Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry Typings of Edible Oils through Spectral Networking of Triacylglycerol Fingerprints

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Supporting Information

ABSTRACT: Adulteration of edible oils by the manufacturers has been found frequently in modern societies. Due to the complexity of the chemical contents in edible oils, it is challenging to quantitatively determine the extent of adulteration and prove the authenticity of edible oils. In this study, a robust and simple MALDI-TOF-MS platform for rapid fingerprinting of triacylglycerols (TAGs) in edible oils was developed, where spectral similarity analysis was performed to quantitatively reveal correlations among edible oils in the chemical level. Specifically, we proposed oil networking, a spectral similarity-based illustration, which enabled reliable classifications of tens of commercial edible oils from vegetable and animal origins. The strategy was superior to traditional multivariate statistics due to its high sensitivity in probing subtle changes in TAG profiles, as further demonstrated by the success in determination of the adulterated lard in a food fraud in Taiwan. Finally, we showed that the platform allowed quantitative assessment of the binary mixture of olive oil and canola oil, which is a common type of olive oil adulteration in the market. Overall, these results suggested a novel strategy for chemical fingerprint-based quality control and authentication of oils in the food industry.

INTRODUCTION

Since the introduction of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), it has been profoundly applied to the analysis of different kinds of biomolecules, including proteins, peptides, metabolites, carbohydrates, and lipids. MALDI produces mostly singly charged ions with only minimal fragmentations, giving relatively simple spectra at m/z > 500. Therefore, the detection of intact biomolecules and the subsequent spectral interpretation of complicated chemical mixtures become feasible using MALDI-TOF-MS.

Food characterization is one of the prominent applications of MALDI-TOF-MS. For example, whey proteins have been proposed as biomarkers for identifying bovine and ewe milk adulteration of water buffalo mozzarella cheese, and peptides can serve as biomarkers to determine meat authenticity. In these cases, only one or very few ion peaks were used as the markers for the assessments of food contents. However, for the adulteration by combining two or more chemically similar mixtures, a single biomarker may not be sufficient as many ion species are likely present. In this context, MS spectral profiles, for example, a set of peaks, are thus used to represent as the markers of specific substances. Data processing by multivariate analysis on MS spectral profiles helps us capture important spectral features as it simplifies the complexity in high-dimensional MS profiles while retaining significant patterns. Principle component analysis (PCA), the most common approach for the preliminary classification of sample groups, can simplify the complexity in high-dimensional MS profiles while retaining significant patterns. However, when the number of sample groups becomes large, PCA could only offer obscure discrimination, often leading to ambiguous and inconclusive classifications. Supervised models, for example, partial least-squares discriminant analysis (PLS-DA), enable multiclassification for complex datasets, whereas the classification results are highly dependent on parameter optimization.

Compared to qualitative statistics, spectral similarity analysis allows the quantitative assessment of resemblance among multiple spectra. In particular, cosine similarity analysis, one of the simplest mathematical operations, provides a strategy to measure mass spectral similarity in the form of a cosine value (cos θ). In general, the cos θ value is the normalized dot product between a reference spectrum and a target spectrum, in which the MS spectra are viewed as multidimensional vectors. In the past years, cosine similarity analysis has been widely used as a scoring system when searching tandem mass (MS/MS) spectra against databases in
metabolomics and proteomics evaluating MS spectral reproducibility, and assessing oil quality.

Edible oils are a mixture of lipids of plant, animal, or marine origin. Each type of edible oil has its characteristic fatty acid (FA) composition, while the majority of FAs exist in the form of triacylglycerols (TAGs) that contribute to 95% weight of edible oils. Edible oils provide essential nutrients in daily life. However, the quality control of edible oils is not fully secured in the food industry, causing numerous oil fraud events worldwide. One of the common issues is oil adulteration, in which expensive edible oils are mixed with cheap ones. The gutter oil event involves the use of recycled cooking oils, which can cause potential health problems. Driven by the emergence in determining the authenticity of edible oils, many analytical approaches have been thus proposed in recent years. However, many of the targeted detections of biomarkers or toxins showed less effectiveness to solve modern edible oil frauds because of unpredicted alterations of chemical compositions in abnormal oils. As a result, developing techniques that allow the investigation of chemical fingerprints has become popular and promising. In particular, MALDI-MS plays a critical role in chemical profiling of edible oils as it provides ease in sample preparation, high-throughput analysis without chromatographic separation, high sensitivity, and broad coverage of molecules, such as phospholipids and TAGs.

To date, interpreting chemical fingerprints of edible oils obtained by MALDI-TOF-MS has been demonstrated with multivariate statistics, including hierarchical clustering, PCA, and PLS-DA. In this regard, qualitative differentiations of edible oils were made possible by the visually interpretable plots, but the conclusions inferred by these approaches were largely based on subjective examinations. As a result, an approach allowing quantitative assessments to determine the significant discrimination on samples is still necessary and thus appropriate for developing a precise quality control (QC) system.

In the present study, we demonstrated an approach combining MALDI-TOF-MS and cosine similarity analysis of TAG fingerprints, which allows a rapid and quantitative comparison of edible oils (Figure 1). In addition, we introduced “oil networking”, a visual illustration of TAG similarities, to facilitate classifications of edible oils. The platform was comprehensively demonstrated by a dataset of edible oils from various vegetables and animals and further utilized for the detection of the adulterated oils. Details of the sample preparation, instrumental settings, mathematical processing, and data interpretation are elaborated in the following sections.

Results and Discussion

Rapid Profiling of TAG Fingerprints in Edible Oils with MALDI-MS. The workflow for MALDI-TOF-MS-based approach to investigate TAG fingerprinting of edible oils was demonstrated as shown in Figure 1. Briefly, edible oils were dissolved in chloroform, mixed with 2,5-dihydroxybenzoic acid (DHB) matrix solution, and deposited onto the stainless steel target plate for subsequent MALDI-TOF-MS analysis. Details of sample preparation are elaborated in Experimental Section and Supporting Information. To evaluate the efficacy of the method, we tested a QC sample consisting of palm oil and soybean oil (v/v = 3/5), which contains the main TAG species commonly found in most edible oils. Figure 2A shows the MALDI-TOF-MS spectrum of the QC sample, where multiple TAG species were observed in the form of [M + Na]+ ions with a good signal-to-noise ratio (S/N). Specifically, these TAGs were resolved as three major groups of the total carbon number of S0 (m/z 850–870), S2 (m/z 870–890), or S4 (m/z 890–910) and pairwise spectral similarities were evaluated based on the cosine similarity.
890−920), and the degree of saturation (i.e., the number of carbon−carbon double bonds) varied as indicated by the m/z shift of 2 in each group. These results were consistent with the literature, in which TAGs of edible oils are readily detected using MALDI-TOF MS. The TAG species, including the carbon chain lengths and the number of double bonds, are putatively identified and summarized in Table S1.

Fingerprint-Based Quality Control. To realize the instrumental stability in obtaining oil TAG fingerprints using our MALDI-TOF-MS method, we tested 15 technical replicates of QC samples in three consecutive days. As a result, the MALDI-TOF-MS spectra of 15 QC samples were obtained, showing highly similar TAG fingerprints (Figure S2). Herein, we applied cosine similarity analysis to quantitatively realize technical variations among these spectra. The 15 TAG fingerprints were normalized by total ion intensities and averaged to serve as the consensus spectrum. Subsequently, pairwise cosine similarity analyses were performed between the consensus spectrum and each of the 15 replicates (Table S2). Such a process allowed us to construct the Shewhart QC chart (Figure 2B), which showed the variations of spectral similarities, denoted as cos θ values, in the 15 technical replicates. We also obtained the mean similarity (μ) and its standard deviation (σ) as 0.99716 and 0.00149, respectively. In fact, the defined similarity of zero (cos θ = 0) indicates that the two fingerprints are absolutely different, whereas two identical fingerprints yield a similarity of unity (cos θ = 1). In this regard, we concluded that our MALDI-TOF-MS platform enabled the routine acquisition of oil TAG fingerprints with great reproducibility. Furthermore, we defined the resolving power of our platform to differentiate two nonidentical TAG fingerprints as cos θ = 0.99269 (μ−3σ, the red dashed line in Figure 2B); that is, for two TAG fingerprints of the similarity lower than 0.9927, they were significantly considered non-identical in this study.

Oil Networking of Various Edible Oils. The proposed platform combining MALDI-TOF-MS and cosine similarity analysis could be implemented to study real oil samples. As a pilot study, we collected 16 common species of edible oils from the local market, including 15 vegetable oils and 1 animal oil, and their TAG fingerprints were thoroughly investigated (Figure S3). Subsequently, cosine similarity analyses were performed on each pair of TAG fingerprints (Table S3). Herein, we demonstrated oil networking as a visual strategy to systematically categorize edible oils based on their TAG similarities. Such MS spectral networking has been profoundly used for investigating similarities of tandem mass spectral (MS/MS) fragments in metabolomics studies and was used for the analysis of chemical fingerprints acquired in the full MS level in this study. Figure 3 shows the resulting oil network where 16 edible oil samples, denoted as nodes, were connected if the paired TAG similarities were higher than 0.80. The oil network reflected the relationship of the TAG profiles of each oil. First, we showed that four oils, including hazelnut oil, camellia oil, canola oil, and olive oil, were clustered based on a dominant C54:3 TAG (m/z 907.8) in their MALDI-TOF-MS spectra. Importantly, hazelnut oil, camellia oil, and canola oil are frequent targets for the identification of adulterated olive oils because they have similar FA profiles and physicochemical properties. The respective TAG species herein were in agreement with those obtained by ambient ionization sources, such as desorption electrospray ionization (DESI) and direct analysis in real time (DART), where TAGs were present in the form of [M + NH4]+ ions.

In the central part of the network, there were 10 other edible oils clustered separately. This stark contrast was not surprising as they were mostly made up of the same TAG species, such as

Figure 3. Oil network of the standard edible oils. The edible oils, denoted by nodes, were connected by edges if the pairwise TAG similarities were higher than 0.80. The color and thickness of edges were adjusted according to the cosine similarity. The complete pairwise TAG similarities are available in Table S3.
unsaturated C54 TAGs and some minor C52 TAGs, instead of C54:3 TAG. We further pointed out that black sesame oil and sesame oil shared the most similar TAG fingerprints ($\cos \theta = 0.9932$) in the current oil network. In fact, black sesame oil and sesame oil are both produced from sesame seeds, whereas a roasting step is applied in processing the former. Additionally, a previous report showed that there was no obvious difference in the FA compositions in TAGs of sesame oils prepared from unroasted and roasted seeds, and this could also be true in the TAG fingerprint. Interestingly, palm oil formed an isolated node due to its distinct TAG fingerprint consisting of abundant C50:1 TAG (m/z 855.7) and C52:2 TAG (m/z 881.7). Lard possessed predominant C52:2 TAG and C52:1 TAG (m/z 883.7) in its MALDI-TOF-MS spectrum, making it also segregated from the others. These results showed the effectiveness of our cosine similarity networking-based strategy as the PCA and hierarchical clustering analysis to the present dataset also showed similar cluster profiles (Figure S4).

**Classification of Edible Oils with Oil Networking.** The obtained TAG fingerprints then serve as the standard dataset for classifications to the new oil samples. In this study, we tested additional 21 edible oil samples from 6 plant sources present in the prebuilt dataset. The resulting MALDI-TOF-MS spectra are provided in Figures S5–S10. For ease of discussion, the newly tested samples were marked with capital letters in the end of labels, such as soybean A (Figure S6) and canola B (Figure S8). First, PCA and hierarchical clustering were preliminarily applied to the combined TAG fingerprints, giving the TAG similarities in the oils of the same species (Figure S11). To quantify the TAG similarities, we subsequently applied cosine similarity analysis to the combined dataset of 37 edible oils. The pairwise TAG similarities are shown in Table S4, and the similarity correlations are visualized as an oil network in Figure 4, where oils of TAG similarities higher than 0.95 were connected. Remarkably, in the oil network, most of the edible oils from the same species were closely clustered. For example, canola oil, olive oil, camellia oil, and hazelnut oil were all mainly made of C52:2/C54:3 mixtures, and their corresponding nodes were thus clustered. In-depth inspection of the pairwise TAG similarities revealed that 19 of the 21 newly tested samples, except for grapeseed A and olive E, showed the highest TAG similarities to their same-origin oils in the prebuilt dataset (Table S4). Although the TAG fingerprint of grapeseed A had a high similarity to that of the standard grapeseed oil ($\cos \theta = 0.984$), it was more similar to those of the soybean oils, as inferred by the network. In this case, it might be the consequence that soybean oil and grapeseed oil had similar FA chain compositions in TAGs, in which C18:2 FA was the most dominant species followed by C18:1 FA and C16:0 FA. For olive E, interestingly, it had a distinct TAG fingerprint (Figure S9). As a result, it had a relative low TAG similarity compared to other oils and thus presented as an independent node in the network. In fact, among all the olive oil samples, olive E was the only one produced through the refining process, which probably altered its TAG composition. Collectively, we demonstrated the capability of spectral networking to effectively classify edible oils based on spectral similarities in their TAG fingerprints.

**Applying Oil Networking for Gutter Oil Differentiation.** In 2014, a gutter oil scandal occurred in Taiwan, in which the lard was adulterated with the recycled cooking oil. In this fraud, however, the official examinations of edible oils by the Taiwan Food and Drug Administration (TFDA), including the detection of toxic contaminants and heavy metal substances, had failed to capture the adulterated lards in advance. With the lack of an officially effective strategy to solve the problem, we thus hypothesized that TAG fingerprints could be used as markers to differentiate the adulterated lard from the natural one. In this regard, we further incorporated six adulterated lard oil samples (TFDA A–F) and one commercial...
lard (Lard A) into the previous oil network (Figures S12 and S13). Notably, we found that all the lard samples had similar TAG fingerprints and thereby clustered closely, independent with other oils (Figure 5A; the full network is available in Figure S13). Subsequent inspection of the pairwise TAG similarities showed that the two normal lards had indistinguishable TAG profiles (cos $\theta = 0.9940$, higher than the defined resolving power of 0.9927), while they were significantly differentiated from the adulterated samples (cos $\theta < 0.990$) (Figure 5B and Table S5). Importantly, such precise differentiation was complementary to the results using PCA and hierarchical clustering, where quantitative discrimination between the normal and gutter oils was not feasible (Figure S14). Overall, these results indicated that the changes in the chemical profiles of the gutter oils might be very subtle, making it challenging to verify through multivariate analysis. We believe that, as demonstrated by the representative fraud in Taiwan, the innovative oil networking platform is of immediate usefulness in identifying adulterated edible oils.

Quantitative Assessment of the Canola–Olive Oil Mixture. Adulteration of edible oil by intentionally adding a cheaper one has been a common issue in the food industry, where the most challenging task is to characterize, as the virgin and cheaper ones usually possess a similar chemical nature. Here, we further investigated the ability of our platform for the analysis of oil mixtures. First, we built an adulterated oil model by manually adding the canola oil (the cheaper oil) into the extra virgin olive oil. As a result, six oil samples with various proportions of the canola oil (0, 20, 40, 60, 80, and 100%) were readily tested with our platform, and their TAG fingerprints were revealed (Figure 6A). For each sample, its TAG similarity was calculated against the pure olive oil sample (i.e., 100% olive or 0% olive). The resulting TAG similarities were plotted against oil compositions to construct a calibration curve (Figure 6B), in which how the TAG fingerprint of the pure olive oil altered upon the addition of the canola oil was revealed. Interestingly, we found that the change of TAG similarity was not linearly related to the mixed proportion of the canola oil; instead, a quadratic function fitted the curve with $R^2 \approx 0.99$. This observation could be simply understood because the nature of cosine similarity was the calculation of a dot product between two vectors but not a linear mathematical operation. More importantly, here, it was the TAG fingerprint that served as the marker to determine the adulterated proportions. Compared to the reported methods using the intensity ratio between two compounds to detect the targeted adulteration, the demonstrated spectral similarity analysis shows great potential in preventing unknown adulteration.

Figure 5. TAG similarity analysis between the normal lards and the lards adulterated with gutter oils. (A) In the present network, one commercial lard (Lard A) and six adulterated lard oil samples (TFDA A–F) were incorporated and showed high TAG similarities to the standard lard. (B) Paired TAG similarities between the standard lard and the tested lard samples.

Figure 6. Quantitative analysis of the olive–canola oil mixture. The olive oils were manually added with various quantities of the canola oils, giving six samples with the olive oil proportions ranging from 0 to 100%. (A) Representative TAG fingerprints of the mixtures. (B) Pairwise TAG similarities were assessed between each sample and the pure oil (100% olive oil, shown as a red line; 100% canola oil, shown as a blue line). Error bars represent standard deviations of six technical replicates. The coefficients of the fitted quadratic functions were as follows: $a, -0.13$; $b, 0.31$; $c, 0.82$; $a', -0.19$; $b', 0.37$; $c', 0.82$. TAG similarity was calculated against the pure oil sample (i.e., 100% olive or 0% olive). The resulting TAG similarities were plotted against oil compositions to construct a calibration curve (Figure 6B), in which how the TAG fingerprint of the pure olive oil altered upon the addition of the canola oil was revealed. Interestingly, we found that the change of TAG similarity was not linearly related to the mixed proportion of the canola oil; instead, a quadratic function fitted the curve with $R^2 \approx 0.99$. This observation could be simply understood because the nature of cosine similarity was the calculation of a dot product between two vectors but not a linear mathematical operation. More importantly, here, it was the TAG fingerprint that served as the marker to determine the adulterated proportions. Compared to the reported methods using the intensity ratio between two compounds to detect the targeted adulteration, the demonstrated spectral similarity analysis shows great potential in preventing unknown adulteration.
because multiple compounds as well as their relative abundances were comprehensively taken into concern.

## CONCLUSIONS

A reliable MALDI-TOF-MS platform for the rapid analysis of TAG fingerprints in edible oils was demonstrated. Herein, cosine similarity analysis was incorporated into the pipeline, allowing quantitative differentiations of edible oils from various sources. Empowered by the sensitivity to probe subtle but crucial changes in the TAG fingerprints, the platform thus provides systematic classifications of the edible oils with robustness. Such an innovative approach paved a new way to comprehensively define the authenticity of edible oils, as further demonstrated by its application in solving a notorious fraud of adulterated lard in Taiwan. The data processing algorithm to create the profiling-based networking is also supported for future uses. On top of that, the mixture of canola oil and olive oil, which is a common form of oil adulteration in the market, was proved to be easily recognized quantitatively. This work provides an ability to externalize and fingerprint-quality control of edible oils in the chemistry level. Such a robust and simplified approach may enable standardized tests and typings of agricultural products and manufacture foods at a low cost.

## EXPERIMENTAL SECTION

### Materials and Chemicals.
Oil samples including olive oil, camellia oil, hazelnut oil, canola oil, rice bran oil, black sesame oil, pumpkinseed oil, peanut oil, sesame oil, corn oil, palm oil, sunflower oil, soybean oil, grapeseed oil, and lards were purchased from the local supermarket. The lard samples with adulteration of gutter oils were provided by the Taiwan Food and Drug Administration (TFDA). All samples were stored in the dark under 4 °C. 2,5-Dihydroxybenzoic acid (DHB) and trifluoroacetic acid (TFA) were purchased from Alfa Aesar (Heysham, U.K.). Acetone was purchased from Duksan Pure Chemicals (Ansan, Korea). Cesium iodide (CsI) was purchased from Sigma-Aldrich (Missouri, USA). Acetonitrile (ACN) and chloroform (CHCl₃) were purchased from Avantor (Pennsylvania, USA).

**Sample Preparation for MALDI-TOF-MS.** Oil samples were dissolved in chloroform to 100 mg/mL, and 3 μL of each oil sample was added into 27 μL of DHB solution (20 mg/mL in acetone and 0.2% TFA) and vortexed. An aliquot of 1 μL of the mixture was loaded onto the Bruker MTP AnchorChip 384 plate. For mass calibration, CsI solution (1 M in 50% ACN) was added into an equal volume of DHB solution (10 mg/mL in 50% ACN and 0.1% TFA), and 1 μL of the mixture was loaded onto the target plate. All samples were dried under vacuum for at least 10 min prior to analysis.

**Instrument Parameters of MALDI-TOF-MS.** All experiments were performed using a MALDI TOF/TOF mass spectrometer (Autoflex Speed MALDI TOF/TOF system, Bruker Daltonics) equipped with a frequency-tripled Nd:YAG SmartBeam-II laser (355 nm) and operated in positive polarity and reflectron mode. FlexControl 3.4 software was used for spectral acquisition. The spectra were acquired using the following instrumental parameters: mass range at m/z 400–1500, deflection suppressed up to m/z 380, laser power at 70%, shots accumulated to 1000 replicates, laser frequency at 200 Hz, detector gain set at 10X (2950 V), laser attenuator at 80%, and laser modulator set to medium.

### Cosine Similarity Analysis.

The spectral similarity between two spectra was evaluated by pairwise cosine similarity. Taking two spectral vectors \( \vec{A} \) and \( \vec{B} \), for example, the cosine similarity was calculated by the normalized dot product: \( \cos\theta(\vec{A}, \vec{B}) = (\vec{A} \cdot \vec{B}) / \|\vec{A}\|\|\vec{B}\| \).

**Data Visualization by Oil Networking.** Raw MALDI-MS spectra were preliminarily viewed by flexAnalysis 3.3 software (Bruker Daltonics) and exported as .txt files for spectral processing using OriginPro 8.5 software. Each spectrum within the mass range of m/z 850.2–950.2 (TAG fingerprint region) was extracted and dimensionally reduced to evenly spaced m/z 1.0 by the averaged intensity, resulting in a 100-dimension vector. For each edible oil sample, three technical replicate spectra were processed similarly, normalized, and averaged to create a consensus spectral vector. The TAG fingerprint dataset was processed with a laboratory-built MATLAB code to create data files required for data visualization using Cytoscape (3.7.0). The code is available at https://drive.google.com/drive/folders/1fH4u8x3d6f54nXyTr13mNk4FQp8lvp?usp=sharing.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02433.

Supporting materials including MALDI-MS spectra of the tested oil samples, results of multivariate analysis, and pairwise cosine similarities (PDF)

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### Author Contributions

T.-H.K. and M.-S.K. contributed equally to this work. T.-H.K. and M.-S.K. performed all the experiments. T.-H.K., M.-S.K., H.Y., and H.-H.C. analyzed the data. The manuscript was written by T.-H.K., M.-S.K., C.-H.C., and H.-J.C.

### Notes

The authors declare no competing financial interest.

All the raw data supporting the findings of this study are available from the corresponding authors upon reasonable request.

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