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Determination of Some Metallic Elements and their Effect on Physical Properties of Edible Olive Oil in Palestine

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Dedication

This thesis is dedicated to my parents, brothers, and sisters.

With respect and love.

Acknowledgement

I'd like to express my sincere appreciation to my supervisor, Prof. Issam Rashid Abdelraziq for his helpful efforts and continual encouragement. My thanks will be extended to my co- supervisor Dr. Mohammed Abu- Jafar, for his cooperation which helped me in the completion of this research.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Determination of Some Metallic Elements and their Effect on Physical Properties of Edible Olive Oil in Palestine

اقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص،باستثناء ما تمت الإشارة إليه حيثما ورد، وان 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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Date: التاريخ: 26/3/2015

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List of Abbreviations and Symbols

cP	Centipoise
cSt	Centistokes
DIR	Daily Intake Rate
E_a	Activation Energy
EIEB	Extraction Induced by Emulsion Breaking
EPA	Environmental Protection Agency
Eq.	Equation
ETA-AAS	Electro-Thermal Atomization Atomic Absorption Spectrometry
ETA-AS	Electro-Thermal Atomic Absorption Spectrometry
FAO	Food and Agriculture Organization
FFA	Free Fatty Acids
Fig.	Figure
FIA	Flow Injection analysis
g	Gram
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IOC	International Olive Council
J	Joule
K	Kelvin
N	Newton
Pa	Pascal
R	Gas Constant
RF	Radio Frequency
RfDo	Reference Dose Oral
rpm	Revolution Per Minute
s	Second
T	Temperature
TMAH	Tetra-Methylammonium Hydroxid
WHO	World Health Organization
WLF	Williams-Landel-Ferry
ρ	Mass Density
η_D	Dynamic Viscosity
η_k	Kinematics Viscosity

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Abstract

The physical properties such as: density, refractive index, viscosity, and acidity of samples of olive oil from different geographical locations and heights in Palestine were measured. The measured physical properties are in agreement with the international and local assigned value. The concentration of Al, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn elements in olive oil samples are measured by inductively coupled plasma mass spectrometry ICP-MS. It was found that Magnesium (Mg) is the most concentrated metal detected (294.7-783.0μg/g), followed by concentration of sodium (Na) (73.4-390.7μg/g) and potassium (K) (23.1 -168.9μg/g).

Concentrations of iron, copper and lead in Palestinian olive oil don't agree with concentration of International Olive Council (IOC). The differences in concentration in metals of olive oil depend on several factors among the type of olive tree, storage age, height and geographical location. There is a positive relation between the concentration of metals in olive oil and physical properties as density, refractive index, viscosity, and acidity.

The daily intake rate of these metals shows no risk to human health according to US Environmental Protection Agency (EPA) report.

Chapter One

Introduction

1.1 Olive Oil

Olive oil is a fat that is widely used in pharmaceuticals, cosmetic and cooking. Olive oil is popular in cooking due to its cholesterol lowering effect. Unlike animal fats that have cholesterol effect on humans (Llorent-Martinez *et al*., 2011; Zhu *et al.,* 2011).

The quality of olive oil depends on the regional conditions of the producing country. Freshness, storability and toxicity of olive oil can be evaluated by determining the levels of several trace metals in the oil (Zhu *et al.,* 2011).

Individual metals or metals compounds can affect human health. There are essential metals for human body like sodium, potassium, calcium, magnesium, iron, copper and zinc (Seiler *et al*., 1994). There are harmful elements like cadmium, chromium, lead, mercury, selenium and silver. These metals are called heavy metals which exist in the environment at low levels but if they accumulate in large quantities they become dangerous and cause many health problems (Martin and Griswold, 2009). It is important to determine the metals in olive oil and their concentration since olive oil is an essential component in our daily life.

Generally, plants, trees, workers and people living near industrial sites that use heavy metals or their components are getting the chance to be affected by these metals. Metals get into human body by ingestion (eating or drinking) or inhalation (breathing) (Martin and Griswold, 2009).

The effect metal levels appear in the oxidation rate of olive oil, which increases by increasing the levels of Fe, Mn, and Cu. The oxidation process may increase carcinogenic effect and develop pathological effects on the digestive system (Llorent-Martinez *et al.*, 2011; Zhu *et al.*, 2011).

1.2 Previous Studies

Vegetable oils are important for global nutrition and metals concentration can affect human health, so many researchers are interested in studying the edible vegetable oils. However, there are several studies on determination of metals in vegetable oil especially olive oil due to the evidence of its beneficial health effect.

There are some studies on determination of inorganic metals in edible olive oil according to geographical origin. Zeiner and his group determined the elements in edible olive oil from different geographical places in Croatia country by using ICP-AES to carry out the concentration of element in large amount. The ETA-AAS was used to determine the concentration of the element in small amounts in olive oil these elements are Al, Co, Cu, K, Mn and Ni. Zeiner found that the concentration of elements in small amount affected according to their geographical origin in Croatia (Zeiner *et al.*, 2005).

The extra virgin olive oil of different geographical places in Spain was studied by Cabrera and his group. The results showed that the differences in the concentration of Cu, Cr, Fe and Ni were according to geographical origin. The concentration of the metals was measured by ETA-AAS. Their study showed the dependency of the trace element content of extra virgin olive oil on their geographical origin, which can be used for their local characterization (Cabrera *et al*., 2012).

Robaina and his team determined the concentration of chromium (Cr) and manganese (Mn) in twelve samples of edible oils by using ETA-AS. The concentration was found for Cr about 66 ng/L and for Mn about 36 ng/L (Robaina *et al.*, 2012).

Benincase and his group studied the elements of Italian virgin olive oils from different regions aiming to develop a reliable method for traceability of the origin of olive oils. Benincase found that the ICP-MS afford a simple and rapid way to trace the geographical origin of olive oil (Benincasa *et al*., 2007).

A study done by Zhu and his group to determine the health risk of eight heavy metals Cu, Zn, Fe, Mn, Cd, Ni, Pb and As in edible vegetable oil by using ICP-AES. They observed that the concentration of iron (Fe) was the highest among other metals in the investigated samples, which was ranging between 16.2 to 45.3 µg/g. By measuring the dietary intakes of the heavy metals they found that the concentration that they got does not have any danger on human health (Zhu *et al.*, 2011).

Pehlivan and his group used ICP-AES to analyze edible vegetable oils, they found the highest metal concentration in virgin olive oil is for zinc (Zn) with concentration of 0.0523 µg/g (Pehlivan *et al*., 2008).

A method proposed by Cindric and his team to determine the inorganic metals in various edible oils. Cindric used ICP-AES for measuring the concentration of Fe, Mg, Zn, Ca and Na. Also they measured the concentration for Al, Cu, Co, Cr, K, Ni, Mn and Pb by using GFAAS. These methods were developed analytical procedure for oil characterization (Cindric *et al*., 2006).

Buldini and his team developed a procedure to determine some inorganic species in edible vegetable oil by using the ion chromatography technique (Buldini *et al*., 1997).

The change in concentration of inorganic metals such as Cu, Cd, Pb and Zn in the virgin olive oil according to the olive cultivars and period of harvest was studied by Angioni and his group. They used the ICP-OES. The only metal that affected the types and the stages of ripening olive was zinc. In addition to that, zinc and lead showed variability within cultivars (Angioni *et al*., 2006).

In Turkey, Bakircioglu and his team determined some elements in edible oils (olive oil, sun flower, hazelnut, canola and corn). ICP-OES was used to analysis the oil samples. The maximum concentration of elements was for iron 12.588 μg/g in hazelnut oil while in olive oil iron concentration was about 8.820 μg/g (Bakircioglu *et al.,* 2013).

Bakircioglu and his partners developed a new procedure only to determine zinc concentration in different types of edible oils. The procedure was extraction induced by emulsion breaking EIEB before determination by flow injection flame atomic absorption spectrometry (Bakircioglu *et al.*, 2014).

Sahan and his group determined a series of inorganic metals for ninety-two black and green olive samples using the inductively coupled plasma mass spectrometry ICP-MS. They obtained different concentrations for Mg, Fe, Zn, Sn and Pb in two types of black and green olive (Sahan *et al*., 2007).

Dugo studied the inorganic anion (Cl^-, F^-, Br^-, I^-) in seed oils and in olive oils produced from de-stoned olives and traditional extraction method carrying out the result by ion exchange chromatography. They obtained that the inorganic anions presence higher in olive oil from whole fruits than the pulp tissue specially the chloride anion (Dugo *et al*., 2007).

Savio and his partners studied the elements in edible oil from Argentine by using ICP-MS. The samples before analysis they solubilized with TMAH, the highest concentration in olive oil was antimony (Sb) element with concentration about 2.03μg/g (Savio *et al*., 2014).

ICP-MS was used by Beltran and his team to study elements transfer from soil to olive oil in south western Spain. They concluded that the elements concentration can be used for geographical traceability (Beltran *et al*., 2014).

Chen and his group developed a method to analyze only the level of copper in the edible oil sample. They used a graphite furnace atomic absorption spectrometer and diluted the sample with 2% lecithin-cyclohexane (Chen *et al*., 1999). Chen developed a method to study the concentration of arsnic in edible oil. The samples were diluted with n-heptane and then analyzed by a graphite furnace atomic absorption spectrometer (Chen *et al*., 2003).

In their study, Llorent-Martinez and his group used ICP-MS to investigate the element level in different types of vegetable oils from Spain. It was the first time in Spain vegetable oils analysis by ICP-MS after the microwave digestion and using a small amount of reagent 5 ml of NHO_3. The reagent reduced the potential environmental contamination and shortest treatment time. Llorent-Martinez concluded that the content of trace metals is related to the type of oil, and its production method (Llorent-Martinez *et al*., 2011).

Fasina and his team have measured the viscosities of 12 vegetable oils as a function of temperature from 5°C to 95°C. They observed that the viscosities of the samples were exponentially decreased with increasing the temperatures. The three models of Williams-Landel-Ferry WLF, power low and Arrhenin were used to describe the temperature effect on viscosity. The best fit of the data was given by WLF (Fasina *et al*., 2006).

In her study, Nierat determined the dynamic viscosity of olive oil samples from Palestine as a function of temperature. Nierat proposed three and multi-constants formulas to describe the relation between the viscosity and temperature (Nierat *et al*., 2014). Another study done by Abromovic and Klofular to measure the dynamic viscosity as function of temperature of different types of vegetable oils. The temperature range between 298.15K to 328.15K. They proposed empirical relations to describe the dynamic viscosity dependence on temperature (Abromovic and Klofular, 1998).

In his study, Stanciu proposed a polynomial or exponential dependence between viscosity and temperature of vegetable oil using the Andrade equation. The four constants equation was determined by the polynomial or exponential fitting (Stanciu, 2012).

Density of vegetable oils was studied by Rodenbush and his group. They developed a way to estimate the density of oil based on the fatty acid properties and oil composition, then from the density data they predicted the viscosity of oil (Rodenbush *et al*., 1999).

Density function of temperature was studied by Noureddini and his group for several types of vegetable oils. They presented correlation constants to calculate the density of oil in temperature range from 24°C -110°C (Noureddini *et al*., 1992). Biodiesel samples of different percentages of blend biodiesel and petrodiesel was studied by Ateeq. The density, refractive index, flash point and viscosity of the biodiesel are measured and compared with the standard values (Ateeq, 2015).

Acidity studies by Mariotti and Mascini, they proposed a method to determine the acidity of the extra virgin olive oil by flow injection FIA titration, and this method presented an interesting way to determine of free fatty acids in oil (Mariotti and Mascini, 2001).

In her study, Nierat proposed fitting equation to describe the relationship between the acidity and storage age of olive oil samples collected from different regions in Palestine (Nierat *et al*., 2014; Nierat, 2012). Bahti studied the acidity of olive oil from Palestine for different crops, he conclude that the acidity increased with storage age (Bahti, 2014).

Dobbou studied the effect of packing material and storage time on the quality of the olive oil. The results showed that the best storage material for olive oil is stainless container or dark glass (Dabbou *et al*., 2011).

1.3 Objectives

The aim of this work is to:

- Study the concentration of metals in edible olive oil from different geographical locations and heights in Palestine.
- Find a relationship between metal concentration in edible olive oil and storage age of the edible olive oil.
- Determine the physical properties of olive oil as density and viscosity as a function of temperature, also the refractive index and acidity of the olive oil samples from different geographical regions and different storage ages.

Chapter Two

Theoretical Formulation

In this chapter, we shall present the parameters used for our calculation, inductively coupled plasma mass spectrometry, density, refractive index, viscosity, viscosity as a function of temperature, percentage of Free Fatty Acids.

2.1 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry ICP-MS is a fast, accurate, and extremely sensitive analytical technique which is used for detecting and analyzing trace and ultra-trace elements. ICP-MS consists sample introduction part, ion generation in the ICP, plasma/vacuum interface plasma employs the ionization source, ion focusing, ion separation and measurement part.

The processes in the inductively coupled plasma mass spectrometry ICP-MS from sample introduction to mass analysis is represented by Fig.(2.1).

At the Beginning, samples introduced into plasma as aerosol droplets, and then plasma dries the aerosol and dissociates the molecules forming singly charged particles. These particles are directed towards the mass spectrometer mass filtering instrument.

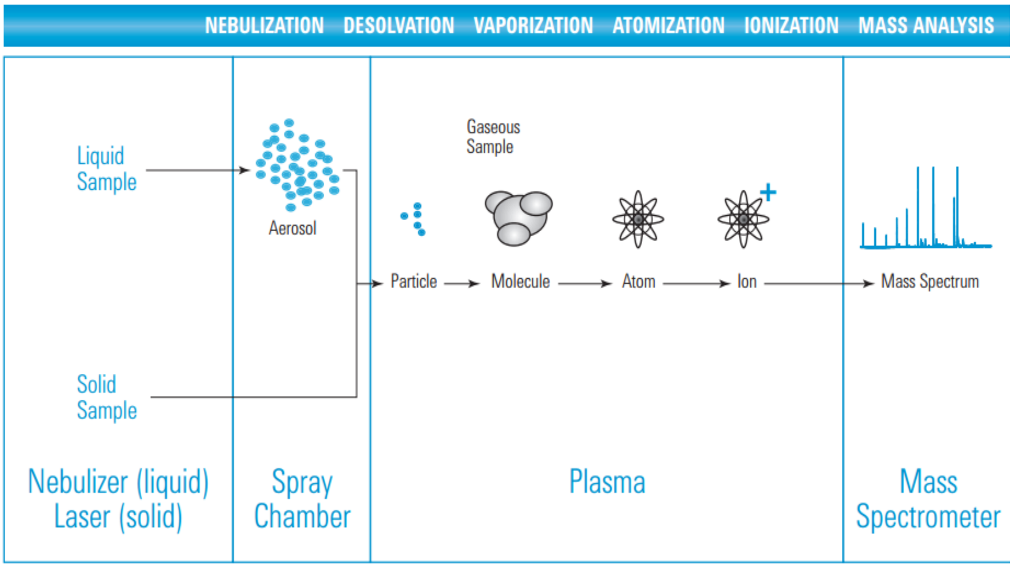

Fig. (2.1): The inductively coupled plasma mass spectrometryICP-MS processes (Agilent, 2005).

2.2 Density

Density of substance is the value of the mass in gram over the volume in cm^3. The density of virgin olive oil is about 0.910- 0.916 g/cm^3 at 20°C (Codex, 2001). Palestinian standard determines the density of virgin olive oil about 0.910 - 0.916 g/cm^3 at 20°C (PS188, 1997).

2.3 Refractive Index

Refractive index (n) is defined as the ratio of the speed of light in vacuum (c) to the speed of light in medium (v). Mathematically it can be written as (Avison, 1989).

$$n = \frac{c}{v} \tag{2.1}$$

According to codex standard for olive oil the refractive index at 20°C is about 1.4677-1.4706 this value for virgin olive oil (Codex, 2001).

Refractive index at 20°C for virgin olive oil according to Palestinian standard is about 1.4677-1.4705 (PS188, 1997).

2.4 Viscosity

One of the fundamental characteristic properties of all liquids is the viscosity. Viscosity is defined as the internal resistance of liquid to flow or shears. It can be defined as a drag force which determines the frictional properties of the fluid.

Viscosity of fluid can be affected by both temperature and pressure. There are two distinct forms of viscosity dynamic (Absolute) and kinematic viscosities (Viswanth *et al.*, 2007).

2.4.1 Dynamic Viscosity

Dynamic viscosity is determined as the ratio of shear stress to the rate deformation. The shear stress is defined as the force over cross section, where deformation is defined as the difference of velocity over a sheared distance (Viswanth *et al.*, 2007). The dynamic viscosity can be written as

$$\eta_D = \frac{\tau}{\gamma} \qquad (2.2)$$

Where η_D is the dynamic viscosity in Pascal-second (Pa.s), $\gamma = \frac{du}{dx}$ is the rate of deformation which also known as the shear rate with unit (1/s), and τ is shear stress with unit (N/m^2).

2.4.2 Kinematic Viscosity

Kinematic viscosity is defined as the ratio of dynamic viscosity to mass density (ρ) of liquid at that temperature and pressure. Kinematic viscosity is represented by the following equation (Viswanth *et al.*, 2007).

$$\eta_k = \frac{\eta_D}{\rho} \tag{2.3}$$

Where η_k is kinematic viscosity in centistokes (cSt).

The liquids flow depends on viscosity so the liquids divided into two categories: Newtonian and non-Newtonian liquids.

a- Newtonian liquid is defined when the viscosity of liquid does not change remains constant, and it is independent of the applied shear stress.

b- Non-Newtonian liquid is defined when viscosity depending on the applied shear force and time (It changes at different shear rate) (Viswanth *et al.*, 2007).

Non-Newtonian has two groups. The first one is "the time independent" in which the viscosity does not change as function of time when it is measured at a specific shear rate (James, 1996). An example of time independent is pseudoplastic material like olive oil (Akhtar *et al.*, 2009; Giap *et al.*, 2009).

The second is "the time dependent" where the viscosity of fluid changes as a function of time, an example of that is the thixotropic materials like yogurt (James, 1996).

2.5 Viscosity as a Function of Temperature

The Arrhenius type relation was used to fit the effect of temperature on dynamic viscosity which is given as (Fasina *et al.*, 2006).

$$\eta_D = \eta_{\infty,T}\, e^{\frac{E_a}{RT}} \tag{2.4}$$

Where $\eta_{\infty,T}$ is the viscosity at infinite temperature in unit (Pa.s), E_a is the activation energy in unit (J/mol), R is the gas constant in unit (J/mol.K), and T is the absolute temperature in Kelvin (Fasina *et al.*, 2006; Giap *et al.*, 2009).

Arrhenius relationship has failed to give real representation phenomena for all fluids, because of the complex nature of fluid. There are large deviation in measured viscosity and theoretical calculation of viscosity (Viswanth *et al.*, 2007).

There are several researchers who proposed alternative equations to describe the viscosity as function of temperatures like De-Guzman, Duhan, Abramovic, Klofutar and Andrade.

2.5.1 Two Constants Relation

De-Guzman proposed a relation for the viscosity as function of temperature, which is (De-Guzman *et al.*, 1913).

$$\eta_D = Ae^{\frac{B}{T}} \tag{2.5}$$

Where A and B are positive constants.

Equation (2.9) was used in logarithmic form by Duhan, which is (Duhan, 1979).

$$\ln \eta_D = A` + \frac{B`}{T} \tag{2.6}$$

A` and B` are constants.

The effect of temperature on dynamic viscosity is also studied by Abramovic, that he proposed the following relationship (Abramovic and Klofutar, 1998).

$$\log \eta_D = \frac{A}{T} - B \tag{2.7}$$

Where A and B are constants evaluated for olive oil to be A = 1558.2 K and B = 3.433.

2.5.2 Three Constants Relation

Abramovic used Andrade relationship to form three constants equation to describe the relation between viscosity and temperature, which is represented mathematically by the following equation.

$$ln\,\eta_D = A + \frac{B}{T} + CT \quad (2.8)$$

A, B and C are constant evaluated by Andrade for olive oil to be A is -32.72, B is 7462.27 K and C is 0.04 K^{-1} (Abramovic and Klofutar, 1998; Andrade, 1930).

2.6 Percentage of Free Fatty Acids (%FFA)

There are many factors that affect the fatty acid composition in olive oil like the maturity of fruit, cultivar, climate, and altitude. The degree of acidity (free fatty acid) depends on the degree of breaking down of triacylglycerols which is one of olive oil components (Boskou, 2006).

International olive council (IOC) established standards of olive oil according to the limit of the percentage of free fatty acid (% FFA) in the oil which is given in Table (2.1) (IOC, 2015).

Table (2.1): Classification of olive oil

Category	**% FFA**
Refined Olive Oil	< 0.3
Extra Virgin Olive Oil	≤ 0.8
Virgin Olive Oil	≤ 2.0
Ordinary Olive Oil	≤ 3.3
Lampante Oil	> 3.3

Chapter Three

Methodology

The olive oil samples used in this study were collected from six different Palestinian regions (Yatta, Yasid, Meithalun, Saida, Allar, Jenin) and produced in Palestinian mills for olive oil from the crop of 1997 to 2012.

The entire samples were kept at the same conditions at room temperature in dark place and packed in closed plastic bottles. The concentration of metals in edible olive oil samples from different regions and different ages were determined by using the inductively coupled plasma mass spectrometry ICP-MS.

The viscosities of all samples were measured as function of temperatures from 15°C to 45°C. The densities of all samples were measured at temperature 28°C. The densities of Yatta crop 2012, Yasid crop 2011, Meithalun crop 2010, Saida crops 1997and 2012, Allar crop 2012 and Jenin crop 2010 samples were measured as function of temperature from 15°C to 50°C. Refractive indices of all samples were measured at two different temperatures at 28.7°C and at 35°C.

Titration method was used to measure the % FFA of all olive oil samples from different ages and regions.

The concentration of metals in olive oil samples and the physical properties of olive oil (viscosity, density, refractive index and FFA) were discussed to find a relation between them.

3.1 Experimental Apparatus

3.1.1 Inductively Coupled Plasma Mass Spectrometer ICP-MS

The quality and quantity of metals in edible olive oil was measured by using Perkin Elmer Elan 9000 ICP-MS. It is a powerful device that has the ability to detect and quantify up to 70 elements of periodic table from different types of samples like water, or soil. ICP-MS detects the elements at parts per-trillion level. Fig.(3.1) shows the Perkin Elmer Elan 9000 device.

Fig. (3.1): Perkin Elmer Elan 9000 ICP-MS

ICP-MS instrument consist of several parts; sample introduction, ion generation, vacuum interface (plasma), ion focusing, and finally mass spectrometer. We shall discuss each part separately.

3.1.1.1 Sample Introduction Part

All the samples that are typically introduced into the ICP-MS system are liquids. Liquid samples require breaking into small droplets they are called aerosol before they can be introduced into the argon plasma. The small droplets are produced by passing the sample through pneumatic nebulizer (Agilent, 2005).

3.1.1.2 Ion Generation in the ICP

The aerosol is passed into the plasma, plasma is generated by passing argon through a series of concentric quartz tubes that are called ICP torch, which are wrapped at one end by a radio frequency (RF) coil. A RF generator produces a high frequency current, which creates an intense magnetic field that causes collisions between free electrons and argon atoms, producing ions and more electrons. During the travel of aerosol droplets into the plasma, they are rapidly dried, decomposed, vaporized and atomized. They are ionized by the removal of one electron from each atom (Agilent, 2005).

3.1.1.3 Plasma/Vacuum Interfaces

The positively charged ions that are produced in the plasma are extracted by a pair of interface cones in a vacuum system. These cones are metal plates allowed the ions to pass through it. The interface cones have typically 1mm diameter or less.

3.1.1.4 Ion Focusing

as the ions pass through the vacuum system there are electrostatic lenses keep the ions focused in a compact ion beam until the ions receive to the final chamber, where the mass spectrometer (MS) and detector (Agilent, 2005).

3.1.1.5 Mass Spectrometer

It is used to detect the ions produced by ICP. Mass spectrometer works as mass filter to isolate a specific mass-to-charge ratio ($\frac{m}{q}$) ion from the multi ion beam. The individual ion beam that has specific charge will be directed to the detector to measure the individual ion currents. The ion current magnitude is proportional to the analyzer ion population from the multi ion beam.

3.1.1.6 Ion Detection Part

The detector counts and stores each mass to charge ($\frac{m}{q}$) signal then create a mass spectrum. The spectrum gives a qualitative identification of molecule that measured and the magnitude of each peak in the spectrum provides quantitative result the concentration of elements in sample (Taylor, 2001).

3.1.2 Density Apparatus

The densities of samples were determined by using 10-mL volume pycnometer. The density determined by measuring at first the mass of pycnometer when it is empty, and then measuring the mass of pycnometer when full with olive oil. The difference in masses divided by 10 gives the density of the olive oil sample. Fig.(3.2) shows the pycnometer and HR-200 analytical balance apparatus.

Fig. (3.2): Pycnometer and HR-200 analytical balance

The pycnometer mass was measured by using HR-200 analytical balance with accuracy of $\pm$ 0.00005.

3.1.3 Refractive Index Apparatus

Refractive index of the olive oil samples was determined by using a digital apparatus the way 2sABBE at two different temperatures at 28.7°C and at 35°C. The accuracy of this apparatus is $\pm 0{,}0002$, Fig(3.3) shows the way 2sABBE device.

Fig. (3.3): A digital refractometer the way 2sABBE

3.1.4 Viscosity Apparatus

Viscosity at different temperatures was measured by using the digital rotational viscometer DV-I and the UL-ADAPTER. The digital viscometer has seven spindles and different rotational speeds. The spindle zero was used for measuring the viscosity of olive oil sample, and set at rotational speed 60 rpm. The spindles have ability to measure viscosity range from 100 to 13,300,000 cP with accuracy ± 1%. While the UL- ADAPTER has ability to measured viscosity range from 1 to 2000 cP (Brookfield, 1999). Fig.(3.4) shows the DV-I viscometer device.

Fig.(3.4): DV-I viscometer

3.1.5 Free Fatty Acids Measurement

Free fatty acids FFAs of olive oil samples were measured by a recommended method which is the titrimetric method (Horwitz, 2000).

Acid value FFAs was calculated by finding the mass of KOH (mg units) that is needed to neutralize one gram of oil sample which is dissolved in ethanol ether mixture, and by standard KOH solution which titrates the mixture.

The following three major steps are needed to calculate the acidity value.

Step one: The preparation of KOH solution with 0.1 molarity.

- Exactly 0.56 g of KOH is transferred into 100-mL volumetric flask, KOH in a solid form is dissolved in absolute ethanol.
- In 50 mL of distilled water 0.204 g of dry primary standard KHP is dissolved in 250 mL conical flask.
- 3 drops of phenolphthalein is used to titrate the dissolved KOH. The KOH changes from colorless to pink color.
- The last 2 steps were repeated 3 times. The average of KOH molarity was taken, which calculated from the following relation:

$$KOH\ molarity = \frac{KHP\ weight\ \times 1000}{Molecular\ weight\ of\ KHP \times KOH\ volume(ml)}$$

Step two: Preparation of ethanol-ether mixture.

- In conical flask 50 mL of ether is mixed with 50 mL of ethanol. Three drops of phenolphthalein are added to the mixture, and then the mixture is titrated with ehanolic KOH until reaches the pink color.

Step three: Calculation the acid value.

- In 250-mL conical flask weight 5 mg of olive oil sample and then 50 mL of ethanol ether is transfered to the conical flask, next three drops of phenolphthalein added.
- The solution of oil in ethanol-ether mixture is titrated by ehanolic KOH until the solution reaches the pink color.
- The acid value is determined by the following relation :

$$Acid\ value = \frac{volume\ of\ KOH(ml) \times Molarityof\ KOH \times 56.1}{wt.of\ sample\ (g)}$$

Free fatty acid percentage calculated by:

$$\%\ FFA = \frac{Acid\ value}{1.99}$$

3.2 Sample Preparation

ICP-MS technique requires preparing the sample before entering the analysis system to determine the concentration and the types of metals in the sample. The way that is used in this study is the digestion by nitric acid (HNO_3).

- A 0.5 g of olive oil sample is transferred into special tubes (These tubes can bear the heat).
- A 2 mL of NHO_3 is transferred into the tube, next all the tubes were placed at the heater 5 minutes at 70°C to remove the entire vapor in the tubes before closing them.
- The tubes were closed with stoppers, and the temperatures of the tubes increased from 75°C to 100°C gradually 2 degree each hour. The final step was adding hydrogen peroxide (H_2O_2) to the tubes. The temperatures of the tube increased from 75°C to 100°C gradually 2 degree each hour. Finally the olive oil samples were ready to be inserted into ICP-MS device to determine the elements concentration.

3.3 Daily Intake of Metals Calculation

The concentration of metals is essential for evaluating the potential dietary toxicity of olive oil which evaluated by determination of daily intake of metals, there are several health problems that can be developed as a result of excessive uptake of dietary metals. The daily intake rate (DIR) of metals that olive oil supply to human body can be calculated by the following relation (Orisakwe *et al.*, 2012)

$$DIR = \frac{M_C\ (\mu\text{g/g})\ \times\ D_i(\text{kg/person})}{M(\text{kg})} \qquad (3.1)$$

Where M_c is metal concentration in olive oil (μg/g), D_i is daily intake of olive oil (kg/person), and M is average body mass in (kg). Table (3.1) represents the reference dose oral (RfDo) values, these values were used to generate guideline values (daily intake of metals) for the metals analyzed (EPA, 2015).

Table (3.1): The reference dose oral (RfDo) values for metals

Metal		**RfDo (μg/g.day)**
Aluminum	Al	1
Cadmium	Cd	$1X10^{-3}$
Copper	Cu	$4\ X10^{-2}$
Iron	Fe	$7\ X10^{-1}$
Manganese	Mn	$2.4\ X10^{-2}$
Nickel	Ni	$2\ X10^{-2}$
Lead	Pb	$3.57\ X10^{-3}$
Zinc	Zn	$3\ X10^{-1}$

Chapter Four

Results and Data Analysis

4.1 Physical Properties

The results of measured physical properties are presented in this chapter, density, refractive index, viscosity and FFAs.

4.1.1 Density

The densities of olive oil samples from different regions and different storage ages were measured at temperature 28°C and represented in Table (4.1).

Table (4.1): The measured density for the different olive oil samples

City	Region	Altitude (m)	Storage age(year)	Density (g/cm^3)
Hebron	Yatta	818	2	0.91068
Nablus	Yasid	698	3	0.91784
Jenin	Meithalun	382	7	0.91241
	Meithalun	382	4	0.91549
Tulkarem	Saida	379	17	0.91740
	Saida	379	6	0.91810
	Saida	379	4	0.91810
	Saida	379	2	0.91911
Tulkarem	Allar	238	16	0.91300
	Allar	238	2	0.91862
Jenin	Jenin	187	7	0.91678
	Jenin	187	4	0.91754

According to Table (4.1) the highest density was of Saida sample of 2012 crop 0.91911 g/cm^3, and the lowest value was for Yatta sample of 2012 crop 0.91068 g/cm). The altitude of Yatta is 818m which is the highest altitude of all samples. It seems that there is inverse relationship between the density of the olive oil sample and the altitude of the region.

The density of 2 year storage age Saida olive oil sample as function of temperature is shown in Fig.(4.1)

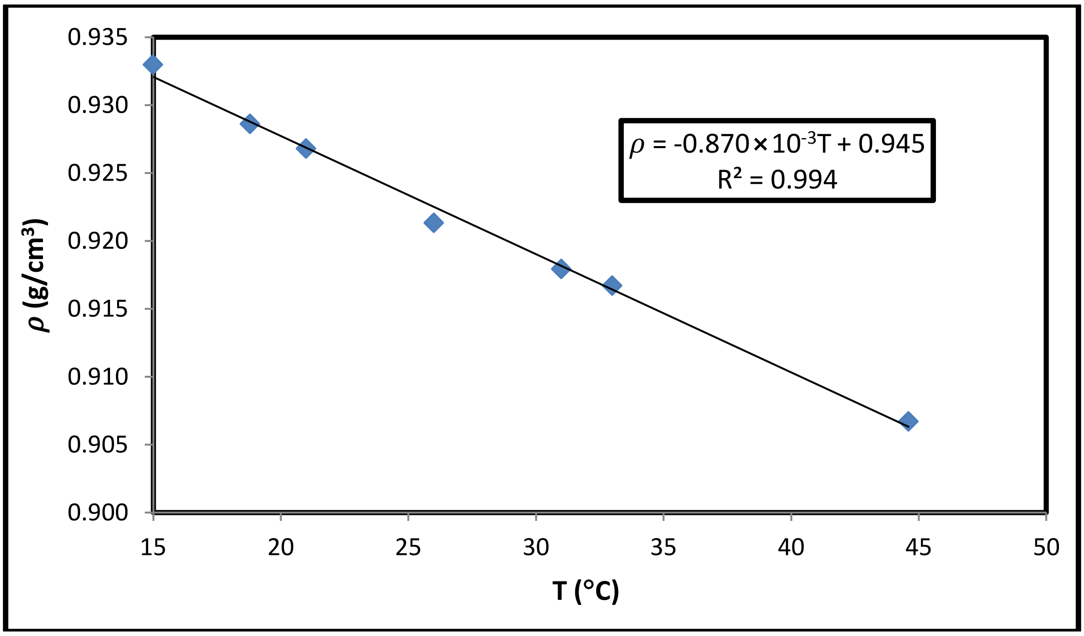

Fig.(4.1): The measured density for Saida sample from 2012 crop versus temperatures

The density as function of temperatures gives a linear relation, the negative slope of the equation in Fig.(4.1) indicates rate change of density with temperature is of the form $\rho = -0.870X10^{-3}T + 0.925$.

R^2 regression indicates how much the data is closed to the line of best fit.

The densities versus temperature for some samples from different regions are given in Appendix A.

4.1.2 Refractive Index

The refractive index values of olive oil samples of different regions and different storage ages were measured at two different temperatures of 28°C and at 35°C as represented in Table (4.2).

Table (4.2): Refractive index for the different olive oil samples

City	Region	Altitude (m)	Storage age (year)	n (28°C)	n (35°C)
Hebron	Yatta	818	2	1.4647	1.4637
Nablus	Yasid	698	3	1.4641	1.4634
Jenin	Meithalun	382	7	1.4628	1.4626
	Meithalun	382	4	1.4633	1.4631
Tulkarem	Saida	379	17	1.4615	1.4611
	Saida	379	6	1.4635	1.4631
	Saida	379	4	1.4630	1.4628
	Saida	379	2	1.4639	1.4633
Tulkarem	Allar	238	16	1.4629	1.4623
	Allar	238	2	1.4633	1.4630
Jenin	Jenin	187	7	1.4626	1.4617
	Jenin	187	4	1.4637	1.4636

Table (4.2) shows that at temperature 28°C the highest value of refractive index for Yatta sample of 2 years storage age is 1.4647. The lowest value for Saida sample of 17 years storage age is 1.4615. It seems that the rise in temperature causes decrease in the refractive index value, as the temperature of oil sample increases the sample becomes less dense and the speed of light in the sample increases so the refractive index decreases. The altitude of Yatta is 818m and Yatta sample has the highest value of the refractive index. The 2 year storage age Saida sample that has an altitude of 379m and Allar with an altitude of 238m have refractive index of 1.4639 and 1.4633, respectively. It seems there is a direct proportion between the altitude of the area and the refractive index value of the sample.

The refractive index values for four olive oil samples of Saida represented in Fig.(4.2)

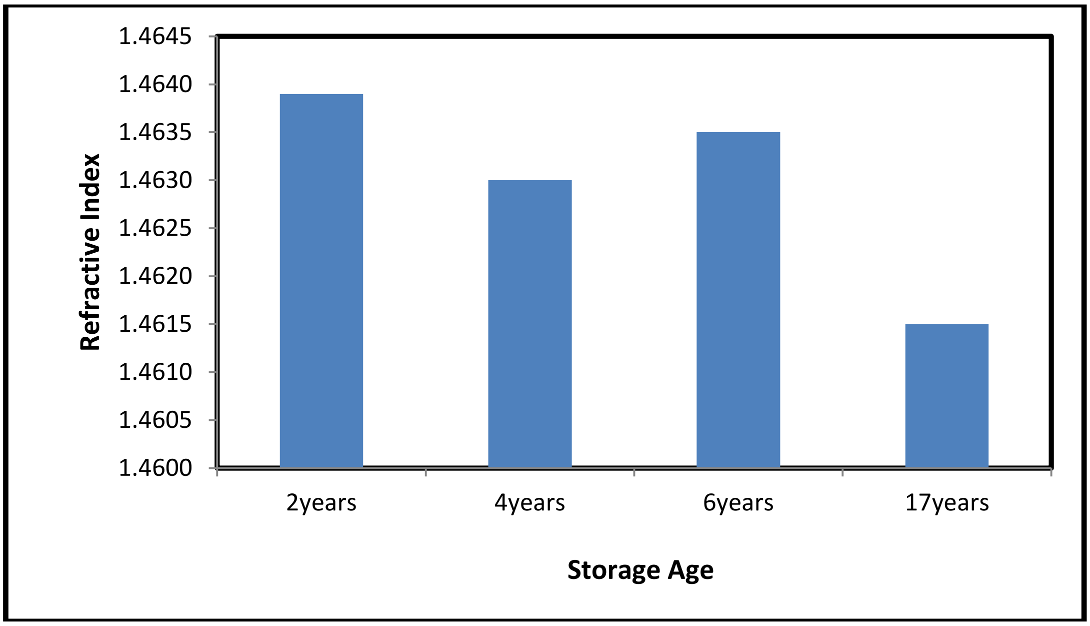

Fig.(4.2):The refractive index values of Saida samples of different storage ages

One can notice from Table (4.2) and Fig.(4.2) that the refractive index decreases as the storage age increases for the sample from the same region, like Allar's sample of 17 years storage age the refractive index is 1.4615 and for 2 years storage age is 1.4633.

The differences between the values of the refractive index is bigger than the accuracy of the digital refractometer which is $\pm$0,0002**.**

4.1.3 Viscosity

The dynamic viscosity of olive oil samples of different regions and different storage ages were measured between 15°C to 45°C. The measured viscosities of Saida sample (2012) are given in Table (4.3).

Table (4.3): The dynamic viscosity (cP) of Saida region for 2012 crops

T(°C)	η (cP) Saida(2012)
15.0	100.1
17.0	90.5
19.0	80.4
21.0	72.4
23.0	65.9
25.0	59.7
27.0	54.5
29.0	49.8
31.0	45.7
33.0	41.4
35.0	37.5
37.0	34.6
39.0	31.9
41.0	29.6
43.0	26.8
45.0	24.4

Table (4.3) shows that the viscosity of the olive oil sample is decreases as the temperature increases. The viscosity as function of temperature of Saida 2012 olive oil crop sample is shown in Fig.(4.3).The other samples are shown in Appendix B

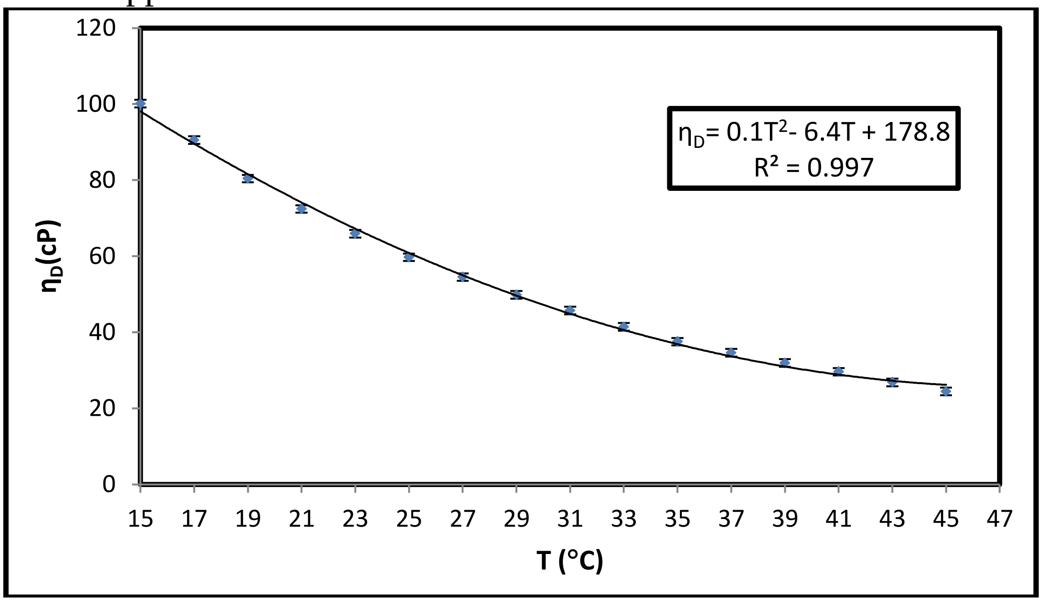

Fig.(4.3): Dynamic viscosity versus temperatures of Saida sample of 2012 crop

The best fit for the experimental data of dynamic viscosity as function of temperature of Saida's sample of 2012 crop is $\eta_D = 0.1T^2 - 6.4T+178.8$

4.1.4 Free Fatty Acids (FFAs)

FFA percent of olive oil samples for different regions and different storage ages were measured at temperature 28°C. The results are shown in Table (4.4).

Table (4.4): %FFA for the different olive oil samples

City	Region	Altitude	Storage age(year)	FFA (%)
Hebron	Yatta	818	2	1.20
Nablus	Yasid	698	3	1.32
Jenin	Meithalun	382	7	3.32
	Meithalun	382	4	2.30
Tulkarem	Saida	379	17	13.80
	Saida	379	6	4.53
	Saida	379	4	2.84
	Saida	379	2	2.34
Tulkarem	Allar	238	16	6.46
	Allar	238	2	2.59
Jenin	Jenin	187	7	3.05
	Jenin	187	4	0.94

The FFA percent of olive oil samples increase with increasing storage age of the sample. The maximum percent of FFA recorded for Saida sample of 17 years storage age and the minimum percent recorded for Jenin sample of 4 years storage age. The FFA percent of the sample compared with the altitude area shows no relationship between the altitude and the FFA percent.

Fig.(4.4) represents the FFA percent for Saida's sample of different storage ages 2, 4, 6 and 17 years.

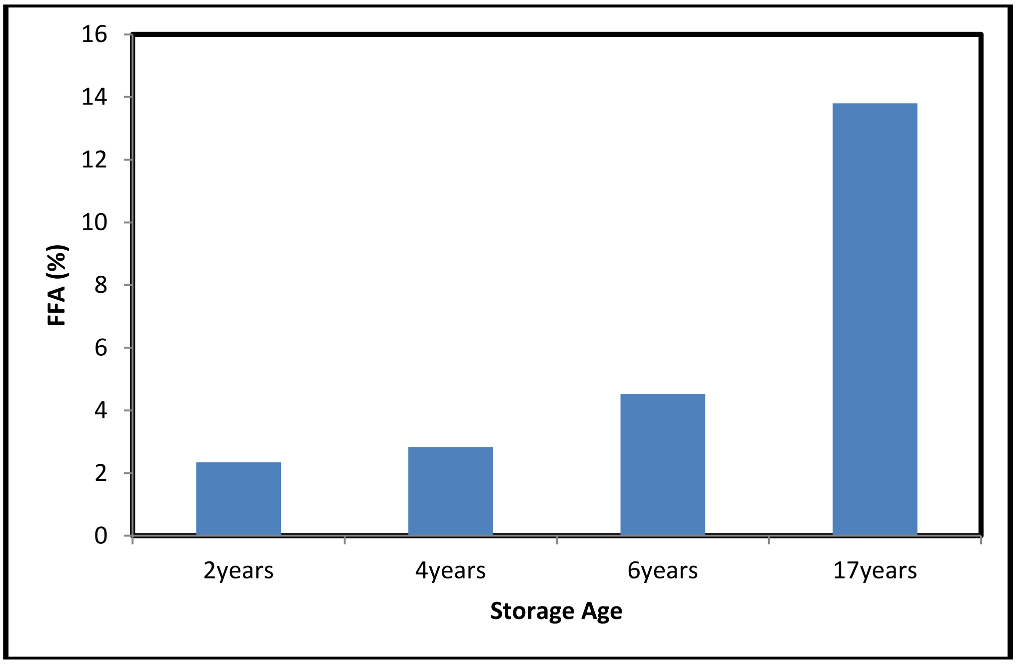

Fig.(4.4): The % FFA for Saida's samples for different storage age

The storage age of the olive oil samples increases the FFA percent for the same region.

4.2 Concentration of Metals

In this study, 11 metals were studied in 12 olive oil samples. The concentrations of the metals in the samples are given in Tables (4.5.a) and (4.5.b).

Table (4.5.a): Concentration of metals in olive oil (µg/g)

Metal		Allar 1998	Allar 2012	Jenin 2007	Jenin 2010	Meithalun 2007	Meithalun 2010
Aluminum	Al	16.1	11.6	19.9	17.4	46.3	21.2
Cadmium*	Cd	1.1	0.5	1.6	1.3	17.7	1.2
Copper	Cu	1.7	1.6	1.9	2.3	2.0	1.6
Iron	Fe	35.4	32.8	85.9	60.3	90.1	50.6
Potassium	K	31.0	25.0	86.5	168.9	130.2	35.9
Magnesium	Mg	530.0	303.0	624.8	702.0	440.5	345.7
Manganese	Mn	0.7	0.6	1.3	1.0	1.4	0.8
Sodium	Na	115.4	102.2	237.6	390.7	266.6	107.3
Nickel	Ni	0.6	0.7	1.3	1.2	1.7	1.0
Lead	Pb	0.2	0.2	0.3	0.3	0.8	0.2
Zinc	Zn	36.6	25.3	116.7	61.6	59.9	55.5

***The row multiplied by 10^{-2}**

Table (4.5.b): Concentration of metals in olive oil (µg/g)

Metal		Saida 1997	Saida 2008	Saida 2010	Saida 2012	Yasid 2011	Yatta 2012
Aluminum	Al	12.0	15.7	15.3	11.9	12.0	6.5
Cadmium*	Cd	0.7	0.6	0.0	0.1	0.5	0.6
Copper	Cu	2.2	1.6	1.1	1.2	1.7	1.4
Iron	Fe	33.2	40.9	18.5	21.8	44.0	25.1
Potassium	K	27.2	23.1	28.4	28.1	33.1	28.1
Magnesium	Mg	360.4	294.7	473.0	540.6	629.0	783.0
Manganese	Mn	0.5	0.6	0.4	0.5	0.9	0.6
Sodium	Na	73.4	92.4	139.0	188.0	232.4	176.4
Nickel	Ni	1.0	0.8	0.3	0.6	0.7	0.4
Lead	Pb	0.8	0.2	0.0	0.4	0.2	0.1
Zinc	Zn	22.4	26.8	13.7	17.9	53.6	24.3

***The row multiplied by 10^{-2}**

The range of the measured concentrations of metals in olive oil samples are shown in Table (4.6).

Table (4.6): The range of the measured concentrations of metals

Metal	Range (µg/g)
Mg	294.7-783.0
Na	73.4-390.7
K	23.1-168.9
Zn	13.7-116.7
Fe	18.5-90.1
Al	6.5-46.3
Cu	1.1-2.3
Ni	0.3-1.7
Mn	0.4-1.4
Pb	0.0-0.8
Cd*	0.0-1.7

*** The row multiplied by 10^{-2}**

Variations in concentration of metals were observed among Palestinian olive oil samples from different regions and different storage ages. These variations could be affected by soil, fertilizers, maturation and processing methods, or may be affected by weather and environmental conditions (rain, temperature, wind).

The maximum concentration in all samples is detected for Mg which ranged from 294.7 to 783.0 µg/g. Results indicate that concentrations of Mg may change according to maturation and processing methods. Concentrations of Mg in olive oil sample were compared with other studies. In Zeiner's study the concentrations of Mg is ranged between 2.91-3.62 µg/g (Zeiner *et al.*, 2005). Nergiz and Engez reported that the range of Mg concentration in green olive is between 114 - 373µg/g (Nergiz and Engez, 2000).

Concentration of elements may affect the quality of olive oil as storability, freshness or toxicity. The levels of Cu, Fe, and Zn cause an increase in the rate of oxidation of oil. The concentration levels of these elements in olive oil samples are given in Figs.(4.5)- (4.7).

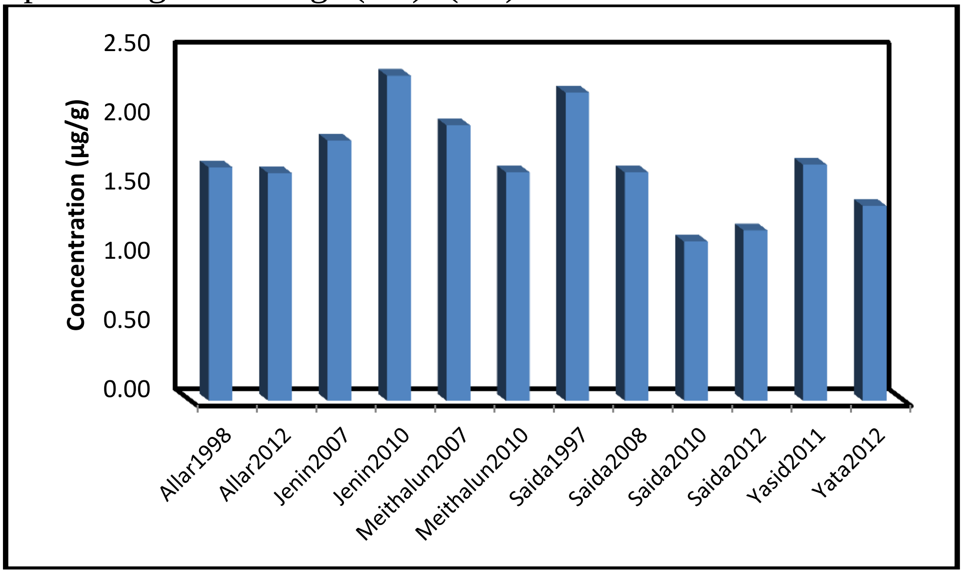

Fig.(4.5): Concentration of copper Cu in different olive oil samples

Fig.(4.5) shows that the levels of copper Cu in olive oil samples vary between 1.1 to 2.4 µg/g. The concentration of Cu is influenced by fertilizers and fungicides which are added to olive trees to fight fungal disease. Moreover a small concentration of Cu can act as a catalyst in oxidation process so the Cu concentration should be controlled because it influences the olive oil quality (Sahan *et al.*, 2007).

Palestinian standard recommends the concentration of Cu in olive oil not to be more than 0.4 µg/g (PS188, 1997). Our values varied between 1.1 and 2.4 µg/g which are more than value of Palestinian standard. The Turkish local food standards recommend the limit of concentration of Cu 6 µg/g

(TSE, 2003). Our results are less than 6 μg/g so they agree with Turkish standards.

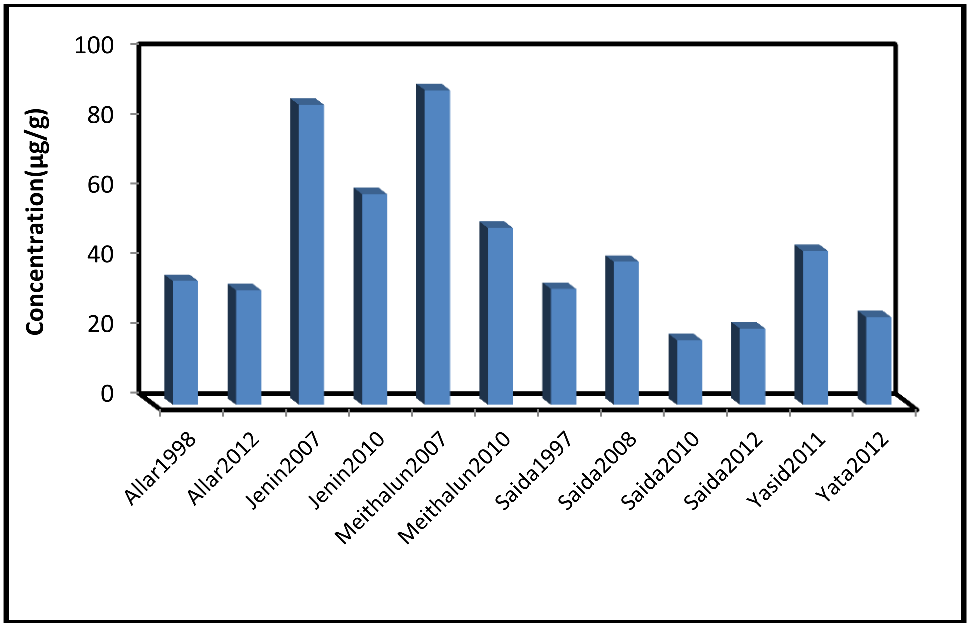

Fig.(4.6): Concentration of iron Fe in different olive oil samples

Fig.(4.6) shows the levels of iron Fe in olive oil samples which vary between 18.5 and 90.1 μg/g. Our results were higher than those of other studies but close to Ziena and his group results which are about 10.76–180.06 μg/g (Ziena *et al.*, 1997). The values of Fe metal influenced by the maturation, production condition and variety properties (Sahan *et al.*, 2007). Palestinian standard recommends the concentration of Fe element in olive oil to be 5μg/g. Our values of Fe are varied between 18.5 and 90.1 μg/g which are more than of Palestinian standard (PS188, 1997).

Fe is essential element to human nutrition according to FAO/ WHO the provisional tolerable daily intake for adult (60kg) is about 48mg (Zhu *et al.*, 2011).

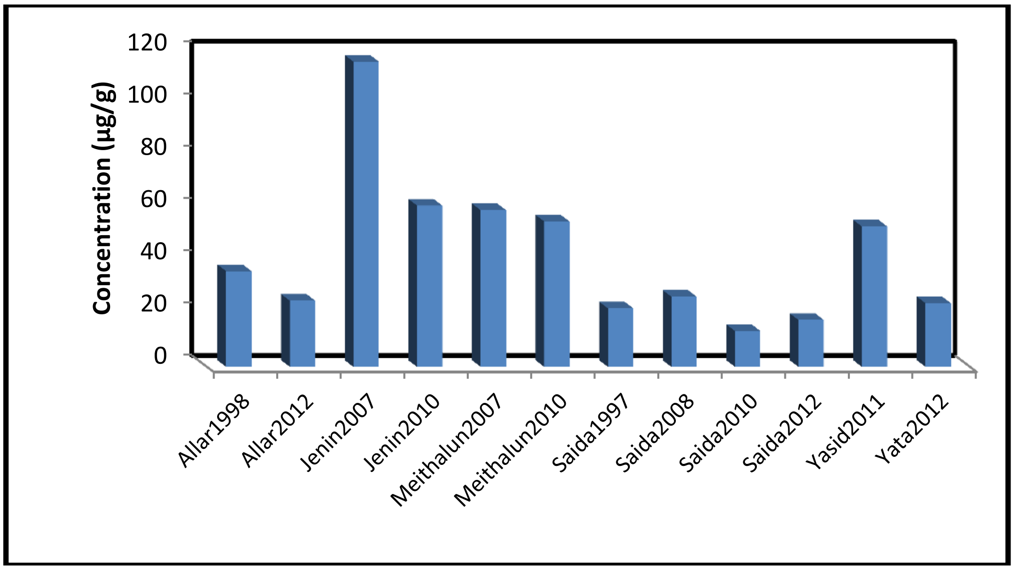

Fig.(4.7): Concentration of zinc Zn in different olive oil samples

Fig.(4.7) shows the concentration of zinc Zn in the analyzed samples varied between 13.7 and 116.7 µg/g. This value is higher than values obtained by other studies. The international and the Palestinian standard do not mention the allowed concentration of Zn in olive oil, but according to FAO/ WHO the allowed provisional tolerable daily intake of Zn element for adult (60kg) is about 60mg (Zhu *et al.*, 2011).

The concentration levels of the 11 metals in olive oil from the same region but different storage age are shown in Figs.(4.8) – (4.9).

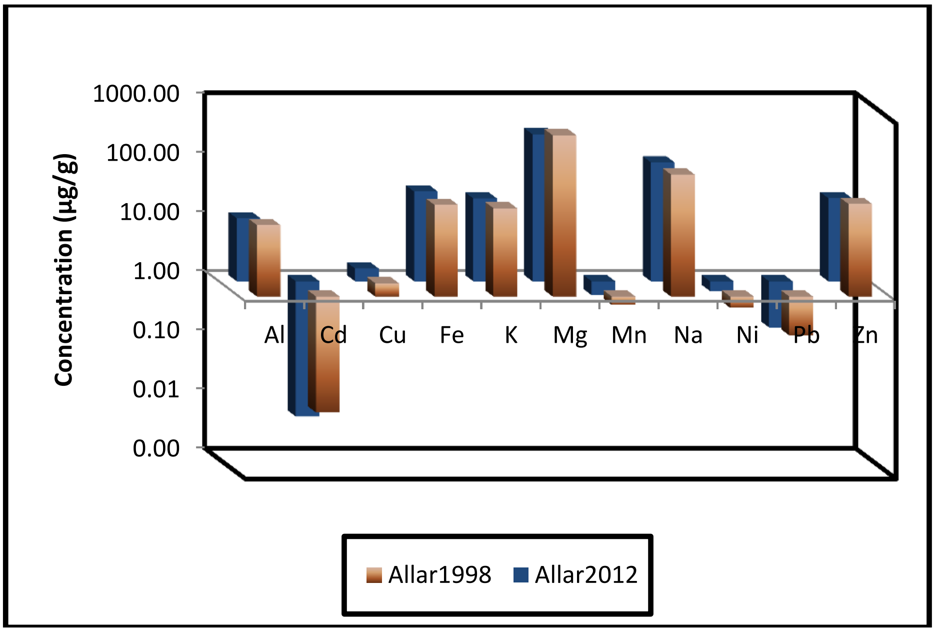

Fig.(4.8): The comparison between the levels of metals for two different storage age olive oil samples of same region(Allar)

The upper columns in Fig.(4.8) represents the metals that have high concentrations in Allar olive oil samples which range between 1 and 1000μg/g. The lower columns represent the metals that have low concentrations which range between 0.001 and 1μg/g. Fig.(4.8) shows that the concentrations of metals in Allar's samples change from one year to another. There are small variations in the concentration of metals, olive oil sample of 16 years storage age has more metals than the sample of 2 years storage age.

The comparison between the levels of metals for two different storage age olive oil samples from same region are given in Appendix C.

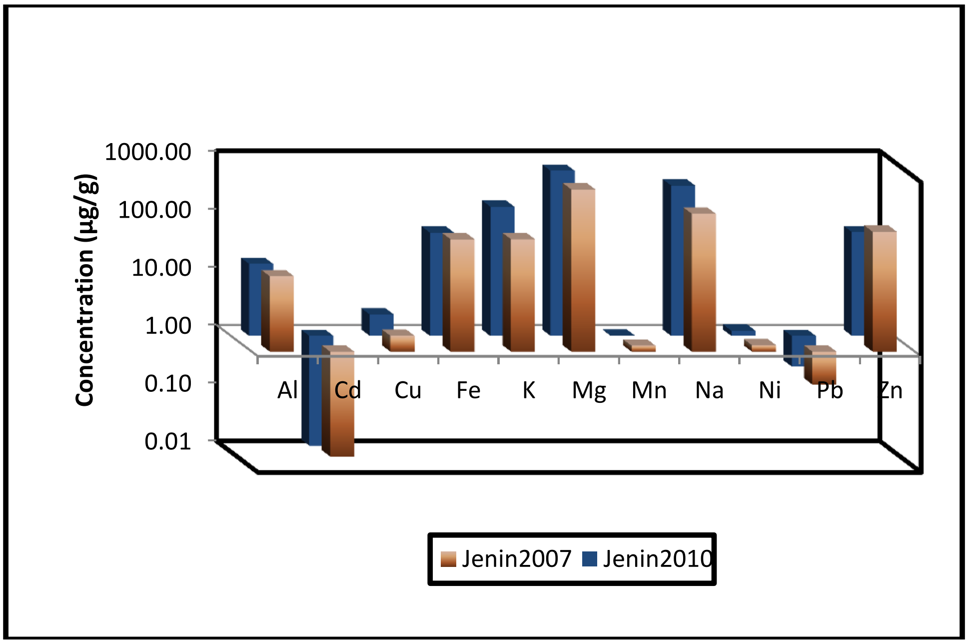

Fig.(4.9): The comparison between the levels of metals for two different storage age olive oil samples of same region (Jenin)

Fig.(4.9) shows a variation in the concentration of metals in Jenin samples where sample of 4 years storage age has more concentration of metals than sample of 7 years storage age. Figs.(4.8)- (4.9) shows that the change in the concentrations of metals is not due to the storage age period.

4.3 Concentration of Metals and the Physical Properties

4.3.1 Concentration of Metals with the Density

The effect of concentration of metals in olive oil on density as function of temperature is shown in Figs.(4.10) – (4.12).

4.3.1.1 The Effect of Cu Concentration on Density

Fig.(4.10) represent the effect of Cu concentration on the sample density. It is observed that the concentration of Cu in Jenin's sample of 2010 crop (2.3µg/g) is higher than Saida's sample of 2012 crop (1.2 µg/g).

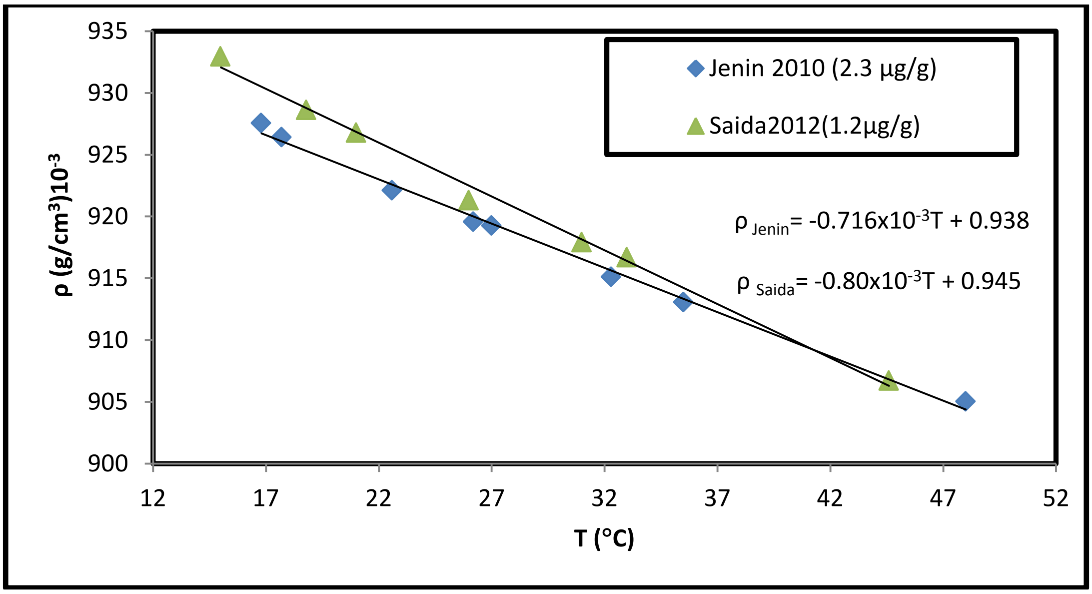

Fig.(4.10): The effect of two different concentrations of copper (Cu) on the density as function of temperature

The change rate of the density with temperature for Jenin's sample is fit by

$$\rho_{\text{Jenin}} = -0.716\times10^{-3}T + 0.938 \qquad (4.1)$$

While the change rate of the density with temperature for Saida's sample is fit by

$$\rho_{\text{Saida}} = -0.80\times10^{-3}T + 0.945 \qquad (4.2)$$

The change rate of the density with temperature for Saida's sample is higher than the change rate of Jenin's sample. The sample that has more concentration of Cu has less change rate of density with temperature.

4.3.1.2 The Effect of Fe Concentration on Density

The effect of Fe concentration in olive oil sample on density is represented in Fig.(4.11).

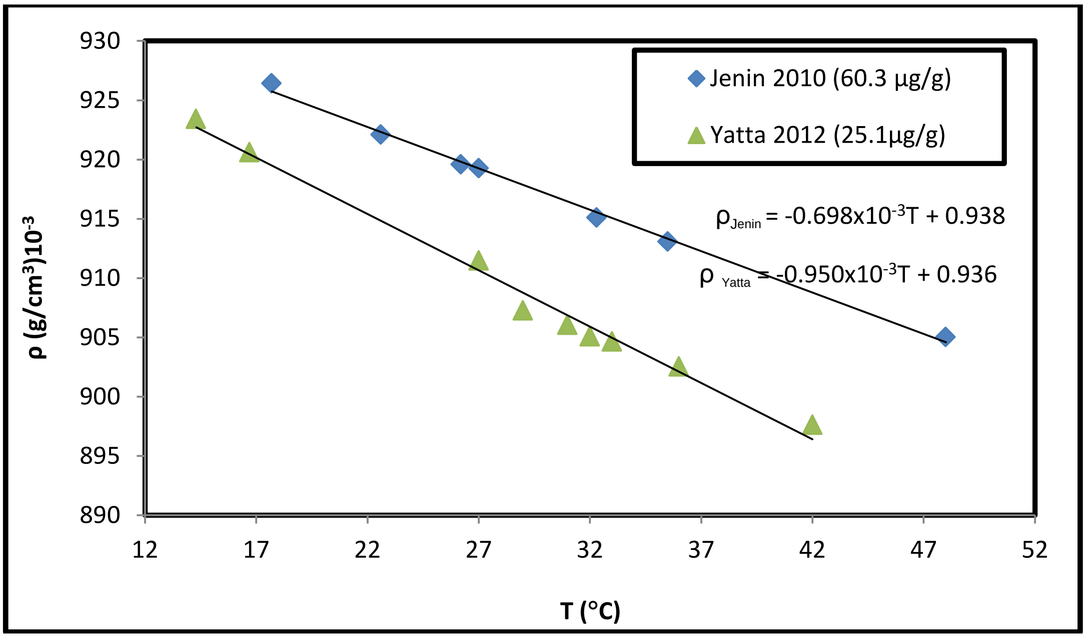

Fig.(4.11): The effect of two different concentrations of iron (Fe) on the density as function of temperature

Jenin's sample of 2010 crop has higher concentration of Fe than Yatta's sample of 2012 crop. At room temperature the density of Jenin's sample is higher than Yata's sample may because Jenin's sample has more Fe concentration than Yatta's sample. The density of Fe element at room temperature is (7.874 g/cm^3) which is considered to be high value compared with elements in the periodic table .

The relationship between the density and temperature for Jenin 2010 crop sample is represented by the following equation

$$\rho_{Jenin} = -0.698\times10^{-3}T + 0.938 \quad (4.3)$$

And the relationship for the 2012 Yatta crop given by

$$\rho_{\ Yata} = -0.950\times10^{-3}T + 0.936 \quad (4.4)$$

Eq.(4.3) and (4.4) show that the change rate for the density with temperature for Yatta's sample is higher than the change rate of Jenin's sample. It seems that there is an inverse relation between the change rates for the density with temperature and the concentration of Fe element.

4.3.1.3 The Effect of Zn Concentration on Density

The effect of concentration of Zn in olive oil sample on density represent in Fig.(4.12).

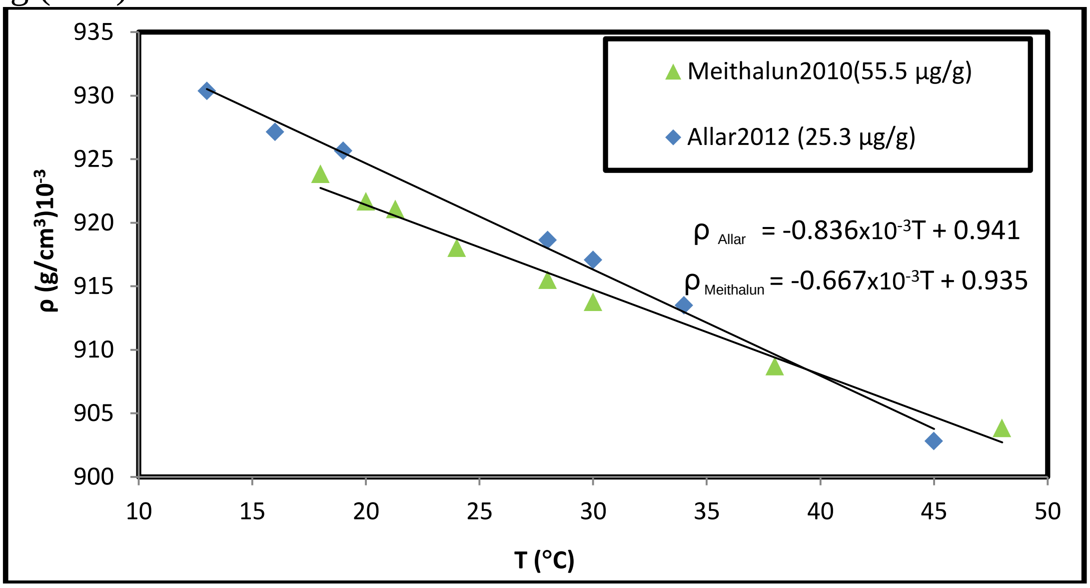

Fig.(4.12): The effect of two different concentrations of zinc Zn on the density as function of temperature

The relationship between the density and temperature for 2012 crop Allar sample is represented in the following equation

$$\rho_{\text{Allar}} = -0.836\times10^{-3}T + 0.941 \qquad (4.5)$$

And the relationship for 2010 crop Meithalun sample is given by

$$\rho_{\text{Meithalun}} = -0.667\times10^{-3}T + 0.935 \qquad (4.6)$$

Eq.(4.5) and (4.6) show that the change rate for the density with temperature for Allar's sample higher than the change rate of Meithalun's sample. Meithalun's sample of 2010 crop has higher concentration of Zn than 2012 crop Allar's sample. It seems that the sample density is not affected by Zn concentration, where the storage age affected the sample density.

4.3.2 Concentration of Metals and the Refractive Index

The refractive index values of 12 samples of olive oil compared with the concentrations of 11 elements. The refractive index values are represented in Table (4.2). The highest value of refractive index is for Yatta 2012 olive oil crop, while the lowest value is for 1997 crop Saida sample. This difference in the refractive index may refer to the storage age, and it may refer to the concentration of metals. It is observed that olive oil from Yatta has the highest concentration of magnesium (Mg) (782.0 μg/g) and Saida has (360.4μg/g). Also Yatta has concentration of sodium Na (176.4 μg/g) and Saida has (73.4 μg/g) the lowest concentration value of Na in all samples.

The refractive index of olive oil samples of 2012 crop at 28°C decreased in the order Yatta (1.4647), Saida (1.4639) and Allar (1.4633).The concentration of Mg for these samples also decreased the obtained results are (783.0, 540.6, 303.0 μg/g, respectively). The concentration of Na is arranged in a decreasing order as (176.4, 188.0, 102.2 μg/g, respectively). It seems that the concentrations of Mg and Na affect the refractive index value for the olive oil while the concentration of Mg affect is more than Na.

Refractive index values for Jenin, Meithalun and Saida 2010 crops and concentration of Mg represented in Table (4.7).

Table (4.7): Refractive index value with concentration of Mg.

Samples of 2010 Crop	**Refractive Index**	**Concentration of Mg (μg/g)**
Jenin	1.4637	702.0
Meithalun	1.4633	345.7
Saida	1.4630	473.0

The concentration of Mg in Saida olive oil is higher than Meithalun, the refractive index of Saida sample may be affected by the concentration of Cu, Fe and Zn where the concentration of these elements in this sample is the lowest compared with other samples.

4.3.3 Concentration of Metals with Viscosity

The highest and the lowest values of concentration of each of the 11 metals change form sample to another. The comparison between the viscosity as function of temperature for two samples of olive oil that have the highest and the lowest value of metals are represented in Figs.(4.13) - (4.15).

4.3.3.1 The Effect of Cu Concentration on Viscosity

Fig.(4.13) shows the effect of the concentration of Cu on the viscosity of olive oil**.**

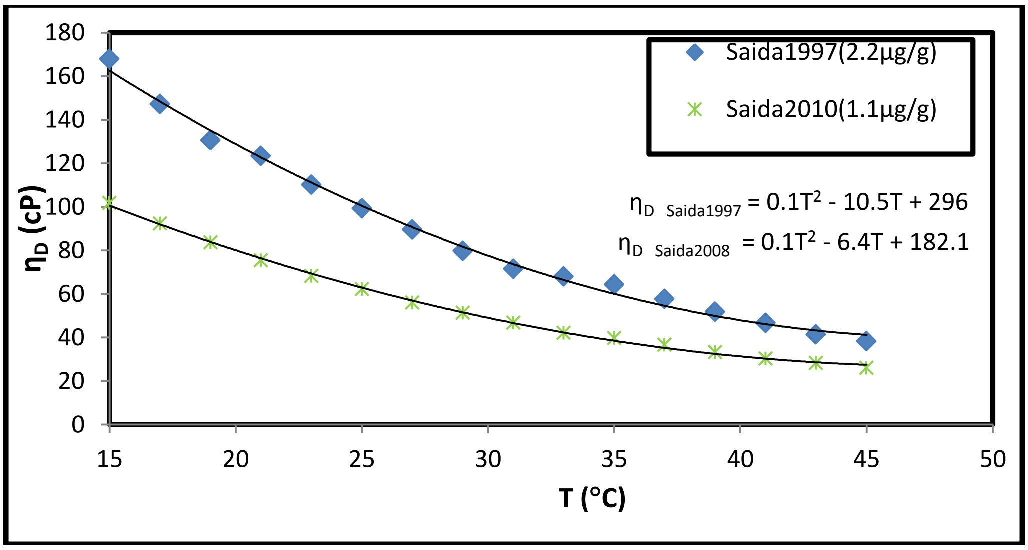

Fig. (4.13): The effect of the highest and lowest concentrations of copper Cu on viscosity as function of temperature

The best fits of the experimental data for Saida's sample of 1997 crop represented by quadratic equation

$$\eta_{D\ Saida1997} = 0.1T^2 - 10.5T + 296.0 \qquad (4.7)$$

The best fits for Saida's sample of 2010 crop represented

$$\eta_{D\ Saida2010} = 0.1T^2 - 6.4T + 182.1 \qquad (4.8)$$

The Eq.(4.7) shows the change rate of the viscosity with temperature of 1997 crop Saida sample (which has concentration of Cu equals 2.2µg/g) larger than 2010 crop Saida sample (which has the lowest concentration of Cu 1.1µg/g). It seems that the concentration of Cu may affect the change rate of the viscosity of the samples.

4.3.3.2 The Effect of Fe Concentration on Viscosity

Fig.(4.14) shows the effect of the concentration of Fe on the viscosity of olive oil.

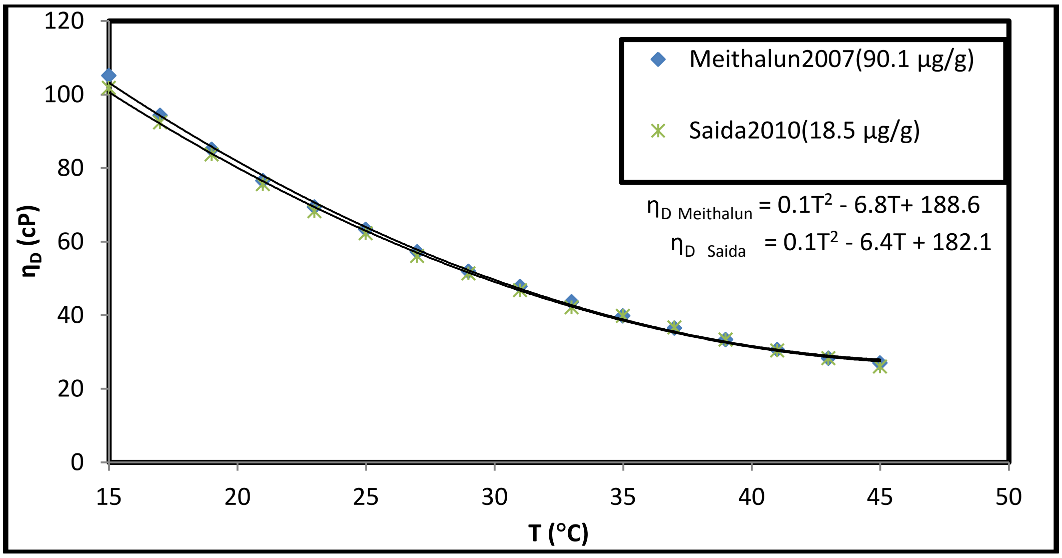

Fig. (4.14): The effect of the highest and lowest concentration of iron Fe on viscosity as function of temperature

2007 crop Meithalun sample has the highest concentration of Fe (90.1µg/g). The best fit of the experimental data for viscosity is given as

$$\eta_{D\ Meithalun} = 0.1T^2 - 6.8T + 188.6 \qquad (4.9)$$

The 2010 crop Saida sample has the lowest concentration of Fe (18.5 µg/g). The best fit of the experimental data for viscosity is given as

$$\eta_{D\ Saida} = 0.1T^2 - 6.4T + 182.1 \qquad (4.10)$$

The change rates of the viscosity with temperature from the two Eq. (4.9) and (4.10) are small. It seems that the concentration of Fe may not affect the viscosity of the olive oil.

4.3.3.3 The Effect of Zn Concentration on Viscosity

Fig.(4.15) shows the effect of concentration of Zn on the viscosity of olive oil.

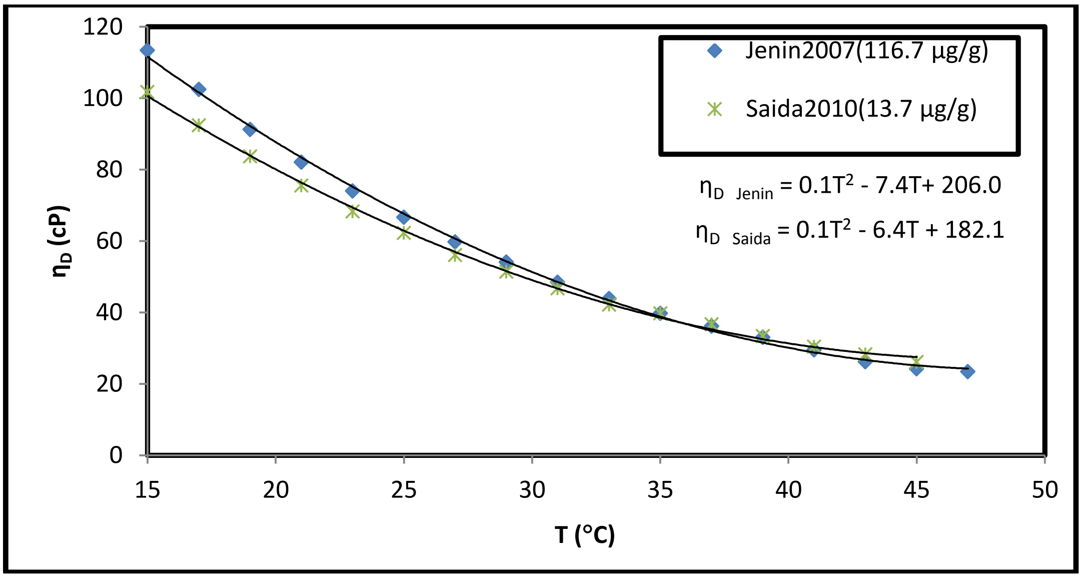

Fig. (4.15): The effect of the highest and lowest concentrations of zinc Zn on viscosity as function of temperature

The highest concentration of Zn is found in the 2007 crop of Jenin sample (116.7μg/g), while the lowest in the 2010 crop of Saida sample (13.7μg/g). The best fitting for the viscosity function of temperature for the Jenin olive oil represented by the following empirical equation.

$$\eta_{D\ Jenin} = 0.1T^2 - 7.4T + 206.0 \qquad (4.11)$$

The best fit for the viscosity function of temperature for Saida olive oil represented by the following empirical equation

$$\eta_{D\ Saida} = 0.1T^2 - 6.4T + 182.1 \qquad (4.12)$$

The change rate of the viscosity with temperature from Eqs.(4.11) and (4.12) is small so we expect that the concentration of Zn does not affect on the viscosity.

4.3.4 Concentration of Metals with %FFA

The FFA percents of 12 olive oil samples compared with the concentrations of 11 elements in the samples. It is observed that the FFA percent of olive oil of Saida 1997 crop is (13.8%) and Allar sample of 1998 crop is (6.46%) they have nearly the same storage age but there is a big difference in FFA percent, this difference may refer to Cu concentration where Saida has 2.2 μg/g of Cu and Allar has 1.7μg/g. Sahan reported that low concentration of Cu might have affect on lipids in olive oil (Sahan *et al*., 2007) which may affect on the FFA percent.

FFA percents of olive oil samples are represented in Table (4.4). The increase in concentration of some metals in olive oil (Cu, Fe and Zn) affect the oxidation rate of olive oil and this increase in concentration may affect the FFA percent.

Jenin samples have different storage ages 7 and 4 years and different concentrations of metals. The sample of 7 years storage age has concentration of Cu 1.9 μg/g, Fe 85.9 μg/g and Zn 116.7 μg/g, and FFA percent 3.07%. While 4 years storage age sample has metals concentration of Cu 2.3 μg/g, Fe 60.3 μg/g and Zn 60.6μg/g, and FFA 0.94%. The large differs in the FFA percents of Jenin samples referring to the storage age and may be also referred to the concentration of metals. Where 7 years storage age sample has the highest concentration of Zn compared with all samples.

Saida samples of 4 and 2 years storage ages have nearly the same FFA 2.84% and 2.34%, respectively. This close value in FFA percent may refer to the concentrations of Cu, Fe and Zn. The concentrations of these elements in the 4 years storage age sample are the lowest compared with all samples.

4.4 Daily Intakes of Metals

Daily intake of metals from olive oil consumptions depends on the amount of olive oil consumption and the metals concentration in olive oil.

The Palestinian adult consumes about 4.8 kg of olive oil per year which means 13.2 g per day. Eq.(3.1) is used to calculate daily intake rate of 8 metals by consuming 13.2g of olive oil per day. The resulted values were displayed in Tables (4.8.a) and (4.8.b).

Table (4.8.a): The calculated DIR of metals (μg/g.day)

Metals	Allar 1998	Allar 2012	Jenin 2007	Jenin 2010	Meithalun 2007	Meithalun 2010
Al	$3.0 X10^{-3}$	$2.2 X10^{-3}$	$3.8 X10^{-3}$	$3.3 X10^{-3}$	$8.7 X10^{-3}$	$4.0 X10^{-3}$
Cd	$2.1 X10^{-6}$	$9.8 X10^{-7}$	$2.9 X10^{-6}$	$2.4 X10^{-6}$	$3.3 X10^{-5}$	$2.3 X10^{-6}$
Cu	$3.1 X10^{-4}$	$3.1 X10^{-4}$	$3.5 X10^{-4}$	$4.4 X10^{-4}$	$3.7 X10^{-4}$	$3.1 X10^{-4}$
Fe	$6.7 X10^{-3}$	$6.2 X10^{-3}$	$1.6 X10^{-2}$	$1.1 X10^{-2}$	$1.7 X10^{-2}$	$9.5 X10^{-3}$
Mn	$1.4 X10^{-4}$	$1.1 X10^{-4}$	$2.4 X10^{-4}$	$1.9 X10^{-4}$	$2.6 X10^{-4}$	$1.6 X10^{-4}$
Ni	$1.2 X10^{-4}$	$1.3 X10^{-4}$	$2.4 X10^{-4}$	$2.3 X10^{-4}$	$3.3 X10^{-4}$	$1.9X10^{-4}$
Pb	$4.3 X10^{-5}$	$3.1 X10^{-5}$	$5.1 X10^{-5}$	$5.6 X10^{-5}$	$1.5 X10^{-4}$	$4.5 X10^{-5}$
Zn	$6.9 X10^{-3}$	$4.8 X10^{-3}$	$2.2 X10^{-2}$	$1.2 X10^{-2}$	$1.1 X10^{-2}$	$1.1 X10^{-2}$

Table (4.8.b): The calculated DIR of metals (μg/g.day)

Metals	Saida 1997	Saida 2008	Saida 2010	Saida 2012	Yasid 2011	Yatta 2012
Al	$2.3 X10^{-3}$	$3.0 X10^{-3}$	$2.9 X10^{-3}$	$2.2 X10^{-3}$	$2.3 X10^{-3}$	$1.2 X10^{-3}$
Cd	$1.2 X10^{-6}$	$1.2 X10^{-6}$	$3.8 X10^{-8}$	$1.1 X10^{-7}$	$9.4 X10^{-7}$	$1.1 X10^{-6}$
Cu	$4.2 X10^{-4}$	$3.1X10^{-4}$	$2.2 X10^{-4}$	$2.3 X10^{-4}$	$3.2 X10^{-4}$	$2.7 X10^{-4}$
Fe	$6.3 X10^{-3}$	$7.7 X10^{-3}$	$3.5 X10^{-3}$	$4.1 X10^{-3}$	$8.3 X10^{-3}$	$4.7 X10^{-3}$
Mn	$9.9 X10^{-5}$	$1.2 X10^{-4}$	$6.7 X10^{-5}$	$8.5 X10^{-5}$	$1.6 X10^{-4}$	$1.1 X10^{-4}$
Ni	$1.82 X10^{-4}$	$1.4 X10^{-4}$	$6.1 X10^{-5}$	$1.1 X10^{-4}$	$1.3 X10^{-4}$	$8.2 X10^{-5}$
Pb	$1.6 X10^{-4}$	$3.8 X10^{-5}$	$3.21 X10^{-6}$	$7.6 X10^{-5}$	$4.6 X10^{-5}$	$2.1 X10^{-5}$
Zn	$4.2 X10^{-3}$	$5.1 X10^{-3}$	$2.6 X10^{-3}$	$3.4 X10^{-3}$	$1.0 X10^{-2}$	$4.6 X10^{-3}$

The results in Tables (4.8.a) and (4.8.b) suggest that the DIR of Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in olive oil are all far below the permitted values reported by US EPA in Table (3.1). Consuming 13.2 g of Palestinian olive oil generally does not pose any health problems on humans. The elements K, Mg, and Na are essential elements that human body needs in large quantities.

Chapter Five

Discussion and Conclusion

The present study provides quantitative analysis of concentration of metals in olive oil from Palestine and some physical properties of olive oil (density, refractive index, viscosity and %FFA).

The physical properties (density and refractive index) of olive oil samples from Palestine agree with the international standard. As shown in Table (5.1).

Table (5.1): The measured density and refractive index in this work and the standard values

Physical Properties	Our Result	Codex Standard (Codex, 2001)	Palestinian Standard (PS 188, 1997)
Density (g/cm^3)	0.91068 - 0.91911	0.910 - 0.916	0.910 - 0.916
Refractive index	1.4647 - 1.4615	1.4677-1.4706	1.4677-1.4705

The Measured dynamic viscosity of olive oil at different temperatures of Saida's sample of 2012 crop and previous study are shown in Table (5.2).

Table (5.2): The measured dynamic viscosity in this work and the other Studies (Peri, 2014)

Our Result		Previous Result	
T (°C)	Dynamic Viscosity	T (°C)	Dynamic Viscosity
15	100.1	15	105.0
19	80.4	20	84.0
25	59.7	25	69.0
35	37.5	35	44.0
39	31.9	40	36.3

The differences in dynamic viscosity values may be referred to the differences in fatty acid composition of olive oil, the storage age for the samples, and may the differences in the concentration of metals in olive oil. There are some studies on determination of concentration of metals in edible vegetable oil (specially the olive oil). IOC reported concentration of metals in olive oil for iron (Fe) less than 3μg/g, copper (Cu) less than 0.1μg/g, lead (Pb) 0.1μg/g and arsenic (As) 0.1μg/g (IOC, 2015).

Metals of Mg, Na, K are present in our study in a wide concentrations range in olive oil. IOC did not put a limit of concentration for these metals. Mg, Na, K are essential metals sustain biological growth for any living organism. The daily recommend quantity of Mg 400 mg, Na 2400 mg, K 3500 mg (Chen, 2012).

Metals of Cd, Cu, Fe, Mn, Ni, Pb, and Zn are heavy metals that are linked in people's mind to toxic metals. In fact any substance that living organism needs depend on concentration of the substance if above a certain level it become hazardous. EPA determined the reference dose oral (RfDo) of heavy metals. The calculate DIR for these metals in this study does not exceed the recommend limits by US EPA. Concentration of Pb in Palestinian olive oil range between 0.0 and 0.8 μg/g, IOC recommends the concentration of Pb is 0.1 μg/g this value is smaller compared with Palestinian values, but the calculate DIR for Pb metal range 1.6 $X10^{-4}$ to 3.2 $X10^{-6}$ (μg/g.day) it is less than the allowed quantity of Pb according to US EPA 3.6 $X10^{-3}$ (μg/g.day) (EPA, 2015).

Concentration of metals in Palestinian olive oil are over the limit that established by IOC. Tables (5.3) represent concentration of metals in Palestinian olive oil and other works.

Table (5.3): Concentration of metals for this work and other works

Metal	Palestinian olive oil (µg/g)	IOC (µg/g) (IOC, 2015)	Previous studies	
			(Zeiner *et al*.,2005)	(Zhu *et al*.,2011)
Fe	18.5 - 90.1	3	13.10-18.46	34.1
Cu	1.1 - 2.3	0.1	0.00-5.45	0.265
Pb	0.0 - 0.8	0.1	-	0.013
As	-	0.1	-	0.012

High concentration of metals in olive oil may refer to the concentration of metals in water that used to irrigate olive trees, the production methods and the weather conditions (temperature rain and wind).

Concentrations of metals may affect the physical properties of the olive oil. It seems that the concentration of Cu, Fe and Zn may affect the density and the FFA percent of olive oil. The concentration of Cu may affect the viscosity of olive oil. The concentration of Mg and Na may affect the refractive index of olive oil.

Future work is indeed to study the effect of the container material on the physical properties of the olive oil and the concentration of metals. The concentration of metals in olive oil needs more study on other samples from Palestine. As future work it is interesting to study the concentration of metals in soil of Palestine to determine how the concentrations of metals in soil affect the concentration of metals in olive oil.

Appendix A

The mass densities for some samples as function of temperature are shown in Figs.(A.1) – (A.5).

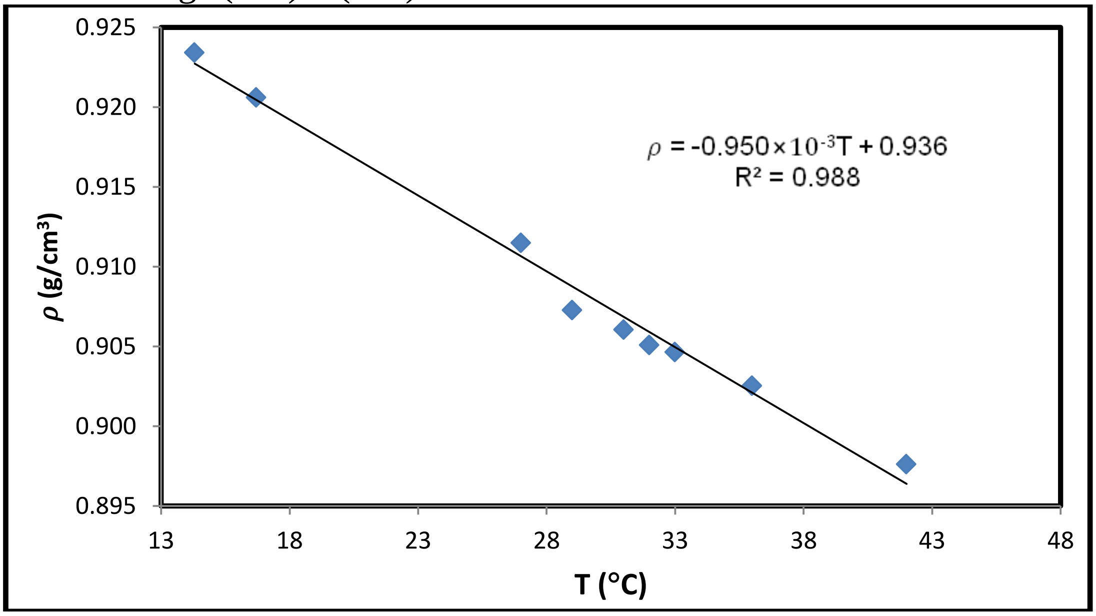

Fig.(A.1): The measured density for Yatta sample from 2012 crop versus temperatures

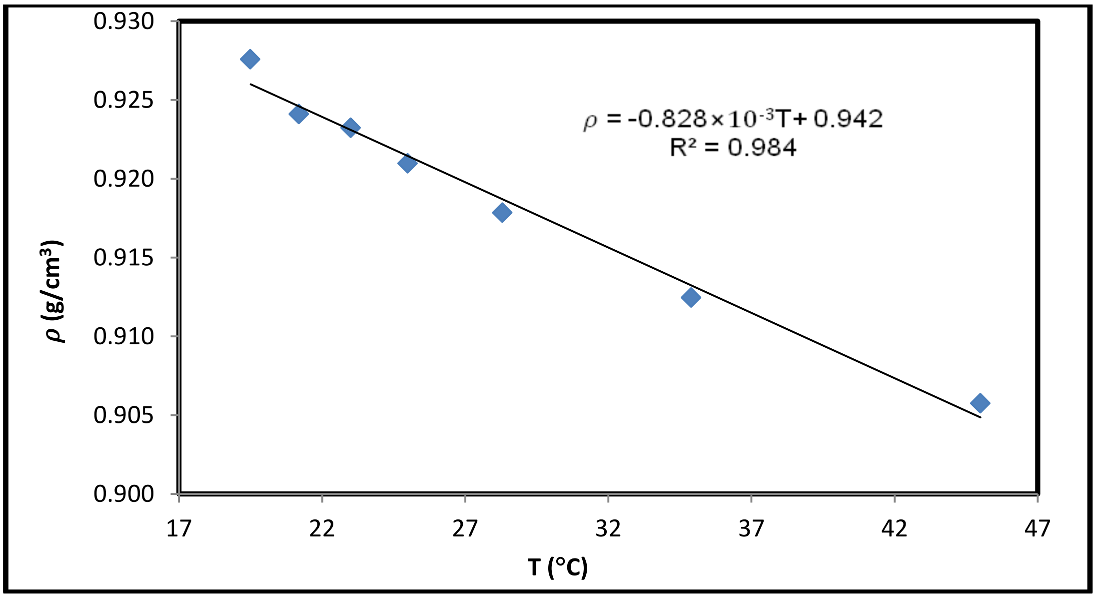

Fig. (A.2): The measured density for Yasid sample from 2011 crop versus temperatures

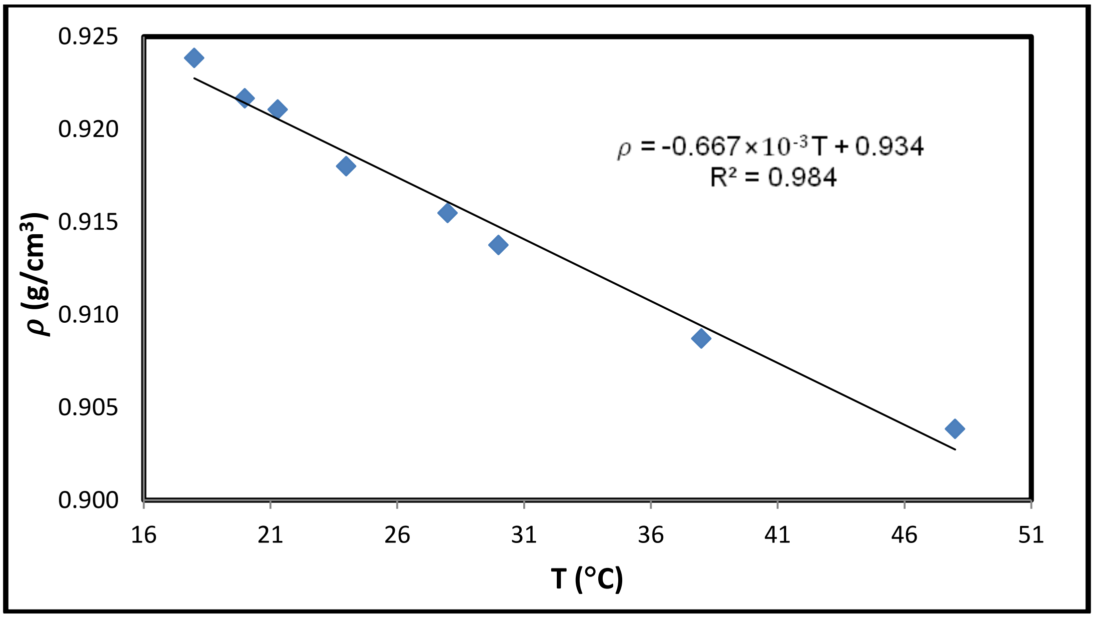

Fig. (A.3): The measured density for Meithalun sample from 2010 crop versus temperatures

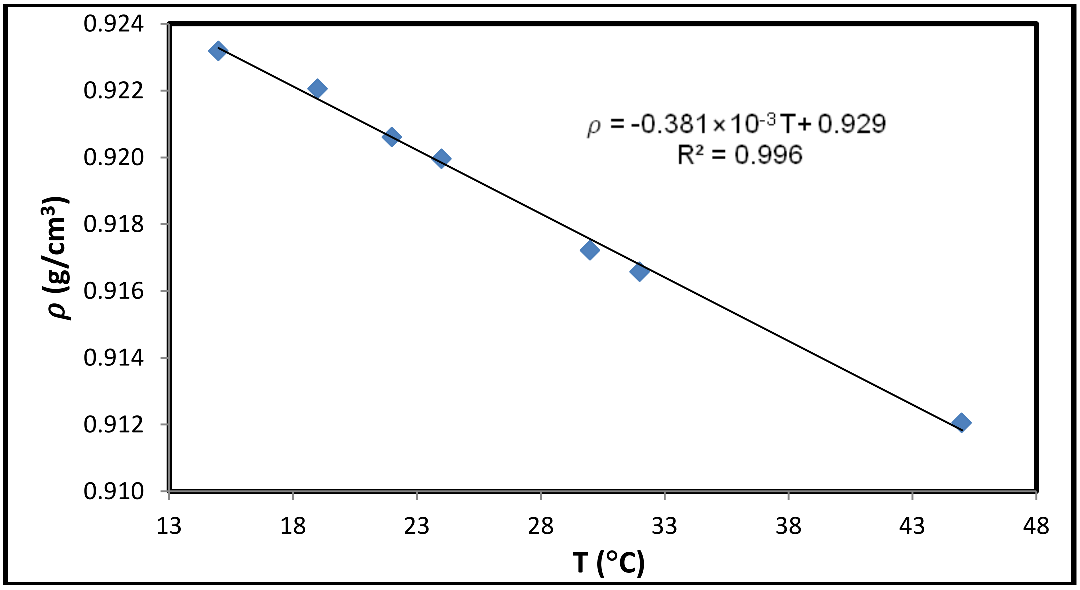

Fig. (A.4): The measured density for Saida sample from 1997 crop versus temperatures

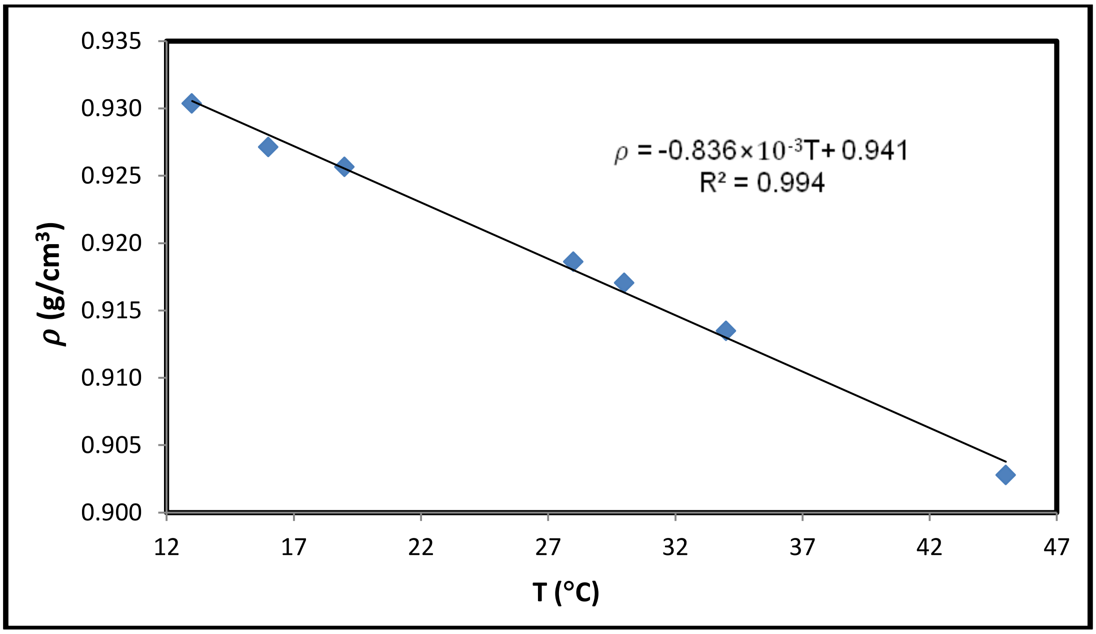

Fig. (A.5): The measured density for Allar sample from 2012 crop versus temperatures

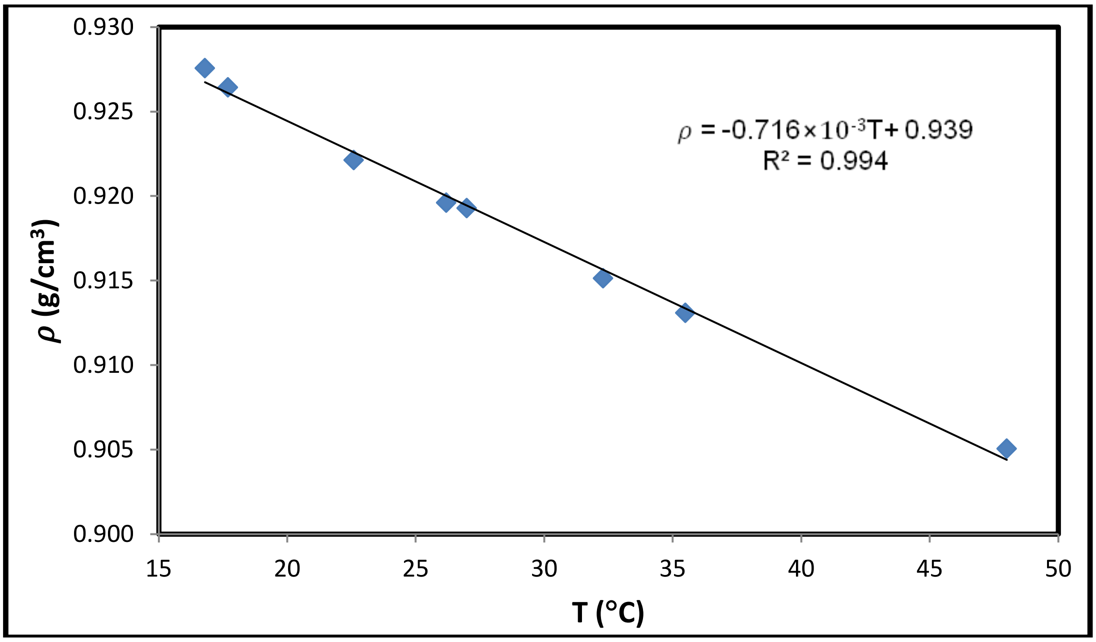

Fig. (A.6): The measured density for Jenin sample from 2010 crop versus temperatures

Appendix B

The dynamic viscosity of the 10 samples of olive oil versus temperatures are represented in Figs.(B.1) – (B.10).

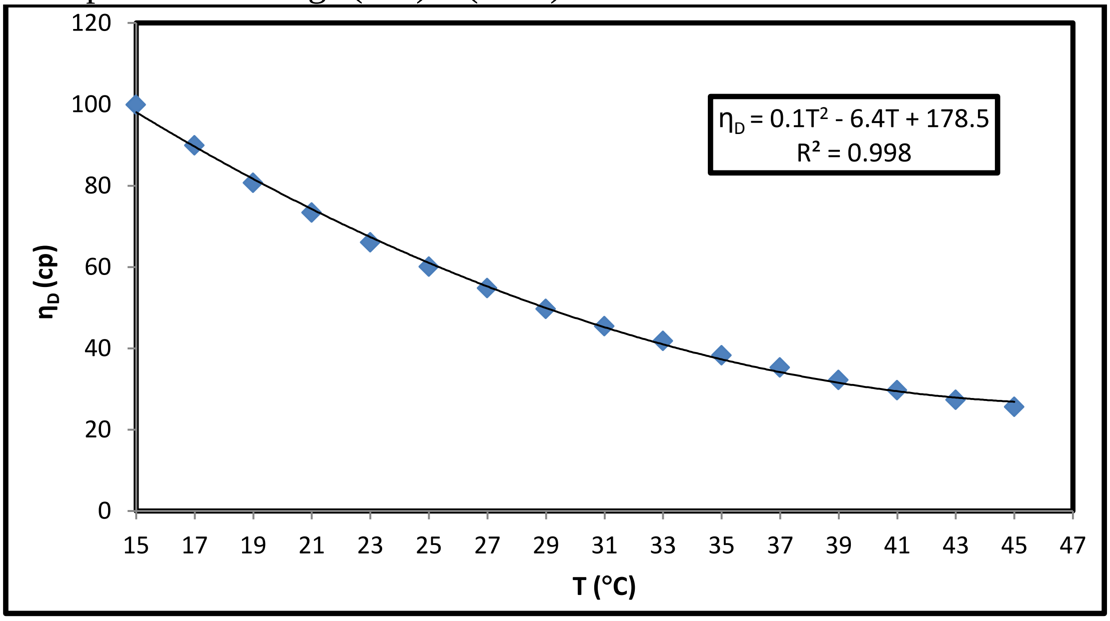

Fig.(B.1): Dynamic viscosity versus temperatures of Yatta sample 2012 crop

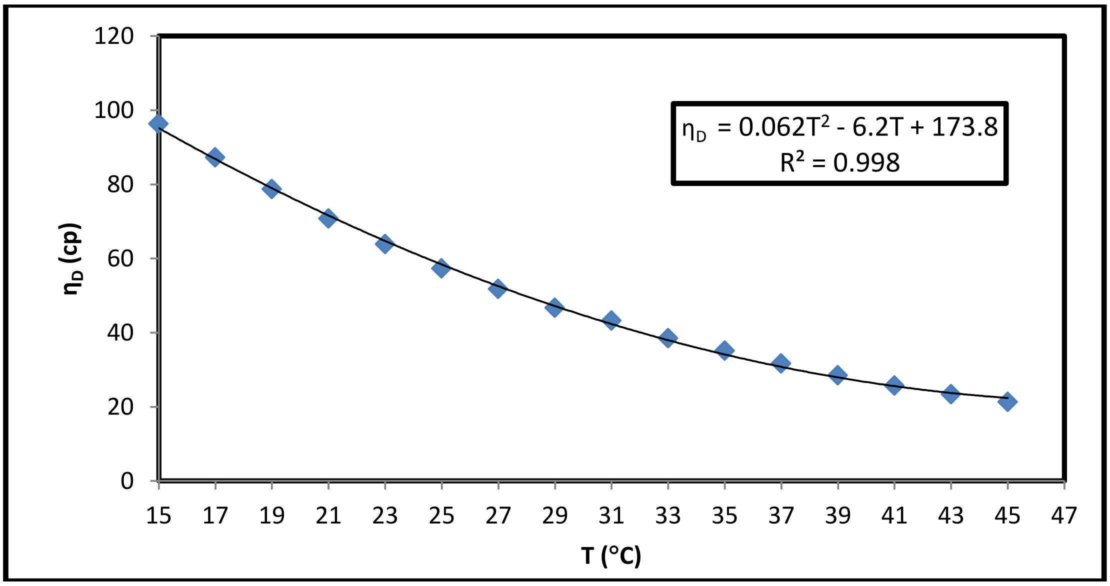

Fig.(B.2): Dynamic viscosity versus temperatures of Yasid sample 2011 crop

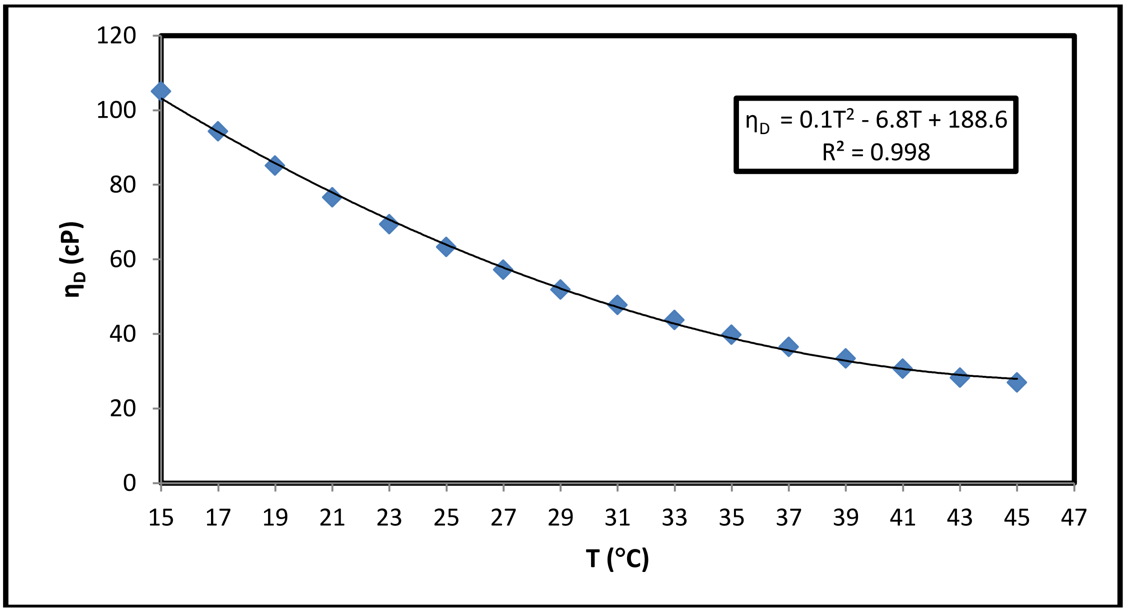

Fig.(B.3): Dynamic viscosity versus temperatures of Meithalun sample 2007 crop

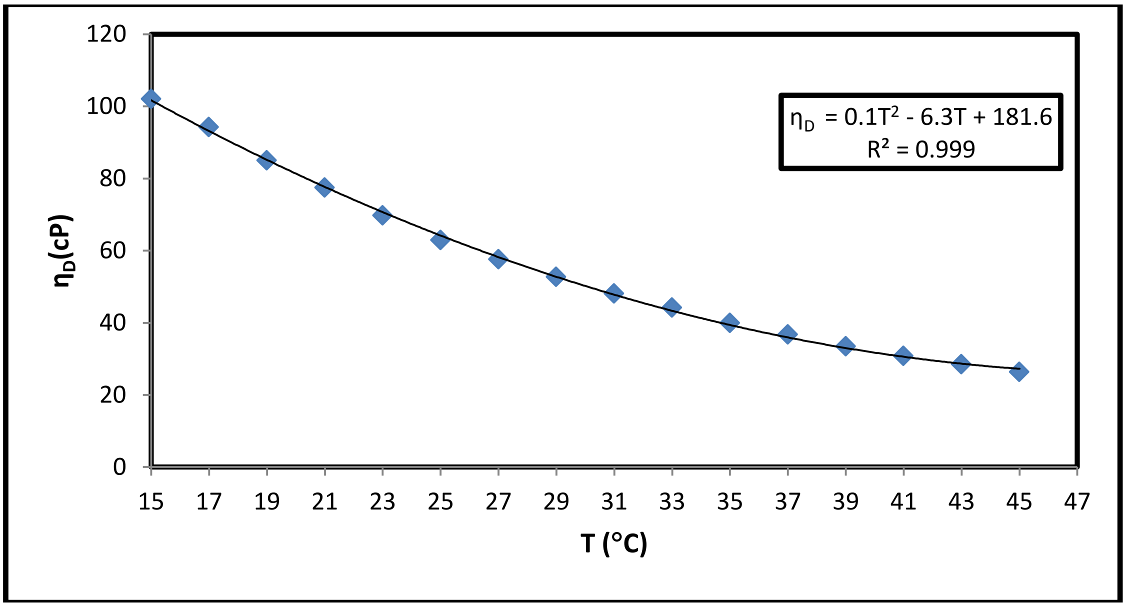

Fig.(B.4): Dynamic viscosity versus temperatures of Meithalun sample 2010 crop

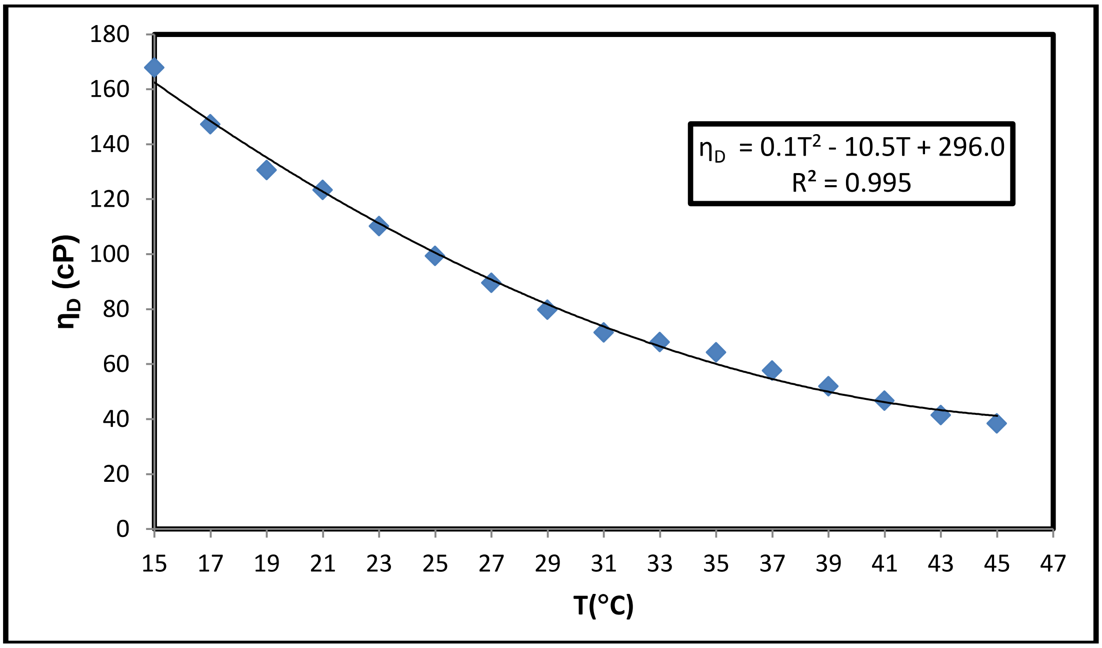

Fig.(B.5): Dynamic viscosity versus temperatures of Saida sample 1997 crop

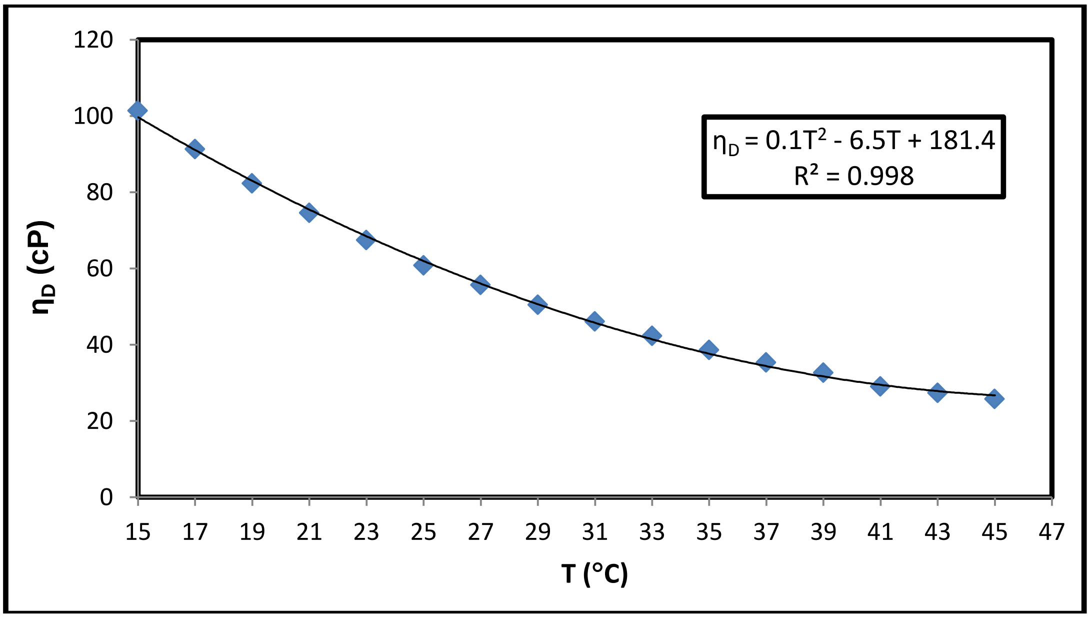

Fig.(B.6): Dynamic viscosity versus temperatures of Saida sample 2008 crop

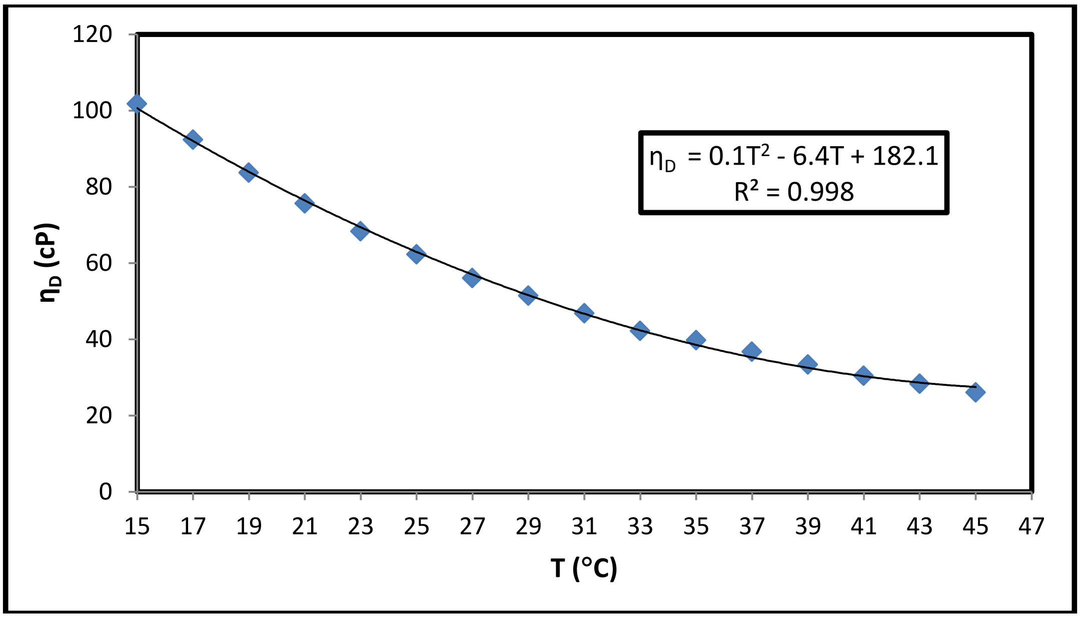

Fig.(B.7): Dynamic viscosity versus temperatures of Saida sample 2010 crop

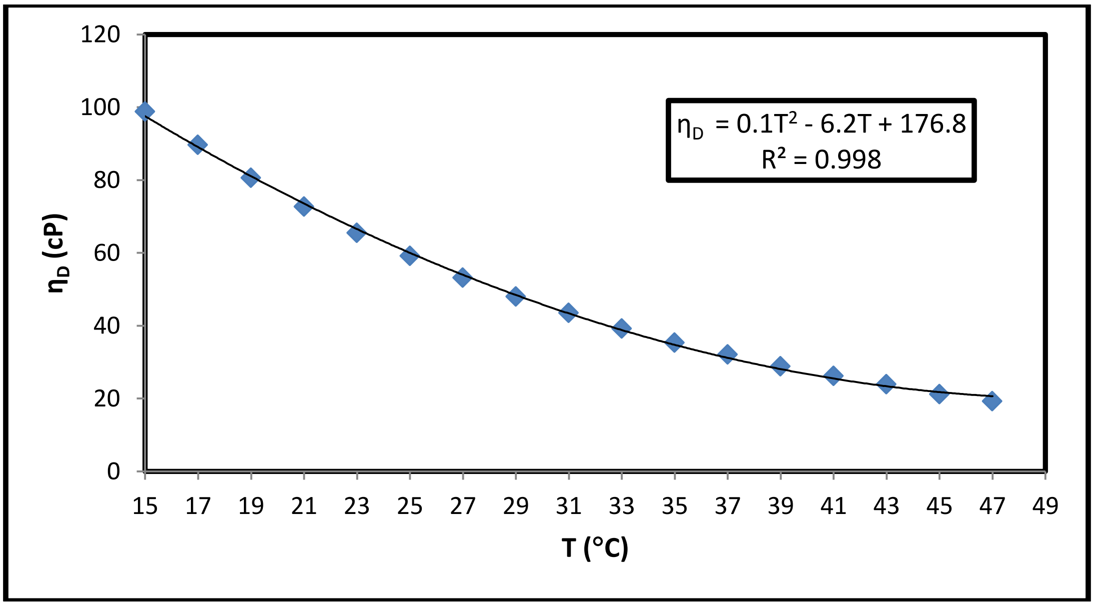

Fig.(B.8): Dynamic viscosity versus temperatures of Allar sample 1998 crop

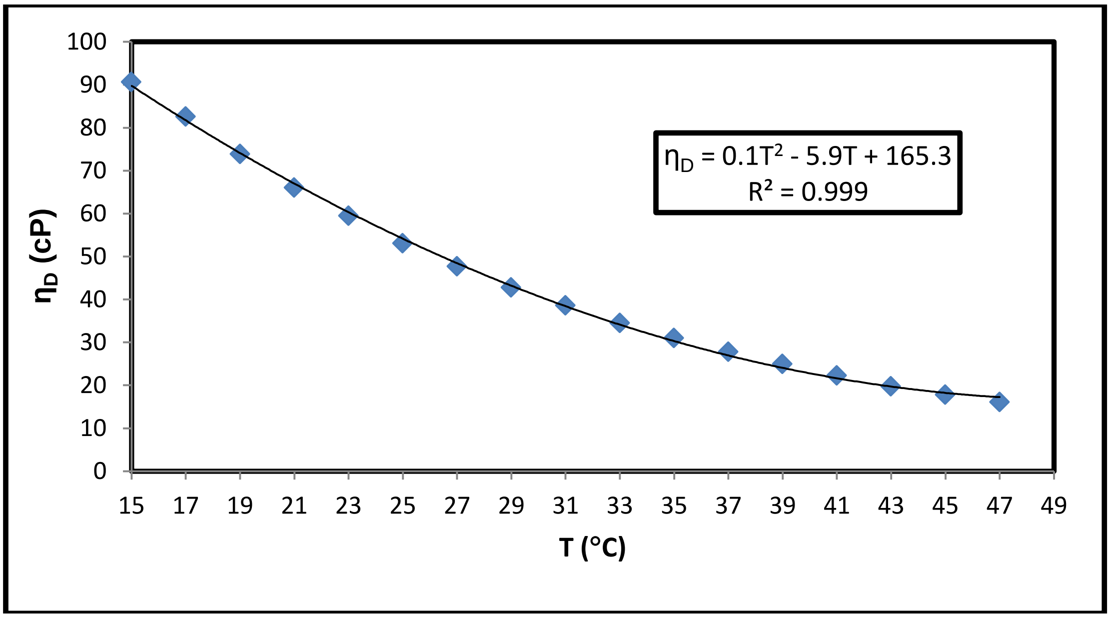

Fig.(B.9): Dynamic viscosity versus temperatures of Allar sample 2012crop

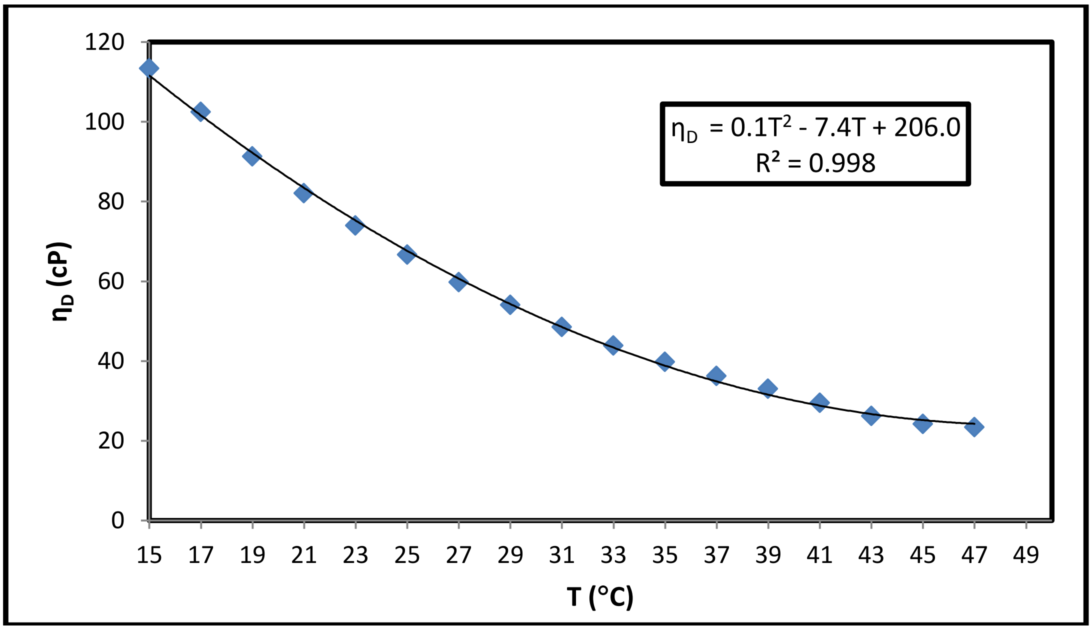

Fig.(B.10): Dynamic viscosity versus temperatures of Jenin sample 2007crop

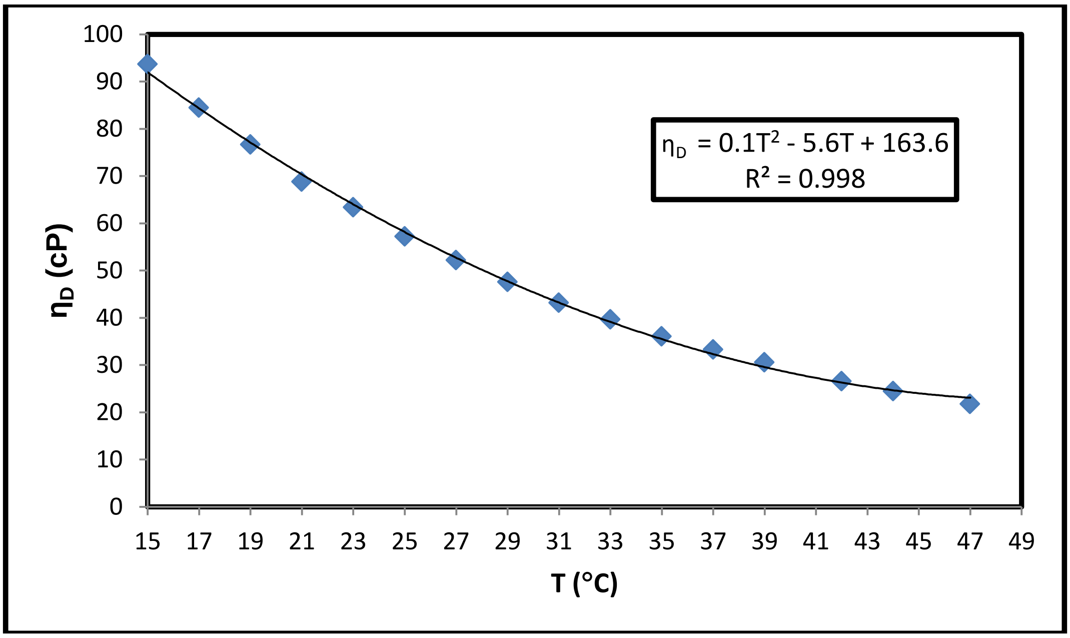

Fig.(B.11): Dynamic viscosity versus temperatures of Jenin sample 2010 crop

Appendix C

The comparison between the levels of metals in olive oil samples for two different storage age of the same region are represented in Figs.(C.1)-(C.3).

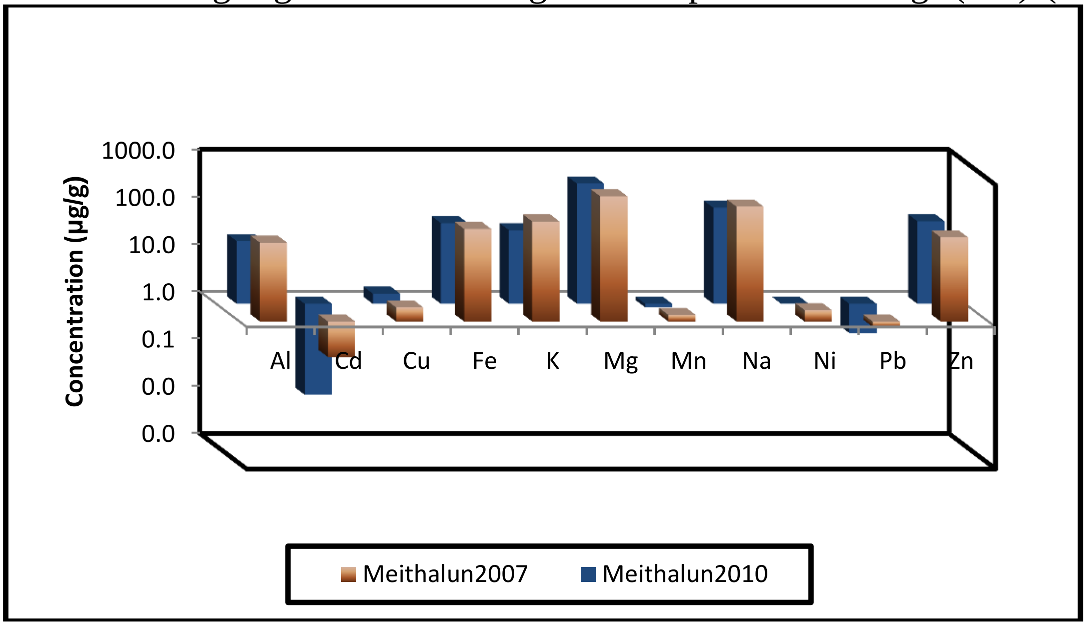

Fig.(C.1): The comparison between the levels of metals for two different storage age olive oil samples of same region(Meithalun)

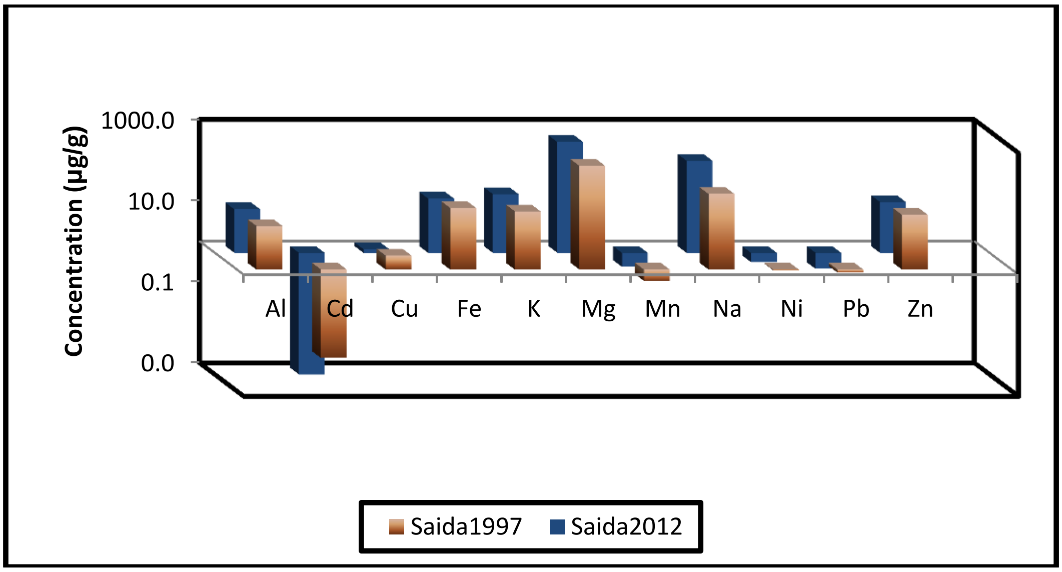

Fig.(C.2): The comparison between the levels of metals for two different storage age olive oil samples of same region(Saida)

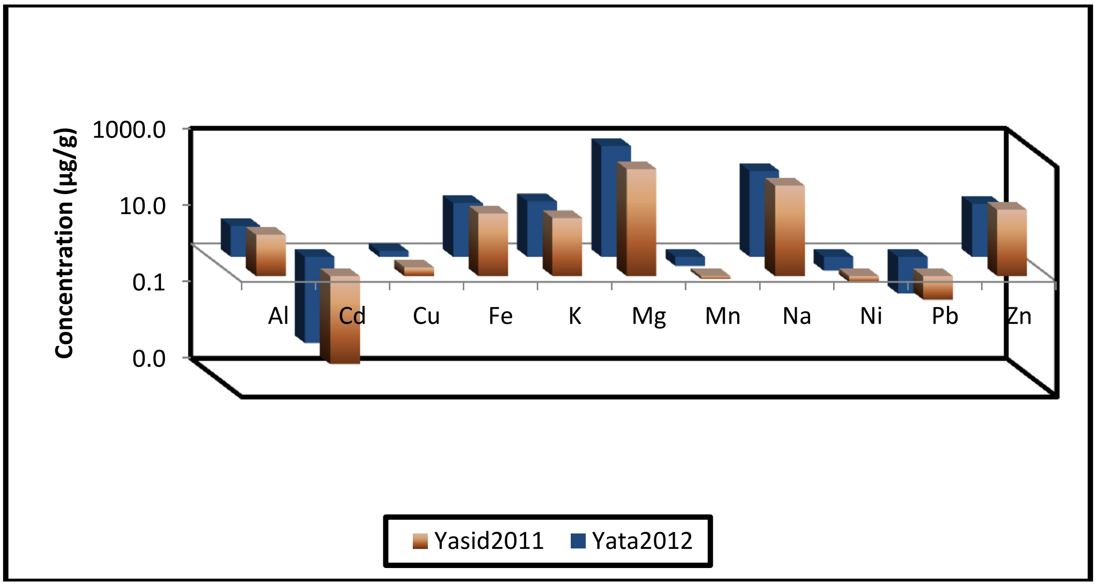

Fig.(C.3): The comparison between the levels of metals for two different storage age olive oil samples of Yasid and Yatta

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جامعة النجاح الوطنية

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تحديد بعض العناصر المعدنية وأثرها على الخصائص الفيزيائية لزيت الزيتون الصالح للأكل في فلسطين

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الفيزياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين

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الملخص

الخصائص الفيزيائية: الكثافة، معامل الانكسار، اللزوجة والحموضة لعينات زيت الزيتون من مناطق جغرافية ومن ارتفاعات مختلفة من فلسطين تم قياسها. الخصائص الفيزيائية التي تم قياسها تتطابق مع المعايير العالمية والمحلية. تركيز كل من العناصر Zn Pb, Ni, Na, Mn, Mg, K, Fe, Cu, Cd, Al تم قياسها بواسطة مطياف الكتلة البلازمي ICP-MS. اكبر تركيز للمعادن وجد للمغنيسيوم Mg بمعدل يتراوح بين (294.7 -783.0 ميكروغم/غم) ، ثم تركيز الصوديوم Na (73.4 -390.7 ميكروغم/غم) ، البوتاسيوم (23.1 -168.9 ميكروغم/غم).

تركيز الحديد، النحاس و الرصاص في زيت الزيتون الفلسطيني لم تتفق مع قيم المجلس العالمي لزيتونIOC. الاختلاف في تركيز المعادن في زيت الزيتون الفلسطيني يعتمد على نوع شجر الزيتون، مدة التخزين، الارتفاع والمنطقة الجغرافية.

معدل الاستهلاك اليومي من هذه المعادن لا يشكل أي خطر على صحة الإنسان وفقا لوكالة حماية البيئة الأمريكية.