APPLICATION NOTE

Mass Spectrometry

Author:

Avinash Dalmia

PerkinElmer, Inc.
Shelton, CT

Rapid Measurement of Extra Virgin Olive Oil Adulteration with Olive Pomace Oil with No Sample Preparation Using DSA/TOF

Introduction

Food adulteration or food crime occurs when an ingredient is replaced partially or fully with something different – without the knowledge of the consumer. Most of the time, food adulteration occurs to improve profits by diluting higher value products with lower value materials. The price of extra virgin olive oil (EVOO) is about 3-5 times higher than food grade olive pomace oil and therefore can be found to be blended with lower quality olive pomace oil. EVOO is extracted by mechanical pressing of high quality olive fruit, while olive pomace oil is the residue oil that is extracted by chemical solvents from previously pressed olive mash. Further, olive pomace oil is highly refined to remove chemical impurities. Both EVOO and olive pomace oil have similar triglyceride composition and therefore it is difficult to distinguish them on this basis. In the past, time consuming GC methods with sample preparation have been used to show that the average amount of ethyl ester of oleic acid (EEOA) in extra virgin olive oil and refined lampante olive oil (similar to refined olive pomace oil) is 27.9 mg/kg and 770 mg/kg, respectively[1]. It has also been reported that the ethyl esters of fatty acids in extra virgin olive oil were less than 32 mg/kg, whereas the ethyl esters of fatty acids in olive pomace oil were far higher; in the range of 500-40000 mg/kg[2]. The higher amounts of EEOA in olive pomace oil can be attributed either to heat treatment in processing or to lower quality of olive fruits. Both EVOO and olive pomace oils have similar amounts of free oleic acid (OA)[3]. Therefore, the measurement of ratio of EEOA to oleic acid in EVOO can be used as a way to detect its adulteration with olive pomace oils and other lower quality olive oils, which have a higher content of EEOA in them. In this work using a Direct Sample Analysis™ Time-of-Flight mass spectrometry system (DSA/TOF), we developed a method with no sample preparation to determine adulteration of EVOO with olive pomace oil by measuring the ratio of EEOA to OA.

PerkinElmer®
For the Better

Experimental

Five samples of extra virgin olive oils, two samples of olive oil blends and two samples of olive pomace oil were purchased from a local supermarket. All oils were tested without any sample preparation with DSA/TOF. One microliter of each sample was pipetted directly onto a glass tube compatible with the AxION® DSA™ system, for ionization and analysis. All samples were analyzed within 30 seconds of sample introduction.

To obtain high mass accuracy, the AxION 2 TOF mass spectrometer was calibrated before each analysis by infusing a mass calibrant solution into the DSA source at 10 µl/min. 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:	2 Spectra/s
Data Acquisition Time:	5 s
Capillary exit voltage:	150 V
DSA source temperature:	350 °C
Drying gas flow rate:	4 L/min

Results

Figures 1 and 2 show the mass spectra for the EVOO sample 3 and olive pomace oil sample 2 in positive ion mode using DSA/TOF, respectively. The mass spectra show the response ratio for EEOA to OA were 0.018 and 0.63 in EVOO sample 3 and olive pomace oil sample 2, respectively. Therefore, the higher response ratio for EEOA to OA in EVOO can be used as a way to determine adulteration of EVOO with olive pomace oil using DSA/TOF. Table 1 shows EEOA to OA response ratio for 5 EVOO samples, 2 olive oil blend samples (a mixture of EVOO and olive pomace oil) and 2 olive pomace oil samples. The average response ratio for EEOA to OA in EVOO samples was 0.023 with standard deviation of 0.005. Therefore, if an EVOO sample showed the response ratio for EEOA to OA at a value higher than 0.032 (calculated using value of average + 2 times standard deviation for EEOA to OA response ratio in extra virgin olive oil) with DSA/TOF, it would indicate that it might be either adulterated with olive pomace oil or any oil containing a higher level of EEOA than EVOO. Table 1 also shows that the response ratio for EEOA to OA for 2 olive oil blend samples and 2 olive pomace oils was higher than 0.032, suggesting that these samples were either blends of EVOO and olive pomace oil or olive pomace oil samples. Figure 3 demonstrates that the response ratio for EEOA to OA increased with addition of olive pomace oil sample 2 from 10 to 75 % in extra virgin olive oil 3. This demonstrated further that the higher response ratio of EEOA to OA in EVOO can be indicative of its adulteration with olive pomace oil using DSA/TOF.

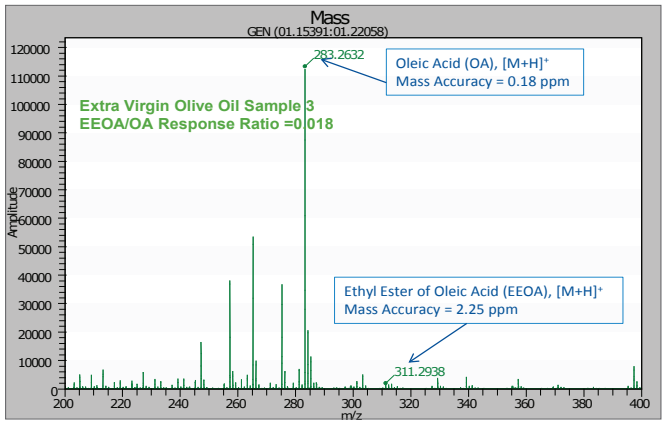

Figure 1. Mass spectra of extra virgin olive oil sample 3 in positive ion mode using DSA/TOF.

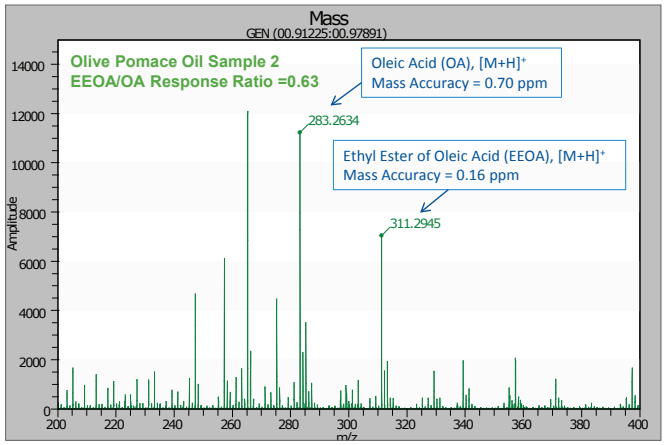

Figure 2. Mass spectra of olive pomace oil sample 2 in positive ion mode using DSA/TOF.

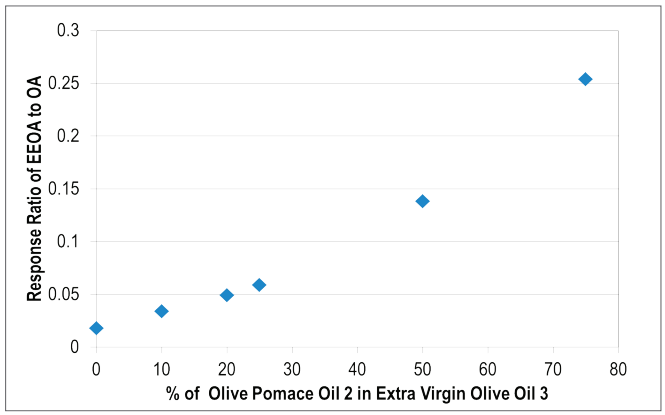

Figure 3. Effect of olive pomace oil adulteration in extra virgin olive oil on EEOA to OA response ratio.

Table 1. Measured values of response ratio of EEOA to OA in different olive oil samples with DSA/TOF.

Sample No.	Sample Description	EOA/OA Response Ratio
1	Extra Virgin Olive Oil 1	0.028
2	Extra Virgin Olive Oil 2	0.023
3	Extra Virgin Olive Oil 3	0.018
4	Extra Virgin Olive Oil 4	0.018
5	Extra Virgin Olive Oil 5	0.028
6	Olive Oil Blend 1	0.083
7	Olive Oil Blend 2	0.037
8	Olive Pomace Oil 1	5.45
9	Olive Pomace Oil 2	0.63

Conclusion

In this application, we developed a rapid method for screening EVOO adulteration with olive pomace oil using DSA/TOF. The data showed that the higher response ratio for EEOA to OA in EVOO can be used to detect its adulteration with olive pomace oil. All samples were tested with no sample preparation and with an analysis time of less than 30 seconds per sample. In comparison to other established techniques such as LC/MS and GC/MS[1-2,4-7], DSA/TOF would decrease operating costs and analysis time.

References

1. Carmen Perez-Camino M., Cert A., Romero-Segura A., Cert-Trujillo R., Moreda W., Alkyl esters of fatty acids a useful tool to detect soft deodorized olive oils, J. Agric. Food. Chem., 2008, 56, 6740-6744.
2. Carmen Perez-Camino M., Moreda W., Mateos R., Cert A., Determination of esters of fatty acids with low molecular weight alcohols in olive oils, J. Agric. Food. Chem., 2002, 50, 4721-4725.
3. Olive oil product grade definitions available at; http://www.oliveoilsource.com/page/product-grade-definitions.
4. 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.
5. 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.
6. 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.
7. 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.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

012035_01 PKI