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Application News

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MALDI-TOF Mass Spectrometry

Simple and Rapid Identification of Vegetable Oils Using a Benchtop MALDI-TOF Mass Spectrometer and eMSTAT Solution™ Statistical Analysis Software

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometers (MALDI-TOF MS) feature simple and rapid detection of low molecular to high molecular weight compounds in a wide range of samples. MALDI-TOF MS is widely used to determine molecular weights of synthesized products and natural substances in R&D laboratories and quality control sectors. In addition, utilizing the feature of MALDI-TOF MS which can detect multiple components in a wide mass range as singly-charged ions (1 component = 1 peak), an attempt is being made to use the instrument for profiling property changes of food and biological specimens.

This article introduces an example of simple and rapid identification of vegetable oils, using a benchtop MALDI-TOF MS and the eMSTAT Solution statistical analysis software.

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Materials and Methods

Samples were prepared by diluting six kinds of commercially available vegetable oils (three olive oils, flaxseed oil, sunflower seed oil, and grape seed oil) to 1 mg/mL using chloroform. Each sample was mixed with an equal volume of matrix solution and cationization agent, spotted onto a reusable MALDI target slide and dried.

The matrix was prepared by dissolving 2,5-dihydroxybenzoic acid (DHB, 10 mg/mL) in methanol, and the cationization agent was prepared by dissolving sodium iodide (1 mg/mL) in tetrahydrofuran. Samples were analyzed using the MALDI-8020 benchtop MALDI-TOF mass spectrometer (Fig. 1). The peak lists obtained from the mass spectra were subjected to multivariate analysis using the eMSTAT Solution software to identify each oil type.

Results

The mass spectra of six vegetable oil samples are shown in Fig. 2. Mainly sodium-adducted molecules originated from diacylglycerols (DAGs) are detected near *m/z* 600, and triacylglycerols (TAGs) are detected near *m/z* 900.

The major constituent fatty acids of the detected TAGs are inferred based on references as listed in Table 1.

Fig. 1 MALDI-8020 Benchtop MALDI-TOF MS

Table 1 Compounds Inferred from Major Peaks Detected in the Mass Spectra of Vegetable Oils[1), 2)]

Observation *m/z*	Inferred Compounds
873.7	C55:6 (PLnLn)*
875.7	C55:5 (PLLn)
877.8	C55:4 (PLL/PLnO)
879.8	C55:3 (PLO/PLnS)
881.5	C55:2 (POO/PLS)
895.6	C57:9 (LnLnLn)
897.7	C57:8 (LLnLn)
899.7	C57:7 (LLLn)
901.5	C57:6 (OLLn/SLnLn)
903.8	C57:5 (OOLn/OLL)
905.5	C57:4 (SLL/OOL)
907.5	C57:3 (OOO/SOL)

* (In parentheses) L = linoleic acid, Ln = linolenic acid, O = oleic acid, P = palmitic acid, S = stearic acid

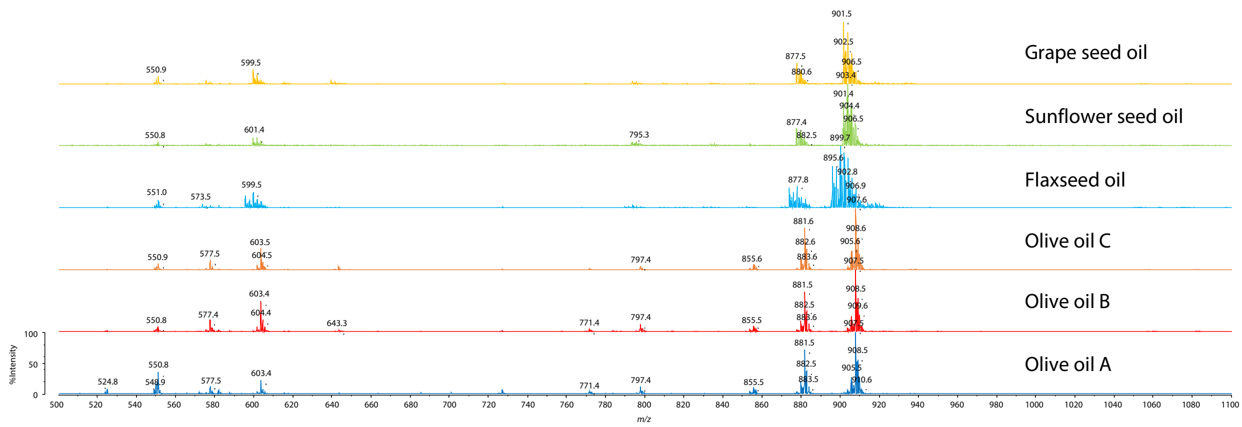

Fig. 2 Mass Spectra of Vegetable Oils

Fig. 3 shows the results (score plot) of multivariate analysis (algorithm: PLS-DA) of the peak lists of vegetable oil samples, which were detected by the MALDI-TOF mass spectrometer, using the eMSTAT Solution software. The samples can be classified into three groups: three olive oils of the high oleic type, flaxseed oil of the high linolenic type, sunflower seed oil and grape seed oil of the high linoleic type, indicating the major constituent fatty acid of each vegetable oil. From the results of the loading plot (Fig. 4), we can see that peaks at *m/z* 907 of the high oleic type, those at *m/z* 903 of the high linoleic type, and those at *m/z* 899 of the high linolenic type contribute to the grouping.
Next, we created a discrimination model (algorithm: Random Forest) to enable discrimination of the acid type of the major constituent fatty acid in an unknown vegetable oil using the measured data of the vegetable oil samples (upper figure in Fig. 5). We used the discrimination model to perform discriminant analysis of olive oils made by different manufacturers (other than those of the oils used for creating the model). All samples are identified correctly as the high oleic type (lower figure in Fig. 5).

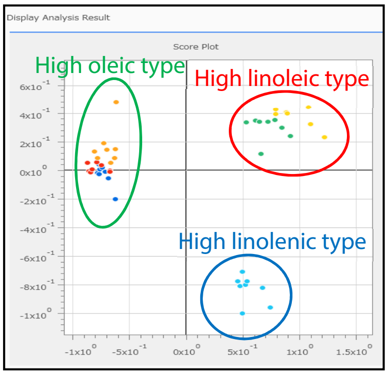

Fig. 3 Results of Multivariate Analysis of Vegetable Oils (Score Plot)
●Olive oil A ●Olive oil B ●Olive oil C ●Flaxseed oil
●Sunflower seed oil ●Grape seed oil

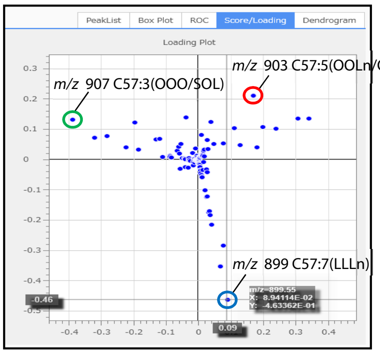

Fig. 4 Results of Multivariate Analysis of Vegetable Oils (Loading Plot)

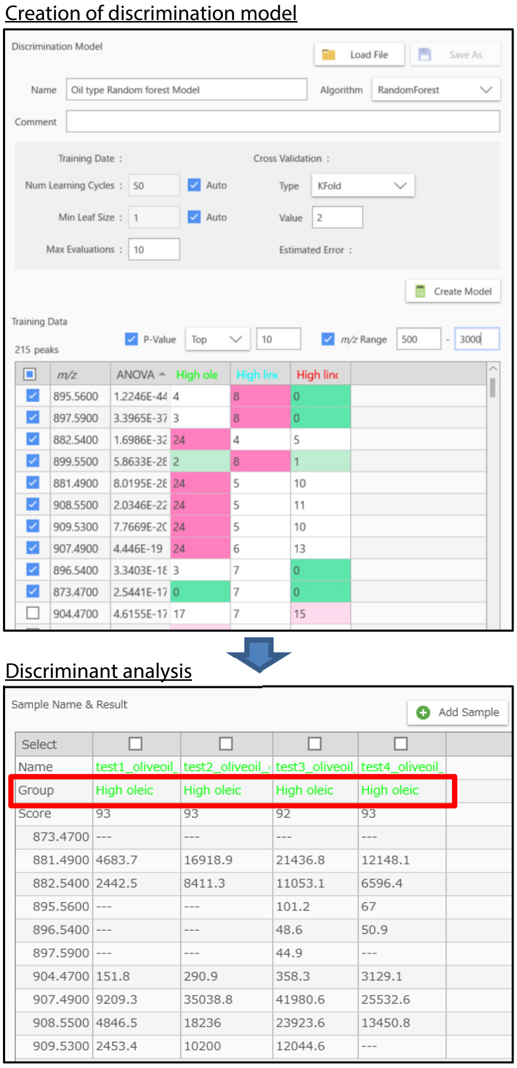

Fig. 5 Discriminant Analysis of Vegetable Oils (Upper: created discrimination model, Lower: discriminant analysis results of olive oils)

Conclusion

This article demonstrates that simple and rapid grouping of vegetable oils by the major constituent fatty acid can be performed using the MALDI-8020 benchtop MALDI-TOF mass spectrometer and statistical analysis software. In this analysis, fats were measured and we assume that this technique can be applied to a variety of samples including proteins, glycans, synthetic products, and biological specimens.
The benchtop MALDI-8020 features compactness and capabilities sufficient for molecular profiling, and its future dissemination in simple and rapid evaluation of properties in versatile samples is expected.

<References>
1) Ohtani, H, Yamahashi, Y, Ishida, Y: 2010. Curing Behavior Analysis of Drying Oil using Matrix-assisted Laser Desorption Ionization Mass Spectrometry (in Japanese). 58th Annual Conference on Mass Spectrometry, Japan
2) Picariello G, Paduano A, Sacchi R, Addeo F, 2009. Maldi-tof mass spectrometry profiling of polar and nonpolar fractions in heated vegetable oils. *J. Agric. Food Chem.*, 57 (12), pp. 5391-5400

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