# Analytical Methods

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ARTICLE TYPE

# Coupling neutral desorption sampling to dielectric barrier discharge ionization mass spectrometry for direct oil analysis

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Rapid analysis of viscous oil samples is of great interest in food science and food industry. Herein, neutral desorption sampling in conjunction with dielectric barrier discharge ionization mass spectrometry (ND-DBDI-MS) has been established for fast and accurate identification of various hogwash oil (HHO) and edible oil samples at ambient conditions. The mass spectra in the negative ion detection mode were recorded in the mass range of *m/z* 50-500 Da, and characteristic substances responsible for the classification were identified using MS/MS experiments. Particularly, free fatty acids (e.g., oleic acid, linoleic acid, palmitic acid, etc.), typical representatives for oil quality, were successfully measured and used as decisive markers to differentiate HHO from qualified edible oil samples with help of principal component analysis (PCA). Methodological reproducibility was characterized in terms of statistical method such as cluster analysis (CA). The experimental results show that ND-DBDI-MS is an important tool for rapid analysis of highly complex viscous samples such as oil samples, providing potential applications in food safety analysis.

## Introduction

Due to the high viscosity and complex matrices, distinguishing HHO from normal edible oils for food safety supervision and monitoring in a fast yet reliable fashion remain challenging. As reported, after derivatization mainly by methylation, fatty acids as the indicator of purity have traditionally been used for oil differentiation with help of gas chromatography (GC) or GC/mass spectrometry (MS).[1-6] Liquid chromatography (LC)/MS has also been used for the analysis of edible oils. For example, 3-chloropropane-1,2-diol fatty acid esters (3-MCPDEs) and glycidyl fatty acid esters in edible oils have been measured by LC-MS,[7] liquid chromatography time-of-flight mass spectrometry (LC/TOF-MS)[8] and LC-MS/MS.[9] The fatty acids composition in three different vegetable oils (soybean oil, groundnut oil and coconut oil) was analyzed by high performance liquid chromatography (HPLC) after oil samples extraction.[10] Also, Raman spectroscopy was used for the quantitative analysis of adulteration of extra virgin olive oil improved by Bayesian framework least squares support vector machines.[11] The polar components in oils, including the fatty acids, after a simple extraction with methanol/water solution, were analyzed by direct infusion ESI-MS.[2] Besides, a method based on an ambient-ionization direct analysis in real-time (DART) coupled to a high-resolution TOF-MS[12] has been applied to the quick analysis of aqueous methanol extracts of oil samples, successfully distinguishing good and adulterated oil samples. However, sample preparation such as extraction and dilution procedures required by aforementioned methods are normally time-consuming and/or laborious, not to mention the high possibility of losing/destroying volatile and labile substances.

More recently, a novel method based on neutral desorption extractive electrospray ionization mass spectrometry (ND-EESI-MS)[13, 14] has been used for analysis of the viscous samples such as ionic liquid, edible oil,[15] honey, toothpaste,[16] cosmetics[17] and in-vivo analysis without sample preparation.[18] EESI tolerates extremely complex matrices and reduces ion suppression effects, providing long-term stability and sensitivity for the analysis of high viscous samples.[18-20] In addition, surface desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS) combined with back propagation neural networks has been established for edible oil analysis, but the mass spectra of oils recorded using DAPCI-MS showed less information in the negative ion detection mode.[21]

Dielectric-barrier discharge (DBD) normally generated in inert gases (such as Ar and He) produce non-equilibrium low temperature (close to room temperature)[22] plasma. In spite of the low temperature, LTP contains a magnitude of reactive species including high-energy electrons in the range of 1~20 eV[23] with higher density of $10^{14}$~$10^{15}$ $cm^{-3}$.[24, 25] This creates a mild microplasma environment with an ideal energy range for ionization of molecular species by electron-impact reactions[26] without suffering too severe heat effects, making DBDI a relatively soft ionization technique.[27-29] For example, DBDI-MS has been applied to the direct detection of the trace explosives (such as TNT, RDX and PETN) on solid surfaces.[30] DBDI or so-called LTP show a powerful desorption and ionization ability of trace compounds in complex matrices, such as melamine in

milk,[31] agricultural chemicals in food,[32] abused drugs[32] in biological matrices (saliva, urine or hair extract), free fatty acids, phenolics and volatiles in olive oil sample[33] as well as caffeine, urea and uracil in raw human urine sample.[34]

In previous studies, a versatile neutral desorption (ND) device was demonstrated to be useful for the release of analytes liberated from solid, fluid, human skin or greasy surface.[19, 20, 35] Highly viscous oil sample could be sampled for DBDI-MS analysis with nitrogen gas beam gently introduced into the sealable ND device. Various oil samples were evaluated by the ND-DBDI-MS in the negative ion mode. The volatile and nonvolatile fatty acids, representative for oil quality, in oil samples including rap oil, tea oil, HHO 1 and 2 were analyzed directly. The experiment combines the advantages of both ND and DBDI to realize a strong desorption and ionization of the highly viscous complex matrix of edible oil by separating the sampling process and the ionization process in both space and time. Principal component analysis (PCA) and cluster analysis (CA) were applied to probe the differentiation and reproducibility of the analytical method.

## Experimental section

### 2.1 Reagents and materials.

Oleic acid (A.R. grade) was purchased from Chinese Chemical Reagent Co., Ltd. (Shanghai, China). The two HHO samples were provided by the Industry and Commerce Bureau (Beijing, China). A total of 8 samples for 4 types of oil (including 3 rap oils, 3 tea oils, HHO 1 and HHO 2) were differentiated in this work. And all qualified edible oil samples were randomly selected from local supermarkets in Nanchang, China. All the qualified edible oil products were quality-guaranteed products with various expiration dates. Note that no clear color differences were observed among those oil samples and their pH values are generally similar, sitting in the range of 4.8 to 5.1. High-purity argon gas (Guoteng gas co., Ltd, Nanchang, China) and nitrogen (Guoteng gas co., Ltd, Nanchang, China) from a cylinder serve as the plasma supporting gas and ND carrier gas, respectively.

### 2.2 ND-DBDI-MS method analysis.

All experiments were carried out using a home-made DBDI source coupled to a commercial linear ion trap mass spectrometer (LTQ-XL, Finnigan, San Jose, CA) equipped with Xcalibur data processing system (as shown in Figure 1). A cylindrical DBD ionization source was made of a quartz tube (1.0 mm i.d., 2.0 mm o.d., 110 mm long), and two separated copper wires were connected to the outside of the ceramic tube as outer ring electrodes. The wall of the insulating ceramic tube serves as the dielectric barrier to improve the stability and homogeneity of the high-frequency discharge. The distance between the two electrodes was set to be 20 mm and that between the inlet of mass spectrometer and the adjacent electrode was set to be 15 mm. The DBD was ignited when the two ring electrodes of DBD were connected to a high-voltage alternating current (AC) power supply (neon power supply, Hongbao Electric Co., Wenzhou, China) at a suitable voltage (tunable 45~120 V, 43.1 kHz). The neon power supply was connected to a touch regulator (model: TDGC2-500VA, Xianglei Electric Co., Wuhan, China) for controlling the input voltage. The distance (a) between DBDI source and the ion entrance of the LTQ instrument was set at 1.5

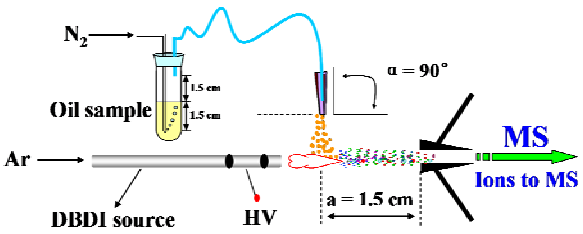


**Fig. 1** Schematic diagram of the ND-DBDI-MS for oil samples. Note that the diagram is not proportionally scaled and the distances (a) and the angle (α) were experimentally optimized to achieve better ionization efficiency.

cm, the angle (α) between the sample channel and the MS inlet at 90°, to minimize carry-over effects. The experiments indicated that stable plasma was created when the argon flow rate was controlled at around 500 ml $min^{-1}$. The input voltage (50 V) and argon (flow rate 500 mL/min) as working gas were used to generate plasma, and the analytes were ionized and then detected by MS. It should be mentioned here that the input voltage rather than the output voltage of the neon power supply was used for the optimization of the DBD ionization process due to the fact that it is practically difficult to obtain the exact value of the output voltage or current of the neon power supply, i.e., the voltage directly applied in the generation of the micro-plasma and for the ionization of the oils samples because of the fluctuation of the high-frequency discharge.

About 2 mL oil sample in a glass vial (4 mL, Aigilen Instrument Co., Ltd.) was impacted by a pure nitrogen gas beam (room temperature, velocity 300 m/s, flow 14.7 mL/s) ejected from an aperture (PEEK tube, ID 0.25 mm) for the desorption sampling. The distance of the ND gas emitter outlet under the oil sample surface was 1.5 cm, and the distance between the desorbed analytes inlet and the oil sample surface was also 1.5 cm. The desorbed analytes were sampled as a viscous flow (velocity 4.7 m/s, flow 14.7 mL/s) into the DBDI source using the sample transfer line (PTFE tube, ID 2 mm), and then analytes were heated by a high capillary temperature (i.e., 270 °C) from the MS instrument. In MS/MS experiments, parent ions were isolated with 1.0 mass/charge unit width, and collision-induced dissociation (CID) was performed with 18-24% arbitrary units of collision energy for 30 ms.

### 2.3 Processing of mass spectral data.

The raw mass spectra data obtained from ND-DBDI-MS fingerprints of the oil samples ranging from *m/z* 50 to 500 and recorded with an averaged time of 1 min. To evaluate reproducibility of our data, each type oil sample was sampled 15 times. For qualified edible oils, individual rap oil (or tea oil) sample was sampled 5 times, so a total of 15 times were obtained from 3 rap oil (or tea oil) samples. All data were background subtracted using the Xcalibur software of the LTQ-XL instrument and then exported to Microsoft Excel. After min-max normalization, the *m/z* values were used as independent variables and the signal intensities of the full scan mass fingerprint as dependent variables for the PCA analysis using MATLAB (version 7.0, Mathworks, USA). Hierarchical cluster analysis was also performed by MATLAB software using the same mass spectral data to output the rescaled distance of different samples by the internal euclidean distance algorithm.

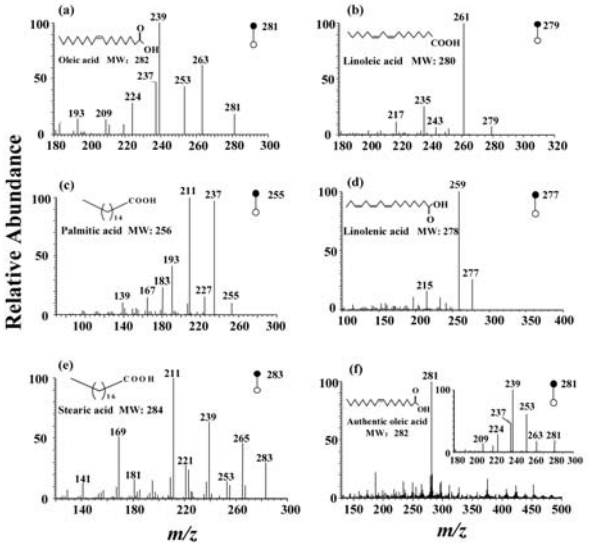


**Fig. 2** ND-DBDI-MS of the oil samples in the negative ion detection mode. (a) MS/MS spectrum of the oleic acid (*m/z* 281); (b) MS/MS spectrum of the linoleic acid (*m/z* 279); (c) MS/MS spectrum of the palmitic acid (*m/z* 255); (d) MS/MS spectrum of the linolenic acid (*m/z* 277); (e) MS/MS spectrum of the stearic acid (*m/z* 283). (f) ND-DBDI-MS spectra of authentic oleic acid. (Inset) MS/MS spectra of oleic acid signal.

## Results and disscussion

### 3.1 ND-DBDI-MS characterization of oil sample

The negative ion detection mode was employed in view of major acidic substances in oil, readily generating deprotonated molecular ion peaks $[M-H]^-$. Due to their high impact for oil quality evaluation, free fatty acids are taken as the main focus of current study. Note that some free fatty acids such as oleic, linoleic and palmitic acids in edible oil were previously observed in the MS/MS spectrum using ESI,[2] LTP,[33] DESI[36] ion sources. A slightly different fragment pattern of deprotonated molecular ion peaks were created under different experimental conditions (e.g., high voltage, collision energy). As shown in Figure 2, the structure identification of the main fatty acids was exhibited according to the ND-DBDI-MS/MS experiments. For instance, the precursor ions *m/z* 281 generated major product ions of *m/z* 239, 253, 263, 237 and 224 by subsequent loss of $CH_3CH{=}CH_2$, $CH_2{=}CH_2$, $H_2O$, $CO_2$ and $C_4H_9$ respectively with 20% CE (Figure 2a). These observations were in a good agreement with the characteristic fragment ion peaks of authentic oleic acid sample (Figure 2f). Furthermore, the other diagnostic anions common for the four oils are those of *m/z* 279, 255, 277 and 283, tentatively identified as deprotonated linoleic acid, palmitic acid and stearic acid, respectively (Figure 2b~e).

The characteristic fragmentation pattern provides the fundamental chemistry evidence for the specific detection of fatty acids in oil sample. Therefore, ND-DBDI-MS is a powerful and reliable method for the analysis of highly complex and viscous matrices such as oil samples. More importantly, to ensure more stable signals and excellent repeatability for differentiation, crucial parameters including DBDI source input voltage, heated capillary temperature of LTQ instrument and desorption gas $N_2$ flow rate; **α** (the angle between ND sampling outlet and MS inlet) and **a** (the distance between ND sampling outlet and MS inlet)

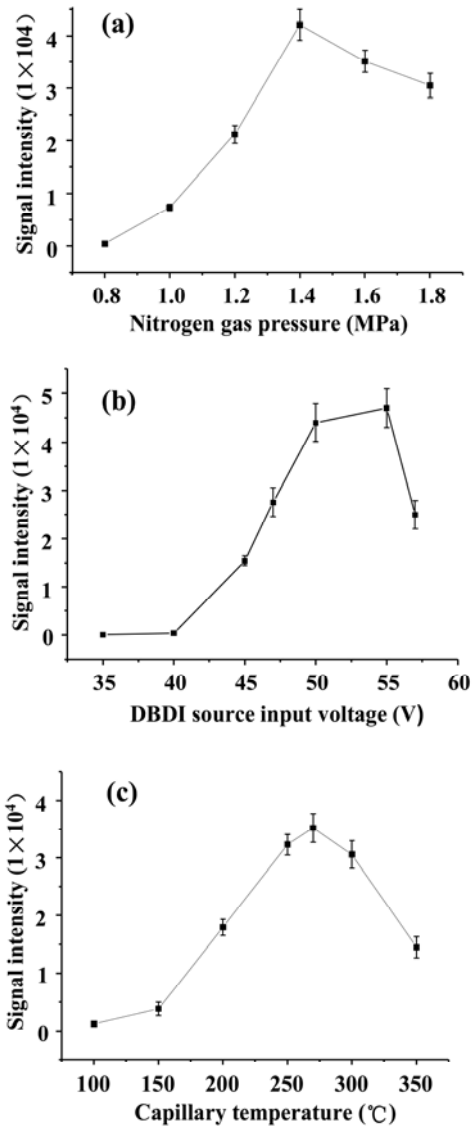


**Fig. 3** Optimization of ND-DBDI-MS working parameters for the oil samples. (a) effects of DBDI input voltage on signal intensity (*m/z* 281); (b) effects of nitrogen pressure on signal intensity; (c) effects of the temperature of the heated capillary on signal intensity.

were adjusted for signal optimization.

### 3.2 Optimization of the ND-DBDI-MS source

The ND-DBDI-MS working parameters were further optimized by following the *m/z* 281 intensity of rap oil sample. As shown in Figure 3, the nitrogen gas flow rate, DBDI source input voltage and the heated capillary temperature were investigated systematically. In practice, each data point of the voltage was measured 6 times, and the standard deviations (SD) were used to represent the measurement uncertainties.

The nitrogen gas pressure is the key factor for ND sampling. As shown in Figure 3a, the strongest signal was obtained at 1.4 MPa. This observation is rationalized that $N_2$ gas with a lower pressure tended to desorb inadequate amounts of analytes for detection, while too high pressure would strongly decrease the residence time of analytes intercepting the DBDI reactive zone. Most stable signal intensity were given when DBDI source input

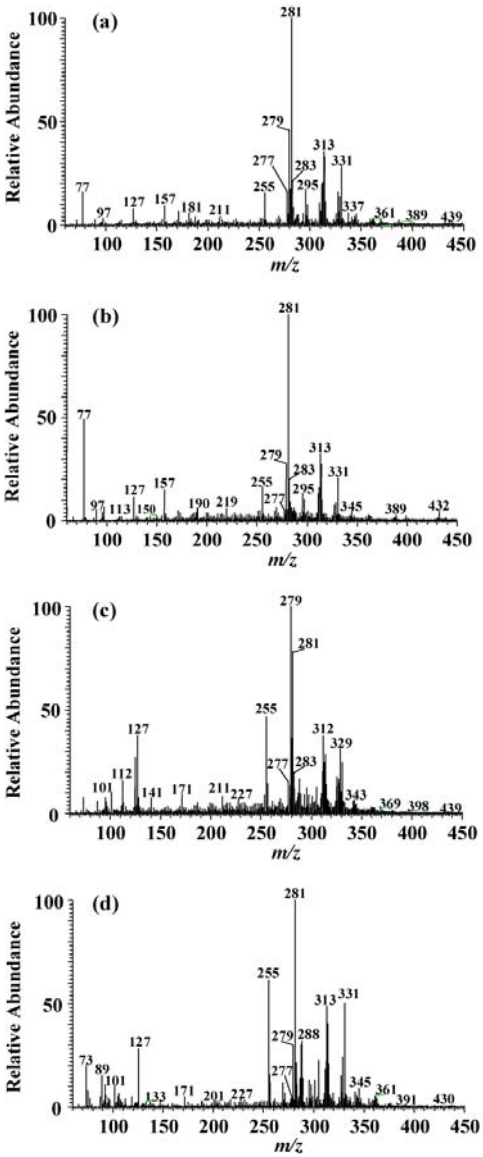


**Fig. 4** ND-DBDI-MS mass spectra of edible oil and HHO in the negative ion detection mode. (a) Rap oil; (b) Tea oil; (c) HHO 1; (d) HHO 2.

voltage was set at 50~55 V (Figure 3b). A reduction of signal intensity and external discharge were observed when the voltage was set above 55 V, possibly due to stronger fragmentation induced by the high energy input to the plasma. In addition, the temperature of heated capillary also possesses a great impact on the detection for oil samples (Figure 3c). The results showed that the signal peaked at ~270 °C. Excessive temperature could cause the decomposition of oil samples as the temperature being set higher than 270 °C in our case.

In short, a highly stable signal of *m/z* 281 was established when $N_2$ flow was regulated to 1.4MPa, DBDI source input voltage optimized to 50 V, and capillary temperature at 270 °C. Besides, **α** was set to 90° and distance **a** was optimized to 1.5 cm. Other working conditions were optimized automatically by the LTQ instrument, the following measurements were performed under the optimized parameters.

### 3.3 Representative mass spectra

Under the optimized working conditions, the spectra of four

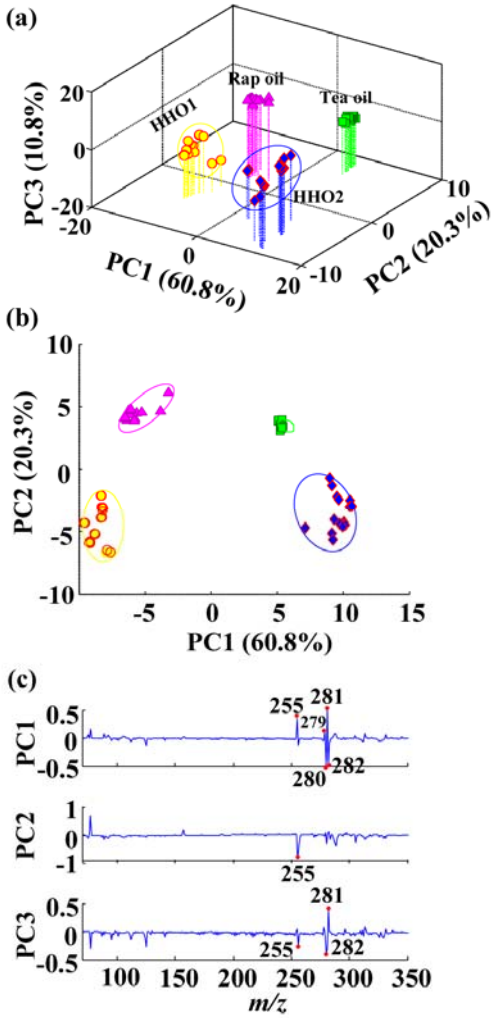


**Fig. 5** PCA results of four types of oil samples including rap oil, tea oil, HHO 1 and 2 in the negative ion detection mode using ND-DBDI-MS mass spectral fingerprints. (a) 3-D PCA score plots achieved using the MS data recorded in the range of *m/z* 50-500; (b) Score plots of PC1-PC2 results; (c) PCA loading results for the first three PCs using the MS data recorded in the range of *m/z* 70-350 (there are no differential signals in *m/z* 350-500). Note that the circles shown serve to guide the readers' eye.

types of oil samples (*i.e.*, rap oil, tea oil, HHO 1 and HHO 2) were directly recorded by ND-DBDI-MS under the negative ion detection mode. And the average signal-to-noise ratio (S/N) of the present work has been calculated to be 24 by sampling all types of oils, showing a reliable signal evaluation. The mass spectra recorded in the mass range of *m/z* 50-500 Da (background subtracted) showed a magnitude of peaks, as plotted in Figure 4. The mass spectral of each oil samples are considerably different in terms of peak density and signal intensity. Abundant peaks in the mass range over *m/z* 400 were not detected, possibly because those large molecules can not be efficiently desorbed from oil samples due to their low vapor pressure or possible affinity to the very complicated matrix. Therefore, the compounds detected in the mass range from 70 to 400 are taken as characteristic mass spectral fingerprints of the oil products. For instance, the well-known fatty acids such as oleic (*m/z* 281), linolenic (*m/z* 277), linoleic (*m/z* 279) and palmitic acid (*m/z* 255) observed in all oil

**Table 1**. The percentage of relative intensity (RI) and relative standard deviations (RSDs) based on five main characteristic substances of oil samples in the negative ion detection mode.

| Samples | Oleic Acid (*m/z* 281) | | Linolenic Acid (*m/z* 277) | | Linoleic Acid (*m/z* 279) | | Palmitic Acid (*m/z* 255) | | Stearic Acid (*m/z* 283) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | RI (%) | RSD (%) n=9 | RI (%) | RSD (%) n=9 | RI (%) | RSD (%) n=9 | RI (%) | RSD (%) n=9 | RI (%) | RSD (%) n=9 |
| **Rap Oil** | 100 | - | 15.4 | 6.0 | 41.3 | 6.1 | 15.2 | 12.5 | 14 | 10.3 |
| **Tea Oil** | 100 | - | 5 | 5.8 | 28.8 | 7.5 | 16.4 | 8.3 | 9.7 | 8.4 |
| **HHO 1** | 50.5 | 11.1 | 15.6 | 11.2 | 100.0 | - | 36.8 | 10.5 | 33 | 11.8 |
| **HHO 2** | 95.1 | 1.9 | 5.6 | 11.1 | 33.7 | 5.9 | 60.4 | 11.2 | 19 | 5.0 |

samples are almost similar to the reported data.[2, 37]

The signal peaks at *m/z* 255, 277, 279, 281, 283, 313, etc. were observed in both edible oil and waste oil samples, probably because of some very similar chemical compositions contained in the 4 types of samples. For instance, oleic acid, which is one of the monounsaturated fatty acids (MUFA), reached the highest abundance in the tea oil and rap oil with 100% relative intensity, while in the HHO the dietary MUFA promotes a healthy blood lipid, mediates blood pressure, and favorably modulates insulin sensitivity and glycemic control.[38] Particularly, palmitic acid (*m/z* 255) and stearic acid (*m/z* 283) are saturated fatty acids (SFA) with higher levels generally present in animal fat. Table 1 showed that relative intensities of the two kinds of main SFA (palmitic acid and stearic acid) in HHO are much higher than the ones in edible oil, probably due to the different manufacture processes or different sources of raw materials (e.g., derived from some waste animal fats, etc.). There are studies which have proven the intimate relationship between saturated fatty acids, serum cholesterol and coronary heart disease (CHD), that the high content of saturated fatty acids may therefore be a risk factor for coronary heart disease (CHD).[39-41] Consequently, less MUFA and high SFA content in the HHO sample may lead to a disturbance to human health due to its poor quality.

### 3.4 Differentiation of oil samples

In contrast, the source of raw materials and oil processing procedures pose large differences among the complex HHO varieties, while various types of edible oils could possess fingerprinting chemical compositions in case of different origins. As shown above, the mass spectral fingerprints of samples tested were reasonably different. At present, mass spectrometry combined with chemometric methods have been successfully applied for the identification and distinction of complex samples.[15, 42] PCA,[43] a popular multiple variance statistical tool, was thus used to better visualize the differences between the MS data of oils in our study. Meanwhile, statistical method CA[44] was further used for reproducibility evaluation.

As shown in Figure 5, differential PCA score and loading plots were obtained from representative 60 data points from 4 types of oil samples (8 individual samples), which was used to validate the feasibility of for rapid differentiation of oil samples by ND-DBDI-MS. As the result, those four types of edible oil and HHO samples were successfully separated into four clusters visualized by the PCA score plots (Figure 5a). The percentages of variances explained by PC1, PC2, and PC3 were 60.8%, 20.3%, and 10.8%, respectively. And these PCs represented ~92% of the total variances. The overlap of the 15 data points each type sample restricted in a narrow scope indicated good reproducibility of the analysis. In the PC1-PC2 scoring graph (Figure 5b), the edible oil samples and HHO samples were clearly differentiated on the axis of PC2, in which palmitic acid (*m/z* 255) acts as the main contributor. Hence, the graph exhibits that HHO may contain high content saturated fatty acids which may attribute to its poor quality.

In Figure 5c, the PCA loading plots of the 4 types of oils showed the outstanding differential peaks such as *m/z* 281, 255, 279, 282, 280, etc., which mainly contributed to the distinction of the samples. Those peaks of significant abundances in the PCA loading plots are potentially molecular markers for quality evaluation of oil products. Indeed, the distribution of the characteristic ions indicates that separation of samples using three PCs is mainly based on the considerably different signal intensity of major fatty acids probably due to the source of raw materials and oil processing procedures, resulting in the different MS fingerprinting data visualized by PCA, which are conventionally regarded as a fingerprint linked to the oil purity. Theoretically, all major peaks, contributing heavily to the differentiation of various oil samples, could be authenticated by tandem mass spectrometry. However, structural identification of all of those peaks will far exceed the scope of this study. In brief, the content of the primary free fatty acids such as oleic, linoleic, and palmitic acid has been demonstrated to be a major quality determining factor.

In the final phase, cluster analysis (CA), one of the statistical methods, is a pattern recognition technique used to form object groups having variables of similar values. The main advantage of CA over visualization techniques such as PCA is that it provides numerical values of the similarity between objects.[45] In this work, hierarchical cluster analysis was carried out based on the fingerprints from *m/z* 50 to 500 in order to evaluate the number of subsets of similar samples. As it can be seen in Figure 6, cluster 1-3 and cluster 7 correspond to rap oils and HHO 1, independently of cluster 4-6 and cluster 8 which correspond to tea oils and HHO 2. We supposed that the HHO samples might be deep processed and/or adulterated with edible oil. And the reason why HHO samples were not located in the similar cluster might be different sources of raw materials and processing procedure. The measurement consistency were verified by relative standard deviation (RSD) of oleic acid in rap oil, tea oil, HHO 1 and 2 at 8.6%, 6.4% 10.1%, 12.2% (n=9), respectively. Therefore, ND-

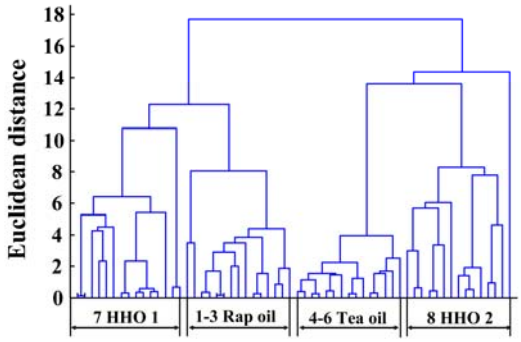


**Fig. 6** Cluster analysis results of raw data recorded by using ND-DBDI-MS from 8 oil products.

DBDI-MS method coupled with chemometric and statistical methods can be applied for quick differentiation of oil samples with better detection stability and confidence.

## Conclusions

Herein, a powerful and reliable ND-DBDI-MS is proposed as the alternative method to be used for the analysis of complex and viscous matrices such as oil sample. The qualified edible oil and HHO samples were rapidly differentiated by PCA without any sample pretreatment and no other chemicals for extraction in the whole testing process. Simultaneously, the statistical repeatability of the method also has been confirmed by CA. As demonstrated, the content of the primary nonvolatile fatty acids such as oleic, linoleic, palmitic acid, etc. is a major quality criterion. Furthermore, the relative intensity of two saturated fatty acids (i.e. palmitic acid and stearic acid) observed in HHO were much higher than edible oil therefore may be a risk for disease caused by higher cholesterol. The experimental data shows that ND-DBDI-MS has been proved to be a rapid tool for determination and identification of HHO with high sensitivity and strong desorption ability. Particularly, neutral desorption is a soft sampling method exceptionally suitable for the in vivo analysis even remote analysis of biological samples from complex surfaces (e.g., food, plants, skin), possibly providing some extended applications of low-temperature plasma in multiple disciplines such as biology, the life sciences and food quality monitoring field.

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## Notes and references

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1 C. Ruiz-Samblás, L. Cuadros-Rodríguez, A. González-Casado and F. P. Rodríguez-García, *Anal. Methods*, 2012, **4**, 753-758.
2 R. R. Catharino, R. Haddad, L. G. Cabrini, I. B. Cunha, A. C. Sawaya and M. N. Eberlin, *Anal. Chem.*, 2005, **77**, 7429-7433.
3 J. O. Lay, R. Liyanage, B. Durham and J. Brooks, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 952-958.
4 M. Monfreda, L. Gobbi and A. Grippa, *Food Chem.*, 2012, **134**, 2283-2290.
5 E. D. Dodds, M. R. McCoy, L. D. Rea and J. M. Kennish, *Lipids*, 2005, **40**, 419-428.
6 S. Thurnhofer and W. Vetter, *J. Agric. Food Chem.*, 2005, **53**, 8896-8903.
7 M. R. Blumhorst, M. W. Collison, R. Cantrill, H. Shiro, Y. Masukawa, S. Kawai and K. Yasunaga, *J. Am. Oil Chem. Soc.*, 2013, 1-8.
8 K. Hori, N. Koriyama, H. Omori, M. Kuriyama, T. Arishima and K. Tsumura, *LWT-Food Sci. Technol.*, 2012, **48**, 204-208.
9 K. Yamazaki, M. Ogiso, S. Isagawa, T. Urushiyama, T. Ukena and N. Kibune, *Food Addi. Contam. A*, 2013, **30**, 52-68.
10 A. Sodamade and O. Bolaji, *Chem. Materials Res.*, 2013, **3**, 26-29.
11 W. Dong, Y. Q. Zhang, B. Zhang and X. P. Wang, *Anal. Methods*, 2012, **4**, 2772-2777.
12 L. Vaclavik, T. Cajka, V. Hrbek and J. Hajslova, *Anal. chim. acta*, 2009, **645**, 56-63.
13 W. S. Law, H. W. Chen, J. H. Ding, S. P. Yang, L. Zhu, G. Gamez, K. Chingin, Y. L. Ren and R. Zenobi, *Angew. Chem.-Int. Ed.*, 2009, **48**, 8277-8280.
14 X. Li, B. Hu, J. H. Ding and H. W. Chen, *Nat. protoc.*, 2011, **6**, 1010-1025.
15 W. S. Law, H. W. Chen, R. Balabin, C. Berchtold, L. Meier and R. Zenobi, *Analyst*, 2010, **135**, 773-778.
16 J. H. Ding, H. W. Gu, S. P. Yang, M. Li, J. Q. Li and H. W. Chen, *Anal. chem.*, 2009, **81**, 8632-8638.
17 X. L. Zhang, Y. Liu, J. H. Zhang, Z. Hu, B. Hu, L. Y. Ding, L. Jia and H. W. Chen, *Talanta*, 2011, **85**, 1665-1671.
18 H. W. Chen, B. Hu and X. Zhang, *Chin. J. Anal. Chem.*, 2010, **38**, 1069-1088.
19 H. W. Chen and R. Zenobi, *Nat. protoc.*, 2008, **3**, 1467-1475.
20 X. Li, B. Hu, J. H. Ding and H. W. Chen, *Nat. protoc.*, 2011, **6**, 1010-1025.
21 Z. Q. Zhou, T. T. Zhang, B. Jia, Y. Z. Ouyang, X. W. Fang and H. W. Chen, *Chin. J. Anal. Chem.*, 2011, **39**, 1665-1669.
22 X. Lu, Q. Xiong, Z. Tang, Z. Jiang and Y. Pan, *Ieee T. Plasma Sci.*, 2008, **36**, 990-991.
23 X. J. Xu, *Thin Solid Films*, 2001, **390**, 237-242.
24 F. Fanelli, *Plasma Process. Polym.*, 2009, **6**, 547-554.
25 C. Sarra-Bournet, G. Ayotte, S. Turgeon, F. Massines and G. Laroche, *Langmuir*, 2009, **25**, 9432-9440.
26 H. L. Chen, H. M. Lee and M. B. Chang, *Plasma Process. Polym.*, 2006, **3**, 682-691.
27 S. Olenici-Craciunescu, A. Michels, C. Meyer, R. Heming, S. Tombrink, W. Vautz and J. Franzke, *Spectrochim. Acta B*, 2009, **64**, 1253-1258.
28 A. Michels, S. Tombrink, W. Vautz, M. Miclea and J. Franzke, *Spectrochim. Acta B*, 2007, **62**, 1208-1215.
29 H. Hayen, A. Michels and J. Franzke, *Anal. chem.*, 2009, **81**, 10239-10245.
30 N. Na, C. Zhang, M. Zhao, S. Zhang, C. Yang, X. Fang and X. Zhang, *J. Mass Spectrom.*, 2007, **42**, 1079-1085.
31 G. Huang, W. Xu, M. A. Visbal-Onufrak, Z. Ouyang and R. G. Cooks, *Analyst*, 2010, **135**, 705-711.
32 J. S. Wiley, J. F. Garcia-Reyes, J. D. Harper, N. A. Charipar, Z. Ouyang and R. G. Cooks, *Analyst*, 2010, **135**, 971-979.
33 J. F. Garcia-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.
34 J. D. Harper, N. A. Charipar, C. C. Mulligan, X. Zhang, R. G. Cooks and Z. Ouyang, *Anal. chem.*, 2008, **80**, 9097-9104.
35 H. W. Chen, B. Hu, Y. Hu, Y. F. Huan, Z. Q. Zhou and X. L. Qiao, *J. Am. Soc. Mass Spectrom.* , 2009, **20**, 719-722.
36 M. Li, H. Chen, X. Yang, J. M. Chen and C. L. Li, *Atmos. Environ.* , 2009, **43**, 2717-2720.
37 B. Brügger, G. Erben, R. Sandhoff, F. T. Wieland and W. D. Lehmann,

*P. Natl. Acad. Sci.*, 1997, **94**, 2339-2344.
38 L. G. Gillingham, S. Harris-Janz and P. J. H. Jones, *Lipids*, 2011, **46**, 209-228.
39 M. R. Flock, M. H. Green and P. M. Kris-Etherton, *Adv. Nutr.* , 2011, **2**, 261-274.
40 P. W. Parodi, *Int. Dairy J.* , 2009, **19**, 345-361.
41 D. J. Pehowich, A. V. Gomes and J. A. Barnes, *W. Indian Med. J.*, 2000, **49**, 128-133.
42 H. W. Chen, H. Z. Liang, J. H. Ding, J. H. Lai, Y. F. Huan and X. L. Qiao, *J. Agric. Food Chem.* , 2007, **55**, 10093-10100.
43 H. Abdi and L. J. Williams, *Wiley Interdisciplinary Reviews: Computation. Stat.*, 2010, **2**, 433-459.
44 A. Scott and M. Knott, *Biometrics*, 1974, 507-512.
45 F. Guimet, R. Boqué and J. Ferré, *J. Agric. Food Chem.*, 2004, **52**, 6673-6679.