protonated *E*-2-hexenal constitutes the peak at *m*/*z* 99 and is visible in all three different primary ESI spray solvents. This also means that the ion peak at *m*/*z* 181, which gives rise to different fragmentation patterns in the presence of different primary ESI spray solvents, must be due to the presence of isobaric compounds in the EVOO sample. The results demonstrate that by adjusting the composition (polarity) of the primary ESI spray solvent, compounds with different polarities present in extra virgin olive oil can be differentially extracted.

The simultaneous detection of volatile compounds such as at *m*/*z* 99 and 81 (*E*-2-hexenal) which contribute to the distinctive fruity fragrance of EVOO[53,54] and non-volatile phenolic compounds (Fig. 3b–d) such as sinapic acid at *m*/*z* 225, coumaric acid at *m*/*z* 165 and tyrosol at *m*/*z* 121 $(M + H–H_2O)^+$ illustrates the capability and versatility of this microjet sampling EESI technique to generate and analyse aerosol which is shown to contain a surprisingly rich molecular profile of the EVOO. Our technique was applied to obtain ESI-MS fingerprints of EVOO, adulterated EVOO, and rancid EVOO.

EVOO adulteration and aging

As exemplified in Fig. 4, MS fingerprints produced by EESI-MS for the 4 different types of oils analysed (EVOO, SSO, SFO and RSO) are easily distinguishable. In the mass range of 50–500 Da, different types of edible oils produce numerous diagnostic ions which allow direct classification of each type of edible oil without any sample preparation or separation prior to detection. Major diagnostic ions for SFO are at *m*/*z* 187, 302, and 340, whereas for rapeseed oils are *m*/*z* 88, 258, 286, 319, 350 and 427. The identification of these compounds is not within the scope of this study and is ongoing. Higher peak intensities and more compounds are observed in the mass spectra of EVOO and SSO. Some of these additional signals are likely to be attributed to the fragrant compounds inherent of EVOO and SSO. The compounds released from EVOO display diagnostic ions at *m*/*z* 81, 99, 319, 334, 356 and 387. Table 1 summarizes the diagnostic ions of EVOO detected by microjet sampling EESI-MS.

Using the EESI mass spectral fingerprints, 4 different types of pure edible oils and 3 adulterated EVOO samples (adulterated with 5% of edible oils), which are indistinguishable by scent, were successfully separated with high confidence by Principal Component Analysis (PCA) (Fig. 5). The projection of the clusters into the plane spanned by Principal Component 1 and Principal Component 2 were unsatisfactory. However, in a 3-D PCA plot, a clear separation and classification of pure EVOO from adulterated EVOO is obtained. EVOO adulterated with SFO and RSO are grouped near each other, whereas the cluster consisted of EVOO with 5% SSO is isolated from both EVOO and SFO/RSO.

When EVOO ages and oxidizes, it usually becomes rancid. Rancid EVOO is most commonly detected by taste. A MS spectrum of rancid EVOO was obtained with our EESI-MS technique. A higher abundance of an ion at *m*/*z* 111 is observed in the rancid EVOO (Fig. 6). A MS/MS experiment was performed on this ion and it was identified as protonated *trans-trans*-2-4-heptadienal. This EVOO oxidation indicator, originating from the β-scission of the 11-hydroperoxide oleate and 1-octen-3-ol[53,55] which produces the octanal fragment, was found to fragment

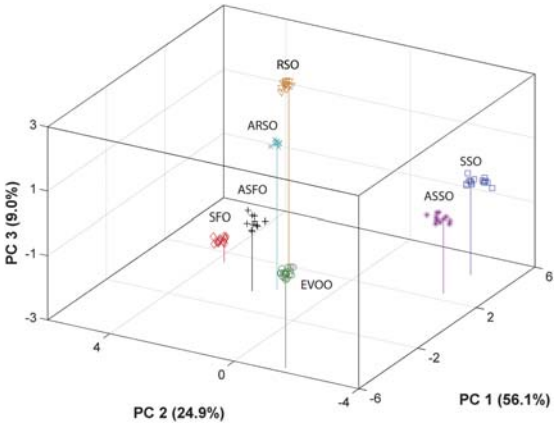

Fig. 5 Score plot of Principal Component Analysis of the mass spectra obtained from 4 edible oils and adulterated EVOO. EVOO: extra virgin olive oil, SSO: sesame oil, RSO: rapeseed oil and SFO: sun flower oil. ASSO: EVOO adulterated with SSO, ARSO: EVOO adulterated with RSO and ASFO: EVOO adulterated with SFO. Each point represents measurement of 1 edible oil sample.

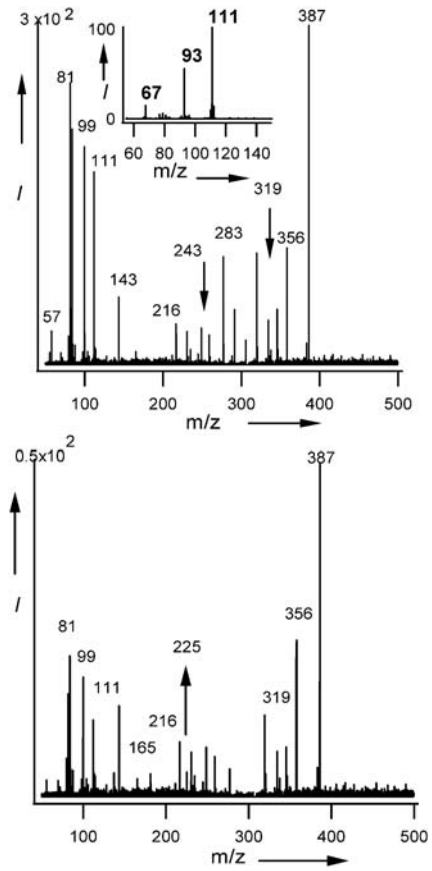

Fig. 6 Chemical fingerprint of rancid EVOO (top) and rancid EVOO (bottom) extract. Inset: CID spectrum of *trans-trans*-2,4-heptadienal.

further to ions at *m/z* 93 and 67 with the loss of H_2O and C_2H_2, respectively (Fig. 6 inset). Besides, the signal intensity of the ion at *m/z* 143 is observed to be elevated in rancid EVOO. This ion can be attributed to protonated nonanal which contributes to the fatty and waxy smell of the rancid EVOO. Nonanal also derives from the homolytic β-scission of the 9-hydroperoxide and 10-hydroperoxide oleate. These results were in accordance with the decreased signal of oleic acid in the rancid EVOO.[53,55]

Due to the intricate matrix of EVOO and its viscosity, solvent extraction or dilution is usually necessary prior to MS analysis. However, a mass spectral profile of only the extracted part of the sample is obtained (Fig. 6b). Due to the intrinsic selectivity of the extraction method, polar compounds such as phenolic acids at *m/z* 181, 165, 137 and 121 were detected in the rancid EVOO extract. For example, as shown in Fig. 6, a significant reduction in the intensities of EVOO oxidation indicators and *E*-2-hexenal in the extract of rancid EVOO is observed. Moreover, volatile compounds at *m/z* 81 and 99 were significantly reduced in intensity in the mass spectrum of the rancid EVOO extract. This result supports our previous hypothesis that, due to the selectivity of the extraction method used, loss of significant characteristic information of the olive oil samples is observed.[29]

Conclusions

In conclusion, a simple, yet powerful method based on microjet sampling EESI-MS was developed for rapid characterization of EVOO (pristine, rancid, aged, and adulterated) and other edible oils without the need for any sample pre-treatment. By adjusting the composition (polarity) of the primary ESI spray solvent, compounds with different polarities present in the EVOO can be differentially extracted, hence providing complementary molecular information of EVOO. The simultaneous detection of volatile, semi- and non-volatile compounds present in EVOO indicates that information about the molecular composition of EVOO could be obtained without notable discrimination when direct characterization was performed with this microjet sampling technique. Phenolic acids, fatty acids, oxidation indicators (such as *trans-trans*-2,4-heptadienal and nonanal) which are responsible for the organoleptic properties and the nutrition value of EVOO are detected. Data from positive ion mode EESI proved to be sufficient to provide a clear classification and fingerprinting of EVOO, adulterated EVOO or rancid EVOO; no further experiments were conducted in negative ion mode at this stage. This technique could be a potentially attractive tool to investigate and characterize viscous liquid samples such as gels, polymers as volatile, semi-volatile and non-volatile compounds with different polarities could be extracted and detected by microjet sampling EESI-MS.

Acknowledgements

W.S. Law is grateful for financial support from an ETH Postdoctoral Fellowship and from the Eidgenössische Stipendienkommission für ausländische Studierende (ESKAS). Financial support from the Swiss National Science Foundation (Switzerland, grant no 200020-124663) and the Sino-Swiss Science and Technology Cooperation (grant no IZLCZ2 123987) are highly appreciated. Partial financial support from MOST (China, grant no. 2009 DFA41880) is gratefully acknowledged.

References

1 B. F. Cravatt, G. M. Simon and J. R. Yates III, *Nature*, 2007, **450**, 991–1000.
2 R. Aebersold and M. Mann, *Nature*, 2003, **422**, 198–207.
3 B. Domon and R. Aebersold, *Science*, 2006, **312**, 212–217.
4 J. M. Wiseman, S. M. Puolitaival, Z. Takats, R. G. Cooks and R. M. Caprioli, *Angew. Chem., Int. Ed.*, 2005, **44**, 7094–7097.
5 J. M. Wiseman, D. R. Ifa, L. Zhu, C. Kissinger, N. E. Manicke, T. G. Peter and G. Cooks, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 18120–18125.
6 T. R. Northen, O. Yanes, M. T. Northen, D. Marrinucci, W. Uritboonthai, J. Apon, S. L. Golledge, A. Nordstrom and G. Siuzdak, *Nature*, 2007, **449**, 1033–1036.
7 D. H. Min, W. J. Tang and M. Mrksich, *Nat. Biotechnol.*, 2004, **22**, 717–723.
8 A. Venter, M. Nefliu and G. Cooks, *TrAC*, 2008, **27**, 284–290.
9 H. W. Chen, G. Gamez and R. Zenobi, *J. Am. Soc. Mass Spectrom.*, 2009, **20**, 1947–1963.
10 G. A. Harris, L. Nyadong and F. M. Fernandez, *Analyst*, 2008, **133**, 1297–1301.
11 G. Cooks, Z. Ouyang, Z. Takats and J. M. Wiseman, *Science*, 2006, **311**, 1566.
12 C. Y. Pierce, J. R. Barr, R. B. Cody, R. F. Massung, A. R. Woolfitt, H. Moura, H. A. Thompson and F. M. Fernandez, *Chem. Commun.*, 2007, 807–809.
13 C. Petucci, J. Diffendal, D. Kaufman, B. Mekonnen, G. Terefenko and B. Musselman, *Anal. Chem.*, 2007, **79**, 5064–5070.
14 P. Nemes and A. Vertes, *Anal. Chem.*, 2007, **79**, 8098–8106.
15 B. Shrestha and A. Vertes, *Anal. Chem.*, 2009, **81**, 8265–8271.
16 P. Nemes, A. A. Barton and A. Vertes, *Anal. Chem.*, 2009, **81**, 6668–6675.
17 J. D. Harper, N. A. Charipar, C. C. Mulligan, X. R. Zhang, R. G. Cooks and Z. Ouyang, *Anal. Chem.*, 2008, **80**, 9097–9104.
18 M. Huang, Z. Ouyang and R. G. Cooks, *Chem. Commun.*, 2009, 556–558.
19 Y. Y. Liu, Z. Q. Lin, S. Zhang, C. Yang and X. R. Zhang, *Anal. Bioanal. Chem.*, 2009, **395**, 591–599.
20 S. Lin, M. Huang, H. Chang and J. Shiea, *Anal. Chem.*, 2007, **79**, 8789–8795.
21 M. Huang, H. Hsu, C. Wu, S. Lin, Y. Ma, T. Cheng and J. Shiea, *Rapid Commun. Mass Spectrom.*, 2007, **21**, 1767–1775.
22 H. W. Chen, A. Venter and R. G. Cooks, *Chem. Commun.*, 2006, 2042–2044.
23 H. W. Gu, H. W. Chen, Z. Z. Pan, A. U. Jackson, N. Talaty, B. W. Xi, C. Kissinger, C. Duda, D. Mann, D. Raftery and R. G. Cooks, *Anal. Chem.*, 2007, **79**, 89–97.
24 H. W. Chen, A. Wortmann, W. H. Zhang and R. Zenobi, *Angew. Chem., Int. Ed.*, 2007, **46**, 580–583.
25 H. W. Chen, S. Yang, A. Wortmann and R. Zenobi, *Angew. Chem., Int. Ed.*, 2007, **46**, 7591–7594.
26 L. Zhu, G. Gamez, H. W. Chen, H. X. Huang, K. Chingin and R. Zenobi, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 2993–2998.
27 K. Chingin, H. Chen, G. Gamez, L. Zhu and R. Zenobi, *Anal. Chem.*, 2009, **81**, 123–129.
28 L. Zhu, G. Gamez, H. Chen, K. Chingin and R. Zenobi, *Chem Commun*, 2009, **559**.
29 W. S. Law, H. Chen, J. H. Ding, S. Yang, L. Zhu, G. Gamez, K. Chingin, Y. Ren and R. Zenobi, *Angew. Chem., Int. Ed.*, 2009, **48**, 8277–8280.
30 A. Bendini, L. Cerretani, A. Carrasco-Pancorbo, A. M. Gomez-Caravaca, A. Segura-Carretero, A. Fernandez-Gutierrez and G. Lercker, *Molecules*, 2007, **12**, 1679–1719.
31 N. IOOC International Olive Oil Council.COI/T.20/Document 15/ Rev.1 (Organoleptic Assessment of Olive Oil. Resolution RES-3/75-IV/96, 1996.
32 R. Aparicio and J. Harwood, *Handbook of Olive Oil Analysis and Properties*, 2000, Aspen Plublisher Inc., Gaithersburg, Maryland.
33 M. I. Covas, V. Ruiz-Gutierrez, R. Torre, A. Kafatos, R. M. Lamuela-Raventos, J. Osada, R. W. Owen and F. Visioli, *Nutr. Rev.*, 2006, **64**, S20–S30.
34 I. S. Arvanitoyannis and A. Vlachos, *Crit. Rev. Food Sci. Nutr.*, 2007, **47**, 441–498.
35 R. Capasso, *Phytochem. Anal.*, 1999, **10**, 299–306.
36 D. Ryan, D. R. Robards, P. Prenzler, D. Jardine, T. Herlt and M. Antolovich, *J. Chromatogr., A*, 1999, **855**, 529–537.
37 R. Japón-Luján and M. D. Luque De Castro, *J. Agric. Food Chem.*, 2008, **56**, 2505–2511.
38 A. Carrasco Pancorbo, C. Cruces-Blanco, A. S. Carretero and A. F. Gutierrez, *J. Agric. Food Chem.*, 2004, **52**, 6687–6693.
39 R. R. Catharino, R. Haddad, L. G. Cabrini, I. B. S. Cunha, A. Sawaya and M. N. Eberlin, *Anal. Chem.*, 2005, **77**, 7429–7433.
40 J. F. Cavalli, X. Fernandez, L. Lizzani-Cuvelier and A. M. Loiseau, *J. Agric. Food Chem.*, 2003, **51**, 7709–7716.
41 F. Pena, S. Cardenas, M. Gallego and M. Valcarcel, *J. Chromatogr., A*, 2004, **1052**, 137–143.
42 J. M. Snyder, E. N. Frankel and E. Selke, *J. Am. Oil Chem. Soc.*, 1985, **62**, 1675–1679.
43 J. L. Gómez-Ariza, A. Arias-Borrego and Garca-Barrera, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 1181–1186.
44 M. J. Lerma-García, G. Ramis-Ramos, J. M. Herrero-Martinez and E. F. Simo-Alfonso, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 973–978.
45 M. J. Lerma-García, J. M. Herrero-Martinez, G. Ramis-Ramos and E. F. Simo-Alfonso, *Food Chem.*, 2008, **107**, 1307–1313.
46 R. Goodacre, S. Vaidyanathan, G. Bianchi and D. B. Kell, *Analyst*, 2002, **127**, 1457–1462.
47 J. Danel and R. B. Cody, Detection of Lipid Using Direct Analysis in Real Time Mass Spectrometry. http://www.jeolusa.com/PRODUCTS/AnalyticalInstruments/MassSpectrometers/AccuTOFDART/tabid/230/Default.aspx.
48 J. F. García-Reyes, F. Mazzoti, J. D. Harper, N. A. Charipar, S. Oradu, Z. Ouyang, G. Sindona and R. G. Cooks, *Rapid Commun. Mass Spectrom.*, 2009, **23**, 3057–3062.
49 M. K. Koch, A. Vossnacke, J. Starflinger, W. Schutz and H. Unger, *J. Aerosol Sci.*, 2000, **31**, 1015–1028.
50 Y. M. Kuo and C. S. Wang, *J. Aerosol Sci.*, 1999, **30**, 1171–1179.
51 F. H. Joseph, C. B. William, J. B. Barry and E. A. Rolph, *Multivariate Data Analysis*, Prentice Hall, 2009, 7th Edition, 816.
52 R. M. Balabin, R. Z. Safieva and E. I. Lomakina, *Chemom. Intell. Lab. Syst.*, 2007, **88**, 183.
53 E. Aprea, F. Biasioli, G. Sani, C. Cantini, T. D. Mark and F. Gasperi, *J. Agric. Food Chem.*, 2006, **54**, 7635–7640.
54 R. Fall, T. Karl, A. Jordan and W. Lindinger, *Atmos. Environ.*, 2001, **35**, 3905–3916.
55 M. T. Morales, J. J. Rios and R. Aparicio, *J. Agric. Food Chem.*, 1997, **45**, 2666–2673.

