APPLICATION OF SOME METHODS FOR DETECTING ADULTERATION IN OLIVE OIL

By

RANIA IBRAHIM MOHAMMAD ALMOSELHY
B.Sc. Agric. Sc. (Food Technology), Ain Shams University, 2000

A thesis submitted in partial fulfillment
of
the requirements for the degree of

MASTER OF SCIENCE

in

Agricultural Science
(Food Science and Technology)

Department of Food Science
Faculty of Agriculture
Ain Shams University

2010

Approval Sheet

APPLICATION OF SOME METHODS FOR DETECTING ADULTERATION IN OLIVE OIL

By

RANIA IBRAHIM MOHAMMAD ALMOSELHY

B.Sc. Agric. Sc. (Food Technology), Ain Shams University, 2000

This thesis for M.Sc. degree has been approved by:

Prof. Dr. Adel Zaki Mohammad Badee ------------------------------------

Prof. Emeritus of Food Science and Technology, Faculty of Agriculture, Cairo University

Prof. Dr. Mamdouh Helmy El-Kalyoubi -----------------------------------

Prof. Emeritus of Food Science and Technology, Faculty of Agriculture, Ain Shams University

Prof. Dr. Magda Habeeb Allam ---

Prof. Emeritus of Food Science and Technology, Faculty of Agriculture, Ain Shams University

Date of Examination: 29/8/2010

APPLICATION OF SOME METHODS FOR DETECTING ADULTERATION IN OLIVE OIL

By

RANIA IBRAHIM MOHAMMAD ALMOSELHY

B.Sc. Agric. Sc. (Food Technology), Ain Shams University, 2000

Under the supervision of:

Prof. Dr. Magda H. Allam

Prof. Emeritus of Food Science and Technology, Department of Food Science, Faculty of Agriculture, Ain Shams University (Principal Supervisor)

Prof. Dr. Atef A. Kotb

Prof. of Food Science and Technology, Department of Food Science, Faculty of Agriculture, Ain Shams University

Prof. Dr. Ahmad A. El-Sharkawy

Head of Research Emeritus of Oils and Fats Technology, Food Technology Research Institute, Agricultural Research Center

ABSTRACT

Rania Ibrahim Mohammad Almoselhy. Application of Some Methods for Detecting Adulteration in Olive Oil. Unpublished M.Sc. Thesis, Department of Food Science, Faculty of Agriculture, Ain Shams University, 2010.

This study aimed to maintain the high quality of olive oil by investigating some analytical methods as a powerful tool to determine extra virgin olive oil adulteration with relatively cheap seed and vegetable oils such as sunflower oil, corn oil and refined olive oil.

The analytical methods ranged from the familiar manual physical and chemical tests such as refractive index (RI) which gives a good idea about the degree of unsaturation of the oil under investigation, as well as its correlation with iodine value (IV); acid value (AV) as indication of free fatty acid content of the oil; peroxide value (PV) which determines the amount of primary oxidation products and UV absorbencies at 232 and 270 nm, that measure the formation of conjugated dienes and trienes, respectively due to the formation of secondary oxidation products.

The analytical methods extended to the more sophisticated instrumental methods of analysis such as chromatographic separation and determination techniques which involved gas chromatography (GC) with flame ionization detector (FID) in order to investigate the composition of the fatty acids of the oils under investigations.

Fourier Transform Infra Red (FTIR) spectroscopic determination technique was employed and applied as a potent, nondestructive and effective analytical tool to study its potency to investigate the functional groups with their relative absorbencies or transmittances according to their concentrations in samples and their characteristic fingerprints. FTIR spectroscopy was used also to determine extra virgin olive oil adulteration with sunflower, corn and refined olive oils in their binary admixtures at different concentrations of 0, 5, 10, 20, 30, 40, 50, 100%; w/w.

FTIR spectral data collected in MIR range 4000-400 cm^{-1} showed major peaks representing triglyceride functional groups which could be observed around 2925 cm^{-1} [C–H stretching (asymmetry)], 2854 cm^{-1} [C–H stretching (symmetry)], 1747 cm^{-1} [C=O stretching], 1463 cm^{-1} [C–H bending (scissoring)], 1238, 1163, 1118 and 1097 cm^{-1} [C–O stretching] and 722 cm^{-1} [C–H bending (rocking)]. A peak around 1653 cm^{-1} is attributed to C=C stretching (*cis*). The spectral region (1300-1000 cm^{-1}) which contains FTIR fingerprints of the used oils was found to be very useful in detecting extra virgin olive oil adulteration.

A band shift at 3005 cm^{-1}; assigned to C–H stretching vibration of *cis*- double bond (=C–H) characteristic to extra virgin olive oil, was observed at higher wavenumbers with increasing adulterant concentration which allowed the determination of adulteration of extra virgin olive oil.

The absorption intensity values of the spectral bands at 1163 cm^{-1} (assigned to C–O stretching vibration and CH_2 bending vibration) increased with increasing adulterant concentration.

There was a pronounced shift of the peak at 912 cm^{-1} (assigned to –HC=CH– of *cis*- double bond, bending out-of-plane) for extra virgin olive oil to higher wave numbers with increasing adulterant concentration.

Absorbance ratios (R1118/1097 and R1747/2925 cm^{-1}) decreased with increasing the concentrations of added adulterant oils (sunflower, corn and refined olive oils) with a fairly good linear relationship.

The spectral region selected between 1800-900 cm^{-1} mostly represented the combination of C–H bending, C=O stretching and C=C stretching and hence it was directly related to the unsaturated C=C bond. It played a very important role in the discriminant analysis.

In conclusion, FTIR spectroscopy proved its potency to detect extra virgin olive oil adulteration at 5% level of adulterant oils (sunflower, corn and refined olive oils) which is much lower than the limit at which there exists a threatening of adulteration of extra virgin olive oil.

KEY WORDS: Adulteration; extra virgin olive oil; FTIR spectroscopy; UV spectroscopy; GC analysis; sunflower oil; corn oil; refined olive oil.

ACKNOWLEDGMENT

In the beginning; I would like to express my deep gratefulness, thankfulness and indebtedness to Allah who enabled me to accomplish this research work to come to light in its final form.

I wish to acknowledge the prior and continuing efforts of my teachers and colleagues, especially the major contributions of the Principal Supervisor; **Prof. Dr. Magda H. Allam**; Prof. Emeritus of Food Science and Technology, Faculty of Agriculture, Ain Shams University, for her great help in a thoroughly professional approach, sincere guidance, valuable comments, scientific supports and continuous supervision. Her constant interest and input have had a significant impact on the final structure of this work to be presented in an excellent form.

Acknowledgement is extended to **Prof. Dr. Atef A. Kotb**; Prof. of Food Science and Technology, Faculty of Agriculture, Ain Shams University and **Prof. Dr. Ahmad A. El-Sharkawy**; Head of Research Emeritus of Oils and Fats Technology, Food Technology Research Institute, Agriculture Research Center, for their precious technical recommendations concerning the experimental work.

I am highly thankful to all the staff members in Food Technology Research Institute, Agriculture Research Center for providing the necessary laboratory facilities, instrumentation availability and valuable contribution to carry out the experimental work.

Finally, I wish to express my sincere gratitude and appreciation to my family for their persistent encouragement, support and sympathy.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

APCI	Atmospheric Pressure Chemical Ionization
APPI	Atmospheric Pressure Photospray Ionization
ATR	Attenuated Total Reflectance
AV	Acid Value
CEC	Capillary Electrochromatography
CL	Chemiluminescence
CLA	Conjugated Linoleic Acids
CO	Corn Oil
CVA	Canonical Variate Analysis
DEPT	Distortionless Enhancement by Polarization Transfer
DSC	Differential Scanning Calorimetry
DTGS	Deuterated Tri-Glycine Sulfate
ECN	Equivalent Carbon Number
ED	Energy-Dispersive
EEFM	Excitation–Emission Fluorescence Matrices
EEFS	Excitation–Emission Fluorescence Spectroscopy
ESI	Electrospray Ionization
EVOO	Extra Virgin Olive Oil
FA	Fatty Acid
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FIR	Far-IR
FTIR	Fourier Transform Infra Red
GC	Gas Chromatography
GC–FID	Gas Chromatography – Flame Ionization Detector
GC-MS	Gas Chromatography–Mass Spectrometry
GILS	Genetic Inverse Least Squares
GLC	Gas Liquid Chromatography
HPLC	High-Performance Liquid Chromatography

HPLC-APCI-MS	High-Performance Liquid Chromatography combined with Atmospheric Pressure Chemical Ionization coupled with Mass Spectrometry
HT-GC	High Temperature – Gas Chromatography
ID	Internal Diameter
IOOC	International Olive Oil Council
IV	Iodine Value
LC-MS	Liquid Chromatography with Mass Spectrometry
LDA	Linear Discriminant Analysis
MIR	Mid-infrared
MRI	Magnetic Resonance Imaging
MS	Mass Spectroscopy
MSC	Multiplicative Signal Correction
MUFA	Mono-unsaturated Fatty Acid
NIR	Near-infrared
NMR	Nuclear Magnetic Resonance
OPO	Olive–Pomace Oil
OSC	Orthogonal Signal Correction
PCA	Principal Component Analysis
PCR	Principal Component Regression
PDO	Protected Denomination of Origin
PLS	Partial Least Square
PLS-DA	Partial Least Square-Discriminant Analysis
PR	Pattern Recognition
PRESS	Prediction Residual Error Sum of Squares
PUFA	Poly-unsaturated Fatty Acid
PV	Peroxide Value
QC	Quality Control
QqTOF	Quadrupole Time-Of-Flight
R	Absorbance Ratio
ROO	Refined Olive Oil