

Mass Spectrometry

Author:

Avinash Dalmia

PerkinElmer, Inc.
Shelton, CT

Rapid Measurement of Olive Oil Adulteration with Seed Oils with Minimal Sample Preparation Using DSA/TOF

Introduction

Olive oil is a valuable product that is traditionally produced in Mediterranean countries and now in the United States (particularly California), and has nutritional advantages concerning cardiovascular

disease prevention^{1,2}. Due to its high nutritional value, it is offered at a higher price than other seed oils. For this reason, it is sometimes adulterated with other cheaper seed oils.

Olive oil and other oils are composed mainly of triacylglycerols. These molecules are derived from the esterification of three fatty acid molecules with a glycerol molecule. The main triglyceride in olive oil is triolein (OOO); whereas the main triglyceride in seed oils (soybean, corn and sunflower) is trilinolein (LLL). Therefore, the measurement of ratio of trilinolein to triolein in olive oil can be used as a way to detect its adulteration with soybean and other seed oils, such as corn and sunflower, which have a higher content of trilinolein and lower amount of triolein in comparison to olive oil³. Using this strategy with a Direct Sample Analysis™ Time-of-Flight mass spectrometry system (DSA/TOF), we detected adulteration of olive oil with soybean and corn oil. In the past, methods employing gas chromatography/mass spectrometry (GC/MS) and high performance liquid chromatography (HPLC) hyphenated to MS (HPLC/MS) were implemented for this purpose⁴⁻⁷. These methods are time consuming, expensive and require extensive sample preparation, method development and derivatization. In this work, we demonstrated that the AxION® Direct Sample Analysis (DSA™) system integrated with the AxION 2 Time-of-Flight (TOF) mass spectrometer can be used for rapid screening of adulteration of olive oil with seed oils such as soybean and corn oil with minimal sample preparation.

Experimental

Olive oil, soybean and corn oil were purchased from a local supermarket. All oils were diluted to 1 % in iso-propanol. After dilution, the oils were mixed in different proportions to simulate the adulteration of olive oil with soybean oil and corn oil at different percentages of 5, 10, 25 and 50 %. To obtain excellent mass accuracy, the AxION 2 TOF instrument was calibrated before each analysis by infusing a calibrant solution into the DSA source at 10 $\mu\text{l}/\text{min}$. Five μl of each sample was pipetted directly onto the stainless steel mesh of the AxION DSA system for ionization and analysis. All samples were analyzed within 30 seconds.

The DSA/TOF experimental parameters were as follows:

Mass spectrometer: PerkinElmer AxION 2 TOF MS
 Ionization source: PerkinElmer AxION Direct Sample Analysis (DSA)
 Ionization mode: Positive
 Flight Voltage: -8000 V
 Mass Scan Range: 10-1100 Da
 Acquisition Rate: 5 Spectra/s
 Capillary exit voltage: 150 V
 DSA source temperature: 300 °C
 Drying gas flow rate: 4 L/min

Results

Figures 1, 2 and 3 show the mass spectra for a 1 % solution of olive, soybean and corn oil in iso-propanol in positive ion mode using DSA/TOF, respectively. The mass spectra shows that the main triglyceride in olive oil is triolein; whereas the main triglyceride in soybean and corn oil is trilinolein. The data shows that the response ratio for trilinolein to triolein (LLL/OOO) was 0.033, 4.25 and 9.2 in olive oil, soybean oil and corn oil, respectively. Therefore, the higher response ratio for trilinolein to triolein in olive oil can be used to detect adulteration of olive oil with soybean or/and corn oil using DSA/TOF. This is supported further by data in Figure 4 which shows that the response ratio of trilinolein to triolein increased when the addition of soybean oil went from 5 to 50 % in eight different olive oils. Similarly, Figure 5 shows that the response ratio of trilinolein to triolein increased with increase in corn oil adulteration from 5 to 50 % in eight different olive oils.

The extensive data collected in this work shows that average response ratio for trilinolein to triolein in olive oils was 0.033 with standard deviation of 0.013. Therefore, if an olive oil showed the response ratio for LLL/OOO at a value higher than 0.072 (calculated using value of average + 3 times standard deviation for LLL/OOO response ratio in olive oil) with DSA/TOF, it would indicate that it might be adulterated with soybean or corn oil, or any oil containing a higher level of trilinolein than olive oil.

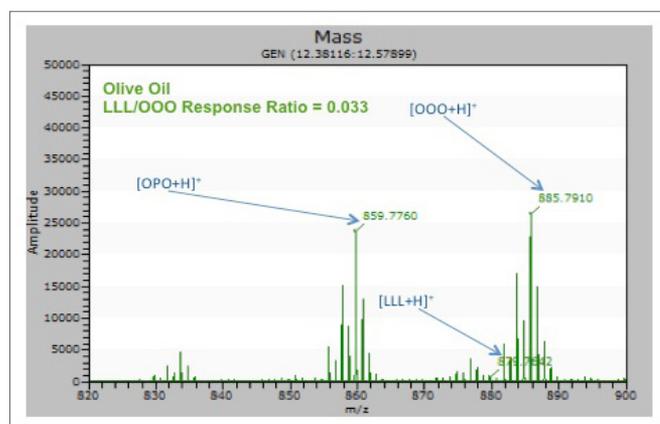


Figure 1. Mass spectra of olive oil in positive ion mode using DSA/TOF.

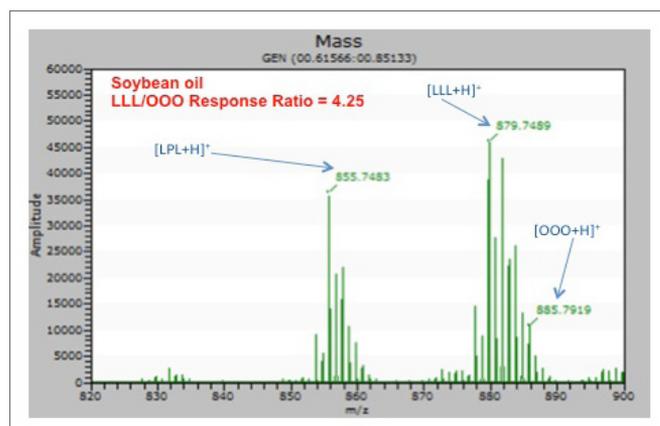


Figure 2. Mass spectra of soybean oil in positive mode using DSA/TOF.

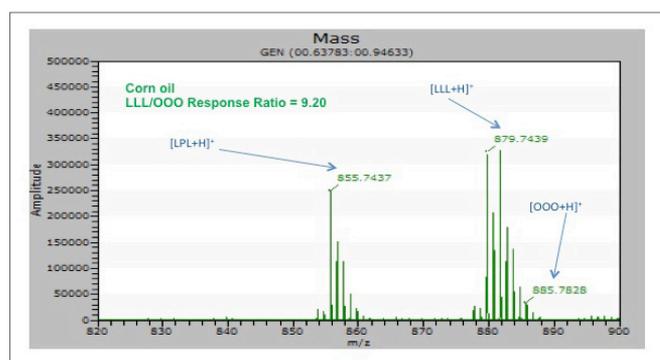


Figure 3. Mass spectra of corn oil in positive mode using DSA/TOF.

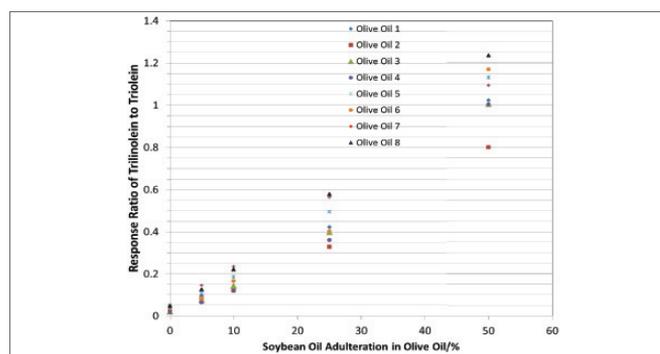


Figure 4. Effect of olive oil adulteration with different levels of soybean oil on response ratio of trilinolein to triolein.

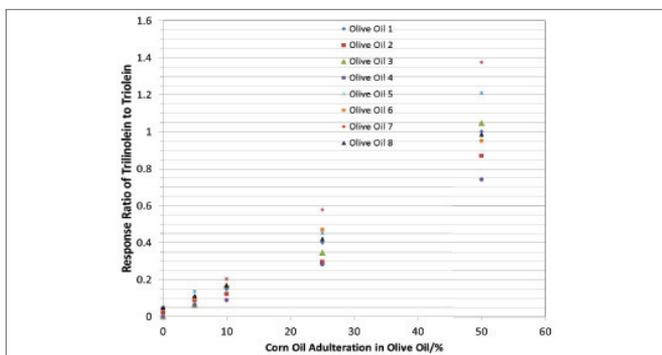


Figure 5. Effect of olive oil adulteration with different levels of corn oil on response ratio of trilinolein to triolein.

Conclusion

This application shows a rapid method for screening olive oil adulteration with other seed oils such as soybean and corn oil using DSA/TOF. The data showed that the higher response ratio for trilinolein to triolein in olive oil can be used to detect its adulteration with soybean or corn oil. All samples were screened with minimal sample preparation and in 30 seconds per sample. In comparison to other established techniques such as LC/MS and GC/MS, DSA/TOF can improve laboratory productivity and decrease operating costs and analysis time.

References

1. Garcia-Gonzalez L. D., Aparicio-Ruiz R., Aparicio R., Virgin olive oil - chemical implications on quality and health, *Eur. J. Lipid Sci. Technol.*, 2008, 110, 602-607
2. Sotiroudis T. G., Kyrtopoulos A. S., Anticarcinogenic compounds of olive oil and related biomarkers, *Eur. J. Nutr.*, 2008, 47, 69-72.
3. Fasciotti M., Annibal D. P. N., Optimization and application of methods of triacylglycerol evaluation for characterization of olive oil adulteration by soyabean oil with HPLC-APCI-MS-MS, *Talanta*, 2010, 81, 1116-1125.
4. Salivaras E., McCurdy R. A., Detection of olive oil adulteration with canola oil from triacylglycerol analysis by reversed-phase high-performance liquid chromatography, *JAOCS*, 1992, 69, 935-938.
5. Gromadzka J., Wardencki W., Trends in edible vegetable oils analysis. Part B. Application of different analytical techniques, *Pol. J. Food Nutr. Sci.*, 2011, 61, 89-99.
6. Andrikopoulos K. N., Giannakis G. I., Tzamtis V., Analysis of olive oil and seed oil triglycerides by capillary gas chromatography as a tool for the detection of the adulteration of olive oil, *J. Chrom. Sci.*, 2001, 39, 137-145.
7. Ezzatpanah H., Ghavami M., Ghasemi B. J., Vanak P. Z., Detection and quantification of adulteration in olive Oils by global method and extinction coefficient, *Australian Journal of Basic and Applied Sci.*, 2010, 4, 6254-6255.