ANA 3: Analysis of Vegetable Oil Authentication and Adulteration

Chairs: P. Delmonte, US FDA, USA; and L. Reimann, Eurofins, USA

Detection of the Addition of Vegetable Oils to Olive Oils by Comparison of Theoretical and Experimental TAG. W. Moreda, M.C. Pérez-Camino, and R. Gómez-Coca, Instituto de la Grasa (CSIC), Seville, Spain.

The fraudulent addition of vegetable oils to olive oil has been produced in the last years. The analytical methods and maximum limits included in the European Union Commission regulations (EEC/2568/91) referred to the olive oil allow the detection of some vegetable oils oil only in high proportions. The triacylglycerol (TAG) composition of seed oils shows differences respecting to the olive oil, in particular the increase of TAG containing linoleic acid and the decrease of those containing palmitic and linolenic acid.

The method compare the TAG composition determined by HPLC and that theoretically calculated from the fatty acid composition, assuming a 1,3-random 2-random distribution of fatty acids in the glycerol moiety, with a restriction for saturated fatty acids in the 2-position. In olive oils, differences between experimental and theoretical values were negligible, whereas in seed oils, significant differences were found in some TAG.
Taking in account the differences the following algorithms were calculated: K1, $\Delta P3$, L3, R1exp, $\Delta R1$, L4 and R2. An excel file was developed to perform all the calculations and comparisons, resulting in a genuine or non-genuine answer. The percentage of detection is reduced considerably to 2-12% depending of the percentage of linoleic acid of the olive oil.

Evaluation of the Authenticity of Olive Oil in the U.S. Market Through the Analysis of the Triglyceride Composition. P. Delmonte, L. Vaclavik, A.R. Fardin Kia, M.M. Mossoba, and A. Krynitsky, U.S. Food and Drug Administration, College Park, MD, USA.

Olive oil, in its various grades, is an expensive commodity often economically adulterated by addition of less expensive oils. Among the various methodologies developed over the decades for the detection of extraneous oils in olive oil, the evaluation of the triglyceride profile has been the most promising approach. In this study olive oil samples were collected from the U.S. market and analyzed according to the International Olive Council "Global Method", and also the calculation of the equivalent carbon number 42 (ECN 42), and the determination of the fatty acid composition. The chromatographic conditions were then adjusted to improve the resolution of partially or fully co-eluting triglycerides. In addition to the chromatographic separation-based approach, a rapid fingerprinting of intact triglycerides was performed using the direct analysis in real time ambient ionization technique coupled to high resolution mass spectrometry (DART–HRMS). The simple dilution of olive oil samples with non-polar solvent was the only sample preparation needed prior to DART–HRMS analysis. The data obtained by the above methods were compared using multivariate statistical tools.

Rapid Analysis of Olive Oil Using FTIR and FTNIR. K. Kramer, N. Wang, and K. Ma*, Eurofins QTA Inc., Cincinnati, OH, USA.

The capability of FTIR and FTNIR for olive oil for chemistry analyses and authentication identification were investigated. Olive oils with various grade were received from various origins. These samples were scanned on FTNIR and FTIR instruments with optimized condition. Typical traits such as Total polyphenols, FFA, Pyropheophytins (PPP), Peroxide value, Tocopherols, and Diacylglycerides were evaluated. This report is the first part of the series study of rapid analysis of olive oil quality.

Using Stable Isotope Ratio Analysis of C, O, and H to Determine the Origin of Extra-Virgin Olive Oil. F. Camin[1,2], [1]FEM-IASMA Research and Innovation Centre, San Michele all'Adige (TN), Italy, [2]ICQRF MIPAAF, Roma, Italy.

The isotopic composition of plant material is related to the climatic conditions and geographical characteristics of the area in which the plants are grown. The isotope ratio of C depends on botanical origin, availability of water, relative humidity and temperature; whereas the isotope ratios of H and O reflect the isotopic composition of groundwater, average precipitation and the extent of evapotranspiration.

In this talk, I will show how stable isotope ratio analysis can be applied to determine the origin of extra-virgin olive oil, discussing the advantages and drawbacks. I will present the analysis of bulk oil using Isotope Ratio Mass Spectrometry (IRMS) and of certain sub-components using GC-IRMS,

discussing combination with other techniques (such as trace element and fatty acid analysis and ^{1}H-NMR profiling). The possibility of discriminating between PDO/PGI extra-virgin olive oils in Italy, between different countries of origin in Europe (Italy, France, Spain, Portugal, Greece, Cyprus) and between Italian and Tunisian olive oils will be investigated.

A Combined ^{1}H and ^{13}C NMR Method to Determine All Characteristics and Origin Tests of Edible Oils. B.W.K. Diehl, Spectral Service AG, Cologne, Germany.

The combination of 1H and 13C NMR using high field cryo NMR devices enables the simultaneous determination of most quality parameters in the analysis of edible oils. The following items can be determined within a low cost 30 minutes analysis: Peroxide value (POV), Anisidinic value (AV), Iodine value (IV), Acid value (FFA), fatty acid composition, Sterols, Tocopheroles, mono- and diglycerides, wax, phospholipids, secondary compounds like sesamol, cinnamic acid, terpenes etc. The analysis is useful for the origin test of edible oils and for the routine quality control.

Characterization of Volatile Compounds of Virgin Olive Oil Produced in the United States. H. Zhu[1], S. Tang[1], C. Shoemaker[1], and S. Wang[2], [1]Department of Food Science and Technology, University of California Davis, Davis, CA, USA, [2]University of California Davis Olive Center, Davis, CA, USA.

The unique and desirable flavors of virgin olive oil are mainly contributed by volatile compounds, which are highly affected by the olive variety, olive ripening stage and geographical origin. Several studies have been done to classify virgin olive oils according to their geographical origins by volatile profile, however, such information has yet to be collected for olive oils that are produced in the United States. In this study, major volatiles in single variety virgin olive oils from different producing regions in the United States are characterized and quantified by solid phase microextraction-gas chromatography/mass spectrometer (SPME-GC/MS). The volatile compositions are compared with those from previous studies on the European olive oils. Statistical analyses are applied to determine the key volatile compounds that are able to discriminate the oils from varieties, ripeness, and cultivation regions.

Multiple Analytical Approaches for Discriminating the Geographic Origin of Asian Sesame Oils. B.H. Kim, Chung-Ang University, Anseong, Gyeonggi-Do, Republic of Korea.

False indications of the geographic origin of sesame products became an issue of public concern in Korea. Chinese and Indian sesame seeds occupy ~81% of Korea's sesame imports during 2009-2010. They frequently appear in Korean local markets as domestically cultivated products. This has created the need for analytical methods to accurately distinguish Korean sesame oil from the oil obtained from imported sesame seeds. The aim of this study was to characterize the geographic origin of Asian sesame oils using a combination of methods to analyze different types of oil components such as fatty acids, lignans, triacylglycerols, and carbon, hydrogen, and oxygen stable isotopes. The analytical data were obtained from 84 roasted oil samples that were prepared from 51 Korean, 19 Chinese, and 14 Indian sesame seeds harvested during 2010-2011 and distributed in Korea during the same period. Canonical discriminant analysis, a type of multivariate statistical analysis method was used for analyzing multiple outcome variables. By applying two canonical discriminant functions, >90% of the sesame oil samples were correctly classified by their geographic origin, indicating that multiple analytical approach is a useful tool for the traceability of the oils.

Identification and Quantification of Tetraacylglycerols in Lesquerella Oil by HPLC and MS. J.T. Lin, United States Department of Agriculture, Albany, CA, USA.

Tetraacylglycerol (an acylglycerol estolide) contains an acyl chain attached to the hydroxyl group of another acyl chain attached to the glycerol backbone. Lesquerolic acid (Ls) is the main fatty acid in lesquerella oil and may be used industrially for the manufacture of biodegradable industrial products. Electrospray ionization mass spectrometry of the lithium adducts of acylglycerols in the HPLC fractions of lesquerella oil was used to identify thirteen tetraacylglycerols. They were LsLsLsLn, LsLsLsL, LsLs-OH20:2-O, LsLsLsO, LsLsLnLn, LsLsLLn, LsLsOLn, LsLsLL, LsLsOL, LsLsOP, LsLsOO, LsLsLS and LsLsOS. For the four tetraacylglycerols containing one normal fatty acid (non-hydroxy fatty acid), LsLsLsLn, LsLsLsL, LsLs-OH20:2-O and LsLsLsO, the normal fatty acids were all directly attached to the glycerol backbone, not to the hydroxyl group of fatty acids. We propose that the biosynthetic precursors

(triacylglycerol acyltransferase) of these four tetraacylglycerols were LsLsLn, LsLsL, LsLsO (Ls-OH20:2-O) and LsLsO individually. Quantitations of these tetraacylglycerols were by HPLC with evaporative light scattering detector and MS of HPLC fractions (comparing the ion signal intensities). The highest content of these tetraacylglycerols was LsLsLsO at about 0.3% in lesquerella oil.

Characterization of TAGs in Edible Oils with UltraPerformance Convergence Chromatography. J. Yang and G. Isaac, Waters Corporation, Milford, MA, USA.

Natural oils and fats are complex mixtures consisting primarily of triacylglycerols (TAGs). Chromatographic separation of TAGs is a challenging task since a large number of TAG species may exist in oils and fats. TAG profile can be used to assess the quality and the authenticity of oil and fat products. UltraPerformance Convergence Chromatography™ (UPC^2) leverages the unique properties of compressed CO_2 at or near its supercritical state, such as low viscosity and high diffusivity, and sub-two micron particle packed columns to improve separation efficiency, speed, and selectivity. The low polarity of compressed CO_2 also makes UPC^2 suitable for TAG analysis. Time-of-flight (Tof) mass spectrometry with MS^E simultaneously collects the exact-mass of precursor ions and their corresponding fragment ions, which is convenient for identification and structural elucidation. TAGs in three common edible oils, peanut, sunflower seed, and soybean oils, were separated on a UPC^2 C18 column using the ACQUITY UPC^2 system with a gradient elution. All TAGs eluted within 15 minutes and showed baseline separation for all the major TAGs. TAG peaks were identified using the accurate mass spectra collected by QTOF MS with MS^E. The method optimization, peak assignment using accurate mass data, and TAG elution order under UPC^2 conditions will be discussed.