Mass Spectrometry

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

Introduction

Among edible oils, olive oil shows important and outstanding characteristics due to its differentiated sensorial qualities (taste and flavor) and higher nutritional value. It is an important oil that is high in nutritional value due to its high content of antioxidants (including vitamin E)[1]. Several health benefits, such as its ability to lower LDL cholesterol and its anti-inflammatory activity, associated with its consumption were initially observed among Mediterranean people[2,3]. Olive oil is one of the most adulterated food products of the world due to its relatively low production and higher prices as compared to vegetable and 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 and these fatty acids determine the fatty acid composition of oils. Olive oil contains more oleic acid and less linoleic and linolenic acids than other vegetable and seed oils. Oleic acid is a monounsaturated fatty acid, whereas linoleic and linolenic acids are polyunsaturated fatty acids. The main fatty acids in olive oil are: oleic acid (65-85%), linoleic acid (4-15%), palmitic acid (7-16%) and linolenic acid (0-1.5%). The main fatty acids in soybean oil are: oleic acid (19-30%), linoleic acid (48-58%), palmitic acid (7-12%) and linolenic acid (5-9%)[4,5]. Therefore, the ratio of linoleic and linolenic acid to oleic acid in olive oil can be used as a way to detect its adulteration with soybean oil and other seed oils such as corn, safflower, sunflower and sesame oil, which have a higher content of linoleic and linolenic acids and lower amount of oleic acid in comparison to olive oil[6]. Using this strategy with the AxION® Direct Sample Analysis™ Time-of-Flight mass spectrometry system (DSA/TOF), we detected adulteration of olive oil with soybean oil.

The addition of vegetable and seed oils of low commercial and nutritional value to olive oil results in frequent problems for regulatory agencies, oil suppliers and consumers. A lot of scientific effort has been spent to develop rapid, reliable, cost effective analytical approach for measurement of adulteration of olive oils with other oils. In the past, methods employing gas chromatography/mass spectrometry (GC/MS) and high performance liquid chromatography (HPLC) hyphenated to MS (HPLC/MS) have been implemented for this purpose[7,8,9,10]. 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 soybean oil. The advantages of this method, compared to conventional techniques, are that no chromatography is required, the combination of direct sampling from the olive oil is done with minimal or no sample preparation and mass spectra results are generated in seconds.

Experimental

Olive oil and soybean oil were purchased from a local supermarket. Both oils were diluted to 1% in iso-propanol with 10 mM ammonium acetate. After dilution, the oils were mixed in different proportions to simulate the adulteration of olive oil with soybean oil at different percentages of 5, 10, 25 and 50. All oils and their mixtures were measured with an AxION 2 DSA/TOF system with minimal sample preparation. Five µl of each sample was pipetted directly onto the stainless steel mesh of the AxION DSA system for ionization and analysis. The DSA/TOF experimental parameters were as follows: corona current of 5 µA and heater temperature of 350 °C. The AxION 2 TOF MS was run in negative ionization mode with flight voltage of 8000 V and capillary exit voltage of -120 V for the analysis. Mass spectra were acquired in a range of m/z 100-700 at an acquisition rate of 5 spectra/s. All samples were analyzed within 30 sec. 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 µl/min.

Results

Figure 1 and Figure 2 show the mass spectra for a 1% solution of olive oil and soybean oil in iso-propanol with 10 mm ammonium acetate in negative ion mode using DSA/TOF, respectively. The mass spectra shows that the fatty acids, oleic, linoleic and linolenic, are present in both oils, but their relative amount is different in the two oils. The data shows that the response ratio for linoleic acid to oleic acid (L/O) was 0.18 and 1.86 in olive oil and soybean oil, respectively. Also, the response ratio for linolenic acid to oleic acid (Ln/O) was 0.017 and 0.29 in olive oil and soybean oil, respectively. Therefore, the higher response ratio for linoleic and linolenic acid to oleic acid can be used to detect adulteration of olive oil with soybean vegetable oil using DSA/TOF. This is supported further by data in Figure 3 which shows that response ratio of linoleic and linolenic acid to oleic acid was higher roughly by a factor of 2 for olive oil adulterated with 10 % soybean vegetable oil in comparison to olive oil. Figures 4 and 5 show that the response ratio for linoleic acid and linolenic acid to oleic acid increased, with
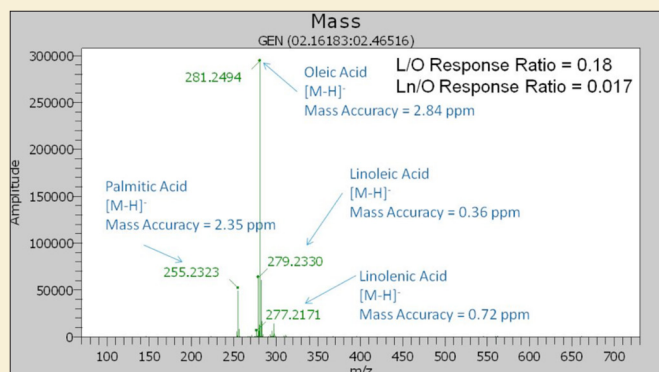

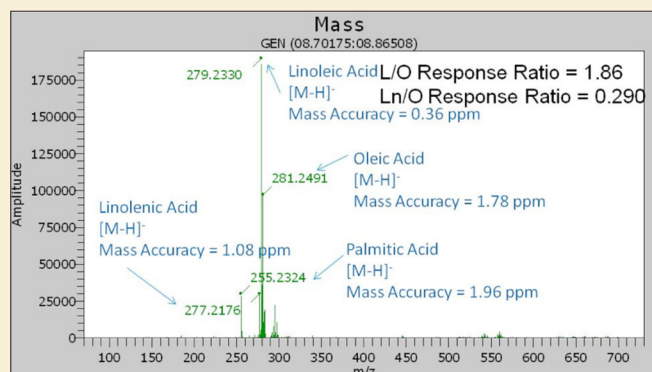*Figure 1.* Mass spectra of olive oil diluted by a factor of 100 in negative mode using DSA/TOF.

Figure 2. Mass spectra of soybean oil diluted by a factor of 100 in negative mode using DSA/TOF.
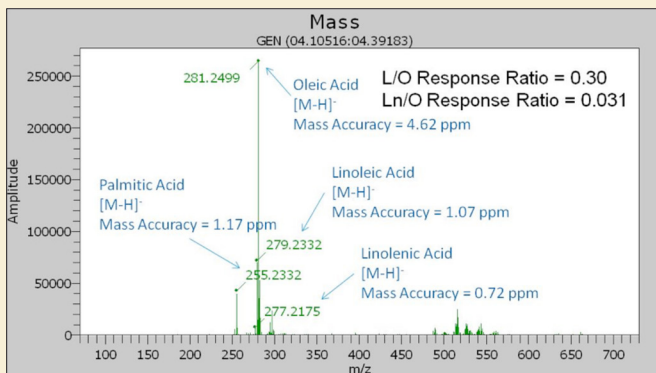
Figure 3. Mass spectra of olive oil adulterated with 10 % soybean oil diluted by a factor of 100 in negative mode using DSA/TOF.
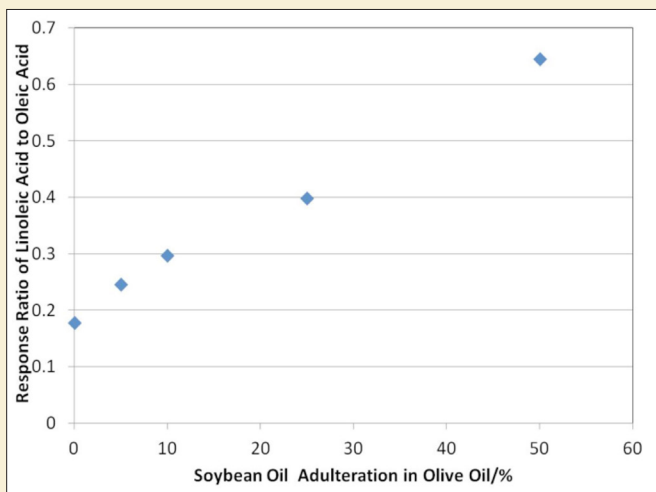

Figure 4. Effect of olive oil adulteration with different levels of soybean oil on response ratio of linoleic acid to oleic acid.
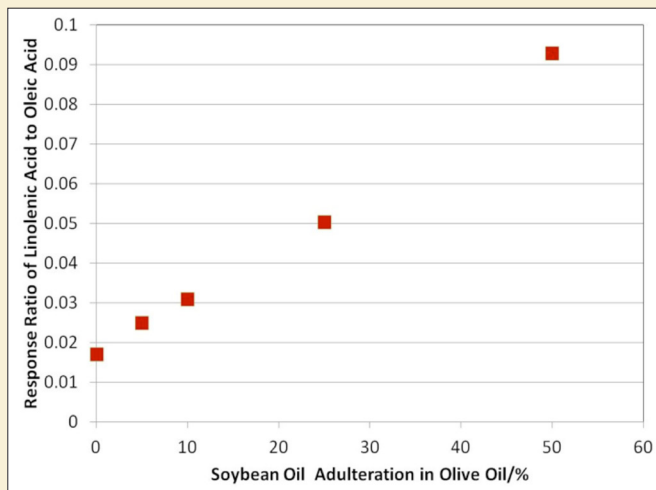

Figure 5. Effect of olive oil adulteration with different levels of soybean oil on response ratio of linolenic acid to oleic acid.

an increase in adulteration of olive oil with soybean oil from 5 to 50 %. This further confirmed that adulteration of olive oil with soybean oil can be detected by measuring the response ratio for linoelic and linolenic acid to oleic acid with DSA/TOF. All mass measurements showed good mass accuracy with an error of less than 5 ppm.

Conclusion

This work shows the first work for rapid screening of adulteration of olive oil with soybean oil using DSA/TOF. The data showed that the higher response ratio for linoleic and linolenic acid to oleic acid in olive oil can be used to detect its adulteration with soybean oil. The mass accuracy of all measurements was less than 5 ppm with external calibration. All samples were screened with minimal sample preparation, in 30 sec per sample. In comparison to other established techniques such as LC/MS and GC/MS, DSA/TOF will improve laboratory productivity and decrease operating costs and analysis time.

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