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Quality Assessment of Oil from Olive Trees Irrigated by Waste Water Using Fluorescence Spectroscopy

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Dedication

This thesis is dedicated to my husband Dr. Mahmoud Obaid,

to my parents with all love, as well as,

to my brother and sisters,

to my daughter dear Zaina,

to everyone who helped me,

to everyone who gave me a good support.

With respect and love.

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الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Quality Assessment of Oil from Olive Trees Irrigated by Waste Water Using Fluorescence Spectroscopy

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما وُرِد، وأن هذه الرسالة ككل أو جزء منها لم يقدم من قبل لنيل أية درجة أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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List of Abbreviations and Symbols

M13	Sample from Misseli of trees irrigated by rain water of crop 2013.
H13	Sample from Hawara of trees irrigated by rain water of crop 2013.
M14	Sample from Misseli of trees irrigated by rain water of crop 2014.
H14	Sample from Hawara of trees irrigated by rain water of crop 2014.
A14	Sample from Anabta of trees irrigated by reclaimed waste water of crop 2014.
D14	Sample from Deir Sharaf of trees irrigated by waste water of crop 2014.
λ_{max}	Maximum wavelength.
λ_{ex}	Excitation wavelength.
λ_{em}	Emission wavelength.
λ_{abs}	Absorption wavelength.
K232	UV Absorption at maximum wavelength 232.
K270	UV Absorption at maximum wavelength 270.
FFA	Free fatty acid.
IOOC	International olive oil council.
IOC	International olive council.
AOAC	Association of official analytical chemists.
EEC	European commission regulation.
PCA	Principal component analysis.
RWW	Reclaimed waste water.
TWW	Treated waste water.
WW	Well water.
BC	Before Christ.
cP	Centipoises.
cSt	Centistokes.
Pa.s	Pascal – second.
ε	Molar Absorptivity.
η	Dynamic viscosity or absolute viscosity.
ν	Kinematic viscosity.
ρ	Mass density of liquid.
γ	Shear rate.
τ	Shear stress.
PVC	Pressure viscosity coefficient.
c	Constant speed of light (3×10^8 m/s).
ha	Hectares.
t	Tons.
nm	Nanometer.
VOO	Virgin olive oil.
EVOO	Extra virgin olive oil.
EHD	Elasto-hydrodynamic.
Nt	Total nitrogen.

KHP	Potassium hydrogen phthalate.
FTIR	Fourier transforms infrared spectroscopy.
NMR	Nuclear magnetic resonance.
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductive coupled plasma mass spectrometry.
AAS	Atomic absorption spectrometry.
GF-AAS	Graphite furnace atomic absorption spectrometry.

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Abstract

This work focuses on the effect of irrigation of Palestinian olive oil on the emission and absorption wavelengths using the fluorescence spectroscopy technique. In addition, the effect of irrigation of olive oil on the physical properties: viscosity, refractive index, acidity, and mass density were measured.

The results for emission spectra of olive oil samples indicated that the olive oil samples irrigated by rain water contain vitamin E more than other samples irrigated by different types of water. The olive oil samples irrigated by waste water contain chlorophyll a and b more than that for reclaimed waste water than that for rain water. The results for absorption spectra of olive oil samples from trees irrigated by waste water have high intensity at wavelength range (380-480 nm). This indicates that the samples of olive oil from trees irrigated by waste water contain amount of chlorophylls more than other samples from trees irrigated by rain and reclaimed waste water.

The results for physical properties of olive oil samples for different irrigation types of water were measured. The results of viscosity for samples irrigated by waste water of crop 2014 are greater than the viscosity of olive oil irrigated by other types of water. The experimental result of acidity for olive oil samples of trees irrigated by waste water was the highest and was classified as Lampante oil. The acidity of olive oil samples of trees irrigated by rain water of crop 2013 are greater than acidity for samples irrigated by rain water of crop 2014. The results of density of olive oil samples of crop 2014 have the highest value.

This study is the first time to be conducted in Palestine. It gives an indication about the quality assessment of oil from olive trees irrigated by waste water using fluorescence spectroscopy**.**

Chapter One

Introduction

The olive is the fruit of the olive tree and belongs to the family oleaceae. Its cultivation dates back to antiquity, and the cultivation of the olive tree and the production of olive oil remain an essential part of farming practices in the Mediterranean basin today. The olive tree flowers in spring, which develops into the nature drupe between October and January, depending on the area (Owen *et al*, 2000).

The first traces of olive tree cultivation have been individualized in Palestine they go back to 3500 BC. Nowadays, olive groves can also be found in many regions, such as United States, Argentina, New Zealand, and Australia (Vossen, 2007). There are about 800 million olive trees in the world, covering about 9 million hectares (ha), with the annual olive fruit production being about 13.7 million tons (t) (Tsimidou *et al*, 2003).

New techniques and equipment for removing the oil from the drupe have been developed to obtain the oil. At the same time extracting impurities and harmful substances this is the same as it was in the days of the Roman Empire (Calabriso *et al*, 2011). Drupe size and shape depend on the cultivar and agricultural conditions. In general, the olive contains the following components: 50% water, 20–25% oil or greasy material, 20% carbohydrates, 6% cellulose, and 1.6% proteins (Nergiz, Engez, 2000).

The Mediterranean diet rely on olive oil as the principal source of fat, they reduce risk of cardiovascular disease, type 2 diabetes, obesity, hypertension and with protection against brain unrest, and age-related disease. (Holzapfel, 2015; Menendez *et al*, 2013)

Virgin olive oils (VOO) are harvested directly from olive fruit by mechanical or physical means, that do not lead to changes in the oil and not undergone any treatment other non-washing, decanting, centrifuging, and filtration. Several types of virgin olive oil exist: extra virgin (highest quality), virgin, ordinary virgin, refined, and olive oil (Boskou, 2007). Olive oil is an edible blend of virgin olive oil and refined olive oil (Tsimidou *et al*, 2003).

Virgin olive oil is a vegetable oil, the chemical composition consists of major components include glycerols (98%) of the total oil weight, and minor components about (2%) of the total oil weight, include more than 230 chemical compounds (Servili *et al*, 2002; Boskou, 2007). Polyphenols are an important functional minor component of virgin olive oils and they are responsible for the key sensory characteristics of bitterness and pungency (Andrewes *et al*, 2003; Kontou, 2015).

The chemical characteristics of olive oil depend on several factors, these factors are clustered into four main groups according to rating Aparicio and Luna (Aparicio & Luna, 2002), environmental (soil, climate), cultivation (ripeness), technological (fruit storage), and agronomic factors (fertilization, irrigation). The irrigation factor is a major determinant of olive oil quality (Gomez-Rico *et al*, 2007). In general, quality is defined as “the combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of that product by the user" (Gould, 1992).

In the past 20 years, the olive oil production has spread to non-traditionally producing countries, leading to an increased olive and olive oil trade. However, this is not always accompanied by the production and marketing of high-quality olive oil, so many efforts have to be made to olive oil with preserved content of minor components that are mainly responsible for the healthy properties of olive oil (Calabriso *et al*, 2011).

At present, search for analytical methods to show the quality and safety of food is a major challenge in the nutrition field. Extra virgin olive oil (EVOO) is a high quality product that is beneficial to human health. This type of oil produced by exposure of olives a mechanical process and that shows special features of odor and taste. Therefore, determination properties of EVOO by analytical instrument are crucial for the oleic section in order to prevent fraud (García-Gonzalez & Aparicio, 2010).

Studies have shown that irrigation can increase olive production, thereby increasing total oil production per tree (Lavee *et al*, 1990; Moriana *et al,* 2003; Bedbabis *et al*, 2010).

The analysis of vegetable oils by the determination of classic parameters, such as acidity, ultraviolet absorption, and the fatty acid composition, are the basis for international types of water for the quality of oil (Corona *et al*, 2009).

In recent years, a remarkable growth in the use of fluorescence in food analysis has been observed, vegetable oils including olive oil form an important group of food products for which fluorescence was successfully applied (Christensen *et al*, 2006; Sadecka & Tothova, 2007; Karoui & Blecker, 2011).

Fluorescence spectroscopy is a well-established analytical tool in many areas (biochemical, medical and chemical research fields) for analyzing organic compounds (Rye *et al*, 1993).

The fluorescence analysis of olive oil get benefit from the presence of natural fluorescent components, including phenolic compounds, tocopherols and pheophytins, and their oxidation products. Analytical applications of fluorescence to olive oils include discrimination between the various quality grades, adulteration detection, Quantification of fluorescent components, control thermal and photo-oxidation and quality changes during storage (Sikorska *et al*, 2012).

A unique feature of fluorescence, primarily multidimensional character, another important advantage of fluorescence is higher sensitivity (Christensen *et al*, 2006). The sensitivity of fluorescence is 100-1000 times higher than that of the absorption techniques, which making fluorescence spectroscopy a very sensitive method, wherefore the fluorescence properties of compound are characterized by two types of spectra: excitation and emission (Guilbault, 1999).

Application of fluorescence to quality assessment of olive oils was proposed already in the beginning of the 20th century (Sidney & Willoughby, 1929; Glantz, 1930). In recent years, few papers were published on the use of fluorescence to assess adulteration detection of virgin olive oils. Adulteration of virgin olive oils has been common cheat practice that makes them cheaper oils. The most common cheating found in virgin olive oil are refined olive oil, pomace oil, residue oil, seed oils, and nut oils. Fluorescence technique was used to detect adulteration of virgin olive with other oils (Poulli *et al*, 2007).

Types of water used for irrigation:

Rain water:

Water (chemical formula: H_2O) is a transparent fluid which forms the world's streams, lakes, oceans and rain, and is the major constituent of the fluids of organisms. As a chemical compound, a water molecule contains one oxygen and two hydrogen atoms that are connected by covalent bonds.

Waste water:

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. Wastewater can originate from a combination of domestic, industrial, commercial or agricultural activities and surface runoff or storm water (Tilley *et al*, 2014).

Wastewater contains a number of pollutants and contaminants, including: plant nutrients (nitrogen, phosphorus, potassium); pathogenic microorganisms (viruses, bacteria, protozoa and helminthes); heavy metals (e.g. cadmium, chromium, copper, mercury, nickel, lead and zinc); organic pollutants (e.g. polychlorinated biphenyls, poly-aromatic, hydrocarbons and pesticides); biodegradable organics (BOD, COD) and micro-pollutants (e.g. medicines, cosmetics and cleaning agents). All of these can cause health and environmental problems and can have economic/financial impacts when improperly or untreated wastewater is released into the environment (Hanjra *et al*., 2012).

Reclaimed waste water:

The aim of treatment is to reduce the level of pollutants in the wastewater before reuse or disposal into the environment, the standard of treatment required will be location and use-specific.

Reclaimed water or recycled water is former wastewater (sewage) that is treated to remove solids and impurities, and used in sustainable landscaping irrigation, to recharge groundwater aquifers, to meet commercial and industrial water needs, and for drinking. The purpose of these processes is water conservation and sustainability, rather than discharging the treated water to surface waters such as rivers and oceans (Bischel *et al*, 2013).

Sometimes reclaimed waste water contains higher levels of nutrients such as nitrogen, phosphorus and oxygen which may somewhat help fertilize garden and agricultural plants when used for irrigation. The usage of water reclamation decreases the pollution sent to sensitive environments. It can also enhance wetlands, which benefits the wildlife depending on that eco-system, also helps to stop the chances of drought as recycling of water reduces the use of fresh water supply from underground sources (Zhang *et al*, 2012).

1.1 Previous studies

1.1.1 Fluorescence of olive oil

Spectroscopic techniques are ideal as new analytical methods since they are fast, simple, cost effective and non-destructive, which have widely been applied to olive oil analysis. First study has been made on the fluorescence of olive oils under ultraviolet light; all pure virgin oils were found to display a yellow fluorescence under ultraviolet light, while all refined oils show a blue fluorescence. A study showed the effect of added carotene that gave the yellow fluorescence of the virgin oil that could be obtained with oils adulterated with refined oil (LeRoy Glantz, 1930).

One important characteristic of a multicomponent fluorescent system was obtained by measuring simultaneous scanning of both excitation and emission wavelengths, keeping a constant difference between them. This investigation by fluorescence techniques was made by Lloyd (Lloyd, 1971).

Scott *et al* used total luminescence spectra of four different types of edible oils, extra virgin olive, non-virgin olive, sunflower and rapeseed oils and measured the spectra of undiluted oil samples in the excitation range from (350 to 450 nm) and in the emission range from (400 to 720 nm) (Scott *et al*, 2003). Total Luminescence Spectroscopy was used to different edible oils and to control oil quality (photo-oxidation). Sikorska and his team studied several vegetable oils available in the Polish market. The results indicated the capability of the luminescence techniques to characterize vegetable oil products and to investigate the effect of photo-oxidation on like products (Sikorska *et al*, 2004).

Results presented in Kongbonga *et al* demonstrated the ability to analyze vegetable oils with cheap and easy method by fluorescence spectroscopy at excitation wavelength (λ_{ex} = 370 nm). Some properties of vegetable oils have been studied using Principal Component Analysis (PCA), to distinguish between the refined and unrefined oils. The study showed the possibility to detect alteration of some desired oils as the argan or the extra virgin olive oils (Kongbonga *et al*, 2011).

In a recent study, Sikorska *et al* reviewed several applications of fluorescence spectroscopy. Examples were differentiation between quality grades; detection of adulteration; authentication of geographic origin; quantification of fluorescent components; monitoring photo-oxidation and assessment of quality changes of olive oil during storage (Sikorska *et al*, 2012).

The aim of Guzmán *et al* study was to use fluorescence spectroscopy that provided information on quality parameters for periodic control and used for a general characterization of olive oils. The results were promising due to providing useful information that can be used for the rapid and easy monitoring of oil quality and showed the potential use of fluorescence instruments for the overall evaluation of olive oil quality (Guzmán *et al*, 2015).

1.1.2 Viscosity of olive oil

Viscosity has been widely studied by scientists and engineers for various purposes. Viscosity is influenced by many factors, such as system of irrigation, temperature, shear rate, moisture, molecular weight, pressure and time of storage, or any combination of these factors (Giap *et al*, 2009; Stanciu, 2012).

Abramovic and Klofutor studied the dynamic viscosities for several mixtures of refined and unrefined vegetable oils which were determined at temperatures from 298.15 K to 328.15 K. They presented relations describing the temperature dependence on dynamic viscosity (Abramovic, Klofutor, 1998).

Biresaw and Bantchev studied the pressure viscosity coefficient (PVC) of ten vegetable oils samples. PVC was estimated using two different methods, the first method was analysis of oil physical properties (viscosity and density); and the second was analysis of Elasto-hydrodynamic (EHD) film thickness data. The results of their study showed that the PVC values of vegetable oils decreased with increasing temperature, and increased with increasing viscosity of the tested oils (Biresaw & Bantchev, 2013).

1.1.3 Refractive index

Refractive index represents a fundamental property in physics, chemistry and biology, and is one of the most significant parameters. Yunus *et al* studied the refractive index and FTIR spectra of virgin coconut oil and virgin olive oil at wavelength range from (491.0-667.8)nm at room temperature. They found that the refractive index of virgin olive oil is higher than all other oils (Yunus *et al*, 2009).

1.1.4 Acidity of olive oil

Fourier transform infrared (FTIR) spectroscopy was proposed as a new technique to determine free fatty acids (FFA) in olive oil. The range of FFA contents of olive oil samples by adding oleic acid of several virgin and pure olive oils, from (0.1 to 2.1)% (Bertran *et al*, 1999).

In Vlachos *et al* work, FTIR spectroscopy was used as an effective analytical tool in order to determine extra virgin olive oil adulteration (Vlachos *et al*, 2006). Another advanced technique to detect fatty acid composition and triacylglycerol molecule with high resolution is nuclear magnetic resonance (NMR). NMR allows the determination of a large number of components with small amount of olive oil samples (Hidalgo *et al*, 2003).

Fatty acid in olive oil components varied according to manufacturing regions and depends on ripeness stage. Gharsallaoui and his group assessed the impact of irrigation by treated waste water on the Tunisian olive oil quality. The results showed that the free fatty acids and the carotene content of the oils do not depend on the irrigation system, but on the duration of olive storage. On the contrary, the irrigation system affects the oxidation state of the oils and their fatty acid composition (Gharsallaoui *et al*, 2013).

1.1.5 Trace metals

Many reports described the harmless effect of trace elements on oil when the trees were irrigated with waste water. This is because of the presence of high concentrations of microorganisms such as bacteria, fungi, viruses, helminthes and heavy metals found in waste water such as arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc (Akpor *et al*, 2010).

The aim of Zeiner *et al* study was to verify the different trace elements in oils from different origins. Some of their elements are essential for human nutrition such as (Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Zn), some of these elements affect the oxidative stability of edible oils (Cu, Fe, Mn, Ni, Zn) and some elements exist in oils due to environmental contaminations (Cu, Pb) (Zeiner *et al,* 2005).

Quality of edible oils can be determined from the concentrations of different trace elements (Ashraf, 2014). Ashraf determined the concentrations of copper, zinc, iron, manganese, cadmium, lead and arsenic in edible vegetable oils consumed in the Kingdom of Saudi Arabia (KSA), using inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GF-AAS) (Ashraf, 2014).

The most commonly used techniques for the determination of metals in olive oil samples were inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) (Zhenli *et al*, 2005). The quality of olive oil samples of different irrigation types of water in Palestine estimated the concentration of several trace elements using inductively coupled plasma-mass spectrometry (ICP-MS) (Odeh *et al*, 2015).

1.2 Research significance

The study is gaining importance through:

- ❖ Using fluorescence spectra of olive oils that contain information about fluorophores that are important for oil quality.
- ❖ Finding a correlation between fluorescence spectra (emission wavelength (λ_{em}) with oil components, which may change by irrigating olive trees with waste water compared to other more pure water.
- ❖ Studying the chemical and physical properties of olive oil samples irrigated by rain water and waste water: viscosity, acidity, density and refractive index at measuring different temperatures.

1.3 Objectives

The technical objectives of this study are to:

- ❖ Analyze olive oil irrigated by rain, reclaimed and waste water by fluorescence spectroscopy technique.
- ❖ Analyze olive oil irrigated by rain, reclaimed and waste water by UV-Visible spectrophotometer technique at different temperatures.
- ❖ Study the chemical and physical properties of olive oil samples irrigated by rain, reclaimed and waste water such as viscosity, density, refractive index and acidity at different temperatures.

- Compare the chemical and physical properties of olive oil samples irrigated by rain, reclaimed and waste water with standard values.

1.4 Olive oil samples

The samples of olive oil used in this study were collected from different regions of the northern part of West Bank, Palestine (Nablus area) as follows:

- Two samples of crop (2013-2014) from Hawara town which is 9 km south of Nablus, and two others from Misseli village which is 14 km south of Nablus, where the trees were irrigated from rain water.
- One sample of crop 2014 from Anabta which is 18 km west of Nablus, where the tree was irrigated by reclaimed waste water.
- One sample of crop 2014 from Deir-Sharaf which is 9 km north west of Nablus where the tree was irrigated by waste water coming from a small valley (Wadi-Zomer).

Table (1.1): Classification of samples according to their irrigation ways.

Region	Sample	Type of irrigation	Crops
Deir-Sharaf	D14	Waste water	2014
Anabta	A14	Reclaimed waste water	2014
Misseli	M14	Rain water	2014
Misseli	M13	Rain water	2013
Hawara	H14	Rain water	2014
Hawara	H13	Rain water	2013

Chapter Two

Theory

2.1 Olive oil composition

European Commission (EC) Regulation 2568/91 and subsequent amendments (EC 2632/94, EC 656/95, and EC 2472/97) set the limits for compositions of olive oil and for absorption at different wavelengths. These limits are very strict and aim at protecting perfect quality of olive oil from adulteration (Tsimidou *et al*, 2003; IOC, 2015).

The Codex Alimentarius Commission, IOOC, and the Commission of the European Union provide identity and synthetic characteristics for olive oil. The primary compound triacylglycerol, was determined by reversed phase liquid chromatography, the main triacylglycerols found in olive oil are: (55-83)% oleic acid, (7.5 - 20)% palmitic acid, (0.5 - 5)% stearic acid, (0.3-3.5)% palmitoleic acid, (3.5 - 21)% linoleic acid and fatty acid. The olive oil composition may differ from sample to sample, depending on the region of production, climate, and the irrigation system. Other secondary components such as, tocopherols which are the main source of vitamin E in olive oil, squalene ($C_{30}H_{50}$) is the major olive oil hydrocarbon, phytosterols are functional ingredients and inhibit the absorption of cholesterol in the body during digestion, carotenoids, phenolic compounds that affect to stability and flavor, chlorophylls that are responsible for the yellow/green color of the oil (CAC, 1993; IOOC, 1999; commission of the European Communities, 1991).

Type of grades of oil extracted from the olive fruit. (IOC, 2015)

-Virgin olive oil, the oil produced by mechanical means only. The term virgin oil including extra virgin, virgin, ordinary virgin and lampante virgin olive oil products, depending on quality.

-Refined olive oil, the olive oil obtained from virgin olive oil by refining methods. It has a free acidity (oleic acid) not more than 0.3 grams per 100 grams. The refining process removes color, odor and flavor from olive oil.

- Olive oil, the oil consisting of a blend of refined olive oil and virgin olive oil valid for consumption. It has a free acidity (oleic acid), of not more than 1 gram per 100 grams.

2.2 UV-Visible Spectrophotometry

Absorption spectra of chemical species (atoms, molecules, or ions) are generated when a beam of electromagnetic energy is passed through a sample. The chlorophyll molecules absorb only a few selected photons in the blue and red regions of the visible part of the electromagnetic spectrum. The energies of these absorbed photons cause electrons to be excited. The primary objective of this process is the fact that when the red and blue photons that chlorophyll absorbs are subtracted from white light, the resulting beam of light leaving the solution appears green to our eye. This indicates that the oil is not adulterated. A spectrophotometer is an instrument designed to make this measurement. This device effectively "counts" the number of photons that enter a sample and compares it with the number of photons that exit the sample (Hardesty & Attili, 2010).

2.3 The Beer-Lambert law:

Think of a solution of a chemical species that absorbs light of a particular wavelength. Two interesting cases: First, a beam of light of a suitable wavelength passes through a relatively dilute solution then the same beam of light passes through a highly concentrated solution. The photons will encounter a great number of absorbing chemical species that gives a low % transmittance and a high absorbance. Secondly, the beam of light is allowed to encounter the solution for a long period of time. Low % transmittance and a high absorbance are expected. Light travels at a constant speed, $c = 3 \times 10^8$ m/s, this means that the absorbance should be proportional to the path length of the beam through the sample (Hardesty & Attili, 2010).

These two cases allow establishing the following proportionality: (Beer-Lambert Law)

$$A = \varepsilon \times I \times C \qquad (2.1)$$

l(cm) = path length, and C(M) = molar concentration of the absorbing chemical species. The proportionality constant is called the Molar Absorptivity ε (M^{-1} cm^{-1}). This technique is used by chemists and scientists of many fields. The Beer-Lambert law allows to measure the absorbance of a particular sample and to deduce the concentration of the solution from that measurement. (www.physics.uoguelph.ca/~pgarrett/Teaching.html)

2.4 Viscosity

Liquid viscosity is important in the design of process equipment for the fatty acid industry. It is an important parameter in estimating the efficiency of distillation columns for the separation of fatty acids (Noureddini *et al*, 1992).

2.4.1 Types of viscosity

All liquids have a natural internal resistance to flow termed viscosity. Viscosity is the result of frictional interactions within a given liquid, commonly expressed in two different ways: (Barron, 2014)

1- Dynamic viscosity

Dynamic viscosity is defined as resistance to shear and flow, which represents the ratio between shear stress and shear rate. It is also known as absolute viscosity.

$$\eta = \tau / \gamma \tag{2.2}$$

η represents dynamic viscosity in pascal-second (Pa. s), τ is the shear stress and γ is the shear rate. Equation (2.2) shows that viscosity decreases as shear rate increases (Diamante *et al*, 2014).

2- Kinematic viscosity

Kinematic viscosity requires a knowledge of the density (ρ), and is given by equation (2.3)

$$\nu = \eta / \rho \tag{2.3}$$

where ν is the kinematic viscosity in centistokes (cSt) and η is the dynamic viscosity, ρ is mass density of liquid in g/cm^3.

2.4.2 Units of viscosity

Viscosity is commonly expressed in poise (P) and centipoises (cP), where cP = 0.01P. Dynamic viscosity is measured in Pascal- second (Pa.s) equivalent to $N.s/m^2$ in SI units, in cgs unit poise and centipoises named after physicist Jean Louis Marie Poiseuille (1799 - 1869).

Kinematic viscosity is measured in cgs unit stokes (St), or centistokes, which is named after George Gabriel Stokes, 1St = 1 cm^2/s (Astle, *et al*, 1988).

2.5 Refractive index

The importance of optical measurement methods in various technologies is increasing. The advantage of these methods is that physical quantities can be measured without disturbing the system. Refractive index is a dimensionless quantity, defined as the ratio between the speed of light in vacuum(c) and that in a given medium (v).

$$n = c/v \tag{2.4}$$

Refractive index is affected by factors such as, density, wavelength of the light source and temperature of material. Each material has a refractive index that differs from other (Thormahlen *et al*, 1985).

2.6 Acidity

Acidity represents the degree of decomposition fatty acid that defines in general formula $CH_3(CH_2)_nCOOH$. Generally, determination of free fatty acid (FFA) level is an important parameter to monitor the quality and validity of the products, the FFA are likely to increase as time passes and temperature is raised.

According to the European Commission Regulation (EC 2568/91), olive oil classification is based on the degree of acidity, expressed in terms of oleic acid weight percentage: extra virgin and virgin olive oil must present degrees of acidity lower than 1 and 3.3%, respectively. Whereas lampante olive oil acidity is above 3.3% (Qutub *et al*, 2010).

Table (2.1): Categorization of olive oil quality according to % FFA (Calabriso *et al*, 2011).

Type of Olive Oil	Free Acidity (% Oleic Acid)
Extra- Virgin olive oil	≤0.8
Virgin olive oil	≤2.0
Ordinary Virgin olive oil	≤3.3
Lampante Virgin olive oil	>3.3

Chapter Three

Methodology

Olive oil samples were collected from some regions in Palestine including Deir Sharaf, Anabta, Misseli and Hawara. The samples were obtained from trees which were irrigated with different water sources (rain, reclaimed and waste water). Some samples were from crops of 2013 and 2014, and others from 2014 only.

The samples from crops of 2014 were obtained and collected using the traditional way, stored and kept under the same conditions (closed plastic bottles placed in dark place at room temperature).

Olive samples irrigated by rain, reclaimed and waste water analyzed by fluorescence spectroscopy technique at room temperature, and by UV-visible spectrophotometer technique at measuring different temperatures. The viscosity and density of olive oil samples were obtained and analyzed in wide range of temperatures (15-50°C), refractive indices were measured over the range (15-40°C), and acidity was studied by a titrimetric method at room temperature.

Measurements

3.1 Fluorescence Spectrophotometry

Fluorescence is the interaction of electromagnetic radiation with matter and that along with phosphorescence it can provide important information about molecular structure and chemical interactions (Roche Institute of Molecular Biology, Nutley, New Jersey, 1969).

The Perkin-Elmer LS-50B Luminescence Spectrometer, as shown in Fig(3.1), is a complete workstation for a very wide variety of sensitive biochemical studies, including fluorescence, phosphorescence, and bio-chemi-luminescence. Wavelength Accuracy is ± 1nm. Fluorescence spectroscopy detects concentrations as low as one part per trillion. This is 10,000 times more sensitive than absorption spectroscopy (Jameson *et al*, 2003).

Fig(3.1): Fluorescence Spectrometer

3.2 UV-Visible spectrophotometry

Spectroscopic methods are the main tool of modern chemistry for the identification of molecular structures. In organic chemistry, spectroscopic methods are used to determine and confirm molecular structures, to monitor reactions and to control the purity of compounds (Poulli *et al*, 2009).

UV-3101PC spectrophotometer as shown in Fig(3.2), was used to detect the presence of chromophores like dienes, aromatics, polyenes, and conjugated ketones, etc. Photometric accuracy was ±0.002 and wavelength accuracy was ±0.3 nm.

Fig (3.2): UV-Visible spectrophotometer

3.3 Viscosity apparatus

The measurement of viscosity is of significant importance in both industry and academia (Viswanath *et al,* 2007).

Viscosity of olive oil samples was measured using NDJ-1 Rotational Viscometer shown in Fig.(3.3). The measurement accuracy was (± 5% Newton liquid).

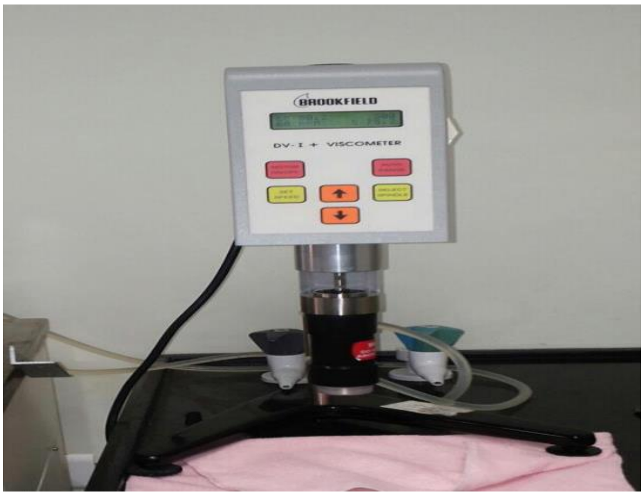

Fig.(3.3): NDJ-1 Rotational Viscometer

3.4 Refractive index apparatus

A refractometer measures the range to which light is bent, when it moves from air into a sample. The refractive index is a unit less number, between 1.3000 and 1.7000 for most compounds, and is normally determined to five digit precision. The index of refraction depends on both the temperature of the sample and the wavelength of light (Hanson, 2003).

The refractive index was measured using a digital refractometer at different temperatures (15 – 40)°C, because the device is sensitive and do not incur high temperatures. The accuracy of this apparatus was ±0.0002. The digital Refractometer is shown in Fig.(3.4).

Fig.(3.4): Digital Refractometer

3.5 Density apparatus

Density determination by pycnometer is a very accurate method. The pycnometer (Fig.3.5) is a glass flask with a close-fitting ground glass stopper with a capillary hole through it. This hole releases a spare liquid after closing a top-filled pycnometer and allows getting a certain volume that measured with a high accuracy (Chang, 1988).

The density was measured by taking the mass difference between a full Pycnometer of oil and an empty one divided by 10 cm^3, at different temperatures over the range of (15-50)°C. The Pycnometer mass was measured using analytical balance with accuracy of ±0.00005.

Fig.(3.5): Pycnometer

3.6 Temperature apparatus

Digital thermometers are temperature-sensing instruments that are easily portable, have constant probes, and a comfortable digital display (Rout, 2011). The temperature of all oil samples was estimated using Digital prima long thermometer, which is shown in Fig (3.6). The accuracy of the thermometer was ±1.0%, which measures the temperature that ranges from -20°C up to +100°C.

Fig.(3.6): Digital Thermometer

3.7 Acidity measurements

Determination of acid value of olive oil by using titrimetric method. The content of fatty acids was analyzed by measuring the acid value. Acid value of oil is defined as mg KOH required neutralizing 1 g oil dissolved in ethanol-ether mixture and titrated with standard KOH solution (AOAC 1997).

Procedure:

A) Preparation and standardization of 0.1 M ethanolic KOH solution:

1. About 0.56 g of solid KOH were transferred into a 100-mL volumetric flask and were dissolved in absolute ethanol.
2. A 0.204 g sample of dry primary standard KHP (Molar mass =204.22 g/mol) were accurately weighed and then transferred into a 250 mL conical flask and dissolved in ~ 50 mL of distilled water.
3. 3 drops of phenolphthalein indicator were added and the solution was titrated with KOH solution drop wise near the endpoint until a change in color from colorless to pink color was observed.
4. Steps 2 and 3 were repeated three times.
5. The average molar concentration of KOH solution was calculated.

$$KHP + KOH \rightarrow K_2P + H_2O$$

$$\text{Molarity of KOH} = \frac{weight\ of\ KHP\,(g) \times 1000}{204.22 \times ml\ of\ KOH} \qquad (3.1)$$

B) Preparation of ethanol-ether mixture:

1. 50 mL absolute ethanol and 50 mL ether were mixed in a conical flask.

2. 3 drops of phenolphthalein solution were added, and then titrated with ethanolic KOH solution to soft pink color.

C) Determination of acid value of oil:

1. 5g of olive oil samples were weighted in a conical flask.
2. 50mL ethanol – ether mixture with a concentration of 1:1 were added.
3. 3 drops of phenolphthalein were added.
4. The resulting solution was titrated with standard KOH with a permanent soft pink color that appears for a few seconds (Nierat *et al*, 2012).

Finally, the acid values of olive oil samples and free fatty acid (FFA) were determined according to equations (3.2 and 3.3):

$$\text{Acid value} = \frac{standerd\ solution\ KOH(ml) \times MolarityKOH \times 56.1}{weight\ of\ sample\ (g)} \qquad (3.2)$$

Acid value which is defined as mg KOH necessary to neutralize 1 g sample, also expressed in terms of % free fatty acids as oleic acid:

$$\%\ \text{FFA (as oleic acid)} = \frac{acid\ value}{1.99} \qquad (3.3)$$

Chapter Four

Results and Discussion

4.1 Fluorescence spectra results

Fluorescence spectroscopy technique was applied to resolve the pure spectra and energy gap for olive oil samples irrigated by different types of water. In this study, the emission spectra of olive oil samples of crop 2014 irrigated by different types of water with λ_{ex} = 350 nm and at room temperature were plotted in Fig. (4.1).

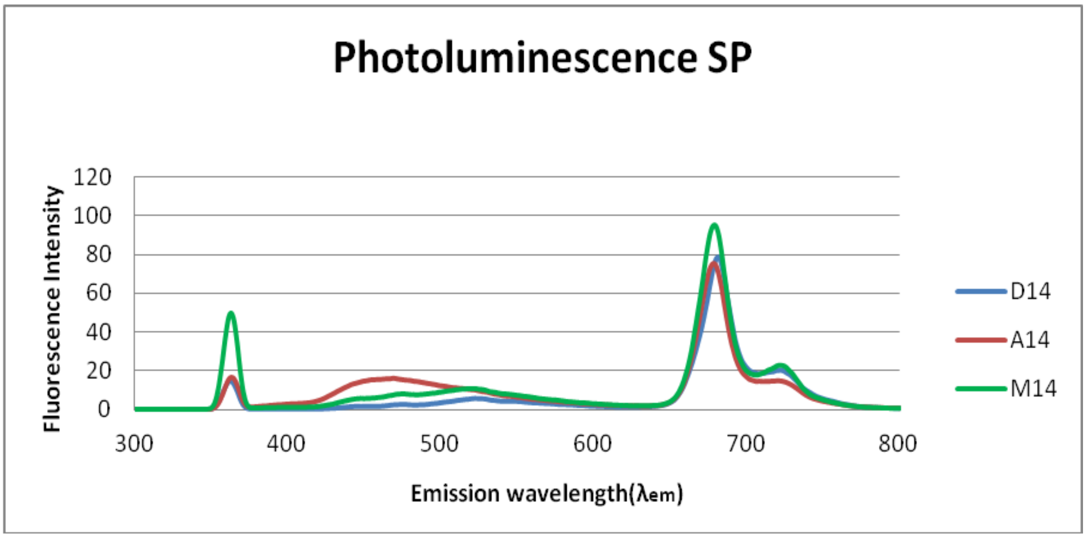

Fig. (4.1): Emission spectra of olive oil samples of crop 2014 irrigated by different types of water with λ_{ex} = 350 nm at room temperature.

Fluorescence spectra of olive oils contain information about fluorophores (tocopherols, phenolic compounds, and chlorophylls) that are important for oil quality (Eitenmiller *et al*., 2011; Ward *et al*., 1994; Undenfriend, 1962 ; Diaz *et al*., 2003; Tena *et al*., 2009; Tsimidou *et al*., 2003).

Table (4.1): The measured emission bands of olive oil samples irrigated by different types of water with λ_{ex} = 350 nm.

Region	**Type of irrigation**	**Samples**	**λ_{em} (nm)**	**Fluorescence Intensity**	**1st band (nm)**
Misseli 2014	Rain water	M14	362	49.862	350 – 430
Deir Sharaf 2014	Waste water	D14	362	14.791	
Anabta 2014	Reclaimed waste water	A14	363	16.570	
					2nd band (nm)
Misseli 2014	Rain water	M14	522	10.743	450 – 590
Deir Sharaf 2014	Waste water	D14	522	5.710	
Anabta 2014	Reclaimed waste water	A14	469	16.124	
					3rd band (nm)
Misseli 2014	Rain water	M14	679	85.432	600 – 750
Deir Sharaf 2014	Waste water	D14	681	78.973	
Anabta 2014	Reclaimed waste water	A14	678	75.422	

The emission bands of olive oil samples irrigated by different types of water with λ_{ex} (350 nm) are represented in table (4.1). The first band from 350 nm to 430 nm shows that the sample irrigated by rain water show the highest intensity (49.862). This indicates that this sample contains vitamin E more than the other two samples irrigated by other types of water. This oil is good and useful for eating. The second band from 450 nm to 590 nm shows that the sample irrigated by reclaimed waste water contains oxidized products from vitamin E more than the sample irrigated by waste water. (λ_{ex}= 350 nm) with maximum emission wavelength at 522 nm may partly originate from compounds of the vitamin E group, or their derivatives formed upon oxidation (Kyriakidis & Skarkalis, 2000).

Emission bands of olive oil samples at different excitation wavelengths were compared with other studies in table (4.2).

Table (4.2): Fluorescent components of olive oil with their emission bands.

Fluorescent component	$\lambda_{em.}$ (nm)	Reference
Chlorophylls	600 - 700	Duputy *et al*., 2005.
Vitamin E	300 - 350	Sikorska *et al*., 2005.
Phenols	300 - 390	Zandomeneghi *et al*., 2005.
Oxidized products from vitamin E	400 - 600	Duputy *et al*., 2005.

Table 4.3 shows that the olive oil sample irrigated by rain water contains vitamin E more than that for waste water and reclaimed waste water. This consistent with previous results. The olive oil sample irrigated by waste water contains chlorophyll a and b more than that for reclaimed waste water than that for rain water. Also, the olive oil sample irrigated by reclaimed waste water contains tyrosol and caffeic acid more than the other samples irrigated by the other two types of water. These results indicate that water contained organic matter and nutrients.

Table (4.3): Fluorescence properties of olive oil components in samples irrigated by different types of water at different excitation wavelengths.

Olive oil components		λex [nm]	λem [nm]	Fluorescence Intensity		
				M14	**D14**	**A14**
Vitamin E	α-Tocopherol	295	320	0.219	0.061	0.123
	β-Tocopherol	297	322	0.225	0.053	0.133
	δ-Tocopherol	297	322	0.225	0.053	0.133
	γ- Tocopherol	297	322	0.225	0.053	0.133
Chlorophylls	Chlorophyll *a*	436	668	6.177	18.047	6.504
	Chlorophyll *b*	405	669	13.719	42.397	17.824
Phenolic compounds	Vanillic acid	270	349	0	0.014	0.003
	Tyrosol	270	420	0.001	0.022	0.025
	Caffeic acid	270	457	0.005	0.035	0.038

Fig. 4.2 and table 4.4 represent the emission bands of olive oil samples from same region irrigated by rain water of different crops. The first band from 350 nm to 430 nm of olive oil samples of crop 2013 contains vitamin E more than sample of crop 2014. The second band from 450 nm to 590 nm of olive oil samples of crop 2013 contains oxidized products from vitamin E more than samples of crop 2014. The third band from 600 nm to 750 nm of olive oil samples of crop 2013 contains less chlorophylls than in crop 2014.

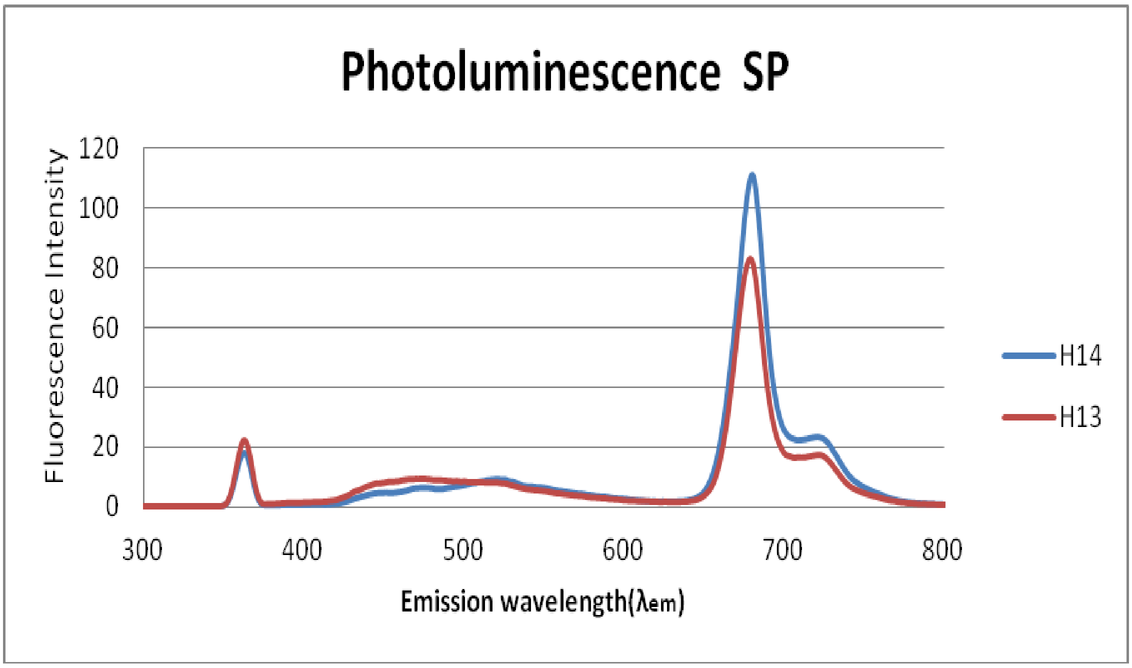

Fig (4.2): Emission spectra of olive oil samples (Hawara town) irrigated by rain water of crops 2014 and 2013 with λ_{ex} = 350 nm.

Table (4.4): The measured emission bands of olive oil samples irrigated by rain water of different crops with λ_{ex} = 350 nm.

Region	Type of Irrigation	Samples	λ_{em}(nm)	Fluorescence Intensity	1st band(nm)
Hawara 2014	Rain water	H14	362	17.976	350 – 430
Hawara 2013	Rain water	H13	362	22.234	
					2nd band(nm)
Hawara 2014	Rain water	H14	474	6.361	450 – 590
Hawara 2013	Rain water	H13	474	9.321	
					3rd band(nm)
Hawara 2014	Rain water	H14	680	111.009	600 – 750
Hawara 2013	Rain water	H13	679	82.799	

Table 4.5 shows the fluorescence properties at different excitation wavelength of olive oil samples irrigated by rain water of different crops. The most important result indicates that the sample of crop 2014 contains vitamin E more than sample of crop 2013.

Table (4.5): Fluorescence properties of olive oil components in samples irrigated by rain water of crops 2014 and 2013 at different excitation wavelength.

Olive oil components		λex [nm]	λem [nm]	Fluorescence Intensity	
				H14	**H13**
Vitamin E	α-Tocopherol	295	320	0.319	0.101
	β-Tocopherol	297	322	0.352	0.119
	δ-Tocopherol	297	322	0.352	0.119
	γ- Tocopherol	297	322	0.352	0.119
Chlorophylls	Chlorophyll *a*	436	668	8.143	10.547
	Chlorophyll *b*	405	669	29.819	56.921
Phenolic compounds	Vanillic acid	270	349	0.003	0
	Tyrosol	270	420	0.011	0.011
	Caffeic acid	270	457	0.044	0.063

4.2 UV-Visible Spectrophotometer results

4.2.1 The absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at room temperature.

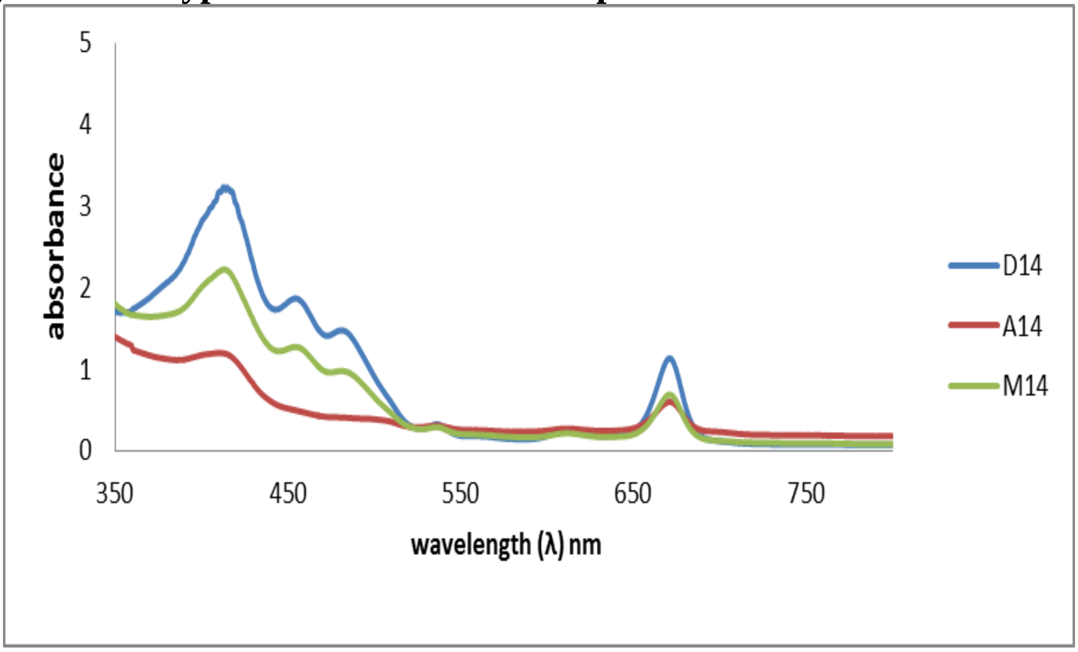

Fig. (4.3): Absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at room temperature.

Fig. 4.3 shows that the absorption spectra of olive oil samples of trees irrigated by different types of water. Over wavelength range (350-750 nm) the sample irrigated by waste water has high absorbance. These results indicate that the sample irrigated by waste water contains amount of chlorophyll more than other samples of trees irrigated by rain water and reclaimed waste water.

The absorption spectra of olive oil samples of crop 2014 of trees irrigated by different types of water at different temperatures are shown in appendix A. The results indicate that the samples irrigated by waste water, rain water and reclaimed water have high absorbance at low temperature (15-30°C), and at high temperature (35-50°C) the absorbance was low especially in samples of trees irrigated by waste water.

4.2.2 The absorption spectra of olive oil samples irrigated by different types of water at different temperatures of crop 2014.

The absorption spectra of olive oil samples of crop 2014 irrigated by waste water (D14) at different temperatures, are shown in Fig. 4.4.

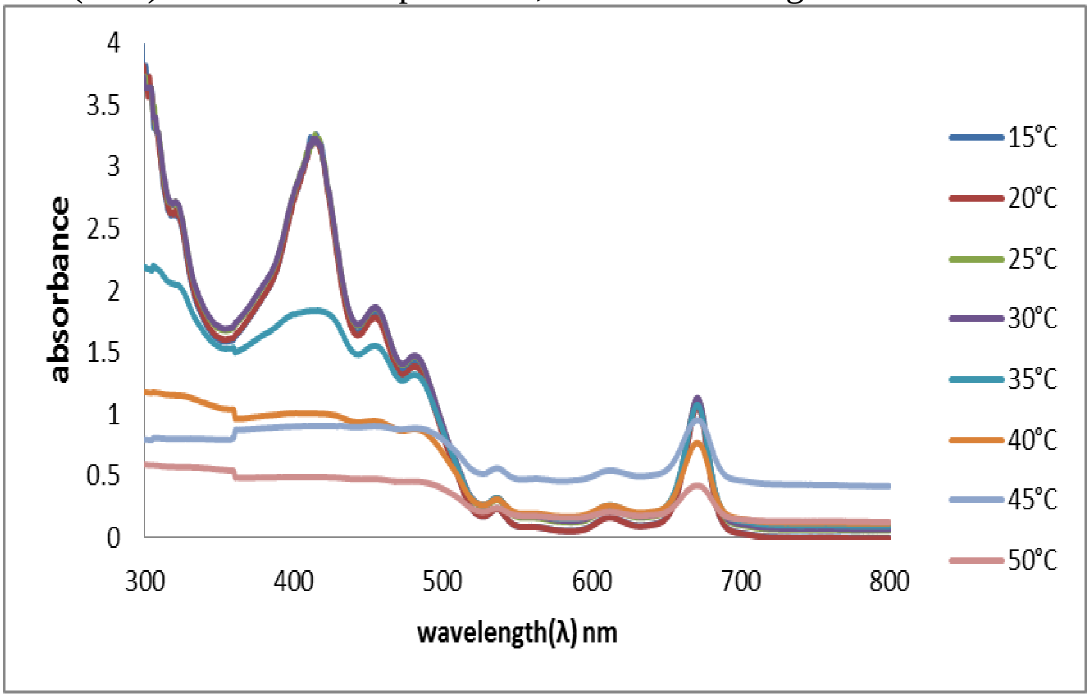

Fig. (4.4): Absorption spectra of olive oil samples (Deir-Sharaf) irrigated by waste water at different temperatures of crop 2014.

Absorption spectra of olive oil samples of crop 2014 irrigated by reclaimed water (A14) at different temperatures are shown in (Fig. 4.5).

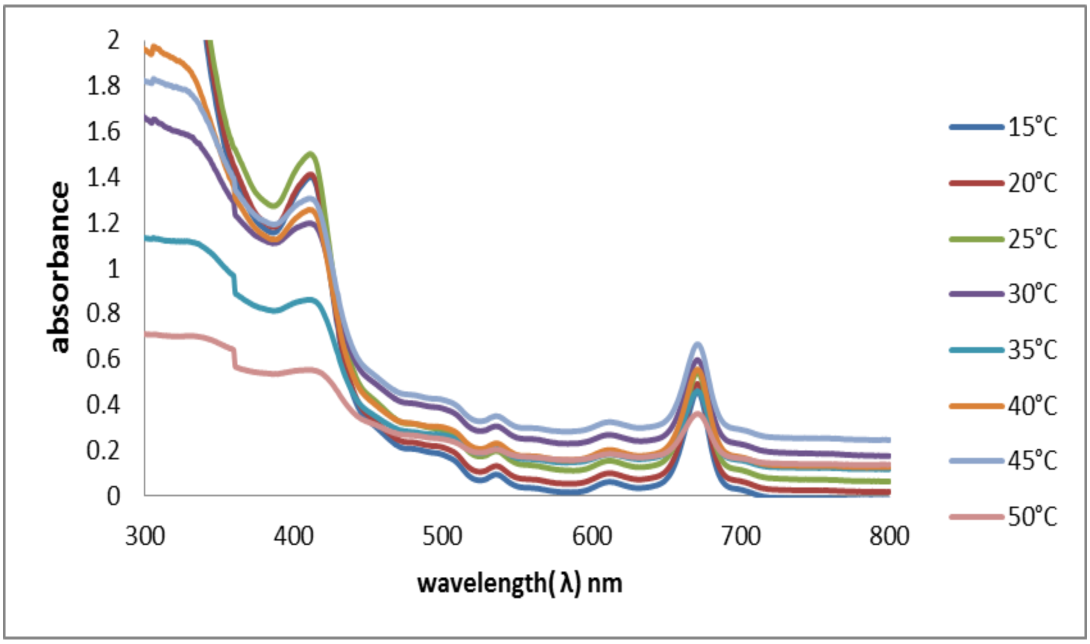

Fig (4.5): Absorption spectra of olive oil samples (Anabta) of crop 2014 irrigated by reclaimed water at different temperatures.

Absorption spectra of olive oil samples of crop 2014 from trees irrigated by rain water (M14) at different temperatures are shown in (Fig 4.6).

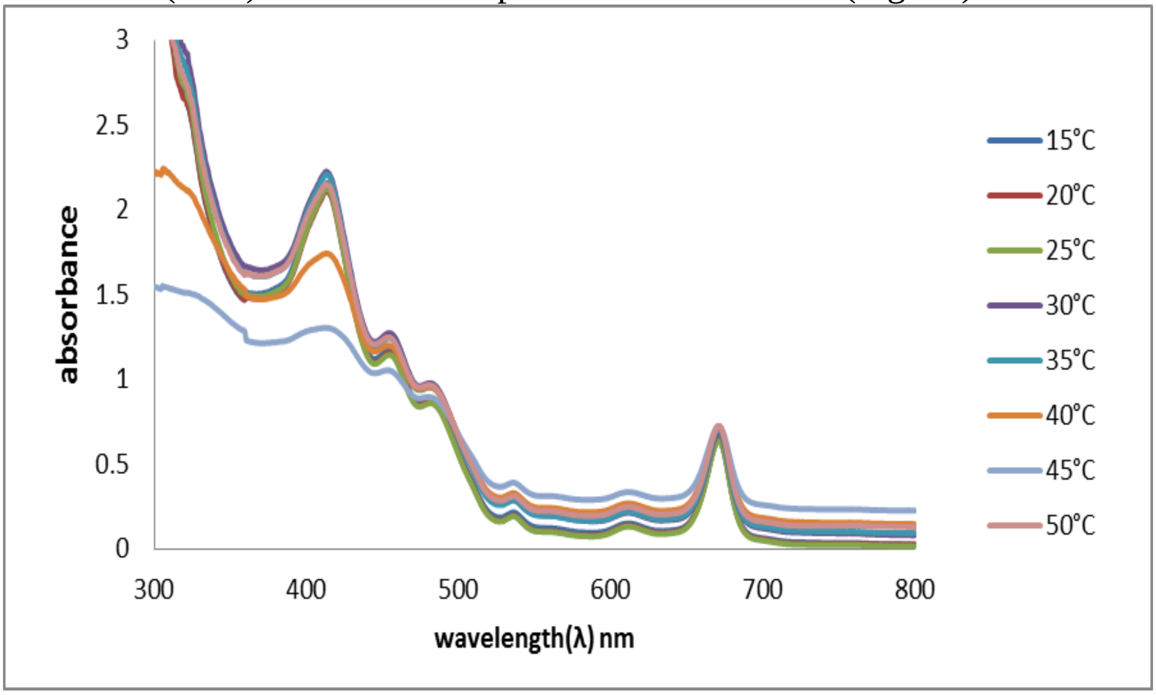

Fig (4.6): Absorption spectra of olive oil samples (Misseli village) irrigated by rain water at different temperatures of crop 2014.

Figs. 4.4-4.6 show the absorption spectra of samples irrigated by different types of water of crop 2014. All three samples irrigated by (waste, reclaimed and rain water) at low temperatures (15-35°C), have almost the same absorbance over wavelength range (380-480 nm). The absorption spectra of samples at high temperatures (40-50°C), have lower absorbance. This is because at high temperatures, the stability of phenolic compounds is affected by cracking the hydroxyl functional group and increase the acidity of samples.

4.2.3 The absorption spectra at different temperatures of olive oil samples of crops 2014 and 2013 irrigated by rain water.

Figs. 4.7 and 4.8 demonstrated the absorption spectra at different temperatures of olive oil samples of crops 2014 and 2013 respectively irrigated by rain water from Hawara town (H14).

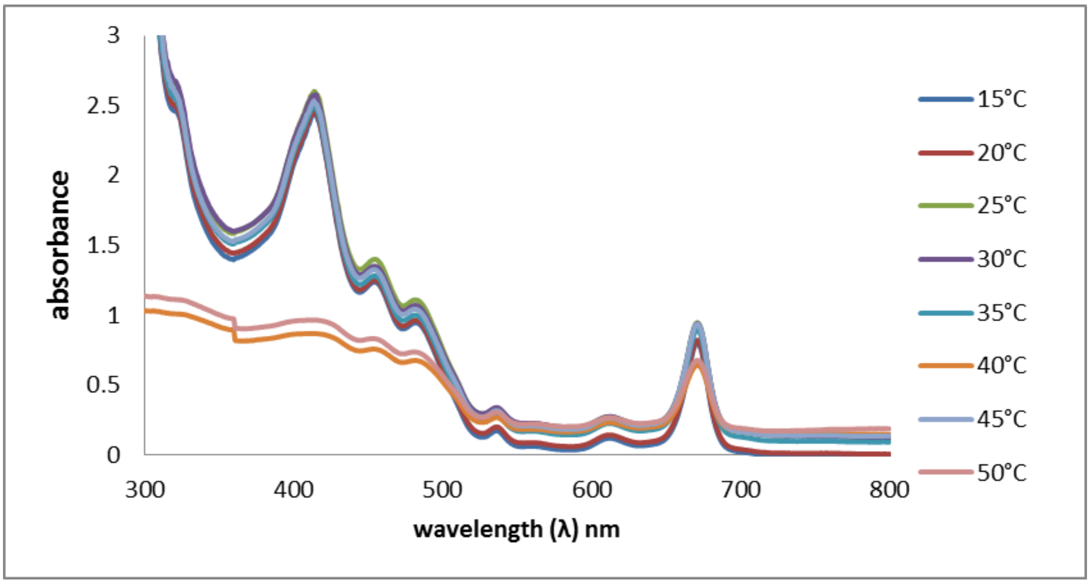

Fig (4.7): Absorption spectra at different temperatures of olive oil samples (Hawara town) of crop 2014 irrigated by rain water.

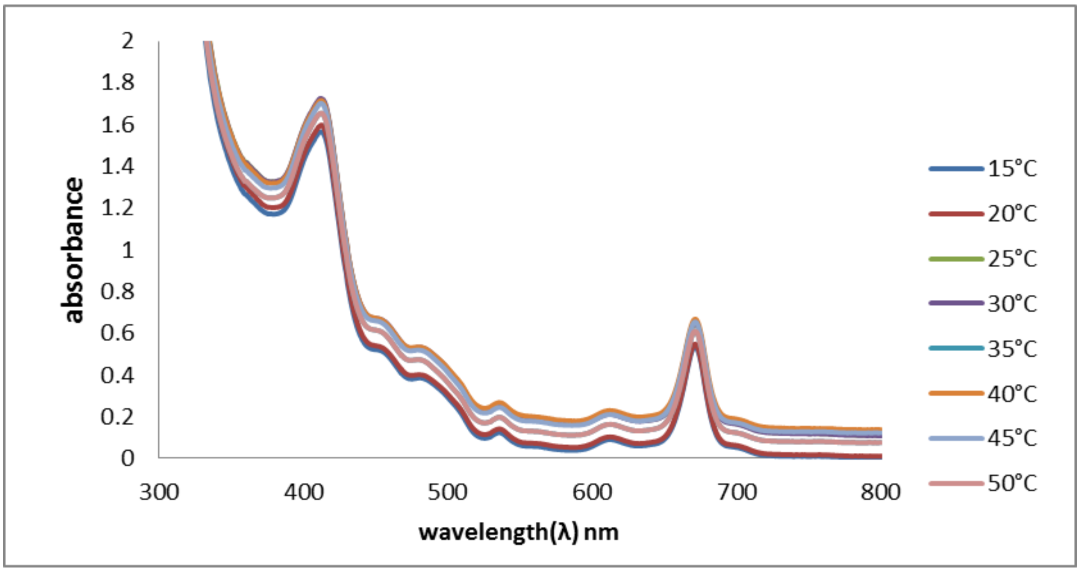

Fig (4.8): Absorption spectra at different temperatures of olive oil samples (Hawara town) of crop 2013 irrigated by rain water.

The olive oil sample of trees irrigated by rain water of crop 2013 have the same absorbance with almost the same wavelength at all different temperatures. The samples of crop 2014 showed the same spectra at low temperatures, but at high temperatures the absorbance decreases. The explanation for this behavior is that at higher temperatures the oil components will cracking in hydrogen bonding which producing new compounds with a new absorption wavelength, and increased accumulation of industrial pollutants.

4.3 The physical properties of samples of crop 2014 of trees irrigated by different types of water.

4.3.1 Viscosity results

The viscosity results in (cP) at different temperatures of olive oil samples of crop 2014 of trees irrigated by different types of water are shown in table (4.6).

Table (4.6): Measured viscosity of olive oil samples of crop 2014 of trees irrigated by different types of water.

Temperature (℃)	Viscosity in (cP) of D14	Viscosity in (cP) of A14	Viscosity in (cP) of M14
15.0	96.0	94.4	88.0
20.0	80.2	73.6	68.4
25.0	58.6	56.5	52.6
30.0	46.7	43.4	41.0
35.0	37.3	33.5	31.4
40.0	30.3	25.7	24.2
45.0	24.6	19.5	18.5
50.0	21.1	15.0	14.2

The relation between viscosity of olive oil samples and temperatures of trees irrigated by different types of water of crop 2014 is shown in Fig.(4.9).

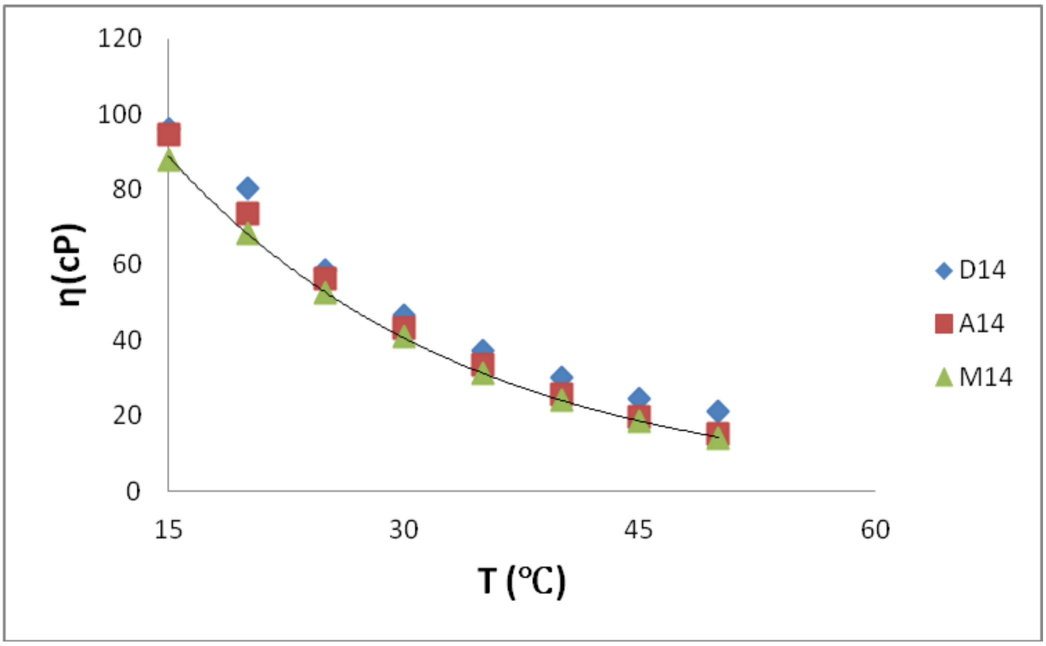

Fig.(4.9): The viscosity of samples at different temperatures of trees irrigated by different types of water of crop 2014.

The viscosity is inversely proportion to temperature as shown in Fig (4.9). This study demonstrated that the viscosity of olive oil samples of trees irrigated by waste water was higher than by reclaimed waste water than by rain water. Our measured viscosity of sample irrigated by rain water at 20°C was 68.4 cP, which was considered to be the standard for other different measurements. The small discrepancy in the values might be due to the influence of the fatty acid composition of olive oil. The viscosity is influenced by the wax content and composition which is affected by cultivar, crop year, and processing (Boskou, 2007).

4.3.2 Refractive index results

The refractive index results at different temperatures of olive oil samples of crop 2014 of trees irrigated by different types of water are shown in table (4.7).

Table (4.7): Measured refractive index at different temperatures of olive oil samples of crop 2014 with trees irrigated by different types of water.

Temperature (°C)	Refractive Index of D14	Refractive Index of A14	Refractive Index of M14
15.0	1.4675	1.4669	1.467
20.0	1.4671	1.4667	1.4664
25.0	1.4669	1.4665	1.4661
30.0	1.4666	1.4662	1.4659
35.0	1.4664	1.4659	1.4655
40.0	1.4662	1.4655	1.4652

The relation between refractive indices of olive oil samples and temperatures of trees irrigated by different types of water of crop 2014 are represented in Fig (4.10).

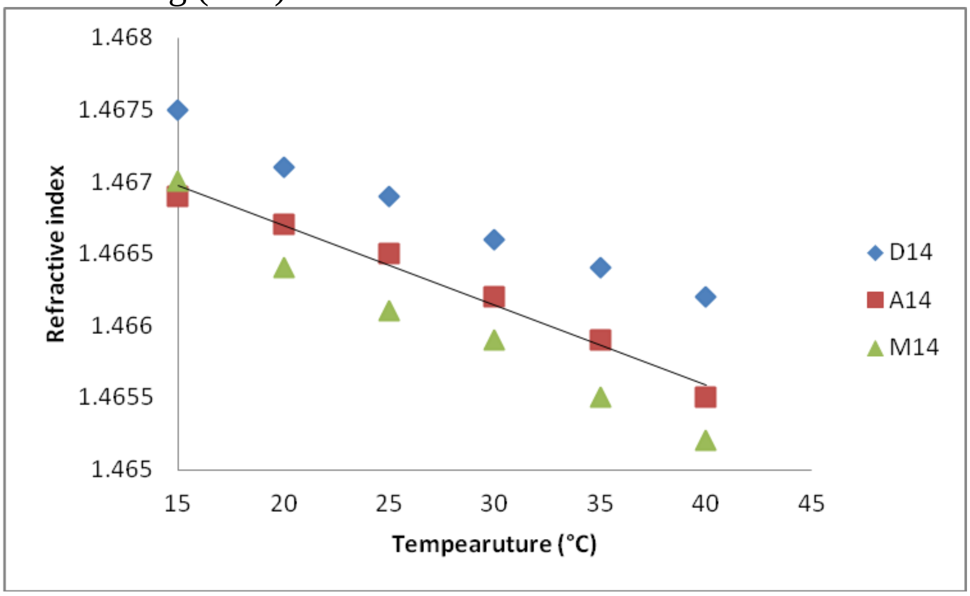

Fig.(4.10): Measured refractive index of olive oil samples of trees irrigated by different types of water at different temperatures of crop 2014.

Fig. 4.10 indicates that the refractive indices of olive oil samples of trees irrigated by waste water at different temperatures increased more than those for reclaimed waste water and for rain water. At 20°C our measured refractive index for sample irrigated by rain water is 1.4670, which is in the range of standard value (1.4677 - 1.4706) (Codex Standard, 2001). The refractive index is higher for sample irrigated by waste water.

4.3.3 Acidity results

The % acidity results of olive oil samples of trees irrigated by different types of water of crops 2014 and 2013 were measured. The data are shown in table (4.8).

Table (4.8): The % acidity results and classification of olive oil samples of crops 2014 and 2013.

Region	Type of irrigation	Sample	Crops	%FFA	Olive oil classification
Deir Sharaf	Waste water	D14	2014	3.79	Lampante oil
Anabta	Reclaimed waste water	A14	2014	2.95	Ordinary virgin olive oil
Misseli	Rain water	M14	2014	1.65	Virgin olive oil
Misseli	Rain water	M13	2013	2.32	Ordinary virgin olive oil
Hawara	Rain water	H14	2014	1.69	Virgin olive oil
Hawara	Rain water	H13	2013	2.32	Ordinary virgin olive oil

Acidity is expressed in terms of % free fatty acids (oleic acid). The acidity of olive oil is highest (3.79) for samples of trees irrigated by waste water of crop 2014 and classified as Lampante oil. The overall results in this study indicated that the acidity of the analyzed olive oil samples are also higher for samples irrigated by reclaimed waste water which were greater than samples irrigated by rain water of crop 2014. The values of acidity of olive oil samples of trees irrigated by rain water (1.65) and classified as virgin olive oil. The acidity of olive oil affected by different factors such as method and period of storage of oil, cultural techniques employed for oil extraction and irrigation system.

4.3.4 Mass density results

The mass density results in (g/cm^3) at different temperatures of olive oil samples of crop 2014 of trees irrigated by different types of water are shown in table (4.9).

Table (4.9): Measured mass density in (g/cm^3) at different temperatures of olive oil samples of crop 2014 of trees irrigated by different types of water.

Temperature (°C)	Density (g/cm^3) of D14	Density (g/cm^3) of A14	Density (g/cm^3) of M14
15.0	0.9225	0.9212	0.9167
20.0	0.9208	0.9196	0.9161
25.0	0.9156	0.9152	0.9123
30.0	0.9118	0.9121	0.9101
35.0	0.9086	0.9074	0.9061
40.0	0.9022	0.9046	0.9021
45.0	0.8986	0.9003	0.8973
50.0	0.8962	0.8988	0.8952

The effect of temperature on density of olive oil samples of crop 2014 of trees irrigated by different types of water, are shown in Fig. (4.11).

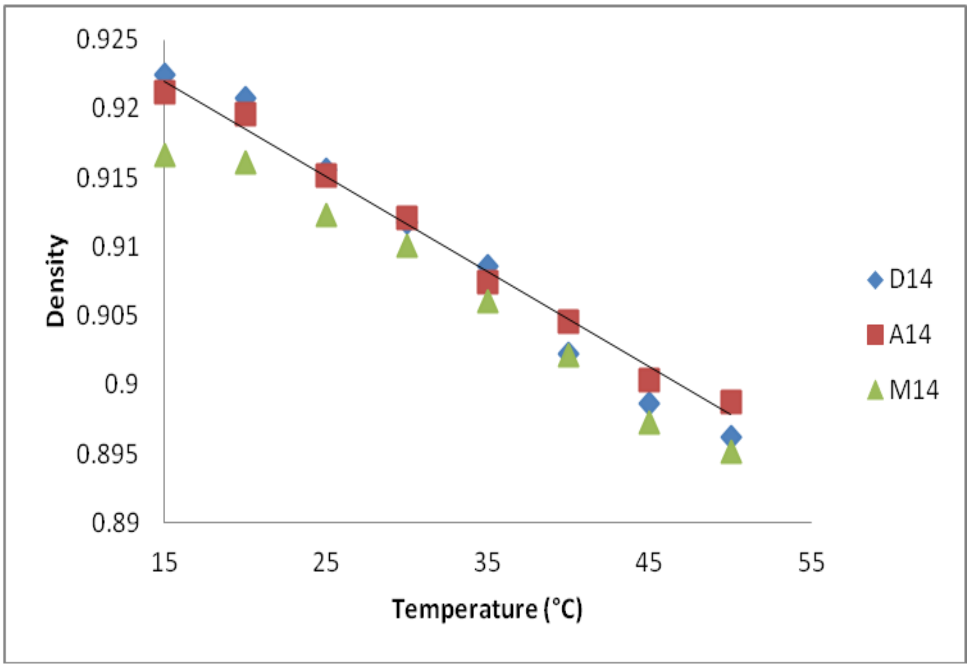

Fig.(4.11): The effect of temperature on density of olive oil samples of crop 2014 of trees irrigated by different types of water.

Fig. 4.11 shows that the densities of olive oil samples of trees irrigated by waste water and reclaimed waste water at different temperatures are higher than for samples irrigated by rain water. The densities decreased as the temperature increased. The measured density value for sample irrigated by rain water at 20°C was (0.9161) g/cm^3 which was in the range of standard values (0.910 – 0.916) g/cm^3 (Codex Standard, 2001). The highest value of the measured density at 20°C was 0.9208 g/cm^3 for sample irrigated by waste water, which was greater than the standard value (0.910 – 0.916) g/cm^3. The density of samples irrigated by waste water is higher than that of samples irrigated by rain water.

4.4 Comparing the physical properties of different crops of samples the same region irrigated by rain water.

The results for the physical properties of olive oil samples from same region of different crops irrigated by rain water are given in table (4.10).

Table (4.10): Measured viscosity, density, refractive index and acidity of olive oil samples (H14 and H13), of trees irrigated by rain water of crops 2014 and 2013.

Temperature (°C)	Viscosity(cP) of H14	Density in (g/cm^3) of H14	Refractive Index of H14	Acidity (%FFA) of H14
15.0	93.9	0.9167	1.4671	1.69 at room temperature
20.0	73.3	0.9161	1.4670	
25.0	55.8	0.9123	1.4667	
30.0	43.1	0.9101	1.4666	
35.0	33.4	0.9061	1.4665	
40.0	25.8	0.9021	1.4663	
45.0	19.9	0.8973	-	
50.0	14.8	0.8952	-	
Temperature (°C)	**Viscosity(cP) of H13**	**Density in (g/cm^3) of H13**	**Refractive Index of H13**	**Acidity (%FFA) of H13**
15.0	87.5	0.9164	1.4675	2.32 at room temperature
20.0	66.6	0.9157	1.4673	
25.0	50.8	0.9120	1.467	
30.0	38.8	0.9100	1.4668	
35.0	30.0	0.9058	1.4666	
40.0	23.0	0.9017	1.4664	
45.0	17.5	0.8962	-	
50.0	14.5	0.8935	-	

In this comparison, the viscosity of olive oil sample of trees irrigated by rain water of samples of crop 2014 is more than for sample of crop 2013. The differences in viscosity values may be referred to the differences in fatty acid composition of olive oil, storage age for the samples and the difference from one location to another according to their irrigation system

(Giap *et al*, 2009; Stanciu, 2012). The densities of samples irrigated by rain water of crop 2014 are more than samples of crop 2013. The refractive indices of samples irrigated by rain water of crop 2014 are more than samples of crop 2013. The acidity of olive oil sample irrigated by rain water of crop 2014 is (1.69) and classified as virgin olive oil. The acidity of olive oil sample irrigated by rain water of crop 2013 is (2.32) and classified as ordinary virgin olive oil. The storage period affects the oxidation of olive oil samples (Gharsallaoui *et al*, 2013).

Chapter Five

Conclusions

Determining the quality of olive oil using fluorescence technique was achieved for the first time in Palestine, according to our knowledge. This technique was applied to resolve the pure spectra and find a correlation between fluorescence spectra (λ_{em}) with oil samples, which changed by different irrigation types of water (rain water, reclaimed water and waste water).

- The results from emission spectra of olive oil samples show that irrigated by rain water contain vitamin E more than other samples irrigated by other two types of water. The olive oil sample irrigated by waste water contains chlorophyll a and b more than that for reclaimed waste water and than that for rain water.
- The results from absorption spectra of olive oil show that the sample of trees irrigated by waste water has high intensity over the wavelength range (380-480 nm). This indicates that the sample of olive oil of trees irrigated by waste water contains amounts of chlorophylls more than other samples of trees irrigated by rain and reclaimed waste water.
- The viscosities for the sample irrigated by waste water of crop 2014 were greater than the viscosities of olive oil irrigated by reclaimed water and rain water at different temperatures.

- The acidity of olive oil samples of trees irrigated by waste water of crop 2014 is (3.79%) and classified as Lampante oil. The acidity of olive oil samples of trees irrigated by rain water of crop 2014 is (1.69%) and classified as virgin olive oil.
- The densities of olive oil samples of trees irrigated by rain water for crop 2014 were lower than samples of trees irrigated by waste water for crop 2014 at different temperatures.
- The viscosities, densities and refractive indices of olive oil samples irrigated by different types of water decreased as temperatures increased.

Suggestions for future work

The following recommendations are suggested for the future works:

- Prepare a study to measure many samples of olive oil from other areas in Palestine that suffer from pollution in water and soil.
- To study the spectra of the olive oil samples at high temperatures then lower the temperature and study the spectra at low temperatures to see the impact of heating then cooling on the components of olive oil.
- To provide competent laboratories to evaluate olive oil quality in Palestine. For example fluorescence spectrometer, that has competent accuracy and sensitivity for the analysis of samples for effective results.

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Appendix A

A.1: The absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at measuring temperatures.

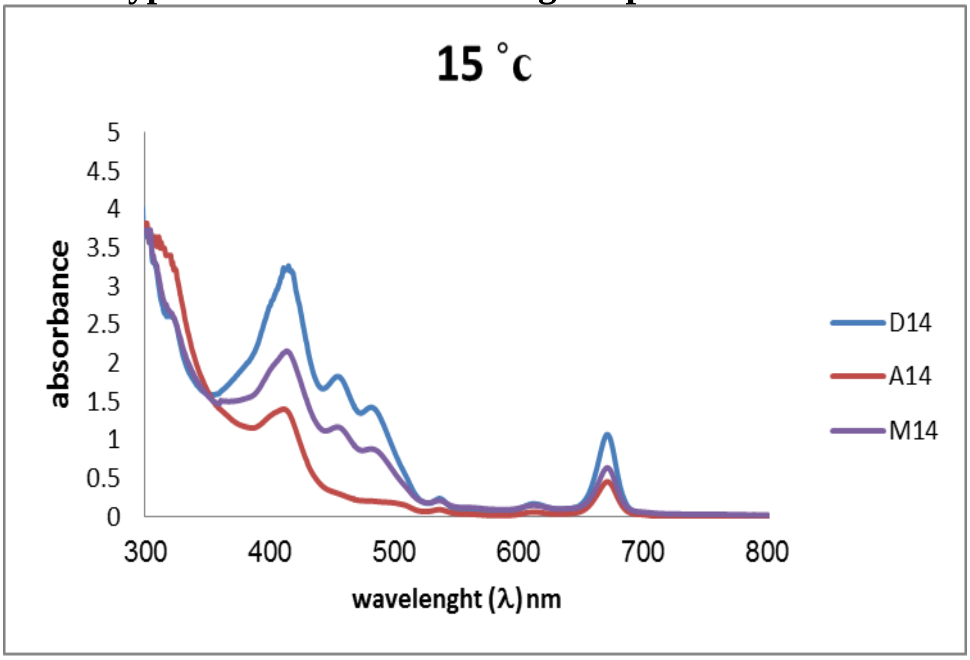

Fig (A.1.1): Absorption spectra of olive oil samples irrigated by different types of water at 15°C of crop 2014.

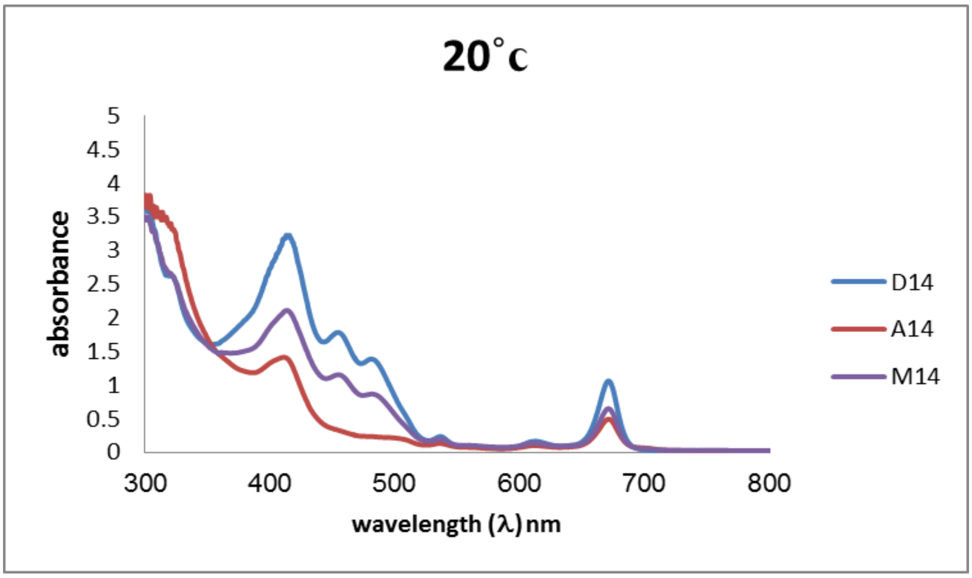

Fig (A.1.2): Absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at 20°C.

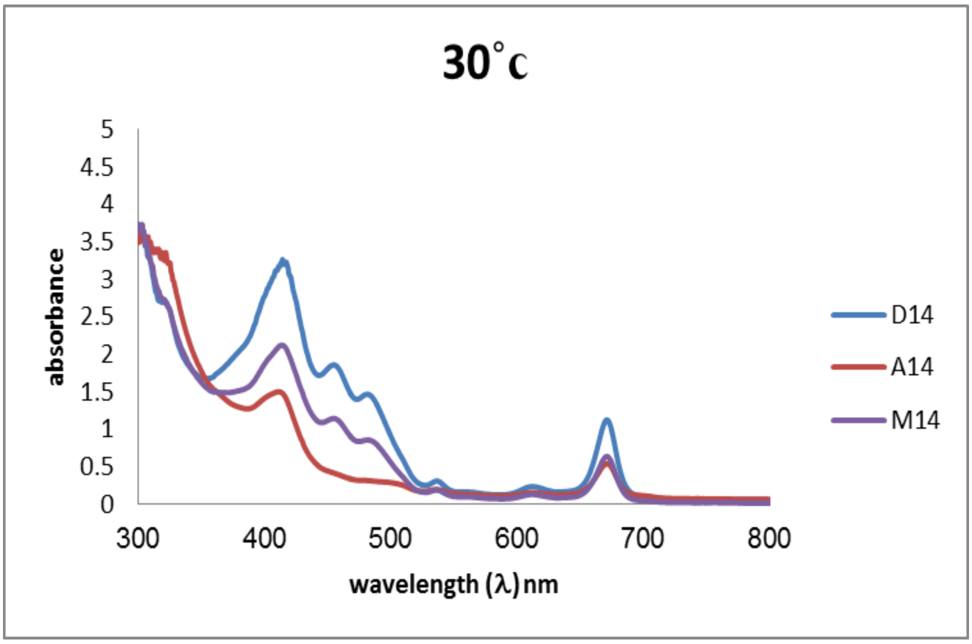

Fig (A.1.3): Absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at 30°C.

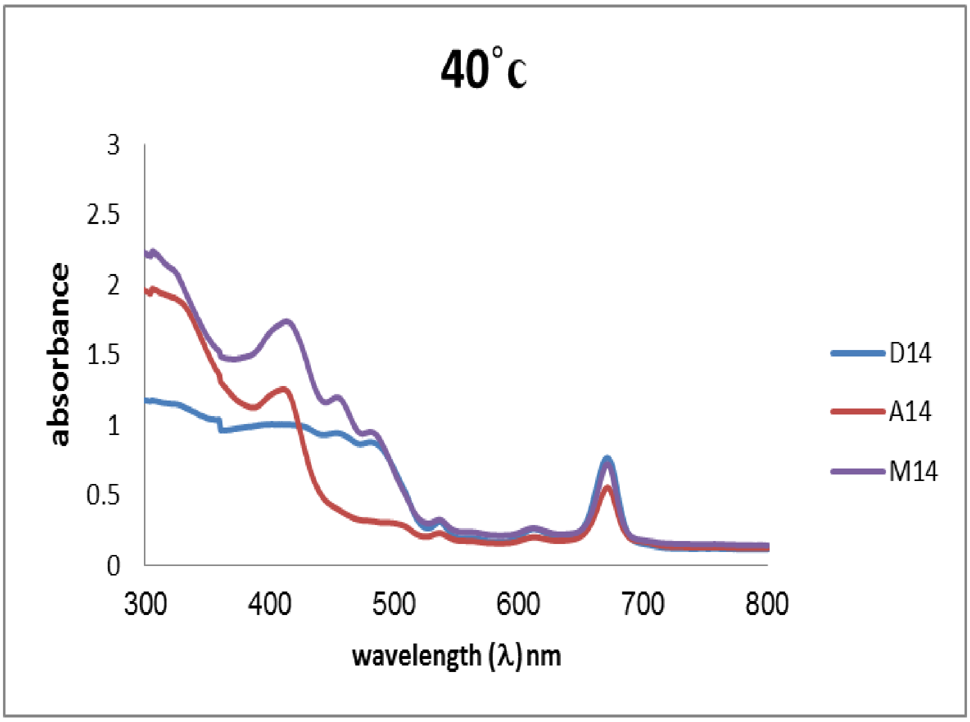

Fig (A.1.4): Absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at 40°C.

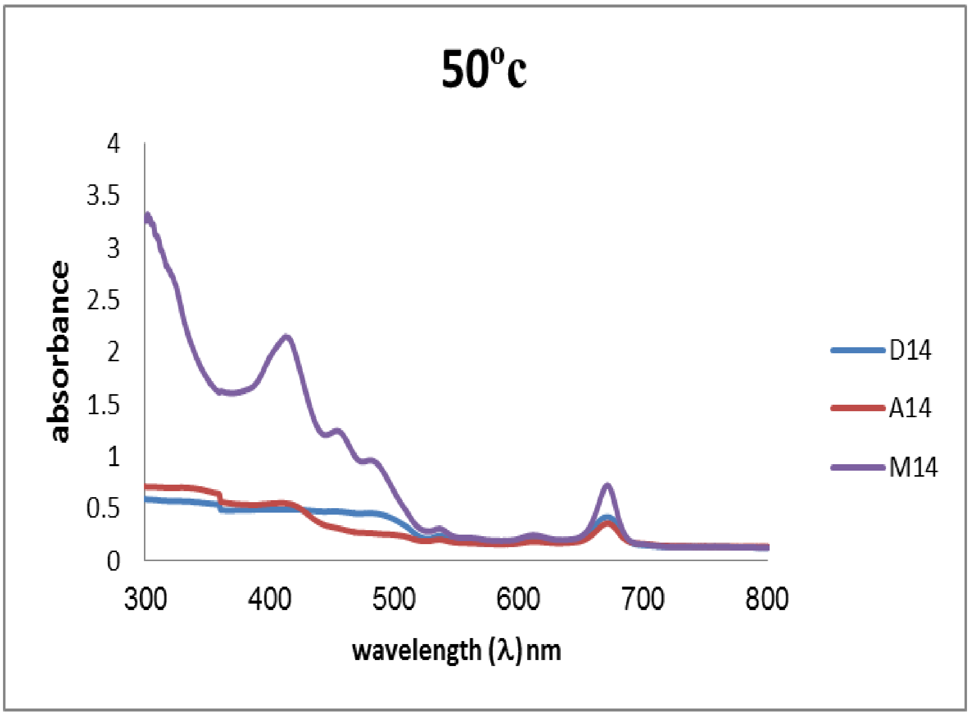

Fig: (A.1.5): Absorption spectra of olive oil samples of crop 2014 irrigated by different types of water at 50°C.

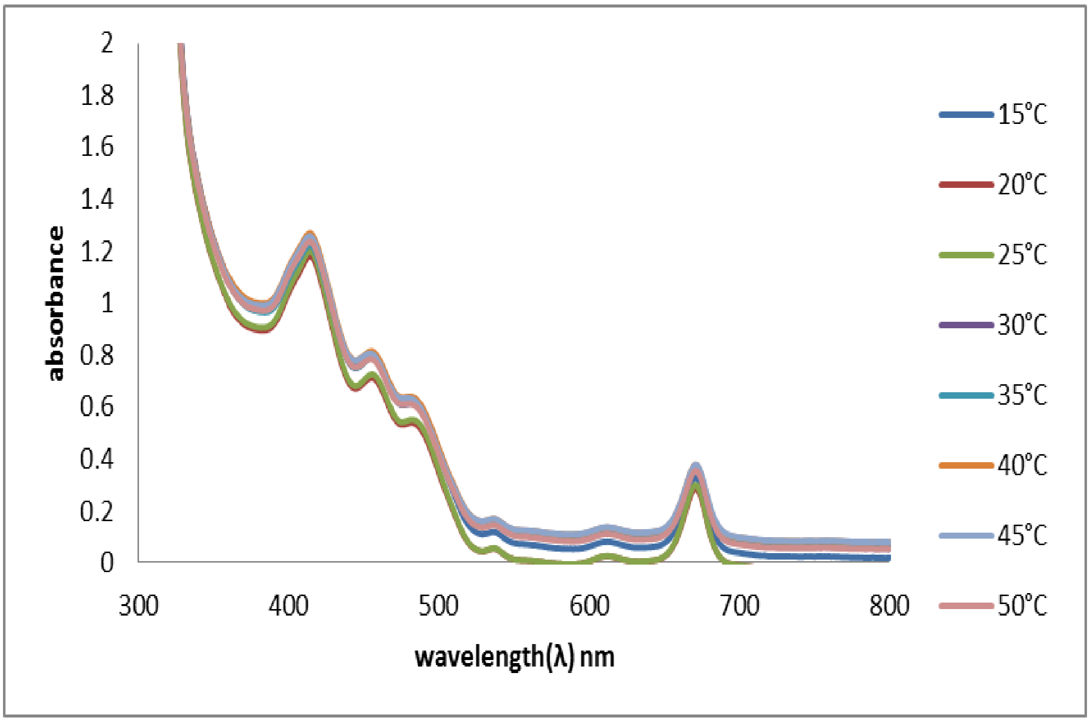

Fig (A.1.6): Absorption spectra of olive oil samples (Misseli village) of crop 2013 irrigated by rain water at different temperatures.

جامعة النجاح الوطنية
كلية الدراسات العليا

تقييم جودة زيت الزيتون من الأشجار المروية بمياه الصرف الصحي باستخدام تحليل المضان الطيفي

إعداد
ولاء عدنان عبد الرحيم دروبي

إشراف
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قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.
2016

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أ. د. عصام راشد عبد الرازق

الملخص

تركز هذه الدراسة على تأثير أنواع الرّي (مياه الأمطار ، مياه مكررة ، مياه الصرف الصحي) على زيت الزيتون الفلسطيني على انبعاث وامتصاص الاطوال الموجية باستخدام تقنية تحليل المضان الطيفي، بالإضافة إلى دراسة الخصائص الفيزيائية لعينات زيت الزيتون المروية بأنواع مختلفة: قياس اللزوجة، معامل الإنكسار، الحموضة والكثافة.

وأشارت نتائج أطياف انبعاث عينات زيت الزيتون أن عينة زيت الزيتون المروية بمياه الأمطار تحتوي على فيتامين E أكثر من عينات أخرى تروى بأنظمة رّي مختلفة. عينة زيت الزيتون المروية بمياه الصرف الصحي تحتوي على الكلوروفيل أ و ب أكثر من العينة المروية بمياه الصرف الصحي المعالجة وهذه بدورها أكثر من المروية بمياه الأمطار. بينت نتائج أطياف الامتصاص ان عينة زيت الزيتون من الأشجار المروية بمياه الصرف الصحي لديها كثافة عالية في نطاق الطول الموجي (480-380) نانومتر، وهذا يشير إلى أن عينة الزيت المأخوذة من أشجار مروية بمياه الصرف الصحي تحتوي على كمية كلوروفيل أكثر من عينة زيت مأخوذة من أشجار مروية بمياه الأمطار ومياه الصرف الصحي المعالجة.

أشارت نتائج الخواص الفيزيائية لعينات زيت الزيتون المروية بأنظمة رّي مختلفة الى ان اللزوجة لعينة زيت زيتون من أشجار مروية بمياه الصرف الصحي من محصول 2014 هي أكبر من لزوجة زيت الزيتون من أشجار مروية بأنظمة رّي أخرى. الحموضة لعينات زيت الزيتون من الأشجار المروية بمياه الصرف الصحي هي الأعلى (3.79 %). حموضة عينات زيت الزيتون من الأشجار المروية بمياه الأمطار من محصول عام 2013 هي أكبر من حموضة العينات المروية

بمياه الأمطار من محصول عام 2014. نتائج الكثافة لعينات زيت الزيتون من المحاصيل 2014 لديها أعلى قيمة.

هذه الدراسة هي الأولى من نوعها في فلسطين تم الاعتماد فيها على مطيافية المضان، وقد أعطت طريقة بسيطة وسهلة لتحديد جودة زيت الزيتون. وقد استخدم جهاز أطياف المضان لمعرفة ما إذا كان زيت الزيتون من حقول أشجار الزيتون المروية بمياه الامطار أو بمياه الصرف الصحي.